REGEMP 2022: Waikato Regional Geothermal Monitoring Programme

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Keywords: *REGEMP, geochemistry, Waikato Region*

ABSTRACT

Waikato Regional Council collects and records monitoring data on geothermal features in the Waikato Region. Among other information, the database contains more than 2400 chemical analyses of geothermal features with variable analytical suites included, some dating back more than 100 years. Every few years more samples throughout the region are collected and analysed, and along with data from other sources, interpreted to determine regional temporal and spatial trends.

This paper presents an interpretation of the REGEMP dataset 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 area is depleted in S compared to Tongariro and TVZ area. 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.

Summary recommendations include that major cation and anion ratios (as displayed in ternary diagrams) be used as the key tools to interpretation of the REGEMP dataset, and that alternative monitoring datasets such as satellite data or drone based thermal imaging should be considered.

1. REGEMP HISTORY

The Waikato Regional Geothermal Geochemical Monitoring Programme REGEMP (Huser and Jenkinson, 1996) was initiated in 1996. It contained analyses of geothermal and volcanic gas and water from 38 springs and 13 fumaroles throughout the Waikato Region. Although the intention was to repeat it every two years, no further work was done until 2007, when a review of the programme was undertaken to take account of modern sampling and analysis methods and data sources, giving rise to REGEMP II (Luketina 2007). Sampling, analysis, interpretation, and reporting under the new regime were undertaken in 2008, 2010, 2013, 2018 and 2022 (Webster-Brown and Brown, 2008, 2010; Golder Associates Ltd, 2013; Wilson, 2018; Pope and Christenson, 2022). This paper summarized the results of the 2022 report.

2. BACKGROUND

This review is a desktop study of the REGEMP data base provided by Waikato Regional Council (WRC), and 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 axes, 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.
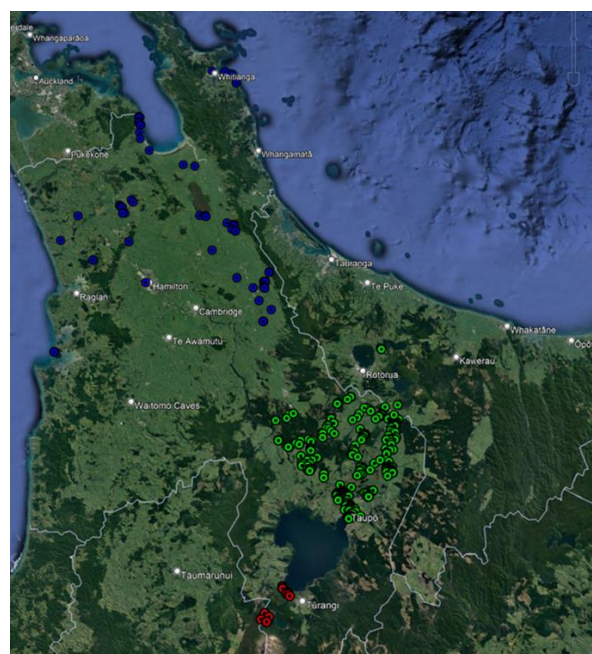

Figure 1: Map of REGEMP database sample locations made using Google Earth. Colours reflect the region the sites were attributed to: blue = North Waikato, green = Taupo Volcanic Zone, red = Tongariro. White lines show Regional boundaries.

For the purposes of this study, the geothermal features that have been studied were divided into three areas based on their locations. The points below 38.9439 °S were designated as the

Tongariro area, and the North Waikato includes features north of 38.063. The Taupo Volcanic Zone (TVZ) was determined to be between these two areas and our analysis includes the Hells Gate systems north of Rotorua in the Bay of Plenty Region (Figure 1).

Pope and Brown (2014) have previously completed a study of variability of geothermal features for the Waiotapu geothermal field including spatial and temporal trends. The findings of that 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.

The report that this paper summarises, including additional graphs, is available on request from WRC and eventually will be made publicly available in a WRC Technical Report.

