

# Chapter 11 - Groundwater Chemistry And Quality

## Introduction

The majority of drinking water in the Marlborough District is sourced from groundwater. It is therefore essential that the quality of the groundwater resources are maintained and just as essential to have enough groundwater in the right place at the right time.

Marlborough's groundwater is generally of a very high quality. The most common exceptions are seasonally elevated nitrate levels or microbial contamination as a result of intensive landuse or human settlement. High levels of naturally occurring manganese, iron, arsenic, chloride, boron and sodium can occur in some aquifers.

Analysing samples of well water for its chemical composition not only determines its suitability for human consumption, but also provides an insight into aquifer mechanics. The levels of certain chemicals for example, can be used to estimate the residence time of groundwater. Knowledge of how these chemicals vary spatially can also tell us a lot about underground flow patterns.

For comparing the chemical composition of different groundwaters in this publication, the fractions of the major ions are plotted in a pie graph showing the concentration in milliequivalents per litre. This allows the groundwater to be categorised geochemically as a particular water type. The proportions reflect the fraction of each of the main dissolved minerals in groundwater.

## Groundwater quality and potability

When assessing water quality it is important to know what the water is intended to be used for, as some waters will be suitable for crop irrigation, but not for human consumption. For instance the presence of water-borne microbes can make a drinking water supply unpotable, but it may be satisfactory for the irrigation of a vineyard. Municipal or community drinking supplies have the strictest quality requirements that are governed by the 2005 Ministry of Health guidelines.

Historically groundwater in Marlborough has been noted for its high quality, but as greater depths are explored in new areas and analysed for new parameters, more examples of poorer quality groundwater are being found.

A 2001 survey identified for the first time the presence of naturally occurring substances in groundwater such as arsenic and boron at concentrations that can cause harm to human health. These recent investigations show there is still more to be discovered about Marlborough's aquifers, particularly about deeper aquifers and their chemical composition.

Most of Marlborough's long standing water quality issues are aesthetic rather than life threatening. Two of the most commonly occurring contaminants of this type are iron and manganese. These contaminants commonly affect older waters originating from deep, confined aquifers with sluggish flow; although they can affect younger groundwaters such as those associated with the Rarangi wetlands.

The common denominators for the presence of high iron and manganese levels are either chemically reduced conditions linked to a lack of oxygen, or long contact times between groundwater and the aquifer forming gravels. Both factors cause groundwater to naturally become more mineralised.

The degree of mineralisation found in Marlborough generally doesn't compare with the advanced evolution that occurs in parts of the Great Artesian Basin of Australia, or the High Plains (Ogallala) Aquifer system of North America, where groundwater moves over hundreds of kilometres over a long period of time. Local aquifers are too small and groundwater is generally too young to have progressed to this level of evolution.

A characteristic of the shallower groundwaters beneath the western Wairau Plain around Renwick or Woodbourne that has long been known about is its low pH and naturally corrosive nature of the water.

All of Blenheim's municipal groundwater supplies are treated with lime to increase the pH of groundwater to make it chemically neutral.

Contaminants such as manganese, iron and arsenic are absent from these areas of shallow groundwater because they are naturally insoluble in the acidic conditions.

Land-uses have had differing impacts on Marlborough groundwater quality from benign to significant. This largely reflects the natural characteristics of the local aquifer. High rates of through-flow associated with the Wairau Aquifer tends to dilute agricultural nutrient levels in groundwater, where the same land use practices applied in the Southern Valleys Aquifers would tend to cause nutrient levels to persist for longer.

Aquifer structure is an important factor in relation to aquifer contamination. The unconfined Rarangi Shallow Aquifer, for example, is more susceptible to contamination than the confined Wairau Aquifer underlying Blenheim.

Some chemical traits can be natural or man-made and a distinguishing factor as to their origin is residence time.

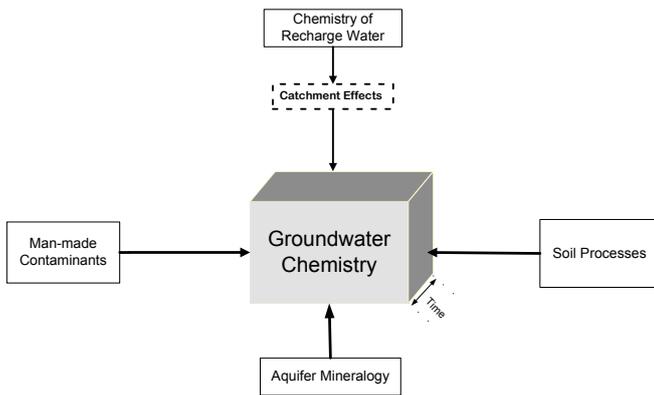


Figure 11.1: Influences on groundwater chemistry.

Younger groundwaters are more commonly associated with landuse contamination, while problems involving older waters are more likely to result from natural evolution processes (Fig. 11.1).

A growing realisation of the natural interdependence between groundwater and rivers or wetlands has led to a greater emphasis by the MDC on a whole catchment approach to understanding freshwater quality.

## Factors influencing groundwater chemistry

The chemical composition of groundwater is determined by a number of influences. These include the mineralogy of the rock types forming catchments or aquifers, overlying landuses, proximity to the coast, source of recharge water, soil type, aquifer structure and the time water has been underground away from atmospheric processes.

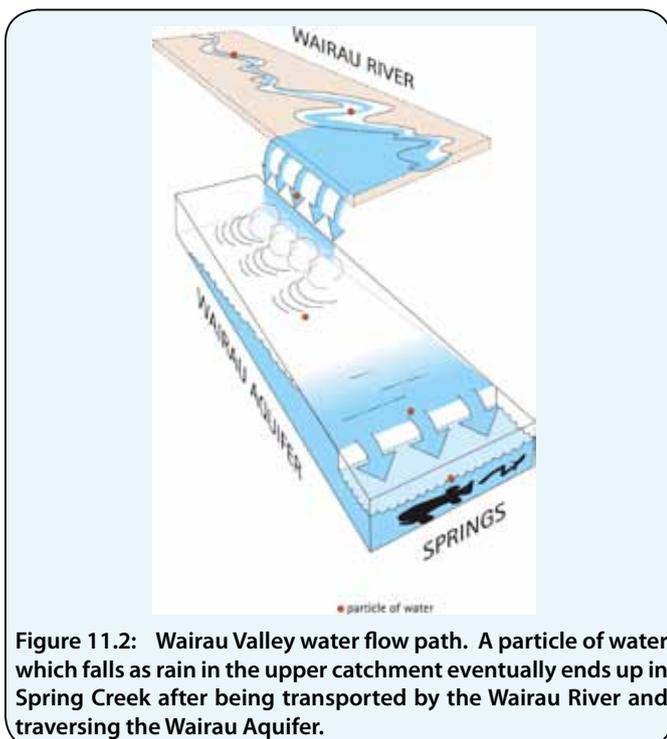


Figure 11.2: Wairau Valley water flow path. A particle of water which falls as rain in the upper catchment eventually ends up in Spring Creek after being transported by the Wairau River and traversing the Wairau Aquifer.

The biggest influence on the chemistry of Marlborough groundwaters are naturally occurring processes and to understand groundwater chemistry, it is necessary to be familiar with them.

One of the peculiarities of New Zealand aquifers are the localised differences in groundwater quality. This reflects New Zealand's unique combinations of geology, source of recharge water, subsurface flow patterns and overlying landuse. Marlborough is no exception.

Groundwater in Marlborough that has been recently recharged, either by rain or river water, will have a similar chemistry to its source water. It is only as groundwater becomes isolated from the oxidising influence of the atmosphere, and over time naturally evolves, that it becomes geochemically distinct.

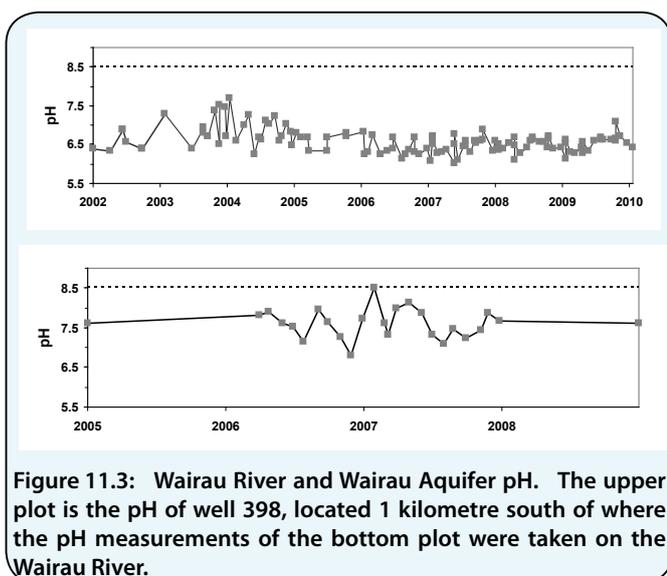
Generally all aquifer recharge water is chemically dilute with naturally low concentrations of dissolved salts. This changes as rainwater leaches natural salts from the soil on its downwards path to the water table.

River water has a low mineral content. As recharge of the Wairau Aquifer is dominated by this river water it also has low levels of dissolved minerals. The downside of the process of Wairau Aquifer recharge by the Wairau River is that it also provides a potential direct avenue for groundwater contaminants (Fig. 11.2).

Major changes in groundwater quality first occur in the soil or unsaturated zone above the water table and are driven by biochemical processes (Freeze and Cherry - 1979). The soil's influence is more apparent on groundwaters recharged by vertically infiltrating rainwater. Its effect however, may be less important where river recharge is dominant and the influence of the organic rich soil horizon is less and the Wairau River is a good example of this.

The soil zone represents a thin layer within the hydrological cycle, but it strongly influences the chemistry of surrounding groundwater due to its unique ability to generate carbonic acid ( $H_2CO_3$ ) which is formed when carbon dioxide ( $CO_2$ ) combines with water.

Carbon dioxide is more abundant in the soil layer than anywhere else in the travel path of groundwater, incorporating atmospheric  $CO_2$  arriving as rainfall, and as by-products of decomposing organic matter. This makes the soil layer a natural acid factory and many compounds or minerals in the unsaturated zone become dissolved as this water naturally drains downwards (Freeze and Cherry - 1979).



The acidification of new recharge water lowers the pH of groundwater once it arrives at the water table. The Wairau River channel water is naturally slightly alkaline, but Wairau Aquifer groundwater beneath the north-western Wairau Plain has a pH as low as 6 (Fig. 11.3).

The next major change in groundwater chemistry occurs at the water table. With increasing distance below the surface, oxygen becomes more scarce as the natural diffusion of atmospheric gases slows down.

Once saturated conditions below the water table are encountered, very little new oxygen is added and what remains is consumed by natural processes (Freeze and Cherry - 1979) (Fig. 11.4).

A number of natural biochemical and geochemical processes consume oxygen within the saturated zone. The most important involve microbes which rely on oxygen to survive and organic matter to eat. Both microbes and organic matter must be plentiful in Wairau Plain aquifers because we see high rates of natural denitrification in groundwater.

If groundwater ends up in a confined aquifer it is likely that all of the oxygen will at some point be consumed via biochemical reactions and what are known as anaerobic conditions are reached. At this point microbes need to find an alternative source of oxygen to sustain the metabolism of the food they are digesting, and turn to substitute compounds including nitrate, sulphate and iron or manganese complexes.

Another natural process which affects groundwater composition locally is cation exchange. This involves the movement of minerals from groundwater to clay particles forming the aquifer and vice versa. In Marlborough calcium ( $\text{Ca}^{++}$ ) dissolved in groundwater is commonly replaced by either potassium ( $\text{K}^+$ ), sodium ( $\text{Na}^+$ ) or magnesium ( $\text{Mg}^{++}$ ) salts adsorbed onto clays forming the aquifer structure.

This covers the full range of chemical environments found in Marlborough. While some processes are instantaneous, others occur incrementally over time-frames of hundreds or thousands of years.

