Waikato Regional Council Technical Report 2022/45

REGEMP II Regional geothermal geochemistry monitoring interpretation 2022

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

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September 2022

Document #: 24602703

Peer reviewed by:
Chris Eager Date September 2022

Approved for release by:
Michelle Begbie Date September 2022

Verum Group

Regional monitoring geothermal interpretation

Prepared for
Waikato Regional

August 2022
J000009

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Client address	Waikato
Distribution (other than client)	none
Date of Issue	7th September 2022

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Document tracking

Version	Date	Changes made	Reviewer(s)
1	19/8/22	Minor	NN
2	26/8/22	Minor	KL
3	30/8/22	Review meeting	JP/KL

Contents

1. Scope and Introduction

Waikato Regional Council collect monitoring data on geothermal features in the Waikato Area and compile the data into a database REGEMP. This data base contains about 2393 analyses of geothermal features with variable analytical suites included. The author has been asked to deliver a regional interpretation of the data including identification of spatial or temporal changes, variation or continuity within the dataset.

The purpose of the review is to:

- Provide regional geochemical interpretation.
- Identify geothermal features or anomalies within the dataset that might be important for future sampling plans.
- Identify other geochemical datasets that would be useful for integration in this database and might strengthen interpretations.
- Identify other data sources that might improve interpretation.

2. Methods

2.1 Background

This review is a desktop study of a data base provided by Waikato Regional Council (REGEMP), publicly available and published literature that the authors find relevant. Raw analysis data have been preserved in mass based chemical concentration units for reporting most dissolved components (mg/L) because stoichiometric relationships are not required for most of the interpretations made in this report. Plotting of data used Sigma Plot and Microsoft Excel software. Where analyte concentrations fell below detection limits, a value of half the detection limit was used where practicable, however due to differences in detection limits across the analytical methods that have been used in the database, this could introduce some bias. For data that is plotted using logarithmic axis, all values that fell below detection limits have been excluded.

Geothermal geochemistry is best interpreted directly on geothermal discharges such as springs and fumaroles. Interpretation of samples from streams that include geothermal components is less certain of overprints from geochemical or biogeochemical processes that are specific to the earth’s surface. This might also include climate and rainfall effects, adjacent land uses such as agriculture or forestry and the effects of infrastructure such as road or hydrothermal developments. The REGEMP dataset had been split into springs and streams based on the authors interpretation of sample site descriptions with streams removed from interpretation.

The geothermal features that have been studied were divided into three regions based on their locations. The points below 38.9439 °S were designated as the Tongariro region, the North Waikato included features north of 38.063. The Taupo Volcanic Zone was determined to be between these two regions, and also included the Hells Gate systems north of Rotorua (Figure 1).

The authors has previously completed a study of variability of geothermal features for the Waiotapu Geothermal field including spatial and temporal trends. The findings of this study are used for comparison to the regional dataset supplied that is available for this report. This study can provide context for the variability that occurs within a small part of the region compared to the variability included in the REGEMP dataset.

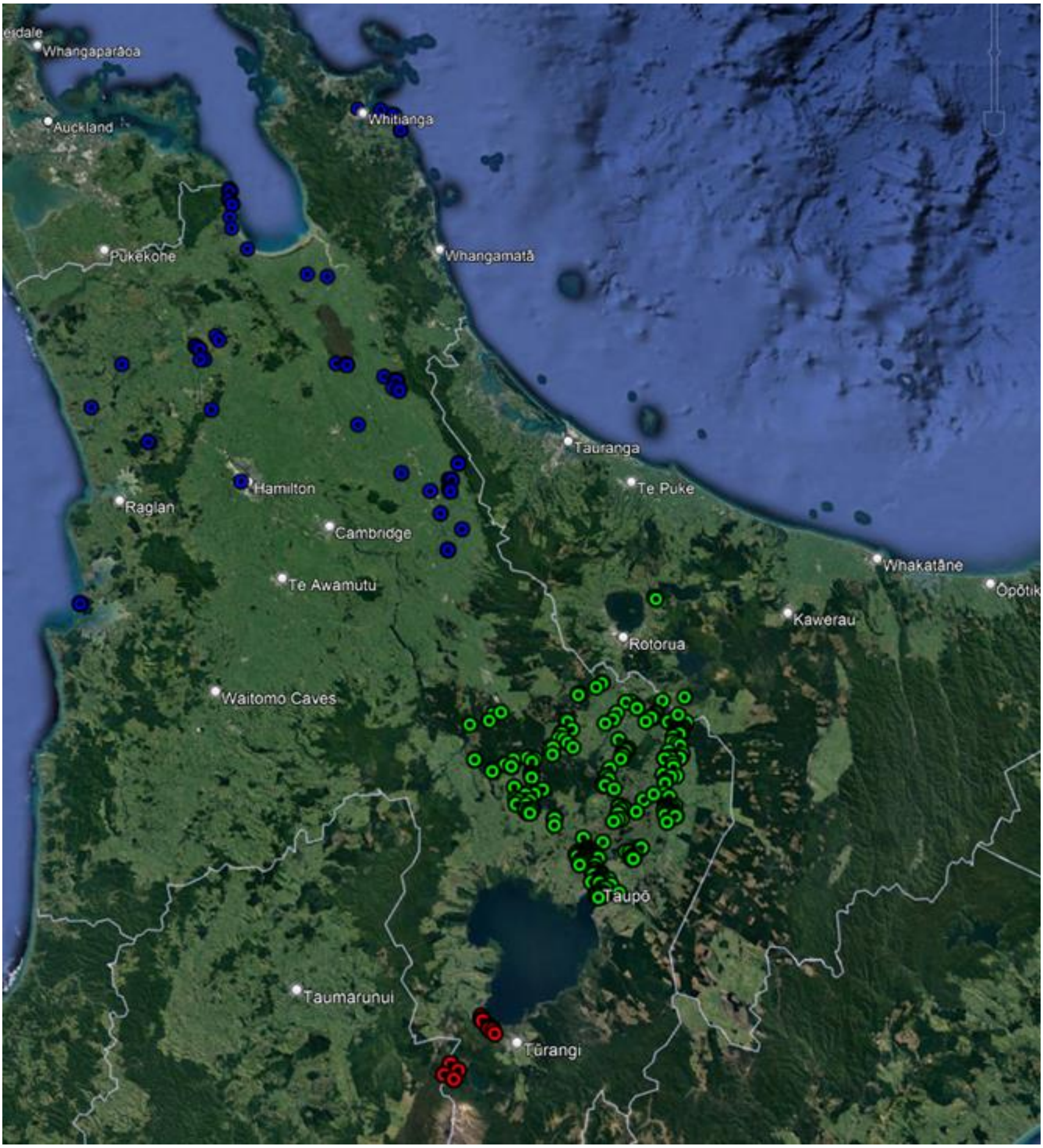


Figure 1: Map of REGEMP database sample locations made using Google Earth. Colours reflect the region the sites were attributed to: blue = North Waikato, green = Taupo Volcanic Zone, red = Tongariro.

3. Results – Regional interpretations

3.1 Introduction

Geothermal systems in the Waikato region have a magmatic heat source related to the Taupo Volcanic zone and develop in the upper 1-2 km of the crust. The magma discharges volatiles and entrains local groundwater into a convection system and delivers upwelling of hydrothermal fluids to the upper portions of the crust, and often to the earths surface as discharges of water or gas (Henley & McNabb, 1978; Eastoe & Guilbert, 1992). Typically the dissolved concentrations of components in geothermal fluids are derived from the crustal rocks through which the mobilized fluids travel (Ellis & Mahon 1967). As the fluids ascend they cool through conductive or adiabatic processes. Where boiling occurs, a gas/steam phase separates from the residual hydrothermal fluid and can migrate to the surface separately (Henley, 1984; Nicholson, 1993).

3.2 Major anion geo-chemistry: Cl^- - HCO_3^- - SO_4^{2-}

The major anions in geothermal systems are usually Cl^- SO_4^{2-} and HCO_3^-. The concentrations of these components can range through several orders of magnitude (Table 1) and are controlled by two main factors.

1. Source water. Most geothermal systems in New Zealand are sourced from deep terrestrial groundwater with some input from volatiles that escape magma in volcanic areas (Henley & McNabb, 1978). Some geothermal systems have seawater or brines included in the source fluids.
2. Geothermal processes. Anion concentrations are controlled by processes that occur as hydrothermal fluids ascend. Chloride is conservative, it remains dissolved in the hydrothermal liquid phase becoming residually enriched as steam is separated through boiling. SO_4 and HCO_3^- mostly arise from gas phases (H_2S, SO_2 and CO_2) that preferentially separate into the steam and gas phase during boiling. If the steam phase interacts with anoxic shallow groundwater H_2S and HCO_3^-/CO_3^{2-}, rich springs occur. If the steam and gas phase interacts with oxygenated shallow groundwater then SO_4 rich springs occur. If the steam phase does not interact with shallow groundwater then fumaroles occur (Henley, 1984; Nicholson, 1993).

Coastal geothermal systems in New Zealand can also be influenced by seawater. Webster-Brown and Brown (2007) concluded that geothermal systems at Kawhia and on the Coromandel Peninsula had seawater contributing to the elevated Na, Cl, Mg, K and SO_4 concentrations that were observed. This was also observed in the current dataset, and the Kawhia system has been considered separately in the following tables.

Component	REGEMP	n=758 (exc. Kawhia)		Kawhia	n=5		Waiotapu	n=155	
	Cl^-	HCO_3^-	SO_4^{2-}	Cl^-	HCO_3^-	SO_4^{2-}	Cl^-	HCO_3^-	SO_4^{2-}
Maximum	6,585	7700	1952	11540	93	724	2198	1360	2790
Minimum	<5	<1	<1	8700	40	210	3	0	3.5
Mean	739	560	94	9844	64	486	695	162	276
Median	320	145	41						

Table 1. Maximum, minimum and mean concentrations of major anions in REGEMP, Kawhia and Waiotapu (after Pope and Brown 2014). The range of concentrations in major anions is larger in REGEMP than the range of concentrations that are found in a single geothermal field. Repeat sampling of features with neutral chloride chemistry in all datasets skews the average concentration data toward higher Cl.

Plots of the major anion data on a ternary diagram (Figure 2) indicate strong regional trends in the dataset. The data from the Central TVZ plots in all parts of the ternary diagram indicating geothermal features of any composition are possible. Data from the North West area are almost all concentrated along the Cl-HCO_3 axis of the anion diagram with very few springs containing significant proportions of SO_4. Data from the Tongariro area are mostly concentrated along the Cl-HCO_3 axis of the diagram with a subset of samples showing mixed Cl-SO_4 composition.

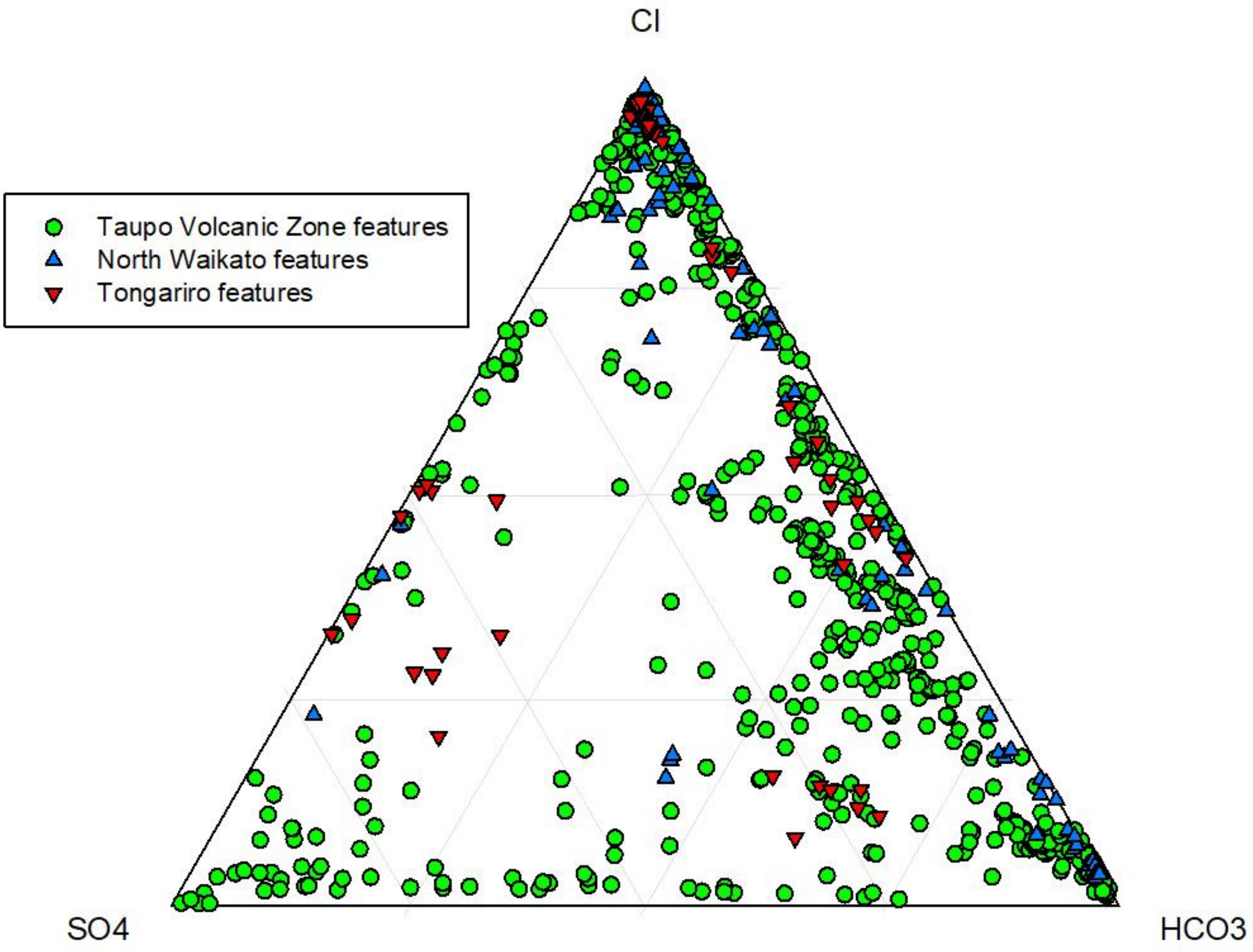


Figure 2. Regional major anion ternary plot. Ternary diagrams of this type are developed from anion proportionality and mass-based concentration units.

Assuming there is no bias in the sampling these regional trends probably indicate that there are different source water characteristics in the North West region compared to the Central TVZ and Tongariro areas. Central TVZ and the Tongariro regions can be linked to specific active volcanic centers, whereas in the North West area the geothermal activity is further from active volcanism. It is possible that the main source of S in geothermal systems is magmatic and this is less abundant in geothermal systems that are more distal to volcanic activity. CO_2 rich fluids are often referred to a 'peripheral' when considering a particular geothermal field, and this applies in a regional sense for the entire TVZ compared to NW geothermal systems.

Further subdivision of the dataset available to the Waikato Regional Council into geothermal fields indicates that spatial trends and patterns in major anion geochemistry are characteristic for different fields but overlap (Figure 3).

