Waikato Regional Council Technical Report 2022/23

Waikato groundwater quality state of environment to 2020

www.waikatoregion.govt.nz
ISSN 2230-4363 (Online)

Prepared by:
John Hadfield

For:
Waikato Regional Council
Private Bag 3038
Waikato Mail Centre
HAMILTON 3240

November, 2022

Peer reviewed by:		
Dr Lisa Scott	Date	November 2022

Approved for release by:		
Mike Scarsbrook	Date	August 2023

Disclaimer

This technical report has been prepared for the use of Waikato Regional Council as a reference document and as such does not constitute Council's policy.

Council requests that if excerpts or inferences are drawn from this document for further use by individuals or organisations, due care should be taken to ensure that the appropriate context has been preserved, and is accurately reflected and referenced in any subsequent spoken or written communication.

While Waikato Regional Council has exercised all reasonable skill and care in controlling the contents of this report, Council accepts no liability in contract, tort or otherwise, for any loss, damage, injury or expense (whether direct, indirect or consequential) arising out of the provision of this information or its use by you or any other party.

Acknowledgement

John Hughey and Sajeewa Herath are gratefully acknowledged for their field monitoring contribution and database management and Asaeli Tulagi for coordinating laboratory services. Mat Allen and Magali Moreau (GNS Science) are thanked for advice on R scripts. Lisa Scott (Environment Canterbury) and Jonathan Caldwell are thanked for providing helpful review comment.

Table of contents

List of figures

List of tables

Executive Summary

Groundwater quality in the Waikato region is highly variable, reflecting the diversity of hydrogelogic settings and hydrochemical conditions. The impacts of land-use activities are commonly, clearly evident and exceed safe concentrations for drinking water at many sites.

Groundwater is extensively used in the Waikato region for purposes including drinking water supply, irrigation, stock water and industry. It also importantly sustains surface water flows and influences its quality. Progressive land-use intensification threatens groundwater quality and its long-term sustainable management.

The monitoring of groundwater quality enables changes in state and trend to be identified. It also reflects the efficacy of management of this resource and provides information for future policy development.

This report describes the state of groundwater quality in the Waikato for the five years to the end of 2020 and trends over an 18-year period from 2003 to 2020. Information is derived from data collected from a regional network of 110 state of environment (SOE) wells, including 10 wells which are part of the National Groundwater Monitoring Programme (NGMP). Less frequent data is also collected from a network of 80 ‘Community’ or rural school water supply wells.

The primary issue in respect to manageable groundwater quality is nitrate contamination. Nitrate commonly exceeds the drinking water guideline, with median concentrations being over the maximum acceptable value at 11% of the SOE monitoring network sites. The highest concentrations are associated with market gardening and dairy farming activities. These account for all exceedances except for one point-source location related to effluent from a woolshed. Areas with highest concentrations are the basalt aquifers of Pukekohe and Pukekawa and parts of the alluvial aquifers of the Hauraki Plains and Hamilton Basin. Areas of relatively low intensity land-use activity such as the Coromandel Peninsula, by contrast, have noticeably lower nitrate concentrations. Data from the Community supply network indicates that nitrate-N trends at these wells are predominantly increasing.

Other anthropogenic contaminants of concern include pesticides and emerging organic contaminants (EOCs). Data from 2020 shows pesticides detected at 22.5% of SOE wells with 2.5% being in excess of the drinking water guidelines. EOCs were detected at 91% of SOE sites sampled and many of these have no guideline values.

Naturally occurring determinants which are routinely monitored and exceed health guidelines, include arsenic and manganese. Median results exceed maximum acceptable values for arsenic at 5.5% and manganese at 4% of the SOE wells monitored.

Waikato groundwaters also commonly exceed aesthetic guideline values, which are of nuisance value rather than health significance. SOE network wells typically have acid waters and therefore tend to have high plumbosolvency or tendency to corrode metal piping. Elevated median iron and manganese concentrations exceeding guidelines at about 20% of wells can lead to nuisance staining and sometimes taste issues.

Sub-regional differences are noted reflecting varied hydrogeologic settings. Relatively large inter-quartile concentration ranges for bicarbonate, calcium and hardness in the Coromandel and Waipa catchment areas, for example, reflect the presence of some shelly sediments in the former and limestone in the latter. The prevalence of relatively higher sodium, chloride and conductivity in the Coromandel area reflects the coastal influence.

Groundwater quality trends are mixed with rates of change correlated with concentration. Although there are similar numbers of nitrate increases and decreases regionally (~31%), the trends vary substantially sub-regionally. Nitrate increases predominate in the northern basalt aquifers (~67%) along with many other major ions. This contrasts with a similar proportion of decreases (~69%) in nitrate and other major ions in the shallow monitoring wells of the Hamilton Basin. Other areas are more balanced although there are more increases (37%) than decreases (~22%) in nitrate concentration trends in the Hauraki area.

Nitrate concentrations decrease with depth. Shallow groundwater may have a range of nitrate concentrations influenced by factors such as land-use and redox conditions. The latter have been categorised into aerobic, anaerobic (characterised by an absence of detectable nitrate), mixed and indeterminate conditions. The mixed category can have high nitrate concentrations while including some anaerobic characteristics, such as notable iron and manganese concentrations. Investigation has shown these often reflect wells screened across both aerobic and anaerobic zones. Wells with indeterminate redox character may have older groundwater or be largely devoid of land-use influences.

There are several key determinants, such as nitrate, calcium, magnesium and sulphate, which have higher concentrations in younger groundwaters, particularly the last ~50 years. These increases may be inferred to relate to anthropogenic rather than geogenic influences.

The fundamental importance of monitoring network design is indicated by distinctions between datasets from different networks e.g. regional SOE and the ‘Community’ network of rural schools. The latter has more anaerobic conditions represented and is on average deeper. It therefore has significantly lower nitrate concentrations. The current networks are due to be reviewed and representation optimised for monitoring objectives.

1 Introduction

1.1 Background

The water resources of the Waikato are of fundamental importance to the health and wellbeing of the wider environment as recognised in the concept of Te Mana o te Wai. Groundwater comprises the vast majority of freshwater in the region and notably extensively sustains surface water flows. It is widely used for potable water supply, irrigation, industrial and many other purposes.

There are considerable land-use pressures on the larger environment which can influence the quality of groundwater resources across the region. Information derived from monitoring the state and trends of groundwater quality assists resource management decision-making. It can also indicate the effectiveness of policy initiatives.

This report describes the state of groundwater quality and identifies trends across the region. An electronic copy of this report can be obtained from the Waikato Regional Council website: www.waikatoregion.govt.nz/publications.

1.2 Report content

This report initially provides a brief description of the hydrogeologic settings within the region. The groundwater quality monitoring networks are then documented. The methods of sampling and data analysis are also reported. Before discussing results there is a section describing influences and pressures on groundwater quality.

Regional groundwater quality state and trends are reported for five and 18 year periods to 2020 respectively. They are also considered on a sub-regional basis for key determinants to illustrate the spatial variation in groundwater chemistry. There is a focus on nitrate, which is the most ubiquitous and important manageable contaminant. Factors which influence its occurrence and distribution are described. These include land-use, redox conditions and the age of the water.

The occurrence of other selected contaminants including micro-organisms, pesticides and emerging contaminants are also described. The suitability of groundwater resources in the region for potable drinking water supply, stock watering, and irrigation use is also described by comparison with relevant water quality standards.

Finally, some policy response mechanisms are briefly described and considered in respect to the information presented.

2 Hydrogeologic settings

2.1 Introduction

The Waikato region (land area 24,666 km^2) extends from the Lake Taupo catchment in the south to the basalt fields of Pukekawa and Pukekohe in the north and includes the Coromandel Peninsula. The regional extent and variation of settings are illustrated in a simplified geology map derived from the GNS Q maps series in Figure 1 (based in part on Edbrook, 2005). These have been broken down for description into seven sub-regional units (Figure 2). Whilst these units are pragmatic sub-divisions of the region, they still encompass considerable variation and multiple aquifers. They are similar to Freshwater Management Unit boundaries.

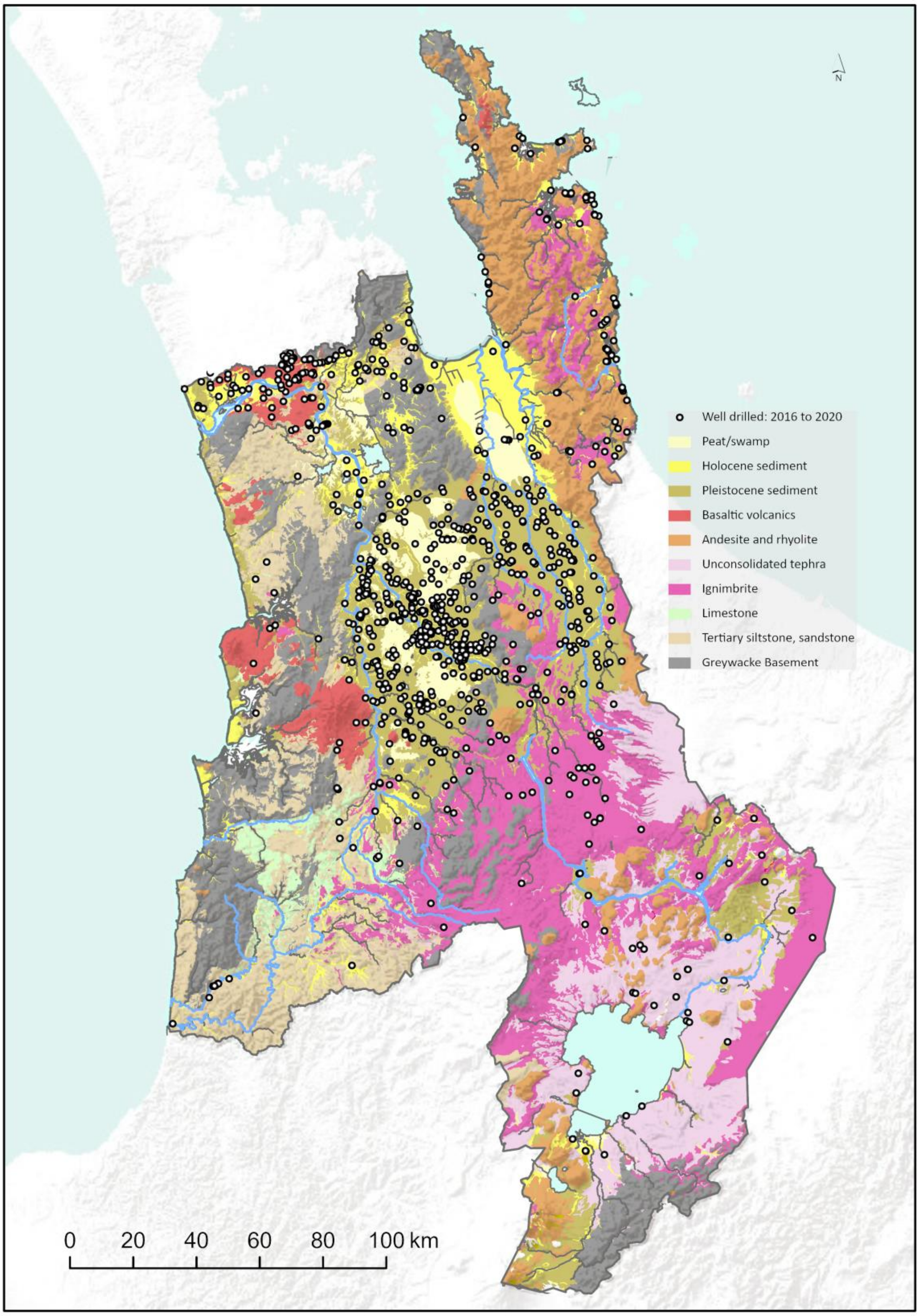


Figure 1 **Simplified geology of the Waikato Region with wells completed 2016–2020.**

It is evident that the distribution of groundwater wells is influenced by topography and geology. The density of wells, largely reflecting groundwater resource development, is also largely consistent with land-use intensity. The seven sub-regions used in subsequent hydrogeologic setting description and state and trend reporting are illustrated in Figure 2. It is noted that the focus in the Lower Waikato are the northern areas of Pukekohe, Pukekawa and Waiuku. ‘Northern areas’ is subsequently used to describe these areas in reporting.

There are a series of West Coast catchments to the west of the Waipa and Lower Waikato (Northern areas) which have not been explicitly reported. These are areas of lower land-use intensity for which monitoring data is sparse. It is apparent from the geology map that these catchments predominantly comprise sedimentary rock formations. These typically comprise Tertiary and Jurassic stratigraphic units which are of relatively low permeability and have therefore have not been substantially developed, as represented by the well distribution. Water supplies in this area are typically reliant on surface waters. There are, however, minor exceptions with some relatively higher yielding limestone and volcanic aquifers.

The vulnerability of Waikato groundwater is illustrated in Figure 3 below. It was derived using DRASTIC, a system developed by the National Water Well Association and the Environmental Protection Agency in the United States to provide a standardised method for estimating the potential for groundwater contamination. DRASTIC is an acronym derived from the seven hydrogeologic factors considered to be the primary controls of groundwater contamination (Aller et al.,1987). These factors are as follows: Depth to water, Recharge, Aquifer media, Soil media, Topography, Impact of the vadose zone and hydraulic Conductivity. A numerical ranking system for groundwater vulnerability has been devised using these factors. The DRASTIC system includes several weights(w) and ratings(R) which are assigned to ranges of the seven selected hydrogeologic factors. As the DRASTIC scores increase toward a possible maximum of 230, the vulnerability of the aquifer increases. DRASTIC was designed to enable subjective estimation for some parameters based on professional judgement where data is not available. The ratings developed relate to the shallowest aquifer and a GIS based approach was used for interpolation (Fryer and Chalmers, 1999).

Figure 2 Location of sub-regions

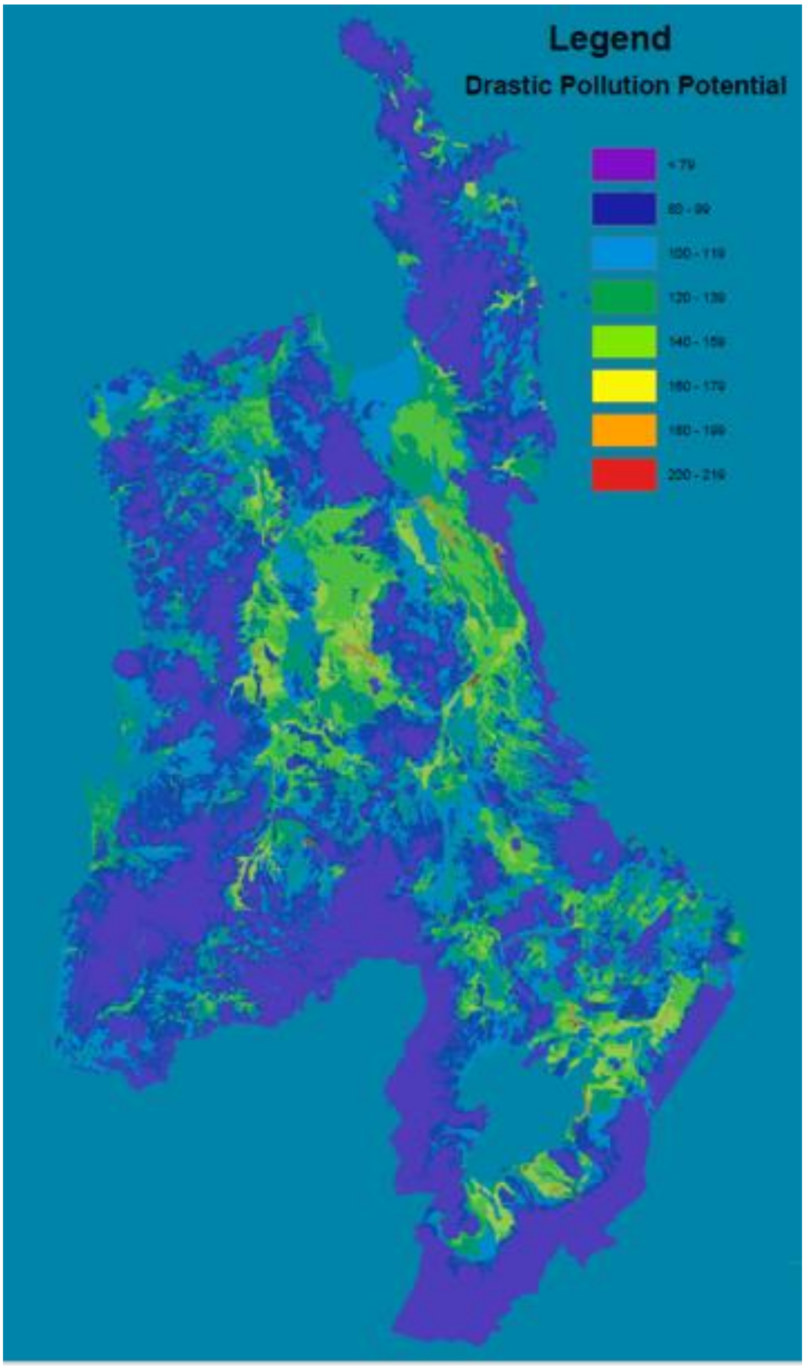


Figure 3 **Vulnerability of groundwater in the Waikato region based on the DRASTIC system.**

2.2 Lake Taupo catchment

Lake Taupo is the largest in New Zealand (620 km^2) and is formed in a caldera largely shaped by a massive eruption about 26,500 years ago. Catchment geology is dominated by young (<0.4 Ma), locally derived, rhyolitic pyroclastics (Figure 4). The sequence in the western catchment is relatively simple with surficial Oruanui ignimbrite overlying a large thickness of Whakamaru ignimbrite. The latter is sufficiently welded in places to have moderate vertical fracture development and to form impressive cliffs along the western lake-front.

East of Kawakawa Bay faulting is common and there is a more complex sequence of ignimbrites, fall deposits, localised lava extrusions and lacustrine sediments (Wilson, 2000). The unwelded Oruanui ignimbrite overlies this broad grouping of rhyolite pyroclastics. Occasional paleosols, punctuate these formations marking periods of cessation in volcanic activity and may act as localised aquitards. The youngest, unwelded, Taupo ignimbrite forms surficial deposits which are often unsaturated (Hadfield et al., 2001).

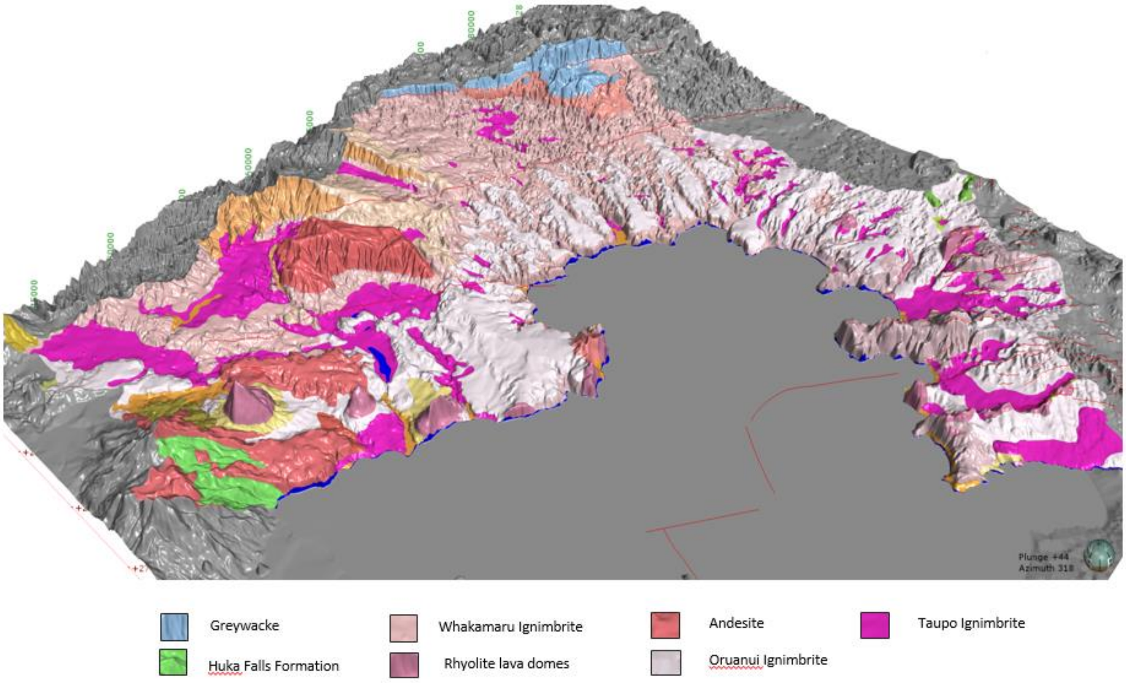


Figure 4 Geology of the northern and western Lake Taupo catchments (based largely on Leonard et al., 2010)

The lake is the sink for groundwater which is recharged from rainfall in the catchment. Groundwater flow in the area is consistent with topography although more subdued. Some divergent flow away from headlands such as the Kawakawa Rd area and toward valleys and bays such as Kinloch is evident. A recharge regime generally exists in the catchment. This is indicated by a strong relationship between the measured depths to static groundwater level and well depth (i.e. water levels typically get deeper with well depth). Vertical head gradients vary considerably with some large differentials (> 50 m) occasionally being observed. Groundwater acts as a pathway for nutrients generated from land use to migrate to the lake directly or indirectly via base-flow dominated streams (Hadfield et al 2007). Pastoral land-use development has largely occurred in the western and northern catchments. Nitrogen leaching estimates in the catchment are now well documented as part of a nitrogen management system.

2.3 Upper Waikato catchment

The Upper Waikato geology is dominated by Pleistocene volcanics with a sequence of eruptions in the last ~3-400,000 years superimposed (Wilson et al., 2009). Aquifers in this sub-region predominantly comprise ignimbrites but also related volcanoclastic sediments. The geology has been summarised by White et al (2015) in Figure 5.

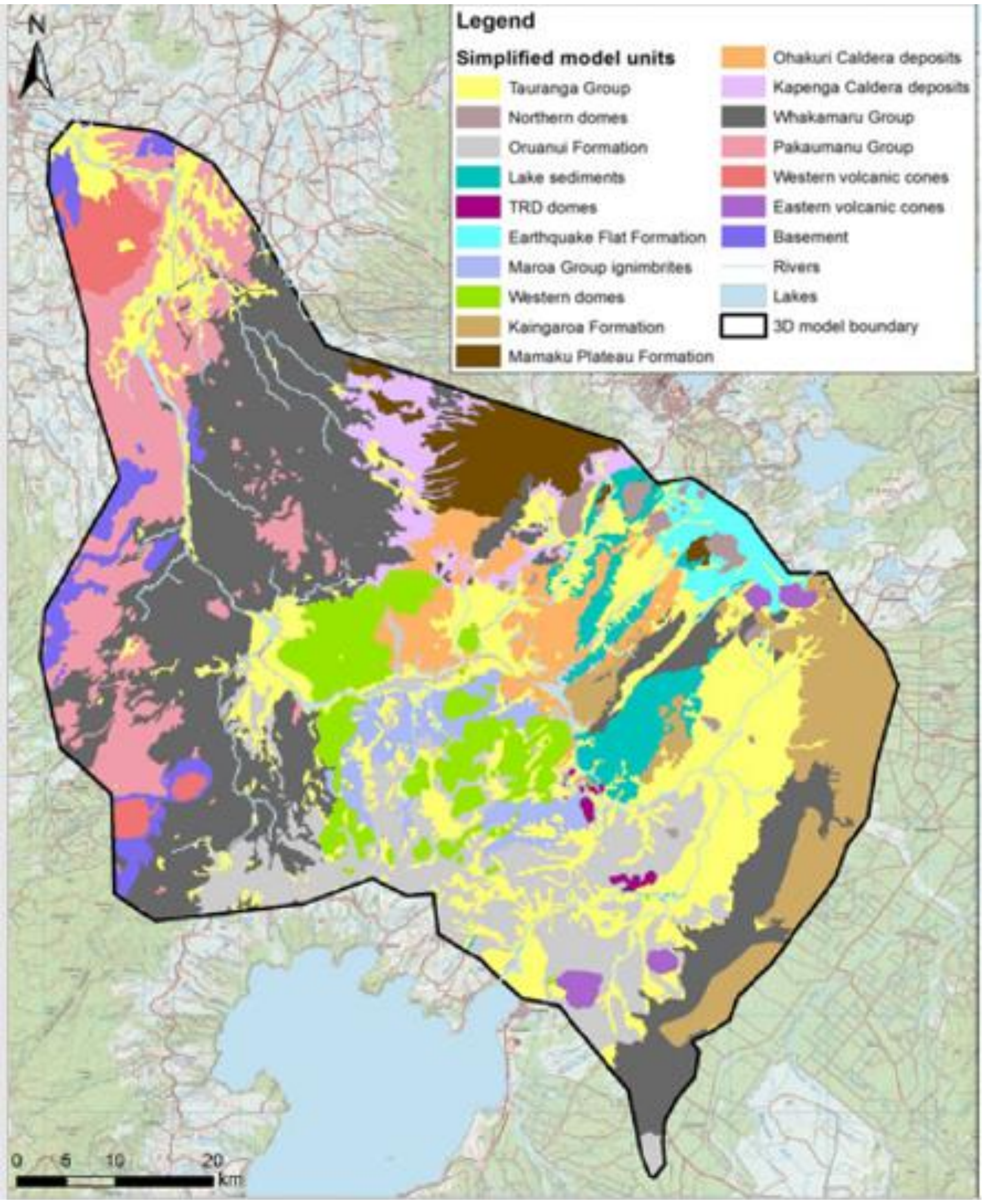


Figure 5 Geology of the Upper Waikato

The hydrogeology of the Reporoa Basin is described by Piper (2005). On the edges of the basin the geology is relatively simple with Taupo Ignimbrite overlying uplifted Rangitaiki Ignimbrite in the eastern Basin and Paeroa Ignimbrite on the western side. Rangitaiki Ignimbrite is welded and fractured. The central Basin is characterised by a complex sequence of pyroclastic Taupo and Oruanui Ignimbrites overlying lacustrine sediments of the Huka Formation. These in turn overlie the ignimbritic Waiora Formation. Water balance estimates show that in many of the basin sub-catchments groundwater flow is predominantly intercepted by large springs, which commonly sustain streamflow. This baseflow dominance is further seen in regard to nutrient contribution to streams in work by Stenger et al., 2022. Numerical groundwater flow and nitrogen transport modelling of the basin with spatially variable redox conditions and denitrification has been undertaken by Sarris et al., (2019).

Groundwater in the Tokoroa area is derived from a series of ignimbrite sheets of which the Waiotapu and Whakamaru ignimbrites are the most important. Lower permeability and deeper, Marshall Ignimbrite, has also been used for dairy factory supply at Lichfield. The Waiotapu aquifer in the Tokoroa (typically 20-50 m thick) underlies ~20-30 m of less permeable but more extensive Whakamaru ignimbrite. Transmissivity of the highly fractured and confined Waiotapu aquifer was found to range between 340 and 2,500 m^2 d^{-1}, which is about ten times higher than for the overlying Whakamaru aquifer. Groundwater velocity in the Waiotapu aquifer was estimated to be between 5 m d^{-1} and 16 m d^{-1} near Kinleith (Bird, 1987). The high quality ambient groundwater in the area enabled a large contaminant plume to be delineated extending from the Kinleith pulp and paper mill northward for about 12 kms (Carter Holt Harvey, 1997).

Several phases of numerical groundwater flow and nitrogen transport modelling has been undertaken in the Upper Waikato to assess potential future nitrogen concentrations for management (Weir and Rajanayaka, 2014). Rajanayaka et al (2020) estimated some 77% of surface water is derived from groundwater and the mean residence time in the domain is about 50 years (ranging from five to just over a 100 years). Nitrogen loads were shown to be increasing with the greatest uncertainties relating to historic land-use and the extent of denitrification in the catchment.

Recent land uses include 53% pasture and 32% production forestry with 13% in native vegetation and minor urban development (~1%). Forestry and farming are the predominant land uses with substantial forest to dairy conversions and land use intensification in recent years (Waikato Regional Council, 2019b).

2.4 Hauraki

The Hauraki Plains form part of a young continental rift structure bounded by major normal faults. A large thickness of predominantly Tauranga Group sediments deposited by ancient Waikato River channels infills this major elongated depression structure to a substantial depth (Hochstein and Nixon, 1979). The plains are bounded to the west by poorly permeable greywacke of the Hapuakohe and Pakaroa Ranges, and to the east by the Kaimai Ranges comprising predominantly andesitic and rhyolitic rock formations. A schematic block diagram of Hauraki geology by Houghton and Cuthbertson (1989) is presented in Figure 6.

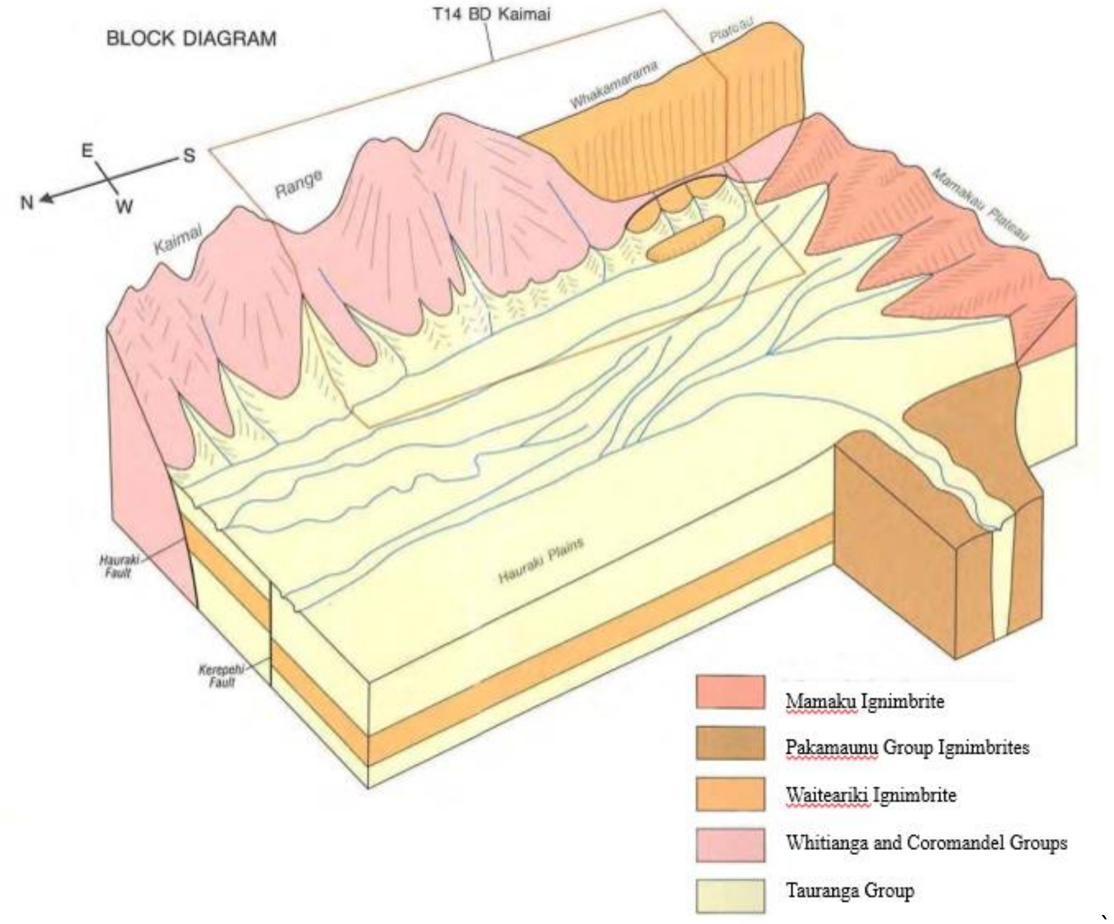


Figure 6 Schematic block diagram of Hauraki geology

Alluvial sediments beneath the plains may be described as a large, leaky, hydraulic system comprising numerous lensoidal aquifers of volcanoclastic sediments and reworked distal ignimbrites. There is a general trend of decreasing sediment size and topographic gradient toward the north. Substantial peat deposition is common north of Te Aroha.

Three-dimensional geological modelling by White et al., (2018) identified hydrogeological units relevant for groundwater modelling. These include Holocene sediments that are approximately 30 m thick at the coast and generally thin towards the south. Volcaniclastic sediments of the Pleistocene, Hinuera Formation are extensively exposed in the southern plains. Mamaku Ignimbrite forms headwater sub-catchments of the Waihou River further south toward the Mamaku Plateau. Other units include Waiteariki Ignimbrite in the Kaimai Ranges and below southern parts of the plains. Greywacke and Coromandel volcanics constitute hydrogeologic basement.

Groundwater flows northward along the Hauraki Plains toward the Firth of Thames as illustrated in Figure 7 (Hadfield in Rosen and White eds, 2001). Recharge is from rainfall predominantly in the southern catchment. Groundwater in the lower lying northern plains discharges through artesian upwelling and leakage to streams and wetlands. Much of the groundwater flow northward comes to the surface where the topographic gradient shallows and the Hinuera Formation meets finer Holocene sediments, as evident by sub-catchment groundwater outflows (White et al., 2018).

Groundwater yields are typically less than 200 $m^3 d^{-1}$ and generally increase toward the south with the most productive well producing about 10,000 $m^3 d^{-1}$. The highly variable nature of the sediments is reflected in a large range of transmissivities measured from less than 5 $m^2 d^{-1}$ to about 25,000 $m^2 d^{-1}$.

Although the highly variable nature of the Hauraki aquifers is reflected in substantial groundwater quality variation, there are strong spatial trends along the plains. Progressively reducing conditions toward the north are indicated by reduced nitrate and dissolved oxygen, and relatively increased ammonium concentrations (Figure 7). Excessive iron concentrations, which are a constraint on groundwater use, generally increase in association with peat content toward the north. Iron staining gives a practical indication of reduced conditions where high nitrate concentrations are absent (Hadfield, 1993).

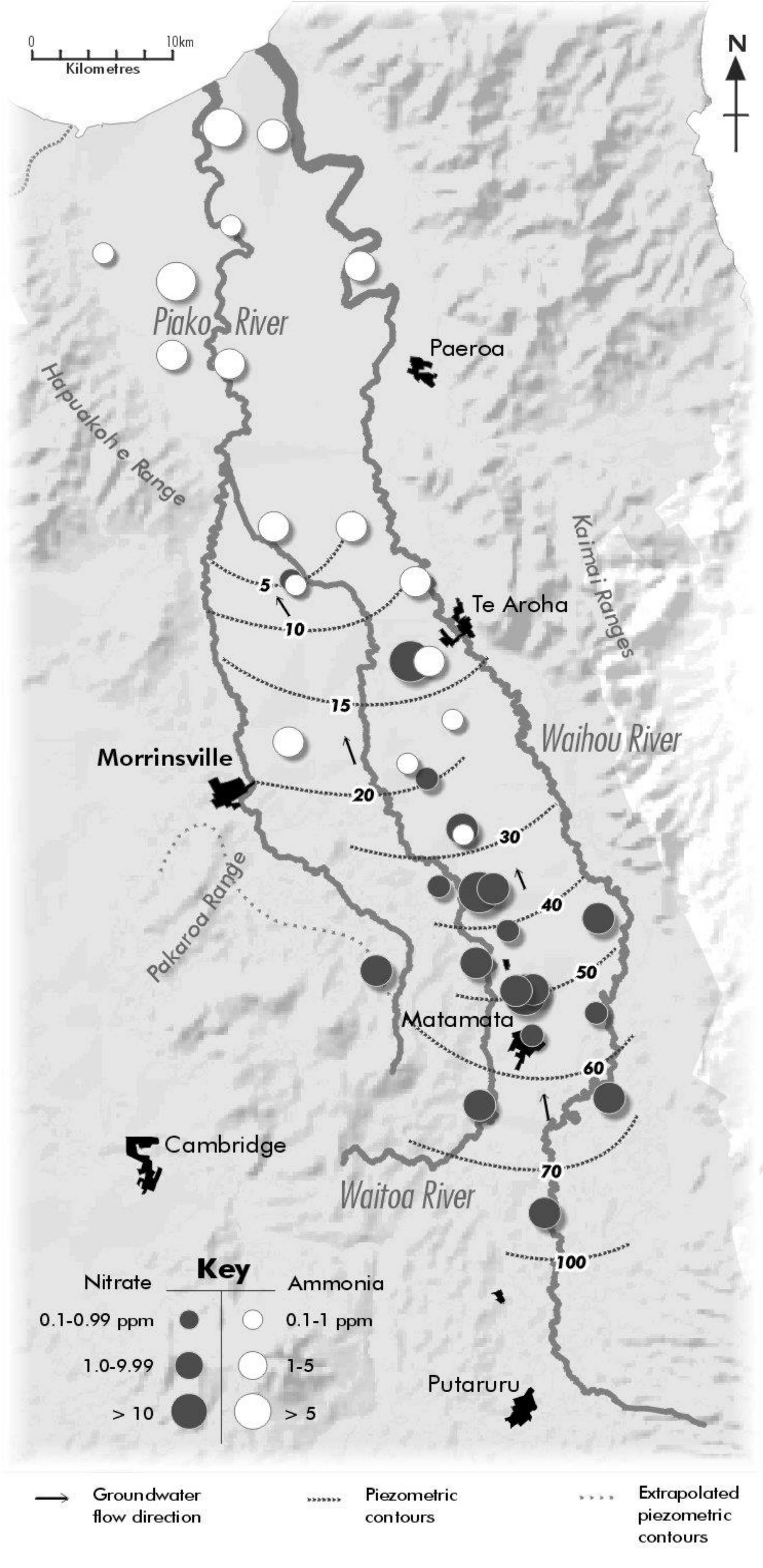


Figure 7 Piezometric contours and historic (1992) nitrate-N distribution in the Hauraki Plains (Hadfield, 2001).

Stochastic, numerical, groundwater flow and nitrogen transport modelling of the Hauraki catchment by Hemmings et al., (2022) was carried out to inform nutrient management and allocation issues. It explored aspects including the temporal evolution of nitrate flux to the Firth of Thames, as well as surface water groundwater exchange. Stream losses occur particularly in the upper Waihou catchment towards the ignimbritic, Mamaku Plateau. Reaches gaining from groundwater include parts of the Waitoa and Piako Rivers. Model simulation suggests a conceptual global 20% nitrate load reduction would potentially result in a six to nine % reduction at the Firth. Denitification may account for some 12 to 30% of load reduction generally.

Work by Stenger et al., (2022) used Bayesian modelling of surface water quality, flow and tritium monitoring data to estimate the relative contributions of nitrogen from near surface, shallow groundwater and deeper groundwater components. This showed that shallow pathways are more important for the Piako River at Kiwitahi compared to the deeper, baseflow component of the Waihou River at Okauia.

2.5 Coromandel

The Coromandel Peninsula is dominated by the Coromandel Range, which divides the eastern and western draining catchments from Colville in the north to Waihi in the south (Figures 1 and 2). Geology comprises predominantly volcanic rocks of the Coromandel and Whitianga Groups. Andesites and dacites of the Tertiary age, Coromandel Group are found throughout the peninsula, while ignimbrites and rhyolites of the Whitianga Group are more typical in the eastern Coromandel, south of Whitianga (Edbrooke, 2001). These rocks are poorly fractured and generally yield only small volumes of groundwater. Nevertheless, some Coromandel settlements, including Whangamata, Hahei and Onemana, are reliant on groundwater from fractured rock aquifers. These aquifers typically have very low transmissivities in the range 5 to 15 $m^2 d^{-1}$.

Alluvial sediments have infilled stream valleys forming localised terrace deposits. Small coastal sand aquifers are also important for groundwater supply. Settlements such as Pauanui, Cooks Beach, Matarangi, Whiritoa and Whangapoua have developed on such pocket aquifers. These coastal sand aquifers are more transmissive with a mean hydraulic conductivity of 15 $m\ d^{-1}$ reported at Pauanui and about 20 $m\ d^{-1}$ estimated at Matarangi (Hadfield, 2001).

Groundwater demand in these areas is highly seasonal and increasing. There have been recent isolated incidences of salinity increase, such as at Opoutere, Hahei and Whangamata. This highlights the potential for wider saltwater intrusion risks, particularly given relatively large drawdowns from pumping. Sentinel well monitoring has been established in many of these aquifers and investigations undertaken with the objective to estimate safe yield.

Pauanui is an example of a shallow, sand barrier, aquifer system which must be cautiously managed for both water supply and subsurface, highly treated, wastewater discharge. Careful management of these vulnerable coastal aquifers is required to avoid saltwater intrusion and safeguard them for future potable use (Hadfield et al., 2015).

2.6 Hamilton Basin

The Hamilton Basin is a large graben flanked by greywacke ranges (Pakaroa and Hakarimata) and infilled with a thick sequence of largely alluvial Tauranga Group sediments distributed by the ancestral Waikato River (Kear and Schofield, 1978). The basement morphology exhibits considerable relief. To the western side, predominantly marine Tertiary sediments were deposited (Marshall and Petch, 1985). The substantial and more recent, terrestrial, Tauranga Group of sediments is derived from rhyolitic volcanics in the Upper Waikato and Taupo areas. This group, which forms the broad alluvial plain of the Hamilton Basin was deposited as a large composite fan that stretches from the Maungatautari Gorge near Cambridge in the south to

Taupiri in the north (McCraw, 2011). Pumice dominated late Quaternary Hinuera Formation alluvium blankets the plain almost burying hills of earlier Quaternary alluvium and non-welded distal ignimbrites. Substantial peat development has occurred in low areas covering nearly half of the Hinuera surface (Edbrooke, 2005).

The highly variable and frequently pumiceous, Tauranga Group includes finer silts and clays as well as common peat layers. It comprises two subgroups being the late Pliocene to middle Quaternary Walton Subgroup and the younger Piako Subgroup (Kear and Schofield, 1978). The former is highly variable and includes primary and reworked distal ignimbrites. The Piako Group comprises more fluvial sediments including lensoidal, pumiceous sand aquifers (Edbrooke, 2005).

The most productive aquifers in the basin are lenses of well-sorted sand and gravel. Aquifer transmissivity estimated from Tauranga Group supplies tested ranges from about 10 m^2 d^{-1} to 1000 m^2 d^{-1} but is typically less than 100 m^2 d^{-1} (Marshall and Petch, 1985). Groundwater velocity for typical pumiceous sands of the Hinuera Formation has been measured at about 0.2 to 1 m d^{-1} (Hadfield and Smith, 2000).

Groundwater is recharged from rainfall and discharges predominantly by flow to incised streams. Isotopic analyses suggest that groundwater flux is predominantly in shallow aquifers (<5 years old) and groundwater in deeper aquifers is considerably older (up to thousands of years. Groundwater contributes up to 85% of the base flow of local streams draining the basin (Marshall and Petch, 1985).

Groundwater quality in the Hamilton Basin is highly variable. Excessive nitrate concentrations were already noted as being common in shallow, unconfined, aquifers by Marshall (1986). He also reported high iron concentrations in deeper and peaty sediments.

2.7 Waipa

The Waipā River is the major western tributary of the Waikato River with a catchment area of 306,569 ha. The alluvial lowlands in the northern and central catchment graben of the Waipa catchment are more intensively developed for dairy farming. Up-faulted greywacke basement and tertiary formations to the west are less permeable. Some limestone formations of the Te Kuiti Group provide localised groundwater resources in karst terrain. There are also a few notable basaltic andesite volcanic cones (including Pirongia and Te Kawa) of the Alexandra Group Volcanics associated with faulting in the west (Edbrook, 2005). Greywacke basement is shallower and variously exposed to the south. These are overlain by ignimbrites of the Pakamanu Group in the south-east. The distribution of geological formations is summarised in Figure 8 (White et al., 2015).

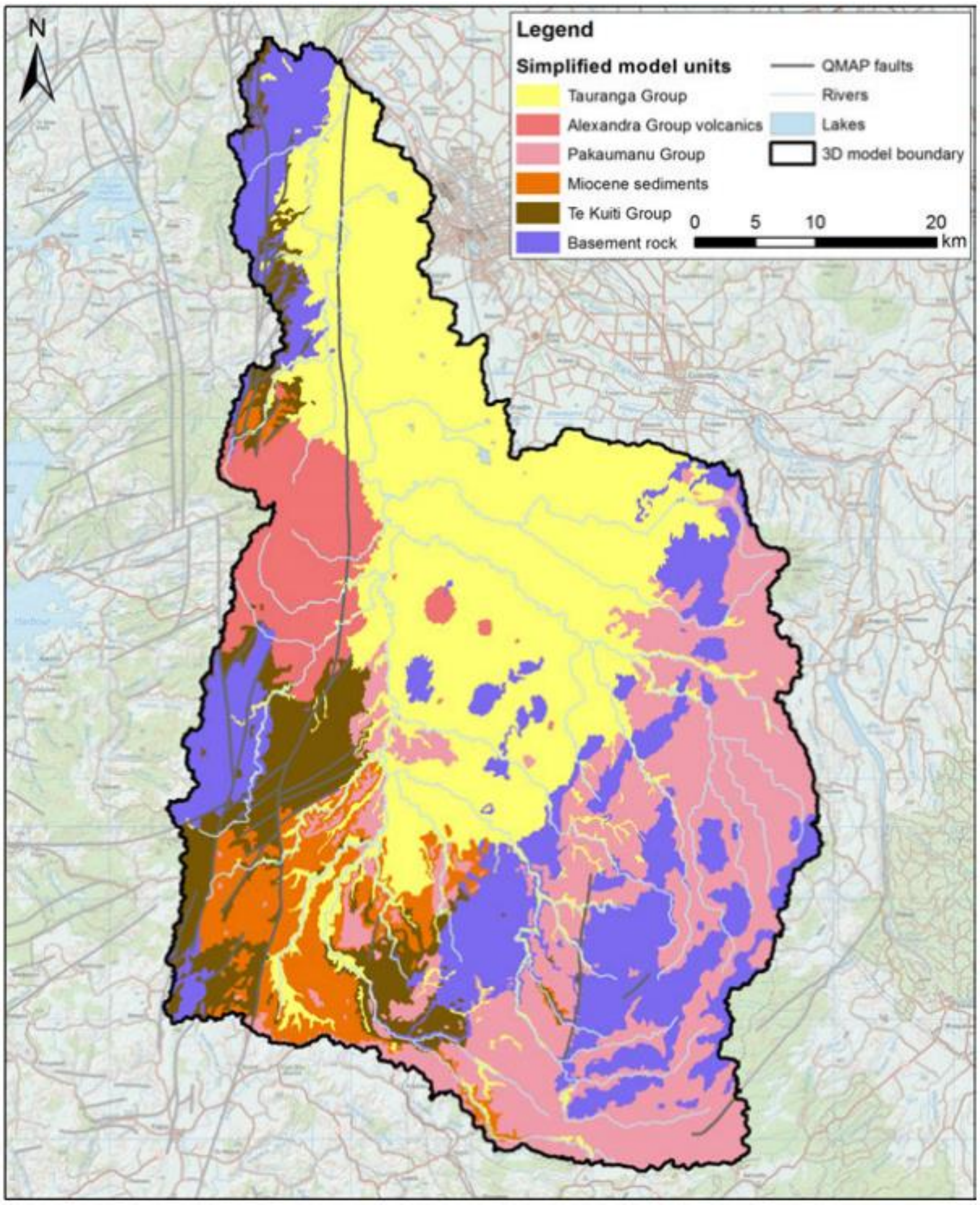


Figure 8 **Geological map of the Waipa catchment**

Groundwater supplies are predominantly derived from the thick Quaternary Tauranga Group sediments, particularly in the lower catchment. Other aquifers include Miocene sediments and limestones (associated with Waitomo caves), and Alexandra Group volcanics.

Preliminary groundwater modelling of the Waipa catchment shows groundwater flow is strongly influenced by the Waipa River which acts as the only groundwater sink (Rawlinson et al., 2016). A considerable portion of net rainfall in the Waipa catchment enters the groundwater system. Mean rainfall recharge for the Waipa Catchment from multiple estimates indicates an uncertainty of 70.7 % ± 10% m^3 s^{-1} (Rawlinson et al., 2015). Baseflow was estimated to be 60% to 80% of river flow (White et al., 2015).

2.8 Northern area

The Pukekohe, Waiuku and Pukekawa areas in the north of the Waikato Region are hydrogeologically complex. The generally low angle topography is strongly influenced by Pleistocene basaltic volcanism with numerous volcanic cones and tuff rings. The basalt aquifers vary substantially in their hydraulic properties dependent upon fracturing with measured transmissivities ranging from 7 m^2 d^{-1} to 5,600 m^2 d^{-1}.

Alluvial Tauranga Group sediments separate shallow basalt aquifers from deeper Kaawa Formation, which is the other major local aquifer north of the Waikato River. Fine silty sediments at the base of the Tauranga Group form an effective but discontinuous aquitard (Figure 9).

The Pliocene, sometimes shelly, marine sand/sandstone Kaawa Formation can reach 300 m in thickness and typically has a local permeability of about 1 m d^{-1}. The Kaawa Formation is limited southward and eastward by uplift on the Waikato and Drury faults respectively. It is underlain by the Miocene, Waitemata Formation. These sandstone and siltstone, flysch sediments are generally regarded as local hydrogeologic basement but can yield small groundwater supplies.

Piezometric contours for shallow aquifers in the Pukekohe area reflect topography as shown in Figure 9 (Hadfield in Rosen and White eds, 2001). The largely confined Kaawa Formation is recharged via vertical leakage over much of the area particularly under Pukekohe Hill. Leakage across the overlying aquitard is estimated to range up to 100 mm and average 50 mm annually. Negative head gradients across the aquitard, however, indicate a discharge regime occurs generally below the 20 m topographic contour.

Water resources are intensively used in the Pukekohe and Pukekawa areas, particularly for market gardening during the summer months. Streams are sustained by groundwater during periods of drought. The five-year recurrent daily low flow specific discharge is about 2.8 l s^{-1} km^{-2}. Streamflow responds promptly to variation in shallow aquifer storage indicating close interaction (Petch et al., 1991).

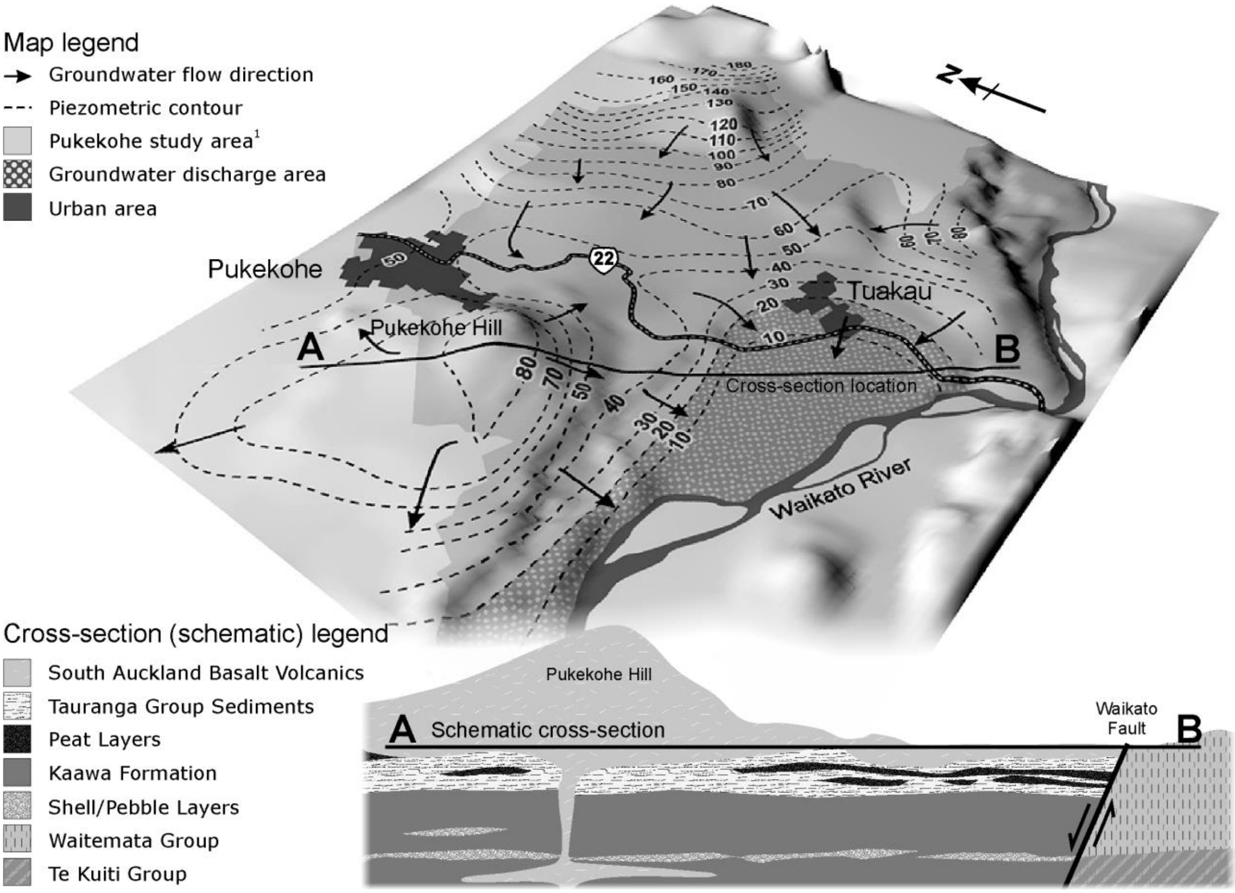


Figure 9 **Piezometric surface for shallow aquifers in the Pukekohe area and geological section**.

Abstraction of groundwater in Pukekawa is more reliant (~90%) on the numerous, discontinuous, basalt aquifers given the absence of Kaawa Formation in this area (Bell et al., 1991). Numerical groundwater flow modelling undertaken by Thornburrow (2018), indicated that groundwater abstraction impacts local stream low flows although some 40% of the depletion effects are to surface waters outside the immediate basalt plateau area.

More recent three-dimensional, geological modelling of the northern area has been undertaken by White et al., (2019). This work utilised both Auckland and Waikato data to review the distributions and characteristics of Franklin area aquifers. It builds on work undertaken as part of the Healthy Rivers project (White et al., 2015).

Groundwater quality in the basalt aquifers is naturally very high but shallow aquifers are becoming increasingly degraded from intensive land use effects e.g. nitrate and pesticide contamination. The Kaawa Formation is less vulnerable to contamination and continues to have relatively higher water quality.

2.9 West Coast

Groundwater resources in the western sub-region from northern Taranaki to Port Waikato are not substantially developed and are not specifically addressed. Intensive land use is limited to some alluvial lowlands and much of the greywacke and Tertiary limestone, sandstone, and siltstone formations predominantly comprising the geology are poor yielding. Dissolution of limestone by underground water has led to notable karst development in the Waitomo area (Ford and Williams, 2007).

3 Groundwater quality monitoring programme

3.1 Monitoring networks

The groundwater quality monitoring programme derives information from two monitoring networks (Figure 10). It provides an indication of groundwater quality across the region including spatial and temporal trends, as required by the Resource Management Act (Hadfield, 2011 and 2013).

The principal state of environment (SOE) network comprises 110 wells, the majority of which are monitored annually. A subset of 37 wells are monitored quarterly and of these 10 are part of the National Groundwater Monitoring Program (NGMP). Routine groundwater quality monitoring in the region commenced in 1995 involving 30 wells and increased to 108 wells within two years. A second ‘Community’ network was established in 2000. This currently comprises a minimum of 80 rural schools which are monitored every two years.

