1 Fairway Drive
Avalon
PO Box 30 368
Lower Hutt
New Zealand
T +64-4-570 1444
F +64-4-570 4600
www.gns.cri.nz

Flaxbourne catchment groundwater residence time, flow pattern, and hydrochemistry trends

Uwe Morgenstern
Dougal Townsend
Chris Daughney
Peter Davidson

GNS Science report 2007/14
April 2007

Institute of Geological and Nuclear Sciences Limited

BIBLIOGRAPHIC REFERENCE

Morgenstern, U., Townsend, D., Daughney, C., Davidson, P., 2007. Flaxbourne catchment groundwater residence time, flow pattern, and hydrochemistry trends, *GNS Science Report,* 2007/14, 56p.

U. Morgenstern, GNS Science, Lower Hutt
D. Townsend, GNS Science, Lower Hutt
C. Daughney, GNS Science, Lower Hutt
P. Davidson, Marlborough District Council, Blenheim

ISSN 1177-2425
ISBN 978-0-478-09978-2

CONTENTS

FIGURES

TABLES

APPENDICES

SUMMARY

Water demand is increasing in Marlborough province due to population growth but more significantly through increases in the area of irrigated crops. In water short catchments like the Flaxbourne on the semi-arid East Coast, vineyard expansion is driving the demand for water. There is significant perennial flow in the upper catchment, which subsequently becomes discontinuous in the middle reaches and reappears near the coast. A combination of shallow groundwater associated with the Flaxbourne Rivers or its tributaries is used by irrigators at Ward.

Little water storage potential is afforded by the greywacke basement rocks in Marlborough, which have the greatest surface outcrop extent. Unconformably overlying Late Cretaceous rocks are slightly less compacted and therefore may contain greater pore space and better storage potential, but these rocks are relatively limited in surface outcrop extent. Paleogene clastic rocks are relatively fine-grained; Miocene and Pliocene rocks are also fine-grained or cemented and these rocks have little storage potential. The best water storage potential is afforded by Quaternary alluvial and colluvial gravels. These are generally open, clast-supported gravels but because they are thin and/or confined within valleys incised into bedrock, they probably do not form volumetrically substantial aquifers. Most of the Quaternary gravel units are thin, and a cross section indicates that there are no connections between catchments.

All investigated waters in the Flaxbourne area are young with mean residence times (MRT) <5 yrs (Table 2) indicating little groundwater storage. Older groundwaters were observed only in the Tachalls/Needles area, with mean residence times at West 53 yrs, at Wiffen seep 120 yrs, and at Peter test bore 38 yrs. However, the old waters at Wiffen seep and Peter test bore are not an indication of larger groundwater storage capacity because the water flow rate is very low and therefore the old age is just a result of near stagnant groundwater flow in an aquifer with low hydraulic conductivity. Only West has a considerable water flow and older age and therefore indicates a larger groundwater storage reservoir in relation to its total flow.

The groundwater samples collected in this investigation have several unusual chemical characteristics, for example high concentrations of boron, bromide, chloride, fluoride, bicarbonate, potassium, magnesium, sodium and/or sulphate, and low concentrations of calcium. Hierarchical cluster analysis (HCA) indicates that the samples from the Flaxbourne catchment have very different chemistry compared to the samples from either the Tachalls or Needles catchments

The chemical composition of the groundwater can help to determine origin and recharge source of the water. However, the chemical composition of the groundwater can also be influenced by anthropogenic and geogenic 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 geogenic influence on hydrochemistry, the various water chemistry parameters are plotted against mean residence time. By isolating anthropogenic and geogenic trends, spatial hydrochemistry patterns (depending on local geologic formations) become more obvious with the result that groundwater flow patterns and connections between different groundwater systems can be better identified.

Little impact of landuse is evident in the water samples. Only a few samples in the lower Flaxbourne catchment and at Ward show elevated levels of sulphate, and only two samples

at Ward and Tachalls have elevated nitrate. Low nutrient concentrations are likely to be partially a product of strong microbial degradation processes with denitrification and sulphate reduction.

The samples at Tachalls that cover a wider age range of 1 to 120 yrs mean residence time show evolving hydrochemistry, with increasing Ca, SiO_2, F, Br, and Hg with increasing contact time of the water with the rock in the aquifer.

Needles and Tachalls show evidence of hard-water influence from the mio-plio Awatere group, probably due to dissolution of calcareous fossils/shell layers. The waters around Ward indicate that their origin is not the same mio-plio Awatere group but the plio Awatere group south of Ward. The Flaxbourne waters indicate that their origin is from the Greywacke catchment of the Flaxbourne River.

Flaxbourne and Tachalls/Needles are strongly anaerobic environments (including the surface waters). Some water samples indicate strongly reducing conditions, excess HCO_3 from organic matter, and high methane concentrations. This suggests that this aquifer system is formed from ancient swamps. Only south of Ward we found oxic groundwater, indicating that this is an aquifer containing little organic matter.

There are extremely high boron concentrations observed in the pond and Peter’s test bore. High boron concentration in groundwater is often an indicator of geothermal activity or fault influence. However, water temperatures are not elevated, and no active fault structure has been mapped in the vicinity, suggesting that geothermal or fault origin of the boron is unlikely. In addition, the ratio of chloride to boron is lower than would be expected for a geothermal source, and although fluoride concentrations are above average relative to groundwater in other parts of the country, the fluoride concentrations are not as high as would be expected for geothermal or fault influence.

The high observed B concentrations are associated with strongly reducing groundwaters. We conclude that the high boron concentrations arise from water-rock interaction involving strongly anaerobic conditions in organic-rich sediments, and greywacke. It is likely that the strongly reducing aquifer conditions have the reason that this aquifer system is formed from ancient swamps, as suggested by the following facts: High methane concentrations, excess HCO_3 from organic matter, and this area is likely to be subsiding (Ward syncline).

Indications of sources for the investigated waters are as follows:

Flaxbourne River: Low ionic concentrations in all of these water samples reflect low mineral solubility in the greywacke catchment. The residence time of the water in the catchment is les than 2 years. No significant groundwater reservoir is indicated by the investigated samples. Hydrochemistry within the short residence time is slightly evolving in the series Upper catchment tributary, Upper catchment river, lower catchment River. The whole catchment is an anaerobic environment.

Taimate well: The hydrochemistry of this water is nearly identical to the Flaxbourne River nearby indicating that the water is sourced from the Flaxborne River.

West domestic well: This groundwater system forms a separate system compared to all other samples. This water is oxic and therefore originates from a ‘clean’ aquifer with little organic matter and significant storage capacity. The recharge area is likely to be the plio Awatere group south of Ward. High nitrate and excess air also indicate recharge from the local farm area. High SF_6 in relation to tritium indicates unconfined aquifer condition.

Wiffen seep: While this water is the only old water with mean residence time of 120 yrs, it does not originate from a large groundwater system because of the low flow. The old age is likely to be caused by extremely slow groundwater flow due to low hydraulic conductivity. The water does not show any evidence of flow along an active fault. However, this water seems to be connected to a stable groundwater system in some distance because this seep never dries up in the summer.

Wiffen domestic well: Hydrochemistry is similar to the other waters in the Tachalls/Needles area. Zero excess air and young age suggests recharge from a stream. However, no stream sample for comparison is available because the nearby stream was not flowing at the time of sampling.

Peter test bore: This water originates from a highly anaerobic aquifer. Excess HCO_3 from organic matter and high methane concentrations suggests that this aquifer system is formed from ancient swamps. The old age (MRT 38 yrs) is a result of slow groundwater flow, and excess SF_6 compared to tritium indicates unconfined or semi-confined aquifer. There is no hydraulic connection to the creek, as indicated by hydrochemistry signature and that this well does not produce significant amounts of water. The hydrochemistry with extremely high boron is therefore assumed to represent the local anaerobic aquifer.

Peter irrigation well: This well is close to the creek and is a good producer of water. Hydraulic connection to the stream is therefore likely, and hydrochemical signature suggests that this water is a mixture of about 10% local groundwater and 90% creek water.

Needless Creek: Compared to the other river waters, this creek water is slightly older with MRT 4.5 years. Good agreement between SF_6 and tritium indicates confined aquifer condition.

Evans domestic well: Smilar hydrochemistry between the well and creek water suggests that Evans well has a hydraulic connection to the nearby creek.

Pond at Chapman seep: This water is completely depleted in oxygen despite the open surface to air. Despite that this pond has no visible outflow it is not stagnant water because chemical components and ^{18}O are only slightly enriched by evaporation. The age is ambiguous but the young age (mean residence time of 1 year) is the most likely one (as opposed to 40 yrs). Hydrochemistry suggests similar origin as Peter test bore from the highly anaerobic local aquifer.

KEYWORDS

Groundwater dating, tritium, CFCs, SF_6, groundwater flow, groundwater recharge source, hydrochemistry evolution, nitrate contamination, boron, anthropogenic impact on groundwater.

1.0 INTRODUCTION

Water demand is increasing in Marlborough province due to population growth and through increases in the area of irrigated crops. In water-short catchments like the Flaxbourne on the semi-arid East Coast, vineyard expansion is driving the demand for water.

Relatively little is known about the hydrology of the Flaxbourne catchment. There is significant perennial flow in the upper catchment, which subsequently becomes discontinuous in the middle reaches. The Flaxbourne River and tributaries appear only in the lowland areas. Shallow groundwater associated with the Flaxbourne River or its tributaries is used by irrigators at Ward. Resource management decisions are being made without sound understanding of sustainable limits for water allocation.

Marlborough District Council requires a baseline hydrological assessment to identify sources and flow characteristics within the Flaxbourne catchment groundwater system. This information will be used to build a conceptual groundwater flow model, and eventually to guide in water allocation practice.

The objective of the study is to identify:

- Sources of water recharge in the catchment, i.e. is the Flaxbourne Catchment water derived solely from rainfall runoff in the upland catchment area plus what falls directly on the lowland flats, or is there a tectonic contribution (Clarence Fault etc).
- Mean Residence Times of the groundwater, i.e has Flaxbourne Catchment water a low residence time as suggested by earlier reports, and is there limited storage associated with the veneer of gravels overlying mudstone?
- It was also hoped to resolve some long-standing salient issues such as the origin of recharge to well P29w/0146 (Needles Creek) and in more general terms the importance of fault generated recharge (West dam). However, P29w/0146 could unfortunately not be included in this study because access to the well was not possible.

The isotopic and chemistry signature of the groundwater is used to identify residence times and flow characteristics of the groundwater system. Tritium, CFCs and SF_6 are used for age dating, and ^{18}O, N_2, Ar, CH_4 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 EASTERN MARLBOUROUGH

2.1 PHYSIOGRAPHY

The physiography of Marlborough is dominated by active tectonics. The most salient geological feature of Marlborough is the Marlborough Fault System, which comprises a series of NE-striking, active dextral strike-slip faults. The topography is accordingly cut into a series of elongate blocks, with valleys delineated by the faults and high mountain ranges in between (Figure 1). Major rivers are controlled by the faulting pattern and most flow in a NE direction towards the coast. The highest peak in the region is the 2885 m Mt. Tapuae-o-Uenuku, which consists of an erosion-resistant plutonic body intruded into the host greywacke of the Inland Kaikoura Range.

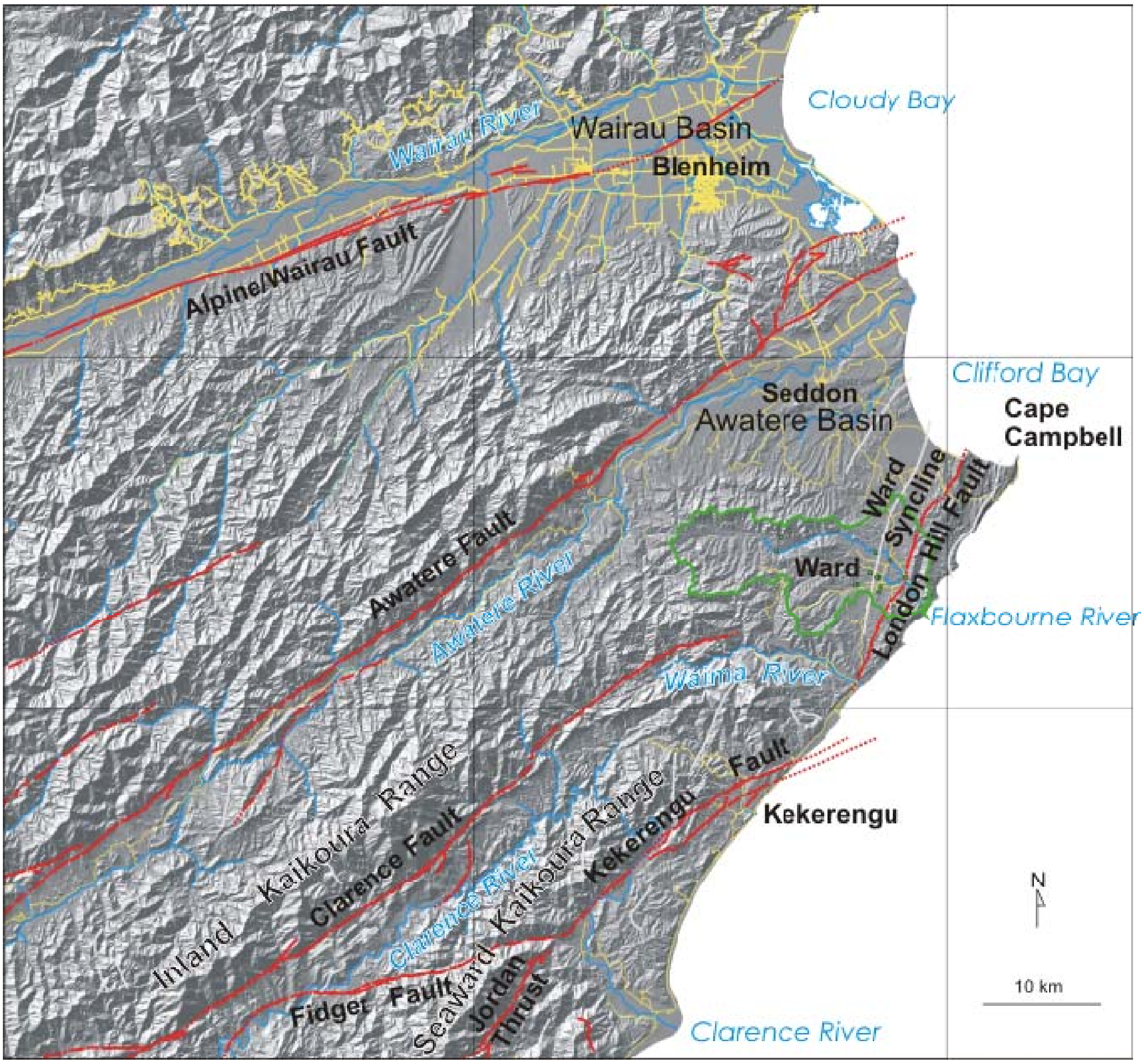

Figure 1. Physiography of the eastern Marlborough region. The region is structurally divided into NE-trending fault-bound blocks by the active Marlborough Fault System (shown in red), comprising the major Alpine/Wairau, Awatere, Clarence and, further south, Hope faults. Other active faults include the Fidget, Kekerengu and London Hill faults, and the Jordan Thrust, which may act as relay structures between the major faults of the Marlborough Fault System. Deformation in the style of half-graben has allowed the preservation of Late Cretaceous to Neogene rocks along the footwalls (SE sides) of the major faults and northward tilting has preserved relatively thick Late Neogene to Quaternary rocks in the Wairau and Awatere basins. Geological data from Begg & Johnston 2000 and Rattenbury et al. in press. Outline of the Flaxbourne River catchment shown in green and sample sites shown by green dots.

Tectonic uplift is highest in the mountain ranges and lower near the coast. As a result of northward tilting of the fault blocks, the Wairau and Awatere valleys have Neogene rocks preserved at their NE ends near the coast. These areas are also sites of significant local Quaternary sedimentation.

The general climate on this part of the South Island's east coast is dry due to a rain-shadow effect with the prevailing wind direction from the north-west. Coastal showers are common when the wind direction is from the south.

2.2 STRUCTURE

Marlborough is dominated by a NE-SW –oriented structural grain, which includes bedding strike ridges and both active and inactive faults. Major active faults include the dextral strike-slip Wairau, Awatere, Clarence and Hope faults, which collectively make up the Marlborough Fault System (Figure 1). Other faults, such as the east-west -striking Haldon Hills and Flaxbourne faults, cut across the dominant structural grain (Figure 2).