3. RESULTS – REGIONAL INTERPRETATIONS

3.1 Introduction

Geothermal systems in the Waikato Region have a magmatic heat source related to the TVZ 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 Earth's 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 Chloride (Cl^-), Sulphate (SO_4^{2-}), and Bicarbonate (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 Hydrogen Sulphide, Sulphur Dioxide and Carbon Dioxide (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 interact 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 their elevated Na, Cl, Mg, K and SO_4 concentrations. This was also observed in the current dataset, and the Kawhia system has been considered separately in the following tables.

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-HCO3 axis of the anion diagram with very few springs containing significant proportions of SO4. Data from the Tongariro area are mostly concentrated along the Cl-HCO3 axis of the diagram with a subset of samples showing mixed Cl-SO4 composition.
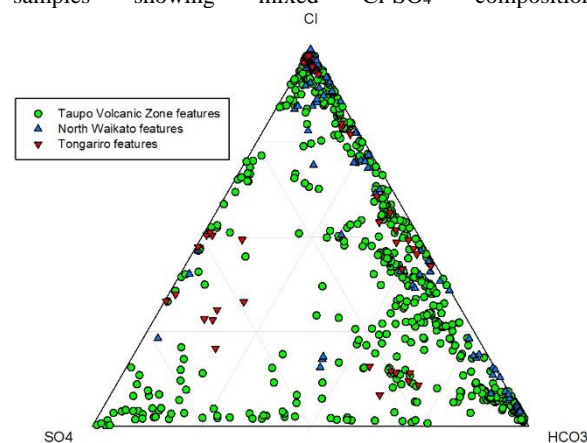

Figure 2. Regional major anion ternary plot. Ternary diagrams of this type are developed from anion proportionality and mass-based concentration units.

Assuming there is no bias in the sampling these regional trends likely indicate that there are different source water characteristics in the North West region versus the Central TVZ and Tongariro areas, which can be linked to specific active volcanic centres, whereas in the North West area the geothermal activity is further from active volcanism. It is possible that the main source of Sulphur (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 as 'peripheral' when considering any 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).

Major anion data for Waiotapu, Waikite and Reporoa including Golden Springs (Figure 4) also indicate that the major anion ratios can be characteristic for different areas.

In general, springs in the Waiotapu geothermal area plot along the Cl-SO4 axis of the diagram while water from smaller fields close by plot in different positions along the Cl-HCO3 axis of the diagram. Comparison of the REGEMP dataset to the Waiotapu dataset also indicates two main features:
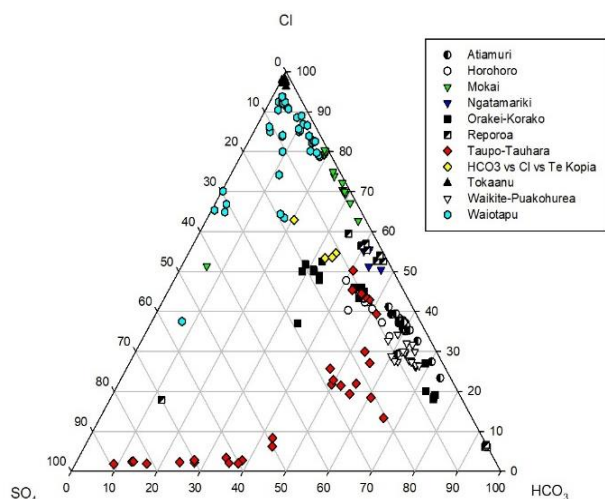
Figure 3. Selected REGEMP data plotted by geothermal field. Duplication of samples from the same spring is included in this dataset.

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 by surface processes such as climate, rainfall, farming forestry or infrastructure.

3.3 Major Cation geo-chemistry: 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. However, sometimes other cations can be more abundant. Most cations, metals and metalloids in geothermal systems are sourced through leaching and alteration of reservoir host rocks. Generally, 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 likely processes affecting fluid chemistry after it leaves the reservoir.

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.