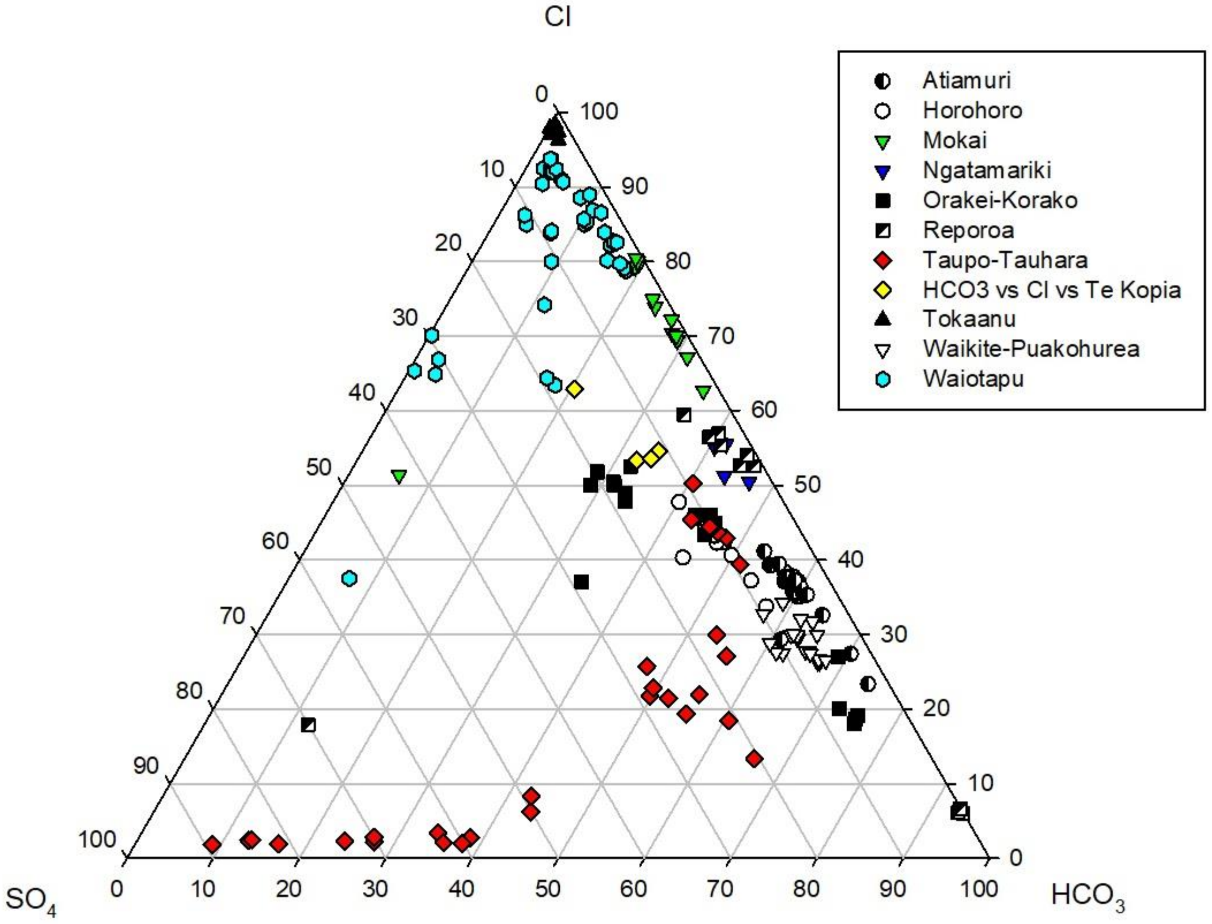


Figure 3. Selected REGEMP data plotted by geothermal field. Duplication of samples from the same spring is included in this dataset.

Major anion data for the Waiotapu district (Figure 4) that includes one large geothermal field (Waotapu) and several small geothermal fields (Reporoa, Waikiti and Golden Springs) also indicates that the major anion ratios can be characteristic for different areas. In general the springs in the main Waiotapu geothermal area plot along the Cl-SO_4 axis of the diagram while water from smaller fields close by plot in different positions along the Cl-HCO_3 axis of the diagram. Comparison of the REGEMP dataset to the Waiotapu dataset also indicates two main features:

1) The REGEMP dataset is biased away from sampling of acid sulphate springs. Springs with pH < 4.5 plot on the Cl-SO_4 axis because HCO_3 reacts to form CO_2 below this pH. The Waiotapu dataset shows that there can be many low pH springs in natural geothermal systems, however the REGEMP dataset does not contain many of these types of springs.
2) The REGEMP dataset contains a group of features that plot along the SO_4-HCO_3 axis. These features are likely to contain mixed geothermal fluid types and probably include samples from small streams draining geothermally active areas or springs where subsurface processes are

complex. Where these samples represent small streams the chemistry could be influenced of surface processes such as climate, rainfall, farming forestry or infrastructure.

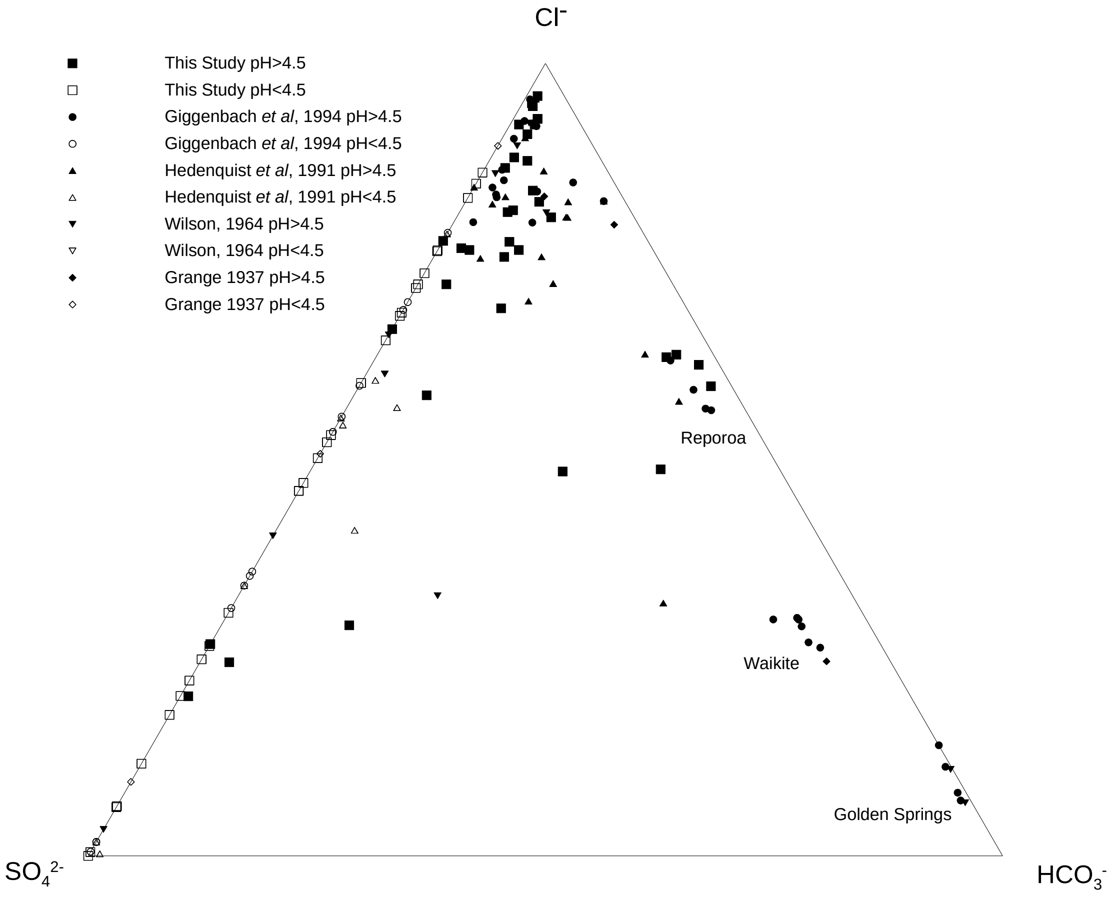


Figure 4. Waiotapu major Anion plot (from Pope and Brown 2014)

Recommendations: Waikato Regional Council complete further analysis of major anion trends to:

1. Investigate if there is a consistent change in geothermal system source fluid or spring chemistry in the North West compared to the Tongariro and Central TVZ.
2. Can major anion chemistry be used to further classify and distinguish geothermal fields and does this add interpretive value for the dataset.
3. Consider re-assessing the sampling sites to include more acid sulphate springs. Overall the dataset is seems low on acid sulphate springs, in contrast to a relatively complete dataset collected for Waiotapu.
4. Investigate in detail the origin of samples that plot with mixed SO_4 and HCO_3. It is likely that some of these features are small streams and therefore monitoring these sites includes variation from the surrounding surface environment (climate, farming, forestry, roads) as well as geothermal variations.

3.3 Major Cation Geochemistry: Na, K, Ca and Mg

The alkaline earth and alkali metals, Na, K, Ca and Mg, are usually considered the major cations in geothermal systems. Although, sometimes other cations can be much more abundant. Most cations, metals and metalloids in geothermal systems are sourced through leaching and alteration of reservoir host rocks. In general, as geothermal fluids rise out of reservoir zones additional leaching of cations is less likely because fluids cool through adiabatic or conductive processes. Thus boiling (separation of volatile phases and residual enrichment of dissolved components) and precipitation of secondary minerals become the most likely processes affecting fluid chemistry after it leaves the reservoir.

Component	Regemp	n=1333		Kawhia	n=5		Waiotapu	n=155	
	Na	K	Mg	Na	K	Mg	Na	K	Mg
Maximum	4675	610	215	4290	200	350	1214	164	44000
Minimum	3.3	0.2	<0.005	3200	90	123	11	2.8	6.2
Mean	526	64	4.3	3771	140	238	446	43.7	1505
Median	225	20	1.89						

Table 2. Maximum, minimum and mean concentrations of major cations in REGEMP, Waiotapu (after Pope and Brown, 2014). The range of concentrations in major cations across the REGEMP database is greater than the range of concentrations that are found in at the single geothermal field Waiotapu, however the variation across 3 orders of magnitude at Waiotapu adds context to the variability across the region.

For these major cations, silicate minerals such as the feldspar, mica, carbonate and clay mineral groups are most likely to control concentration (Giggenbach, 1988). Thermodynamic evaluation of the solubility of these groups of minerals under hydrothermal conditions (~100-320°C) led to the formation of geothermometry relationships so that geothermal reservoir temperatures can be calculated by analysis of major cation concentrations in some springs. There are many geothermometry relationships proposed with different applicability and strengths and weaknesses under different geothermal regimes (refs).

Cation concentrations in springs are suitable for geothermometry if they preserve equilibrium with respect to minerals such as albite, adularia (feldspars) muscovite, quartz, chlorite, calcite. The mineral systems that are commonly equilibrated in deep reservoirs in New Zealand geothermal systems include albite, adularia, muscovite, and chlorite. This system has been identified through core samples collected geothermal reservoir zones. For these minerals, the concentrations of Na, K are likely to reflect the deepest part of the reservoir because albite and adularia are only likely to be at equilibrium at high temperature. Mg and Ca could equilibrate with chlorite or calcite at lower temperature.

Geothermometry relationships for the Na, K, Mg system (Giggenbach, 1988) in equilibrium with albite, adularia, muscovite and chlorite can be summarized on a ternary diagram (Figure 5). The REGEMP dataset indicate that most springs are undersaturated with respect to cation geothermometers. This is not surprising because only springs that cool adiabatically (boiling) will preserve mineral equilibrium conditions from the geothermal reservoir. Samples that plot between the full equilibrium line and the partial equilibrium line are likely to preserve information from the geothermal reservoir in the ratios Na, K and Mg. Samples that plot toward the Mg apex of the diagram are not appropriate for geothermometry interpretation and represent dilute geothermal fluids.

A Na, K, Mg cation geothermometry plot for the REGEMP data (Figure 5) shows that most samples are undersaturated with respect to albite, adularia, chlorite and muscovite, because they fall beneath the equilibrium line. This plot also shows regional trends in the cation geothermometry data, Taupo volcanic zone cations plot throughout the diagram indicating multiple reservoirs occurring at different temperatures, Tongariro reservoir temperatures cluster toward the hot end of the Ternary diagram and North Waikato samples plot with a moderate temperature.

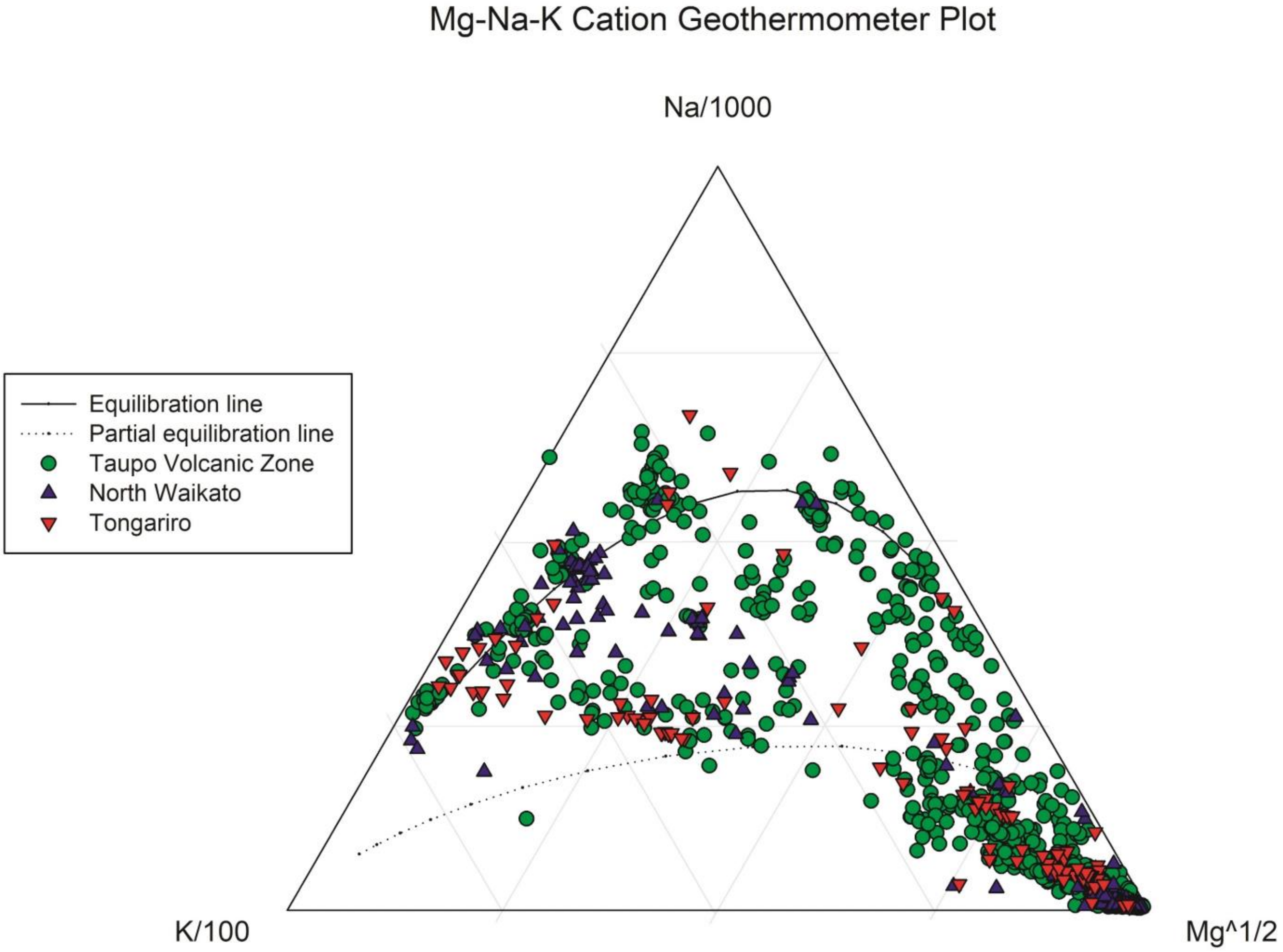


Figure 5. Regional ternary plot of K-Na-Mg. The full equilibrium line reflects concentrations of Na-K-Mg with respect to albite-adularia-muscovite-chlorite. Partial equilibrium line indicates maximum dilution by Mg rich water where Na-K geothermometry remains applicable. Ternary diagrams of this type are developed from cation concentrations expressed proportionality from mass-based units (mg/L).

