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ABSTRACT

The hydrogeology in the Linkwater area is influenced by cyclically alternating climate and associated variations in sea level and vegetation, and by tectonic processes resulting in regional subsidence. Schist-derived gravel predominates, and is interbedded with brown and yellow clay. Drillholes record the presence of blue silt and clay deposits of swamp or lake origin across much of the Linkwater lowlands. There are no known well-sorted river gravel deposits with a potential to form continuous or semi-continuous aquifers.

Cullen Creek is the most important stream with the most extensive catchments and thus the potential to transport significant quantities of debris. Channelised alluvial gravel, sand and silt deposits are present to a depth of 80 m, forming the more permeable aquifers beneath the Linkwater area and Mahakipawa Valley; they also provide hydraulic connection to the present creek courses so that seepage from surface flow contributes to groundwater recharge. Surface water flow along Cullen Creek occurs only during high and steady rainfall. Under normal conditions surface waters infiltrate creek bed deposits and the bed is "dry". Downstream surface flow can be re-established through spring feed along the creek bed.

Groundwater derived from surface water on the northern and southern slopes infiltrating into aquifers beneath the stream bed are likely to provide a more reliable water supply than water table wells. Large quantities of groundwater occur within schist bedrock. This groundwater was an ongoing problem to the gold mining operations in the Cullen Creek catchment. Piezometric contours derived from random well water measurements show the groundwater flow pattern follows ground surface contours. The logs of wells to the east of Linkwater School indicate poorly sorted gravel and increasing clay and silt deposits towards Okiwa Bay at the head of Queen Charlotte Sound.

All samples collected from the streams and from the vicinity of the upper Cullen Creek have tritium ratios between 1.6 and 1.9, which is considered the range of tritium in rain in this area and represents young water with mean residence times of less than 3 years. The remaining samples have tritium ratios below 1.6 and therefore have mean residence times of 3 years or more. For samples with a rainfall recharge signature (as determined from hydrochemistry and gases), water age shows an excellent correlation of increasing age with depth. Preferential flow paths in hydraulic connection to Cullen Creek, on the other hand, are indicated by short water residence times at all depths for the samples with stream recharge signature.

From the excess air data, a relatively clear pattern with regards to the recharge source emerges. Waters that are not collected from the vicinity of Cullen Creek have elevated or high excess air, indicating recharge by local rainfall. In contrast, samples collected near Cullen Creek have excess air concentrations close to zero, indicating stream recharge. $\delta^{18}\text{O}$ results support the recharge sources identified from tritium and the gases Ar and N_2 .

Comparison of the Linkwater samples to the New Zealand national state of the environment dataset clearly indicates that the Linkwater groundwater samples have several unusual chemical characteristics: low electric conductivity and low concentrations of calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulphate and/or silica. Conversely, well 0485 has relatively high concentrations due to the influence of human activity in the well's recharge area. The patterns in hydrochemistry assessed with the aid of hierarchical cluster analysis support the recharge sources identified by the isotopes and gases.

Water age, excess air and recharge temperature, conductivity, $\delta^{18}\text{O}$, and major ions and nutrients allow for a clear differentiation between groundwater with a signature of young stream water (Cullen Creek), and a signature of local rain-recharged water:

- stream signature with recharge from Cullen Creek for samples #15, 16, 18, and 22 to 25 (wells 0472, 0276, CUL-2, 0495, 0447, 0494, CUL-3).
- signature for recharge via local rain for samples #19 to 21, 26, 27 and 29 (0493, 0485, 0235, 0496, 0492, 0247).

All **groundwaters along Cullen Creek** show a strong stream-water signature, indicating hydraulic connection to Cullen Creek and the presence of channelised alluvial gravel deposits along Cullen Creek. The two groundwater seeps from Jones mine shaft and from Cullen Creek upstream of the bridge also have a strong stream-water signature, indicating that these are re-emerging waters that infiltrated into the creek bed further up valley.

All groundwaters with stream signatures are very young, with mean residence times of less than 3 years, indicating rapid flow in these confined channels. Only well 0472 (#15), furthest down the valley, is slightly older, with a mean residence time of about 6 years, as a result of the further distance to the recharge source and probably lower permeability of sediments down valley. The hydrochemistry of all of these wells is very similar, with low ion concentrations. Low nutrient concentrations demonstrate very little anthropogenic impact and reflect the relatively pristine conditions of Cullen Creek water. These groundwaters are mostly oxidic, indicating relatively clean gravels with too little organic matter to cause anoxic conditions.

The **samples with a signature of rain recharge** in the lowland are older than the stream-signature groundwaters and cover a wide age range of mean residence times, ranging from 3 to >110 years. They show an evolving hydrochemistry, with increasing Ca, SiO_2 , F, P, Mg, Na, and alkalinity/hardness/bicarbonate with increasing contact time of the water with the aquifer material. With increasing residence time in the aquifer these waters become anoxic.

The youngest of the rain recharge signature groundwaters, 0485 (#20) and 0496 (#26), show a high anthropogenic impact. Sample #20 is affected the most, with high nutrient concentrations of K, SO_4 , and NO_3 , and also elevated cadmium and zinc. The older the water, the less it is affected by nutrients. The very old water from well 0235 (#21) has a very unusual hydrochemistry.

Old groundwater ages within the small area indicate stagnant groundwater flow conditions due to the clay-bound gravels. None of the lowland rain-recharged groundwaters shows evidence of origin from well-sorted river gravel deposits that would allow fast flow from recharge sources. This is in agreement with the fact that no such deposits were found in the bore logs.

KEYWORDS

Linkwater, Hydrogeology, Groundwater dating, tritium, CFCs, SF_6 , groundwater flow, groundwater recharge source, hierarchical cluster analysis, nitrate contamination, anthropogenic impact on groundwater.

1.0 INTRODUCTION

Water demand in the Marlborough Sounds Linkwater catchment is increasing due to pasture irrigation by dairy farmers. Little is known about the geology and the hydrology of the area. Resource management decisions are being made without a sound understanding of sustainable limits. Groundwater is the main potential source for irrigation water at Linkwater.

Marlborough District Council requires a baseline hydrological assessment of the flow characteristics of the Linkwater catchment to guide day-to-day allocation practice and advice to Council. While this may be regarded as a baseline study, according to Marlborough District Council consent records, a significant amount of water (around 10,000 m³/day) has already been allocated at Linkwater.

It is assumed that Linkwater catchment water is derived predominantly from local rainfall, either directly onto the flats or as surface run-off from the adjacent ranges via Cullens Creek and other smaller creeks. The variation in well depth at Linkwater suggests that there are different water-bearing formations, ranging from shallow flow through the alluvial gravels recharged by seepage from Cullens Creek or recent rainfall, to medium and deep aquifers that may contain older water.

The objective of this study is to establish the hydrogeology of the Linkwater area, and groundwater flow patterns from the isotopic and chemical signature of the water, including the sources of catchment recharge and mean residence times of the water in the catchment. Tritium, chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆) are used for age dating, and δ¹⁸O, N₂, Ar, CH₄ and a full chemical assessment at all sites (including arsenic, nutrients and heavy metals) are used along with the age data to identify flow characteristics.

2.0 HYDROGEOLOGY OF THE LINKWATER DISTRICT, MARLBOROUGH SOUNDS

2.1 Marlborough Sounds Geology

Linkwater is a low-lying 5 km long alluvial plain between Okiwa Bay at the head of Queen Charlotte Sound and the Mahakipawa Arm of Pelorus Sound near Havelock at the head of the sound (Figure 1). The maximum elevation of the Havelock to Picton road (Queen Charlotte Drive) crossing Linkwater is 17 m above sea level.

The Marlborough Sounds were formed as a result of the northeast tilting of the Marlborough Sounds crustal block, which is located north of the Wairau Fault in the Wairau Valley. The sounds were formed when valleys occupied by rivers during the last glacial period (Otiran) between 14,000 to 70,000 years ago were inundated by the transgressing sea during the postglacial sea-level rise which lasted until 7,500 years ago.

During low sea-level stands throughout parts of the Quaternary Period (last 1.8 million years), the North and South Islands of New Zealand were connected by an isthmus extending from the Marlborough Sounds across Cook Strait to Kapiti Island and the Horowhenua coast (Te Punga 1953a, 1953b). This land bridge was last severed through sea-level rise following the last glaciation, forming Cook Strait and the Marlborough Sounds.

The landscape and topography of Pelorus and Queen Charlotte sounds are the result of the drowning of river valleys cut during low sea-level stands (such as during the last glaciation; Cotton 1955) throughout the Quaternary, when the Cook Strait land bridge was in place and the sea level was up to 130 m below present-day sea level. At the start of the last glaciation about 70,000 years ago, the Pelorus River flowed south from Havelock down the Kaituna Valley to join the Wairau River (Lauder 1970; Mortimer & Wopereis 1997). At Havelock the Pelorus River was joined by a west-flowing tributary that flowed down the valley that is now Mahau Sound and the Mahakipawa Arm. Evidence for the Kaituna Valley being the former Pelorus River course includes Pelorus River-derived schist gravel (“green gravels”) penetrated by a well on the north bank of the Wairau River about 2 km downstream from the State Highway 8 bridge. These schist gravels are at the stratigraphic level of the Speargrass Formation (Otiran Glaciation), which has greywacke-sourced gravels delineated by Brown (1981a and 1981b) in water wells on the adjacent Wairau Plain (Mortimer & Wopereis 1997).

Cotton (1955) proposed a similar Queen Charlotte Sound-derived river flowing south down the Tuamarina Valley to the Wairau River valley. Whether the relic Queen Charlotte Sound river ever flowed west into the Pelorus River system through Linkwater is important when considering the occurrence of aquifers of the Linkwater catchment.

Sometime during the last glaciation (70,000 years to 7500 years ago) the Pelorus River abandoned the 20 km long Kaituna Valley course. Why it stopped flowing south down the Kaituna Valley is not known, but Mortimer and Wopereis (1997) put forward two possibilities: 1) The Pelorus River was not able to maintain its south-flowing course due to northeast tilting of the Marlborough Sounds block; or 2) There was headwater capture of the Pelorus River by a river occupying what is now Pelorus Sound, resulting from erosion of weaker schist bedrock in the Hikapu Reach of Pelorus Sound. This is an area where the schist bedrock is susceptible to erosion due to cataclasis (fracturing) associated with the Kenepuru and Queen Charlotte faults. These faults have not been active since the last interglacial (ca. 80,000 years; Begg & Johnston 2000).

2.2 Linkwater Catchment Geology

The depositional geology of the river sediments, including gravel deposits that form aquifers underlying the Linkwater area, is influenced by climate change over the last 200,000 years of the late Quaternary period, with alternating glacial and warm interglacial periods producing fluctuations in sea level and vegetation cover, and tectonic processes that mainly resulted in regional subsidence.

All drillhole log descriptions are dominated by alluvial materials, indicating that the sea has not transgressed into the Linkwater lowlands for any substantial time during the period represented by the sedimentary record.

The sequence of strata penetrated by test bores and water wells in the Linkwater area provides important information about the late Quaternary geology of the Marlborough Sounds and the groundwater resources of the Linkwater catchment. The cross section compiled from well logs shows the distribution of sediments across Linkwater from west to east (Figure 2).

Schist-derived gravel interbedded with brown and yellow clay dominates the well log descriptions, including the deepest explored depth of 77 m in a test bore (P27/w440) sited about 400 m southeast of the Cullensville Road – Queen Charlotte Drive intersection (Figure 1). Also very obvious in the cross section is a group of wells that penetrate a stratum comprising swamp/wood/peat/organic material in association with blue silt and clay deposits at a depth close to present-day sea level.

A sample of peat and wood collected by Paul Wopereis, L & M Mining Limited, from a depth of 16 m in testbore P27/w440 was submitted for radiocarbon dating and paleoenvironment determination using palynology (pollen content analysis). A freshwater depositional environment was indicated, and an age of >25,000 years before present (BP) within the degree of uncertainty covers the period of the last glaciation during which the sea level was substantially lower than that of today.

The maximum extent of the freshwater body (swamp or lake) that occupied the Linkwater area during the late Quaternary was defined by plotting all wells penetrating organic material and also those wells penetrating blue silt or clay (Figure 3; Wopereis unpublished). The blue colour of the sediment is attributed to reduction of iron oxides in the presence of organic matter, a condition commonly observed in wells penetrating late Quaternary fluvial deposits associated with beds with high organic content such as swamp or lake deposits. The Linkwater lake/swamp occupied most of the Linkwater area but did not extend to the coast to the head of either Queen Charlotte Sound or Pelorus Sound (Figure 3). The lake could have formed as a result of last glaciation fan deposition by Cullen Creek (formerly known as Mahakipawa Stream) cutting off flow of a river draining west across Linkwater, fed by other creeks and streams that drain north and south into the Linkwater area. Today, Cullen Creek flows directly into Mahakapawa Arm, whereas all other westward-flowing creeks and streams in the Linkwater catchment drain into a swamp at the head of the arm about 1 km north of Cullen Creek (Figure 1). Cullen Creek is the most important stream in the Linkwater catchment, both in terms of its catchment area and flow, as monitored at the head of Mahakipawa Valley.

The sediment age of >25,000 years BP eliminates the possibility that the lake/swamp is a postglacial feature unless the dated sample is a reworked sample, which is unlikely in a fluvial depositional environment. This means that the lake/swamp sediments are associated with deposition during a period of warmer climate (interstadial) during the last glaciation about 25,000 – 60,000 years ago. This last glacial interstadial warming is marked by deposits of wood, vegetation and carbonaceous material up to 10 m thick within last glaciation Waiwhetu Artesian Gravels in the Hutt Valley (Brown & Jones 2000), and similar organic beds occur within last glacial gravels underlying other coastal alluvial plains, including the Canterbury Plains near Christchurch and the Heretaunga Plains in Hawkes Bay. The radiocarbon age and the presence of organic-rich sediments suggest that the Linkwater lake/swamp was the result of the warmer interstadial climate during the last glacial interstadial.

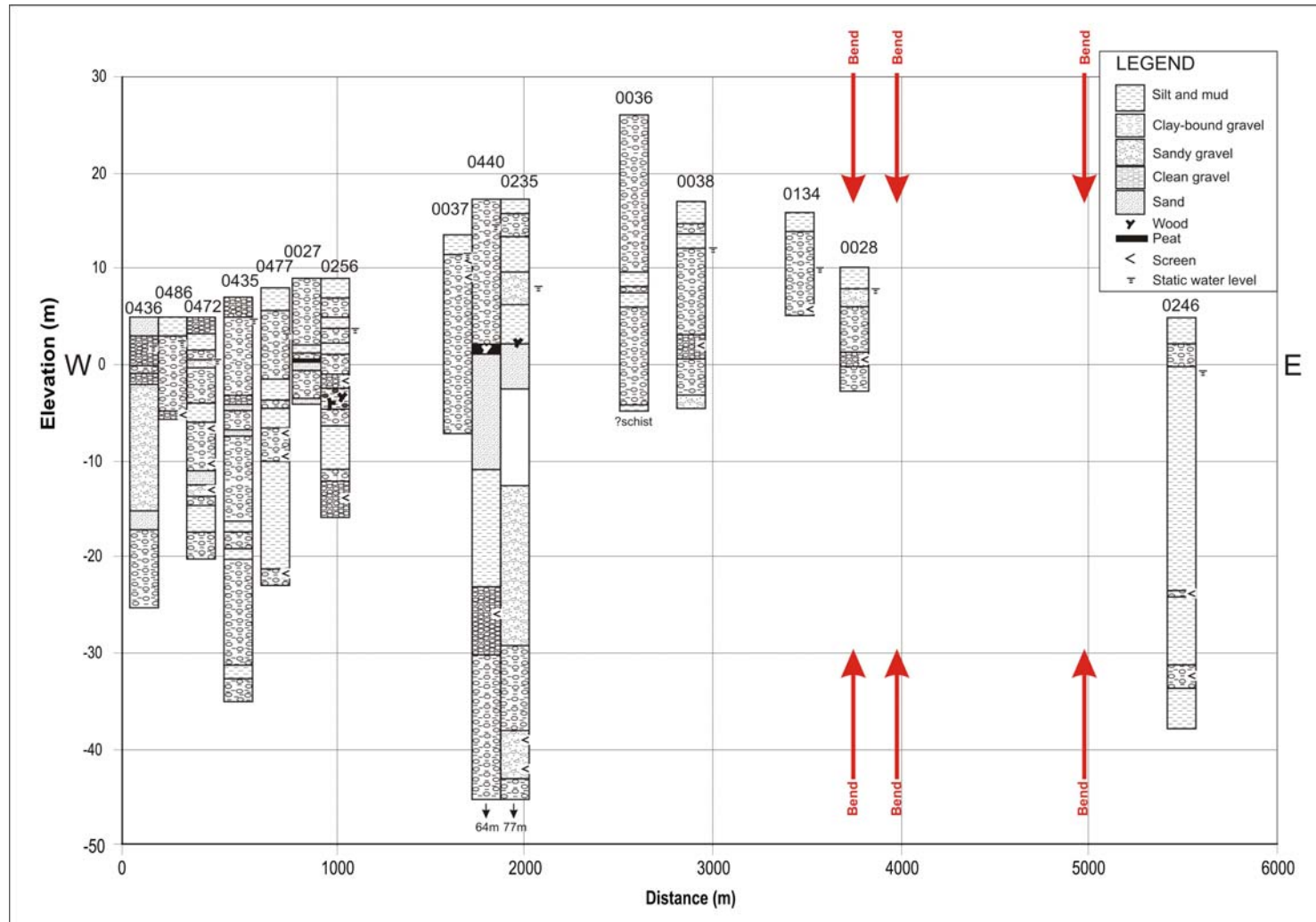


Figure 2. Cross section of the Linkwater area generated from drillhole logs. The section line and locations are shown on Figure 1, along the road from west to east, and drillhole logs are projected onto the section line at right angles. The elevations of the logs are relative to sea level. Turns in the road along the length of the section line are marked by red arrows.