The SOE network is intended to represent a broad range of groundwater characteristics rather than investigate the impacts on quality of specific point source discharges. The networks, particularly with the addition of the rural schools, are widely distributed throughout the region. Groundwater aquifer systems are three dimensional and substantial changes in groundwater quality often occur with depth. Groundwater may therefore be monitored at the same location at various depths.

The SOE network tends to overly represent vulnerable aquifers with relatively young groundwater in aerobic condition. The initial 30 wells focused primarily on nitrate occurrence in shallow groundwater and excluded wells with anaerobic conditions. Given also, that where possible, water supply wells are drilled to avoid poor quality water and less permeable formation, such situations are expected to be under-represented in the network. There are also few wells representing ambient conditions apart from where older groundwater may be sampled. It is noted that some water quality records may not be long enough to show gradual trends which may be occurring in deeper and older groundwater.

Apart from the spatial distribution, an important criterion is that wells are properly documented to inform interpretation. This is with regard primarily to both well construction and geology. Some early exceptions are progressively being rectified. Wide diameter wells have recently been replaced. These often had very little associated well log information and were difficult to sample. The replacements, by contrast, were fully cored and are narrow (50 mm) in diameter. An overlap period is, however, required before these will be substituted into the monitoring dataset. Monitoring well construction and other details are provided in Appendix I.

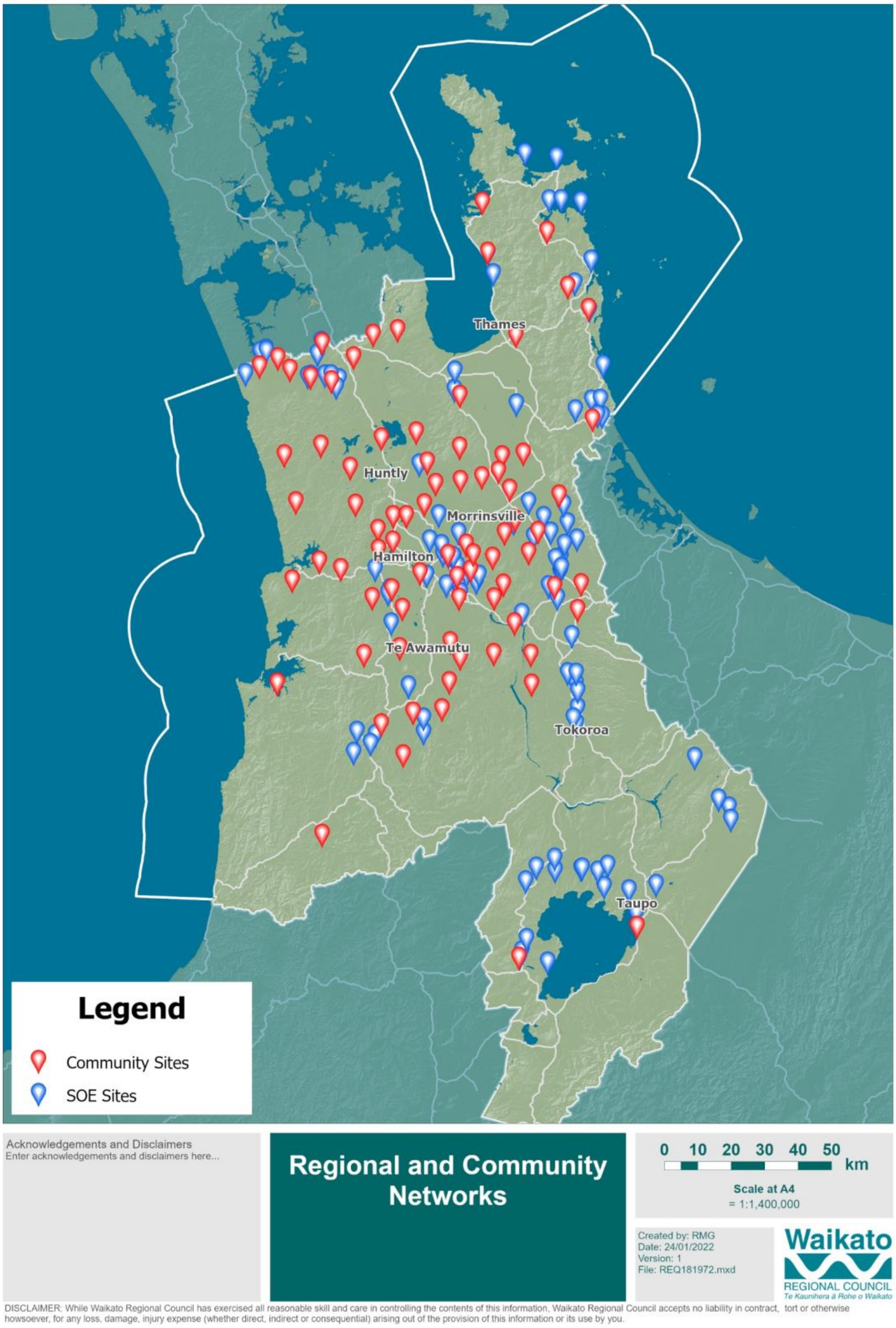


Figure 10 SOE (Regional) and Community groundwater quality monitoring networks

There are currently relatively fewer dedicated sampling wells in the SOE network and therefore monitoring is more dependent on available access to predominantly privately owned sites. Consequently, there have been replacements and changes over time resulting in variations in data records as sites are substituted.

Monitoring of the community network was initiated following an investigation of community water supplies in the Waikato region undertaken at that time (Hadfield and Nicole, 2000). It was found there was little focus on source water monitoring or protection (which was recommended in the report). The community network reported here comprises 80 rural schools which are monitored every two years due to logistic constraints. This monitoring has obvious community interest. It also provides an objectively determined, well distributed, network on public land. It was therefore expected to be a stable network with dependable access. It has not been as reliable as initially thought, however, given changes with rural school closures and supply replacements. Also, as these supplies are required to meet drinking water guidelines, they tend to be shut down once exceedances occur. Some, which continue to be used for other non-potable supply, remain in the network. Many of the school supply wells were drilled long before regional council drilling management or database archiving and thus have limited information with only half having driller's logs (Appendix 1).

Under the Water Services Act smaller community water supplies such as schools will be required to monitor their source water as part of a multi-barrier consideration for protection. This information will be supplied to WRC by Taumata Arowai. This will build on the valuable data already collected and promote further collaboration for supply and resource protection.

There are site sheets for each monitoring well documenting the location with finder diagrams, photos of the wells and pumping equipment. They also describe aspects of note for sampling and list any safety and health concerns and requirements. A characteristic of monitoring non-dedicated wells is that logistics frequently change, and site sheets must be continually updated.

Monitoring network design is fundamentally important and a review of the SOE network is planned to optimise the programme. One approach is to investigate how representative the current network is of a larger set of all available data using a selected determinant, as described by Farlin et al., (2019). The most efficient network optimisation would involve the least change of sites to achieve acceptable representation. An obvious focus for consideration is nitrate-N given the importance of this ubiquitous, manageable, contaminant both in respect to health and the environment. The current use of both quarterly and lower annual frequency monitoring allows greater spatial representation within logistic constraints, while allowing some seasonal consideration. Many trends in groundwater are very long-term and buffered and therefore do not require as high frequency monitoring as that required for surface waters. High frequency case investigations using in-situ probes (e.g. nitrate-N) can, however, provide insights for interpretation.

It is noted that there are other datasets related to specific groundwater quality investigations, such as for the Lake Taupo catchment and Coromandel coastal aquifer studies, which are not included or discussed in this report. Also there has been reporting of groundwater quality related to sub-catchments within the Waikato River catchment in support of Plan Change 1 e.g. by White et al., (2015).

3.2 Sampling procedures

As mentioned, wells are monitored quarterly, annually or biennially dependent on the network. Sampling is carried out by WRC's Environmental Monitoring team using a range of in-situ pumps and introduced pumping equipment. A typical sampling set up involves the use of a multi-parameter, digital, water quality meter and flow cell. Upload of field data to the database is via a mobile phone application. Three annular volumes are flushed prior to sampling to remove stagnant water and field parameters are checked during this process to ensure equilibrium has been reached. Sampling procedures largely followed the national protocol for state of the environment groundwater sampling in New Zealand introduced by the Ministry for the Environment in 2006 (MfE, 2006). A notable exception was that pH continued to be analysed only in a controlled laboratory environment until 2017. Before 2006 conductivity, temperature and inconsistent dissolved oxygen (D.O.) measurements were taken in the field. D.O. was not relied upon due to in-situ pumping effects.

More recently protocols have been adjusted to adhere to the National Environmental Monitoring Standards for groundwater quality introduced in 2019 (NEMS, 2019). This includes sensor calibration and field stabilization criteria for sample collection. The following pre-sampling criteria apply to field determinants: temperature +/- 0.2°C, conductivity +/- 5% if <= 100 uS/cm and +/- 3% if > 100 uS/cm, pH +/- 0.1 pH units and dissolved oxygen +/- 0.3 mg/L.

Collected samples are kept cool (~4° C) and transported to Hill Laboratories in Hamilton for analysis. Microbial samples are delivered within 24 hours. NGMP samples are sent to the Geological and Nuclear Sciences (GNS) laboratory at Wairakei.

3.3 Data suite and analysis

Chemical analysis is undertaken at IANZ-accredited laboratories. The ion charge balance error is routinely calculated for samples at the laboratory. Charge balance errors over the standard 5% threshold are reviewed, attributed and may uncommonly require re-analysis. Quality assurance checks are also made before all the water quality data from field measurements and laboratory analysis is stored in the council's water quality archiving database (Wiski). More recently this has involved automated comparison with expected determinant ranges.

The current suite of SOE determinants which are analysed is listed in Appendix II, Table II.1 along with their associated methods and detection limits. The SOE state and trend analysis presented here, however, has been carried out using 14 selected determinants. These comprise the major ions, pH, electrical conductivity, nitrate-N, ammonium-N, iron, manganese and boron (except the last two for the NGMP wells). Although there are more determinants measured in the current routine SOE suite many do not have sufficient records for trend analysis. The groundwater quality programme has recently been transitioning from a predominance of total analysis to also include a greater number of field-filtered dissolved determinants. Total analysis is required for comparison with the drinking water standards to determine potability. Dissolved concentrations, however, better reflect likely migration from an environmental perspective. Dissolved iron and manganese have been routinely analysed since 2008. The dissolved fraction of several other major ions has been added since 2017, although these records are insufficient to report here.

Dissolved reactive phosphorous has been analysed on an occasional basis. This is due to the slow concentration changes expected, reflecting long residence times required for the dissolution from minerals in formation (Scott and Wong, 2016). It has now, however, been routinely included since 2014 given an interest in providing nationally consistent reporting.

Apart from the SOE state and trend analysis there are numerous other parameters which are discussed in section 6, primarily in respect to potability. These include pesticide analysis of over a hundred compounds, which are analysed on a much less frequent basis. Similarly, E-coli is not measured on a routine basis as described in section 6. There have also been other selected specific investigations which are briefly described in the same section. These include specific studies of parameters of concern including arsenic, glyphosate and recently a much wider group of emerging contaminants.

Data from the three components of the SOE groundwater quality network (quarterly, NGMP and annual) were collated for the period 2003 to 2020 for analysis. This period of 18 years allows components such as Taupo monitoring to be included and provides the most widespread representation of sites. Given the Community network is only monitored every two years the full available record was used from 2000 to 2020. Initial data examination was undertaken using an automated spreadsheet from GNS (Daughney, 2010). This allowed outliers to be identified and obvious anomalies to be examined. These occasionally led to corrections relating to data entry. It is noted that there are various gaps in individual monitoring records and sometimes changes also in analysis methods and associated detection limits. Methods were aggregated where appropriate and detection limits maintained.

Trend analysis was carried out using R scripts obtained from the LWP trends library in 2021 described by Snelder and Frazer (2019). These tools for water quality analysis require the plyr, NADA and gam packages. Left sensored (below detection) data are replaced by imputed values based on non-sensored data as described by Helsel (2012). Trends may be calculated with a range of confidence intervals, which are a measure of the precision of detection. Trends with 95% confidence have predominantly been used, although wider intervals are described and sometimes reported in Section 5. Widening the intervals results in the detection of trends with less precision although such trends would be detected in more parameters and at more sites and vice-versa (Helsel and Hirsch, 1992).

4 Influences on groundwater quality

4.1 Introduction

The hydro-chemical composition of groundwater may be influenced by numerous factors. Its chemical character initially reflects recharge conditions and then progressively evolution along flow pathways. Ion concentrations typically increase during migration due to water-rock interaction and other groundwater processes. Influences include natural conditions such as soil type, aquifer geology, and geothermal affects. Anthropogenic impacts from land-use activities are fundamentally important in respect to manageable aspects of groundwater quality.

Apart from factors mentioned here, the interaction between groundwater and surface waters may influence the water quality of both. Streams gain or lose water to the ground depending on the local flow regime. The water quality of streams particularly during low flow may strongly reflect its sustaining groundwater contribution (Stenger et al., 2022).

4.2 Recharge and geochemical processes

Groundwater recharge in the Waikato region is typically derived from rainfall. The local rainwater chemistry thus influences groundwater chemistry, particularly of shallow aquifers in recharge areas. Sodium and chloride concentrations, for example, vary spatially influenced by proximity to the coast. (Drever, 1988).

The chemical composition of rainwater in the Taupo area was investigated by Timperley and Vigor-Brown, (1986). The mean annual concentrations of major ions in rainwater have been compared with mean 2001 concentrations for selected groundwater groupings based on geology in Figure 11 (Hadfield et al., 2001). The sub-parallel relationship exhibited in the Schoeller plot implies that the groundwaters are of a generally similar character, although significantly evolved from rainwater (Zaporozec, 1972). The divergence in relative bicarbonate concentration between rainwater and groundwater reflects normal carbonic acid leaching of rhyolitic formation.

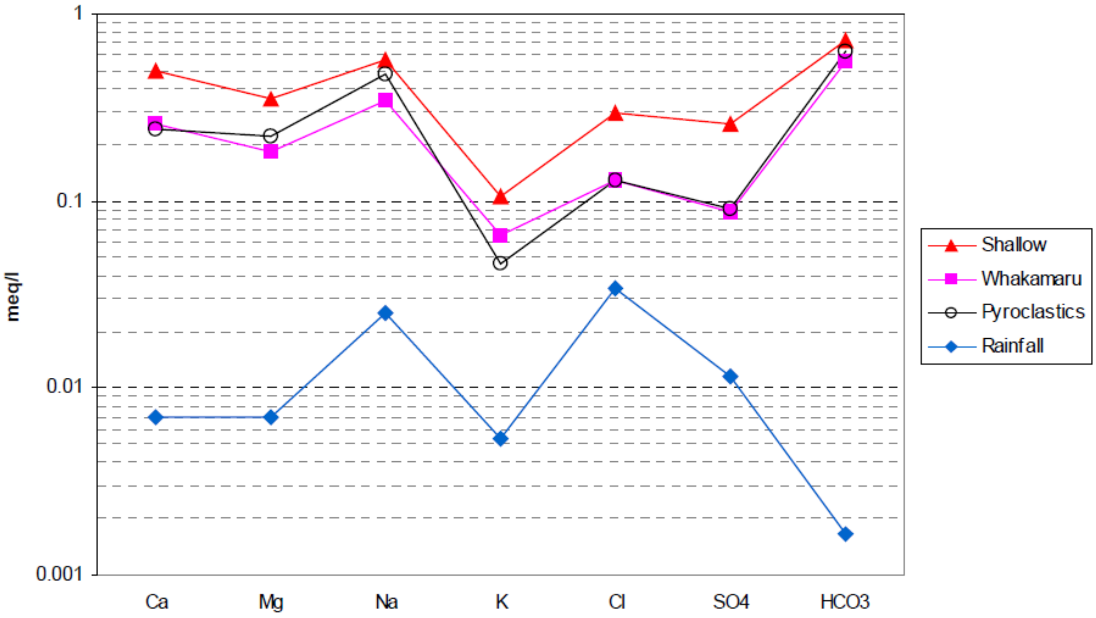


Figure 11 Schoeller plot of rainfall and mean chemistry for groundwater groupings

Water infiltrating into the ground is altered chemically even before it reaches the water table. Uptake of CO_2 by water to form HCO_3 is one of the major alterations processes within soil and may be expressed as follows:

$$CO_2 + H_2O = H_2CO_3 \text{ and } H_2CO_3 = H^+ + HCO_3^-$$

CO_2 is brought into solution in the soil, where it has a higher partial pressure than in the atmosphere, caused primarily by root and microbial respiration. The soil exerts a strong influence on the chemistry of infiltrating water and is capable of generating relatively large amounts of acid (Palmer and Cherry, 1984).

After recharge at the water table, groundwater migrates through a sequence of formations and mineral assemblages. The composition of these formations and the order in which they are encountered control the groundwater chemistry. The length of the flowpath and the groundwater velocity are also strong influences on chemical character. The most important reactions in the evolution of groundwater chemistry are mineral dissolution and precipitation, redox reactions and cation exchange (Freeze and Cherry, 1979).

Dissolution results in the progressive weathering of minerals releasing cations and dissolved silica in the process. Mineral dissolution generally proceeds in several steps each releasing cations into solution. Ion exchange primarily involves clay minerals which absorb cations such as calcium, magnesium, and potassium, in preference to sodium, which is released into solution. A progressive increase in sodium ratios along the groundwater flowpath indicates substantial cation exchange is occurring (Appelo and Postma, 1993).

Groundwater undergoes a complex series of chemical reactions with the formations through which it migrates (Hounslow, 2018). Reconstruction of the sequence of chemical reactions responsible for the observed groundwater chemistry, by way of mass balance calculations requires detailed information and is not addressed in this report.

4.3 Redox conditions

Redox conditions are important in respect to nitrogen transformation and attenuation of the principal manageable contaminant of concern being the oxidised form nitrate-N. The processes involved are therefore considered in more detail. Redox reactions effectively involve the transfer of electrons between dissolved, gaseous or solid constituents. In groundwater every oxidation (electron loss) is balanced by reduction (electron gain). In order for the reduction of inorganic constituents to occur some other component must be oxidised. The constituent oxidised is often (but not always) organic matter, catalysed by bacteria (Korom, 1992).

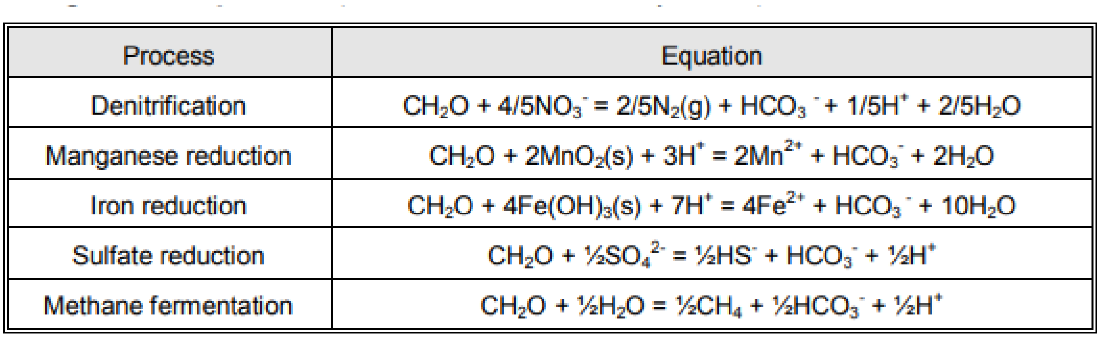
Groundwater redox levels are essentially determined by the relative rates of the introduction and consumption of dissolved oxygen. Oxygen is introduced by circulation but is not readily replenished due to isolation from the atmosphere. Consumption of oxygen is primarily by bacterially mediated decomposition of organic matter and to a lesser extent by other hydro-chemical reactions. There are four factors identified by Drever (1988), as being most important in determining redox conditions:

(i) the oxygen content of recharge water,
(ii) the availability and reactivity of organic matter and other potential reductants,
(iii) the existence of potential redox buffers in the aquifer and
(iv) groundwater circulation rate.

Infiltration through organic rich soils may readily deplete the dissolved oxygen in recharging groundwater. Further oxidation of organic matter can still occur once dissolved oxygen has been consumed. In its absence, the oxidising agents which are progressively reduced are; nitrate, manganese oxides, iron hydroxides, sulphate and others. The groundwater environment becomes progressively more reduced as these oxidising agents are consumed. Organic constituents may be anaerobically degraded should conditions become sufficiently reduced.

Table 1 (Freeze and Cherry, 1979), lists a sequence of redox reactions which progress downwards from aerobic oxidation to methane fermentation. These reactions proceed at a significant rate provided there is a supply of consumable organic matter and bacteria have sufficient nutrients.

Table 1 **Some redox reactions that consume organic matter and reduce inorganic compounds**



Process	Equation
Denitrification	$CH_2O + 4/5NO_3^- = 2/5N_2(g) + HCO_3^- + 1/5H^+ + 2/5H_2O$
Manganese reduction	$CH_2O + 2MnO_2(s) + 3H^+ = 2Mn^{2+} + HCO_3^- + 2H_2O$
Iron reduction	$CH_2O + 4Fe(OH)_3(s) + 7H^+ = 4Fe^{2+} + HCO_3^- + 10H_2O$
Sulfate reduction	$CH_2O + \frac{1}{2}SO_4^{2-} = \frac{1}{2}HS^- + HCO_3^- + \frac{1}{2}H^+$
Methane fermentation	$CH_2O + \frac{1}{2}H_2O = \frac{1}{2}CH_4 + \frac{1}{2}HCO_3^- + \frac{1}{2}H^+$

Both dissolved and solid-phase organic carbon along a groundwater flow-path can provide reactants for such processes as sulphate reduction. Increases in iron and manganese in groundwater from wells near organic-carbon sources results from dissolved organic matter participating in metal oxide reduction (Freeze and Cherry, 1979). Oxidation of only a small amount of organic matter in groundwater can result in the consumption of all available dissolved oxygen. The decomposition of organic matter may be represented by the following reaction in the presence of bacteria and free oxygen.

$$O_2(g) + CH_2O = CO_2(g) + H_2O$$

There has been considerable investigation of both the distribution of favourable conditions for, and processes involved in, denitrification in the Waikato region, particularly in the Taupo catchment. This has included coring of shallow formation to identify anaerobic conditions using the Childs' test (Childs, 1981). Anaerobic conditions were confirmed at a depth of less than five metres below the water table at nearly 60% of 14 sites investigated in the Lake Taupo Catchment. Similar investigations in other parts of the Waikato region (e.g. Hauraki and Hamilton Basin) have also shown redox chemistry results consistent with Childs' testing indications. It is noted that nitrate is not detected in groundwater samples obtained from piezometers specifically isolated to anaerobic zones.

Further work included a series of "push-pull" tracer tests to confirm that nitrate injected into the anaerobic zones actually attenuated, and to estimate rates (Hadfield and Korom 2012). In-situ mesocosms were also used in Taupo to enable longer term geochemical modelling to determine electron donor contributions. This indicated that while organic carbon in paleosols is important, denitrification may be more widespread with both autotrophic and heterotrophic denitrification occurring in the Lake Taupo catchment (Korom et al. 2016).

Martindale at al. (2019) went a step further and showed where denitrification was actively occurring naturally. This involved measuring two noble gases (neon and argon) to differentiate excess N_2 gas produced via denitrification from atmospherically derived dissolved N_2 gas. Results showed eight of ten sites selected in Taupo had measurable excess N_2 indicative of denitrification. Substantial investigation of an intensively instrumented Waihora hillslope study site at Taupo further detailed complex variations in vertical redox gradient, denitrification potentials and their biogeochemical and hydrological controls (Barkle et al. 2011, Stenger et al. 2018).

Recent re-drilling (coring) of 18 shallow SOE wells predominantly in the Hamilton Basin further demonstrated the importance of understanding the hydrogeological and notably redox conditions. Despite these wells being shallow (<10 m), four encountered previously unknown redoxclines (Hadfield, 2021). Redoxclines are boundaries with strong redox gradients from upper oxygenated to lower anoxic water.

Four categories are used to classify the redox status of groundwater monitored in the SOE and Community network sites. Apart from aerobic and anaerobic categories, mixed and indeterminate categories are also designated. The criteria for these are loosely based on the work of McMahon and Chapelle (2008) and are as follows:

- Aerobic: NH_4, dissolved Fe and dissolved Mn all non-detect and NO_3-N > 1 ppm
- Anaerobic: Two of NH_4, dissolved Fe and dissolved Mn detected and NO_3-N non-detect
- Mixed: Two of NH_4, dissolved Fe and dissolved Mn detected and NO_3-N detected > 1 ppm
- Indeterminate: not meeting the criteria above and may reflect older waters or little land-use loading

It is noted that dissolved oxygen has not been used as part of these criteria given data may be unreliable due to in-situ pumping effects. The prevalence and influence of redox characteristics on monitored groundwater are described in more detail in section 5.

The spatial distribution of redox conditions within the region has been predicted (Figure 12) based on available groundwater chemistry and related formation characteristics using linear discriminant analysis (Close, 2015). Reduced (anaerobic) conditions are predicted to dominate in the low lying poorly drained areas of the lower Waikato basins and Waipa catchment. Oxic (aerobic) conditions, by contrast, are indicated to be more common in elevated terrain, particularly parts of the Upper Waikato. Reduced conditions occur more commonly with depth in the Hamilton Basin and with distance northward along the Hauraki Plains (not shown). Larger scale national mapping of predicted redox categories using statistical learning methods has been carried out by Wilson et al., (2020).

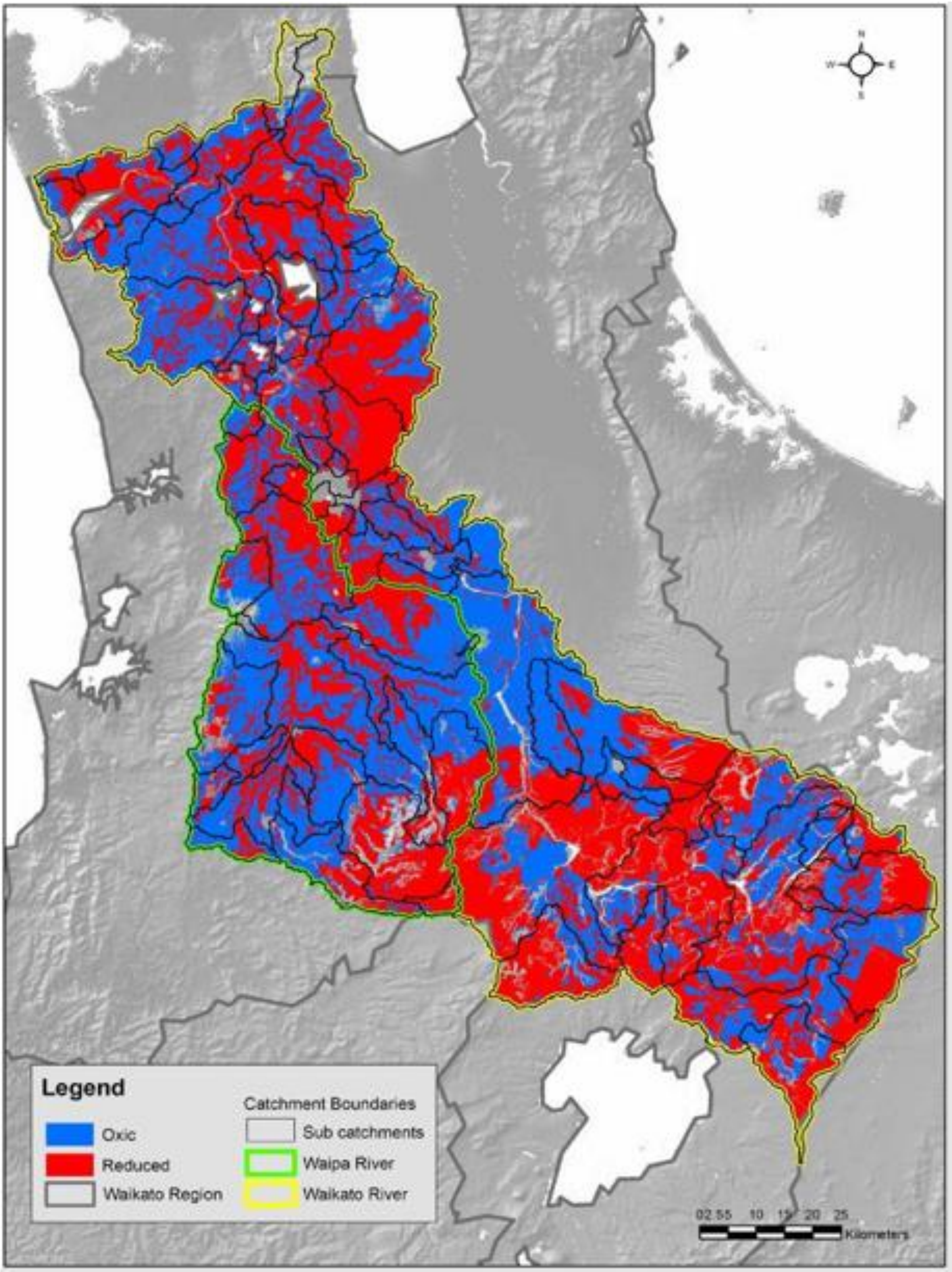


Figure 12 **Spatial prediction of oxic and reduced conditions in shallow groundwater (< 25 m depth) in the Waikato and Waipa catchments**

4.4 Groundwater age

The age of groundwater can influence its quality in that it reflects the progress of processes. There may be a considerable lag between the effects of land-use at the ground surface and impacts on older groundwaters. Groundwater age can be estimated by measuring the cosmogenic isotope tritium (half-life of 12.3 years) and other atmospheric tracers such as CFCs and SF_6 to reduce ambiguity. Tritium is a conservative tracer in groundwater. It is not affected by chemical or microbial processes, or by reactions between the groundwater, soil sediment and aquifer material. Tritium is a component of the water molecule and age information is therefore not distorted by any processes occurring underground (Malosezewski and Zuber, 1982).

The interpretation depends on mixing processes underground. Samples comprise a mixture rather than a discrete age reflecting variable flowpaths. It can be useful to estimate not only the mean residence time (MRT) but also fractions of water such as that recharged since farming was introduced to an area (Morgenstern, 2007).

The age of groundwater in the SOE monitoring network is highly variable (Appendix 1). For the 85 sites where groundwater age estimates are available the mean residence times (MRTs) range from 0.2 years to greater than 250 years. The median is about 22 years and the interquartile range (IQR) is about 44 years (from 6.4 to 50 years MRT).

There is no simple linear relationship between groundwater age and well depth, although age may generally increase with depth within a recharging regime. Similarly, there is no simple linear relationship between age and nitrate-N concentration in wells. Typically, however, there is a wedge-shaped distribution showing groundwater older than the significant development of farming is low in nitrogen, whereas younger groundwaters range in concentration dependent on land-use influence and attenuation.

Estimating the travel time through the unsaturated/vadose zone is a component in determining the overall lag time between land use intensification and the associated impacts on groundwater and surface water quality. The following figure shows modelled time of travel through the vadose zone into shallow groundwater. Most of the lower Waikato, Hamilton and Waipa basins have vadose travel times estimated to be less than 10 years, whereas elevation over 100 m in the Upper Waikato may have travel times of some 30 years (Wilson and Hadfield, 2017).

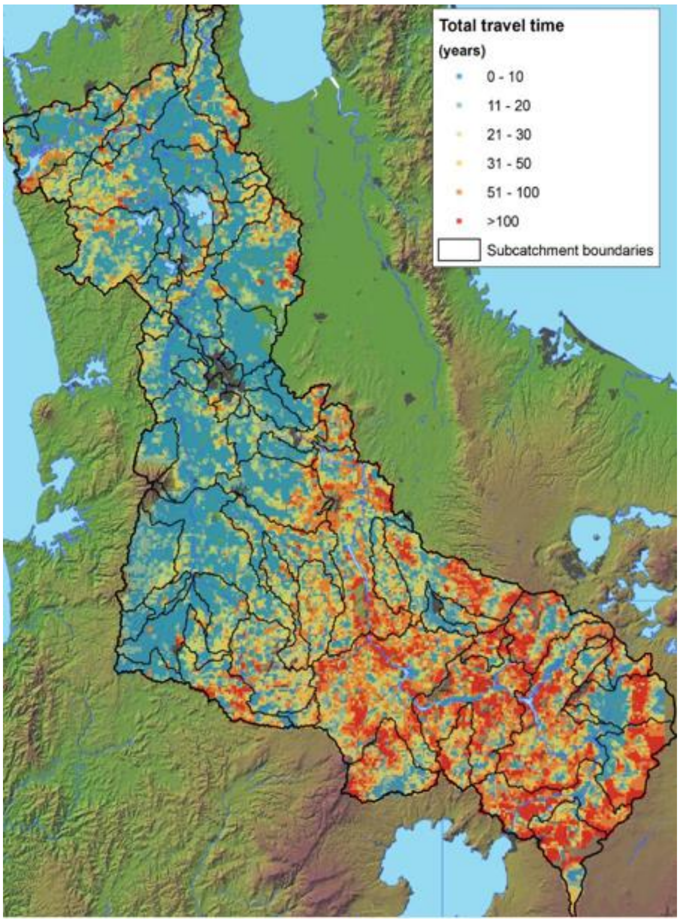


Figure 13 **Estimated travel time through the vadose zone into the unconfined aquifer**

Numerical modelling typically indicates that in the Waikato there are substantial lags before full nitrogen equilibrium with land-use loading is reached. Simulation assuming conservative nitrogen transport inferred lags of some 250 years in the northern Lake Taupo catchment (Hadfield, 2007) and 900 years in the Upper Waikato catchment (Weir and Rajanayaka, 2014). Half of this simulated change, however, was predicted to occur within about 30 years and 40 years respectively. Further Upper Waikato modelling work by Rajanayaka et al., (2020), indicated that about three quarters of surface water is sourced from groundwater, which is likely to account for most of the total nitrogen load. The mean residence time of contributing groundwater was estimated to average about 50 years and range from about 5 to 101 years. Taking attenuation into account in the northern Lake Taupo catchment substantially reduces lag times as well as the nitrogen loads (Vant and Hadfield, 2022). Stochastic analysis of nitrogen transport, including attenuation, in the west Lake Taupo catchment (Hemmings, 2021) and Hauraki area (Hemmings et al., 2022) illustrate substantial uncertainty in both lags and losses of nitrogen during transport in these domains.

Recent work by Stenger et al., (2022) using a Bayesian modelling approach for hydrograph separation and contaminant load partitioning showed that lag from groundwater nitrogen input to surface water may be less than often assumed. This approach utilises surface water quality monitoring data and targeted age-dating to estimate young (shallow) and older (deeper) groundwater pathway contributions. It generally showed that mass flux from young groundwater was often relatively important. Related research by Ehrhardt et al., (2021), however, although indicating relatively short transit times in many European catchments, cautioned that substantial nitrogen retention is likely to buffer remediation initiatives.

4.5 Land-use

The predominant land cover in the Waikato region is exotic grassland (53% in 2018), about half of which was used for dairy farming and the remainder for drystock. Indigenous forest cover accounted for 28% of the region with exotic forestry comprising about 12%. Cropland is estimated to be about 1% of the regional land area of 2,466,629 ha (Jones and Borman, 2022).

There is considerable land cover variation across the region. Most sub-regions are dominated by grassland pasture although Lake Taupo catchment and Coromandel are dominated by indigenous forest. Cropland cover predominantly occurs in the Lower (Northern) and Central Waikato, with the latter having the most urban development.

Net land-use change over the period 1996-2018 is indicated in Figure 14 (Jones and Borman, 2022). Increases, denoted by positive area change, were notably to pasture, cropland and urban development.

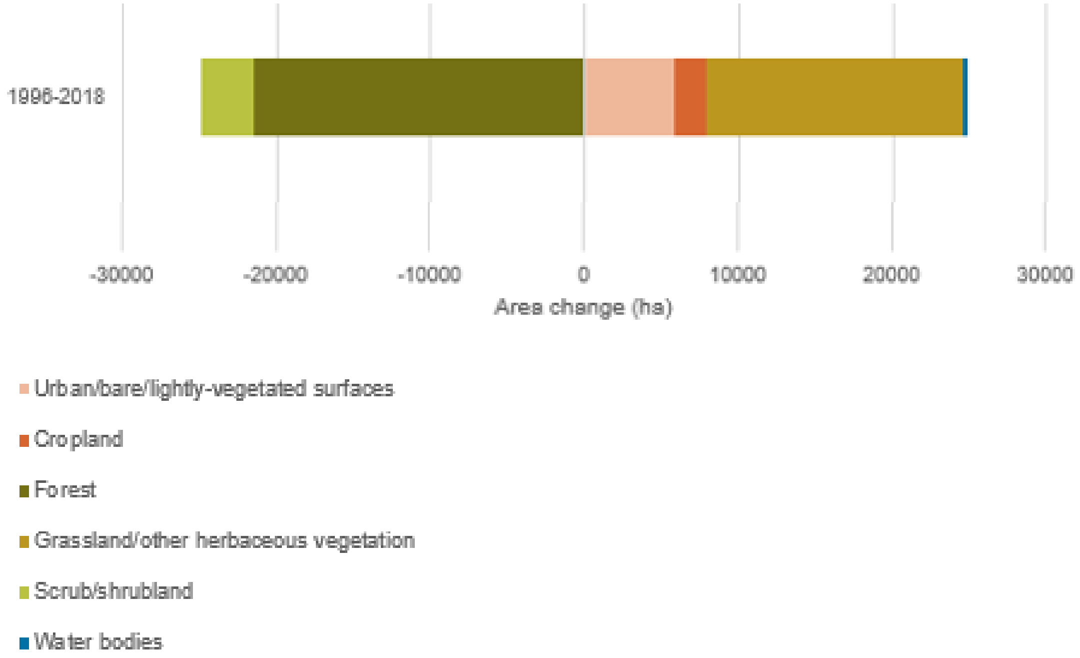


Figure 14 **Net land-use change 1996-2018.**

Land use intensification since 2001 has put greater pressure on existing soil and water resources (Hill and Borman, 2022). Intensification of existing pastoral land-use was the greatest driver of regional change (2001 to 2018), followed by planted forest conversion to pasture. This has included a notable “pine to pasture” shift in the Upper Waikato resulting in a net change of 49,525 ha from 2001 to 2018 (Hill and Borman, 2022; Figure 15). During the same period there has been a net decrease in pastoral land in the Lake Taupo catchment (-6,120 ha). This has involved conversion to forestry, via the Lake Taupo Protection Trust, as part of initiatives to protect water quality (under variation 5 of the Regional Plan).

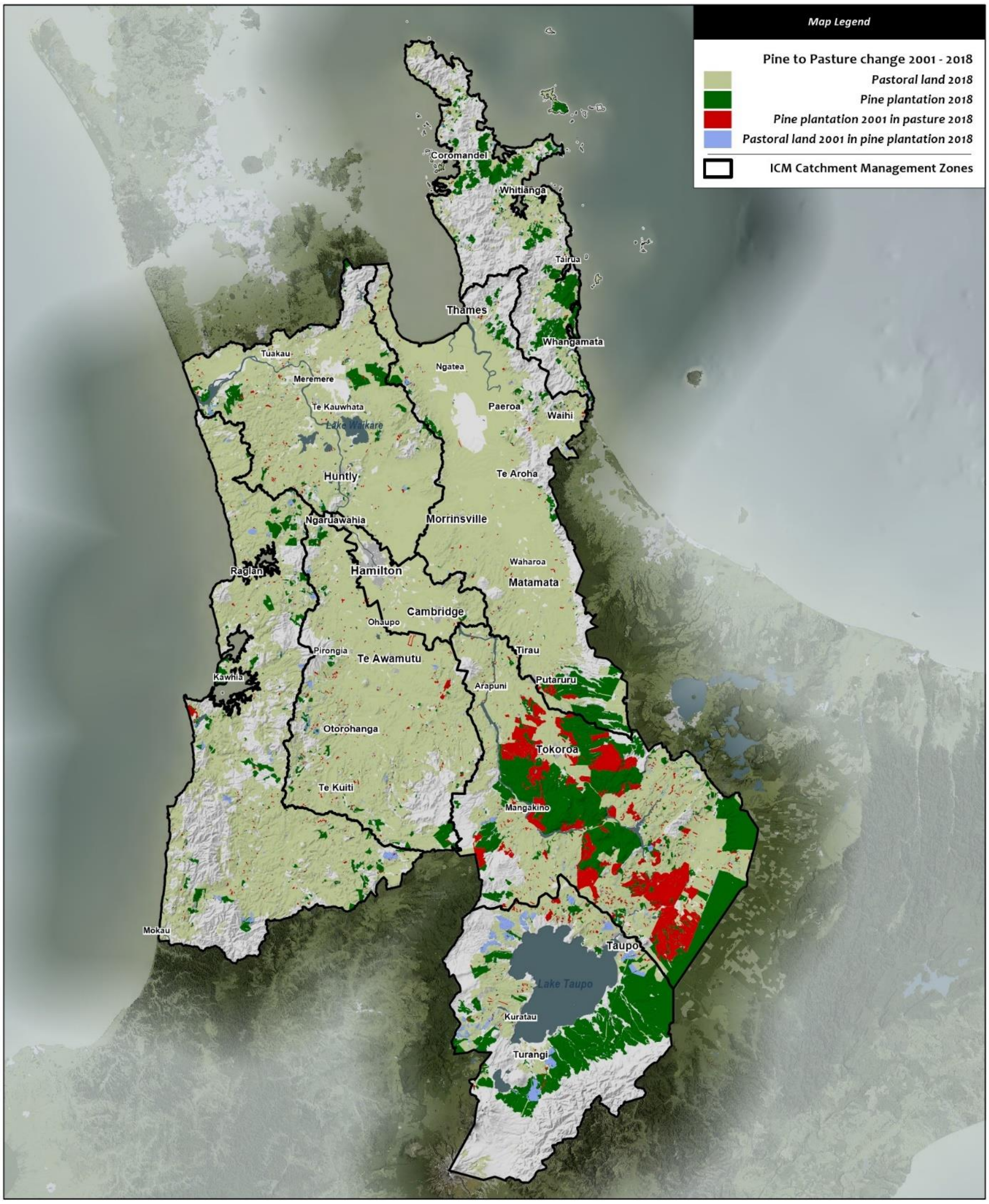


Figure 15 Land-use change between forest and pasture 2001 to 2018.

There has also been conversion of non-dairy pastoral land to dairy. The number of dairy cows in the Waikato has increased by 43% in the period 1990 to 2019, going from 1.28 M to 1.82 M (Statistics NZ, 2021). The intensification of land-use is illustrated in Figure 16 (Hill and Borman, 2022).

Such diffuse anthropogenic pressures as well as other point sources have consequences in groundwater quality contamination. Point sources include septic tanks, landfills, leaky underground storage tanks, industrial sites, sheep dips and woolsheds but are not addressed further here as they are not intentionally targeted by SOE monitoring. Although theoretically manageable, remediation of groundwater contamination is very difficult, and protection (or at least mitigation) is much more cost effective.

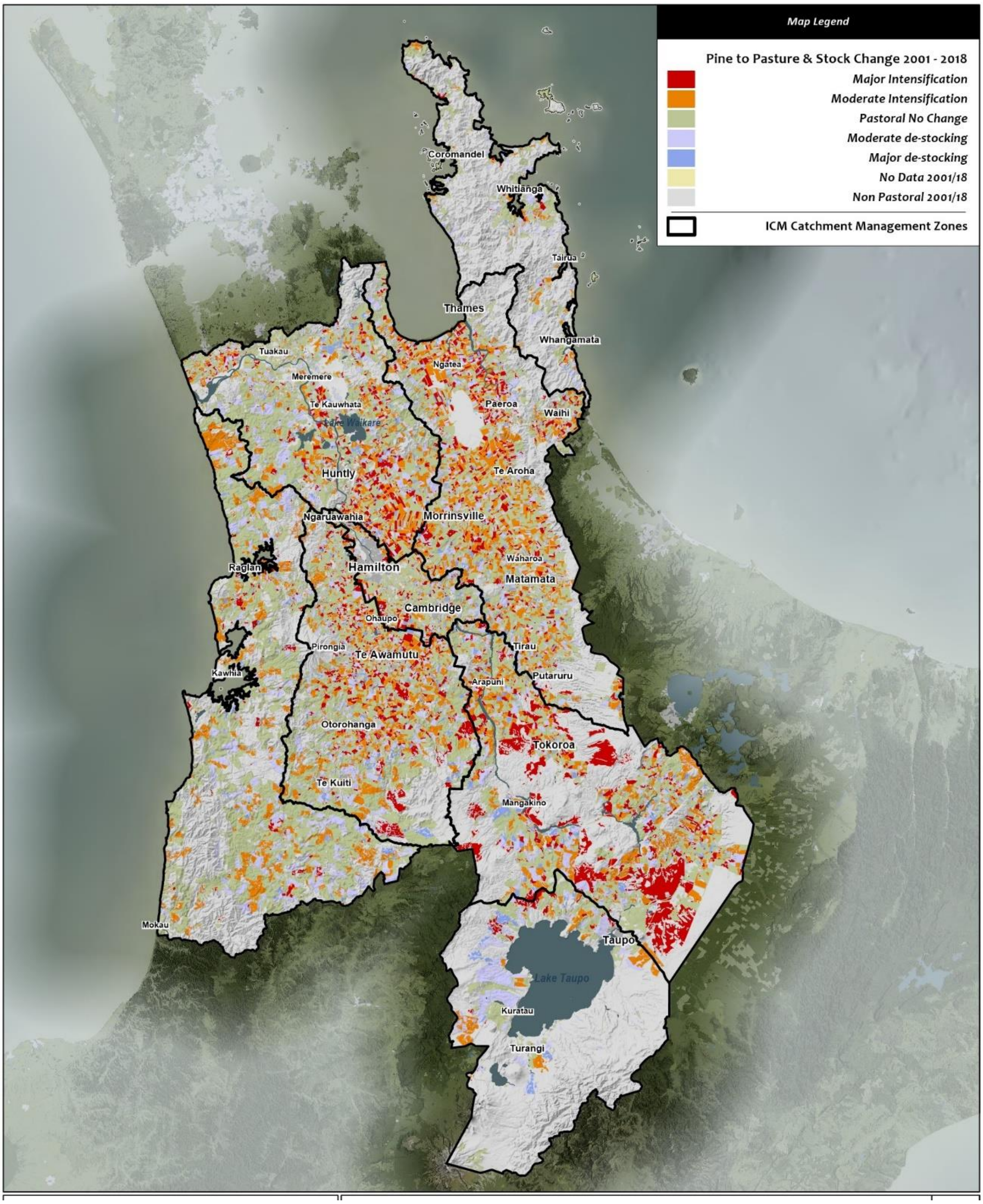


Figure 16 Map of pastoral land intensity change from 2001 to 2018.

5 Results and discussion

Groundwater quality monitoring results are presented initially on a sub-regional basis and then brought together in respect to regional state and trends. In general, sub-regional spatial characteristics are reported rather than differences on an aquifer basis given their complexity and statistical constraints, although some hydrogeologic groupings are noted. There is a particular focus on nitrate occurrence and factors influencing it.

Trend analysis uses data from an 18-year period from 2003 to 2020. Analysis of state is focused on the five years from 2016 to 2020. For sites where monitoring is less frequent than quarterly, data can be very limited such that a simple median is used.

5.1 Taupo groundwater quality

A total of 17 wells in the Lake Taupo catchment are monitored as part of the SOE network. The type and general character of these groundwaters is presented in a tri-linear Piper diagram using USGS software (Winston, 2000). Major ion milli-equivalent ratios are plotted in Figure 17. Median values being a measure of central tendency are used to derive the ratios.

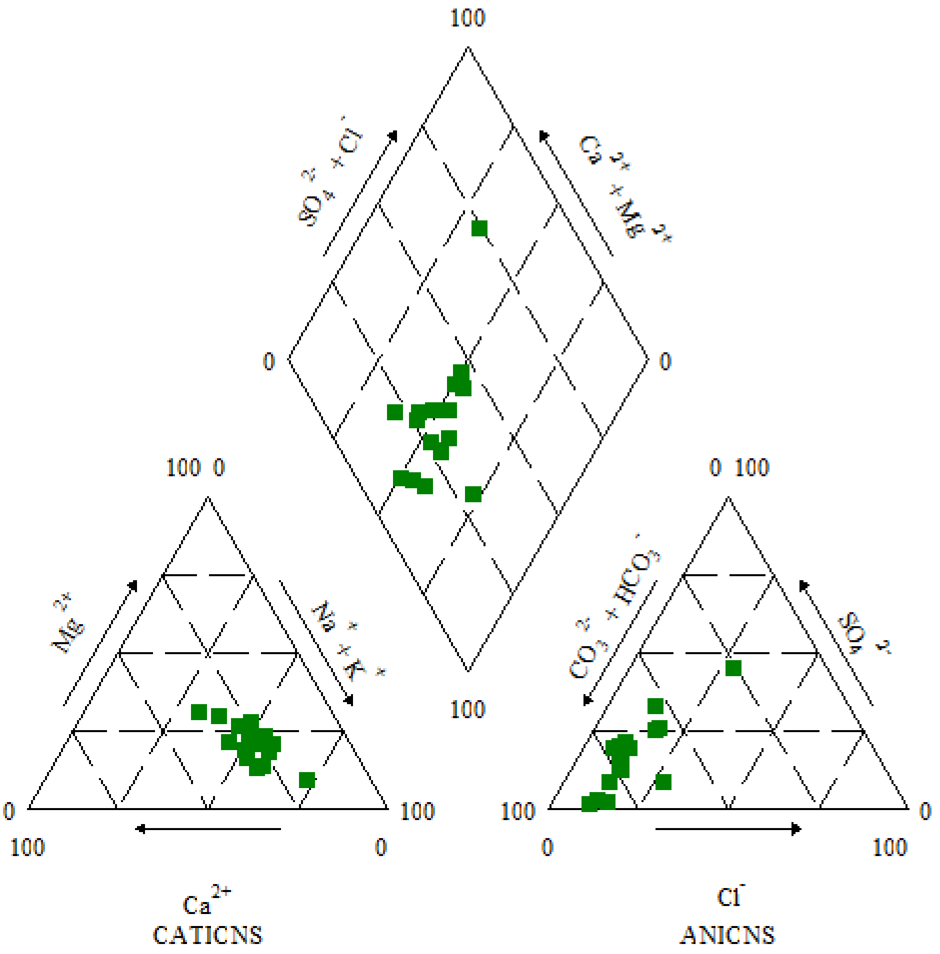


Figure 17 **Piper diagram of Taupo groundwater quality**

The Piper diagram shows that groundwaters of the Taupo catchment are predominantly of bicarbonate type in respect to anions and tending toward sodium type for cations. The overall water type is mixed although bicarbonate dominated. This reflects the hydrogeologic setting which is comprised predominantly of rhyolitic or acid volcanics. There is however one exception. This well (68_320) has been investigated and was shown to be influenced by a point source discharge from a nearby woolshed (Hadfield and Barkle, 2004). This anomaly can also be seen in Figure 20, being the only well to exceed the drinking water guideline for nitrate (based on annual data).

Median values for key parameters for the period 2016-2020 are listed in Appendix III. This data further illustrates the anomalous nature of the high nitrate concentrations at 68_320. All other median nitrate-N values are substantially lower being generally below 2.5 mg/l with two exceptions near 4 mg/l. These exceptions are sites of dairy and dry-stock activities. Other major ion median concentrations are low with relatively little variability. It is noted that nitrate concentrations are strongly correlated with calcium, chloride, magnesium, sulphate and total dissolved solids (TDS) which also reflect land-use effects, as discussed in more detail in section 5.8.

Redox conditions are also indicated in Appendix III for the four different categories that were described earlier in section 4. The designated colours for the wells are green for aerobic conditions, red for anaerobic, yellow for mixed and grey for indeterminate status. It is clear from field investigation that redox conditions strongly influence nitrate concentrations in Taupo and regionally. This is given there has been no detection of nitrate within monitoring wells designed to be isolated to anaerobic conditions identified by core testing (described in section 4.3). Further research has shown evidence of both autotrophic and heterotrophic conditions in the Taupo catchment (Hadfield and Korom, 2012). The distributions of parameter concentrations in the Taupo sub-region are compared graphically in box plots against other regions later in this report (section 5.8). This clearly indicates that Taupo monitoring wells have relatively low concentrations for the selected determinants.

Trends in nine key determinant concentrations for the Taupo catchment sites are illustrated in the mirror bar graph (Figure 18) below (analysis described in Appendix II). These represent the percentage of increasing and decreasing trends with 95% confidence for the period 2003 to 2020. Trend information is provided in Appendix IV. The trends are mixed with the most significant percentages of increases being for bicarbonate, sodium and potassium. Of note, given its importance to lake management, there are slightly more decreases in nitrate-N concentration than increases.

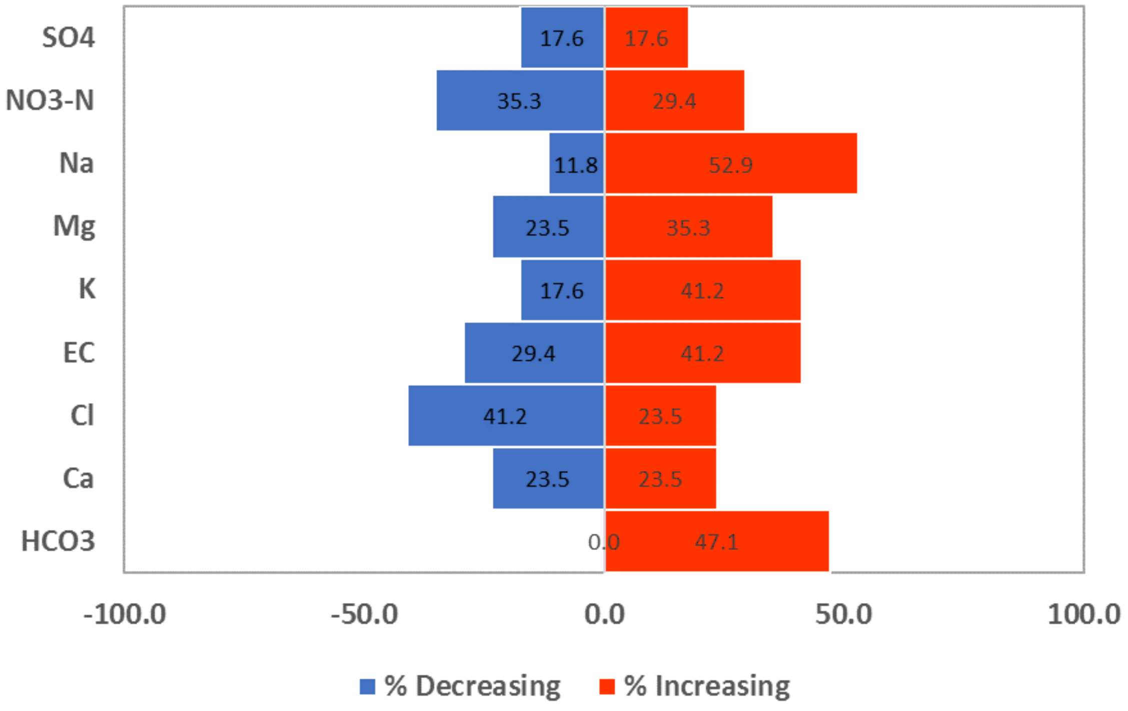


Figure 18 Mirror bar plots of key determinant trends in the Taupo sub-region

The rate of change in nitrate concentrations for those wells with trends of 95% confidence is illustrated below in Figure 19. The majority of significant Taupo monitoring well trends represented are gradual with greater reductions than increases.

