

Chapter 12 - Environmental Isotopes

Introduction

Two of the fundamental things we need to know about groundwater are where has it come from, and how long has it been underground. The most common way of determining its origin and residence time below the surface is by using natural and man-made tracers. These tracers are substances which accompany the water molecule from the upper atmosphere through the deepest aquifers.

Groundwater tracers include dissolved gases and isotopes of atoms associated with water. Various methods have been applied in Marlborough over the past 40 years or so to help answer these questions and these powerful but cost effective tools have helped unravel the mysteries of groundwater flow in Marlborough. It is not uncommon for the only information about groundwater to come from a well or for a newly discovered aquifer system to be its chemical or isotopic properties.

Because tracers require specialist laboratories to analyse and interpret their presence, investigations usually involve a collaborative approach between the DSIR, or their modern equivalent GNS Science and the MDC.

Environmental isotopes

Some elements such as oxygen have more than one atomic species and these are called isotopes. For example naturally occurring oxygen has three stable isotopes: ^{16}O , ^{17}O and ^{18}O , and many radioactive isotopes.

Isotopes can either be radioactive, which means they decay over time, or stable meaning they do not decay. Some radioactive isotopes have half-lives of only seconds or minutes, whilst others decay slowly over periods of thousands of years.

Isotopes originate from a variety of sources both natural and man-made. All of the stable isotopes and some of the radioactive types have been present since the formation of the earth over 4 billion years ago and are called primordial isotopes (The AAEC - 1978). Another category are cosmogenic isotopes which are continually created by interaction between the earth's atmospheric gases and the sun's rays.

Humans have also been responsible for adding isotopes to the environment through the atmospheric testing of nuclear weapons in the 1950s and 1960s. These fall-out products were released into the upper atmosphere and fell to earth in rainfall. There are also inadvertent releases of isotopes such as the Chernobyl accident in 1986.

Stable isotopes are used to reveal the origin of groundwater or other components such as nutrients. Because radioactive isotopes change their mass over time, they are used as clocks to determine the residence times of water underground (Rosen & White - 2001).

Generally, isotope results are far more meaningful as a series of measurements in space or time rather than in isolation. In other words, a single measurement is of limited value unless there are repeat measurements or observations at different locations within a catchment. Their hydrological meaning is normally interpreted in a regional context alongside other information and in particular the chemistry of the groundwater.

Stable isotope methods

Stable isotopes are conservative in nature. Once they enter groundwater they aren't modified by natural processes such as reduction or oxidation. This makes them ideal tracers to identify and track the source of groundwater recharge or its flowpath.

They are also commonly used to identify the origin of nutrients in groundwater such as nitrates. The way they are used and interpreted differs slightly in each case, but they rely on differences in the chemical or physical behaviour of different isotopes. To compare values from around the world they are expressed as a ratio relative to an internationally recognised standard.

Oxygen-18 ($\delta^{18}\text{O}$)

The two most commonly applied stable isotope tracers in hydrological studies in Marlborough are oxygen-18 (^{18}O) and deuterium (^2H). Because they form part of the water molecule, they are almost ideal tracers.

The oxygen isotope method relies on the preferential increase in the lighter isotope molecule (H_2^{16}O) compared to the heavier isotope molecule (H_2^{18}O). The ratio of the two molecules changes as water undergoes changes in state from liquid to vapour or solid, and back to liquid as it moves through the hydrological cycle. Separation of isotopes during phase changes (isotopic fractionation) is affected by temperature, with greater fractionation at lower temperature.

Results are expressed as differences between the ratios of the two isotopic molecules compared to an international standard known as the Vienna Standard Mean Ocean Water (VSMOW). Because of the way this difference or delta (δ) is defined in units of parts per thousand (‰), seawater has a $\delta^{18}\text{O}$ value of 0‰ and freshwaters have negative values because they contain less ^{18}O than water in the sea.

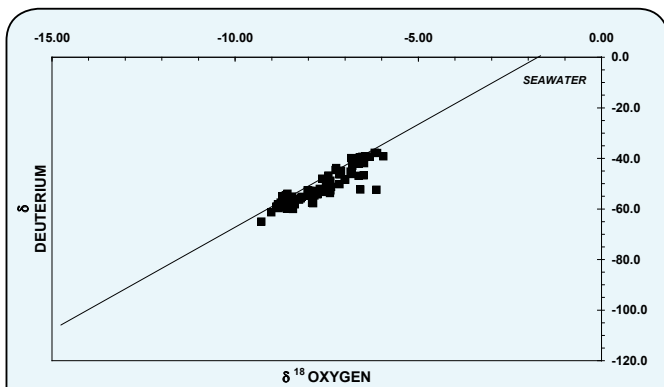


Figure 12.1: Deuterium and Oxygen-18 values for Marlborough freshwaters. Seawater is near the top right hand corner, with the most negative values furthest to the left representing water that has originated at high altitude in the alpine catchments of the Upper Wairau River. This high altitude water has evolved from seawater whereas values closer to the origin are locally derived runoff from low altitude hills or rainfall. Local factors other than condensation can cause the ratio to diverge from the global relationship. The two values to the right of the line represent samples from Wairau Valley whose $\delta^{18}\text{O}$ values have been modified locally through evaporation.