In comparison to Waiotapu Na, K, Mg geothermometry (Figure 6) REGEMP data shows trends for low temperature equilibrium conditions in some reservoirs and also trends in samples that plot above the full equilibrium line. Samples that plot above the equilibrium line were first identified by Hedenquist (1989) and confirmed by Pope and Brown (2014) and relate to Mg depletion in reservoirs compared to equilibrium with chlorite. REGEMP data indicate there is a trend in this Mg depletion with respect to Chlorite and therefore probably mineralogical control of the Na, K, Mg contents of these samples. It is unclear what mineral might cause this, possibly chloritoid (Pope and Brown, 2014).

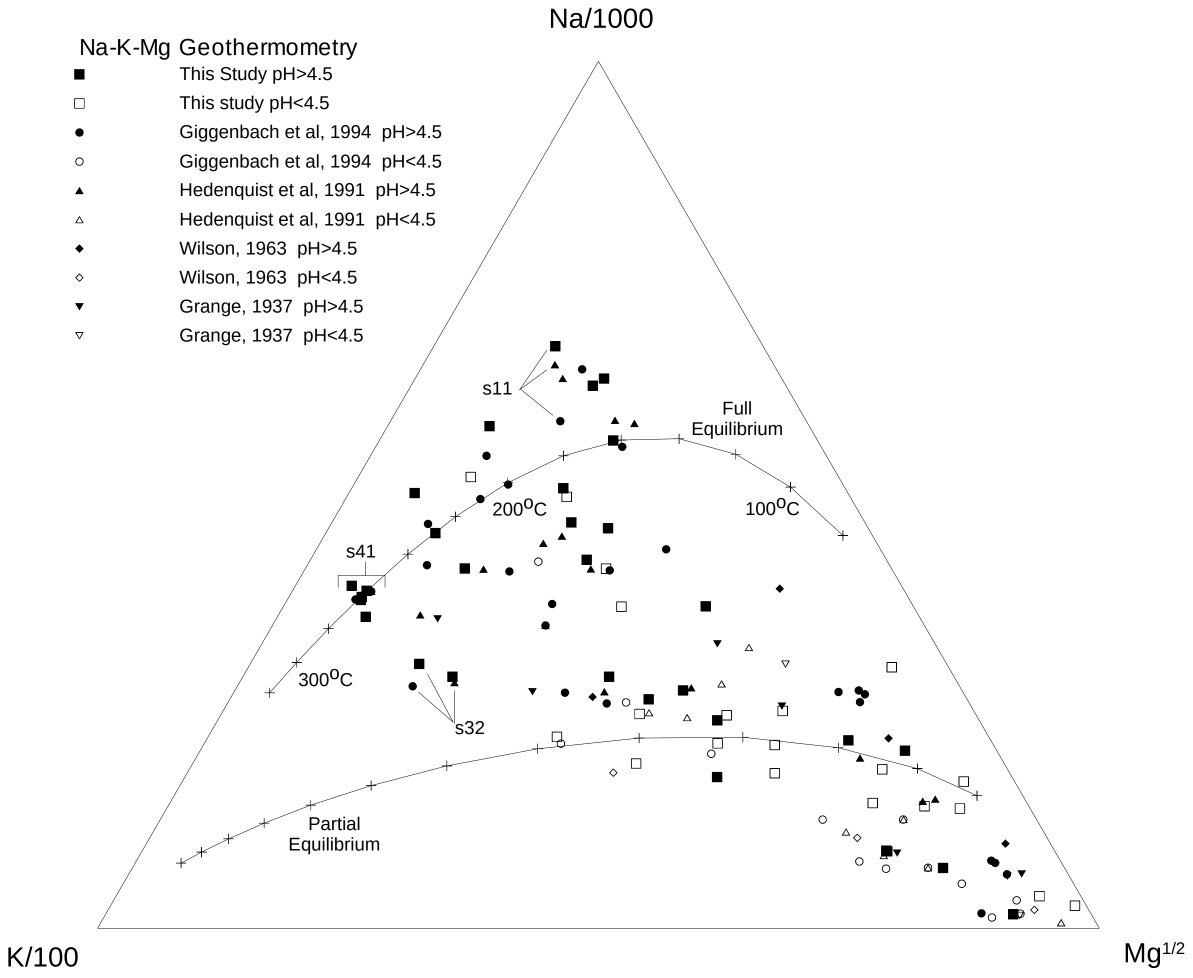


Figure 6. Ternary plot of Na-K-Mg plot for the Waiotapu Geothermal field (after Pope and Brown 2014).

The data presented for Waiotapu shows clustering of springs where cation chemistry is relatively stable. However, it also shows the limit of geothermometry for assessing reservoir temperature from a small sample set. The temperature range for samples that plot close to the full equilibrium line is between 160 and 260°C.

Analysis of the Na, K and Mg concentrations in selected springs from REGEMP (Figure 7) indicates that individual geothermal features show two types of chemical pattern through time.

1. Strong clustering occurs at hot springs with stable chemistry for example Mokena Geyser, Champagne Pool, and MK3.
2. Variation in chemistry with samples plots on a linear trend toward the Mg apex of the diagram such as Waipumahana, Manaroa Pool and Manganese Pool.

Variation in chemistry parallel to the Na-K axis of the diagram at individual features is much lower than toward the Mg axis. This indicates that most variation in individual spring chemistry comes from changes in the dilution by mixing with ground water.

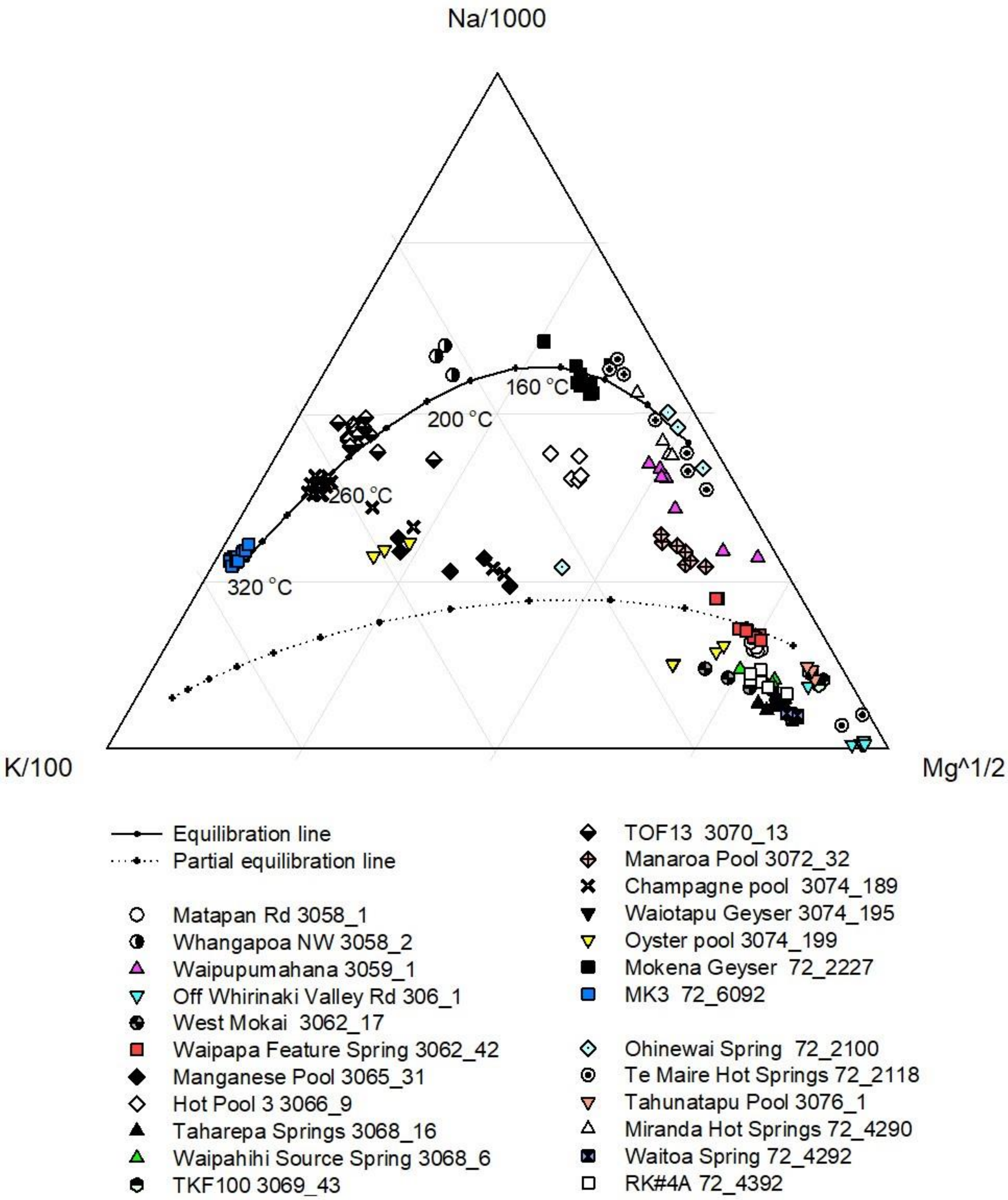


Figure 7. Plot of K-Na-Mg for selected springs throughout the REGEMP dataset

Recommendation: Waikato Regional Council complete further analysis of major cation trends to:

1. Investigate if there is a mineralogical reason for a suite of samples to plot above the full equilibrium line and in a position that is depleted in Mg compared to equilibrium with Chlorite.
2. Investigate the dilution trends that occur in regional data and spring specific data.

4. Results – Temporal trends

4.1 Introduction

Springs where there are multiple analyses over time enable assessment of the stability of geothermal geochemistry or trends in chemistry with time. We assessed the major cation and anion chemistry of 20 springs with the longest monitoring periods and have selectively presented this data below. There are additional datasets for other geothermal features that could be presented in this manner if required. Monitoring periods range up to 117 years for Mokena Geyser. Trends with time are variable, some springs have stable chemistry, some springs show gradual changes with time while other springs have step changes. The datasets span several generations in analytical technologies and sampling procedures and there is related uncertainty within the datasets. We have not tried to quantify analytical uncertainty. Springs with both stable chemistry and variable chemistry are presented. The dataset is presented with elapsed time since first sampling along the x axis and all graphs are aligned so that the time scale can be read from the pH Graph for all subsequent cation and anoin graphs at each feature.

4.2 Springs with temporal changes in chemistry

Waipahihi (3068_6)

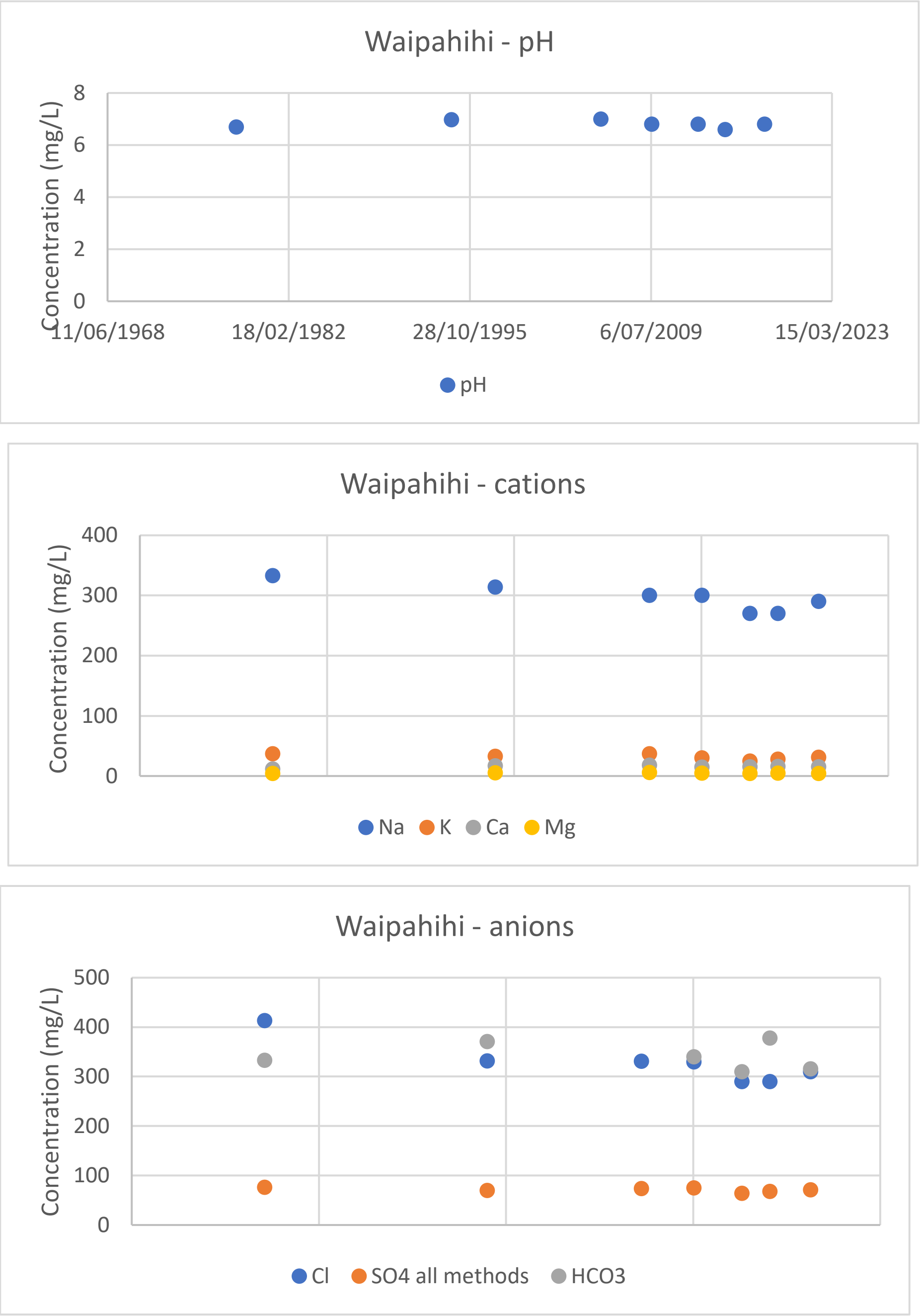


Figure 8 Trends in concentration of components at Waipihihi

Waipahihi has one of the strongest trends in the geothermal dataset collected. Strong downward trends in Cl and Na indicate decreasing component of deep geothermal fluid at this spring. Geothermal extraction is does not cause this trend (pers. Comm. Katherine Luketina WRC) and so this appears to be natural change in spring chemistry with time. Taharepa spring is close to Waipahihi but this spring has stable chemistry (Figure 22).