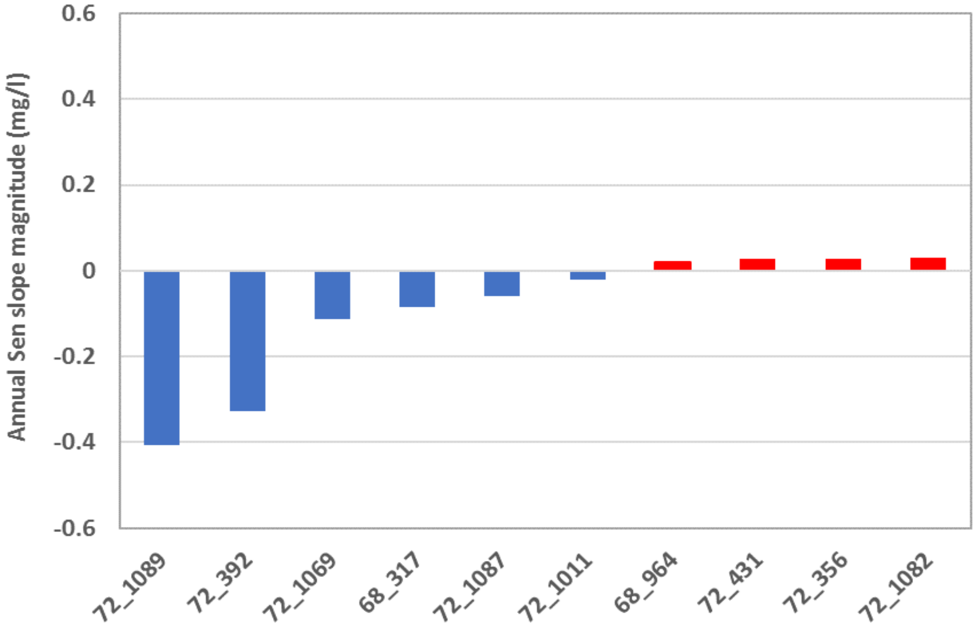


Figure 19 Magnitude of NO3-N concentration change for Taupo wells with trends of 95% confidence

Figure 20 below shows groundwater quality state and trends in the Lake Taupo catchment. Upward facing arrows indicate increasing concentration trends, downward arrows show decreasing trends and no arrow is where there is no significant trend. It is apparent that monitoring is focused on the northern and western lake catchment. This is where agricultural land-use has predominantly developed. It is noted that monitoring well 72_1006 has a mean residence time (MRT) age of about 75 years and is therefore less likely to show the effect of land-use change. Also, piezometer 72_1072 is the only anaerobic site but the symbol is not visible below that of adjacent piezometer 72_1087.

Figure 20 Nitrate-N state and trend for SOE wells in the Lake Taupo catchment.

5.2 Upper Waikato groundwater quality

There are 13 wells sampled routinely in the Upper Waikato catchment as part of the SOE monitoring programme. The tri-linear Piper diagram below shows the type and general character of these groundwaters (Figure 21). Once again bicarbonate and sodium dominate the water type. This reflects the acid volcanic tephra formations in this area. Most of these wells have been drilled into ignimbrite aquifers with some related volcanoclastic sediments.

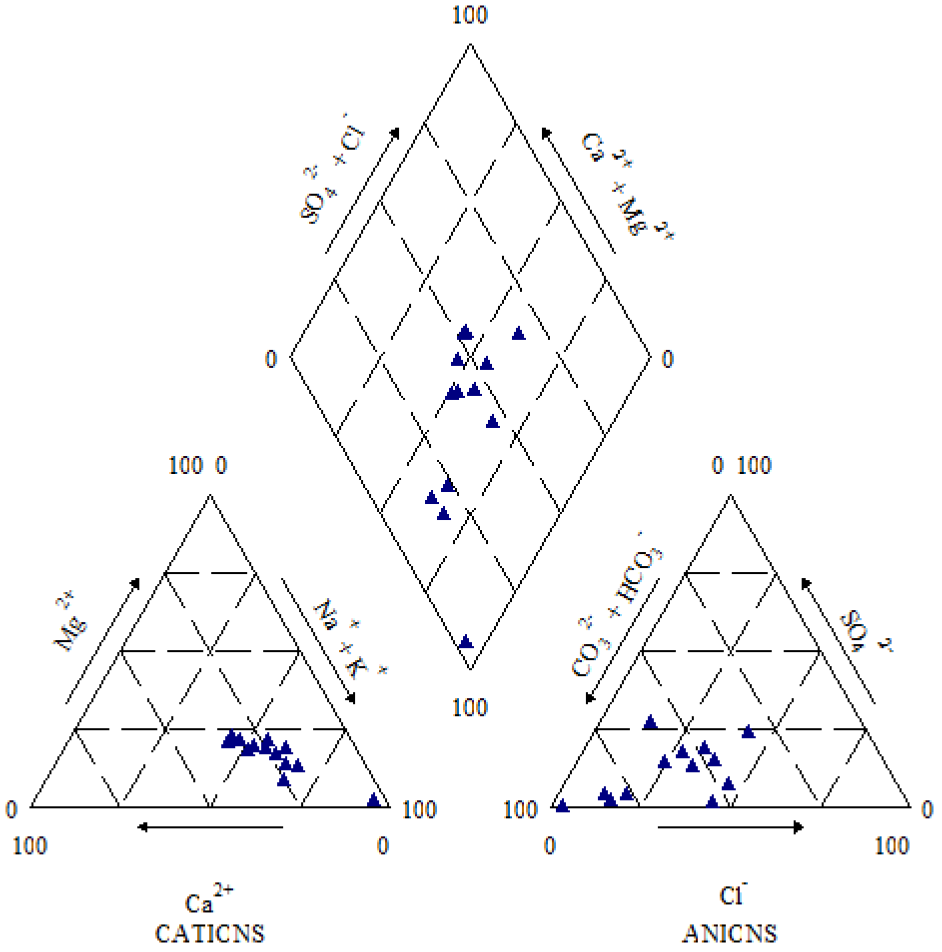


Figure 21 **Piper diagram of Upper Waikato groundwater quality**

Median values for key parameters for the period 2016-2020 are tabulated for the Upper Waikato in Appendix III. There is high quality ambient groundwater in this catchment (Bird, 1987). Groundwater age data are available for nine of the 13 wells and ranges from 15 to 200 years with a median MRT of 31 years. There are four wells with nitrate-N concentrations above half the maximum acceptable value (MAV) for drinking. These are associated with dairy land-use and two of these have mixed redox status. The majority of wells have groundwater in aerobic condition with two each being of anaerobic and indeterminate category status. It is noted that nitrate concentrations are strongly correlated with calcium and potassium and moderately with magnesium, chloride and sulphate which is consistent with land-use effects.

The mirror bar graph below (Figure 22) shows trends with 95% confidence in nine key determinant concentrations for the Upper Waikato monitoring wells. The trends are mixed and well balanced. This also applies to nitrate-N concentrations with the same number of significant increases and decreases (three of each). The rates of concentration change are modest being generally less than 0.4 mg/l annually.

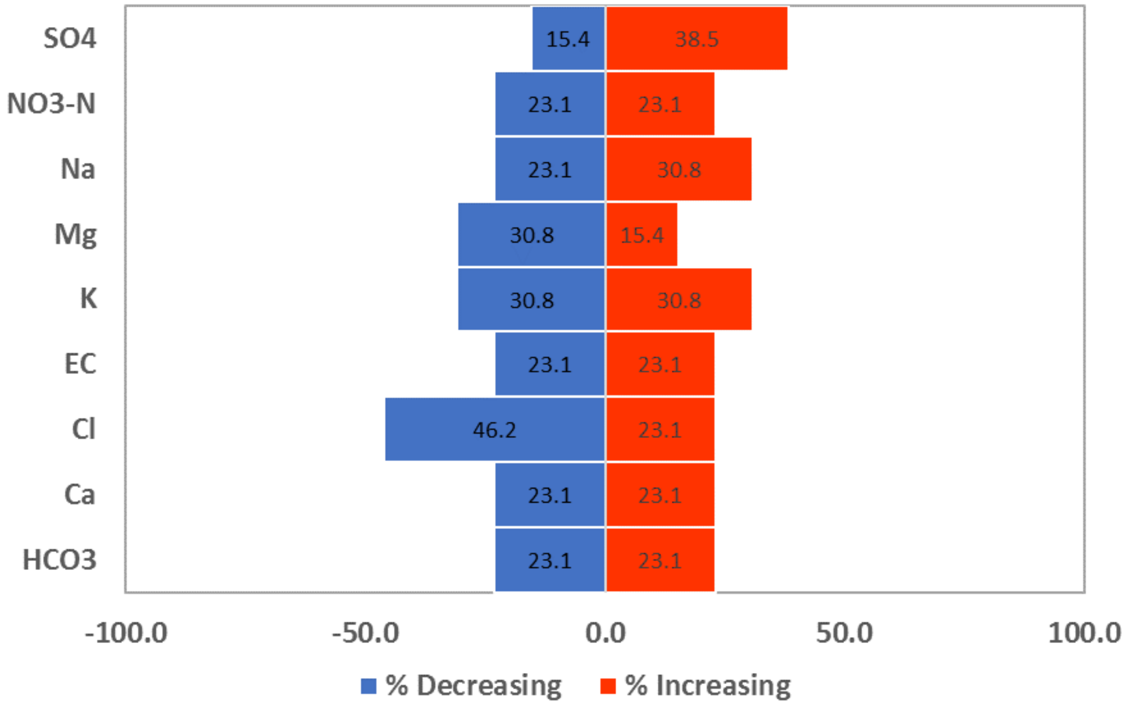


Figure 22 Mirror bar plot of key determinant trends in the upper Waikato sub-region

Monitoring is predominantly in the Reporoa and Tokoroa/Putaruru areas, which Figure 15 in section 4.5 shows has been extensively developed for dairy grazing. This includes recent widespread forest to dairy conversion in recent times (Hill and Borman, 2022). Figure 23 shows the distribution of median nitrate-N concentrations. No MAV exceedances are indicated but there are clear land-use impacts with four wells having nitrate-N concentrations over half the drinking water guidelines.

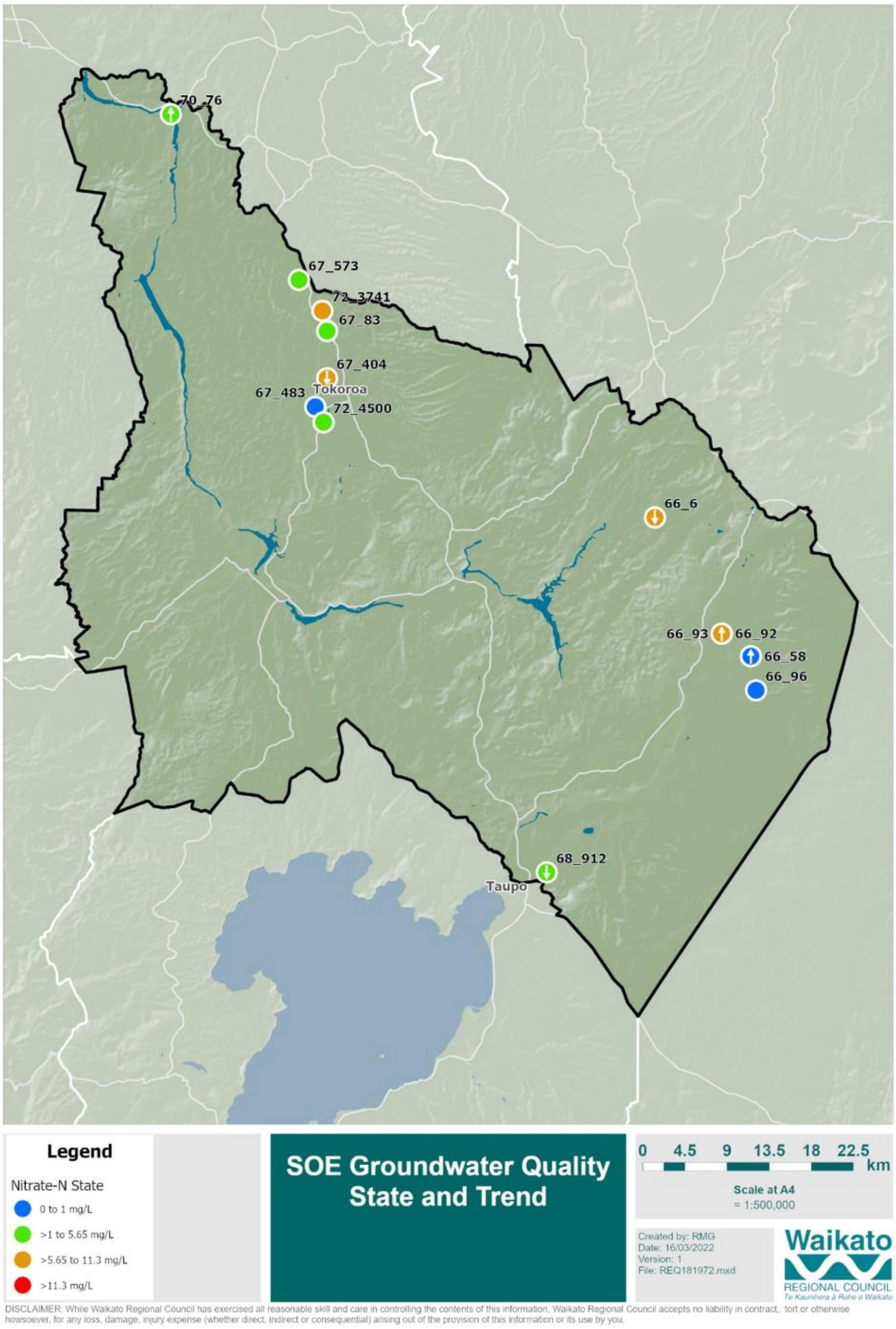


Figure 23 Nitrate-N state and trend for SOE wells in the Upper Waikato

5.3 Hauraki SOE groundwater quality

A total of 27 wells in the Hauraki sub-region are routinely monitored as part of the SOE monitoring programme. Their major ion chemistry ratios are presented in the tri-linear Piper diagram below. It indicates a reasonably mixed distribution of groundwater types. Sodium and potassium cations are well represented, and bicarbonate dominates the anions. Once again this reflects acid hydrolysis of the predominant rhyolitic or acid volcanic tephra formations in much of the upper catchment and related sediments in the plains further north. Two slightly anomalous sodium chloride type groundwaters (wells 64_43 and 63_78) are from fractured rock aquifers. Well 63_43 is drilled into greywacke basement and investigation showed it to also have very high radon concentrations.

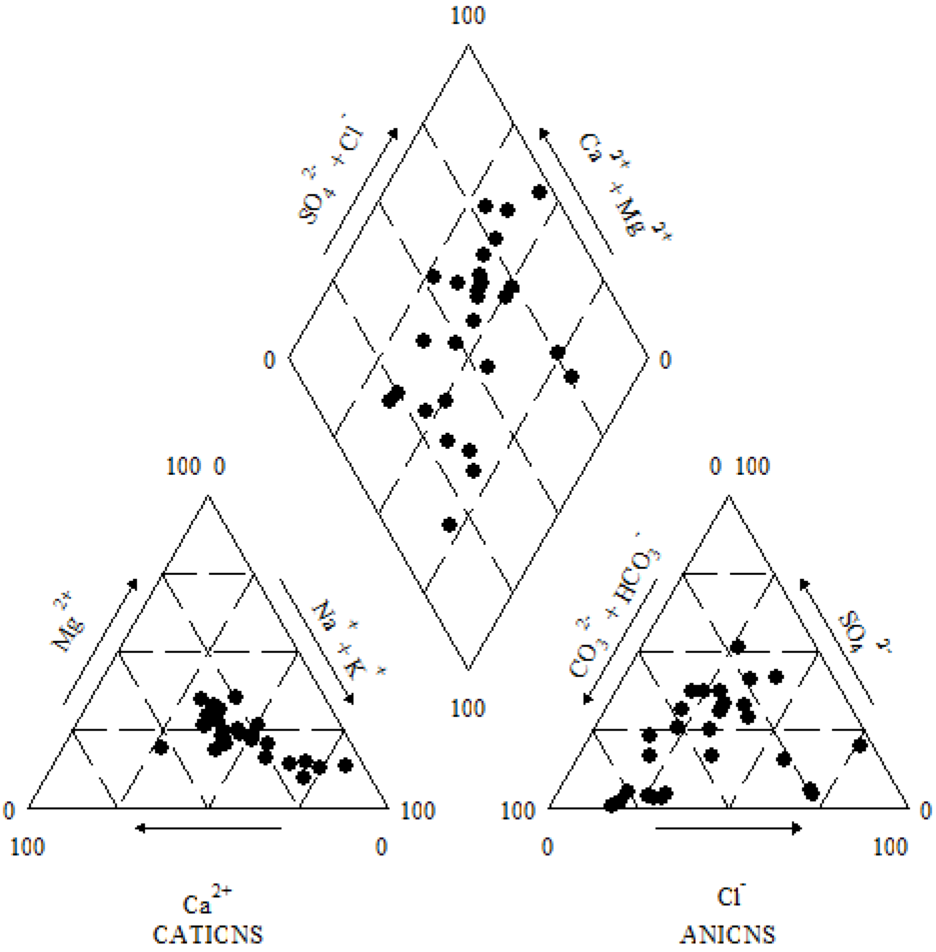


Figure 24 Piper diagram of Hauraki groundwater quality

Median values for key parameters monitored in the Hauraki for the period 2016-2020 are tabulated in Appendix III. Groundwater age estimates are available for all but one of the 27 sites. These range from seven to 260 years with a median MRT of 34.5 years. There are five wells (18.5%) with nitrate-N median concentrations above half the MAV for drinking. Three of these are associated with dairy land-use, another site is used for market gardening and the last is a disused school supply. A little over half (16) of the sites have groundwater in an aerobic redox category, two are anaerobic, three are of mixed status and six are indeterminate. This mixture is reflected in the range of nitrate-N concentrations evident. Nitrate concentrations are strongly correlated with calcium and TDS and moderately correlated with potassium, magnesium and sulphate, all being typical indicators of land-use effects.

Figure 25 below shows the percentage of increasing and decreasing trends with 95% confidence in nine key determinant concentrations for monitoring wells in the Hauraki sub-region. It is apparent that there are more increasing trends, with an exception being chloride. This suggests some overall degradation reflecting increasing land-use intensity.

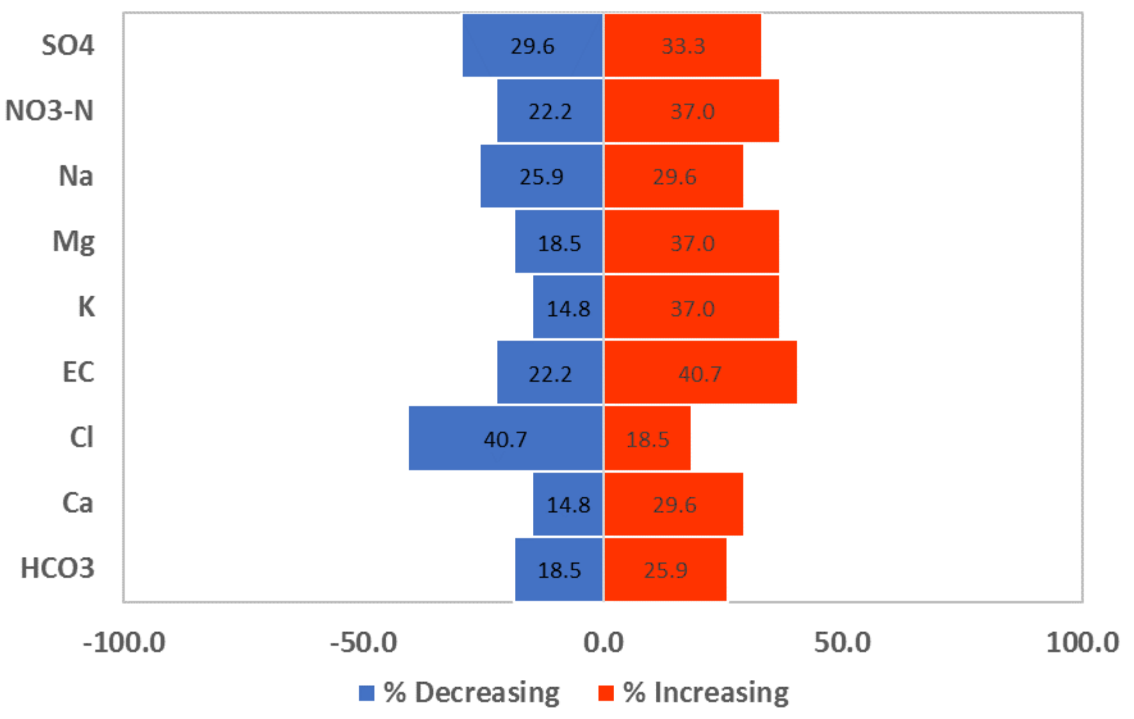


Figure 25 Mirror bar plots of key determinant trends in the Hauraki sub-region

The rate of nitrate-N concentration change is further illustrated below in Figure 26. The trends are mixed with some rates being relatively rapid (> 0.5 mg/l annually). There is one exceptionally high rate site which likely represents point source contamination.

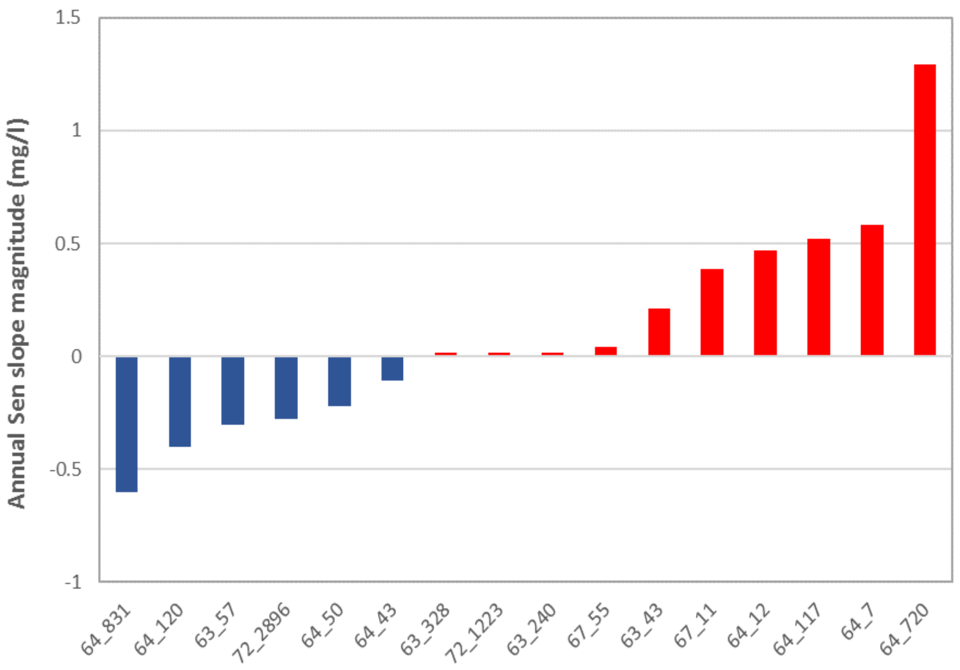


Figure 26 Magnitude of NO3-N concentration change for Hauraki wells with trends of 95% confidence

Figure 27 shows that the highest concentrations of nitrate-N tend to occur in the southern Hauraki Plains. Aquifers towards the southern plains tend to have coarser, 'cleaner' sediments with more prevalent aerobic conditions.

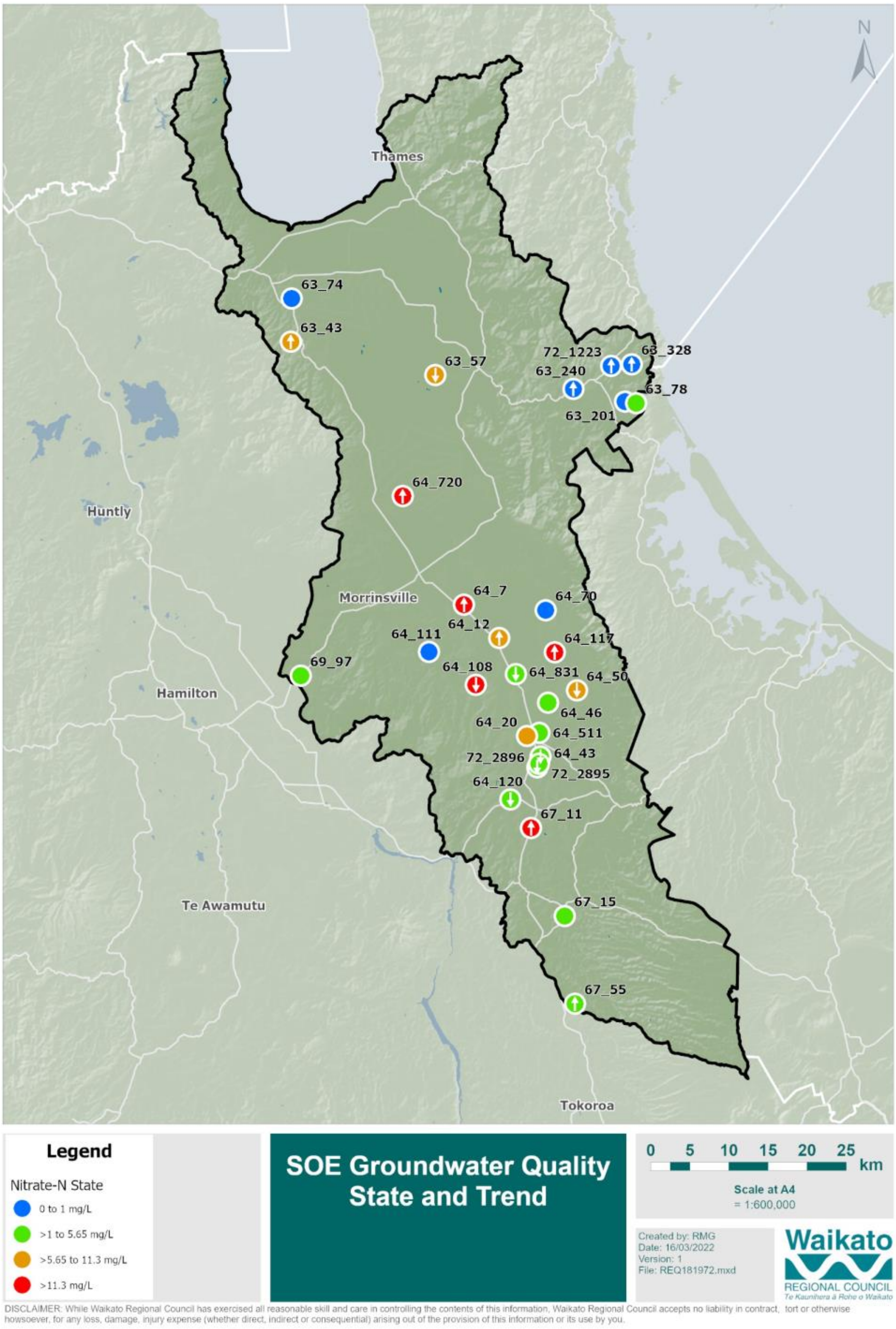


Figure 27 Nitrate-N state and trend for SOE wells in the Hauraki catchment

5.4 Coromandel SOE groundwater quality

A total of 11 wells in the Coromandel sub-region are monitored as part of the SOE network. The type and general character of these groundwaters is presented in the tri-linear Piper diagram of major ion milli-equivalent ratios using median values (Figure 28).

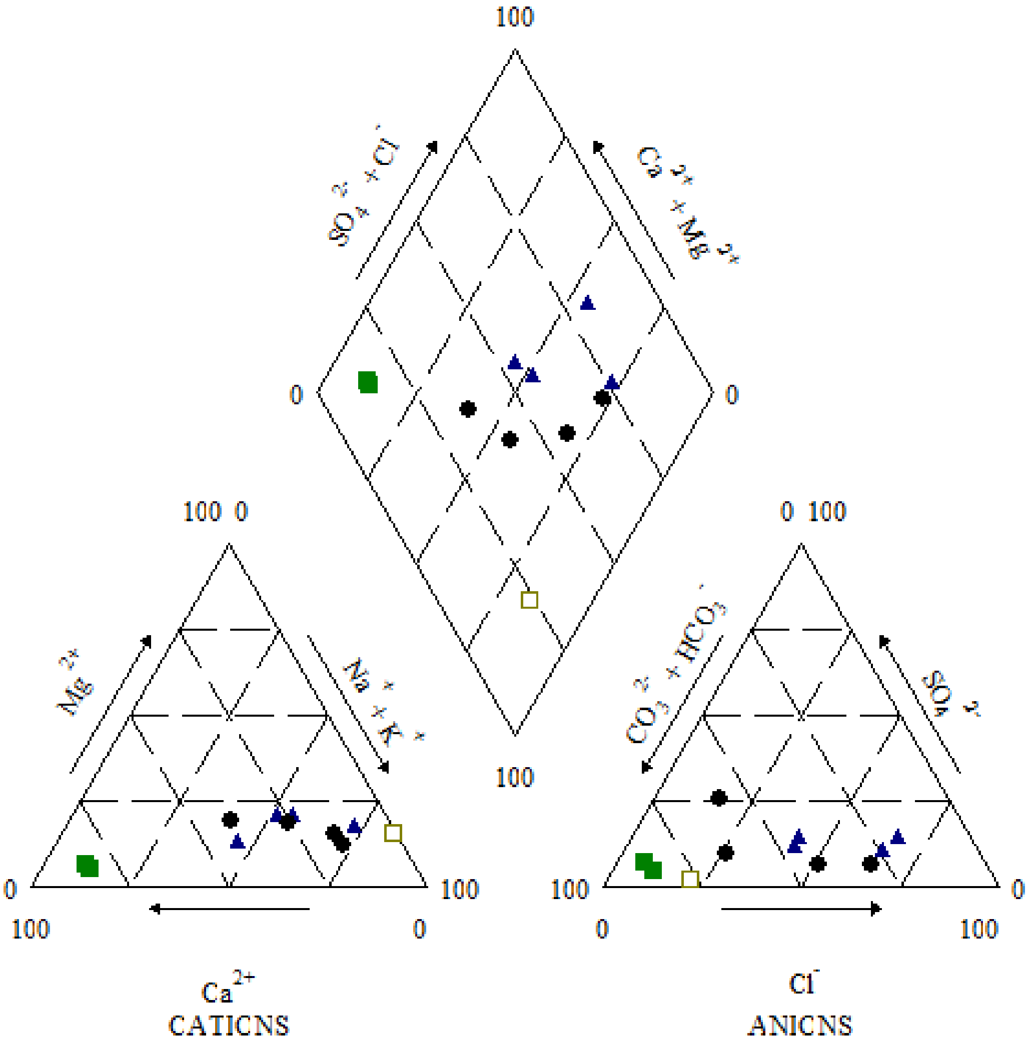


Figure 28 **Piper diagram of Coromandel groundwater quality**

It is evident that there is considerable variation in chemical character with substantial ranges in calcium, sodium, bicarbonate and chloride. This reflects the coastal proximity of many sites and the dissolution of calcium from shell content in some sandy aquifers. The cation distribution shows both sodium type (seven wells) and calcium type (two wells - green squares) waters. The anion distribution indicates the presence of bicarbonate type (five wells) and chloride type waters (four wells). In combination, sodium chloride type waters are more prevalent than magnesium bicarbonate waters.

The two wells denoted by green squares (60_12 and 60_124) are both very shallow, unconfined, sand aquifers with calcium bicarbonate rich alkaline waters from the influence of shell dissolution. The other well which is notably different is well 60_167 (white square), which is again in a sand aquifer almost 20 m deep but has anaerobic, iron rich water. Although it has a relatively high bicarbonate concentration, calcium is very low resulting in a sodium bicarbonate type water. The fractured, volcanic rock, aquifers are denoted by black circles. They show generally similar ionic character to the other sandy aquifers (triangles) apart from the exceptions already mentioned.

Median concentrations of selected determinants are presented in Appendix III. There is relatively little agricultural land-use development in the Coromandel area and this is reflected in low concentrations of nitrate-N and other ions such as potassium. It is notable also that there is no correlation between nitrate and the other determinants listed. The TDS and related conductivity are relatively high and vary with coastal influence. There is overall little indication of anthropogenic influence in the major ion chemistry. Rather it tends to reflect the aquifer formation and recharge conditions. While the aquifers are dominated by siliceous sands and volcanic (rhyolitic and sometimes andesitic) fractured rock, it is noted that the coastal origin and proximity appears to be a stronger influence.

The mirror bar graph in the following Figure 29 illustrates trends with 95 % confidence in key parameters over a period of 18 years to 2020. These trends are roughly balanced and show no indication of overall degradation. Consistent with this, nitrate-N median concentrations are relatively low (2.5 mg/l or less). There are three significant (95%) decreases and two increases. One of the latter is at the only dairy farming site monitored. The rates of change are also minimal with an annual Sen slope of less than 0.1 mg/l except for one site identified with a moderate Sen slope of 0.28 mg/l annually.

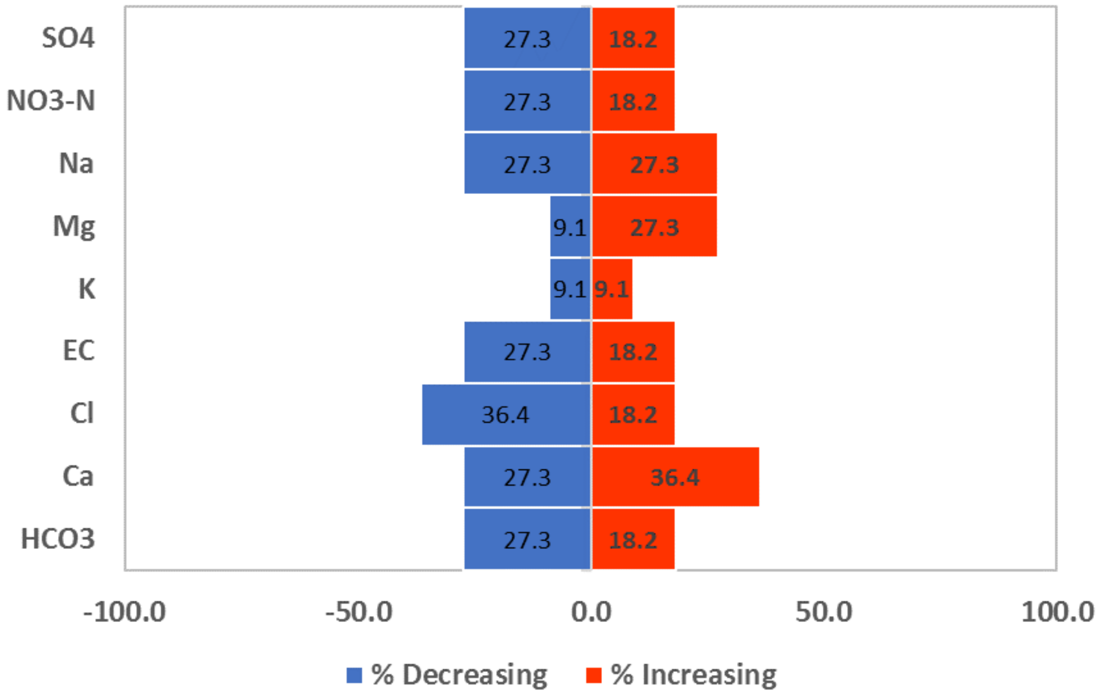


Figure 29 Mirror bar plots of key determinant trends in the Coromandel sub-region

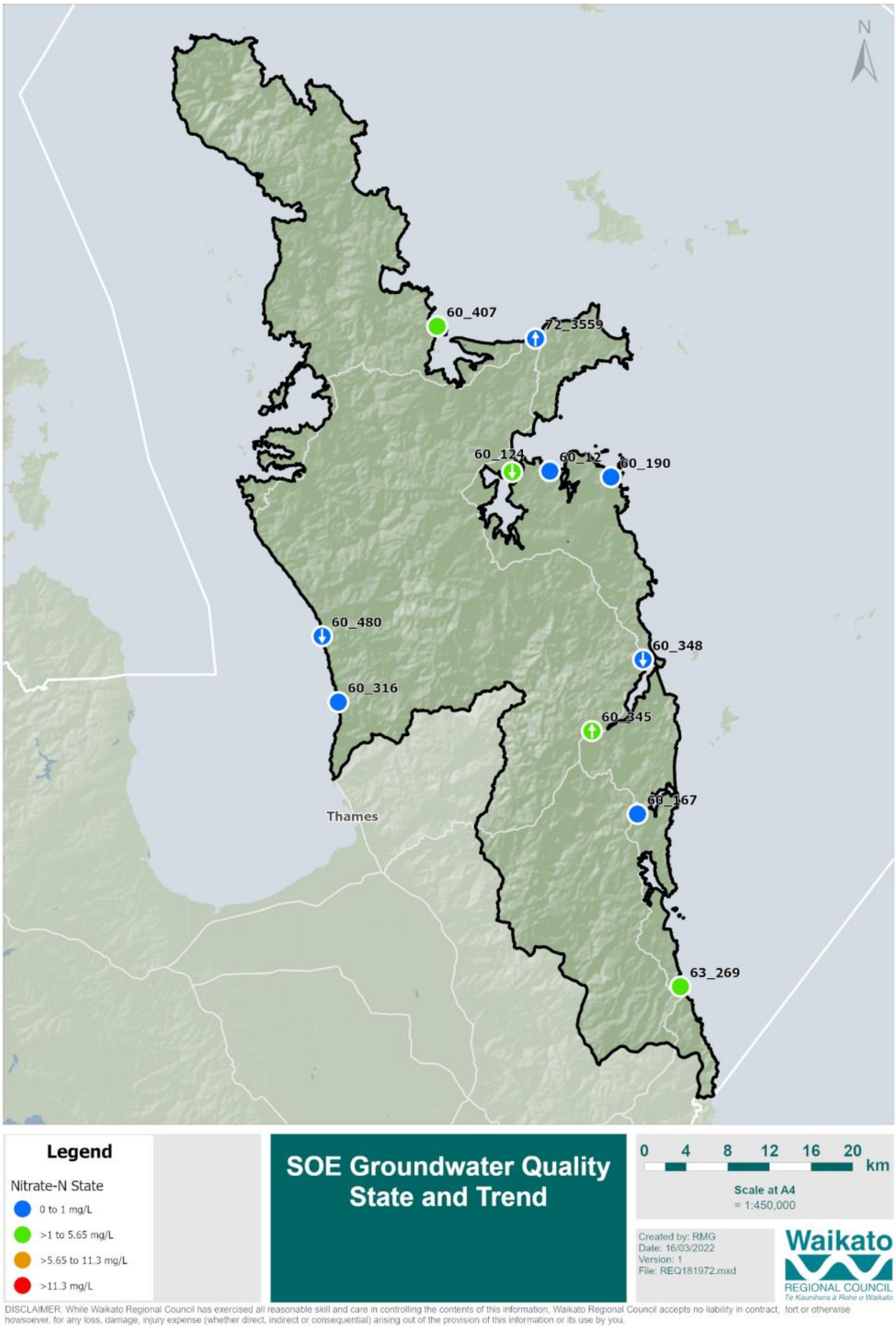


Figure 30 Nitrate-N state and trend for SOE wells in the Coromandel catchment

5.5 Hamilton Basin SOE groundwater quality

A total of 16 wells are monitored in the Hamilton Basin sub-region as part of the SOE monitoring programme. These are all shallow, with a mean of 6.5 m, and are constructed in the Hinuera Formation of the Tauranga Group. The distribution of major ion milli-equivalent ratios in the tri-linear Piper diagram using median values shows a mixed water type is most common (Figure 31). The bicarbonate dominance of some other areas is diminished and may reflect that the geology predominantly comprises sediments which have been transported further from their volcanic sources.

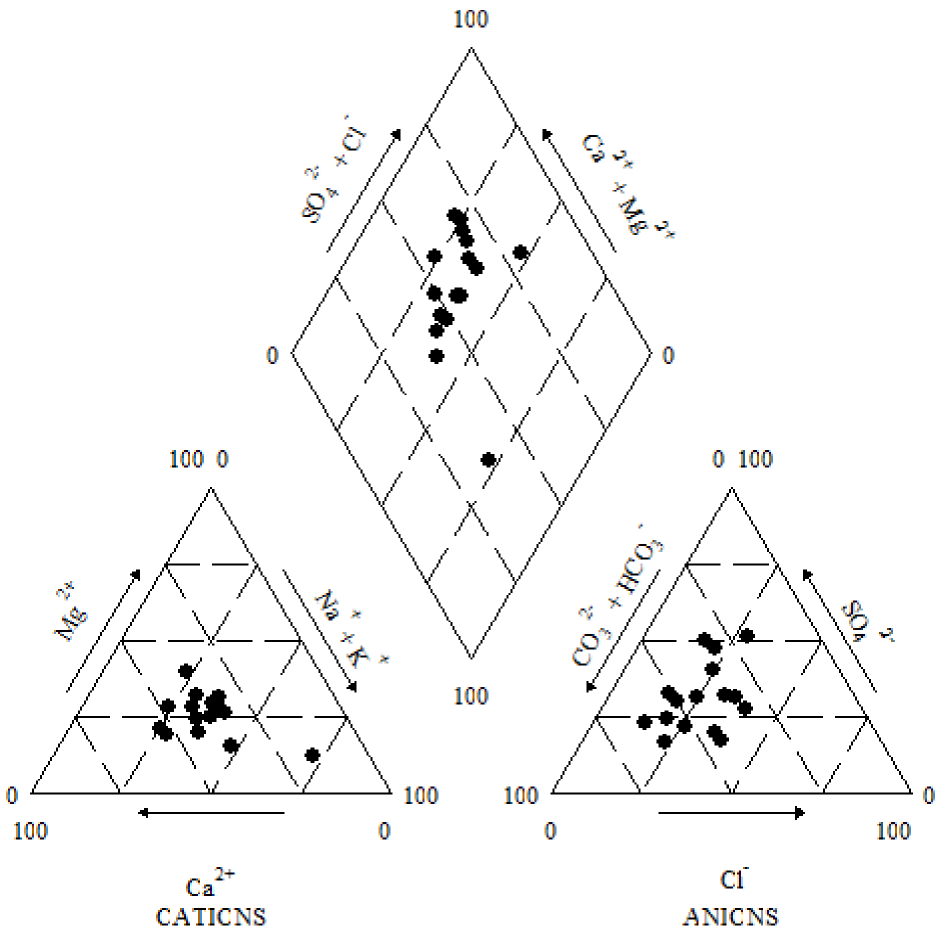


Figure 31 **Piper diagram of Hamilton Basin groundwater quality**

Median concentrations for key parameters monitored in the Hamilton Basin for the period 2016-2020 are listed in Appendix III. The Hamilton Basin monitoring wells are primarily in unconfined, sand aquifers and many were part of an original 'Nitrate' monitoring network. Three quarters of them are in aerobic environments and no anaerobic conditions are represented. The remaining conditions are mixed except for one which is indeterminate. There are seven MRT groundwater age estimates available and these range from 0.2 to 39 years with a median of 3 years. This indicates that the monitoring sites largely reflect recent land-use activities.

There is one well (69_19) with a nitrate-N median concentration above the MAV for drinking. This site is in horticultural use. There are another 10 sites (~two thirds) which have nitrate-N concentrations above half the MAV. Nitrate-N is not well correlated with other parameters with the highest having moderate correlations with calcium and TDS only.

The mirror bar graph below (Figure 32) clearly shows that groundwater quality represented by nine key parameters below is generally improving in the monitoring wells in the Hamilton Basin. The percentage of decreasing trends with 95 % confidence (2003-2020) substantially outweighs the percentage of increases, notably including nitrate-N. It is noted that there has been common de-intensification of land-use at many of these monitoring sites. These shallow wells on the fringes of Hamilton and Cambridge have typically changed land-uses from dairy to lifestyle and horse studs.

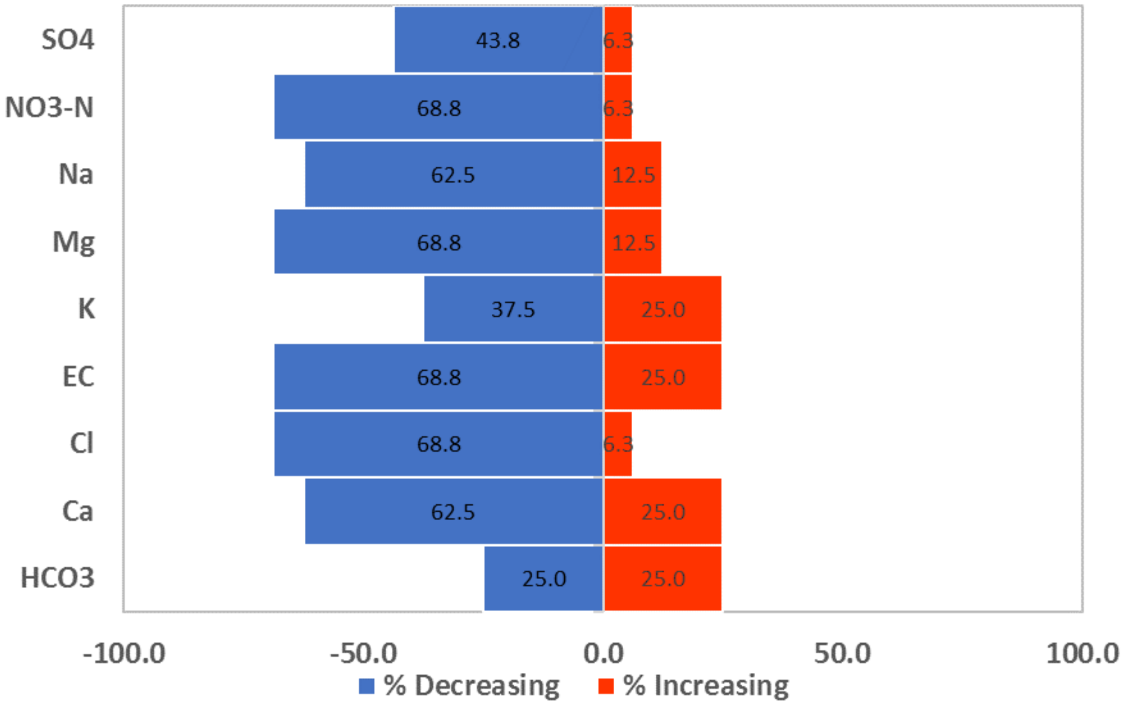


Figure 32 **Mirror bar plot of key parameter trends (with 95 % confidence) in the Hamilton Basin sub-region.**

The rates of change in nitrate-N are illustrated further below (Figure 33) and as mentioned shows only one well (69_19) with an increasing concentration trend. The remainder have decreasing trends, some of which are relatively rapid. The distribution of these monitoring wells is illustrated in Figure 34 and shows that most are in the vicinity or south of Hamilton. A network redesign could reconsider the three-dimensional distribution of these wells.

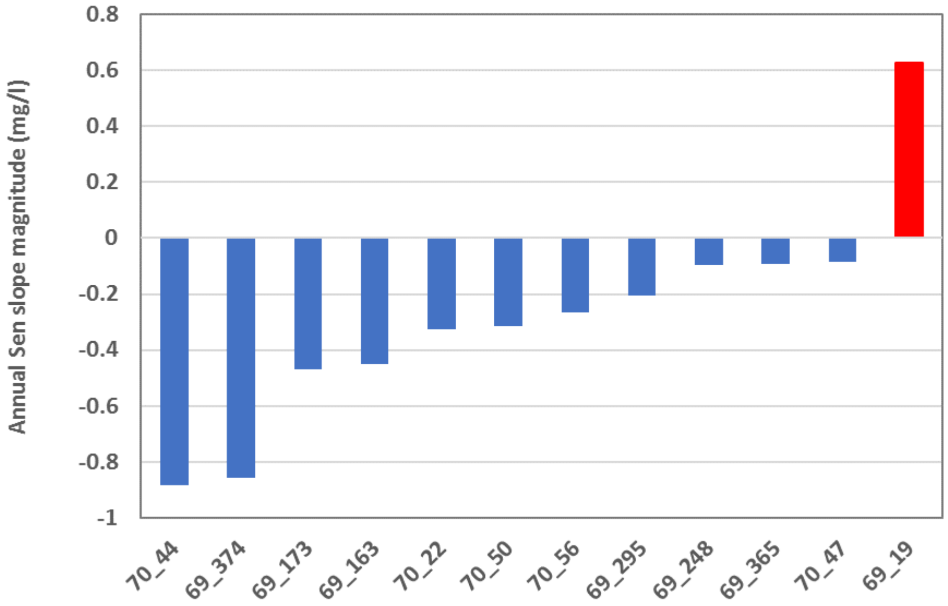


Figure 33 **Magnitude of NO3-N concentration change for Hamilton Basin wells with trends of 95% confidence**

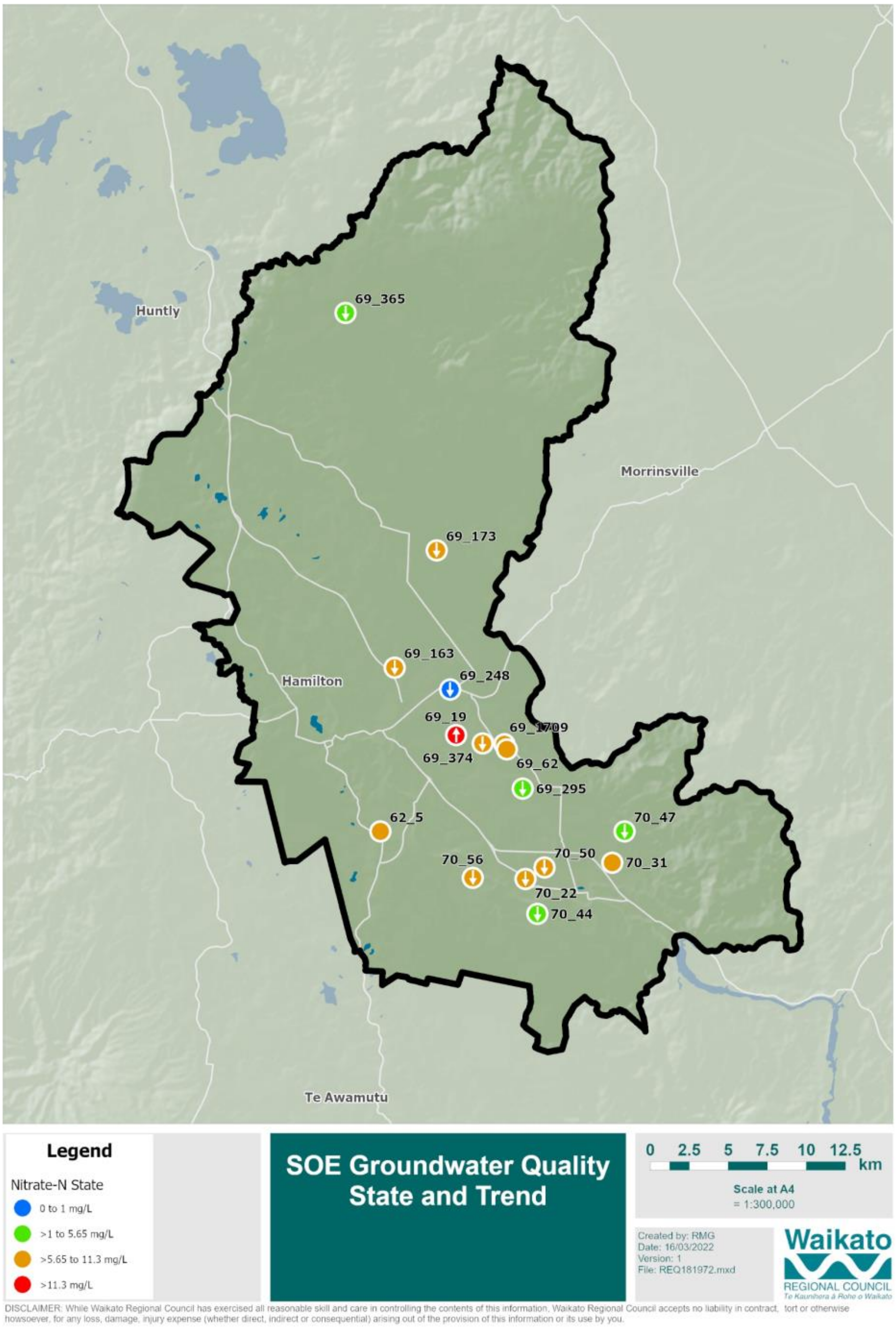


Figure 34 Nitrate-N state and trend for SOE wells in the Hamilton Basin catchment

5.6 Waipa SOE groundwater quality

There are 12 wells monitored in the Waipa catchment as part of the SOE network. The characteristic of notable difference in this catchment's major ion chemistry ratios is the prevalence of calcium bicarbonate type waters. These represent about half of the wells with the remainder being of mixed character. The calcium bicarbonate character reflects the presence of Tertiary formations. These comprise limestones, calcareous sandstones and siltstones which occur towards the western side of the catchment. The four wells in Figure 35 with highest calcium and bicarbonate concentrations are constructed in limestone aquifers.

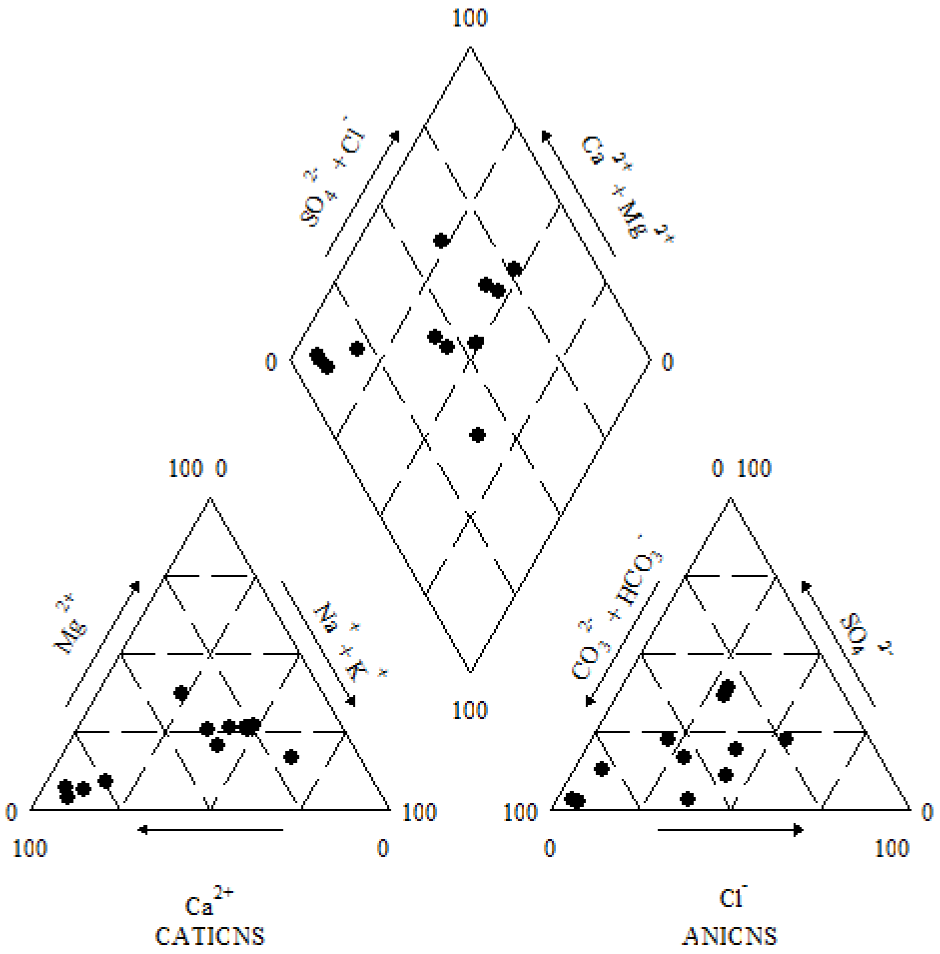


Figure 35 **Piper diagram of Waipa groundwater quality**

Median values for key parameters monitored in the Waipa catchment for the period 2016-2020 are listed in Appendix III. The Waipa monitoring wells range in depth from 2.25 m to 105 m with a median of 10.3 m. As mentioned, four of these are drilled into limestone aquifers and five derive their supplies from alluvial sands. Just over half of the wells exhibit aerobic groundwater characteristics with the remainder being indeterminate. There are five groundwater age estimates available, all of which have MRTs of 10 years or less.