Ocean water is constantly being evaporated to form water vapour which rises and condenses as it moves inland as cloud, before falling to earth as rain or snow. It then recharges aquifers directly, or after running off into rivers which lose flow to groundwater. If condensation and precipitation are the only processes involved, then the isotope ratio is fixed and samples fall on a straight line known as the global meteoric line. All values worldwide match the global meteoric line but their exact position will vary depending on local factors. As a rule of thumb $\delta^{18}\text{O}$ values are more negative in winter and at higher altitudes or latitudes.

This isotope tool is the most widely used under Marlborough conditions with measurements from the late 1960s onwards. Between 1968 and 1984, tritium and $\delta^{18}\text{O}$ measurements of 125 water samples from wells, springs and rivers in the Wairau Catchment were made by the DSIR as part of hydrological investigations.

The Oxygen-18 method has been used to confirm the source of recharge for the Rarangi Shallow Aquifer which is overwhelmingly from rainfall (GNS Science - 2004) and (Taylor - 2004). This method also demonstrated that Wairau River channel flow normally plays a minor role in recharging riparian aquifers at Kaituna (Taylor - 2004), and on the south-bank at Wairau Valley (Taylor - 2003).

Sufficient $\delta^{18}\text{O}$ results have been collected to also define characteristic signatures based on their mean value. For example the mean $\delta^{18}\text{O}$ value of Wairau River water is -8.86‰ and lowland rain is -7.01‰ (Fig. 12.1). Care is needed however, when applying these representative figures because large variations in individual measurements do exist.

An example of this is the $\delta^{18}\text{O}$ values of rainwater collected in early 2010 from the roof of the MDC Seymour Square office of -8.31‰ and -8.57‰ which differ markedly from the mean value of -7.0 . The likely explanation is the differing composition of water forming these weather systems. This example highlights the natural variability of individual measurements relative to the mean. To account for this variability, ranges are given as a guide in Table 12.1.

Experience from across Marlborough aquifers shows that $\delta^{18}\text{O}$ values are relatively constant over time in medium depth groundwaters. Shallow aquifer values are more likely to vary significantly and mirror river or rainfall values. The $\delta^{18}\text{O}$ values associated with river water tend to be more consistent than rainfall values.

Water Source	Mean Delta ^{18}O Range (‰)
Predominantly Wairau River recharge	-8.6 to -9.2
Wairau River with some rainfall recharge	-8.0 to -8.6
Rainfall with some Wairau River recharge	-7.4 to -8.0
Predominantly rainfall recharge	-6.8 to -7.4

Table 12.1: Average Wairau Plain $\delta^{18}\text{O}$ ratios

Sources of Wairau Plain groundwater

The use of isotope tracers and dating methods have been central to developing the current understanding of regional groundwater flow patterns beneath the Wairau Plain. This extract from the 2006 GNS Science review of the Oxygen-18 measurements collected since the 1960s, succinctly summarises what they tell us about the behaviour of the predominant Wairau Aquifer system:

"In the west and close to the Wairau River, groundwater has $\delta^{18}\text{O}$ values like that of the river. With distance from the river and towards the coast, the $\delta^{18}\text{O}$ values of shallow groundwater in the unconfined aquifer become more positive as land surface recharge with less negative $\delta^{18}\text{O}$ values contributes to flow. The infiltrating surface water carries nitrate and other landuse related chemicals downwards to groundwater. At deeper levels, the groundwater is unaffected by water infiltrating from the surface, and retains its distinctive river $\delta^{18}\text{O}$ signature when it rises to the surface near the coast."

Contributions from local rainfall resulting in less negative $\delta^{18}\text{O}$ values become more significant on the margins of the main Wairau Aquifer at Rarangi and in the side valleys such as at Tuamarina. In the Southern Valleys catchments recharge is from either rainfall or losses from local ephemeral rivers such as the Omaka, Fairhall and Taylor Rivers.