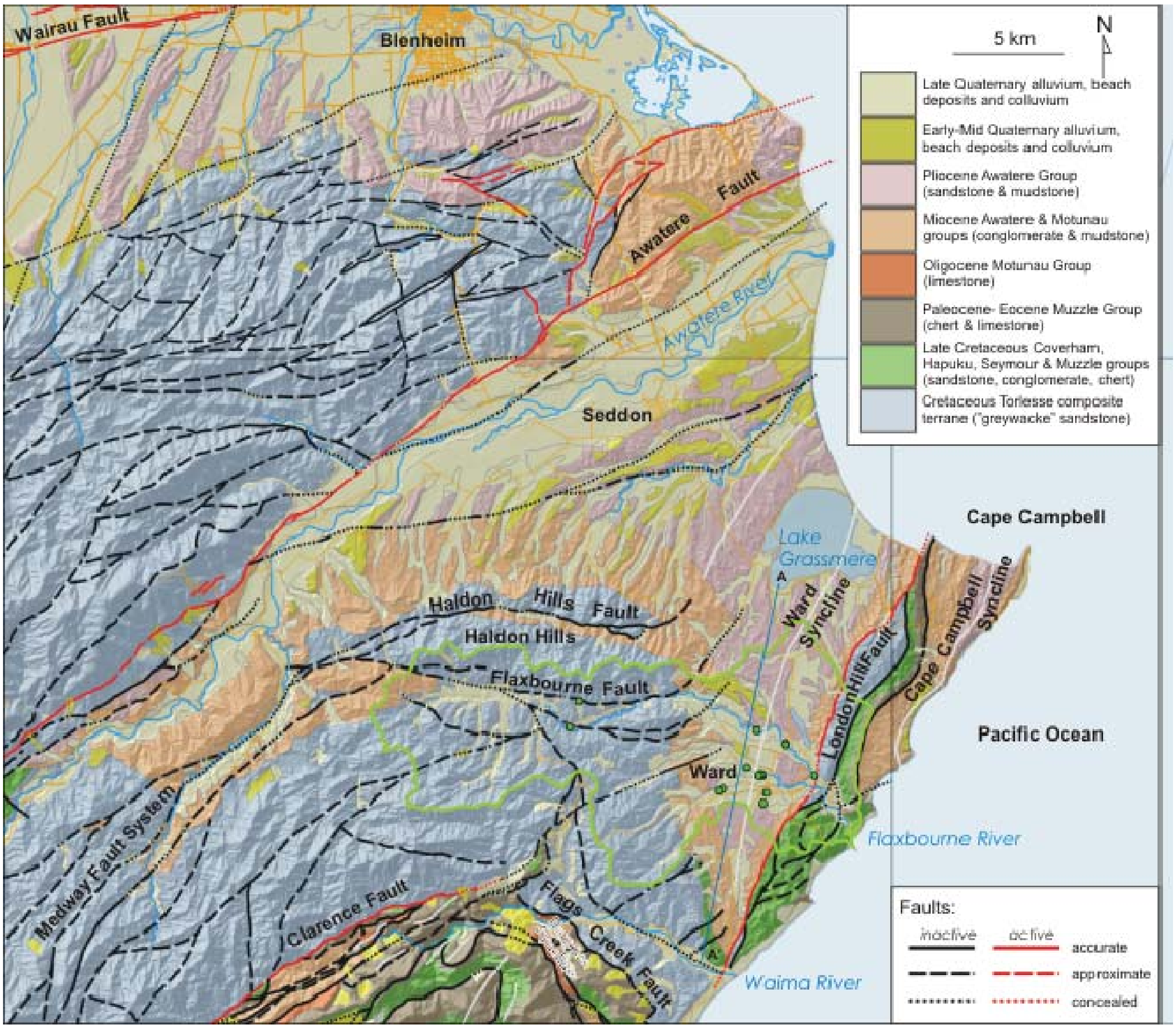

Figure 2. Geology of the lower Awatere Valley - Ward area, illustrating the distribution of rock units of varying age based on QMAP data (Begg & Johnston 2000; Rattenbury et al. in press). The map pattern reflects mostly Late Miocene to Quaternary faulting and folding, and the development of localised basins along the fault traces during the Late Miocene and Pliocene. Quaternary Uplift of the Haldon Hills may be a consequence of folding due to the onshore termination of the active Clarence Fault (Roberts 1995; Townsend 2001). The Flaxbourne River has maintained its course towards the Pacific Ocean despite the activity of the Ward Syncline and the London Hill Fault (Townsend & Little 1998). Outline of the Flaxbourne River catchment shown in green and sample locations shown by green dots. Blue line shows position of cross-section A-A' (Figure 5).

Many of the active faults appear to have had a long history of movement, e.g. prior to the middle Cretaceous, the Clarence Fault had developed a wide shear zone which was then cut by Ngaterian-aged (90-100 Ma) intrusive dikes (Crampton et al. 1998). Subsequent reactivation as a thrust fault in the Early Miocene preceded its current phase of dextral strike-slip motion (Townsend 2001). Another example of multiple episodes of faulting deformation is the London Hill Fault, which today is a thrust fault that dips moderately to the ESE. Paleogene normal activity, however, is inferred from stratigraphic differences on either side of the fault (Townsend & Little 1998).

The onshore termination of the active Clarence Fault is an unusual case whereby strain accommodated by strike-slip deformation in the south is transferred to other modes of deformation, such as uplift/subsidence and vertical-axis rotation of crustal-scale blocks in the north. Paleomagnetic evidence from Late Miocene and Pliocene rocks of the lower Awatere Valley suggests that a crustal block that is approximately 20 km^2 has rotated clockwise about a vertical axis by as much as 44° since the Pliocene (Roberts 1992, 1995). The Awatere, Clarence, Flags Creek and London Hill faults form the boundaries of the rotating block and the Ward and Narrows synclines possibly accommodate strain near its edges (Figure 2; Townsend 2001).

Haldon Hills and Flaxbourne River

Uplift and erosion of the Haldon Hills during the Quaternary has exposed a core of Torlesse terrane rocks. Directions of Late Quaternary tilting based on stream drainage patterns surrounding the Haldon Hills suggests that the shape of the uplifting area is a broad dome centred to the north of the Clarence Fault termination (Figure 3; Townsend 2001). This uplift has caused the gradient of the upper reaches of the Flaxbourne River to have become “disconnected” from the gradient of the lower reaches. A profile of the Flaxbourne River (Figure 4a) shows that about midway along its length, its gradient becomes much steeper than in the upper or lower reaches and the river cuts through a gorge formed in Torlesse terrane bedrock. This gorge coincides with the along-strike projection of the Clarence Fault. Just below the gorge, Miocene strata and Middle Quaternary terraces are tilted towards the east on the western limb of the Ward Syncline. Only younger terraces are preserved near the axis of the syncline; the older ones have apparently been buried (Figure 4b). The Flaxbourne River has maintained its course to the Pacific Ocean despite the activity of the Ward Syncline and London Hill Fault.

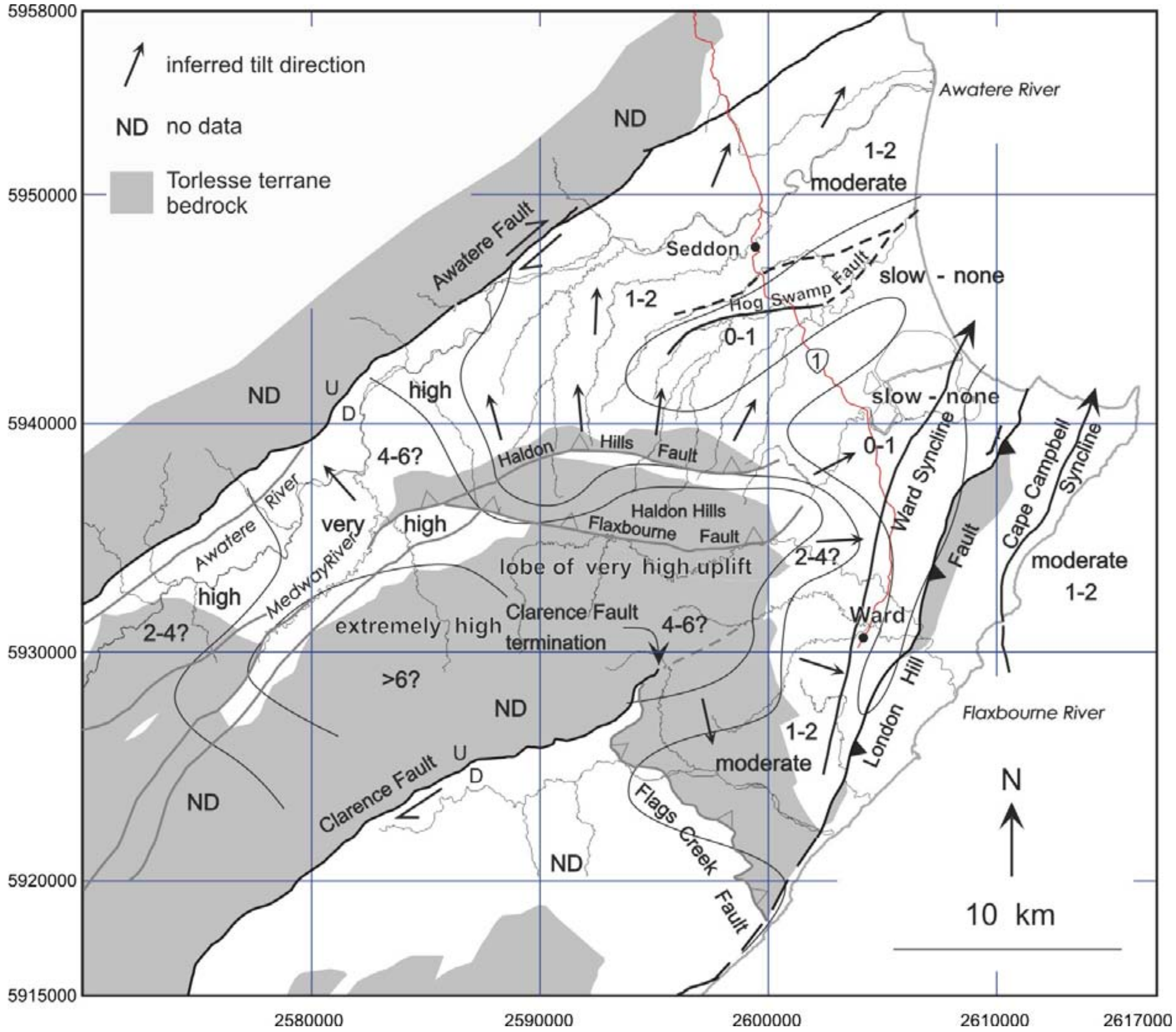

Figure 3. Approximation of contemporary uplift rates in NE Marlborough (after Townsend 2001). Numbers are rates of uplift (in mm a-1) extrapolated from uplifted coastal marine terraces (see Ota et al. 1995) and constrained by the pattern of Late Quaternary river incision and terrace tilting inland. High rates of uplift to the north and west of the Clarence Fault termination indicate uplift and crustal thickening to accommodate enhanced compressive tip stress in this region. Lack of active surface structures suggests that the deformation may be occurring by folding or by slip on blind faults. Low rates of uplift in the Blind River-Lake Grassmere area attest to active structures such as the Hog Swamp Fault and the Ward Syncline. This pattern is superimposed on a regional NNE tilt of 2° per million years since the last c. 120 ka.

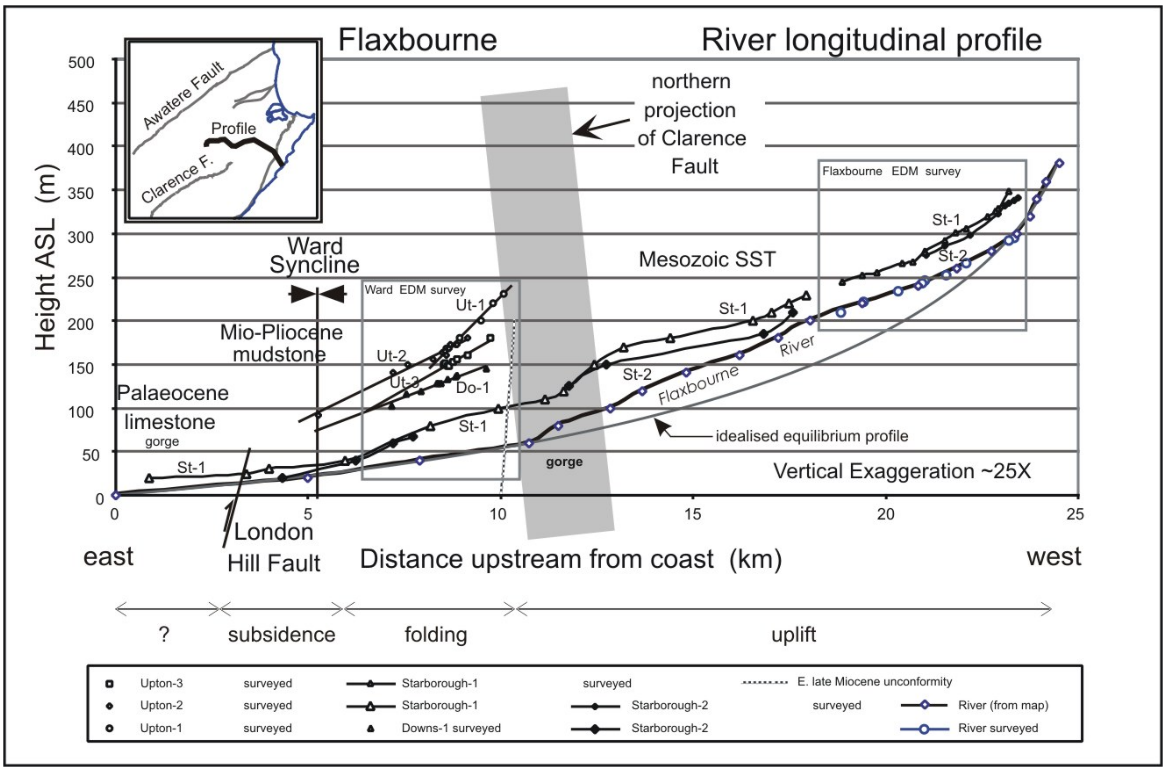

Figure 4a. Longitudinal profile of the Flaxbourne River (after Townsend 2001), showing tilting of terrace surfaces across the northern projection of the Clarence Fault (see inset). The obvious change in slope of the river (at ~12 km) defines a knickpoint, that may be related to the more resistant Torlesse bedrock, to which the upper part of the river is grading. Tilted terraces in the central region appear to define a monocline, with the greatest change in slope occurring at the projected position of the Clarence Fault (shaded band). The pattern of elevation changes is consistent with down-warping in the Ward Syncline and a ~15 km wide broad doming to the west of the projected Clarence Fault position. Abbreviations of terrace names are: Ut -1: Upton 1; Ut -2: Upton 2; Ut -3: Upton 3; Do -1: Downs 1; Do -2: Downs 2; St -1: Starborough 1; St -2: Starborough 2.

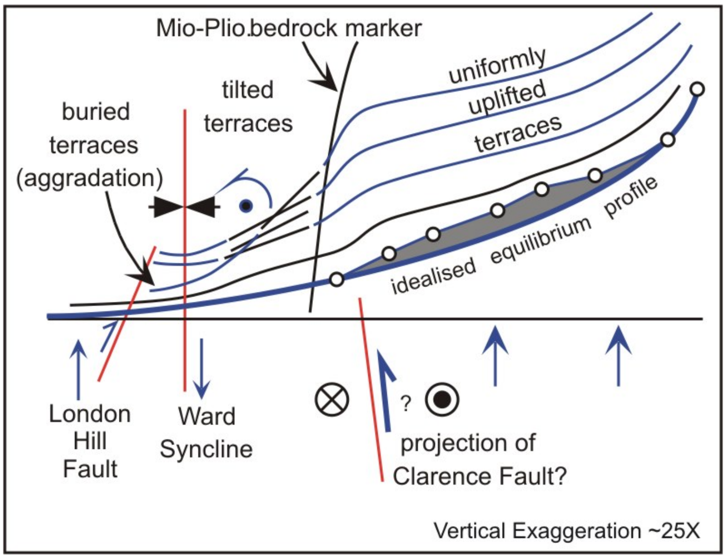

Figure 4b. Schematic representation of Figure 4a (above) showing differential uplift of fluvial fill terraces above a growing monocline. The upper catchment is constantly attempting to grade to the equibrium level, but uplift over and upstream from the fold axis (possibly cored by a blind reverse fault) requires that the stream incises all the way to the headwaters (shaded region). This pattern of deformation produces parallel, uplifted terraces upstream from the fold axis and tilted, sometimes buried terraces downstream.

2.4 MAJOR ROCK TYPES

Torlesse composite terrane

The dominant rock type by far in eastern Marlborough is massive sandstone or interbedded sandstone and argillite, or “greywacke” of the Torlesse composite terrane. These rocks also include minor components of basalt, chert and limestone. The age of the Torlesse terrane in Marlborough ranges from Late Jurassic to middle Cretaceous, though most is Cretaceous (Rattenbury et al. in press). These rocks have been subjected to multiple phases of deformation since their deposition, and therefore contain many faults, folds and joints. Due to the deformation, bedding is generally steeply dipping.

Distribution: Torlesse composite terrane makes up the high mountain ranges and most of the inland part of eastern Marlborough (Figure 2).

Hydrogeology: Induration and cementation of these rocks has removed most of the primary pore space between sand grains. There is some, although not great, potential for water storage along joint planes.

Late Cretaceous rocks

These rocks include conglomerate, well-bedded sandstone and siltstone, poorly-bedded sandstone and chert. The conglomerate is usually matrix-supported and generally only a minor component that grades up into sandstone. These clastic rocks unconformably lie on Torlesse terrane, often with a sharp angular discordance. Pelagic chert was deposited as basins deepened towards the end of the Cretaceous.

Distribution: Late Cretaceous rocks are relatively limited in distribution (Figure 2). They crop out in narrow, fault-bound strips, or more extensively in the coastal hills east of ward.

Hydrogeology: Most of these rocks are well-compacted, semi-indurated or contain bedding-plane shear. Therefore they have little potential for water storage. Some of the well-sorted sandstones which are relatively less-compacted and contain many joints (e.g. Seymour Group) have limited potential for water storage, but these are spatially limited in extent.

Paleocene to Eocene rocks

Paleocene to Eocene rocks include well-bedded, micritic limestone and marl, and minor sandstone and pillow basalt of the Muzzle Group. The limestone, which is very fine-grained and often recrystallised, is composed mainly of foraminifera tests. Interbedded with the limestone, the calcareous marl contains a high proportion of bentonitic clay. This clay preferentially acts as slip-planes during tectonic deformation and it is often associated with Quaternary landslides.

