

**A Review on the Impact of Irrigation
on Age Dating and Geochemistry
of Shallow Groundwater
- implications for the Wairau Plains**



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**A Review on the Impact of Irrigation
on Age Dating and Geochemistry
of Shallow Groundwater
- implications for the Wairau Plains**

A report prepared for Marlborough District Council

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By

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1 Executive Summary

A recent review highlighted the possibility that irrigation with older water, particularly if deeper groundwater is used, could cause the water from a particular well to appear older than it actually is, if the irrigation retained some or much of its age signature. A literature review, carried out as part of this EnviroLink report, did not reveal any published studies on the effect of irrigation method and source on age dating of shallow groundwater. One relevant unpublished study was a vadose zone tracing experiments where the leaching water, which was irrigated using drip irrigation, was found to retain its groundwater tritium age signature (ESR, unpublished data). This experiment indicated that the irrigation water had retained its “old water” age signature and had not re-equilibrated at the soil surface. This is not surprising as the irrigation method was drip irrigation which permits little opportunity for contact with the atmosphere. It is not known whether methods such as border strip or spray irrigation will result in re-equilibration at the soil surface. It is also expected that age tracers with differing degrees of volatility may re-equilibrate at different rates.

A work plan to determine how much of the age signature is retained for the different tracers and different irrigation application systems has been developed as part of this EnviroLink project. The necessary funding for this work has been approved and this research is planned to be carried out within the next year.

This EnviroLink study also examined the effect of using deep groundwater sources for irrigation. There is an increasing use of deep groundwater for irrigation purposes in Marlborough and elsewhere in New Zealand. A literature review has been carried out on the effect of using deep groundwater sources for irrigation, focussing on the geochemical aspects. Much of the overseas literature deals with high levels of dissolved minerals and, for anoxic waters, high levels of As, B, Fe and Mn.

The deeper groundwaters in the Wairau Valley have an extremely wide variation in age. The older groundwaters have increased levels of dissolved minerals, including As and B although levels of Fe and Mn are generally low. The As level in one well exceeds the MAV of 10 µg/L and As levels are > 50% of the MAV for 4 other wells. High levels of B (> 0.1 mg/L) are only observed in the Deep Wairau Aquifer and the northern fringe of the confined section of Wairau Aquifer. There are no wells with B concentrations above the MAV for drinking water.

The sodium adsorption ratio (SAR) is a measure of the suitability of water for use in agricultural irrigation. High levels of Na relative to the Ca and Mg can cause a decrease in infiltration and permeability of the soil to water leading to problems with crop production. Some of the deeper groundwaters have SAR values >3 which indicates that care is needed with respect to using this water for irrigation purposes.

A long term monitoring programme for the Deep Wairau Aquifer has been developed. It is proposed that the annual sampling continue for well 3278 and that every five years a more comprehensive sampling programme should be carried out for all the wells located in the Deep Wairau Aquifer.

Recommendations

- The arsenic levels in some of the deep wells in the Deep Wairau Aquifer and the fringe areas of the Wairau confined aquifer can be elevated and approach the MAV of 10 µg/L. Well 980 in the Deep Wairau Aquifer has an As value of 18 µg/L but there is only 1 analysis of As for this well and it should be repeated to confirm this level. If any of the wells with As concentrations >50% of the MAV are used for drinking purposes then the owners should be advised.
- Some of the levels of SAR in the deep groundwater in the Wairau Valley are in the range where care is needed with respect to using this water for irrigation purposes. It is recommended that someone with appropriate soil expertise is asked to review the effect of irrigation using groundwaters with SAR values > 3 on the soils in the Wairau Valley.
- Some levels of B in the deep groundwater in the Wairau Valley are in the range of 0.5 – 1.0 mg/L which may cause problems for sensitive crops. As grapes are an important crop in Marlborough and the guidelines from Lenntech suggest some problems may occur if groundwater with these levels of B were used for irrigation, We recommend that someone with the necessary expertise is asked to review this aspect
- It is recommended that age determinations be carried out for selected wells, including well 3667, in the northern fringe of the confined Wairau Aquifer to confirm the reason for the change in groundwater quality in this area. It would be necessary to have more than one age determination over a 5 – 10 year period to confirm whether the water is becoming younger.
- It is recommended that the long term monitoring programme for the Deep Wairau Aquifer as described in section 6 is implemented.

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2 Introduction

A recent review of existing knowledge on vadose zone travel processes and their impact on groundwater quality (Close, 2010) has just been completed for Environment Canterbury (the review is available on their website). A number of related issues, including age dating of shallow groundwater, were considered as part of that review.

The review highlighted the possibility that irrigation with older water, particularly if deeper groundwater is used, could cause the water from a particular well to appear older than it actually is, if the irrigation retained some or much of its age signature. There was an example noted where water irrigated from groundwater using a drip irrigation system retained its age signature and caused the water sampled down the profile to show a high apparent age.

Retention of age signature by the irrigation water could explain some of the groundwater having older ages than expected. It may also provide an explanation for the SF₆ showing the youngest age, followed by CFC-12, then CFC-11 and then tritium, as the more volatile tracers will re-equilibrate fastest and retain less of their age signature. The input of irrigation is significant in Canterbury, with estimates of the amount of irrigation ranging from 48 – 86% of the rainfall input, as calculated using data from 1960 to 2009. The drier locations had higher inputs of irrigation as would be expected. This rough estimate indicates that the input of irrigation is significant and could have an important influence on the apparent age of the shallow groundwater, depending on how much the age signature of the irrigation water is retained through the application process. Although Canterbury has the highest levels of irrigation, these issues will be of significance throughout New Zealand, particularly along the east coast regions such as Hawkes Bay, Marlborough, Nelson and Otago.

Initial discussions and a preliminary literature search has indicated that there is little information and that few, if any, experiments have been carried out to determine how much of the age signature is retained for the different tracers and different irrigation application systems. A more in depth literature review has been carried out as part of this study.

