Journal of Hydrology (NZ) 50 (2): 313-338 2011

Nitrate sources and residence times of groundwater in the Waimea Plains, Nelson

Michael K. Stewart[1], Glenn Stevens[2], Joseph T. Thomas[2], Rob van der Raaij[3], Vanessa Trompetter[3]

[1] *Aquifer Dynamics & GNS Science, PO Box 30368, Lower Hutt, New Zealand. Corresponding author: M.Stewart@gns.cri.nz*
[2] *Tasman District Council, Private Bag 4, Richmond, New Zealand*
[3] *GNS Science, PO Box 30368, Lower Hutt, New Zealand*

Abstract

Nitrate concentrations exceeding Ministry of Health potable limits (11.3 mg/L nitrate-N) have been a problem for Waimea Plains groundwater for a number of years. This work uses nitrogen isotopes to identify the input sources of the nitrate. The results in relation to nitrate contours have revealed two kinds of nitrate contamination in Waimea Plains groundwater – diffuse contamination in the eastern plains area (in the vicinity and south of Hope) attributed to the combined effects of the use of inorganic fertilisers and manures for market gardening and other land uses, and point source contamination attributed to a large piggery to the south of Hope.

Once nitrate is introduced to a groundwater system it can take many years for it to be flushed out. Tritium measurements in wells are interpreted to give mean residence times, and the spread of residence times around the mean, for groundwater in different parts of the plains. Mean ages are youngest in the area south of Hope, where nitrate concentrations are highest, and increase to the south, west and north. The age distributions have been used to produce a nitrate input history for the Upper and Lower Confined Aquifers by simulating the nitrate measurements in the various wells. The timing of the derived nitrate input history shows that both the diffuse sources and the point source were present from the 1940s, which is anecdotally the time from which there were increased nitrate sources on the plains. The large piggery was closed in the mid-1980s.

Unfortunately, major sources of nitrate (including the piggery) were located on the main groundwater recharge zone of the plains in the past, leading to contamination of the Upper and Lower Confined Aquifers. The contamination travelled gradually northwards, affecting wells on the scale of decades. Input of nitrate to the groundwater has been decreasing since about 1988 due to closure of the piggery. The resulting decrease in nitrate concentrations is now also gradually travelling northward. Groundwater to the south and west already had relatively low nitrate because of river and/or rainfall recharge with low nitrate concentrations. Improved monitoring and practices (e.g., best management practices and nutrient budgeting) need to be encouraged among market gardeners and other land users, taking special account of the location of the groundwater recharge areas around and south of Hope.

Keywords

Age dating; nitrate concentration; nitrogen isotopes; tritium; groundwater flow

Introduction

The Waimea Plains (lying southwest of Nelson City) are an area of intensive farming and horticulture of some 75 km^2 (Fig. 1). Groundwater from unconfined and two major confined aquifers is used extensively for irrigation. The Hope Gravel Lower Confined Aquifer unit supplies a large part of the township of Richmond's drinking water supply (Johnston, 1979; Dicker, 1980; Fenemor, 1988). Summer drawdown has a significant effect on usage and optimum allocation of the resource is an issue. Water quality is generally good, except for nitrate concentrations which often exceed the limit for potable waters (11.3 mg nitrogen/L H_2O, Ministry of Health, 2005). This paper uses geochemical methods to investigate the sources of nitrate and its residence times in groundwater in the plains.

Nitrate concentrations higher than the drinking water standard are not uncommon in groundwater in New Zealand, and many other parts of the world. Several surveys of nitrate concentrations in groundwater in the Waimea Plains have been carried out (Stanton and Martin, 1975; Fenemor, 1987; Dicker *et al.*, 1992; Ware, 2000; Stevens, 2005). With intensification of farming and horticulture, better understanding of nitrate sources is needed to allow better management of groundwater resources. There are many possible sources of nitrate contamination within groundwater systems, such as natural soil organic matter, inorganic nitrogenous fertilisers, dairy and pastoral farming, animal manure applied to land (dairy shed effluent, chicken manure, blood and bone), septic tanks and municipal sewage effluent. Which of these are the major nitrate contributors is often not clear.

Identification of nitrate sources by means of nitrogen isotopes has been applied by a number of researchers (e.g., Fogg *et al.*, 1998; Kendall, 1998). $\delta^{15}N$ values often allow good discrimination between animal sources and inorganic fertiliser or natural nitrate sources, but not between fertiliser and natural sources or between animal and human sources. Variability of $\delta^{15}N$ values within a single source type limits the ability to distinguish between sources, and groundwater nitrate can often come from more than one source type, both adding to the possible confusion.

Tritium and CFC concentrations have been used to determine groundwater residence times, which show when the water and dissolved nitrate entered the system (Stewart and Morgenstern, 2001). Tritium ($T={}^3H$) is a component of the water molecule and therefore almost an ideal tracer. It is produced naturally in the atmosphere by cosmic rays, and large amounts were released into the atmosphere by nuclear weapons tests in the late 1950s and early 1960s, giving rain and surface water a relatively high tritium concentration, particularly in the Northern Hemisphere. In the Southern Hemisphere, there is now almost no bomb-peak tritium remaining in groundwater systems, either because of radioactive decay and dispersion, or because bomb-tritium has completely passed through short-residence-time hydrological systems. Instead, groundwater can now be dated using the natural decay of cosmic ray tritium because sufficiently precise tritium measurements are available (Morgenstern and Taylor, 2009; Stewart *et al.*, 2010; Morgenstern *et al.*, 2010). Other tracers (CFCs and SF_6) are providing new methods of age-dating groundwater (Plummer and Busenberg, 1999). The steady increases of CFCs and SF_6 in the atmosphere since 1940 and 1970 respectively potentially tag subsurface waters with their dates of last exposure to the atmosphere.

Being able to combine identification of nitrate sources with determination of when

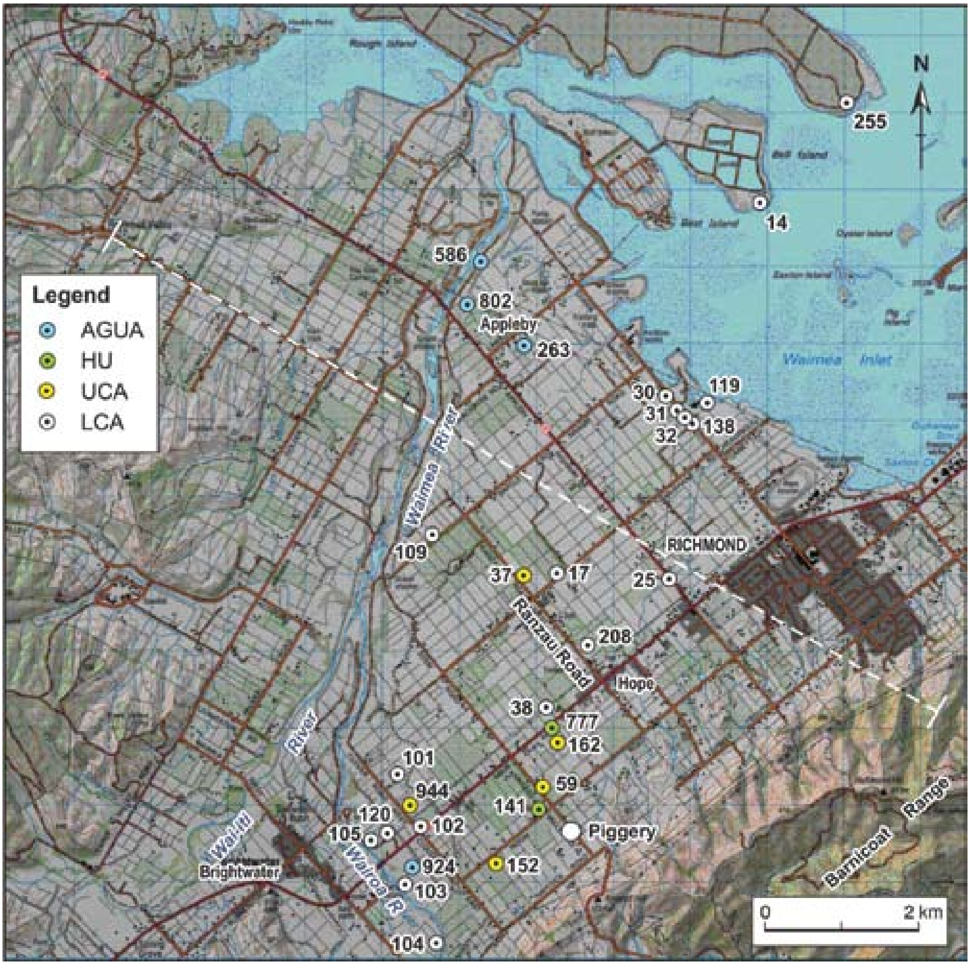

Figure 1 – Map of the Waimea Plains showing the locations of wells sampled for nitrogen isotopes, and tritium and/or CFC concentrations. The trace of the cross section in Figure 2 is shown as a dashed line.

the nitrate entered the groundwater system offers a powerful means of investigating nitrate contamination problems (Böhlke and Denver, 1995, Katz *et al.*, 2001; Moore *et al.*, 2006). The objectives of this work are to investigate the input sources of nitrate to Waimea Plains groundwater using nitrogen isotopes, to estimate groundwater residence times using tritium concentrations, and to combine them to deduce the history of nitrate input on the plains and infer future changes. This will help to establish the connections between groundwater nitrate and land use, and contribute to better understanding and management of the groundwater.

Previous work

Hydrogeology

The late Quaternary terrestrial gravel underlying the Waimea Plains, which is up to 60 m thick, has been divided into several formations (Johnston, 1979). These unconformably overlie clay-bound Moutere Gravel of late Pliocene or early Pleistocene age. Neither the Moutere Gravel nor older formations are considered likely to yield appreciable quantities of groundwater. Only the Hope Gravel (late Pleistocene) and Appleby Gravel (Holocene) are important as sources of groundwater (Fig. 2).

The Hope Gravel occupies most of the valley cut in the Moutere Gravel by the Waimea River and is mainly a tight, poorly sorted, clay-bound gravel up to 55 m thick (Fig. 2). However at two levels beneath the Plains it contains large lenses of sorted, less clay-bound gravel which, along with minor lenses elsewhere in the formation, contain confined aquifers. In the east, Stoke Fan Gravel derived from the Barnicoat Range (500 m) to the east of the plains interdigitates with and partly overlies the Hope Gravel (Fig. 2).

After deposition of the Hope Gravel, the rivers cut down into and reworked the surface gravel and deposited the well-sorted Appleby Gravel underlying the floodplains of the Wai-iti, Wairoa and Waimea Rivers and in the delta of the Waimea River. Adjacent to the coast the sea removed the upper part of the Hope Gravel to form a sea cliff up to 12 m high that extends eastward from the Waimea River near Appleby towards Richmond. On the seaward side of this cliff, while the Appleby Gravel was being deposited, small streams draining the eastern part of the Waimea Plains deposited relatively poorly-sorted gravel mapped as the Pugh Gravel Member of the Appleby Gravel.

The Appleby Gravel is generally highly permeable and forms unconfined aquifers (referred to as the Appleby Gravel unconfined aquifers or AGUA). The gravel is up to 14 m thick on the coast but thins inland to 6 m thick in the lower Wai-iti valley and 3 m thick at the Brightwater Bridge over the Wairoa River. The unconfined aquifers rest unconformably on the clay-bound gravel with no appreciable loss of water into the Hope Gravel, except near the mouth of the Wairoa Gorge and near Appleby. The Pugh Gravel Member of the AGUA lies adjacent to the coast between the Waimea River delta and Richmond. Water yield from the aquifers is generally high, but in the Pugh Gravel Member permeability and consequently water yield decreases rapidly in an easterly direction.