Hydrogeology

Because of its fine-grained nature, there is little potential for the limestone to store water. Few cave systems are known within this lithology, and those present (e.g. at Kaikoura) are small. This is probably due to the tectonic instability of the region, thus there has not been enough time to form any large cave systems. However, due to deformation (mainly folding) the limestone contains many closely-spaced joints and sometimes spaces between bedding planes. There may be, therefore, some storage potential where it is moderately deformed. The bentonitic clay (marl) has the ability to absorb water and therefore may have some storage potential.

Oligocene to Pliocene rocks

In the south these rocks consist of a basal silty or sandy limestone which rests unconformably on Paleogene limestone and grades up into massive siltstone or marl (the Motunau Group). A sequence of Early Miocene massive calcareous siltstone, interbedded siltstone and sandstone, and massive sandstone with conglomerate lenses rests conformably on the Oligocene limestone. In the north Middle Miocene to Pliocene conglomerate, sandstone, interbedded siltstone and mudstone of the Awatere Group rests unconformably on Torlesse composite terrane. East of the London Hill Fault Late Miocene and Pliocene rocks are faulted against Paleogene limestone.

Hydrogeology: These Neogene rocks are usually cemented or mildly compacted, therefore do not contain much pore space. In the south the conglomerates are typically mass-emplaced debris flow deposits and are often matrix supported. Some of the conglomerate units in the north are clast supported and may have limited potential to store water. The massive sandstone units have the potential to store water, but these are typically thin, and substantial aquifers probably do not exist.

Middle Quaternary rocks

Older alluvial terrace remnants preserved in the lower Awatere Valley and to the north of Ward include moderately- to well-sorted gravels, usually with a capping unit of loess. These gravels also include older beach deposits preserved near the coast (e.g. Ota et al. 1995). The gravels are generally open, clast-supported gravels with high porosity and permeability. They lie unconformably on all older rock types which, by contrast, are impermeable.

Hydrogeology: These rocks may contain abundant groundwater due to their clast-supported nature and open pore space, but because of their relatively limited spatial extent, any aquifers may not be large and flow may be inconsistent.

Late Quaternary rocks

These rocks include alluvial and colluvial gravels which may or may not contain a capping unit of loess. They are generally well-sorted, clast supported gravels with high porosity and permeability. They also include young beach deposits fringing the coastline and surrounding Lake Grassmere (Ota et al. 1995; Figure 2). They lie unconformably on all older rock types.

Hydrogeology: Late Quaternary gravels are the most extensively-preserved gravel unit in eastern Marlborough. They also occupy the modern valley floors and therefore have the most potential to carry large amounts of groundwater where aquifers are connected. Figure 5 shows a cross-section from Lake Grassmere to the Waima River across the lower reaches of the Flaxbourne River. This section indicates that most of the Quaternary gravel units are thin and are therefore not connected between catchments. Photo 1 shows an example of the thin gravel layer overlaying the mudstone (papa).

2.5 SUMMARY OF HYDROGEOLOGY

Little water storage potential is afforded by the greywacke basement rocks in Marlborough, which have the greatest surface outcrop extent. Unconformably overlying Late Cretaceous rocks are slightly less compacted and therefore may contain greater pore space and better storage potential, but these rocks are relatively limited in surface outcrop extent. Paleogene clastic rocks are relatively fine-grained; Miocene and Pliocene rocks are also fine-grained or cemented and these rocks have little storage potential. The best water storage potential is afforded by Quaternary alluvial and colluvial gravels. These are generally open, clast-supported gravels but because they are thin and/or confined within valleys incised into bedrock, they probably do not form volumetrically substantial aquifers.

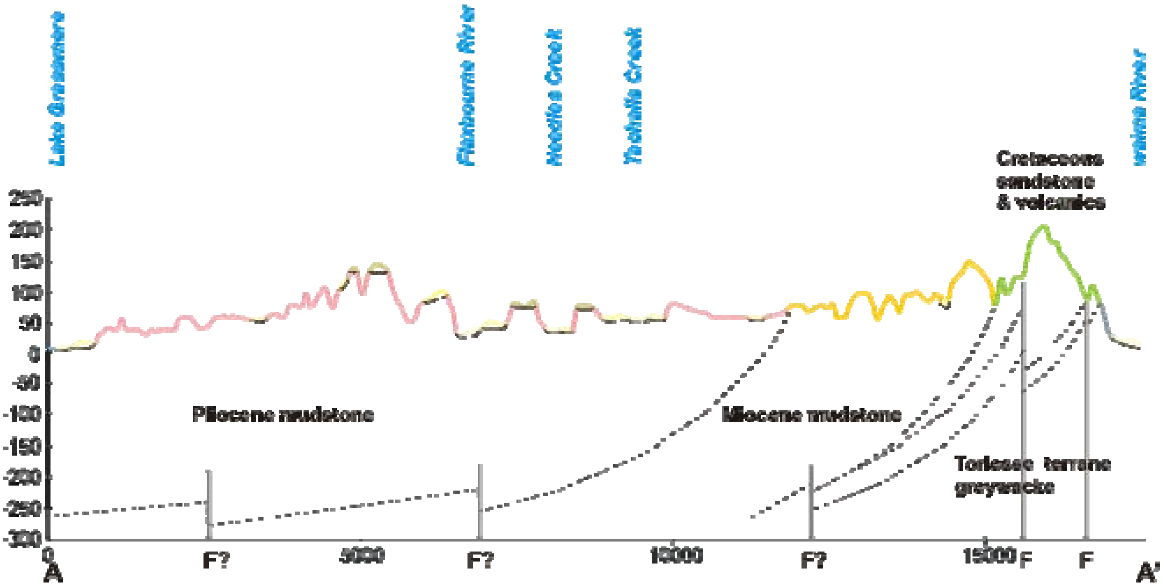

Figure 5. Schematic cross-section A-A' between Lake Grassmere and the Waima River. Older Quaternary gravel remnants form thin caps to the ridges and younger gravels in-fill the valley bottoms. Aquifers are apparently not connected between valleys. See Figure 2 for location.

Photo 1. View from Evan's house to the river with exposed gravel and papa formation.

3.0 SAMPLE LOCATION AND BORE DATA

Sample locations are shown in Figure 6, with photographs of sites in Appendix 1. Only a few wells were available, and these were shallow (<6 m). Therefore, a number of surface waters had to be included in this study. Additionally, two samples from the upper reaches of the Flaxbourne River were included to identify its isotopic and chemistry signature and its contribution to the groundwater system. Geographic and bore data are summarized in Table 1. Information on screens and classification on confinement of the aquifer is scarce.

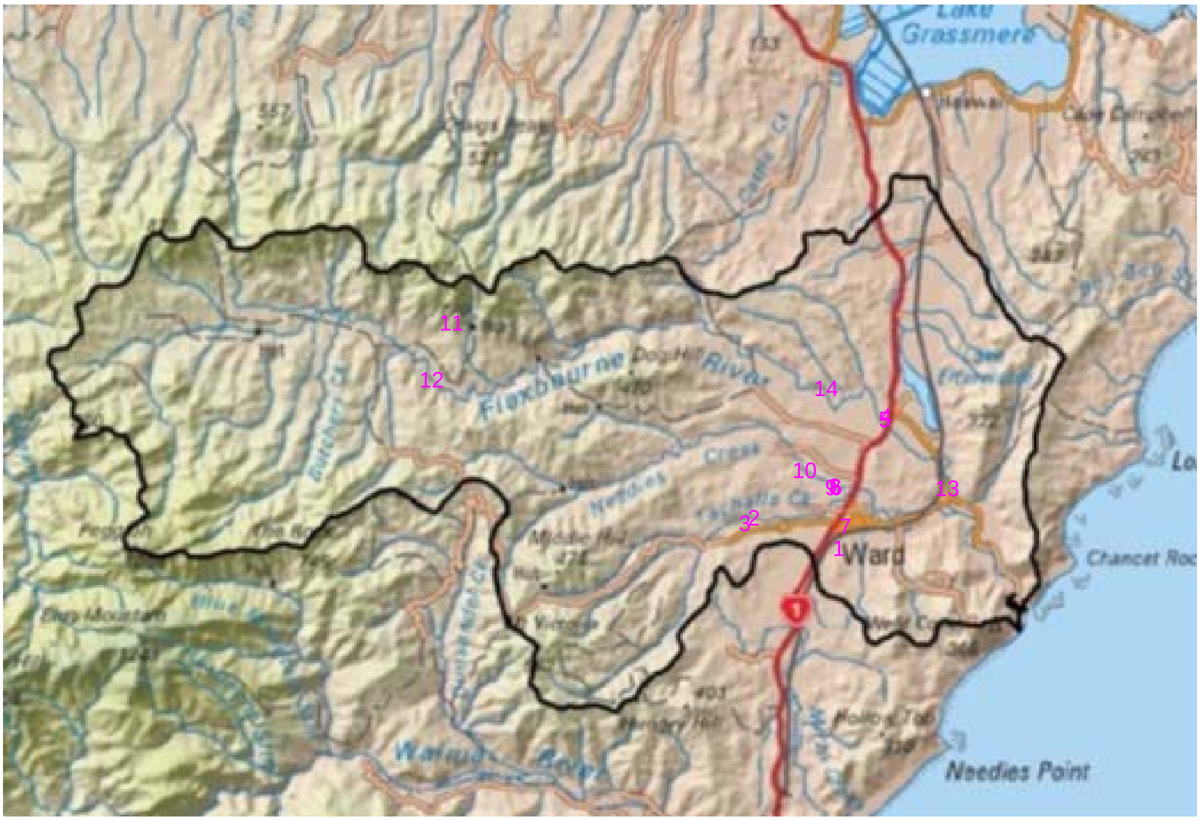

Figure 6. Flaxbourne topographic catchment and sample location.

Table 1. Sample, geographic, and bore data.

#	Well_ID	Name	East	North	well depth m	water level m	Screen [m] top	bottom	confined?	Remark sampling
1	P29w/0187	West domestic well	2604185	5929963	3.5	1.2	none	none	unconfined	domestic well near seeps, sheep farming around
2	P29w/0164	Wiffen domestic well	2602362	5930586	2.5	1.45	?	?	unconfined	Tachalls Creek, domestic well
3	TAC-1	Wiffen seep	2602168	5930482	na	na	na	na		constant flow, never drying up, appears to have higher flow in dry conditions
4	P29w/0087	Taimate stock scheme	2605202	5932646	4 ?	?	?	?	unconfined	water supply bore, stock farming
5	FLX-2	Flaxbourne River @ SH1	2605173	5932581	na	na	na	na		40m from #4, stock farming
6	P29w/0188	Peter irrig. Bore 1 near Needles Creek	2604126	5931203	5.8	1.2	?	?	?	irrigation well, removed plastic suction pipe befor sampling
7	WAR-1	Pond at Chapman seep	2604327	5930408	na	na	na	na		semi-stagnant pond
8	NED-2	Needles Creek @ Peter's culvert	2604097	5931227	na	na	na	na		stream
9	P29w/0189	Peter test bore 2	2604014	5931202	5	1.4	?	?	?	unused irrigation well, dries up sometimes
10	P29w/0163	Evans domestic well	2603451	5931547	?	?	?	?	?	good yielding bore, sample via pressure tank
11	FLX-4	Flaxb River tributary upper catchment	2595859	5934540	na	na	na	na		altitude 303 m
12	FLX-5	Flaxbourne River in upper catchment	2595432	5933383	na	na	na	na		altitude 157 m
13	FLX-6	Flaxbourne River @ Beach Rd Ford	2606513	5931182	na	na	na	na		
14	FLX-7	Flaxbourne River @ Corrie Downs	2603911	5933212	na	na	na	na		

Table 2. Isotope and age data. Low dissolved oxygen results (anaerobic environment) are highlighted. E%PM is the fraction of mixed flow within the total flow volume.

#	Well_ID	Date Sampl.	Temp °C	DO mg/l	Cond uS/cm	pH	Code TMB	TR 2005scale	sigTR	18O ‰	SF6	CFC11 pptv	CFC12	recharge temp °C	excess air mL(STP)	CH_4 µmol/L	E%PM estimat	MRT y
1	P29w/0187	21/02/2006	13.3	5.6	645	6.4	41	1.11	0.04	-6.93	4.89	84.2	364	9.7	-0.9	0	70	53
2	P29w/0164	21/02/2006	15.6	0.2	753	6.02	42	1.77	0.06	-6.59	6.03	25.6	339	11.8	0.2	0	70	3
3	TAC-1	21/02/2006	15.6	6.3	1005	7.3	43	0.383	0.036	-7.47	na	na	na	na	na	na	70	120
4	P29w/0087	21/02/2006	14.7	2.6	351	6.4	44	1.92	0.06	-6.64	5.75	179	464	12.9	1.0	0	70	1.5
5	FLX-2	21/02/2006	22.2	8.0	406	7.8	45	1.89	0.06	-6.52	5.63	194	464	15.6	0.1	0	70	1.5
6	P29w/0188	21/02/2006	13.4	0.1	688	6.8	46	1.91	0.06	-6.39	6.54	0.5	48.9	12.8	1.5	5	70	1.5
7	WAR-1	22/02/2006	16.8	0.2	605	6.45	47	1.91	0.06	-2.12	na	na	na	na	na	na	**70**/35	**1**/40
8	NED-2	22/02/2006	17.4	3.3	718	7.27	48	1.79	0.06	-6.03	5.14	157	410	15.3	1.4	0	70	4.5
9	P29w/0189	22/02/2006	14.1	0.2	745	6.05	49	1.38	0.05	-6.98	2.36	30	75	13.8	1.2	265	70	38
10	P29w/0163	22/02/2006	13.9	0.4	671	6.76	50	1.94	0.06	-6.61	6.24	59	296	12.2	3.6	3	70	1
11	FLX-4	22/02/2006	16.7	6.2	151	7.9	51	2.00	0.05	-7.55	5.55	228	486	16.2	-0.3	0	70	<1
12	FLX-5	22/02/2006	24.6	8.0	251	8.44	52	1.97	0.05	-5.82	5.92	226	487	20.3	1.5	0	70	<1
13	FLX-6	23/02/2006	17.9	2.1	457	6	53	1.92	0.04	-6.13	6.13	178	547	16.8	0.4	0	70	1.5
14	FLX-7	23/02/2006	15.4	6.4	354	6.34	54	2.06	0.07	-6.41	6.02	165	449	14.0	-0.6	0	70	<1

4.0 RESULTS

4.1 ISOTOPES, GASES, AND AGE DATING

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

Table 2 provides a summary of the field parameters, and results of tritium, SF_6 and CFC, and ^{18}O, Ar, N_2, CH_4 analyses, together with the age interpretation. The original analysis reports for CFCs, SF_6 are provided in Appendix 2.

None of the samples show tritium, CFC or SF_6 concentrations above their expected natural occurrence indicating no or very little contamination by local sources. CFC concentrations in the stream waters in the lower reaches, however, are significantly lower than equilibrium concentration with current air (Appendix 2). This indicates that CFCs are degraded in this environment and can only be used for dating in a limited way. Also in wells CFCs are too low according to their tritium and SF_6 age. High methane concentrations in the Evans and Peter bores 1+2 indicate CFC degradation by methane-producing bacteria, observed also by Happell et al. (2003). In Peter bore 1 for example, CFCs are nearly completely degraded while the concentrations should be close to equilibrium concentration with current air. CFC11 is more strongly affected than CFC12.

The tritium ratios of the samples are shown in Figure 7. Most of the river and related samples have tritium ratios between the mean TR of Kaitoke and Christchurch rain. No tritium rain data are available for the Flaxbourne catchment but it can be assumed to be 2.15 TR, close to Christchurch rain. Most samples have TR close to rain and therefore have mean residence times less than 1.5 years (Table 2). Only samples West (#1), Wiffen seep (#3), and Peter test bore 2 (#9) are significantly older with MRT 53, 120, and 38 years, respectively. The sample from Needles Creek (#8) is slightly older (MRT 4.5 yrs) than the river and related samples.

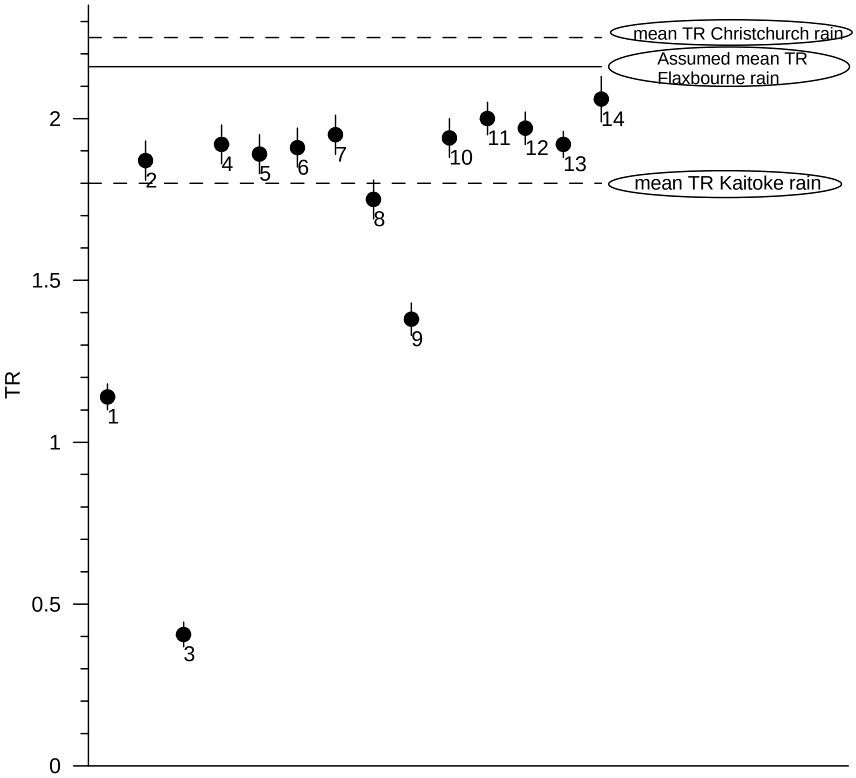

Figure 7. Tritium ratios (see Table 1 for sample codes).