A second aspect of this study concerns the effect of using deep groundwater sources for irrigation. There is an increasing use of deep groundwater for irrigation purposes in Marlborough. This trend is also happening in other regions around New Zealand. Old deep groundwater often is anoxic with low levels of oxygen and elevated levels of iron, manganese, and sometimes arsenic. These compounds can have a negative impact on the crop as they can precipitate on the plant surface when the water contacts the atmosphere. Other aspects include induced recharge of water with different geochemistry into the shallow aquifer with potential to alter the groundwater chemistry and flow patterns. The different geochemistry may cause problems with blockage of pumps, well screens, irrigation equipment and the plants or soil to which it is applied.

A literature review has been carried out on the effect of using deep groundwater sources for irrigation, focussing on the geochemical aspects. Factors likely to cause problems have been identified and discussed. A long term monitoring programme for the Deep Wairau Aquifer has also been developed.

This study reports on two literature reviews on the related topics of: (1) the effect of irrigation method and source on age dating of shallow groundwater, and (2) the effect of using deep groundwater sources for irrigation.

As there was insufficient information available from the literature on the effect of irrigation method and source on age dating of shallow groundwater, this study has also scoped out what would be needed to answer the above question and a work proposal and plan has been developed.

3 Literature review of the effect of irrigation method and source on age dating of shallow groundwater

3.1 Brief review of Age Dating of Groundwater

During the past 60 years, a number of chemical substances have been released into the atmosphere in sufficient quantities to allow their use as tracers. The substances such as chlorofluorocarbons (CFCs) and SF₆, dissolve in precipitation and tritium as part of the water molecule of atmospheric moisture, become incorporated in the water cycle (Stewart et al., 2002). Measurement of their concentrations in groundwater enables comparison with the historical levels in the atmosphere and can provide an estimate of how long it has been since the water was in equilibrium with the atmosphere and thus the likely age of the groundwater.

The basis for using these chemicals to date water and the assumptions associated with this technique have been described by Stewart et al. (2002), and are summarised briefly here. Age-dating using tritium is based on radioactive decay of tritium after rainwater penetrates the ground during recharge. The half-life of tritium is 12.3 years. Tritium concentrations in rainfall peaked in tritium concentration in the 1960s and early 1970s due to nuclear weapons testing and has steadily decreased since that time. Age-dating of groundwater using dissolved gases is possible due to the steady increase in atmospheric CFC and SF₆ concentrations since their production began in the 1940s. The measured concentrations in groundwater are used to calculate the corresponding atmospheric concentrations using Henry's Law and the recharge temperature, and the age is determined by comparing these with the atmospheric record (Stewart, 2006).

There are several assumptions involved in assigning an age of a water sample from the measurements of tracers. Tritium is assumed to be at equilibrium with the atmosphere when entering the soil or subsurface and the age is estimated from that point. There is some opportunity for re-equilibration in the vadose zone but this is assumed to be small. For the gases such as CFCs and SF₆ (Plummer et al., 2000) several studies have shown that there is significant equilibration in the vadose zone. Cook and Solomon (1997) state that usually the CFCs are assumed to be at equilibrium with the atmosphere at the groundwater table but that for thick unsaturated zones that may not be the case. If the unsaturated zone thickness is < 5 m then the time lag is negligible. If the water emerges into surface waters such as rivers, then re-equilibration with the atmosphere is insignificant for tritium, and for the gases also does not occur immediately but the age signal is lost gradually. This can be seen in the age of river water such as the Waimakiriri River (4 years old; Stewart et al., 2002) and the Wairau River (50% is about 8 years old; (Taylor et al., 1992). If this river recharges a groundwater system or is used for irrigation then the water will appear older than it would have been with full re-equilibration at the time of recharge.

This is particularly relevant for irrigation from groundwater and the implications of this process have not yet been fully considered. If the water retains a measure of its age signature as it moves through the soil, vadose zone and into the groundwater then it may appear older than it would have been with full re-equilibration at the time of recharge. The extent to which it retains its age signature will depend on the type of irrigation system and the volatility of the tracer. Border strip (flood) irrigation and drip irrigation encourage less exchange with the atmosphere compared to spray irrigation and, among the spray systems, finer droplets and low application rates will promote more equilibration. With respect to tracer volatility, tritium (water) is by far the least volatile followed by CFC-11, CFC-12 and then SF₆ (Stewart, 2010, pers comm). Tritium is unlikely to be significantly altered by re-equilibration,

whereas the others are increasingly likely to be completely reset. Lack of equilibration will have a relatively minor effect (< 5 years) on reported ages for areas where the irrigation water is sourced from surface waters, but may have a more significant effect where irrigation is sourced from deeper older groundwater. It is currently not known how much re-equilibration with atmosphere occurs for the different spray irrigation systems, and therefore the extent that the irrigation water retains its previous age signature.

3.2 Studies on the effect of irrigation method and source on age dating of shallow groundwater

An extensive literature review did not reveal any published studies on the effect of irrigation method and source on age dating of shallow groundwater. The one study that we are aware of was part of the Integrated Research for Aquifer Protection (IRAP) vadose zone tracing experiments. They observed that the leaching water, which was irrigated using drip irrigation, was found to retain its groundwater tritium age signature (ESR, unpublished data). A description of the sites and the modelling of the transport of a tracer, bromide, through the vadose zones at the Lincoln and Dunsandel sites has been reported by Dann et al. (2010). A brief description of the Lincoln site and the key results from the age dating of water collected from the vadose zone profile are given here.

