

Interpretation of Geochemical Data (REGEMP II) and Recommendations for Further Monitoring

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Executive summary

A preliminary assessment of the 2005/06 dataset collected from geothermal features in the Waikato region as part of REGEMP II has been undertaken. The 2005/05 dataset has been combined with the dataset from 1993/94 from Huser and Jenkinson (1996), and with data for features in Tongariro National Park and Tokaanu made available from the GEONET program administered by GNS Science. In combining these different datasets some assumptions have had to be made with regard to site locations and analytical data. Some data collected in the most recent survey have been removed from the combined dataset in the interests of consistency and relevance to geothermal monitoring (for example, nutrient data and sites of non-geothermal nature). The final dataset used in this assessment is presented in Appendix 1.

A general assessment of spatial trends demonstrated chemical changes consistent with the presence of high-temperature, deep-seated geothermal fluid systems in the central part of the region (the Taupo volcanic zone), low-temperature systems in the north, and more steam-heated systems further south. Several features stand out as having unusual geochemistry for the region, such as Te Aroha, Tokaanu and a number of high-temperature features in the middle of the region. All available grid references have been converted to full NZMS 260 coordinates (seven figure easting and northing coordinates), with a view to future GIS treatment of the data.

Temporal changes were assessed for those features with multi-year data available. The only such features to show a distinctive trend were Horohoro (decreasing contribution from groundwater sources), and Ketetahi (an apparent decreasing contribution from steam-heated fluids).

Data correlations confirmed the close association of components of the deep-seated geothermal fluids and the common fluid source and evolution of features in the Taupo volcanic zone (TVZ). Few correlations were evident in the components of the steam-heated fluids.

The stable isotope data that does not lie on the meteoric water line can be mainly explained in terms of evaporation in hot springs or dilution of deep geothermal waters by meteoric waters. Nearly all of the waters from the small low-temperature hot springs in the northern Waikato area are sourced from meteoric waters. Waingaro springs and the Mokena geyser at Te Aroha are exceptions. The stable isotopes from Te Puia at Kawhia show dilution of seawater by meteoric water. Stable isotopes from Soda Springs show that these waters probably originate from higher altitudes.

Silica and cation geothermometers have been calculated for all data. There is reasonable correlation between the quartz geothermometer and the Na/K/Ca geothermometer only for high-temperature fluids. Nearly all quartz geotemperatures calculated for the low-temperature hot springs in the northern Waikato area predict temperatures greater than 100°C at depth. For those features in all areas that have been sampled over time, there is no significant change in their calculated geothermometer temperatures.

A number of recommendations have been made to optimise the results which can be gained from this monitoring programme, and to reduce the effort required in the long term. The principal recommendations are as follows.

- For the **full suite**, monitor the parameters shown in Appendix 1 once every four years.
- Every two years, monitor a **minimum suite** of; Temp, pH, Li, Na, Cl, Mg, SO₄, F, B and HCO₃. This is based on the **minimum suite** recommended in Huser and

Jenkinson, but includes Li (as an indicator of correlated parameters Cs, As and Sb), B and F (independent variables of environmental interest).

- Select only a small number of significant features to be sampled in the larger geothermal systems; the features should be chosen with a view to longevity, ease of access and be representative of both deep geothermal fluid and steam-heated fluids where possible.
- Accurate GPS coordinates should be measured and recorded, and used to confirm the same feature is sampled each time. If the next sampling includes samples from the 1993/94 survey that were not sampled in 2005/06, then the grid coordinates listed in Appendix I should be checked with the newer measured GPS coordinates.

1 Introduction

In October 2007, GEOKEM was asked to provide an initial assessment of 2005/06 fluid geochemistry data collected for geothermal features in the Waikato region, as part of REGEMP II (Regional Geothermal Geochemistry Monitoring Programme II). The REGEMP initiative began in 1993/94, and data compiled for and collected as part of this initiative was reported by Environment Waikato in 1996 (Huser and Jenkinson). This initial dataset was comprehensive and provided a good platform from which to launch a routine monitoring programme. However, due to other commitments monitoring was unable to be resumed again until 2005/06, when REGEMP was restarted (Luketina, 2007).

The data collected by Environment Waikato in 2005/06 does not duplicate many of the sites sampled in 1993/94, and includes others. This is partially because it is envisaged that data known to be collected from some features in 2005/06 by GNS Science will ultimately become available to Environment Waikato and may be incorporated into the dataset at a later date (duplication of effort is avoided). Also the suite of analytes differs somewhat from that of the 1993/94 survey, and is more extensive moving beyond the suite of analytes usually determined for geothermal activity or geothermal sustainability monitoring. As a result there is some disparate data collected that has no relationship to other collected data. This may detract from the focus of the programme on the analytes that are common and deviate from the objectives of the monitoring programme.

GEOKEM was asked specifically to:

- obtain all available relevant monitoring data from GNS Science
- identify and discuss temporal and geographical trends in the data
- identify and discuss any correlations between chemical species
- interpret the stable isotope (^{18}O and 2H) data
- provide recommendations (for example, site and analyte choice and sampling frequency) for future surveys.

The sources of information provided by Environment Waikato for this assessment included:

- the REGEMP (Huser and Jenkinson, 1996) and REGEMP (II) reports (Luketina, 2007)
- MS Excel spreadsheet containing all REGEMP (II) fluid analytical data collected in 2005/06, and a correlation matrix compiled by Dr Nick Kim using this data
- MS Excel spreadsheet containing all REGEMP fluid analytical data collected in 1993/94 (and previous data available at this time).

Additional information obtained for this assessment included data from GNS Science under the GEONET program for Tongariro National Park features and Tokaanu from 1981-2006. The data collected by GNS Science for other features included in the REGEMP network is unfortunately not available at this time.

2 Data compilation and assumptions

The first step was to combine the data from all sources into a single spreadsheet, from which temporal and spatial trends could be assessed. In order to create a single, relevant dataset the following actions and/or assumptions were made.

- The following samples were deleted from the 2005/06 spreadsheet as there was no relevant geochemical data available: 241.3 (collected in 2006), 64-07 (1988), 64-842 (1992), 72-2942 (1870?). These were all from the north of the region.
- Features with no geothermal influence were deleted from the Tongariro National Park data from GNS Science. These included Tama Lakes and Blue Lake.
- The following parameters were removed from the 2005/06 database on the grounds that they were either:
 - a) of little relevance in geothermal geochemical monitoring; A254F, CuTR, Drawdown, HardT, Bore WL, MnTR, NNN, NO₂, NO₃, Pump dur, Pump rate, Transmis, Turb-N, and ZnTR, or
 - b) were a different way of measuring the more commonly determined parameter in the dataset, and thus not comparable over time or space; Hg Diss (generally reported as HgT), B TR (B Diss), Br Diss (Bromine), FeTR (Fe Diss), Free CO₂, Si R F (SiTot D), TDS (Cond or Sal).
- At Wigmore Spring where different analytes were determined in 2005 and 2006, it has been assumed that Ca = Ca Diss, K = K Diss, Mg = Mg Diss, Na = Na Diss. It is a reasonable assumption as concentrations of the major ions rarely differ significantly between unfiltered and filtered samples.
- It has been assumed that Si Tot D (reported as SiO₂) is the same as SiO₂ in the 1993/94 dataset.
- It has been assumed that ALK (alkalinity, reported as CaCO₃) measured in the 2005/06 data is predominantly comprised of HCO₃ and so can be compared to HCO₃ reported in the previous 1993/94 dataset and in the GNS Science data. ALK has been recalculated as, and reported as, HCO₃ for this assessment (see Appendix 1).
- The H₂S Tot in the 1993/94 dataset has been assumed to be equivalent of S Tot (presumably reported as H₂S?) in the 2005/06 dataset. This column has been labelled S Tot (total sulphide reported as H₂S). The H₂S column (unionised H₂S) in the 2005/06 dataset had been calculated from S Tot, so is not necessary to include this in the primary data compilation.

Finally, for plotting data it has been assumed that <DL values (< detection limit) are = DL. This has led to ambiguity when it comes to analytes for which DL has changed with time or the methods used, for example as for H₂S and As, but is a commonly accepted approach for plotting such data.

3 Spatial and temporal trends

3.1 Spatial trends

For this analysis, all available data (as shown in Appendix 1) have been included. The spatial analysis below includes commentary on the likely origin of selected components and their implications. The interpretation is broadly similar to that described in Huser and Jenkinson (1996) and Luketina (2007), based on:

- deep geothermal fluids: higher pH-Na-Cl-Si-Li-Rb-Cs assemblages
- steam-heated fluids: lower pH, higher H₂S-NH₄-SO₄ and K (leached from rocks during acid alteration)
- meteoric waters (including groundwaters): higher Mg, HCO₃
- specific local or regional bedrock/aquifer characteristics: high B, F.

3.1.1 One dimensional spatial analysis: north to south

A north-south transect through the Waikato region has been taken, and features labelled 1 to 32 depending where upon this transect they fall (these labels are also given in the Appendix 1 table). In this way, general geochemical trends as one moves from the north (Coromandel – Hahei and Hot Water Beach features) to the south (Tongariro National Park) become apparent, as do individual features with unusual geochemistry. These graphs are shown in Figure 1a - f. Originally, these graphs were plotted with the northing as the x coordinate, but this tended to group together many of the TVZ data.

Systems with distinctive geochemistry

The coastal systems at Coromandel and Kawhia show the clear influence of seawater with high Na, Cl, Mg, K and SO₄. In this case, a predominant geothermal origin can not be attributed to these ions. However, the features at Hot Water Beach also have high Li, Rb and Cs – higher than would be expected if these trace ions originated from seawater, indicating a deep geothermal fluid input. The Kawhia springs more closely resemble the composition of seawater.

Te Aroha is an unusual system, high in Na, K, HCO₃, SO₄ and B.