No long-term tritium data were available for robust age interpretation and identification of mixing parameters. Therefore, mixing parameters had to be chosen based on other New Zealand aquifers with similar hydrogeologic situations. To describe age distributions the exponential-piston-flow model (Appendix 2) was used, which describes sufficiently the age distribution of groundwaters in many parts of New Zealand. A fraction of 70% mixed flow within the total flow volume was assumed. The Kaitoke tritium input function was used for age interpretation with scaling factor 1.2.

Most samples have un-ambiguous age interpretations. Only the sample at pond has an ambiguous result because no samples for CFCs and SF6 could be taken. Mean residence time could be 1yr for 70% mixed flow, or 35yrs for 35% mixed flow. High boron in this sample (see below) indicates origin from the highly anaerobic aquifer and therefore an older age seems possible. However, a fraction of mixed floe of only 35% seems unlikely, therefore the young age solution is more realistic.

Argon, nitrogen, and related recharge temperatures and excess air are shown in Figure 8. Most river samples have excess air close to zero, which is expected for water in equilibrium with air. Only the Flaxbourne River in the upper catchment is in disequilibrium with air, which is likely due to a temperature effect. This water had an unusually high temperature of 25 ^{o}C during sampling. Slow and shallow river flow could cause relatively rapid warming of the water at the right angle to the sun, with the gasses not yet in equilibrium.

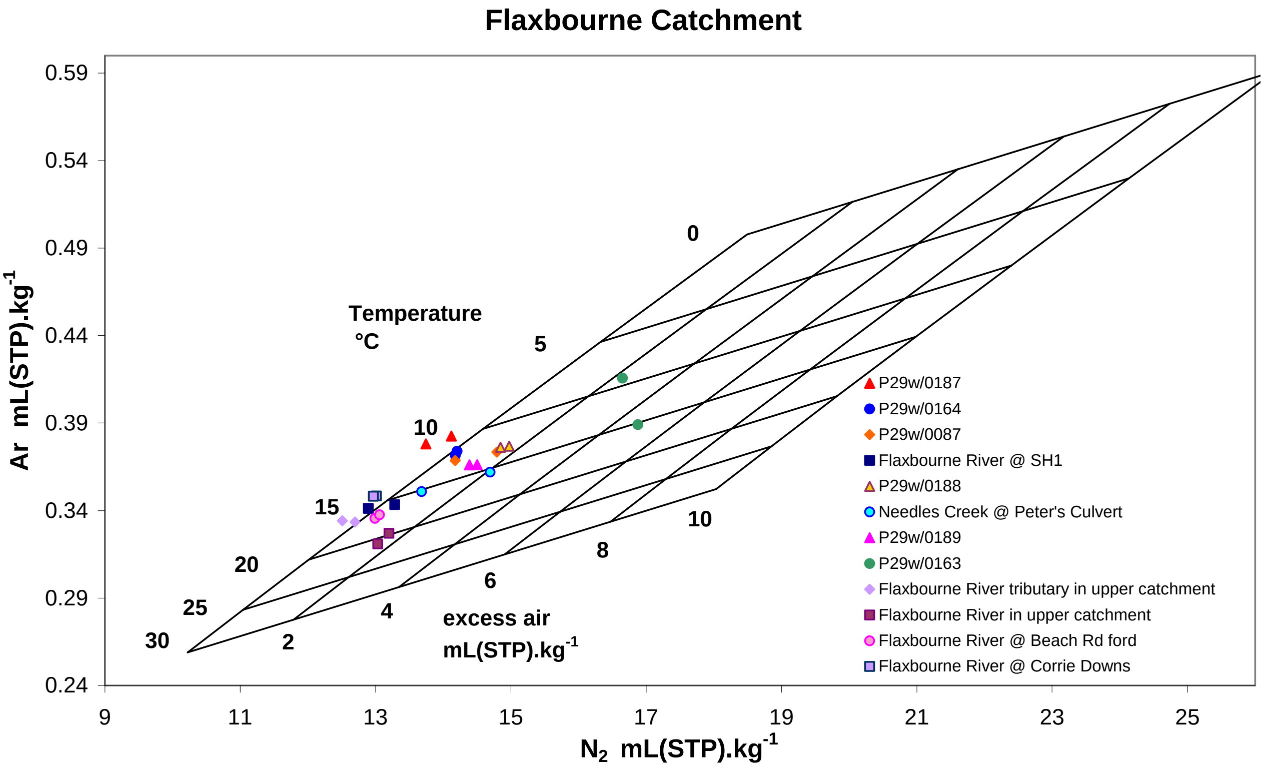

Figure 8. Argon, nitrogen, and related recharge temperatures and excess air.

West and Wiffen domestic wells have excess air close to zero, and Peter irrigation bore 1 and test bore 2 have elevated excess air. Taimate stock scheme, Needles Creek, and West are inconclusive. The result for Evans domestic well is likely to be influenced by the pressure tank. This water had to be sampled after passing through the pressure tank because no sampling point was available upstream of the pressure tank.

While in a previous study (Morgenstern 2005) excess air could be used to distinguish between river and rain recharge source, the data in the Flaxbourne catchment are too scarce. In addition, the nitrogen concentrations may also be affected by denitrification processes in this strongly anaerobic environment. Therefore, no conclusion can be made in term of recharge source.

All investigated waters in the Flaxbourne area are young with mean residence times (MRT) <5 yrs (Table 2) indicating little groundwater storage. Older groundwaters were observed only in the Tachalls/Needles area, with mean residence times at West 53 yrs, at Wiffen seep 120 yrs, and at Peter test bore 38 yrs. However, the old waters at Wiffen seep and Peter test bore are not an indication of larger groundwater storage capacity because the water flow rate is very low and therefore the old age is just a result of near stagnant groundwater flow in an aquifer with low hydraulic conductivity. Only West has a considerable water flow and older age and therefore indicates a larger groundwater storage reservoir in relation to its total flow.

High SF_6 in relation to tritium at West and Peter test bore indicates unconfined aquifer conditions. At Needless Creek, good agreement between SF_6 and tritium indicates confined aquifer conditions.

4.2 HYDROCHEMISTRY

Chemistry and faecal coliforms data, provided by Marlborough District Council, is listed in Table 3.

Table 3. Chemistry and faecal coliform (FC) data. Brown highlighting in # column indicates groundwater samples (bores and seeps), whereas no highlighting indicates surface water samples. Unusual concentrations for groundwater samples are highlighted: dark green – very low, light green – low, pink – high, red – very high. Total concentrations of cations and anions and anion-cation balance (An-Cat) calculated according to Freeze and Cherry (1979).

#	Well_ID	B	Br	Ca	Cl	F	Fe	HCO3	K	Mg	Mn	Na	NH4-N	NO3-N	DRP	SiO2	SO4	Alk	pH	Hard.
		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 as CaCO3	pH units (lab)	mg/L as CaCO3
1	P29w/0187	0.05	0.35	41	80	0.47	0.003	150	1.9	9.1	0.001	65	0.005	6.6	0.008	17	28	120	7.2	141
2	P29w/0164	0.22	0.23	2	87	0.25	0.11	210	13	62	0.003	61	0.011	0.006	0.028	14	72	170	7	208
3	TAC-1	0.13	0.5	18	160	0.72	0.006	240	120	56	0.005	4.2	0.018	8.5	0.023	17	65	200	7.8	214
4	P29w/0087	0.07	0.15	24	33	0.2	0.005	110	1	7.8	0.001	30	0.005	0.025	0.009	12	30	90	6.9	107
5	FLX-2	0.07	0.15	29	36	0.17	0.005	120	1.6	8.8	0.003	33	0.005	0.002	0.004	13	36	100	8.1	119
6	P29w/0188	1.8	0.21	2.6	67	0.28	0.73	260	16	55	0.003	55	0.1	0.005	0.005	14	38	210	7.6	203
7	WAR-1	17	0.15	24	110	0.29	1.6	130	2.9	62	0.003	3.8	0.01	0.003	0.089	11	1.7	110	7	130
8	NED-2	0.094	0.21	2.6	66	0.34	0.09	260	17	58	0.003	57	0.008	0.006	0.026	15	37	210	7.7	212
9	P29w/0189	18	0.29	3.4	59	0.59	16	320	3.3	57	0.005	57	1.5	0.008	0.01	34	5.3	260	7	216
10	P29w/0163	0.25	0.18	2.6	57	0.27	0.1	230	16	58	0.003	50	0.023	0.018	0.011	12	52	190	7.8	211
11	FLX-4	0.028	0.15	12	8.5	0.17	0.021	63	0.06	3.6	0.003	12	0.005	0.016	0.021	14	7.1	52	7.7	45
12	FLX-5	0.09	0.15	18	9.9	0.23	0.014	110	1.2	5.7	0.003	24	0.009	0.02	0.008	10	12	94	8.7	83
13	FLX-6	0.08	0.16	35	49	0.19	0.006	120	1.7	9.7	0.001	34	0.005	0.002	0.006	13	35	100	7.5	127
14	FLX-7	0.07	0.15	30	27	0.17	0.011	120	1.3	7.5	0.016	24	0.005	0.002	0.005	12	25	100	7.6	106

#	Well_ID	Tot. Cations	Tot. Anions	An-Cat	FC	As	Cd	Ni	Cr	Cu	Pb	Al	Zn
		meq/L	meq/L	%	cfu/100 ml	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	P29w/0187	5.67	5.80	-1.18	5	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.003	< 0.005	0.005
2	P29w/0164	8.19	7.44	4.83	5	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.005	< 0.005	0.011
3	TAC-1	8.76	10.47	-8.88	5	0.001	< 0.0005	< 0.0005	< 0.001	< 0.003	0.002	0.004	0.004
4	P29w/0087	3.17	3.38	-3.22	5	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.002	< 0.003	0.005
5	FLX-2	3.65	3.75	-1.39	20	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.005	< 0.005	0.002
6	P29w/0188	7.49	7.13	2.47	5	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.005	< 0.005	0.09
7	WAR-1	6.60	6.87	-2.01	270	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	0.008	0.016	0.02
8	NED-2	7.82	6.93	6.05	20	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.005	< 0.005	0.035
9	P29w/0189	8.10	8.72	-3.68	1	0.012	< 0.0005	< 0.001	< 0.003	< 0.005	0.0005	0.001	0.1
10	P29w/0163	7.49	6.50	7.05	1	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.005	0.011	0.076
11	FLX-4	1.42	1.44	-0.62	100	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.005	< 0.2	0.001
12	FLX-5	2.44	2.36	1.78	160	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.005	0.004	0.007
13	FLX-6	4.07	4.10	-0.39	35	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001	< 0.003	< 0.005	0.005
14	FLX-7	3.19	3.27	-1.18	460	0.001	<0.0005	<0.0005	<0.001	<0.001	<0.003	<0.005	0.005

5. DISCUSSION

5.1. OVERVIEW OF HYDROCHEMISTRY

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. This comparison is based on data collected through the National Groundwater Monitoring Programme (NGMP), which includes 112 groundwater monitoring sites around the country (Daughney and Reeves, 2005).

This comparison to the NGMP data clearly indicates that the groundwater samples collected in this investigation have several unusual chemical characteristics (this comparison could not be made for surface water samples). For example, many of the groundwater samples collected in this investigation have high concentrations of boron, bromide, chloride, fluoride, bicarbonate, potassium, magnesium, sodium and/or sulphate. Concentrations that exceed the 75th and 95th percentiles in the NGMP are highlighted in pink and red, respectively, in Table 3. Many of the groundwater samples collected in this study also have relatively low concentrations of calcium, highlighted in light green or dark green in Table 3 to indicate values below the 25th and 5th percentiles in the NGMP, respectively. The most exceptional high or low concentrations in the groundwater samples from this study are as follows:

- Exceptionally high boron concentrations of 1.8 and 18 mg/L are observed at Sites 6 and 9, respectively. A very high boron concentration of 17 mg/L is also found at one surface water site (Site 7). For comparison, the health-related maximum allowable value is 1.4 mg/L under the New Zealand Drinking Water Standards (Ministry of Health, 2005).
- Groundwater calcium concentrations are exceptionally low at Sites 2, 6, 9 and 10. For comparison, the 5th percentile in the NGMP is 5.1 mg/L.
- An exceptionally high chloride concentration of 160 mg/L is found at Site 3 (the 95th percentile in the NGMP is 87.8 mg/L). Several of the surface water samples have comparably high chloride concentrations.
- Fluoride concentrations at Sites 1, 3 and 9 are 0.47, 0.72 and 0.59 mg/L, respectively. For comparison, the 95th percentile in the NGMP is 0.3 mg/L.
- An exceptionally high iron concentration of 16 mg/L is found at Site 9 (the 95th percentile in the NGMP is 2.6 mg/L).
- Potassium concentrations at Sites 2, 3, 6 and 10 are 13, 120, 16 and 16 mg/L, respectively, all of which exceed the 95th percentile in the NGMP (8 mg/L).
- Magnesium concentrations at Sites 2, 3, 6, 9 and 10 are also exceptionally high, being measured as 62, 56, 55, 57 and 58 mg/L, respectively. For comparison, the 95th percentile in the NGMP is 26.6 mg/L.
- Exceptionally high sulphate concentrations of 72, 65, 38 and 52 mg/L are found at Sites 2, 3, 6 and 10 (the 95th percentile in the NGMP is 30.3 mg/L).

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 hydrochemical facies. Here, HCA is performed using the methods of Daughney and Reeves (2005), based on the log-transformed measured concentrations of 15 analytes: bromine, calcium, chloride, fluoride, iron, bicarbonate, potassium, magnesium, manganese, sodium, ammoniacal-nitrogen, nitrate-nitrogen, dissolved reactive phosphorus, silica and sulphate. Note that HCA simply categorises water samples based on the concentrations of parameters considered, and does not provide any information about causes of any patterns observed. 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 9. 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 2 and 8 have very similar hydrochemistry, because they are joined by a line that is low on the Distance axis. Likewise, Sites 4, 5 and 13 have similar hydrochemistry, but it is very different from the hydrochemistry at Sites 2 and 8.

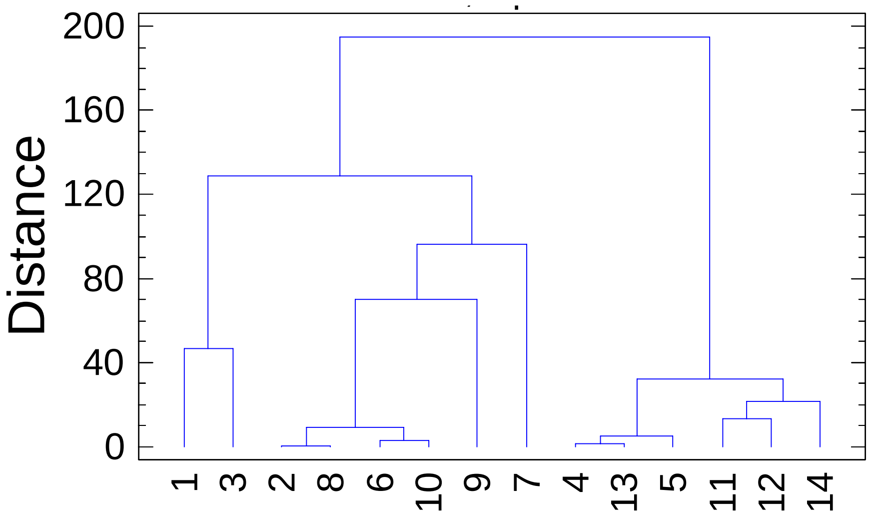

Figure 9. Dendrogram produced by hierarchical cluster analysis. Numbers along the x-axis correspond to site identification numbers in Table 3.

HCA indicates that the samples from the Flaxbourne catchment have very different chemistry compared to the samples from either the Tachalls or Needles catchments. On the dendrogram, all of the sites from the latter two catchments are grouped together on the left (namely Sites 1, 2, 3, 6, 7, 8, 9 and 10) and all of the sites from the Flaxbourne catchment are grouped together on the right (namely Sites 4, 5, 11, 12, 13 and 14). An examination of the hydrochemistry indicates that the samples from the Tachalls and Needles catchments have higher concentrations of potassium, sodium, magnesium and fluoride and lower concentrations of calcium compared to the samples from the Flaxbourne catchment (Table 3). Cation ratios also differ, as indicated by a Piper diagram (Figure 10). These differences in hydrochemistry suggest that the Flaxbourne catchment is a different hydrologic flow system than the Tachalls and Needles catchments (see further discussion below).

HCA also reveals some variations in hydrochemistry within the Tachalls and Needles catchments. The dendrogram indicates that Sites 2, 6, 8 and 10 have similar chemistry (Site 2 is in the Tachalls catchment whereas the other three are in the Needles catchment). These four sites are all characterised by magnesium-sodium-bicarbonate-chloride type waters with unusually low calcium concentrations. Site 7 (Tachalls) and Site 9 (Needles) also have magnesium as the dominant cation, but they are hydrochemically differentiated from other sites in the Tachalls and Needles catchments by extremely high concentrations of boron. Sites 7 and 9 are also unusual in the Tachalls and Needles catchments in that they have strongly reduced (i.e. anoxic) waters, indicated by the high concentrations of iron and ammoniacal nitrogen in combination with low concentrations of sulphate. The hydrochemical signature at Sites 7 and 9, in particular the high boron concentration, may indicate a geothermal influence or extensive interaction between the water and greywacke. Sites 1 and 3 (Tachalls) are differentiated from other sites in the catchment by relatively high concentrations of nitrate-nitrogen. The measured nitrate-nitrogen concentrations almost certainly indicate that the water at these sites has been impacted by human and/or agricultural activities. Based on the hydrochemistry data alone, it is not possible to conclusively determine whether the Tachalls and Needles catchments represent isolated flow systems (this topic is discussed in more detail below).