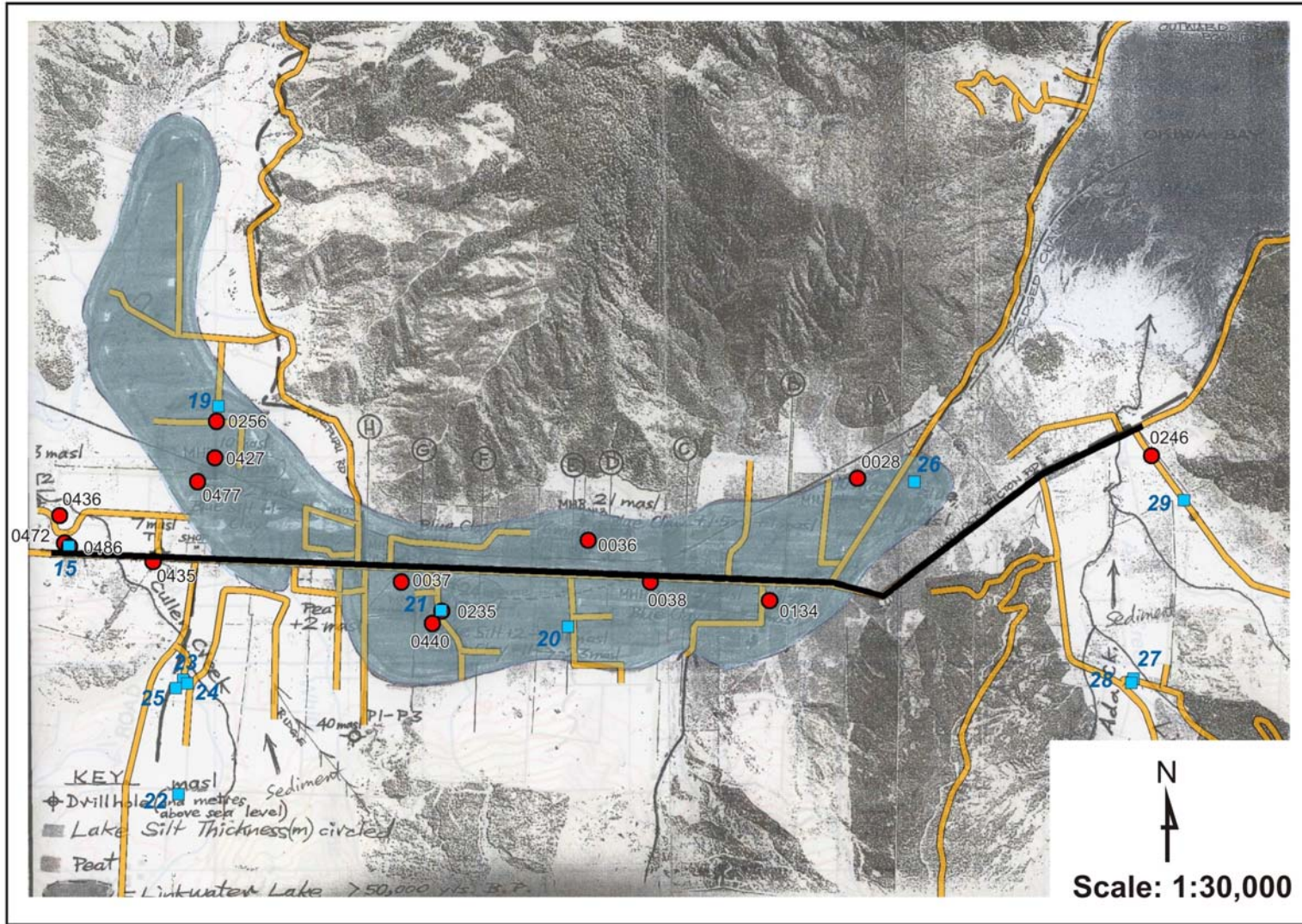


Figure 3. Inferred extent of the last glacial interstadial lake/swamp in the Linkwater area (Paul Wopereis, L & M Mining Limited, unpublished map).

2.3 Hydrogeology

The Linkwater well logs and the graphic well log cross section (Figures 1 and 2) do not indicate the presence of any well-sorted gravel deposits with a potential to form a continuous or semi-continuous aquifer within the valley sediments underlying the Linkwater catchment. The lack of well-sorted gravels forming extensive aquifers precludes the possibility of a major river such as the Pelorus River flowing through the area between Pelorus and Queen Charlotte Sounds during the late Quaternary. The discontinuous and anisotropic character of the Linkwater catchment aquifers is more typical of channel deposition by small local rivers rather than deposition and reworking of sediments by a large river flowing through the valley.

Because of the regional northeast tilting of the Marlborough Sounds Block, the creeks and streams flowing north into the Linkwater area have more extensive catchments, wider valleys and higher flows than those flowing south from catchments on the southern slopes of Mount Oliver. Thus, flooding in north-flowing creeks such as Cullen Creek has the potential to transport and deposit significant quantities of debris derived from the erosion of rocks in the catchment headwaters. Reworking of these flood deposits of gravel, sand and silt would have resulted in channels of well-sorted river gravel. Geophysical surveys (magnetic and seismic) (Modriniak & Marsden 1938) identified possible former river channels and river channel profiles in the schist basement to depths of up to 80 m in the Mahakipawa Valley. These former river channel gravel deposits have the potential to form the more permeable aquifers underlying the Linkwater area and Mahakipawa Valley and also facilitate hydraulic connection to the present creek courses so that surface flow seepage can contribute to groundwater recharge.

Piezometric contours derived from episodic well water level measurements show that the groundwater table elevation is a subdued reflection of the topography, and that the groundwater divide is located near the Linkwater School. The logs of wells to the east of the groundwater divide report poorly sorted gravel and increasing clay and silt deposits towards Okiwa Bay at the head of Queen Charlotte Sound. This may be further evidence of the significance of Cullen Creek for the hydrogeology of the Linkwater area.

2.4 Source of Groundwater

Groundwater in the Linkwater catchment is potentially derived from three recharge sources:

1. local rainfall,
2. infiltration of creek and stream flow, and
3. schist basement rock groundwater derived from inflow through fault fractures, cracks, joints and fissures.

Water levels of wells screening shallow water table aquifers show an immediate response to rainfall events, suggesting that these wells contain rainfall-recharged groundwater. These wells are the most likely wells to run dry during drought conditions and are also most vulnerable to contamination.

For Cullen Creek, flow is maintained only when there is steady and sufficient rainfall in the headwaters. Otherwise, surface flow infiltrates into the creek bed and the river is "dry." In

downstream reaches of Cullen Creek, flow can be re-established by springs feeding the creek. This suggests that water from surface flow in Cullen Creek and other creeks and streams draining the slopes north and south of Linkwater could infiltrate through their beds into the aquifers underneath the Linkwater area. As already outlined, buried palaeoriver channels may provide preferential groundwater recharge conduits to anisotropic semi-confined and confined aquifers. Groundwater derived from a river recharge source is likely to have convoluted flowpaths and as a result, fluctuations in recharge caused by variations of catchment rain and creek flow volume are smoothed out. Wells screening aquifers recharged by this source of water thus provide a more reliable water supply than water table wells.

Isotope and chemistry data can indicate whether the rate of groundwater flow is slow enough to register an age difference. A study in the Speeds – Tuamarina valleys aquifers, from which Picton obtains part of its water supply, showed that the flow rate in the valley aquifers was too fast to register tritium decay (Brown et al. 1985).

Large quantities of groundwater occur in the schist bedrock. In the past, this groundwater component was an ongoing problem to the gold mining operations in the Cullen Creek catchment (Johnston 1993). The groundwater is contained within faults and random lattices of fractures, joints, crevices and cracks in the schist and this can result in high pressures and flows. Groundwater from schist could flow into valley aquifers and even contribute surface flow to creeks and streams. In the Tuamarina Valley groundwater study, only one well at the head of the valley tapped groundwater with a low tritium content, suggesting slow circulation, possibly through fracture joints and fault zones (Brown et al. 1985).

2.5 Aquifer pump tests

Three aquifer pumping tests (two in Mahakipawa Valley and one in Linkwater 400 m from the Mahakipawa Arm shoreline) provide some indication with regards to the hydraulic properties of the aquifers (Royds Consulting 1995). Relatively low transmissivities ranging from 1000 – 4500 m²/day were derived from the analysis of the recovery period at the pumped well. Storativities indicated semi-confined aquifer conditions. Pumping-induced changes in slope of the drawdown curves indicate a heterogeneous aquifer system, with the pumping-induced cone of depression intersecting aquifer boundaries, including schist rock at the valley sides. From the available data, it is not possible to determine whether any of the aquifer tests achieved a sustainable “steady state”, with pumped groundwater derived from water table aquifers, and semi-confined former river channel and schist bedrock aquifers.

No aquifer test data is available from the eastern part of the Linkwater catchment near the Queen Charlotte Sound. It is likely that the aquifers in this part of the catchment will be less permeable because their sediments were deposited by streams with lower flow rates than Cullen Creek in the western sector of Linkwater catchment.

2.6 Summary of Hydrogeology

Deposition in the Linkwater area is influenced by cyclically alternating climate and associated variations in sea level and vegetation, and by tectonic processes resulting in regional subsidence. Schist-derived gravel interbedded with brown and yellow clay predominate. Drillholes record the presence of blue silt and clay deposits of swamp or lake origin across

much of the Linkwater lowlands. There are no known well-sorted river gravel deposits with a potential to form continuous or semi-continuous aquifers.

Cullen Creek is the most important stream, because in the Linkwater catchment north-flowing streams have the most extensive catchments and thus the potential to transport significant quantities of debris. Channelised alluvial gravel, sand and silt deposits are present to a depth of 80 m, forming the more permeable aquifers beneath the Linkwater area and Mahakipawa Valley; they also provide hydraulic connection to the present creek courses so that seepage from surface flow contributes to groundwater recharge. Surface water flow along Cullen Creek occurs only during high and steady rainfall. Under normal conditions surface waters infiltrate creek bed deposits and the bed is “dry”. Downstream surface flow can be re-established through spring feed along the creek bed.

Surface water in Cullen Creek and other streams from catchments on the northern and southern slopes infiltrate aquifers beneath the Linkwater area. Buried former river channels may provide preferential groundwater recharge conduits to anisotropic semi-confined and confined aquifers. Groundwater derived from this recharge source is likely to provide a more reliable water supply than water table wells. Large quantities of groundwater occur within schist bedrock. This groundwater was an ongoing problem to the gold mining operations in the Cullen Creek catchment. Groundwater in the bedrock is confined within faults and random lattices of fractures, foliation, joints, crevices and cracks in the schist and can result in high pressures and flows.

Piezometric contours derived from random well water measurements show the groundwater flow pattern follows ground surface contours, with the groundwater divide being near Linkwater School. The logs of wells to the east of the “divide” indicate poorly sorted gravel and increasing clay and silt deposits towards Okiwa Bay at the head of Queen Charlotte Sound.

3.0 SAMPLE LOCATION AND BORE DATA

Sample locations are shown in Figure 1, and photos of the sites and the surrounding area are shown in Appendix 1. The samples include a series of wells and springs in the western Linkwater catchment that may be related to surface/subsurface flow of Cullen Creek, and a sample from upper Cullen Creek representing a potential recharge source. Another series of samples from wells and an irrigation pit represent the lower central catchment, and one sample is from Ada Stream, a potential recharge source in the east.

Geographic locations and bore data are summarized in Table 1. Information on screen intervals and classification of confinement of the aquifer is scarce.

Table 1. Sample locations, well log data, and comments related to sampling conducted in this investigation.

#	Well_ID	Name	East	North	Altitude m	well water		Screen [m]		confinement from bore logs	Remark sampling
						depth m	level m	top	bottom		
15	P27w/0472	Templeman	2581296	5990571	5	16.1	4.47	6.8	16.1	may be partly confined	irrigation well, not being used
16	P27w/0276	Jones test well (upper valley)	2581592	5988544	33	50?	6.91	slotted full length		unconfined?	test-well, casing plastic
17	CUL-1	Cullen Creek @ Cullensville	2581511	5987860	42						brown transparent algae in stream
18	CUL-2	Jones mine shaft seep	2581600	5988396							seep from old mine shaft, large flow c.3 l/s, dairy farm
19	P27w/0493	Jenkins domestic well	2582018	5991248		18	5.21	15.8	18	?	domestic and milk shed, submersible pump with 2 m plast pipe
20	P27w/0485	Gardiner irrigation well	2583705	5990181	28	4.8	3.68	4.4	4.8	probably unconfined	dairy farm irrigation well, large diam concrete well
21	P27w/0235	Parkes irrigation well	2583091	5990260	18	77	c.9	56.5	76.5	probably partly confined	supply dairy farm, irrigation, stock, domestic
22	P27w/0495	Morrison test well	2581825	5989370	21	33	6.62	18	21	semi-confined	yield too low for irrigation, water not clearing after 30 min pumping
23	P27w/0447	Morrison original test well	2581847	5989925	15	39	5.05	6	17	semi-confined	water contains clay when pumping hard, not used
24	P27w/0494	Morrison domestic well	2581868	5989906		8.3	4.17	5.5?	8.3	semi-confined	sampled from suction pump with pressure tank disconnected
25	CUL-3	Cullen Creek upstream of bridge	2581811	5989883		na	na	na	na	unconfined?	spring or upwelling, very constant through driest summers
26	P27w/0496	Delany irrigation pit	2585377	5990882	12	3	c. 1.5	c.1.5	c.3	unconfined	water seeping into the pit from strong seeps around the pit
27	P27w/0492	Shallcrass irrigation well	2586432	5989930	23	44	10.09	?	?	?	new well, not yet pumped, we pumped 30mins, water de-gassing
28	ADA-1	Ada Stream @ Shallcrass bridge	2586423	5989909	19	na	na	na	na	unconfined?	
29	P27w/0247	Coleman domestic well	2586676	5990793	12	40	5.5	24.5	38	possibly conf.	reported as iron rich water, sampled from plastic pipe

4.0 RESULTS

4.1 Age Tracers Tritium, CFCs and SF₆

A summary of the methodology of groundwater age dating is outlined in Appendix 2.

Table 2 provides a summary of the tritium, SF₆, CFC, δ¹⁸O, Ar, N₂, and CH₄ analytical results, and the field parameters (water temperature, dissolved oxygen and conductivity). The age distribution results are listed in the last two columns. The original analysis reports for CFCs and SF₆ are provided in Appendix 3.