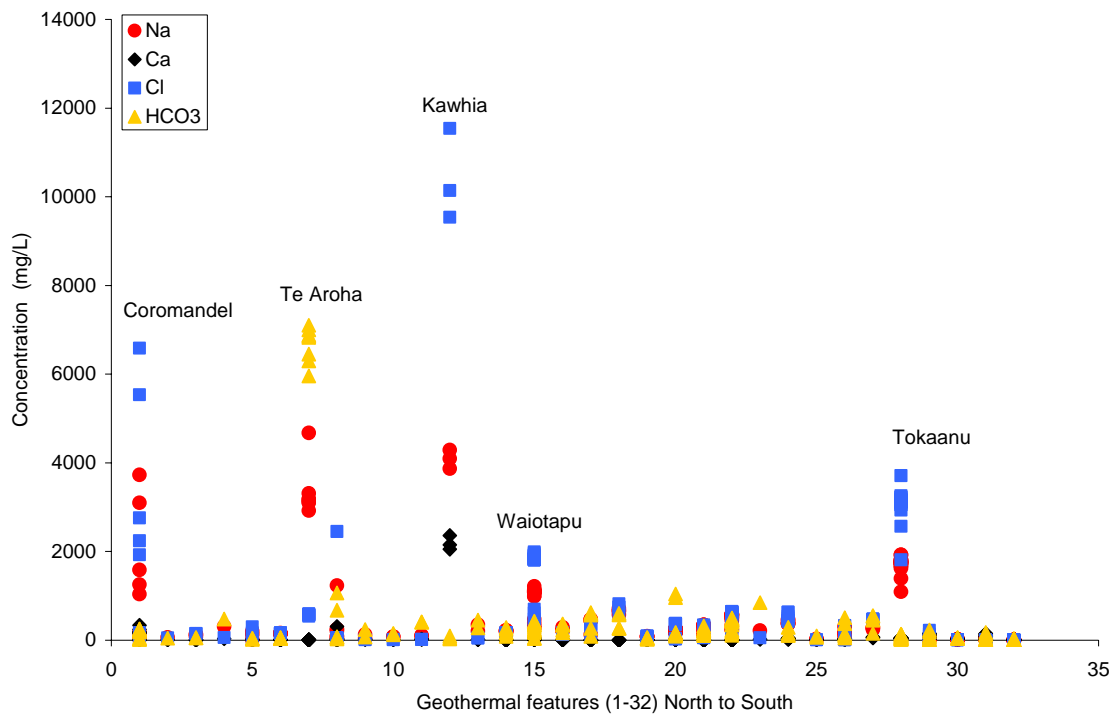
Larger geothermal systems such as Waiotapu and Rotokawa display a range of compositions from low pH, high H₂S, SO₄, NH₄ and K (and occasionally Fe) from steam-heated waters, as well as Na-Cl-Si-As rich deep-seated fluids.

Mid-region features outside or on the edge of the TVZ (Te Maire, Atiamuri, Orakeikorako and Horohoro) appear to have consistently higher F, possibly reflecting regional aquifer characteristics or bedrock geology.

South of Lake Taupo, Tokaanu has high Na-Cl, Li, K and B, As, Cs, effectively a deep-seated geothermal fluid assemblage but with higher B. The Tongariro National Park (TNP) systems on the other hand (Ketetahi, No Name Spring and Emerald Lakes), tend to have the low pH, high SO₄ and Fe assemblage typical of steam-heated features. Ketetahi also has high B similar to Tokaanu, and the Emerald Lakes have surprisingly high As concentrations.

Figure 1: North-south geochemical trends

a)



b)

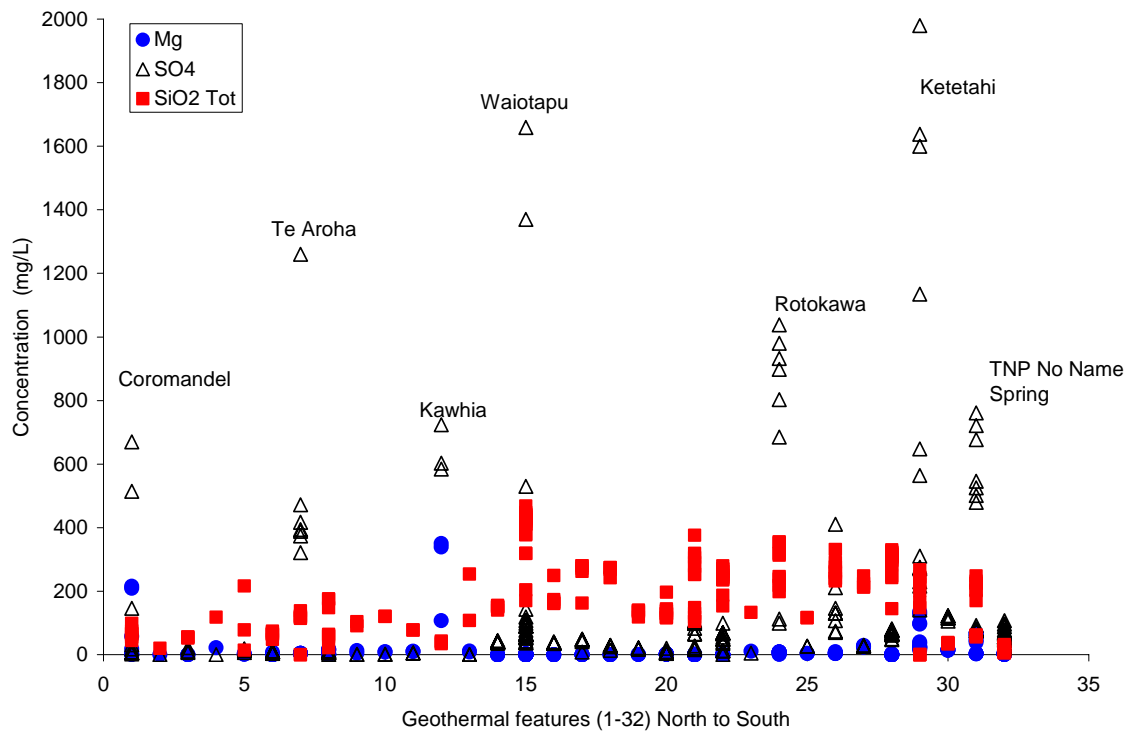
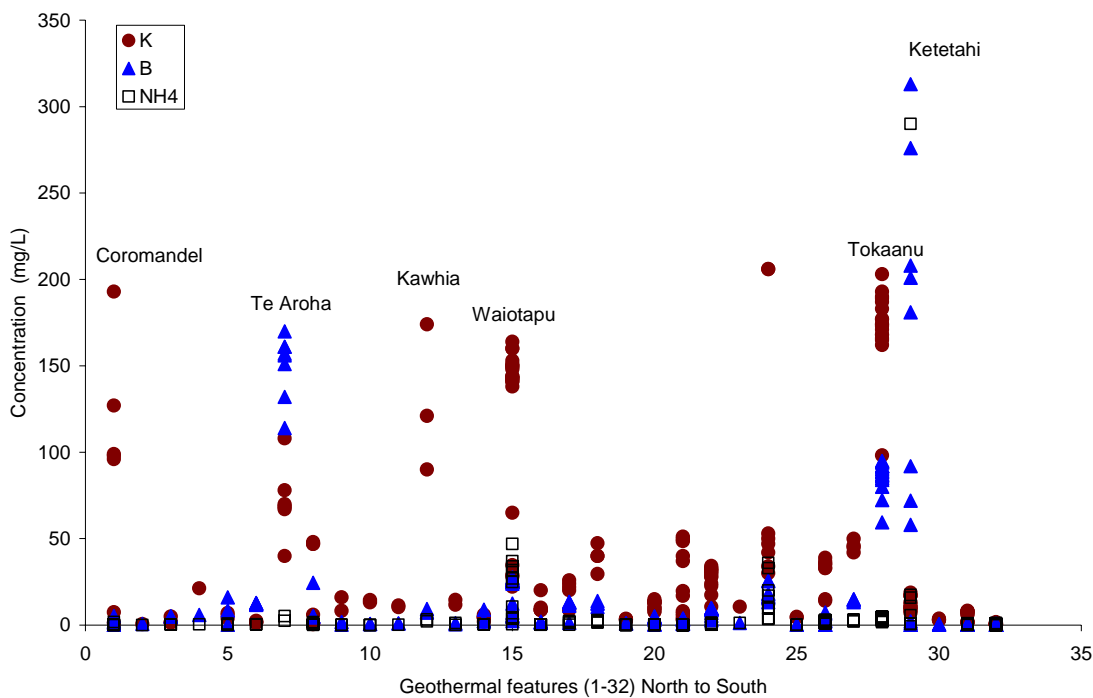


Figure 1 (continued)

c)



d)

