From Rain through River Catchment to Aquifer: The Flow of Water through the Wairau Hydrologic System

U Morgenstern, P Davidson, DB Townsend, PA White
RW van der Raaij, MK Stewart, M Moreau, C Daughney

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U Morgenstern, GNS Science, PO Box 30368, Lower Hutt 5040, New Zealand
P Davidson, Marlborough District Council, PO Box 443, Blenheim, New Zealand
D Townsend, GNS Science, PO Box 30368, Lower Hutt 5040, New Zealand
P White, GNS Science Wairakei Private Bag 2000, Taupo, 3352, New Zealand
R van der Raaij, GNS Science, PO Box 30368, Lower Hutt 5040, New Zealand
M Stewart, GNS Science, PO Box 30368, Lower Hutt 5040, New Zealand
M Moreau, GNS Science Wairakei Private Bag 2000, Taupo, 3352, New Zealand
C Daughney, MFE, PO Box 10362, Wellington 6143, New Zealand (formerly GNS Science)

www.gns.cri.nz

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However, Radon-222 can also be removed from groundwater due to absorption on organic matter in the aquifer (Morgenstern et al. 2012). This can clearly be seen in the groundwater near the coast in the centre of the valley, which has low ^{222}Rn but is reasonably old (MRT = 11 years) and originates from a highly anoxic environment indicative of high organic matter content, as indicated by a high methane concentration. Similar conditions are likely at the well with low ^{222}Rn northwest of Renwick, which also has a high methane concentration and ^{222}Rn concentration even lower than the youngest groundwaters next to the river.

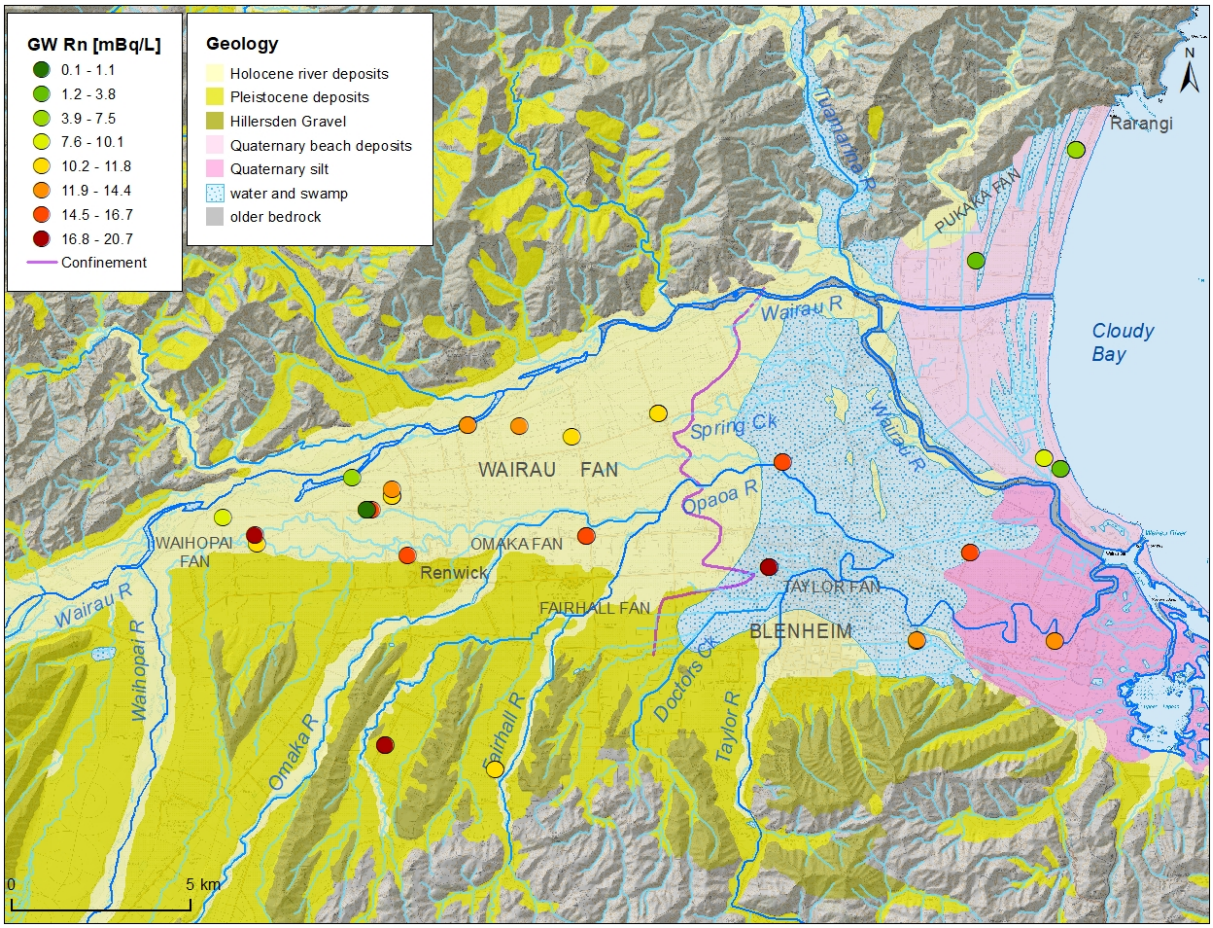

Figure 4.9 Spatial distribution of Radon-222.