HCA also shows that there are some slight variations in hydrochemistry between the monitoring sites within the Flaxbourne catchment. Notably, the dendrogram indicates that Sites 4, 5 and 13 (lower catchment) have slightly different chemistry compared to Sites 11, 12 and 14 (upper catchment). An examination of the hydrochemistry shows that the water samples from the lower catchment have higher conductivity and higher concentrations of calcium, sodium, magnesium and chloride. This is consistent with an increase in water-rock interaction along the course of the river, which would lead to higher concentrations of most major ions in the lower catchment compared to the upper catchment. The samples from the upper catchment also have higher ratios of fluoride to chloride, which may indicate the effect of water-rock interaction with the greywacke rocks found there.

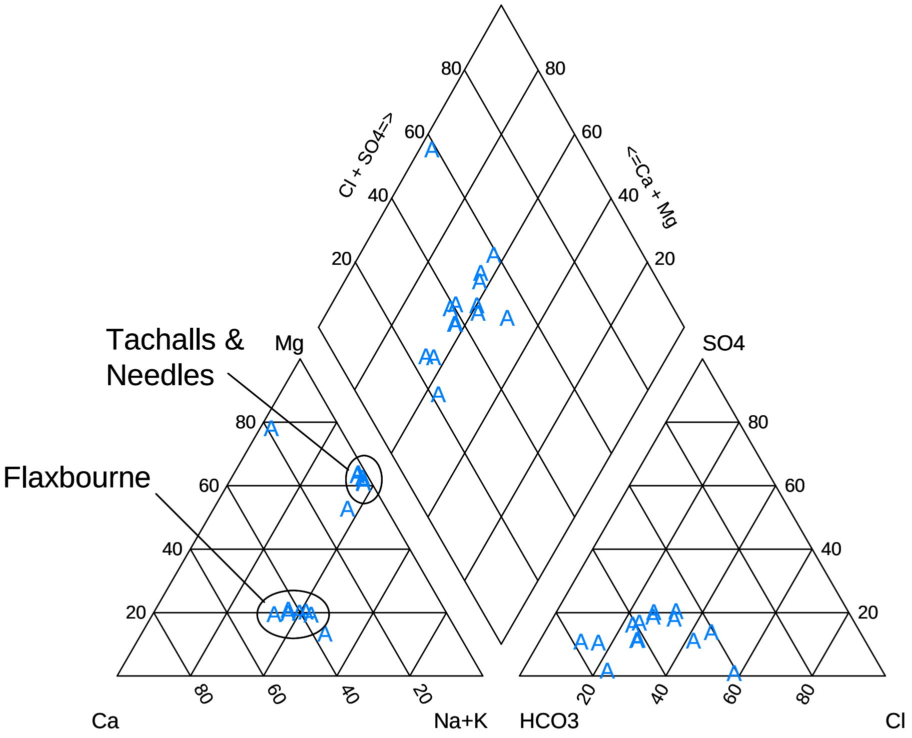

Figure 10. Piper diagram.

5.2 TIME TRENDS IN HYDROCHEMISTRY

As stated above, the chemical composition of the groundwater can help to determine origin and recharge source of the water. However, the chemical composition of the groundwater can also be influenced by anthropogenic and geogenic 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 geogenic influence on hydrochemistry, the various water chemistry parameters are plotted against mean residence time (MRT). By isolating anthropogenic and geogenic trends, spatial hydrochemistry patterns (depending on local geologic formations) become more obvious with the result that groundwater flow patterns and connections between different groundwater systems can be better identified.

Note that interpretation of such graphs must be made with caution. First, it is important to take into account the spatial variations in hydrochemistry (e.g. differences between catchments described above). Thus all graphs presented below use a colour code, to distinguish between sub-catchments, and between surface and groundwater:

Flaxbourne River (# 5, 11-14)
Flaxbourne groundwater (# 4)

Needles Creek (# 8)
Needles groundwater (# 6, 9, 10)

Tachalls pond (# 7)
Tachalls groundwater (#1-3)

Plotting the different groundwater parameters against their mean residence times is for this sample set is a good means to compare the samples according to their residence time because all mean residence times were calculated with the same mixing model. With spatial variations borne in mind, plotting the various hydrochemistry parameters against MRT can help to elucidate groundwater flow patterns and connections between different groundwater systems.

Figure 11 shows the water temperature at sampling, conductivity, pH, and the recharge temperature and excess air as calculated from Ar and N_2.

The **measured temperature** at sampling is for all groundwaters within a narrow range between 13 and 16^{o}C, close to the local mean annual temperature of 13^{o}C. The surface waters have higher variation in measured temperature of 15-25^{o}C, with an unusually high temperature in the Flaxbourne River in the upper catchment and at SH1. These high temperatures are likely to be caused by slow and shallow river flow with high sun exposure. These effects could be very localised, depending on exposure and angle to the sun.

The **calculated equilibrium temperatures** from Ar and N_2 of the surface waters (Sites 8, 11, 13, 14) are similar to the measured temperatures, except that the calculated temperatures are significantly lower for Flaxbourne River in the upper catchment and at SH1 indicating disequilibrium. All young groundwaters are within a narrow range of 12 to 13 ^{o}C calculated recharge temperature. The older groundwaters show slightly higher variation of 10 to 14 ^{o}C.

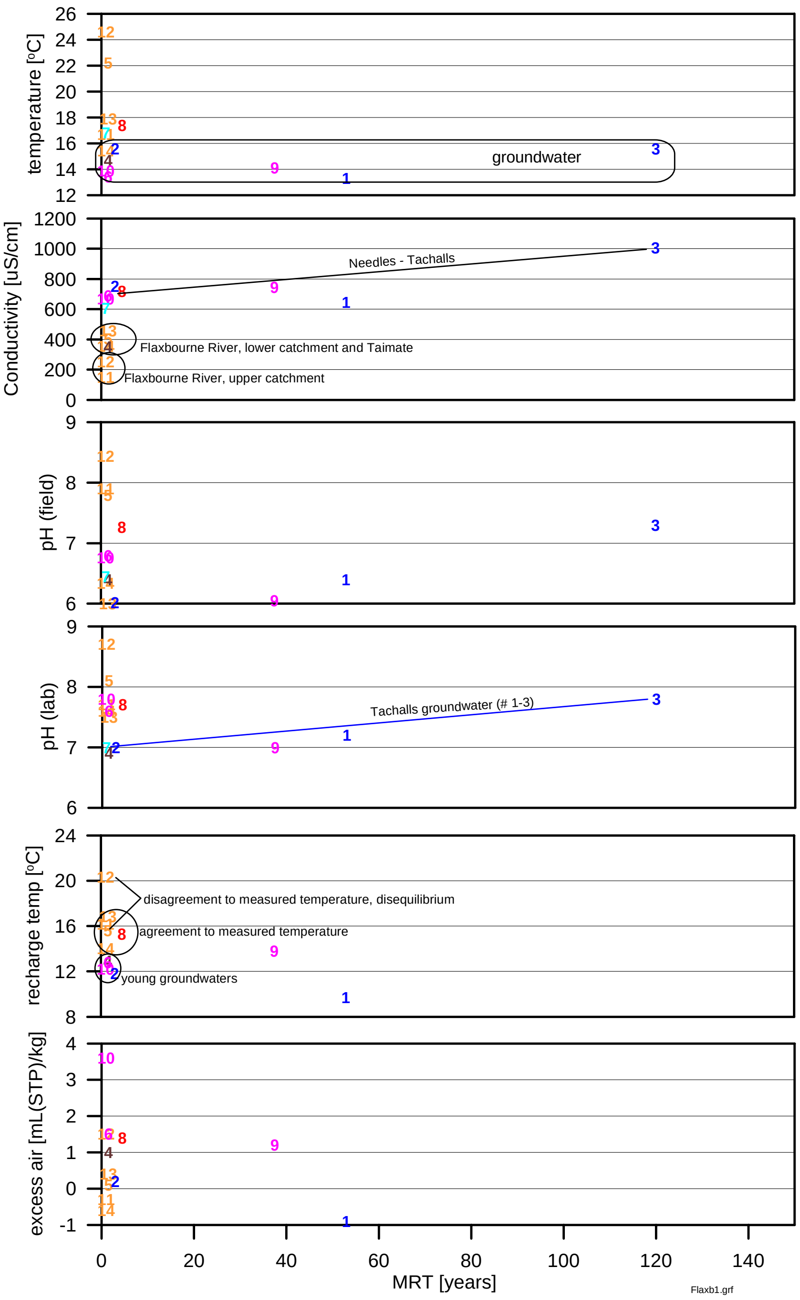

Figure 11. Water temperature, conductivity, pH, and calculated recharge temperature and excess air versus mean residence time.

The **conductivity** is lowest for river and groundwater in the Flaxbourne catchment, indicating young water and reflecting the origin of the water from a catchment of mostly greywacke with low mineral solubility. Conductivity is lowest in the upper Flaxbourne tributary (Site 11), indicating lowest water-rock interaction and therefore lowest residence time. Conductivity in the upper Flaxbourne River (Site 12) is slightly higher indicating slightly longer residence time. Flaxbourne River in the lower catchment (Sites 5, 13, 14) and Taimate (Site 4) have again slightly higher conductivity indicating slightly longer residence time (time of water-rock interaction).

For the Tachalls and Needles catchments, the conductivity of the young waters is significantly higher compared to the samples of comparable age from the Flaxbourne catchment. This indicates that the rocks in the Tachalls and Needles catchments have higher solubility limits and also dissolve more rapidly. As in the Flaxbourne catchment, the older groundwaters in the Needles and Tachalls catchments show an increase in conductivity over time, due to increased mineral dissolution with longer contact time.

pH measured in the field and in the lab both show similar trends. In the Flaxbourne River and in some Needles Creek and groundwater samples a relatively high pH (lab) of 7.5 - 8.5 is observed. Tachalls groundwaters (Sites 1-3), the only samples with a wide range of MRT of 1-120 yrs, indicate increasing pH over time, starting at pH 7 for young (MRT 1yr) groundwater and raising to pH 8 for old (MRT 129 yrs) groundwater. This pH increase 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).

Excess air data are too scarce to allow for a time trend analysis.

Hardness, Bicarbonate, and Alkalinity (Figure 12) of the waters from Needles and Tachalls catchments are generally high, showing evidence of hard-water influence from the Miocene-Pliocene Awatere group, probably due to dissolution of calcareous fossils/shell layers or cements. The water south of Ward is intermediate in alkalinity and hardness, suggesting that its origin is not from the Miocene-Pliocene Awatere group but from the Pliocene Awatere group south of Ward. This sampling site is situated near the toe of a fan consisting of older gravels (probably Oxygen Isotope Stage 4; 60-70 ka) as mapped by Townsend 2001. The fan emanates from hills to the south east of Ward which are made up from Late Cretaceous sandstone, conglomerate and chert (Figure 2). The sampling sites in the Needles and Tachalls catchments are on a Last Glacial outwash fan (OI Stage 2) associated with the much larger Tachalls Creek, which drains the hills to the west of Ward. These different gravels have different source areas and therefore probably different compositions, as also indicated by the different chemistry signature of their waters.

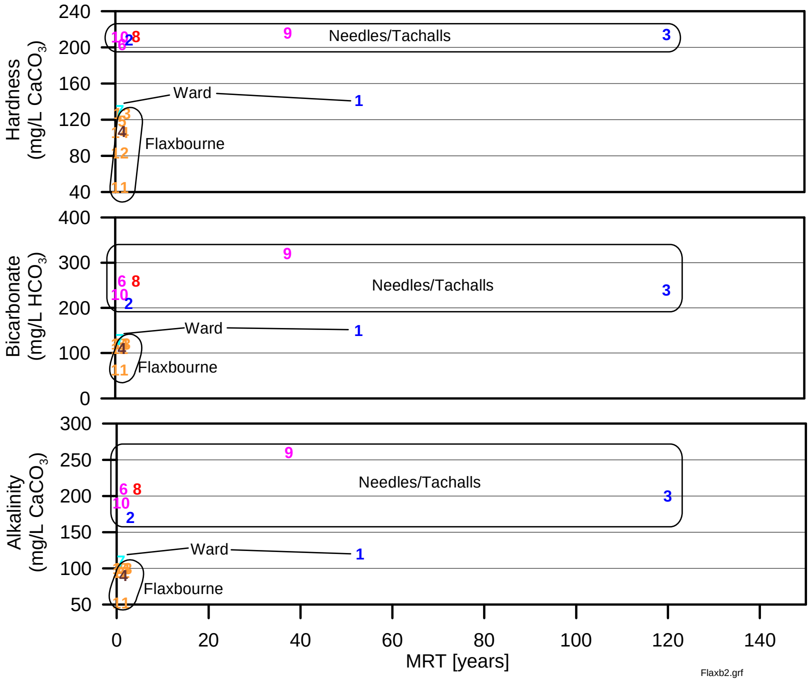

Figure 12. Hardness, bicarbonate and alkalinity balance versus mean residence time.

The Flaxbourne waters have significantly lower alkalinity and hardness values, suggesting that they are derived from a completely different rock type, the greywacke in the Flaxbourne catchment. The Flaxbourne River tributary in the upper catchment (Site 11) has the lowest values, indicating that it is the least evolved (youngest) water.

Total cation and anion concentrations are plotted against mean residence time in Figure 13. In the Flaxbourne area the total ion concentrations are about a factor of three lower compared to the Tachalls/Needles area. This is consistent with observations based on conductivity described above. There are no significant relationships between the anion-cation balance and mean residence time. This is to be expected, because the anion-cation balance is simply a measure of analytical accuracy, and should theoretically be zero for any water sample.

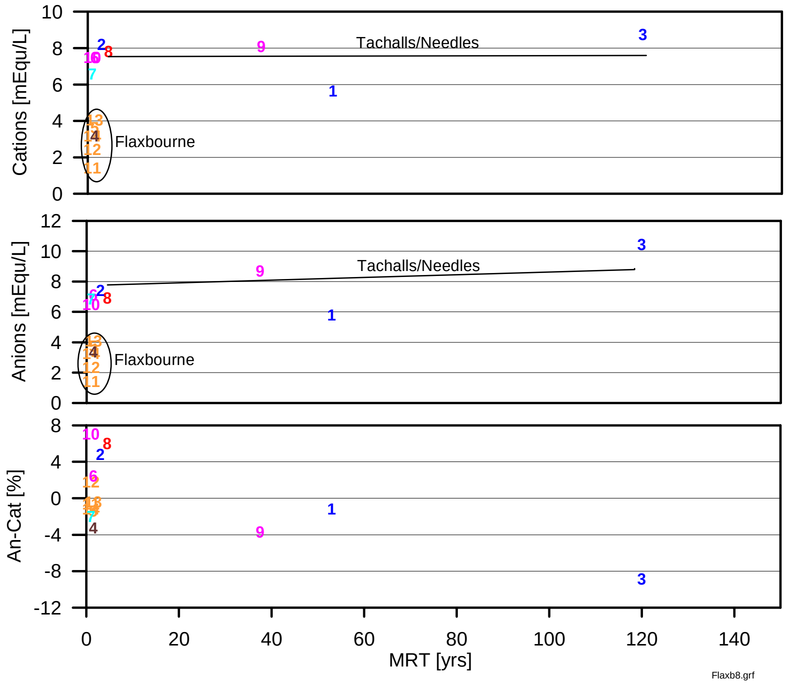

Figure 13. Total cations, total anions and anion-cation balance versus mean residence time.

Figure 14 shows concentrations of dissolved oxygen, iron, and manganese versus mean residence time. Note that microbial respiration tends to deplete **dissolved oxygen** along a groundwater flow path, providing that 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 reduced conditions.

None of the water samples are saturated with dissolved oxygen (saturation concentration is c. 9 mg/L at these water temperatures). Even the surface waters are considerably depleted in oxygen despite of the contact of the water with air. This indicates that in this catchment the processes that lead to oxygen removal are so strong that oxygen equilibrium concentration with air cannot be reached. This conclusion is supported by the CFC results (Table 2). CFCs are also below equilibrium concentration, indicating that these anaerobic processes are so strong that also CFCs are degrading so quickly that equilibrium with air cannot be reached. SF_6 is in equilibrium with air, but SF_6 is not affected by anaerobic processes. Lower oxygen concentrations in Taimate compared to the river is likely due to additional oxygen removal in the aquifer, probably due to similar processes that are operating in more complete isolation from the atmosphere.

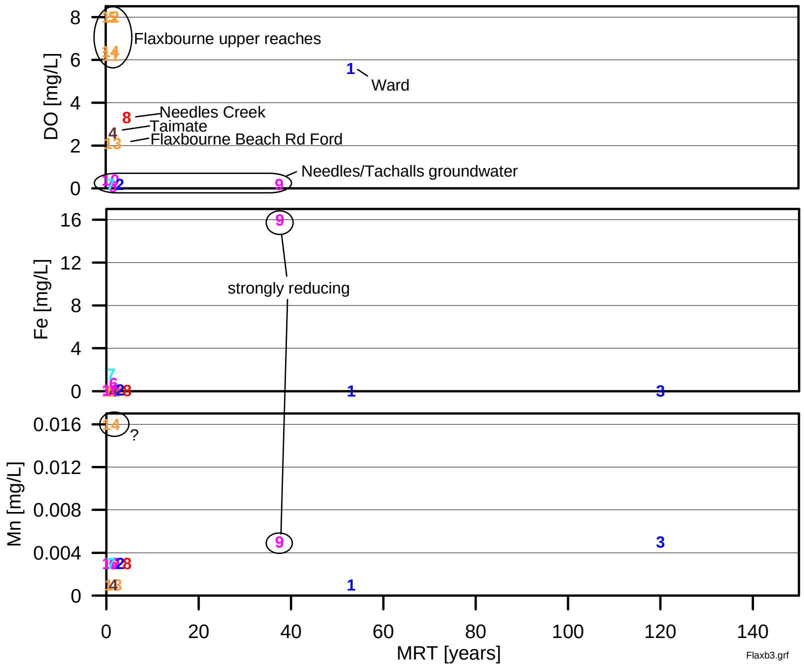

Figure 14. Dissolved oxygen, iron and manganese versus mean residence time.