Cation concentrations in springs are suitable for geothermometry if they preserve equilibrium with respect to minerals such as albite, adularia (feldspars) muscovite,
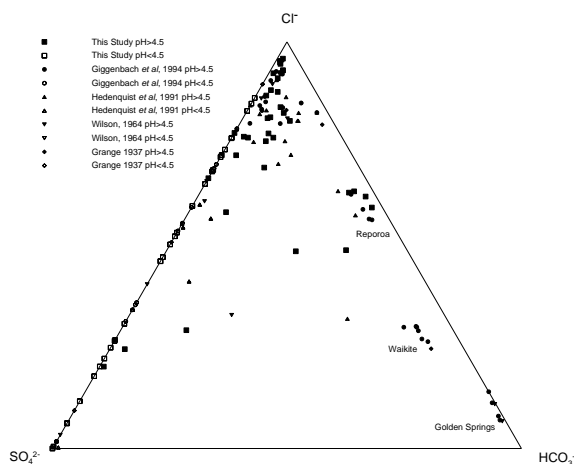
Table 1. Maximum, minimum and mean concentrations of major anions in REGEMP, Kawhia and Waiotapu (after Pope and Brown 2014). The range of concentrations in major anions is larger in REGEMP than that found in a single geothermal field. Repeat sampling of features with neutral chloride chemistry in all datasets skews the average concentration data toward higher Cl.

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

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						

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

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 in 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 (Table 2) 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, TVZ 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.

In comparison to Waiotapu Na, K, Mg geothermometry (Figure 6) REGEMP data shows trends for low temperature equilibrium conditions in some reservoirs and 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).
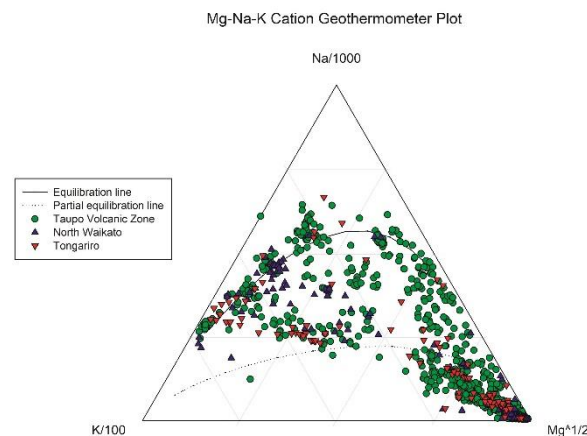

Figure 5. Regional ternary plot of K-Na-Mg. The full equilibrium line reflects concentrations of Na-K-Mg with respect to albite-adularia-muscovite-chlorite. Partial equilibrium line indicates maximum dilution by Mg rich water where Na-K geothermometry remains applicable. Ternary diagrams of this type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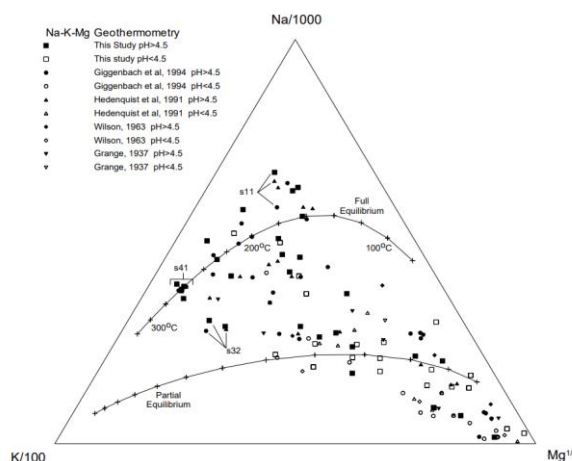

Figure 6. Ternary plot of Na-K-Mg plot for the Waiotapu Geothermal field (after Pope and Brown 2014).

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 temporal chemical pattern:

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

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such as Waipupumahana at Whangairorohea, Manaroa Pool at Waikite and Manganese Pool at Orakei Korako.

