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Age and Source of Groundwater from Isotope Tracers

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INTRODUCTION

As methods for analysing isotopes and chlorofluorocarbons continue to develop, increasingly useful information is being gained on groundwater systems (Clarke and Fritz 1997; Kendall and McDonnell 1998; Cook and Herczeg 1999). Stable isotopes are used as fingerprints to reveal groundwater sources and sources of dissolved nitrate and other constituents. Radioactive isotopes and dissolved chlorofluorocarbons (CFCs) are used as clocks to determine the residence times of water underground.

Stable isotopes in the water molecule are conservative tracers and have been used mainly to determine the sources of groundwater. Meteoric processes, for example, modify the stable isotope composition of water so that recharge waters from a particular environment have a characteristic isotopic signature. This signature serves as a natural tracer for the provenance of the groundwater. Likewise, the distinctive isotopic compositions of nitrogen, carbon and sulphur from different sources help to identify sources and processes affecting dissolved species such as nitrate, bicarbonate and sulphate in groundwater.

The decay of radioactive isotopes (such as tritium and carbon-14) provides a measure of the underground residence time of groundwater, and thus its sustainability. Tritium has become the standard for definition of "modern groundwater". Modern groundwater contains tritium and therefore has been recharged in the past few decades. This means it is part of an active hydrological cycle and exploitation of the resource is potentially sustainable. Dating by CFCs is an exciting new development, which complements tritium dating in the ten to fifty-year age range (Plummer and Busenburg 1999).

Groundwater containing zero tritium is submodern or older; it is not being actively recharged or simply has long flow paths and low flow velocities. Carbon-14 dating is the method used most often for dating tritium-free groundwater. Dating in this age range is important to establish the long-term potential for aquifer recharge.

Stable isotopes, radioactive isotopes, and CFCs have been used in New Zealand in a number of studies. The purpose of this chapter is to give a short background of isotopic techniques used in New Zealand and to illustrate the recent studies that have been undertaken to address the following aspects of groundwater movement, recharge and contamination.

Sources of groundwater and constituents - determining recharge sources for Canterbury, Takaka and Waimea Plains groundwater, and sources of nitrate for Canterbury and Waimea Plains groundwater.

Groundwater residence times - studies from Canterbury, Lower Hutt Valley, Takaka and Waimea Plains show whether water is being actively recharged or being mined.

Better conceptual and digital flow models of systems - age and source data help to elucidate the nature of the groundwater flow system at Canterbury, Lower Hutt Valley, Takaka and Waimea Plains, and validate digital flow models in Canterbury.

History of contamination - combining better dating methods with groundwater contami-

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nation studies gives exciting prospects of determining contaminant-input histories, as well as transport and degradation rates of contaminants. Canterbury and Waimea Plains examples are described.

Young water fraction - a groundwater drinking water supply is considered secure against bacteriological contamination if it is of sufficient age for bacteria and viruses to have decayed. Examples from Canterbury are given.

Isotopic research commenced in New Zealand in the late 1940s in the then Department of Scientific and Industrial Research. A team led by T. Athol Rafter and Gordon J. Ferguson established one of the first successful carbon-dating laboratories in the world (Rafter 1953; Ferguson 1953). State-of-the-art stable isotope and tritium measurement capabilities followed (Hulston and McCabe 1962; Taylor et al. 1963). These facilities have been maintained and developed in the Institute of Nuclear Sciences (created in 1959 with Athol Rafter as its first director) and since 1992 in the Institute of Geological and Nuclear Sciences. The University of Waikato set up an Isotope Unit in 1973 with radiocarbon and stable isotope measurement capabilities.

STABLE ISOTOPE TRACERS

Oxygen and hydrogen isotopes in water

Oxygen-18 (^{18}O) and deuterium ($^{2}H \equiv D$) are ideal tracers for water because they are constituent atoms of water molecules. ^{18}O and D concentrations in water are expressed as δ values with respect to a water standard in units of per mil (‰), where

$$\delta(‰) = (R_{sample} / R_{VSMOW} - 1) \times 1000 \qquad (1)$$

and R is the $^{18}O/^{16}O$ or D/H ratio of the sample or standard. The standard (VSMOW or Vienna Standard Mean Ocean Water) is held at the International Atomic Energy Agency in Vienna. Measurement errors are ±0.10‰ for $\delta^{18}O$ and ±1.0‰ for δD (one standard deviation).

Compared to all other water bodies, the ocean is relatively uniform in isotopic composition and therefore a good starting point for discussing the hydrological cycle of ^{18}O and D. Temperature-related separation or fractionation during evaporation or condensation cause variations in ^{18}O and D in environmental waters (Craig 1961; Dansgaard 1964). As water evaporates from the ocean surface, its heavy and light isotopes separate appreciably and oceanic vapour becomes strongly depleted in ^{18}O and D relative to the ocean. The balancing increase in the ^{18}O and D concentration of the ocean is negligible, owing to the immense water content of the ocean relative to the amount of water evaporated.

This isotopic separation (described by a separation factor α) is made up of two parts. The first is an equilibrium separation factor $\alpha_e = R_c/R_v$ at the ocean surface (where R_c refers to the condensed phase, in this case liquid water, and R_v to water vapour). The second is a kinetic separation factor α_k due to different rates of diffusion of the isotopic water molecules away from the ocean surface. These are related by

$$\alpha = \alpha_k \cdot \alpha_e \qquad (2)$$

Marine vapours sampled at Baring Head, near Wellington (Fig. 7.1) illustrate the consequence of kinetic fractionation; these samples are all depleted in ^{18}O and D compared

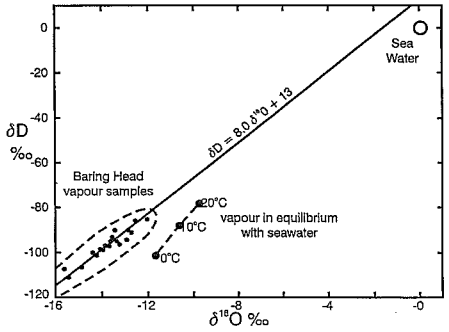

Figure 7.1: *Plot of δD versus $\delta^{18}O$ values for sea water, water vapour in isotopic equilibrium with sea water at the indicated temperatures, and actual atmospheric vapour sampled at Baring Head, near Wellington. The line is an average straight line through points (not shown) for many New Zealand precipitation samples.*

to equilibrium vapour. Fig. 7.1 is an example of the linear δ–diagram commonly used to show isotope relationships in hydrological studies, with $\delta^{18}O$ plotted as the x-axis and δD as the y-axis. Ocean water occupies a small region close to the origin, and most other waters occupy the negative quadrant as they have negative $\delta^{18}O$ and δD values.

The condensates from marine vapours, such as those shown in Fig. 7.1, plot nearer the origin of the δ–diagram, while the remaining vapour plots further away. The fractionation factors applying in atmospheric condensation processes are close to the equilibrium factors, so the relative changes of $\delta^{18}O$ and δD correspond to the ratio $(\alpha_e(D) - 1)/(\alpha_e(^{18}O) - 1)$, which is close to 8 for the range of temperatures in the atmosphere. As a consequence, condensates and depleted vapours plot near a straight line of slope of about 8 in the δ–diagram. However, the 'memory' of the extra kinetic fractionation during evaporation from the ocean surface is not lost, so that this line does not pass through the origin, but has a positive intercept (symbol d) on the δD axis, i.e.

$$\delta D = 8\delta^{18}O + d \qquad (3)$$

From global measurements Craig (1961) determined d to be +10‰ on average. We have found that d is about +13‰ for New Zealand (Stewart and Taylor 1981).

As rainfall is extracted from atmospheric vapour by condensation due to reduction in temperature, the ^{18}O and D concentrations of the remaining vapour become more and more depleted. This is the basis of the general rule that the δ values of precipitation are more negative at lower temperature. Consequently, δ values of precipitation vary with season, with more negative δ values in winter, and with altitude and latitude, with more negative δ values at higher altitudes and latitudes. Climate change also causes variations, with more negative δ values during colder periods.