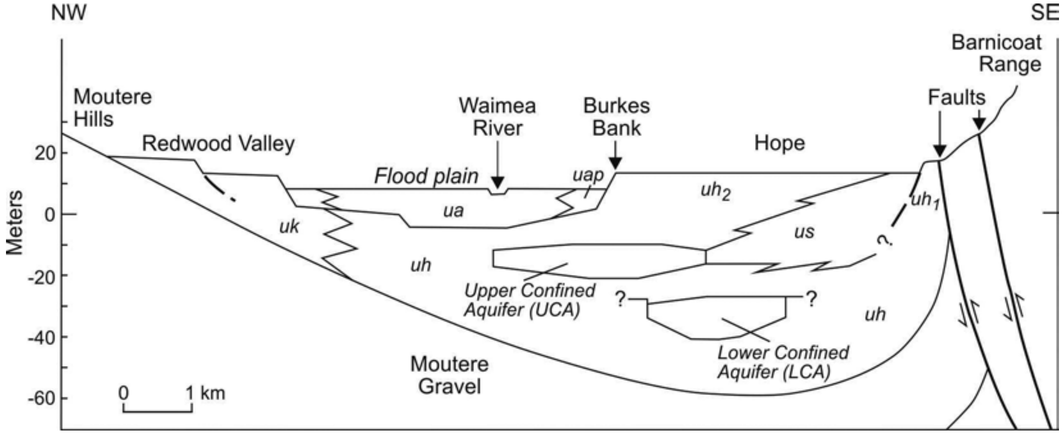

Figure 2 – Schematic cross-section from NW to SE through the central part of the Waimea Plains showing late Quaternary units (from Dicker *et al.*, 1992). (ua – Appleby Gravel, uap – Pugh Gravel Member, uh – Hope Gravel, us – Stoke Fan Gravel). The line of the cross section is shown on Figure 1.

At various levels within the Hope Gravel, particularly within 15 m of the surface, and in the Stoke Fan Gravel, water-bearing gravels no more than 0.4 m thick form minor confined and unconfined aquifers (HU). The aquifers are generally not continuous, their distribution is not well-defined or predictable, and they commonly fail during periods of prolonged dry weather. Geological data and water analyses suggest that some of them in the Hope area are connected to the deeper confined aquifer units. Northeast of the state highway near Appleby, the now buried sea cliff truncates some of these minor aquifers. Water from the aquifers rises to the surface and partly recharges the unconfined aquifers in the Pugh Gravel.

The 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 (UCA) and the Lower Confined Aquifer (LCA) (Johnston, 1979; Dicker, 1980). Each unit consists of a number of aquifers separated by less permeable, commonly sandy gravel layers. The UCA is within a few metres of the surface at the mouth of the Wairoa Gorge and extends north beneath the Waimea Inlet at a depth of about 18-32 m. This unit has not been located in holes drilled in the Wai-iti Valley. It is about 0.9 km wide near the gorge, and increases to 1.8 km wide in the north. Piezometric level measurements indicate recharge from the Wairoa River occurs at the mouth of the gorge where the capping gravels are absent and the Appleby Gravel overlies the unit (Dicker, 1980). To the east away from the rivers, recharge is mainly from rainfall and largely in the area near Hope (Dicker *et al.*, 1992; Stewart *et al.*, 1981). Beneath the Waimea Inlet the unit widens considerably into the now-buried delta of the Waimea River. Between Appleby and the coast, much of the clay-bound Hope Gravel capping the unit has been removed, so the Appleby Gravel rests on the UCA and the aquifers become one hydraulic unit. Further north, where Holocene marine sediments overlie the buried delta, salt water has infiltrated the aquifers. As a result the aquifers contain up to 6000 g/m^3 of chloride, are not artesian, and show large tidal fluctuations in static level.

The LCA is at a depth of 26 m near the mouth of the Wairoa Gorge and extends northeast to the coast where it is at a depth of about 30-40 m below the surface. Like the UCA, the unit has not been located in the Wai-iti Valley. Beneath the plains the unit is of similar dimension to the UCA. Water level is artesian at the coast, with a tidal influence of 1.5 m, reducing to 10 mm inland near Brightwater. The unit pinches out towards the Wairoa Gorge. The LCA provides much of the water for the Richmond township in the northeast of the plains, and is used extensively for irrigation on the plains.

By modelling the water-bearing layers in three dimensions, White and Reeves (1999) observed three major aquifer structures consistent with, but different in detail to the aquifers described by Dicker *et al.* (1992). The first is a near-surface structure that covers most of the Waimea Plains and estuary consistent with the AGUA, unconfined HU and northern parts of the UCA. The second underlies the Wairoa and Waimea Rivers and is generally consistent with the mid and southern parts of the UCA. The third is a deeper structure east of the Waimea River and under the estuary consistent with the LCA.

Nitrate concentrations in groundwater

Nitrate concentrations have been of concern since the work of Stanton and Martin (1975). Their results for samples collected in 1969-1972 are given in Figure 3. Samples were collected from wells with a range of depths, and similar patterns are seen for both the 7.5-15 m and >15 m depth ranges. The survey would have included some wells penetrating the UCA, but not the LCA. The highest concentrations occupy a very narrow N-S band now known to be on the east side of the UCA. This is surrounded by a broader nitrate anomaly now known to be in the Appleby Gravel unconfined, and the Hope Gravel unconfined and upper confined aquifers.

Later surveys of the nitrate concentrations were carried out in 1978, 1986, 1994, 1999 and 2005 by the Tasman District Council (Fenemor, 1987; Dicker *et al.*, 1992; Ware, 2000; Stevens, 2005). Figure 4a gives a contour plot of the 2005 survey results for the UCA (Stevens, 2005). The narrow band of high concentrations on the east of the UCA still exists, although maximum concentrations are now lower than before and the band has

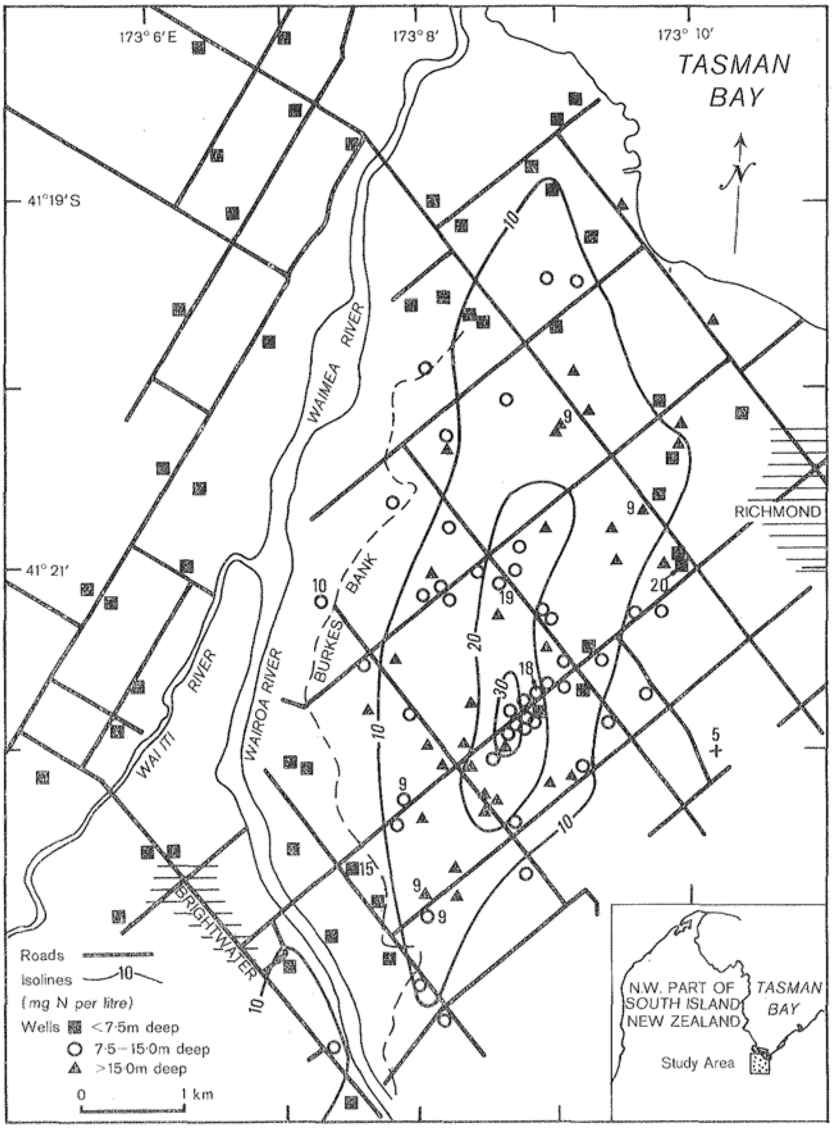

Figure 3 – Map showing distribution of nitrate in wells on the Waimea Plains in 1969-1972 (from Stanton and Martin, 1975).

extended mainly to the north but also to the south. The concentration decreases towards the Waimea River on the west side of the band. In the north, high concentrations are now seen in the Appleby Gravel unconfined aquifers, where the capping gravel overlying the UCA pinches out and the two aquifers become one (Fig. 4b). Nitrate concentrations in the LCA (Fig. 4c) show a broad anomaly elongated towards the northeast that has remained relatively static from 1986 to 2005, except that maximum concentrations have decreased. The source of nitrate to the LCA is considered to be recharge from the UCA where it overlies the LCA in the Ranzau Rd area (Stevens, 2005).

Figure 4a-c – Maps showing distribution of nitrate in wells in 2005 (from Stevens, 2005).

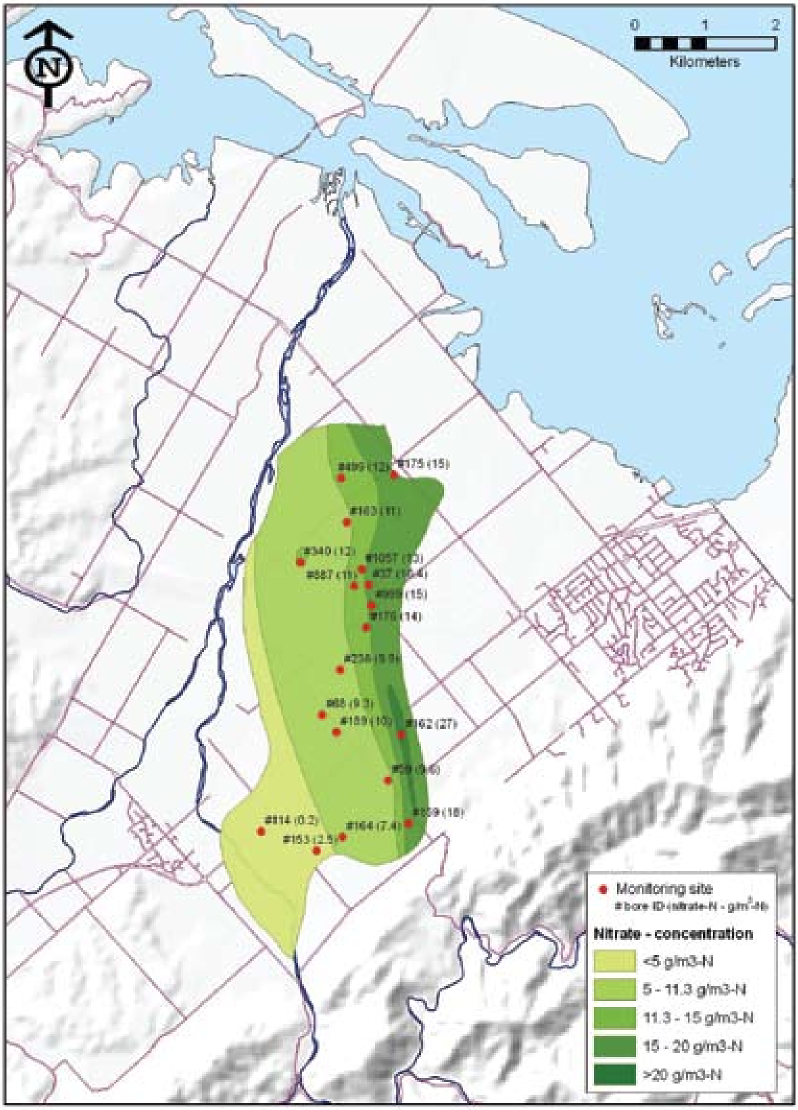

Figure 4a – Upper Confined Aquifer

Oxygen-18 concentrations in groundwater indicate water recharge source when the potential sources have different ^{18}O concentrations (Stewart *et al.*, 1981; Stewart and Morgenstern, 2001). Rainfall on the Waimea Plains and in streams draining the eastern hills have average $\delta^{18}O$ values of -6.2‰, while the three rivers from higher altitude (Waimea, Wai-iti and Wairoa Rivers) have an average $\delta^{18}O$ of -7.2‰. The groundwater $\delta^{18}O$ values show that the unconfined aquifers (the Appleby Gravel and Hope Gravel unconfined aquifers) are recharged by river water near the Waimea and Wairoa Rivers and by direct rainfall or eastern streams away from them. The UCA