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.
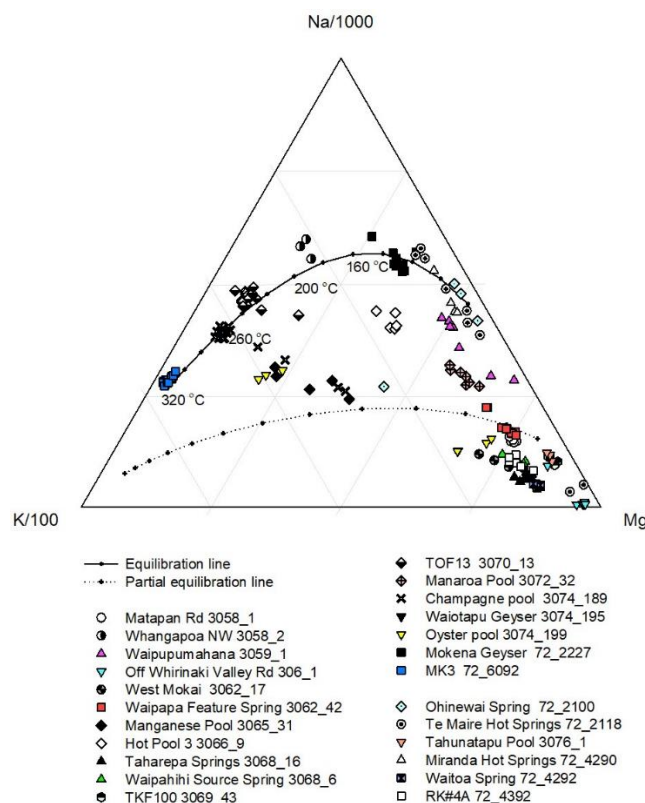

Figure 7. Plot of K-Na-Mg for selected REGEMP springs

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 at Te Aroha. 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 anion graphs at each feature.

4.2 Springs with temporal changes in chemistry

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. Large-scale geothermal extraction from the Wairakei-Tauhara Geothermal System does not appear to be the reason for this trend 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.

Manaroa Pool at Waikite has a subtly increasing trend in Na concentration and decreasing concentration of Mg.

Whangapoa Pool North West at Atiamuri has a sharp decrease in pH between an early sample in 1978 and more recent samples. Other major component concentrations are stable. Forestry activity, land-use changes, and restoration projects over the last ~ 30 years adjacent to the pool could influence chemistry (See Figure 10).

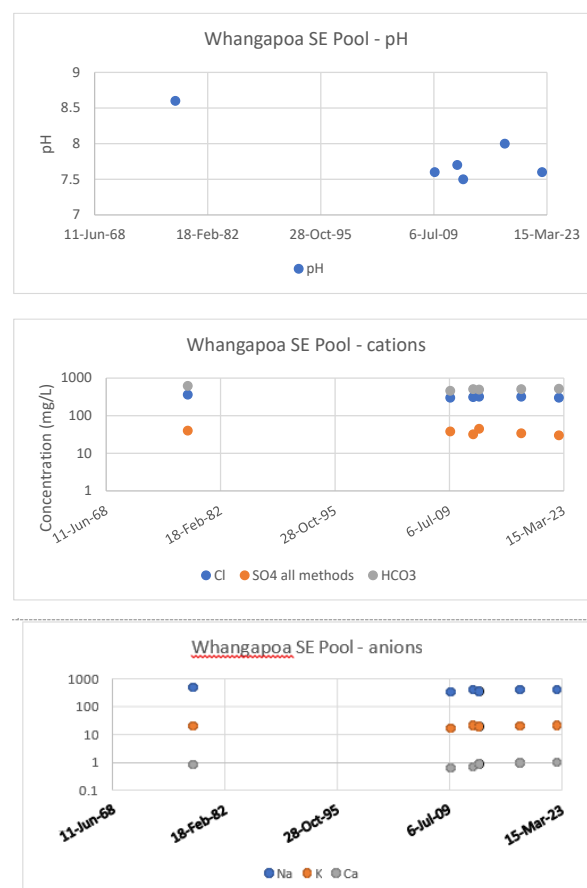Due to space restrictions, only the Whangapoa SE pool graphs are shown here.

Figure 10. Trends at Whangapoa SE Pool

Champagne Pool at Waiotapu 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 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 are 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 at Waiotapu 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.

4.3 Springs with stable chemistry

These included Map of Australia at Orakei Korako, Mokena Geyser at Te Aroha, Opal Hot Spring at Okauia, Taharepa at Tauhara, and Te Maire at Naike.

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.

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.

In general, Cl, Na, K are most stable parameters measured, whereas pH, Ca, Mg, SO4 and HCO3 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.