All samples except one have tritium, CFC and SF₆ concentrations below or near their expected natural occurrence, indicating no or insignificant contamination by local sources. Only the water in well 0496 (#26) is contaminated with CFC from local sources. CFC concentrations in the stream water of Cullen Creek are near equilibrium concentration with current air (Appendix 2), indicating that CFCs are not significantly degraded in this stream environment. For wells 0485, 0235, 0495, and 0492 (#20-22, 27), elevated Fe and Mn concentrations (Section 5) indicate anoxic groundwater conditions with the potential for CFC degradation. However, this does not cause ambiguity in age interpretation. Well 0235 (#21), with a presence of methane (Table 2), indicates highly anoxic conditions with a high likelihood of CFC degradation. However, this water does not contain tritium or SF₆ and is therefore old water without ambiguity.

The tritium ratios of all samples are shown in Figure 4a. All samples collected from the streams and from the vicinity of the upper Cullen Creek have tritium ratios between 1.6 and 1.9, which is considered the range of tritium in rain in this area and represents young water with mean residence times of less than 3 years (Table 2). The remaining samples have tritium ratios below 1.6 and therefore have mean residence times of 3 years or more. Sample 0235 (#21) has a tritium ratio close to the detection limit. The indicated mean residence time of 110 years is a lower limit, and the water could be significantly older.

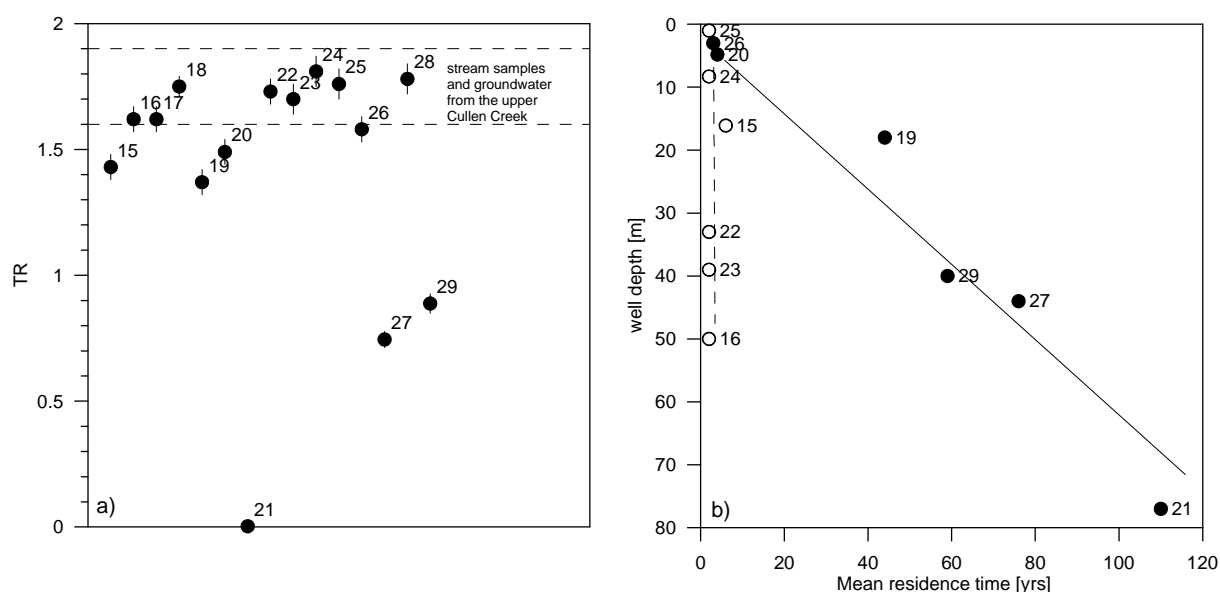


Figure 4. a) Tritium ratios. See Table 1 for sample codes. b) Well depth versus mean residence time for samples with a rain recharge signature (full symbols, full line) and for samples with stream recharge signature (hollow symbols, dotted line).

Table 2. Isotope and age data. Samples with chemistry indicating anaerobic environment are highlighted in red. E%PM is the fraction of mixed flow within the total flow volume; MRT is the mean residence time (see Appendix 2).

#	Well_ID	Date sampling	Temp °C	DO mg/L	Cond uS/cm	Sample code TMB	TR	±TR	δ ¹⁸ O ‰	SF6	CFC11 ± pptv	CFC12 ±	recharge temp °C	±	excess air mL(STP)	±	CH4 μmol/L	±	E%PM estimate %	MRT y		
15	P27w/0472	6/03/2006	12.1	4.7	77	55	1.43	0.05	-6.41	3.75	212	5	451	6	9.2	0.4	0.24	0.06	0	80	6	
16	P27w/0276	6/03/2006	11.7	4.3	76	56	1.62	0.05	-6.23	4.73	197	1	451	5	11.7	0.1	1.16	0.04	0	80	2	
17	CUL-1	6/03/2006	17.4	8	76	57	1.62	0.05	-6.22		233	13	473	39	15.0	1.0	-0.28	0.08	0	80	2	
18	CUL-2	6/03/2006	14.4	1.8	81	58	1.75	0.04	-6.2	5.38	170	3	394	6	12.3	0.5	-0.11	0.85	0	80	2	
19	P27w/0493	6/03/2006	12.8	3.5	106	59	1.37	0.05	-5.81	2.58	122	1	267	1	8.9	0.2	1.78	0.09	0	45	44	
20	P27w/0485	6/03/2006	14.1	5.6	141	60	1.49	0.05	-5.43	4.46	198	--	394	--	10.5	--	-3.04	--	0	80	4	
21	P27w/0235	6/03/2006	12.8	0.1	306	61	0.003	0.021	-6.58	0.03	15	22	38	50	8.7	2.8	2.64	2.14	7.7	1.1	50	110
22	P27w/0495	7/03/2006	12.2	1.2	73	62	1.73	0.05	-6.52	4.76	171	2	459	3	9.4	0.1	0.60	0.18	0	80	2	
23	P27w/0447	7/03/2006	12.4	7.8	76	63	1.7	0.06	-6.26	4.96	211	1	477	3	10.0	0.1	0.94	0.09	0	80	2	
24	P27w/0494	7/03/2006	12.1	6.6	76	64	1.81	0.06	-6.31	4.66	232	7	505	15	11.6	0.5	-2.61	0.20	0	80	2	
25	CUL-3	7/03/2006	12.7	6	73	65	1.76	0.06	-6.21	5.41	227	4	500	8	10.6	0.3	0.52	0.05	0	80	2	
26	P27w/0496	7/03/2006	15	6.3	109	66	1.58	0.05	-5.86	4.79	411	21	1487	76	12.2	1.5	0.70	0.69	0	80	3	
27	P27w/0492	7/03/2006	13.2	1.3	157	67	0.745	0.032	-6.35	1.67	43	0	105	0	10.5	0.1	4.57	0.05	0	70	76	
28	ADA-1	7/03/2006	22	6	75	68	1.78	0.06	-5.69										0	50	1	
29	P27w/0247	7/03/2006	12.5	1.3	144	69	0.888	0.039	-6.54	0.55	53	1	123	2	10.2	0.4	1.44	0.18	0	70	59	

No long-term time-series tritium data were available for a robust age interpretation and identification of mixing parameters. Therefore, mixing parameters had to be chosen based on other New Zealand aquifers with similar hydrogeologic properties. The exponential-piston-flow model (Appendix 2), which successfully characterised the age distribution of groundwaters in many parts of New Zealand (Morgenstern & Taylor 2009), was used to describe the groundwater age distribution. The Kaitoke tritium input function was used for age interpretation. All samples have un-ambiguous age interpretations (Table 2).

The tritium ratios of the groundwater samples in the upper Cullen Creek are similar to the stream samples with very young residence times, indicating that these samples are recharged by Cullen Stream.

Figure 4b shows well depth versus mean residence time, individually for the samples with a rain recharge signature and a stream recharge signature (see Section 6 for rain versus stream recharge source). For samples with a rainfall recharge signature, water age shows an excellent correlation of increasing age with depth. This is also an indication for rain recharge, independent from the hydrochemistry signature. Preferential flow paths in hydraulic connection to Cullen Creek, on the other hand, are indicated by short water residence times at all depths for the samples with stream recharge signature.

4.2 Argon and Nitrogen

Argon, nitrogen, and related recharge temperatures and excess air are shown in Figure 5. Each water sample was sampled and measured twice, with good reproducibility of the data. Only sample 0235 (#21) has an unusual large variation. This sample is from a highly anoxic environment in which various microbial reactions can affect the gas concentration. The large variation is therefore likely to be caused by anaerobic reactions during sample storage.

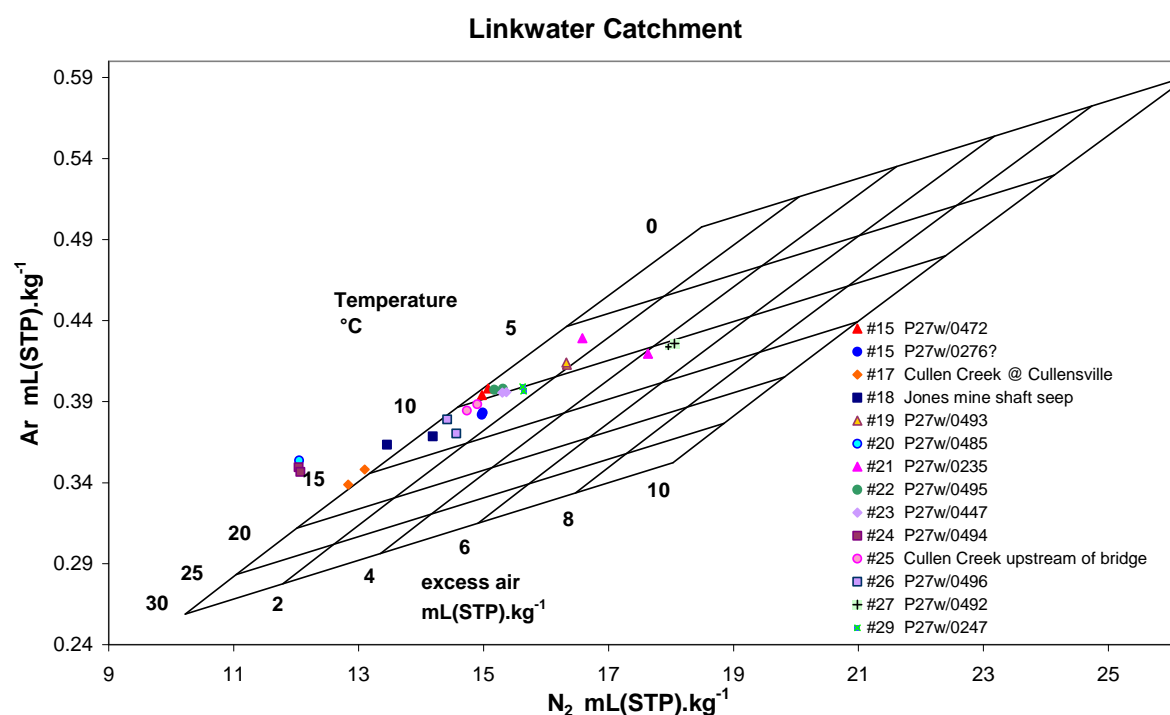


Figure 5. Argon, nitrogen, and related recharge temperatures and excess air. Raw gas results are listed in Appendix 3.

Ar and N₂ concentrations of the stream sample Cullen Creek (#17) are in the expected range: excess air is close to zero, as expected for a water sample with contact to air; and the temperature derived from Ar and N₂ concentrations of 15°C compares reasonably well with the 17°C measured in the stream at the time of sampling. Agreement is not expected to be better because slow and shallow river flow can cause relatively rapid temperature changes of the water with changing angle to the sun, so the gasses are not always in equilibrium with air.

Water samples 0485 (#20) and 0494 (#24) have Ar and N₂ concentrations that are slightly too low, which results in calculated negative excess air. For sample 0494, this can be related to degassing during sampling. As there was no access for the Grundfos sampling pump to the well, the water had to be sampled from the installed suction pump (see photo Appendix 1), which causes a quick pressure change from positive to negative which can result in degassing. There is no obvious reason for degassing of sample 0485, but the chemistry of this water also indicates that this water has evolved in an anaerobic environment with possible gas disturbance. Sample 0496 (#26) is likely to have been exposed to air contact, which would cause the gas concentrations to shift toward equilibrium with the current temperature and excess air. Despite that the water was collected from the deeper part of the well in the irrigation pit, water seeped into the pit from the immediate surrounding of the pit and significant air contact is possible before the water reaches the well.

From the remaining Ar and N₂ data, a relatively clear pattern with regards to the recharge source emerges. Waters that are not collected from the vicinity of Cullen Creek have elevated or high excess air, indicating recharge by local rainfall, because water recharged through an unsaturated zone often picks up excess air during infiltration. The recharge temperatures are relatively constant with gas equilibrium around the mean annual temperature, which also suggests that local rainfall recharge dominates. In contrast, samples collected near Cullen Creek have excess air concentrations close to zero, indicating that stream recharge without passage of the water through an unsaturated zone occurs here (Morgenstern 2005). The high variability of the recharge temperature also indicates recharge from streams, because water temperature varies seasonally in streams. Groundwater samples with particular strong signals of stream recharge are 0472 (#15), 0276 (#16), CUL-2 (#18), 0495 (#22), 0447 (#23), and CUL-3 (#25) (Figure 6).

4.3 Oxygen-18

The $\delta^{18}\text{O}$ results (Table 2) support the recharge sources identified from tritium, excess air and recharge temperatures. Water related to Cullen Creek is typically more negative (-6.2 to -6.5‰), due to the depletion of the heavier isotope ¹⁸O in higher altitude rainfall compared to lower altitude rain (-5.4 to -5.9‰). Exceptions to the typically more negative $\delta^{18}\text{O}$ values of rainfall-recharged groundwater are noticeable in deep groundwater well 0235 (#21), possibly indicating rainfall recharge at higher altitudes in the mountain ranges with related long travel times. Also, groundwater samples 0492 (#27) and 0247 (#29) from the eastern part of the catchment are more depleted, possibly indicating the dominance of air masses with a different isotopic signature as the principal source of precipitation in this area. Figure 7 shows $\delta^{18}\text{O}$ versus mean residence time, with the samples recharged by Cullen Creek forming a cluster with young age and high negative $\delta^{18}\text{O}$.

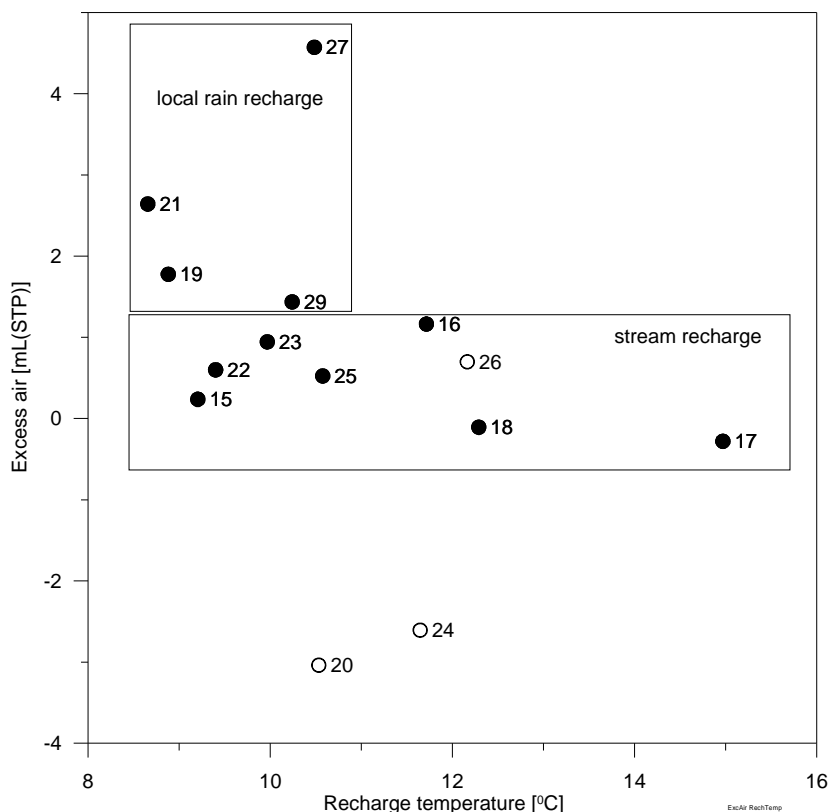


Figure 6. Excess air versus recharge temperature. The two boxes indicate the likely recharge source. Open symbols are samples that may be affected by degassing or air contact and therefore are not considered in the interpretation.