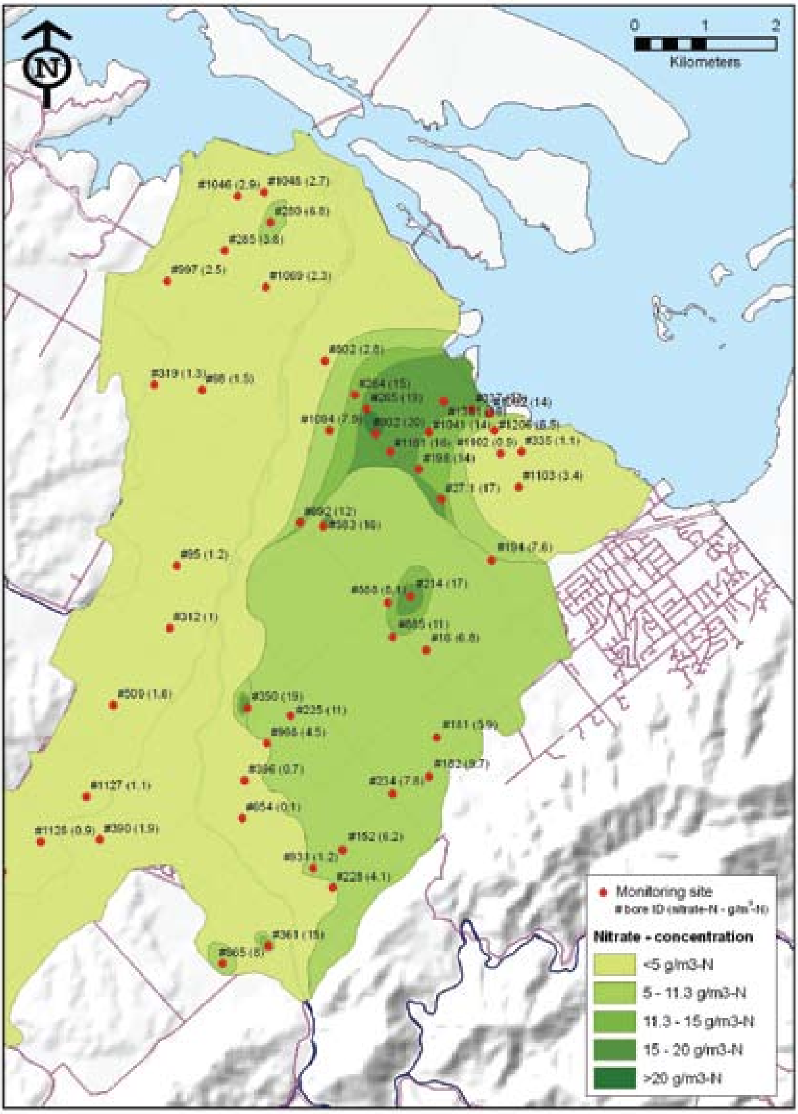

Figure 4b – Appleby Gravel Unconfined Aquifer and Hope Minor Confined and Unconfined Aquifers

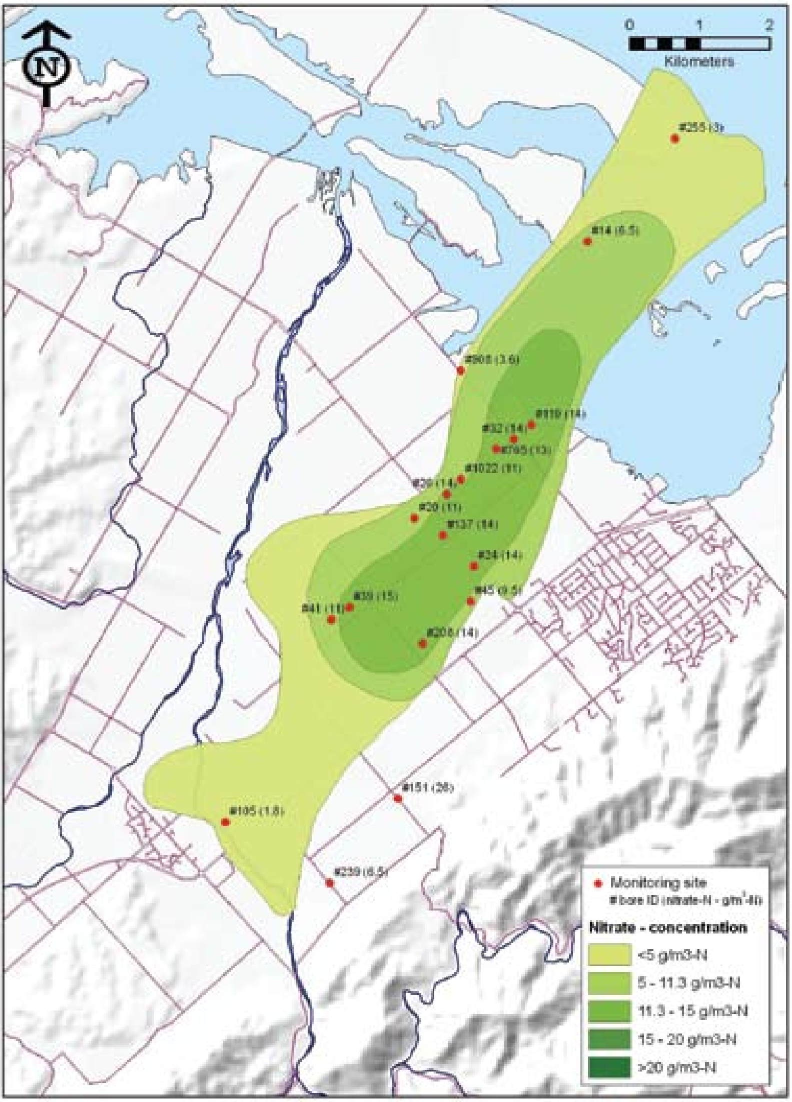

Figure 4c – Lower Confined Aquifer

has a narrow zone along the rivers showing predominantly river recharge, which grades through a mixed zone into recharge by rainfall and eastern streams on the centre and east of the plains. The LCA has mixed recharge (i.e., water from both rivers and rainfall) in the south adjacent to the Wairoa River, which is probably derived from the UCA where it communicates with the LCA. The aquifer appears to be blind further to the south. Mainly river recharge is seen close to the Waimea River in the central reach and offshore (Bells and Rabbit Islands). Rainfall recharge is received from the UCA in the Ranzau Rd area (as also shown by the nitrate concentrations). This water flows northeast. Mixed zones are seen on east and west sides of this flow.

Methods

Sampling and measurement

Samples were collected from wells in the region between Brightwater and Rabbit Island (Fig. 1). The wells typically have screens extending a few metres from the bottom. Sampling and analysis methods are described in more detail in Stewart and Thomas (2008), which covered approximately the same period of study (1972 to 2008). Samples for chemical analysis were collected by standard techniques and analysed for nitrate and sulphate concentrations at the Cawthron Institute and as part of the National Groundwater Monitoring Project run by GNS Science. Nitrate concentrations are expressed as nitrate-N (mg nitrogen/L H2O).

Samples for 15N analysis were collected in 1 L jars, poisoned with HgCl to prevent microbial loss of nitrate, and stored in a freezer until analysis. After a preliminary oxidation step to remove organic matter, 15N was measured by evaporating the sample to dryness and analysing the precipitate in an elemental analyser/mass spectrometer system. Nitrogen isotope ratios are reported in per mil (‰) relative to the international standard (AIR), which has a ratio close to that of atmospheric nitrogen (which is almost constant), where

$$\delta^{15}N = [(^{15}N/^{14}N)_{Sample}/(^{15}N/^{14}N)_{AIR}-1].1000 \qquad (1)$$

Analytical error is ±0.5‰, based on duplicate measurements.

Water was collected in 28 mL glass bottles for ^{18}O measurements. Care was taken to seal the bottles tightly to prevent evaporation. ^{18}O measurements were made by isotopically equilibrating 2 mL of the water with CO_2 gas at 29°C for two hours. The CO_2 was analysed in a stable isotope mass spectrometer (Hulston *et al.*, 1981). The ^{18}O concentrations are expressed as $\delta^{18}O$ values, where

$$\delta^{18}O = [(^{18}O/^{16}O)_{Sample}/(^{18}O/^{16}O)_{VSMOW}-1].1000 \qquad (2)$$

and VSMOW (Vienna Standard Mean Ocean Water) is the international standard water. Measurement errors are ±0.1‰.

Tritium samples were collected in 1.1 L glass bottles. Tritium measurements were made by electrolytically enriching the water in tritium by a factor of 70, and counting in an ultra low-background Quantulus liquid scintillation counter (Hulston *et al.*, 1981; Morgenstern and Taylor, 2009). Tritium concentrations are expressed as tritium units (TU) (where I TU means a $^{3}H/^{1}H$ ratio of 1×10^{-18}). Measurement errors have varied greatly during the long period of the study and are given in Table 2.

To sample for CFC concentrations, water samples were isolated from air and preserved in the field by sealing them into 62 mL borosilicate glass ampoules at the well site. Measurements of the dissolved CFC concentrations in the water were made by gas chromatography using a purge and trap method, and electron capture detector (van der Raaij, 2003). Measurement and use of CFC concentrations for dating groundwater is described by Plummer and Busenberg (1999).

Residence time determination

Sampling of water in a groundwater system (e.g., from a well or spring) results in mixing, i.e., combining of water following different flowpaths through the system. Hence, the water in a sample does not have a single underground residence time, but has a distribution of residence times. This distribution is described by a flow model, which reflects the average conditions in the unsaturated and saturated zones of the system.