Fig. 7.2 shows contours of the average annual δD values of precipitation throughout New

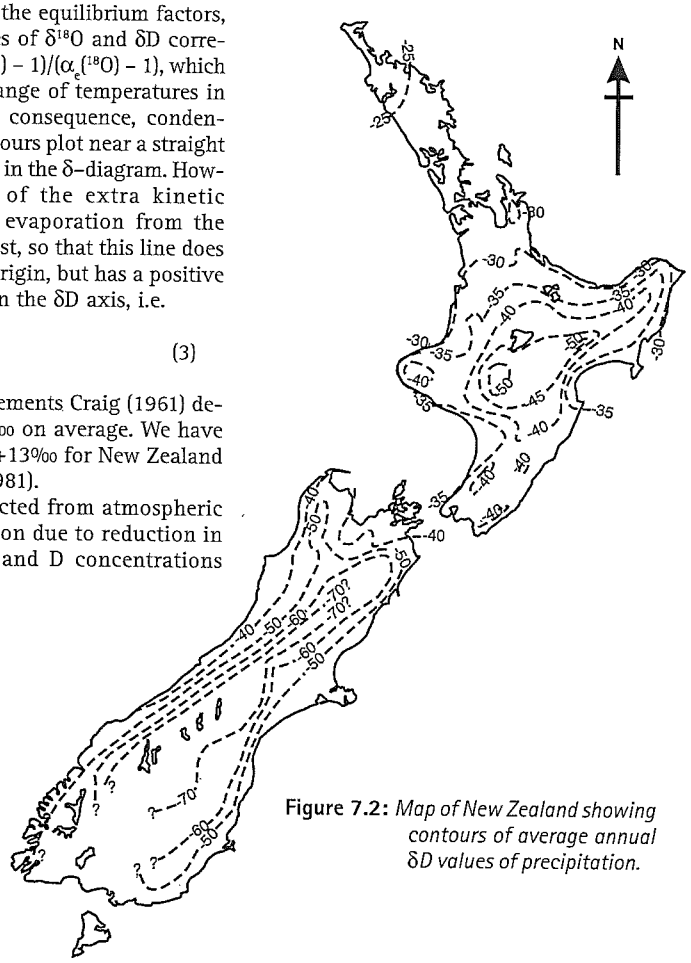

Figure 7.2: *Map of New Zealand showing contours of average annual δD values of precipitation.*

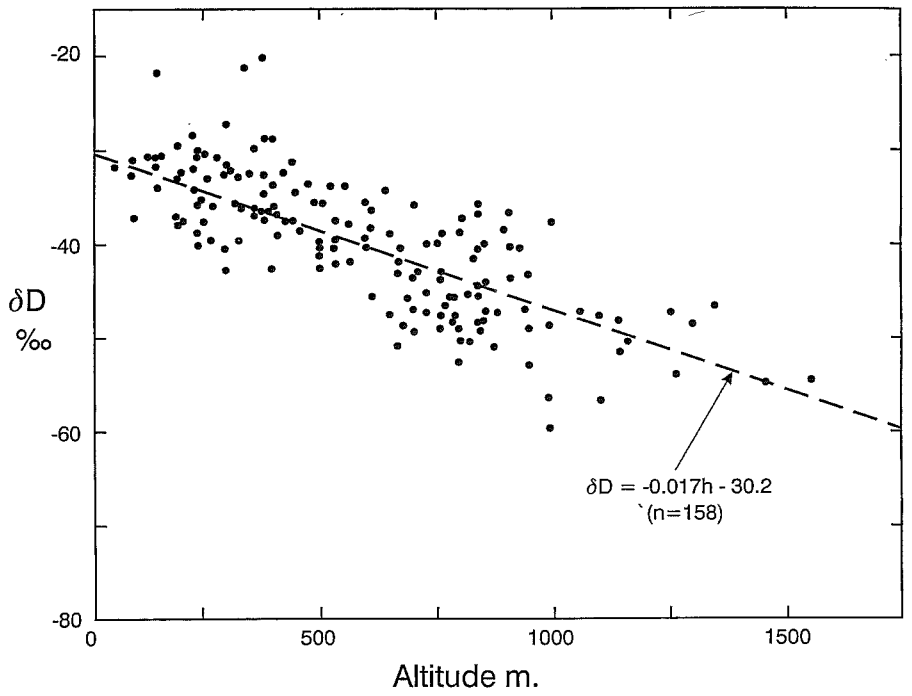

Figure 7.3: *δD values of river samples plotted against estimated mean altitudes of their catchments in the North Island and westerly zones of the South Island of New Zealand.*

Zealand (Stewart et al. 1983). Average annual δD values smooth out the seasonal variations. The highest (least negative) δD values are found at low elevations north of Auckland and the lowest (most negative) δD values at the highest elevations in the South Island, reflecting the effects of altitude and latitude.

Good correlations are found between δD and altitude, and δD and latitude for river samples (Figs. 7.3 and 7.4), as proxies for annual precipitation samples for westerly climatic zones (i.e. all of the North Island and all areas except Canterbury and Otago in the South Island). The equations of lines fitted to the data are:

$$\delta D = -0.017h - 30.2 \text{ and } \delta D = -1.76L + 41.6, \quad (4)$$

where h is the altitude in metres, and L is the latitude South in degrees. On average, δD decreases by 1.7‰ for each 100-m increase in altitude, and by 1.8‰ for each degree increase in latitude. The data used for the latitude correlation had first been adjusted to sea level using the altitude correlation.

Correlations for $\delta^{18}O$ in westerly zones are:

$$\delta^{18}O = -0.0021h - 5.40 \text{ and } \delta^{18}O = -0.22L + 3.58, \quad (5)$$

showing that $\delta^{18}O$ decreases by 0.21‰ for each 100-m increase in altitude, and by 0.22‰ for each degree increase in latitude. The relatively uniform behaviour of $\delta^{18}O$ and δD in westerly zones is due to the prevailing westerly circulation over the Tasman Sea. The d value of +13‰ results from the influence of dry air from Australia, which picks up moisture rapidly (and moisture with a higher α_k) as it passes over the Tasman Sea before reaching New Zealand.

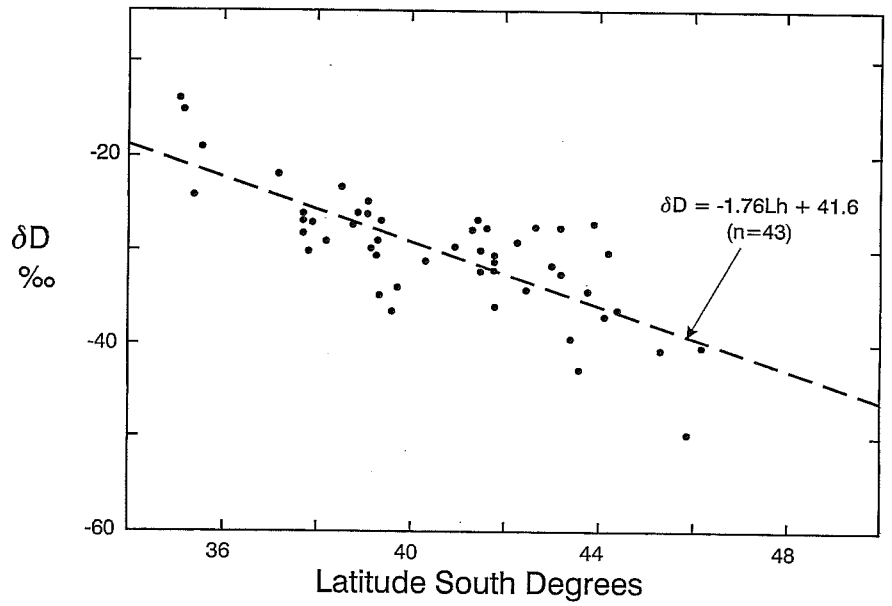

Figure 7.4: *δD values of river samples plotted against mean latitudes of catchments in westerly zones of New Zealand at sea level.*

Easterly climatic zones (Canterbury and Otago) do not fit the relationships derived for westerly rainfall (Stewart et al. 1983). The δ values are more negative for a given altitude or latitude than they are for westerly rainfall: this is because easterly rainfall is from southeasterly sources or from westerly air masses that have been 'wrung out' on passing over the main divide in the South Island. The relationship between the δ values is also different, with

$$\delta D = 8\,\delta^{18}O + 10 \quad (6)$$

applying more closely for Canterbury and Otago precipitation.

The δ values of groundwater can be useful indicators of the source of recharge to a groundwater system. Two main sources of recharge are seepage from rivers or infiltration of rainfall. The average δ value of a river can be significantly different from the average δ value of low altitude rainfall, if the rivers derive their water from high altitude catchments (e.g. rivers on the Canterbury Plains). This enables the groundwater recharge source to be identified from $\delta^{18}O$ or δD.

Variations in $\delta^{18}O$ and δD in rainfall are used to study transport times of water through a catchment into a stream or through a soil to an underlying aquifer. Studies at Maimai Catchment on the West Coast (Stewart and McDonnell 1991; McDonnell et al. 1999) showed that during storms headwater streams predominantly discharged the water resident in the catchment rather than the current rainfall, even though their response to the rainfall was very rapid. The mean residence time of water in the catchment was three months. Another study in the Pukekohe region near Auckland (Rosen et al. 1999) showed that soil water residence times were at least six months.

Carbon, nitrogen and sulphur isotopes

Carbon has two stable isotopes (^{12}C and ^{13}C) and one radioactive isotope (^{14}C, see below). Carbon-13 is an excellent tracer of carbonate

evolution in groundwaters, because there are large variations in the various carbon reservoirs (Clarke and Fritz 1997). Carbon isotope ratios are given as per mil (‰) relative to a marine carbonate standard (VPDB); marine carbonates have only limited variations in carbon isotope ratios.

$$\delta^{13}C\ (‰) = [(^{13}C/^{12}C)_{Sample}/\ (^{13}C/^{12}C)_{VPDB} - 1] \times 1000 \quad (7)$$

Carbon and oxygen isotopes in carbonate minerals have been used very successfully to reveal past temperatures, because long sequences of carbonates are preserved in chronological order in sediments and chemical deposits. Temperature-related variations, most commonly in the oxygen isotope ratios, are used to extract temperature records covering the period when the deposit was being laid down. The oxygen-isotope record from foraminifera in ocean cores has revealed in unparalleled detail the multiple succession of glacials and interglacials that have occurred in the Pleistocene (see, for example, Emiliani 1966). Hendy and Wilson (1968) pioneered the application of the method to stalactites from several New Zealand cave systems. They derived a detailed temperature record that revealed differences between Northern and Southern Hemisphere temperature histories.