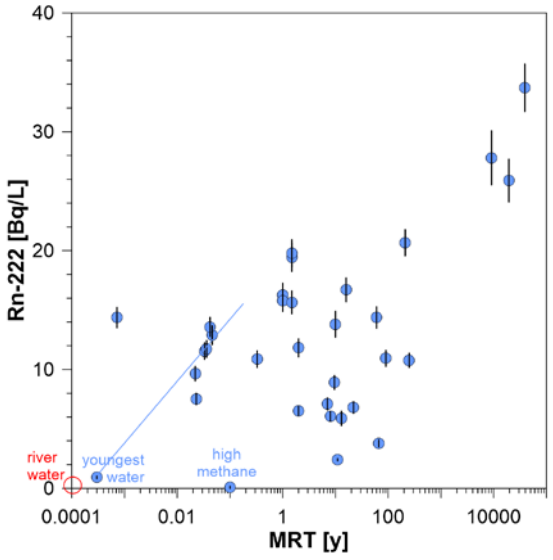

Figure 4.10 Radon-222 concentrations vs. MRT.

Figure 4.10 shows the ^{222}Rn concentrations versus MRT. Most groundwaters have ^{222}Rn concentrations between 5 and 20 mBq/L. The youngest water and the water with high methane (labelled in Figure 4.10) have low ^{222}Rn concentrations, as expected. Most of the young groundwaters with ages below 0.06 years, the age range where a gradual ^{222}Rn increase would be expected due to re-saturation of low-^{222}Rn river water, do show a trend with age (blue line). Close et al. (2014) utilised a similar ^{222}Rn increase to estimate flow velocities. However, the ^{222}Rn versus age data in Figure 4.10 show that care must be taken, as the radon transfer from the minerals into the water is not a uniform process. Other conditions, such as the radium concentration of the minerals and the ability to release the ^{222}Rn, appear to result in a high variability of ^{222}Rn concentrations. In addition, ^{222}Rn can also be absorbed by organic matter, which limits the use of ^{222}Rn-ingrowth as an age tracer.

4.1.2 River and Stream Transit Time

To characterise the transit time of water through the various geologic formations in the Wairau Plain and hydraulically connected river catchments, the age tracer tritium was measured in samples collected from rivers and streams. Samples were collected from the wider catchments of the Wairau and Tuamarina Rivers that flow through and potentially interact with the Wairau Plain aquifers, and from spring-fed streams within the Wairau Plain. For streams and rivers that were sampled only once or twice, low and average baseflow conditions were chosen for sampling because this allows identification of the oldest water in the flow system. The oldest water typically dominates river flow during the summer months when demand for the water resource is greatest, including recreation, and when water quality is of greatest concern. Understanding the transit times of water in catchments and groundwater storage is vital for assessing the impact of contamination in order to protect riverine ecosystems, and for validating groundwater flow models for assessment of potential consequences of groundwater pumping for these rivers.

The transit time of the water through the Wairau River catchment has already been characterised by Taylor et al. (1992) using the tritium response of the river following the tritium bomb peak (Section 3.1) in the 1960s. The first tritium measurements of river water were made in 1968, post-dating the tritium bomb peak in precipitation by only three years. We would like to emphasise that only due to the foresight of the hydrologists/geologists at this time in taking up these tools so early do we now have such invaluable data to understand the water dynamics through this river catchment. They found that, following the bomb peak, tritium concentrations of the river declined much more slowly than those of rain, suggesting a lagged response and indicating a large groundwater store in the upper catchment and large transit times of the water in the order of years. This was confirmed by the damping of the seasonal tritium and stable isotope variability in the river. Both tritium decay and variability of tritium and stable isotopes indicated the presence of both a delayed and a non-delayed water component in the river.

Trials by Taylor et al. (1992) using lumped parameter models indicated that to fit the measured data, a tritium input scaling factor of significantly greater than 1.35, compared to Kaitoke (Section 3.1) is necessary for the Wairau Plain. This seemed high at the time, given that the Wairau River catchment lies only 200 km south-west of Kaitoke (Figure 2.2). However, our recent measurements of tritium in Blenheim rain (Figure 4.2) confirmed a high tritium scaling factor for this area. The input scaling factor for Blenheim was 1.22, demonstrating that a scaling factor of 1.35 for the high-mountain catchment is realistic.

These trials by Taylor et al. (1992) also indicated that the non-delaying and delaying catchment reservoirs contribute about equally to the flow, with a residence time of about eight years for the delaying reservoir. With these age distribution parameters, the delayed tritium response of the Wairau River could be matched sufficiently to the bomb-tritium pulse in rain. To refine these parameters after the hydrologic system returned to natural tritium levels, when the bomb tritium had decayed and potential uncertainty from local differences in bomb-tritium input had vanished, we again collected samples from 2002 onwards, and through the first half of 2015 with weekly resolution, to enable matching with the seasonal tritium variability. Figure 4.11 shows the hydrologic status of the Wairau River catchment at the time of sampling, including daily mean values for rain, river flow and water level at nearby well 3009.

The groundwater at well 3009 is recharged from the river and, with its location near Spring Creek (Figure 2.7), represents the groundwater near the end of its flow path through the unconfined aquifer. The water level of well 3009 closely mimics the river flow, demonstrating a close hydraulic connection of the Wairau Aquifer to the Wairau River (Davidson and Wilson 2011; Wöhling et al. 2018).