Tracer inputs to the groundwater (e.g., tritium, CFC or nitrate concentrations in the recharge water) are modified by passing through the hydrological system (as represented by the flow model) before appearing in the output. The convolution integral and an appropriate flow model are used to relate the tracer input and output. The convolution integral is given by

$$C_{out}(t) = \int_{0}^{\infty} C_{in}(t-\tau)h(\tau)\exp(-\lambda t)d\tau \qquad (3)$$

where C_{in} and C_{out} are the input and output concentrations in the recharge and well discharge respectively. t is calendar time and the integration is carried out over the residence times τ. $h(\tau)$ is the flow model or reaction function of the hydrological system. λ (= $\ln 2 / T_{½}$) is the tritium decay constant ($T_{½}$ is the half-life of tritium – 12.32 years). CFCs and nitrate do not decay unless there is chemical degradation in the system.

This work uses the exponential-piston flow model. The exponential-piston flow model combines a section with exponential residence times followed by a piston flow section to give a model with parameters of mean residence time (τ_m) and exponential volume fraction (f) (parameters slightly modified from Maloszewski and Zuber, 1982). The response function is given by

$$h(\tau) = 0 \qquad \text{for } \tau < \tau_m (1\text{-}f) \qquad (4a)$$

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

where f is the ratio of the exponential to the total volumes, and $\tau_m(1\text{-}f)$ the time required for water to flow through the piston flow section. An alternative flow model (the dispersion model) was tried, but found not to fit the tritium measurements as well as the exponential-piston flow model.

The parameters (τ_m and f) are determined by fitting the simulation to the data points. f specifies the spread of residence times around τ_m. A value f=100% gives the well-mixed or exponential model (in which part of the incoming water contributes immediately to the well discharge along with a range of older waters from the aquifer), while f=0% gives the piston flow model in which all of the water reaching the well has the same age. f had relatively high values (85 to 100% for the Waimea Plains), showing that the well samples (including those from the 'confined' aquifers) have wide age distributions, which are most unlike piston-flow distributions.

Results and discussion

Nitrogen-15 and nitrate sources

The locations of wells sampled for nitrogen isotopes are given in Figure 1, and the results of the measurements in Table 1. The wells were sampled in 1998-1999, and two were resampled in 2006. Although $\delta^{15}N$ values were measured on all of the samples listed in Table 1, measurements of nitrate-N were not made on the actual samples from WWD208 and 14 in 1999. These have been extrapolated from nitrate data given later in the paper (Fig. 10).

Identification of nitrate sources by means of nitrogen isotopes has been applied by a number of researchers (e.g., Fogg *et al.*, 1998; Kendall, 1998; Stewart *et al.*, 2006). Fogg *et al.* (1998) listed $\delta^{15}N$ values for soil water beneath animal waste, inorganic fertiliser, natural (soil organic nitrogen), and sewer septic sources. They found values typically ranged from +8 to +25‰, –3 to +2‰, –3 to +10‰, and +7 to +15‰ respectively for these sources. Groundwater at these sites had $\delta^{15}N$ values in close agreement with the soil water samples.

Table 1 – $\delta^{15}N$ values and nitrate concentrations of groundwater samples from the Waimea Plains.

Well WWD	Well Owner	Sample Date	Grid Reference	Screened Depth m	NO_3 - N mg/L	$\delta^{15}N$ ‰	$\delta^{18}O$ ‰	SO_4 mg/L
Unconfined Aquifer (AGUA)								
924	TDC Brightwater	2/98	N27/20338104	6.5 – 9.2	0.5	5.2	-6.30	3.5
524	Kempthorne	2/98	N27/21578742	9.7 – 16.7	4.7		-6.75	15.4
586	TDC	2/98	N27/21408901	8.5 – 11.5	0.4	3.8	-6.89	3.9
802	Waiwest	3/99	N27/21258816		1.4	6.9	-6.69	9.1
802		2/98			1.3	5.4	-6.56	8.3
802		9/99			2.2	3.3	-6.64	9.0
Upper Confined Aquifer (UCA)								
228	Puklowski	2/98	N27/21368066	8.1 – 9.1	6.5		-6.43	22.0
152	Greenhough	2/98	N27/21478128	12.0 – 28.7	6.7	3.3	-6.56	17.9
944	Sowman	2/98	N27/20368188	12.2 – 13.7	0.5	4.0	-6.90	4.8
59	Zwart - mode 1	3/99	N27/22018222	9.0 – 15.0	17	8.9	-6.43	
59	Zwart - mode 2	9/99			9	5.5	-6.57	13.8
134	Wai-west	2/98	N27/20838250	17.0 – 20.0	0.2		-6.26	1.7
37	Milson	2/98	N27/21858498	19.0 – 23.8	19.8	7.9	-6.27	32.0
37		3/99			19.8	9.9	-6.03	34.0
37		9/99			18.9	9.0	-6.28	34.0
37		6/06			15.3	6.2		
1023	Gull	2/98	N27/21868628	15.0 – 17.0	9.4		-6.56	20.5
Lower Confined Aquifer (LCA)								
117	Hoddy	2/98	N27/22038365	29.0 – 44.8	6.8		-6.89	11.3
208	Buck	2/98	N27/22688409	30.4 – 36.4	20.4	6.7	-6.47	31.0
208		3/99			17	7.7	-6.52	
208		6/99			17		-6.54	
208		9/99			17	7.7	-6.56	
25	TDC Appleby	2/98	N27/23798497	30.0 – 36.0	9.2	4.8	-6.80	15.2
1022	King	2/98	N27/23408660	28.0 – 34.5	13.5		-6.51	19.3
138	TDC Queen St	2/98	N27/24028694	28.5 – 31.0	12.8	4.7	-6.62	20.2
32	TDC Queen St	2/98	N27/23768724	32.0 – 38.1	12.3	5.8	-6.54	20.0
32		3/99			12.6	6.0	-6.47	21.4
32		6/99			13.2	6.3	-6.56	22.0
32		9/99			13.0	5.6	-6.45	21.0
32		6/06			12.6	4.2		
30	TDC Queen St	2/98	N27/23768724	26.5– 36.6	8.0	3.1	-6.78	11.1
14	TDC Bells Island	2/98	N27/25008984	38.5 – 54.0	5.7	5.0	-6.95	7.1
14		3/99			6	5.3	-6.90	
14		9/99			6	4.3	-7.02	
255	TDC Rabbit Island	2/98	N27/26279131	47.0 – 56.6	3.2	5.8	-7.07	3.9

Denitrification, i.e., transformation of nitrate to nitrogen gas, can occur in anaerobic conditions. As well as reducing the nitrate concentration, this can increase the $\delta^{15}N$ value of the remaining nitrate (Kendall, 1998). However, conditions within the unconfined and Hope Gravel Upper Confined aquifers in the Waimea Plains are normally aerobic and denitrification is not expected (Stevens, 2005). Mildly anaerobic conditions are known to occur within the LCA, mainly north of Lower Queen St, where some denitrification can occur.

Figure 5a plots $\delta^{15}N$ against nitrate concentration. The $\delta^{15}N$ values of possible nitrate contamination sources are shown on the right, the natural soil $\delta^{15}N$ at low nitrate concentration is given on the left. Natural sources generally produce less than 1 mg/L in New Zealand groundwaters according to Close *et al.* (2001), while Daughney and Reeves (2005) found that median nitrate-N was 0.7 mg/L for pristine oxidised groundwater. The latter authors estimated that concentrations above 1.6 mg/L (75th percentile) were indicative of anthropogenic impacts. A trend line (based on two mixing curves using equation 5) has been fitted to the sample points (Fig. 5a). This shows approximately constant $\delta^{15}N$ values up to a nitrate-N concentration of 10-15 mg/L, followed by increasing $\delta^{15}N$ values with increasing nitrate concentrations. The mixing curves are described by the equation (Kendall, 1998)

$$\delta^{15}N = b - a / C_n \qquad (5)$$

where C_n is the nitrate-N concentration, and a and b are constants. Equation 5 shows that the $\delta^{15}N$ of the mixture approaches b, as C_n increases (b approximates to the $\delta^{15}N$ value of the high-nitrate end member (i.e., contaminant), while a describes the shape of the mixing curve). The constant portion of the trend indicates input of nitrate derived from both inorganic fertiliser and animal sources in subequal amounts, with a diffuse input of nitrate over the plains (where rainfall infiltrates) producing the broad nitrate anomaly in the Hope Gravel UCA. The second portion (fitting the results for WWD37 and 208) shows increasing input of animal-derived nitrate, with a mean $\delta^{15}N$ of 15.5‰ producing the narrow band of high concentrations identified in Figures 3 and 4. The extreme narrowness of this band suggests that it comes from a point source of high intensity upstream (i.e., to the south). This plume had become less intense by the date of sampling (1998–1999).

Increased input of nitrate to the Waimea Plains (and particularly the Hope region) started in the 1940s (from anecdotal evidence). The two wells sampled for $\delta^{15}N$ inside the plume (WWD37 and 208), have young mean residence times showing active recharge (from rainfall as shown by $\delta^{18}O$ values, Table 1). The point source of high nitrate input was certainly well established by the 1960s (see Fig. 3), and continued during the 1970s and 1980s (Fig. 4). A large piggery (Stratfords) housing the equivalent of c 1000 50-kg pigs (Baker, 1988) was active in the area during this time and is considered the likely cause of the point source (see location in Fig. 1). Market gardening was widespread in the Hope area and quantities of manure, along with inorganic fertilisers, were applied to the soil to improve growth. These are considered to have produced the diffuse nitrate contamination of groundwater in the area.

The plot of $\delta^{18}O$ versus nitrate (Fig. 5b) shows that the nitrate is carried into the aquifers by rainfall recharge. In the UCA, low nitrate waters can be either from river or rainfall recharge. In the LCA, the low nitrate waters are from the rivers. Sulphate and nitrate concentrations (Fig. 5c) show a good correlation, particularly for the LCA. The correlation can be explained by mixing of water containing nitrate and sulphate in a fixed proportion (i.e., rainwater that has leached nitrate from soil south of Hope) with water low in nitrate and sulphate.

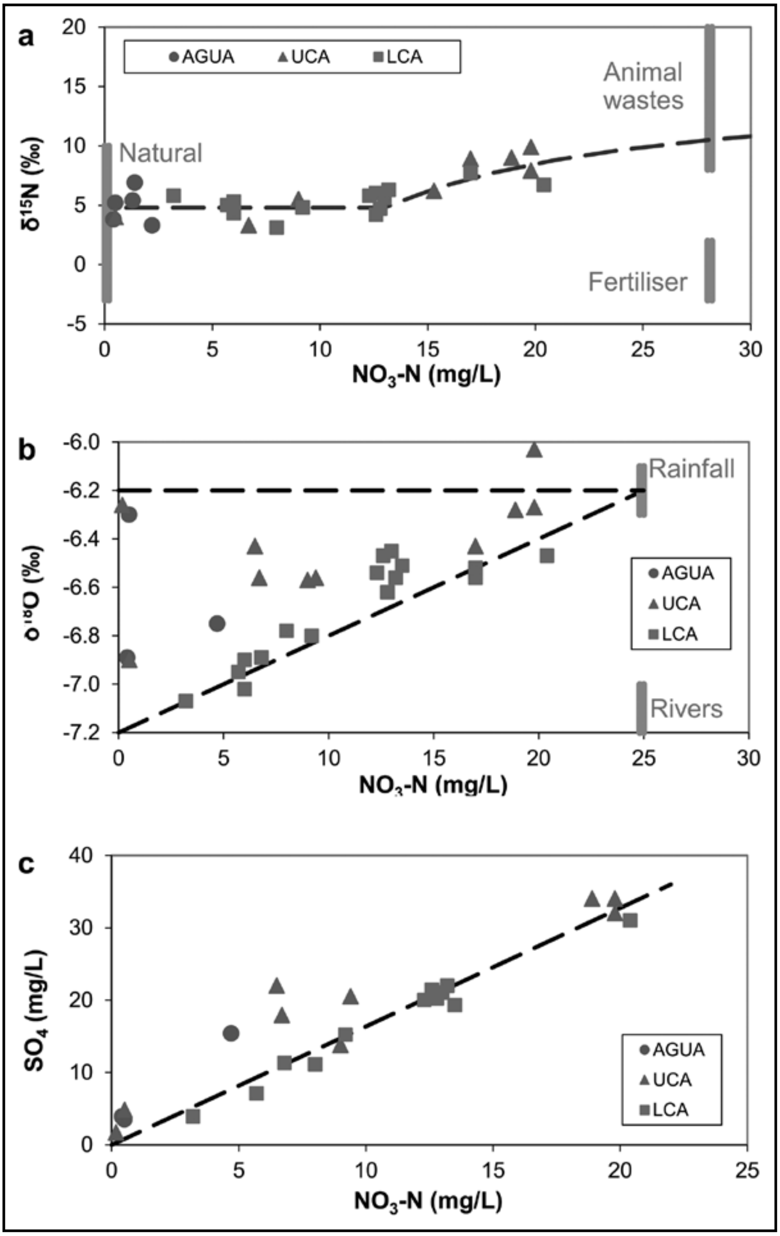

Figure 5a-c – Plots of $\delta^{15}N$, $\delta^{18}O$ and sulphate versus nitrate-N (AGUA – Appleby Gravel Unconfined Aquifer, UCA and LCA – Hope Gravel Upper and Lower Confined Aquifers).