The groundwaters at Needles/Tachalls are completely depleted of oxygen, but there is high dissolved oxygen at Ward. This indicates that the Ward sample is from a different groundwater system. Note that also the pond is completely depleted in oxygen, probably due to microbial or algal resipiration under more-or-less stagnant flow conditions.

The low oxygen concentration observed in Needles Creek is likely because the creek water is predominantly older groundwater (MRT 4.5 yrs) that emerges into the creek just upstream of the point where the sample was collected. Thus the gases in the water had not yet time to equilibrate with air. This is also indicated by the fact that also SF_6 is lower than equilibrium concentration.

The sample from the lower Flaxbourne River at Beach Road Ford also has very little oxygen. However, this significantly lower oxygen concentration (compared to the other river samples) may have been caused by the collection of the sample early in the morning after limited balancing photosynthetic oxygen production by the aquatic fauna during the night.

High **Iron** and **Manganese** concentrations at several sites indicate a reducing environment (Sites 2, 6, 7 and 9). Note that 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 (see further discussion below).

Boron and ^{18}O are plotted against mean residence time in Figure 15. There are extremely high **Boron** concentrations observed in the pond (Site 7) and Peter's test bore 2 (Site 9) (cf. drinking water maximum allowable value of 1.4 mg/L). Boron is also elevated in Peter irrigation bore (Site 6). All 3 waters with high boron occur in a small localised area north of Ward. Many of the other sites also have boron concentrations above what would be expected for the "average" groundwater in New Zealand.

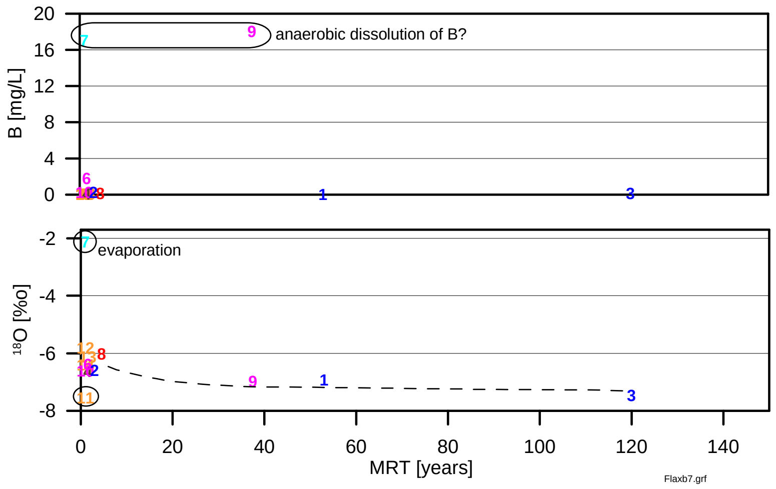

Figure 15. Boron and ^{18}O versus mean residence time.

There are several possible causes of high boron concentrations, some of which can be ruled out. Seawater intrusion or connate seawater can be excluded as the cause of high boron because sodium and chloride concentrations are not considerably elevated. The high boron in the pond is unlikely to be a result of increasing concentration of solutes due to evaporation. Even though the pond has no visible outflow, evaporation is insignificant as indicated by the low ^{18}O enrichment and also by the lack of enrichment of other elements.

High boron concentration in groundwater in other regions of New Zealand is often an indicator of geothermal activity because normally high-temperature processes are necessary to cause increased B dissolution from the rock matrix. However, water temperatures are not elevated, and no active fault structure has been mapped in the vicinity, suggesting that geothermal or fault origin of the boron is unlikely. In addition, the ratio of chloride to boron is lower than would be expected for a geothermal source (Christenson et al., 2002), and although fluoride concentrations are above average relative to groundwater in other parts of the country, the fluoride concentrations are not as high as would be expected for geothermal or fault influence.

Similarly high boron concentrations had also been found in the Pukehou formation along the Kapiti Coast (Morgans and Hughes 2001), with the suggestion that the high B is derived from the greywacke basement. This might explain the high boron concentrations in the area north of Ward.

The high observed B concentrations are associated with strongly reducing groundwaters (elevated iron, sulphate nearly completely removed – see below, and high methane). On the other hand, groundwater in the Tachalls area from a less reducing environment does not show high B despite much older age and longer contact time with the aquifer material. However, strongly reducing environment is not the only condition necessary for high B. In the Wairarapa, we found many groundwaters from highly reducing aquifers with extremely high methane and absolutely no SO_4 but these were not elevated in boron (Morgenstern 2003).

In conclusion, two conditions seem necessary for the high B concentrations: (1) contact with greywacke, and (2) extremely strongly reducing environment.

It is likely that the strongly reducing aquifer conditions have the reason that this aquifer system is formed from ancient swamps, as suggested by the following facts: High methane concentrations, excess HCO_3 from organic matter (see below), and this area is likely to be subsiding (Ward syncline, Figure 4b).

High boron concentrations can be found in groundwater associated with organic-rich sedimentary rocks. Interaction with organic material could give rise to the strongly reduced nature of the samples. However, there is little information available about the organic content of rocks within this area. While it is most likely that the high boron concentrations arise from water-rock interaction involving organic-rich sediments and greywacke, but without additional sampling and research, it is not possible to determine this process accurately.

The lower B and Fe concentrations in the Peter irrigation well (relative to Sites 7 and 9) are probably the result of dilution with stream derived water. This bore is very close to the stream and produces a high quantity of water. The surrounding groundwater indicates a highly anaerobic environment with high B in the water, while the stream water is low in B. Assuming that the local groundwater contains about 18 mg/L boron, the boron concentration in the Peter irrigation well (1.8 mg/L) indicates dilution of about a factor 10. A calculation based on iron indicates a similar ball-park dilution factor of about factor 20. The young age of water in the Peter irrigation well also supports a mainly stream origin. On its way from the stream to the well, the water travels through an anaerobic environment that nearly completely degrades the CFCs.

The **^{18}O** concentration for most young groundwaters is within a narrow range -6 to -7‰. Only the Flaxbourne tributary (Site 11) is outside this range. This is likely due to seasonal ^{18}O variation, which is also an indication that this water is very young, because the seasonal variation is not yet smoothed out. The pond water (Site 7) is affected by evaporation (as to be expected in such an open and still water body) but only slightly. The older groundwaters seem to have slightly more negative ^{18}O values than the younger groundwaters.

Potassium, dissolved reactive phosphate, sulphate, ammonia and nitrate are plotted against mean residence time in Figure 16. **Potassium** can be derived via water rock interaction or from human or animal wastes, or from fertilisers. Potassium concentrations are low in the Flaxbourne catchment, indicating absence of fertiliser use in the upper catchment and low geogenic input. The Flaxbourne tributary has lowest potassium concentration, which is consistent with the shortest contact time of the water with the rock matrix. In comparison, potassium concentrations are higher and more varied in samples from the Needles and Tachalls catchments, which could be a result input from a variety of sources, including fertilisers, human or animal wastes, or natural water-rock interaction. The seep (Site 3) has extremely high potassium, which is probably related to contamination above the seep. In contrast, potassium concentration in the pond (Site 7) is also low, possibly indicating uptake by plants in the pond. There are a number of sites at which the ratio of potassium to sodium is suggestive of fertiliser input (Figure 17).

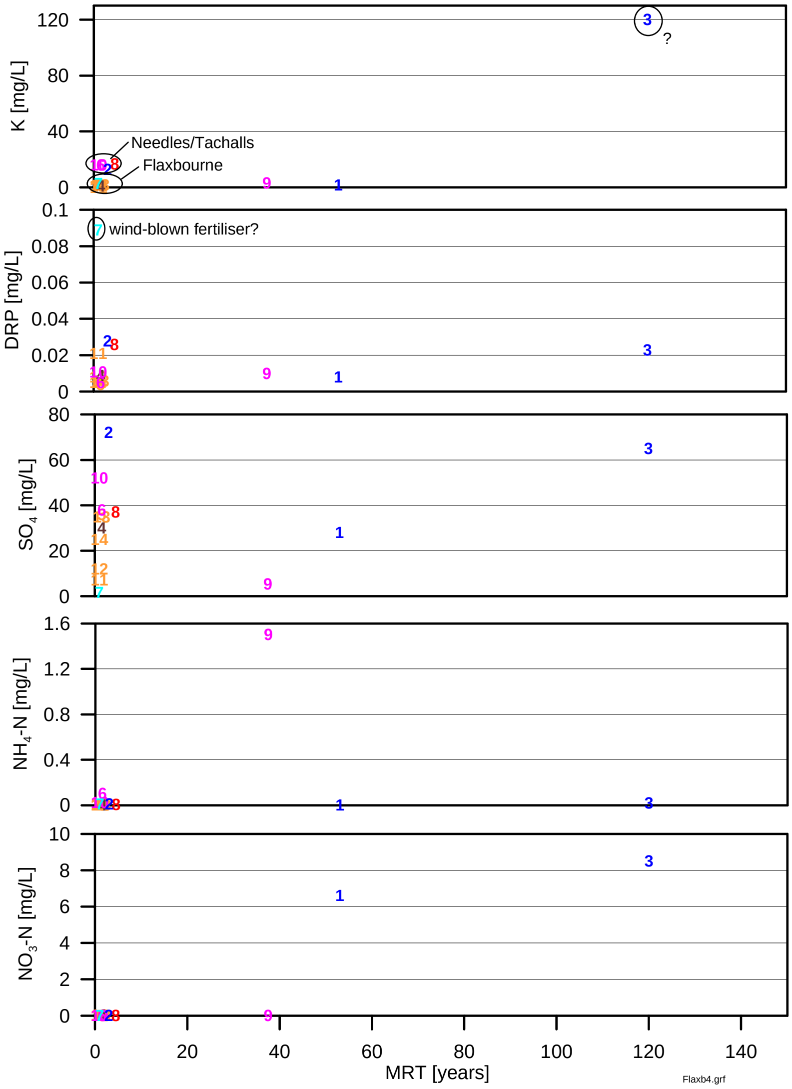

Figure 16. Potassium, dissolved reactive phosphate, sulphate, ammonia and nitrate versus mean residence time.

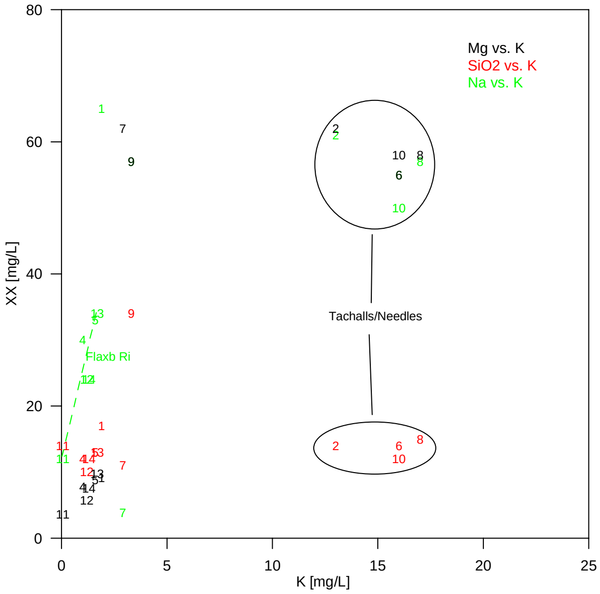

Figure 17. Mg, SiO2, and Na vs. K.

Dissolved reactive phosphate is low in most samples (Figure 16). Phosphorus as an essential plant nutrient is applied as fertiliser in agriculture areas. However, it is taken up by plants in the top soil, and adsorbed by mineral surfaces in the unsaturated zone. Low DRP concentrations measured in this investigation demonstrate that very little (if any) anthropogenic phosphorus finds its way into the groundwater in the study area. Low phosphorus concentrations in the old groundwaters indicate that it is also not available from geogenic sources. Only the pond (Site 7) contains relatively high DRP, which could be a result of air-born fertiliser.

Relatively high **sulphate** concentrations are observed in most of the water samples (Figure 16). The major sulphate source appears to be geogenic because most of the sulphate data plot close to the seawater concentration dilution line with Mg (Figure 18) controlled by mineral equilibration. However, the samples from the lower Flaxbourne catchment and the Ward area indicate additional anthropogenic source of sulphate (added as gypsum to fertilisers). Anthropogenic excess sulphate appears to be 10-20 mg/L. The samples from the upper Flaxbourne catchment plot on the seawater concentration dilution line indicating only geogenic sulphate origin and absence of sulphate reduction. The Flaxbourne tributary (Site 11) has lowest concentrations indicating youngest age (least contact time between water and rock).

Many of the samples from the Tachalls and Needles catchments show clear evidence of anaerobic sulphate reduction. All of these waters are anoxic. Needles samples are generally more reduced (i.e. less sulphate) than Tachalls samples. Strongly reducing conditions in the Tachalls catchment are also indicated by higher iron and methane concentrations (see above). Sulphate in the pond (Site 7) and Peter test bore (Site 9) is nearly completely removed, indicating an extremely reducing environment. As noted above, samples from these same sites also have very high boron concentrations. The sulphate and magnesium concentrations in the sample from West (Site 1) near Ward suggest that this water is not related to the Tachalls/Needles groundwater system.

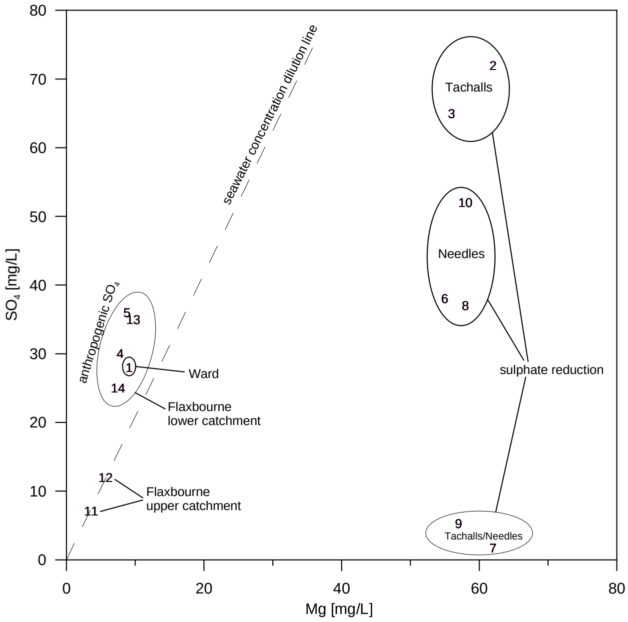

Figure 18. Sulphate versus magnesium. Dashed line is seawater concentration dilution line (Rosen 2001).

Only two samples have high concentrations of **nitrate-nitrogen** (Figure 16): West (Site 1) and Wiffen seep (Site 3). High nitrate-nitrogen in groundwater usually indicates impact from farming (particularly dairy). Normally, this only affects young groundwaters that have been recharged since farming was established. The water at West is young enough (MRT 41 yrs) that it can show the impact of farming. The high nitrate concentration suggest that this water is recharged on the farmland above the well and seeps. Note that this is the only groundwater that is not anoxic. Therefore nitrate is unlikely to be affected by denitrification. The high nitrate concentration at Wiffen seep seems surprising because this water is very old (MRT 120 yrs). However, the high nitrate concentration is probably derived from animal wastes near the seep (animals use the seep for drinking and will therefore be close around the seep for considerable time).

Ammonium (Figure 16) is high in Peter test bore (Site 9), and elevated in Peter irrigation bore. Elevated ammonium is typically the result of nitrogen mineralization in anaerobic aquifers, following depletion of nitrate-nitrogen due to microbial denitrification. Despite the absence of ammonia in the other samples, no conclusion can be made about the original nitrate concentration, because there is the possibility for denitrification without ammonia production. The relatively lower ammonium concentration in Peter irrigation well is, similar to boron and iron, likely to be a result of dilution of local groundwater from a strong anaerobic environment with stream water (see above). The measured ammonium concentrations indicate a dilution factor of about 15.

Silica concentrations in this area are generally low and typical for groundwater in New Zealand (Figure 19). Only Peter test bore (Site 9) has a slightly elevated silica concentration, although even this concentration is not unusual for New Zealand groundwaters. There is no strong evidence for a systematic increase in silica concentration over time (such patterns have been observed in other regions of the country, Morgenstern et al. 2004). The samples from the Flaxbourne River have the lowest silica concentrations, as expected for the greywacke catchment. The lowest values are in the upper catchment, indicating youngest age. Silica concentration in many New Zealand aquifers is found to be correlated to sodium concentration (Rosen, 2001), which applies to most of the Flaxbourne samples (Figure 20). The samples from the Needles and Tachalls catchments show a similar correlation but with higher sodium concentration.

Fluoride concentrations are lowest in the Flaxbourne area (Figure 19). The Tachalls groundwaters (Sites 1-3) show increasing fluoride concentration as a function of mean recharge time, suggesting that the fluoride is derived from water-rock interaction.

There is a good correlation between **bromide** and chloride, with most values plotting near the seawater concentration dilution line (Figure 21). This indicates that the two elements are derived from the same source for most samples. Only the pond the result may indicate Br removal in the pond, or Cl concentration.