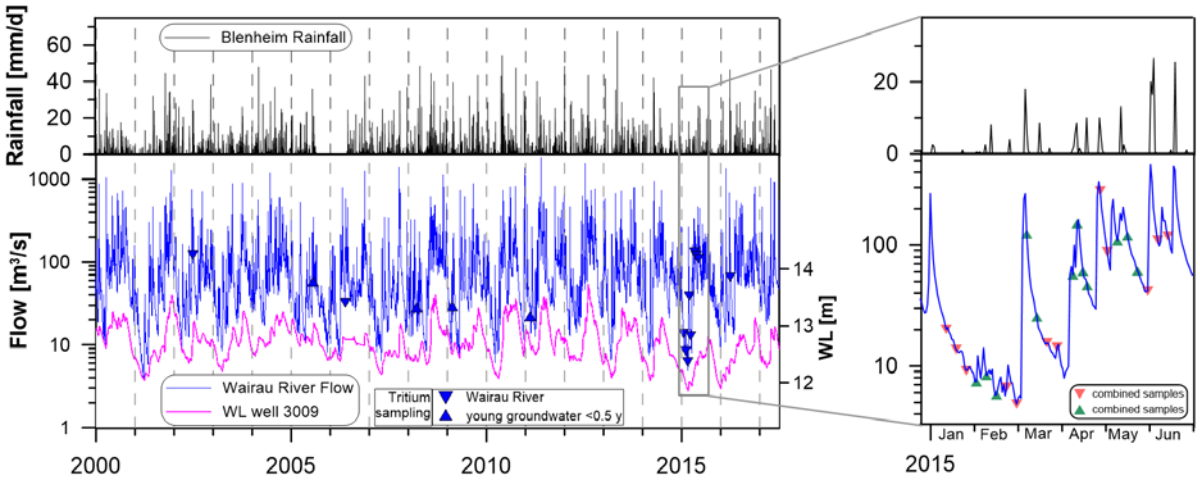

Figure 4.11 Daily rainfall at Blenheim rain gauge and mean Wairau River flow at SH 1 (Figure 2.3) and mean daily water level above median sea level (WL) at well 3009 (Figure 2.7). The river flows at the times of tritium sampling (Wairau River and related young groundwaters) are shown as triangles. The insert on the right shows the period of frequent tritium sampling (approximately weekly), with 2–4 samples combined into one tritium sample (consecutive samples in same colour) to obtain a more averaged tritium concentration for this period.

For the Wairau River and the streams with automatic flow gauges, the related flow duration curves covering the tritium sampling periods are shown in Figure 4.12. The circles show the flows at the time of tritium sampling. The flow of the Wairau River between 2000 and 2016 ranged from 2.8 to 1557 m^3/s, varying with annual rainfall, with a median flow (Q50) of 53.4 m^3/s. Flow at Spring Creek between 2013 and 2015 ranged from 2.7 to 5.3 m^3/s, with a median flow of 3.5 m^3/s. During dry conditions, the Wairau River flow can be as low as low Spring Creek flow. Flow at Murphys Creek in 2015 ranged between 0.6 and 1.3 m^3/s, with a median flow of 0.8 m^3/s. For Doctors and Fulton Creeks the flow was not measured at the time of sampling, but flow duration curves based on previous monitoring are shown.

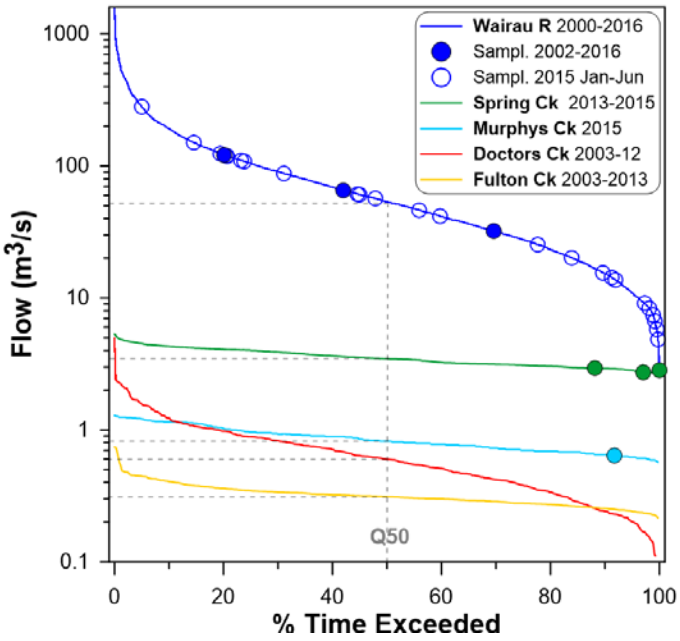

Figure 4.12 Flow duration curves: for the Wairau River and Spring and Murphy Creeks over the times representative for the tritium sampling; for Doctors and Fulton Creeks over a decade. The circles show the flow at the time of tritium sampling. Murphys, Doctors and Fulton Creeks were sampled on 4/3/15; Spring Creek on 15/3/13 and 6/3/15.

In contrast to the flashy nature of the Wairau River and Doctors Creek, due to hill run-off in their catchments, the gentle slope of the flow duration curves of groundwater fed Spring, Murphys and Fulton Creeks, with low extrema on both ends, indicate the baseflow nature of the creeks; their flows are buffered by a relatively large groundwater flow reservoir. The stream samples were collected at low baseflow conditions; however, as the flow does not vary significantly, they can also be considered to represent average flow conditions, except for Doctors Creek. For the Wairau River, both the samples taken over the long-term and the high-resolution samples collected through the first half of 2015 cover average flow conditions, representing the 5th to 100th percentiles of stream flows between 2000 and 2016.

The tritium response of the Wairau River following the tritium bomb peak and the natural cosmogenic tritium levels after the bomb tritium had decayed are shown in Figure 4.13.