Age determination

Tritium

The locations of wells sampled for tritium (and in some cases for CFCs) are given in Figure 1, and the results of the measurements in Table 2. The wells were sampled at various times between 1972 and 2005. Mean residence times (MRTs) were determined from tritium for four wells (WWD208, 32, 14, 255) tapping the LCA, for which there are time sequences of measurements, some of which were collected before 1990. The early data, combined with later data, give the most robust age interpretations, because of the high values following the tritium bomb peak. The data are plotted in Figures 6a-d, together with the input concentrations (i.e., the tritium concentrations in rainfall) and simulations using the exponential piston flow model. It can be seen that the simulations fit the data very well and yield well-defined mean residence times (see model parameters in Table 2). Well WWD208 contains very young water (MRT ~ 8 months), WWD32 has MRT of 33.5 years, and WWD14 and 255 have much older waters with MRTs of 110 and >150 years respectively. The best-fitting exponential piston flow models have wide distributions of residence times (shown in Fig. 6e). The parameter (f) has values ranging from 100% for the youngest to 85% for the oldest. f is theoretically the ratio of the exponential to the total volumes in the system, but in practice describes the spread of residence times around the mean. Such wide distributions mean that water follows a wide variety of flowpaths to each well.

Applying the same exponential piston flow models to the other wells for which there is only one tritium measurement per well, yields the mean residence times given in Table 2. The values of f were chosen based on the age of the water with the youngest having f=100% and the oldest f=85%, as shown by the results for the four wells above. Having only one tritium measurement can sometimes cause ambiguous ages (i.e., more than one mean residence time can produce good fits to the data point). However, in this case the ages determined were unique for all of the wells except WWD38, because the parameter f was specified based on the four examples given above.

The two HU wells (WWD777, 141) were unambiguously young (MRTs of 0.5 and 0.1 years respectively), as also were the two AGUA wells (WWD263 and 802) with MRTs of 2 and 1.1 years. Three wells were sampled from the UCA (WWD59, 162 and 37). WWD59 is in the upstream part of the aquifer, and contains unambiguously older water (36 years). WWD162 gave an unambiguous tritium mean residence time of 17 years, but this is considered to represent only one of two types of water with different nitrate concentrations that alternated in the well (see below). The other type of water, although not sampled for tritium, is considered to have been very young, based on its high nitrate concentration (mode 1 water, Table 2). (Such a mode change could have occurred, for example, if water resident in the nearby aquifer originally supplying the well (with MRT=17 years) was displaced by much younger water recently arrived from the surface.) The third well WWD37 yielded a relatively young mean residence time of 4.5 years (three measurements were available for this well).

The remaining wells are all from the LCA. The wells are ordered along the aquifer from south to north in Table 2. The first six wells (WWD104, 103, 105, 101, 120 and 102) were all sampled in the late 1970s and have tritium concentrations increasing from south to north, but all less than the ambient level at the time. They have unique tritium mean residence times decreasing from 71 to 22 years along the aquifer, showing that recharge is derived north of this group of wells. WWD38 had tritium at the ambient level and two possible age interpretations (MRT=1 or

Table 2 – Tritium concentrations and model parameters for groundwater samples from the Waimea Plains.

Well WWD#	Well	Date Collected	Depth m	Distance km	Tritium TR	MRT yr	f %	IDF	NO3-N mg/L	δ18O ‰
Unconfined Aquifers (AGUA & HU)										
141	Hope School	19/12/72	18.3	2.0	14.2 ± 0.9	0.1	100		–	-6.4
777		19/12/72	12.2	3.0	15.2 ± 0.9	0.5	100		–	-6.2
263		19/12/72	2.1	8.0	18.6 ± 1.1	2	100		–	-6.7
802	Waiwest	14/06/99		8.6	2.40 ± .07	1.1	100		1.3	-6.6
802		12/06/05			1.82 ± .06				1.0	
802		17/12/08			1.79 ± .05				4.9	
Upper Confined Aquifer (UCA)										
59	Zwart – mode 1	14/06/99	15.2	2.3	–			0.51	17	–
59	Zwart – mode 2	14/06/99			1.52 ± 0.05	36	98	0.29	10	-6.3
162	Mode 1	19/12/72	25.3	2.9	–	1*	100	1.00	43	–
162	Mode 2	19/12/72			10.0 ± 0.6	17	100	0.60	22	-6.3
37	Milson	14/06/99	24.3	5.0	2.05 ± 0.06	4.5	100	0.54	19.4	-6.2
37		11/06/05			1.47 ± 0.05				16.1	
37		17/12/08			1.48 ± 0.04				13.7	
Lower Confined Aquifer (LCA)										
104	Baigents	3/02/75		0.3	1.9 ± 0.2	71	90		1.5	-7.0
103	Waimea County	26/2/75	26.2	1.0	3.0 ± 0.4	62	94		0.5	-6.6
105	Railway	3/08/75	30.5	1.6	4.6 ± 0.4	42	96		1.7	-6.7
120	Near 105	31/1/78	32.9	1.7	4.3 ± 0.3	41	96		1.5	–
102	Sowman No. 2	24/2/75	34.3	1.8	7.5 ± 0.6	22	99		1.1	-6.8
101	Sowman No. 1	14/2/75	33.2	2.4	5.8 ± 0.8	33	98		1.9	-6.7
38	Woodford	30/8/73	34.1	3.3	13.4 ± 0.8	1	100	1.00	28.4	–
208	Ranzau Rd	19/12/72	30.5	4.1	15.8 ± 1.0	1	100	0.70	19.9	-6.4
208		14/3/83	32.6		3.93 ± 0.20				19.0	-6.5
208		15/06/99	36.9		2.16 ± 0.06				20.4	-6.5
17	Pughs Rd	17/11/72		5.0	10.5 ± 0.6	16	100	0.23	5.5	-6.6
109	Bartletts Rd	16/4/75		6.4	1.4 ± 0.4	78	89		1.0	-7.4
32	RBC#2	17/11/72	33.5	7.1	6.4 ± 0.4	33.5	98	0.60	10.8	-6.7
32		16/4/75	38.1		6.0 ± 0.5				10.0	-6.4
32		14/06/99			1.70 ± 0.05				13.2	-6.4
32		20/06/05			1.24 ± 0.05				13.2	
32		17/12/08			1.23 ± 0.04				13.5	
31	RBC#3	14/3/83		7.1	2.24 ± 0.15	67	92	0.78	10.0	–
119	Chipmill	26/6/86	37.9	7.3	2.67 ± 0.19	41	96	0.64	14.0	-6.3
14	Bells Island	15/3/83	39.6	9.8	0.71 ± 0.14	110	85	0.60	3.4	-7.0
14		27/6/86	54		1.02 ± 0.10				6.2	-7.0
14		14/06/99			0.488 ± 0.023				5.7	-7.0
255	Rabbit Island	3/02/83		11.2	-0.14 ± 0.11	150	85	0.60	2.0	-7.1
255		20/11/86	59		0.07 ± 0.09				3.2	-7.1

*Water with high NO3-N (43 mg/L) in this well is considered to have had an MRT of 1 year.

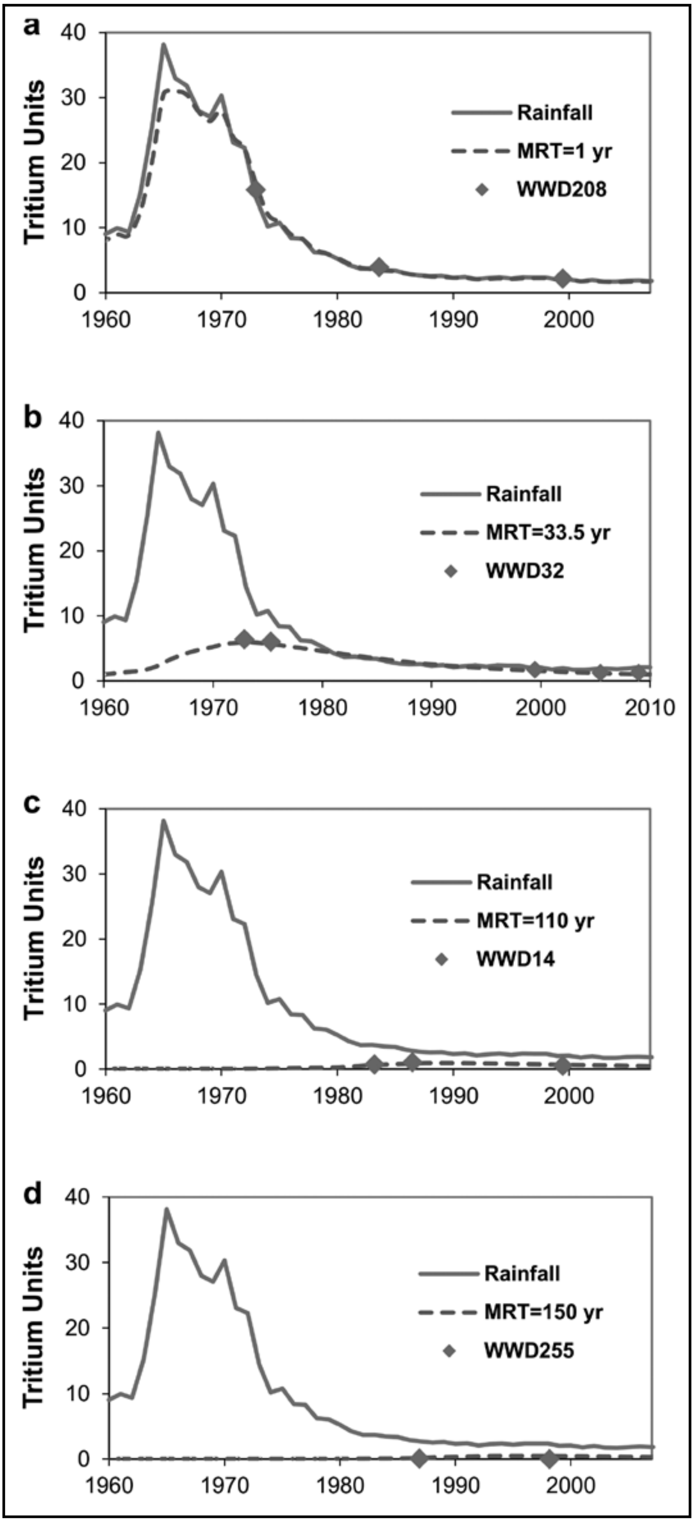

Figure 6 a-d – Tritium measurements and age simulations versus calendar time for wells WWD208, 32, 14 and 255.