There are no sites with nitrate-N median concentrations above the MAV for drinking. There are, however, two above half the MAV standard. These are at a dairy and a horticultural site. Nitrate concentrations correlate strongly with chloride and moderately with potassium, magnesium and TDS.

It may be inferred from the mirror bar graph below (Figure 36) that groundwater quality in the Waipa catchment, as represented by the wells monitored, is generally degrading. It is evident that the percentage of trends which are increasing with 95 % confidence (2003-2020) is greater than those that are decreasing for all parameters except sulphate. This includes nitrate-N. It may be concluded that the effects of land-use intensification are becoming more apparent.

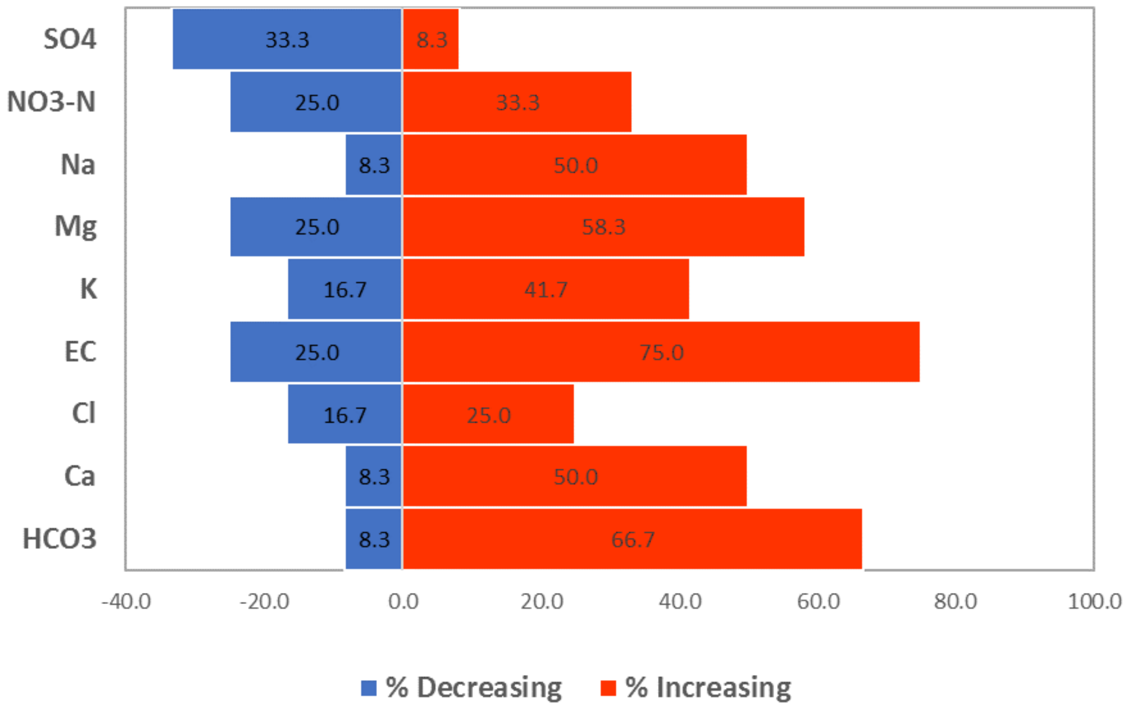


Figure 36 **Mirror bar plot of key determinant trends (with 95 % confidence) in the Waipa catchment.**

The rates of significant nitrate-N change plotted below shows mixed trends with modest increases being slightly more prevalent (Figure 37).

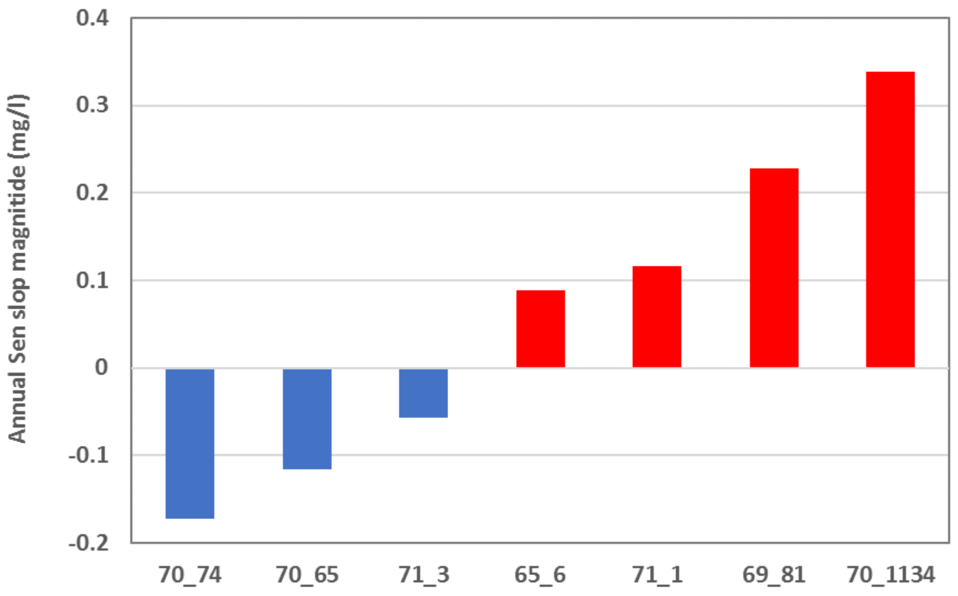


Figure 37 **Magnitude of NO3-N concentration change for Waipa wells with trends of 95% confidence**

The nitrate-N state and trend map below (Figure 38) shows that the higher concentrations are in the more intensively farmed northern catchment. The four wells in limestone aquifers with highest calcium and bicarbonate concentrations are in the south-west corner of the catchment (wells 71_3, 71_4, 71_5 and 72_2138).

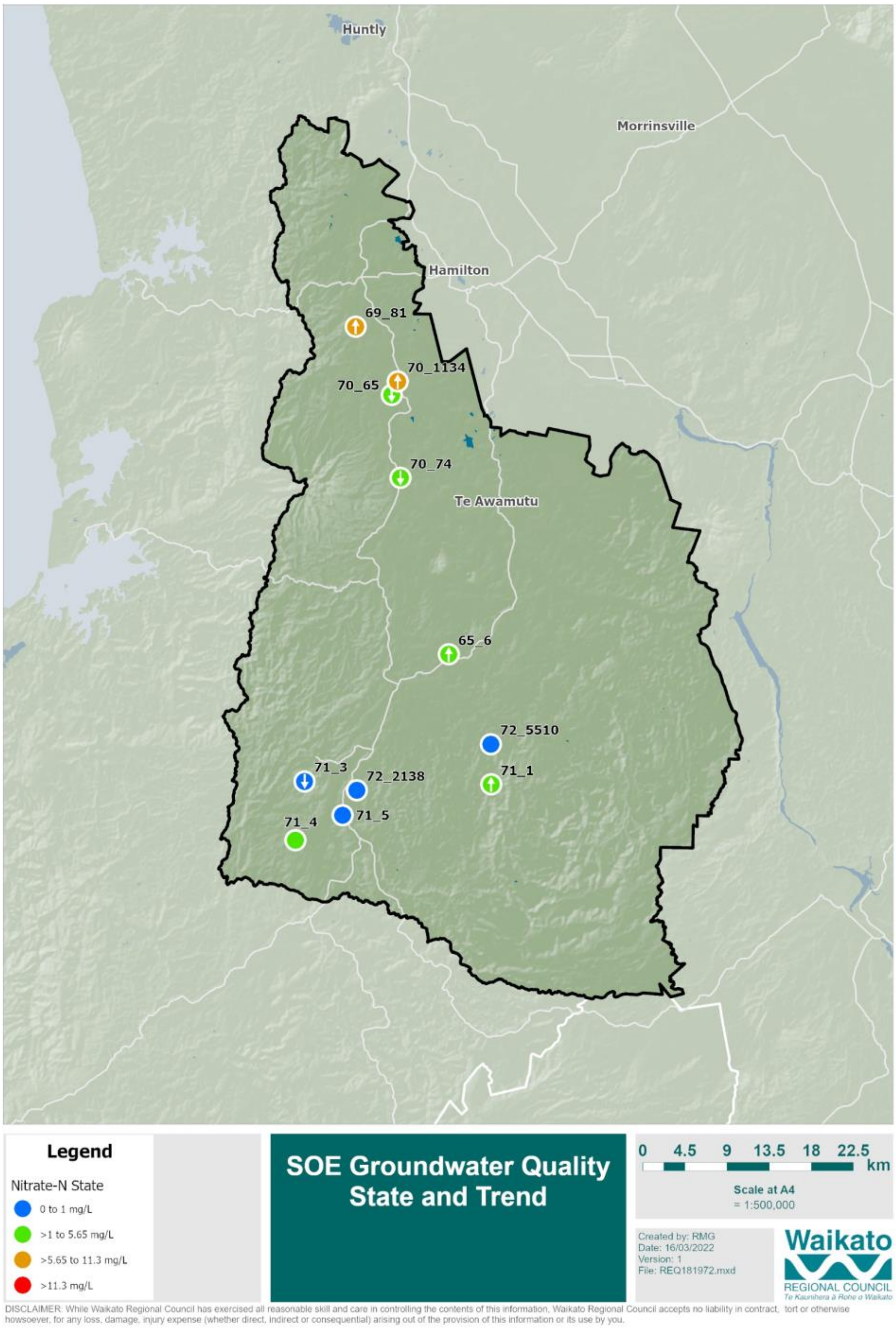


Figure 38 Nitrate-N state and trend for SOE wells in the Waipa catchment

5.7 Northern SOE groundwater quality

A total of 14 wells are monitored in the Northern sub-region as part of the SOE network. As previously described, this area primarily comprises the southern Pukekohe, Pukekawa and southern Waiuku areas and borders the Auckland region. The monitoring wells range in depth from 6 m to 52 m with a median of 26 m. All of the wells are constructed in basalt aquifers with the exception in one which is the shallowest and described as having been dug manually into sand. The majority (10) have aerobic groundwater characteristics, with two being of mixed character and the remaining two being in the indeterminate category (as indicated in Appendix III). There are estimates of MRT for all these wells. They range from four to 130 years with a median of about 18 years (ambiguous ages for three sites have been averaged).

The type and general character of these groundwaters is presented in the Piper tri-linear diagram of major ion milli-equivalent ratios (Figure 39). These groundwaters plot as chloride type in respect to anions likely as a consequence of the coastal influence on recharge given predominantly westerly winds, which may be accentuated by intensive land-use. The cations are relatively high in magnesium reflecting the prevalence of basaltic aquifers. Overall, the water type is mixed with a tendency toward sodium chloride type waters. Although these monitoring wells are predominantly in alkali, South Auckland basalt field aquifers, there are other important formations locally present which are under-represented in this network. These notably include the Kaawa Formation and to a lesser extent the Tauranga Group of sediments. Comparative water chemistry for these formations is reported by Ringham et al., (1990).

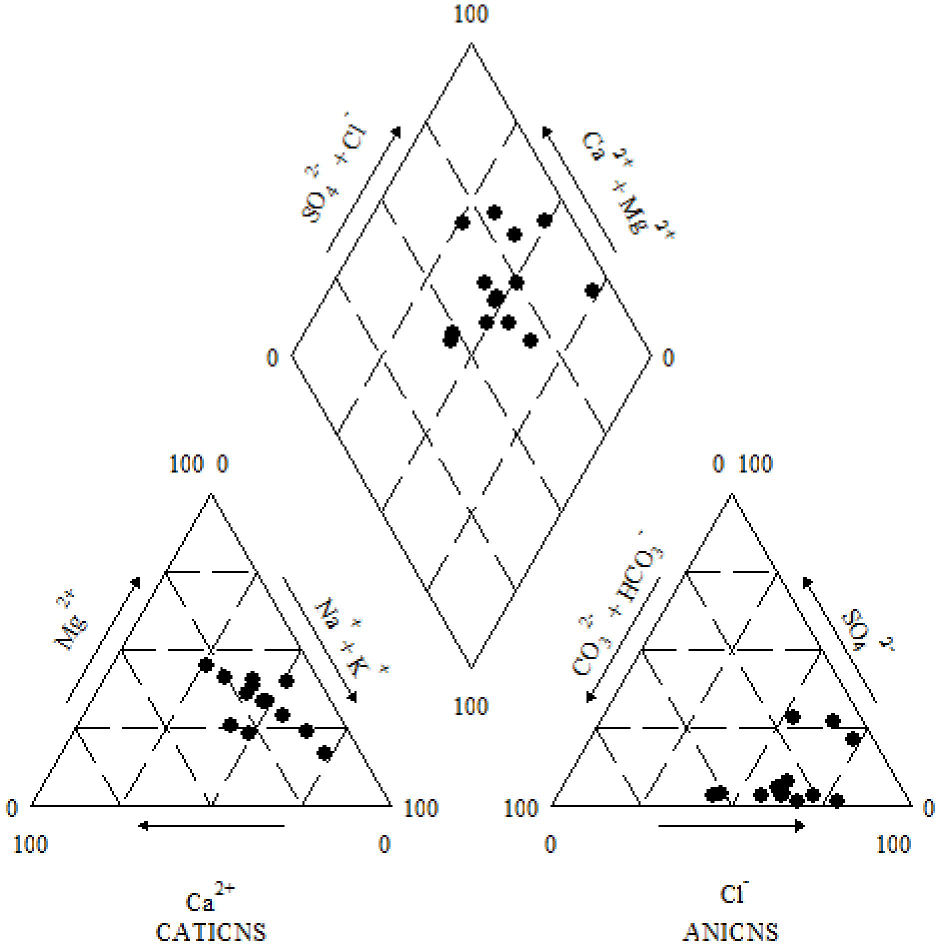


Figure 39 Piper diagram of Northern groundwater quality

Median values (2016-2020) for selected Northern sub-catchment determinants are listed in Appendix III. Median nitrate-N concentrations for the period 2003-2020 exceed the MAV for drinking at five of the wells (36%). A further seven (50%) are over half the MAV concentration. On the basis of our current understanding of land-use, all five of the sites with median nitrate-N concentrations exceeding the MAV for drinking water relate to horticultural (market gardening) activities. It is noted that one of these (61_135) is a small lifestyle block but it is nevertheless surrounded by market gardening. The only strong correlation with nitrate-N in the northern area is with magnesium although there are moderate correlations with calcium and TDS.

The mirror bar graph in Figure 40 shows that seven of the nine selected determinants are exhibiting substantially higher percentages of increasing concentration trends than decreasing trends (with 95 % confidence over the period 2003-2020). This indicates overall degradation of groundwater quality in the Northern sub-region. Importantly this includes nitrate-N, which is commonly exceeding drinking water guidelines, as already described. The degree of groundwater quality degradation appears to reflect the very high intensity market gardening land-use in this sub-region. Two exceptions are decreasing trends in sulphate and bicarbonate concentrations.

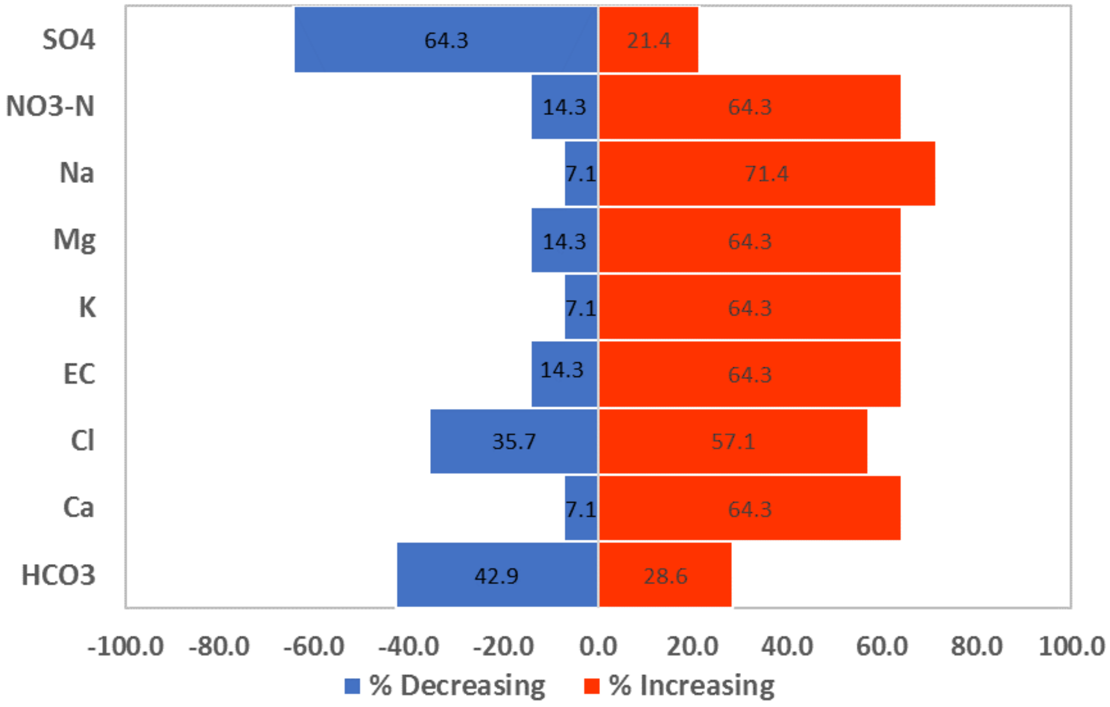


Figure 40 **Mirror bar plot of key determinant trends (with 95 % confidence) in the Northern sub-region.**

The rates of nitrate-N change for northern wells with significant trends are illustrated in Figure 41. This shows increasing trends predominating with many moderate to high rates over 0.2 mg/l annually.

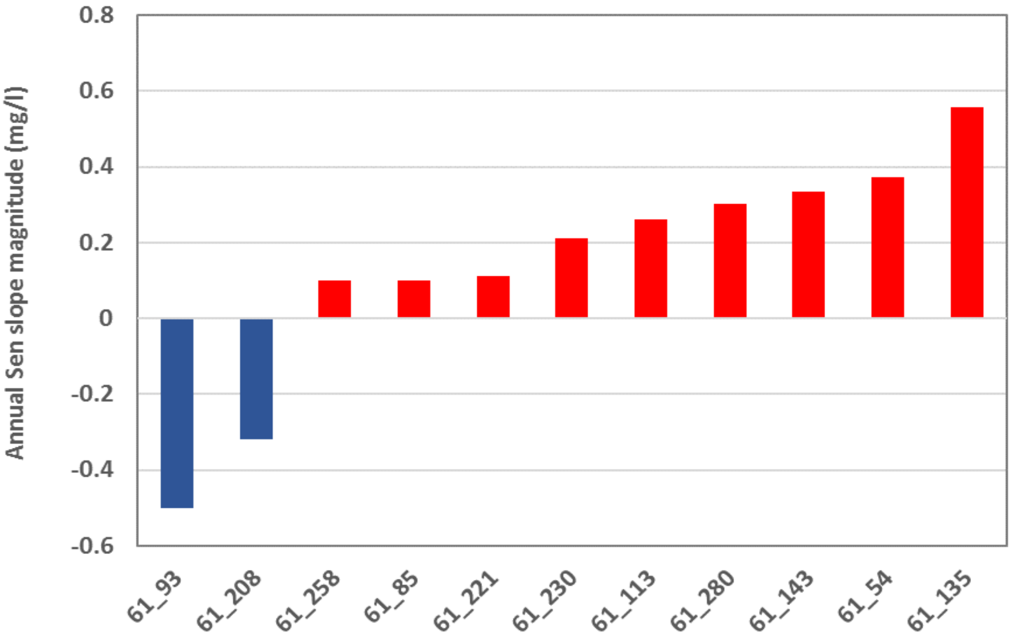


Figure 41 **Magnitude of NO_3-N concentration change for Northern wells with trends of 95% confidence**

The nitrate-N state and trend map (Figure 42) for the northern areas (which includes Pukekohe, Pukekawa and Waiuku) shows they are relative hot spots of nitrate-N contamination for the region. The rates of increase are also relatively high for the region.

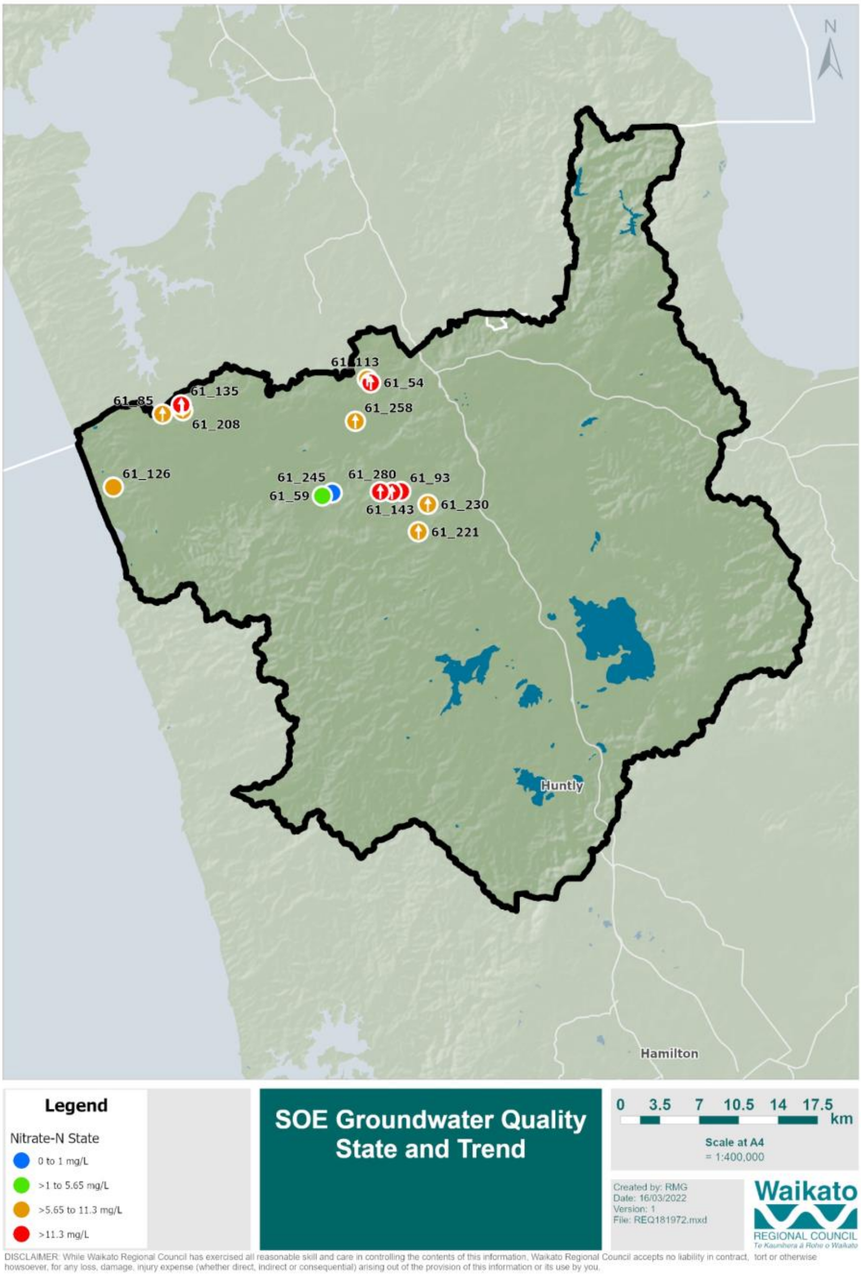


Figure 42 Nitrate-N state and trend for SOE wells in the Northern catchments

5.8 Regional groundwater quality characteristics

Groundwater quality state and trends discussed in respect to sub-regional areas are brought together in this section for a regional overview. Comparisons are also made between the network components of the groundwater quality monitoring programme with inference regarding network design. Some of this detail is provided in Appendix IV.

Firstly, major ion chemistry ratios for the total 110 wells comprising the regional SOE monitoring network are illustrated together in the Piper -linear diagram in Figure 43. The greater diversity of water types is evident. Bicarbonate waters tend to dominate anion chemistry reflecting the extensive rhyolitic acid volcanic formation in the region. An exception is the basaltic aquifers monitored in the Northern sub-region. Sodium ions are well represented in cation chemistry likely reflecting progressive cation exchange. Relatively higher magnesium presence is evident in the Northern sub-region. Calcium type water in respect to cations reflects the limestone aquifers of the south-western Waipa catchment and some shell rich shallow sand aquifers in the Coromandel. The most prevalent overall water type is mixed, and the multiplicity of chemical characteristics is apparent.

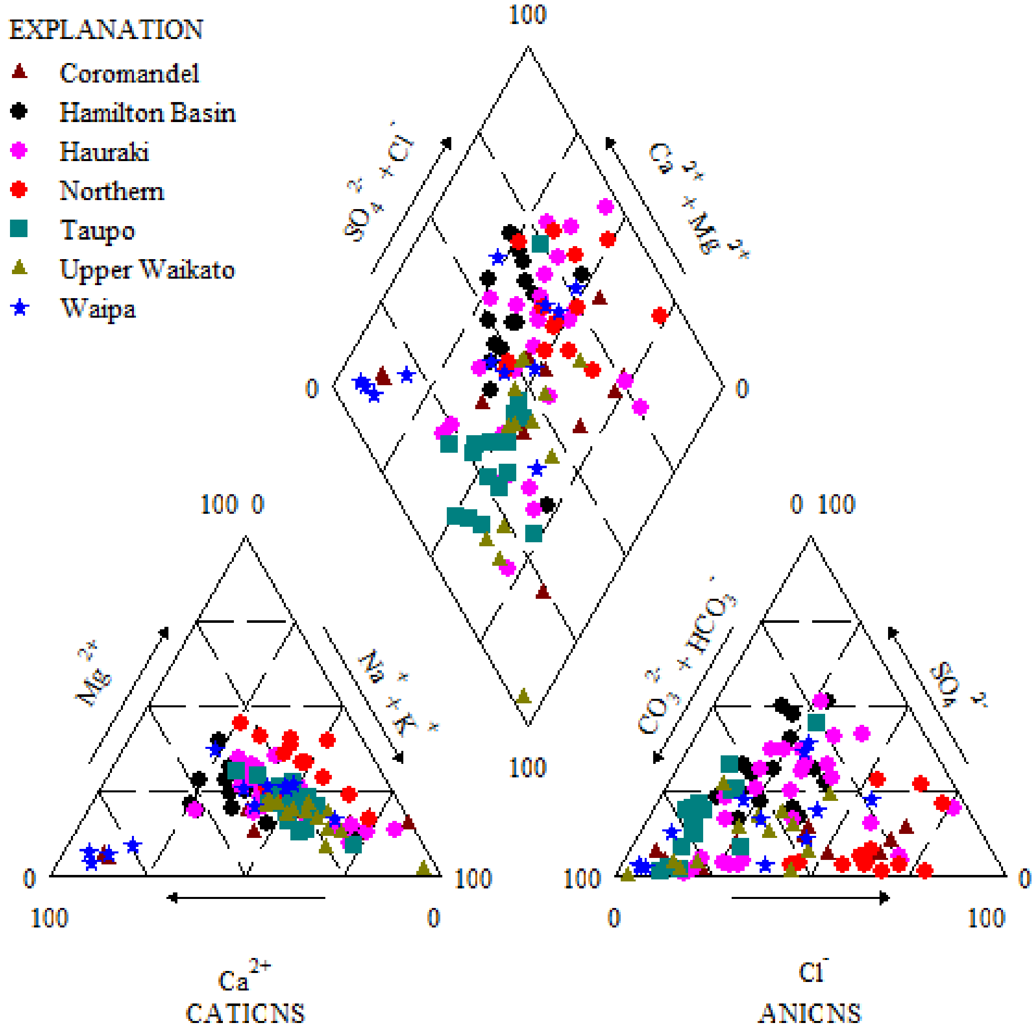


Figure 43 Piper diagram of the regional SOE groundwater quality monitoring network

For comparison between key determinant concentration ranges of sub-regions a series of box plots are presented in Figures 44 to 52. This data is from the 18 years of monitoring from 2003-2020 and has been annualised for aggregation. Data which falls outside one and a half times the inter-quartile range (IQR) are treated as outliers. Left sensored or below detection results were simply halved for these Figures.

Relatively large IQRs are apparent for bicarbonate in the Coromandel and Waipa areas. This reflects the inclusion of shelly coastal sands in Coromandel aquifers and limestone aquifers in the Waipa catchment. The bicarbonate concentrations in the Northern sub-region, being largely representative of basaltic aquifers, are significantly lower than in other areas where more rhyolitic or acid volcanic formations and associated sediments are more typical.

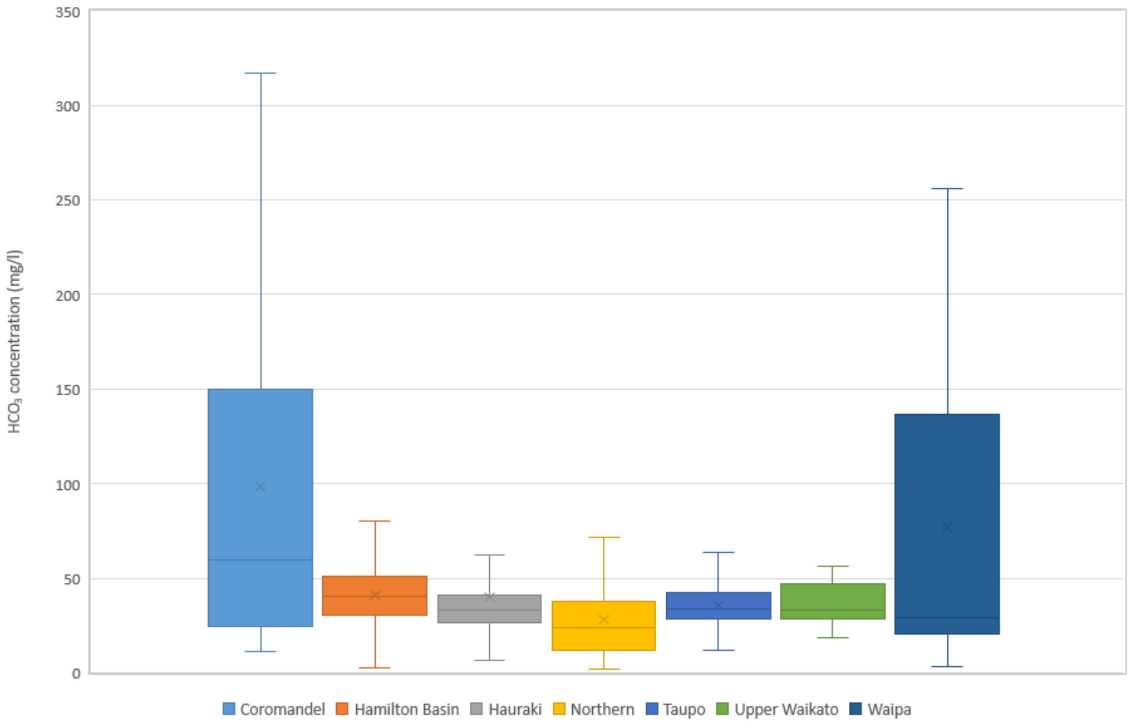


Figure 44 Sub-regional box plots of bicarbonate concentration (2003-2020)

Calcium IQRs are similarly largest in the Coromandel and Waipa areas for the same reasons as above (i.e. the presence of shelly coastal sand and limestone aquifers respectively). The lowest calcium concentrations and range are in Taupo reflecting the domination of young siliceous volcanic formations.

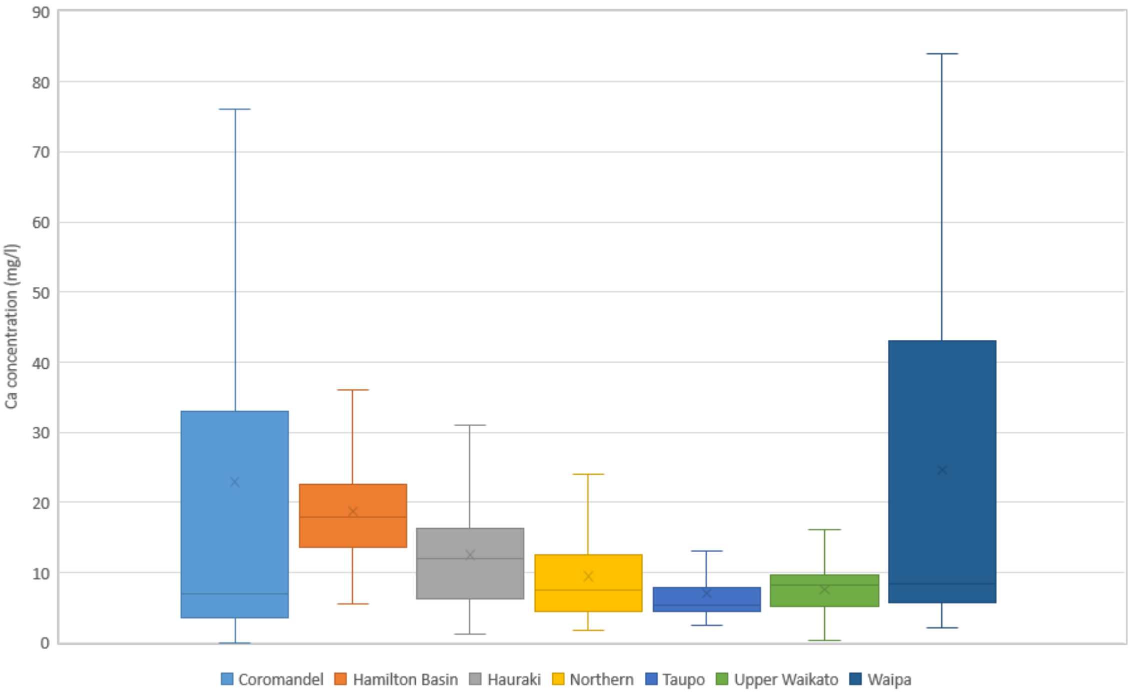


Figure 45 Sub-regional box plots calcium concentration (2003-2020

The highest median and largest chloride concentration IQRs are in the Coromandel and Northern areas. The Coromandel distribution is consistent with coastal proximity of the aquifers monitored. The relatively high concentrations in the Northern sub-region are also likely a consequence of the coastal influence on recharge given predominant westerly winds, which may be accentuated by intensive land-use. The lowest chloride concentrations and smallest range is in the Lake Taupo catchment. This is consistent with its distant location from the coast and modest land-use development.

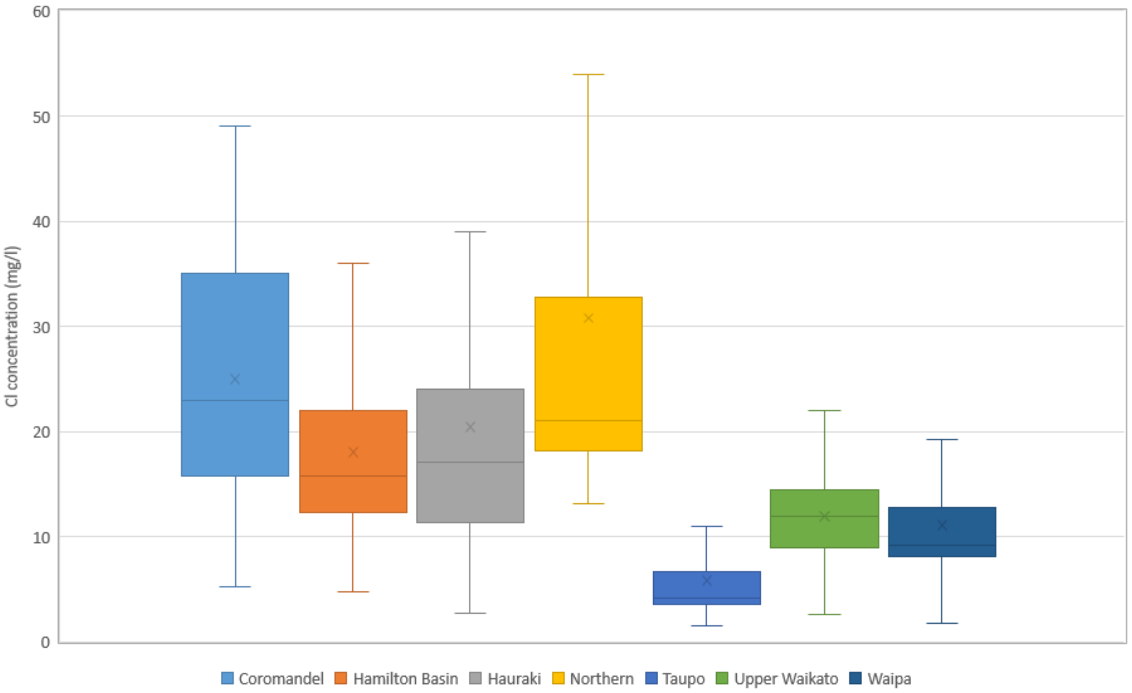


Figure 46 Sub-regional box plots of chloride concentration (2003-2020)

Electrical conductivity typically indicates the concentration of total dissolved solids in natural waters (assuming predominantly inorganic content). There is a strong correlation between electrical conductivity and chloride regionally, which is evident in the distributions. Other ions can also contribute to conductivity and moderate correlations also occur with calcium, magnesium, sodium, nitrate and sulphate. It appears that the subregional conductivity differences are predominantly reflecting the same influences as that for chloride.

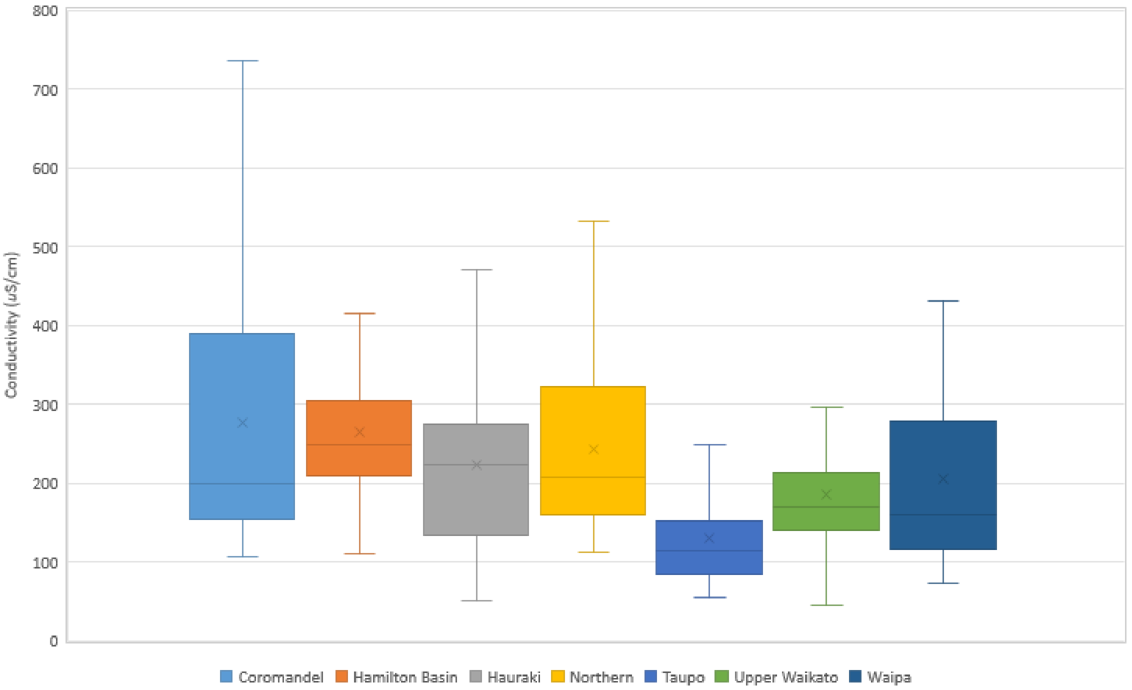


Figure 47 Sub-regional box plots of electrical conductivity (2003-2020)

Potassium is common in many formations although more so in those that are sedimentary than volcanic. Being important for plant growth it is also present in many fertilisers. Potassium may be readily attenuated in groundwater, however, through ion exchange. Higher concentrations are shown to be more prevalent in aquifers in Hamilton Basin, Hauraki and Upper Waikato than the Northern areas and Coromandel.

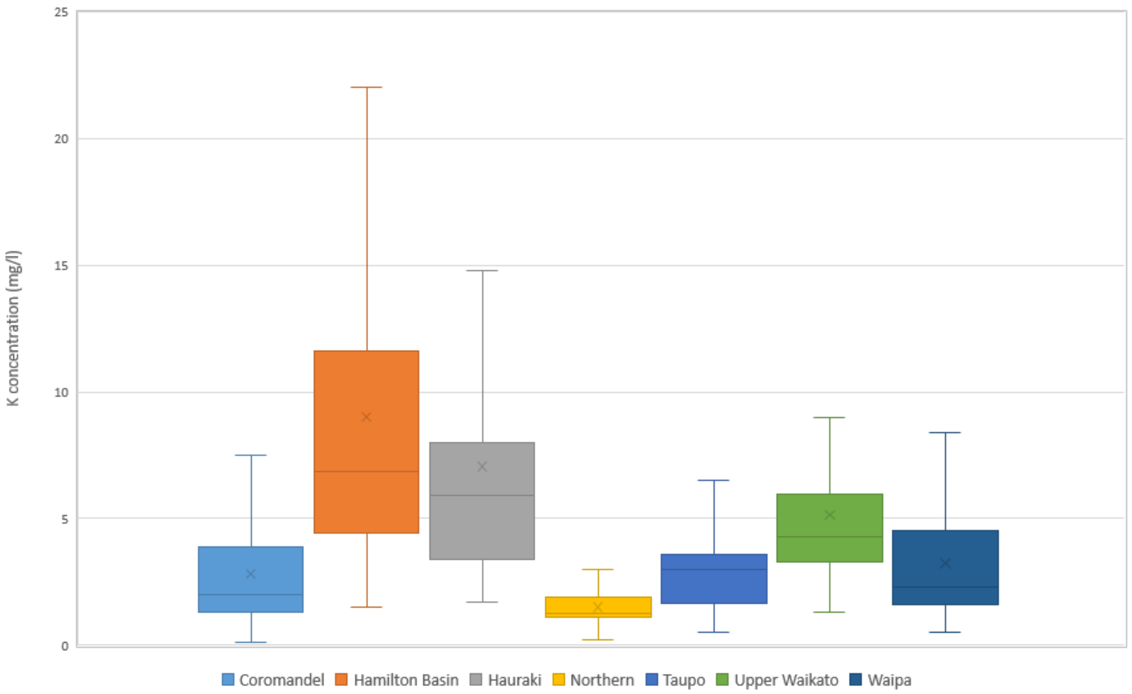


Figure 48 Sub-regional box plots of potassium concentration (2003-2020)

Higher magnesium concentrations in the Northern areas and Hamilton Basin and to a lesser extent Hauraki compared to other sub-regions are apparent in Figure 49 below. Basalts in the Northern areas are rich in ferromagnesian minerals which are a source of magnesium in groundwater (Hem, 1985). The relationship of concentration with age (further below) appears to suggest an anthropogenioc origin, however, rather than one that is geogenic. This may, however, be complicated by comparison with a range of hydrogeologic environments. Although some limestones can be a significant source of magnesium, this appears not to be the case in the Waipa catchment.

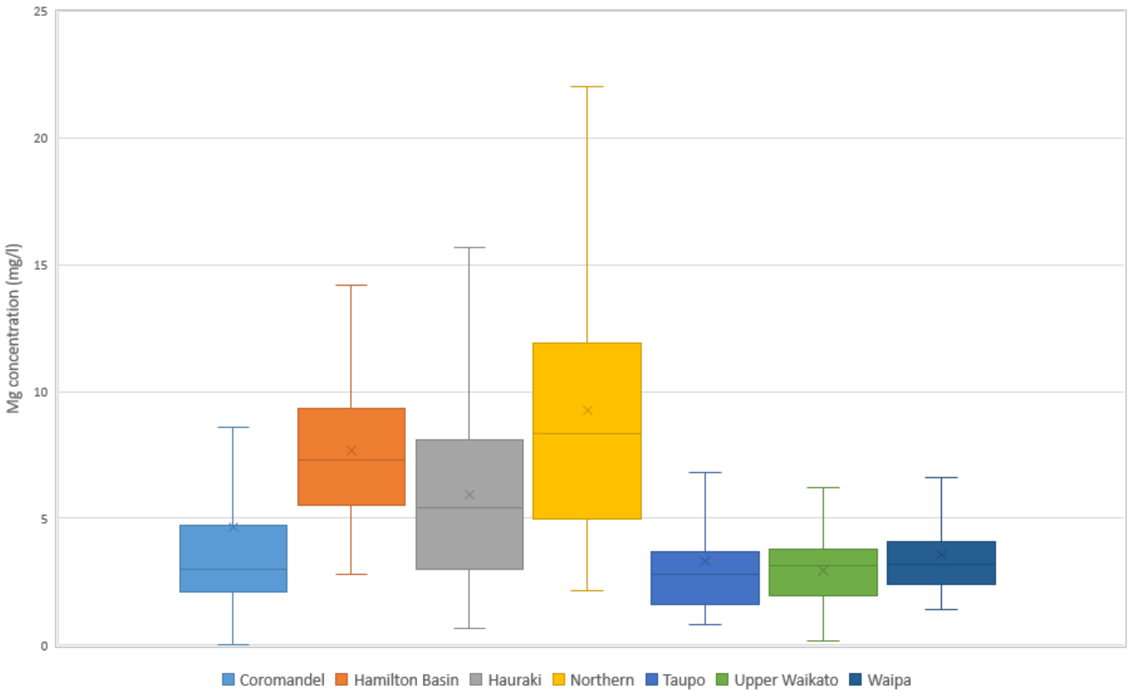


Figure 49 Sub-regional box plots of magnesium concentrations (2003-2020)

The largest IQR and highest median concentration for sodium in Figure 50 is in the Coromandel area. This reflects the coastal proximity of these aquifers. Sodium is more mobile than for example potassium, so is often used as an indicator of human impacts on shallow groundwater. Anthropenic sources of sodium include wastewater and notably animal effluent. Increased dissolution from formation can also occur over time.

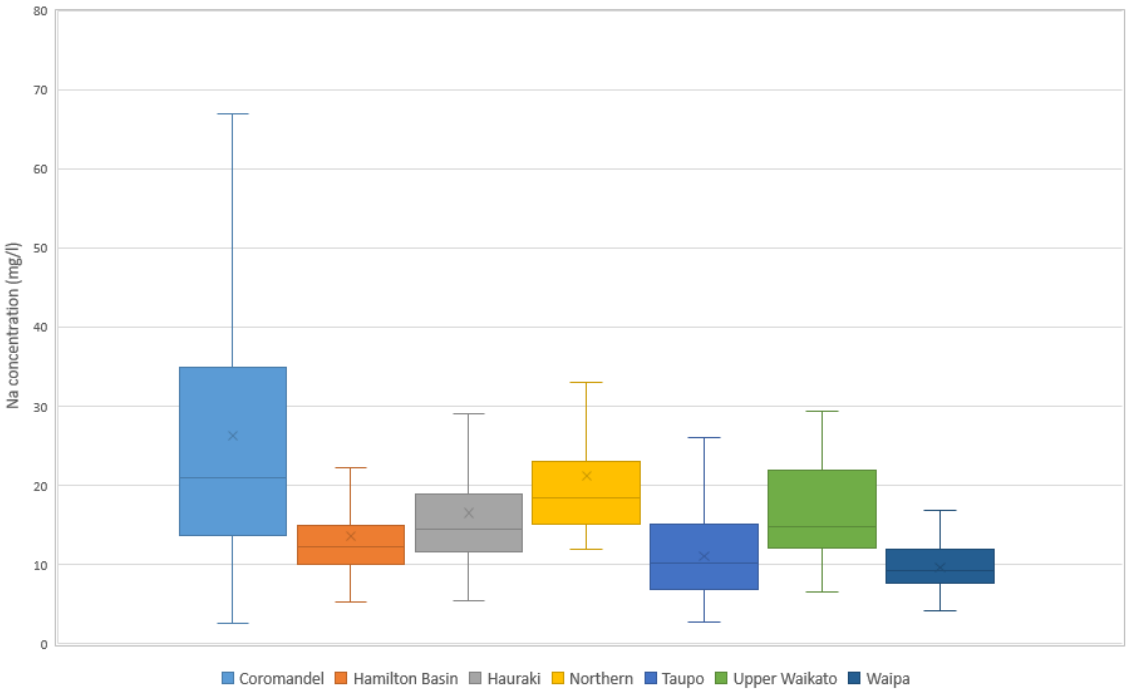


Figure 50 Sub-regional box plots of sodium concentration (2003-2020)

The highest nitrate-N concentrations are shown in Figure 51 to occur in the Northern areas, Hauraki and Hamilton Basin. These are the areas of traditionally most intensive agriculture. Nitrate concentrations correlate moderately with chloride, magnesium and TDS. Apart from land-use loading, the most notable other factor influencing nitrate-N occurrence is attenuation, which is related to the distribution of redox conditions. Lag times can also substantially delay the impact of land-use loading on groundwater quality. These aspects are discussed in more detail later in this section.

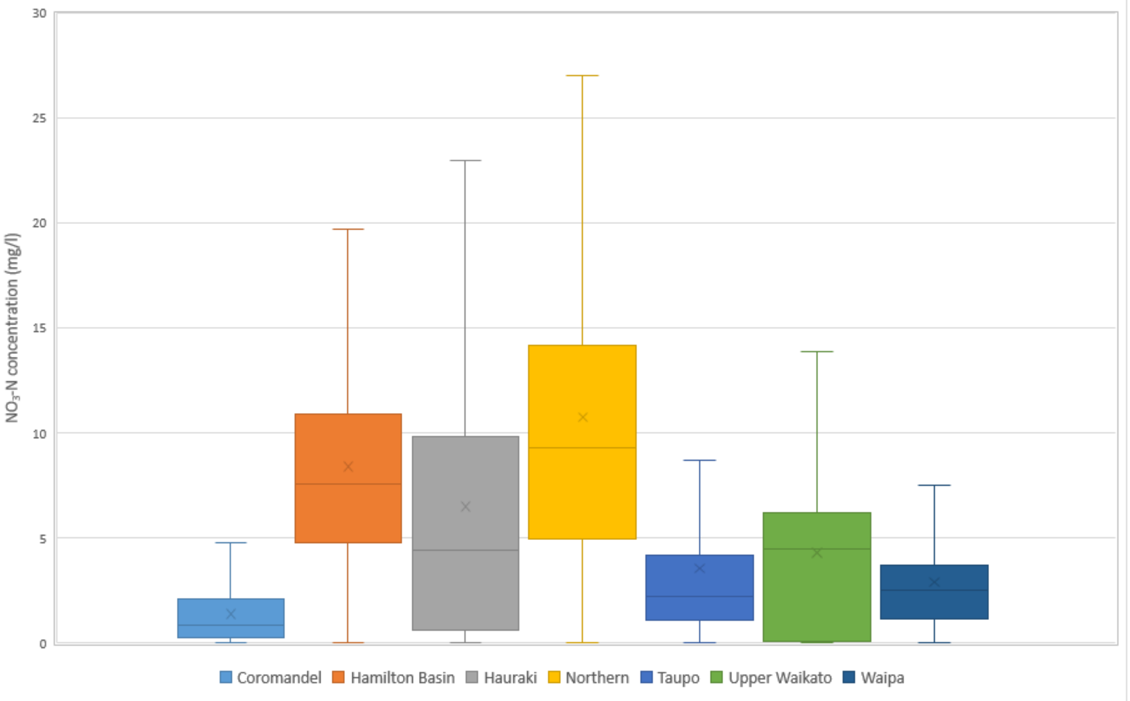


Figure 51 Sub-regional box plots of nitrate-N concentration (2003-2020)

Sulphate concentrations are highest in the Hamilton Basin monitoring wells and lowest in the basalt aquifer dominated Northern areas. In natural waters sulphate is generated from the oxidation of pyrite and dissolution of sulphate minerals such as gypsum. Gypsum is also used in fertilisers. Rosen (2000), found that SO_4 to Mg ratios above that of seawater typically occur from fertiliser use. This is typically the case regionally with a minor exception in the Upper Waikato and a major anomaly with a much lower ratio in the basaltic Northen areas.

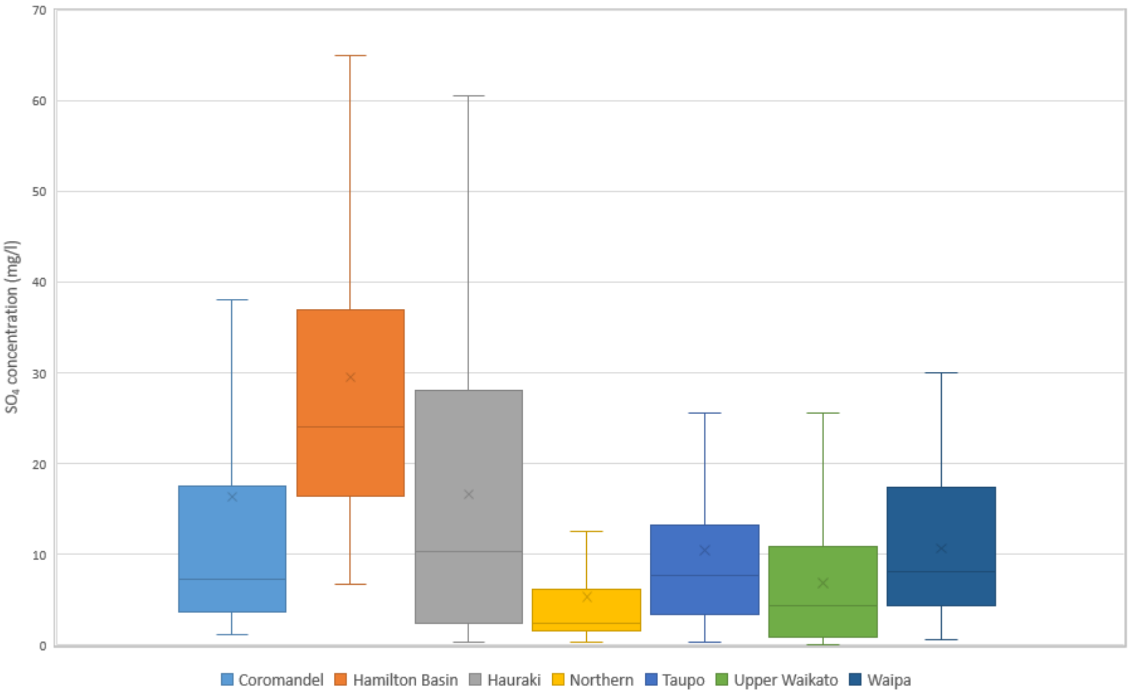


Figure 52 Sub-regional box plots of sulphate concentration (2003-2020)

The percentages of increasing and decreasing key parameter concentration trends (with 95 % confidence, 2003-2020) are shown in Figure 53 for the full regional SOE network. This composite representation is much more balanced than for some sub-regions. Trend information is provided in Appendix IV. There were seven sites not analysed due to a preponderance of left censored data and insufficient unique values. The overall picture suggests a variable mix of degradation and water quality improvement. This is examined further for components of the regional SOE network below. Consideration of the consequences of these trends, such as nitrate, within the larger three-dimensional groundwater domain and receiving surface waters requires further investigation and use of techniques such as modelling (e.g. Hemmings et al., 2022, Rajanayaka et al. 2020, Stenger et al., 2022).