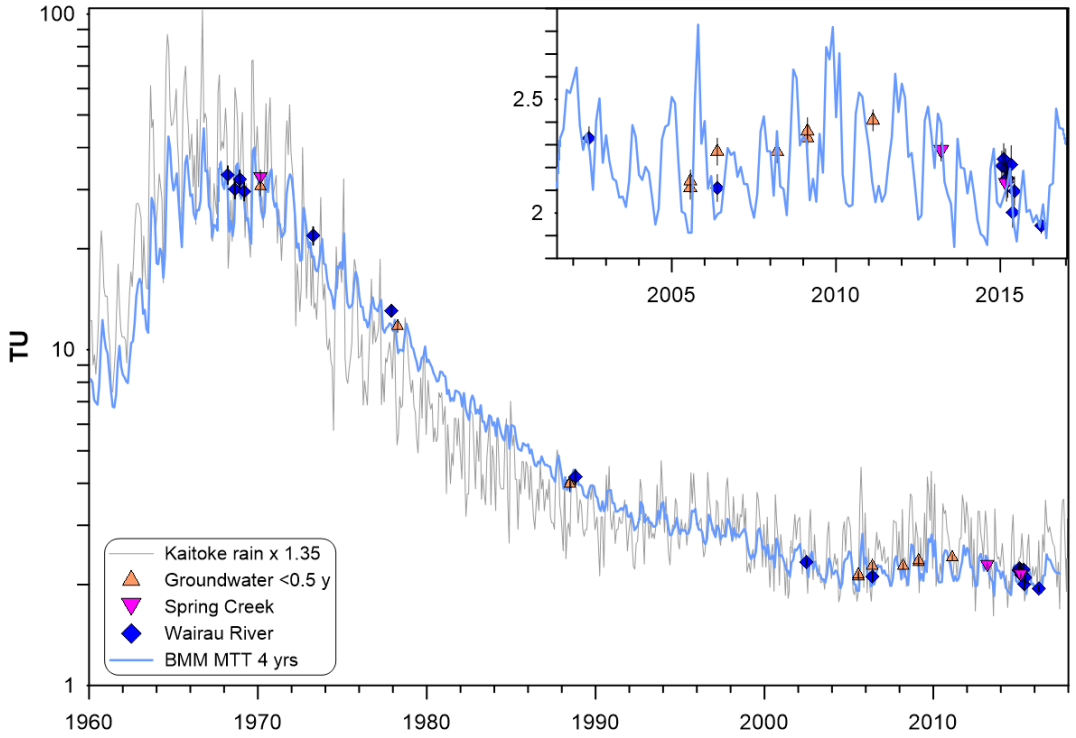

Figure 4.13 Tritium concentrations measured in the Wairau River directly and via Spring Creek, and in groundwaters younger than 0.5 years, in comparison to the tritium concentrations in rain. Both Spring Creek and the young groundwater are the subsurface expression of the river. A scaling factor of 1.35 was applied to the Kaitoke tritium record. A binary mixing model (BMM) with a mean transit time of four years matches all measured data, the delayed tritium response of the river after the tritium bomb spike and the recent data, including seasonal variability (insert).

The Wairau River catchment discharges a mixture of both very young (months) and older (years) water, evidenced by both the appreciable seasonal variability of the stable isotopes and tritium, and the history of the river's tritium concentrations, respectively. The binary mixing of very young water and eight years old water, proposed by Taylor et al. (1992) on the basis of the pre-1990 data, produces a very good fit to both the delayed tritium response of the river after the tritium bomb spike in the 1970s and 1980s and the recent post-2010 data, which are no longer influenced by bomb tritium. Both the river's delayed response to the bomb tritium and the lower tritium concentrations of the river water compared to rain since 2010 clearly show the presence of old water and, consequently, involvement of a large groundwater flow reservoir in the river flow system.

Taylor et al. (1992) attributed this delaying flow reservoir within the upper Wairau River to large deposits of scree and alluvium infilling U-shaped glacial valleys, which dominate the headwater areas of the Upper Wairau catchment, and V-shaped non-glacial valleys in the lower reaches. Our results show that such a scenario is realistic. The Holocene gravels in the Wairau Plain are extremely transmissive, allowing active groundwater flow down to a great depth of c. 50 m (Section 4.1.1) and basically form an underground extension of the river. These Holocene deposits form an extensive coverage within the stream and river channels of the upper Wairau River (Figure 2.1).

Note that during the period 1995–2005, the tritium concentrations in the river and rain water were similar to each other. During this time, which spans the return of the hydrologic system from elevated bomb tritium concentrations to natural cosmogenic low tritium concentrations, tritium was not sensitive enough to identify the old groundwater on the basis of single tritium measurements. The time-series data covering longer periods, and also including the seasonal variability, could be used to overcome this restriction. However, such time-series data are now

no longer required in the southern hemisphere; single tritium measurements of river water in 2015 indicate lower tritium concentrations in the river compared to rain. This is also already the case in parts of the northern hemisphere, where the tritium bomb fallout was significantly larger (Figure 3.3, Gusyev et al. 2016).

Due to the partial decay of the elevated tritium from the high-altitude catchments during the four-year mean transit time through the river's groundwater flow system, the tritium concentration of the river at the Wairau Plain matches that of the low-altitude rain (Figure 4.2). Therefore, the same scaling factor for the Kaitoke tritium rain record of 1.22 can be used for Wairau Aquifer recharge from local rain and from the river.