## Chemical composition of groundwater

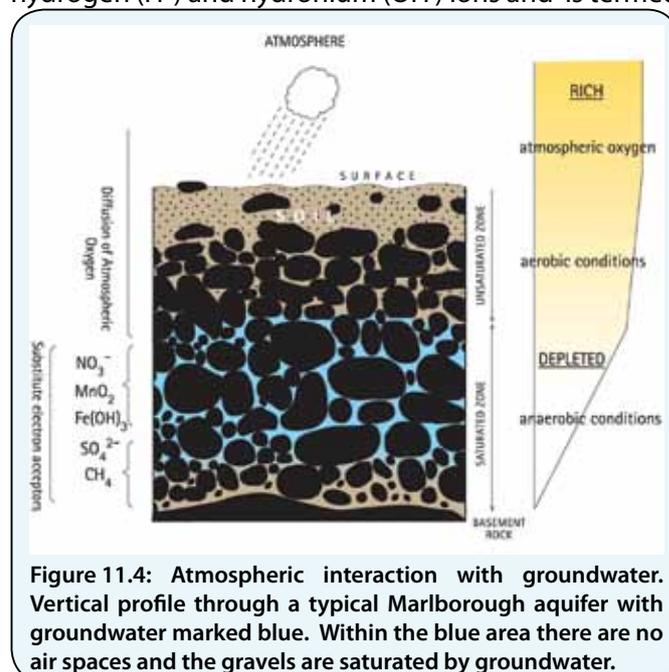
Groundwater contains many chemicals both naturally occurring and man-made. Some of which are present in large quantities whereas others occur as trace concentrations. Some are also very small in size and are chemically dissolved in the water while larger particles are commonly suspended. Since 2004 the MDC has followed the lead of the National Groundwater Monitoring Programme (NGMP) and filtered all groundwater samples to only measure the dissolved fraction.

The following sections describe each of the main chemicals found in Marlborough groundwaters, how these vary from site to site, and what this tells us about aquifer dynamics or the influence of landuses. In each case a plan view of the Wairau Plain shows the distribution of median concentrations in deeper groundwaters, excluding the Rarangi Shallow Aquifer. These maps show the pattern of specific chemicals and are used by the MDC to identify the dominant issues in relation to groundwater composition.

At present the understanding of the geochemistry of lesser developed aquifer systems away from the Wairau Plain is in its infancy and it will take several years to buildup a complete picture.

## pH

pH is a measure of the acidity or alkalinity of groundwater. pH 7 groundwater has equal numbers of hydrogen ( $\text{H}^+$ ) and hydroxide ( $\text{OH}^-$ ) ions and is termed



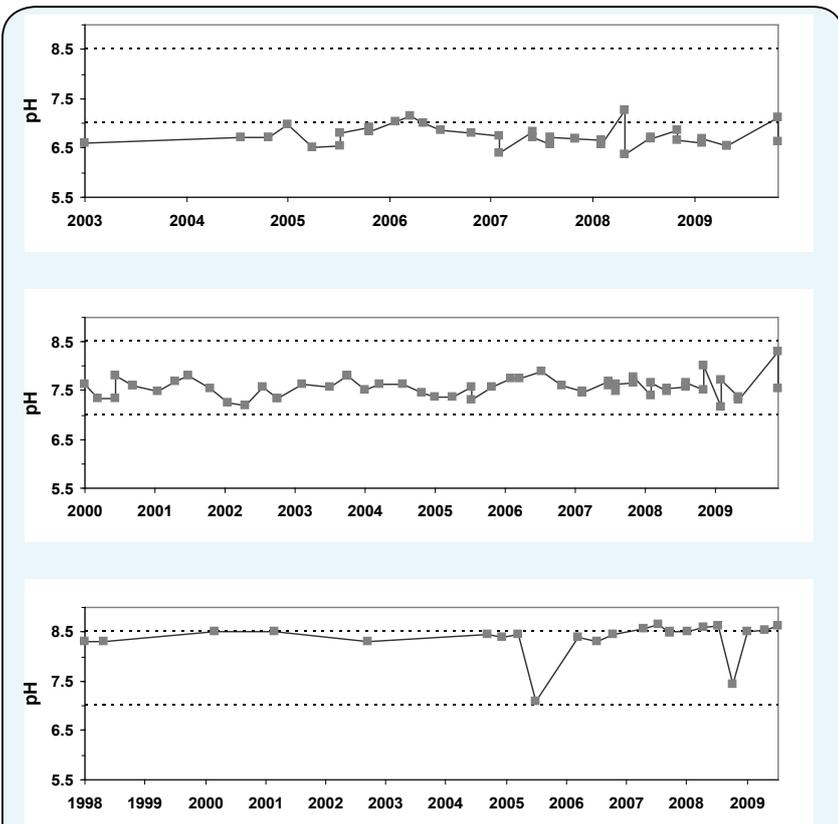


Figure 11.5: Wairau Plain groundwater pH variation. The top graph represents groundwater from a well tapping the unconfined Wairau Aquifer at Wratts Road (well 3009). This well has a low pH which typifies the unconfined Wairau Aquifer from the Waihopai River confluence east to Blenheim or Woodbourne. The middle plot shows moderately evolved groundwater (well 1945) from the Omaka Aquifer in Hawkesbury Road. This well represents groundwater from more isolated, semi-confined conditions. The bottom plot shows water from the Deep Wairau Aquifer (well 3278) beneath Fairhall. Note: The time series are over slightly different periods.

neutral. pH of rainfall is slightly acidic at 5.7 and tends to evolve to more neutral conditions in the environment.

pH is important because it controls many of the chemical reactions involving groundwater and it also strongly influences the presence or absence of arsenic, iron, manganese and nitrogen.

Generally acidic groundwaters are corrosive in nature, while alkaline groundwaters tend to be incrusting. For this reason the MDC treats its municipal water supply to correct the low natural pH of the groundwater supplied to Blenheim households. The aim of the treatment is to reduce corrosion of water mains and household plumbing.

The pH of Marlborough groundwaters is variable and reflects both the nature of the recharge water, catchment geology and its evolutionary history (Fig. 11.5). While surface waters such as

the Wairau River are generally slightly alkaline, nearby shallow groundwater has a pH of 6 to 7 due to the acidifying influences of natural soil and atmospheric processes. This compares with pH values of between 7 and 8 for older groundwaters in confined aquifers near the Cloudy Bay coast, the deeper levels of the Southern Valleys Aquifers and the Deep Wairau Aquifer (Fig. 11.6). Higher pH is caused by increased bicarbonate ( $\text{HCO}_3^-$ ), a by-product of natural reduction reactions taking place in confined aquifers, or carbonate rich rock types such as those found in the Flaxbourne River catchment.

### Electrical conductivity

Electrical conductivity is widely used as an indicator of the dissolved solids or salts in groundwater. Electrical conductivity has the advantage of being easy to measure in the field using a portable meter which is comparable with values from other regions. The more dissolved salts a groundwater contains, the easier it passes electrical current and the higher its conductivity becomes.

This is illustrated by the close match between dissolved ions and electrical conductivity for a survey of North Bank related waters in 2009 (Fig. 11.7).

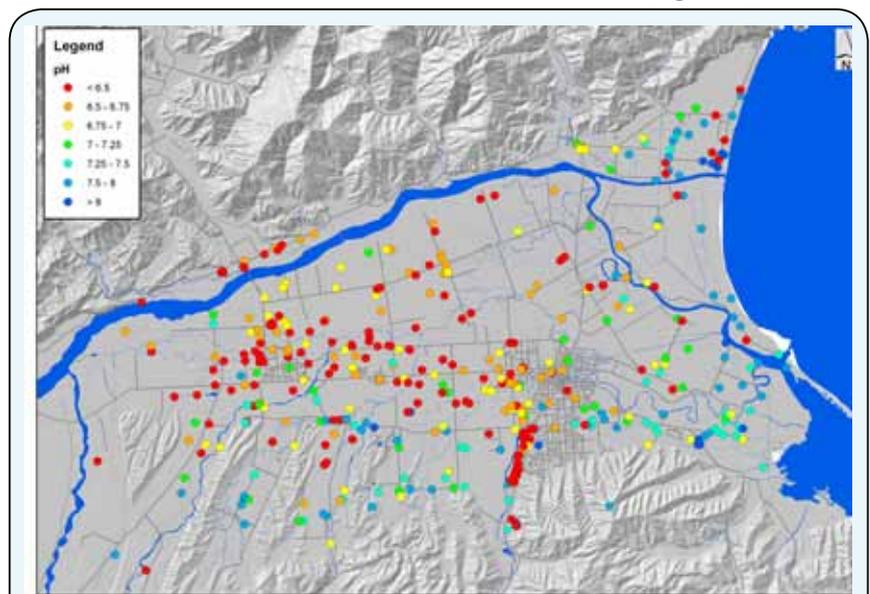


Figure 11.6: Median pH of Wairau Plain groundwater (Excluding Rarangi Shallow Aquifer). Younger, low pH groundwater dominates the central area marked by red or yellow dots, with alkaline groundwaters on the fringes in blue or green associated with confined groundwaters. The groundwater of confined aquifers located on the edges of the Wairau Plain is older and naturally more evolved. The evolution process has produced higher concentrations of bicarbonate, which increases pH marked by blue or green dots.

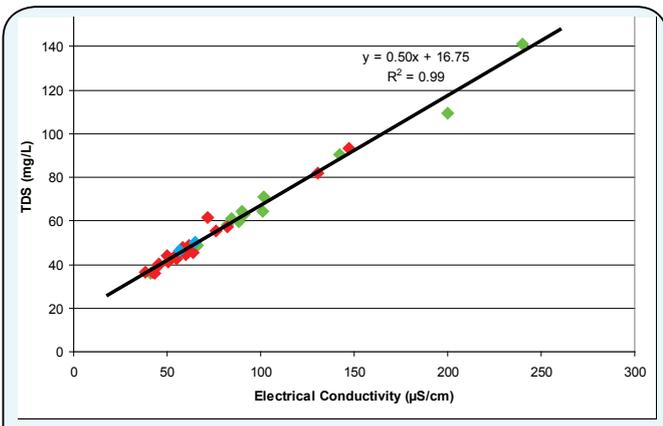


Figure 11.7: Total dissolved solids versus electrical conductivity (Botting - 2010). Red points are surfacewater sites, green are groundwater sites and blue is the Wairau River. Groundwaters shown in green have higher concentrations of salts and as a consequence have higher electrical conductance compared to that of river waters. One of these parameters can be predicted from the other based on the simple linear relationship between them.

A clear regional flow pattern exists for the conductivity of Wairau Plain groundwaters. A pronounced tongue of dilute water with conductivity values of less than 10 mS/m, extends in a north-west to south-east direction in the Rapaura area. This corresponds with the fastest moving groundwater which has had less opportunity to dissolve minerals. Conductivity values increase on the margins of the valley, as groundwater flow slows and rates of mineralisation increase (Fig. 11.8).

Higher conductivity values in shallower wells are caused by a combination of overlying landuses and aquifer processes. By contrast the conductivity of deeper groundwater at Rarangi or Riverlands only reflects natural aquifer reactions due to their isolation. High values in the Taylor Pass area represent measurements from landfill leachate monitoring wells.