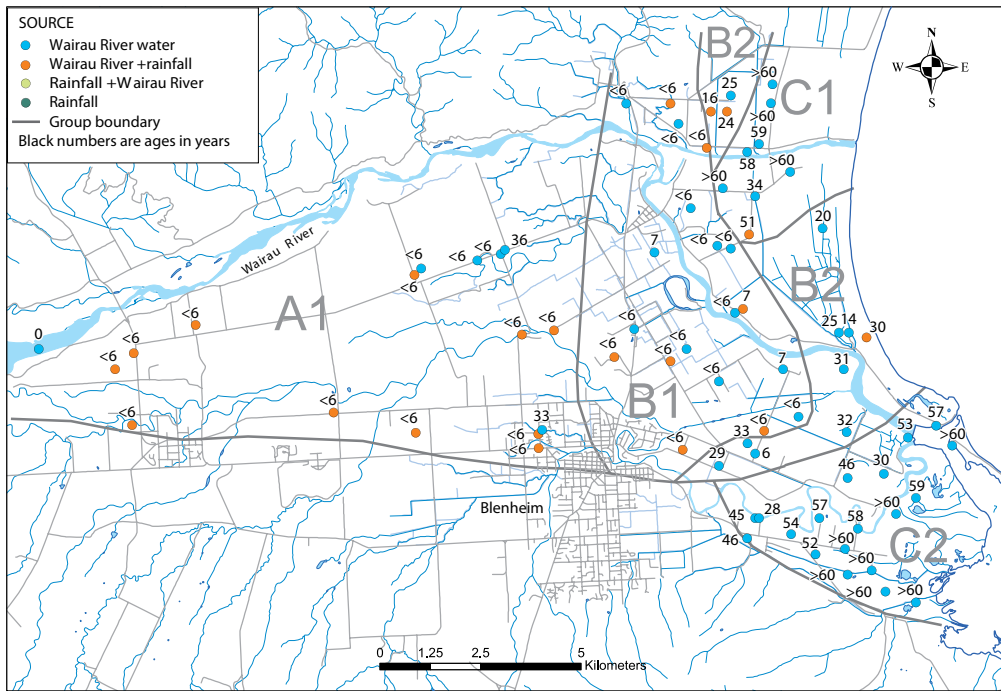


Figure 12.2: Northern Wairau Plain groundwater residence time and recharge source

These patterns are illustrated by Figure 12.2 for Wairau River recharged groundwater and Figure 12.3 for the Southern Valleys and Rarangi. The coloured dots denote the source of recharge and the number, the age of groundwater from that well in years. How these groundwater ages were derived is discussed in detail in the following section on tritium.

The Wairau Aquifer is subdivided into three age based sectors. Young recently recharged groundwater of less than about five years characterises sector A and is dominated by Wairau River recharge water close to the present day channel.

Old groundwater with residence times of 50 years or more typifies sector C. These groundwaters started life as Wairau River losses north-west of Renwick, and have travelled a much deeper flowpath through the less permeable Speargrass Formation which has isolated them from surface influences. They have retained their Wairau River signature despite having traversed beneath the entire length of the Wairau Plain.

As Cloudy Bay is approached, water is forced upwards through

the confining layer to become flow in the Opawa River, Diversion or the many wetlands in the coastal area. The ages of groundwater at Rarangi and Riverlands are symmetrical about a line bisecting the middle of the Wairau Plain from east to west. This reflects similarities in geology and aquifer structure.

Intermediate aged groundwater is associated with sector B beneath the central Cloudy Bay coast and shows that local gravels transmit groundwater more rapidly because they

are thicker or more permeable than at Riverlands and Rarangi. This sector has a confined structure, but still contains relatively young water compared to group C.

The green dots indicate that a mix of river and rainfall recharge is supplying wells tapping the complex Taylor River Fan aquifers. The grey horizontal boundary marks the dividing line between predominantly Wairau River recharged groundwater to the north and the Southern Valleys Catchment dominated groundwaters to the south.

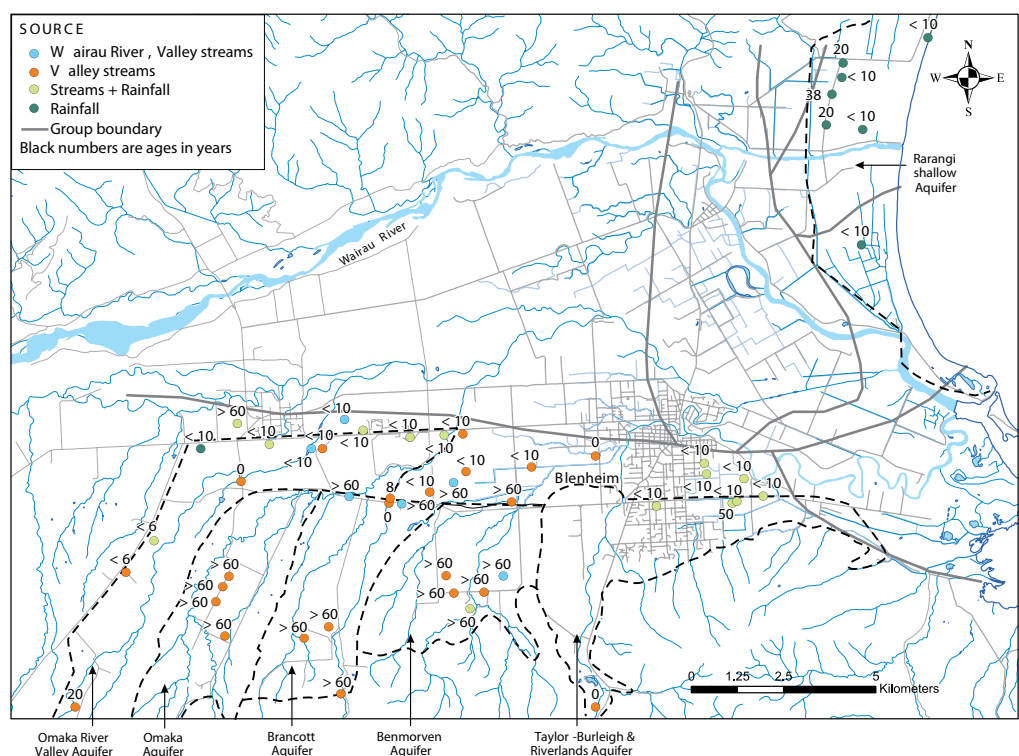


Figure 12.3: Southern Wairau Plain groundwater residence time and recharge source

These results are consistent with the flow patterns indicated by groundwater chemistry and well water level surveys. Together they form a unifying concept of Wairau Plain groundwater flow. As a rule, younger groundwater is associated with permeable gravel formations and unconfined aquifers, while older water is found in confined aquifers.