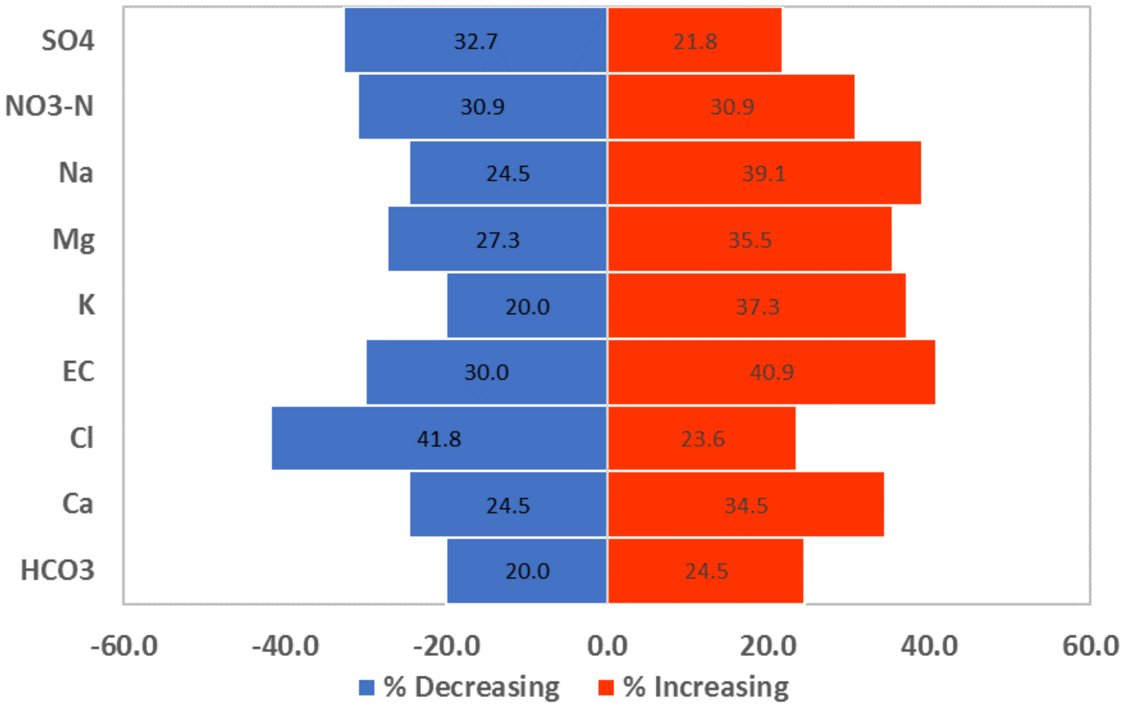


Figure 53 Mirror bar plot of key determinant trends (with 95 % confidence) in the regional SOE network.

For a national comparison of nitrate-N concentrations MfE and Stats NZ report that for the period 2009 to 2018 improving nitrate-N trends were evident at 49 % of sites and 38 % had worsening trends (Figure 54).

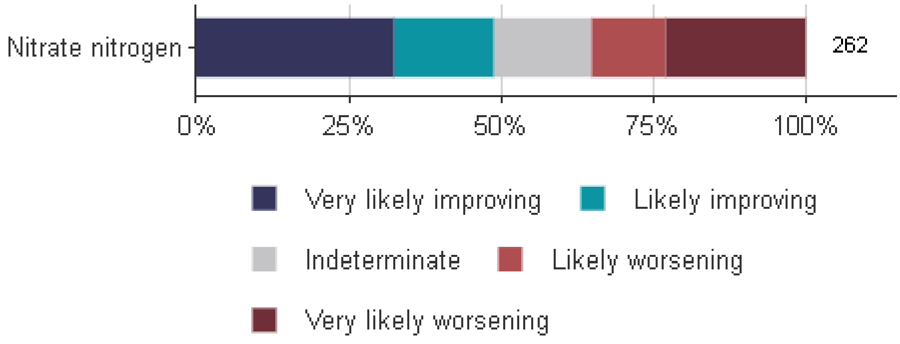


Figure 54 National nitrate-N trends 2009-18 (MfE and Stats NZ)

More detailed comparison is made between trends in the four network components of the regional groundwater quality monitoring programme in Appendix IV. These components comprise 27 SOE wells which are monitored quarterly, 10 wells which are part of the NGMP and also monitoried quarterly, 73 SOE wells sampled annually and the "Community network' of 80 rural schools monitored every two years. The column graphs for 14 determinants in the appendix include a larger range of trend confidence intervals derived using script from Land and Water People (Snelder and Frazer, 2019).

To illustrate further the differences between the SOE and Community networks, nitrate-N concentrations and well depths are compared using 2020 annual data (given monitoring frequency differences) in Figure 55 below.

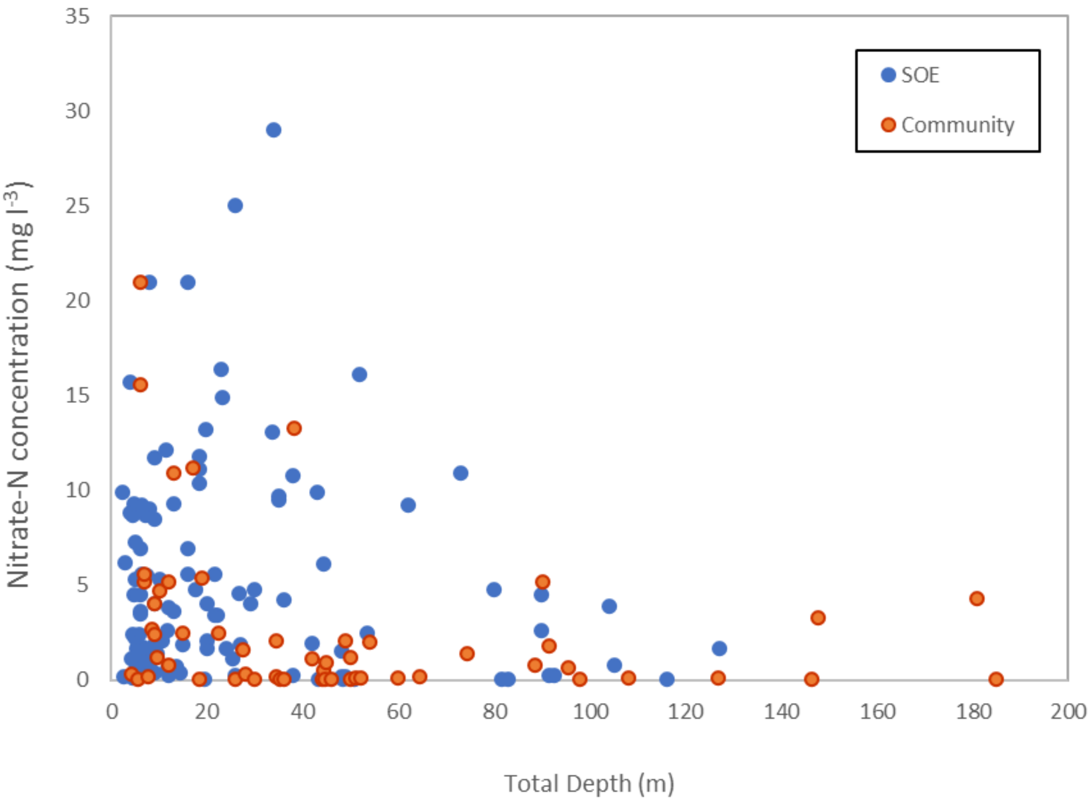


Figure 55 **Nitrate-N concentrations in 2020 versus well depth for SOE and Community wells**

Nitrate-N concentrations compared using 2020 data are significantly higher in the SOE network than the community network with medians of 3.60 and 0.91 respectively (Mann Whitney p <0.001). Well depths are also different with the median for the SOE and Community networks being 16.05 and 35.40 m respectively (p < 0.001).

Anaerobic groundwater is more commonly found in the Community network (~23 %) than the SOE network (~5.5 %). As a corollary, SOE network wells are more frequently aerobic (~55 %) compared to the Community network (34 %). As evident, higher nitrate concentrations are more prevalent in shallower wells where aerobic conditions are more likely. Such differences highlight the need for explicit consideration of important factors such as redox conditions in monitoring network design. Other influences on nitrate occurrence include land-use loading and lag times.

Figure 56 shows a nitrate-N versus depth graph, similar to that shown above but with redox categories indicated. This illustrates that aerobic conditions are less likely at greater depth. Clearly the redox conditions in groundwater strongly influences the occurrence of nitrate. Under anaerobic conditions nitrate concentrations are typically below detection. Nitrogen, if detectable, is generally present at low levels in the ammonium form. Nitrate-N typically volatilises essentially to nitrogen gas via denitrification. Denitrification, as described in section four, is a microbially mediated process which requires an available electron donor, typically particulate organic carbon or iron sulphides (Korom, 1992, Hadfield and Korom 2012).

Although the occurrence of nitrate and dissolved iron are typically mutually exclusive (requiring opposite redox conditions), there are numerous wells where a mixture of conditions may occur. Some of these have been investigated and found to result from well screening across both anaerobic and aerobic zones (Hadfield, 2021).

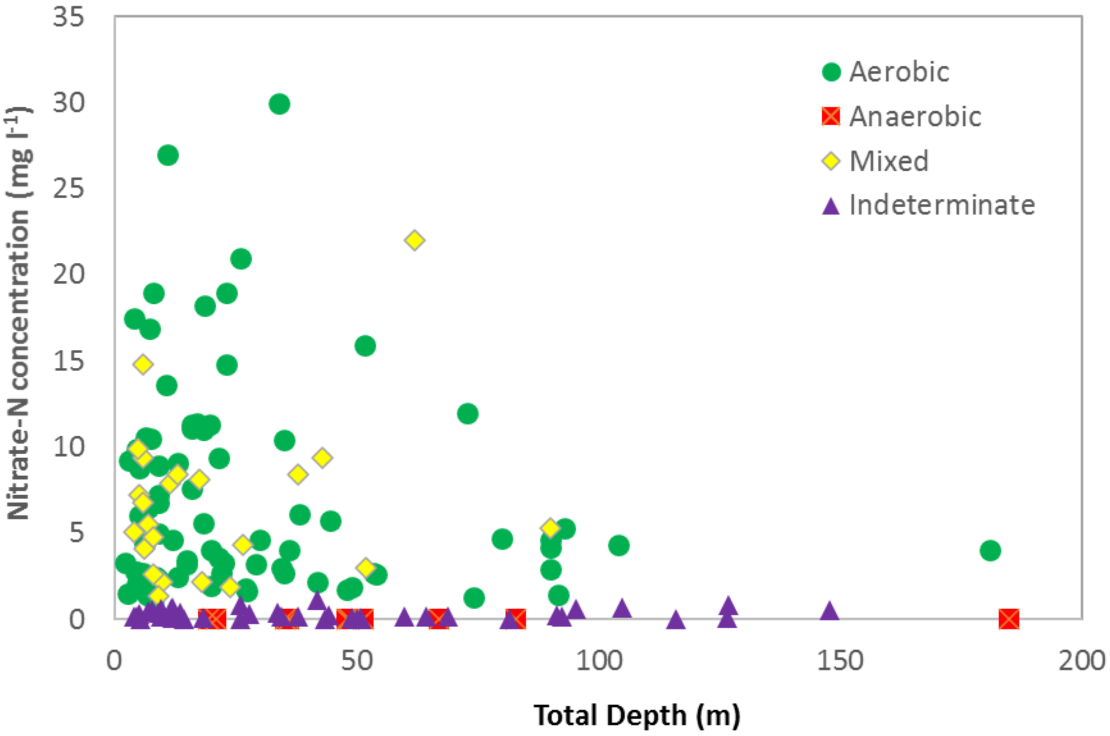


Figure 56 **Nitrate-N concentration versus depth for the regional and community networks showing redox categories**

The regional SOE network distribution for nitrate-N state and trends is illustrated in Figure 57. It is evident that the highest concentrations occur in the northern areas (Pukekohe, Pukekawa and Waiuku), the southern Hauraki Plains and Hamilton Basin. The concentrations in these relatively intensively farmed areas contrast with low nitrate-N concentrations in less developed Coromandel and Taupo sub-regions. It is noted that higher concentrations and all MAV exceedances are associated with dairy farming or market gardening areas (with one exception being a point-source from a woolshed in Taupo). Regional state and trend maps of other key determinants are provided in Appendix V.

The equivalent map of nitrate-N state and trend from the Community network shows a more subdued concentration distribution (Figure 58). This in part reflects that groundwater exceeding the drinking water MAV is not used for potable school supply (although sometimes it still may be used for other purposes). It also, however, reflects differences in network composition such as well depth and representation of redox categories as described above. It nevertheless follows somewhat similar patterns with higher concentrations in the central region areas. This dataset includes wells from the west of the region, which all have low nitrate concentrations.

Whilst overall the trends from the SOE network are mixed (30.9% degrading and 30.9% improving), the Community network shows more degrading trends (22.5%) than improving (6.25%). The Community network records now provide useful trend information despite only being monitored biennelly.

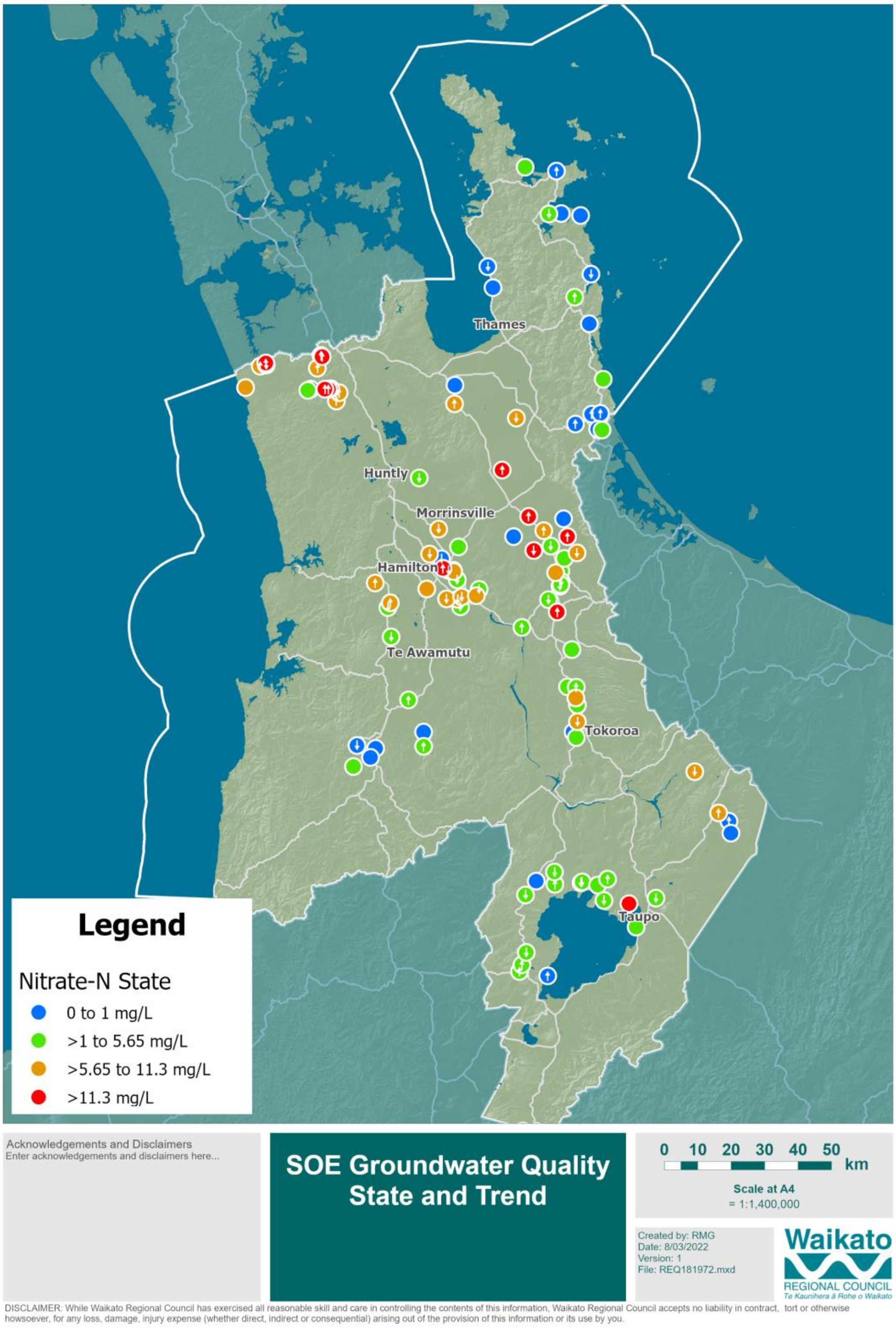
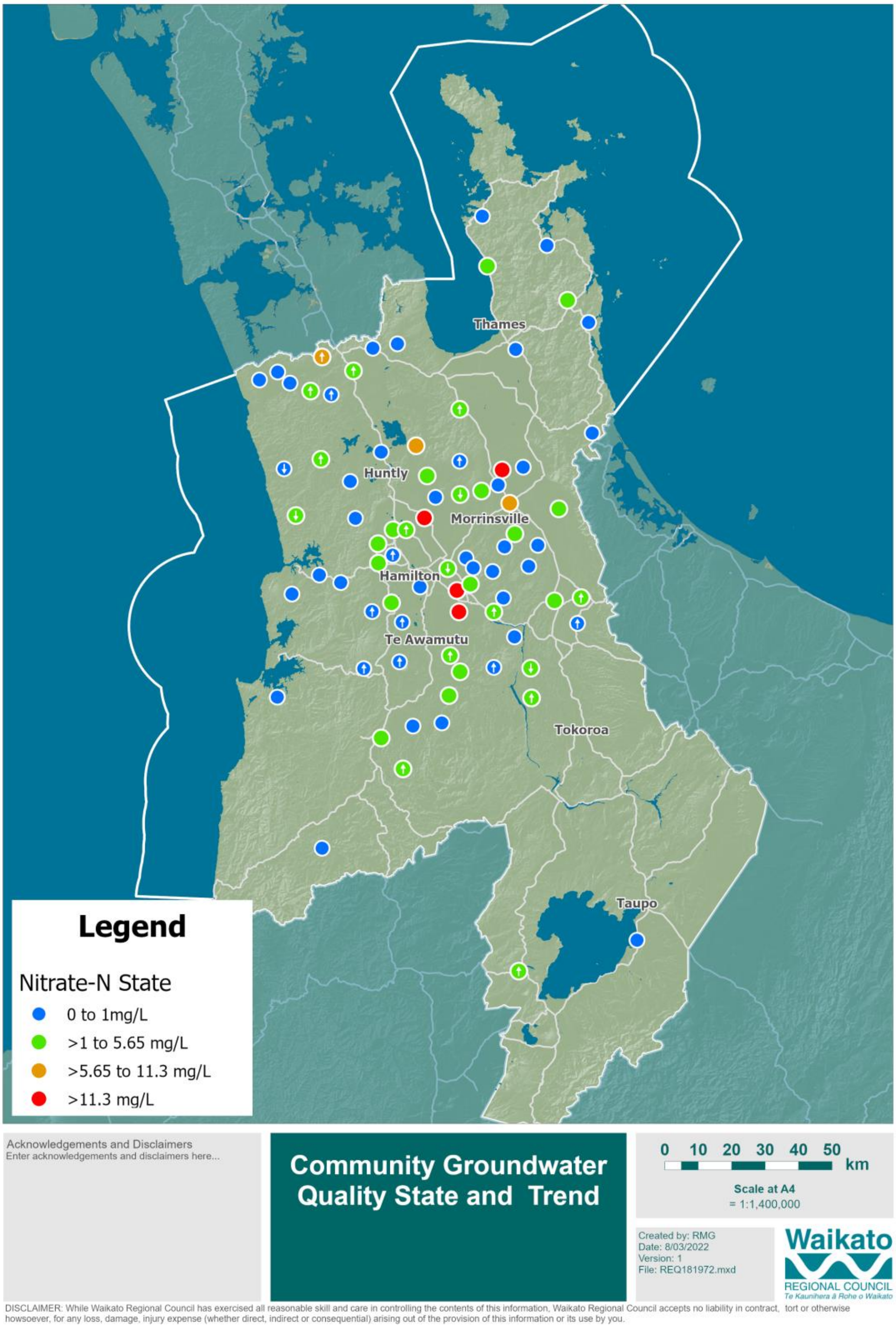


Figure 57 Nitrate-N concentration state and trend for the SOE groundwater quality network



DISCLAIMER: While Waikato Regional Council has exercised all reasonable skill and care in controlling the contents of this information, Waikato Regional Council accepts no liability in contract, tort or otherwise howsoever, for any loss, damage, injury expense (whether direct, indirect or consequential) arising out of the provision of this information or its use by you.

Figure 58 **Nitrate-N state and trend for the Community groundwater quality network**

The magnitude of the trend slopes for nitrate-N with 95% confidence are illustrated spatially for both the SOE and Community networks in the map below (Figure 59) and summarised in Appendix IV. Although the trends are mixed there are some spatial patterns. For example, relatively high rates of concentration increase predominate in the northern basalt aquifers. By contrast concentration trends are predominantly decreasing in the Hamilton Basin.

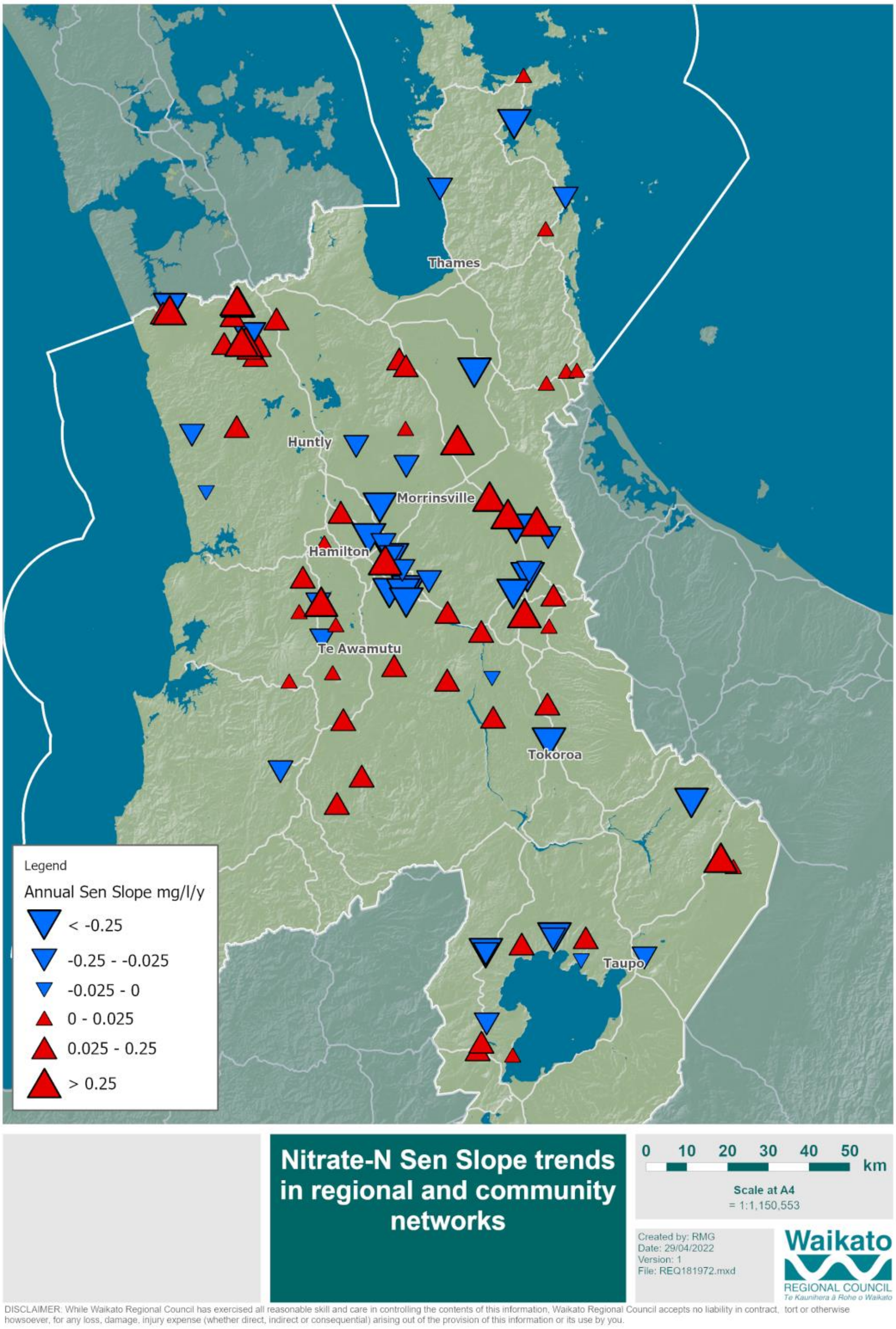


Figure 59 Nitrate-N Sen slope trends of 95% confidence for the SOE and Community groundwater quality network.

The figure below (Figure 60) shows the magnitude of nitrate-N concentration changes of 95% confidence (increases or decreases) plotted against well depth. The redox categories of these rates are also indicated. It is apparent that there is no simple linear relationship but rather a wedge shape indicating high rates of change are less likely to occur at depth. More rapid changes are more likely at shallow depth but may or may not occur dependent on other factors such as redox conditions and land-use loading. The largest changes occur in aerobic conditions followed by mixed redox conditions. Very low rate significant change is by definition occurring in the indeterminate category. As expected, there are no significant trends in wells with anaerobic conditions. The wedge shape in this graph is very similar to that in Figure 56 of nitrate-N concentration versus depth. This is because there is a strong linear relationship between the rate of change (Sen slope) and concentration.

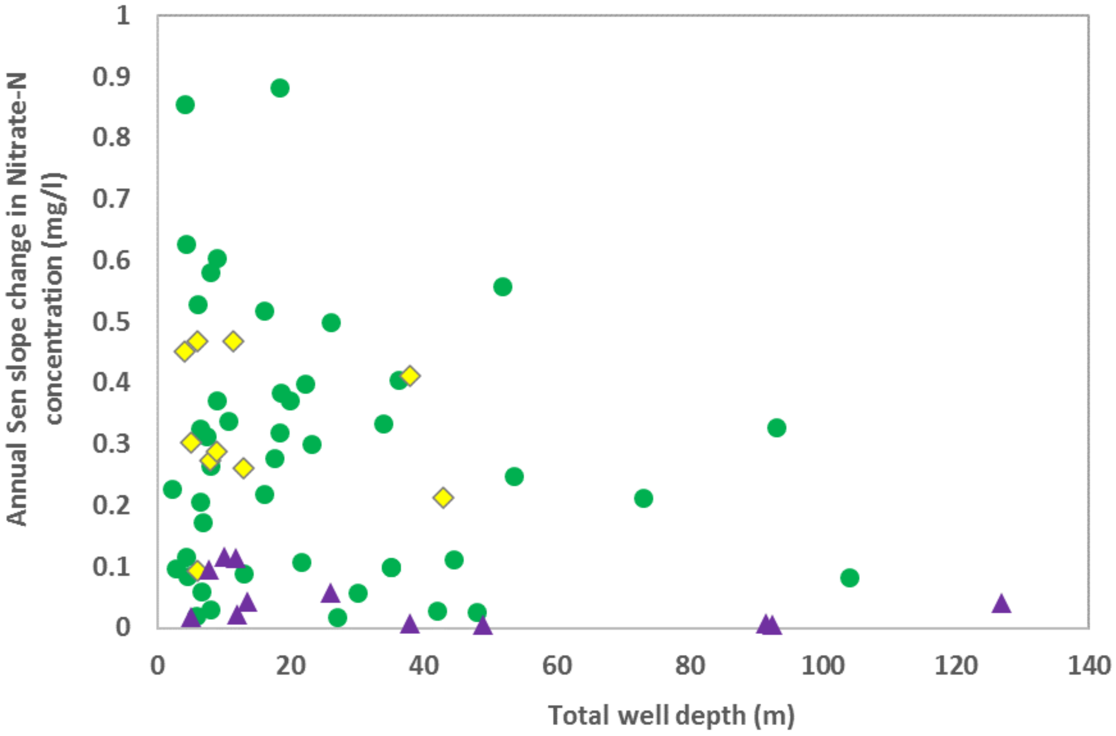


Figure 60 **Magnitude of nitrate-N concentrations change and well depth**

Relationships between groundwater age and the concentrations of groundwater quality parameters can help differentiate between geogenic and anthropogenic influences. Concentrations which increase with age typically reflect geogenic sources. By contrast, impacts from land-use are likely when higher concentrations occur in younger waters. The age of land-use impacted groundwater can be used to infer the timing of land-use activities, such as farming, impacting groundwater quality (Morgenstern, 2007).

The following figure (Figure 61) shows SOE network concentrations for selected groundwater quality determinants plotted against groundwater age. It is apparent that higher calcium, magnesium and sulphate concentrations occur in younger groundwaters indicating land-use effects probably related to fertiliser use and liming. The concentration distributions all suggest intensification in the last 50 years. By contrast pH is increasing with age reflecting evolving biochemical reactions.

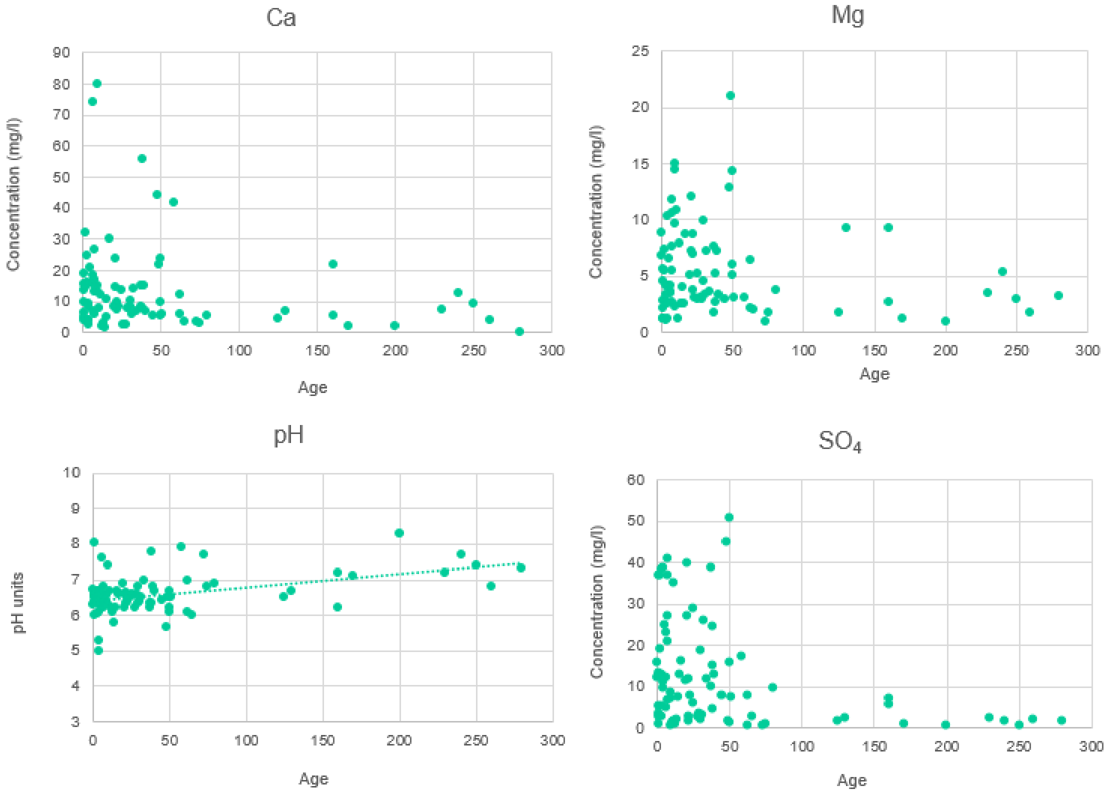


Figure 61 **Selected SOE network water quality determinant concentrations plotted against groundwater age (MRT in years)**

Of the nine key determinants described earlier the most significant correlations (although still weak) are for nitrate, sulphate and pH. The first two are negatively correlated with age and pH has a positive correlation. Higher concentrations of chloride, potassium, sodium and TDS also occur in younger groundwater, although unlike the previous three, their relationships are not significant. It is noted that potassium may be relatively reduced from groundwater by ion exchange.

Nitrate-N concentrations are plotted against groundwater age (MRT in years) in Figure 62. This shows that rather than a simple linear relationship between groundwater age (mean residence time) and nitrate concentrations, there is typically a wedge-shaped distribution. This indicates that older groundwater (e.g. pre-farming) has low concentrations, whereas younger groundwater concentrations range depending on land-use intensity and denitrification. Numerical modelling indicates that the full realisation of the effects of land-use intensification and change may not become evident for a considerable time. Such simulation enables current monitoring to be understood in the context of future scenario prediction.

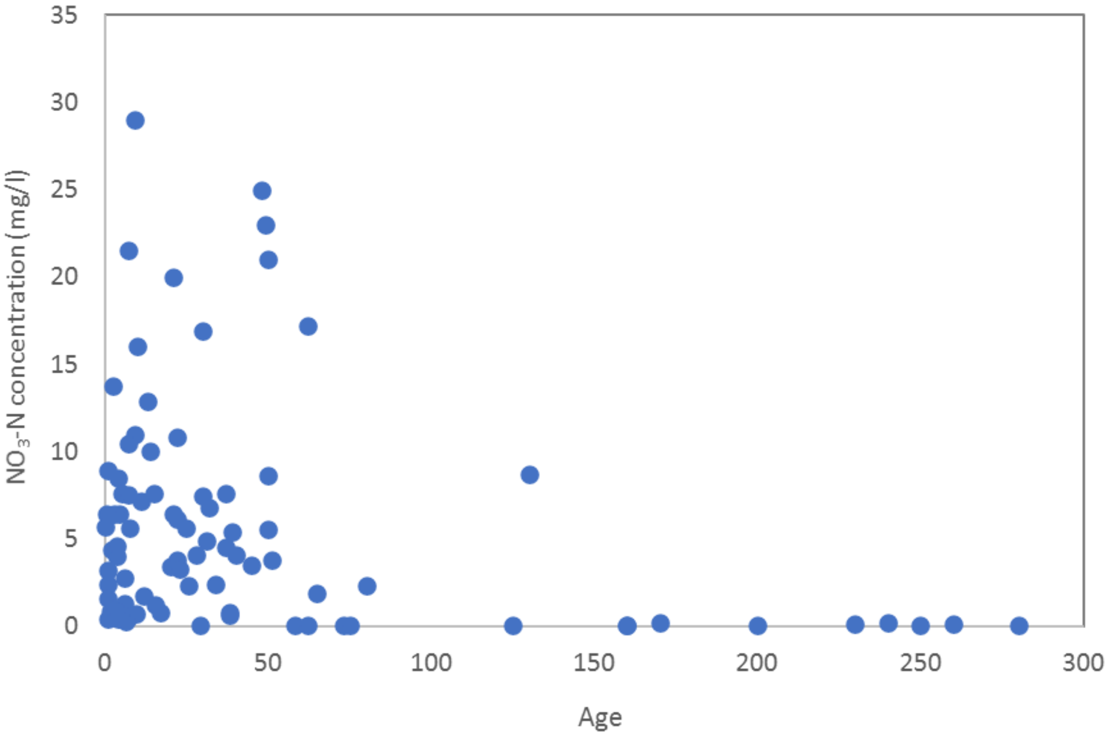


Figure 62 NO$_3$-N concentration plotted against groundwater age (MRT in years)

6 Groundwater quality impacts

6.1 Introduction

This section describes groundwater quality impacts by comparison with available standards and guidelines for use. Regional Councils have responsibilities for groundwater resource management under the RMA and drinking source water management under the Water Services Act (WSA), 2021. The relevant standards relate to microbial contaminants, inorganic and organic contaminants and there are also aesthetic guidelines relating to nuisance rather than health concerns. The occurrence of micro-organisms in the Waikato region is briefly discussed, exceedances of inorganic standards described along with the detection of pesticides and emerging contaminants in groundwater.

It is noted that there are no National Objectives Framework (NOF) bands established for groundwater quality under the National Policy Statement for Freshwater Management (NPSFM) currently (MfE, 2020). Groundwater does, however, contribute indirectly to impacts on surface water quality, particularly during low flows.

Also, importantly the drinking water standards and guidelines have recently been reviewed by Tuamata Arowai and some very minor changes in respect to this reporting will come into effect toward the end of 2022 (Water Services Regulations, 2022) but are not addressed here. Statistical issues that relate to the Drinking-water Standards used here are described in Appendix 2 of the Guidelines for Drinking-water Quality Management (MoH, 2019).

6.2 Microbial contamination

The occurrence of micro-organisms in drinking water is the top priority groundwater concern from a health perspective as their presence can lead to rapid and major outbreaks of illness, sometimes with fatal consequences. The current drinking water standards (MoH, 2018) includes an MAV for the microbial indicator bacteria *Escherichia Coli*, which should be less than 1 per 100 mls of sample. These organisms are from the gut of warm-blooded animals and are an indicator that other pathogenic organisms including viruses, protozoa and other bacteria may be present. *E. coli* are the preferred indicator group because they are easy to detect and count and have better survival in fresh water than enterococci. Specific measurement of viral occurrence, such as MS2, is by comparison expensive and difficult.

WRC does not monitor *E-coli* on a routine basis as part of the groundwater quality monitoring programme. This may be reviewed for national consistency. It is currently considered that a poor sanitary seal at the well-head and cross contamination are relatively important mechanisms for *E*-coli detections in the Waikato. Thus occurrences may not reflect the state of groundwater more widely.

E-coli surveys are, however, undertaken on a four-yearly basis as one of numerous environmental indicators. A total of 82 sites are currently monitored comprising a mix of SOE and rural school wells. The wells were originally selected based on the following criteria:

- vulnerability to contamination from the land surface assessed using the DRASTIC index (Aller et al., 1987);
- availability of in-situ pumps to minimise the potential to introduce contamination during sampling;
- availability of well log and construction information, and;
- spatial distribution and representation of a range of land uses.

Of the 82 wells sampled in 2020 about 9% of narrow diameter wells (100 mm or less) and two thirds of wide diameter wells (at least 900 mm) had *E-coli* detected (Figure 63 below). These sites comprised 21 schools and 61 SOE wells.

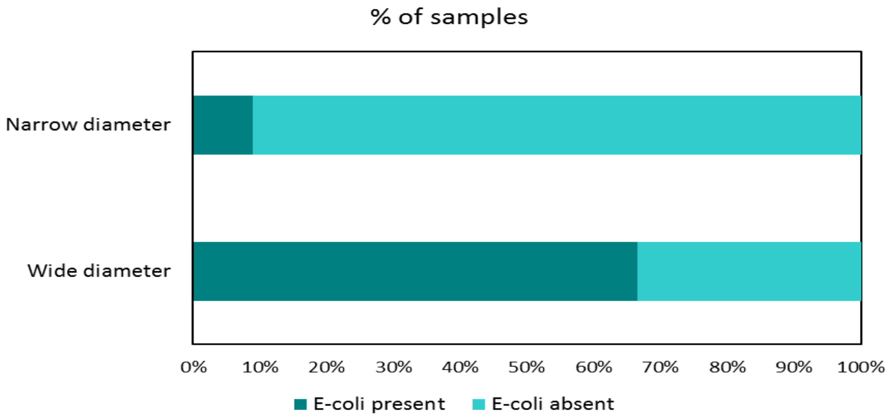


Figure 63 **Percentage of wells where E-coli was detected in 100 mls of groundwater in 2020**

These results suggest that well construction and completion to achieve a sanitary seal are of fundamental importance. The Waikato region is relatively well protected naturally from the ground surface, as shown in the vulnerability mapping in Figure 3. A study by Pang (2003) showed that pumice sand aquifers readily attenuate bacteria. Tracer testing using viruses and bacteria in coastal sands at Pauanui (Coromandel) showed very high attenuation rates of about six log within a distance of only three metres of travel (Hadfield et al., 2014, Pang et al., 2020). There are, however, settings where microbial transport through the aquifer is more likely. These may include shallow groundwater with little soil cover and relatively faster travel times such as in fractured rock or karst systems. Conduits such as soak holes and offal holes may also short-circuit natural protection. A precautionary approach involving proper laboratory microbial testing is recommended.

6.3 Inorganic contaminants

The drinking-water standards define maximum acceptable values (MAVs) that if not exceeded will ensure water is safe for consumers to drink all their lives without becoming ill (Nokes, 2008). For carcinogenic chemicals, the MAVs generally represent a risk of one additional cancer incidence per 100,000 people ingesting the water at that concentration for a lifetime of 70 years (MoH, 2019). Guidelines for drinking-water quality management for New Zealand (MoH, 2019) includes datasheets for related determinants. A datasheet for nitrate is included as an example in Appendix VIII.

Table 2 below lists the maximum acceptable values (MAVs) for inorganic determinants of health significance from the Ministry of Health Drinking-water Standards (MoH, 2018). The following abbreviations are used:

ATO	Concentrations of the substance at or below the health-based guideline value that may affect the water's appearance, taste or odour.
DBP	Disinfection by-product. Any difficulty meeting a DBP MAV must never be a reason to compromise adequate disinfection. Trihalomethanes and haloacids are DBPs. Some DBPs may also have other sources.
PMAV	Provisional MAV (because it is provisional in the World Health Organisation (WHO) Guidelines or the WHO has no guideline value but the DWSNZ has retained a MAV or developed its own).

Table 2 **Maximum acceptable values for inorganic determinants of health significance (MoH, 2018)**

Name	MAV (mg/L)	Remarks
antimony	0.02	
arsenic	0.01	For excess lifetime skin cancer risk of 6 x 10^{-4}. PMAV, because of analytical difficulties
barium	0.7	
boron[1]	1.4	
bromate	0.01	For excess lifetime cancer risk of 7 x 10^{-5}. PMAV
cadmium	0.004	
chlorate	0.8	PMAV. Disinfection must never be compromised. DBP (chlorine dioxide)
chlorine	5	Free available chlorine expressed in mg/L as Cl_2. ATO. Disinfection must never be compromised
chlorite	0.8	Expressed in mg/L as ClO_2. PMAV. Disinfection must never be compromised. DBP (chlorine dioxide)
chromium	0.05	PMAV. Total. Limited information on health effects
copper	2	ATO
cyanide	0.6	Total cyanides, short-term only
cyanogen chloride	0.4	Expressed in mg/L as CN total. DBP (chloramination)
fluoride[2]	1.5	
lead	0.01	
manganese	0.4	ATO
mercury	0.007	Inorganic mercury
molybdenum	0.07	
monochloramine	3	DBP (chlorination)
nickel	0.08	
nitrate, short-term[3]	50	Expressed in mg/L as NO_3. The sum of the ratio of the concentrations of nitrate and nitrite to each of their respective MAVs must not exceed one
nitrite, long-term	0.2	Expressed in mg/L as NO_2. PMAV (long term)
nitrite, short-term[3]	3	Expressed in mg/L as NO_2. The sum of the ratio of the concentrations of nitrate and nitrite to each of their respective MAVs must not exceed one
Selenium	0.01	
Uranium	0.02	PMAV

Notes:

1. The WHO guideline value (provisional) is 0.5 mg/L.
2. For oral health reasons, the Ministry of Health recommends that the fluoride content for drinking-water in New Zealand be in the range of 0.7–1.0 mg/L; this is *not* a MAV.
3. Now short-term only. The short-term exposure MAVs for nitrate and nitrite have been established to protect against methaemoglobinaemia in bottle-fed infants.
4. For information about determinants of possible health significance but which do not have a MAV, refer to the datasheets in the Guidelines.

There are five parameters that are monitored routinely which have MAVs of health significance. These are arsenic, boron, copper, manganese and nitrate-N. The MAVs apply to total concentrations as shown rather than dissolved fractions. Table 3 below presents the percentage of wells in the SOE and Community networks which have exceeded the relevant MAVs at least once in the last five years. The percentage of five-year medians concentrations exceeding the MAVs are also shown in subsequent Table 4.

Table 3 **Percentage of wells with groundwater which exceeded MAVs at least once from 2016-2020.**

Determinant	As	B	Cu	Mn	NO_3-N
MAV (mg/l)	0.01	1.4	2	0.4	11.3
SOE Quarterly	3.70	0.00	0.00	3.70	37.04
NGMP[1]	Na	na	na	0.00	50.00
SOE Annual	5.48	0.00	0.00	5.48	13.70
SOE All[2]	5.00	0.00	0.00	5.00	22.73
Community	2.50	2.50	0.00	6.25	5.00

[1] NGMP manganese concentration is dissolved

[2] All available

[3] Boron MAV will change to 2.4 mg/l at the end of 2022

Table 4 **Percentage of wells with median groundwater concentrations which exceeded MAVs 2016-2020.**

Determinant	As	B	Cu	Mn	NO_3-N
MAV (mg/l)	0.01	1.4	2	0.4	11.3
SOE Quarterly	0	0.00	0.00	3.70	11.10
NGMP[1]	na	na	na	0.00	20.00
SOE Annual	5.48	0.00	0.00	4.11	9.59
SOE All[2]	5.48	0.00	0.00	4.00	10.91
Community	2.50	1.25	0.00	6.25	5.00

[1] NGMP manganese concentration is dissolved

[2] All available

Arsenic is a toxic but naturally occurring determinant which exceeded the drinking water PMAV at about 5% of regional SOE wells and 2.5% of community wells in the five years to 2020. It is noted that this is a provisional MAV because of scientific uncertainties and the value is most directly related to excess lifetime skin cancer risk of 6×10^{-4} (MoH, 2019).

An investigation of arsenic occurrence in Waikato groundwater by Piper and Kim (2006), involved analysis of samples from 302 wells. About 10% of Waikato groundwater samples in this study exceeded the PMAV and about 19% exceeded half the PMAV. The highest non-compliance was in the Reporoa Basin (33%), with the Taupo (12%) and Coromandel (9%) areas also being prevalent. Only 2% of samples exceeded the PMAV in the remainder of the Waikato.

Elevated arsenic concentrations were related to the direct influence of geothermal sources and the reductive dissolution of subsurface iron and manganese oxides, which may influence variation. Other point sources of arsenic not represented here may include copper chromium arsenic (CCA) treatment of timber and legacy use in sheep dips until the 1950s.

A significant positive correlation with arsenic was found with lithium, ammonia, dissolved iron and manganese concentrations. The majority (70%) of samples were found to be in the arsenate form with the remainder being in the more mobile and toxic arsenite form. It was recommended that, due to temporal variation, groundwater from new drinking-water wells in the Waikato should be tested quarterly for the first year to assess the potential range in arsenic concentrations (Piper and Kim, 2006).

Boron typically enters groundwater through the dissolution of minerals such as tourmaline in igneous and sedimentary rocks and may be associated with geothermal fluids (GNS, 2015). The MAV of 1.4 mg l^{-1} is likely to change to 2.4 mg l^{-1} in 2022. MoH (2019) describe the MAV as being related to developmental toxicity. There are no exceedances at SOE sites but a few concentrations are above half MAV.

Copper has not exceeded the MAV of 2 mg l^{-1} (related to liver and gastric illnesses). Geological settings for the natural occurrence of copper include volcanic areas. Geothermal waters in the Taupo Volcanic Zone can contain concentrations up to about 3 mg l^{-1} (GNS 2015).

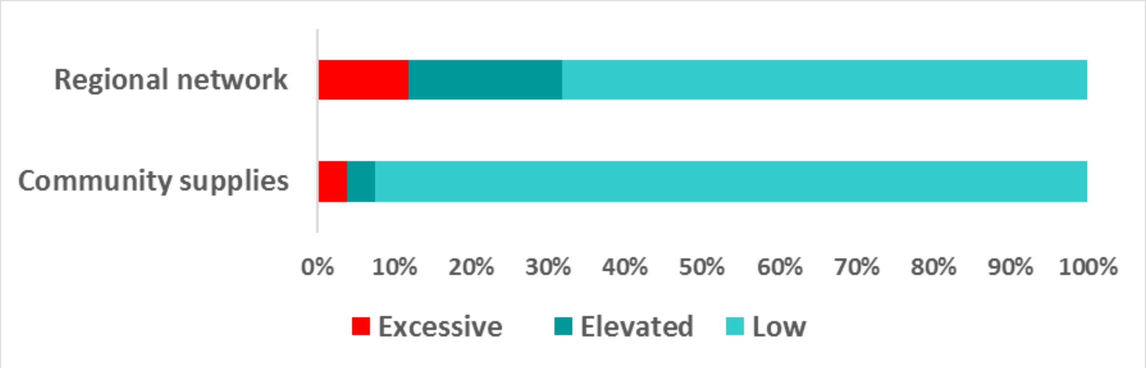
Manganese is naturally occurring and is classified as a parameter of health significance. It is ubiquitous in the environment, being a minor constituent of many igneous minerals, particularly basalts, but may also substitute in small amounts for calcium in limestones. Concentrations in groundwaters can become elevated in anaerobic conditions or peaty environments usually in association with iron (Daughney, 2003). It exceeded the drinking water MAV of 0.4 mg l^{-1} at about 5% of SOE wells monitored. Manganese can be readily treated, typically with aeration and sand or other filters.

Nitrate-N concentrations, above low ambient levels, are of anthropogenic origin and therefore essentially differ from the other inorganic contaminants discussed in that they are manageable. High concentrations of nitrate in drinking water can pose health issues. A health concern regarding nitrate is the formation of methaemoglobinaemia (blue-baby syndrome). Methaemoglobinaemia occurs when nitrate is reduced to nitrite in the stomach of infants, and nitrite is able to oxidise haemoglobin to methaemoglobin, which is then unable to transport oxygen around the body. This can cause cyanosis and asphyxia. The basis of the current MAV is described in the determinant datasheet (MoH, 2019) in Appendix VIII. For drinking water, the New Zealand Drinking Water Standards set a Maximum Acceptable Value (MAV) of 50 milligrams per litre (mg/l) for nitrate, which is equivalent to 11.3 mg/l nitrate-nitrogen (MoH, 2018).

Recent studies have also raised other health concerns related to lower concentrations of nitrate. For example, a recent Danish study identified a correlation with colorectal cancer risk and recommended an upper limit of 0.87 g/m^3 for nitrate-nitrogen (Schullehner et al. 2018). Chambers et al., (2022) also discuss other research related to health and carcinogenic risk and related epidemiological evidence. The Ministry of Health set up a task force to review the implications of new evidence for New Zealand and whether this would require a review of NZ's drinking water standard for nitrate. No change has been signalled at this stage.

It is apparent from Table 3 that groundwater in SOE wells commonly (22%) exceeded the nitrate-N MAV at least once from 2016-2020. Median concentrations from the same five-year period also exceeded the MAV at 11% of SOE wells. Exceedances occurred at 5% of 'Community' (rural school) network wells. The differences between these networks were discussed in section 5.8.

Apart from the exceedances reported above, nitrate-N in groundwater is also reported by WRC as one of a suite of environmental indicators on a biennial basis. The most recently reported (2020) nitrate indicator is presented below (Figure 64) based on 110 Regional (SOE) wells and 80 Community (rural school) wells.



Where: Excessive is > MAV 50 ppm (> 11.3 ppm NO_3-N)
Elevated is < MAV 50 ppm and > 25 ppm (<11.3 and > 5.65 ppm NO_3-N)
Low is < half MAV

Figure 64 **Nitrate-N concentration indicator**

The indicator reports nearly 12% of the Regional (SOE) groundwater monitoring network wells exceeded the maximum acceptable value (MAV) for potable supply. A further 20% of wells had nitrate concentrations over half the MAV. The remaining two thirds (68.18%) have 'low' concentrations below half the MAV. Three quarters of these wells had concentrations greater than 0.87 ppm (mentioned in the paper by Schullehner et al., 2018).

Exceedances of the nitrate MAV occurred at 3.75 % of the community supply wells. None of these wells are now used for potable supply but rather for other purposes. A similar percentage are described as elevated and a total of 92.5 % have concentrations below half MAV. About half (50.62%) of community supplies have nitrate concentrations over 0.87 ppm.

WRC also contributes data to the Ministry for the Environment (MfE) and Statistics New Zealand to produce a national groundwater quality indicators. This is part of New Zealand's Environment Reporting Series updated for MfE's 'Our Freshwater 2020' (MfE and Stats NZ, 2020). For the five-year period 2014–18, 19 % of 433 sites (non-blue) failed to meet the nitrate-nitrogen drinking water standards on at least one occasion (Figure 65). The colours indicate the frequency at which the MAV was exceeded (e.g. mauve indicates these sites exceeded the MAV at least 25% of the time). Median nitrate-N concentrations were greater than 3 ppm at 44 % of 424 sites, indicating concentrations were influenced by industrial agriculture based on Daughney and Reeves (2005) and Morgenstern and Daughney (2012). This compares with 53.64 % for the most recent Waikato regional data.

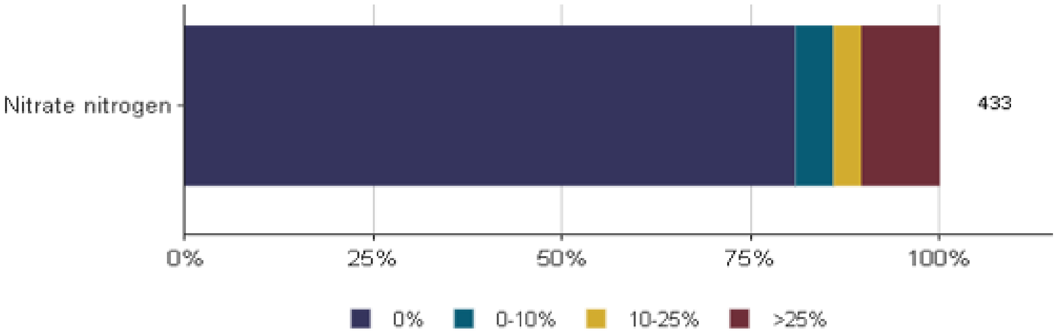


Figure 65 **Nitrate-N exceedances of MAV (MfE and Stats NZ)**

It is noted that the treatment of nitrate for community supplies is difficult as it is not removed by typical methods. Dilution with lower nitrate concentration water is one approach used (e.g. at Pukekohe). Reverse osmosis and anion exchange treatment technologies are available for small volumes such as domestic applications but are expensive for larger applications (MoH, 2019). Reverse osmosis also results in a large loss of water.