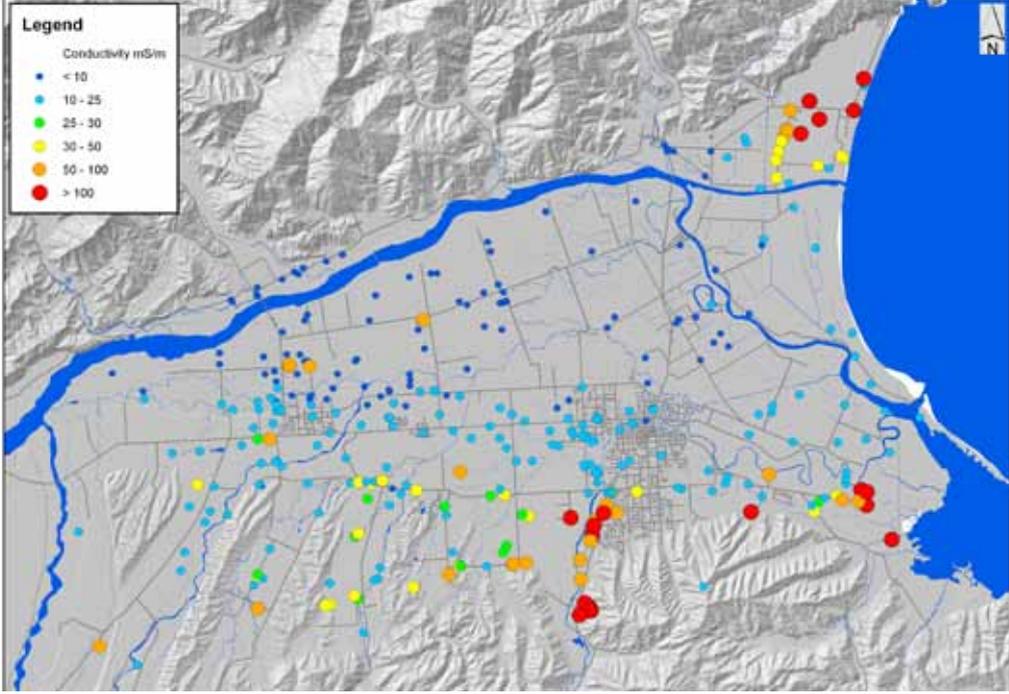


Figure 11.8: Median electrical conductance values excluding Rarangi Shallow Aquifer.

### Dissolved oxygen

Generally river or rain waters are saturated with atmospheric oxygen. The amount of oxygen in local groundwaters can range from virtually no oxygen in the isolated confined aquifers at Riverlands, to the fully saturated shallow aquifers that are open to the atmosphere near Renwick.

Aquifers which are less isolated from the atmosphere with an unconfined structure, have higher levels of oxygen. An exception to this is the large range in dissolved oxygen concentrations observed within the Rarangi Shallow Aquifer (RSA). These range from anaerobic conditions at an inland well (4442), to moderately aerobic conditions at wells closer to the coast (3668). While the RSA has an unconfined structure that is open to the atmosphere, biochemical processes associated with the wetlands are likely to consume much of the free oxygen. This explains the presence of the anaerobic conditions inland. Coastal areas have fewer wetlands and dissolved oxygen levels are higher (Fig. 11.9).

Measuring natural dissolved oxygen levels in groundwater in the field is not straightforward as pumping can cause aeration which can artificially raise dissolved oxygen levels.

### Alkalinity

Alkalinity is a measure of the ability of a substance to neutralise acids. The key elements contributing to alkalinity are bicarbonate and carbonate. The main sources of these are from natural reactions between water and carbon dioxide, or as by products of naturally occurring reduction processes.

Carbonaceous rocks are also a source of alkalinity but they are rare in Marlborough with only localised outcrops of limestone ( $\text{CaCO}_3$ ) influencing groundwaters in parts of the Flaxbourne and Waima/Ure catchments.

Another natural source of alkalinity are shells found in marine sediments such as the Papa mudstones of the East Coast, or the marine clay confining layer underlying the Lower Wairau Plain.

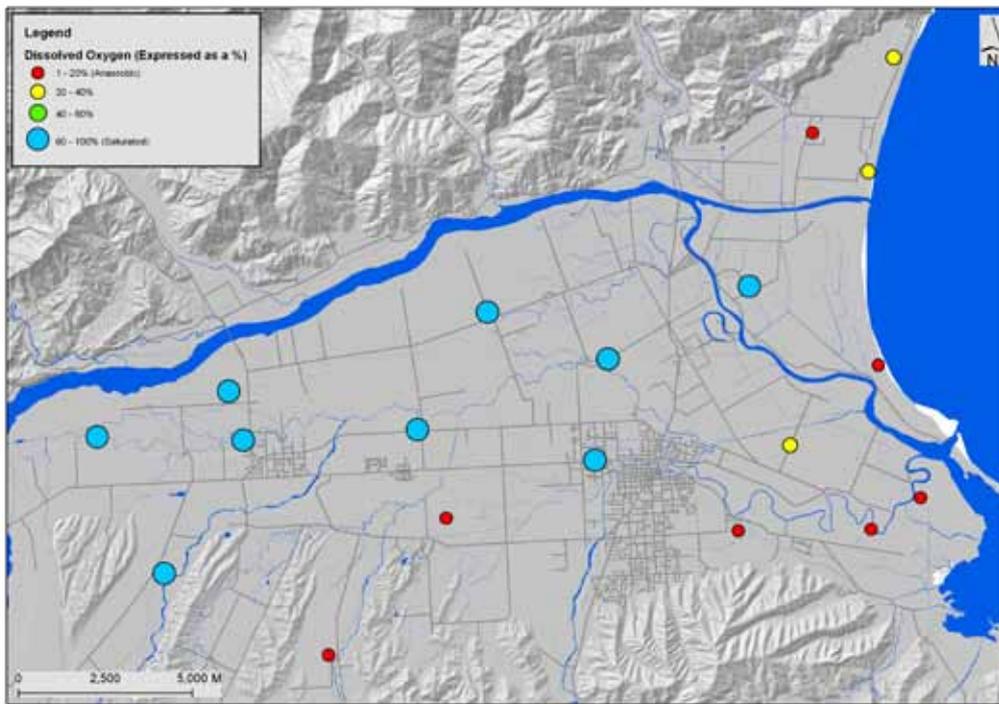


Figure 11.9: Wairau Plain groundwater dissolved oxygen levels

Alkalinity values are relatively low in absolute terms for most Wairau Plain groundwaters. Concentrations increase away from the main axis of groundwater flow beneath the Wairau Plain due to increasing levels of bicarbonate ( $\text{HCO}_3^-$ ) produced by natural reduction reactions (Fig. 11.10).

Alkalinity is controlled by varying proportions of bicarbonate ( $\text{HCO}_3^-$ ), carbonate ( $\text{CO}_3^{2-}$ ) and carbonic acid ( $\text{H}_2\text{CO}_3$ ). Bicarbonate is the predominant species in Marlborough aquifers due to the pH range of local groundwaters. The concentration of alkalinity in groundwater is normally expressed as the equivalent amount of either calcium carbonate ( $\text{CaCO}_3$ ) or bicarbonate ( $\text{HCO}_3^-$ ).

A plot of bicarbonate versus calcium on a milliequivalent basis is a good way of checking its source in Marlborough groundwaters (Fig. 11.11). If the sample is principally from calcium-carbonate rock deposits, it will fall on the 1 to 1 line dashed line (Rosen - 2001).

### Magnesium

Local rocks are the main source of magnesium in Marlborough groundwater. As rocks are eroded and transported by rivers

as alluvial sediments, they slowly dissolve and release magnesium and other chemicals into the groundwater over time. A small amount of magnesium may also come from the use of agricultural fertiliser.

The pattern of magnesium concentrations is consistent with older groundwater and natural evolution processes, rather than landuse effects (Fig.11.12). Concentrations in Southern Valleys groundwaters are relatively high by international standards.

### Calcium

Calcium is one of the most common components of young Marlborough groundwaters, but it is at relatively low concentrations by world standards. Many fossil shells making up the coastal marine sediments beneath Cloudy Bay are formed of calcium carbonate. These shells dissolve over time and enrich the calcium concentration of the local groundwater. Calcium can also originate as lime in agricultural fertilisers.

In the Ward area calcium levels are higher than the regional average due to the presence of shell-rich, marine mudstone and some carbonate rocks.

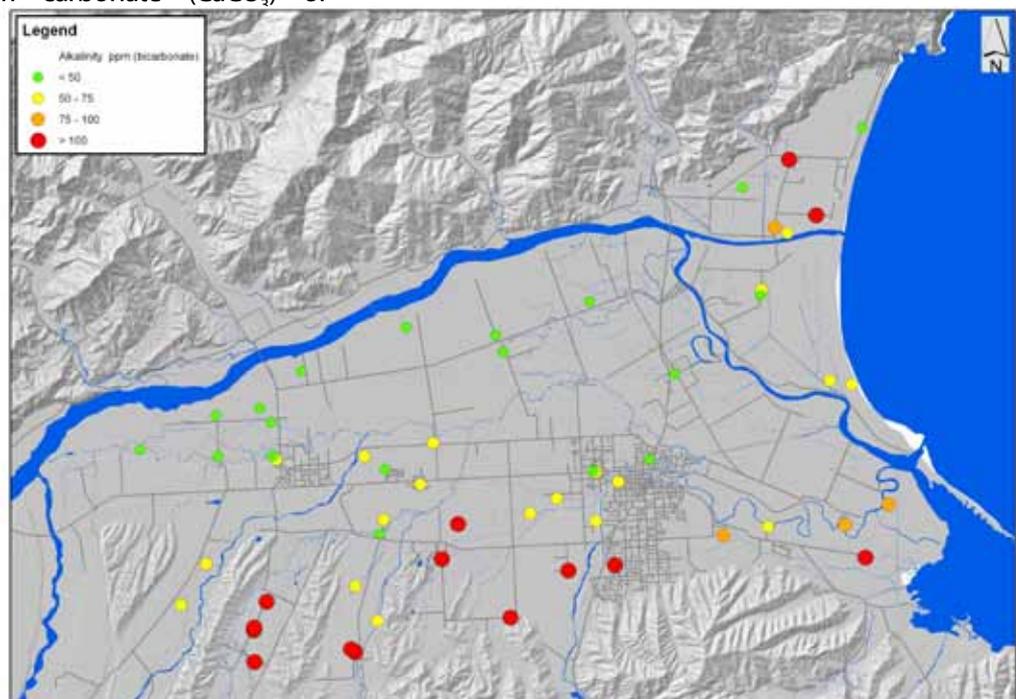


Figure 11.10: Median alkalinity concentrations excluding Rarangi Shallow Aquifer

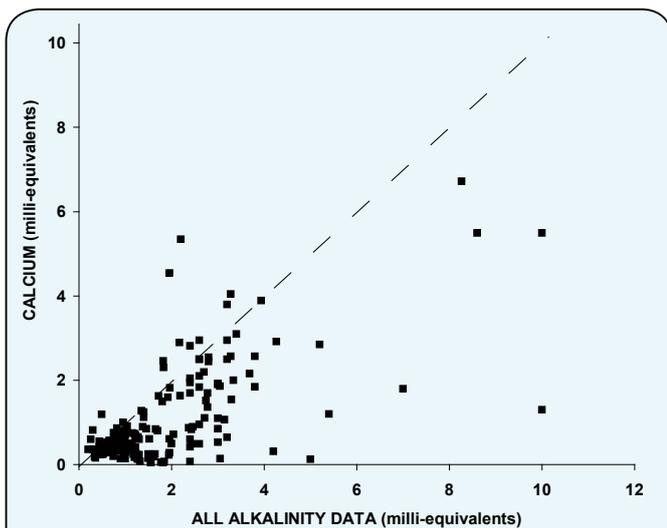


Figure 11.11: Mean calcium versus bicarbonate concentration for all aquifer waters in Marlborough. Most of the points do not fall on the line but are relatively enriched in bicarbonate, confirming they are mostly by-products of soil organic processes or reduction reactions. This is consistent with the relative scarcity of carbonate rock formations in Marlborough. However some Rarangi Shallow Aquifer waters are significantly influenced by calcium carbonate ( $\text{CaCO}_3$ ) presumably due to contact with fossil shell beds.

The concentration of calcium in groundwater is low across the northern Wairau Plain. This reflects the background levels of the Wairau River recharge water, which dominates this area. Calcium increases on the edges due to natural water rock interaction (Fig. 11.13).

Calcium is also removed from groundwater as it flows from west to east beneath the Wairau Plain due to cation exchange. This involves the exchange of calcium in groundwater with magnesium or sodium, on clay particles forming the aquifer. This may explain the lower concentrations associated with deeper groundwater in the coastal area, in what are calcium rich sediments.