The Lincoln site is located on a slightly undulating silt loam soil with a thickness of approximately 1 m. The site has most recently been used for cropping and prior to this, dryland sheep grazing. The gravel vadose zone at Lincoln generally consists of coarse alluvial sandy gravel interspersed with lenses of pure sand and open-frameworks gravels. The groundwater level was approximately 9 m below ground level at the time of the study. The site was instrumented with 12 ceramic suction cup samplers at depths ranging between 1 and 7 m, 3 neutron probe access tubes, time-domain reflectometry (TDR) probes, gas samplers (for an associated study) and groundwater wells. The suction cups were installed in triplicate (in 3 rows with suction cups installed approximately 4 m apart along the row) at depths of 1, 3, 5 and 7 m on a 20° angle from vertical, to enable sampling of undisturbed flow and transport from the surface to the suction cups. The annulus around each access tube was sealed with bentonite to prevent by-pass flow down along the suction cups.

Eight samples were collected from the suction cups at the Lincoln site on 11 February 2005 and analysed for tritium content to give the age of water down the profile. All the samples had much less tritium than would be expected and it was evident that the water used for irrigation, which came from a 41 m deep well, had percolated through the vadose zone profile by the time the samples had been collected. Nearby wells screened at similar depth had zero tritium content indicating old water, consistent with groundwater up-welling from depth in this area. If the old irrigation water is assumed to have a value of zero and the recent rain is assumed to have a value of 2.4 tritium units (TU), then the vadose zone samples had proportions of old water ranging between 26 and 75%. There was slightly more "old" irrigation water near the top of the profile as would be expected but there was lots of variability and the deepest sample still had 49% of "old" irrigation water. These samples were taken 2 months after irrigation commenced at this site and the detection of irrigation water throughout the profile indicates rapid movement of the irrigation water through the profile which was consistent with the observed nitrate and bromide concentrations (Dann et al. 2010). This experiment indicated that the irrigation water had retained its "old water" age signature and had not re-equilibrated at the soil surface. This is not surprising as the irrigation method was drip irrigation which permits little opportunity for contact with the atmosphere.

There was one moderately relevant study that examined the degree of re-equilibration that could take place in the vadose zone for the more volatile age dating tracers. Plummer et al.

(2000) discuss the potential for CFC ages of water recharged through a thick unsaturated zone to appear old relative to time of recharge. They found that, depending on recharge mechanism, water may fully equilibrate with unsaturated zone air during recharge or retain CFC concentrations acquired at the land surface. They found that irrigation with river water high in CFC-11 can cause contamination of unsaturated zone air and shallow groundwater. Age dating using CFCs found water contained as much as 5% to 30% young water mixed with old regional background water.

At present, to the best of our knowledge, there have been no experiments carried out to determine how much of the age signature is retained for the different tracers with different irrigation application systems. A proposal and workplan for this purpose is given in the next section.

4 Proposed work plan to determine how different irrigation systems influence the re-equilibration of age dating tracers prior to entering the soil

The proposed experiments would need to consider the type of irrigation (border, centre pivot, travelling irrigator, drip, etc), the source of irrigation water (surface vs. groundwater), and the experimental design, including the number of samples, season or temperature which would affect the equilibration rate, and the number of tracer compounds to be analysed. The first phase of the experiment would focus on the re-equilibration of age dating tracers prior to entering the soil. The likely changes in tracers and their equilibration with the atmosphere during passage through the soil and vadose zone would also be of interest but would be considered as a separate investigation phase dependant on the results from the first phase.

There is little previous relevant data for this question as shown in the previous section. The IRAP experiment carried out in 2005 and detailed in Close (2010) indicated that the age signature of the irrigation water is largely conserved with drip irrigation. The literature review indicated that there is no other relevant data available.

As there is some information for drip irrigation and is not widely used, it will not be included in this experiment. Three irrigation methods will be tested, namely border, centre pivot, and travelling irrigator. The two types of spray irrigation have different spray droplet sizes and application rates that could influence equilibration processes. The water would be sampled using a container at ground level for the spray irrigators and at distances down the border for the flood irrigation.

An irrigation source of old groundwater would be chosen that would have a zero tritium, CFCs and SF₆ concentrations and provide maximum sensitivity for the experiments. Several candidate sources will be identified and each would be assessed for proximity to the required irrigation systems, land access and land owner co-operation. A single groundwater source may not be possible for all irrigation methods – however we will try to get similar sources in the same vicinity if a single source is not possible.

The temperature and humidity conditions are expected to influence the degree and rate of equilibration. Two contrasting conditions will be chosen based on an inspection of the climate record and the temperature and humidity will be measured accurately on each sampling occasion.

The following tracer compounds will be measured on each sample – Tritium (cost = \$650) and tracer gases which include CFC11, CFC12, SF₆, Ar, N₂, methane (cost = \$660).

Experimental Procedure

For each irrigation method, a sample will be taken from the source entering the irrigation system and sample(s) will be taken from where the water contacts the soil and is infiltrating. The water would be sampled using a container at ground level for the spray irrigators and at distances down the border for the flood irrigation.

The costs for the project have been estimated for duplicate and triplicate samples taken at different locations for the spray irrigation systems and for 2 temperature/humidity conditions. The total cost of the project is \$46,680. It may be slightly less if duplicates rather than triplicate samples are used for the second experiment. This will be determined based on the observed variability from the first experiment.

Funding has been sought from Environment Canterbury and from the Core Purpose funded projects from ESR and GNS. The total budget for the experiments is \$46.7K, so a third (\$15.6K) has been sought from each source. The requested funding has been granted to carry out these experiments and it is planned to carry them out over the next 12 month period.

5 Review of the effect of using deep groundwater sources for irrigation

The key question addressed in this section is “what is the impact of anoxic water and associated chemicals coming into contact with oxic groundwater (for example, the Rarangi Shallow Aquifer) and wetlands and soil?”