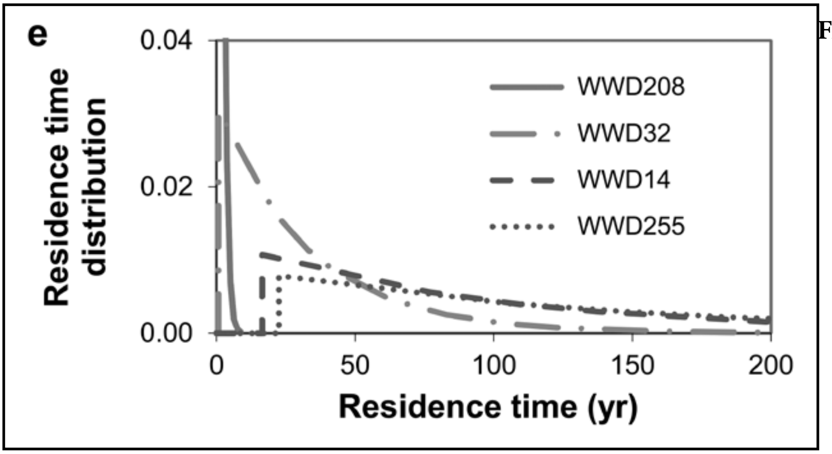

Figure 6e – Residence time distributions of the simulations.

9 years, both with f=100%). In this case, the very young age is considered correct, based on its high nitrate concentration (see below). The other wells (WWD109, 17, 31 and 119) all gave unique mean residence times. Figure 7 shows the mean residence times plotted, with symbol size reflecting mean residence time (with the youngest having the largest symbols). The figure emphasises the importance of recharge in the central eastern plains area (north and south of Hope).

Figure 8 shows various quantities plotted against distance north and northeast along the LCA aquifer. Low nitrate is seen in waters near the Wairoa and Waimea Rivers, high nitrate is seen around 3 km north, which then gradually drops off to the north. Well WWD109 on the west is affected by river input. The mean residence times (Fig. 8b) also show a clear and distinctive pattern with distance. Ages decrease from 70 years along the aquifer to about the 3 km point (where the age is about 1 year for wells WWD38 and 208), then increase strongly towards the sea, with the offshore wells (Bells Island WWD14 and Rabbit Island WWD255) having the oldest ages (greater than 100 years). Both nitrate concentrations and mean residence times show dilution with increasing amounts of low-nitrate, old water towards the north. The $\delta^{18}O$ values also show a clear trend with distance along the aquifer. The Waimea River has mean $\delta^{18}O$ of -7.2‰, while rainfall on the plains has a mean of -6.2‰. The pattern in Figure 8c shows increasing recharge from rainfall towards the central part of the aquifer, while river recharge is important at the ends of the aquifer.

CFC/SF6 results

Mean residence times estimated from the CFC measurements from 1998 and 1999 do not agree with the tritium results in some cases. Applying the same exponential-piston flow models as were used to determine the tritium mean residence times leads to contrary results for some wells where both the tritium and CFC concentrations were measured on 14/6/99 (Table 3). Many of the samples contain excess CFC-12 (i.e., more CFC-12 than could have come from the atmosphere). In fact, some of the Waimea Plains samples had the highest CFC-12 concentrations we have ever measured. Apart from the samples containing excess CFC-12, all of the others gave younger CFC-12 ages than would be estimated from the CFC-11 concentrations, suggesting that they are also contaminated in CFC-12 to a lesser degree. The source of the CFC-12 contamination is considered to be agricultural chemicals used on the plains.

Although less prone to contamination, the CFC-11 results are not very satisfactory either. No excess concentrations were observed, but there is still poor agreement with the

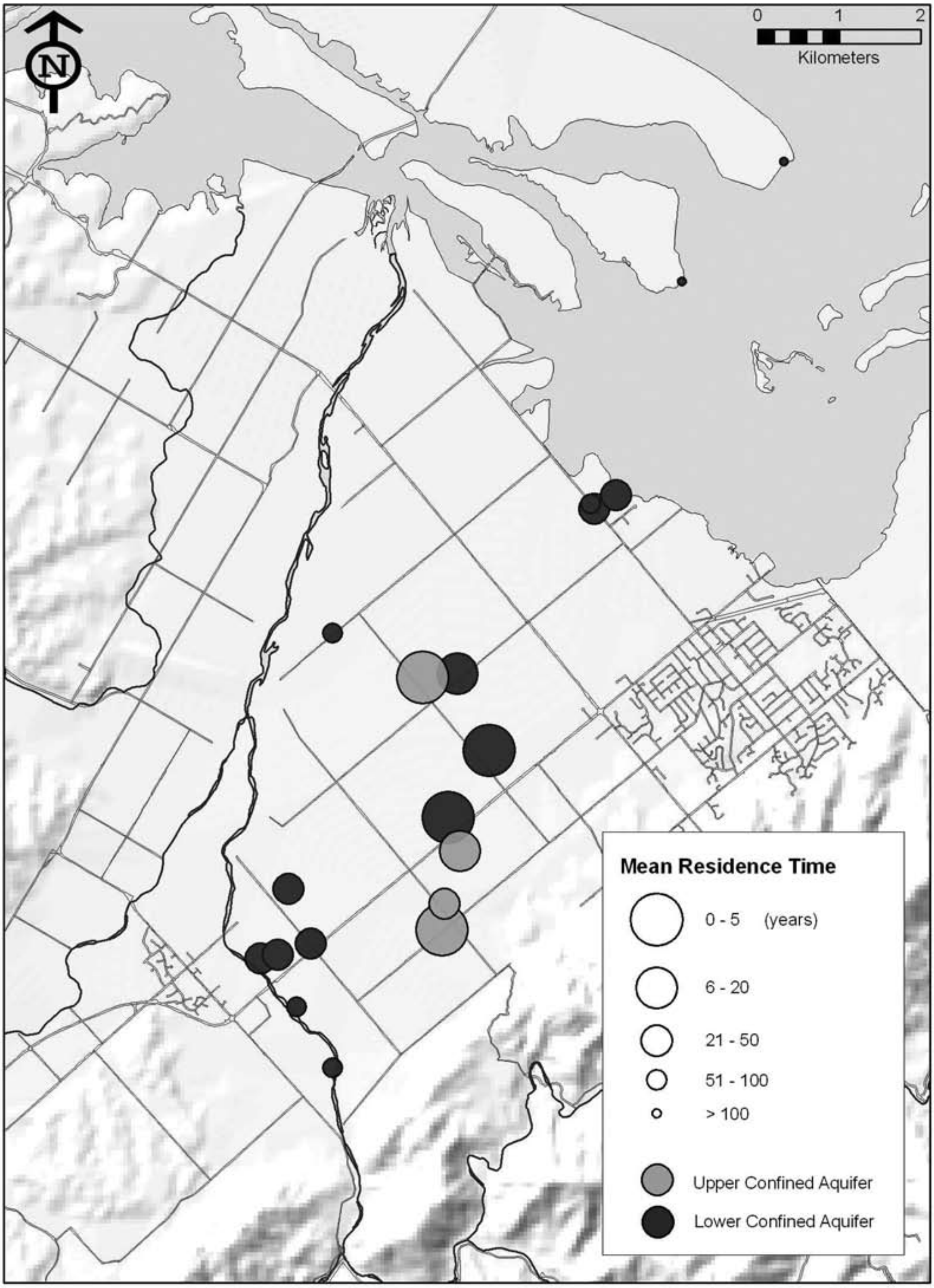

Figure 7 – Map showing mean residence times (MRTs) of groundwater in the Upper Confined Aquifer and Lower Confined Aquifer.

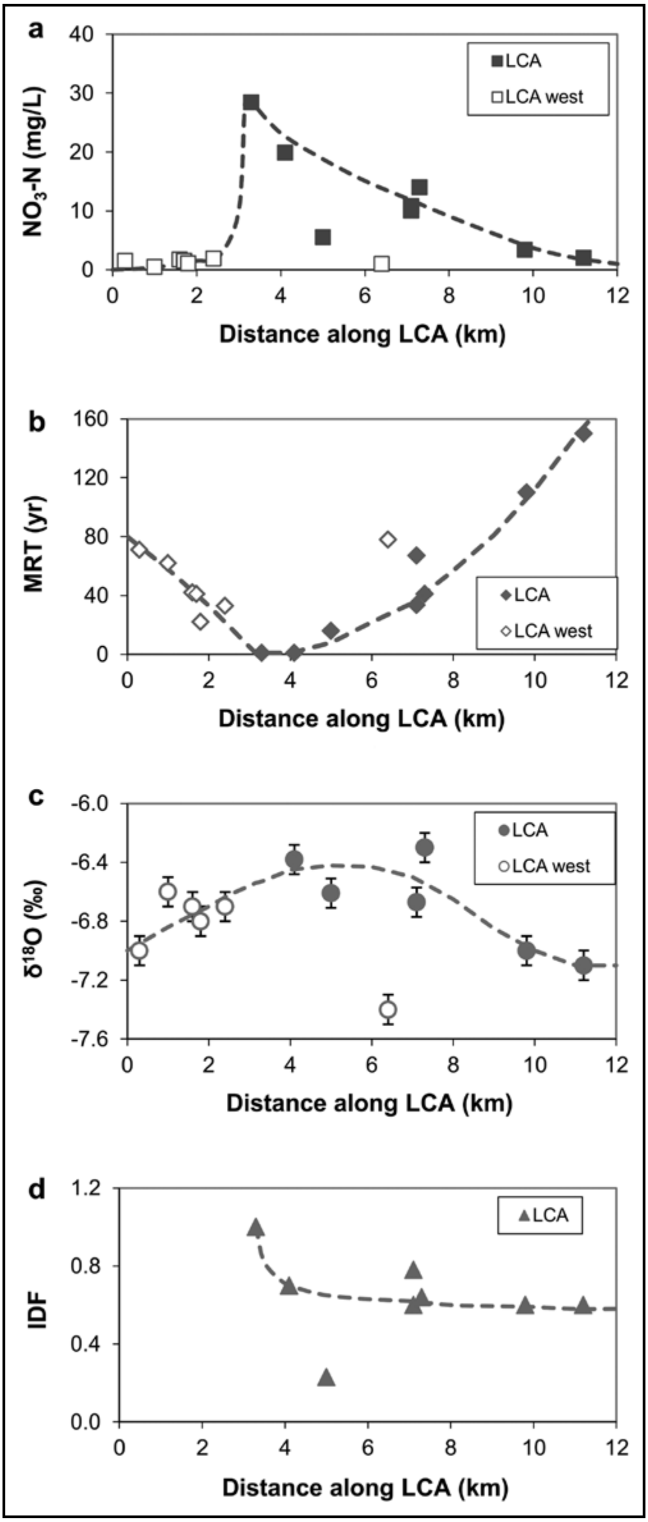

Figure 8 a-d – Plots of NO_3-N, mean residence time (MRT), $\delta^{18}O$ and isotope dilution factor (IDF) versus distance north along the Lower Confined Aquifer. Open symbols mark wells on the west side of the LCA where they are affected by river recharge.

tritium mean residence times for several wells. When the CFC-12 results are badly contaminated, it appears that the CFC-11 results are also likely to be disturbed. No SF_6 measurements were made on 14/6/99, but measurements on 13/6/05 and 17/12/08 for three wells allowed mean residence times to be estimated and concentrations to be extrapolated back to 14/6/99 (Table 3).