Sodium and **chloride** (Figure 22) are elevated compared to rain water. The groundwater samples from the Tachalls and Needles groundwaters have sodium concentrations that are typically about a factor of two greater than the samples from the Flaxbourne catchment. The Tachalls/Needles data indicate that sodium concentration increases with age. The nearly constant sodium-chloride ratio therefore indicates a single source for both elements, which is probably gradual dissolution of mineral salts within the aquifer. The old water from Wiffen seep has unusually low sodium concentration coupled with an unusually high chloride concentration. This probably reflects the addition of chloride in the form of animal wastes, which is consistent with the high nitrate concentration also measured at this site (see above).

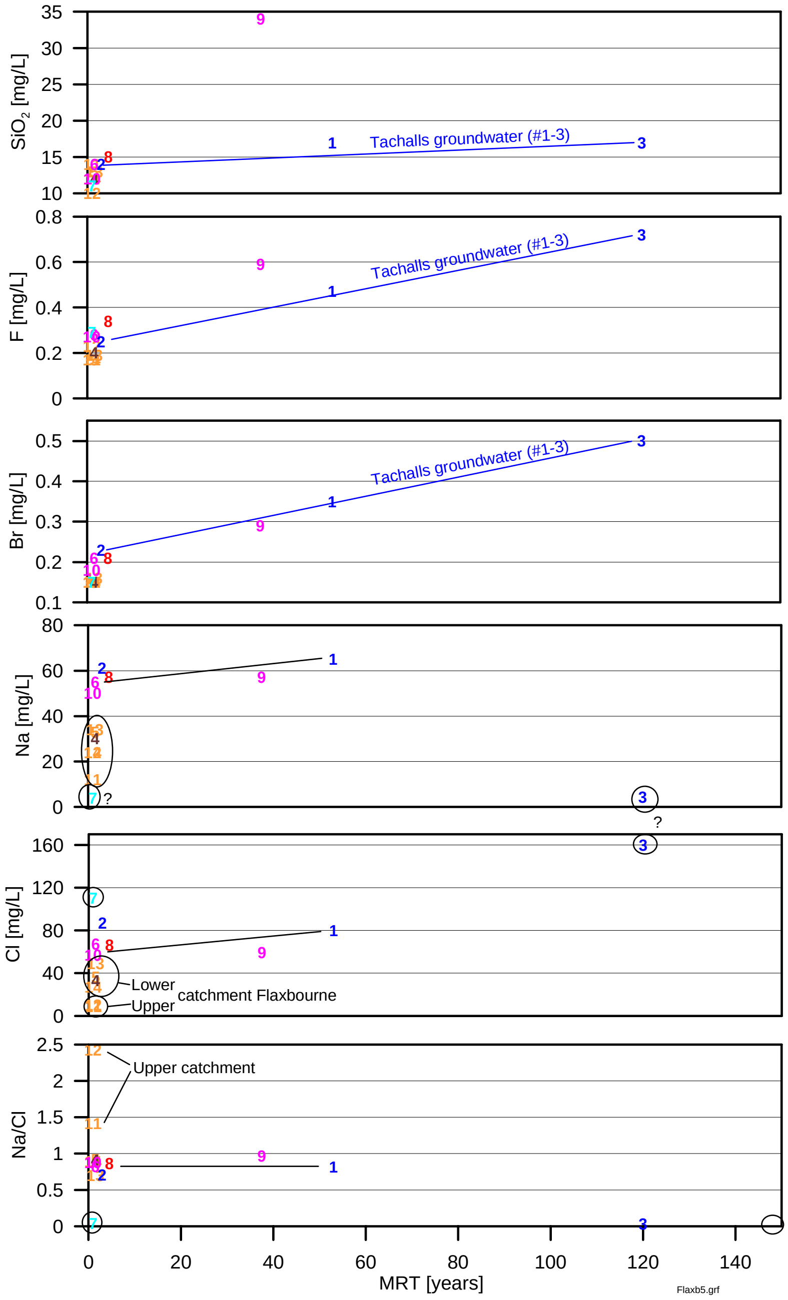

Figure 19. Silica, fluoride, bromide, sodium and chloride versus mean residence time.

There is a good correlation between sodium and magnesium for the samples from the Flaxbourne catchment (Figure 22), implying the two elements are derived from the same source (water-rock interaction). The samples from the Needles and Tachalls catchments also display a good correlation between sodium and magnesium, though with higher magnesium concentrations compared to the Flaxbourne catchment. The difference in sodium-magesium ratio reflects the different rock types within the various catchments.

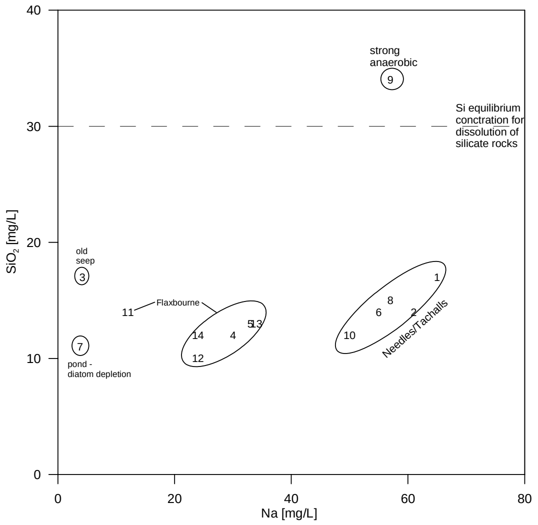

Figure 20. Silica versus sodium concentration. The dashed line represents Si equilibrium concentration for dissolution of silicate rocks (Rosen 2001).

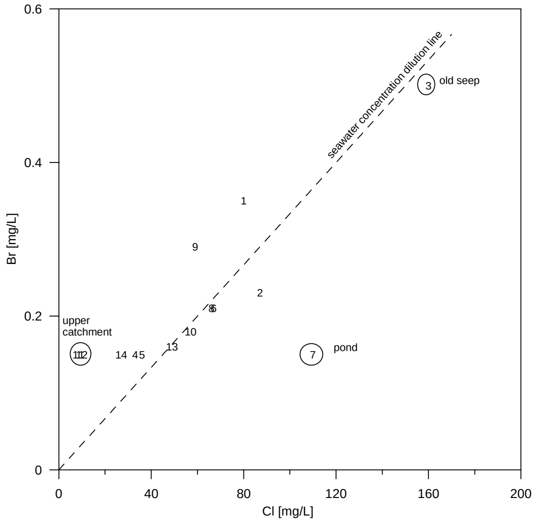

Figure 21. Bromide versus chloride. The dashed line is seawater concentration dilution line (Rosen 2001).

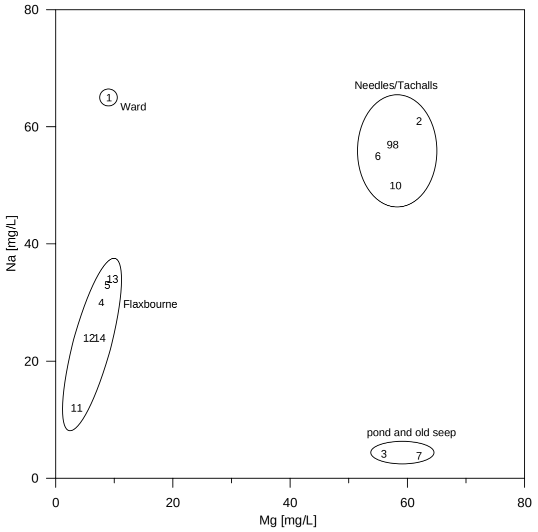

Figure 22. Sodium versus magnesium.

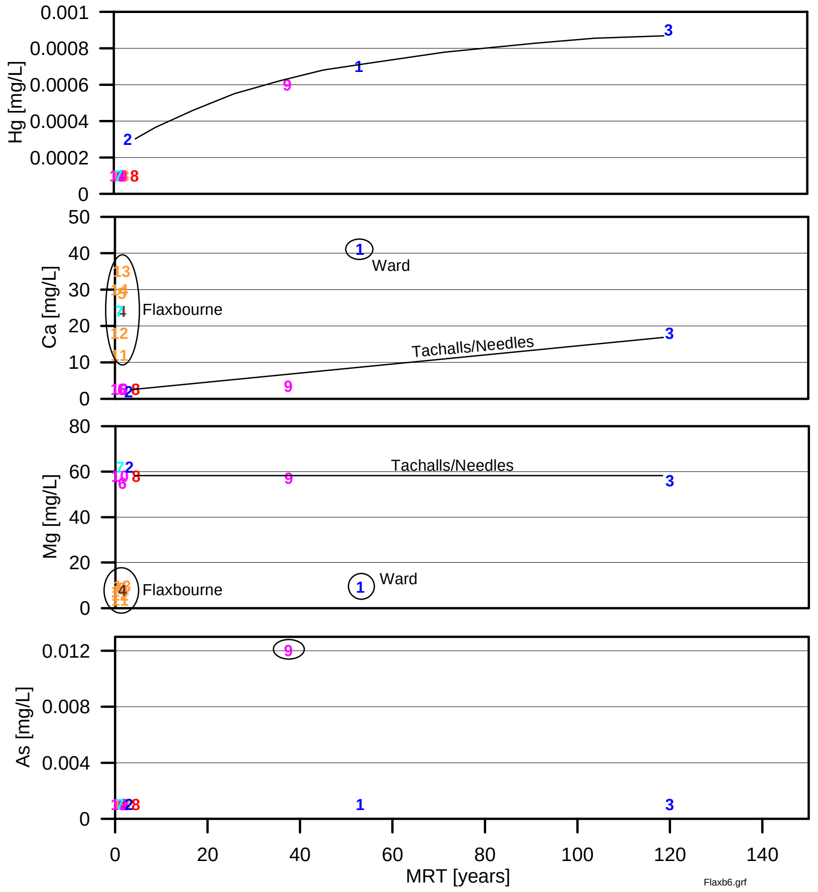

Figure 23. Mercury, calcium, magnesium and arsenic versus mean residence time.

Mercury is below detection limit for most samples (Figure 23). However, the Tachalls groundwaters and Peters test bore show an increase over time which probably indicates a geogenic source due to leaching from the Miocene-Pliocene Awatere group.

Calcium concentrations are very low in several of the samples from the Tachalls and Needles catchments, but the concentrations increase over time. This time trend indicates a geogenic origin of calcium in these samples. The samples from the Flaxbourne area have relatively higher calcium concentrations. In agricultural areas large amounts of CaO (lime) may be added to pastures to adjust soil pH, and magnesium may be added with fertilisers. Evidence of elevated calcium is detected only at Ward.

Most samples are near saturation with respect to calcite (Figure 24). Several of the samples from anoxic environments have excess bicarbonate relative to the calcite equilibrium line. The most likely reason is that bicarbonate is accumulated during microbial oxidation of organic carbon. This is the same process that tends to deplete oxygen, solubilise iron and manganese and remove sulphate.

Magnesium is very low in the Flaxbourne and Ward samples and constantly high in the Needles and Tachalls samples, independent of groundwater age. West (Site 1) at Ward is also very low in magnesium, indicating that this site is possibly associated with a different groundwater flow system.

Arsenic is detected only in Peter test bore (Site 9). This arsenic may originate from the vineyard upstream (CCA-treated posts), or it may be naturally released into solution as a result of the solubilisation of iron (arsenic is often associated with iron oxide minerals, and then released into solution along with the iron as a result of microbial respiration).

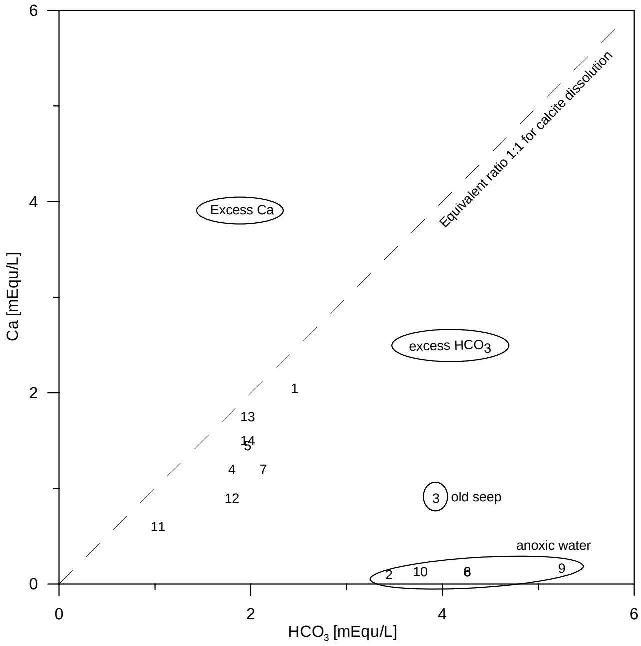

Figure 24. Calcium versus bicarbonate.

6.0 GROUNDWATER FLOW FROM WATER ISOTOPE AND CHEMISTRY SIGNATURE, AND HYDROGEOLOGIC EVIDENCE

Tachalls/Needles, Flaxbourne, and Ward form separate groundwater systems based on the different hydrochemistry signature. This is in agreement with hydrogeologic evidence which indicates that most of the Quaternary gravel units are thin and are therefore not connected between sub-catchments.

Little impact of landuse is evident on hydrochemistry. Only a few samples in the lower Flaxbourne catchment and at Ward show elevated levels of sulphate, and only two samples at Ward and Tachalls have elevated nitrate. Low nutrient concentrations are likely to be a product of strong microbial degradation processes with denitrification and sulhate reduction.

The samples at Tachalls that cover a wider age range of mean residence times 1–120 yrs show evolving hydrochemistry, with increasing Ca, SiO_2, F, Br, and Hg with increasing contact time of the water with the rock in the aquifer.

Needles and Tachalls show evidence of hard-water influence from the mio-plio Awatere group, probably due to dissolution of calcareous fossils/shell layers. The waters around Ward indicate that their origin is not the same mio-plio Awatere group but the plio Awatere group south of Ward. The Flaxbourne waters indicate that their origin is from the Greywacke catchment of the Flaxbourne River. The Flaxbourne River tributary in the upper catchment is the least evolved (youngest) water.

Flaxbourne and Tachalls/Needles are strongly anaerobic environments (including the surface waters). Some water samples indicate strongly reducing conditions, excess HCO_3 from organic matter, and high methane concentrations. This suggests that this aquifer system is formed from ancient swamps. It is possible that the drainage of Needles/Tachalls creeks have been dammed at some time in the recent past, perhaps forming a localised swamp in the vicinity of the town of Ward. There is a constriction in the valley width immediately downstream from Ward, and locally some swampy ground. This swamp may have extended farther up-valley as far as the locations of sites 7 & 9. Possible causes of valley damming are minor landsliding from the block of Tertiary mudstone to the NE of Ward, subsidence in the core of the Ward Syncline and/or uplift along the London Hill Fault

Only south of Ward we found oxic groundwater, indicating that this is an aquifer containing little organic matter.

Unusual chemistry signature (particularily extremely high B) is normally observed at geothermal or fault influence. However, this unusual chemistry in this catchment seems to be a result of strongly reducing conditions in an aquifer with high content of organic matter and with methane producing bacteria in contact with greywacke. It is unlikely that any of the investigated waters is fault impacted. There is no active fault mapped in the vicinity.

Wiffen seep is the only very old water. However, because of the small flow this does not represent a significant groundwater reservoir. Of the investigated samples, only the groundwater sample at Ward with a significant flow and age indicates significant groundwater storage. All other investigated samples are young and therefore do not indicating any significant groundwater reservoir in relation to their total flow.

Indications of sources for the investigated waters are as follows:

Flaxbourne River: Low ionic concentrations in all of these water samples reflect low mineral solubility in the greywacke catchment. The residence time of the water in the catchment is les than 2 years. No significant groundwater reservoir is indicated by the investigated samples. Hydrochemistry within the short residence time is slightly evolving in the series Upper catchment tributary, Upper catchment river, lower catchment River. The whole catchment is an anaerobic environment.

Taimate well: The hydrochemistry of this water is nearly identical to the Flaxbourne River nearby indicating that the water is sourced from the Flaxborne River.

West domestic well: This groundwater system forms a separate system compared to all other samples. This water is oxic and therefore originates from a 'clean' aquifer with little organic matter and significant storage capacity. The recharge area is likely to be the plio Awatere group south of Ward. High nitrate and excess air also indicate recharge from the local farm area. High SF_6 in relation to tritium indicates unconfined aquifer conditions.

Wiffen seep: While this water is the only old water with mean residence time of 120 yrs, it does not originate from a large groundwater system because of the low flow. The old age is likely to be caused by extremely slow groundwater flow due to low hydraulic conductivity. The water does not show any evidence of flow along an active fault. However, this water seems to be connected to a stable groundwater system in some distance because this seep never dries up in the summer.

Wiffen domestic well: Hydrochemistry is similar to the other waters in the Tachalls/Needles area. Zero excess air and young age suggests recharge from a stream. However, no stream sample for comparison is available because the nearby stream was not flowing at the time of sampling.

Peter test bore: This water originates from a highly anaerobic aquifer. Excess HCO_3 from organic matter and high methane concentrations suggests that this aquifer system is formed from ancient swamps. The old age (MRT 38 yrs) is a result of slow groundwater flow, and excess SF_6 compared to tritium indicates an unconfined or semi-confined aquifer. There is no hydraulic connection to the creek, as indicated by the hydrochemistry signature and that this well does not produce significant amounts of water. The hydrochemistry with extremely high boron is therefore assumed to represent the local anaerobic aquifer.

Peter irrigation well: This well is close to the creek and is a good producer of water. Hydraulic connection to the stream is therefore likely, and the hydrochemical signature suggests that this water is a mixture of about 10% local groundwater and 90% creek water.

Needless Creek: Compared to the other river waters, this creek water is slightly older with MRT 4.5 years. Good agreement between SF_6 and tritium indicates confined aquifer conditions.

Evans domestic well: Similar hydrochemistry between the well and creek water suggests that Evans well has a hydraulic connection to the nearby creek.