There is an increasing use of deep groundwater for irrigation purposes in Marlborough. This trend is also happening in other regions around New Zealand. Old deep groundwater often is anoxic with low levels of oxygen and elevated levels of iron, manganese, and sometimes arsenic. These compounds can have a negative impact on the crop as they can precipitate on the plant surface when the water contacts the atmosphere. Other aspects include induced recharge of water with different geochemistry into the shallow aquifer with potential to alter the groundwater chemistry and flow patterns. The different geochemistry may cause problems with blockage of pumps, well screens, irrigation equipment and the plants or soil to which it is applied. The use of deep groundwater can also induce recharge of water with different geochemistry into the aquifer from which the water was withdrawn, which can alter the groundwater flow patterns.

A brief literature review has been carried out on the effect of using deep groundwater sources for irrigation, focussing on the geochemical aspects. Much of the overseas literature deals with high levels of dissolved minerals and, for anoxic waters, high levels of As, B, Fe and Mn.

A particular focus over the past 10-15 years has been the occurrence of high levels of arsenic (As) in parts of South and South-east Asia, such as Bangladesh, India, Cambodia, Vietnam (Brammer and Ravenscroft, 2009; Harvey et al., 2006). In these areas the principal mode of As contamination is by reductive dissolution whereby As adsorbed to iron oxyhydroxides in sediments is liberated into the groundwater when microbial degradation of organic matter reduces ferric iron to the soluble ferrous form. Reports indicate that there is significant variability in As concentrations in Bangladesh. One survey measured As > 50 µg/L in 25% of wells and >10 µg/L in 50% of wells while another survey of 456 irrigation wells measured As > 100 µg/L in 50% of wells and >200 µg/L in 14% of wells (Brammer and Ravenscroft, 2009). These levels of As not only have significant health effects when used for

drinking purposes but rice, which is the principal irrigated crop in this region, is very susceptible to As toxicity and is the most important source of As in the human diet (Brammer and Ravenscroft, 2009).

High levels of As have also been observed in other areas of the world. Appleyard et al. (2006) report an area of shallow groundwater near Perth, Australia where changes in pumping and land use have resulted in the groundwater becoming more acidic and reduced. Levels of As have increased significantly in the last 10-20 years and, in a selection of domestic wells with acidic conditions, ranged between 1 and 800 µg/L. Sampling of monitoring wells in the area showed As levels up to 7000 µg/L. There were two groundwater zones with high As levels; a shallow reduced zone with acidic conditions and a deep reduced zone with neutral to alkaline conditions. High As concentrations have also been reported in a shallow (25-30 m thick) Mississippi River Valley alluvial aquifer in Arkansas (Sharif et al., 2008). Levels of As ranged from < 0.5 to 77 µg/L, with 18% of wells exceeding the 10 µg/L drinking water standard. Reductive dissolution of iron oxyhydroxide was suggested as the dominant As release mechanism. In contrast to this mechanism, Busbee et al. (2009) showed that high As levels in a shallow aquifer in Idaho, USA, occur under oxic conditions. The shallow aquifer contained As levels in excess of 50 µg/L together with oxygen levels around 4 mg/L, high nitrate levels (8 mg/L) and low dissolved Fe (<0.02 mg/L). The high As levels resulted from increased recharge due to crop irrigation in a semi-arid environment which leached As, in the form of arsenate, from surficial soil and sediments that are visibly stained with iron oxides.

These levels of As reported in the overseas studies are generally much greater than the levels observed in the Wairau valley (Table 1). However, they do provide some useful background and context.

A number of studies have examined the effects of irrigation with waters of differing salinity and sodium and calcium composition on the quality of the underlying shallow groundwater. Kass et al. (2005) studied recharge to shallow groundwater following irrigation with either a wastewater or freshwater source for a coastal aquifer in Israel. The wastewater was more saline and contained more sodium compared to the freshwater source and interacted with the clayey soil and subsoil quite differently to produce different composition in the shallow groundwater. The study showed the need to assess both the composition of the irrigation water as well as the lithology to determine the resulting groundwater quality.

The sodium adsorption ratio (SAR) is a measure of the suitability of water for use in agricultural irrigation, as determined by the concentrations of solids dissolved in the water (Wikipedia, accessed July 2011).

The formula for calculating sodium adsorption ratio is:

$$\text{SAR} = [\text{Na}^+] / \{([\text{Ca}^{2+}] + [\text{Mg}^{2+}]) / 2\}^{1/2}$$

where sodium, calcium, and magnesium are in milliequivalents/liter.

Although SAR is only one factor in determining the suitability of water for irrigation, in general, the higher the sodium adsorption ratio, the less suitable the water is for irrigation. Irrigation using water with high sodium adsorption ratio may require soil amendments to prevent long-term damage to the soil. If irrigation water with a high SAR is applied to a soil for years, the sodium in the water can displace the calcium and magnesium in the soil. This will cause a decrease in the ability of the soil to form stable aggregates and a loss of soil structure and tilth. This will also lead to a decrease in infiltration and permeability of the soil to water leading to problems with crop production.

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Table 1: Means of selected chemical parameters for selected wells for Wairau Valley aquifers.