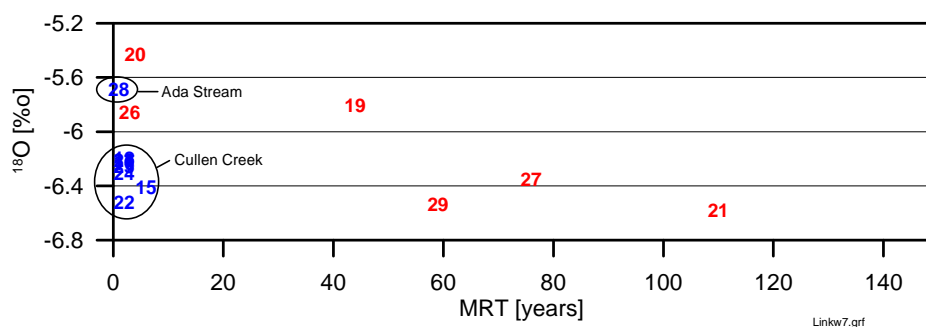


Figure 7. $\delta^{18}\text{O}$ versus mean residence time (MRT). Colour code: red – rain signature, blue – stream signature.

4.4 Hydrochemistry

Chemistry data, provided by Marlborough District Council, are compiled in Table 3.

4.4.1 National Context

A national context for the hydrochemistry of the samples collected in this study can be provided by comparison to groundwater from other parts of New Zealand. The Ministry for the Environment (2007) has recently compiled a national dataset consisting of groundwater quality data obtained during the period 1995 to 2006 from over 1000 sites comprising the state of the environment (SOE) monitoring programmes operated by all 15 regional authorities in New Zealand.

Comparison to the national SOE dataset clearly indicates that the groundwater samples collected in this investigation have several unusual chemical characteristics relative to groundwater samples from other parts of New Zealand (this comparison could not be made for surface water samples). For example, compared to the national SOE dataset, many of the groundwater samples collected in this investigation have low electric conductivity and low concentrations of calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulphate and/or silica. Sites with low concentrations of the aforementioned substances are highlighted in light green or dark green in Table 3 to indicate values below the 25th and 5th percentiles in the national SOE dataset, respectively. Conversely, a small number of samples collected as part of this investigation have relatively high concentrations of certain parameters; concentrations that exceed the 75th and 95th percentiles in the national SOE dataset are highlighted in pink and red, respectively, in Table 3. The most exceptional high or low concentrations in the groundwater samples from this study are as follows:

- Electric conductivity values range from 73 to 81 $\mu\text{S}/\text{cm}$ at Sites 15, 16, 18 and 22 to 24. These conductivity values are exceptionally low relative to the national SOE dataset, for which the 5th percentile is 88 $\mu\text{S}/\text{cm}$ (i.e. 95% of all SOE groundwater monitoring sites across New Zealand have conductivity values above 88 $\mu\text{S}/\text{cm}$). The low electric conductivity values observed at the aforementioned groundwater monitoring sites in the Linkwater catchment point toward a young age and recharge derived from primarily river/creek seepage, in agreement with the age tracer and $\delta^{18}\text{O}$ data (see Sections 4.1 to 4.3). For comparison, the electric conductivity values measured in the stream samples in the Linkwater catchment range from 73 to 75 $\mu\text{S}/\text{cm}$.
- Electric conductivity values measured at Sites 19, 20, 26 and 29 are also relatively low, spanning the range between 106 and 144 $\mu\text{S}/\text{cm}$. For comparison, the 25th percentile in electric conductivity in the national SOE groundwater quality dataset is 145 $\mu\text{S}/\text{cm}$. The slightly higher electric conductivity at these sites, compared to Sites 15, 16, 18 and 22 to 24, suggests that a component of recharge is derived from rainfall (rain accumulates salts and nutrients as it passes through the soil zone, all of which contribute to increased electrical conductivity). The suggestion that rainfall comprises a component of recharge at Sites 19, 20, 26 and 29 is in agreement with the $\delta^{18}\text{O}$ data (see Section 4.3), and also in agreement with the slightly higher concentrations of potassium, sodium, chloride and/or nitrate, relative to Sites 15, 16, 18 and 22 to 24, which likely receive most of their recharge from river seepage.
- Bicarbonate (HCO_3) concentrations are exceptionally low at Sites 20 and 26, having values of 16 and 18 mg/L, respectively. Both of these values are below the 5th percentile in the national SOE groundwater dataset (20 mg/L). The low bicarbonate concentrations at Sites 20 and 26 might be an artefact of degassing during sampling, which would cause release of CO_2 in the form of gas. Note that degassing during sampling at these sites is also suggested by the argon and nitrogen data (see Section 4.2).
- The groundwater at Site 20 has a nitrate concentration of 4.7 mg/L, which is slightly higher than the 75th percentile in the national SOE groundwater dataset (4.4 mg/L). The elevated nitrate concentration at Site 20 is likely to be caused by the predominance of rainfall recharge, as described above, and the influence of human activity in the well's recharge area. It is not possible from the nitrate concentration alone to determine if the nitrate is derived from fertiliser, septic tank leakage, manure or some combination of these.

- The groundwater at Site 20 also has concentrations of magnesium, chloride, silica, boron, manganese and phosphate that exceed the corresponding 75th percentile values in the national SOE dataset. The elevated concentrations of these substances in the groundwater are consistent with recharge being derived from local rainfall, as discussed above.

4.4.2 Variations in Hydrochemistry within the Study Area

The patterns and variations in hydrochemistry within the study area can be assessed with the aid of hierarchical cluster analysis (HCA). HCA is a multivariate statistical method that can be used to assign groundwater monitoring sites to distinct “water types” (i.e., hydrochemical facies). Here, HCA is performed using the methods of Daughney and Reeves (2005), based on the log-transformed measured concentrations of the major ions calcium, magnesium, sodium, potassium, bicarbonate, chloride and sulphate. This HCA analysis included all samples, both from groundwater and surface water sites.

The results of HCA are displayed in the form of a dendrogram in Figure 8. The terminus of each vertical blue line represents a single monitoring site. Sites and groups of sites are joined together by horizontal blue lines. The height of each horizontal line on the Distance axis indicates the similarity of sites or groups of sites that it connects. Horizontal lines that are positioned low down on the Distance axis join sites with the most similar chemistry. For example, HCA indicates that sites 15, 16, 17, 18 and 22 have very similar hydrochemistry, because they are joined by a line that is low on the Distance axis. Likewise, Sites 27 and 29 have similar hydrochemistry, but it is very different from the hydrochemistry at Sites 15, 16, 17, 18 and 22.

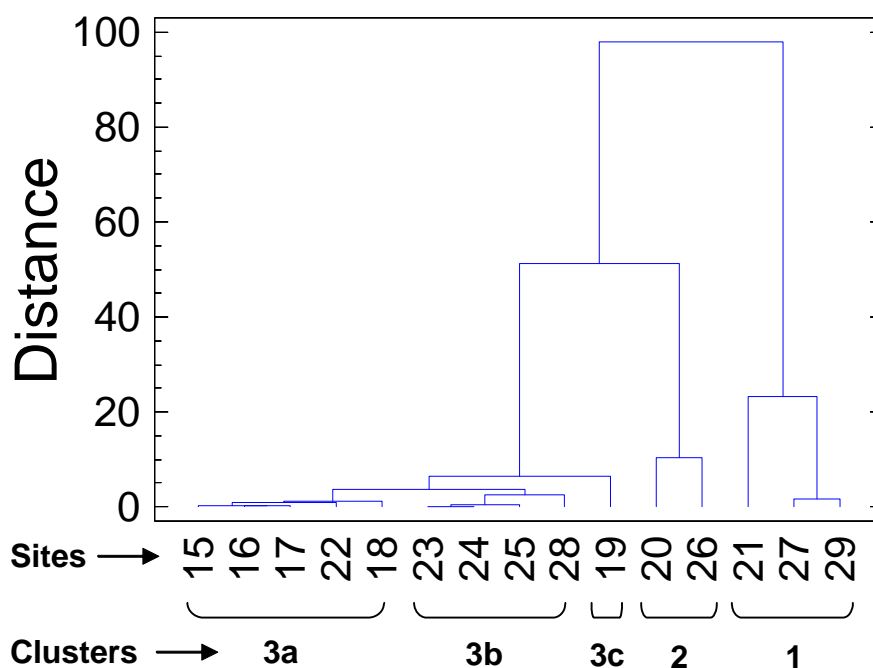


Figure 8. Dendrogram produced by hierarchical cluster analysis. Numbers immediately below the x-axis correspond to site identification numbers in Table 3. The sites are grouped into three main clusters (1, 2 and 3), one of which is partitioned into three sub-clusters (3a, 3b and 3c).

On the basis of HCA, the sites sampled in this investigation can be partitioned into three main clusters, labelled in Figure 8 as Clusters 1, 2 and 3, and Cluster 3 can be further partitioned into three sub-clusters (3a, 3b and 3c). The geographic distribution of sites in the various clusters is displayed in Figure 9. The hydrochemical features that differentiate the clusters and sub-clusters are as follows:

- Cluster 1 includes Sites 21, 27 and 29, which are among the deepest wells sampled in this study. Relative to other sites in the study area, sites assigned to Cluster 1 are typified by higher electric conductivity and concentrations of most major ions. Major ion ratios indicate a predominance of bicarbonate relative to other anions and relatively high concentrations of magnesium relative to calcium and sodium (Figure 10). Groundwater at sites assigned to Cluster 1 is generally anoxic, as shown by low concentrations of dissolved oxygen and nitrate accompanied by measurable but low concentrations of ammonium, iron and/or manganese. The chemical signature for Cluster 1 is consistent with the expectation for older groundwater, in agreement with the age tracer data (Section 4.1).
- Cluster 2 includes Sites 20 and 26, which are the shallowest wells sampled in this study (well depths of 3 and 4.8 m, respectively). Major ion ratios show relatively high proportions of chloride and sulphate relative to bicarbonate and relatively high proportions of potassium relative to calcium, sodium and magnesium (Figure 10). This hydrochemical pattern suggests that recharge is derived predominantly from local rainfall. The nitrate concentration at Site 20 is 4.7 mg/L, which as discussed above is relatively high and suggests that the nitrate is derived from leaching of fertiliser, septic tank leakage, manure or some combination of these.
- Cluster 3 includes the ten remaining sampling sites. The hydrochemistry at these sites is typified by low electric conductivity and low concentrations of most dissolved substances. All of the stream samples collected in this study are assigned to this cluster, which by implication suggests that the groundwater samples in this cluster derive a significant proportion of recharge from river or stream seepage. There are slight variations in hydrochemistry amongst the ten sites, which allows Cluster 3 to be partitioned into three sub-clusters:
 - Cluster 3a includes Sites 15 to 18 and 22. These sites are grouped together on the Piper diagram (Figure 10), indicating that they all have very similar major ion ratios. Sites assigned to Cluster 3a are all associated with Cullen Creek.
 - Cluster 3b includes Sites 23 to 25 and 28. Relative to sites assigned to Cluster 3a, sites assigned to Cluster 3b have slightly lower proportions of bicarbonate relative to chloride and sulphate, although the significance of this small variation in hydrochemistry is unclear. Sites 23, 24 and 25 are located very close to one another and may be located along the same groundwater flow paths. Site 28 is Ada Stream, located in the eastern part of the Linkwater catchment.
 - Cluster 3c includes only Site 19. The hydrochemistry at this site is similar in many ways to the other sites assigned to Cluster 3 (see Figure 10), with the main point of difference being higher concentrations of nitrate and sulphate, suggesting a greater extent of human influence in the well's recharge zone.

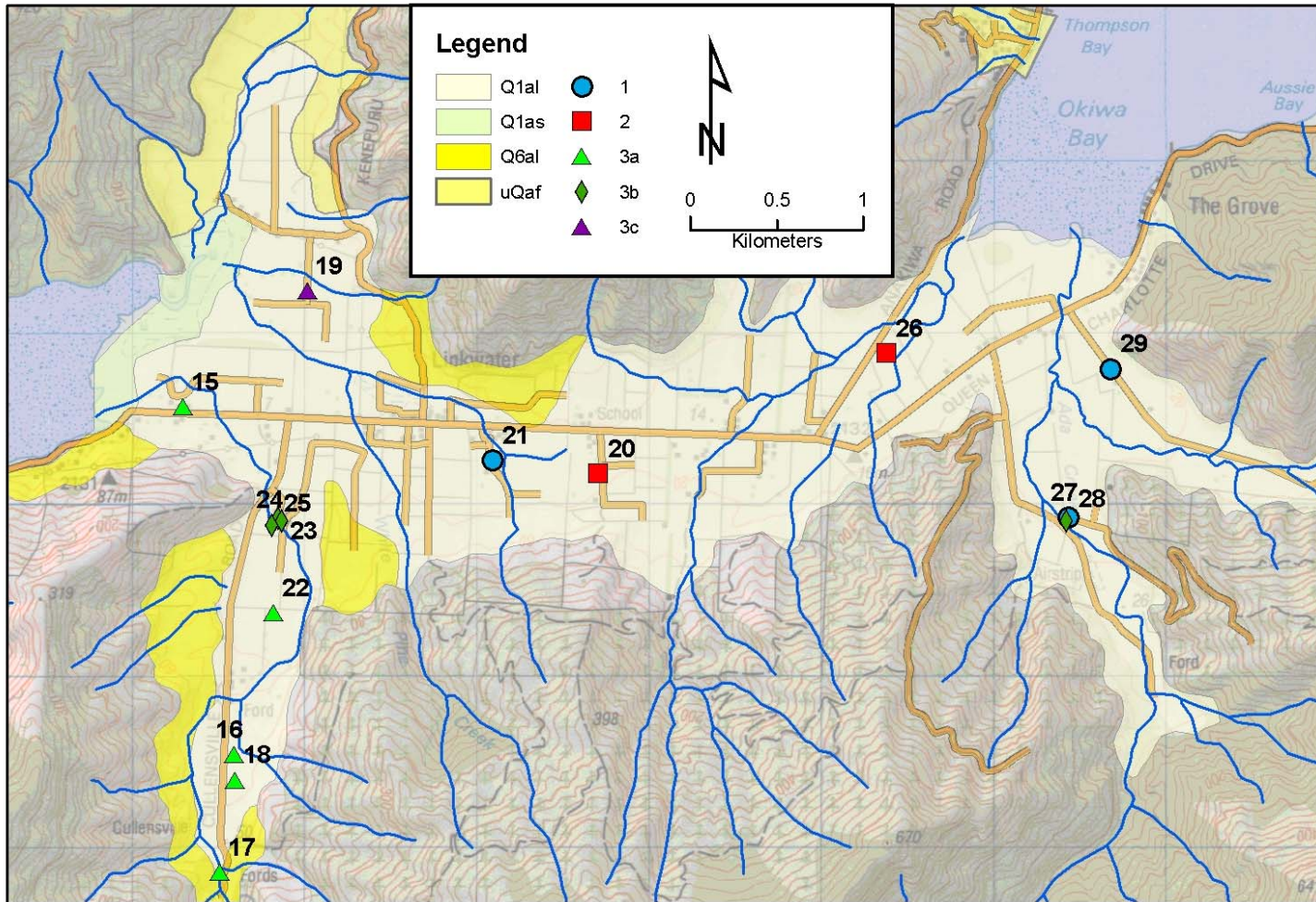


Figure 9. Geographic distribution of sites assigned to clusters defined by hierarchical cluster analysis.