Because $\delta^{18}\text{O}$ generally retains its signature over thousands of years, it was used to identify high altitude derived water from the Wairau River or Waihopai River as the source of recharge for the Deep Wairau Aquifer in 1998, with residence times of tens of thousands of years (Taylor - 2000).

Nitrogen-15 ($\delta^{15}\text{N}$)

Another isotopic tool that has been used successfully locally to identify the source of nitrates is Nitrogen-15. The relative abundance of the heavier nitrogen isotope Nitrogen-15 (^{15}N) to Nitrogen-14 (^{14}N) compared to N_2 in air is expressed in parts per thousand relative to the international standard (Stewart et al - 2001).

The Nitrogen-15 ($\delta^{15}\text{N}$) value of nitrate-nitrogen depends on the source of the nitrate and can identify whether it is from an animal, fertiliser or human source (Stewart - 2004) (Fig. 12.4). Inorganic fertilisers have low $\delta^{15}\text{N}$ values of 0-5 ‰, natural soil organic matter has values of 4-9 ‰ and manure values of 8-20 ‰ (Stewart et al - 2001). This technique has the advantage of being easy and cheap to apply. Care is needed however, when interpreting results from reducing environments where nitrate is being lost from groundwater due to natural denitrification processes.

The Nitrogen-15 method was used by the MDC in 2004 to identify the origin of high or elevated levels of nitrate-nitrogen in shallow groundwaters at Rarangl and near Renwick (Fig. 12.5). Fertiliser was identified as the source in all but one case, at Fault Lake in the Lower Waihopai Valley which was attributed to animal waste.

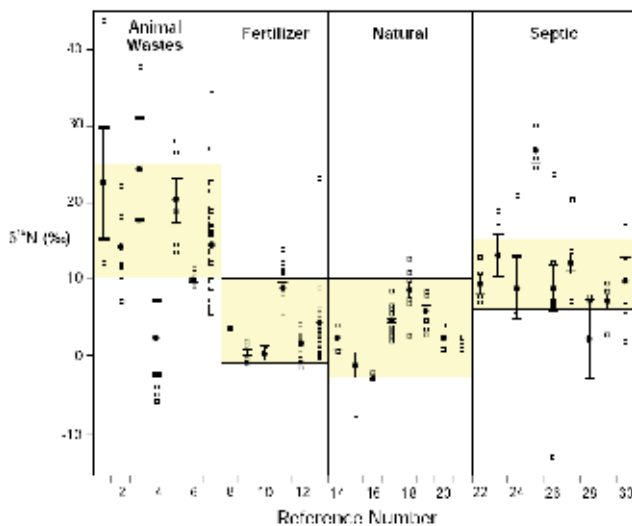


Figure 12.4: $\delta^{15}\text{N}$ signatures (Stewart - 2004)

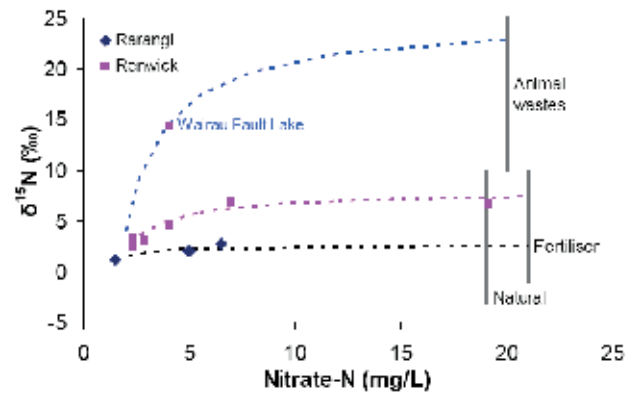


Figure 12.5: Nitrate versus Nitrogen-15 concentrations (Stewart - 2004)

It was observed that the intermittent nature of the spikes in nitrate-nitrogen concentration reflected the seasonal practice of fertiliser use, however it could also be explained by seasonal leaching of historic nutrients associated with winter or spring rains.

The Nitrogen-15 method also helped identify the source of high nitrate concentrations in groundwater from the Lower Brancott Valley in 2001. Nitrate concentrations of 7.2 g/m³ at Woodbourne Farm well 1479, and 9.8 g/m³ at shallow well 2600 in the centre of the valley, corresponded with mean $\delta^{15}\text{N}$ values of 6.6 and 9.1 ‰. These values suggested an animal or human waste source (Stewart - 2001).

Radioactive isotope methods

An important regulatory role of the MDC is to ensure groundwater in the region is used sustainably. Generally aquifers containing old groundwater are poorer natural reservoirs than aquifers with a higher turnover, and a more reliable recharge source.

While radioactive particles attached to water molecules are in the atmosphere, they are constantly being replaced. Once they become part of groundwater and are isolated from their source of replenishment, they decay with time. If we can measure the residual amount of a particular isotope and know its historical variation, then from its decay rate we can estimate the time water has been underground.

However the process isn't quite as simple as it has been described. Groundwater does not have a single age but is normally a mix of water of different ages. This is caused by natural dilution and dispersion of groundwater and has to be taken into account when predicting the age.

Several models are used to account for the possible range of ages including the piston flow approach which assumes limited mixing, while the exponential model reflects significant mixing. Selection of an appropriate

age model requires as much knowledge of the geology, chemistry and hydrology of a groundwater system as possible.