Although not routinely analysed, there have been surveys of other inorganic determinants of health significance. These include antimony, cadmium and fluoride. Cadmium has been included in analysis on three occasions. It has a very low MAV of 0.004 g m^{-3} because it accumulates in the kidneys and has a long biological half-life. Cadmium is present in phosphate fertilisers and may also enter drinking water from the dissolution of galvanised pipes in which it is an impurity associated with the zinc.

Cadmium analyses was included in the summer of 2016-2017 with 81% of 130 samples being below detection. The highest concentration was 0.00077 mg l^{-1} which is still less than 20% of the MAV (median of 0.000125 mg l^{-1}). A total of 84 samples was also taken at rural schools. Of these 90% were below detection. Again, the highest concentration was under 20% of the MAV. Only total concentrations were measured whereas previously dissolved analysis was also included.

Earlier analyses of cadmium in 106 groundwater samples collected in 2010/11 found concentrations also to be low, with none over half the guideline value. A total of 81 samples was also taken at rural schools with about 84% being below detection. The highest concentration was 32% of the MAV. In 2008/9 a total of 101 regional network wells were sampled. Of these, 16 detected total cadmium and there were nine detections in the dissolved phase. The highest concentration was 52% of the MAV.

Antimony was also included in analyses in 2012. The MAV is 0.02 mg l^{-1} and relates to general health concerns with there being limited evidence of its carcinogenicity (MoH, 2019). Antimony is largely derived from mineral dissolution and may be associated with arsenic and hydrothermal influences. An example being at Hahei where antimony precluded the development of a prospective community water supply (URS, 2004). Antimony analysed at a total of 93 wells in 2012 found no exceedances of MAV and only six detections (6.4%). The highest concentration was 0.00087 mg l^{-1} being about 4% of the MAV. Four of these were in the Taupo catchment and one each in Reporoa and Hauraki.

Fluoride has been analysed at 100 SOE wells on a few occasions generally between 2007 and 2012. Its origin includes the dissolution of minerals such as apatite in siliceous, igneous formation and associated compounds are common in geothermal fluids. The MAV for fluoride is 1.5 mg l^{-1} based on health considerations (MoH, 2019). There were no exceedances found with the highest concentration being 0.45 mg l^{-1}. Most of the higher concentrations were found in the geothermally influenced Taupo and Reporoa areas.

6.4 Organic contaminants

MAVs for organic determinants of health significance listed in the drinking water standards are provided in Appendix VI. There is no routine monitoring for organic contaminants, however, regular pesticide surveys are undertaken as part of a larger environmental indicator programme. There has also been substantial investigation of pesticides and emerging contaminants undertaken. Pesticide contamination of groundwater in the Waikato region has been reported by Hadfield and Smith (1999 and 2000). There has also been other related pesticide research within the region (Close et al., 2003). The occurrence of pesticides in groundwater is a concern for human health and may have implications for other uses such as stock watering and crop irrigation. Poor management and use of agrichemicals may also result in contamination of water supplies by pesticides. These may cause a range of both acute and or chronic health effects.

An investigation into pesticide contamination of groundwater commenced in high use areas in the Waikato region in 1995. Aquifers considered to be particularly vulnerable to contamination were targeted. Initially, groundwater samples were collected from 35 sites in the Pukekohe/Pukekawa and Hamilton Basin/southern Hauraki Plains areas in 1995 and 1996. Up to 74% of the wells sampled contained detectable pesticide residues. A total of 20 different, mostly persistent and mobile, pesticide active ingredients were identified. Atrazine, alachlor, diuron, simazine, terbuthylazine and procymidone were most commonly detected. The concentrations of pesticides detected were generally well below the MAVs for drinking water. Notable exceptions were two sites where dieldrin, from nearby former sheep-dips, was detected above MAV.

Subsequent quarterly monitoring of 20 of the sites, undertaken over three years, indicated considerable temporal variation in pesticide concentration and occurrence. A close relationship between pesticides detected in groundwater and those used at the site was apparent in five cases in the Hamilton Basin. The majority of pesticides in use, however, were not detected. Direct entry of pesticides into wells (e.g. during mixing) was indicated at some sites from relatively high concentrations and rapid response. There were also instances where detected pesticides were the result of historic use. Pesticides detected at several sites (at least five) apparently relate to chemical use at a neighbouring property. Much of the pesticide contamination detected was a legacy of past use or poor management practices.

A potable water-supply well near Hamilton is one of two at which dieldrin was detected, at concentrations (up to 0.18 ppb), in excess of the MAV (0.03 ppb). Detailed investigation at this site showed the well exists within a plume of contaminated groundwater, originating from the location of a former sheep dip situated 14m away. Soil around the dip location is heavily contaminated with dieldrin, which persists nearly 40 years after the use of this chemical ceased at the site. Modelling of dieldrin transport indicated that groundwater concentrations were still increasing.

Subsequent to this study, regular four-yearly surveys were introduced as part of an environmental indicator programme. This indicates the proportion of groundwater wells in the Waikato region at which pesticides are detected and where concentrations exceed drinking water guidelines and/or half the drinking water guideline value. Information is derived from 40 regional SOE and 40 community (school) monitoring wells. These wells were selected from the larger networks primarily on their vulnerability to contamination by pesticides from the land surface and secondarily on distribution. Vulnerability was assessed using the DRASTIC index, which provides an arbitrary but consistent score based on seven hydrogeologic factors (Aller et al., 1987). The community network was selected without any consideration of pesticide use. The SOE sites include those that were previously selected based on known chemical use. Pesticide detection is therefore more likely in this group.

The indicator reports pesticide occurrence in groundwater supplies in four categories (Figure 66) relating to drinking water guidelines as described below:

Excessive	pesticides > MAV for drinking water
High	< MAV but > half MAV
Low	detections < half MAV
Non-detect	below detection limits

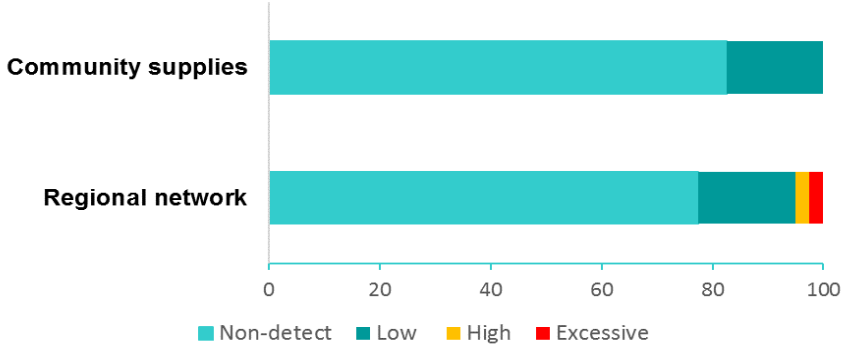


Figure 66 **Pesticide concentration categories relative to MAVs for 40 selected SOE and Community wells using 2020 results.**

Pesticides were not detected at 82.5% of the community wells and were less than half MAV for the remainder. No pesticides were detected at 77.5% of the SOE wells. Of the remainder, concentrations were less than half MAV at 17.5%, between half and MAV at 2.5% and exceeded the MAV at 2.5% of sites. The suite of analysis and their detection limits are available on request. It is noted that there are national surveys of pesticide occurrence that Waikato data contributes to (Close and Humphries, 2016 and 2019).

The first regional baseline survey of the occurrence of emerging organic contaminants (EOCs) in New Zealand groundwater was conducted in the Waikato in 2018 (Moreau et al., 2019). EOCs are manufactured compounds, used for a range of purposes, that are a rising concern for freshwater quality, human and aquatic health.

A wide-screening approach of 723 compounds was used and a novel randomised design stratified to groundwater age categories (MRT) to inform future monitoring. In total 61 sites were sampled, which included 51 baseline sites from the SOE network and for comparison 10 targeted sites located in the vicinity of known likely EOC sources.

EOCs were widely detected at 91% of the SOE wells sampled with concentrations ranging from 0.1 to 11,000 ng l^{-1}. Groupings of EOCs comprised the following numbers of compounds: pesticides (48), pharmaceuticals (11), industrial (10), preservatives/food additives (3) and personal care products (1). Although similar diversity and concentration ranges of EOCs were observed at the targeted sites, there were also additional drugs of abuse and life-style compounds. Higher concentrations and more types of EOCs were detected at sites in the youngest age category, although detections occurred across all three MRT categories being: 1–11 years; 11–50 years and 50–250 years (Moreau et al., 2019). The spatial distribution of EOC detections are shown in Figure 67. The size of the circle is proportional to the number of detected compounds with a scaled example provided in the legend.

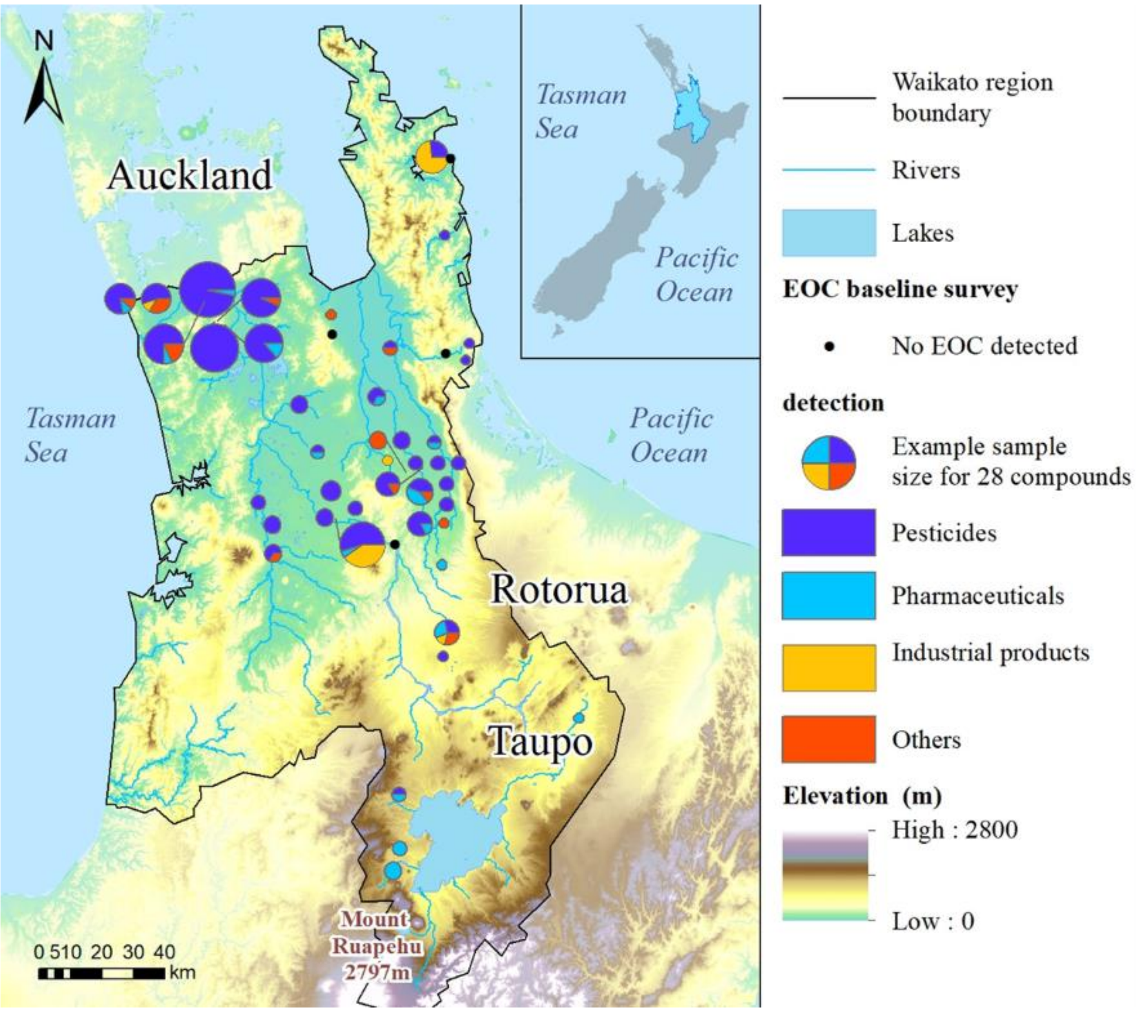


Figure 67 **Spatial distribution of EOC detections at SOE groundwater sites.**

There are currently no drinking-water or environmental guideline values for the majority of the EOC compounds detected. The concentrations of the 73 compounds found were comparable to those reported in international literature with 28 being above the EU maximum admissible concentration for pesticides. (Loos et al., 2010; Lapworth et al., 2015). The results of this survey will be used to inform future targeted EOC monitoring in the region.

6.5 Aesthetic properties and other guidelines

The public perception of supplies typically relates to aesthetic qualities rather than standards set with respect to health risk. Guideline values for aesthetic determinants, generally relate to taste or staining nuisance issues (MoH, 2018).

Exceedances of aesthetic guidelines for routinely monitored parameters are summarised in Table 5 below. Median concentrations at monitoring wells exceeded aesthetic guidelines for five determinants with pH, manganese and iron being the most common. The vast majority of wells have groundwater with median pH levels which are more acidic than the guideline range and are therefore considered to have high plumbosolvency or tendency to corrode metal piping. Iron and manganese concentrations in excess of their guidelines typically occur together and are prevalent in anaerobic conditions. They are considered likely to lead to nuisance staining and sometimes taste issues. The occasional exceedances for hardness occur at wells in limestone or are influenced by shelly formation. Other occurrences are minor with occasional copper exceedances at one well 72_392 likely to relate to pipework.

Table 5 **Percentage of SOE wells with groundwater which exceeded aesthetic guidelines from 2016-2020.**

Determinant	GV (mg/l)	At least one exceedance	Median exceedance
NH_4-N	1.5	2.0	1.0
Cl	250	0.0	0.0
Cu	1	1.0	0.0
Hardness	200[1]	4.0	2.0
Fe	0.2	41.8	21.8
Mn	0.04[2]	24.5	18.2
pH	7 – 8.5	87.3	83.6
Na	200	0.0	0.0
SO_4	250	0.0	0.0
TDS	1000	0.0	0.0

[1] scaling threshold; taste threshold is 100 to 300 g/m^3
[2] staining threshold; taste threshold at 0.1 g/m^3

The Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000) also provide useful trigger value concentrations for considering the suitability of groundwater for other uses. This includes potential impacts on ecosystem health. For example, these guidelines indicate that nitrate concentrations for stock water of less than 400 mg/l (or ~90 mg/l as nitrate-N) should not be harmful to animal health. The ANZECC guidelines may also be referred to in respect to the suitability of groundwater for irrigation purposes. Trigger values for the prevention of damage to crops varies dependent on crop sensitivity. Chloride and sodium trigger values for sensitive crops, for example, are 175 mg /l and 115 mg /l respectively. None of the SOE wells have median concentrations (2016-20) exceeding these values. Other guidance for irrigation includes long-term values for iron and manganese of 0.2 mg/l and short term (up to 20 year) trigger values of 10 mg/l. Sodium adsorption ratio guidance is also provided.

7 Management response

It is noted that groundwater quality remediation is difficult, expensive and very slow. Protection is therefore much more effective and cost efficient. The Council's response to date, aimed at improving water quality, includes developing the Waikato Freshwater Strategy to manage fresh water more effectively. It focusses on three themes; focussed advocacy, smarter methods, and better information. The Freshwater Strategy builds on existing Waikato Regional Council freshwater initiatives. These include 'Variation 5' or Taupo-nui-a-Tia project for the protection of Lake Taupō. Also, the Healthy Rivers/Wai Ora project now proposed under Waikato Regional 'Plan Change 1'. There are also the Waipa Catchment Plan, Zone and Catchment Management plans, and the Waikato Waipa River Restoration Strategy for ecosystem outcomes.

'Plan Change 1' focuses on the management of four main contaminants which includes nitrogen. It introduces stricter controls, including resource consents requirements, for farms that have medium tohigh nitrogen leaching. If nitrogen leaching is high, it must be reduced and addressed via a farm environment plan. Variation 5 and the subsequent Plan Change 2 focus on nitrogen management in the Lake Taupo catchment. These policies and rules now sit in section 3.10 of the Regional Plan. They include a cap on the manageable nitrogen load to the lake from its catchment at 2001 levels. A trading system has also been set up that allows for the transfer of nitrogen discharge rights within the catchment. A Trust was established which has used $80M of public funding to remove the potential discharge of an estimated 20% of the manageable nitrogen load to the lake. This was done by purchasing the rights to discharge 170 tonnes of nitrogen per year, to be retired. This has resulted in 6675 ha of farmland (~12%) being permanently converted to forestry.

While these policy tools were developed to manage ecosystem health, the reduction of nitrate-nitrogen in the waterways also has benefits for drinking water. Other legislation relating to drinking water includes the NES for human drinking water sources (gazetted in 2007), which is currently being reviewed. It essentially requires regional councils to manage activities for the protection of registered community supplies. The recent enactment of the Water Services Act (2021) and establishment of Taumata Arowai as a new drinking water authority also has implications for Council management of groundwater quality for drinking water source protection. The use of multiple barriers to protect against supply contamination is included and aims to decrease risks and the reliance on supply treatment.

As mentioned, the current groundwater quality monitoring programme is due to be reviewed. The Parliamentary Commissioner for the Environment in 2019 reviewed environmental reporting in New Zealand and found several shortcomings. Recommendations included the development of a comprehensive, nationally coordinated environmental monitoring system. It is intended that national direction being developed will be taken into account in the imminent review of groundwater quality monitoring in the Waikato. Also changes in relevant legislation and anticipated increased related collaboration with, for example, water suppliers is also likely to influence future design.

References

Aller L, Bennett T, Lehr JH, Petty RJ, Hackett G 1987. DRASTIC: A standardised system for evaluation of ground water pollution potential using hydrogeologic settings. Washington DC, Environmental Protection Agency.

Appello AJ, Postma D 1993. Geochemistry, groundwater and pollution. Rotterdam, Balkema.

Archer M, Palmer H, McKenzie A 2019. Upper Waikato Zone Plan. Waikato Regional Council Policy Series 2019/20. Hamilton, Waikato Regional Council.

Australian and New Zealand Environmental Conservation Council 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Volume 1: The guidelines. Artarmon, NSW, ANZECC.

Baker M, Wilson N, Hales S 2022. Nitrate in drinking water and cancer risk: the biological mechanism, epidemiological evidence and future research. Australian and New Zealand Journal of Public Health, 46(2): 105-108.

Barkle GF, Wohling T, Stenger R, Mertens J, Moorhead B, Wall A, Clague J 2011. Automated equilibrium tension lysimiters for measuring water fluxes through a layered volcanic vadose profile in New Zealand. Vadose Zone Journal. 10: 749–759.

Bell A, Cochrane P, Depledge D, Maggs G 1991. Pukekawa-Onewhero area water resources. Waikato Regional Council Technical Report 1991/29. Hamilton, Waikato Regional Council.

Bird GA 1987. A study of the groundwater resources of the Tokoroa region. Waikato Valley Authority Technical Publication no. 47. Hamilton, Waikato Valley Authority.

Carter Holt Harvey 1997. Discharges to groundwater from Kinleith pulp and paper mill wastewater treatment system: assessment of environmental effects. # 3788792. Tokoroa, Carter Holt Harvey Pulp & Paper.

Chambers T, Douwes J, Mannetje AT, Woodward A, Baker M, Wilson N, Hales S 2022. Nitrate in drinking water and cancer risk: the biological mechanism, epidemiological evidence and future research. Australian and New Zealand Journal of Public Health. 2022 Apr 1; 46(2): 105-8.

Childs CW 1981. Field tests for ferrous iron and ferric-organic complexes (on exchange sites or in water-soluble forms) in soils. Australian Journal of Soil Research 19: 175-180.

Close M E, Magesan G N, Lee R, Stewart MK, Hadfield J C 2003. Field study of pesticide leaching in an allophanic soil in New Zealand. 1: Experimental results. Soil Research 41: 809-824.

Close ME 2015. Prediction of subsurface redox status for Waikato Healthy Rivers - plan for change: Waiora He Rautaki Whakapaipai. Waikato Regional Council technical report 2018/34. Hamilton, Waikato Regional Council.

Close M, Humphries B 2016. The 2014 national survey of pesticides in groundwater in New Zealand. Journal of Hydrology (New Zealand) 55(2):73-88.

Close M, Humphries B 2019. National survey of pesticides and emerging organic contaminants (EOCs) in groundwater 2018. Porirua, Institute of Environmental Science and Research Ltd.

Daughney C, Reeves R 2005. Analysis of temporal trends in New Zealand's groundwater quality based on data from the National Groundwater Monitoring Programme. Journal of Hydrology (New Zealand) 45(1): 41-62.

Daughney CJ 2003. Iron and manganese in New Zealand's groundwater. Journal of Hydrology (New Zealand) 42(1): 11-26.

Daughney C, Wall M 2007. Groundwater quality in New Zealand : state and trends 1995-2006. GNS Science Consultancy report 2007/23. Wellington, Ministry for the Environment.

Daughney C 2010. Spreadsheet for automatic processing of water quality data: 2010 Update – Calculation of percentiles and tests for seasonality. GNS Science Report 2010/42. Lower Hutt, Institute of Geological and Nuclear Sciences.

Drever JI 1988. The geochemistry of natural waters. 2nd ed. Englewood Cliffs NJ, Prentice Hall.

Edbrooke SW 2001. Geology of the Auckland Area: Scale 1: 250 000. 1:250 000 geological map no. 3. Lower Hutt, Institute of Geological & Nuclear Sciences.

Edbrooke SW 2005. Geology of the Waikato area: Scale 1: 250 000. 1:250 000 geological map no. 4. Lower Hutt, Institute of Geological and Nuclear Sciences Limited.

Ehrhardt S, Ebeling P, Dupas R, Kumar R, Fleckenstein JH, Musolff A 2021. Nitrate transport and retention in Western European catchments are shaped by hydroclimate and subsurface properties. Water Resources Research 57(10): e2020WR029469.

Farlin J, Gallé T, Pittois D, Bayerle M, Schaul T 2019. Groundwater quality monitoring network design and optimisation based on measured contaminant concentration and taking solute transit time into account. Journal of Hydrology. 573: 516-573.

Ford D, Williams P 2007. Karst hydrogeology and geomorphology. Chichester, Wiley.

Freeze R A, Cherry JA 1979. Groundwater. Englewood Cliffs NJ. Prentice Hall.

Fryer K, Chalmers L 1999. Report to accompany the thesis : 'The drastic need for vulnerability mapping; a case study of the Waikato Region's groundwater resources using DRASTIC-GIS'. Commissioned by Environment Waikato. Hamilton, Waikato Regional Council (Environment Waikato).

Hadfield JC 1993. Groundwater chemistry of the Piako catchment, Hauraki Plains. Environment Waikato Technical Report 1993/7. Hamilton, Waikato Regional Council (Environment Waikato).

Hadfield JC, Smith D 1999. Pesticide contamination of groundwater in the Waikato region. Environment Waikato Technical Report 1999/9. Hamilton, Waikato Regional Council (Environment Waikato).

Hadfield JC, Nicole D 2000: Community groundwater supply source protection. Environment Waikato Technical Report 2000/10. Hamilton, Waikato Regional Council (Environment Waikato).

Hadfield J, Smith D 2000. Pesticide contamination of groundwater supplies in the Waikato region. Water: 10.

Hadfield J 2001. Waikato. In: Rosen MR, White PA eds. Groundwaters of New Zealand. Wellington, New Zealand Hydrological Society, 315-326.

Hadfield JC, Nicole DA, Rosen MR, Wilson CJN, Morgenstern U 2001. Hydrogeology of Lake Taupo Catchment – Phase 1. Environment Waikato Technical Report 2001/01. Hamilton, Waikato Regional Council (Environment Waikato).

Hadfield JC 2003. Hauraki groundwater quality trends 1992-2002. Environment Waikato Internal Series Report 2003/1. Hamilton, Waikato Regional Council (Environment Waikato).

Hadfield JC, Barkle G 2004. Contrasting effects of nitrogen discharge to groundwater from a woolshed and nearby wastewater plant in Taupo catchment. Hydrological Society Conference proceedings, Queenstown

Hadfield JC, Hughey J, Piper J 2005. Coromandel coastal aquifer management. Hydrological Society Conference Proceedings.

Hadfield JC 2007. Groundwater flow and nitrogen transport modelling of the northern Lake Taupo catchment. Environment Waikato Technical Report 2007/39. Hamilton, Waikato Regional Council (Environment Waikato).

Hadfield JC, Morgenstern U, Piper JJ, Brebbia CA, Kungolos A 2007. Delayed impacts of land-use via groundwater on Lake Taupo, New Zealand. WIT Transactions on Ecology and the Environment 103: 293-303.

Hadfield J 2011. Groundwater quality monitoring 2010-2011. Waikato Regional Council Technical Report 2011/14. Hamilton, Waikato Regional Council.

Hadfield JC, Korom S 2012. Mechanisms of groundwater denitrification, Taupo. NZ Hydrological Society Conference proceedings, Nelson.

Hadfield J 2013. Groundwater quality monitoring 2012-2013. Waikato Regional Council Technical Report 2013/1. Hamilton, Waikato Regional Council.

Hadfield J, Close M, Hughey J, Mackenzie M, Pang L, Weaver L 2014. Virus tracer testing in a shallow coastal aquifer, Pauanui. NZ Hydrological Society Water Symposium, Blenheim.

Hadfield JC 2018. Groundwater field investigations over the 2014-15 summer in support of the Healthy Rivers project. Waikato Regional Council Technical Report 2018/32. Hamilton, Waikato Regional Council.

Hadfield JC 2021. Redox consideration in Waikato groundwater monitoring. NZ Hydrological Society Conference proceedings, 30 November – 3 December 2021, Wellington.

Hamilton L 2008. Force of nature : : mind, body, soul, and, of course, surfing. New York, Rodale.

Helsel DR 2012. Statistics for censored environmental data using MINITAB and R. 2nd ed. Hoboken, NJ, Wiley.

Helsel DR, Hirsch RM 1992. Statistical methods in water resources. Studies in Environmental Science v. 49. Amsterdam, Elsevier.

Hemmings B, Cameron S, White J, Rawlinson Z 2022. Regional groundwater modelling in the Hauraki Plains, Waikato. GNS Consultancy Report 2022/06. Lower Hutt, GNS Science.

Hemmings BJC 2021. West Lake Taupo nitrate transport modelling and preliminary uncertainty quantification. GNS Science Consultancy Report 2021/103. Lower Hutt, GNS Science.

Hill R, Borman D 2022. Pastoral land-cover and intensity changes in the Waikato Region 2001-2018. Waikato Regional Council Technical Report 2022/51. Hamilton, Waikato Regional Council.

Hochstein MP, Nixon IM 1979. Geophysical study of the Hauraki Depression, North Island, New Zealand. New Zealand Journal of Geology and Geophysics 22(1): 1-19.

Houghton BF, Cuthbertson AS. 1989. Kaimai [map]. Wellington (NZ): Department of Scientific and Industrial Research. 1 folded map + 1 booklet, scale 1:50,000. (Geological map of New Zealand 1:50,000; sheet T14 BD).

Hounslow AW 2018. Water quality data: analysis and interpretation. Boca Raton FL, CRC Press.

Jones H, Borman D 2022. Land cover in the Waikato region, 1996-2018. Waikato Regional Council Technical Report 2022/18. Hamilton, Waikato Regional Council.

Kear D, Schofield JC 1978. Geology of the Ngaruawahia Subdivision. New Zealand Geological Survey Bulletin 88. Wellington, Department of Scientific and Industrial Research, New Zealand.

Korom SF 1992. Natural denitrification in the saturated zone: A review. Water Resources Research 28, (6): 1657–1668.

Korom S, Gelles L, Hadfield JC, Barkle G 2016. Geochemical modelling of electron donors involved in denitrification in the Lake Taupo catchment. Water Infrastructure and the Environment Conference proceedings, Queenstown.

Lapworth DJ, Baran N, Stuart ME, Manamsa K, Talbot JC. 2015. Persistent and emerging micro-organic contaminants in Chalk groundwater of England and France. Science of the Total Environment, 203: 214–225.

Land, Air, Water Aotearoa 2023. https://www.lawa.org.nz/ [accessed 16/08/2023]

Leonard GS, Begg JG, Wilson CJN, Leonard GS 2010. Geology of the Rotorua area : scale 1:250,000. 1:250 000 geological map no. 5. Lower Hutt, GNS Science.

Loos R, Locoro G, Comero S, Contini S, Schwesig D, Werres F, Balsaa P, Gans O, Weiss S, Blaha L, Bolchi M, Gawlik BM. 2010. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Research 44(14): 4115-4126.

McCaw J 2011. The wandering river: landforms and geological history of the Hamilton Basin. Geoscience Society of New Zealand guidebook ; No. 16. Wellington, Geoscience Society of New Zealand.

McMahon PB, Chapelle FH 2008. Redox processes and water quality of selected principal aquifer systems. Groundwater 46(2): 259-271.

Maloszewski P, Zuber A 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers. Journal of Hydrology 57:207-231.

Marshall TW 1986. Groundwater chemistry characteristics of the Mangaonua-Mangaone catchments. Waikato Valley Authority Technical Report 86/2, Hamilton, Waikato Valley Authority.

Marshall TW, Petch RA 1985:. A study of the groundwater and surface water resources of the Hamilton Basin. Waikato Valley Authority Technical Publication no. 30. Hamilton, Waikato Valley Authority.

Martindale H, van der Raaij R, Daughney CJ, Singh R, Jha N, Hadfield J 2019. Assessment of excess N2 for quantifying actual denitrification in New Zealand groundwater systems. Journal of Hydrology (New Zealand) 58: 1–17.

Ministry for the Environment 2006. A national protocol for state of the environment groundwater sampling in New Zealand. Ministry for the Environment, Wellington.

Ministry of the Environment 2020. National Policy Statement for Freshwater Management. Wellington, Ministry for the Environment.

Ministry for the Environment & Stats NZ 2020. New Zealand's Environmental Reporting Series: Our freshwater 2020. Available from www.mfe.govt.nz and www.stats.govt.nz.

Ministry of Health 2018. Drinking-water standards for New Zealand 2005. Rev. ed. Wellington, Ministry of Health.

Ministry of Health 2019. Guidelines for drinking water quality management for New Zealand. Wellington, Ministry of Health.

Moreau M, Hadfield J, Hughey J, Sanders F, Lapworth DJ, White D, Civil W 2019. A baseline assessment of emerging organic contaminants in New Zealand groundwater. Science of the Total Environment, 686: 425-439.

Morgenstern U 2007. Lake Taupo catchment groundwater age distribution and implications for future land-use impact. Environment Waikato Technical Report 2007/49. Hamilton, Waikato Regional Council.

Morgenstern U, Daughney CJ 2012. Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification–The National Groundwater Monitoring Programme of New Zealand. Journal of Hydrology 456: 79-93.

Mroczek E, Climo M, Evans D 2015. The composition of high temperature geothermal fluids in New Zealand producing geothermal fields. GNS Science Report 2014/68. Lower Hutt, GNS Science.

National Environmental Monitoring Standards 2019. National Environmental Monitoring Standards, Water Quality, Part 1 of 4: Sampling, Measuring, processing and Archiving of Discrete Groundwater Quality Data. Wellington, National Environmental Monitoring Standards.

Nokes C 2008. A guide to the Ministry of Health drinking-water standards for New Zealand. Porirua, Institute of Environmental Science and Research Ltd..

Palmer CD, Cherry JA 1984. Geochemical evolution of groundwater in sequences of sedimentary rocks. Journal of Hydrology, 75: 27-65.

Pang L, Close M, Goltz M, Sinton L, Davies H, Hall C, Stanton G 2003. Estimation of septic tank setback distances based on transport of E. coli and F-RNA phages. Environment International 29: 907-921.

Pang L, Abeysekera G, Hanning K, Premaratne A, Robson B, Abraham P, Sutton R, Hanson C, Hadfield J, Heiligenthal L, Stone D, McBeth K, Billington C 2020. Water tracking in surface water, groundwater and soils using free and alginate-chitosan encapsulated synthetic DNA tracers. Journal of Water Research 184 (2020) 116192.

Parliamentary Commissioner for the Environment, 2019. Focusing Aotearoa New Zealand's environmental reporting system. Wellington, Parliamentary Commissioner for the Environment.

Petch RA, Bell AR, Depledge D, Hadfield JC, Maggs GR, Ringham KL 1991. An assessment of ground and surface water resources in the Pukekohe/Tuakau area. Waikato Regional Council Technical Report 1991/12. Hamilton, Waikato Regional Council.

Piper J 2005. Water resources of the Reporoa Basin, Environment Waikato Technical Report 2005/57. Hamilton, Waikato Regional Council (Environment Waikato).

Piper J, Kim N 2006. Arsenic in groundwater of the Waikato Region. Environment Waikato Technical Report 2006/145. Hamilton, Waikato Regional Council (Environment Waikato).

Rajanayaka C, Weir J, Barkle G, Griffiths G, Hadfield J 2020. Assessing changes in nitrogen contamination in groundwater using water aging: Waikato River, New Zealand. Journal of Contaminant Hydrology, 234 (2020) 103686.

Rawlinson ZJ, Westerhoff RS, White PA, Schaller K, Moore C 2015. Estimation of rainfall recharge to groundwater in the Waipa River catchment from three independent models. GNS Science Consultancy Report 2015/212. Taupo, GNS Science.

Rawlinson ZJ 2016. A preliminary groundwater model of the Waipa catchment. GNS Consultancy Report 2016/1134. Taupo, GNS Science.

Ringham KL, Cochrane PR, Petch RA 1990. Groundwater chemistry of the Northern Waikato District. Waikato Regional Council Technical report 1990/5. Hamilton, Waikato Regional Council.

Rosen MR 2000. Hydrochemistry of New Zealand's aquifers. In: Rosen MR, White PA eds. Groundwaters of New Zealand. Wellington, New Zealand Hydrological Society, 77-110.

Sarris TS, Scott D, Close M, Humphries B, Moore C, Burbery L., Rajanayaka C, Barkle G, Hadfield JC, 2019. The effects of denitrification parameterization and potential benefits of spatially targeted regulation for the reduction of N-discharges from agriculture. Journal of Environmental Management 247: 299-312.

Schullehner J, Hansen B, Thygesen M, Pedersen CB, Sigsgaard T 2018. Nitrate in drinking water and colorectal cancer risk: A nationwide population-based cohort study. International Journal of Cancer. 2018 Jul 1;143(1):73-79. doi: 10.1002/ijc.31306.

Scott L, Wong R 2016. Dissolved phosphorus in Canterbury groundwater. In: Currie LD, Singh R (eds.) Integrated nutrient and water management for sustainable farming. http://flrc.massey.ac.nz/publications.html. Occasional Report No. 29. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand.

Snelder T, Fraser C 2019. [Water quality trend analysis functions for R | LWP (landwaterpeople.co.nz)](https://landwaterpeople.co.nz) The LWP-Trends Library; v2101 April 2021, LWP Ltd Report.

Statistics New Zealand 2021. Livestock numbers. https://www.stats.govt.nz/indicators/livestock-numbers/ [accessed 16/08/2023]

Stenger R, Clague JC, Morgenstern U, Clough TJ 2018. Vertical stratification of redox conditions, denitrification and recharge in shallow groundwater on a volcanic hillslope containing relict organic matter. Science of the Total Environment 639: 1205–1219.

Stenger R, Park J, Morgenstern U, Hadfield J, Rivas A, Clague J 2022. Combining surface water monitoring, age-dating, and parsimonious modelling to unravel water and contaminant pathways through catchments. In: Christensen CL, D.J. Horne DJ, Singh R (eds.). Adaptive strategies for future farming. Occasional Report No. 34. Palmerston North, Farmed Landscapes Research Centre, Massey University.

Taumata Arowai 2022. New Standards, Rules, and Aesthetic Values. https://www.taumataarowai.govt.nz/for-water-suppliers/new-compliance-rules-and-standards/ [accessed 16/08/2023]

Thornburrow BR 2018. Pukekawa aquifer: groundwater flow modelling. Waikato Regional Council Technical Report 2017/18. Hamilton, Waikato Regional Council.

Timperley MH, Vigor-Brown RJ 1986. Water chemistry of lakes in the Taupo volcanic zone, New Zealand . New Zealand Journal of Marine and Freshwater Research 20: 173:183.

URS 2004. Hahei groundwater supply – Grierson Close supply bore completion report to Thames Coromandel District Council. Auckland, URS Ltd.

Vant B, Hadfield J 2022. Water quality of Lake Taupo and its catchment. Waikato Regional Council Technical Report 2022/04.Hamilton, Waikato Regional Council.

Water Services Act New Zealand 2021. Public Act 2021, no. 36.

Water Services (Drinking Water Standards for New Zealand) Regulations 2022.

Weir J, Rajanayaka C. 2014. Groundwater modelling of the Upper Waikato catchment: Stage Four prepared for Waikato Regional Council. #3388289. Christchurch, Aqualinc Research Limited.

Weir J, Rajanayaka C 2014. Groundwater modelling of the upper Waikato catchment: stage 5. Client report prepared for Waikato Regional Council. Aqualinc Research Ltd. Report C14061/1. Waikato Regional Council Internal Series 2015/51. Hamilton, Waikato Regional Council.

White P, Tschritter C, Rawlinson Z, Moreau M, Dewes K, Edbrooke S 2015. Groundwater resource characterisation in the Waikato River Catchment for the Healthy Rivers Project. Waikato Regional Council Technical Report 2018/33. Hamilton, Waikato Regional Council.

White PA, Raiber M, Tschritter C 2018. Geological model and water budget of the Hauraki Plains, Waikato region. Waikato Regional Council Technical Report 2018/04. Hamilton, Waikato Regional Council.

White P, Moreau M, Mourot F, White J, Johnson K, Hill M 2019. Groundwater in the Franklin area. GNS Consultancy Report 2019/81. Wairakei, GNS Science.

Wilson CJN 1993. Stratigraphy, chronology, styles and dynamics of late Quaternary eruptions from Taupo volcano, New Zealand. Philosophical Transactions of the Royal Society of London 343: 205-306.

Wilson CJN 2000. The 26.5 ka Oruanui eruption, New Zealand: an introduction and overview. Journal of Volcanology and Geothermal Research 112(1-4): 133-174.

Wilson CJN, Gravley DM, Leonard GS, Rowland JV 2009. Volcanism in the Central Taupo volcanic zone, New Zealand: Tempo, styles and controls. In: Thordarson T, Self S, Larsen G, Rowland SK, Hoskuldsson A (eds.) Studies in volcanology: the legacy of George Walker. The Geological Society of London on Behalf of the International Association of Volcanology and Chemistry. 225-247.

Wilson S, Hadfield J 2017. A methodology for estimating vadose zone transit time and its implications. NZ Hydrological Society Conference proceedings, Napier.

Wilson SR, Close ME, Abraham P, Sarris TS, Banasiak L, Hadfield JC 2020. Achieving unbiased predictions of national-scale groundwater redox conditions via data oversampling and statistical learning. Journal of the Total Environment vol. 705 (2020): 135877.

Winston RB 2020. GW_Chart version 1.30: U.S. Geological Survey Software Release, 26 June 2020.

Woods R, Jowett I, Nathan R, Williamson J, Pattle A, Mulholland M, Basheer G, Collins D, Schmidt J, Thornburrow BR, Joynes S 2010. Summary of the effects of land use change between Taupo and Karapiro on the flood hydrology of the Waikato River catchment. Environment Waikato Technical Report 2009/21. Hamilton, Waikato Regional Council (Environment Waikato)

Zaporozec A 1972. Graphical interpretation of water quality data. Ground Water, 10: 32-43.

Appendix I:

Table I.1 SOE Well information

Well	Easting	Northing	Network	Sub-region	Well Depth (m)	Casing depth (m)	Lithology	Confinement	Water age (y MRT)	Land-use
60_12	1844556	5919551	NGMP	Coromandel	9	2	Sand	Unconfined	1.5	Urban
60_124	1840947	5919496	Annual	Coromandel	6	3	Sand	Unconfined		Urban
60_167	1852989	5886648	Annual	Coromandel	19.5	16.7	Sand	Semi-confined	280	Urban
60_190	1850412	5918971	Annual	Coromandel	43.4	31.8	Ignimbrite	Confined	>160	Motor camp
60_316	1824237	5897395	Annual	Coromandel	7	1	Gravel	Unconfined	17	Urban
60_345	1848609	5894615	Annual	Coromandel	27	13	Ignimbrite	Unconfined	65	Dairy
60_348	1853509	5901466	Annual	Coromandel	13.5	6.5	Sand	Unconfined	7	Park/Reserve
60_407	1833744	5933465	Annual	Coromandel	5	na	Sand	Unconfined		Urban
60_480	1822694	5903703	Annual	Coromandel	7.7	na	Gravel	Unconfined		Urban
61_113	1772785	5877132	Quarterly	Northern	13	10	Basalt	Unconfined	4	Horticultural
61_126	1750224	5867527	Quarterly	Northern	6.09	dug well	Sand	Unconfined	4.5	Dairy
61_135	1756268	5874857	Annual	Northern	51.82	19.56	Basalt	Unconfined	40/**19**	Horticulture
61_143	1774986	5867077	Annual	Northern	34	12	Basalt	Confined	9	Horticultural
61_208	1756403	5874333	Quarterly	Northern	18.3		Basalt	Unknown	9	Horticultural
61_221	1777329	5863554	Quarterly	Northern	44.5	20	Basalt	Unconfined	11/40/**22**	Agriculture
61_230	1778168	5865992	Annual	Northern	43	18.3	Basalt	Unconfined	50	Horticultural
61_245	1769666	5867027	Annual	Northern	14.5	8.5	Basalt	Unconfined	4	Horticultural
61_258	1771729	5873388	NGMP	Northern	35	24.8	Basalt	Unknown	130	Agriculture
61_280	1773947	5867124	Annual	Northern	23.2	15.5	Basalt	Confined	10	Forestry

Well	Easting	Northing	Network	Sub-region	Well Depth (m)	Casing depth (m)	Lithology	Confinement	Water age (y MRT)	Land-use
61_54	1773105	5876816	Annual	Northern	19.8	14.32	Basalt	Unknown	13	Agriculture
61_59	1768799	5866755	Quarterly	Northern	26.6	19.5	Basalt	Confined	11 or 45	Urban
61_85	1754596	5874016	NGMP	Northern	35	19.56	Basalt	Confined	22	Horticultural
61_93	1775757	5867144	NGMP	Northern	26	19	Basalt	Unconfined	49	Forestry
62_5	1804339	5807285	Annual	Hamilton Basin	6.2	2.5	Sand	Unconfined		Horticultural
63_201	1855436	5855078	Annual	Hauraki	48	26	Ignimbrite	Unknown	125	Horticultural
63_240	1848801	5856703	Annual	Hauraki	91.5	58.5	Ignimbrite	Confined	>240	Horticultural
63_269	1857103	5870063	Annual	Coromandel	20	16.7	Sand	Confined	25.5	Urban
63_328	1856283	5859856	Annual	Hauraki	49	19.5	Ignimbrite	Confined	>230	Agriculture
63_43	1812638	5862736	Annual	Hauraki	73	26	Greywacke	Confined	14	Agriculture
63_57	1831153	5858445	Quarterly	Hauraki	5	3	Sand	Unconfined	11	Agriculture
63_74	1812774	5868267	Annual	Hauraki	50.8	26.2	Greywacke	Confined	>160	Dairy
63_78	1856828	5854849	Annual	Hauraki	24	13	Ignimbrite	Confined	12	Dairy
64_108	1836338	5818794	Quarterly	Hauraki	23	18.5	Sand	Confined	62	Horticultural
64_111	1830324	5823013	Annual	Hauraki	83	58.3	Ignimbrite	Confined	250	Dairy
64_117	1846414	5822940	Quarterly	Hauraki	16	8	Sand	Unconfined	7	Dairy
64_12	1839325	5824778	Quarterly	Hauraki	11.5	9.5	Sand	Unconfined	7	Dairy
64_120	1840767	5804097	NGMP	Hauraki	22.2	6	Sand	Unconfined	3.5	Dairy
64_20	1842870	5812211	Quarterly	Hauraki	9	5.2	Sand	Unconfined	21	Horticultural
64_43	1844608	5809570	Quarterly	Hauraki	21.6	18.6	Sand	Unconfined	50	Urban
64_46	1845549	5816478	Quarterly	Hauraki	12.1	10	Sand	Unknown	37	Urban
64_50	1849273	5818083	Quarterly	Hauraki	16.1	14.3	Pumice	Unknown	32	Dairy
64_511	1844481	5812637	NGMP	Hauraki	21.5	18.5	Pumice	Unknown	51	Dairy
64_7	1834814	5829066	Annual	Hauraki	7.92	4.26	Pumice	Unconfined	50	Dairy
64_70	1845280	5828355	Quarterly	Hauraki	11.8	9.1	Pumice	Unconfined	38	Dairy
64_720	1826969	5842949	NGMP	Hauraki	6	2.8	Pumice	Unknown	48	School

Well	Easting	Northing	Network	Sub-region	Well Depth (m)	Casing depth (m)	Lithology	Confinement	Water age (y MRT)	Land-use
64_831	1841441	5820147	Annual	Hauraki	9	3	Pumice	Unconfined	20	Dairy
65_6	1798912	5774127	Annual	Waipa	13	9.5	Ignimbrite	Unconfined		Dairy
66_58	1894718	5737933	Annual	Upper Waikato	38	32.5	Ignimbrite	Unconfined	>170	Dairy
66_6	1884465	5752752	Quarterly	Upper Waikato	38	32	Pumice	Unconfined	30	Dairy
66_92	1891614	5740353	Annual	Upper Waikato	48.5	17.2	Gravel	Unconfined	73	Dairy
66_93	1891606	5740344	Annual	Upper Waikato	8	2	Gravel	Unknown	26 or 48	Urban
66_96	1895259	5734282	Annual	Upper Waikato	116	104	Pumice	Unconfined	200	Urban
67_11	1843403	5800440	Quarterly	Hauraki	18.5	15.5	Pumice	Unknown	45/**2.5**	Dairy
67_15	1847726	5789195	Quarterly	Hauraki	20	13	Pumice	Unconfined	45	Agriculture
67_404	1849448	5767601	Annual	Upper Waikato	9		Ignimbrite	Unconfined	15	Dairy
67_483	1848177	5764568	Annual	Upper Waikato	53.6	34.7	Ignimbrite	Confined	29	Dairy
67_55	1849019	5777956	Annual	Hauraki	127	65	Ignimbrite	Confined		Agriculture
67_573	1846468	5778103	Annual	Upper Waikato	90	45.5	Ignimbrite	Confined		Dairy
67_83	1849477	5772624	Annual	Upper Waikato	80	58	Ignimbrite	Unknown		Dairy
68_301	1855521	5718798	Annual	Taupo	53.6	49	Ignimbrite	Confined	80	Dairy
68_317	1850484	5719524	Annual	Taupo	104	71	Ignimbrite	Unknown	40	Dairy
68_320	1864824	5713198	Annual	Taupo	62	46	Ignimbrite	Unknown	21?	Motor camp
68_912	1872912	5714845	Annual	Upper Waikato	53.6	34.7	Ignimbrite	Unknown		Urban
68_964	1840522	5691618	NGMP	Taupo	5	2	Sand	Unknown	1	Agriculture
69_163	1805259	5817785	Annual	Hamilton Basin	4	3.5	Sand	Unconfined		Dairy > Lifestyle
69_1709	1812293	5812858	NGMP	Hamilton Basin	5	2.5	Gravel	Unconfined	0.2	Dairy
69_173	1807943	5825299	Quarterly	Hamilton Basin	6	4	Pumice	Unconfined	3	Dairy
69_19	1809206	5813466	Annual	Hamilton Basin	4.3	2.1	Pumice	Unconfined		Agriculture
69_248	1808811	5816377	Annual	Hamilton Basin	2.75	1.1	Pumice	Unconfined		Horticultural
69_295	1813461	5810020	Annual	Hamilton Basin	6.35	4.4	Pumice	Unconfined		Horticultural
69_365	1802116	5840499	Quarterly	Hamilton Basin	6	2.5	Pumice	Unconfined	2	Horticultural

Well	Easting	Northing	Network	Sub-region	Well Depth (m)	Casing depth (m)	Lithology	Confinement	Water age (y MRT)	Land-use
69_374	1810888	5812909	Annual	Hamilton Basin	4.16	2	Sand	Unconfined		Horticultural
69_62	1812458	5812552	Annual	Hamilton Basin	9.15	na	Sand	Unconfined		Dairy > Lifestyle
69_81	1788964	5809114	Quarterly	Waipa	2.25	1	Unknown	Unknown	1	Dairy
69_97	1813907	5819939	Annual	Waipa	4.71	3.3	Sand	Unconfined		Horticultural
70_1134	1793458	5803246	NGMP	Waipa	10.6	4	Sand	Unconfined	0.3	Hort > Lifestyle
70_22	1813640	5804238	Quarterly	Hamilton Basin	6.42	3.5	Sand	Unconfined	5	Hort > Lifestyle
70_31	1819208	5805288	Annual	Hamilton Basin	5.2	na	Sand	Unconfined		Dairy > Horses
70_44	1814410	5801988	Quarterly	Hamilton Basin	18.3	na	Sand	Unknown	39	Dairy
70_47	1819994	5807279	Quarterly	Hamilton Basin	4.5	2.5	Sand	Unconfined	1	Dairy
70_50	1814851	5804983	Annual	Hamilton Basin	7.3	na	Sand	Unconfined		Dairy > Lifestyle
70_56	1810275	5804321	Quarterly	Hamilton Basin	8	5.1	Sand	Unconfined	7	Dairy
70_65	1792806	5801812	Quarterly	Waipa	4.3	na	Unknown	Unknown	6	Dairy
70_74	1793754	5792965	Quarterly	Waipa	6.71	3.66	Sand	Unconfined	1	Urban
70_76	1832786	5795802	Quarterly	Upper Waikato	30	na	Ignimbrite	Unknown	31	Dairy
71_1	1803433	5760260	Annual	Waipa	10	4	Sand	Confined	3.5	Agriculture
71_3	1783525	5760572	Annual	Waipa	26	6.5	Limestone	Confined	9.5	Forestry
71_4	1782518	5754292	Annual	Waipa	90	26	Limestone	Unknown	6	Dairy
71_5	1787575	5756958	Annual	Waipa	81.6	36.8	Limestone	Confined	58	Dairy
72_1006	1837116	5719976	Annual	Taupo	5.43	2.43	Tephra	Semi-confined	75	Agriculture
72_1008	1842613	5722653	Annual	Taupo	8	2	Ignimbrite	Unconfined	15.5	Agriculture
72_1011	1857370	5714209	Annual	Taupo	5.88	2.3	Ignimbrite	Unconfined		Agriculture
72_1069	1833951	5715883	Annual	Taupo	11.7	2.7	Ignimbrite	Unconfined	4	Agriculture
72_1072	1834190	5698624	Annual	Taupo	21	14.5	Ignimbrite	Confined	62	Agriculture
72_1081	1832115	5692948	Annual	Taupo	4.6	0.45	Sand	Unconfined	1	Urban
72_1082	1832842	5694923	Annual	Taupo	7.98	1.99	Ignimbrite	Unconfined		Agriculture
72_1087	1834175	5698626	Annual	Taupo	6.6	0.6	Ignimbrite	Unconfined	3	Agriculture

Well	Easting	Northing	Network	Sub-region	Well Depth (m)	Casing depth (m)	Lithology	Confinement	Water age (y MRT)	Land-use
72_1089	1833951	5715871	Annual	Taupo	36.2	na	Ignimbrite	Confined	22	Agriculture
72_1223	1853668	5859634	Annual	Hauraki	92.5	19.1	Ignimbrite	Confined	260	Urban
72_2138	1789097	5759639	Annual	Waipa	105	49	Limestone	Confined	38	Dairy
72_2895	1844402	5808665	Annual	Hauraki	16	10	Sand	Unconfined	7.5	Horticulture
72_2896	1844188	5808223	Annual	Hauraki	17.5	11.5	Sand	Unconfined	25	Horse stud
72_3559	1843181	5932275	Annual	Coromandel	12	6	Sand	Unconfined	6.5	Coastal settlement
72_356	1858456	5720549	Annual	Taupo	42	37	Ignimbrite	Confined		Urban
72_3741	1848980	5774796	Annual	Upper Waikato	78	64	Ignimbrite	Unknown		Dairy
72_392	1850808	5719734	Annual	Taupo	93	19.2	Ignimbrite	Unconfined	34	Agriculture
72_431	1842718	5719019	Annual	Taupo	48	45.7	Ignimbrite	Confined		Agriculture
72_4500	1849099	5762891	Annual	Upper Waikato	29.1	6.5	Ignimbrite	Unconfined	5 or 41	Dairy
72_5510	1803401	5764550	Annual	Waipa	9.5	7.5	Sand	Unknown		Dairy
72_9095	1867014	5706240	Annual	Taupo	10	na	Sand	Unconfined		Urban

Table I.2 Community well data

Well	Easting	Northing	Sub-region	Lithology	Total Depth (m)	Casing Depth (m)
60_13	1840336	5910051	Coromandel	Ignimbrite	98	53.3
60_236	1820981	5918764	Coromandel	Gravel	5.5	3.5
60_260	1822604	5903833	Coromandel	Sand	9	6.5
60_290	1852748	5886988	Coromandel	Rhyolite	44.6	26
60_393	1846533	5893578	Coromandel	Rhyolite	42	19.5
60_478	1831006	5878983	Hauraki			
61_1255	1775888	5865381	Northern		91.4	
61_1679	1772725	5846115	Northern	Limestone	91.6	
61_1680	1761799	5843241	Western		44.1	29.1
61_1727	1759880	5872227	Northern	Sandstone	146.22	132.2
61_1728	1782504	5872549	Northern	Basalt	57.5	32.1
61_1729	1754378	5869784	Northern			
61_1730	1795662	5880655	Northern			
61_1731	1788360	5879281	Northern			
61_182	1769633	5866530	Northern		180.85	
61_761	1773093	5876728	Northern		13.1	
63_390	1814264	5861027	Hauraki			
63_392	1853908	5853933	Hauraki		126.7	76.6
64_32	1814203	5845558	Hamilton Basin	Gravel	12	8.5
64_456	1827617	5819914	Hauraki	Sand	60	44.2
64_744	1814435	5835570	Hamilton Basin	Sand	27.43	19.6
64_751	1825791	5838341	Hauraki	Sand	7.7	6.5
64_807	1837626	5820342	Hauraki	Sand	50	48.5
64_879	1842562	5803814	Hauraki	Sand	9.6	9.15