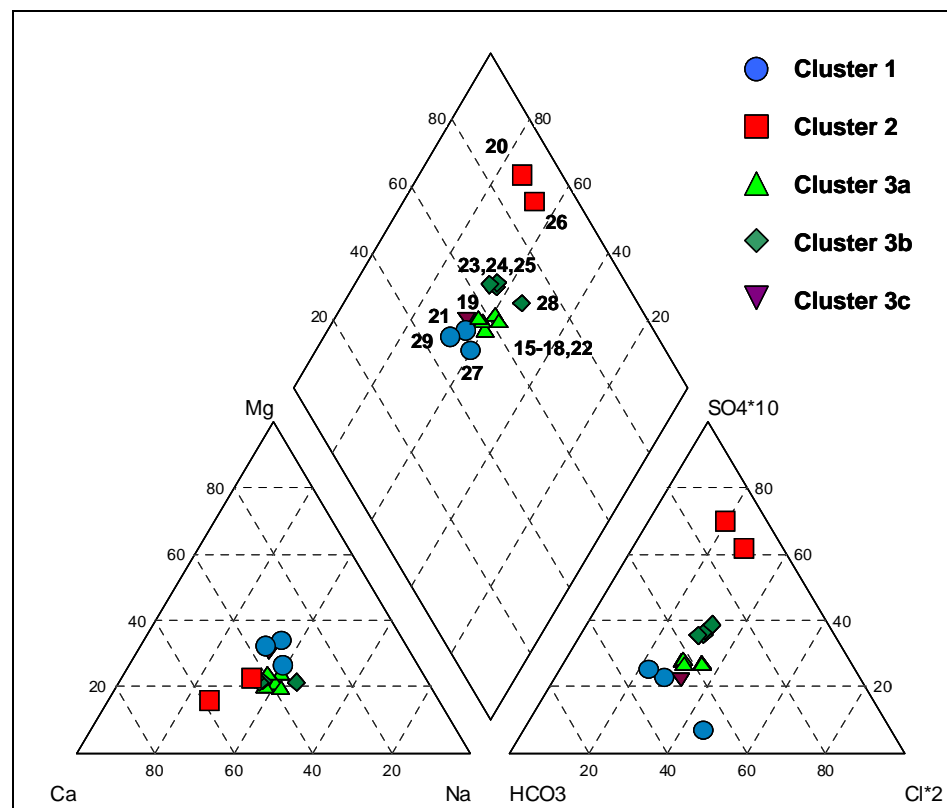


Figure 10. Piper diagram. Sites are labelled in the central diamond field. Note that chloride and sulphate concentrations have been multiplied by 2 and 10, respectively, in order to increase visual separation of points on the diagram.

Table 3. Chemistry data. Brown highlighting in # column indicates stream samples, whereas no highlighting indicates well and seep samples. Unusual concentrations for groundwater samples are highlighted: dark green – very low, light green – low, pink – high, red – very high. Total concentrations of anions and cations (Tot An and Tot Cat, respectively) and charge balance error (CBE) calculated according to Freeze and Cherry (1979).

#	Site Name	Cluster	Ca	Mg	Na	K	HCO3	Cl	SO4	SiO2	B	F	Br	Mn	Fe	NO3-N	NH4-N	PO4-P	Hardness	Alkalinity
			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg CaCO3/L
15	P27w/0472	3a	4.9	1.9	6.2	0.7	32	6.5	1.6	14	0.01	0.05	0.15	0.001	0.005	0.45	0.005	0.021	20	26
16	P27w/0276	3a	5.1	1.6	6	0.7	29	7.8	1.6	10	0.02	0.05	0.15	0.001	0.002	0.1	0.005	0.023	19	24
17	CUL-1	3a	5.7	1.6	5.9	0.7	33	6.8	1.7	11	0.01	0.054	0.15	0.001	0.006	0.013	0.006	0.014	21	27
18	CUL-2	3a	5.4	1.6	6.8	0.8	31	8.4	1.7	11	0.03	0.056	0.15	0.001	0.013	0.07	0.009	0.019	20	25
19	P27w/0493	3c	6.6	3.5	7.1	0.9	38	7.8	1.5	19	0.01	0.05	0.15	0.001	0.003	1.7	0.005	0.033	31	31
20	P27w/0485	2	12	2	6	1.1	16	13	7.8	11	0.01	0.05	0.15	0.034	0.056	4.7	0.022	0.002	38	13
21	P27w/0235	1	18	12	23	1.3	120	33	1.4	34	0.09	0.098	0.15	0.41	0.055	0.035	0.035	0.14	94	96
22	P27w/0495	3a	5.1	1.8	5.4	0.8	29	6.1	1.4	10	0.01	0.05	0.15	0.047	0.17	0.21	0.005	0.002	20	24
23	P27w/0447	3b	5.4	1.7	5.4	0.7	26	7.1	2.2	8.8	0.01	0.052	0.15	0.001	0.005	0.32	0.005	0.018	21	21
24	P27w/0494	3b	5.6	1.7	5.4	0.7	26	7.2	2.3	10	0.01	0.05	0.15	0.001	0.002	0.33	0.005	0.017	21	21
25	CUL-3	3b	5.4	1.7	4.9	0.8	26	6.5	2.1	10	0.01	0.05	0.15	0.002	0.008	0.26	0.008	0.018	21	21
26	P27w/0496	2	7.4	2.3	6.3	2.4	18	9.3	9.3	11	0.01	0.05	0.15	0.003	0.031	1.8	0.014	0.014	28	15
27	P27w/0492	1	10	4.7	13	0.9	68	11	2.5	26	0.02	0.12	0.15	0.017	0.62	0.19	0.005	0.005	44	56
28	ADA-1	3b	4.4	1.7	6.8	0.7	26	8.2	2.7	11	0.01	0.05	0.15	0.001	0.018	0.007	0.014	0.018	18	21
29	P27w/0247	1	9.8	5.4	10	0.9	68	8.3	2.6	26	0.01	0.087	0.15	0.001	0.09	0.31	0.005	0.021	47	56

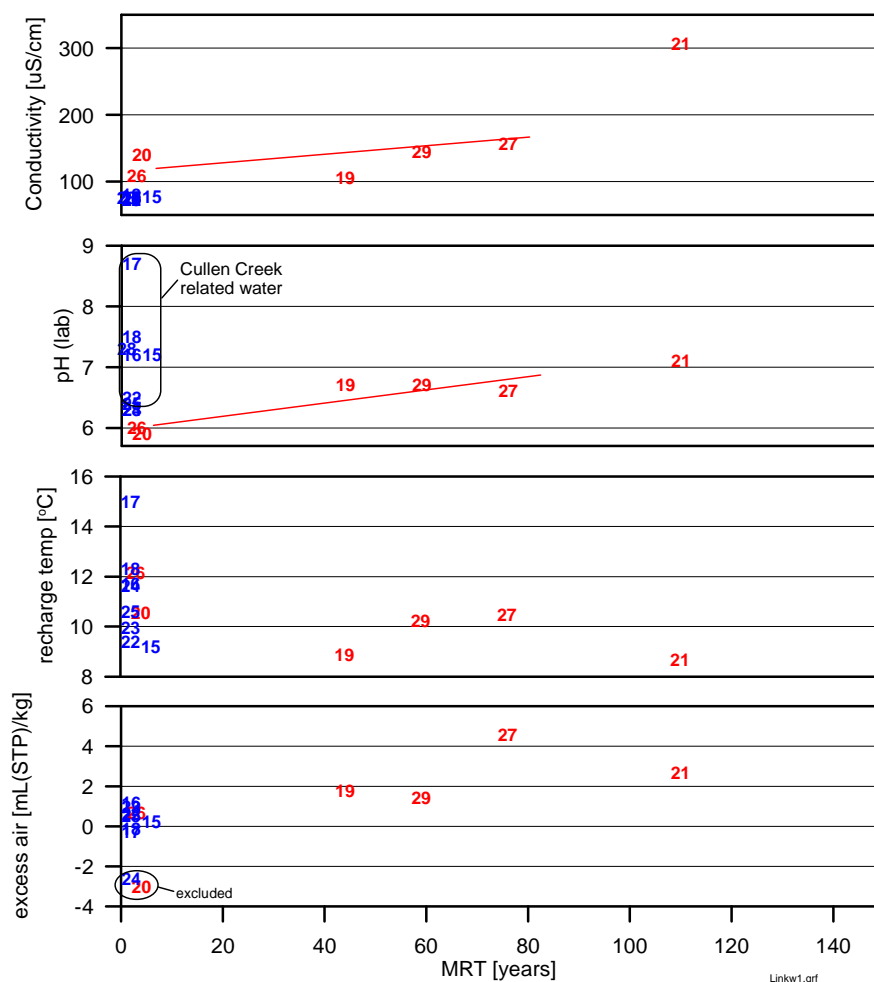
#	Site Name	Cluster	CBE	Tot An	Tot Cat	Temp	DO	Cond	pH	As	Cd	Ni	Cr	Cu	Pb	Al	Zn	Hg
			%	meq/L	meq/L	Deg C	mg/L	uS/cm	pH units	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
15	P27w/0472	3a	-4.44	0.753	0.689	12.1	4.7	77	7.2	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
16	P27w/0276	3a	-4.96	0.735	0.665	11.7	4.3	76	7.2	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
17	CUL-1	3a	-5.59	0.773	0.691	17.4	8	76	8.7	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.008	0.005	<0.0001
18	CUL-2	3a	-4.52	0.786	0.718	14.4	1.8	81	7.5	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
19	P27w/0493	3c	2.35	0.906	0.950	12.8	3.5	106	6.7	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
20	P27w/0485	2	9.61	0.872	1.057	14.1	5.6	141	5.9	< 0.001	0.0008	0.0005	< 0.001	< 0.001	< 0.003	0.022	1.6	<0.0001
21	P27w/0235	1	0.06	2.935	2.938	12.8	0.1	306	7.1	0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
22	P27w/0495	3a	-1.37	0.684	0.666	12.2	1.2	73	6.5	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
23	P27w/0447	3b	-1.44	0.682	0.663	12.4	7.8	76	6.3	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
24	P27w/0494	3b	-1.07	0.687	0.672	12.1	6.6	76	6.3	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
25	CUL-3	3b	-1.4	0.662	0.644	12.7	6	73	6.4	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
26	P27w/0496	2	6.63	0.785	0.896	15	6.3	109	6	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.007	0.005	<0.0001
27	P27w/0492	1	0.3	1.488	1.497	13.2	1.3	157	6.6	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.005	0.005	<0.0001
28	ADA-1	3b	-3.14	0.718	0.675	22	6	75	7.3	< 0.001	0.0005	0.0005	< 0.001	< 0.001	< 0.003	0.011	0.005	<0.0001
29	P27w/0247	1	-0.69	1.414	1.395	12.5	1.3	144	6.7	< 0.001	0.0005	0.0009	< 0.001	< 0.001	< 0.003	0.005	0.007	<0.0001

5.0 TIME TRENDS IN HYDROCHEMISTRY

The chemical composition of the groundwater can help to determine the origin and recharge source of the water. However, the chemical composition of the groundwater can also be influenced by anthropogenic and geological processes: young water can be affected by land use (nutrients, heavy metals), and old water can be affected by evolving hydrochemistry due to increasing contact of the water with the aquifer material. To identify anthropogenic and geological influence on hydrochemistry, the various water chemistry parameters are plotted versus mean residence time (MRT). By separating anthropogenic and geological trends, spatial hydrochemistry patterns that depend on local geologic formations become more obvious, with the result that groundwater flow patterns and connections between different groundwater systems can be better identified.

Groundwater from different recharge sources can follow different trends. To help identifying such trends within a group, the data are plotted in two colours: red for rain-recharged groundwater, and blue for stream water and Cullen Creek-derived groundwater as identified before by the isotopes, gases and hydrochemistry (see also chapter 6).

Figure 11 shows the conductivity and pH, and the recharge temperature and excess air as calculated from Ar and N₂.



Conductivity allows clear differentiation between rainfall and stream recharge sources. All stream waters and Cullen Creek-derived groundwaters have low conductivities (73 - 81 $\mu\text{S}/\text{cm}$), while rain-recharged older groundwaters have higher conductivities (> 106 and up to 306 $\mu\text{S}/\text{cm}$). This reflects the origin of the stream water from catchments of mostly schist with low mineral solubility and the short residence time of the water. Higher conductivities for rainfall-recharged groundwaters in the Holocene alluvial deposits reflect strata with higher mineral solubility and long residence times, resulting in a more evolved hydrochemistry with relatively higher ion concentrations. The data show a clear trend of increasing conductivity with mean residence time.

The **pH** measured in the lab shows high variation for the young Cullen Creek-related waters. The rain-recharged groundwaters follow a trend of increasing pH with mean residence time. An increase in pH with increasing contact time of the water with the aquifer matrix was also observed in other aquifers in New Zealand (Morgenstern 2005, Morgenstern et al. 2004).

The **calculated recharge temperatures** from Ar and N₂ show high variability in the stream-related waters due to seasonal variability in stream water temperature. The rain-recharged groundwaters have a lower recharge temperature variability because they reflect the mean annual temperature in the valley, which is relatively constant over time. The high variability of recharge temperature in the groundwaters with a Cullen Creek recharge signature is an independent indication that these waters are very young (less than 3 years), because the seasonal variability is not yet smoothed out due to mixing, as would be expected in older groundwater.

Excess air data for the stream-related waters show low variability, with values near zero for the stream-related waters. This is expected because stream-recharged groundwater should not contain excess air (Morgenstern 2005). On the other hand, the rain-recharged groundwaters have elevated excess air, indicating influence by unsaturated zone processes. Excess air is constant over residence time.

The rain-recharged groundwaters show a clear trend of increasing **hardness, bicarbonate, and alkalinity** over time, due to increased dissolution of carbonate minerals with time (Figure 12).

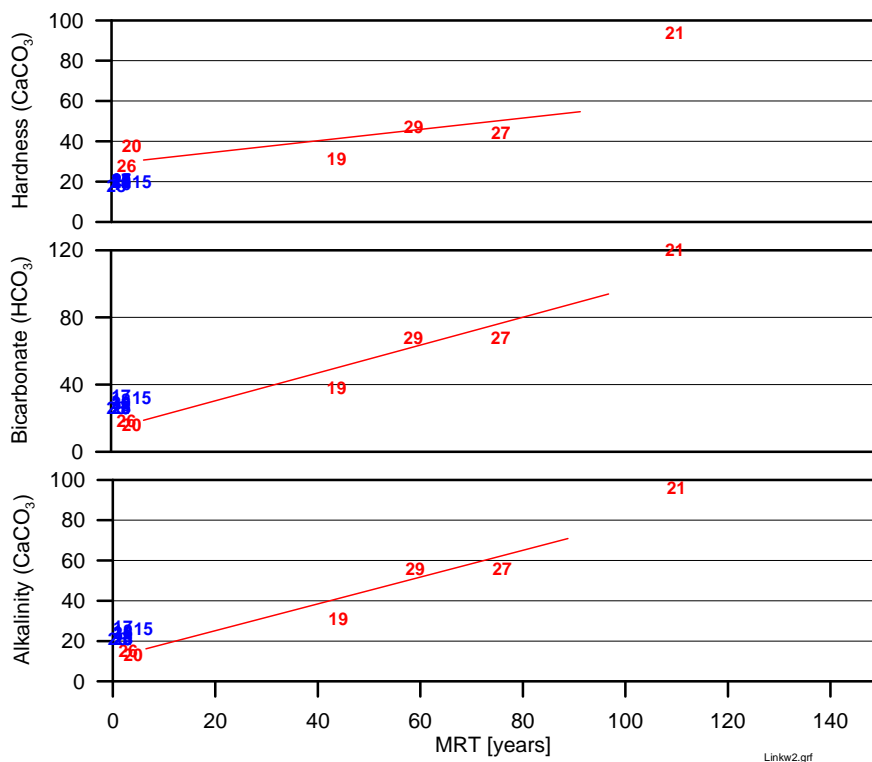


Figure 12. Hardness, bicarbonate and alkalinity versus mean residence time (MRT). Colour code: red – rain signature, blue – stream signature.