Manaroa pool (3073_32)

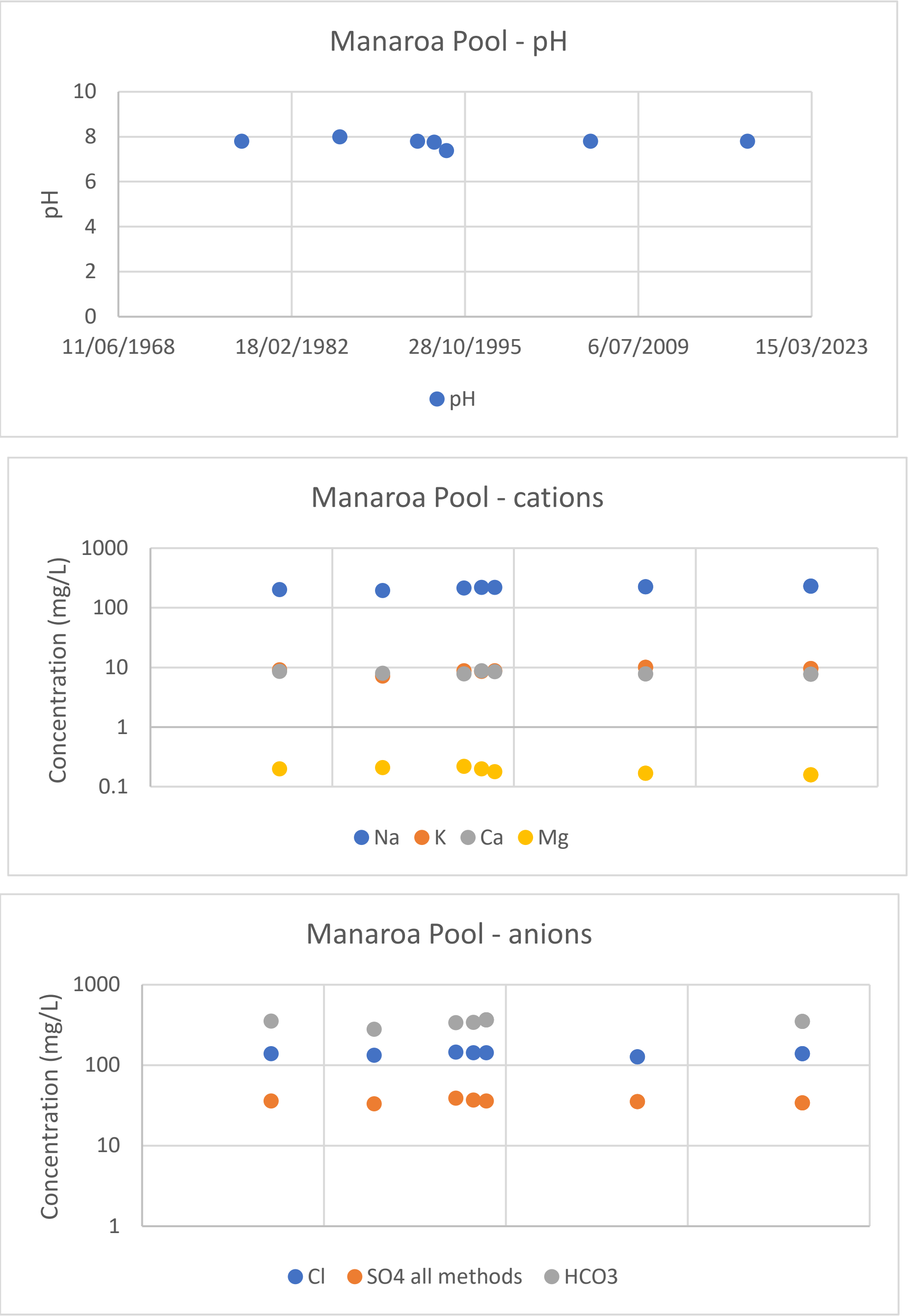


Figure 9 Trends in concentration of components at Manoroa Pool

Manoroa Pool has a subtly increasing trend in Na concentration and decreasing concentration of Mg.

Whangapoa SE Pool (3058_3)

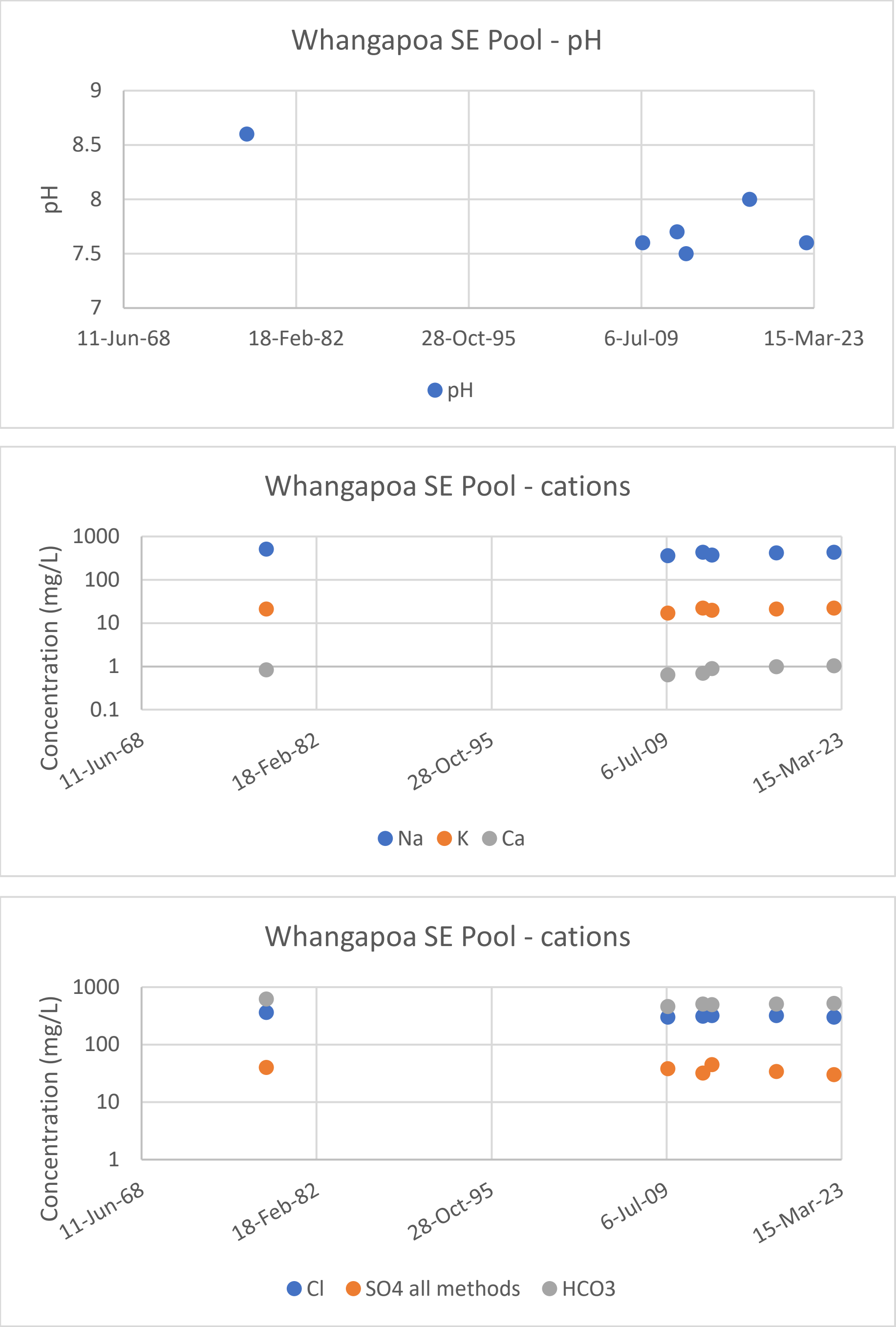


Figure 10 Trends in concentration of components at Whangapoa SE Pool

Whangapoa Pool South East has a sharp decrease in pH between an early sample in 1978 and more recent samples. Other major component concentrations are relatively stable.

Whangapoa NW Pool (3058_2)

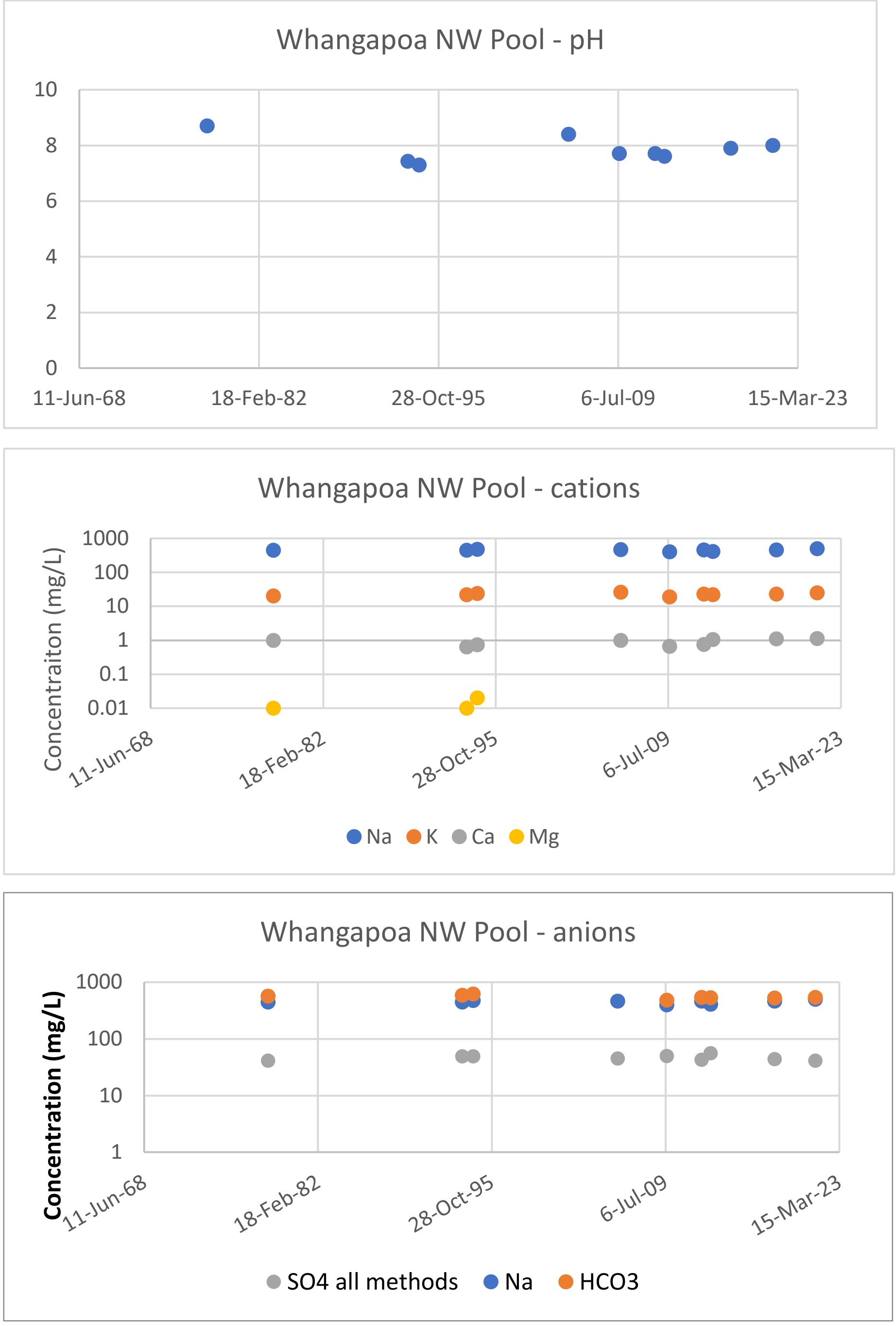


Figure 11 Trends in concentration of components at Whangapoa NW Pool

Whangapoa Pool North West has a sharp decrease in pH between an early sample in 1978 and more recent samples. Other major component concentrations are stable. Forestry activity, landuse changes, and restoration projects over the last ~ 30 years adjacent to the pool could influence chemistry (Pers. Comm. K. Luketina, 2022).

Champagne Pool (3074_189)

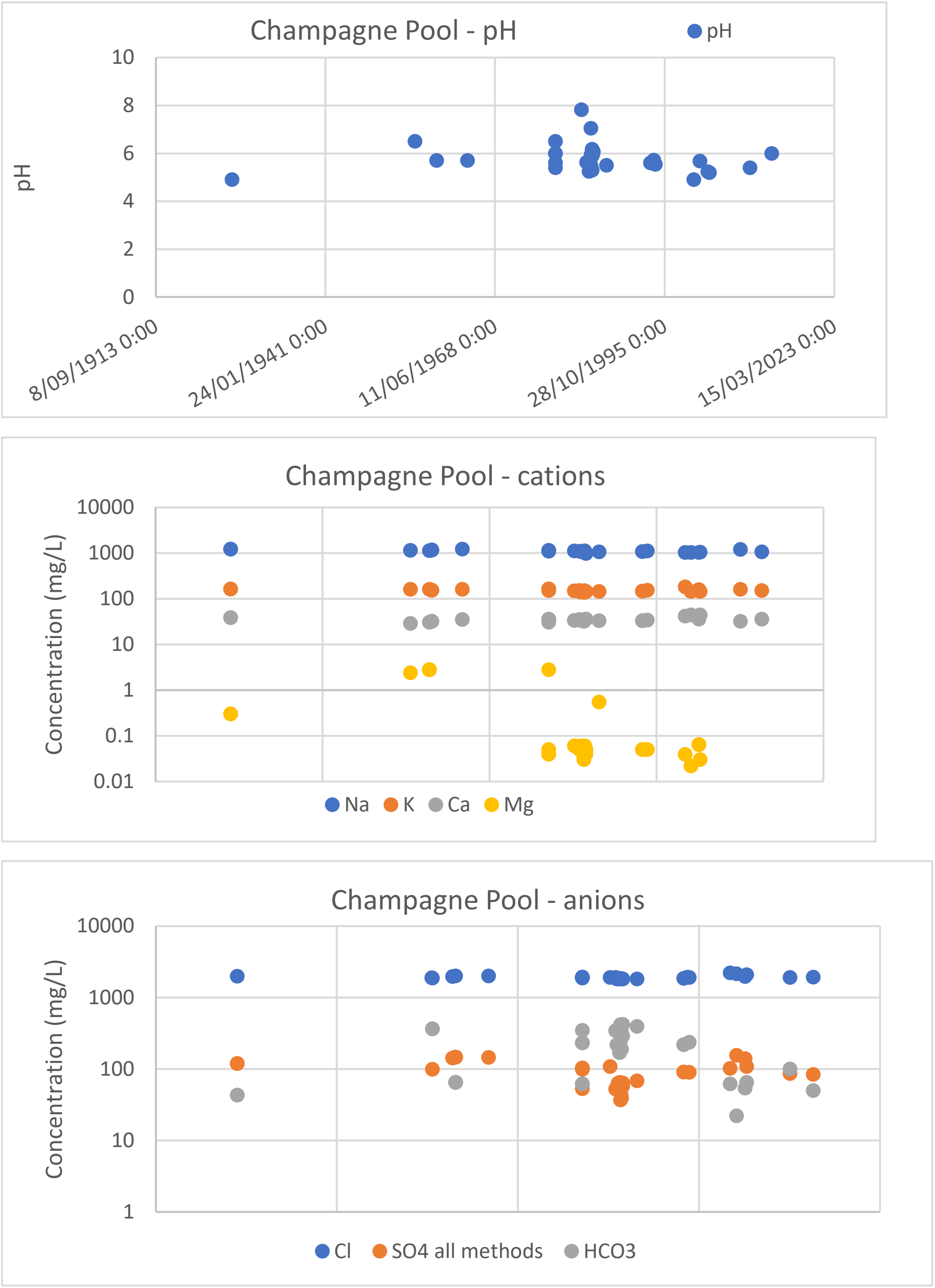


Figure 12 Trends in concentration of components at Champagne Pool

Champagne Pool has variable chemistry, pH varies between about 4.9 and 8. Sulphate and bicarbonate concentrations are also variable. The Mg concentration reduces sharply downward since about the 1990s. This chart includes several data points that are not in the REGEMP database published in (Pope and Brown, 2014) springs.