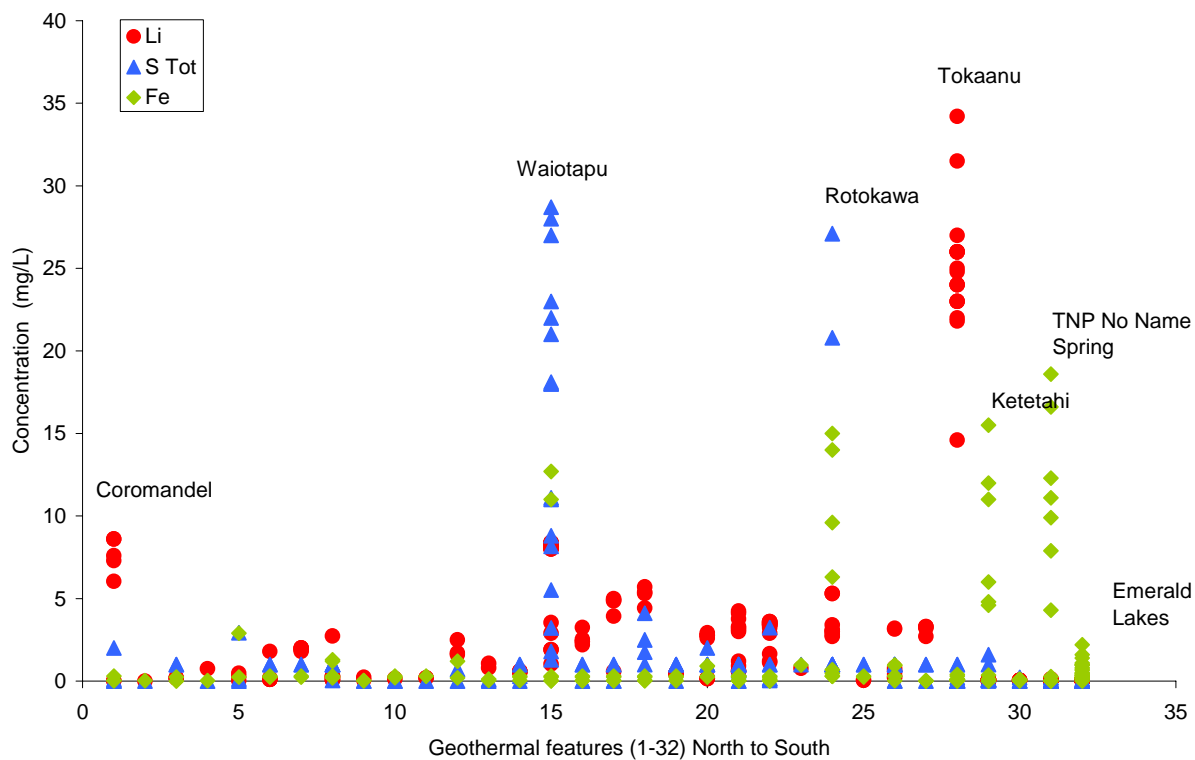
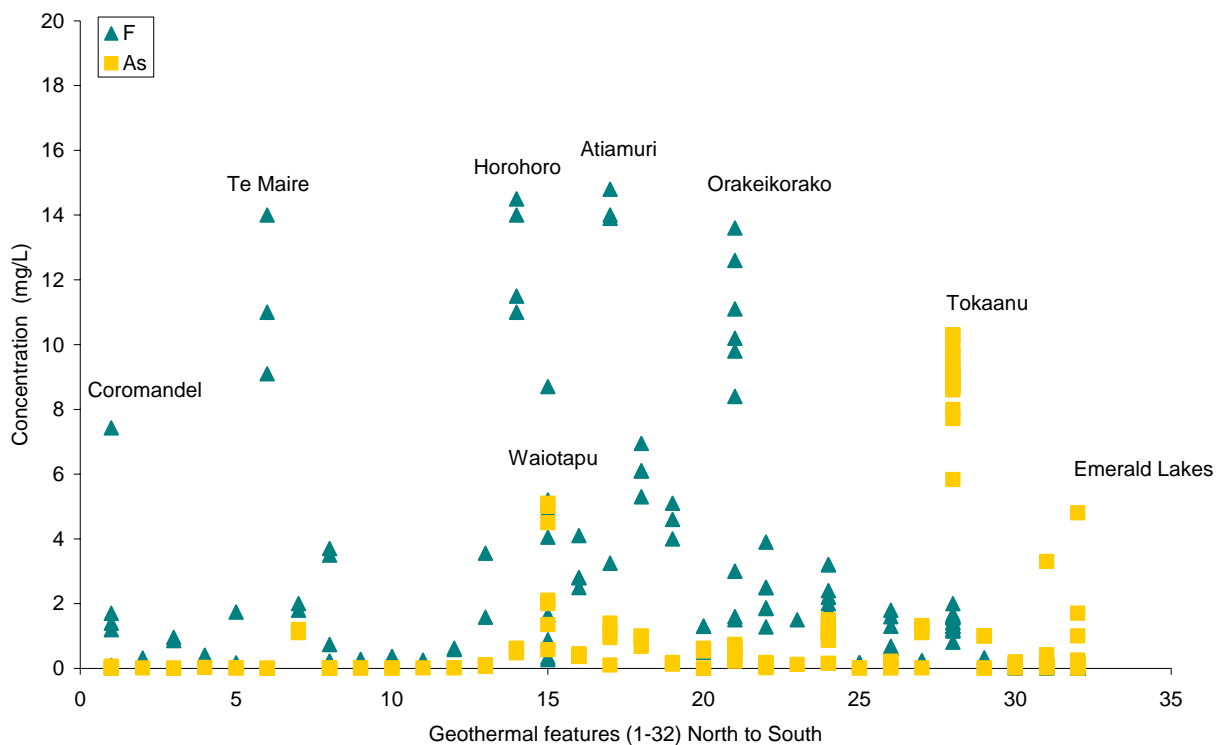
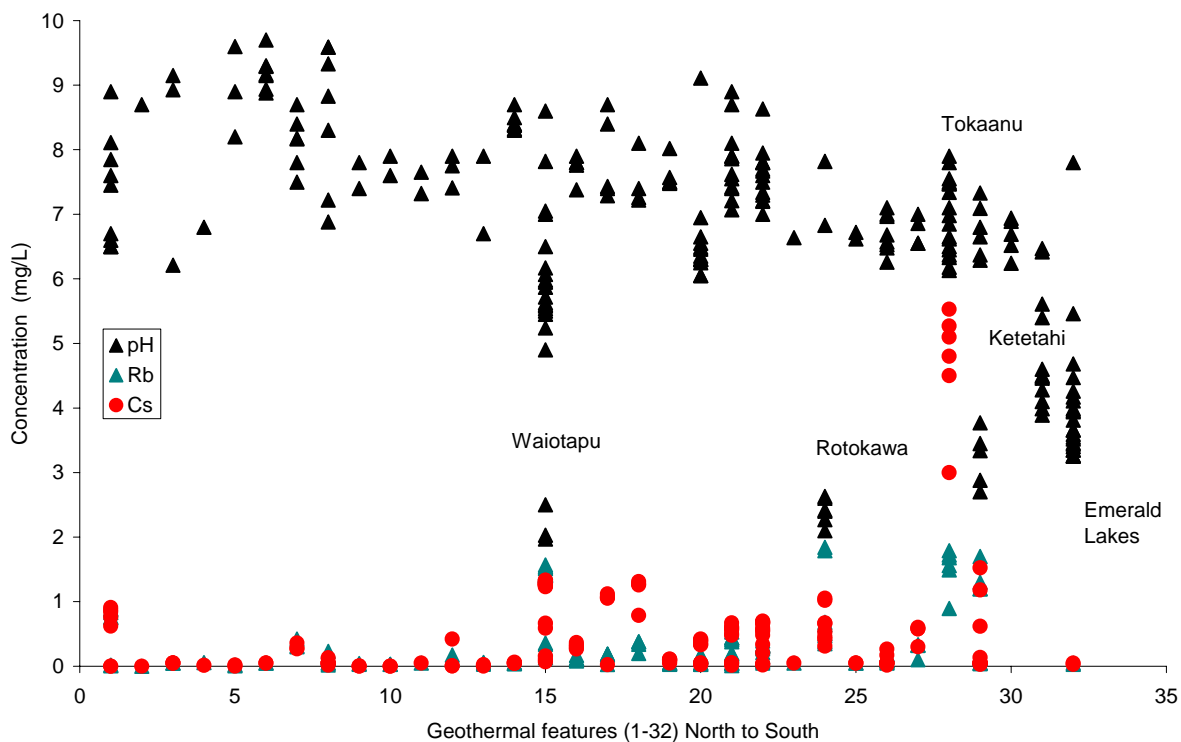


Figure 1 (Continued)

e)



f)



General geochemical trends north to south

Plotting concentration on a log scale, allows general trends to become more apparent, as the influence of the individual systems described above becomes diminished. This is evident on Figure 1f where pH (already a log parameter), demonstrates a general decrease from north to south. Figures 2a–2d show the parameters showing such general spatial trends. Other parameters (such as B) do not show such trends (therefore no plots are shown).

Sodium and Cl show a decrease from north to south in the southern part of the region (Figure 2a), as do HCO_3 and F (Figure 2b). Together with the pH trend, this indicates a diminishing contribution of the deep geothermal fluids to feature geochemistry in the south, where steam heating becomes more apparent. This is further reinforced by consistently high SO_4 concentrations in the south (Figure 2c).

Temperature and SiO_2 show very similar trends, increasing towards the south into the TVZ and TNP, but decreasing in the low-temperature features of TNP in the far south. Parameters such as Li, Rb, Cs, and As show a similar but less obvious trend to SiO_2 , reaching a maximum in the TVZ systems.

In summary, the trends are broadly consistent with the presence of high-temperature, deep-seated geothermal fluid system in the central part of the region (the TVZ), with low-temperature systems in the north, and more steam-heated systems further south.

Figure 2: North-south geochemical trends (log scale)

a)

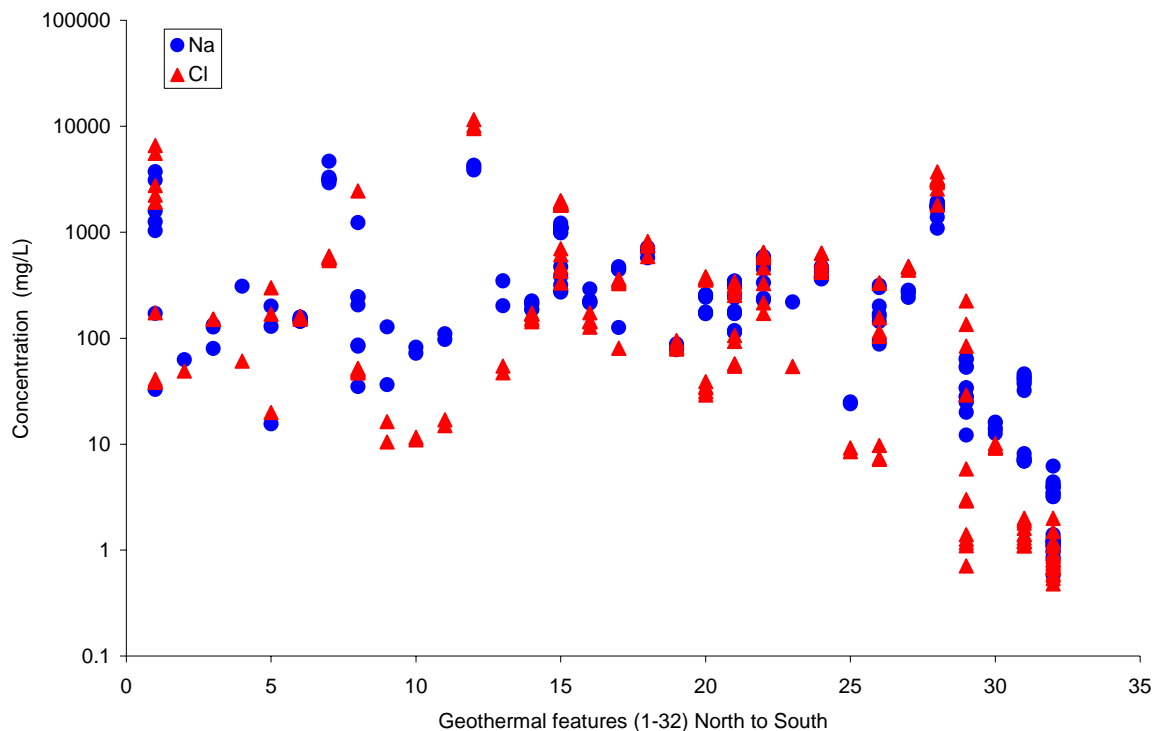
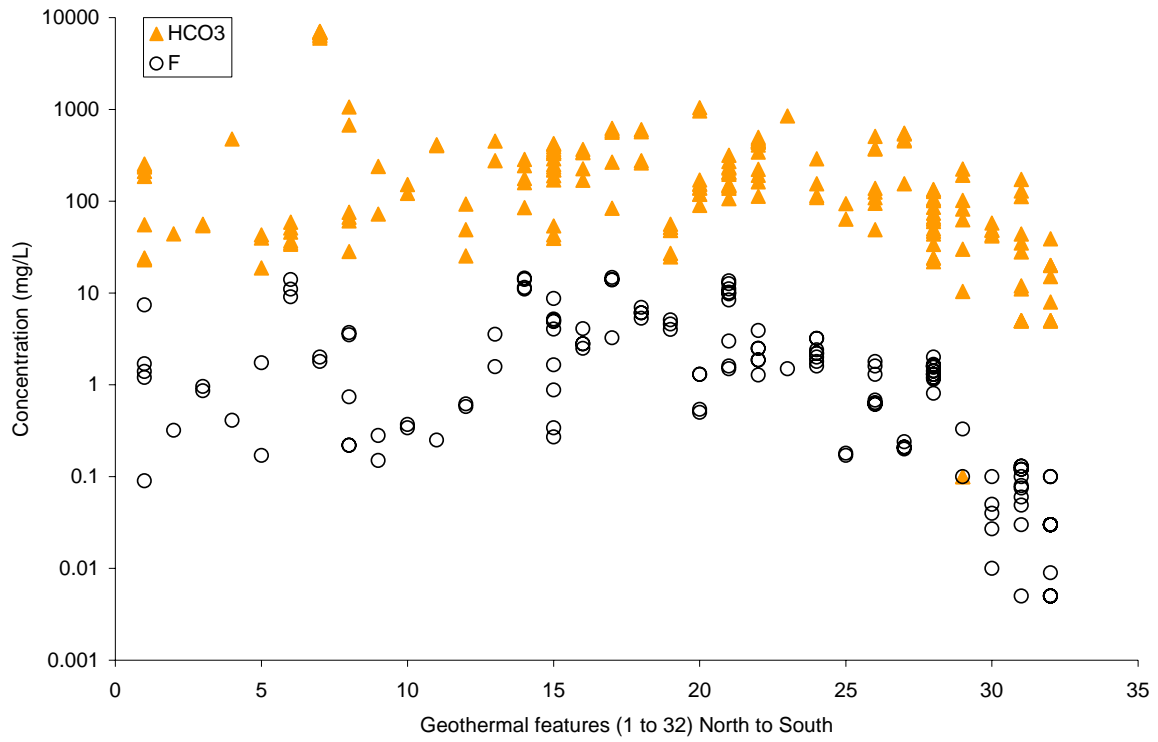