Nitrogen has two stable isotopes (^{14}N and ^{15}N) that have been used to evaluate the sources and processes affecting nitrates in groundwater. This knowledge assists the development of effective management practices to preserve water quality and remediation plans for sites that are already polluted.

The average abundance of ^{15}N in air is constant, with $^{15}N/^{14}N = 1/272$. Nitrogen isotope ratios are reported in per mil (‰) relative to N_2 in atmospheric air, where

$$\delta^{15}N\ (‰) = [(^{15}N/^{14}N)_{Sample}/\ (^{15}N/^{14}N)_{AIR} - 1] \times 1000 \quad (8)$$

and AIR is the internationally accepted gas standard. Oxygen isotopes can also be measured in nitrate, and can sometimes provide more definite information on sources and cycling of nitrate in combination with nitrogen isotopes (Kendall and Aravena, 1999). New Zealand examples of the use of nitrogen isotopes to determine the source of nitrate in groundwater are described below for Canterbury and Waimea Plains.

Sulphur isotopes have been used particularly to determine the origin and fate of sulphate in groundwater, which is a subject of great interest in relation to the effect of "acid rain" on the environment (Krouse and Mayer 1999). Sulphur has four stable isotopes (^{32}S, ^{33}S, ^{34}S and ^{36}S), of which the two most abundant (^{32}S, ^{34}S) are chosen for measurement on the delta scale, defined as

$$\delta^{34}S\ (‰) = [(^{34}S/^{32}S)_{Sample}/\ (^{34}S/^{32}S)_{VCDT} - 1] \times 1000 \quad (9)$$

The standard is VCDT (Vienna Canon Diablo Troilite).

Robinson and Bottrell (1997) used sulphur isotopes to identify sources of sulphate in a number of New Zealand river catchments. Pristine rivers in the South Island (Buller, Wairau) and North Island (Hutt) contained two end-member mixtures of marine sulphate from rainwater and sulphate from oxidation of bedrock sulphides. Some Wairarapa rivers showed input of fertiliser sulphate (from "superphosphate"); in particular, results for the Ruamahanga River showed that the river removes 20% of the sulphate applied as fertiliser to the catchment. The Whangaehu River was shown to contain mainly volcanic sulphate from the Crater Lake of Ruapehu. Geothermal and rainwater sulphates were the main sources to Lakes Taupo and Rotorua via their tributary streams; Lake Rotorua outlets had a higher geothermal sulphate content than the inlets, showing an underwater geothermal input to the lake.

DATING MODERN GROUNDWATER

Good understanding of recharge, flow and storage volume is necessary for sustainable management of groundwater resources. One of the most important pieces of information for understanding groundwater resources is the age, or residence time, of the water underground. The age can give information on groundwater flow rates and paths, the sustainable yield of the resource, and buffering against drought. Furthermore, the age information al-

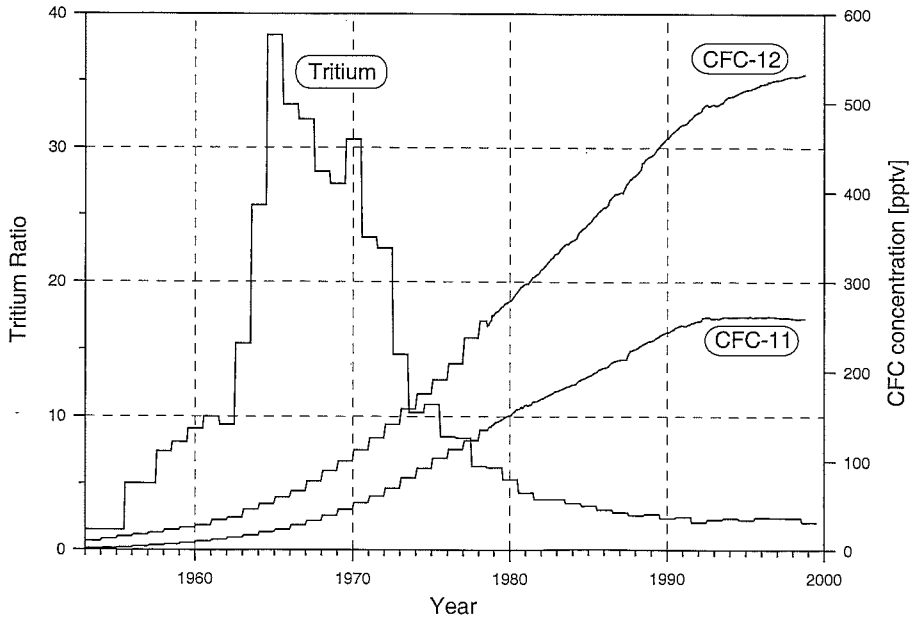

Figure 7.5: *History of tritium concentration in precipitation at Kaitoke, near Wellington, and CFC-11 and CFC-12 concentrations in the atmosphere in the Southern Hemisphere.*

lows assessment of the vulnerability of a groundwater resource to contamination; the fraction of young water gives a quantitative measure of the security of a groundwater resource against bacteriological contamination or against disasters (e.g. floods or volcanic ash). To obtain age information from groundwater, various isotopic and chemical tracers can be applied, depending on the age range and hydrogeologic conditions.

Tritium

The radioisotope tritium (half-life 12.3 years) is the standard dating tool for groundwater in the age range of recent to 100 years. It is the ideal tracer for groundwater because it is a component of the water molecule, and the age information is not distorted by any processes occurring underground, i.e. tritium is not affected by chemical or microbial processes, or by reactions between the groundwater, soil sediment and aquifer material. Tritium is naturally produced in the atmosphere by cosmic rays, but large amounts were also released into the atmosphere in the early 1960s during nuclear bomb tests, giving rain and surface water a high tritium concentration (Fig. 7.5). Surface water becomes separated from the atmospheric tritium source when it infiltrates into the ground, and the tritium concentration in the groundwater then decreases over time due to radioactive decay. The tritium concentration in the groundwater is therefore a function of the time (t) the water has been underground, i.e.

$$C_t = C_o \cdot e^{-\lambda t} \text{ or } t = (1/\lambda) \cdot \ln (C_o / C_t) \quad (10)$$

where C_o is the initial tritium ratio (in the rain water), C_t the tritium ratio in the groundwater after time t, and λ ($= \ln 2 / T_{½}$) the tritium decay constant.

Most applications of the tritium method involved tracing the tritium from nuclear weap-

ons tests through the hydrological cycle. However, since the mid-1980s, atmospheric tritium has declined to the natural cosmogenic level in most parts of the world. This allows tritium to be used now for groundwaters more straightforwardly as a "natural clock", using the decay equation (10), in combination with realistic age distribution models. Additional age information can be gained for very young groundwaters from the seasonal tritium variation, as peaks occur in spring due to an enhanced movement of tritium from the stratosphere to the troposphere.

As a result of the nuclear test peak in atmospheric tritium in the 60s, ages from single tritium determinations can be ambiguous (i.e. the tritium concentration can indicate any of three possible groundwater ages). This ambiguity can be overcome by making a second tritium determination after about 2 years, or by combining the single tritium determination with a second independent dating technique such as chlorofluorocarbons. The bomb tritium peak gives, on the other hand, waters with ages of 20-40 years a very distinct tritium signature that can be used to obtain very precise age information.

Very clear understanding of groundwater flow processes can be gained when historic tritium data (high tritium concentrations in the 60s and 70s) can be combined with recent data (natural levels). Such historic data are available from most of the main aquifers in New Zealand.

Further information about the tritium method is available in Clark and Fritz (1997) or Cook and Herczeg (1999). The tritium method has been applied to New Zealand groundwaters in several studies. In the first study, tritium data prior to the bomb-peak was used to indicate groundwater flow directions and residence times in the Heretaunga Plains aquifer (Grant-Taylor and Taylor 1967). This study also determined the residence time of groundwater in the main supply well in the Hutt Valley aquifer by tracing the tritium from individual bomb-test series. In Taylor and Stewart (1987), tritium data were used in a mixing model to derive mean residence times in the Rotorua geothermal aquifer. Following the bomb-peak period, tritium data were mainly used to distinguish between water recharged before and after1960, and attempts began to calculate groundwater ages for piston flow conditions (Taylor et al. 1989, 1992; Taylor 1994a). Tritium was also used to identify any fraction of recently derived water in old groundwater for carbon isotope studies (Taylor and Fox, 1996; Taylor and Evans 1999).

Sensitive and accurate methods for detecting tritium are needed to use low-level natural tritium as a tracer of the hydrologic cycle. Because of particularly low tritium concentrations in the Southern Hemisphere, a tritium measurement system with extremely high detection sensitivity is required. In New Zealand, the tritium measurement system has a lower detection limit of 0.03-0.04 TU (2-sigma criterion), using ultra low-level liquid scintillation spectrometry, and electrolytic enrichment prior to detection. Reproducibility of standard enrichment is 2%, and an accuracy of 1% can be achieved via deuterium-calibrated enrichment (Taylor 1994b). Tritium concentrations are expressed as tritium units (TU) or as a tritium ratio (TR). One TU (TR = 1) corresponds to one tritium atom per 10^{18} hydrogen atoms. The radioactivity equivalent for one TU in one kg of water is 0.118 Bq. The sampling procedure for tritium involves filling a one-litre bottle (avoiding air contact as much as possible because there is tritium in the air) and securely tightening the cap. No cooling of the sample during collection or transport is necessary.