As with the Wairau River, we found a similar tritium response for the Tuamarina River, which discharges near the coast into the Wairau River, although less data was available. The Tuamarina River water has a significantly longer mean transit time of eight years, compared to four years for the Wairau River. This is demonstrated by the recent tritium levels from 2015 and 2017 that are significantly lower than those of local rain. The data can be fitted reasonably well to a simple EPM with an MRT of eight years and 95% EM. Taylor River had only one measurement in 1978, which showed a similar tritium concentration to rain, but this result is ambiguous without a more recent analysis.

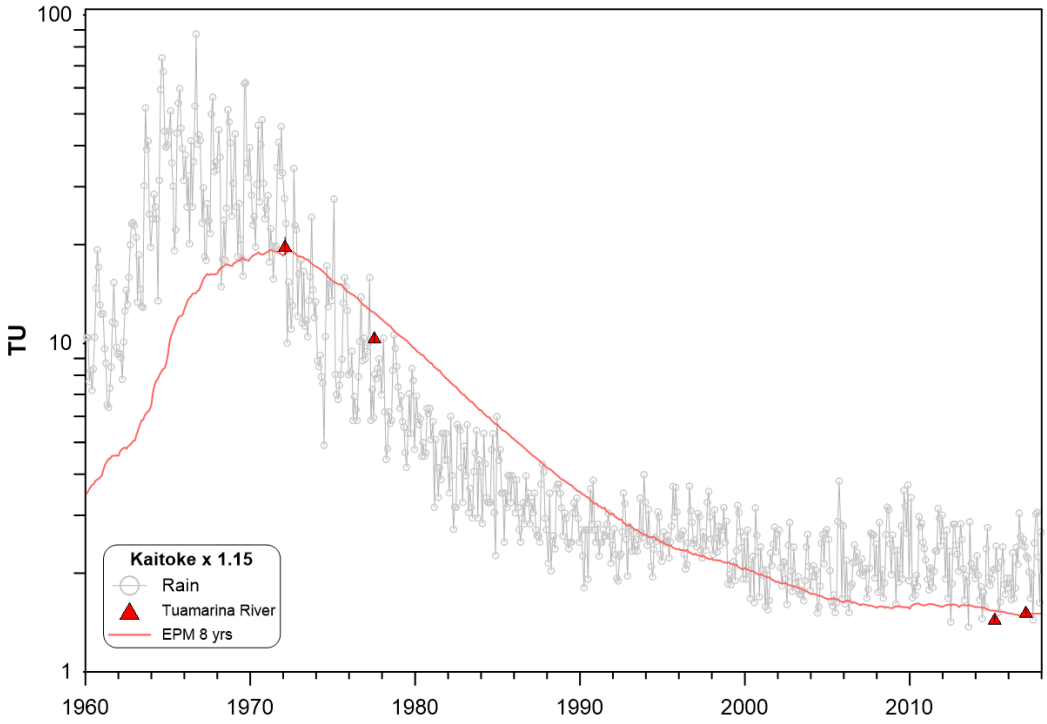

Figure 4.14 Tritium concentrations measured in the Tuamarina River in comparison to the concentrations in rain. A scaling factor of 1.15 was applied to the Kaitoke tritium record, as the Tuamarina catchment lies further north and is closer to Kaitoke and no high elevation mountains shield this sub-catchment from lower-tritium-bearing oceanic moisture. An exponential piston flow model (EPM) with a mean transit time of eight years matches the measured tritium data, the delayed tritium response of the river after the tritium bomb spike and the recent data.

Tritium was also measured in a number of groundwater-fed creeks, and a drain, to obtain an estimate of mean transit time (MTT) of the water through these systems. Spring Creek was measured in 1970 and twice in recent time. The data fit a MTT similar to that of the Wairau River. In Section 4.1.1, it is shown that the water of Spring Creek is an underground expression of the Wairau River, with the water at its discharge point from the groundwater system only 0.33 years older than that of the Wairau River.

Doctors, Fulton and Murphys Creeks, and a drain, were only measured recently, after 2014, when the bomb-tritium had already decayed to insignificant levels and was no longer causing ambiguous age interpretation. The lower tritium concentrations in Doctors Creek and a contributing drain, compared to rain, indicate MTTs of the water of seven and six years, respectively.

Murphys and Fulton Creeks had tritium concentrations similar to those of rain, indicating MTTs of only 1.5 years.

The MTTs for the rivers and streams, in comparison to MRTs of groundwaters, are discussed in Section 4.3.3 and shown in Figure 4.27.

4.2 Hydrochemistry

In the following figures, groundwater hydrochemistry parameters are shown versus MRT to identify drivers of hydrochemistry and the impacts of land use versus natural processes on groundwater quality. Note that all MRTs > 100 years result from data close to the tritium detection limit and may be significantly older (potentially thousands of years). The numbers only indicate the minimum MRT.

During the process of natural groundwater evolution, aquifer matrix minerals are progressively dissolved over time and increasing ion concentrations with groundwater age indicate a geological source due to leaching from the aquifer material. In contrast, high concentrations (in particular those of nutrients) in young groundwater indicate anthropogenic sources from land-use activities.

An overview of the hydrochemical composition of the groundwater from the Wairau Plain in comparison to average New Zealand groundwater composition is listed in Table 4.1. Overall, the Wairau Plain groundwaters have low solute concentrations in relation to average concentrations of New Zealand groundwaters.

Table 4.1 Hydrochemistry statistics, showing number of wells, minimum and maximum concentrations and the 25th, 50th and 75th percentiles for all hydrochemistry data from wells with groundwater age-tracer data. The New Zealand percentiles, shown for comparison, are for groundwater quality data obtained from over 1000 sites collected as part of 'State of the Environment' (SOE) monitoring programmes run by regional authorities and compiled by the New Zealand Ministry for the Environment (2007).