Figure 2 (continued)

b)



c)

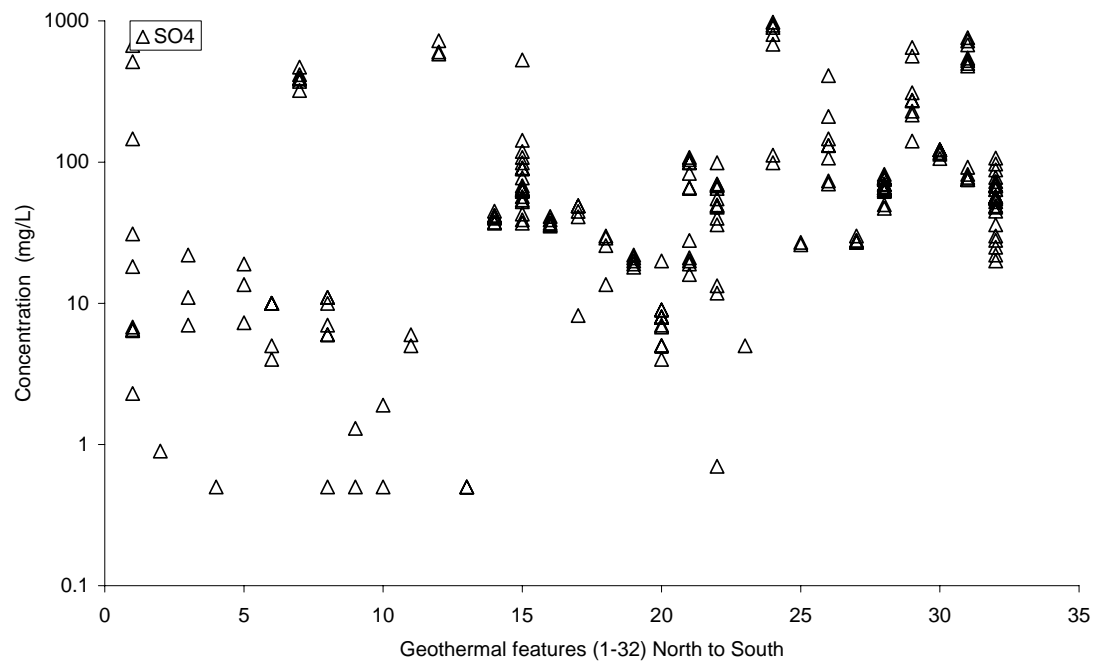
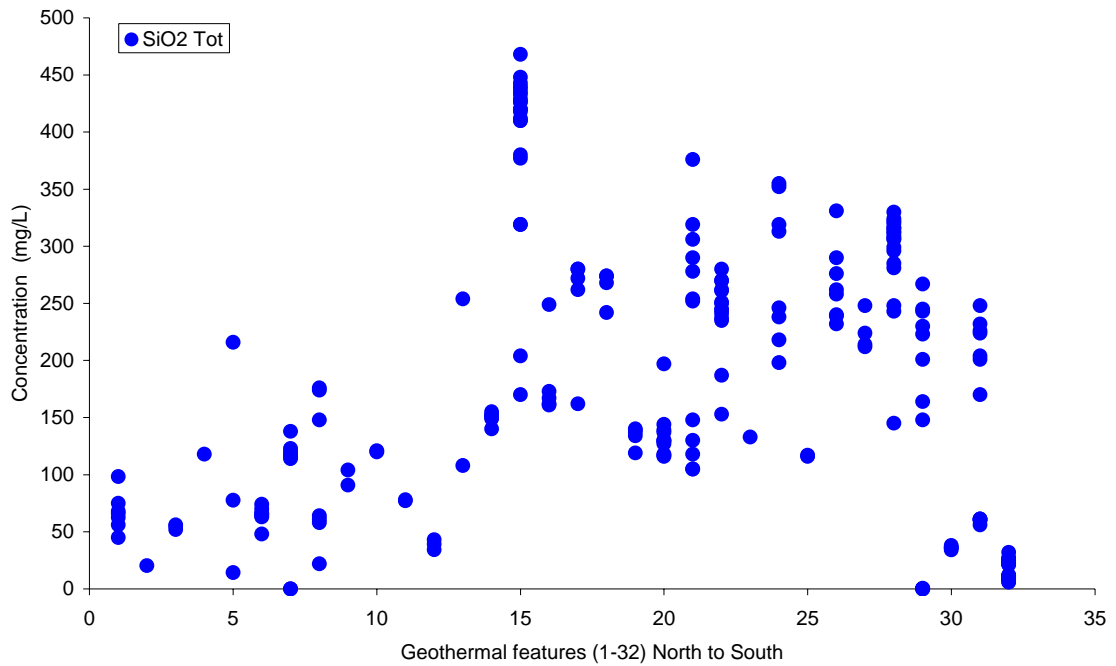
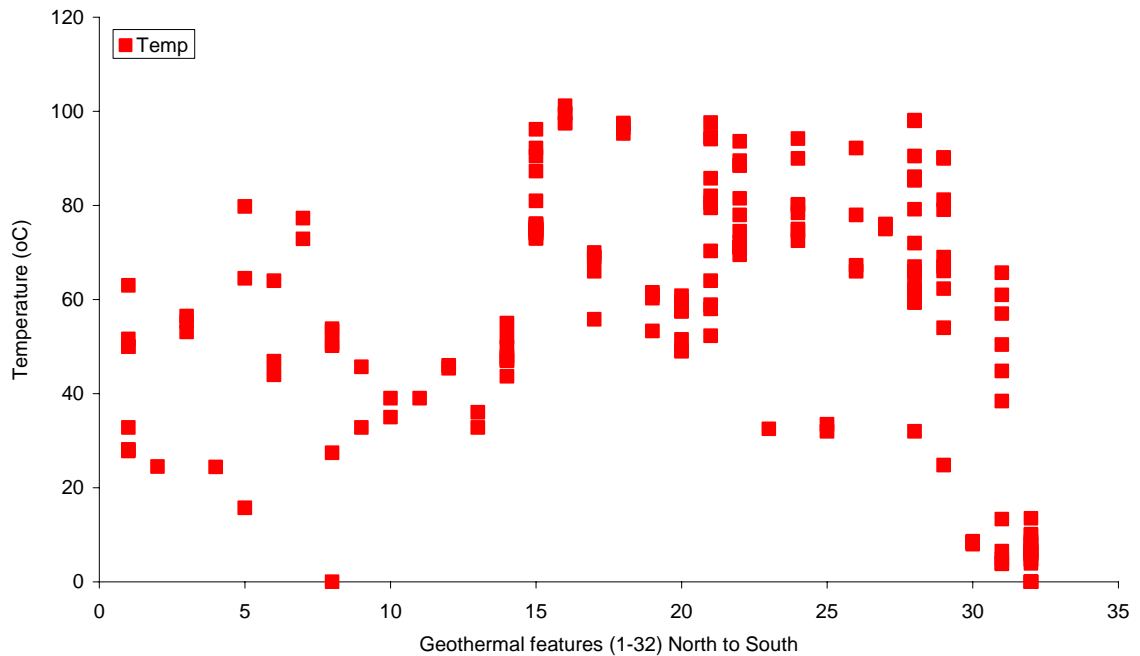


Figure 2 (continued)

d)



e)



3.1.2 Two dimensional analysis

To undertake a full two-dimensional analysis of the data, the map coordinates were expanded to the full NZMS 260 coordinates. Where no map coordinates were present in the supplied table, they were interpreted to be identical to the first coordinates in the series given in the supplied spreadsheets. Using all of the data in Appendix 1, two-dimensional maps with contours can be constructed. The contoured maps for sulphate

concentrations and sodium concentrations are shown in Figures 3a and 3b respectively.

However, as can be seen from Figure 3, the two-dimensional contouring is very biased towards the high concentrations, and the contours are definitely not realistic. This is really a function of the spread of data points and the contouring parameters. This may be improved somewhat when the additional GNS Science data becomes available. Consequently, in the meantime, the one dimensional transects shown in Figures 1 and 2 provide much more information, particularly since the Waikato area is elongated north/south.