Figure 13 shows concentrations of dissolved oxygen, iron, manganese, and boron versus mean residence time. Note that microbial respiration tends to progressively deplete **dissolved oxygen** along a groundwater flow path, if a sufficient amount of suitable metabolic substrate is available (usually organic carbon). This leads to reducing (i.e., oxygen-poor) conditions that can lead to the solubilisation of iron and/or manganese. Therefore, absence of oxygen and presence of iron and/or manganese is an indicator of reducing conditions.

Oxygen saturation concentration with air at the measured water temperatures is about 9 mg/L. Most of the groundwaters have retained a relatively high concentration of oxygen. Of the stream-recharged groundwaters, CUL-2 (#18) and 0495 (#22) are relatively depleted in oxygen, indicating the presence of sufficient organic carbon in the aquifer. The rain-recharged groundwaters show a clear trend of oxygen depletion with time due to evolving microbial respiration. Sample 0235 (#21) is completely depleted in oxygen. Figure 12 shows that these anoxic conditions can be accompanied by elevated manganese and iron. Also, elevated **boron** can be associated with these solubilisation processes due to microbial respiration.

While high **iron** and **manganese** concentrations indicate a reducing environment, above certain thresholds (ca. 0.1 mg/L for iron and 0.01 mg/L for manganese) the actual measured concentration alone does not indicate the oxidation-reduction potential (i.e., the strength or degree of reduction or anoxia). Rather, the oxidation-reduction potential, if not measured directly, must be estimated by comparing the concentrations of several redox-sensitive elements, such as iron, manganese, nitrate-nitrogen, ammoniacal-nitrogen, sulphate and methane.

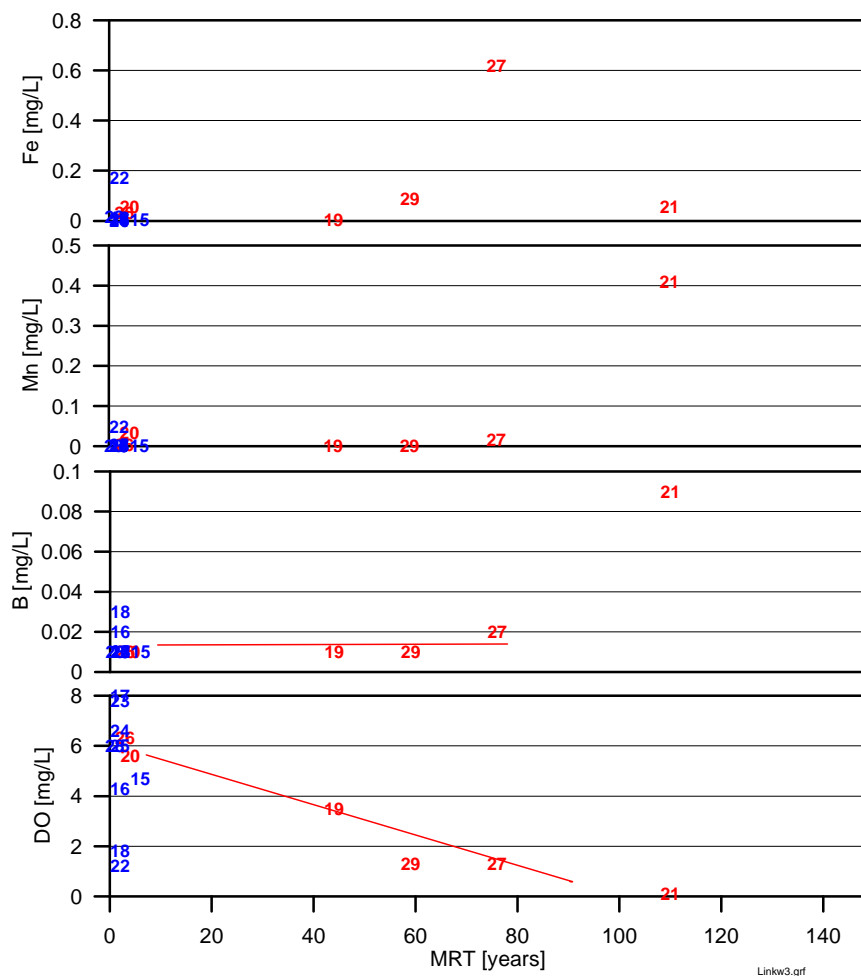


Figure 13. Dissolved oxygen, iron and manganese versus mean residence time (MRT). Colour code: red – rain signature, blue – stream signature.

The nutrients potassium, dissolved reactive phosphate, sulphate, ammonia and nitrate are plotted against mean residence time in Figure 14. **Potassium** can be derived from water-rock interaction, from human or animal wastes, or from fertilisers. Potassium concentrations are low in the Linkwater catchment, indicating low use of fertiliser and low geological input. The young stream-recharged groundwaters have the lowest potassium concentration, which is consistent with the shortest contact time of the water with the rock matrix. The rain-recharged groundwaters have a slightly higher potassium concentration that is constant over time. Only sample 0496 (#26) has an elevated potassium concentration, which may be due to airborne fertiliser input in this open water collection pit.

Dissolved reactive phosphate is low in almost all samples (Figure 14) except the oldest groundwater, indicating geological sources. Phosphorus as an essential plant nutrient is applied as fertiliser in agriculture areas. However, no young land-use affected water has elevated phosphate, indicating that if phosphorus is applied in this area, it is taken up by plants in the top soil, and adsorbed by mineral surfaces in the unsaturated zone. Very little (if any) anthropogenic phosphorus has found its way into the groundwater.

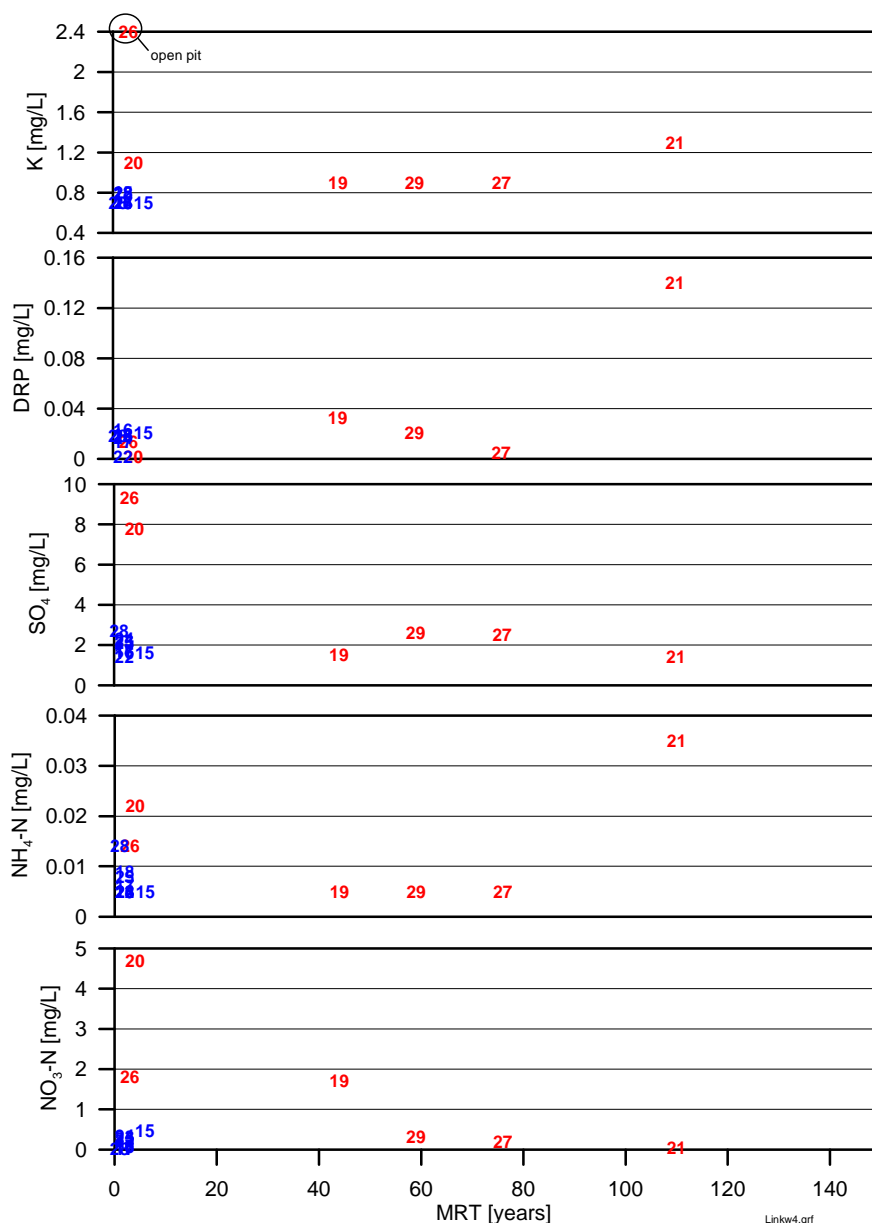


Figure 14. Potassium, dissolved reactive phosphate, sulphate, ammonia and nitrate versus mean residence time (MRT). Colour code: red – rain signature, blue – stream signature.

Also **sulphate** concentrations are low and constant over time (Figure 14) for most of the samples, except for slightly elevated SO_4 in samples 0485 (#20) and 0496 (#26), which again may be related to anthropogenic input. For the stream-recharged samples, the major sulphate source appears to be geological, because all sulphate data plot close to the seawater concentration dilution line, with Mg (Figure 15) controlled by mineral equilibration. Most of the rain-recharged samples appear to be affected by sulphate reduction. With increasing reducing conditions (high Fe, Mn, B and low dissolved oxygen), sulphate is increasingly depleted (data shifted from the seawater concentration dilution line). Samples 0485 (#20) and 0496 (#26) show SO_4 elevated with respect to the seawater concentration dilution line, indicating an anthropogenic source of sulphate (added as gypsum to fertilisers). Anthropogenic excess sulphate appears to be about 4 mg/L.

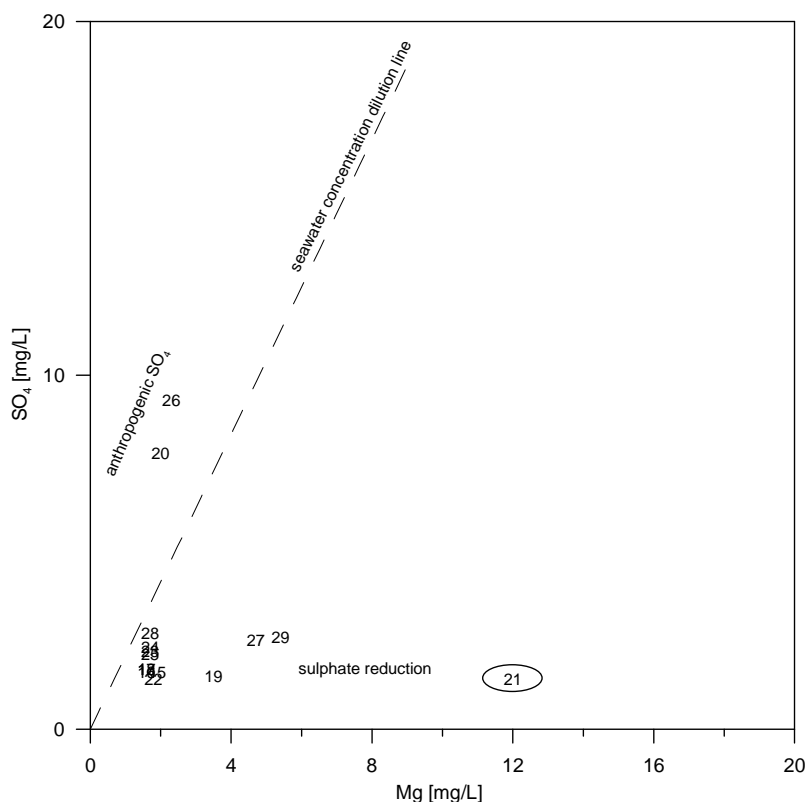


Figure 15. Sulphate versus magnesium. Dashed line is seawater concentration dilution line (Rosen 2001).

Ammonium (Figure 14) is elevated only in sample 0485 (#20), likely due to anthropogenic input, and in the old sample 0235 (#21), as a result of nitrogen mineralization in the anoxic aquifer, following depletion of nitrate-nitrogen due to microbial denitrification.

Nitrate in stream water and stream-recharged groundwater is mostly below 0.3 mg/L $\text{NO}_3\text{-N}$ (Figure 14). The slightly elevated nitrate in wells 0447 (#23), 0494 (#24), and 0472 (#15) (see Table 3) furthest down Cullen Creek indicate a minor contribution of nitrate-bearing rain-recharged water impacted by landuse. The land-use affected young groundwaters 0485 (#20), 0496 (#26) and 0493 (#19) with a rain recharge signature have a relatively high nitrate contamination, up to 4.7 mg/L $\text{NO}_3\text{-N}$. This is an independent indication for groundwater recharged by local rain with landuse impact. The older rainfall-recharged groundwaters with mean residence times of greater than 50 years do not contain any substantial amounts of nitrate, either due to denitrification processes or because there was no nitrate source at the time of recharge.

Fluoride, calcium, magnesium and silica in Figure 16 show increasing ion concentrations with time due to evolving hydrochemistry. These parameters have also in other aquifers of New Zealand correlated well with residence time. The correlation between ion concentration and residence time may therefore be an independent indication of young or old groundwater.

Silica shows a very good correlation with mean residence time (Figure 16). All the young waters have concentrations of about 10 mg/L SiO_2 , increasing to 34 mg/L for the oldest sample. Both rain- and stream-recharged waters follow the same trend. Silica has shown the best correlation with residence time in several aquifers of New Zealand (Morgenstern et al. 2004).

Silica concentration in many New Zealand aquifers is also found to be correlated to sodium concentration (Rosen 2001), which also applies to the Linkwater samples (Figure 17).

Magnesium also shows a good correlation with residence time (Figure 16). A similar correlation is also shown by **calcium**. Only two samples, 0485 (#20) and 0496 #26), do not follow this trend, due to elevated Ca, which is probably caused by fertilisers (as also indicated by elevated SO_4). In agricultural areas, CaO (lime) may be added to pastures to adjust soil pH, and magnesium may be added with fertilisers. **Aluminum** is elevated slightly above background only in the stream samples and in the groundwaters that are elevated in Ca and SO_4 . **Fluoride** also increases with mean residence time, suggesting that F is derived from water-rock interaction.

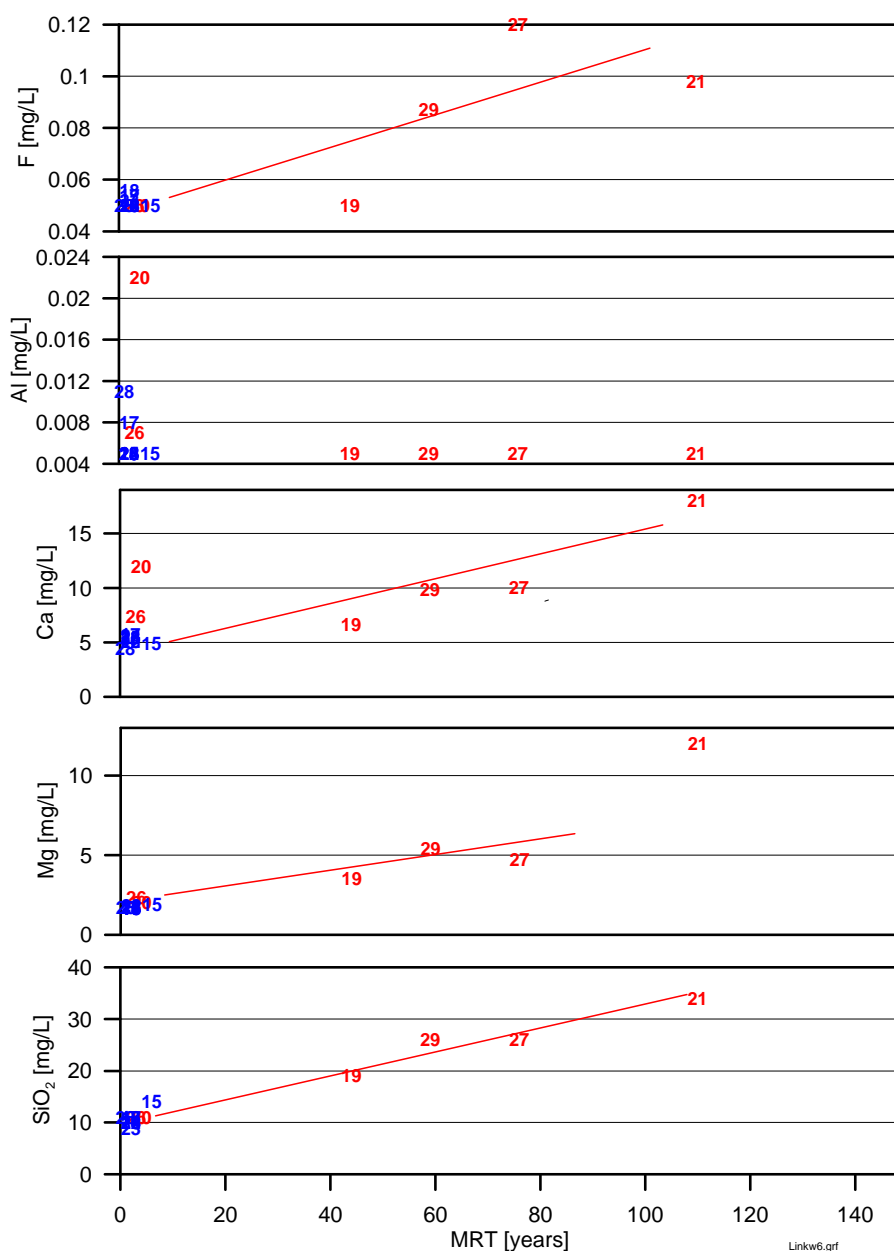


Figure 16. Fluoride, aluminium, calcium, magnesium and silica versus mean residence time (MRT). Colour code: red – rain signature, blue – stream signature.