All types of variations are present, gradual trends, step changes and erratic changes in concentration. Some springs have stable concentrations.
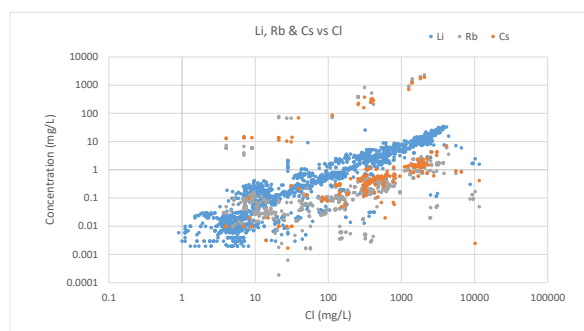

Figure 8: Cl vs Li, Rb and Cs for REGEMP data

5. RESULTS – TRACE ELEMENTS AND ISOTOPES 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 is shown that demonstrates 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

5.2.1 Conservative trace elements

In general trace elements in geothermal systems are leached from the reservoir zone and transported to surface in the geothermal fluid. Alkali metals 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 Lithium, Rubidium and Caesium (Li, Rb and Cs) are unlikely to reach saturation and therefore their concentrations in springs are controlled by the reservoir and dilution either by conductive cooling of the geothermal fluid or through mixing with shallow groundwater. Therefore, strong linear trends occur between Li, Rb and Cs and Cl (Figure 8). 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.

5.2.2 Metalloids and B

The REGEMP database indicates that Boron (B) is relatively conservative, there are several sub trends in the B to Cl ratio that are probably related to different 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 9). 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.
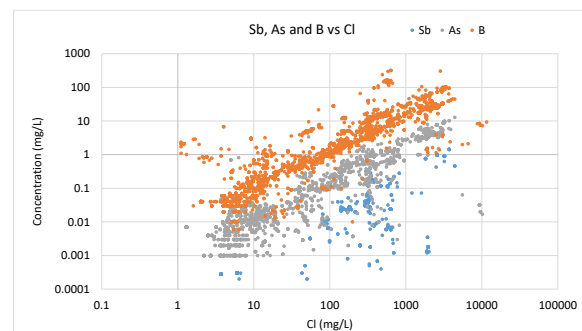

Figure 9: Cl vs B, As and Sb for REGEMP data

5.3 Stable Isotopes

Variations in isotopic compositions of water occur in natural systems as a result 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 10).

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 meteoric water and the heavy waters at Champagne Pool. Many features including Waipahihi Springs and others from 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 meteoric signature is expected. Lighter waters are often a sign of condensation, which is unlikely to be a dominant surface process at these features, although 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 meteoric water line and Standard Mean Ocean Water (SMOW). Evaporative features such as Mokena geyser also show an enrichment in heavy isotopes.
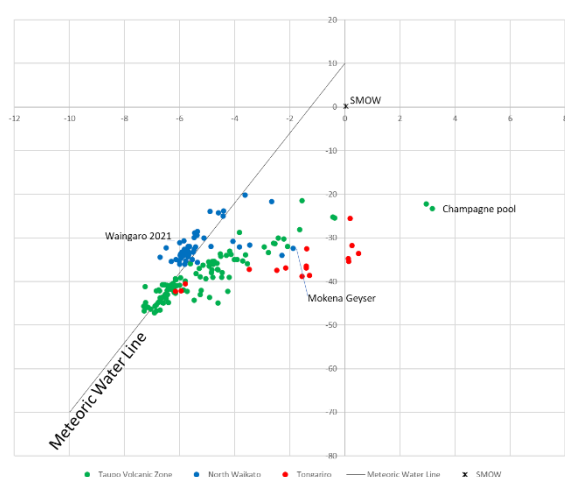

Figure 10. Stable isotopes in geothermal waters.

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 at shallow depths within geothermal systems. The trace element dataset in REGEMP is extensive, containing many interesting relationships that could be developed with specific investigations targeting particular metals or geothermal fields.

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 areas 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 areas. 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 shown on a Na-K-Mg geothermometry plot, which also gives insight into the degree of equilibrium regarding the albite-adularia-muscovite- chlorite mineral system. Springs plotting 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 more restricted area indicating slightly lower reservoir temperatures than 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 affected 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 is best completed in smaller focussed studies on one particular metal in a regional context or for several trace elements in one geothermal field.