Waiotapu Geyser (3074_195)

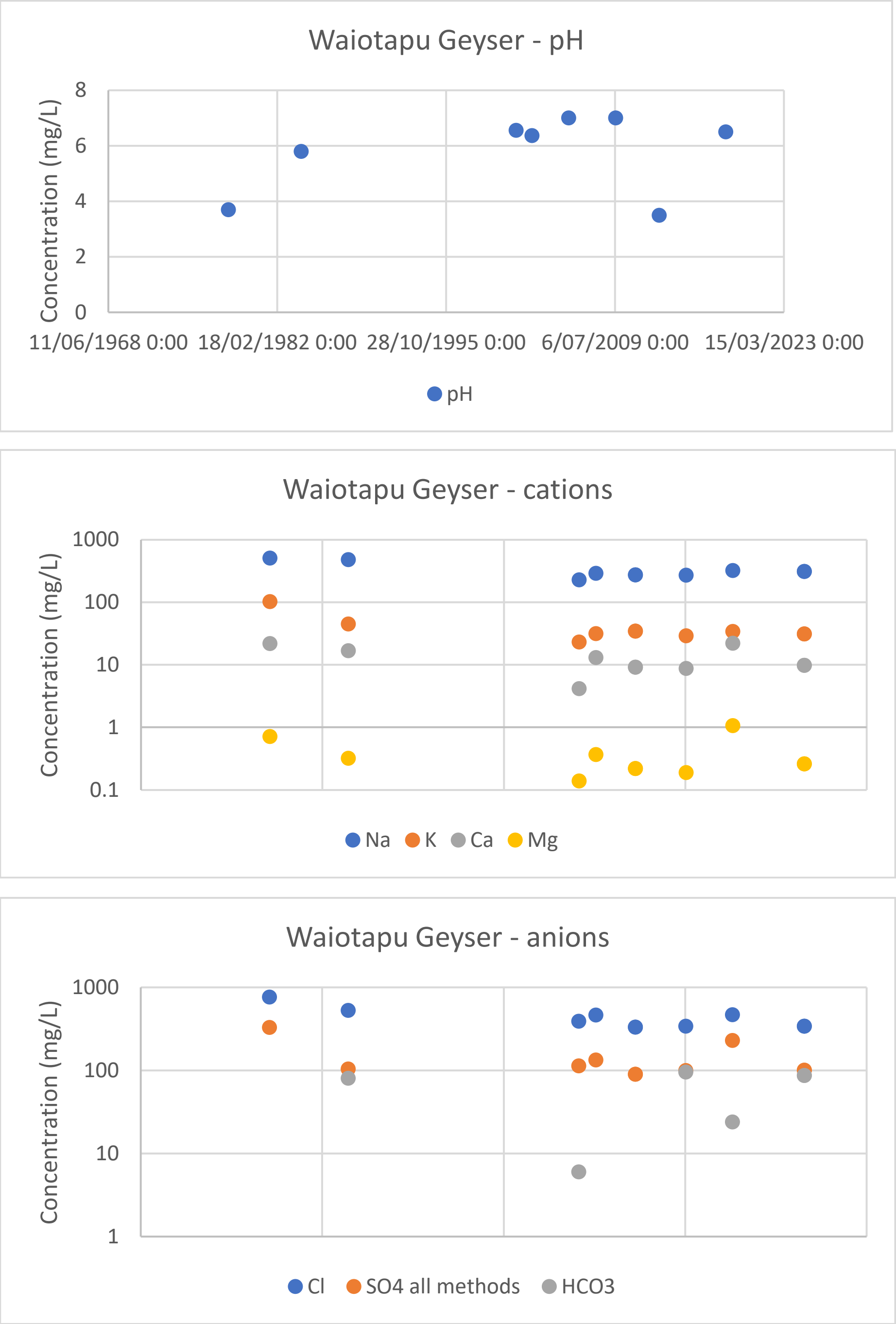


Figure 13 Trends in concentration of components at Waiotapu Geyser

Waiotapu Geyser has the most variable chemistry of all spring sampled, pH ranges from strongly acidic, <4 to >7. The concentrations of cations are variable, especially Ca and Mg which change by about an order of magnitude. The concentrations of anions is also variable especially bicarbonate which varies by more than an order of magnitude. There are no trends in the Waiotapu Geyser dataset to date.

Oyster Pool (3074_199)

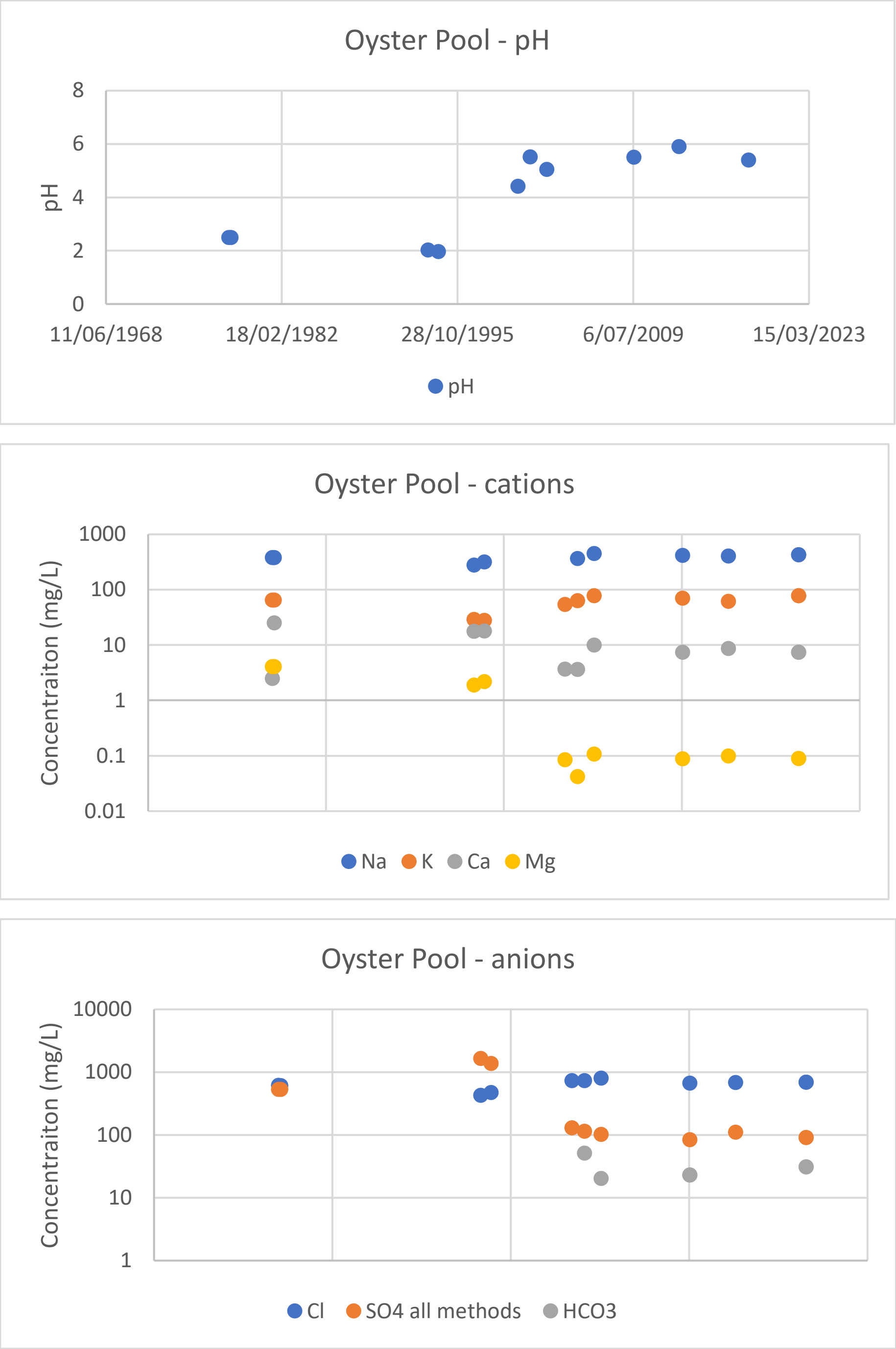


Figure 14 Trends in concentration of components at Oyster Pool 3

Oyster pool has the strongest step change in chemistry of all the springs where data is available. The pH increases from about 2 to >5. Cation concentration have a similar step change with K increasing and Ca decreasing. Similarly anion concentrations change with SO4 decreasing and Cl increasing. The oyster pool chemistry changes from acid sulphate to neutral chloride during the monitoring period.

Waipupumahana Pool (3059_1)

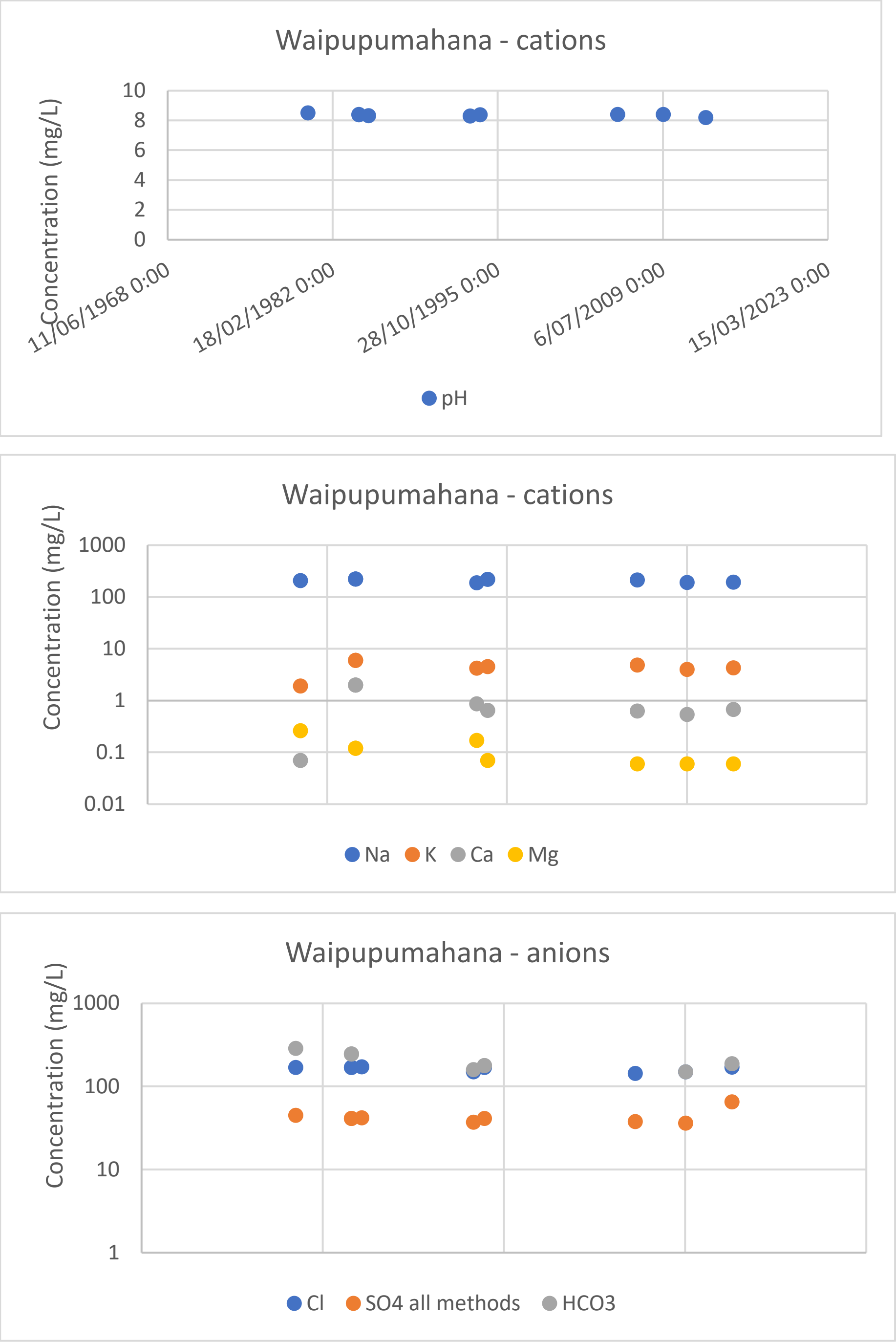
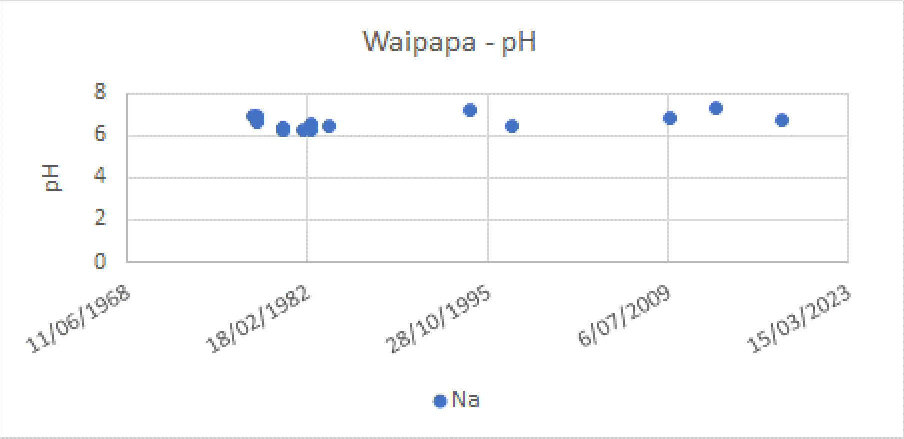
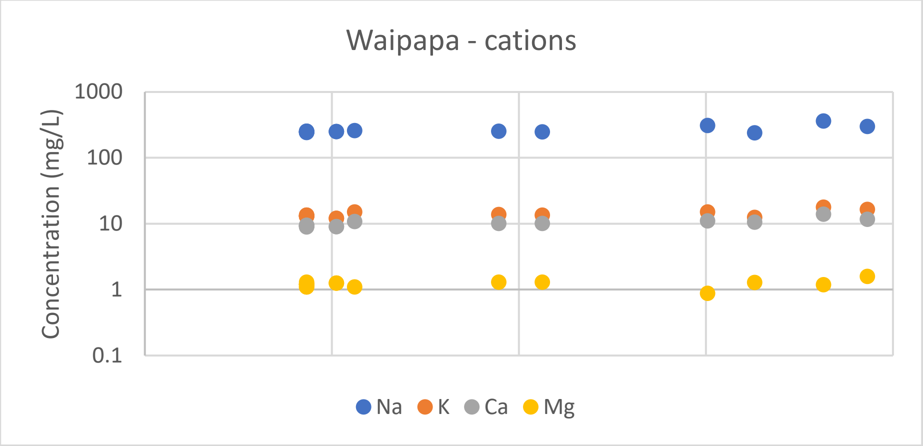


Figure 15 Trends in concentration of components at Waipupumahana

At Waipumahana, the concentrations of Ca, Mg and K vary by about an order of magnitude throughout the sampling period. In addition the concentration of bicarbonate decreases with time.

Waipapa NW Pool (3062_42)





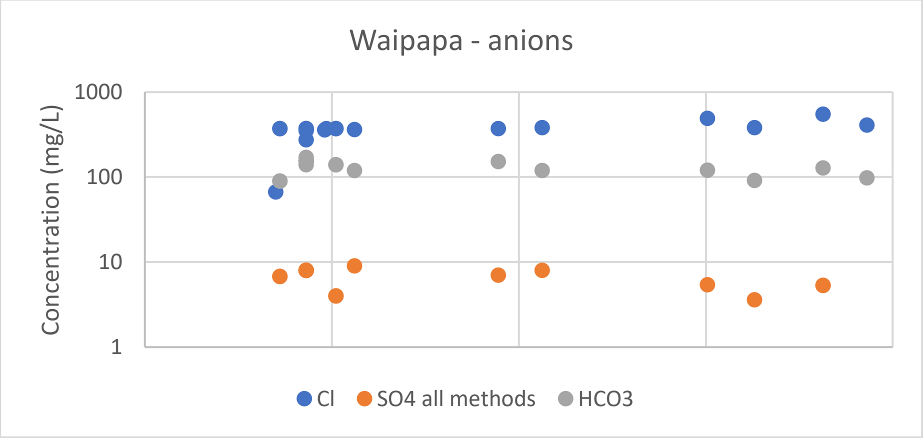


Figure 16 Trends in concentration of components at Waipapa

Waipapa shows large changes in pH and variation in anion concentrations with time. There is no trend in the data collected to date, just variation. Adjacent landuse changes might cause some of the variation in chemistry observed in this spring (Pers. Comm. K. Luketina, 2022).