Sodium and **chloride** concentrations (Figure 18) are in the range expected for rain water. Sodium is consistently low for young groundwater, and shows a good correlation of increasing concentration with time due to continuous water-rock interaction. Chloride, as expected for a conservative tracer, is relatively constant over time. Only the old water of well 0235 (#21) has an unusually high concentration, similar to most of the other chemistry parameters, indicating a different source of the water. Sample 0485 (#20) is slightly elevated, indicating anthropogenic influence.

The slight increase of sodium-chloride ratio over time indicates a geological source of sodium due to gradual dissolution of mineral salts within the aquifer.

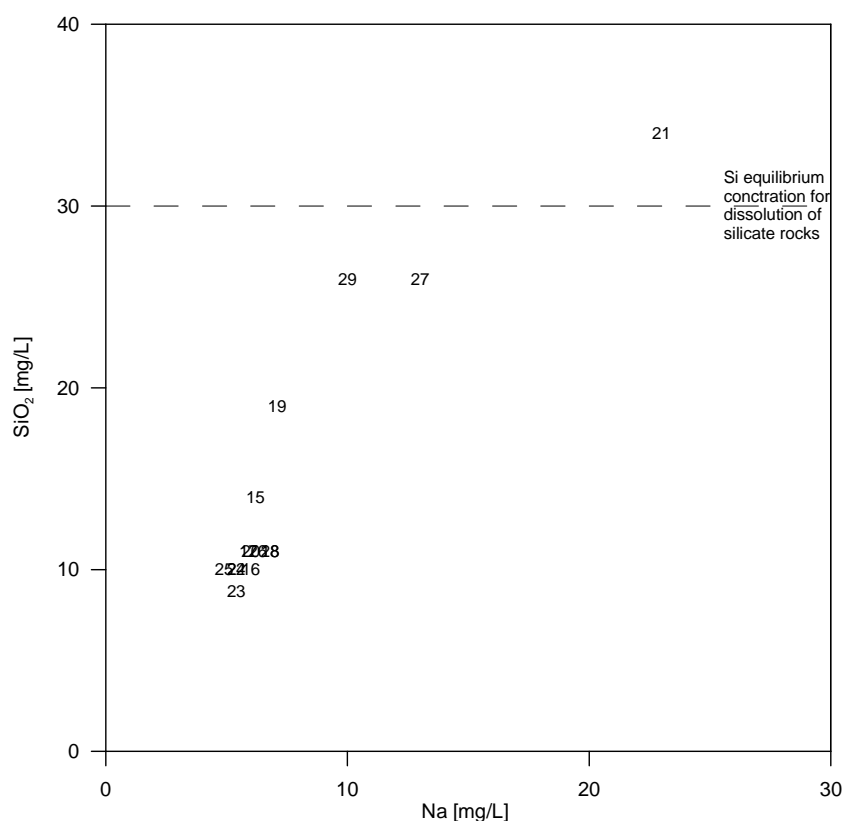


Figure 17. Silica versus sodium concentration. The dashed line represents the Si equilibrium concentration for dissolution of silicate rocks (Rosen 2001).

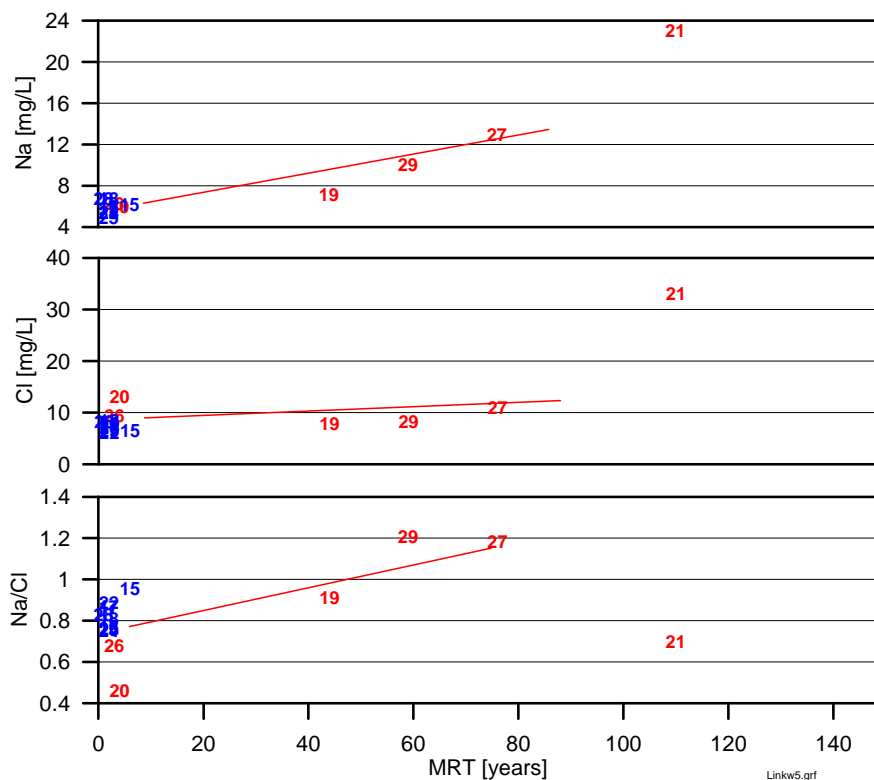


Figure 18. Sodium and chloride versus mean residence time (MRT). Colour code: red – rain signature, blue – stream signature.

6.0 CONCLUSION - GROUNDWATER SOURCES AND FLOW FROM WATER ISOTOPE AND CHEMISTRY SIGNATURES, AND HYDROGEOLOGIC EVIDENCE

All investigated groundwaters have been able to be dated without ambiguity. Excellent trends of increasing ion concentrations with mean residence time for the hydrochemistry parameters that are controlled by time-dependent leaching from geological sources are an independent validation that the age interpretations are correct. No conflicting evidence was observed within the data.

The data allow for a clear differentiation between groundwater with a signature of young stream water (Cullen Creek), and a signature of local rain-recharged water. Indicators for that are conductivity, water age, excess air and recharge temperature via Ar-N, $\delta^{18}\text{O}$, and concentrations of major ions and nutrients. The recharge source, based on the various indicators, is listed in Table 4 for all groundwaters. The indication is very clear, without any conflict between the various indicators. Samples #15, 16, 18, and 22 to 25 have a stream signature and indicate recharge from Cullen Creek, and samples #19 to 21, 26, 27 and 29 have a signature different to the stream water and indicate recharge via local rain. All of the investigated groundwater samples follow the two trends of stream or local rain recharged groundwater, no water was identified with a long-travel fault fracture signature.

Table 4. Recharge source of the different sample locations. S stands for stream recharge signature, R for rain recharge signature; stream water samples are greyed out.

#	Conduct.	Age	Ar-N	18O	Nutrients	HCA
15	S		S	S		S
16	S	S	S	S		S
17						
18	S	S	S	S		S
19	R	R	R	R	R	
20	R			R	R	R
21	R	R	R		R	
22	S	S	S	S		S
23	S	S	S	S		S
24	S	S		S		S
25	S	S	S	S		S
26	R			R	R	R
27	R	R	R			
28						
29	R	R	R			

All **groundwaters along Cullen Creek** show a strong stream-water signature, indicating hydraulic connection to Cullen Creek and the presence of channelised alluvial gravel deposits along Cullen Creek. Young stream-recharged groundwater was found up to well depth 50 m, confirming the presence of former river channels as identified by magnetic and seismic surveys to depth up to 80 m. The two groundwater seeps from Jones mine shaft 0493 (#18), and from Cullen Creek upstream of the bridge CUL-3 (#25) also have a strong stream-water signature, indicating that these are re-emerging waters that infiltrated into the creek bed further up valley. The very localised occurrence of these groundwater outflows supports the hypothesis of preferential groundwater flow along buried former river channels that provide conduits to anisotropic semi-confined and confined aquifers.

All groundwaters with stream signatures are very young, with mean residence times of less than 3 years, indicating rapid flow in these confined channels. Only well 0472 (#15), furthest down the valley, is slightly older, with a mean residence time of about 6 years, as a result of the further distance to the recharge source and probably lower permeability of sediments down valley. The hydrochemistry of all of these wells is very similar, with low ion concentrations. Low nutrient concentrations demonstrate very little anthropogenic impact and reflect the relatively pristine conditions of Cullen Creek water. These groundwaters are mostly oxidic, indicating relatively clean gravels with too little organic matter to cause anoxic conditions.

The wells along Cullen Creek with hydraulic connection to the stream are likely to be a reliable source of water as long as there is sufficient recharge by Cullen Creek. The young age of these waters indicates that these wells are being recharged quickly. Wells 0495 and 0447 are in this group of young stream recharged groundwater, but these wells have low water yield which indicates the channelised nature of these gravel aquifers. These wells do not intercept the channelised gravels, despite that they are close by as indicated by the young age of the groundwater.

The **samples with a signature of rain recharge** in the lowland are older than the stream-signature groundwaters and cover a wide age range of mean residence times, ranging from 3 to 110 years. They show an evolving hydrochemistry, with increasing Ca, SiO₂, F, P, Mg, Na, and alkalinity/hardness/bicarbonate with increasing contact time of the water with the

rock in the aquifer. With increasing residence time in the aquifer these waters become anoxic.

The youngest of the rain recharge signature groundwaters, 0485 (#20) and 0496 (#26), show a high anthropogenic impact. Sample #20 is affected the most, with high nutrient concentrations of K, SO₄, and NO₃, and also elevated cadmium and zinc. The older the water, the less it is affected by nutrients. The very old water from well 0235 (#21) has an unusual hydrochemistry.

Old groundwater ages within the small area indicate stagnant groundwater flow conditions due to the clay-bound gravels. None of the lowland rain-recharged groundwaters shows evidence of an origin from well-sorted river gravel deposits that would allow fast flow from recharge sources. This is in agreement with the fact that no such deposits were found in the bore logs.

7.0 ACKNOWLEDGEMENT

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APPENDICES

APPENDIX 1 — SAMPLING LOCATIONS



#15 P27w/0472 Templeman irrigation well (not used)



#16 P27w/0276 Jones test well





#17 Cullen Creek



#18 Jones mine shaft seep



#19 P27w/0493 Jenkins domestic well (sampled before pressure tank)



#20 P27w/0485 Gardiner irrigation well



#21 P27w/0235 Parkes domestic/stock/irrigation well



#22 P27w/0495 Morrison test well



#23 P27w/0447 Morrison original test well



#24 P27w/0494 Morrison domestic well



#25 Cullen Creek upstream of bridge



#26 P27w/0496 Delany irrigation pit



#27 P27w/0492 Shallcrass irrigation well





#28 Ada Stream @ Shallcrass bridge



#29 P27w/0247 Coleman domestic well

APPENDIX 2 — METHODOLOGY OF GROUNDWATER AGE DATING

Tritium, CFC and SF₆ method

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, giving rain and surface water high tritium concentration at this time (Figure 19). Surface water becomes separated from the atmospheric tritium source when it infiltrates into the ground, and the tritium concentration in the groundwater then decreases over time due to radioactive decay. The tritium concentration in the groundwater is therefore a function of the time the water has been underground. Additionally, detection of superimposed bomb tritium can identify water recharged between 1960 and 1975. Groundwater dating using tritium is described in more detail in Cook & Herczeg (1999) and Stewart & Morgenstern (2001).

As a result of the superimposed atmospheric tritium "bomb" peak in the 1960s, ambiguous ages can occur with single tritium determinations in the age range 15-40 years (i.e. the tritium concentration can indicate any of several possible groundwater ages). This ambiguity can be overcome by using a second tritium determination after about 2-3 years, or combined age interpretation of tritium data and data from an independent dating method, for example CFCs or SF₆. CFC and SF₆ concentrations in the atmosphere have risen monotonously over that time and therefore can resolve tritium ambiguity if they are not altered in the aquifer.

Chlorofluorocarbons (CFCs) are entirely man-made contaminants. They were used for refrigeration and pressurising aerosol cans, and their concentrations in the atmosphere have gradually increased (Figure 19). CFCs are relatively long-lived and slightly soluble in water and therefore enter the groundwater systems with groundwater recharge. Their concentrations in groundwater record the atmospheric concentrations when the water was recharged, allowing determination of the recharge date of the water. CFCs are now being phased out of industrial use because of their destructive effects on the ozone layer. Thus rates of increase of atmospheric CFC concentrations slowed greatly in the 1990s, meaning that CFCs are not as effective for dating water recharged after 1990.

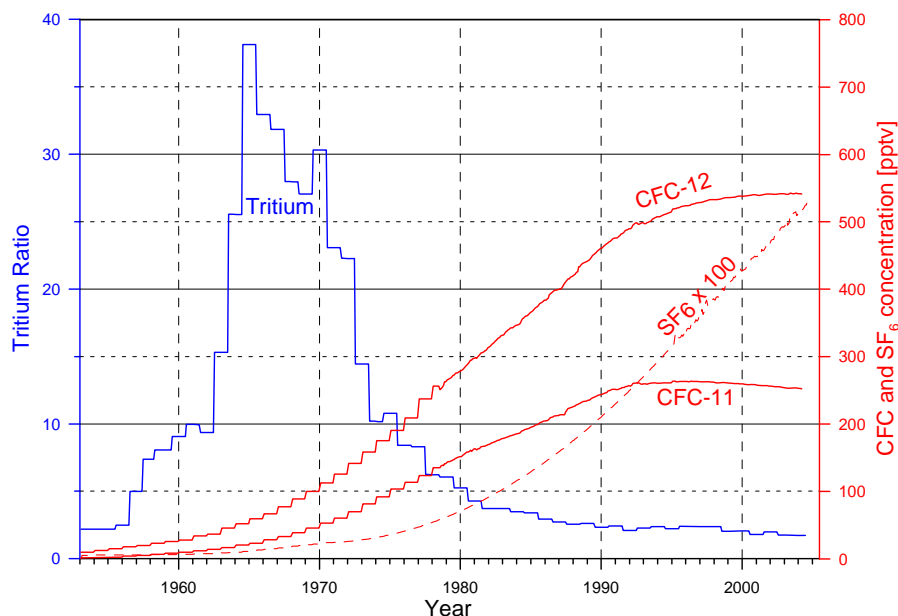


Figure 19. Tritium, CFC and SF₆ input for New Zealand rain. Tritium concentrations are in rain at Kaitoke, 40km north of Wellington (yearly averages), and CFC and SF₆ concentrations are for southern hemispheric air. TR=1 represents a 3H/1H ratio of 10-18, and 1 pptv is one part per trillion by volume of CFC or SF₆ in air, or 10⁻¹². Pre-1978 CFC data are reconstructed according to Plummer and Busenberg (1999), and scaled to southern hemisphere by factor 0.83 (CFC-11) and factor 0.9 (CFC-12). Post-1978 CFC data are from Tasmania. Pre-1970 SF₆ data are reconstructed (USGS Reston), 1970-1995 data are from Maiss and Brenninkmeijer (1998), and post-1995 data was measured in Tasmania.