Pond at Chapman seep: This water is completely depleted in oxygen despite the open surface to air. Despite that this pond has no visible outflow it is not stagnant water because chemical components and ^{18}O are only slightly enriched by evaporation.
The age is ambiguous but the young age (mean residence time of 1 year) is the most likely one (as opposed to 40 yrs). Hydrochemistry suggests similar origin as Peter test bore from the highly anaerobic local aquifer.

7.0 ACKNOWLEDGEMENT

We thank Rob van der Raaij for development work in gas measurements, and analysis of the gases, and for reviewing the report. We also thank Kirsty Hunt for the text processing.

8.0 REFERENCES

Begg, J.G.; Johnston, M.R. 2000: Geology of the Wellington area: scale 1:250,000. *Institute of Geological & Nuclear Sciences 1:250,000 geological map 10*: 64 p.

Busenberg, E., and Plummer, L.N. 1997: Use of sulfur hexafluoride as a dating tool and as a tracer of igneous and volcanic fluids in ground water. Geological Society of America, Salt Lake City, 1997, Abstracts and Programs, v. 29(6), p. A-78.

Christenson, B. W.; Mroczek, E. K.; Kennedy, B. M.; van Soest, M. C.; Stewart, M. K.; Lyon, G. 2002: Ohaaki reservoir chemistry: characteristics of an arc-type hydrothermal system in the Taupo Volcanic Zone, New Zealand. *Journal of Volcanology and Geothermal Research, 115*: 53-82.

Cook, P. and Herczeg, A.L. 1999: Environmental Tracers in Subsurface Hydrology. Kluwer Academic Publishers

Crampton, J.S.; Laird, M.; Nicol, A.; Hollis, C.J.; Van Dissen, R.J. 1998: Geology at the northern end of the Clarence Valley, Marlborough; a complete record spanning the Rangitata to Kaikoura orogenies. *Geological Society of New Zealand and New Zealand Geophysical Society 1998 joint annual conference 101B*: 35.

Daughney, C. J.; Reeves, R. R. 2005: Definition of hydrochemical facies in the New Zealand National Groundwater Monitoring Programme. *New Zealand Journal of Hydrology, 44(2)*: 105-130.

Freeze, R. A.; Cherry, J. A. 1979: Groundwater. Prentice-Hall, New Jersey.

Happell JD, Price RM, Top, Z, Swart, PK 2003. Evidence for removal of CFC-11 CFC-12, and CFC-113 at the groundwater- surface water interface in the Everglades. Journal of Hydrology 279, pp. 94-105

Morgan, M.; Hughes, B. 2001: Regional Groundwater Summaries: Wellington. *In* Groundwaters of New Zealand, M.R. Rosen and P.A. White (*eds*). New Zealand Hydrological Society Inc., Wellington, p. 403

Morgenstern, U., Reeves, R., Daughney, C., Cameron, S., Gordon, D., 2004. Groundwater age and Chemistry, and Future Nutrient Load for Selected Rotorua Lakes Catchments. *Institute of Geological & Nuclear Sciences science report* 2004/31. 74p.

Morgenstern, U Wairarapa Valley Groundwater – Residence time, flow pattern and hydrochemistry trends. Institute of Geological & Nuclear Sciences Science Report 2005/33, 36 pages

Ota, Y.; Brown, L.J.; Berryman, K.R.; Fujimori, T.; Miyauchi, T. 1995: Vertical tectonic movement in northeastern Marlborough: stratigraphic, radiocarbon, and paleoecological data from Holocene estuaries. *New Zealand Journal of Geology and Geophysics, 38(3)*: 269-282.

Plummer, L.N.; Busenburg, E. 1999: Chlorofluorocarbons. Chapter 15 in Environmental Tracers in Subsurface Hydrology. Eds: P. Cook and A.L. Herczeg. Kluwer Academic Publishers. pp. 441-478.

Rattenbury, M.S.; Townsend, D.B.; Johnston, M.R. In Press: Geology of the Kaikoura area: scale 1:250,000. *Institute of Geological & Nuclear Sciences 1:250,000 geological map 13.*

Roberts, A.P. 1992: Paleomagnetic constraints on the tectonic rotation of the southern Hikurangi margin, New Zealand. *New Zealand Journal of Geology and Geophysics 35 (3)*: 311-323.

Roberts, A.P. 1995: Tectonic rotation about the termination of a major strike-slip fault, Marlborough fault system, New Zealand. *Geophysical Research Letters, 22 (3):* 187-190.

Rosen, M.R., 2001, Hydrochemistry of New Zealand's Aquifers. In: Groundwaters of New Zealand (Eds. Rosen MR. and White PW.), The Caxton Press, Christchurch: 161-184

Stewart, M. and Morgenstern U. 2001. Age and Source of Groundwater from Isotope Tracers. In: Groundwaters of New Zealand (Eds. Rosen MR. and White PW.), The Caxton Press, Christchurch: 161-184

Townsend, D.B.; Little, T.A. 1998 Pliocene-Quaternary deformation and mechanisms of near-surface strain close to the eastern tip of the Clarence Fault, northeast Marlborough, New Zealand. *New Zealand journal of geology and geophysics, 41(4):* 401-417.

Townsend, D.B. 2001: Neogene evolution of the Pacific-Australia plate boundary zone in NE Marlborough, South Island, New Zealand. PhD thesis, Victoria University of Wellington, Wellington. 186 p.

APPENDIX 1

#1 West domestic well

#2 Wiffen domestic well

#3 Wiffen Seep

#4 Taimate stock sheme

#5 Flaxbourne River at SH1

#6 Peter irrigation bore 1

#7 Pond at Chapman seep

#8 Needles Creek at Peter’s culvert

#9 Peter test bore 2

#10 Evans domestic well (sampling behind pressure tank, no other sampling point)

#11 Flaxbourne River tributary upper catchment

#12 Flaxbourne River in upper catchment

#13 Flaxbourne River at Beach Road ford

#14 Flaxbourne River at Corrie Downs

APPENDIX 2

METHODOLOGY OF GROUNDWATER AGE DATING

TRITIUM, CFC AND SF_6 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 25). 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 SF_6. CFC and SF_6 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 25). 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.

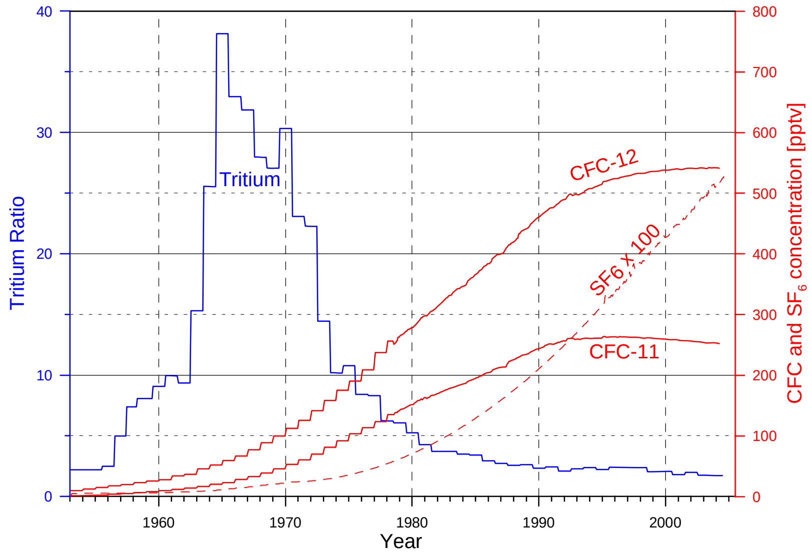

Figure 25. Tritium, CFC and SF_6 input for New Zealand rain. Tritium concentrations are in rain at Kaitoke, 40km north of Wellington (yearly averages), and CFC and SF_6 concentrations are for southern hemispheric air. TR=1 represents a 3H/1H ratio of 10-18, and 1 pptv is one part per trillion by volume of CFC or SF_6 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 SF_6 data are reconstructed (USGS Reston), 1970-1995 data are from Maiss and Brenninkmeijer (1998), and post-1995 data was measured in Tasmania.

Sulphur hexafluoride (SF_6) is primarily anthropogenic in origin, but can also occur in some volcanic and igneous fluids. Significant production of SF_6 began in the 1960s for use in high-voltage electrical switches, leading to increasing atmospheric concentrations (Figure 25). The residence time of SF_6 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 SF_6 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 then CFC-12), and CFC contamination from local anthropogenic sources (CFC-12 is more susceptible to this), Plummer and Busenburg (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 SF_6 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 SF_6 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/SF_6) or two tritium measurements over time are necessary.

Schematic groundwater flow situations are shown in Figure 5. 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 6 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 (yf). The young water fraction younger than 55 years is about 80% in the example in Figure 7 (hatched area).

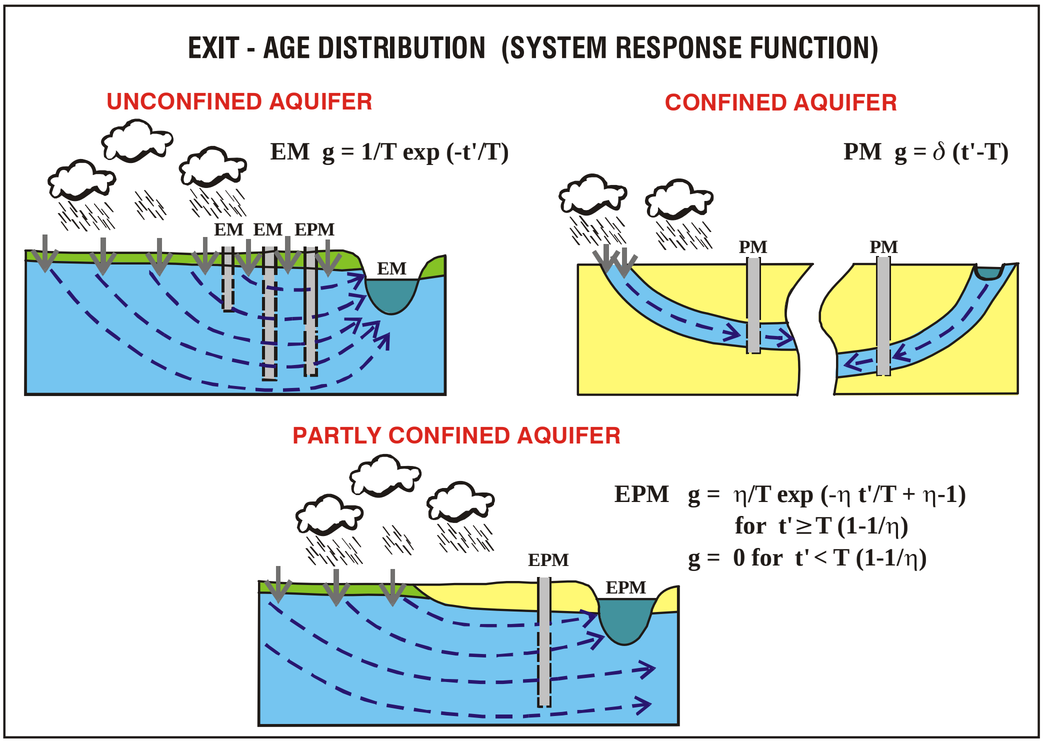

Figure 26. Schematic groundwater flow situations and corresponding age distribution functions (see Maloszewski and Zuber (1982) for theoretical background).

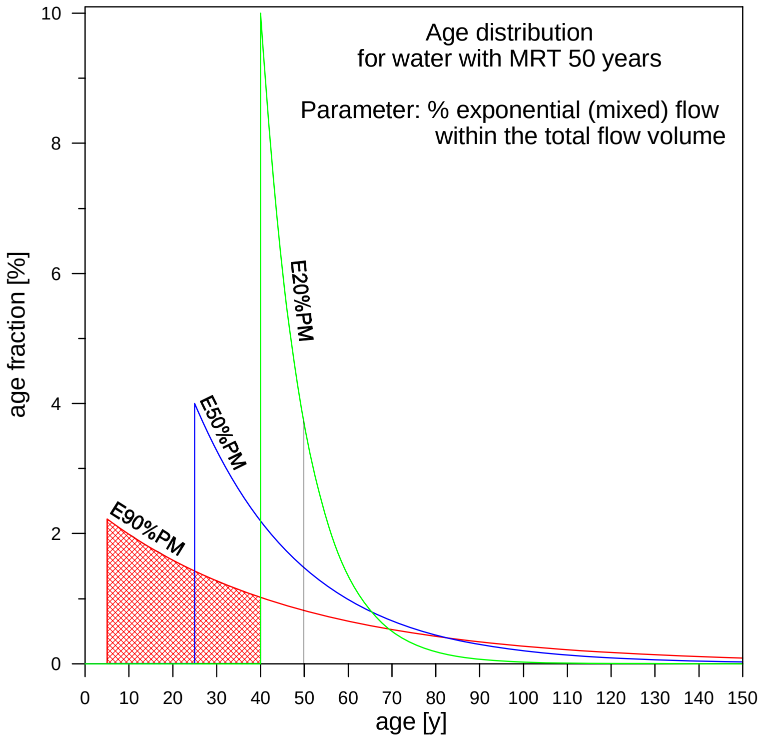

Figure 27. Age distribution for the exponential-piston flow model.

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 SF_6 RAW DATA

Table 4. Raw CFC and SF6 data. See appendix 2 for explanation.

				Measured concentration in solution					**Calculated Atmospheric Partial Pressure in pptv**					**Piston Flow Model Recharge Dates**		
CFC No.	**SF_6 No.**	**Sample Details**	**Sampling Date**	**fmolkg^{-1} SF_6**	**pmolkg^{-1} CFC-11**	**±**	**pmolkg^{-1} CFC-12**	**±**	**SF_6**	**CFC-11**	**±**	**CFC-12**	**±**	**SF_6**	**CFC-11**	**CFC-12**
FMB30	SMB24	P29w/0187	21.02.06	1.79	1.78	0.04	1.98	0.03	4.89	84.2	1.9	364.2	7.4	2002.5	1973.5	1984.5
FMB31	SMB54	P29w/0164	21.02.06 (SF6 10.05.06)	2.30	0.48	0.01	1.68	0.00	6.03	25.6	0.1	338.9	4.1	Contam. (>5%)	1966.0	1983.0
FMB32	SMB26	P29w/0087	21.02.06	2.30	3.21	0.02	2.21	0.01	5.75	179.3	4.2	464.1	7.2	Modern	1982.5	1989.5
FMB33	SMB27	Flaxbourne River @ SH1	21.02.06	1.83	3.02	0.01	1.93	0.01	5.63	194.4	4.4	463.5	4.9	2005.0	1984.5	1989.5
FMB34	SMB28	P29w/0188	21.02.06	2.78	0.01	0.00	0.23	0.00	6.54	0.5	0.0	48.9	0.5	Contam. (>5%)	1950.5	1964.0
FMB35	SMB29	Needles Creek @ Peter's Culvert	22.02.06	2.00	2.47	0.02	1.75	0.04	5.14	156.5	1.8	410.1	6.9	2003.5	1980.0	1987.0
FMB36	SMB30	P29w/0189	22.02.06	0.94	0.51	0.11	0.34	0.07	2.36	29.6	6.1	74.6	15.5	1991.0	1966.5	1967.0
FMB37	SMB31	P29w/0163	22.02.06	3.28	0.98	0.95	1.46	0.28	6.24	58.5	62.7	295.9	108.1	Contam. (>5%)	1971.0	1980.5
FMB38	SMB32	Flaxbourne River tributary in upper catchment	22.02.06	1.66	3.43	0.00	1.96	0.00	5.55	228.0	5.3	485.9	9.0	2005.0	1988.0	1991.0
FMB39	SMB33	Flaxbourne River in upper catchment	22.02.06	2.01	2.81	0.02	1.69	0.02	5.92	225.5	9.8	487.2	21.4	Modern	1987.5	1991.5
FMB40	SMB34	Flaxbourne River @ Beach Rd ford	23.02.06	1.99	2.62	0.02	2.17	0.01	6.13	178.4	0.7	547.1	7.4	Contam. (>5%)	1982.5	Modern
FMB41	SMB35	Flaxbourne River @ Corrie Downs	23.02.06	1.91	2.78	0.01	2.00	0.01	6.02	165.0	1.3	448.8	3.7	Contam. (>5%)	1981.0	1989.0

	Concentration in solution mL(STP).kg^{-1}			
Sample Details	**Ar**	**±**	**N_2**	**±**
P29w/0187	0.380	0.003	13.93	0.27
P29w/0164	0.373	0.002	14.19	0.02
P29w/0087	0.371	0.003	14.48	0.44
Flaxbourne River @ SH1	0.342	0.001	13.09	0.28
P29w/0188	0.377	0.000	14.91	0.09
Needles Creek @ Peter's Culvert	0.356	0.008	14.19	0.72
P29w/0189	0.366	0.000	14.44	0.08
P29w/0163	0.402	0.019	16.77	0.16
Flaxbourne River tributary in upper catchment	0.334	0.001	12.60	0.13
Flaxbourne River in upper catchment	0.324	0.004	13.12	0.12
Flaxbourne River @ Beach Rd ford	0.337	0.001	13.03	0.05
Flaxbourne River @ Corrie Downs	0.348	0.000	12.99	0.03

calculated variables			
temp °C	**±**	**excess air mL(STP).**	**±**
9.7	0.0	-0.9	0.3
11.8	0.3	0.2	0.1
12.9	0.4	1.0	0.7
15.6	0.4	0.1	0.5
12.8	0.1	1.5	0.2
15.3	0.1	1.4	1.0
13.8	0.2	1.2	0.2
12.2	4.3	3.6	1.8
16.2	0.5	-0.3	0.3
20.3	0.8	1.5	0.1
16.8	0.2	0.4	0.0
14.0	0.1	-0.6	0.1