Well	Easting	Northing	Sub-region	Lithology	Total Depth (m)	Casing Depth (m)
64_880	1830794	5823863	Hauraki	Gravel	15	
64_881	1820837	5836676	Hauraki		45	
64_883	1834829	5814065	Hauraki			
64_884	1829150	5832967	Hauraki	Sand	6.9	1.1
64_990	1826905	5842941	Hauraki	Sand	7	5
64_993	1833220	5843733	Hauraki			
64_996	1850525	5804715	Hauraki	Sand	34.5	25.5
65_142	1808925	5767309	Waipa	Rhyolite	64.5	52
65_270	1811090	5775419	Waipa			
65_285	1785627	5783486	Waipa			
67_565	1849449	5796996	Hauraki	Rhyolite	34.5	
67_567	1835711	5774721	Hauraki			
67_602	1835485	5783580	Hauraki			
68_1000	1831915	5693064	Taupo			
68_794	1867227	5702301	Taupo	Sand	26	20
69_1349	1798281	5825062	Hamilton Basin	Sand	49	33
69_1446	1790808	5848273	Northern		18.3	7
69_1809	1816142	5816539	Hauraki	Sand	4.2	
69_1816	1764164	5805815	Western	Mudstone	51.5	49
69_1897	1781500	5839497	Northern	Mudstone	61	52
69_1902	1801227	5850100	Northern	Greywacke	90.2	74
69_2071	1783081	5828451	Hamilton Basin			
69_2072	1810709	5813426	Hamilton Basin			
69_2074	1804516	5841084	Hamilton Basin			
69_2075	1794251	5817462	Hamilton Basin			
69_2079	1778681	5809219	Western		18.3	14.4
69_2080	1789943	5814998	Waipa		18	16.5

Well	Easting	Northing	Sub-region	Lithology	Total Depth (m)	Casing Depth (m)
69_2081	1807027	5834686	Hamilton Basin			
69_2187	1794339	5825063	Hamilton Basin			
69_912	1803659	5828610	Hamilton Basin	Sand	11	6.5
70_1156	1830599	5793008	Upper Waikato		28	14
70_1157	1824507	5800486	Upper Waikato			
70_1158	1793931	5803173	Waipa	Sand	6.9	5.1
70_1159	1814370	5782595	Waipa			
70_1161	1802367	5807972	Hamilton Basin		35.4	21.5
70_1162	1827281	5804608	Hamilton Basin			
70_1164	1811400	5787379	Waipa	Sand	74.3	58.3
70_1187	1814000	5800457	Hamilton Basin	Sand	38.1	28.3
70_1231	1817491	5808756	Hamilton Basin	Sand	8.5	7
70_453	1813431	5806866	Hamilton Basin	Sand	17.07	14.9
70_778	1797082	5797361	Waipa	Sand	51	45.5
70_794	1796298	5785557	Waipa	Sand	44.3	32.5
70_804	1824410	5783847	Waipa	Rhyolite	147.8	48.4
70_951	1824068	5812606	Hamilton Basin	Rhyolite	67	36
70_952	1788075	5800549	Waipa			
71_59	1790795	5762829	Waipa	Limestone	22.5	21.3
71_60	1759690	5774982	Western		52	16.2
71_61	1797339	5753550	Waipa			
71_63	1773089	5729811	Western			
72_1857	1763483	5868821	Northern	Scoria	88.4	52.2
72_2047	1818261	5813640	Hauraki			
72_592	1765254	5829216	Western	Sandstone	50	13
72_5981	1843933	5831234	Hauraki	Sand	10	9
72_739	1772277	5811475	Western	Sand	36	30

Well	Easting	Northing	Sub-region	Lithology	Total Depth (m)	Casing Depth (m)
72_749	1800291	5766332	Waipa	Greywacke	108	39
72_9925	1789804	5820914	Waipa		16	13

Appendix II:

Table II.1 Groundwater quality analysis methods and detection limits

Determinant	Analysis Method	Detection Limits
Alkalinity Total	Potentiometric autotitration to pH 4.5. APHA 2320B.	1.0 mg/l-CACO3
Ammonium-N	Colorimetry,Phenolhypochlorite. FIA. APHA Method 4500	0.01 mg/l-N
Arsenic Total	ICP-MS after HNO3 digestion	0.0011 mg/l
Boron Dissolved	Filtered, ICP-MS	0.005 mg/l
Boron Total Recoverable	ICP-MS after HNO3 digestion. APHA 3125B.	0.0053 mg/l
Calcium Dissolved	Filtered, ICP-MS	0.05 mg/l
Calcium Total	ICP-MS after HNO3 digestion. APHA 3215 B.	0.053 mg/l
Chloride Dissolved	Filtered sample, Ion chromotography. APHA 4110B.	0.5 mg/l
Copper Total Recoverable	ICP-MS after HNO3 digestion. APHA 3125B.	0.00053 mg/l
Dissolved Reactive Phosphorous	Molybdenum blue colorimetry. Flow injection analyser. APHA 4500-P G	0.004 mg/l-P
Conductivity at 25 DegC	Measured in lab by meter @ 25"C. APHA Method 2510B	0.1 mS/m @25°C
Iron Dissolved	Filtered, ICP-MS	0.02 mg/l
Iron Total Recoverable	ICP-MS after HNO3 digestion. APHA 3125B.	0.021 mg/l
pH	Measured in lab by meter. APHA Method 4500-H+ B.	0.1 pH units
Potassium Dissolved	Filtered, ICP-MS	0.05 mg/l
Potassium Total	ICP-MS after HNO3 digestion. APHA 3215 B.	0.053 mg/l
Magnesium Dissolved	Filtered, ICP-MS	0.02 mg/l
Magnesium Total	ICP-MS after HNO3 digestion. APHA 3215 B.	0.021 mg/l
Manganese Dissolved	Filtered, ICP-MS	0.0005 mg/l
Manganese Total Recoverable	ICP-MS after HNO3 digestion. APHA 3125B.	0.00053 mg/l
Nitrate-N	Ion Chromotography. APHA 4110B	0.05 mg/l-N
Sodium Dissolved	Filtered, ICP-MS	0.02 mg/l
Sodium Total	ICP-MS after HNO3 digestion. APHA 3215 B.	0.021 mg/l
Sulphate Dissolved	Filtered sample.Ion chromotography APHA 4110B	0.5 mg/l
Zinc Total	ICP-MS after HNO3 digestion. APHA 3125B/US EPA 200.8	0.0011 mg/l
Calculated parameters:		
Hardness Total	Calculation from Ca and Mg. APHA 2340B.	1.0 mg/l-CACO3
Total Dissolved Solids	Calculated from Electrical Conductivity	2.0 mg/l
Free Carbon Dioxide	Calculation from alkalinity & pH (APHA 4500 CO2D)	1.0 mg/l-CO2
Field measurements:		
Conductivity at 25 DegC	Field Meter	mS/m @25°C
Dissolved Oxygen	Field Meter	mg/l
% Dissolved Oxygen	Field Meter	% Sat
pH	Field Meter	pH
Water Temperature	Field Meter	°C

Appendix III: Median concentrations for selected parameters for sub-regions 2016-2020 (mg/l and pH units)

Taupo

Well	Ca	Cl	HCO_3	K	Mg	Na	NO_3-N	pH	SO_4	TDS
68_301	5.5	3.6	39.0	1.54	3.8	11.9	2.3	6.9	9.6	78
68_317	6.9	6.7	35.4	3.2	3.4	14.8	4.1	6.7	12.8	98
68_320	24	19.2	29.3	3.5	12	22	20	6.6	40	250
68_964	5	3.5	36	2.5	2.8	5.4	0.42	6.56	2.9	78.3
72_1006	2.9	2.8	32.9	1.42	1.8	7.1	0.07	6.8	0.8	42
72_1008	4.9	3.9	26.8	5.4	2.6	7.6	1.2	6.7	12.8	68
72_1011	5.2	4.7	43.9	1.56	3	15	2.4	6.8	7.2	82
72_1069	3.8	3.7	42.7	25	1.23	3.9	0.92	6.3	9.5	82
72_1072	5.8	4	52.5	3.2	2.2	9.6	0.06	7	0.5	65
72_1081	4	4.4	39.0	3.9	1.16	7.4	1.56	6.5	0.8	60
72_1082	4.9	6.5	25.6	3.8	1.57	7.4	1.46	6.4	2.7	55
72_1087	3.9	2.8	24.4	3.1	1.02	6.8	1.03	6.7	5.4	47
72_1089	9.8	3.9	56.1	4.7	3.8	12.6	3.8	6.6	11.9	106
72_356	4.9	4	36.6	2.3	2.4	10.5	1.97	6.6	5.3	66
72_392	6.85	6.1	34.8	2.5	3.6	13.6	2.435	7	11.9	96
72_431	5	3.9	34.2	1.57	2.8	8.4	1.73	6.9	4.4	60
72_9095	6.7	6	58.6	0.57	3.1	18.6	1.57	7.1	9.9	101

Upper Waikato

Well	Ca	Cl	HCO_3	K	Mg	Na	NO_3-N	pH	SO_4	TDS
66_58	2.1	2.4	26.8	1.43	1.19	6.8	0.22	7.1	0.9	36
66_6	10.25	26	33.6	11.6	4.6	24	7.45	6.35	18.9	168
66_92	3.4	4.4	256.2	1.79	0.89	96	0.05	7.7	0.5	270
66_93	8.6	11.6	39.0	11	1.72	19.4	7.6	6.2	9.9	126
66_96	2.2	3.6	31.7	2.6	0.93	7.7	0.05	8.3	0.5	38
67_404	11	14.3	30.5	6.9	4	12.4	7.6	6.2	7.5	123
67_483	7.8	11.9	81.7	4	2.9	24	0.05	6.6	3.4	117
67_573	5.8	12.2	25.6	5	2.6	12.1	4.6	6.2	0.5	93
67_83	8.4	11.2	31.7	3.8	3.4	12.2	4.9	6.4	6	98
68_912	8.4	6.2	45.1	3.3	3.5	16.1	2.8	6.5	16.4	105
70_76	6.1	15.4	26.8	5.4	3.3	13.4	4.9	6.4	3.3	99
72_3741	10.9	13.4	32.9	6	4.6	13.6	7.6	6.4	10.1	122
72_4500	8.5	10.4	43.9	4	3.1	14.2	3.3	6.4	7.9	101

Hauraki

Well	Ca	Cl	HCO_3	K	Mg	Na	NO_3-N	pH	SO_4	TDS
63_201	4.6	10.5	43.92	2	1.75	10.8	0.05	6.5	1.5	73
63_240	12.9	11.2	78.08	2.5	5.4	12.3	0.23	7.7	1.6	111
63_328	7.2	10.9	51.85	2.4	3.55	11.7	0.1	7.2	2.3	83.5
63_43	1.63	23	13.42	4	2.6	28	10	5.8	1.9	128
63_57	12.25	20.5	40.3	7.7	10.8	18.9	7.2	6.7	35	182
63_74	22	20	132.98	3.6	9.2	22	0.07	7.2	7.1	194

Well	Ca	Cl	HCO_3	K	Mg	Na	NO_3-N	pH	SO_4	TDS
63_78	1.9	16.5	9.638	2.1	1.2	12	1.74	6.2	1.8	62
64_108	12.3	22	17.8	9.9	6.4	21	17.2	6.1	7.9	181
64_111	9.4	15.4	124.44	2.7	2.9	40	0.05	7.4	0.5	163
64_117	27	28.5	56.7	40	11.85	14.65	21.5	6.6	37	305
64_12	17.1	31	20.0	6.9	10.6	19.5	10.5	6.3	41	220
64_120	9.2	8.4	32.5	4.75	3.3	10.6	4	6.54	12.8	145.6
64_20	14.5	11.3	37.8	6.8	7.2	12.4	6.4	6.2	27	150
64_43	9.8	15.15	34.2	6.4	5.1	14.05	5.55	6.7	15.9	128.5
64_46	15.4	25	28.1	7.05	7.6	16.15	4.55	6.35	39	174.5
64_50	14	22	29.3	6.9	7.2	14.1	6.8	6.5	26	160
64_511	6.2	6.8	36	5	3.1	10.8	3.8	6.5	7.45	128
64_7	24	19.9	26.84	11.6	14.3	17.3	21	6.2	51	270
64_70	7.75	25.5	32.3	4.6	5.3	16.85	0.64	6.35	24.5	138.5
64_720	44	128	10.8	16.9	12.8	47	25	5.68	45	781
64_831	8.4	6.3	37.82	3.5	5.1	8.4	3.4	6.9	11.5	95
67_11	25	9.8	36.6	9.15	5.55	9.6	13.8	6.5	19.2	184
67_15	5.55	12.5	26.8	7.7	3	11.35	3.5	6.45	7.75	94
67_55	1.72	5.2	19.764	3.6	0.98	6.8	1.19	6.7	0.7	41
72_1223	4	10	36.6	3.5	1.69	12.6	0.16	6.8	2	67
72_2895	13.4	19.7	35.38	7.7	5.5	14.5	5.6	6.4	27	156
72_2896	13.7	14.45	37.82	7.75	5.3	14.75	5.65	6.5	29	150

Coromandel

Well	Ca	Cl	HCO_3	K	Mg	Na	NO_3-N	pH	SO_4	TDS
60_12	32	6.7	92	1.3	1.2	4.8	0.87	8.06	3.6	180
60_124	96.5	13.9	286.7	2.4	4.65	12.75	2.08	7.6	19	355
60_167	0.19	15.25	93.3	2.455	3.16	31.75	0.05	7.3	1.6	133
60_190	5.6	41	31.7	8.3	2.7	26	0.05	6.2	5.5	141
60_316	30	34	141.5	1.26	8.7	35	0.8	6.6	16.3	250
60_345	3.3	16.8	24.2	4.1	2	14.7	1.88	6	2.8	79
60_348	6	15.4	26.8	1.4	2.7	12.3	0.52	6.2	6.9	78
60_407	7	31	14.5	1.86	3.8	18.3	2.5	6.7	8.9	118
60_480	38	42	256.2	5.2	16.9	93	0.51	7.1	89	490
63_269	2.7	28	17.8	2.5	2.9	22	2.3	6.6	5.9	109
72_3559	18.6	32	59.8	0.71	3.5	23	0.28	6.3	12.1	157

Hamilton Basin

Well	Ca	Cl	HCO_3	K	Mg	Na	NO_3-N	pH	SO_4	TDS
62_5	12.7	17.8	39.04	5.9	7.7	13.3	6.1	6.5	13.5	159
69_163	27	12.1	37.82	13.8	6	8.6	6.6	6.4	46	200
69_1709	13.5	14.3	48	3.9	6.9	13.7	5.7	6.72	15.8	208.1
69_173	16.15	15.75	18.8	21	4.1	11.4	6.4	6.05	38.5	171
69_19	25	21	41.48	5.7	9.1	11.3	13.1	6.5	12.9	193
69_248	7.6	10.5	31.72	2.2	3.9	8.6	0.13	6.4	18	77
69_295	7.95	10.45	78.08	10.8	3.85	37	5.45	6.85	22.5	172.5
69_365	14.9	16.4	40.3	10.9	7.4	12.5	4.35	6.6	37	164.5
69_374	15.8	19.8	31.72	4.2	6.5	11.1	7.9	6.4	24	143

Well	Ca	Cl	HCO_3	K	Mg	Na	NO_3-N	pH	SO_4	TDS
69_62	19.6	32	43.92	4.1	12.8	11.7	7.4	6.7	30	200
70_22	16.35	9.3	50.0	7.7	6.55	14.25	7.6	6.45	25	158
70_31	17.3	15.6	29.28	9.6	6.1	10.6	9.3	6.4	21	159
70_44	15.25	15.25	69.5	6.4	7.3	17.95	5.4	6.8	15.2	164
70_47	18.8	12.6	30.5	7	4.6	6.2	2.4	6.6	37	132
70_50	20	11.3	54.9	13.9	5.5	11.5	10.7	6.6	18.6	186
70_56	15.05	10.3	43.9	4.55	7.7	11.25	7.5	6.8	21	144.5

Waipa

Well	Ca	Cl	HCO_3	K	Mg	Na	NO_3-N	pH	SO_4	TDS
65_6	4.2	11.2	31.72	5.5	2.2	12.8	3.2	6.5	1.3	81
69_81	9.9	24	17.6	9.4	5.7	14.8	8.9	6	13.5	150
69_97	9.2	13	24.4	4.3	4.8	12.1	3.5	6.3	21	111
70_1134	15.5	20.35	32.5	3.35	8.9	8.5	6.4	6.32	12.4	224
70_65	6.9	13	23.1	4.4	4.2	11.6	1.33	6.3	23	101
70_74	6.6	6.7	21.2	1.89	2.2	7.4	3.2	6.4	5.2	71
71_1	4.2	8.4	15.25	1.78	2.8	8.6	4.6	6.1	2.8	67
71_3	80	8.1	256.2	1.21	2.3	8.3	0.71	7.4	7.3	280
71_4	74	8.4	226.92	0.77	3.6	6.2	2.8	7.6	4.9	270
71_5	42	8.1	136.64	2.2	3.1	9.8	0.05	7.9	17.3	184
72_2138	56	7.6	185.44	1.62	2.7	8.3	0.8	7.8	4.6	220
72_5510	8.3	7.5	34.16	2.2	3.4	7.9	0.99	6.4	10.9	81

Northern areas

Well	Ca	Cl	HCO_3	K	Mg	Na	NO_3-N	pH	SO_4	TDS
61_113	8.3	20	4.4	0.31	4.2	16.5	8.5	5.3	11.2	121
61_126	21	54	32.9	4.3	10.25	30	6.45	6.7	39	255
61_135	8.5	25	30.5	1.42	9.9	27	16.9	6.8	2.1	184
61_143	15	27	11.956	2	15	22	29	6.4	0.7	240
61_208	13	66.5	65.9	1.115	14.45	51	11	6.55	8.75	300
61_221	7.2	18.15	37.8	1.185	7	14.95	6.15	6.65	1.8	118
61_230	5.5	18.2	17.568	1.34	6	15.6	8.6	6.1	1.2	114
61_245	2.4	32	4.026	1.72	2.5	20	0.42	5	12.3	106
61_258	6.9	20	39	1.1	9.2	17.4	8.7	6.69	2.4	206.1
61_280	7.9	22	21.228	1.18	9.6	19.3	16	6.3	1.4	159
61_54	3.1	17.4	10.614	1	7.9	18.7	12.9	6.1	1	125
61_59	2.5	17.2	14.6	1.14	3.1	15.3	4.1	6.2	2.8	85
61_85	8.3	32.5	30	1.4	8.75	23	10.8	6.35	2.8	244.3
61_93	22	54	43	2.3	21	22	23	6.51	1.7	421

Appendix IV: Trend analysis summary and network component comparison

A summary of trend analysis for individual SOE wells is provided in the following table. This is followed by a comparison of trends in the four network components of the regional groundwater quality monitoring programme. These components comprise 10 wells which are part of the quarterly NGMP, 27 SOE wells which are also monitored quarterly, 73 SOE wells sampled annually and the “Community network’ of 80 rural schools monitored every two years.

Trend analysis summary for SOE wells

Well	Samples	Prop. Censored	% Confidence	Annual Sen Slope	% Annual Change	Trend Confidence
60_12	59	0.000	53.02	0.000	0.000	As likely as not
60_124	18	0.000	99.85	-0.288	-8.228	Virtually certain improving
60_167	19	0.895	NA	NA	NA	Not Analysed
60_190	18	0.556	93.23	0.000	0.000	Very likely worsening
60_316	18	0.000	91.96	0.016	3.146	Very likely worsening
60_345	18	0.000	95.24	0.019	1.034	Extremely likely worsening
60_348	18	0.000	99.80	-0.043	-6.875	Virtually certain improving
60_407	18	0.000	61.92	0.012	0.531	As likely as not
60_480	18	0.000	99.89	-0.096	-11.199	Virtually certain improving
61_113	64	0.000	100.00	0.262	3.539	Exceptionally likely worsening
61_126	66	0.000	82.74	-0.050	-0.731	Likely improving
61_135	19	0.000	100.00	0.558	3.648	Exceptionally likely worsening
61_143	19	0.000	99.10	0.335	1.154	Exceptionally likely worsening
61_208	68	0.000	100.00	-0.320	-2.463	Virtually certain improving
61_221	64	0.000	100.00	0.113	2.088	Exceptionally likely worsening
61_230	18	0.000	100.00	0.212	2.849	Exceptionally likely worsening
61_245	19	0.211	52.81	0.000	0.000	As likely as not
61_258	66	0.000	100.00	0.099	3.613	Exceptionally likely worsening
61_280	20	0.000	100.00	0.301	2.151	Exceptionally likely worsening
61_54	19	0.000	100.00	0.373	3.585	Exceptionally likely worsening
61_59	59	0.000	94.66	0.015	0.341	Very likely worsening
61_85	65	0.000	100.00	0.101	1.006	Exceptionally likely worsening
61_93	62	0.000	99.99	-0.501	-2.275	Virtually certain improving
62_5	18	0.000	94.44	0.244	4.430	Very likely worsening
63_201	18	0.889	NA	NA	NA	Not Analysed
63_240	18	0.000	100.00	0.007	3.119	Exceptionally likely worsening
63_269	15	0.000	56.15	0.000	0.000	As likely as not
63_328	18	0.105	99.99	0.005	6.263	Exceptionally likely worsening
63_43	17	0.000	99.86	0.212	2.139	Exceptionally likely worsening
63_57	63	0.000	100.00	-0.304	-3.376	Virtually certain improving
63_74	18	0.111	93.25	0.001	1.382	Very likely worsening
63_78	18	0.000	61.95	0.001	0.069	As likely as not
64_108	64	0.000	91.27	-0.060	-0.327	Very likely improving
64_111	18	0.889	NA	NA	NA	Not Analysed

Well	Samples	Prop. Censored	% Confidence	Annual Sen Slope	% Annual Change	Trend Confidence
64_117	62	0.000	99.72	0.518	2.962	Exceptionally likely worsening
64_12	63	0.000	100.00	0.468	6.776	Exceptionally likely worsening
64_120	70	0.000	100.00	-0.400	-7.610	Virtually certain improving
64_20	66	0.014	73.84	0.041	0.649	Likely worsening
64_43	61	0.000	96.13	-0.107	-1.385	Extremely likely improving
64_46	65	0.000	84.15	0.012	0.280	Likely worsening
64_50	59	0.000	99.99	-0.219	-3.128	Virtually certain improving
64_511	66	0.000	90.39	0.014	0.386	Very likely worsening
64_7	18	0.000	99.94	0.581	3.898	Exceptionally likely worsening
64_70	63	0.000	66.61	-0.003	-0.396	As likely as not
64_720	65	0.000	100.00	1.294	8.745	Exceptionally likely worsening
64_831	18	0.000	99.39	-0.604	-14.207	Virtually certain improving
65_6	18	0.000	100.00	0.088	3.836	Exceptionally likely worsening
66_58	19	0.053	100.00	0.007	4.300	Exceptionally likely worsening
66_6	62	0.000	100.00	-0.412	-4.429	Virtually certain improving
66_92	19	0.947	NA	NA	NA	Not Analysed
66_93	19	0.000	99.28	0.273	5.936	Exceptionally likely worsening
66_96	19	0.684	57.23	0.000	0.000	As likely as not
67_11	64	0.000	99.85	0.385	3.252	Exceptionally likely worsening
67_15	62	0.000	74.18	0.005	0.131	Likely worsening
67_404	18	0.000	100.00	-0.371	-3.538	Virtually certain improving
67_483	18	0.944	NA	NA	NA	Not Analysed
67_55	18	0.000	99.99	0.040	4.908	Exceptionally likely worsening
67_573	18	0.000	63.37	0.018	0.392	As likely as not
67_83	18	0.000	67.61	0.008	0.167	Likely worsening
68_301	20	0.000	55.19	0.000	0.000	As likely as not
68_317	20	0.000	100.00	-0.084	-1.742	Virtually certain improving
68_320	19	0.000	85.37	-0.290	-1.451	Likely improving
68_912	18	0.000	100.00	-0.249	-6.551	Virtually certain improving
68_964	68	0.027	100.00	0.019	6.756	Exceptionally likely worsening
69_163	18	0.000	95.22	-0.452	-5.282	Extremely likely improving
69_1709	64	0.000	62.35	0.021	0.434	As likely as not
69_173	65	0.000	99.99	-0.468	-4.525	Virtually certain improving
69_19	18	0.000	99.85	0.627	6.269	Exceptionally likely worsening
69_248	18	0.056	99.06	-0.098	-7.056	Virtually certain improving
69_295	17	0.000	99.54	-0.207	-3.049	Virtually certain improving
69_365	65	0.000	99.84	-0.094	-1.655	Virtually certain improving
69_374	18	0.000	99.88	-0.855	-7.777	Virtually certain improving
69_62	19	0.053	86.85	0.254	3.523	Likely worsening
69_81	62	0.000	98.19	0.228	5.010	Extremely likely worsening
69_97	18	0.000	67.55	0.037	1.390	Likely worsening
70_1134	60	0.000	100.00	0.339	9.419	Exceptionally likely worsening
70_22	63	0.000	99.98	-0.325	-3.202	Virtually certain improving
70_31	17	0.000	79.56	0.041	0.457	Likely worsening
70_44	53	0.000	100.00	-0.883	-8.789	Virtually certain improving
70_47	66	0.000	100.00	-0.084	-2.815	Virtually certain improving
70_50	19	0.000	97.70	-0.314	-2.227	Extremely likely improving
70_56	64	0.000	99.84	-0.265	-2.853	Virtually certain improving

Well	Samples	Prop. Censored	% Confidence	Annual Sen Slope	% Annual Change	Trend Confidence
70_65	66	0.000	99.99	-0.116	-5.852	Virtually certain improving
70_74	66	0.000	100.00	-0.173	-4.239	Virtually certain improving
70_76	66	0.000	100.00	0.057	1.233	Exceptionally likely worsening
71_1	18	0.000	99.98	0.117	2.996	Exceptionally likely worsening
71_3	18	0.000	100.00	-0.057	-6.109	Virtually certain improving
71_4	18	0.000	65.04	0.000	0.000	As likely as not
71_5	18	0.722	NA	NA	NA	Not Analysed
72_1006	19	0.158	75.00	0.000	0.000	Likely improving
72_1008	20	0.000	91.39	-0.127	-4.350	Very likely improving
72_1011	20	0.000	97.73	-0.020	-0.775	Extremely likely improving
72_1069	18	0.000	98.15	-0.113	-8.087	Extremely likely improving
72_1072	19	0.421	64.47	0.000	0.000	As likely as not
72_1081	19	0.316	98.91	0.013	14.220	Extremely likely worsening
72_1082	19	0.053	98.67	0.031	2.679	Extremely likely worsening
72_1087	19	0.000	99.79	-0.059	-3.790	Virtually certain improving
72_1089	17	0.000	100.00	-0.406	-8.112	Virtually certain improving
72_1223	16	0.000	97.17	0.006	4.221	Extremely likely worsening
72_2138	8	0.000	87.61	0.003	0.389	Likely worsening
72_2895	15	0.000	90.95	-0.387	-4.667	Very likely improving
72_2896	15	0.000	96.26	-0.279	-3.895	Extremely likely improving
72_3559	13	0.000	99.28	0.021	9.337	Exceptionally likely worsening
72_356	17	0.000	97.90	0.029	1.578	Extremely likely worsening
72_3741	5	0.000	NA	NA	NA	Not Analysed
72_392	19	0.053	100.00	-0.327	-5.745	Virtually certain improving
72_431	20	0.000	99.94	0.027	1.750	Exceptionally likely worsening
72_4500	12	0.000	75.41	-0.033	-0.999	Likely improving
72_5510	10	0.000	89.48	0.056	6.042	Likely worsening
72_9095	6	0.000	77.38	0.080	5.588	Likely worsening

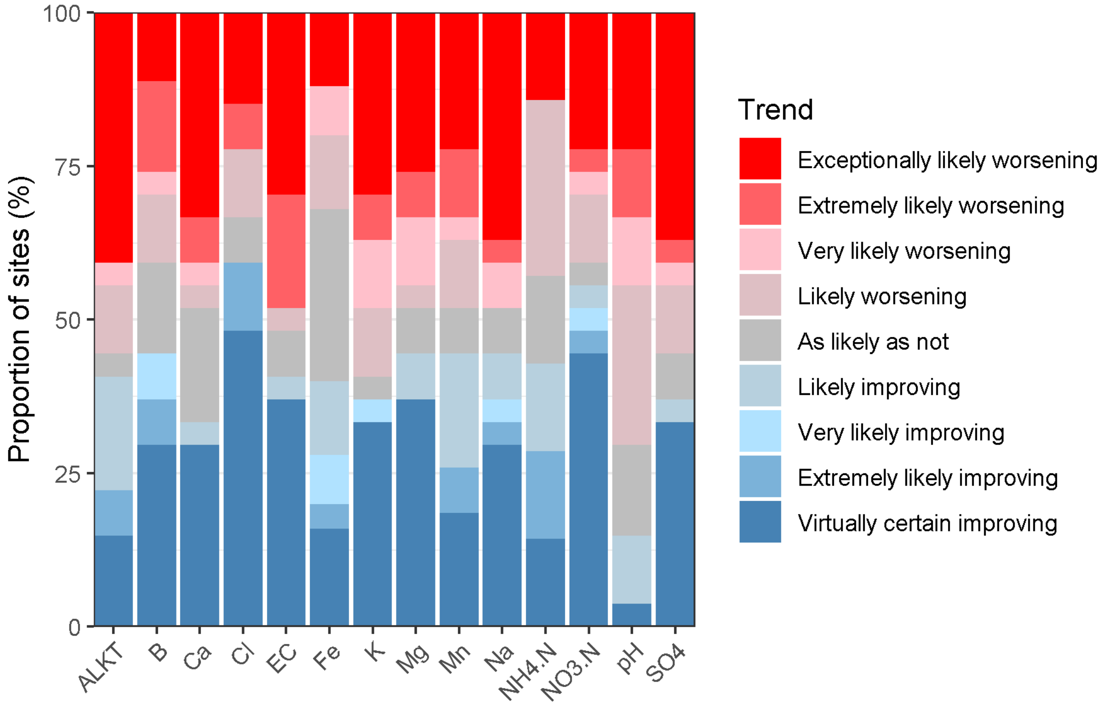
The following column graphs for components of the monitoring programs show the percentage of increasing and decreasing trends for selected determinants with the trend categories relating to the % confidence intervals listed below and derived using script from Land and Water People (Snelder and Frazer, 2019).

Trend category criteria

Categories of trend	% Confidence
Virtually certain improving	99-100
Extremely likely improving	95-99
Very likely improving	90-95
Likely improving	66.6-90
As likely as not	33.3-66.6
Likely worsening	66.6-90
Very likely worsening	90-95
Extremely likely worsening	95-99
Exceptionally likely worsening	99-100

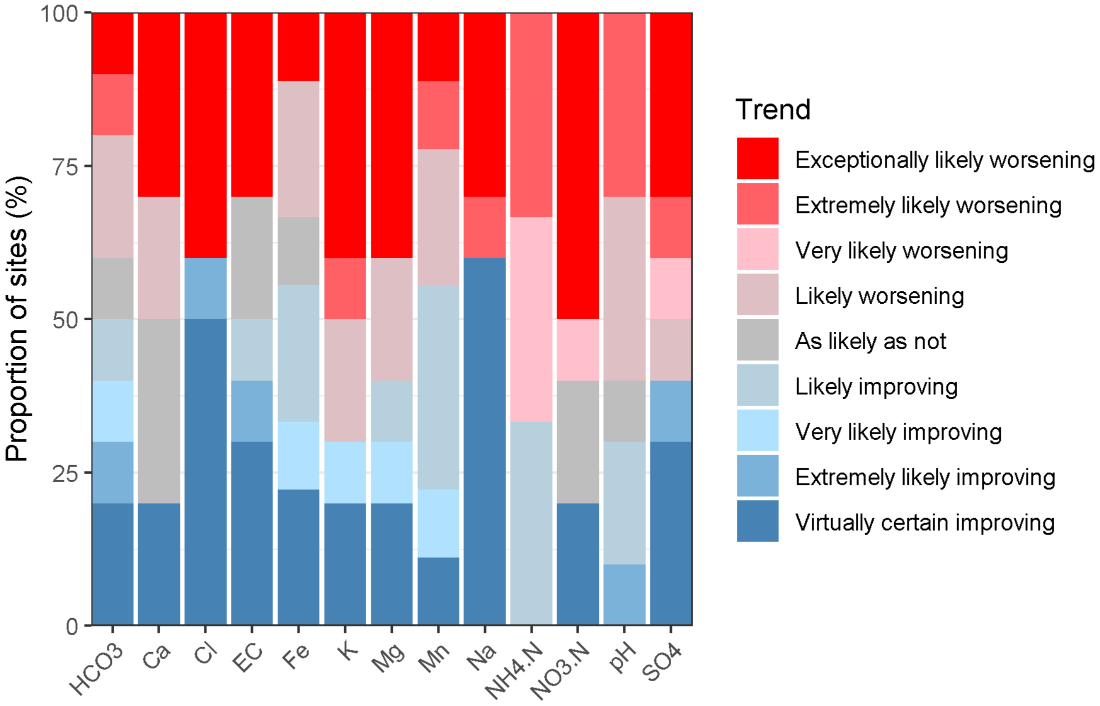
The first graph below shows that for the 27 SOE wells monitored quarterly there are notably more decreasing trends in nitrate-N and chloride. There are also notably more increasing concentration trends in alkalinity and pH. These wells are relatively shallow ranging from 2.2 to

44.5 m with a median of about 12 m. They are also predominantly aerobic, apart from five of mixed category and four indeterminate (no anaerobic condition represented). They comprise relatively young groundwaters (median MRT of nine years) so have generally had time to equilibriate.



Percentage of trends in key chemical parameters for the 27 SOE wells monitored quarterly

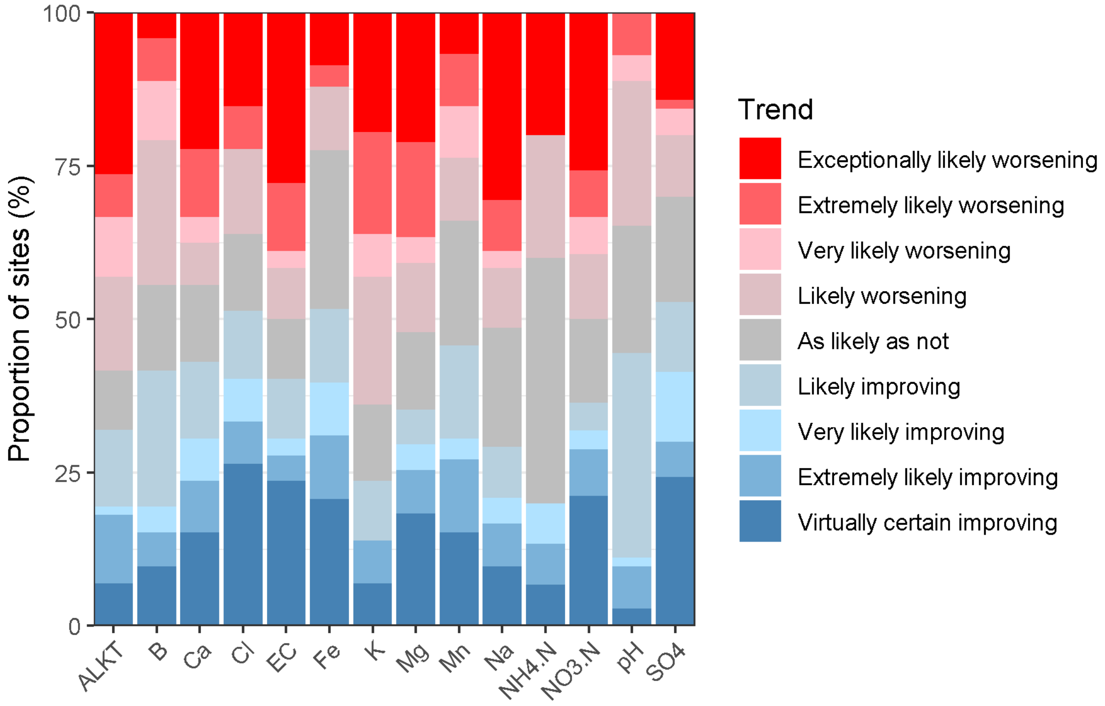
Markedly different trends are indicated in the NGMP well trends illustrated below. For these 10 quarterly monitored wells there are notably more increasing trends in nitrate-N and ammonium-N. There are also more decreasing concentration trends in sodium and chloride. These wells range in depth from 5 to 35 m with a median of about 16 m. They all have groundwaters in aerobic conditions except for two which are indeterminate. The groundwater age represented is relatively young with an estimated median MRT of 13 years.



Percentage of trends in key chemical parameters for the 10 NGMP wells monitored quarterly

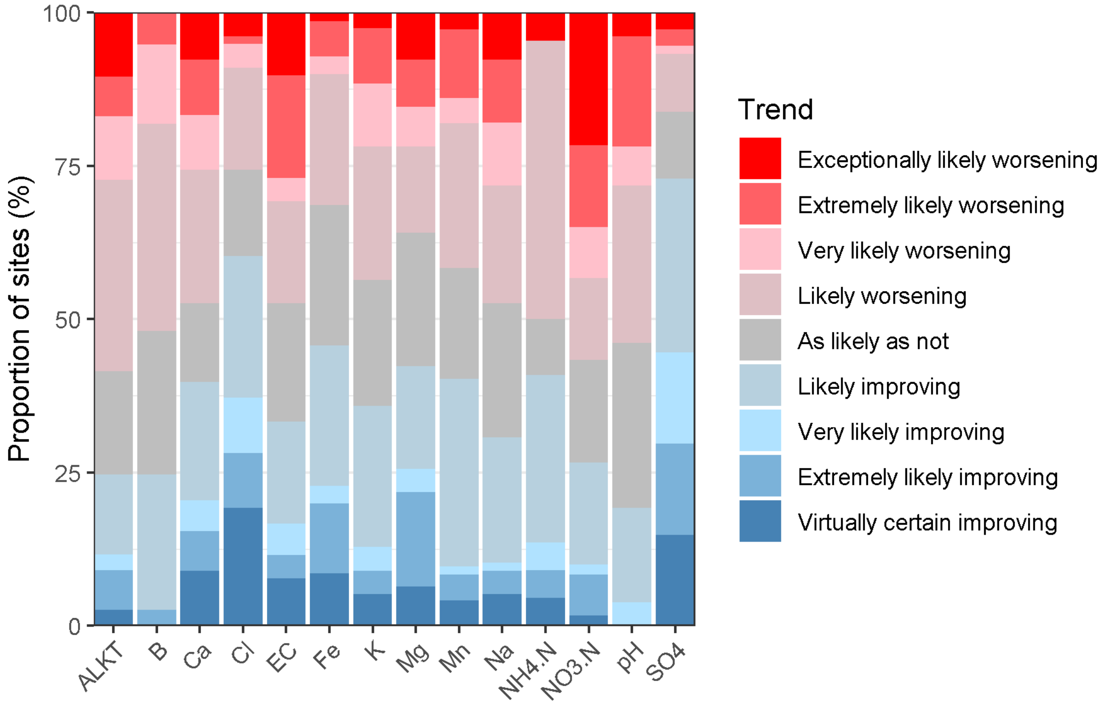
Increasing concentration trends in the annually monitored SOE wells are shown to be more prevalent for nitrate-N, calcium, potassium, magnesium and ammonium-N. Sulphate is an exception with more decreasing concentration trends. These wells range in depth from 2.75 to 127 m with a median of about 20 m. Just over half (55%) of these wells have aerobic groundwater with a further ~10% being of mixed category, ~7% are anaerobic with the remainder being indeterminate. The groundwater age is highly variable (ranging from 1 from to 280 years MRT) with a median MRT of about 27 years (Appendix I).

Differences in trends between these components of the monitoring program underlines the importance of network design. When the above three components of the SOE network are combined as in the mirror bar graph of Figure 53, these differences are essentially seen to balance out. The components are, however, of themselves also mixtures of aquifers and hydrochemical conditons. Some of the influencing factors are considered further in comparison between the larger SOE and Community networks in section 5.8.



Percentage of trends in key chemical parameters for the 73 SOE wells monitored annually

Useful trend information is now derived from the Community network records despite being only monitored biennelly. The chart below notably shows predominant increases in nitrate-N concentrations. Other parameters with a majority of increasing concentration trends include alkalinity and pH. Predominantly decreasing trends are evident for chloride and sulphate. These wells range in depth from 4.2 to 181 m with a median of about 38 m. About 30% of these wells have aerobic groundwater, 21% are anaerobic, 11% mixed and the remaining 38% are indeterminate.



Percentage of trends in key chemical parameters for the 80 Community wells monitored biennially

Appendix V: Regional state and trend maps for selected key determinants

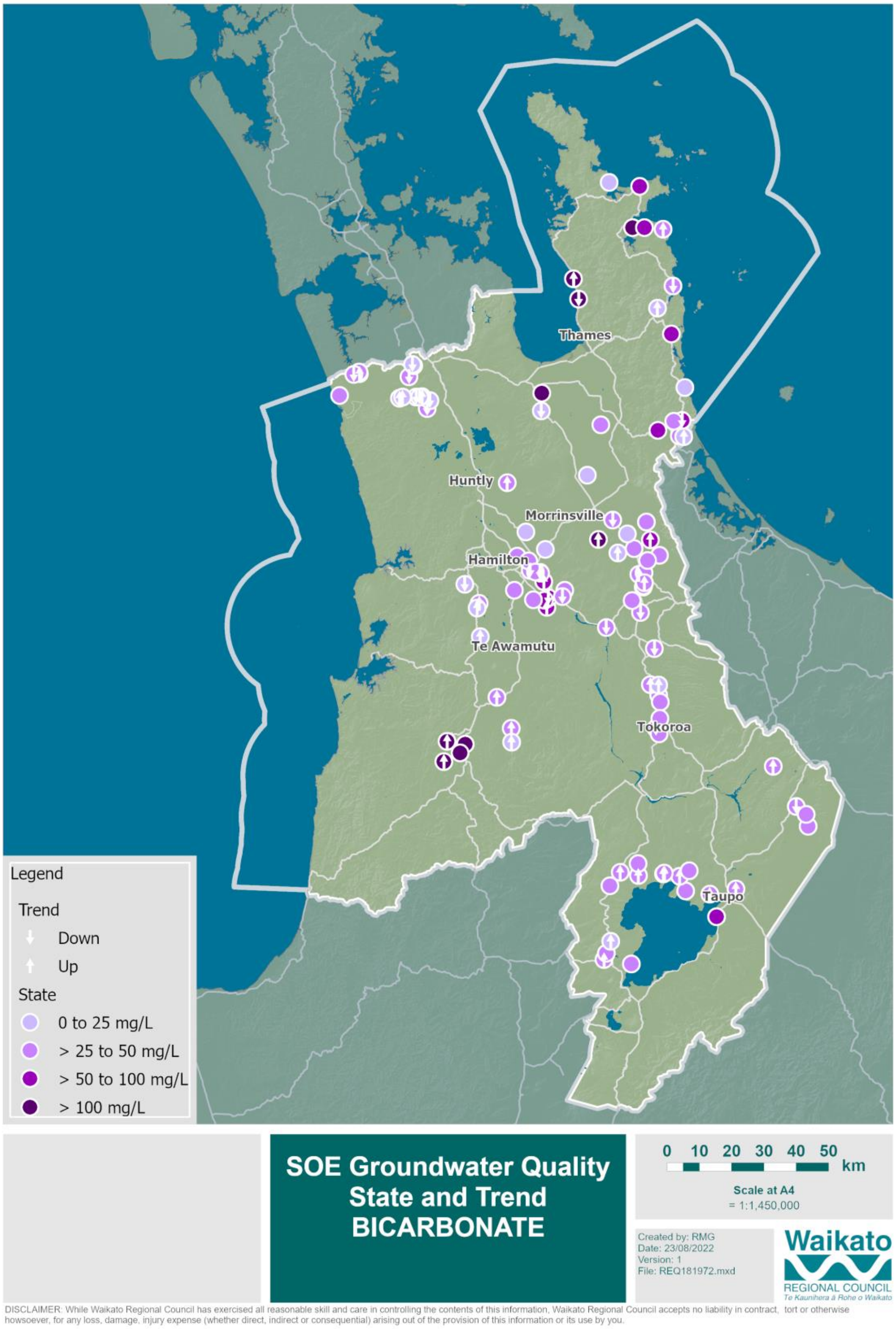


Figure V.1 Bicarbonate state and trend for the SOE groundwater quality network

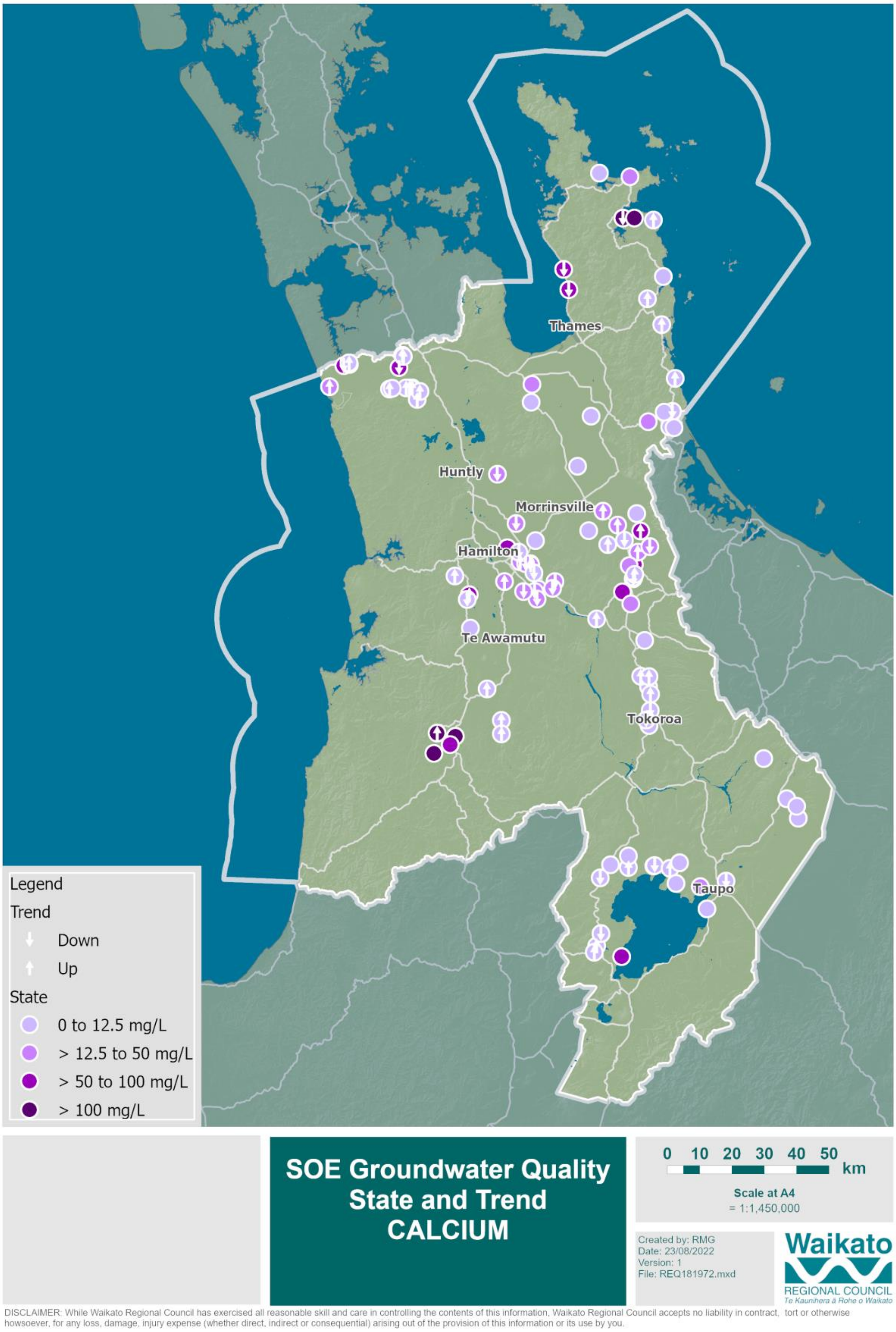


Figure V.2 Calcium state and trend for the SOE groundwater quality network

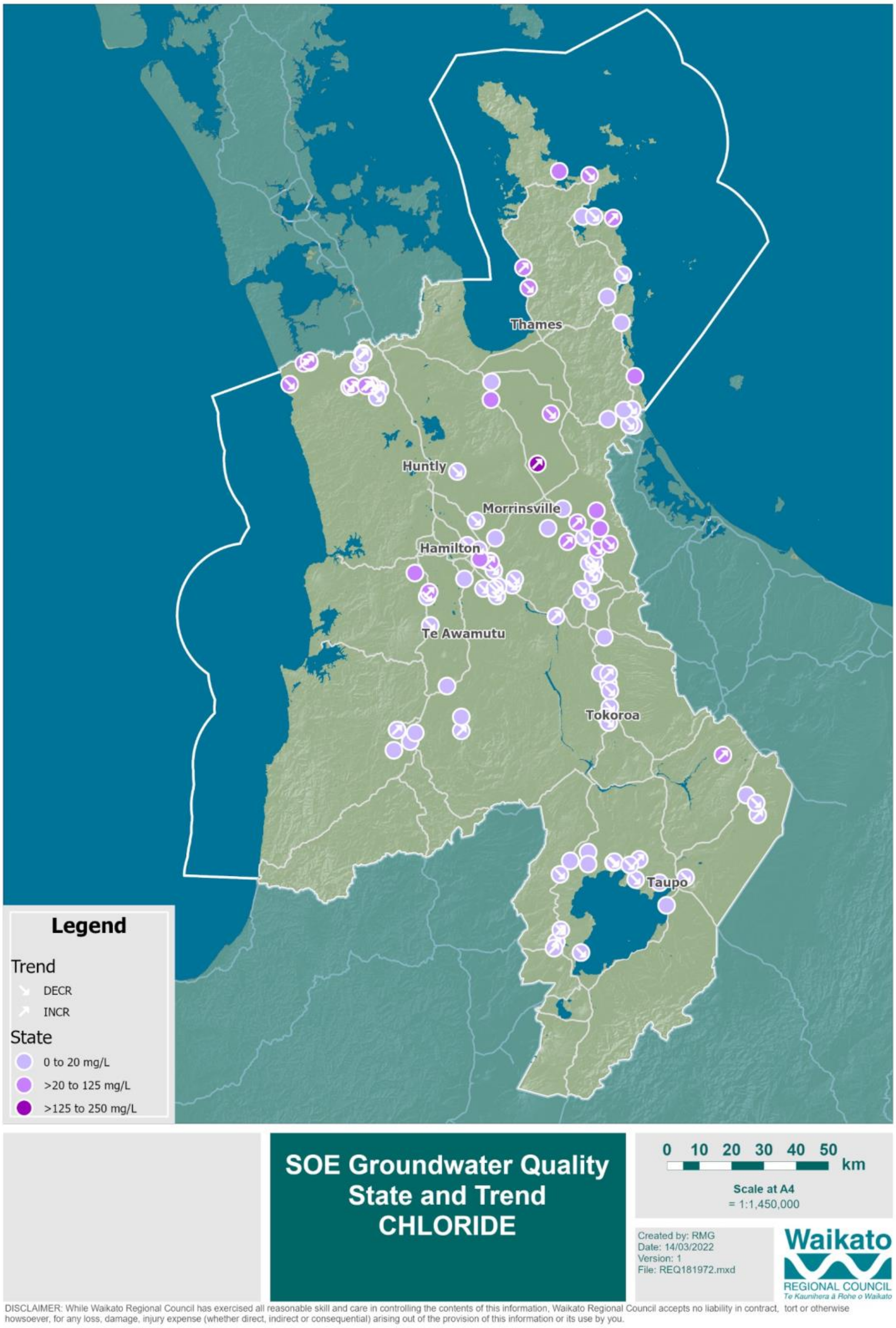


Figure V.3 Chloride concentration state and trend for the SOE groundwater quality network

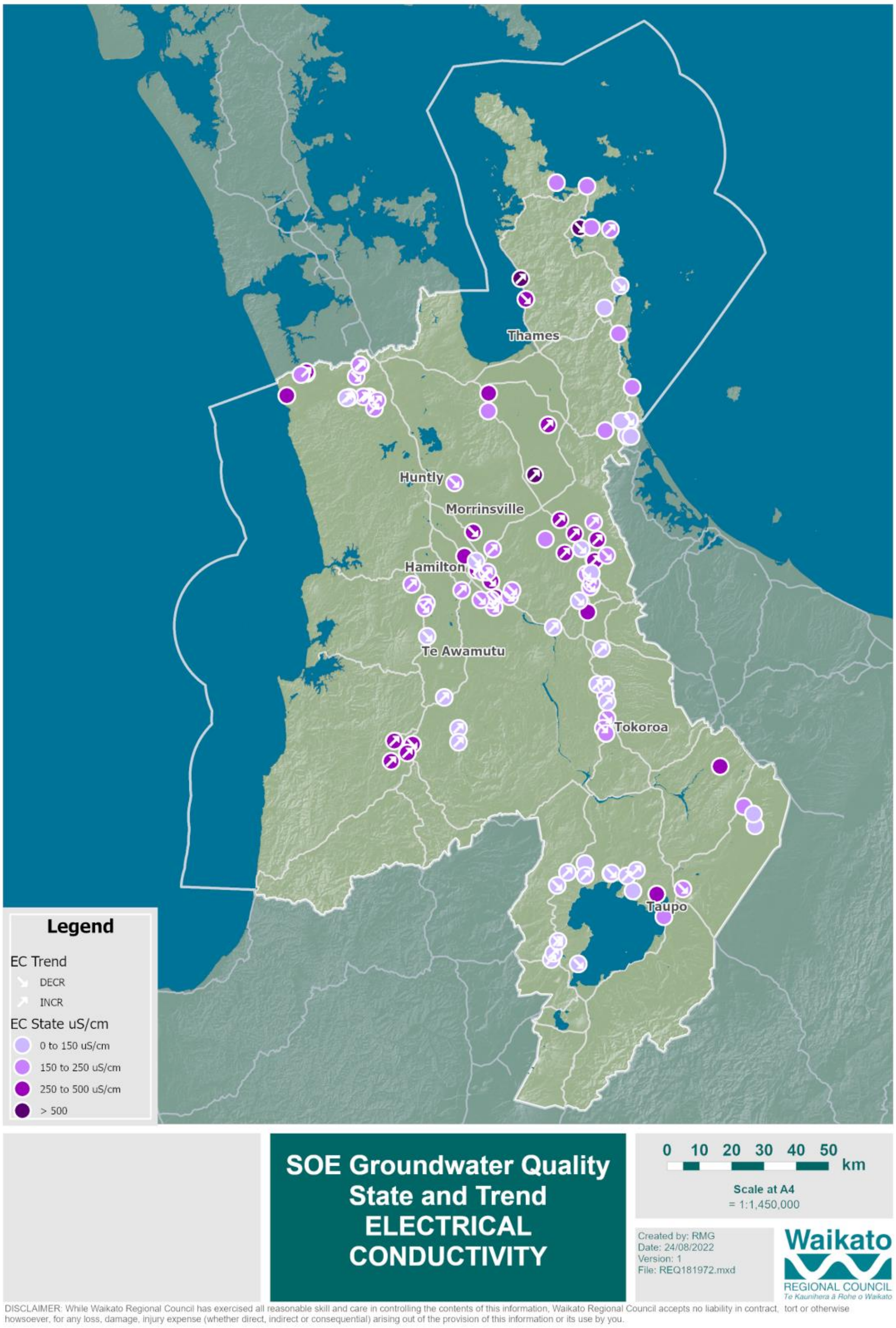


**Figure V.4	Electrical conductivity state and trend for the SOE groundwater quality network**

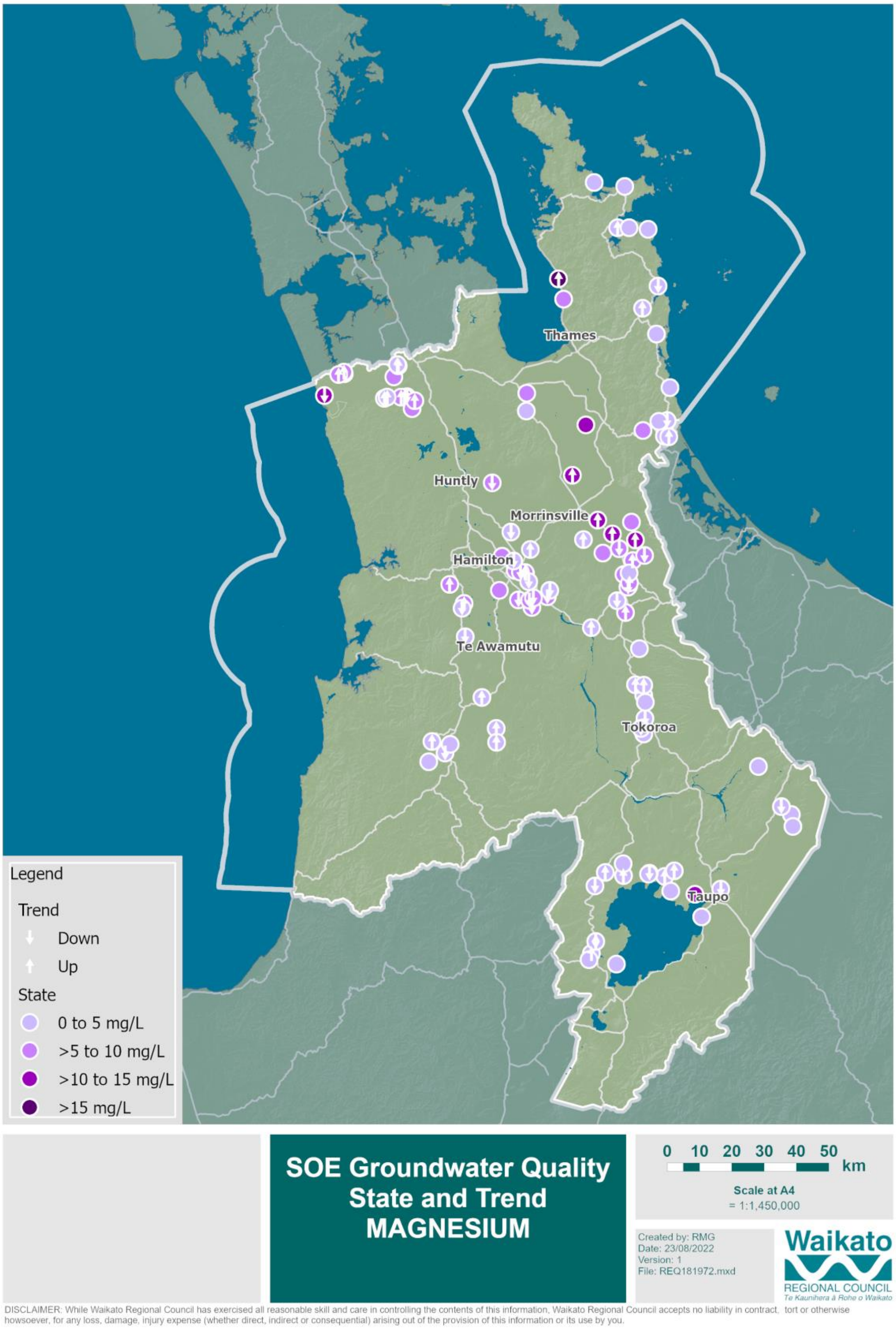


Figure V.5 **Magnesium concentration state and trend for the SOE groundwater quality network**