Sulphur hexafluoride (SF₆) is primarily anthropogenic in origin, but can also occur in some volcanic and igneous fluids. Significant production of SF₆ began in the 1960s for use in high-voltage electrical switches, leading to increasing atmospheric concentrations (Figure 19). The residence time of SF₆ in the atmosphere is extremely long (800-3200 years). It holds considerable promise as a dating tool for post-1990s groundwater because, unlike CFCs, atmospheric concentrations of SF₆ are expected to continue increasing for some time (Busenberg and Plummer, 1997).

Tritium is a conservative tracer in groundwater. It is not affected by chemical or microbial processes, or by reactions between the groundwater, soil sediment and aquifer material. Tritium is a component of the water molecule, and age information is therefore not distorted by any processes occurring underground. For CFCs, a number of factors can modify the concentrations in the aquifer, including microbial degradation of CFCs in anaerobic environments (CFC-11 is more susceptible than CFC-12), and CFC contamination from local anthropogenic sources (CFC-12 is more susceptible to this), Plummer and Busenberg (1999). CFC-11 has been found in New Zealand to be less susceptible to local contamination and age estimates agree better with tritium data. Note that CFC and SF₆ ages do not take into account travel time through unsaturated zones.

The tritium method is very sensitive to the flow model (distribution of residence times in the sample) due to the large pulse-shaped tritium input during 1965-1975. With a series of tritium measurements, and/or additional CFC and SF₆ measurements, age ambiguity can usually be resolved. In that case, both the mean groundwater age and the age distribution can be obtained.

Groundwater mixing models

Groundwater comprises a mixture of water of different ages due to mixing processes underground. Therefore, the groundwater doesn't have a discrete age but has an age distribution or spectrum. Various mixing models with different age distributions describe different hydrogeological situations (Maloszewski and Zuber, 1982). The piston-flow model describes systems with little mixing (such as confined aquifers and river recharge), while the exponential model describes fully mixed systems (more like unconfined aquifers and local rain recharge). Real groundwater systems, which are partially mixed, lie between these two extremes. They can be described by a combination of the exponential and piston-flow models representing the recharge, flow and discharge parts of a groundwater system respectively. The output tracer concentration can be calculated by solving the convolution integral, and the mean residence time (MRT) can be obtained from the tracer output that gives the best match to the measured data. If the second parameter in the age distribution function, the fraction of mixed flow, cannot be estimated from hydrogeologic information, then two independent tracers (tritium and CFC/SF₆) or two tritium measurements over time are necessary.

Schematic groundwater flow situations are shown in Figure 20. The unconfined aquifer situation is described by the exponential model (EM). Flow lines of different length containing water of different age converge in the well or the stream, and the abstracted water has a wide range of ages with an exponential age distribution. The confined aquifer situation is described by the piston flow model (PM) with a narrow range of ages. The partly confined aquifer situation is described by the exponential-piston flow model (EPM). The free parameter is the fraction of exponential flow within the total flow volume (represented by E%PM, where the fraction is given in %), or the ratio η of the total flow volume to the volume of the exponential part. The water has a wide range of ages, but because part of the flow is piston flow, the age distribution has a minimum age (no water can be younger than the time necessary to pass through the piston flow part). The piston flow part can be represented by a partly confined flow with no vertical input of young water from the surface, or it can be represented by a significant unsaturated zone with vertical piston flow toward the water table and mixing of different ages below the water table.

As an example, the age distribution for the exponential-piston flow model for different fractions of mixed flow is shown in Figure 21 for water with a mean residence time of 50 years. Water with a high fraction of exponential flow of 90% has a wide range of ages, starting at 5 years and still significant contributions of old water with ages over 150 years. Despite the mean residence time of 50 years, the major part of the water is younger than 50 years. The water can therefore partly be contaminated before the mean residence time of 50 years has elapsed. About 2% of the water can already be contaminated after 5 years. With each further year, these young fractions accumulate, and increasingly contaminated water arrives at the spring or well. The total fraction of water within a certain age range can be obtained by integrating the age distribution over the specified age range. This is equal to the area below that part of the curve, with the total area below the whole curve being 100% water fraction. The fraction of water that is younger than a specified age is called the young water fraction (y_f). The young water fraction younger than 55 years is about 80% in the example in Figure 21 (hatched area).

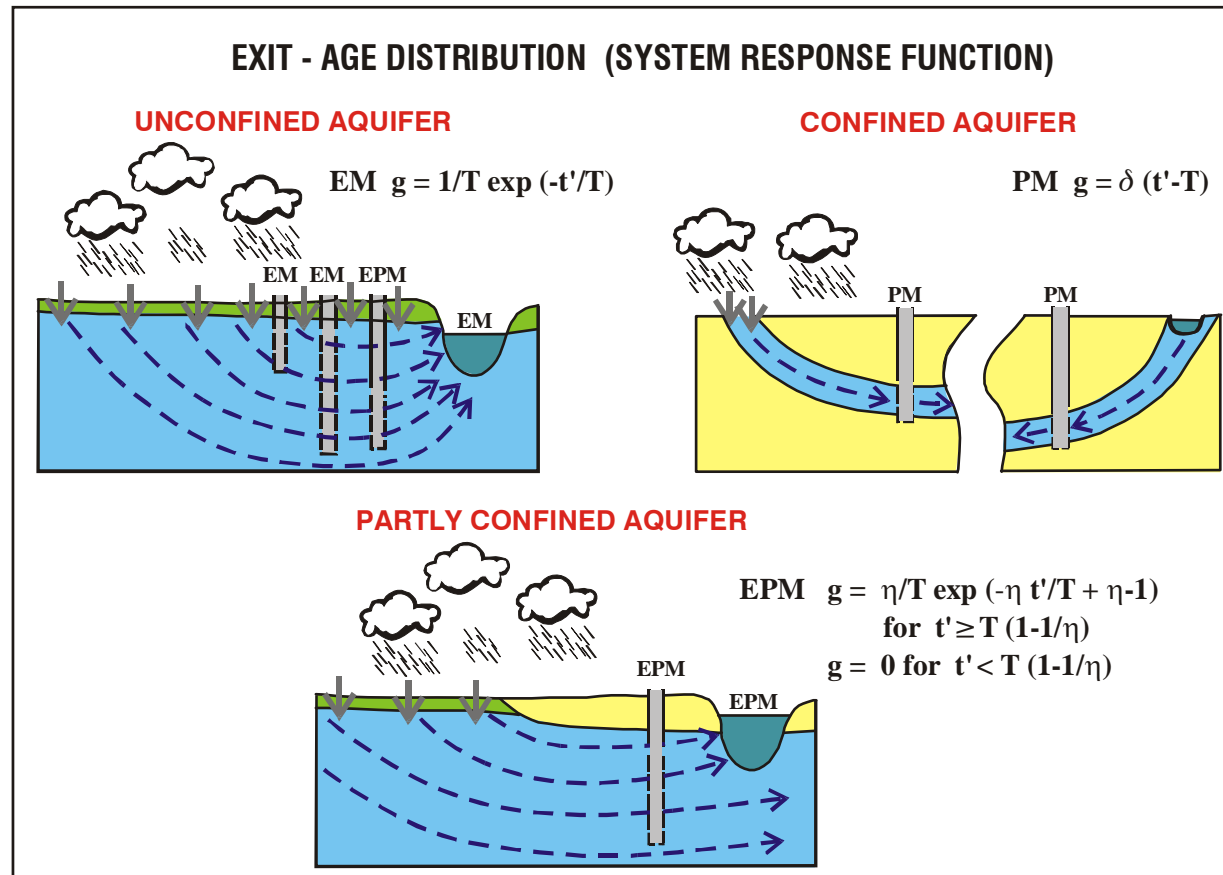


Figure 20. Schematic groundwater flow scenarios and corresponding age distribution functions (see Maloszewski and Zuber (1982) for theoretical background).

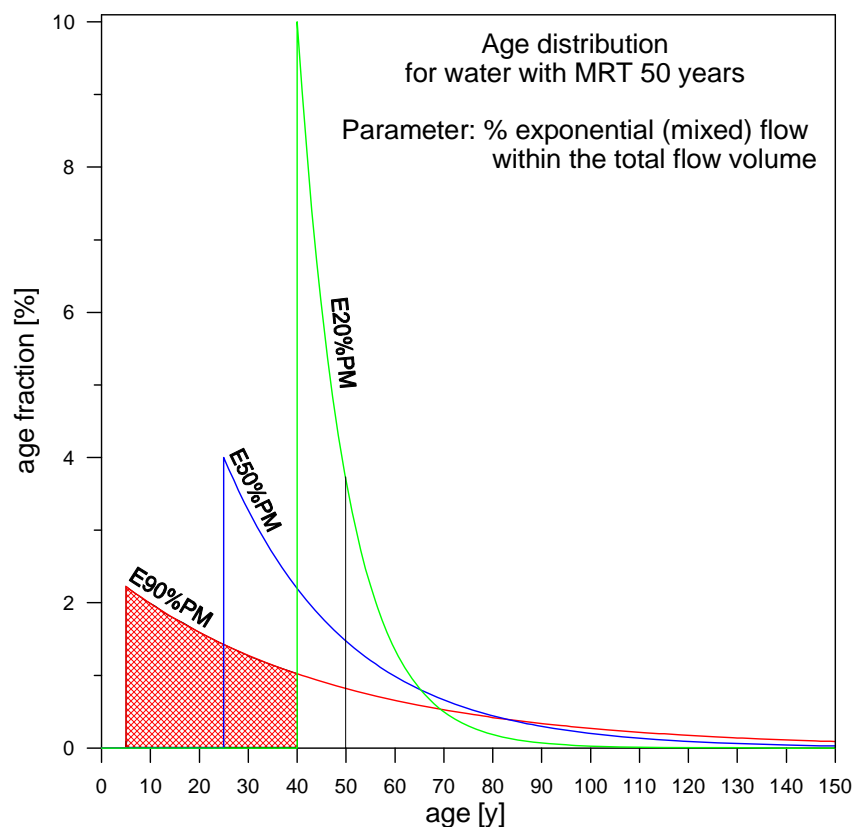


Figure 21. Age distribution for the exponential-piston flow model.

In a flow situation with less exponential flow, the age distribution of the water is less wide-spread. At 50% exponential flow, the minimum age is 25 years, and the water does not contain significant fractions older than 150 years. At only 20% exponential flow, the age distribution is relatively peaked around the mean residence time. The minimum age is 40 years, and there is an insignificant amount of water older than 100 years. This water would just start to show a contaminant introduced 40 years ago, but this contaminant would arrive in a relatively sharp front, with 10% contribution in the first year of arrival after 40 years time.

APPENDIX 3 — CFC AND SF₆ RAW DATA

Table 5. Raw CFC and SF₆ data. See Appendix 2 for explanation.

CFC No.	SF ₆ No.	Sample Details	Sampling Date	Measured concentration in solution					Calculated Atmospheric Partial Pressure in pptv					Piston Flow Model Recharge Dates				
				fmolkg ⁻¹		pmolkg ⁻¹		±	CFC-12	±	SF ₆	CFC-11	±	CFC-12	±	SF ₆	CFC-11	CFC-12
				SF ₆	CFC-11	±	CFC-12											
FMB42	SMB36	P27w/0472	6.03.06	1.60	4.63	0.01	2.55	0.01	3.75	212.1	4.8	450.6	6.2	1997.0	1986.5	1989.0		
FMB43	SMB37	P27w/0276?	6.03.06	2.02	3.76	0.01	2.27	0.01	4.73	197.1	0.9	451.0	4.9	2001.5	1984.5	1989.0		
FMB44	SMB38	Cullen Creek @ Cullensville	6.03.06	--	3.73	0.03	2.02	0.08	--	233.0	13.4	472.8	39.4	--	1988.0	1990.0		
FMB45	SMB39	Jones mine shaft seep	6.03.06	1.94	3.13	0.03	1.91	0.00	5.38	170.1	2.8	393.6	5.5	2004.5	1981.5	1986.0		
FMB46	SMB40	P27w/0493	6.03.06	1.29	2.73	0.01	1.55	0.01	2.58	122.3	1.0	267.0	0.7	1992.0	1976.5	1979.0		
FMB47	SMB41	P27w/0485	6.03.06	1.75	4.02	--	2.08	--	4.46	198.2	--	394.1	--	2000.5	1985.0	1986.0		
FMB48	SMB42	P27w/0235	6.03.06	0.02	0.31	0.44	0.21	0.27	0.03	15.3	21.6	38.2	50.1	<1952.5	1963.0	1962.0		
FMB49	SMB43	P27w/0495	7.03.06	2.09	3.71	0.00	2.57	0.00	4.76	171.4	1.5	458.6	3.3	2002.0	1981.5	1989.5		
FMB50	SMB44	P27w/0447	7.03.06	2.21	4.42	0.01	2.61	0.01	4.96	211.0	0.7	476.6	2.7	2003.0	1986.0	1990.5		
FMB51	SMB45	P27w/0494	7.03.06	1.75	4.42	0.02	2.52	0.02	4.66	231.6	6.7	504.7	15.5	2001.5	1988.0	1993.0		
FMB52	SMB46	Cullen Creek upstream of bridge	7.03.06	2.25	4.60	0.01	2.65	0.00	5.41	227.1	3.8	500.2	7.5	2004.5	1987.5	1992.5		
FMB53	SMB47	P27w/0496	7.03.06	1.91	7.64	0.22	7.30	0.10	4.79	410.9	20.7	1487.0	76.3	2002.0	Hi Cont. (>25%)	Hi Cont. (>25%)		
FMB54	SMB48	P27w/0492	7.03.06	1.00	0.89	0.00	0.58	0.00	1.67	43.4	0.1	105.1	0.0	1987.5	1969.0	1969.5		
FMB55	SMB49	P27w/0247	7.03.06	0.25	1.10	0.01	0.67	0.00	0.55	53.3	0.9	123.2	1.7	1978.0	1970.5	1971.0		

Sample Details	Concentration in solution				μmol.L ⁻¹		calculated variables			
	mL(STP).kg ⁻¹		N ₂		CH ₄		temp	excess air		
	Ar	±	±	±	±	±	°C	±	mL(STP).l	±
P27w/0472	0.396	0.003	15.02	0.07	0		9.2	0.4	0.2	0.1
P27w/0276?	0.383	0.001	14.98	0.01	0		11.7	0.1	1.2	0.0
Cullen Creek @ Cullensville	0.343	0.007	12.97	0.19	0		15.0	1.0	-0.3	0.1
Jones mine shaft seep	0.366	0.004	13.82	0.52	0		12.3	0.5	-0.1	0.8
P27w/0493	0.413	0.001	16.33	0.01	0		8.9	0.2	1.8	0.1
P27w/0485	0.354	--	12.05	--	0		10.5	--	-3.0	--
P27w/0235	0.424	0.007	17.11	0.74	7.7	1.1	8.7	2.8	2.6	2.1
P27w/0495	0.398	0.000	15.24	0.10	0		9.4	0.1	0.6	0.2
P27w/0447	0.396	0.000	15.33	0.05	0		10.0	0.1	0.9	0.1
P27w/0494	0.348	0.002	12.05	0.02	0		11.6	0.5	-2.6	0.2
Cullen Creek upstream of bridge	0.386	0.003	14.82	0.12	0		10.6	0.3	0.5	0.0
P27w/0496	0.375	0.006	14.49	0.10	0		12.2	1.5	0.7	0.7
P27w/0492	0.425	0.001	18.01	0.07	0		10.5	0.1	4.6	0.0
P27w/0247	0.398	0.002	15.63	0.01	0		10.2	0.4	1.4	0.2



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