Tritium – Helium-3 (^3H – ^3He)

Tritium-helium dating is a variant of tritium dating that allows unambiguous ages to be determined from tritium concentrations by using its daughter (helium-3) to eliminate the complicated tritium input function (Torgersen et al. 1979). The method gives good results and generally shows agreement with CFC dates (Ekwurzel et al. 1994), but is expensive and has not been used in New Zealand.

Chlorofluorocarbons and SF_6

Chlorofluorocarbons (CFCs) are entirely man-made contaminants of the atmosphere and hydrological systems. CFCs are used in-

dustrially for refrigeration, air conditioning and pressurising aerosol cans. Their concentrations in the atmosphere have gradually increased from zero in 1940 to the present levels of several hundred pptv (1 pptv is one part per trillion by volume or 10^{-12}). CFC-11 and 12 concentrations in the Southern Hemisphere are shown in Figure 7.5. Because the gases (CFC-11, CFC-12 and CFC-113) are relatively long-lived, they are widely distributed in the atmosphere. CFCs are slightly soluble in water and enter groundwater systems during recharge. Their concentrations in groundwater record the atmospheric concentrations when the water was recharged, thus allowing the recharge date of the water to be determined.

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, three dates are obtained (because there are three CFC species) and these can be compared, giving additional information. Thirdly, CFC concentrations can be measured accurately and relatively easily by modern gas chromatography. The main disadvantage is the relatively difficult sampling techniques required, because air must be rigorously excluded from the sample.

CFCs are now being phased out of industrial use because of their destructive effects on the ozone layer. Thus rates of increase of atmospheric CFC concentrations slowed greatly in the 1990s. This means that CFCs are not as effective for dating water recharged after about 1990.

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 ±2°C results in an error of ±1 year for water recharged before 1970 and ±1-3 years for water recharged between 1970 and 1990. (Plummer and Busenburg 1999).

Thickness of the unsaturated zone - CFCs can be transported more rapidly than water through the unsaturated zone 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 (Plummer and Busenburg 1999).

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, the ages may appear to be too young when very slight contamination occurs. 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.

Despite these potential problems, CFC measurements have given good results in New Zealand. Figure 7.6 shows CFC-derived recharge years for groundwater in Canterbury (Stewart et al. 1997, 1999). The CFC-11 ages are compared with the CFC-12 ages for data collected in 1997-2000. The dates when recharge occurred ranged from 1940 to 1999, with a small number of samples containing excess CFCs from local sources. An approximately linear trend between the results is observed, but the CFC-11 ages tend to be older than the CFC-12 ages.

The CFC results are compared with tritium

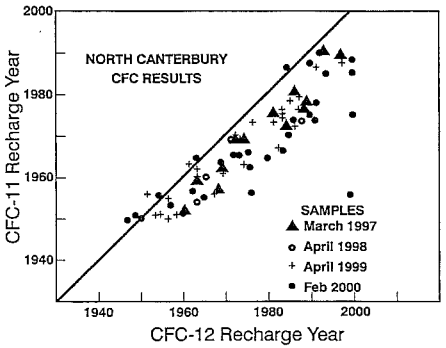

Figure 7.6: *Plot of CFC-11 recharge year versus CFC-12 recharge year for Canterbury groundwater.*

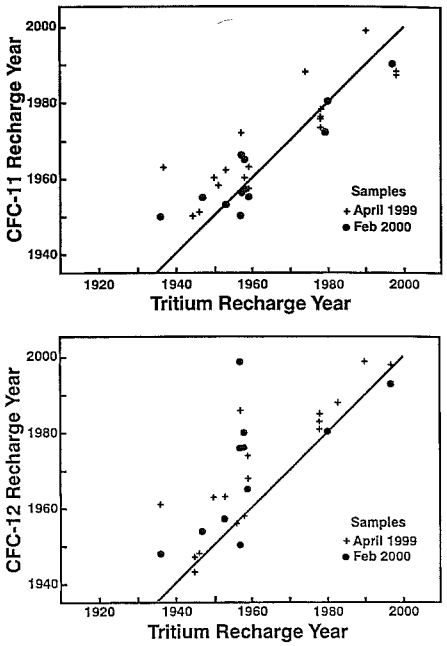

Figure 7.7: *Plot of CFC-11 and CFC-12 recharge years versus tritium recharge years for Canterbury groundwater.*

results in Figure 7.7. Ages were calculated for the tritium results assuming a mixing model with 80% piston flow and 20% exponential flow (see below for an explanation of these terms); ambiguous tritium ages were resolved by considering the hydrogeological conditions or by comparison with the CFC ages. CFC-11 and tritium ages show reasonable agreement, with points scattered about the concordant line, while the CFC-12 ages are generally younger than the tritium ages. This is probably due to a very slight contamination of the CFC-12 concentrations by local sources (at less than the "excess" levels).

Methods for dating groundwater using SF_6 are now being developed. SF_6 concentrations in the atmosphere have increased from zero in 1970 to the present. Concentrations are likely to continue to increase for some time because SF_6 is widely used in electrical switch gear. This should mean that SF_6 is especially useful for dating very young groundwater.

DATING OF OLD GROUNDWATER

Radiocarbon

Radiocarbon is the major tool for dating old groundwater (i.e. groundwater that has no tritium). ^{14}C (half-life 5730 years) is generated by cosmic rays in the atmosphere and introduced into living biomass by photosynthesis, and into the hydrosphere by CO_2 exchange reactions. Consequently, any carbon compound derived from atmospheric CO_2 since the late Pleistocene can potentially be dated by radiocarbon. Radiocarbon dating has provided the chronology used by archaeologists to decipher the history of humanity in the Holocene. It has also been used to provide the chronology of climate change in the late Pleistocene and Holocene.

^{14}C concentration or activity (a) is expressed as percent modern carbon (pmC), where the activity of "modern carbon" is taken as 95% of the activity in 1950 of the NBS oxalic acid standard. Groundwater dating by ^{14}C is complicated both by changes in ^{14}C activity in the atmosphere during the late Pleistocene and Holocene, and by dilution of ^{14}C in groundwater by dead (i.e.^{14}C-free) carbon derived from soils and rocks where carbon-bearing solutions penetrate underground.

Most of the ^{14}C in groundwater is gained from the soil, where CO_2 accumulates by root respiration and decay of vegetation. The ^{14}C in dissolved inorganic carbon (DIC) is susceptible to reaction and dilution with dead carbon from carbonate and other minerals in the soil and groundwater zones. A dilution factor q is used to take account of the resulting dilution of ^{14}C. The age equation is therefore written (in analogy with equation 10)

$$t = (1/\lambda) \cdot \ln (q \cdot a_o / a_t) \qquad (11)$$

where a_o is the initial ^{14}C activity ($q.a_o$ the diluted initial activity in the groundwater), a_t is the ^{14}C activity in groundwater after time t (i.e. when measured) and λ is the carbon-14 decay constant ($1/\lambda = T_{½} / \ln 2 = 8267$ years). The apparent simplicity of this equation is deceptive. Numerous methods have been proposed for estimating q, based on the chemical and ^{13}C composition of the groundwater. A widely accepted modern method involves modelling the geochemical and isotopic evolution of groundwater between initial and final points along a flow path using the *NETPATH* geochemical code (Plummer et al. 1994). This is best suited for regional confined systems where changes between sampling points can be observed.

New Zealand groundwater systems are often recharged by rivers, which impart a different initial ^{14}C signature and dilution factor to the groundwater. This is illustrated by ground-water in deep aquifers under Christchurch, which are recharged by the Waimakariri River (Taylor and Fox 1996). Because the water is recharged from the riverbed, thus largely bypassing the soil, it has low DIC (and other chemical) concentrations. Ages of up to several thousand years were determined for the deep groundwater beneath Christchurch.

Taylor (1997) developed a method for estimating a_o and q, based on the ^{13}C and DIC concentrations in the groundwater. This is applied in a study of deep groundwaters in Taranaki (Taylor and Evans 1999). The study identified Mt Taranaki as the major recharge area both today and for several tens of thousands of years in the past. Residence times of groundwater in the confined Tertiary sandstone/mudstone/shellbed aquifers ranged up to several tens of thousands of years.

APPLICATIONS TO NEW ZEALAND GROUNDWATER SYSTEMS

Isotopic studies of New Zealand hydrological systems have been carried out since the early 1960s, using most of the isotopic methods outlined above. In the following we have selected some New Zealand groundwater systems to illustrate the variety of problems that can be addressed using isotopic methods.

Canterbury Plains

Glacial outwash deposits of the major rivers have built up the Canterbury Plains from the Southern Alps, and fluvial episodes then redistributed the sediments. The plains extend over a 50 km wide by 150 km long area from Timaru to the Waipara River. Quaternary gravel aquifers are widespread and their thicknesses range from 250 m up to 600 m. Groundwater aquifers are unconfined or semi-confined under much of the inner plains, becoming confined near the coast, around Kaiapoi, Christchurch and Lake Ellesmere. Isotope methods are contributing greatly to understanding the recharge sources, residence times, nature of flow, and chemical history of the groundwater system.