Parameter	Units	Wairau Aquifer Data						New Zealand Percentiles		
		No.	Min.	25%	50%	75%	Max.	25%	50%	75%
Ca	mg/L	45	0.825	6.3	6.8	14.1	50	9.6	15.5	30.0
Cl	mg/L	45	1.6	3.25	3.9	11.3	98	7.3	15.3	30.1
HCO_3	mg/L	45	25.9	30	37	95.69	217	40.0	62.7	144.6
K	mg/L	45	0.54	0.63	0.84	1.3	3.55	1.0	1.6	3.7
Mg	mg/L	45	0.515	1.5	2.1	3.8	12.5	2.6	4.6	8.5
Na	mg/L	45	3.4	4.1	7	14.5	95	9.4	15.0	29.6
NO_3-N	mg/L	45	0.0001	0.135	0.25	0.72	2.75	0.00	1.3	4.4
SiO_2	mg/L	45	8.1	9.1	12.4	14.85	22	13.5	17.0	29.5
SO_4	mg/L	45	0.075	2.5	3.8	7.21	20	3.0	6.5	13.0

Parameter	Units	Wairau Aquifer Data						New Zealand Percentiles		
		No.	Min.	25%	50%	75%	Max.	25%	50%	75%
DRP	mg/L	22	0.0055	0.008	0.0155	0.052	0.21	0.01	0.02	0.07
Fe	mg/L	21	0.0025	0.006	0.01	0.06	0.735	0.01	0.03	0.23
Mn	mg/L	27	0.0005	0.0015	0.0025	0.0565	0.22	0.00	0.01	0.24
NH_4-N	mg/L	45	0.0025	0.005	0.0055	0.012	0.72	0.00	0.01	0.06
Cond.	µS/cm	45	54	65.2	110.8	208	550	144.8	210.0	371
pH	-	37	6.14	6.506	6.88	7.354	8.551	6.4	6.8	7.2

4.2.1 Redox Conditions

Fully oxygenated water in equilibrium with air has a DO concentration of c. 10.5 mg/L. In groundwater systems the water is separated from the atmosphere, and in the presence of organic matter or other electron donors (e.g. pyrite) the oxygen is consumed by microbial oxidation reactions. Reduction of oxygen is energetically the most favourable reaction that micro-organisms use, with the result that other reduction reactions (including denitrification) typically do not occur until most of the dissolved oxygen has been consumed. These reactions take time and usually old waters become increasingly anoxic (e.g. Böhlke et al. 2002).

The Wairau Plain dataset does show a clear trend along these lines: groundwater younger than one year contains high DO of c. 6–10 mg/L, beyond one year DO is strongly decreasing with increasing MRT and groundwater older than 100 years has low DO of < 1mg/L, indicating the ubiquitous presence of organic matter in the aquifer to facilitate microbial reactions up to oxygen depletion.

Elevated concentrations of iron, ammonia and methane in groundwater are indicators of highly anoxic conditions (Morgenstern and Daughney 2012) and are observed in the older Wairau Plain groundwaters (Figure 4.15b–d), indicating that those groundwaters have evolved over time towards highly anoxic conditions, up to the stage of methane fermentation. However, this process appears to not only depend on reaction time, but also on preferential occurrence of organic matter in the aquifer and not all old groundwaters have elevated iron, ammonia or methane.

Elevated iron concentrations start to occur after one year of residence time in the groundwater system, when oxygen depletion also starts to occur. Highly anoxic conditions, up to the state of methane fermentation, typically occur in water older than 10 years.