Looking at the results in detail in Table 3, WWD802 from the Appleby Gravel Unconfined Aquifer shows agreement between the tritium, CFC-11 and SF_6 MRTs, while the CFC-12 concentration is only mildly in excess. It appears that the CFC-11 and SF_6 age determination is consistent with tritium where the well is not heavily contaminated in CFC-12. In the UCA, WWD59 is slightly contaminated with CFC-12 and the tritium and CFC-11 residence times show moderate agreement (36 to 48 years), while WWD37 is massively contaminated in CFC-12 and its tritium and CFC-11 mean residence times are completely different (4.5 years compared with

Table 3 – Comparison of mean residence times (MRTs) estimated from tritium, CFC and SF6 measurements. Concentrations measured or extrapolated to 14/6/99 are given.

Well No. WWD#	EPM f %	Tritium		CFC-11		CFC-12		SF6	
		Concn TU	MRT yr	Concn pptv	MRT yr	Concn pptv	MRT yr	Concn* pptv	MRT yr
Appleby Aquifer (AGUA)									
802	100	2.40	1.1	272	~0	696	Excess	3.48	3.5
Upper Confined Aquifer (UCA)									
59	98	1.52	36	95	48	547	~0		
37	100	2.05	4.5	71	68	14,245	Excess	1.93	16
Lower Confined Aquifer (LCA)									
208	100	2.16	1	98	46	4,259	Excess		
32	98	1.7	34	90	50	2,322	Excess	1.13	33
14	85	0.488	110	56	63	579	~0		
255	85	–	>150	56	57	210	32		

*Extrapolated from later measurements

68 years). The SF_6 result, however, is not too far from the tritium result (16 years versus 4.5 years). In the LCA, both WWD208 and 32 are heavily contaminated with CFC-12 and there is poor agreement between the tritium and CFC-11 residence times (with WWD208 being the most affected). The SF_6 mean residence time for WWD32, however, agrees very well with the tritium result. WD14 and 255 are moderately contaminated in CFC-12 and their CFC-11 mean residence times are considerably younger than their tritium residence times.

It is concluded that the tritium results are the most reliable for dating groundwater in the Waimea Plains, with results being consistent over time (Fig. 8). CFC-11 results are unreliable when the CFC-12 is heavily contaminated. The SF_6 results are more resistant to contamination and support the tritium results for WWD802 and 32. Note that the best-fitting exponential-piston flow models for the tritium data have high degrees of mixing of young and old water (i.e., f values ranging from 85–100%). This explains how CFCs could have contaminated even the oldest samples (i.e., WWD 14 and 255).

History and future of nitrate concentration

Interpretation of the tritium results has shown that the waters in the UCA and LCA have wide age distributions, and therefore recent as well as long-past inputs will have influenced the nitrate concentrations. Estimates of the history of nitrate input can be gained by simulating the nitrate concentrations in a well, in the same way that the tritium concentrations are simulated. The nitrate concentrations in wells can also be projected into the future by making assumptions about the future input of nitrate, or for long residence times based on the past nitrate inputs alone.

Figures 9a-c show measurements and simulations of the nitrate concentration for the UCA wells. The simulations are based on an assumed history of nitrate inputs to the UCA illustrated in Figure 9d. This input curve was chosen to produce matches with the nitrate concentrations in WWD162 and 37 (Figs. 9a, 9b). Future nitrate inputs (beyond 2010) are shown dotted (Fig. 9d). Well WWD162 has the highest nitrate concentrations measured, but its nitrate data looks bimodal (Fig. 9a). The single tritium sample in 1972 indicated an mean residence time of 17 years and it is assumed that this applied to the lower-nitrate water (mode 2, Table 2) observed in the 1970s; its fitting curve is shown dotted in Figure 9a. The high-nitrate water (mode 1) is assumed to have a residence time of 1 year in the simulation (Fig. 9a, Table 2). With such a short mean residence time, there is not much difference between the input curve and the predicted nitrate concentration in the well.

An input dilution factor (IDF) has been applied to the input curve to allow matches to be made to the nitrate measurements at wells WWD37 and 59 (Table 2). This means that the average input nitrate concentrations are assumed to be lower than that for WWD162 for these wells, but the time structure is not altered. The lower input concentrations are considered to result from lower average concentrations in the recharge sources (i.e. the high-nitrate water shown in WWD162 is diluted by older water with lower nitrate in these wells). The simulation for WWD37 has an input dilution factor IDF of 0.54, and also a relatively short mean residence time (4.5 years) which means that the predicted nitrate concentration has only a short lag from that in the input (Fig. 9b). The nitrate concentration in this well has been declining during the 1990s and 2000s. The data for both WWD162 and 37 constrain the UCA input curve chosen. The nitrate data for WWD59 also looks bimodal (Fig. 9c). Assuming an

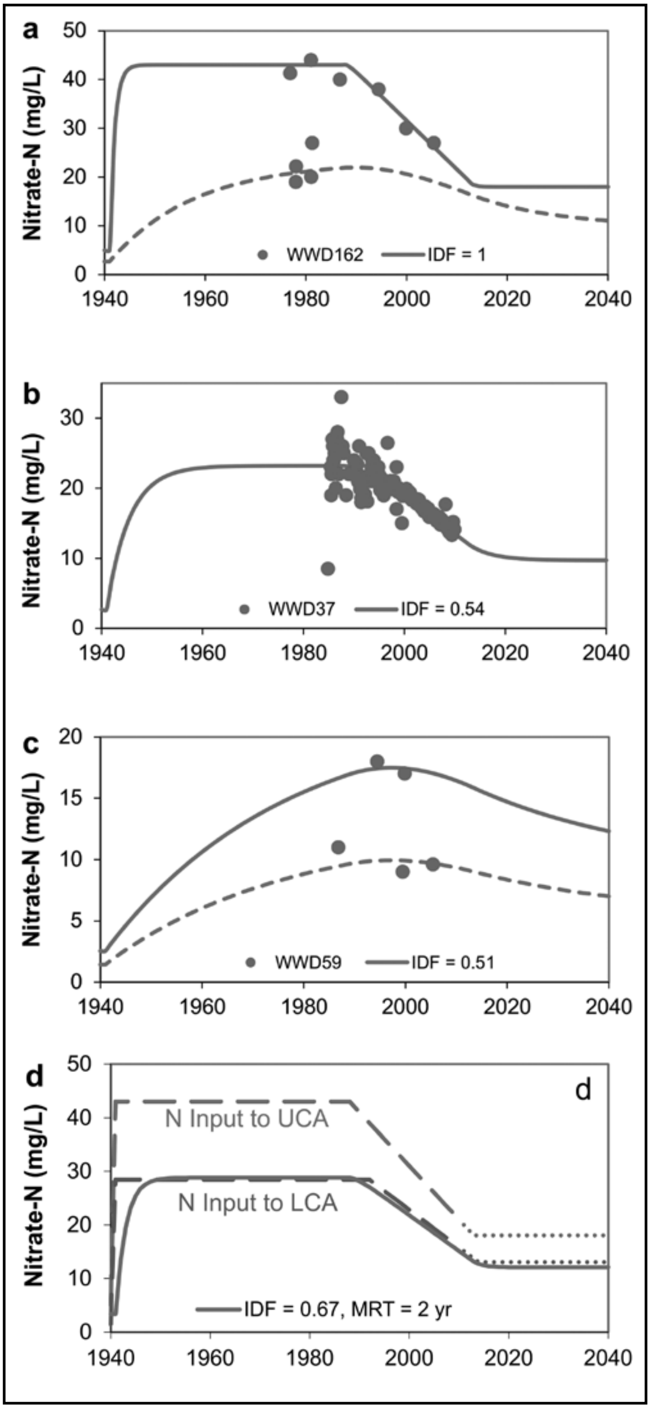

Figure 9a-c – Nitrate-N concentrations in groundwater versus calendar time for the Upper Confined Aquifer (UCA), d) Nitrate input histories for the UCA and LCA.

MRT=36 years applies to both, the higher nitrate group can be simulated using an input dilution factor IDF=0.51, the lower with 0.29. However, it is more likely that the tritium measurement only applies to the lower nitrate and probably older group water (mode 2, Table 2), and that mode 1 water was considerably younger (consistent with its higher nitrate). The two samples collected for $\delta^{15}N$ measurement were apportioned on this basis (Table 1), the higher $\delta^{15}N$ value (8.9‰) then represents mode 1 water and plots on the trend indicating animal wastes input (Fig. 5a).

Figures 10a-f give measurements and simulations for LCA wells. The nitrate input curve for the LCA is given in Fig. 9d. It is the same shape as that for the Hope Gravel UCA, but is only two thirds the height, i.e., The Hope Gravel LCA input curve can be derived from the UCA input curve using an input dilution factor IDF = 0.67, MRT = 2 years. It is chosen to produce fits to the nitrate data for WWD38 and 208. There are only two measurements for WWD38; they fix the height of the input curve. The single tritium measurement for WWD38 could have been interpreted to give either MRT = 1 or 9 years, the former has been chosen as much more likely because of its high nitrate concentrations and because of consistency with the results for WWD208. The data for WWD208 is scattered as expected

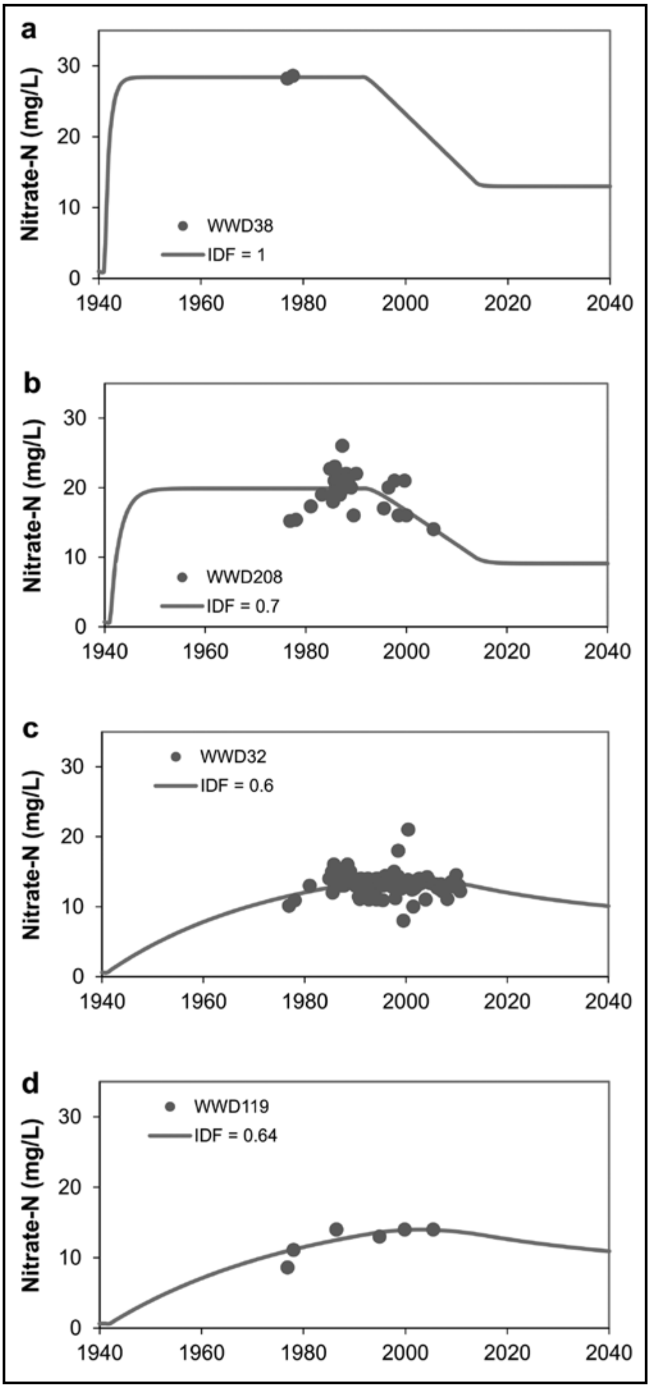

Figure 10 a-d – Nitrate-N concentrations in groundwater versus calendar time for the Lower Confined Aquifer (LCA).