Alpine rivers crossing the plains have high-altitude catchments and therefore low $\delta^{18}O$ values (c.f. equation 5) compared to the higher $\delta^{18}O$ values of precipitation on the plains (Taylor et al. 1989). $\delta^{18}O$ therefore serves as a fingerprint to distinguish river from rainfall-recharged groundwater via the equation:

$$f = (\delta_g - \delta_r)/(\delta_p - \delta_r), \qquad (12)$$

where f is the fraction of groundwater derived from precipitation, and δ_g, δ_r and δ_p are the $\delta^{18}O$ values of the groundwater, rivers and precipitation respectively. Note that δ_r and δ_p are the δ values of groundwater derived from the rivers and precipitation, rather than those of the rivers and precipitation themselves. Average $\delta^{18}O$ values of the alpine rivers (in brack-

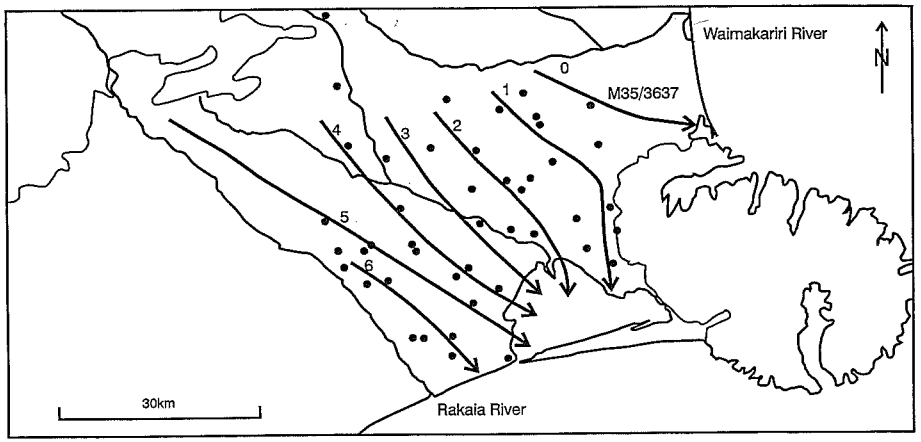

Figure 7.8: *Flowlines in shallow groundwater and sampling locations of CFC concentrations between the Waimakariri and Rakaia Rivers, Canterbury.*

ets) are, from north to south, Ashley (-9.4‰), Waimakariri (-9.4‰), Rakaia (-9.5‰) and Ashburton (-9.6‰) (Taylor et al. 1989). Their compositions are not expected to change much as they infiltrate the ground. Rainfall $\delta^{18}O$ values, however, are affected by soil processes because of higher evapotranspiration in summer than in winter, so δ values measured in water draining through the soil have been used for δ_p rather than the precipitation itself. These are about -7.7‰ near the coast (measured at Harewood Airport and Lincoln) and -9.0‰ inland (Hororata and in foothills rivers such as the Eyre and Selwyn) (Stewart 2001, unpublished data).

Fractions determined from equation 12 show that recharge from the alpine rivers dominates in fluvial gravel aquifers towards the coast, whereas recharge from rainfall and foothill rivers is predominant in the inter-fan areas. In particular, the deeper Christchurch aquifers are recharged by infiltration from the Waimakariri River in its Central Plains reaches, and are consequently protected from pollution as long as the river retains its present pristine condition (Taylor et al. 1989). On the other hand, shallow groundwater (including the unconfined and first confined aquifers under Christchurch) and water recharged to depth by precipitation and irrigation on the unconfined western areas of the Plains are susceptible to agricultural and other pollutants.

Residence times determined from tritium, carbon-14 and CFC concentrations reveal the flows in the groundwater systems (Taylor et al. 1989; Taylor and Fox 1996; Stewart et al. 1997, 1999). Horizontal flows in the near-surface layers are rapid, with very young waters emerging in springs on the west side of Christchurch and Kaiapoi. Vertical flows are more gradual, as they are driven by recharge rates. Taylor et al. (1989) showed that ground-water from deep aquifers under Christchurch had zero tritium. The isotopic and other evidence showed that old artesian groundwater underlying Christchurch ascends from deeper aquifers into the shallowest confined aquifer via gaps in the confining layers or by diffuse flow. Carbon-14 measurements have shown that the residence time of the deepest water under Christchurch is of the order of thousands of years (Taylor and Fox 1996).

Well M35/3637 is a deep well (140 m) located on the western edge of Christchurch, where the groundwater system becomes confined (flowline 0 in Fig. 7.8). It is ideally situated to help reveal the nature of water moving

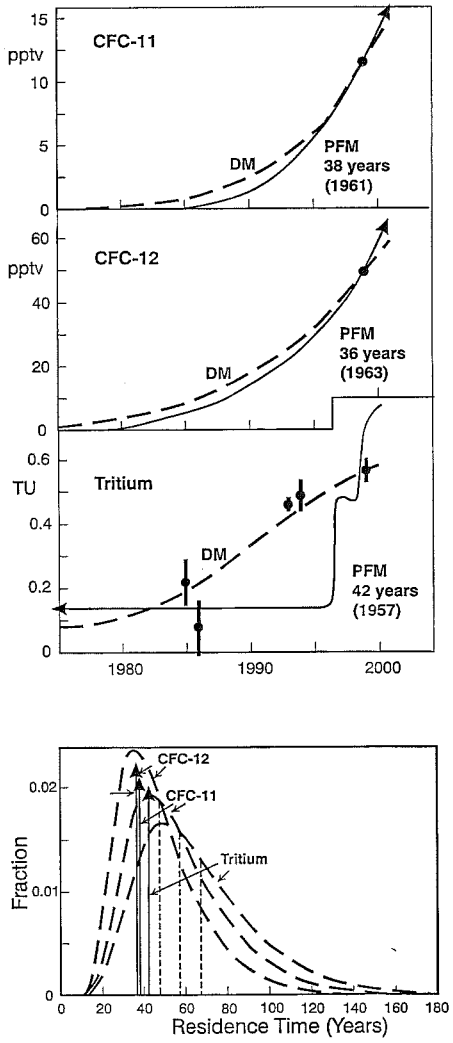

Figure 7.9: *Upper figure: Tritium, CFC-11 and CFC-12 concentrations versus time for well M35/3637. The dots are measured data, curves simulated data. PFM - piston flow model, DM - dispersion model. Lower figure: Residence time distributions for piston flow and dispersion models for well M35/3637.*

towards the important deep confined aquifers under Christchurch and how that water will change in the future. The $\delta^{18}O$ value of -9.33‰ shows that the water is derived from the Waimakariri River. It has very low concentrations of nitrate (0.21 mg/L NO_3-N) and other chemicals.

Five tritium measurements are available for this well between 1985 and 1999, so the age distribution of the water can be defined quite well. These are supplemented by CFC measurements in 1999. The measurements are plotted in Figure 7.9 (upper figure), along with simulations using the dispersion and piston flow models. The dispersion model (with τ = 68 years, D_p = 0.1) gives a reasonable match to all of the tritium points, whereas the piston flow model does not ($\tau \sim 42$ yr). Figure 7.9 (lower) shows the distribution of residence times (i.e. age spectra) of the models. The peak residence times of the dispersion models are about 40 years (in agreement with the piston flow models), but a considerable proportion of older water is also present, probably derived from a greater depth in the system. The results show that good quality but relatively young water (40 years old) is penetrating into the system en route to the deep aquifers under Christchurch. This will preserve the good quality of deep Christchurch water in the future.

CFC measurements have been made on groundwater in the areas between the Waimakariri and Rakaia Rivers (Fig. 7.8), Waimakariri and Ashley Rivers, and Rakaia and Ashburton Rivers (Stewart et al. 1997, 1999). Figure 7.8 shows the locations of wells sampled for CFCs, chemical compositions and other isotopes between the Waimakariri and Rakaia Rivers in 1999. The figure shows flow directions for the shallow aquifers. The CFC age data have been used to define constant age surfaces, showing that young water penetrates more deeply i.e. recharge is greater near the alpine rivers.

The source and age information from $\delta^{18}O$ values and CFCs have been used to validate a large-scale model of Canterbury groundwater flow (White et al. 1999). CFC measurements on eight pairs of wells allowed the travel times of the groundwater between the wells to be determined. These were compared with flow-

model predictions of the travel times. The CFC travel times ranged between 2 and 26 years, with a mean of 10.4 years, in good agreement with the flow-model predicted travel times of 4 to 25.5 years, with a mean of 9.9 years.

The history of chemical contamination of the groundwater is stored within the system and can be accessed by making age and chemical measurements on well waters. An increase in nitrate concentrations is apparent in the early 1950s, as shown by measurements on groundwaters of this age and younger; older groundwaters have low nitrate concentrations. The cause is likely to have been the intensification of farming in the post-war period. This early 1950s nitrate front is passing through the groundwater systems in accordance with their natural flow rates. While it is still observable in the Waimakariri–Rakaia and Waimakariri–Ashley groundwater regions, the front has already essentially passed through the more-rapidly flowing Rakaia–Ashburton groundwater region. Other fronts passing through the systems are those from the "nuclear weapons test" tritium peak in the mid-1960s and the CFC fronts of more recent years. $\delta^{15}N$ values indicate that the increase in nitrate concentrations in the 1950s was due to an increased use of inorganic fertilisers or to clover fixation. It is probable that increased dairy farming in recent years is introducing nitrate with $\delta^{15}N$ reflecting a larger proportion of manure sources.

Lower Hutt Valley

The Lower Hutt groundwater zone is an unconfined/confined aquifer system. The sediments infilling the Lower Hutt Basin include a thick sequence of alluvial gravels deposited by the Hutt River during successive Quaternary glaciations. Layers of fine sediments, which form confining layers for the artesian aquifers, break the succession of alluvial gravels. The major source of recharge to the Lower Hutt groundwater zone is flow loss from the Hutt River. Due to the large number of chemical and microbial analyses undertaken on municipal water supplies, groundwater quality is well defined and generally very good in terms of the drinking water standards (Ministry of Health 2000).