Age estimates are likely to be refined over time as understanding of these processes improves. Dr Uwe Morgenstern at GNS Science is using movement of the tritium plume through the Wairau Aquifer based on measurements at the same wells over many decades, to calibrate the local dispersion model.

Radioactive decay

Radioactive decay is a natural process whereby an element changes to become a related product over time. The mass of a certain element remaining after a given time can be used to calculate how long it has been away from its source in the atmosphere based on the known decay rate.

The following equation describes the process whereby the concentration of a radioactive element at any time (C_t) equals the initial concentration (C_0) multiplied by the exponent to the power of the time (t) and its decay constant (k). The negative sign indicates the concentration declines over time.

$$C_t = C_0 e^{-kt}$$

Because the half life of all radioactive elements is precisely known, we can derive the decay constant. For example, we know that the half life of tritium is 12.3 years which converts to a decay constant of 0.056. The half life is the time it takes for the mass to halve. This means that the typical groundwater in a Riverlands well that is 60 years old would only have 3.5% of the original tritium remaining. A time-span of 60 years was chosen to illustrate the useful time range of tritium after which it's mass is more or less stable.

Tritium (^3H)

Tritium is a radioisotope of hydrogen (^3H), and is the most widely used dating tool for medium to younger groundwaters in New Zealand. Tritium is restricted to dating the ages of groundwaters that are less than about 60 years because of its short half life of 12.3 years. It is the radioactive isotope of hydrogen and is associated with the water molecule. It is conservative in nature meaning it doesn't change chemically during its travel through the hydrological cycle. This characteristic makes it an excellent tracer of groundwater flow.

A characteristic of radioactive elements such as tritium is they decay over time to related products of a different element, in this case helium (^3He). The concentration of tritium is measured in tritium units (TU) with 1 tritium unit corresponding to a ratio of 1 tritium atom (^3H) to 10^{18} normal hydrogen (^1H) atoms.

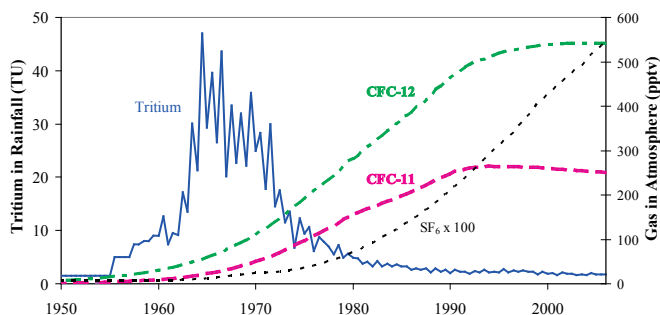


Figure 12.6: Atmospheric tritium, CFC and SF₆ levels 1950 – 2007 (GNS Science)

Development of the dating method locally was pioneered in the 1960s and 1970s by Dr C.B. Taylor of the DSIR. Its application and precision has been further refined in recent years, predominantly by Dr Uwe Morgenstern of GNS Science Ltd (Morgenstern - 2009). Both of these scientists have contributed greatly to understanding Marlborough hydrological processes through applied isotope studies.

Tritium is produced naturally in the atmosphere by cosmic rays, but large amounts were also released into the atmosphere in the early 1960s during nuclear bomb tests. This temporarily raised concentrations in New Zealand rain and surface waters to about 20 times the background level at Kaitoke north of Wellington (Fig. 12.6). The distinction is often made between pre-bomb and post bomb water.

As with all the radioactive tracers, the way in which it works relies on its isolation from the atmosphere and its natural source of replenishment. When the water infiltrates the ground and becomes isolated from the atmospheric tritium source, its tritium concentration decreases over time due to radioactive decay. The tritium concentration of groundwater therefore reflects the time the water has been underground (Morgenstern et al - 2009).

Artificially high tritium levels were incorporated in groundwater as rainfall or river recharge during weapons testing. Tracking the artificially high levels of tritium through the hydrological cycle has proven useful for understanding the movement of groundwater through local aquifer systems. These high values have by 2011 almost returned to pre-bomb levels due to natural radioactive decay (Fig. 12.7).

To assign a date to a sample of groundwater requires a knowledge of the starting concentration in the atmosphere before the water was isolated below the ground and the decay process began. However, the source of recharge for the majority of northern Wairau Plain wells is the Wairau River which has slightly different tritium levels to rainfall due to the runoff characteristics of the catchment whereby some water is retained in the scree slopes causing mixing.

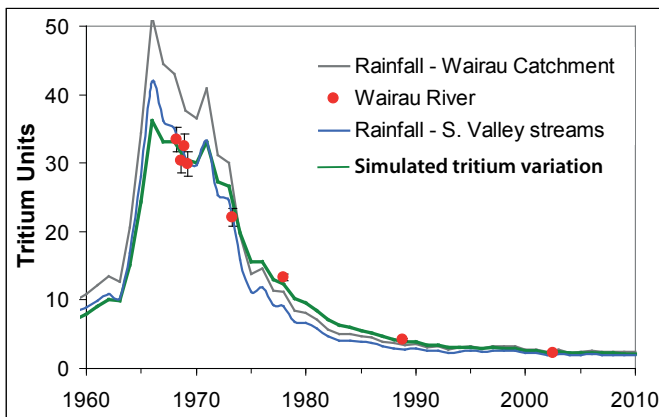


Figure 12.7: Measured and modelled tritium concentrations (Stewart - 2008)

The variation in tritium levels for wells penetrating various parts of the Wairau Aquifer relative to the Wairau River recharge source is shown in Figure 12.8. The young groundwaters of group A associated with the Wairau River marked by the diamonds, show the largest variation in tritium levels. These samples have had the most recent contact with the atmosphere and mirror the atmospheric trend.