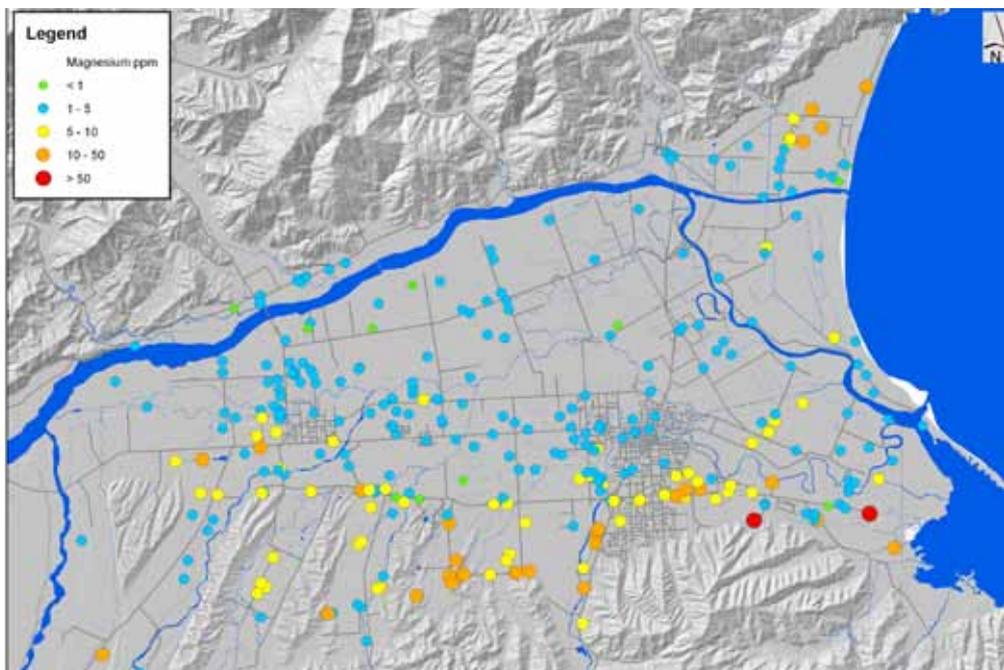


Figure 11.12: Median magnesium concentrations excluding Rarangi Shallow Aquifer

## Hardness

Hard water results from high levels of calcium and magnesium. Hard water makes it difficult for domestic water users to form a lather when washing, and can cause the buildup of scale in boilers when it evaporates. Hardness is defined as the concentration of calcium and magnesium in water expressed as the equivalent of calcium carbonate ( $\text{CaCO}_3$ ).

Most groundwaters in Marlborough are classed as soft with values of less than  $75 \text{ g/m}^3$ . Higher values are associated with highly evolved groundwater at Wairau Valley, in shell beds forming parts of the Rarangi Shallow Aquifer and the Needles Creek Gravels Aquifer (Fig. 11.14).

## Chloride

Most chloride in inland groundwaters originates indirectly from evaporated seawater that enters aquifers as rainfall recharge. Rainfall contains high levels of chloride near the coast and as a consequence it is found at higher concentrations in groundwaters that originate nearer to the coast. This effect does not apply to deeper coastal wells which are recharged from waters that originate inland.

Local exceptions include an evaporite deposit at Wairau Valley related to upwelling saline fault fluids, seaspray in shallow groundwater in coastal wells at Rarangi and interaction with salt rich marine sediments near the coast.

Chloride is dissolved in groundwater as it flows through marine sediments rich in connate salts. While some free flowing formations have been flushed of salts over geological time, the lower permeability Benmorven

Aquifer, which is partially formed of marine clays, retains much of its salt. These salts will persist for a long time to come.

Chloride is a conservative constituent of groundwater. This means that it doesn't readily react with other chemicals, and isn't chemically altered as it travels along its underground flowpath. For this reason it is commonly used by hydrologists to track natural flow patterns.

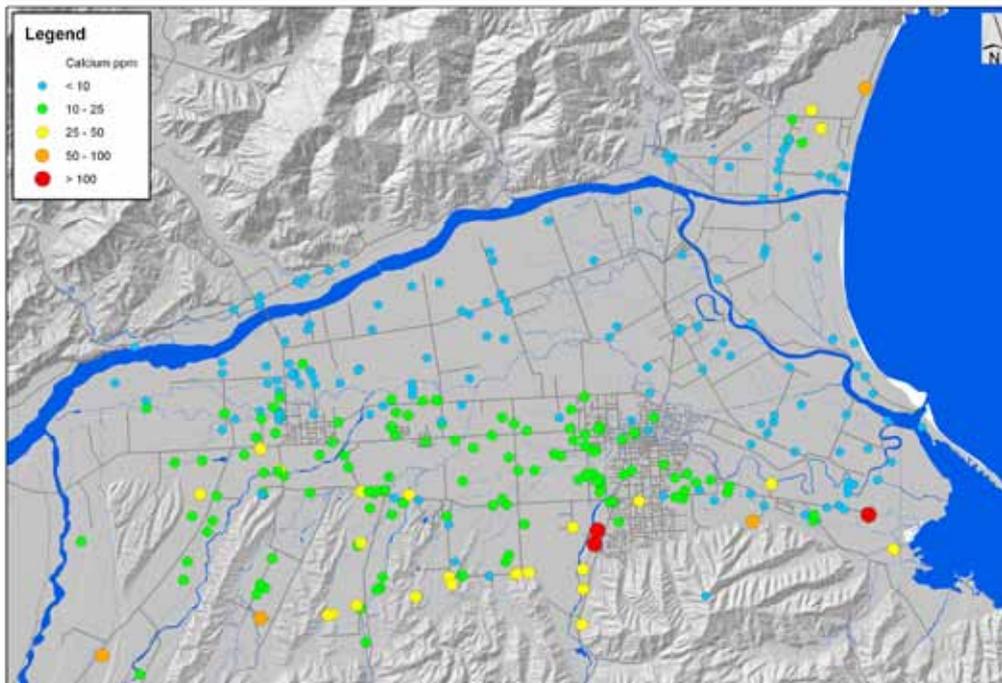


Figure 11.13: Median calcium concentrations excluding Rarangi Shallow Aquifer

Induced changes to natural groundwater flow regimes through increased pumping, shifts in the pattern of aquifer recharge, or changes to soil structure can be reflected in the chemistry of groundwater. Chloride is a good natural indicator of this occurring.

Chloride concentrations are very low for the majority of Wairau Plain groundwaters, but increase sharply on the margins of the Wairau Plain where flow is sluggish and there is more water-rock interaction (Fig. 11.15). Values remain low along the central coastal area despite the chloride rich marine deposits. This suggests these sediments have been flushed of salt over geological time. Some chloride may also be fault related.

One way of determining the origin of chloride is by comparing the ratio of sodium to chloride in groundwater with the natural ratio of these salts in ocean water. If the predominant source is rainfall rather than minerals from local rocks, they will fall on a line known as the seawater concentration dilution line (SCDL) (Fig. 11.16).

### Sodium

The distribution of sodium in Wairau Plain groundwaters is similar to that of chloride. Both salts occur together in marine deposits, although sodium is a more common by-product in groundwater as a result of the breakdown of clay minerals (Fig. 11.17).

### Iron

Iron and manganese are often found together in anaerobic groundwaters in Marlborough. Both are derived from natural water-rock processes rather than landuse activities (Rosen - 2001). Iron and manganese are generally insoluble in the oxygen rich groundwaters that underlie the western Wairau Plain and as a result well owners in areas around Renwick or Rapaura are not affected by their presence.

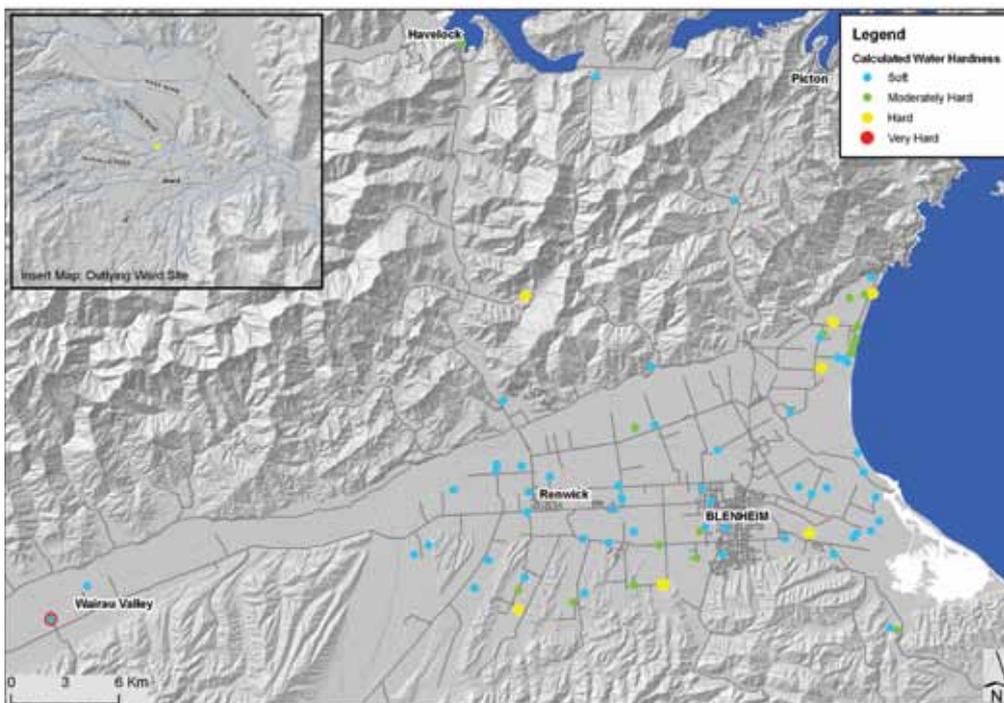
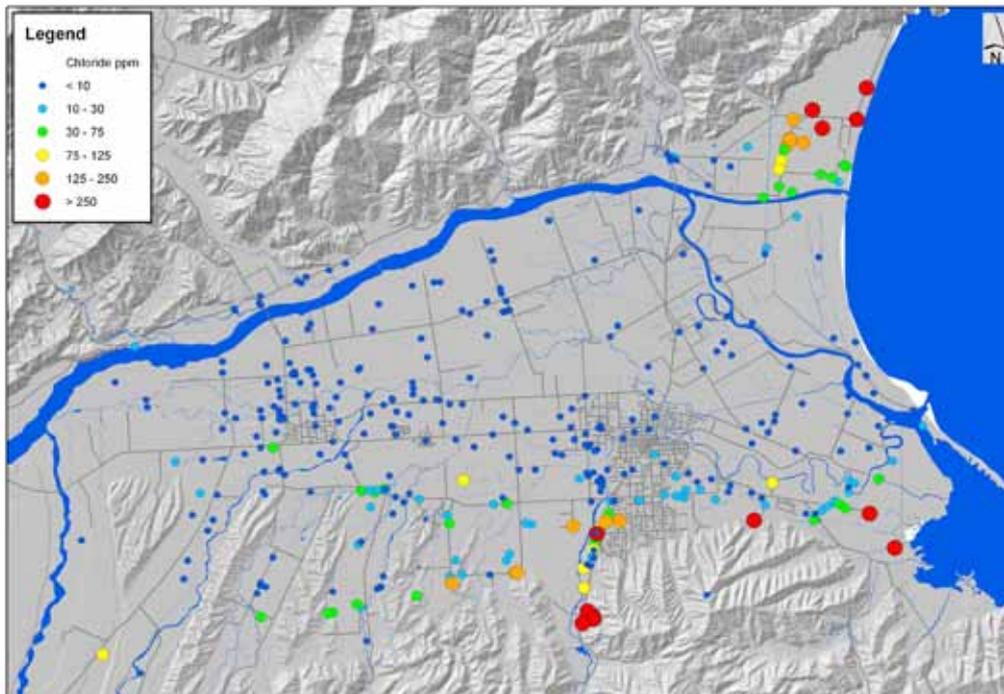


Figure 11.14: Groundwater hardness for all aquifers

Concentrations of iron in groundwater of greater than 0.2 g/m<sup>3</sup> can encrust pumps and cause staining of whiteware and carpets. The concentration of iron in Wairau Plain groundwaters is less predictable than for other parameters (Fig. 11.18). Based on reports from well owners it can also be a seasonal issue, linked to rain events or changes in water table depths.