Aquifer-Well	Well screen (m)	n*	pH	Cond. (mS/m)	Alkalinity (mg/L)	Cl (mg/L)	NO ₃ -N (mg/L)	SiO ₂ (mg/L)	As (µg/L)	B (mg/L)	Fe (mg/L)	Mn (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	SAR	Age (yrs)
MAV or GV			7.0 - 8.5§			250§	11.3		10	1.4	0.2§	0.4	200§				
Wairau –unconfined																	
P28w/3009	5 - 6	26 - 30	6.8	7.1	29#	3.4	0.5	8.7#	<1‡	0.03‡	<0.02	<0.01	3.7	6.8	1.7	0.3	3.5
Wairau- confined																	
P28w/708	? – 43	7 - 16	7.7	22	95	20	<0.05	20.3	5	0.08	0.08	0.06	33	4.8	2.9	2.9	72
P28w/765	34 – 39	17 - 22	7.4	21	94	18	<0.01	20.3	<1	0.07	0.40	0.22	30	5.9	4.2	2.3	52
P28w/1733	46 – 50	22 - 33	8.0	15	74	7.6	<0.03	11.1	-	-	0.62	0.06	18	4.7	4.6	1.4	22
P28w/2107	23 – 24	2	7.7	23	69	20	<0.05	-	-	-	0.07	0.05	22	5.7	5.2	1.6	
P28w/3439	24 – 26	8 - 14	7.7	71	144	129#	<0.01#	21.8	9	0.31	0.22	0.05	99	10	6.8	5.9	
P28w/3667	38 – 40	5 - 11	8.0	32	109	36#	<0.05	16.5	5	0.21	1.7	0.02	61#	0.9#	1.0#	10.6	
P28w/4402	22 – 26	25 - 34	7.1	18.7	94	8.3	0.14	16.7	<1‡	0.04‡	0.44	0.07	12	14	7.4	0.7	9
P28w/4403	34 – 37	24 - 27	7.2	13.7	72	5.4	0.67	13.5	<1	0.03	0.03	<0.005	14	5.6	4.8	1.1	
Rarangi shallow																	
P28w/1634	? – 6	53 - 63	6.9	27	115	18	1.4	15.9	0.8	-	<0.06	<0.01	14	32	5.9	0.6	
Southern Valley Aquifers																	
P28w/1945	15 – 60	42 - 45	7.6	27	148	9.5#	0.06	21.9	<1‡	-	<0.02	0.20	26	17	8.9	1.3	210
P28w/3217	55 – 140	36 - 42	8.1	46	203	38#	<0.03	16.5	<1‡	-	<0.02	0.08	61	31	3.9	2.7	>250
Deep Wairau Aquifer																	
P28w/980	? – 87	1 - 2	8.1	71	180	140	0.002	18	18	0.96	0.48	0.19	115	17	6.7	6.0	39,000
P28w/3278	100 – 189	26	8.4	57	138	97	<0.01	13.7	3.8	0.7	0.02	0.014	97	17	0.5	6.2	19,500
P28w/3287	43 – 250	3 - 7	8.6	34	148	28	<0.15#	12	8	0.21	0.09	0.002	69	8.0	0.2	6.6	
P28w/3291	81 – 151	1 - 2	7.6	36	160	35	0.028	21	2	0.08	0.16	0.09	43	20	8.0	2.0	9,100
P28w/3333	201 – 318	1	7.3	42	144	56	0.08	16	-	0.22	0.56	0.05	68	14	5	4.0	21,000

Note: Alkalinity is expressed as HCO₃; Cond = conductivity @ 25°C; SAR = sodium adsorption ratio; MAV = Maximum acceptable value; GV = Guideline value.

* Range for number of samples.

§ Guideline value for aesthetic purposes

trend in data

‡ less samples for this parameter than for the remainder of the parameters for that well.

Lenntech, a water treatment company based in the Netherlands, (www.lenntech.com – accessed July 2011) states that a SAR value < 3 should give no problem for irrigation, values between 3 and 9 require care, and values > 9 are not suitable for irrigation. They also state that, while low levels of B are essential, higher levels can cause phyto-toxicity in sensitive plants. They indicate that low levels of B (<0.5 mg/L) should be fine for all crops, but levels of B in the range 0.5 – 1.0 mg/L could cause problems for sensitive crops such as peaches onions, wheat and grapes. Some of the effect may depend on the irrigation method as spray systems that apply irrigation to the leaves will enhance the phyto-toxic effect.

Some of the levels of SAR in the deep groundwater in the Wairau Valley, as seen in Table 1, are in the range where care is needed and some levels of B are in the range of 0.5 – 1.0 mg/L which may cause problems for sensitive crops. The likely effect of irrigation with this water on crops is outside the scope of this report and we have no expertise in this area. However as grapes are an important crop in Marlborough and the guidelines from Lenntech suggest some problems may occur if particular groundwater sources (Table 1) were used for irrigation, we recommend that someone with the necessary expertise is asked to review this aspect.

Ayotte et al. (2011) looked at the effects of human-induced changes of groundwater flow patterns for five different aquifer systems in the USA. They showed that there were several mechanisms for this to occur. One example was the mixing of shallow oxidic water with deeper confined anoxic water via wells that had been screened across both aquifers. This mixing resulted in the mobilisation of uranium from solid aquifer materials and the increase in dissolved uranium concentrations at nearby supply wells. Other examples involved changes in land use and pumping rates which could induce changes in groundwater quality.