Conversely the oldest and most isolated groundwater in group C shown by the orange triangles, do not show the influence of the bomb tritium because this water was recharged prior to testing. Group B groundwaters flagged by the yellow squares exhibit intermediate values.

Tritium levels in group A groundwater are the same as the atmosphere because it hasn't had time to decay and this water is classified as having zero age. Estimating the age of older groundwater is not as straightforward, as natural mixing within the aquifer has to be allowed for.

We know from well drilling that the geological formations and the associated groundwater flow beneath the Wairau Plain are stratified. The age of older water is estimated based on a blending which occurs near the coastal boundary as groundwater is forced upwards.

Tritium is becoming more useful again as a water dating tool as the bomb component slowly moves through the hydrological cycle and is replaced by naturally occurring atmospheric levels. In the near future the age ambiguity associated with measurements made on samples from the 1970s to recently will vanish, allowing use of spot samples to fix an age.

Carbon-14 ($\delta^{14}\text{C}$)

Due to the short half life of tritium it is only useful for determining the age of water that is less than about 60 years old. To identify the age of older groundwaters, isotopes with longer half lives are used.

Carbon-14 comes from cosmic rays and is incorporated in plants through photosynthesis and in groundwater via reactions between recharge water and carbon dioxide in the atmosphere.

The element carbon has two stable isotopes: Carbon-12 (^{12}C) and Carbon-13 (^{13}C), and a radioactive isotope carbon-14 (^{14}C) known as radiocarbon. Radiocarbon (^{14}C) has a much greater half life than that of tritium of 5,730 years, and can be used to measure groundwater residence times of up to 50,000 years before present.

The carbon-14 method wasn't applied in Marlborough until the late 1990s when it was used to date water from the Deep Wairau Aquifer. Prior to this only relatively young groundwaters had needed to be dated in Marlborough. This aquifer subsequently turned out to contain some of the oldest water in New Zealand.

Because this technique is used to date old water, the greater time period allows for more mixing or dispersion than with younger groundwaters. This complicates the interpretation of a waters age and for this reason the error associated with predictions is larger and generally an age spectrum rather than an exact date is given.

Age interpretations are complicated by having to allow for background inorganic carbon that comes from carbonate minerals. These minerals are usually so old all the ^{14}C has decayed. If present in significant amounts and unaccounted for, it will dilute the active ^{14}C and suggest an older groundwater age than is really the case.

Dr C.B. Taylor described in detail in a series of reports, the methods he used to account for the dead carbon as part of the interpretation of the ages of groundwater from the Deep Wairau Aquifer (DWA) for the MDC. He identified groundwater from the DWA as having been recharged thousands of years before present using the radiocarbon (^{14}C) dating method (Taylor - 1999).

In 2008 a GNS Science report calculated the residence age of groundwater from the DWA following a decade

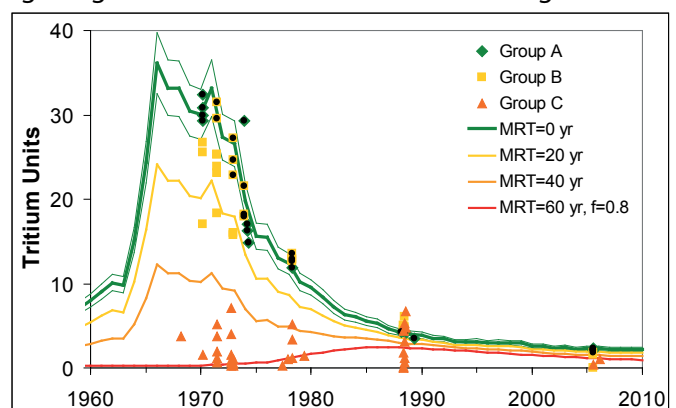


Figure 12.8: Wairau Plain groundwater tritium concentrations and simulated values (Stewart - 2008)

of consented pumping (Fig. 12.9). Results showed that groundwater from the MDC monitoring well at Wairau Hospital (0980) is the oldest in the country having been recharged 39,500 years before today (Morgenstern et al - 2008).

Dissolved gases

Since industrialisation many man-made contaminants have entered the atmosphere and some have been entrained in groundwater. Because they have been introduced so recently and their concentration varied with time, some have proved ideal as groundwater tracers. Dissolved gases are particularly useful for identifying young groundwater ages of the order of several years to decades.

Dr M.K. Stewart from GNS Science in Lower Hutt has largely been responsible for developing gas dating techniques in New Zealand and most of the following commentary is taken directly from his reports prepared for the MDC.

CFCs

The most commonly used gas tracers are Chlorofluorocarbons or CFCs. They are man-made gases which were first widely used from the 1940s as refrigerants, but have been phased out recently because they damage the ozone layer. There are 2 types: CFC-11 and CFC-12.