Reporoa Hot Pool 3 (3066_9)

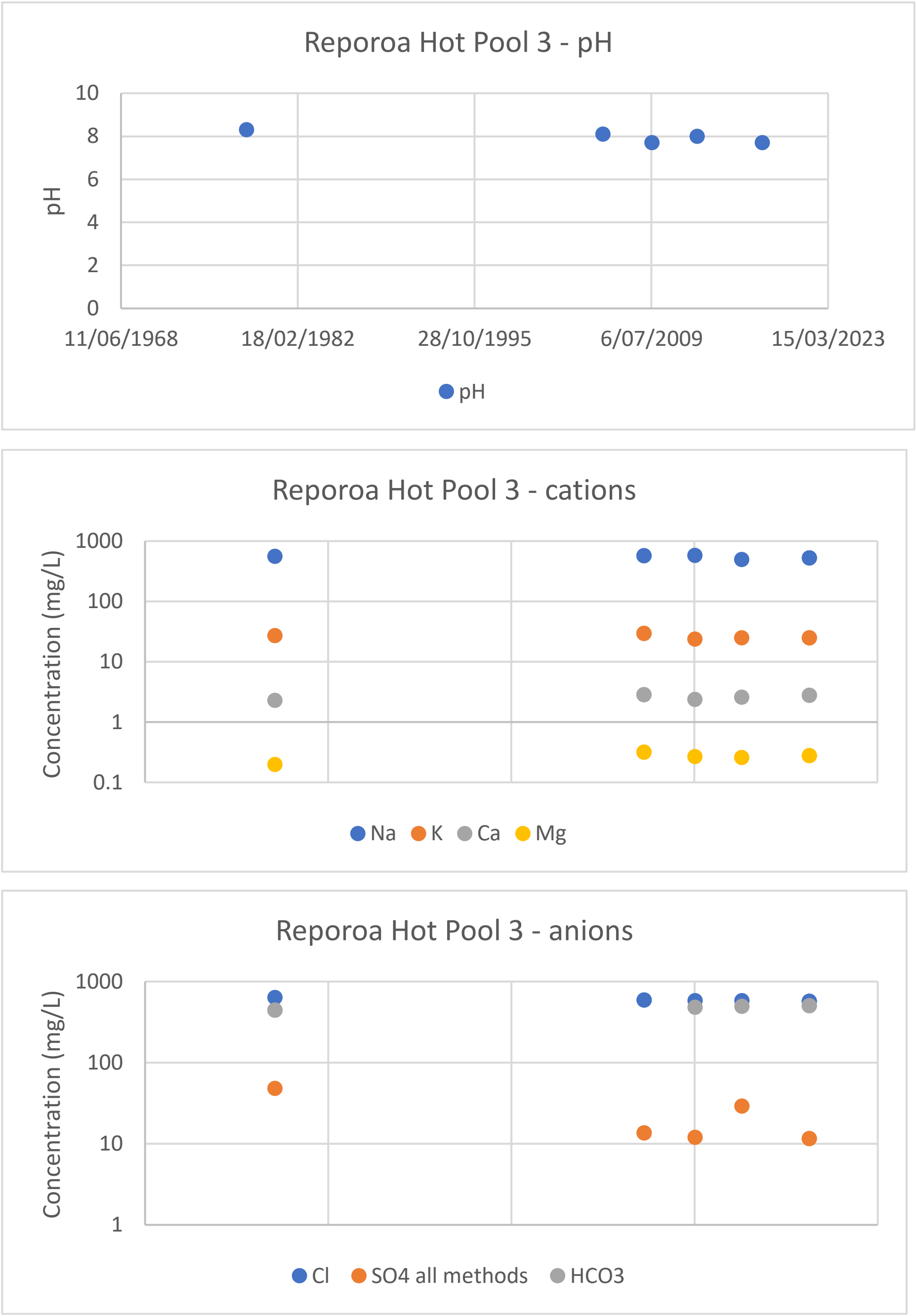


Figure 17 Trends in concentration of components at Reporoa Hot Pool 3

Reporoa Hot Pool 3 has a decreasing pH and decreasing SO_4 concentration but otherwise relatively stable concentration.

Waingaro Hot Pool Bore (72_4292)

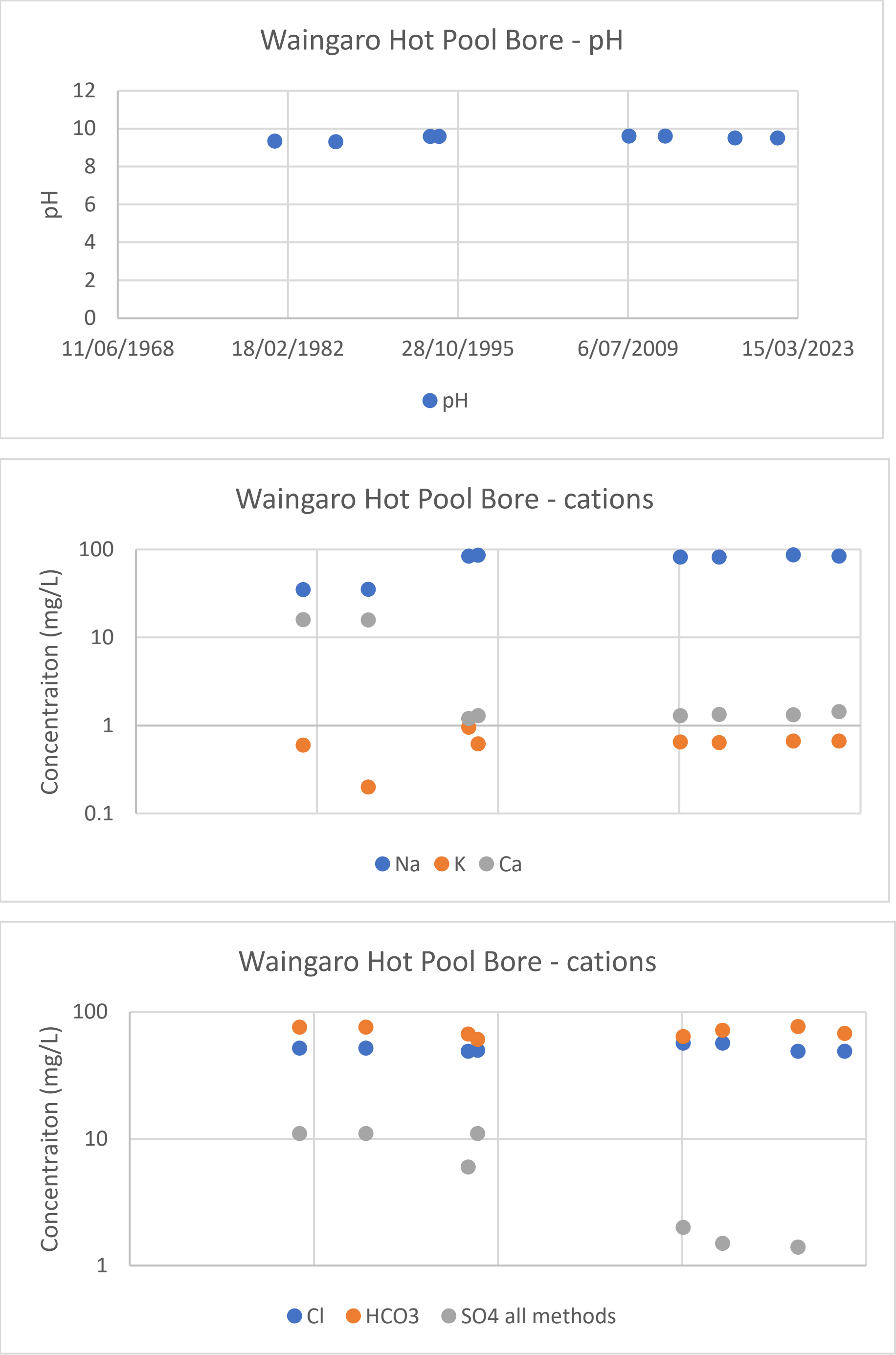


Figure 18 Trends in concentration of components at Waingaro Hot Pool Bore

Waingaro hotpool bore has a step change increase in Na concentration and decrease in sulphate concentration. Otherwise has relatively stable chemistry.

4.3 Springs with stable chemistry

Map of Australia (3065_1)

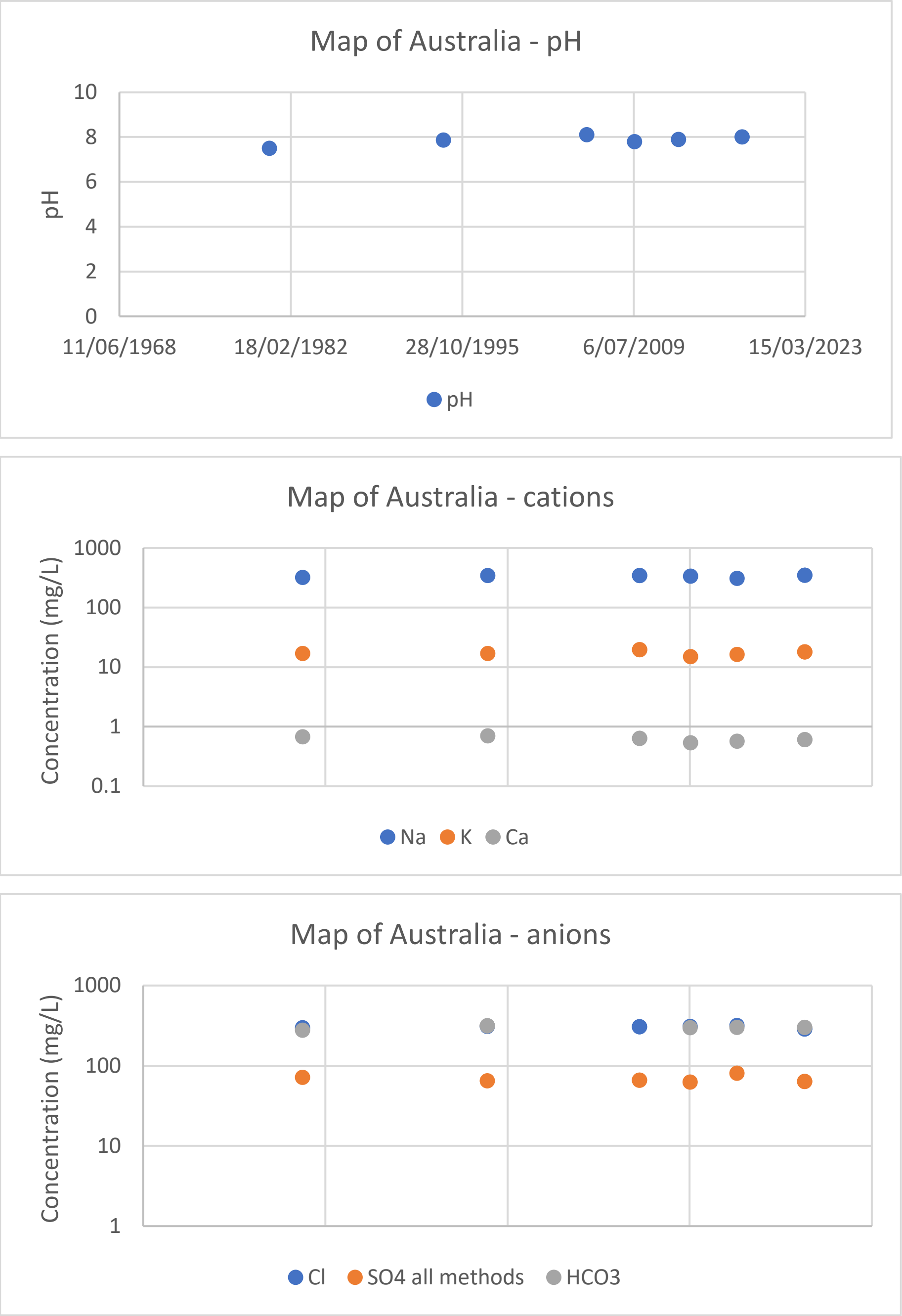


Figure 19 Trends in concentration of components at Map of Australia

Monkena Geyser (72_2227)

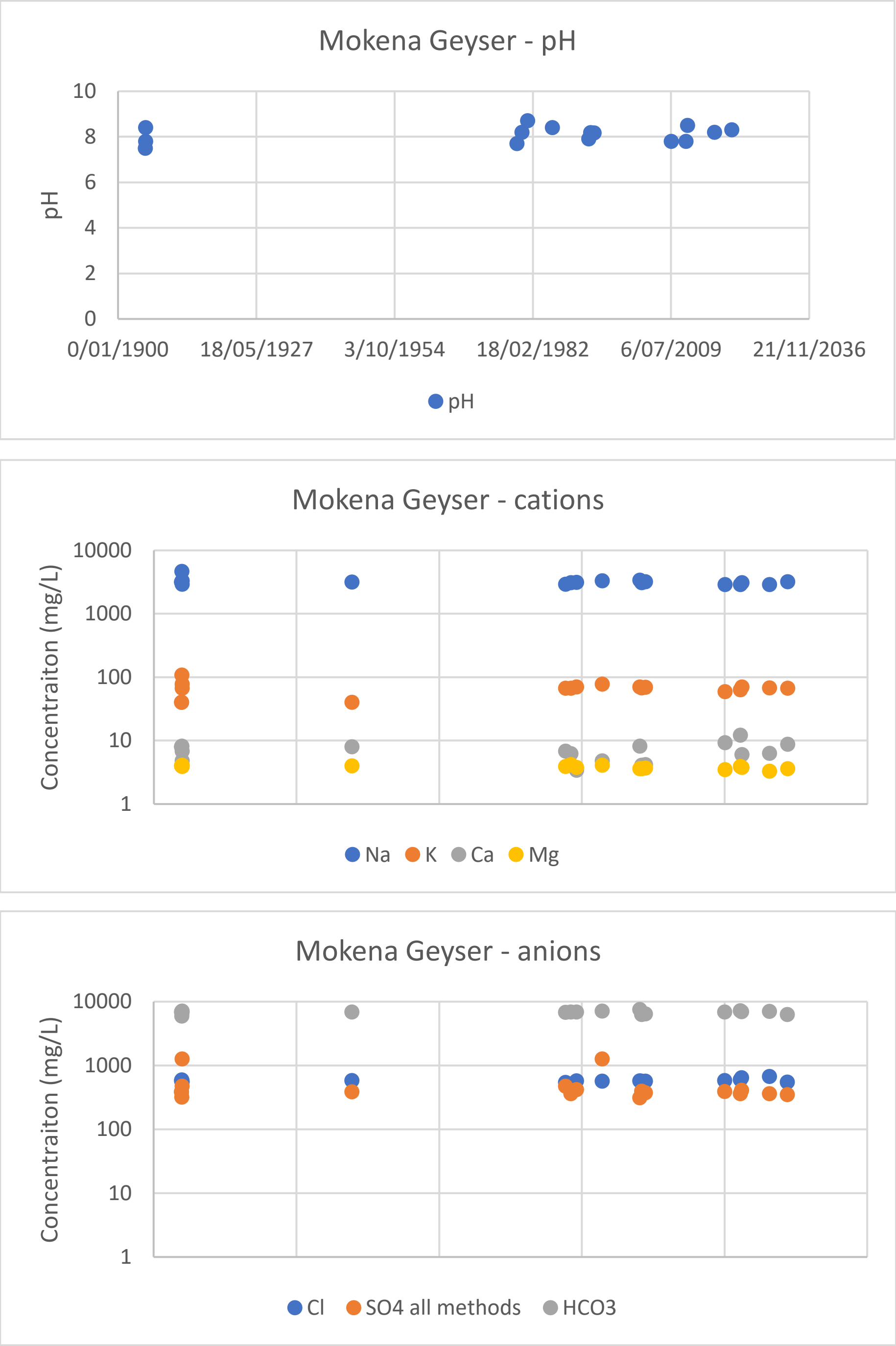


Figure 20 Trends in concentration of components at Mokena Geyser

Opal Hot Spring (72_2013)