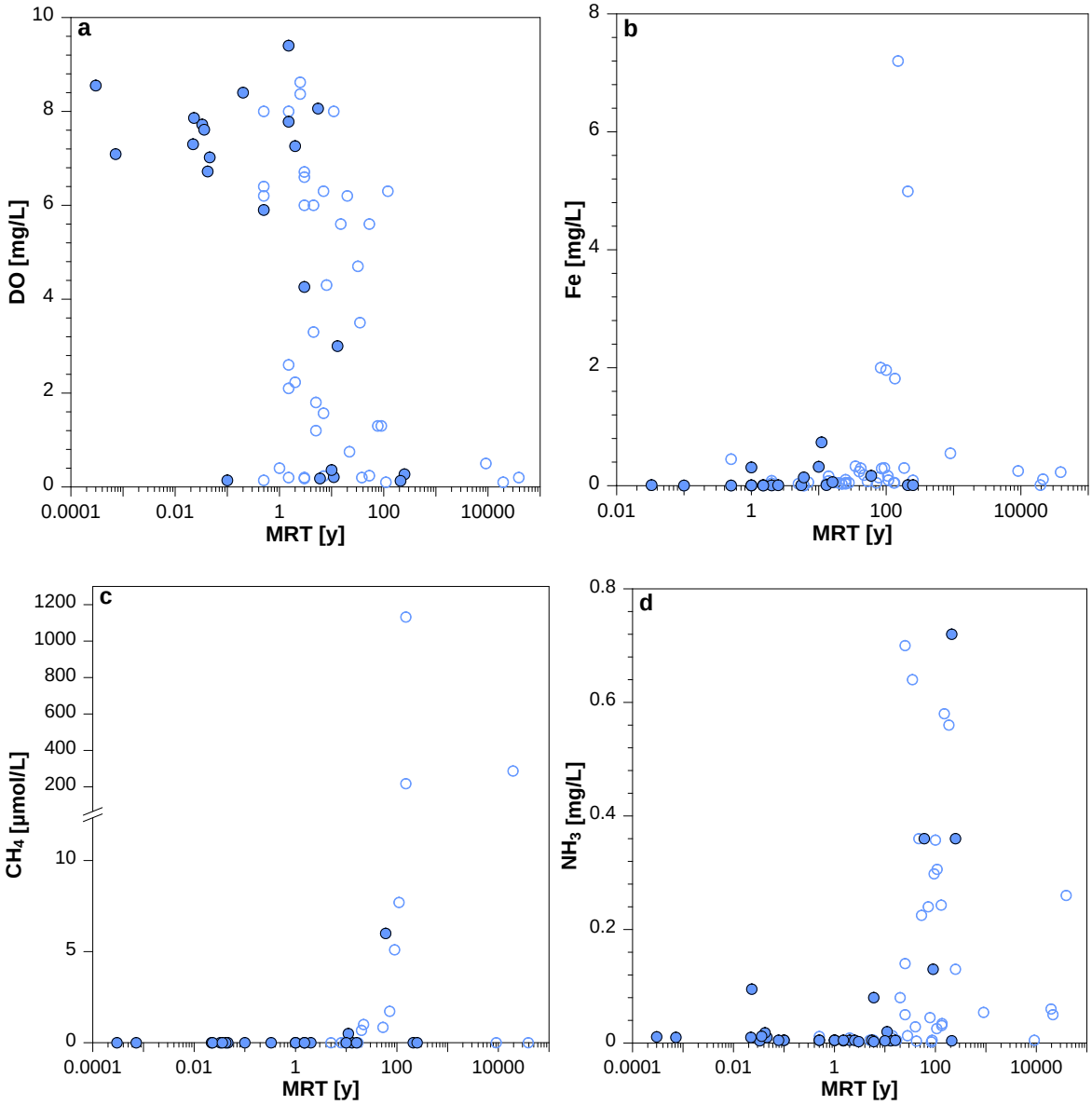

Figure 4.15 Dissolved oxygen (DO), iron (Fe), methane (CH_4) and ammonia (NH_3) concentrations versus mean residence time (MRT) for the Wairau Plain groundwater. This hydrochemistry data originates from various sources over time – solid blue circles indicate more robust recent data.

Figure 4.16 shows the spatial distribution of dissolved oxygen (inner circle) and methane (outer circle) in groundwater. In the unconfined Holocene Wairau Fan, where the groundwaters are younger than one year, DO is typically 6–10 mg/L (green symbols). Towards the coast, in the confined and in the overlying unconfined system, the groundwater becomes increasingly depleted in DO (orange and red symbols) up to the highly anoxic stage of methane fermentation, with consistently high CH_4 in the coastal zone indicating high concentrations of organic matter in these deposits. The groundwaters in the Pleistocene deposits are depleted in oxygen but show a range of methane, from zero up to > 400 µmol/L.

Extremely high hydraulic conductivities, as indicated by extremely young groundwater ages in the Wairau gravel fan, are likely to be a result of clean gravel deposits; these groundwaters show only little depletion in DO, indicating the absence of significant amounts of organic matter that could facilitate microbial reactions.