Higher monitoring values, prior to filtering samples, may be biased by the presence of suspended particles of iron knocked



**Figure 11.15: Median chloride concentrations excluding Rarangi Shallow Aquifer** off the well casing rather than representing iron dissolved in groundwater. This explanation is supported by the differing distribution for manganese which behaves in a similar way chemically.

A less common iron related problem are iron bacteria, which are small living organisms which can co-exist with inorganic iron. These bacteria have the potential to choke the screen of a water well making it unusable. To date iron bacteria have only been positively identified by the MDC in wells at Neal Road, Rarangi and Riverlands. It is thought however, that they are more widespread and have the potential to exist in conditions where iron concentrations are high.

### Manganese

Manganese occurs naturally in groundwater. It can cause staining to whiteware at concentrations above  $0.04 \text{ g/m}^3$ , and affect human health at concentrations of greater than  $0.4 \text{ g/m}^3$ . Levels exceed these thresholds around the margins of the Wairau Plain where groundwater flow is sluggish (Fig. 11.19).

Closed landfills or contaminated sites in the Taylor Pass area also contribute to elevated manganese levels.

Manganese concentrations can be reduced to safe levels through treatment.

Manganese dioxide is a distinct black colour compared to the familiar orange-brown of iron oxide commonly known as rust.

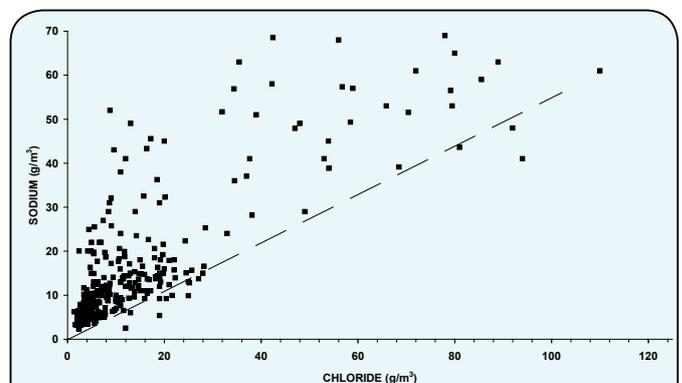
### Nutrients

Nitrogen, sulphate, potassium and phosphorus are all nutrients which occur naturally in local groundwaters, or can also be added by man-made sources. Agricultural fertilisers are the most common source of nutrients in local groundwaters. Other sources include animal and human waste. Nutrients are mostly found in low concentrations in Marlborough groundwaters with the exception of nitrogen and to some extent sulphate.

The Wairau Plain has been intensively farmed since European settlement and artificial nutrients have been used over that 150 year period to maintain soil fertility. To avoid nutrients leaching to groundwater the rate at which fertiliser is applied to land needs to be balanced by plant requirements.

Not only can groundwater be affected, but it can also affect aquifer fed springs. These can potentially become eutrophied and their fauna or flora degraded by higher concentrations of nutrients encouraging algae growth.

Thin alluvial soils underlying the western Wairau Plain or at Rarangi are more vulnerable to leaching of nutrients than heavier soils.



**Figure 11.16: Mean sodium versus chloride concentration for 415 wells representing all of Marlborough aquifers.** The dashed line is the seawater concentration dilution line (SCDL). A few Marlborough groundwaters fall near the line representing recycled seawater, but most are enriched in sodium, presumably as a result of water-rock interaction.

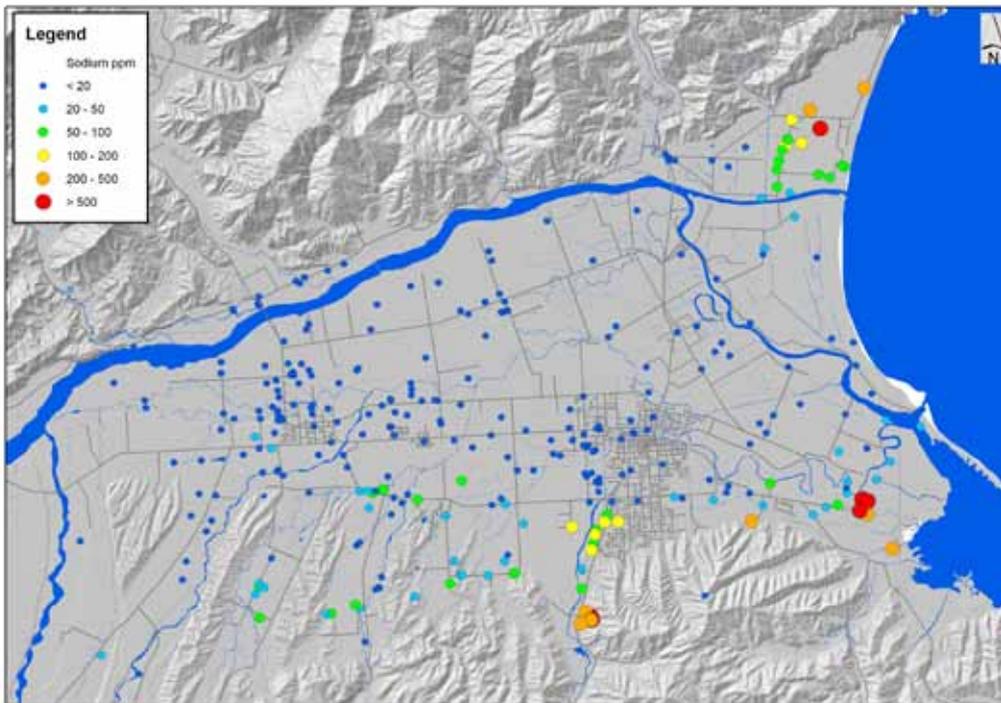


Figure 11.17: Median sodium concentrations excluding Rarangi Shallow Aquifer

Because sulphate and nitrate are subject to natural denitrification processes, their absence in groundwater does not necessarily mean they have not been present. This is especially true of Marlborough groundwaters which are rich in organic material and bacteria, the main agents of denitrification.

### Nitrogen

Nitrogen is the most common contaminant of groundwaters worldwide and also for Marlborough aquifers (Todd - 1980). Its presence normally indicates that overlying landuse practices are affecting groundwater below.

Nitrogen comes in a number of forms and can be reversibly transformed depending on natural conditions. Care is needed in assessing the presence or absence of a particular form of nitrogen due to these natural degradation processes. For instance, low levels in the confined aquifer beneath the Lower Wairau Plain may not mean it was never present.

The most common form of nitrogen in Marlborough aquifers is the oxygenated variety nitrate ( $\text{NO}_3^-$ ). This reflects

the high percentage of local aquifers which are unconfined and connected to the atmosphere. Furthermore, nitrate concentrations aren't limited by natural solubility limits which means that groundwater can dissolve as much nitrogen as overlying landuses can potentially produce. Nitrogen is also very mobile. This means that landuses in the western Wairau Plain can generate nitrate that will naturally accumulate along its flowpath without being altered until the confined aquifer, east of Blenheim.

Groundwater nitrate concentrations of greater than 1 to 3  $\text{g/m}^3$  indicate human inputs and concentrations above 11.3  $\text{g/m}^3$  in drinking water can be harmful to human health and make the water unfit to drink. Nitrate levels in local groundwaters vary considerably both spatially and seasonally.

Nitrate isn't the only form of nitrogen present in local groundwaters. In confined aquifers with oxygen deficient or anaerobic conditions, nitrate is naturally reduced to ammoniacal nitrogen and further to nitrogen gas. This process is called denitrification and it actually improves groundwater quality from a human

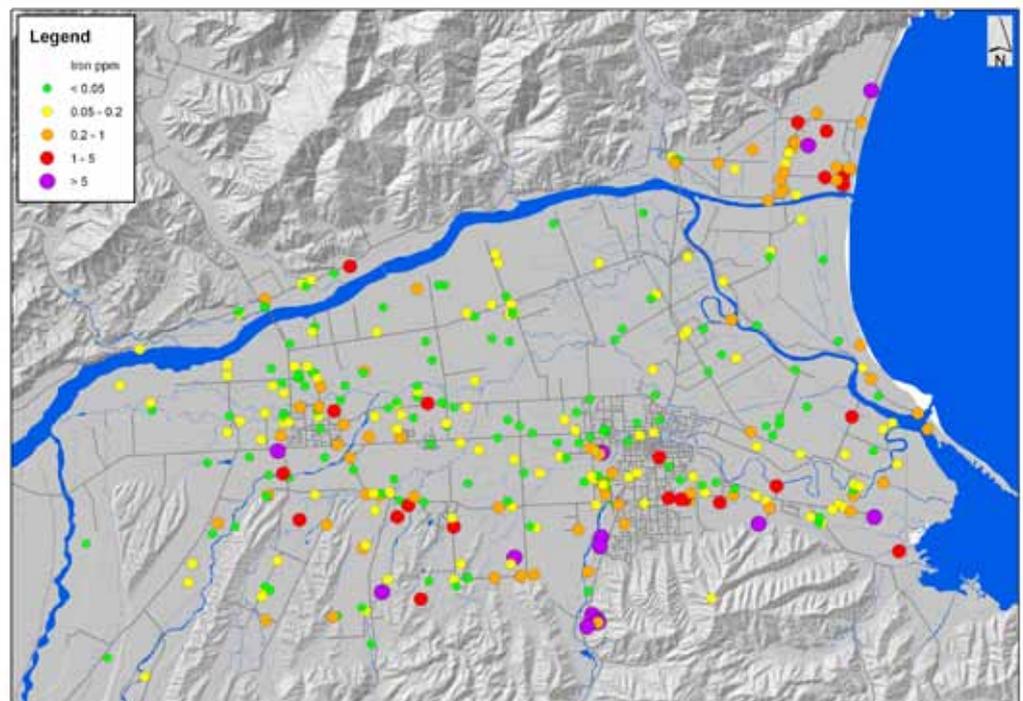


Figure 11.18: Median iron concentrations excluding Rarangi Shallow Aquifer

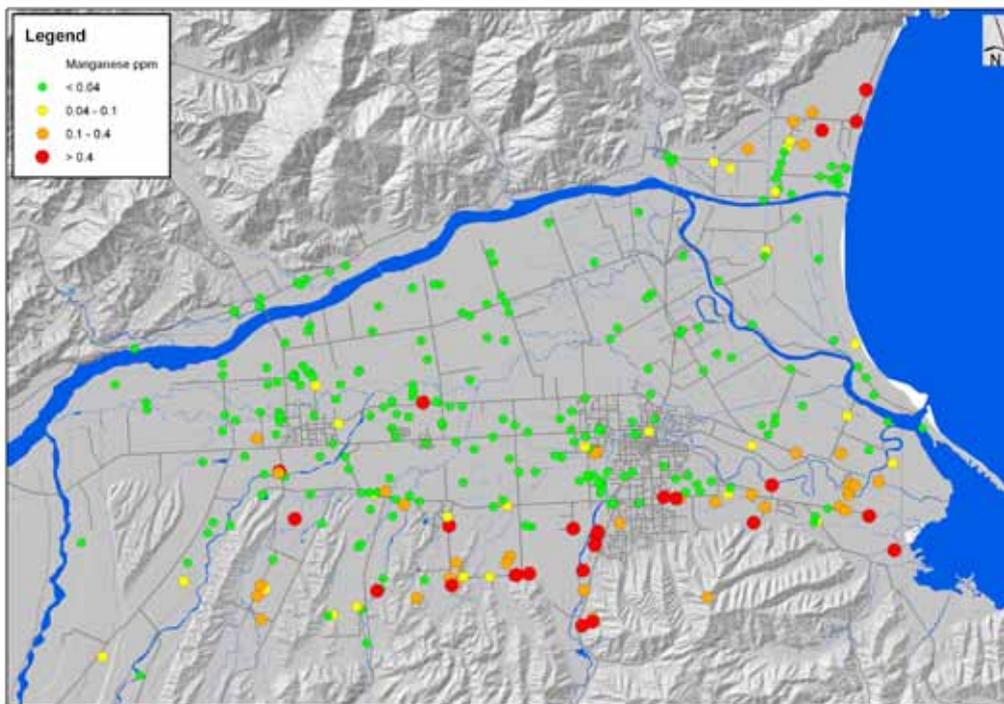


Figure 11.19: Median manganese concentrations excluding Rarangi Shallow Aquifer

health and eutrophication perspective by reducing nitrate levels. However this process can also produce small amounts of the greenhouse gas nitrous oxide if the process does not proceed through to nitrogen, which is the main component of air.