The artesian aquifers of the Lower Hutt basin provide about 35% of the greater Wellington region's water supply. They are recharged by the Hutt River, whose catchments extend 40 km north of Wellington, including the Kaitoke Regional Park at the southern end of the Tararua mountain range. This hydrological system has played an important role in the history of environmental isotope hydrology in the Southern Hemisphere. Environmental isotope data encompassing the period following atmospheric H-bomb tests (mainly 1952-62) are available from rainwater, rivers and groundwater. The long-term observation of tritium allows for understanding the water flow throughout the whole hydrological system from catchment to river, to aquifer, to outflow (Morgenstern, unpublished data).

The tritium signature in the Hutt River is smoothed compared to rain, and is very dependent on the preceding rainfall history. After heavy rain, the tritium signature in the river follows that of the rain, indicating that in rain periods the main component of the river water is derived directly from surface run-off. However, in periods of low rainfall, the main component of the river water at Kaitoke is up to 6 months old. The river water consists mainly of this old component after several days without rain.

The Lower Hutt groundwater system is recharged from the Hutt River between Taita Gorge and Kennedy-Good Bridge, about 7 km from the coast. Groundwater in the upper artesian aquifer (Waiwhetu Gravel) reaches wells at the coast in the centre of the valley after about 3.5 years, based on comparison of tritium records in the river and in a supply well at Hutt Park (Grant-Taylor and Taylor 1967). This is confirmed by matching the measured long-term tritium data from Hutt Park well with the output calculated with a mixing model. The best fit of the data is for groundwater flow mainly described by piston flow, with a portion of approximately 20% mixed flow represented by an exponential model. Modelling the tritium data from different wells results in the following

groundwater flow pattern and age structure. The age of the groundwater in the upper artesian aquifer in the centre of the valley is 0.5±0.2 years close to the recharge area at Avalon; 1.0±0.7 years 3 km from the coast at Waterloo; 3.5±0.5 years near the coast at Hutt Park; and 20±1 years 3 km offshore at Somes Island, in the aquifer extension under Wellington Harbour. The much older groundwater age at Somes Island, compared to onshore data, demonstrates slower flow beneath Wellington Harbour, which can be explained by a combination of lateral widening of the aquifer downvalley and leakage holes within Wellington Harbour near the Hutt River mouth i.e. less water flows through a wider aquifer cross section in the offshore section of the aquifer. The groundwater age near the coast on the western side of the valley is 22±1 years, much older than in the centre, and indicates a slower rate of groundwater flow along the western margin of the Hutt Valley. The age of the water in the deeper artesian aquifer (Moera Gravel) is older than 50 years at both the centre and the side of the valley near the coast.

Waikoropupu Springs, Takaka Valley

The Waikoropupu Springs, comprising the Main Spring and Fish Creek Springs, are the principal outflows from the Arthur Marble Aquifer (Chapter 21). The springs are New Zealand's largest and an impressive sight. They are karstic, tidal and slightly brackish. The springs emerge from Arthur Marble through a cover of Motupipi Coal Measures approximately 4 km south of Golden Bay and 13 m above sea level (Fig. 21.12a in Chapter 21). $\delta^{18}O$ is used to determine the sources of the water in the springs. Dating then helps to gain an understanding of the nature of the system.

Mueller (1992) identified three recharge sources to the Arthur Marble Aquifer—the Takaka River, tributary creeks in Central Takaka including the Waingaro and Anatoki Rivers, and rainfall on Arthur Marble where it outcrops or is covered by permeable rocks. The annual and overall average $\delta^{18}O$ values of these are given in Table 7.1, based on three and a half years of monthly sampling (Stewart and Williams 1981). There is a large difference between the $\delta^{18}O$ values of the Takaka River and rainfall on the Takaka Valley floor, providing a very effective means of discriminating between these sources

Mueller (1992) and Edgar (1998) gave estimates of the net flows to the aquifer (Table 7.2). Mueller estimated total recharge to be 23.4 m^3/s, of which 15.0 m^3/s was discharged by the Waikoropupu Springs and 8.40 m^3/s by submarine springs in Golden Bay. Edgar estimated that total recharge was 14.5 m^3/s (approximately matching the outflow from the springs) and there were no submarine springs (see also Doyle and Edgar 1998). Their recharge models are given in Table 7.2.

Average discharges from the Main Spring and Fish Creek Springs are 10.0 m^3/s and 3.2 m^3/s respectively (Chapter 21). Their average $\delta^{18}O$ values are consistently different: -7.38‰ for Main Spring and -7.64‰ for Fish Creek Springs (Table 7.1). This means that the two springs contain different proportions of the source waters. In particular, Fish Creek Springs contain proportionately more Takaka River water than the Main Spring.

We can calculate the $\delta^{18}O$ values expected for the spring waters from the flows and $\delta^{18}O$ values of the source waters (Stewart, Rosen and Thomas, unpublisahed data; see Table 7.2). Results for the Mueller (–7.72‰) and Edgar (–

Table 7.1 *Mean oxygen-18 concentrations of waters from the Takaka Valley.*

Feature sampled	$\delta^{18}O$ ‰				
	1976	1977	1978	1979*	Mean
Takaka River	-8.73	-8.75	-8.66	-8.53	-8.67
Rainfall	-5.41	-5.43	-5.27	-5.50	-5.40
Main Spring	-7.24	-7.31	-7.48	-7.50	-7.38
Fish Creek Spring	-7.53	-7.67	-7.69	-7.66	-7.64

* *Samples collected January to June only.*

Table 7.2 *Recharge models to the Arthur Marble Aquifer and resulting oxygen-18 values.*

Recharge Source	δ ¹⁸O ‰	Mueller Net flow m³/s	Edgar Net flow m³/s	Preferred Model: Main Spring m³/s	Preferred Model: Fish Creek Spring m³/s	Preferred Model: Total flow m³/s
Takaka River sinks	-8.67	11.0	8.0	3.3	4.7	8.0
Sinks in tributary creeks	-7.20	10.2	4.3	5.0	3.3	8.3
Takaka Valley rainfall	-5.40	2.2	2.2	1.7	1.5	3.2
Total recharge flow (m³/s)		23.4	14.5	10.0	9.5	19.5
Weighted mean δ¹⁸O (‰)		-7.72	-7.74	-7.38	-7.64	-7.51

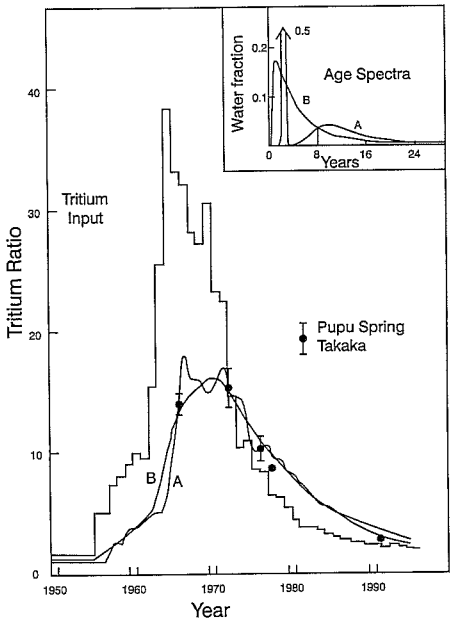

Figure 7.10: *Tritium concentration in the atmosphere and in Waikoropupu Springs from 1950 to 1995. Two models (A and B) are fitted to the data. The inset shows the distribution of residence times in each model.*

7.74‰) recharge models do not agree with the measured values for either the Main Spring or Fish Creek Springs and therefore the models are not feasible. A new model that matches the output of the Main Spring and the observed δ¹⁸O values of the springs, and keeps the input of Takaka River water to the measured amount (8.0 m³/s; see Chapter 21), produces too much Fish Creek-type water (9.5 m³/s instead of 3.2 m³/s). The remainder of at least 6.0 m³/s must be discharged offshore via submarine springs or seeps.

At low flows, when the Fish Creek Springs dry up and the Main Spring flow is reduced, the δ¹⁸O value of the Main Spring becomes more negative, like that of the Fish Creek Springs (Stewart and Downes 1981). In combination with the δ¹⁸O difference between Main and Fish Creek Springs, this suggests that Takaka River-derived water flows preferentially over the top of the Arthur Marble aquifer and/or through larger solution cavities that occur in the upper parts of karstified carbonate rocks.