Figure 3a: Contoured sulphate concentrations

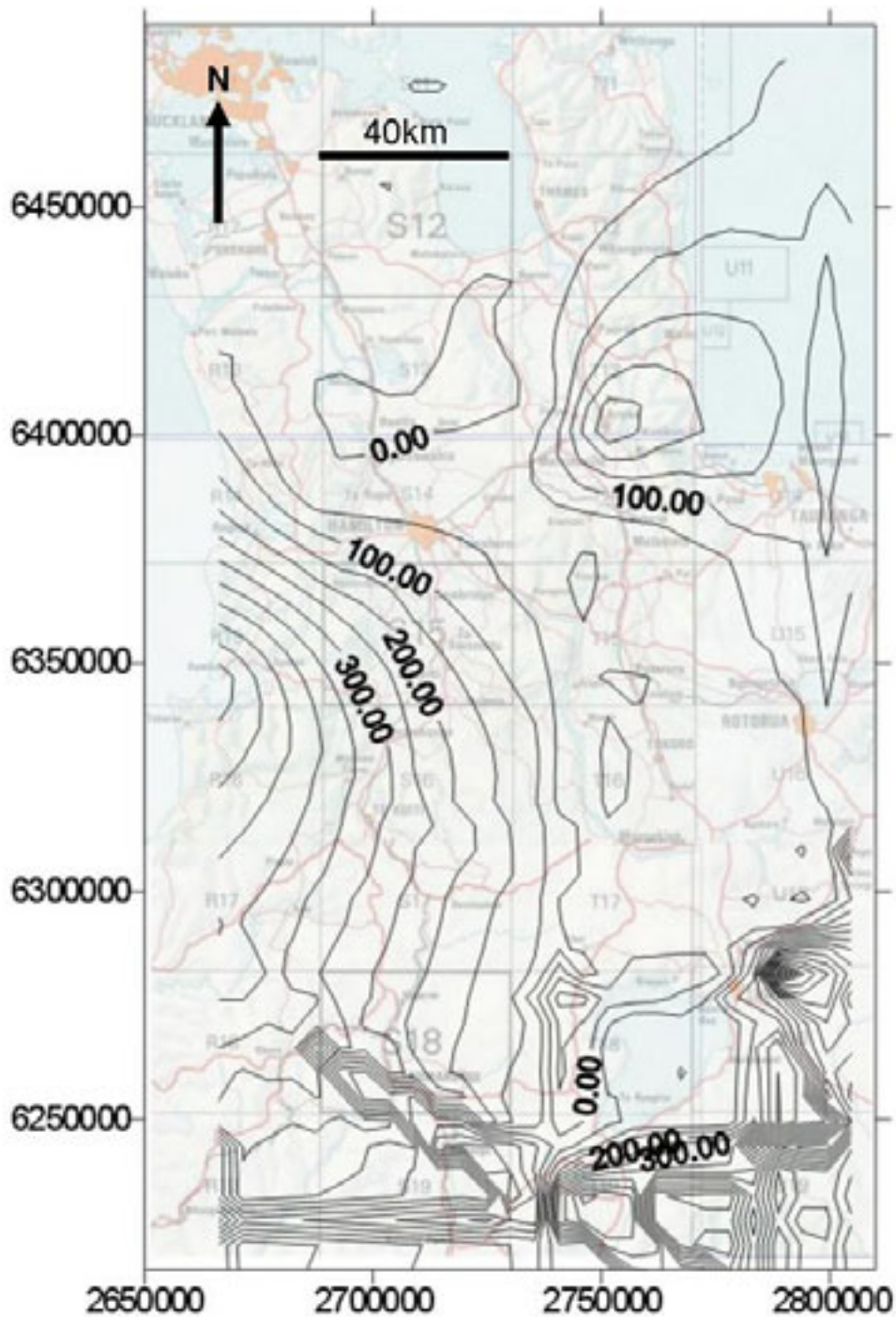
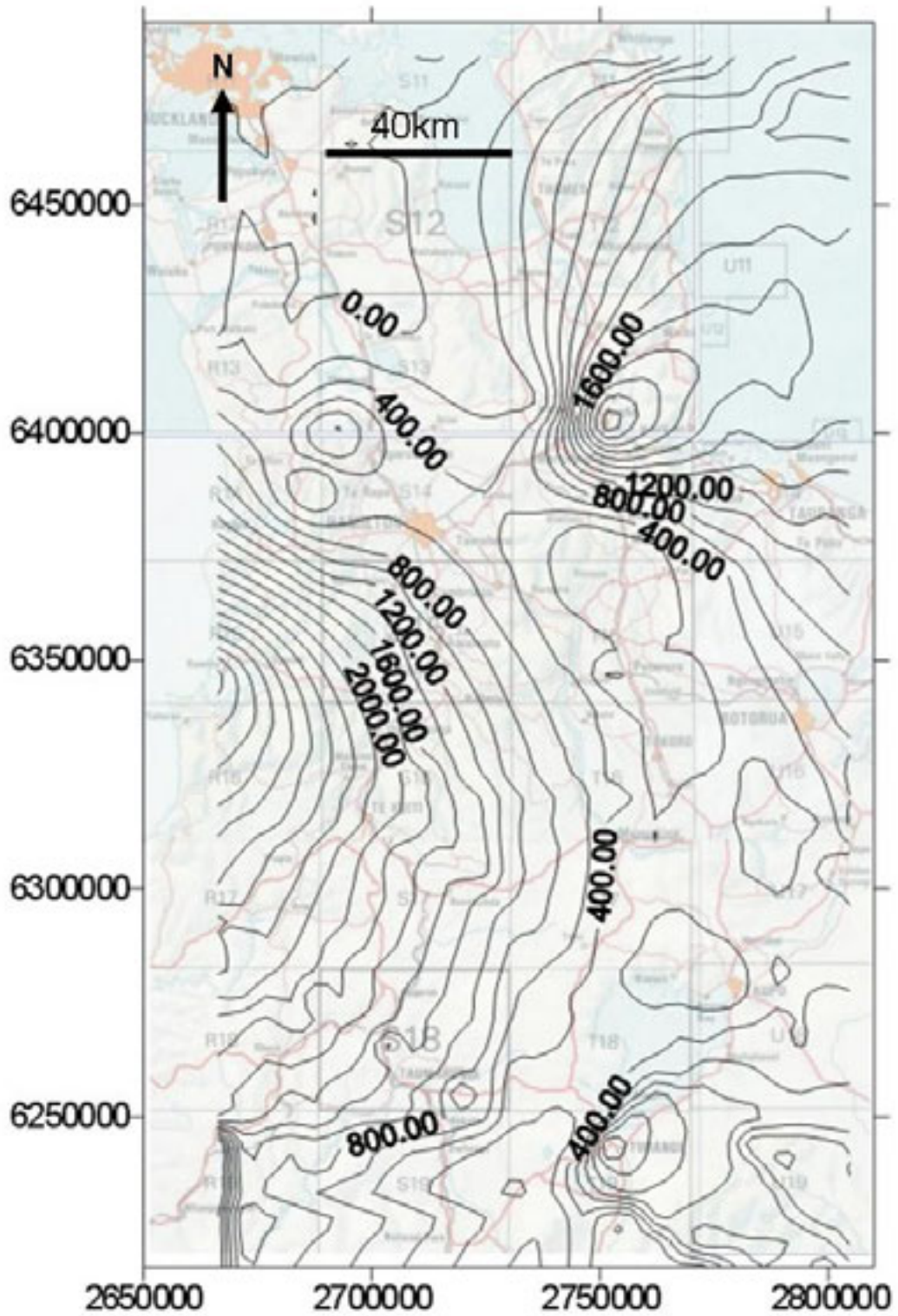


Figure 3b: Contoured sodium concentrations



3.1.3 Recommendations: Spatial survey

It is difficult to make recommendations in the continued absence of recent data for some of the features sampled by GNS Science. However, some suggestions can be made to refine the approach to monitoring and to make sure the same feature is included in each monitoring programme.

- Possible deletion of low temperature, low chloride springs.
- Monitor a single, representative feature (for which previous data is available) for small systems in the north.
- For larger systems, select some representative features. For instance, one deep geothermal fluid feature and one steam-heated feature, for which previous data is available, and monitor these.

3.2 Temporal trends

Only a few of the sites sampled in the 1993/94 survey were included in the current survey. There is also no surety that the feature sampled in 2005/06 was exactly the same feature previously sampled. For those that seem to be, the following comments can be made for these systems, ordered again below from north to south of the region.

Note that the colour scheme on Figure 4, although somewhat garish, is designed to help visual interpretation, with data prior to 1980s represented as black or grey, through the 1980s by red and brown, through the 1990s by orange, yellow and green, and through the 2000s by cooler colours; blue and purple. A log scale has been used so that all parameters can be shown on the one figure and therefore trends can be viewed together.

Feature analysis

Hahei (Figure 4a)

Hahei was not sampled previously, but has been sampled three times over 2005/06, although not all parameters have been measured each time. No trends are evident over this short time scale.

Recommendation: Revert to monitoring the higher temperature, principal feature at Hot Water Beach (as in 1993/94) instead of the cooler springs at Hahei. Every two years.

Kawhia (Figure 4b)

Kawhia has been sampled in 1981, 1994 and 2006 (at 12-13 year intervals). This spring is influenced by seawater as noted previously. There is possibly a decreasing Cl concentration with time, however, other seawater components do not follow this trend. It was noted after the 1993/94 survey that yearly sampling would be necessary to establish a good baseline (Huser and Jenkinson, 1996) and that remains the case. Note that the apparent decrease in S Tot is a change of detection limit.

Recommendation: Continue measurements every two years until a baseline is established, then move to less frequent monitoring (for example, 1/6yrs).

Horohoro (Figure 4c)

It has been assumed that what is now known as Waipupumahana is the same "hot spring" that has been monitored at Horohoro since 1963. In this case there are trends evident in Ca, Mg and HCO₃ concentration which decrease over this period. This suggests less dilution by groundwater sources, in contrast to the findings of Huser and Jenkinson (1996).

Recommendation: Continue monitoring every two years.

Te Kopia (Figure 4d)

No trends are evident in this data spanning 13 years. Again the apparent recent decrease in S Tot is due to a change in detection limit.

Recommendation: Continue monitoring every two years.

Orakei Korako: Waihunuhunu (Figure 4e)

Magnesium appears to have decreased over the 22 year period of sampling, though no other consistent trends are evident (S Tot changes are again due to changing detection limits).

Recommendation: Continue monitoring every two years.

Orakei Korako: Manganese pool (Figure 4f)

Few consistent trends are shown over the 22 year period, although possible increases in F and As are indicated.

Recommendation: It is likely that only one of these Orakeikorako features (which are similar in nature) need to be monitored, every two years. Waihunuhunu has the longer data record.

Ngatamariki: New North Spring (Figure 4g)

The North or New North spring (assuming they are the same feature) has been sampled in 1993, 1994 and 2005. Prior to 1993 a different feature was sampled until buried in a landslide (Huser and Jenkinson, 1996). Although it appears that most parameters (except S Tot) have decreased in the most recent 2005 sampling, further data is needed before a trend can be confirmed.

Recommendation: Continue monitoring every two years.

Tauhara: Taherepa (Figure 4h)

There is too little data for a trends assessment as yet.

Recommendation: Continue monitoring every two years.

Waihi: Whakatara (Figure 4i)

This feature has been monitored over 12 years – no consistent trends are apparent (S Tot again due to changes in the detection limit).

Recommendation: Continue monitoring every two years.

Tokaanu: Taumatapuhpuhi Geyser (Figure 4j)

Too little data for a trend analysis at this stage.

Recommendation: Continue monitoring every two years.