### Nitrate-nitrogen

Nitrate contamination is not a major problem in Marlborough aquifers. Historically there have been hotspots west of Renwick, at Rarangi, in the Lower Fairhall/Brancott Valley, Doctors Creek catchment, and associated with the Wairau Fault in the Lower Waihopai Valley. These persistent levels have been attributed to historic arable or dairy farming. They occur in areas on the southern margin of the main aquifer where groundwater flow rates are lower. Less dilution occurs in these areas compared to the main Wairau Aquifer, where similar land-uses also existed.

Nitrate is subject to natural degradation processes in the anaerobic aquifer conditions found within confined aquifers. This explains why concentrations are low beneath the Cloudy Bay area, or in deeper wells in the Southern Valleys (Fig. 11.20).

Not all elevated nitrate levels can be explained as a legacy of previous land-use. Part of the explanation is likely to involve the introduction of irrigation on thin soils in particular, or short-lived effects associated with landuse conversions. Recirculation of water on irrigated land will leach chemicals both natural and man-made downwards. Its effect will depend on a number of factors including the degree of groundwater flow, depth to the water table and the composition of the soil layer.

It is likely that fertiliser use is now more widespread but at lower application rates than for traditional mixed farming which predominated on the Wairau Plain up until the late 1980s. The almost universal practice of vineyard irrigation is likely to have increased leaching and transport of nutrients to the water table.

Elevated nitrate levels usually occur as short-lived spikes, before returning to their ambient value for that particular aquifer. This is particularly true of reducing conditions when denitrification is the dominant process such as in wetlands or low lying areas of the Rarangi Shallow Aquifer.

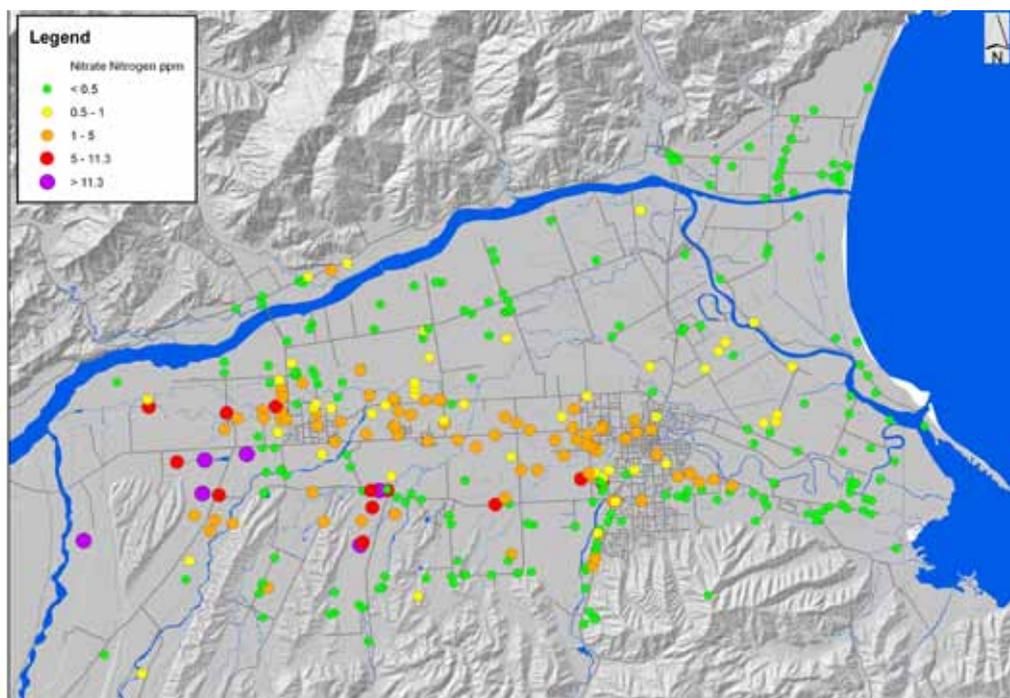


Figure 11.20: Median nitrate concentrations excluding Rarangi Shallow Aquifer

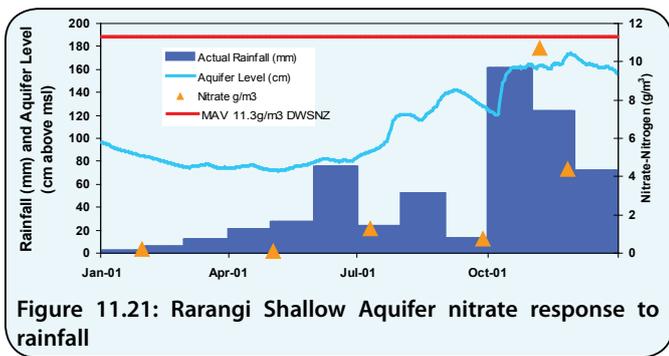


Figure 11.21: Rarangi Shallow Aquifer nitrate response to rainfall

Some of the highest nitrate levels were recorded during the exceptionally wet spring of 2001 when rain maximised the rate of leaching of fertilisers in the soil with nitrate-nitrogen concentration rising in November 2001 at the Rarangi Golf Club well (1634) (Fig. 11.21).

The lack of an increasing trend in nitrates levels suggests the presence of weak reducing chemical conditions, or that it is flushed through the Rarangi Shallow Aquifer (RSA) by newly arriving groundwater.

There is a general trend of decreasing nitrate-nitrogen with increasing well depth across all Marlborough aquifers (Fig. 11.22). This reflects the greater susceptibility of shallow groundwaters to overlying landuses, and the dominant effect of natural denitrification processes on deeper groundwaters.

The most likely explanation for low nitrate-nitrogen levels associated with the permeable Wairau Aquifer is the natural diluting effects of rapid groundwater flow. This is confirmed by high nitrate concentrations in less permeable aquifers underlying similar land-uses.

A recently recognised objective of groundwater management is the need to maintain low nutrient levels to avoid eutrophication of connected surfacewaters,

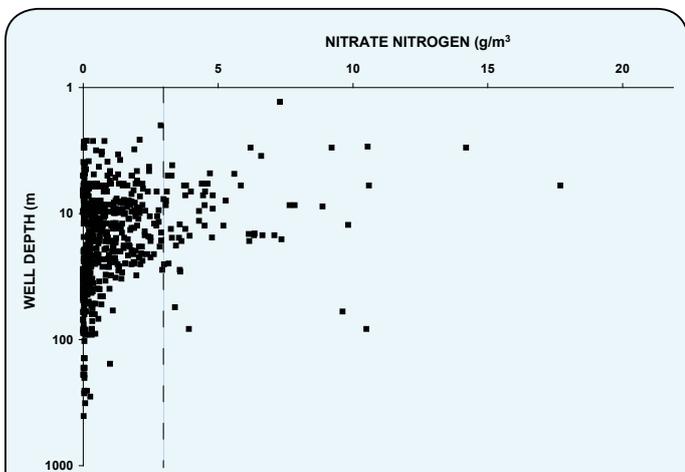


Figure 11.22: Mean nitrate-nitrogen concentration versus depth. Human sources of nitrate-nitrogen are generally linked to wells of less than 20 metres depth, where the dashed line on this plot marks what is generally accepted as the upper limit of naturally occurring concentrations of nitrate-nitrogen (Rosen & White – 2001)

including the Wairau Plain freshwater springs such as Spring Creek.

Nitrate-nitrogen is relatively difficult to remove compared to other contaminants in groundwater. Ion exchange, reverse osmosis, distillation and various biological processes are available, but all are expensive. Blending with water of better quality is commonly used as a treatment.

### Ammoniacal-nitrogen

Under the anaerobic aquifer conditions found in wetlands or confined aquifers, nitrate-nitrogen is reduced to ammoniacal nitrogen. It is also commonly associated with recent impacts of decomposing plant, animal and human waste. The presence of the ammoniacal form of nitrogen is a useful indicator of the previous existence of nitrogen as nitrate.

Ammoniacal nitrogen concentrations of greater than about 0.1 g/m<sup>3</sup>, generally indicate reducing conditions in an aquifer. It flags that other problem chemicals such as iron, manganese and arsenic may also be present.

The distribution of ammoniacal nitrogen clearly marks the boundary of the main areas of aquifer flow beneath the Wairau Plain at Riverlands, Rarangi and south of New Renwick Road (Fig. 11.23). Several of the high values in the Taylor Pass area, represent leachates associated with closed landfills. Even in highly confined parts of the Wairau Aquifer, ammoniacal-nitrogen levels remain below the 0.1 g/m<sup>3</sup> threshold indicating advanced chemically reducing conditions.

### Sulphate

Sulphate exists at relatively low levels in local groundwaters. Most sulphate is assumed to originate from natural processes, but some comes from the use of agricultural or household fertilisers in Marlborough.

Sulphate concentrations in groundwater increase in the Woodbourne and Southern Valleys catchments, but are relatively low in the deeper, confined aquifers beneath Riverlands, Rarangi or the central coast (Fig. 11.24). In absolute terms, sulphate levels are low compared to the Ministry of Health drinking water guideline value of 250 g/m<sup>3</sup> and there is no risk to human health (DWSNZ - 2005).

Higher sulphate levels in Southern Valleys Aquifer wells reflect the use of agricultural fertilisers in combination with a lack of natural flushing. The absence of sulphate in older groundwater in confined aquifers where oxygen is depleted, points to its degradation through natural reduction reactions. These same chemical processes are responsible for denitrification.

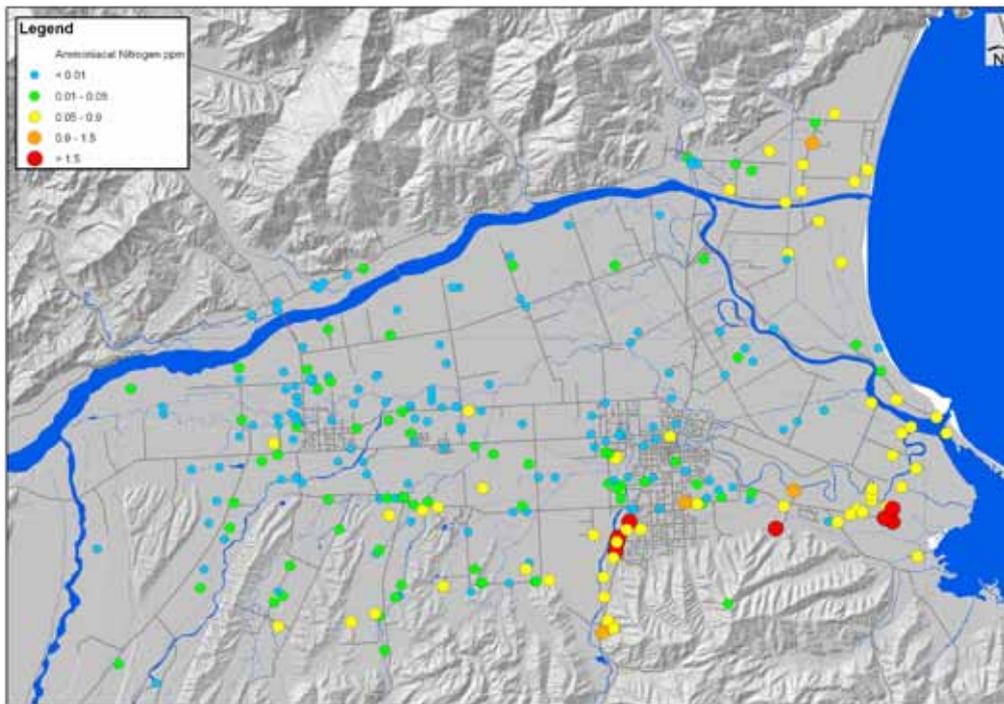


Figure 11.23: Median ammoniacal nitrogen concentrations excluding Rarangi Shallow Aquifer

One way of identifying the source of sulphate in local groundwaters is to compare the ratio of magnesium and sulphate in a particular groundwater sample, to that of seawater.