They are very stable synthetic compounds containing fluorine and chlorine. Their concentration in the atmosphere has grown steadily and peaked in the 1990s.

Water entering an aquifer carries small amounts of these gases in solution, depending on the concentration and the temperature at the time of recharge. Since the average recharge temperature at a given site is constant,

groundwater is labelled by its CFC concentration. The age of the groundwater is given by matching the concentration with the corresponding atmospheric level (Fig. 12.6).

The method has a number of disadvantages including its susceptibility to contamination by ambient CFC gases during sampling, and under anaerobic conditions microbes can also consume CFCs. During an MDC survey of groundwater ages at municipal supply wellfields in 2001, samples from the central town well 3120 and Base Woodbourne well 0662 were contaminated by locally occurring materials in the air. Therefore much more care is needed collecting the water sample than for other tests.

CFCs are becoming less useful for dating recent groundwaters because atmospheric levels are now levelling out (Fig. 12.6). One of CFC's advantages compared to tritium dating had been that it gave unambiguous ages because natural levels had risen monotonically (GNS Science). A common use of CFC-based dating has been to identify the young fraction of groundwater for the purpose of defining drinking water security for human health purposes.

The Drinking Water Standards for New Zealand (DWSNZ 2005) specify that for a groundwater source to be deemed secure, less than 0.005% of water has to have been in the aquifer for less than one year. Two or more samples are taken of groundwater two years apart to determine the young fraction. This is a standard approach used around New Zealand, with all the public water supply wells in Marlborough being tested by the MDC over the past 10 years.

Sulphur hexafluoride (SF₆)

Sulphur hexafluoride (SF₆) is a relatively recently introduced gas used in the electrical industry. It is used for dating very young groundwaters that have been underground for only months or several years, but has not been as widely used in Marlborough as other methods.

Sulphur hexafluoride was used to successfully date the mean residence time of young Rarangi Shallow Aquifer water at five years as part of an MDC survey in 2004 (GNS Science - 2004). In this case it was used instead of the CFC method because the groundwater had been affected by atmospheric CFCs, which is often the case for unconfined aquifer systems.

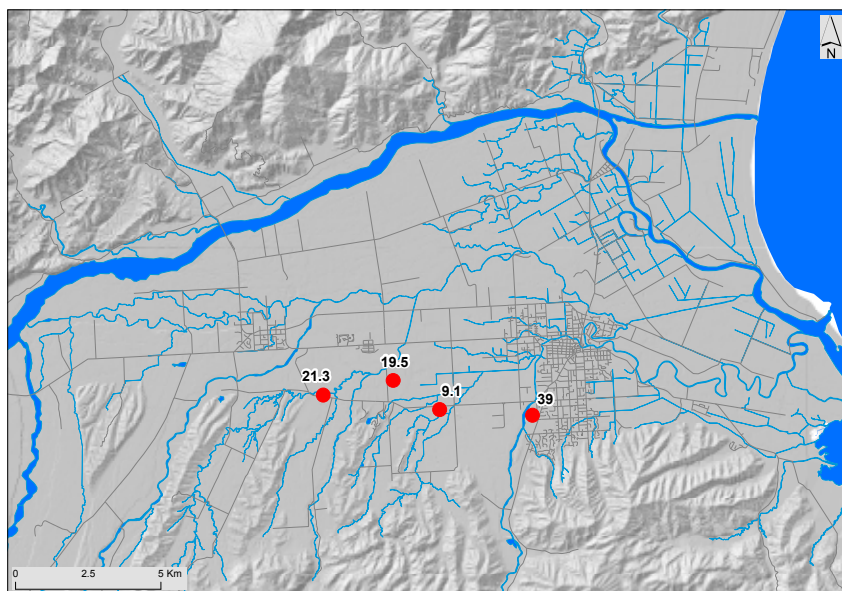


Figure 12.9: Deep Wairau Aquifer ages in thousands of years before present (Morgenstern et al – 2008)

Age interpretation

One of the complicating factors facing scientists when assigning a residence time to a particular groundwater is that in the real world all samples represent a mixture of waters. Groundwaters have a spectrum of ages rather than a discrete time of recharge (Fig. 12.9). For this reason a mean residence time is given based on the estimated degree of mixing that has occurred, which varies between aquifer types.

In confined aquifers groundwater flow approximates the movement of a piston, with slugs of water moving through as a succession of cohorts with limited mixing. In unconfined aquifers there is more mixing due to inputs of rainfall or river recharge from above and the so called exponential flow model is used to generate a spectrum of ages. In reality the natural mixing process often lies somewhere in the middle of these two extremes.

Applications of isotope techniques

Environmental isotope results played a key role in unravelling the hydrogeology of the Tuamarina River/ Waitohi Valley in the early to mid 1980s as part of the joint investigations by the NZGS and the Marlborough Catchment and Regional Water Board (Brown et al - 1985).

These studies proved that most groundwater and water from the Blue Hole Spring or Tuamarina River were of relatively recent origin, indicating rapid flow through the alluvial gravels (Brown et al 1985). The similarity between the $\delta^{18}\text{O}$ values highlighted the interconnection between groundwater, surfacewater and spring-flow which are essentially the same water body. Another finding of fundamental importance was that all water originated from local rainfall.