Measurements of the tritium concentrations in the Main Spring show that the peak residence time of the water is about one year (Stewart and Downes 1981). Figure 7.10 shows the input, measured, and simulated tritium concentrations for two mixing models. The inset shows the residence time distributions of the mixing models, both of which show a high degree of mixing. Such high mixing reflects dual porosities in the aquifer and is typical of karst systems (e.g. Rank et al. 1992). Connected porosity occurs in the small-scale fissures and the porous matrix that provides much of the storage in the system and contributes to baseflow. This provides a large fraction of much older water, so that the mean residence time of the water is eight years. A second porosity is demonstrated by the peaks at about one year in Fig. 7.10, which show that part of the Main

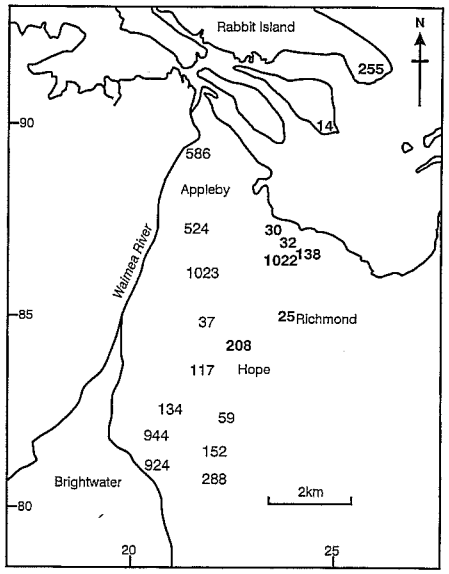

Figure 7.11: *Map of the Waimea Plains, Nelson, showing locations of wells referred to in the text. Wells penetrating the Lower Confined Aquifer are in bold.*

Spring discharge is delivered to the springs through a high-velocity conduit system in the upper levels of the Arthur Marble Aquifer. Takaka River contributes to this flow of young water.

A short flow-through time for Takaka River water is corroborated by the monthly δ¹⁸O measurements (Stewart and Downes 1981). Fish Creek δ¹⁸O showed a recognisable decrease 1.2 years after the δ¹⁸O of the Takaka River went through a pronounced decrease in the winter of 1977. No corresponding decrease was found in the δ¹⁸O of the Main Spring, but this is to be expected if the Takaka River contributes much less water proportionately to the Main Spring than to Fish Creek Springs, as concluded above.

The conceptual model that arises from the isotopic work is one of water penetrating deeply into the Arthur Marble Aquifer from recharge on both sides of the valley where the marble outcrops or is covered by permeable rock. The sources are the mid-valley tributary streams and direct rainfall. Flow is driven by the higher water levels on the flanks of the valley and the water has long residence times in the very large marble reservoir. On this "floats" water from Takaka River, which passes more rapidly through the larger solution cavities in the upper part of the karstified marble. Some of this reaches the springs, but much of it travels down the valley and is discharged in seeps or springs offshore. The Main Spring draws water from deeper in the aquifer than the Fish Creek Springs and hence discharges more of the water from the flanks of the valley.

Waimea Plains

The Waimea Plains, southwest of Nelson City, is an area of intensive farming and horticulture (Fig. 7.11). Groundwater from unconfined and two major confined aquifers are used extensively for irrigation. The Lower Confined Aquifer also supplies a large part of the Richmond Borough Council water supply. Water quality is generally good, except for nitrate concentrations, which exceed the Ministry of Health's recommended upper limit for potable waters (50 g/m³ nitrate, or 11.3 g/m³ nitrate-nitrogen). We have used δ¹⁸O to determine the sources of recharge to the groundwater and δ¹⁵N to investigate the source of the nitrate–knowledge that is important for management of the groundwater resource.

The hydrogeology of the area is summarised in Fig. 21.4 of Chapter 21. The unconfined aquifers are within the Appleby Gravel and the Pugh Gravel Member, adjacent to the coast between the Waimea River delta and Richmond. Hope Minor Confined and Unconfined Aquifers occur to the east of the plains. Two large lenses of sorted gravel within the Hope Gravel are, on the basis of their depth beneath the surface, divided into two major units: the Upper Confined Aquifer and the Lower Confined Aquifer (Dicker et al. 1992).

The predominant source of recharge for each well was assigned on the basis of its δ¹⁸O value (Stewart et al. 1981). Wells with river recharge have δ¹⁸O values in the range -6.8 to -7.4‰ with a mean of -7.02 ± .19‰: this is the same as the Waimea, Wai-iti and Wairoa Rivers,

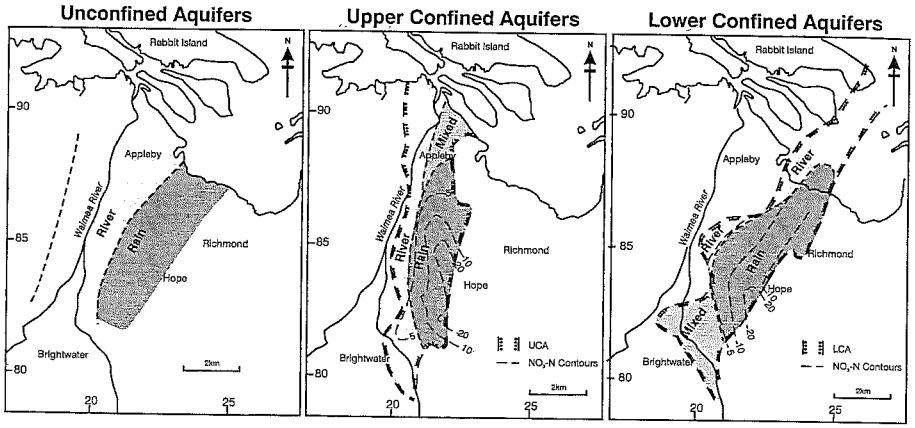

Figure 7.12: *Recharge sources of groundwaters in the Unconfined aquifers, Upper Confined Aquifer and Lower Confined Aquifer of Waimea Plains, Nelson, based on $\delta^{18}O$ to identify river, rainfall or mixed recharge, indicated by shading. Dashed lines show NO_3-N contours for the Upper Confined and Lower Confined aquifers.*

which have $\delta^{18}O$ = -7.1‰ on average. These wells have low nitrate-N concentrations (mean 2.9 ± 2.4 g/m³). Wells with rainfall recharge have $\delta^{18}O$ values in the range -6.0 to -6.6‰ with a mean of -6.44 ± .15‰, in comparison with a measured value for rainfall of -6.2‰. Nitrate-N concentrations vary widely, but contain the highest values observed in the plains (mean: 10.1 ± 6.5 g/m³). Wells with mixed river and rainfall recharge have intermediate $\delta^{18}O$ values (range: -6.6 to -7.0‰, mean: -6.79 ± .12‰) and more equal quantities of river and rainfall recharge. Mean nitrate-N concentration is 7.1 ± 0.7 g/m³.

Fig. 7.12 shows the areal distributions of these recharge sources for each aquifer unit. The unconfined aquifers are recharged by river water near the Waimea and Wairoa rivers, and by rainfall to the east of them. The Upper Confined Aquifer is recharged by the Waimea River in a narrow strip along the river, then gains mixed recharge in the north, where there is no distinction between the Upper Confined Aquifer and the unconfined aquifers. Recharge is mainly from rainfall on the east, away from the rivers. The pattern of recharge for the Lower Confined Aquifer is more complicated. The south zone, adjacent to the Wairoa River, has mixed recharge, showing that the aquifer is not connected to the surface and recharge is from the overlying Upper Confined Aquifer from both river and rain sources. The Waimea River recharges a zone in the middle of the Valley, where the Upper and Lower Confined Aquifers are in contact, and the water flows northeast to the offshore part of the Lower Confined Aquifer (Bells and Rabbit Islands). Rainfall recharge is received from the Upper Confined Aquifer near the Hope area. This water also flows northeast, but does not reach far offshore, probably because of water extraction by wells near the coast and inland. Some influence from this water is seen at Bells Island, however.

Understanding the recharge sources sheds light on the sources of nitrate in the Upper and Lower Confined Aquifers. Clearly nitrate is low in the river-recharged parts of the aquifers and high in rainfall-recharged parts near Hope and northeast of it.

Further understanding can be gained from other geochemical parameters (Fig. 7.13). Sulphate shows a good correlation with nitrate-N for most of the area shown in Fig. 7.11, including all of the Lower Confined Aquifer samples. The correlation can be explained by mixing of groundwater enriched in nitrate and sulphate with groundwater low in nitrate and sulphate. Furthermore, the enriched end member must be a body of water that has a uniform composition and therefore has been resident in the aquifers for a considerable time. The samples that deviate from the line are from the unconfined aquifers or Upper Confined Aquifer in areas away from Hope.

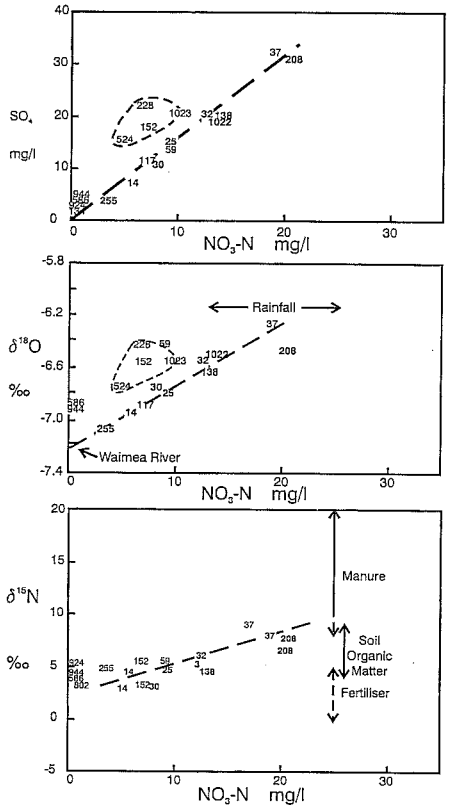

Figure 7.13: *Plots of sulphate, $\delta^{18}O$ in water and $\delta^{15}N$ in nitrate versus nitrate-nitrogen concentration for Waimea Plains groundwaters. The numbers are TDC well numbers (Lower Confined Aquifer wells are in bold). The $\delta^{15}N$ ranges of possible nitrate sources are shown.*

$\delta^{18}O$ versus nitrate-N shows a similar correlation to that with sulphate. The mean $\delta^{18}O$ values of rainfall and Waimea River are shown. Rainfall-derived groundwater enriched in NO_3-N mixes with river water low in NO_3-N to produce the correlation. The sources of the elevated levels of nitrate are clearly distributed on the ground surface in the general region of Hope. Rainfall infiltrating into the Upper Confined Aquifer in the vicinity of Hope carries nitrate at consistent concentration levels through to the Lower Confined Aquifer.