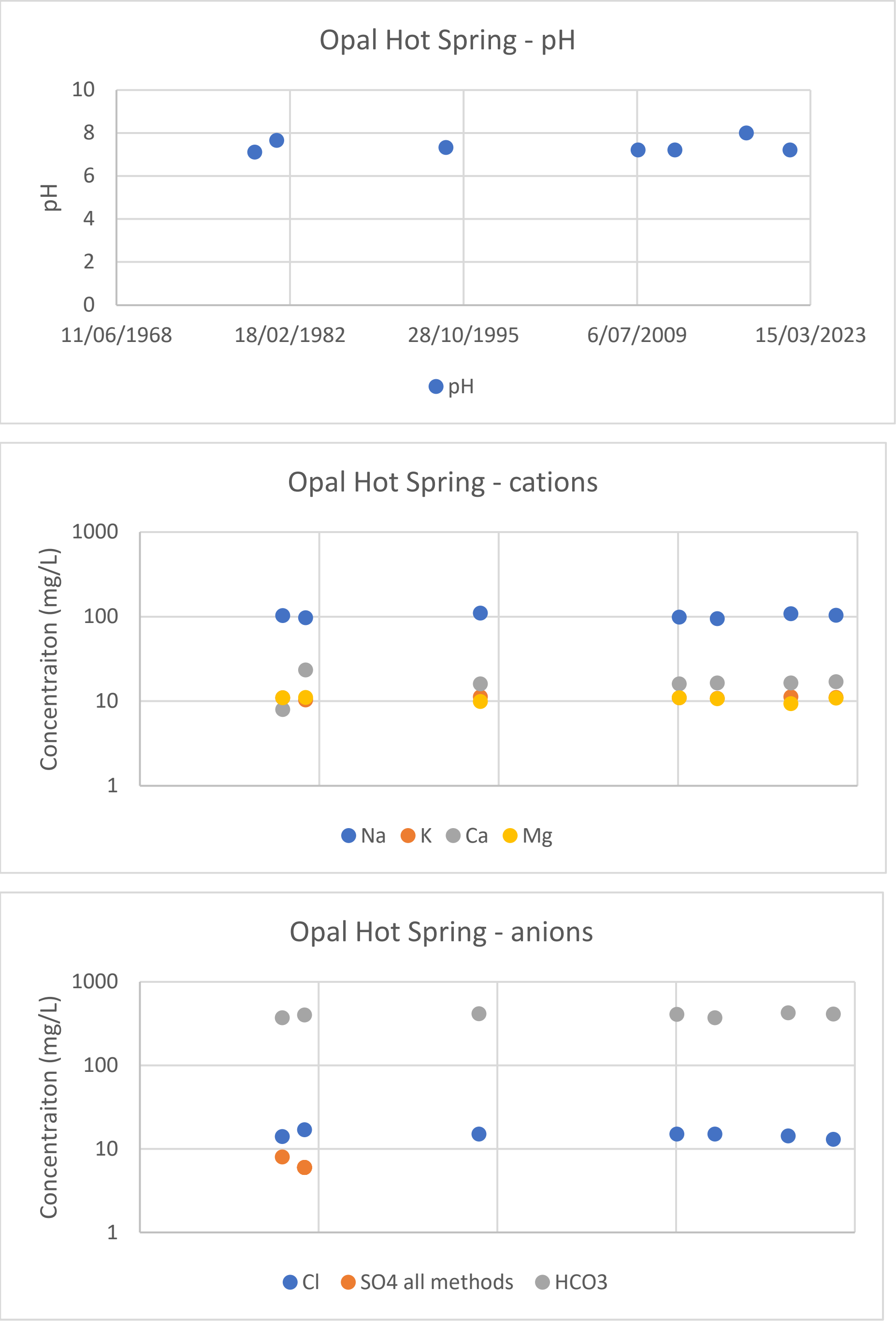


Figure 21 Trends in concentration of components at Opal Hot Spring

Taharepa (3068_16)

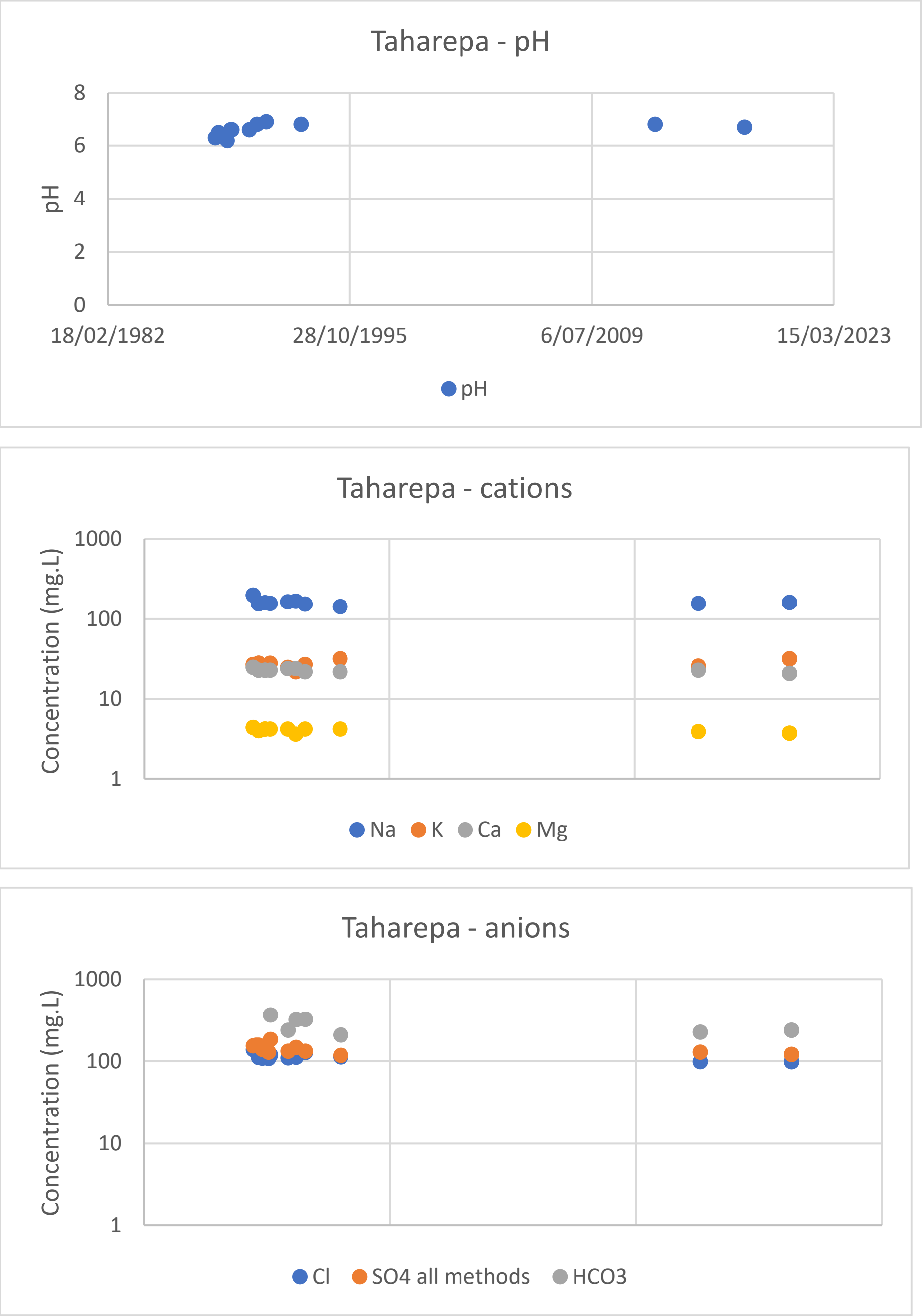


Figure 22 Trends in concentration of components at Taharepa

Ta Maire (72_2118)

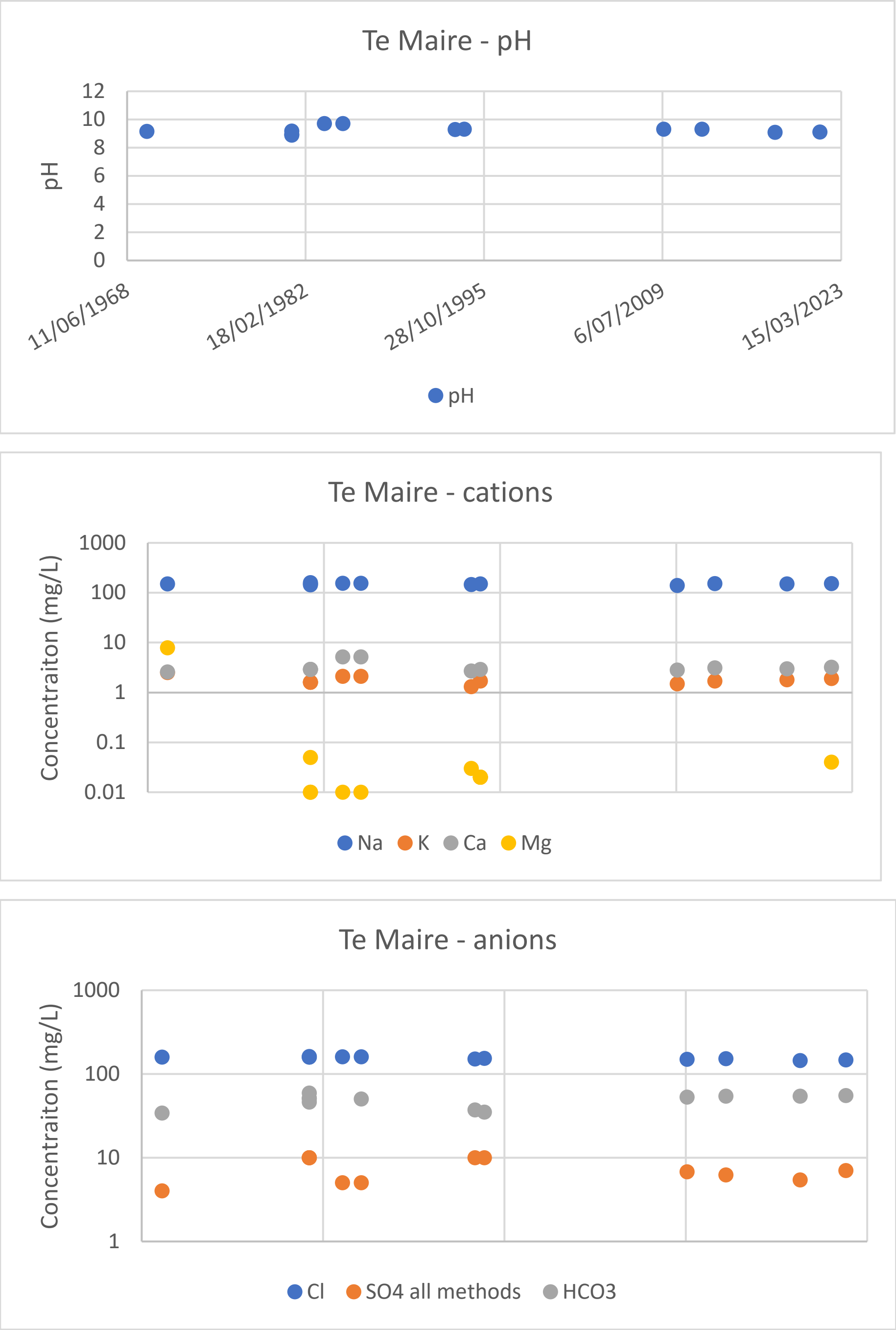


Figure 23 Trends in concentration of components at Te Maire

4.4 Summary of temporal changes

Samples to identify temporal changes within REGEMP are not uniformly or regularly collected and so interpretations are limited and preliminary. It is very likely that large variations in chemistry at some springs have been missed in the REGEMP database.

From a selection of the temporal trend data that is available in REGEMP several generalisations can be made.

1. Over the monitoring periods, typically about 30 years, most springs show some chemical variation or changes that are pronounced on our log scale chemical plots.
2. In general, Cl, Na, K are most stable parameters measured, whereas pH, Ca, Mg, SO_4 and HCO_3 are the most variable. The variable parameters are more likely to be influenced by shallow geothermal processes or groundwater, whereas the stable parameters are likely to be controlled by the geothermal reservoir chemistry.
3. All types of variations are present, gradual trends, step changes and erratic changes in concentration. In addition, some springs have stable concentrations.

Recommendations

1. Continue to collect data and build information on temporal trends information using major cation and anion geochemistry.
2. Select several sites where chemistry is variable (Waipupumahana, Waiotapu Geyser, Champagne Pool) to measure chemical variation at different frequencies (maybe weekly or monthly) or install automated probes for data collection.

5. Results – Trace Elements and Isotopes

5.1 Introduction

The REGEMP database contains trace element analyses for many of the springs that have been sampled. A complete interpretation of trace element data is not possible so a selection of trace elements plots are shown that demonstrate the types of analysis that could be possible with more time to focus on the details and split the dataset different ways to improve interpretation.

5.2 Selected trace element interpretation

Conservative trace elements

In general trace elements in geothermal systems are leached from the reservoir zone and transported to surface through in the geothermal fluid. Alkali metals (Figure 24) are generally conservative in geothermal systems and their concentrations are linked to reservoir conditions. Sodium and K partition into feldspar and micas deep in the geothermal system and possibly into jarosite in acid sulphate parts of the geothermal system. Primary minerals for Li, Rb and Cs are unlikely to reach saturation and therefore their concentrations in springs controlled by the reservoir and dilution either by conductive cooling of the geothermal fluid or through mixing with shallow groundwater. So strong linear trends occur between Li, Rb and Cs and Cl (Figure 24). The secondary trend for Rb and Cs that sits above most of the data possibly reflects an analytical mistake. Many of these values are three orders above where the rest of the data plot and therefore µg/L might have been transposed for mg/L. The samples that plot at the highest Cl concentrations are the sea water system at Kawhia.