Another application of isotope dating is in relation to the security of community drinking water supply schemes. This approach is based on the fact that older groundwaters contain fewer viruses or bacteria due to the natural filtering effect and degradation processes that occur in gravel aquifers. Therefore the age of a groundwater is a good measure of whether it is microbiologically safe for humans to drink.

Knowing the young fraction or the proportion of water that is less than one year old is the way in which the security of public water supplies is graded. Only two of Marlborough's public water supply well fields are considered microbiologically secure based on the Ministry of Health criteria (NZ Ministry of Health 2005). These are the Havelock water supply and the Malthouse Road well-field, both of which penetrate confined aquifers containing older water (PDP - 2002).

A more recent use of groundwater dating techniques by the MDC was to determine if consented abstraction of groundwater from wells is affecting natural flow patterns beneath the Wairau Plain. The record that currently exists is too short to reach any conclusions yet, but based on the declining concentrations of chloride, it is likely that this more dilute water is also younger.

In areas where there is limited hydrological observations, isotope tools have often provided the only information on groundwater characteristics and aquifer properties. One such example is the water bearing gravels associated with the Graham River in Whatamonga Bay, near Waikawa in the Queen Charlotte Sound.

A MDC test well (0518) was drilled in 2008 in search of a supplementary water supply for Picton. This well was

screened at a depth of 23 to 26 metres below the surface and sampled for $\delta^{18}\text{O}$ and tritium in June 2008. A low tritium ratio of 1.51 was measured in groundwater from the well and was ambiguous in terms of its age. It could either represent current atmospheric levels meaning it is very recent, or levels which existed prior to the bomb testing, making it over 50 years old (GNS Science - 2008). Other techniques and more measurements are needed to reconcile the age of the water as

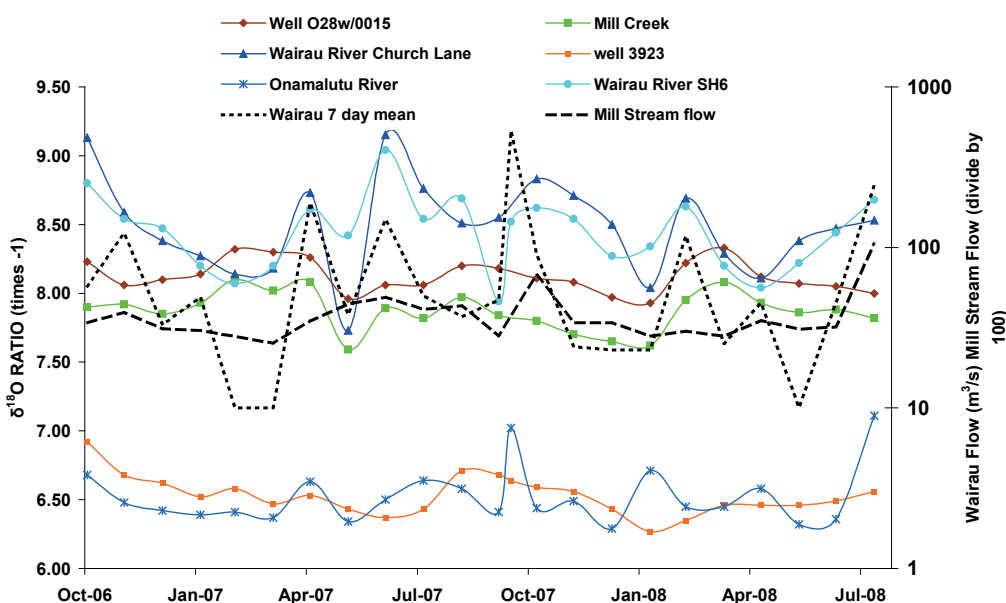


Figure 12.10: Variation in $\delta^{18}\text{O}$ isotope ratio values for the six sampled sites together with Wairau River and Mill Stream flow.

the water chemistry is also slightly ambiguous. This illustrates the need to interpret isotope information in the context of the wider catchment hydrology and geology. It is thought that a short residence time of two to four years is most likely.

Another example is the Oxygen-18 field surveys at Kaituna conducted by the MDC in conjunction with Dr C.B. Taylor. This work established the localised influence of Wairau River recharge water on groundwater along its riparian margin (Taylor - 2004).

To see if this pattern applied elsewhere along the Wairau River axis and to understand localised or shorter term effects, monthly surveys were made by the MDC between 2006 and 2008 at paired surface and groundwater sites elsewhere in the Wairau Valley.

The sites were sampled on the same day each month over this period to understand the relative influence of Wairau River versus local runoff or rainfall (Fig. 12.10).

The Wairau Valley community water supply well O28w/0015 is located on the lower terrace opposite the Wairau Valley Golf Course and was paired with samples from Mill Stream twenty metres away. Irrigation well 3923 is located on the lower terrace at Kaituna, approximately 500 metres north of the Wairau River channel and was paired with water samples from the Onamalutu River. Wairau River water was sampled at the SH6 bridge, and also opposite Church Lane at Wairau Valley, 25 kilometres to the west.

The results showed distinct differences between the stable isotope signature of water from the Wairau River compared to that of its tributaries or nearby groundwater did not only apply at Kaituna, but extended along the south bank of Wairau Valley also.

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