The $\delta^{15}N$ values of possible nitrate sources are shown in the third diagram in Figure 7.13. The sources can be clearly distinguished by their $\delta^{15}N$ values. Inorganic fertilisers have low $\delta^{15}N$ values (0-5‰), natural soil organic matter has values of 4-9‰ and manure has values of 8-20‰ (Sheppard and Lyon 1996). The plot shows that nitrate is from soil organic matter or inorganic fertilisers at low nitrate concentrations, but $\delta^{15}N$ trends towards manure values as nitrate increases. This shows that the high nitrate concentrations are derived mainly from manure sources. In the Hope region, market gardening is widespread and large quantities of chicken manure have been applied to the soil to improve growth, particularly in the 1970s and 1980s. There was also a large piggery in the area until recent years. The market gardens and piggery are the likely sources of much of the nitrate.

Tritium and CFC concentrations have shown that the waters in the Lower and Upper Confined Aquifers have very wide age distributions, as extensive mixing has occurred (Stewart, Thomas and Rosen 2001). The current nitrate concentrations reflect events that occurred in the 1970s and 80s. Refinement of the age dating will give more information on the history of nitrate contamination.

Security of groundwater drinking water supplies

The age of groundwater is a good indicator of its likely biological safety for drinking water. During the time spent underground bacteria and viruses decay, and in addition are affected by filtration and dilution due to flow of the groundwater through a porous medium.

Groundwater comprises a mixture of water of different ages due to mixing processes underground. Therefore the groundwater doesn't

usually have a discrete age, but has an age distribution or spectrum. Various mixing models with different age distributions describe different hydrogeological conditions (Maloszewski and Zuber 1982). The piston-flow model describes systems with little mixing (such as confined aquifers and river recharge), while the one-box, or exponential model, describes fully mixed systems (more like unconfined aquifers and local rain recharge). 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 conditions with only two parameters (the first is the average residence time (τ) and the second the dispersion parameter (D_p), which is a measure of the spread of ages). Those parameters applying to a particular well are chosen to give the best match to the measured data. If information about the hydrologic conditions (and therefore the degree of mixing) is scarce, a minimum of two measurements of either tritium or CFC concentrations, separated in time, is needed to determine the parameters and uniquely specify the age spectrum.

The degree of mixing is specified by the dispersion parameter. A small dispersion parameter (e.g. 0.01) describes a system with a small degree of mixing, as in piston-flow. The distribution of residence times in this case is a symmetrical but very narrow bell-shaped curve. An intermediate value of the dispersion parameter (e.g. 0.1) describes a medium degree of mixing and the distribution of residence times looks like a skewed bell-shaped curve (Fig. 7.9b). A high dispersion parameter (e.g. 1.0) describes a highly mixed groundwater and the distribution of residence times has similarities to an exponential distribution i.e. the distribution is very skewed towards young ages (Fig. 7.10 inset).

What is important for drinking water safety is the fraction of water that is less than one year old, because one year or more is long enough for bacteria and viruses to decay (Ministry of Health 2000). This fraction can be determined from the parameters of the dispersion model fitted to tritium or CFC data. It is denoted by the symbol yf (for "young fraction") and given by

$$yf = \int_0^1 g(t)\, dt \qquad (13)$$

where g(t) describes the age spectrum (Maloszewski and Zuber 1982). A yf of 100% means that all of the water has been underground for less than one year and 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 that 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.

Wells from the Canterbury region with two or more tritium measurements show the use of the method. The Environment Canterbury well numbers are M35/0443, M35/0444, M35/0480 and the tritium results and dispersion model simulations are given in Figure 7.14. Wells M35/0443 and M35/0444 had high tritium concentrations in the 1970s, showing that the waters have mean residence times of 4 and 5 years respectively and a dispersion parameter (D_p) of 0.6. These give young water fractions (yf) of 7.5% and 5.1%, so the well water supplies are not secure. The two tritium measurements from well M35/0480 are fitted with a dispersion model, with a mean residence time of 16 years and D_p of 0.001. The young water fraction is yf = 0.00% and the well water supply is thus secure. Tritium measurements in the 1980s, when much higher tritium concentrations occurred, are especially diagnostic of the model parameters (Fig. 7.14). The dating techniques demonstrate differences in groundwater flow and security, even though all three wells are in the same coastal Waimakariri-Ashley region.

Well M35/3637, on the western edge of Christchurch, is more typical of deeper wells

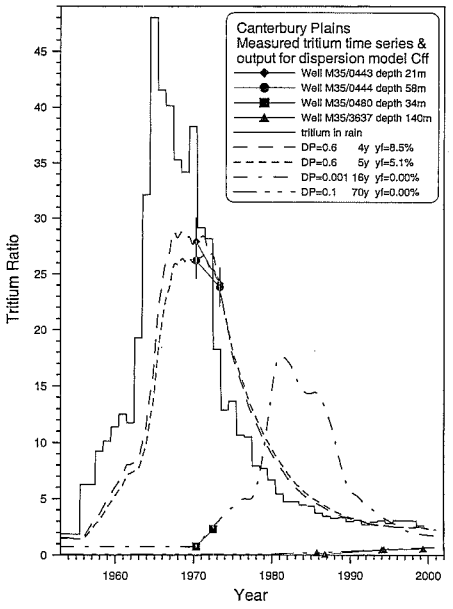

Figure 7.14: *Simulated tritium series for selected age and dispersion parameters compared to measured tritium data for four Canterbury wells.*

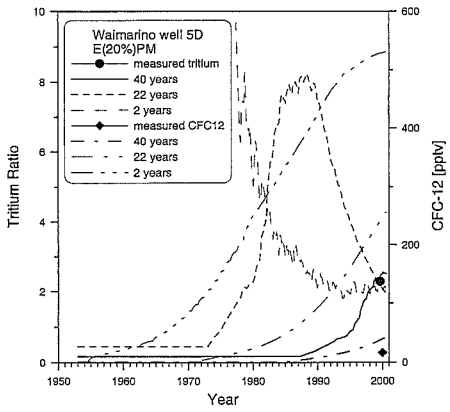

Figure 7.15: *Plot of tritium and CFC-12 measured concentrations and simulated time series for Waimarino well 5D.*

between the Waimakariri and the Rakaia Rivers. Five tritium measurements were made between 1985 and 1999, and CFC measurements were made in 1999. The mean residence time of water is 68 years and D_p is 0.1. These give yf = 0.00% and the well water supply is secure

The tritium concentration of a sample from the Waimarino well (5D) from the Lake Taupo Basin gave an ambiguous age; the age could have been 2, 22 or 40 years (Fig. 7.15; all three simulations pass through the tritium measurement marked by a filled circle). In contrast, only the 40-year simulation fits the CFC-12 measurement; waters younger than this have higher CFC concentrations and older waters have lower concentrations. The CFC-12 result thus shows that the tritium age of 40 years is the correct one. This gives yf = 0.00% and shows that the well water supply is secure. In this example, we have assumed a particular age distribution model because there was only one tritium and one CFC measurement. The model (labelled E20%M) was assumed to be fully mixed in 20% of its volume (representing the recharge portion of the hydrological system) and non-mixed in the remaining 80% of the volume. This is roughly equivalent to a dispersion model with $D_p \sim 0.2$.)

SUMMARY

Isotope studies are coming of age and beginning to fulfil their promise as probes of groundwater systems, both because of gradual improvement in analysis methods and because of the introduction of new methods such as CFC dating. This chapter has described the background and application of environmental isotopes and CFCs that have found most use in New Zealand. Improvements in measuring tritium, combined with the decay of the nuclear testing peak, have improved the effectiveness of tritium for dating recent groundwater. CFC dating has also proven effective, and CFC and tritium dates have shown agreement for Canterbury groundwater. Radiocarbon dating has been applied to some old groundwaters in a number of New Zealand groundwater systems.

Stable isotopes have been used to help identify recharge sources of groundwaters in Can-

terbury, Takaka Valley and Waimea Plains, and the source of nitrate in Canterbury and Waimea Plains groundwater. Age-dating has proven to be a reliable method of determining flow rates in groundwater systems. The results are contributing to improved conceptual models of the systems and have assisted validation of a large-scale groundwater flow model of the Canterbury Plains. The history of water quality changes in the groundwater systems can be investigated by combined age-dating and chemical measurements, as illustrated for Canterbury and Waimea Plains groundwaters. Age-dating is proving to be a reliable method of establishing whether a groundwater supply is secure against contamination by pathogens and thus suitable for drinking water supplies.

As more data is accumulated, monitoring of environmental isotope data is expected to become more valuable, because trends in water ages will reveal changing flow patterns resulting from exploitation of the resource. For example, a trend of decreasing ages in water from deep aquifers under Christchurch over time could show recharge by young water, while increasing ages over time could show that older water is being drawn from greater depth or from offshore parts of the aquifer. Also improvements in techniques such as development of SF_6 dating will allow more precise information to be gained.

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