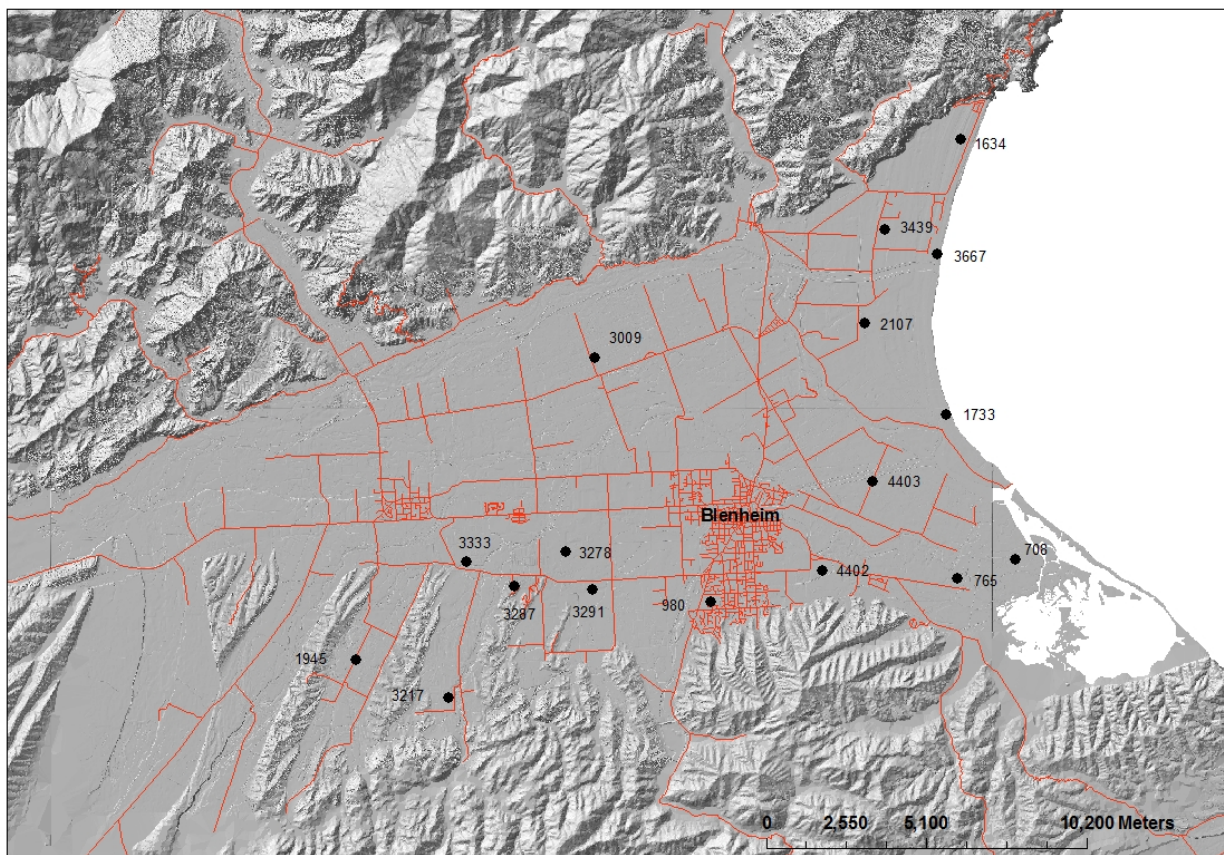


Figure 1: Location of wells from different aquifers in the Wairau Plains.

The deep groundwater in the Wairau valley can be sourced from a number of aquifers and can be mineralised to a variable degree (Table 1). These aquifers include the confined section of the Wairau Aquifer, particularly at the north and south fringes of the aquifer, the Southern Valley aquifers (Deep Brancott, Benmorven, etc) and the Deep Wairau Aquifer. Selected wells from the shallow aquifers, namely the Wairau unconfined aquifer and the Rarangi Shallow aquifer, are shown in Table 1 for comparison. The locations for the wells are given in Figure 1.

The arsenic levels in some of the deep wells in the DWA and the fringe areas of the Wairau confined aquifer can be elevated and approach the maximum acceptable value (MAV) of 10 µg/L (Ministry of Health, 2008). Well 980 in the DWA has an As value of 18 µg/L but there is only one analysis of As for this well and it should be repeated to confirm this level. Boron concentrations are highest in the DWA and 2 wells are > 50% of the MAV. As noted above some of the higher B levels may cause some phyto-toxic effects for sensitive crops.

Iron (Fe) levels are generally low but some wells in the Wairau confined aquifer and the DWA have levels above the guideline value of 0.2 mg/L for aesthetic purposes. All the values for Mn were below the MAV level of 0.4 mg/L but three wells, located in three different aquifers, were around 50% of the MAV (Table 1).

The sodium adsorption ratio was elevated for a number of wells in the Wairau confined aquifer and the DWA. The highest level observed was for well 3667, where the value was > 10. The sodium concentrations are decreasing with time but so are the calcium and magnesium levels so the SAR value remains high. It is recommended that someone with soil expertise is asked to review the effect of irrigation using groundwaters with SAR values > 3 on the soils in the Wairau Valley.

Several of the wells showed increases or decreases in parameter concentrations over time (Table 1). Cl was the most common parameter to display trends in concentration. An example is given in Figure 2 for Cl and Na concentrations for well 3667. The probable cause of these decreases in concentration is induced recharge of higher quality water from the main flow regions of the Wairau Aquifer to stagnant areas on the fringes of the aquifer due to pumping of well 3667. This would imply that the groundwater in well 3667 is becoming younger and it would be worthwhile to check this hypothesis by determining the age of this groundwater on at least 2 occasions over the next 5-10 years.

The ages of groundwater from these wells are given in Table 1 where available. The ages show that groundwater in the unconfined Wairau Aquifer is fairly young (well 3009 – 3.5 years). In the confined section of the Wairau Aquifer the groundwater ages increase and range from 9 years for well 4402 (reasonably close to the confined boundary) to 72 years for well 708 (on the southern fringe of the aquifer and near the coast – Figure 1). There are no ages available for the 3 wells on the northern fringe of the Wairau confined aquifer. This includes well 3667 where significant changes in groundwater quality have occurred over the past 10 years (Figure 2). It is recommended that age determinations be carried out for selected wells in the northern fringe of the confined Wairau Aquifer to confirm the reason for the change in groundwater quality in this area.

The relationship of selected chemical parameters, namely Cl, Na, and SiO₂, with the age of the groundwater was investigated (Figure 3). The data were plotted for all ages and for groundwaters less than 250 years to show the relationship clearly for those periods. Cl and Na showed a good relationship with age for the complete dataset ($r = 0.95$ and 0.89 , respectively), but SiO₂ showed no relationship for the complete dataset ($r = 0.03$). When the analysis was restricted to ages less than 250 years then the correlation for SiO₂ improved significantly ($r = 0.49$) and the correlation for Cl and Na remained strong ($r = 0.69$ and 0.80 , respectively). This indicates that the SiO₂ relationship with age that is being explored should not include groundwaters from the Deep Wairau Aquifer. Cl and Na give a good relationship

with age but care would be needed to avoid contamination with seawater. These graphs and correlations only include a limited number of wells (n=11 for the whole dataset and n = 7 for ages < 250 years) and it would be worthwhile to carry out this analysis for all the available data from the Wairau Valley aquifers.