The mean magnesium and sulphate concentrations have been collected for several hundred samples from a representative series of Marlborough aquifers and there is a wide scatter of results around the seawater concentration dilution line (SCDL) suggests a combination of sources (Fig. 11.25). Many confined aquifer sites lie predominantly below the line with groundwater relatively depleted in sulphate, but this pattern is far from universal. It could be due to the loss of sulphate from groundwater by natural

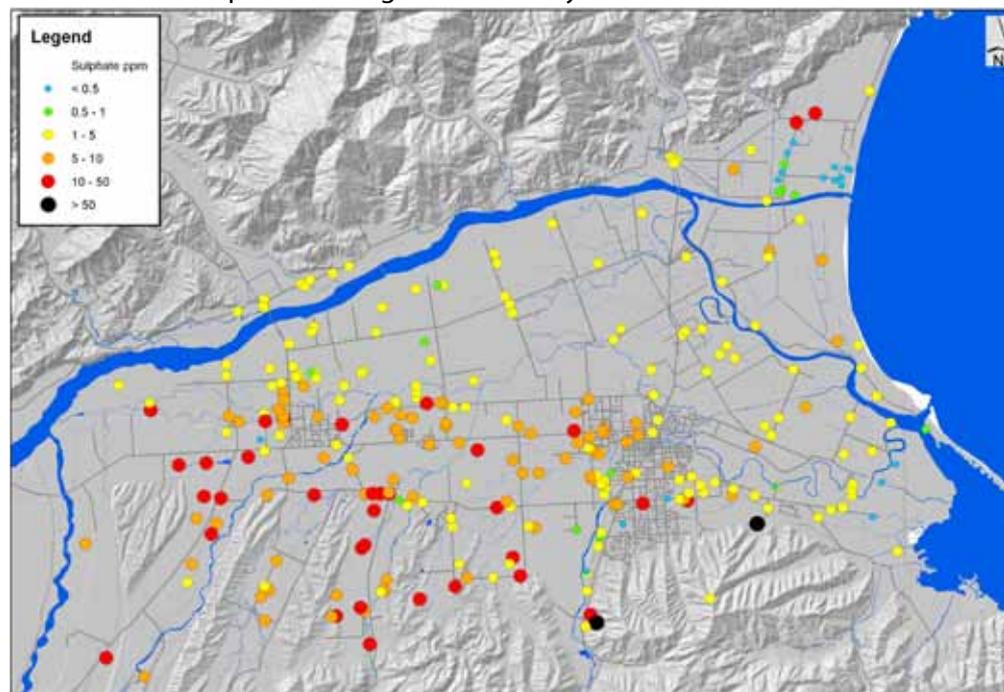


Figure 11.24: Median sulphate concentrations excluding Shallow Aquifer

chemical processes, or the addition of magnesium through ion exchange, or fertilisers. These patterns show that sulphate levels in Marlborough groundwaters can be dynamic, being added as a result of human activities, but with the potential to be degraded by natural processes.

The mean concentration of sulphate declines with depth across all aquifers in Marlborough, with a scarcity of oxygen in confined aquifers leading to a chemical reduction to sulphides (Fig. 11.26). This is a common trend in New

Zealand aquifers and has been documented elsewhere (Rosen - 2001).

### Potassium

Potassium can be added to groundwater through fertiliser use and the breakdown of animal or human waste products. Concentrations of potassium are generally low in New Zealand aquifers because of plant uptake or natural exchange processes that remove it from groundwater (Rosen & White - 2001), and this is true of Marlborough groundwaters.

Potassium concentrations follow a similar pattern to that of other naturally evolved parameters. This suggests that potassium originates as a result of natural water-rock interaction, rather than from agricultural fertilisers. Potassium levels are monitored in case there is an increased contribution from landuses in the future through agricultural processes disturbing the soil structure. The reason for elevated levels in some Rarangi groundwaters remains unexplained.

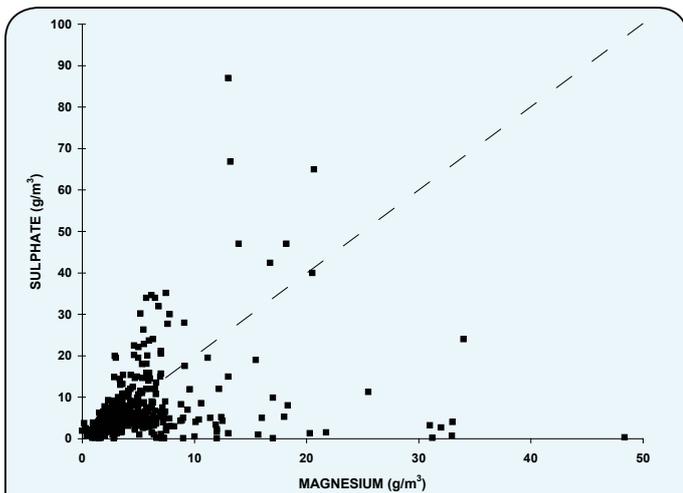


Figure 11.25: Mean sulphate versus magnesium concentration. The dashed line represents the ionic ratio of sulphate to magnesium in ocean water which subsequently becomes incorporated in rain and recycled as groundwater. It is known as the seawater concentration dilution line (SCDL). Sulphate recirculated from seawater falls on this line.

### Phosphorus

Phosphorus originates from the weathering of local rocks and fertiliser use. However there is little evidence of elevated levels in groundwater due to fertiliser use in Marlborough. During the 2006 survey of Linkwater groundwater, low levels were found in all samples except the oldest groundwater, indicating a geological source (GNS Science - 2009). These low levels probably reflect that it is taken up by plants or organic matter, and adsorbed into clay or other particles in the soil in the unsaturated zone, before reaching groundwater.

### Pesticides

Marlborough is economically reliant on its primary industries, and pesticides are widely used as part of agricultural production systems. Apart from isolated incidents related to well head security or spills, very low levels of pesticide have been measured in Marlborough groundwaters.

### Heavy metals

Limited information exists on concentrations of heavy metals in Marlborough groundwaters. However their concentrations do not appear to be a regional issue based on the results available. In common with phosphorous,

heavy metals have an affinity with large particles which they naturally adsorb on to. This means they get locked up in the soil and do not reach the water table.

### Arsenic

Studies of arsenic in Marlborough groundwaters started in 2001 following the discovery of elevated levels in Rarangi Shallow Aquifer water. The elevated arsenic levels were found as part of routine sampling of groundwater by operators of the North Rarangi community water supply well.

The discovery initiated two large scale surveys of all water wells in the Rarangi area in winter 2003 and again in summer 2005. Several hundred wells were sampled on each occasion to measure the spatial distribution of arsenic. These surveys were followed up by three years of monthly sampling at four domestic water supply wells to measure the temporal variation. All of the research to date points to a natural source with the exception of a few sites linked with landuses such as landfills or sheep-dips. Arsenic is now routinely measured as part of the MDC state of the environment groundwater quality monitoring programmes.

A natural source is supported by the distribution of arsenic concentrations within the Marlborough groundwater system which mimics the pattern exhibited by other chemicals that are formed by water-rock interaction rather than landuses (Fig. 11.27). This plot omits results for the Rarangi Shallow Aquifer where most of the intensive research by the MDC has occurred. This is covered in detail in the Rarangi Shallow Aquifer chapter.

A knowledge of arsenic's occurrence in groundwater sourced drinking water is very important as the long-term consumption of groundwater with concentrations above 0.01 g/m<sup>3</sup> is toxic to human health. However the technology exists to reduce levels to safe concentrations. There are not enough measurements to comprehensively map its distribution yet, and the risk factors that control where it occurs are not yet fully understood.

The presence of iron and manganese has been used as an indicator of the existence of arsenic due to similarities in their chemical behaviour. There are many more measurements of these parameters than currently exist for arsenic.

### Silica

Silica is one of the most common rock forming groups of minerals on earth. Its concentration is expressed in terms of SiO<sub>2</sub>. As a mineral it is the building block of most local rocks such as greywacke and argillite.

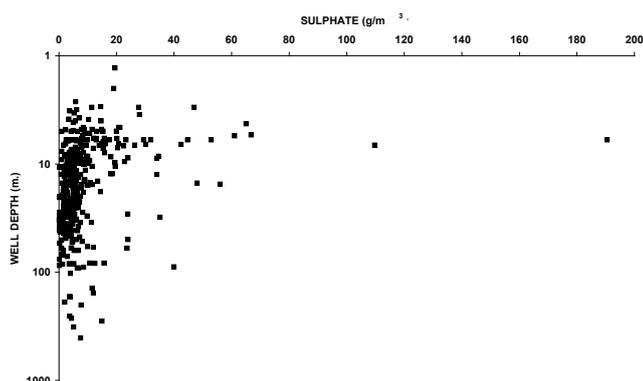


Figure 11.26: Mean sulphate concentration versus depth

However silica is relatively insoluble compared to carbonaceous rocks, and concentrations are generally low in Marlborough groundwaters.

A reasonable correlation exists between silica levels and groundwater age for some aquifer systems such as the Linkwater Aquifer, to allow it to be used as a natural clock. But this is not always the case either worldwide or in Marlborough. Silica concentrations in Deep Wairau Aquifer groundwater with residence times of more than 9,000 years, are lower than for much younger water from the Wairau Aquifer. The explanation probably lies in the solubility equilibrium of silica according to Dr Chris Daughney of GNS Science.

### Boron

Elevated levels of boron are common in Marlborough groundwaters and appear to be mostly due to natural processes such as the breakdown of boron minerals in the basement greywacke rock (Fig. 11.28). Concentrations that can affect human health of above 1.4 g/m<sup>3</sup>, have been recorded in groundwater at Wairau Valley and are likely to be related to natural fluids emanating from the nearby Wairau Fault.

### Microbes

In addition to the dissolved or suspended solids found in groundwater there are also many living organisms present. The largest of these are invertebrates which are visible to the naked eye, however most are microscopic in size. The main categories of these smaller organisms are protozoa, bacteria and viruses.

Groundwater can contain millions of these microbes and while some have no effect on humans, others are harmful to human health and are known as pathogens. Of particular concern are the presence of certain types of protozoa and bacteria in the groundwater where drinking water is sourced. Well known examples of harmful bacteria are *Camphylobacter* and *Salmonella*. Protozoa which can affect human health in New Zealand include *Giardia* and *Cryptosporidium*.

Not as much is known about viruses yet, but many bacteria have

been identified and their risk to human health is well understood from experience. The bacteria *Escherichia coli* (*E. coli*) is commonly used as an indicator of the presence of faecal contamination. *E. coli* originate from the gut of warm blooded animals, but may not adequately indicate the presence of viruses, which are more harmful to human health.

Aquifers act as natural filters which reduce microbial contamination of groundwater, but their filtration ability varies widely (Pang - 2009). Many factors influence their filtration effectiveness. The permeability of the aquifer and velocity of the groundwater are the most important and removal rates decrease with increasing permeability.

It is for this reason that quantifying groundwater travel times is a research priority in Marlborough due to the increasing density of human settlement. While agricultural stock have almost completely disappeared from the Wairau Plain over the past 20 years, human waste from rural residential settlement and process wastes has grown.