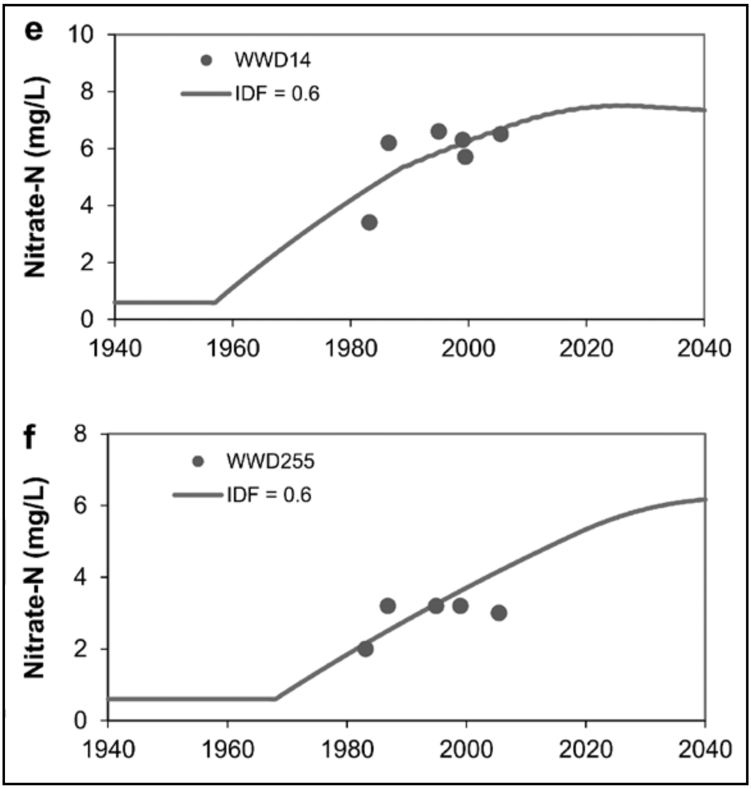

Figure 10 e-f – Nitrate-N concentrations in groundwater versus calendar time for the Lower Confined Aquifer (LCA).

with its short mean residence time (1 year), but the input curve (with input dilution factor IDF = 0.7) allows a fit to the average values. The simulation to the WWD32 data has an input dilution factor IDF of 0.6, its MRT of 33.5 years produces a gradual rise through 1940 to 2000, with a very gentle fall now beginning to take place. The simulation to WWD119 (input dilution factor IDF = 0.64, MRT = 41 years) shows a very similar trend to WWD32. Simulations to WWD14 and 255 are showing rising trends that are likely to continue for 20 years, regardless of future input to the LCA because of their very long mean residence times (110 and >150 years respectively). There may be some small effect from denitrification in this area.

The input dilution factor IDF values are given in Table 2, and are plotted in Figure 8d for LCA wells. The values are relatively constant for many of the wells (being mostly in the range 0.6 to 0.7), showing that the input nitrate concentrations for them are relatively similar. Exceptions are WWD38 with higher nitrate input water, and WWD17 with lower nitrate input water.

Conclusions

1. Nitrate contours of Stevens (2005) and earlier workers in relation to nitrate isotope results in this work have revealed two kinds of nitrate contamination in Waimea Plains groundwater. These are diffuse contamination in the eastern plains area (in the vicinity and south of Hope) attributed to the combined effects of the use of inorganic fertilisers and manures for market gardening and other land uses, and on top of this a strong point source contamination attributed to a large piggery to the south of Hope.

2. Tritium measurements in wells have been interpreted to give mean residence times, and the spread of residence times around the mean, for the groundwater in different parts of the plains. CFC and SF_6 measurements are also discussed. Mean ages are youngest in the area south of Hope, where nitrate concentrations are highest, and increase to the south, west and north.
3. The age distributions have been used to produce a nitrate input history for the Hope Gravel Upper and Lower Confined Aquifers (UCA and LCA) by simulating the nitrate measurements in the various wells. The timing of the derived nitrate input history shows that both the diffuse sources and the point source were present from the 1940s, which is anecdotally the time from which there was increased nitrate input to the plains. The large piggery was closed in the mid-1980s.
4. Management implications of the results: Unfortunately, major sources of nitrate (including the piggery) were located on the main groundwater recharge zone of the plains in the past, leading to contamination of the UCA and LCA aquifers. The contamination travelled gradually northwards, affecting wells on the scale of decades. Input of nitrate to the groundwater has been decreasing since about 1988 due to closure of the piggery. The resulting decrease in nitrate concentrations is now also travelling gradually northward. Groundwater to the south and west already had relatively low nitrate because of river and/or rainfall recharge with low nitrate concentrations. Improved monitoring and practices among market gardeners and other land users need to be encouraged, taking special account of the location of the groundwater recharge areas around and south of Hope.

Acknowledgements

Financial support for this study was provided by Tasman District Council (grants for sampling and measurement), and the Ministry for Science and Innovation through grants to GNS Science (currently Contract C05X0706, “New Zealand Groundwater Quality”, and via Envirolink grant: 924-TSD72). We thank the two anonymous journal referees for their helpful comments.

References

Baker, M.A. 1988: Report on piggery effluent disposal in the Nelson region. Nelson Catchment and Regional Water Board, 12 p.

Böhlke, J.K.; Denver, J.M. 1995: Combined use of groundwater dating, chemical and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. Water Resources Research 31:2319-2339.

Close, M.E.; Rosen, M.R.; Smith, V.I. 2001: Fate and transport of nitrates and pesticides in New Zealand’s aquifers. Pp. 185-220 in Groundwaters of New Zealand, Rosen, M.R.; White, P.A. (eds.). New Zealand Hydrological Society Inc., Wellington.

Daughney, C.J.; Reeves, R.R. 2005: Definition of hydrochemical facies in the New Zealand National Groundwater Monitoring Programme. Journal of Hydrology (NZ) 44: 105-130.

Dicker, M.J.I. 1980: The hydrogeology of the Waimea alluvial basin, Nelson, New Zealand. MSc. Thesis, Dept. of Geology, University of Canterbury.

Dicker, M.J.I.; Fenemor, A.D.; Johnston, M.R. 1992: Geology and groundwater resources of the Waimea Plains, Nelson. New Zealand Geological Survey Bulletin 106, 59 p.

Fenemor, A.D. 1987: Water Quality of the Waimea Plains Aquifers 1971-1986. Nelson Catchment and Regional Water Board internal report.

Fenemor, A.D. 1988: A three-dimensional model for management of the Waimea Plains aquifers, Nelson. Publication No. 18, Hydrology Centre, Department of Scientific and Industrial Research, Christchurch.

Fogg, G.E.; Rolston, D.E.; Decker, D.L.; Louie, D.T.; Grismer, M.E. 1998: Spatial variation in nitrogen isotope values beneath nitrate contamination sources. Ground Water 36 (3): 418-426.

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

Johnston, M.R. 1979: Geology of the Nelson urban area. (1:25,000). *New Zealand Geological Survey urban series Map 1*. Department of Scientific and Industrial Research, Wellington.

Katz, B.G.; Böhlke, J.K.; Hornsby, H.D. 2001: Timescales for nitrate contamination of spring waters, northern Florida, USA. *Chemical Geology 179*: 167-186.

Kendall, C. 1998: Tracing nitrogen sources and cycles in catchments. Chapter 16 in *Isotope Tracers in Catchment Hydrology*. Kendall, C.; McDonnell, J.J. (*eds*.). Elsevier, pp. 519-576.

Maloszewski, P.; Zuber, A. 1982: Determining the turnover time of groundwater systems with the aid of environmental tracers, 1. Models and their applicability. *Journal of Hydrology 57*: 207-231.

Ministry of Health 2005: Drinking water standards for New Zealand 2005. Ministry of Health.

Moore, K.B.; Ekwurzel, B.; Esser, B.K.; Hudson, G.B.; Moran, J.E. 2006: Sources of groundwater nitrate using residence time and isotope methods. *Applied Geochemistry 21*: 1016-1029.

Morgenstern, U.; Stewart, M.K.; Stenger, R. 2010: Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit time with streamflow. *Hydrology and Earth System Sciences Discussions 14(11)*: 2289-2301.

Morgenstern, U.; Taylor, C.B. 2009: Ultra low-level tritium measurement using electrolytic enrichment and LSC. *Isotopes in Environmental and Health Studies 45*: 96-117.

Plummer, L.N.; Busenburg, E. 1999: Chlorofluorocarbons. Chapter 15 in *Environmental Tracers in Subsurface Hydrology*. Cook, P.; Herczeg, A.L. (*eds*.). Kluwer Academic Publishers, p. 441-478.

Stanton, D.J; Martin, J. 1975: Nitrate levels in subsurface waters of the Waimea Plains, Nelson. *New Zealand Journal of Marine and Freshwater Research 9*: 305-309.

Stevens, G. 2005: 2005 Waimea Plains groundwater nitrate survey. *TDC State of the Environment Monitoring Programme Draft Report*, Tasman District Council. 51 p.

Stewart, M.K.; Dicker, M.J.I.; Johnston, M.R. 1981: Environmental isotopes in New Zealand hydrology. Part 4. Oxygen isotope variations in subsurface waters of the Waimea Plains, Nelson. *New Zealand Journal of Science 24*: 339-348.

Stewart, M.K.; Morgenstern, U. 2001: Age and source of groundwater from isotope tracers. Pp. 161-183 in *Groundwaters of New Zealand*, Rosen, M.R.; White, P.A. (*eds*). New Zealand Hydrological Society Inc., Wellington.

Stewart, M.K.; Morgenstern, U.; McDonnell, J.J. 2010: Truncation of stream residence time: How the use of stable isotopes has skewed our concept of streamwater age and origin. *Hydrological Processes 24(12)*: 1646-1659.

Stewart, M.K.; Thomas, J.T. 2008: A conceptual model of flow to the Waikoropupu Springs, NW Nelson, New Zealand, based on hydrometric and tracer (^{18}O, Cl, ^{2}H and CFC) evidence. *Hydrology and Earth System Sciences 12(1)*: 1-19.

Stewart, M.K.; van der Raaij, R.W.; Daughney, C.J. 2006: Use of ^{15}N to identify sources of groundwater nitrate in NGMP samples. Pp. 8-9 in *New Zealand Hydrological Society 2006 Symposium Proceedings*, Christchurch, 20-23 November.

Van der Raaij R. 2003: Age dating of New Zealand groundwaters using sulphur hexafluoride. *MSc Thesis*, School of Earth Sciences, Victoria University of Wellington.

Ware, P. 2000: The spatial and temporal distribution of nitrate within the groundwater system of the Waimea Plains. *Unpublished Honours thesis*, University of Otago.

White, P.A.; Reeves, R.R. 1999: Waimea plains aquifer structure as determined by three-dimensional computer modelling. *Journal of Hydrology New Zealand 38(1)*: 49-75.

Manuscript received 4 May 2011; accepted for publication 15 August 2011