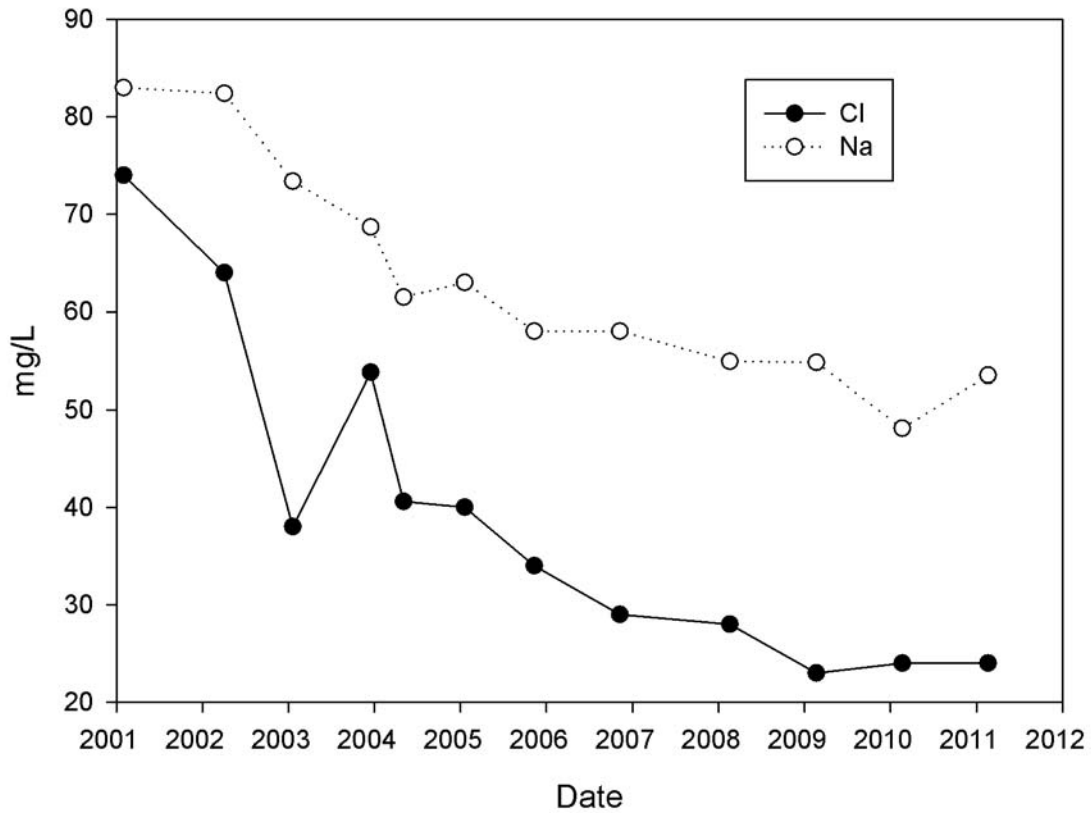


Figure 2: Decrease in Cl and Na concentrations with time for well P28w/3667.