The natural processes of inactivation acting on microbes reach their maximum in the soil profile, causing an exponential decline in numbers. Fine textured soils remove more microbes than coarser grained material, with the exception being soils with macropores that act as natural motorways, expediting their movement. Microbes are leached downwards through the soil, but move horizontally once they arrive at the water table. Microbes persist longer in groundwater than the soil zone because mechanisms such as filtration and adsorption are less effective (Rosen & White - 2001).

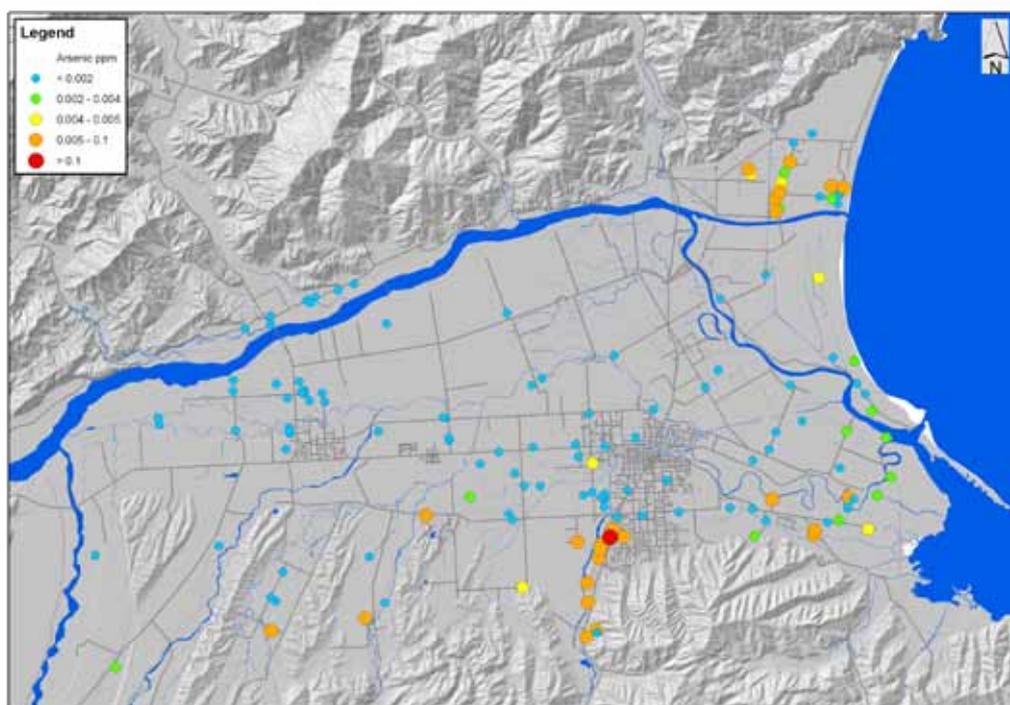


Figure 11.27: Median arsenic concentrations excluding Rarangi Shallow Aquifer

They are also consumed by groundwater invertebrates living in the pore spaces between the gravels.

Fewer microbes survive in finer grained aquifers with slower velocities due to the effect of straining and filtration. The sandy Rarangi Shallow Aquifer for example, is likely to remove more microbes than the Wairau Aquifer, which consists of coarser gravels. These are generalisations as other factors such as the distance to wells which might be affected, rainfall and microbe loading rate will all have a bearing.

Microbe type also affects their survival with different types responding differently under the same conditions. Because viruses are smaller organisms than bacteria and don't rely on nutrients as a food source, they are not as effectively removed by natural filtration and can survive in aquifers with limited food sources (Pang – 2009).

### Microbes locally

There have been surprisingly few reported cases of microbe contamination of local groundwaters or ill health. As part of the MDC state of the environment monitoring programme, the presence of *E. Coli* bacteria in vulnerable aquifers used for drinking water supplies are surveyed regularly throughout the province. Surveys occur in spring when the presence of microbes in groundwater is likely to peak because of higher rainfall rates.

The relative absence of microbes in surveys to date is not necessarily proof they don't occur in local groundwaters. Because they originate from point

sources such as septic tanks but die-off rapidly under certain conditions, they can be localised, and sampling may not always provide a true picture of populations or risk to drinking water.

The risk factors for microbe contamination of groundwater include an unconfined aquifer structure, thin soils with limited organic matter and high water tables close to the surface. These conditions exist at Wairau Valley, Rarangi, Rai Valley, parts of the Wairau Plain and the Tuamarina River Valley.

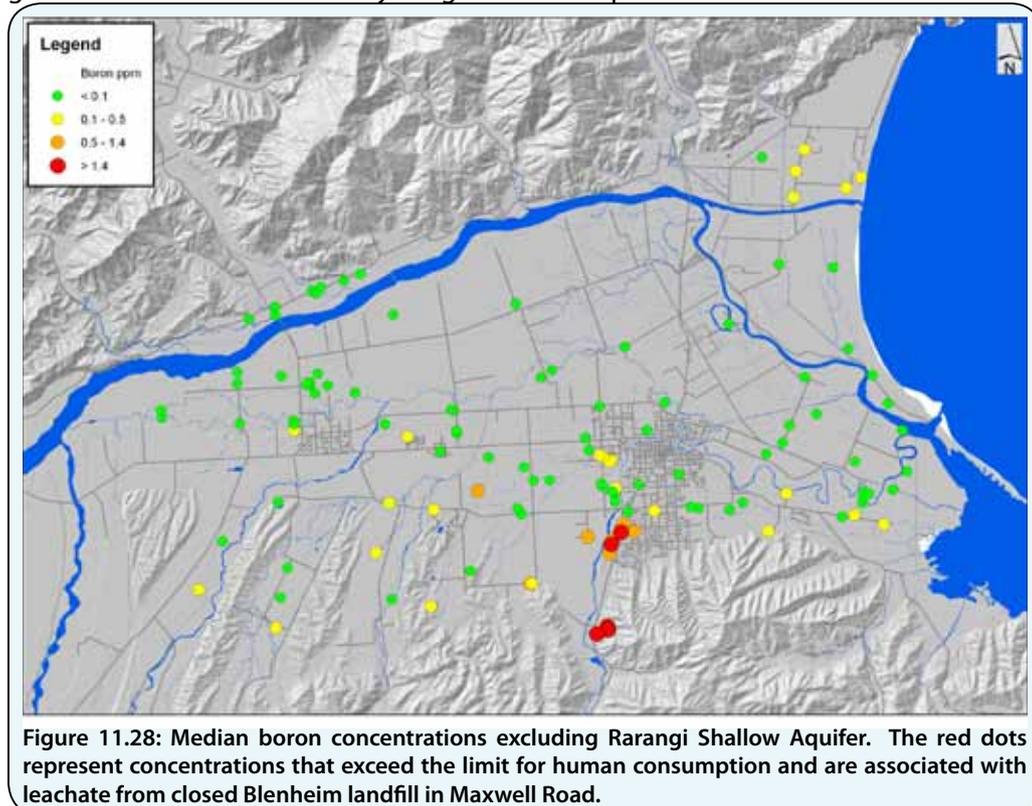
As recently as 2009 the Blenheim municipal water supply was untreated, with groundwater pumped directly from wells into the water mains for distribution to houses for drinking. Ultraviolet treatment of municipal water supplies has now reduced the risk of microbial contamination for the public following an incident at the MDC Middle Renwick Road wellfield in early 2008.

### Groundwater gases

Groundwaters naturally contain varying concentrations of common atmospheric gases such as oxygen ( $O_2$ ), carbon dioxide ( $CO_2$ ), nitrogen ( $N_2$ ), nitrous-oxide ( $N_2O$ ), methane ( $CH_4$ ) and hydrogen sulphide ( $H_2S$ ). Several of these gases such as carbon dioxide and nitrous oxide are greenhouse gases. However the potential contribution to global warming is likely to be low relative to emissions generated by the burning of fossil fuels.

The presence of each gas tells us something about the state and biochemical processes taking place within an aquifer such as how old the water is, and whether reducing or oxidising conditions predominate.

Levels of gases in groundwater from unconfined aquifers are similar to atmospheric concentrations because the two bodies are in contact and reach equilibrium over time. In confined aquifers, groundwater is isolated from the atmosphere and natural processes consume oxygen in particular. By-products of these biochemical reactions include hydrogen sulphide and under advanced reducing conditions, methane.



Hydrogen sulphide has a distinctive rotten egg odour.

From the limited research carried out to date it would appear that groundwater systems act as carbon sinks, storing the carbon dioxide gas generated through interaction between rainfall recharging the aquifer and decomposing organic matter. This is beneficial for soaking up human generated carbon dioxide. This is especially true of groundwater resident in highly confined aquifers that can sequester the carbon dioxide for tens of thousands of years, isolating it from the atmosphere. However a decrease in pressure as groundwater is pumped to the surface will release it through degassing (MacPherson - 2007).

It is difficult to measure the carbon dioxide concentration of groundwater because it changes rapidly on exposure to the atmosphere where it degasses. A bit like opening a can of coke. What is thought to be dissolved gases in local groundwater have been observed at several wells around Marlborough and have the appearance of aerated water.

The most noticeable was well 3177, a failed attempt at locating a domestic supply to a depth of 118 metres in the highly confined Benmorven Aquifer. The second example is the 50 metre deep MDC exploratory well O28w/0219 at Wairau Valley.

A common factor between both wells is that they tap old groundwater within confined aquifers. The nature of these gases is not known but is likely to include methane (CH<sub>4</sub>) based on previous experience at Benmorven and possibly carbon dioxide (CO<sub>2</sub>). All appear to have hydrogen sulphide (H<sub>2</sub>S) present. It is also likely that old groundwater from the Deep Wairau Aquifer contains dissolved gases, but it's water doesn't have an aerated appearance.

## References

- BOTTING, J. 2010. GROUNDWATER FLOW PATTERNS AND ORIGIN ON THE NORTH-BANK OF THE WAIRAU RIVER, A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ENGINEERING GEOLOGY IN THE UNIVERSITY OF CANTERBURY.
- DAUGHNEY, C.J. AND REEVES, R. R. 2005. DEFINITION OF HYDROCHEMICAL FACIES IN THE NEW ZEALAND NATIONAL GROUNDWATER MONITORING PROGRAMME. JOURNAL OF HYDROLOGY (N.Z.) 44: 105-130
- FREEZE, R.A. AND CHERRY, J.A., 1979. GROUNDWATER
- MACPHERSON, G.L. 2007. CO<sub>2</sub> RELEASE FROM GROUNDWATER AND HUMAN POPULATION GROWTH. GEOLOGICAL SOCIETY OF AMERICA DENVER ANNUAL MEETING OCTOBER 2007. DEPT. OF GEOLOGY, UNIVERSITY OF KANSAS

- MORGENSTERN, U, BROWN, L.J, BEGG J, DAUGHNEY, C. AND DAVIDSON P. 2009. LINKWATER CATCHMENT GROUNDWATER RESIDENCE TIME, FLOW PATTERN, AND HYDROCHEMISTRY TRENDS, GNS SCIENCE REPORT 2009/08 MAY 2009
- NEW ZEALAND MINISTRY OF HEALTH, 2005. DRINKING-WATER STANDARDS FOR NEW ZEALAND 2005
- PANG, L. 2009. MICROBIAL REMOVAL RATES IN SUBSURFACE MEDIA ESTIMATED FROM PUBLISHED STUDIES OF FIELD EXPERIMENTS AND LARGE INTACT SOIL CORES, JOURNAL OF ENVIRONMENTAL QUALITY 38: 1531-1559
- ROSEN, M.R. 2001. HYDROCHEMISTRY OF NEW ZEALAND'S AQUIFERS. IN GROUNDWATERS OF NEW ZEALAND, M.R. ROSEN & P.A. WHITE (EDS). NEW ZEALAND HYDROLOGICAL SOCIETY INC., WELLINGTON. Pp. 77-110.
- TODD, D.K. 1980. GROUNDWATER HYDROLOGY
- WISPAS, MARCH 2007 EDITION. N<sub>2</sub>O EMISSIONS FROM GROUNDWATER UNDER AGRICULTURAL LAND USE A CASE STUDY FROM A SANDY AQUIFER IN GERMANY, HORTRESEARCH PUBLICATION