Tokaanu: Teretere and No. 5 Pool (Figure 4k and 4l)

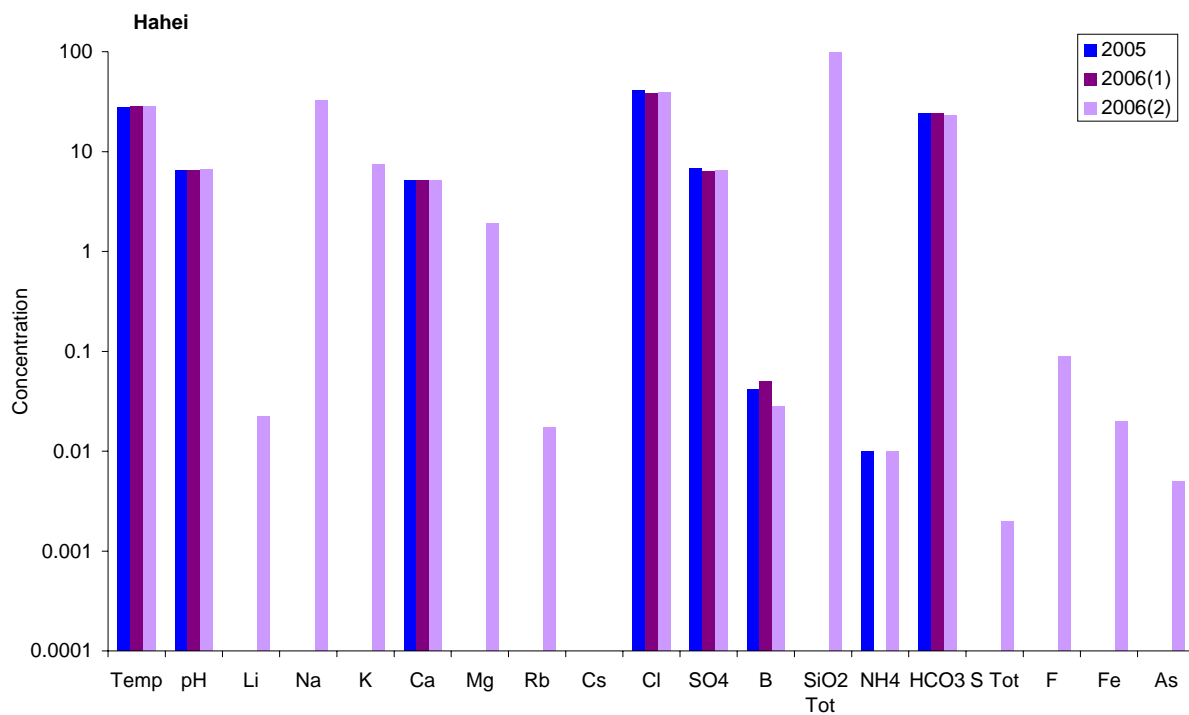
These features have been monitored annually since 2002, and few trends are evident. Magnesium and HCO₃ increase in Teretere, which may indicate increasing dilution by meteoric (ground or surface) water.

Recommendation: Continue monitoring every two years.

Figure 4: Temporal geochemical trends

(The concentration units are mg/L, the temperature unit is °C and the pH is in log units).

a)



b)

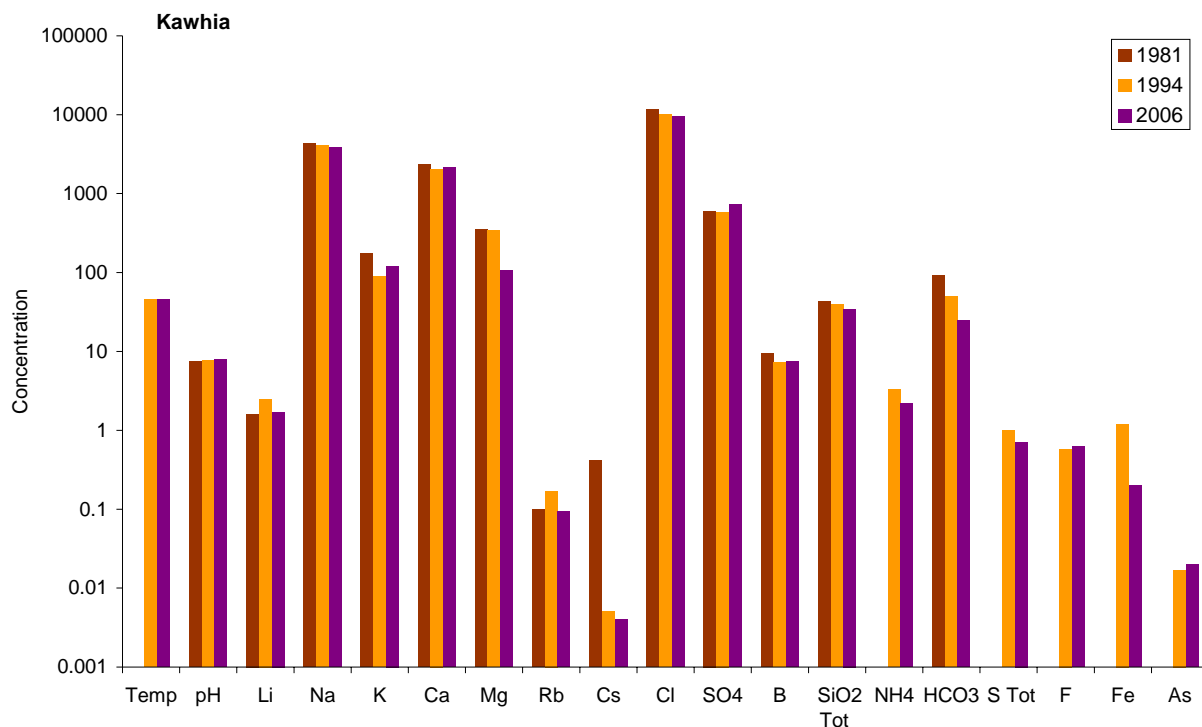
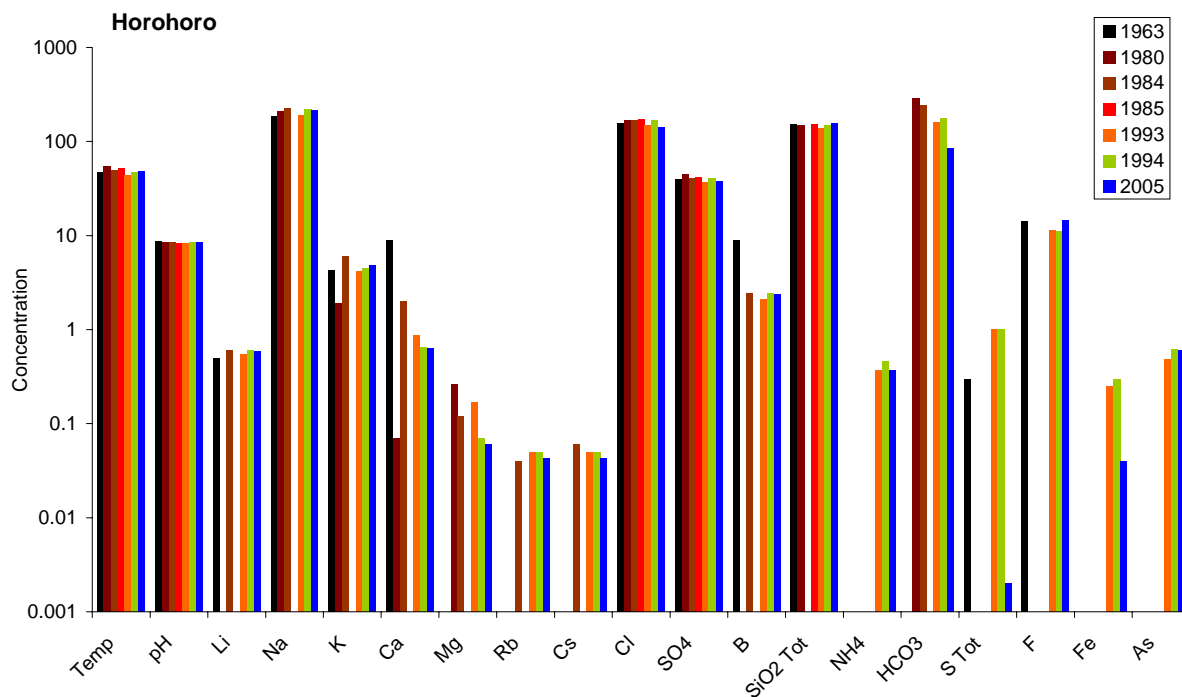


Figure 4 (continued)

(The concentration units are mg/L, the temperature unit is °C and the pH is in log units).

c)



d)

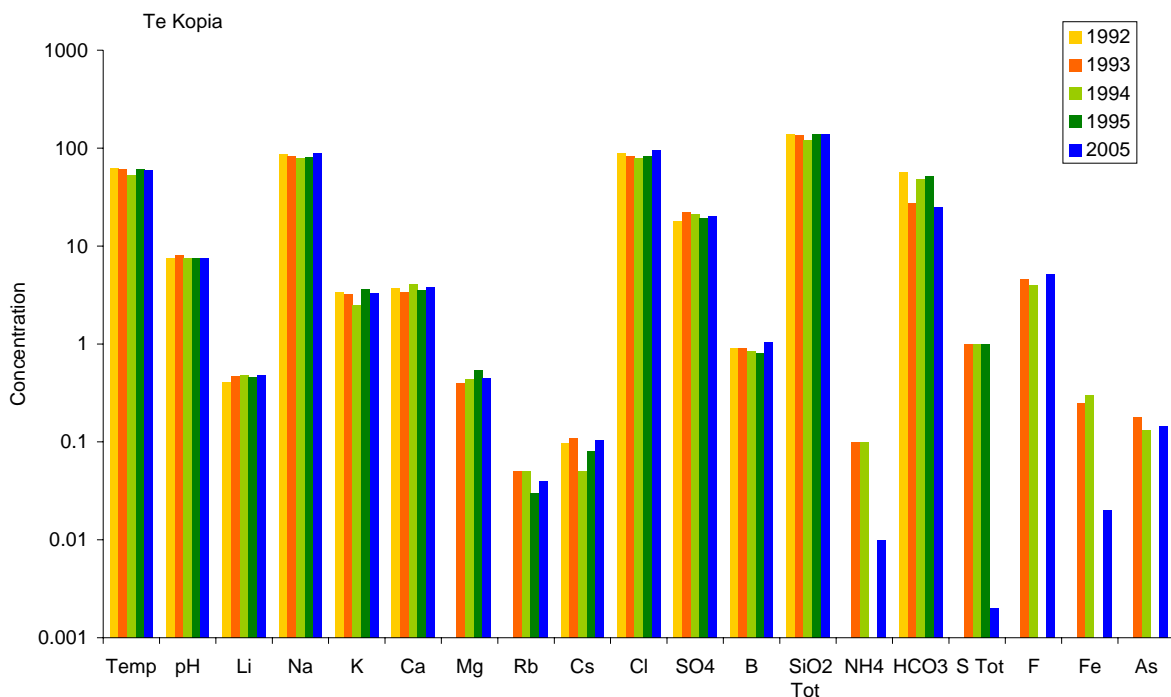
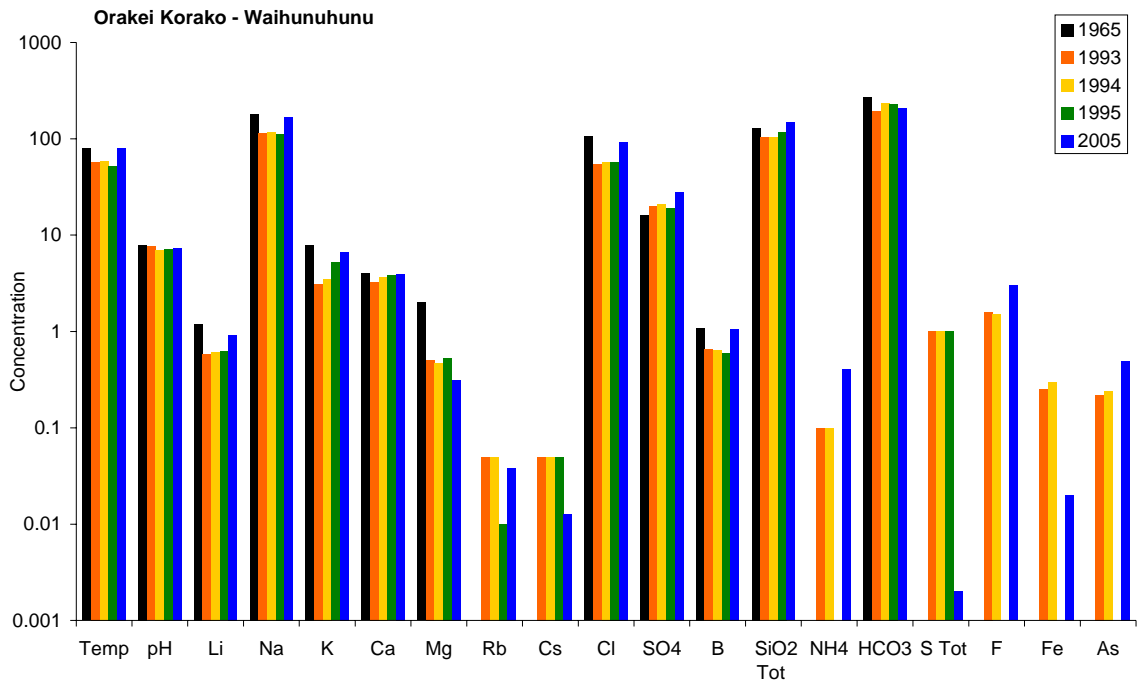