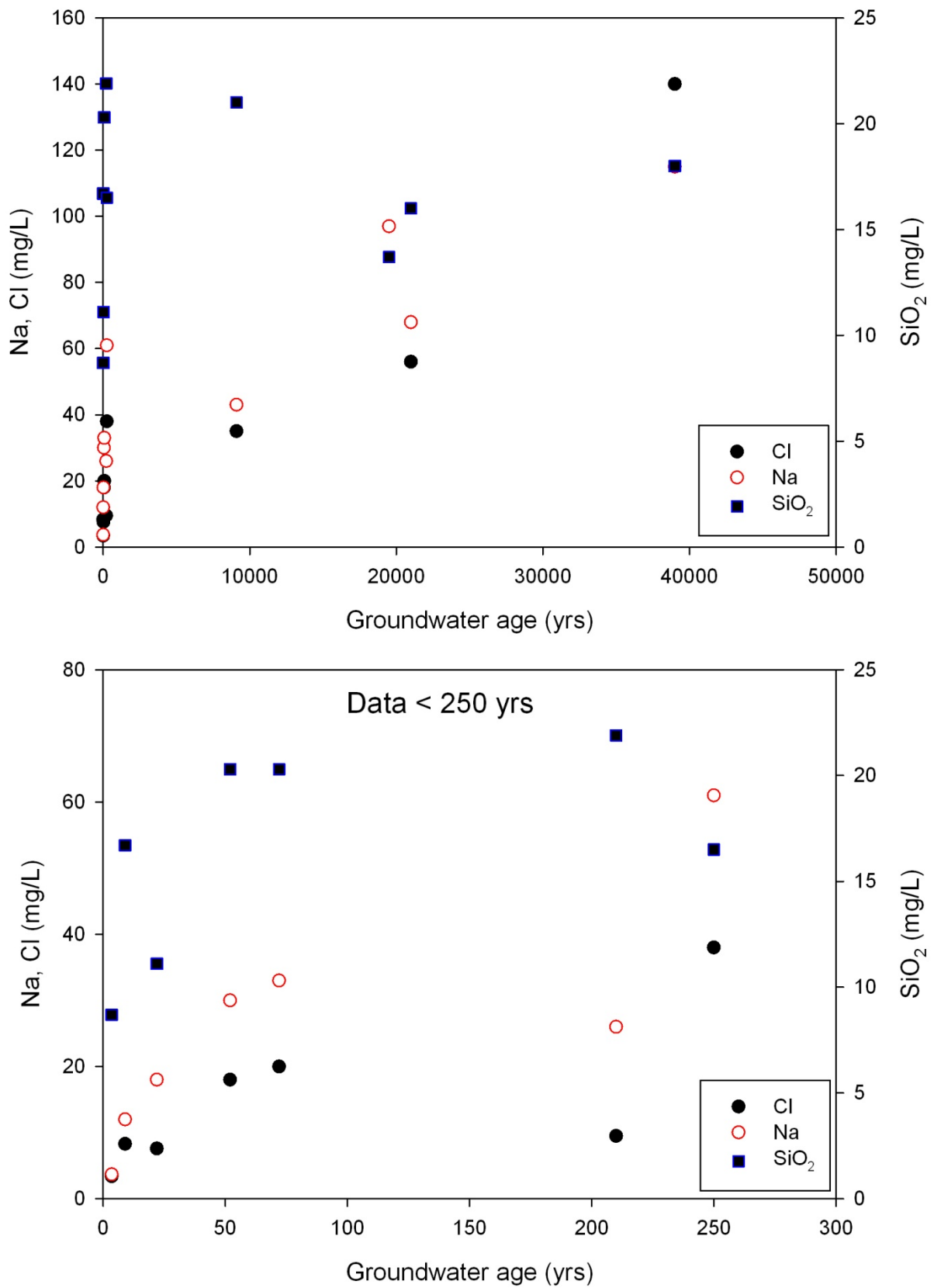


Figure 3: Variation in Cl, Na and SiO₂ concentrations with age (data from Table 1).

6 Development of a long term monitoring programme for the Deep Wairau Aquifer

There is a need to develop a long term (100 year) monitoring programme for the Deep Wairau Deep Aquifer (DWA) with 5 yearly sampling intervals. Currently there are automatic water levels recorders on 5 out of the 7 wells located in the DWA. Well 3278 is the only well that is currently being pumped and this well is monitored quarterly for selected chemical parameters as part of the MDC sampling network.

It is recommended that the annual sampling be carried out for well 3278 and that volumes of water pumped for the DWA are collated on an annual basis. Currently the pumping is confined to well 3278 but if other wells are pumped in the future the pumping information from these wells should also be collated. The samples should be analysed for pH, conductivity, major ions including SiO₂, and the following trace elements – As, B, Fe and Mn.

Every five years a more comprehensive sampling programme should be carried out for all the wells located in the DWA (currently there are 7 wells). If significantly more wells are installed in the DWA then the programme should be reviewed to sample a representative number. Samples should be analysed for age dating (probably using C-14), pH, conductivity, major ions including SiO₂, and the following trace elements – As, B, Fe, Mn, Br, F and ammonia.

7 Summary and Recommendations

A literature review did not reveal any published studies on the effect of irrigation method and source on age dating of shallow groundwater. One relevant unpublished study was a vadose zone tracing experiments where the leaching water, which was irrigated using drip irrigation, was found to retain its groundwater tritium age signature (ESR, unpublished data). This experiment indicated that the irrigation water had retained its “old water” age signature and had not re-equilibrated at the soil surface. This is not surprising as the irrigation method was drip irrigation which permits little opportunity for contact with the atmosphere. It is not known whether methods such as border strip or spray irrigation will result in re-equilibration at the soil surface. It is also expected that age tracers with differing degrees of volatility may re-equilibrate at different rates.

A work plan to determine how much of the age signature is retained for the different tracers and different irrigation application systems has been developed as part of this EnviroLink project. The necessary funding for this work has been approved and this research is planned to be carried out within the next year.

A literature review has been carried out on the effect of using deep groundwater sources for irrigation, focussing on the geochemical aspects. Much of the overseas literature deals with high levels of dissolved minerals and, for anoxic waters, high levels of As, B, Fe and Mn. The deeper groundwaters in the Wairau Valley have an extremely wide variation in age. The older groundwaters have increased levels of dissolved minerals, including As and B although levels of Fe and Mn are generally low. The As level in one well exceeds the MAV of 10 µg/L and As levels are > 50% of the MAV for 4 other wells. High levels of B (> 0.1 mg/L) are only observed in the Deep Wairau Aquifer and the northern fringe of the confined section of Wairau Aquifer. There are no wells with B concentrations above the MAV for drinking water.

The sodium adsorption ratio (SAR) is a measure of the suitability of water for use in agricultural irrigation. High levels of Na relative to the Ca and Mg can cause a decrease in infiltration and permeability of the soil to water leading to problems with crop production. Some of the deeper groundwaters have SAR values >3 which indicates that care is needed with respect to using this water for irrigation purposes.

A long term monitoring programme for the Deep Wairau Aquifer has been developed. It is proposed that the annual sampling continue for well 3278 and that every five years a more comprehensive sampling programme should be carried out for all the wells located in the Deep Wairau Aquifer.

Recommendations

- The arsenic levels in some of the deep wells in the DWA and the fringe areas of the Wairau confined aquifer can be elevated and approach the MAV of $10 \mu\text{g/L}$. Well 980 in the DWA has an As value of $18 \mu\text{g/L}$ but there is only 1 analysis of As for this well and it should be repeated to confirm this level. If any of the wells with As concentrations $>50\%$ of the MAV are used for drinking purposes then the owners should be advised.
- Some of the levels of SAR in the deep groundwater in the Wairau Valley are in the range where care is needed with respect to using this water for irrigation purposes. It is recommended that someone with appropriate soil expertise is asked to review the effect of irrigation using groundwaters with SAR values > 3 on the soils in the Wairau Valley.
- Some levels of B in the deep groundwater in the Wairau Valley are in the range of $0.5 - 1.0$ which may cause problems for sensitive crops. As grapes are an important crop in Marlborough and the guidelines from Lenntech suggest some problems may occur if groundwater with these levels of B were used for irrigation, we recommend that someone with the necessary expertise is asked to review this aspect
- It is recommended that age determinations be carried out for selected wells, including well 3667, in the northern fringe of the confined Wairau Aquifer to confirm the reason for the change in groundwater quality in this area. It would be necessary to have more than one age determination over a $5 - 10$ year period to confirm whether the water is becoming younger.
- It is recommended that the long term monitoring programme for the Deep Wairau Aquifer as described in section 6 is implemented.

8 Acknowledgements

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