6.1 Summary Recommendations

6.1.2 Ratios

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. Assess whether different geothermal features have consistent or variable ratios of major components.
- 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.

6.1.3 Review

Systematically review 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 provides 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.

6.1.4 Focus

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.

6.1.5 Other methods

Alternative monitoring datasets such as satellite data or drone based thermal imaging should be considered.

ACKNOWLEDGEMENTS

REFERENCES

Eastoe, C.J. & Guilbert, J.M. Stable chlorine isotopes in hydrothermal processes. *Geochimica et Cosmochimica Acta,* 56: 4247-4255. (1992).

Ellis, A.J. & Mahon, W.A. Natural hydrothermal systems and experimental hot water/rock interactions. *Geochimica et Cosmochimica Acta,* 28: 1323-1357. (.1964).

Giggenbach, W.F. Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochimica et Cosmochimica Acta,* 52: 2749-2765. (1988).

Giggenbach, W.F. *Isotopic composition of geothermal water and stream discharges. Applications of Geochemistry in Geothermal Reservoir Development,* United Nations Institute for Training and Research and UNITAR/UNDP Centre on Small Energy Resources, United States of America. (1992).

Golder Associates Ltd. *REGEMP II 2013 interpretation of geochemical data.* Waikato Regional Council Technical Report 2013/30. Hamilton,. (2013).

Hedenquist, J.W. & Browne, P.R.L. The evolution of the Waiotapu geothermal system, New Zealand, based on the chemical and isotopic composition of its fluids, minerals and rocks. *Geochimica et Cosmochimica Acta,* 53: 2235-2257. (1989).

Henley, R.W. Chemical structure of geothermal systems. In: R.W. Henley, A.H. Truesdell, P.B. Barton Jr. and J.A. Whitney (Editors), *Fluid-mineral equilibria in hydrothermal systems.* (1984).

Henley, R.W. & McNabb, A. Magmatic vapor plumes and ground-water interaction in porphyry copper emplacement. *Economic Geology,* 73(1): 1-20. (1978)

Huser B, Jenkinson D. *Regional geothermal features monitoring programme.* Waikato Regional Council Technical Report 96/18 (Unpublished Report, Doc No. 791983). Hamilton, Waikato Regional Council. (1996)

Luketina KM. *REGEMP II: Regional Geothermal Geochemistry Monitoring Programme.* Waikato Regional Council Technical Report 2007/36. Hamilton, Waikato Regional Council. (2007).

Nicholson, K. *Geothermal fluids: chemistry and exploration techniques.* Springer Verlag, Heidelberg, 263 pp. (1993).

Pope, J. and Brown, K. Geochemistry of discharge at Waiotapu geothermal area, New Zealand – Trace elements and Temporal Changes. *Geothermics* 51: 253-269. (2014).

Pope, J., McConchie, D., Clark, M., and Brown, K. Diurnal variations in the chemistry of geothermal fluids after discharge, Champagne Pool, Waiotapu, New Zealand: *Chemical Geology,* v. 203, p. 253-272. (2004).

Pope J, Christenson H. *Regional geothermal geochemistry review and interpretation.* Report for Waikato Regional Council, Verum Group Report J000009 (in press). WRC doc number 24602703. (2022).

Reyes, A. G., Christenson, B. W., & Faure, K. Sources of solutes and heat in low-enthalpy mineral waters and their relation to tectonic setting, New Zealand. *Journal of Volcanology and Geothermal Research,* 192(3-4), 117-141. (2010).

Webster-Brown JG, Brown KL. *Interpretation of geochemical data (REGEMP II) and recommendations for further monitoring.* Waikato Regional Council Technical Report 2008/01. Hamilton, (2008).

Webster-Brown JG, Brown KL. *Interpretation of geochemical data (REGEMP II) and recommendations for further monitoring.* Waikato Regional Council Technical Report 2012/07. Hamilton, (2010).

Wilson N 2019. *REGEMP II: interpretation of geochemical data.* Waikato Regional Council Technical Report 2019/05. Hamilton, Waikato Regional Council. (2018).