Figure 4 (continued)

(The concentration units are mg/L, the temperature unit is °C and the pH is in log units).

e)



f)

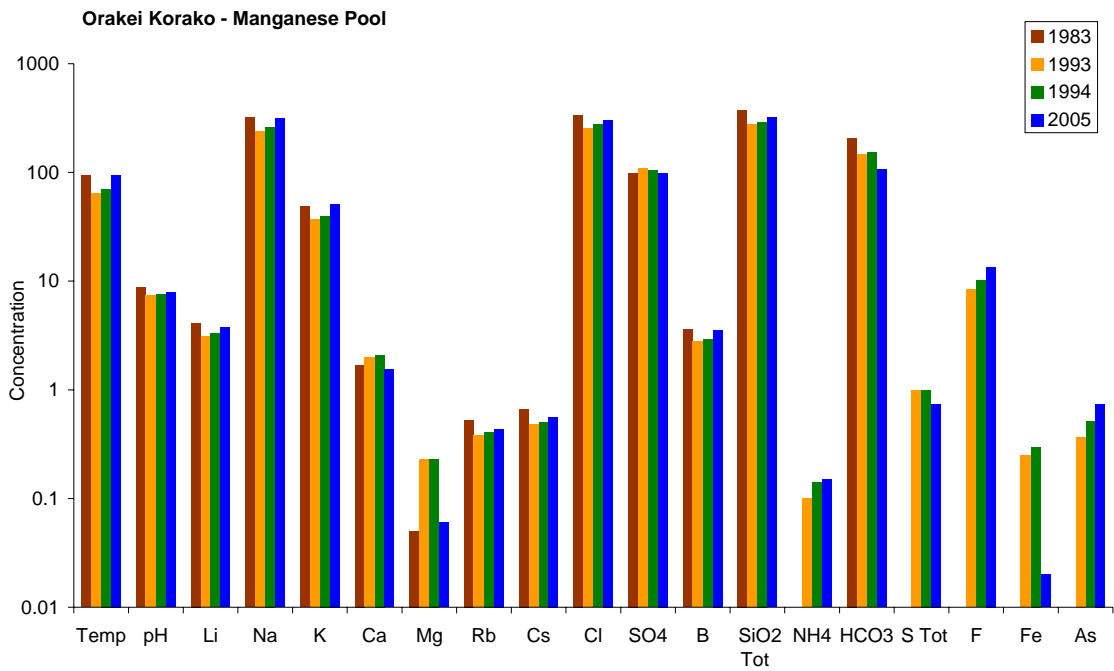
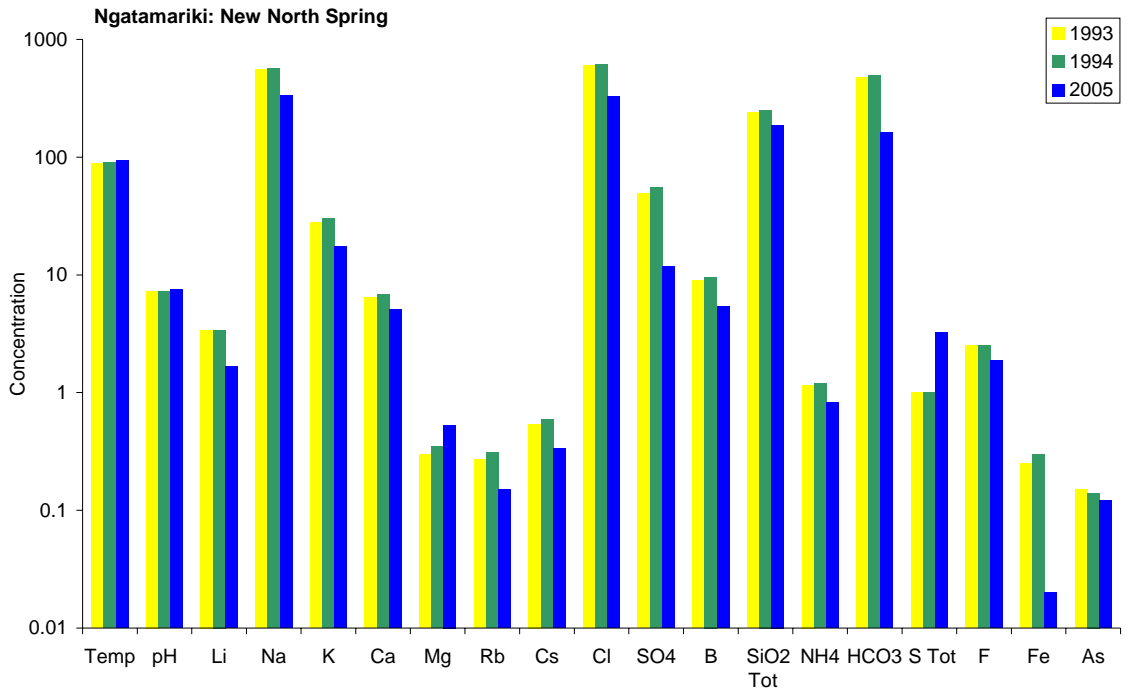


Figure 4 (continued)

(The concentration units are mg/L, the temperature unit is °C and the pH is in log units).

g)



h)

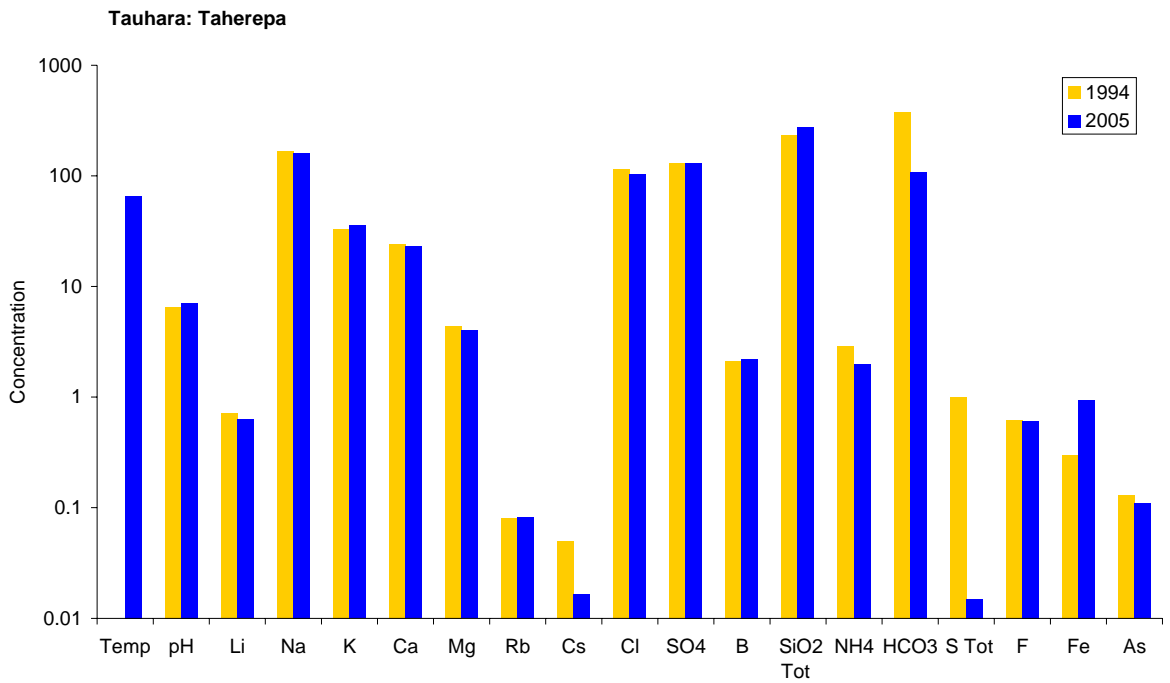
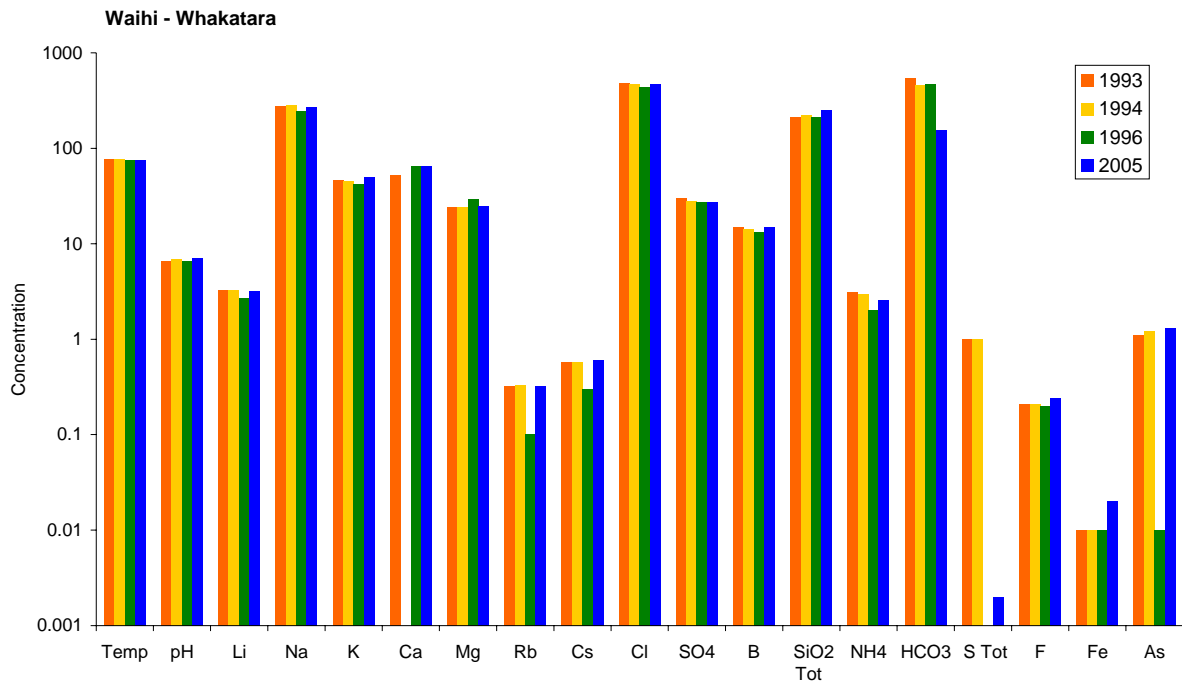