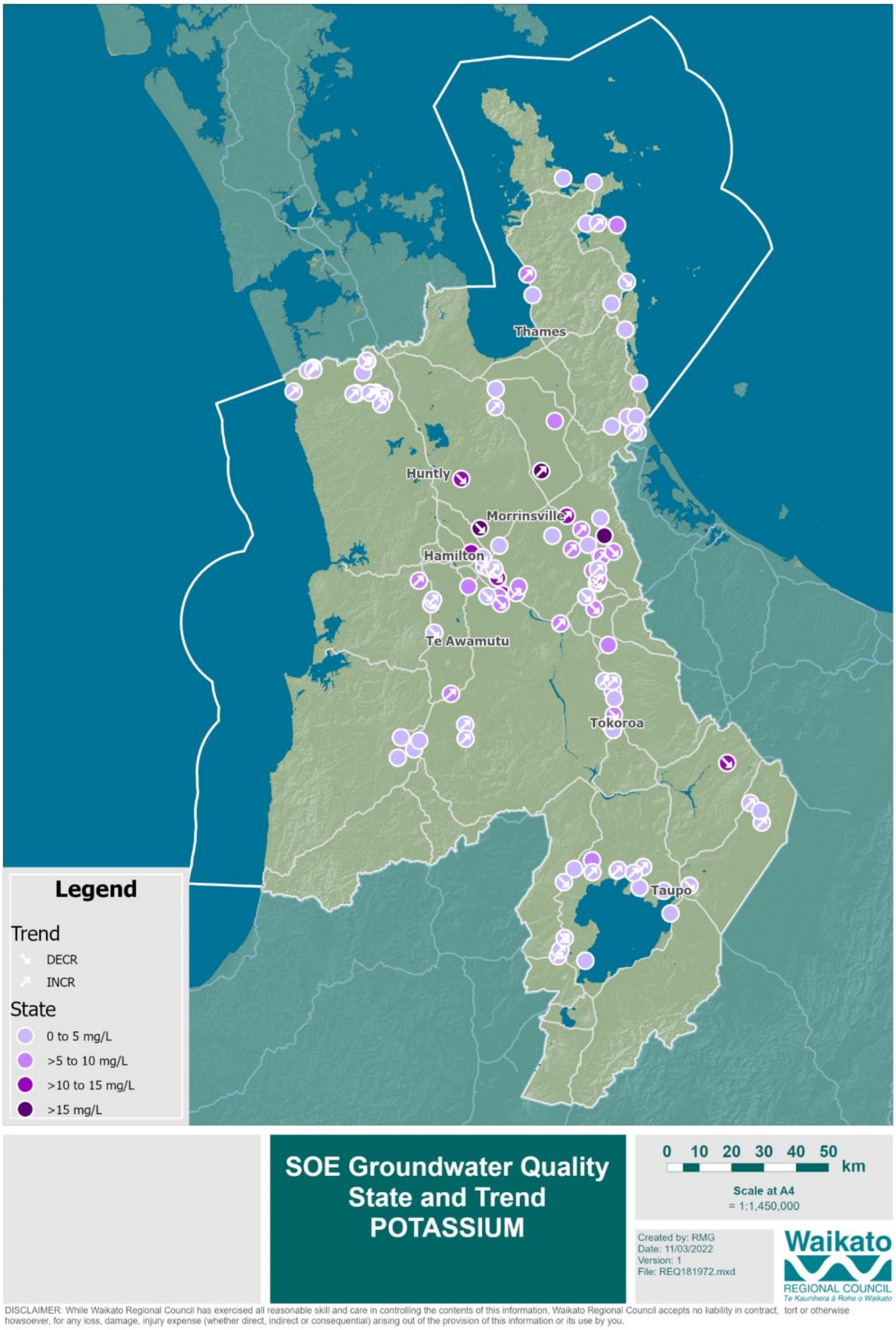
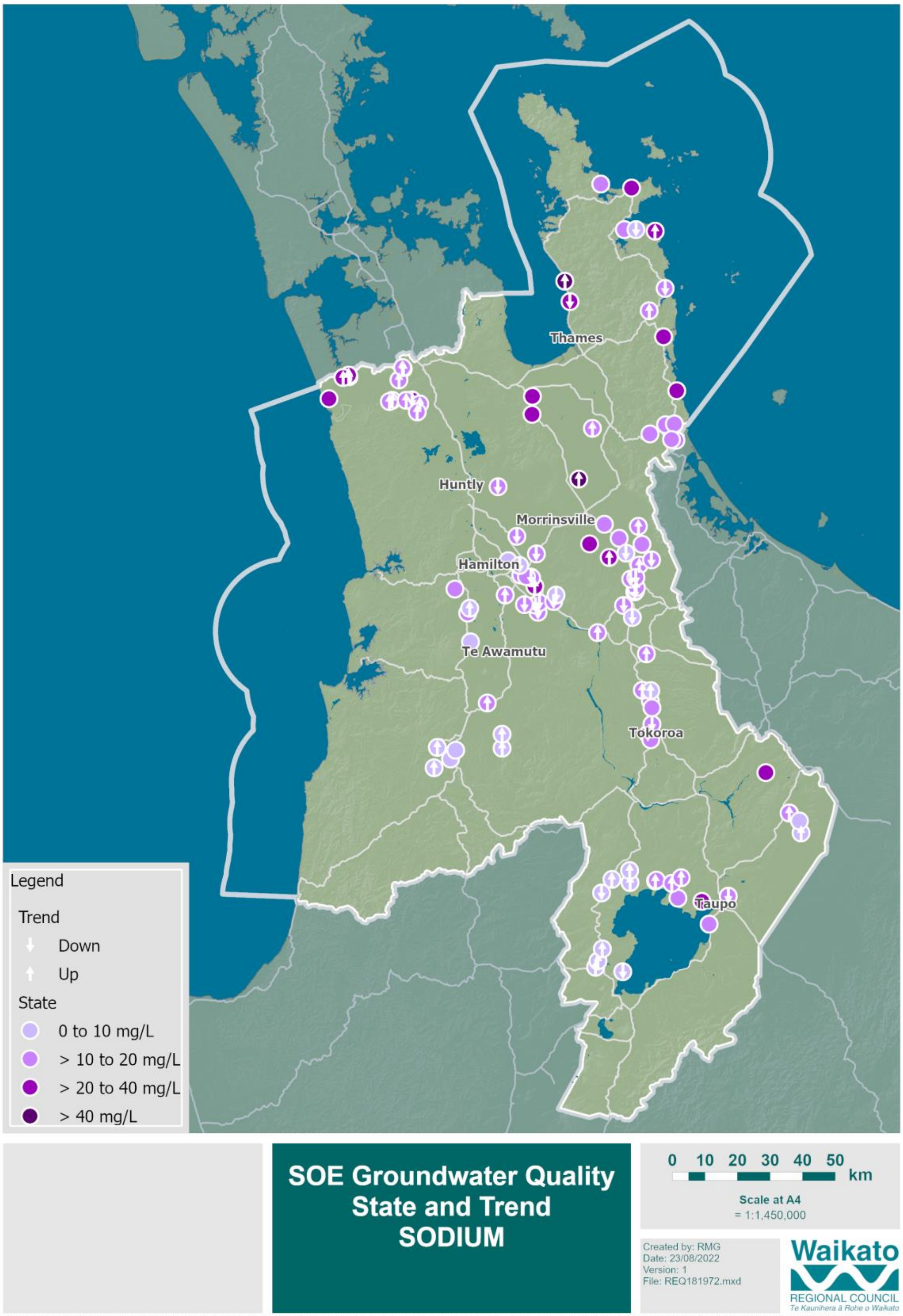


Figure V.6 Potassium concentration state and trend for the SOE groundwater quality network



DISCLAIMER: While Waikato Regional Council has exercised all reasonable skill and care in controlling the contents of this information, Waikato Regional Council accepts no liability in contract, tort or otherwise howsoever, for any loss, damage, injury expense (whether direct, indirect or consequential) arising out of the provision of this information or its use by you.

Figure V.7 **Sodium concentration state and trend for the SOE groundwater quality network**

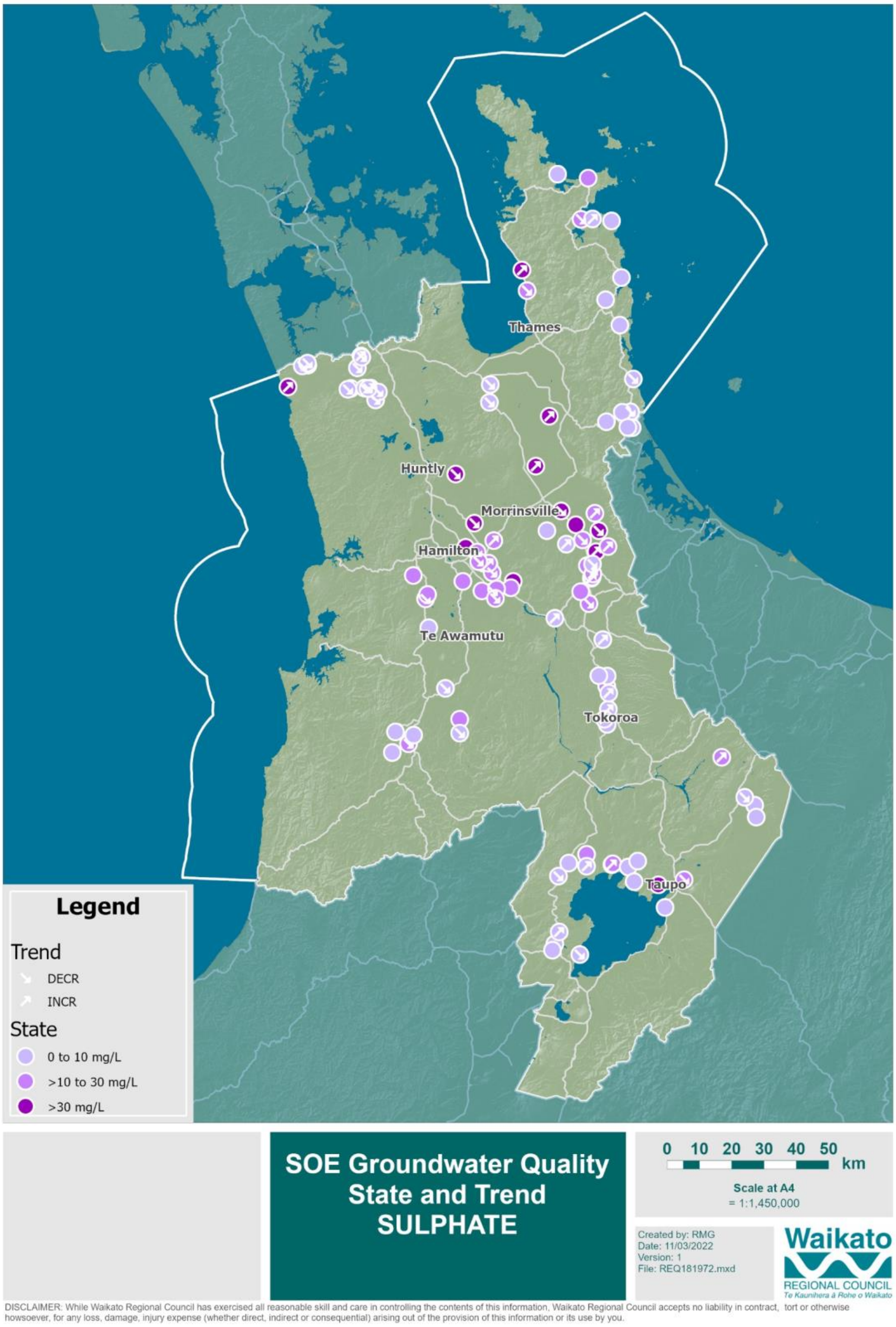


Figure V.8 Sulphate concentration state and trend for the SOE groundwater quality network

Appendix VI: Maximum acceptable values for organic determinants of health significance

Name	MAV (mg/L)	Remarks
acrylamide	0.0005	For excess lifetime cancer risk of 10^{-5}
alachlor	0.02	Pesticide. For excess lifetime cancer risk of 10^{-5}
aldicarb	0.01	Pesticide
aldrin + dieldrin	0.00004	Pesticide. The sum of, not each
anatoxin-a	0.006	Cyanotoxin. PMAV
anatoxin-a(s)	0.001	Cyanotoxin. PMAV
atrazine	0.002	Pesticide. Cumulative for atrazine and congeners
azinphos methyl	0.004	Pesticide. PMAV
benzene	0.01	For excess lifetime cancer risk of 10^{-5}
benzo(α)pyrene	0.0007	For excess lifetime cancer risk of 10^{-5}
bromacil	0.4	Pesticide. PMAV
bromodichloromethane	0.06	For excess lifetime cancer risk of 10^{-5}. THM
bromoform	0.1	THM
carbofuran	0.008	Pesticide
carbon tetrachloride	0.005	
chlordane	0.0002	Pesticide
chloroform	0.4	THM
chlorotoluron	0.04	Pesticide
chlorpyriphos	0.04	Pesticide
cyanazine	0.0007	Pesticide
cylindrospermopsin	0.001	Cyanotoxin. PMAV
2,4-D	0.04	Pesticide
2,4-DB	0.1	Pesticide
DDT + isomers	0.001	Pesticide. Sum of all isomers
di(2-ethylhexyl)phthalate	0.009	
1,2-dibromo-3-chloropropane	0.001	Pesticide. For excess lifetime cancer risk of 10^{-5}
dibromoacetonitrile	0.08	DBP (chlorination)
dibromochloromethane	0.15	THM
1,2-dibromoethane	0.0004	Pesticide. PMAV, for excess lifetime cancer risk of 10^{-5}
dichloroacetic acid	0.05	PMAV. DBP (chlorination)
dichloroacetonitrile	0.02	PMAV. DBP (chlorination)
1,2-dichlorobenzene	1.5	ATO
1,4-dichlorobenzene	0.4	ATO
1,2-dichloroethane	0.03	For excess lifetime cancer risk of 10^{-5}
1,2-dichloroethene	0.06	Total of cis and trans isomers
dichloromethane	0.02	
1,2-dichloropropane	0.05	Pesticide. PMAV
1,3-dichloropropene	0.02	Pesticide. Total of cis and trans isomers. For excess lifetime cancer risk of 10^{-5}
dichlorprop	0.1	Pesticide
dimethoate	0.008	Pesticide
1,4-dioxane	0.05	For excess lifetime cancer risk of 10^{-5}
diuron	0.02	Pesticide. PMAV
EDTA (editic acid)	0.7	

Name	MAV (mg/L)	Remarks
endrin	0.001	Pesticide
epichlorohydrin	0.0005	PMAV
ethylbenzene	0.3	ATO
fenoprop	0.01	Pesticide
hexachlorobutadiene	0.0007	
hexazinone	0.4	Pesticide. PMAV
homoanatoxin-a	0.002	Cyanotoxin. PMAV
isoproturon	0.01	Pesticide
lindane	0.002	Pesticide
MCPA	0.002	Pesticide
mecoprop	0.01	Pesticide
metalaxyl	0.1	Pesticide. PMAV
methoxychlor	0.02	Pesticide
metolachlor	0.01	Pesticide
metribuzin	0.07	Pesticide. PMAV
microcystins	0.001	Cyanotoxin. PMAV. Expressed as MC-LR toxicity equivalents
molinate	0.007	Pesticide
monochloroacetic acid	0.02	DBP (chlorination)
nitrilotriacetic acid (NTA)	0.2	
nodularin	0.001	Cyanotoxin. PMAV
oryzalin	0.4	Pesticide. PMAV
oxadiazon	0.2	Pesticide. PMAV
pendimethalin	0.02	Pesticide
pentachlorophenol	0.009	Pesticide. PMAV
picloram	0.2	Pesticide. PMAV
pirimiphos methyl	0.1	Pesticide. PMAV
primisulfuron methyl	0.9	Pesticide. PMAV
procymidone	0.7	Pesticide. PMAV
propazine	0.07	Pesticide. PMAV
pyriproxifen	0.4	Pesticide
saxitoxins	0.003	Cyanotoxin. Expressed as STXeq PMAV
simazine	0.002	Pesticide
styrene	0.03	ATO
2,4,5-T	0.01	Pesticide
terbacil	0.04	Pesticide. PMAV
terbuthylazine	0.008	Pesticide
tetrachloroethene	0.05	
thiabendazole	0.4	Pesticide. PMAV
toluene	0.8	ATO
trichloroacetic acid	0.2	DBP (chlorination)
trichloroethene	0.02	PMAV
2,4,6-trichlorophenol	0.2	For excess lifetime cancer risk of 10^{-5}. ATO
triclopyr	0.1	Pesticide. PMAV
trifluralin	0.03	Pesticide. Technical grade may contain carcinogens
trihalomethanes (THMs)		The sum of the ratio of the concentration of each THM to its respective MAV must not exceed one The individual members of this group are indicated in the table as THM
vinyl chloride	0.0003	For excess lifetime cancer risk of 10^{-5}
xylenes (total)	0.6	ATO

Name	MAV (mg/L)	Remarks
1080	0.0035	Pesticide. PMAV

Maximum acceptable values for radiological determinants (becquerel per litre)

Radioactive constituents	MAV	Unit
total alpha activity	0.10	Bq/L excluding radon
total beta activity	0.50	Bq/L excluding potassium-40
radon	100	Bq/L

Appendix VII: Guideline values for aesthetic determinants

Determinant	GV	Unit	Comments
aluminium	0.10	mg/L	Above this, complaints may arise due to depositions or discoloration
ammonia	1.5	mg/L	Odour threshold in alkaline conditions
calcium			See hardness
chloride	250	mg/L	Taste, corrosion
chlorine	0.6–1.0	mg/L	Taste and odour threshold (MAV 5 mg/L)
2-chlorophenol	0.0001 0.01	mg/L	Taste threshold Odour threshold
colour	10	TCU	Appearance
copper	1	mg/L	Staining of laundry and sanitary ware (MAV 2 mg/L)
1,2-dichlorobenzene	0.001 0.002	mg/L	Taste threshold Odour threshold (MAV 1.5 mg/L)
1,4-dichlorobenzene	0.0003 0.006	mg/L	Odour threshold Taste threshold (MAV 0.4 mg/L)
2,4-dichlorophenol	0.0003 0.04	mg/L	Taste threshold Odour threshold
ethylbenzene	0.002 0.08	mg/L	Odour threshold Taste threshold (MAV 0.3 mg/L)
hardness (total) (Ca + Mg) as $CaCO_3$	200	mg/L	High hardness causes scale deposition, scum formation. Low hardness (<100) may be more corrosive
	100–300		Taste threshold
hydrogen sulphide	0.05	mg/L	Taste and odour threshold
iron	0.2	mg/L	Staining of laundry and sanitary ware
magnesium			See hardness
manganese	0.04 0.10	mg/L	Staining of laundry Taste threshold (MAV 0.4 mg/L)
monochlorobenzene	0.01	mg/L	Taste and odour threshold
pH	7.0–8.5		Should be between 7 and 8. Most waters with a low pH have a high plumbosolvency. Waters with a high pH have a soapy taste and feel. A pH less than 8 is preferable for effective disinfection with chlorine
sodium	200	mg/L	Taste threshold
styrene	0.004	mg/L	Odour threshold (MAV 0.03 mg/L)
sulphate	250	mg/L	Taste threshold
taste and odour			Should be acceptable to most consumers
temperature			Should be acceptable to most consumers, preferably cool
toluene	0.03 0.04	mg/L	Odour Taste threshold (MAV 0.8 mg/L)
total dissolved solids	1000	mg/L	Taste may become unacceptable from 600–1200 mg/L
trichlorobenzenes (total)	see below		
1,2,3-trichlorobenzene	0.01	mg/L	Odour threshold

Determinant	GV	Unit	Comments
1,2,4-trichlorobenzene	0.005	mg/L	Odour threshold
1,3,5-trichlorobenzene	0.05	mg/L	Odour threshold
2,4,6-trichlorophenol	0.002 0.3	mg/L mg/L	Taste threshold Odour threshold (MAV 0.2 mg/L)
Turbidity	2.5	NTU	Appearance. See compliance criteria for effects on disinfection
Xylene	0.02	mg/L	Odour threshold (MAV 0.6 mg/L)
Zinc	1.5	mg/L	Taste threshold. May affect appearance from 3 mg/L

Appendix VIII: MoH data sheet for nitrate and nitrite

(From Ministry of Health 2019 Guidelines for drinking water quality management in New Zealand)

Nitrate and Nitrite

Maximum Acceptable Value for nitrate (short-term)
Based on health considerations, the concentration of nitrate (as NO_{3-}) in drinking-water should not exceed 50 mg/L. This is protective against methaemoglobinaemia and thyroid effects in the most sensitive subpopulation, bottle-fed infants, and, consequently, other population subgroups.

Maximum Acceptable Value for nitrite (short-term)
Based on health considerations, the short-term concentration of nitrite (as NO_{2-}) in drinking-water should not exceed 3 mg/L. This is protective against methaemoglobinaemia induced by nitrite from both endogenous and exogenous sources in bottle-fed infants, the most sensitive subpopulation, and, consequently, the general population.

Maximum Acceptable Value for nitrate plus nitrite
The sum of the ratios of the concentrations of each to its Maximum Acceptable Value (short-term) should not exceed 1.

DWSNZ (2008): Maximum Acceptable Value for nitrite (long-term and provisional)
Based on health considerations expressed in WHO (2004), the long-term concentration of nitrite (as NO_{2-}) in drinking-water should not exceed 0.2 mg/L. This WHO guideline value for chronic (long-term) effects of nitrite was considered provisional owing to uncertainty surrounding the relevance of the observed adverse health effects for humans and the susceptibility of humans compared with animals.

Note that WHO (2011/2017) no longer includes a long-term (chronic) guideline value for nitrite.

The Prescribed Concentration or Value (PCV) for nitrate in England and Wales is 50 mg/L as nitrate. The Prescribed Concentration or Value (PCV) for nitrite in England and Wales is 0.5 mg/L as nitrite at the consumers' taps and 0.1 mg/L at the WTP. See Notes.

The maximum contaminant level or MCL for nitrate (USEPA 2009/2011) is 10 mg/L as N, and 1 mg/L for nitrite as N, or a total of 10 mg/L. The maximum acceptable concentration in Canada is 10 mg/L for nitrate as N, and 1 mg/L for nitrite as N. *In cases where nitrite is measured separately from nitrate, the concentration of nitrite should not exceed 3.2 mg/L as* NO_2^-.

The Australian Drinking Water Guidelines (NHMRC, NRMMC 2011) state that based on health considerations, the guideline value of 50 mg-NO_3/L (as nitrate) has been set to protect bottle-fed infants under three months of age. Up to 100 mg-NO_3/L can be safely consumed by adults, and by children over 3 months of age. Where a water supply has between 50 and 100 mg-NO_3/L nitrate, active measures are required to ensure that those caring for infants are aware of the need to use alternative water sources in making up bottle feeds for babies under three months of age. Based on health considerations, the concentration of nitrite in drinking water should not exceed 3 mg-NO_2/L (as nitrite).

Note that 50 mg/L nitrate as NO_3^- is equivalent to 11.3 mg/L as N, 3 mg/L nitrite as NO_2^- is equivalent to 0.9 mg/L as N, and 0.2 mg/L nitrite as NO_2^- is equivalent to 0.06 mg/L as N.

Sources to drinking-water

Nitrate and nitrite can enter the aquatic environment from the oxidation of vegetable and animal debris and animal excrement.

Nitrate and nitrite can also enter water from agricultural, domestic and industrial discharges. Nitrate is used in chemical fertilisers, oxidising agents in the chemical industry, in the manufacture of glass, enamels for pottery, matches, pickling meat and in the production of explosives. A major source of nitrate is from municipal wastewaters and septic tanks. Nitrite is also used as a corrosion inhibitor in industry, and as a food preservative, especially for curing meats.

An example of the long-term effect of land use on the nitrate content in groundwater was presented in Figure 17 of Auckland City (2016). Prior to 1977 Pukekohe Borough water was supplied from a shallow spring, Hickey Spring. The nitrate level of the spring progressively increased from 6.5 mg/L as N in 1959 to 20 mg/L in 2015. Other bores in the area are also trending upwards.

From the Treatment Processes

The chlorination of raw waters containing significant amounts of ammonia or nitrite may lead to increases in nitrate through their oxidation. As 70 percent or more of the chlorine consumed during the oxidation of ammonia leads to nitrogen (the gas) production, the increase in nitrate concentrations is likely to be small unless ammonia concentrations are very high.

From the distribution system

Nitrite can be formed chemically in distribution pipes by *Nitrosomonas* bacteria during stagnation of nitrate-containing and oxygen-poor drinking-water in galvanised steel pipes, or if chloramination is used to provide a residual disinfectant but its occurrence is almost invariably sporadic. Nitrification in distribution systems can increase nitrite levels, usually by 0.2–1.5 mg/L.

Forms and fate in the environment

Nitrate and nitrite are naturally occurring ions which make up part of the nitrogen cycle. Nitrate is the oxidised form of combined nitrogen found in natural waters and in dilute aqueous solutions is chemically unreactive. Under anaerobic conditions nitrate may be reduced to nitrite and ammonia. Nitrite is seldom present in surface waters at significant concentrations but may be present in groundwaters. High nitrite concentrations are generally indicative of contamination. Incomplete nitrification of ammonia and denitrification of nitrate result in the biochemical production of nitrite which is generally present only under anaerobic conditions.

Typical concentrations in drinking-water

Nitrate

Nitrate was routinely measured in New Zealand drinking-water supplies as part of the Department of Health three yearly surveillance programme. Of 1908 samples analysed between 1983 and 1989, 14 samples (0.7 percent) contained concentrations equal to or exceeding the 1984 MAV of 10 mg/L (N).

The P2 Chemical Determinant Identification Programme, sampled from 673 zones, found nitrate concentrations to range from “not detectable” (nd) to 30 mg/L as NO_3-N, with the median concentration being 0.2 mg/L (Limit of detection = 0.1 mg NO_3-N/L). The Priority 2 Identification Programme found six distribution zones supplying drinking-water to a total of 1017 people with nitrate at greater than the MAV (Nokes and Ritchie, 2001).

In 2012 the Canterbury District Health Board stated that 33 of 289 wells tested in Canterbury exceeded the MAV for nitrate, the majority being around Ashburton.

26,177 water utilities in the US reported detecting nitrate in tap water since 2004, according to EWG's analysis of water quality data supplied by state water agencies, with the highest concentration being 30 mg/L as N.

Results of a survey of 210 waters (both source and zone) were reported by ESR (2016). Source waters sampled were groundwaters, mainly from dairying districts. Nitrate concentrations were below the limit of detection of the method used in 88 percent of samples. In only 2 percent (3) of source waters, and in none of the zone waters, did the nitrate concentration exceed 50 percent of the MAV. The MAV was not exceeded in any water sampled in this study. The highest reported nitrate concentrations in source waters were found in supplies in the Waikato (27 mg NO_3/L) and Canterbury (27 mg NO_3/L) districts. The highest nitrate concentration found in a zone water was in Canterbury (25 mg NO_3/L) in the Darfield zone.

Nitrite
Nitrite was not measured routinely in New Zealand drinking-water supplies as part of the Department of Health three-yearly surveillance programme.

The P2 Chemical Determinant Identification Programme, sampled from 227 zones, found nitrite concentrations to range from "not detectable" (nd) to 0.088 mg/L, with the median concentration being "nd" (Limit of detection = 0.005 NO_2^- -N mg/L). The Priority 2 Identification Programme found no distribution zones supplying drinking-water with nitrite at greater than the MAV (Nokes and Ritchie, 2001).

2,719 water utilities in the US reported detecting nitrite in tap water since 2004, according to EWG's analysis of water quality data supplied by state water agencies, with the highest concentration being 2.78 mg/L as N.

Removal methods

Nitrate
Nitrate is not removed from water by classical methods of treatment. Ion exchange systems have been developed for removing nitrate, but dilution with water of lower nitrate concentration from another source, where one is available, is commonly used. Reverse osmosis is also effective.

WRF (2016) evaluated the performance of four emerging treatment technologies: (1) a proprietary biological denitrification system (MB-N2), (2) standard ion exchange (IX) resin without brine reuse, (3) nitrate selective IX resin without brine reuse (NSR), and (4) nitrate selective IX resin with an electrochemical denitrification system (IX with ECD). For each alternative, capital, annual operation and maintenance (O&M), and 20-year present worth costs were calculated. When non-cost factors, such as overall safety, process reliability, and treatment history were evaluated, the conventional IX system was ranked higher than the MB-N2 and IX with ECD systems. However, the MB-N2 and IX with ECD systems were more favourable when considering waste disposal and environmental sustainability factors.

Nitrite
Treatment of the water with an oxidising agent such as chlorine will convert the nitrite to nitrate. The nitrate can then be treated as explained for nitrate. The USEPA Maximum Concentration Level (MCL) for nitrite indicates that the concentration at which it might be of concern is ten times less than the MCL for nitrate. The oxidation of high nitrite levels to nitrate therefore will not create an unacceptably high nitrate concentration in the water, unless the nitrate level is already high, or the nitrite level is extremely high.

Household treatment (WHO 2016)

Point-of-use reverse osmosis and point-of-entry anion exchange technologies are available for home or small-volume applications. Certified units are available, but they are costly, require good maintenance and are not readily available in many locations. Point-of-entry anion exchange uses strong base anion exchange resins that are regenerated with sodium chloride. Concurrent sulfate presence will significantly affect nitrate removal performance, as sulfate is preferentially retained and will displace nitrate back into the water if the system is operated beyond its nitrate capacity. Point-of-use reverse osmosis systems are potentially useful, but they operate at low line pressures, so they are much less efficient than high-pressure central desalination systems. Water reject levels can be of the order of up to 80 percent. Point-of-entry reverse osmosis is not used because of the corrosivity of the treated water to pipe and plumbing components (for more information, refer to the WHO website on household water treatment and safe storage at http://www.who.int/water_sanitation_health/water-quality/household/en/).

For individual households that obtain their drinking-water from private wells, residential drinking-water treatment devices are an option for reducing nitrate and nitrite concentrations in drinking-water. Before a treatment device is installed, the water should be tested to determine its general water chemistry and verify the presence and concentrations of nitrate and nitrite in the source water. As bacterial contamination of a well water supply frequently occurs in conjunction with nitrate contamination, the bacterial and chemical aspects of the water quality should be considered prior to selecting a water treatment device, and disinfection is essential.

Analytical methods

Nitrate

Referee method

Cadmium Reduction Method (APHA 4500-NO_3-E).

Some alternative methods

1. Ion Chromatography Method (APHA 4110B; USEPA 300.1).
2 Nitrate Electrode Method (APHA 4500-NO_3 D).

Nitrite

Referee method

Colorimetric Method (APHA 4500-NO_2 B).

Some alternative methods

1. Ion Chromatography Method (APHA 4110 B; USEPA 300.1).

Health considerations

For nitrate, the main sources of exposure are vegetables, especially leafy vegetables. Other food sources include baked and processed cereal products and cured meat. For an average adult consumer who lives in an area with low drinking-water contamination, total exposure to nitrate from food and water is estimated to be about 60 to 90 mg per person per day, of which at least 90 percent is from food. For high consumers of vegetables, the intake of nitrate may reach 200 mg per person per day. Similar intakes could result from high consumption of water contaminated with more than 50 mg/L nitrate (as NO_3^-).

For nitrite, the main source of exogenous human exposure is also food. Important sources include cereal products, vegetables and cured meat. Over the last 30 years, the relative contribution of cured meat to dietary exposure to nitrite for an average consumer has decreased from about 40 percent to about 20 percent. For high consumers of cured meat, the relative contribution may have reached 90 percent. The total intake of exogenous nitrite is estimated to be about 0.75 to 2.2 mg per day for an adult with an average food consumption pattern.

Ingested nitrate is absorbed readily and completely from the upper small intestine. Nitrite may be absorbed directly from the stomach as well as from the small intestine. When nitrate levels in drinking-water exceed 50 mg/L as NO_3^-, drinking-water may become the major source of total nitrate intake, especially for bottle-fed infants.

The toxicity of nitrate in humans is thought to be due solely to its reduction to nitrite. Bacteria are responsible for most of the conversion of nitrate to nitrite in the gastrointestinal system. Consequently, the risk of methemoglobinemia from ingestion of nitrate depends not only on the dose of nitrate, but also on the number and type of enteric bacteria. In healthy adults, available data suggest about 5 percent of a dose of nitrate is reduced to nitrite by bacteria in the mouth. Conversion of nitrate to nitrite may also occur in the stomach if the pH of the gastric fluid is sufficiently high (above pH 5) to permit bacterial growth. This is of concern in adults with diseases such as achlorhydria or atrophic gastritis. It is commonly accepted that infants younger than 3 months may be highly susceptible to gastric bacterial nitrate reduction, as their stomach pH is generally higher than in adults.

The primary health concern regarding nitrate and nitrite is the formation of methaemoglobinaemia, so-called blue-baby syndrome. Nitrate is reduced to nitrite in the stomach of infants, and nitrite is able to oxidise haemoglobin (Hb) to methaemoglobin (metHb), which is then unable to transport oxygen around the body. The reduced oxygen transport becomes clinically manifest when metHb concentrations reach 10 percent or more of normal Hb concentrations; the condition, called methaemoglobinaemia, causes cyanosis and, at higher concentrations, asphyxia. The normal metHb level in infants under 3 months of age is less than 3 percent. Other susceptible groups include pregnant women and people with a deficiency of glucose-6-phosphate dehydrogenase or methaemoglobin reductase. Methaemoglobinaemia in infants also appears to be associated with simultaneous exposure to microbial contaminants, eg, Addison and Benjamin (2004).

Walton (1951) described a survey performed by the American Public Health Association to identify clinical cases of infantile methemoglobinemia that were associated with ingestion of nitrate-contaminated water. A total of 278 cases of methemoglobinemia were reported. Of 214 cases for which data were available on nitrate levels in water, none occurred in infants consuming water containing <10 mg nitrate-nitrogen/L (1.6 mg nitrate-nitrogen/kg/day). There were 5 cases (2 percent) in infants exposed to 11–20 mg nitrate-nitrogen/L (1.8–3.2 mg/kg/day), 36 cases (17 percent) in infants exposed to 21–50 mg/L (3.4–8.0 mg/kg/day), and 173 (81 percent) in infants exposed to >50 mg/L (>8 mg/kg/day). Based on these studies of nitrate contamination and occurrence of methemoglobin the USEPA set the maximum contaminant level or reference dose for oral intake of 10 mg/L nitrate as N (USEPA 1987, revised 1991).

In Hungary in 1975 to 1977, 190 cases of methaemoglobinaemia were reported, 94 percent in infants less than three months of age. The nitrate level in drinking water was more than 100 mg/L in 92 percent of cases and between 40 and 100 mg/L in the remaining 8 percent. In 1982, 96 cases of methaemoglobinaemia were reported. All cases were associated with privately dug wells, and 92 percent of the patients were three months of age or younger. Nitrate levels in drinking water were above 100 mg/L in 93 percent of cases and between 40 and 100 mg/L in the remaining 7 percent (WHO 1985).

For over 50 years, there has existed a widespread belief that nitrate in drinking water is a primary cause of infantile methemoglobinemia. Hunter Comly originally proposed this theory in 1945 in a report in the *Journal of the American Medical Association* after treating several infantile methemoglobinemia victims. Comly proposed that because nitrite is known to react directly with hemoglobin to form methemoglobin, nitrate from drinking water must be converted to nitrite within the gastrointestinal tract of infants. Because many infants did not appear susceptible to methemoglobinemia from nitrate-contaminated water, Comly suggested that the nitrate-to-nitrite conversion might only occur in the presence of a bacterial infection of the upper gastrointestinal tract, where such reactions could occur before nitrate is absorbed. The nitrate-derived nitrite could then react with haemoglobin to form methemoglobin and, in sufficient quantities, lead to the cyanosis of methemoglobinemia. This theory was reinforced by the fact that cyanosis typically subsided once an infant was switched to an uncontaminated water supply. Comly's hypothesis became widely accepted as further research revealed a consistent pattern of elevated well water nitrate levels in infantile methemoglobinemia cases. Limiting infant exposure to nitrate was thus decided to be the most prudent approach to protecting infant health, and a committee from the American Public Health Association conducted a nationwide survey to determine a safe level of nitrate in water. A total of 278 cases with 39 deaths were compiled. The results showed that methemoglobinemia incidence correlated with increasing nitrate levels. Because no infantile methemoglobinemia cases were observed with concentrations <10 ppm nitrate-nitrogen, the United States and the World Health Organization established a maximum contaminant level (MCL) of 10 ppm nitrate-N for nitrate in drinking water. Over the last 20 years, however, a more complex picture of infantile methemoglobinemia causation has emerged which indicates that current limits on drinking water nitrate may be unnecessarily strict. It is now well established that diarrhoeal illness and some gastrointestinal disturbances, typically accompanied by diarrhoea and/or vomiting, can lead to methemoglobinemia in young infants without exposure to high-nitrate drinking water or exposure to abnormal levels of nitrate through food. There many reported infantile methemoglobinemia cases associated with diarrhoea without exposure to nitrate-contaminated water. Because diarrhoea was a prominent symptom in the majority of drinking water linked methemoglobinemia cases, the evidence suggests that diarrhoea and/or gastrointestinal infection/ inflammation, are the principle causative factors in infantile methemoglobinemia. A survey in Germany found that 53 percent of 306 infantile methemoglobinemia cases reported diarrhoea. Contrary to some reports, diarrhoea and vomiting are not symptoms that typically accompany cyanosis, methemoglobinemia due to oxidant drug exposure, or genetic abnormalities in haemoglobin (Avery 1999, and discussed in WHO 2011).

Methaemoglobinaemia in infants appears to be associated with simultaneous diarrhoeal disease. Authorities should therefore be all the more vigilant that water to be used for bottle-fed infants is microbiologically safe when nitrate is present at concentrations near the guideline value or in the presence of endemic infantile diarrhoea. Water should not be used for bottle-fed infants if the concentration of nitrate is above 100 mg/L as NO_3 but can be used if the concentration is between 50 and 100 mg/L if the water is microbiologically safe and there is increased vigilance by medical authorities (WHO 2011).

Current evidence suggests that exposure to nitrate in drinking-water may alter human thyroid gland function by competitively inhibiting thyroidal iodide uptake, leading to altered thyroid hormone concentrations and functions. Although studies found that exposure to nitrate concentrations above 50 mg/L are weakly associated with altered thyroid function, the evidence is limited, conflicting and based on studies with important methodological limitations (from WHO 2016).

The reference dose or RfD (USEPA 1991/2009/2011) for nitrate as N is 1.6 mg/kg/d, and for nitrite as N it is 0.16 mg/kg/d (USEPA 1997/2009/2011).

As at October 2015 and July 2017 ATSDR (http://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls.pdf) quotes a minimal risk level (MRL) for nitrate of:

4 mg/kg/d for acute-duration oral exposure (1–14 days)
4 mg/kg/day for intermediate-duration oral exposure (15–364 days)
4 mg/kg/day for chronic-duration oral exposure (>364 days).

As at July 2017 ATSDR (http://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls.pdf) quotes a minimal risk level (MRL) for nitrite of:

0.1 mg/kg/d for acute-duration oral exposure (1–14 days)
0.1 mg/kg/day for intermediate-duration oral exposure (15–364 days)
0.1 mg/kg/day for chronic-duration oral exposure (>364 days).

Nitrate is not mutagenic in bacteria and mammalian cells *in vitro*. Chromosomal aberrations were observed in the bone marrow of rats after oral nitrate uptake, but this could have been due to exogenous N-nitroso compound formation. Nitrite is mutagenic, causing morphological transformations in in vitro systems.

IARC (2005) stated that "Ingested nitrate or nitrite under conditions that result in endogenous nitrosation is *probably carcinogenic to humans (Group 2A)*. The underlying mechanism is endogenous nitrosation, which in the case of nitrate must be preceded by reduction to nitrite. Nitrate and nitrite are interconvertible *in vivo*. Nitrosating agents that arise from nitrite under acidic gastric conditions react readily with nitrosatable compounds, especially secondary amines and alkyl amides, to generate *N*-nitroso compounds. Many *N*-nitroso compounds are carcinogenic." However, the weight of evidence indicates that there is unlikely to be a causal association between gastric cancer and nitrate in drinking-water.

The livestock guideline value for nitrite (as NO_2^-) is 30 mg/L. Nitrate (as NO_3^-) concentrations less than 400 mg/L in livestock drinking water should not be harmful to animal health; stock may tolerate higher nitrate concentrations in drinking water provided nitrate concentrations in feed are not high. Water containing more than 1,500 mg/L nitrate (as NO_3^-) is likely to be toxic to animals and should be avoided (ANZECC/ARMCANZ 2000). These guidelines were to have been updated in 2012.

Derivation of Maximum Acceptable Values

Nitrate (short-term)
The MAV of 50 mg/L (as NO_3^-) is to protect against methaemoglobinaemia in bottle-fed infants (short-term exposure). In epidemiological studies, methaemoglobinaemia was not reported in infants in areas where drinking-water consistently contained less than 50 mg of nitrate per litre.

The epidemiological evidence for an association between dietary nitrate and cancer is insufficient, and the MAV for nitrate in drinking-water is established solely to prevent methaemoglobinaemia, which depends upon the conversion of nitrate to nitrite. Although bottle-fed babies are the most susceptible, occasional cases have been reported in some adult populations.

Nitrite (short-term)
The short-term MAV of 3 mg/L nitrite (as NO_2^-) is to protect against methaemoglobinaemia in bottle-fed infants. WHO (2017) guideline value for nitrite of 3 mg/L as nitrite (or 0.9 mg/L if reported as nitrite-nitrogen) is based on:

1. no incidence of methaemoglobinaemia at nitrate concentrations below 50 mg/L (as nitrate ion) in drinking-water for bottle-fed infants less than six months of age (assuming body weight of 2 kg)
2. converting 50 mg/L as nitrate to corresponding molar concentration for nitrite
3. multiplying by a factor of 0.1 to account for the estimated conversion rate of nitrate to nitrite in infants where nitrite is formed endogenously from nitrate at a rate of 5–10 percent

4. multiplying by a source allocation factor for drinking-water of 100 percent or 1, as a bottle-fed infant's primary exposure to nitrite is through consumption of formula reconstituted with drinking-water that contains nitrate or nitrite.

As the guideline value is based on the most sensitive subgroup of the population bottle-fed infants less than six months of age), application of an uncertainty factor is not deemed necessary.

Earlier, WHO had stated that animal studies were inappropriate to establish a firm No-Observable-Adverse-Effect Level (NOAEL) for methaemoglobinaemia in rats. Therefore, a pragmatic approach was followed, accepting a relative potency for nitrite and nitrate with respect to methaemoglobin formation of 10:1 (on a molar basis), and a provisional MAV of 3 mg/L had been adopted for nitrite.

Nitrite (long-term)

The long-term MAV had been based on the next paragraph. WHO (2011/2017) now states: "However, owing to the uncertainty surrounding the susceptibility of humans compared with experimental animals, this value which was considered provisional has now been suspended and is being subjected to review in light of evidence on the differences in nitrite metabolism between laboratory rodents and humans".

The 0.2 mg/L (as NO_2^-) MAV in the 2008 DWSNZ (based on WHO 2004) for long-term exposure for chronic effects of nitrite was considered provisional owing to uncertainty surrounding the relevance of the observed adverse health effects for humans and the susceptibility of humans compared with animals. The occurrence of nitrite in the distribution system as a consequence of chloramine use will be intermittent, and average exposures over time should not exceed the provisional MAV. The nitrite MAV (long-term exposure) is based on allocation to drinking-water of 10 percent of JECFA ADI of 0.06 mg/kg of body weight per day, based on nitrite-induced morphological changes in the adrenals, heart and lungs in laboratory animal studies.

Nitrate:Nitrite ratio

Because of the possibility of simultaneous occurrence of nitrite and nitrate in drinking-water, the sum of the ratio of the concentration of each to their short-term MAVs, as shown in the following formula, should not exceed 1:

$$\frac{\mathrm{C(NO_2-)}}{\mathrm{MAV(NO_2-)}} + \frac{\mathrm{C(NO_3-)}}{\mathrm{MAV(NO_3-)}} \leq 1$$

where C = concentration, and MAV = Maximum Acceptable Value.

Note related to short-term MAVs

The short-term MAVs for nitrite and nitrate have been established to protect the health of infants, particularly those that are bottle-fed. Community water suppliers providing drinking-water that exceeds the short-term MAVs will need to find a procedure for advising parents of new-born babies. The WHO (2007) states that in areas where household wells are common, health authorities may wish to take a number of steps to ensure that nitrate contamination is not or does not become a problem. Such steps could include targeting mothers, particularly expectant mothers, with appropriate information about water safety, assisting with visual inspection of wells to determine whether a problem may exist, providing testing facilities where a problem is suspected, providing guidance on disinfecting water or where nitrate levels are particularly high, providing bottled water from safe sources or providing advice as to where such water can be obtained.

The MAV for nitrate in the 1995 and 2000 DWSNZ was 50 mg/L as NO_3^-, and the MAV for nitrite was 3 mg/L as NO_2^-. The 1995 datasheet stated:

> The epidemiological evidence for an association between dietary nitrate and cancer is insufficient, and the MAV for nitrate in drinking-water is established solely to prevent methaemoglobinaemia, which depends on the conversion of nitrate to nitrite. Although bottle-fed babies are the most susceptible, occasional cases have been reported in some adult populations.
>
> As a result of recent evidence of the presence of nitrite in some water supplies, it was concluded that a MAV for nitrite should be proposed. However, the animal studies were inappropriate to establish a firm NOAEL for methaemoglobinaemia in rats. Therefore a pragmatic approach was followed, accepting a relative potency for nitrate and nitrite with respect to methaemoglobin formation of 10:1 (on a molar basis), and a PMAV for nitrite of 3 mg/L is proposed. (The paragraph and formula related to the ratios of each appeared in the 1995 Guidelines as well.)

The Minnesota Department of Health (MDH) has developed health-based rules and guidance to evaluate potential human health risks from exposures to chemicals in groundwater. The chronic health risk limit (exposure greater than 10 percent of a lifetime) for nitrate is 10 mg/L as N.

Bibliography

Addison TM, Benjamin N. 2004. Nitrate and human health. *Soil Use and Management* 20: 98–104.

ANZECC/ARMCANZ. 2000. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. http://www.mfe.govt.nz/publications/water/anzecc-water-quality-guide-02/anzecc-water-quality-guide-02-pdfs.html.

APHA. 2005. *Standard Methods for the Examination of Water and Wastewater* (21st edition). Washington: American Public Health Association, American Water Works Association, Water Environment Federation.

Auckland City. 2016. *Elevated Nitrate Concentrations in Franklin Surface and Groundwater: A review*. Technical Report 2016/015. 93 pp. http://www.aucklandcouncil.govt.nz/SiteCollectionDocuments/aboutcouncil/planspoliciespublications/technicalpublications/tr2016015elevatednitrateconcentrationsfranklinsurfacegroundwater.pdf.

Avery AA. 1999. Infantile methemoglobinemia: re-examining the role of drinking water nitrates. *Environ Health Perspect* 107(7): 583–6. http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1566680/.

AWWA. 1990. *Water Quality and Treatment* (4th edition). Pontius FW (ed). McGraw & Hill.

ESR. 2001. *A Report on the Chemical Quality of New Zealand's Community Drinking Water Supplies*. Client Report FW0120, prepared as part of a Ministry of Health Contract for Scientific Services. 333 pp.

ESR. 2016. *Report on a Survey of New Zealand Drinking-water Supplies for Arsenic and Nitrate*. Client Report FW16030. Prepared by C Nokes and J Ritchie for Ministry of Health. 83 pp.

Environmental Working Group (EWG). Accessed 2010. *National Drinking Water Database: Chemical contaminants*. http://www.ewg.org/tap-water/chemical-contaminants.

Health Canada. 1987. *Guidelines for Canadian Drinking Water Quality – Supporting Documents. Nitrate/Nitrite*. 8 pp. See http://www.hc-sc.gc.ca/home-accueil/search-recherche/a-z-eng.php and http://www.hc-sc.gc.ca/ewh-semt/water-eau/index-eng.php.

IARC. 2005. Ingested nitrates and nitrites. *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans* 94. http://monographs.iarc.fr/ENG/Meetings/index1.php.

IPCS. 1978. Nitrates, nitrites and N-nitroso compounds. *Environmental Health Criteria* 5. INCHEM. International Programme on Chemical Safety. http://www.inchem.org/documents/ehc/ehc/ehc5.htm.

Mattingley BI. 1991. New Zealand Drinking-water Surveillance Programme Data Review, 1983–89. DSIR Chemistry.

MDH. 2009. *Groundwater Values Table*. Minnesota Department of Health (MDH). See: http://www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html.

NHMRC, NRMMC. 2011. *Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy*. Canberra: National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia. 1244 pp. http://www.nhmrc.gov.au/guidelines/publications/eh52.

USEPA (1987, revised 1991). *Nitrate. Integrated Risk Information System (IRIS)*. See: http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.showSubstanceList see also: http://www.epa.gov/iris/subst/0076.htm.

USEPA 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography. 1999. See http://water.epa.gov/scitech/drinkingwater/labcert/methods_index.cfm.

USEPA (1987, revised 1997). Nitrite. *Integrated Risk Information System (IRIS)*. See: http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.showSubstanceList see also: http://www.epa.gov/iris/subst/0078.htm.

USEPA. 2009. *2009 Edition of the Drinking Water Standards and Health Advisories*. Washington, DC: US Environmental Protection Agency. EPA 822-R-09-011. 18 pp. Available at: http://water.epa.gov/action/advisories/health_index.cfm.

USEPA. 2011. *2011 Edition of the Drinking Water Standards and Health Advisories*. Washington, DC: US Environmental Protection Agency. Available at: http://water.epa.gov/action/advisories/health_index.cfm or www.epa.gov/waterscience/.

Walton G. 1951. Survey of literature relating to infant methemoglobinemia due to nitrate-contaminated water. *Am J Public Health* 41: 986–96. Some details quoted in http://www.worh.org/files/AgHealth/envi.pdf.

WHO. 1985. *Health Hazards from Nitrates in Drinking-water*. Report on a WHO meeting. Copenhagen: WHO Regional Office for Europe.

WHO. 1993. *Guidelines for Drinking-water Quality* (2nd edition). Geneva: World Health Organization. Volume 1: Recommendations.

WHO. 2004. *Guidelines for Drinking-water Quality* (3rd edition). Geneva: World Health Organization. Available at: http://www.who.int/water_sanitation_health/dwq/gdwq3rev/en/ see also the addenda.

WHO. 2007. Nitrate and nitrite in drinking-water. *Background Document for Preparation of WHO Guidelines for Drinking-water Quality*. Geneva: World Health Organization (WHO/SDE/WSH/07.01/16). http://www.who.int/water_sanitation_health/dwq/chemicals/nitratesnitrite/en/index.html.

WHO. 2011. *Guidelines for Drinking-water Quality* 2011 (4th edition). Geneva: World Health Organization. Available at: http://http://www.who.int/water_sanitation_health/publications/drinking-water-quality-guidelines-4-including-1st-addendum/en/index.html.

WHO. 2016. Nitrate and nitrite in drinking-water. *Background Document for Preparation of WHO Guidelines for Drinking-water Quality*. Geneva: World Health Organization WHO/FWC/WSH/16.52. 41 pages. http://www.who.int/water_sanitation_health/dwq/chemicals/nitrate-nitrite-background-jan17.pdf.

WHO. 2017. *Guidelines for Drinking-water Quality: Fourth edition incorporating the first Addendum.* Geneva: World Health Organization. 631 pp. http://www.who.int/water_sanitation_health/publications/drinking-water-quality-guidelines-4-including-1st-addendum/en/.

WRF. 2016. *Pilot Testing of Nitrate Treatment Processes with Minimal Brine Waste*. Project #4578. Denver, Colo.: Water Research Foundation. 174 pp. http://www.waterrf.org/Pages/Projects.aspx?PID=4578