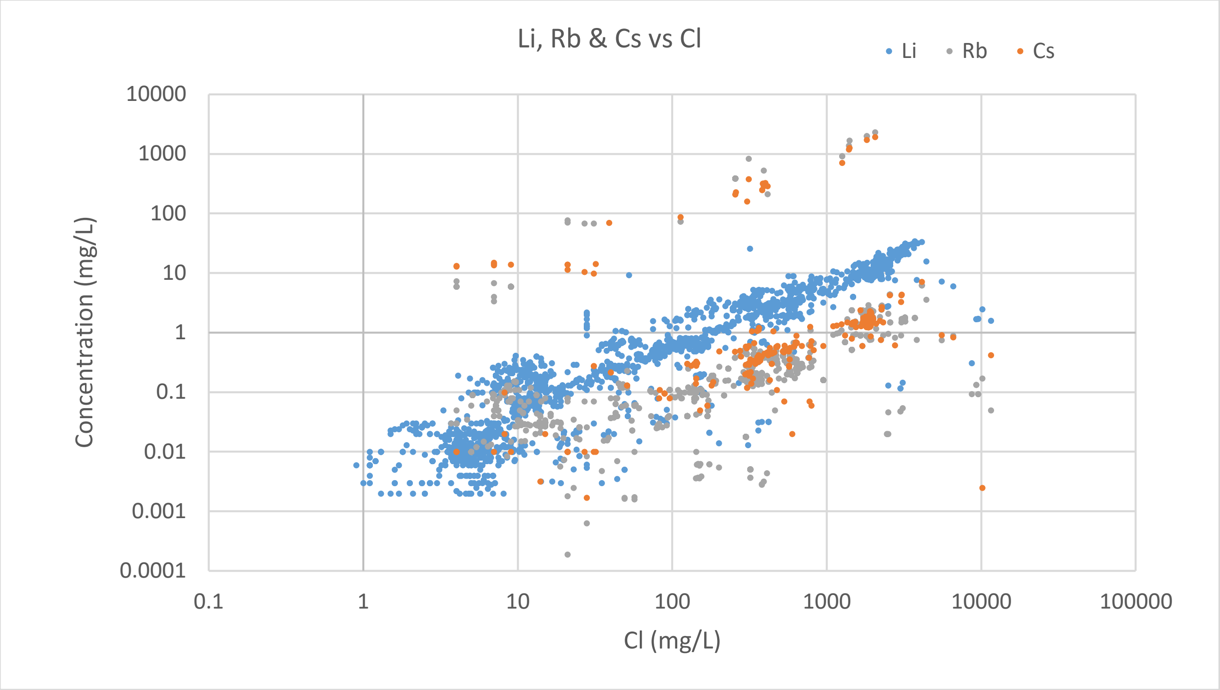


Figure 24 Cl vs Li, Rb and Cs for REGEMP data

Metalloids and B

The REGEMP database indicates that B is relatively conservative, there are several sub trends in the B to Cl ratio that are probably related to different regions and areas where B is relatively enriched or depleted. These trends would benefit from more detailed investigation. Arsenic and Sb are often thought to be relatively conservative in geothermal systems, however, the data indicate that there are processes that deplete geothermal fluids with respect to As and Sb (Figure 25). Some of these processes are documented at springs such as Champagne Pool (Pope et al 2004) . Understanding where these sites are within the region and within geothermal fields would be an interesting next step in interpretation of trace element trends in the REGEMP data.

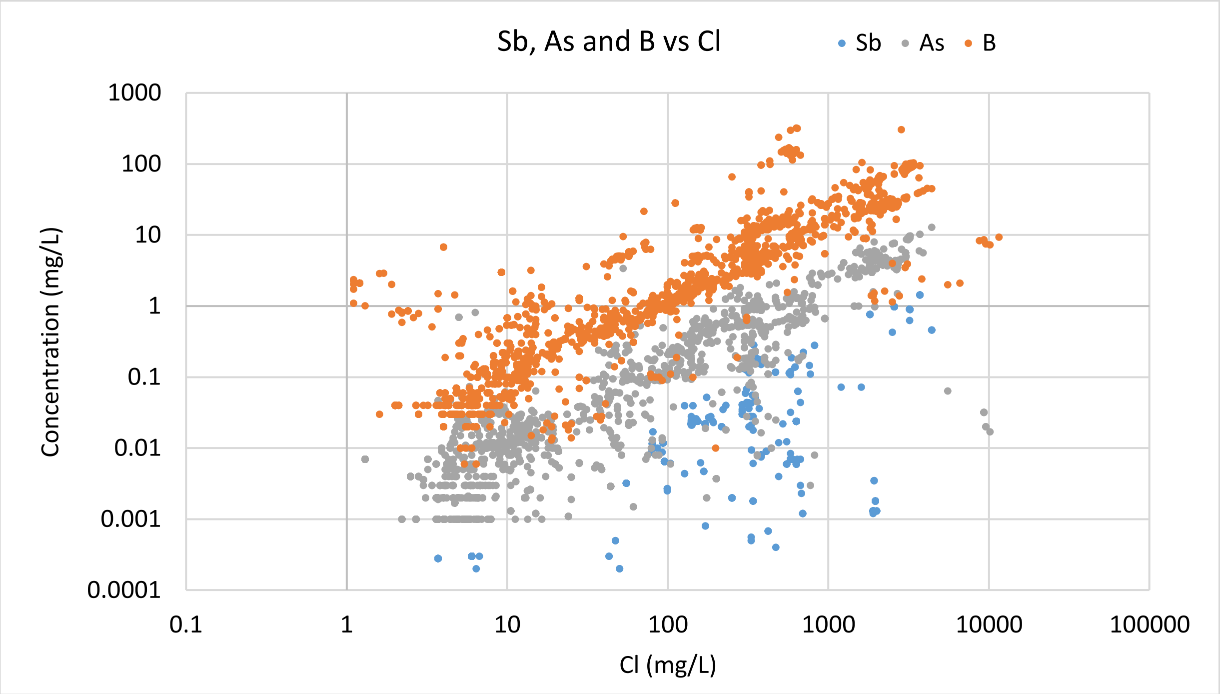


Figure 25 Cl vs B, As and Sb for REGEMP data

5.3 Stable isotopes

Variations in isotopic compositions of water occur in natural systems as a results of naturally occurring interactions between assemblages of water, gas and rock. They are useful as tracers due to concentration differences that occur as a result of temperature, steam separation, water-rock interaction, dilution and mixing (Giggenbach, 1992). The stable isotope composition of geothermal waters in the REGEMP database vary between light and heavy compositions (Figure 26).

Heavy isotopes are dominant at Champagne Pool which reflects a loss of lighter isotopes during boiling. Many of the Taupo Volcanic Zone features including Waiotapu Geyser, RKF4, Oyster Pool, Whangapoa NW Pool, Hot Pool 3 at Reporoa and others fall on a dilution line between metoric water and the heavy waters at Champagne Pool. A large number of features including Waipahihi Springs and others from the Taupo-Tauhara field plot very close to the meteoric water line.

Features from Tongariro also vary from heavy waters sampled from bores (72_2985) to waters with a more meteoric signature (72_2982). Boiling fractionation is unlikely to be prevalent in bore waters, and this variation may reflect dilution of rock interacted water with meteoric water.

The features in the Northern Waikato region often plotted above the meteoric water line. A strong metoric signature is expected. Lighter waters are often a sign of condensation, which is unlikely to be a dominant surface process at these features, however may occur at depth. Loss of heavy water molecules in clay formation and alteration processes could also explain the lighter water at some of the North Waikato features (Reyes et al, 2010). The heavy water detected at Waingaro as reported in Webster-Brown and Brown (2007) may have been an analytical error, as subsequent analysis in 2021 showed the Waingaro feature plotting slightly above the meteoric water line. The composition of waters at Kawhia plot between the meteroric water line and Standard Mean Ocean Water (SMOW). Evaporative features such as Mokena geyser also show an enrichment in heavy isotopes.

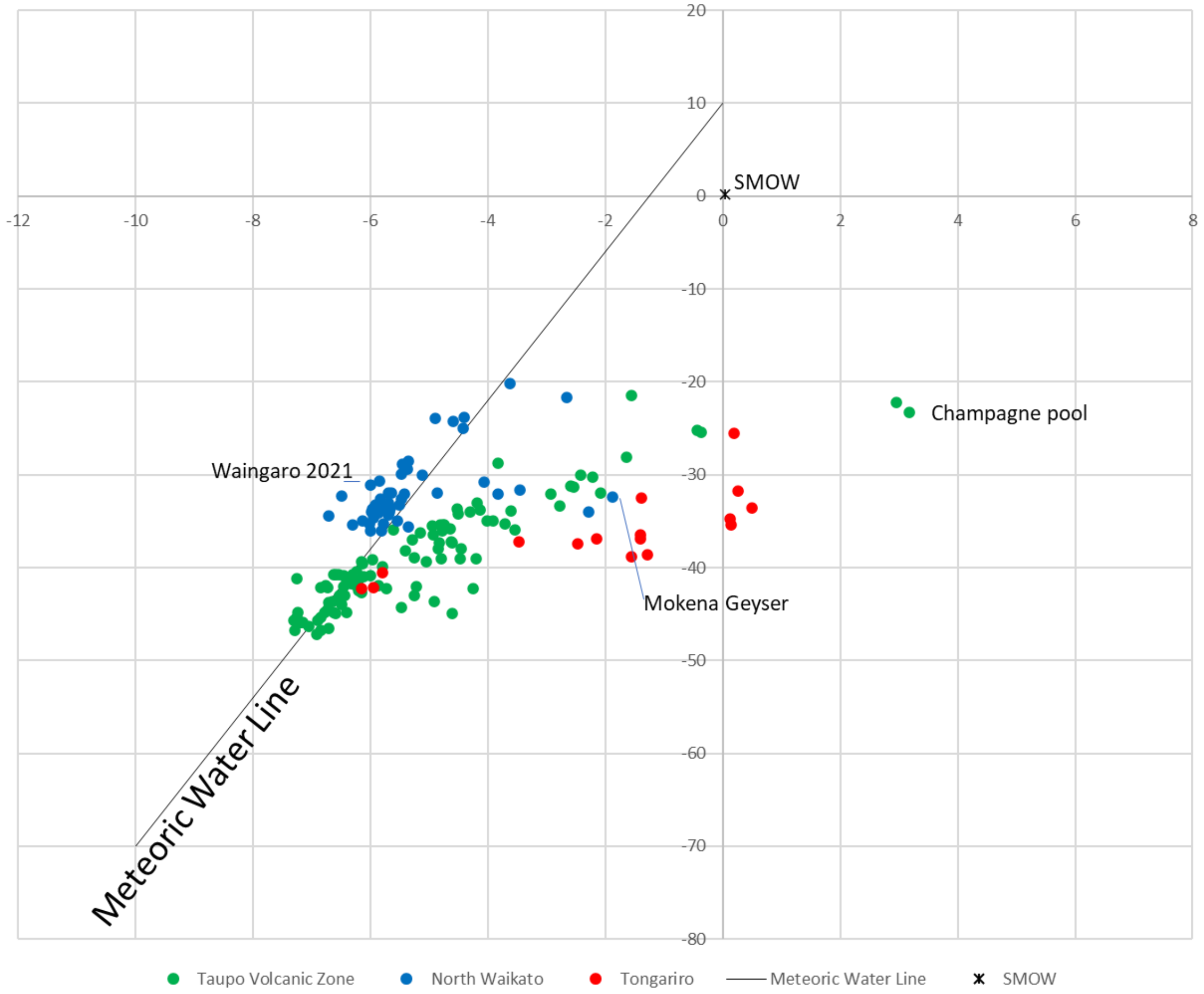


Figure 26. Stable isotopes in geothermal waters.

5.4 Summary

Conservative trends in trace element concentrations with respect to Cl indicate that geothermal reservoir conditions strongly influence trace element concentrations in springs. Many other trace elements do not have conservative relationships with reservoirs when samples of springs are collected and have complex interactions with alteration minerals such as sulphides and carbonates shallow in geothermal systems. The trace element dataset in REGEMP is extensive and contains many interesting relationships that could be developed with specific investigations targeting particular metals or particular geothermal fields.

Recommendations

1. Check the Rb and Cs concentrations in samples that plot 3 orders of magnitude too high.
2. Use the REGEMP data set to define detailed desktop and sampling studies to better understand the controls on concentrations of trace elements and isotopes regionally or locally within geothermal fields. This should involve developing a priority list of geothermal fields or areas for focussed studies by MSc level student projects. An alternative could be to scope future REGEMP review reports to complete high level regional analysis and a focus study on one or two fields or features.
3. Strong fractionation of stable isotopes occurs and often with ranges that relate to different geothermal fields or regions. Further investigation of isotope information at the scale of each geothermal field is recommended.

6. Summary

The REGEMP dataset can be interpreted using classical geothermal classification based on major anions to indicate regional trends in geothermal geochemistry. The major anion plot distinguishes the types of geothermal processes that contribute to spring chemistry. In the REGEMP data the TVZ samples plot throughout the possible composition range on a major anion plot, whereas the North Waikato and Tongariro regions have a more restricted range of compositions. The North Waikato samples are concentrated along the Cl- HCO_3 axis possibly indicating that this region is depleted in S compared to Tongariro and TVZ regions. This could indicate a systematic change in geothermal fluid composition in areas more distal from volcanism. Different geothermal fields also plot in relatively restricted, but overlapping, compositional fields on the major anion plot.

Regional trends in major cation chemistry can be summarised on a Na-K-Mg geothermometry plot. This plot also provides insight into the degree of equilibrium with respect to the albite-adularia-muscovite- chlorite mineral system. Springs that plot between the equilibrium lines can be used for geothermometry whereas springs that plot near the Mg apex are diluted by shallow groundwater. TVZ samples plot throughout the diagram, North Waikato samples plot in a relatively restricted area that indicates slightly lower reservoir temperatures compared to most Tongariro samples. Major cation geothermometry plots for individual geothermal features where there are multiple samples through time can be restricted to relatively tight compositional zones on this plot and sometimes show dilution trends with time by shallow groundwater

Major anions and cations as well as pH measurements can be used to identify changes in spring chemistry with time. Trends over time for springs where samples have been collected for more than 30 years demonstrate several types of variation. Some springs have stable composition through time, but most have either; increasing or decreasing concentrations with time; step changes in chemistry or chemical variability without trend. This variability indicates that the processes that impact chemistry of springs throughout time are variable.

REGEMP contains a large suite of trace element geochemistry, several components are conservative with geothermal reservoir conditions indicated by a strong linear correlation with Cl content. However many trace elements do not have strong conservative trends. This indicates that trace element compositions can be impacted by shallow geothermal processes such as precipitation of secondary minerals where the trace elements can be selectively removed from solution. Interpretation of these complex relationships are best completed in smaller focussed studies on one particular metal in a regional context or for several trace elements in one geothermal field.

Summary Recommendations

Detailed recommendations are made throughout the report adjacent to supporting data. Summary recommendations below include and aggregate main recommendations listed earlier in the report and place them within the context the interpretation completed in this review.

1. Major cation and anion ratios (as displayed in ternary diagrams) are the key tools to interpretation of the REGEMP dataset. In future reports these ratios should be used to:
    - Systematically assess the completeness of the monitoring dataset. Currently the REGEMP dataset is biased toward neutral chloride springs based on comparison to a complete spring sample dataset for Waiotapu geothermal features.
    - Interpret spatial variation at a regional scale.
        - The observation that there are few acid sulphate discharges in the North Waikato should be tested. Does this represent regional discharge of Cl-HCO_3 fluids at sites further from volcanism or sampling bias away from acid sulphate springs
    - Interpret spatial variation at a local scale
        - Assess if different geothermal areas or geothermal fields can be separated or partially separated by a combined interpretation of anion and cation ratios.
    - Interpret spatial variation within a geothermal area of field
        - Assess if different geothermal features have consistent ratios of major components or if they are variable
    - Assess the geothermometry relationship represented by full equilibrium on the cation ternary diagram. Can departures from full equilibrium that relate to Mg depletion be related to another mineral phase or an alternative interpretation of this equilibrium curve.
2. Complete a systematic review of variations with time for features where there are repeated analysis through time using major cation and anion concentrations along with pH. Our review of selected springs with analyses plotted on a true scale time axis provide new insight into temporal trends for the geothermal features. This study would benefit from sensor based continuous monitoring or short interval sampling of major component chemistry on a weekly to monthly basis at selected features.
3. Using the REGEMP data as a start point, commission focussed studies of major cation, anion, trace element and isotope concentrations at the scale of geothermal fields. The most cost effective approach to this would be to partially fund MSc level projects. Alternatively, future REGEMP reviews could include a regional level study and a focus on trace elements and isotopes at a particular geothermal field. A priority list of the best geothermal fields for these studies should be developed.
4. Alternative monitoring datasets such as satellite data or drone based thermal imaging should be considered.

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