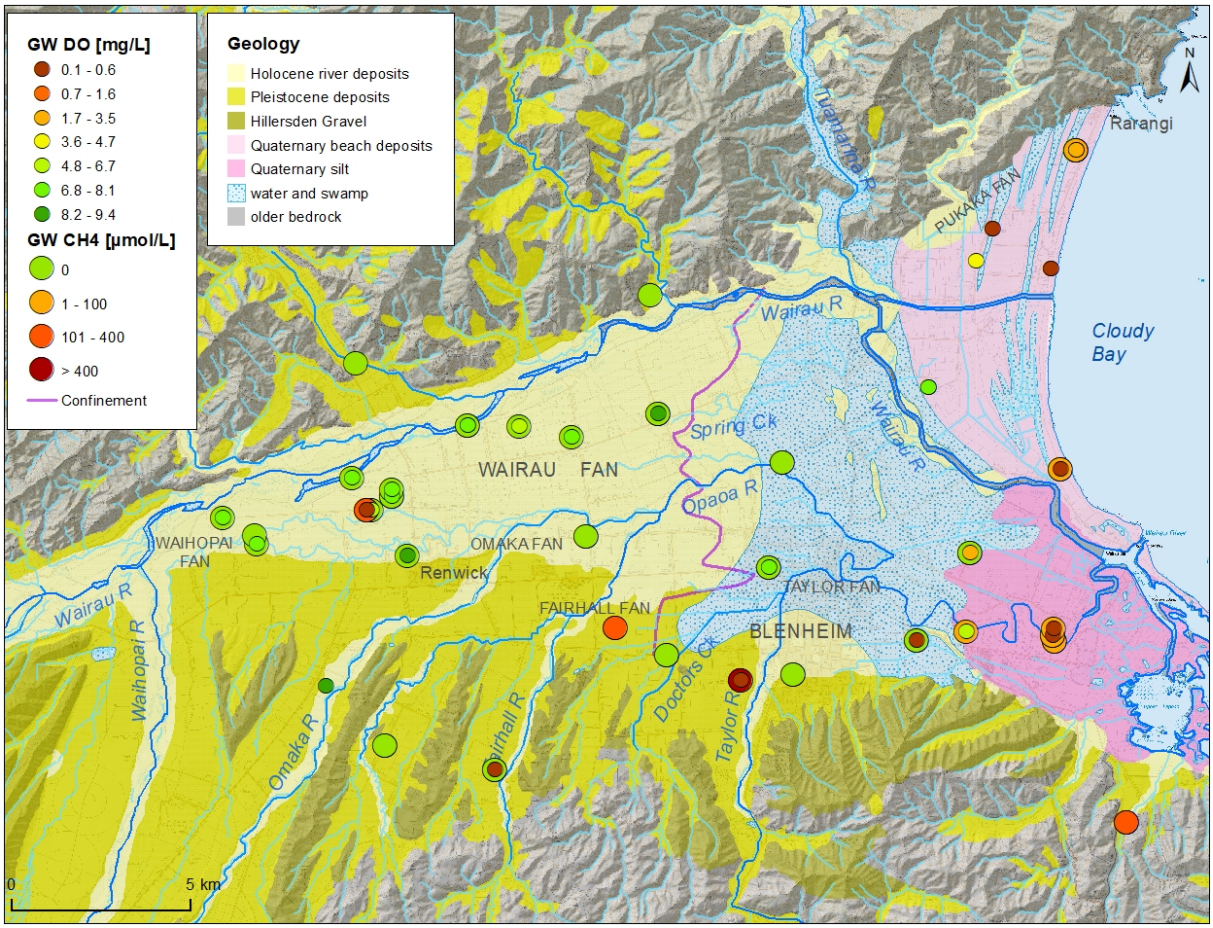

Figure 4.16 Map of dissolved oxygen (DO, inner circle) and methane (CH_4, outer circle) in groundwater. Confining layers reach from the coast up to the confinement line.

However, some localised gravel deposits may have a high content of organic matter, as indicated by the highly anoxic groundwater up to the stage of methane fermentation of well 4724, northwest of Renwick. Note also that this highly anoxic groundwater is very young, indicating that such gravels with high organic matter can be highly hydraulically conductive. While these results indicate that pockets of anoxic conditions with high hydraulic conductivity may exist, the results from this well may be very localised as, when lowering the pump toward the bottom of the well for sampling, it produced alternating oxic and anoxic water at various depths consistently, including oxic water below anoxic water.

4.2.2 Nutrients

The main anthropogenic impacts on groundwater quality in New Zealand started with the onset of industrial agriculture in the 1950s, as deduced from the dataset of the NGMP of New Zealand. Comparison of ion concentrations of recently recharged groundwater, and groundwater that was recharged before 1950, allowed the identification of the pre-industrial baseline groundwater quality and the impacts of land-use activities on groundwater quality (Morgenstern and Daughney 2012).

The NGMP dataset enabled the identification of agricultural contaminants (mostly nutrients) from high-intensity land use, listed in Table 4.2. Comparison of the Wairau Plain data to the NGMP data allows identification of anthropogenic versus geological sources and determination of the impact from high-intensity land use for most of the hydrochemistry parameters.

Table 4.2 Agricultural indicators for high-intensity land use (Morgenstern and Daughney 2012), showing concentration range prior to high-intensity land use, threshold concentrations that indicate high-intensity agricultural land use and observed maximum concentrations. Threshold concentrations in brackets can be ambiguous.

Agricultural Indicator	Concentration Range Prior to High-Intensity Land Use (mg/L)	Threshold Concentration (mg/L)	Observed Maximum Concentration (mg/L)
NO_3-N	0–2.5	2.5	34
SO_4	0–12	12	94
Cl	0–60	(60)	100
Br	0–0.2	(0.2)	1.3
Ca	0–50	(50)	110
Mg	0–15	(15)	54
Cr	0–0.0015	0.0015	0.006

Of the agricultural indicators listed in Table 4.2 that indicate impact by high-intensity land use in New Zealand, only NO_3-N and SO_4 are elevated in the Wairau Plain groundwater, and only marginally. Note the data below represent only the wells that also have age-tracer data, not the entire MDC dataset.

While NO_3-N contamination is not a major problem in Wairau Plain groundwaters, there have been some hotspots with concentrations above 11.3 mg/L, the maximum permittable level for drinking water supplies, attributed to historic arable or dairy farming. These hotspots occurred on the southern margin of the Wairau Fan, where groundwater flow rates and dilution of NO_3-N-loaded water by river-recharged groundwater are lower.

In the wells with water of MRT < 140 years, recharged after the onset of low and high intensity land use, NO_3-N is elevated in about half of the groundwaters between 0.5 and 2.5 mg/L (Figure 4.17a), indicative of low-intensity land use (Morgenstern and Daughney 2012). The youngest groundwaters with MRT < 0.01 years are from wells close to the river and represent river NO_3-N concentrations. Three samples display NO_3-N concentrations above the threshold level of 2.5 mg/L, indicative of high-intensity land use of up to 4.6 mg/L. They are all younger than 10 years and therefore indicate recent nitrate sources.

The few measured groundwaters recharged decades ago at the time of historic arable or dairy farming do not display high nitrate concentrations as observed in other regions of New Zealand (Morgenstern and Daughney 2012). This may imply that a legacy NO_3-N load is not expected to cause drinking water issues. However, a larger sample number in this age range would be required to robustly identify absence of a legacy nitrate load.

About half of the measured groundwaters that are younger than 140 years, and therefore were recharged since low- and high-intensity land use started, have NO_3-N concentrations high enough to cause environmental issues once discharged to the surface. A large fraction of the remainder has low nitrate concentrations, likely only because of high dilution by river water.

SO_4 concentrations of greater than 12 mg/L and up to about 30 mg/L occur in groundwaters with MRTs of 1–140 years (Figure 4.17b), indicating impact by high-intensity land-use activities.