Figure 4 (continued)

(The concentration units are mg/L, the temperature unit is °C and the pH is in log units).

i)



j)

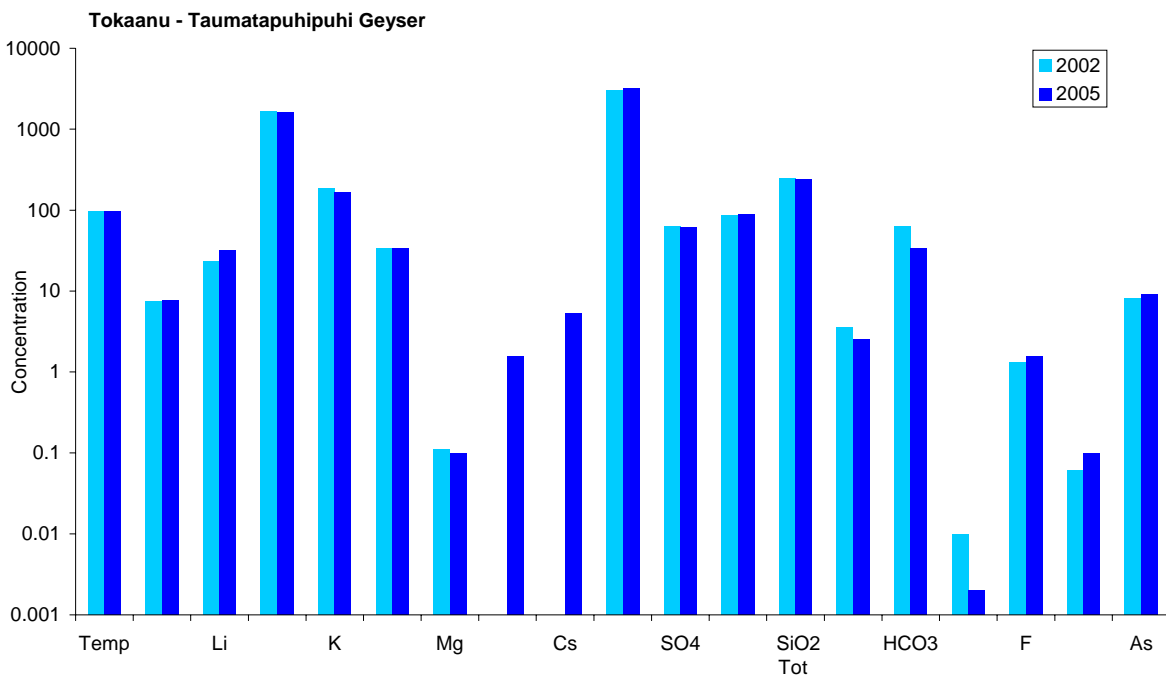
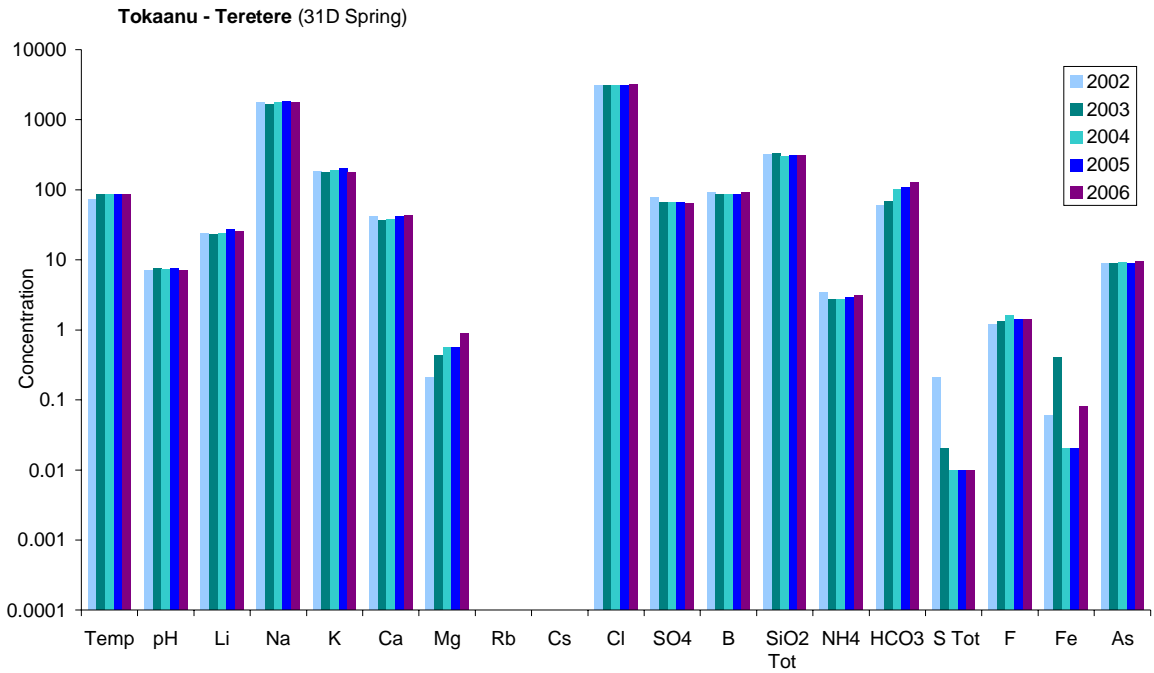


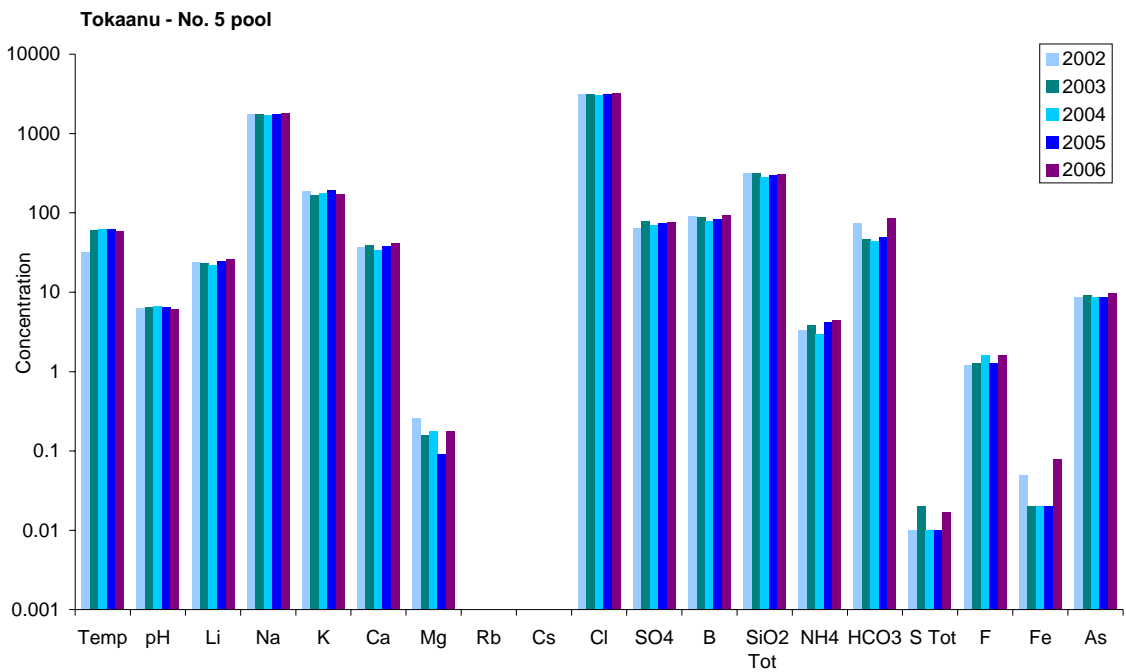
Figure 4 (continued)

(The concentration units are mg/L, the temperature unit is °C and the pH is in log units).

k)



l)



Ketetahi Black Cauldron (Figure 4m)

This has been monitored over a 16 year period, and appears to have fairly variable chemistry. Iron concentrations have decreased markedly and consistently over this period due to the increase in pH, but the apparent decrease in As is due to a changing detection limit. Deep fluid components such as Na, Cl, Cs, Rb have shown recent increases, consistent with an increasing pH also. The SO₄ concentrations have decreased, which together with the rise in pH suggests a decreased contribution of steam-heated fluids. However, these trends would need to be confirmed with further data.

Recommendation: Continue monitoring every two years

No Name Spring (Figure 4n)

This has been monitored annually since 2001 ... and again there is evidence of relatively variable chemistry, but few consistent trends.

Recommendation: Continue monitoring every two years

Lower Emerald Lake (Figure 4o)

Monitoring data is available over a 24 year period and shows significant variability but, again, few consistent trends. Potassium, SO₄ and Fe appear to increase, accompanied by a decrease in pH, suggesting a greater contribution for steam-heated fluid in more recent years. However, Mg and B also increase and the reason for this is less clear.

Recommendation: Continue monitoring every two years

Figure 4 (continued)

(The concentration units are mg/L, the temperature unit is °C and the pH is in log units).

m)

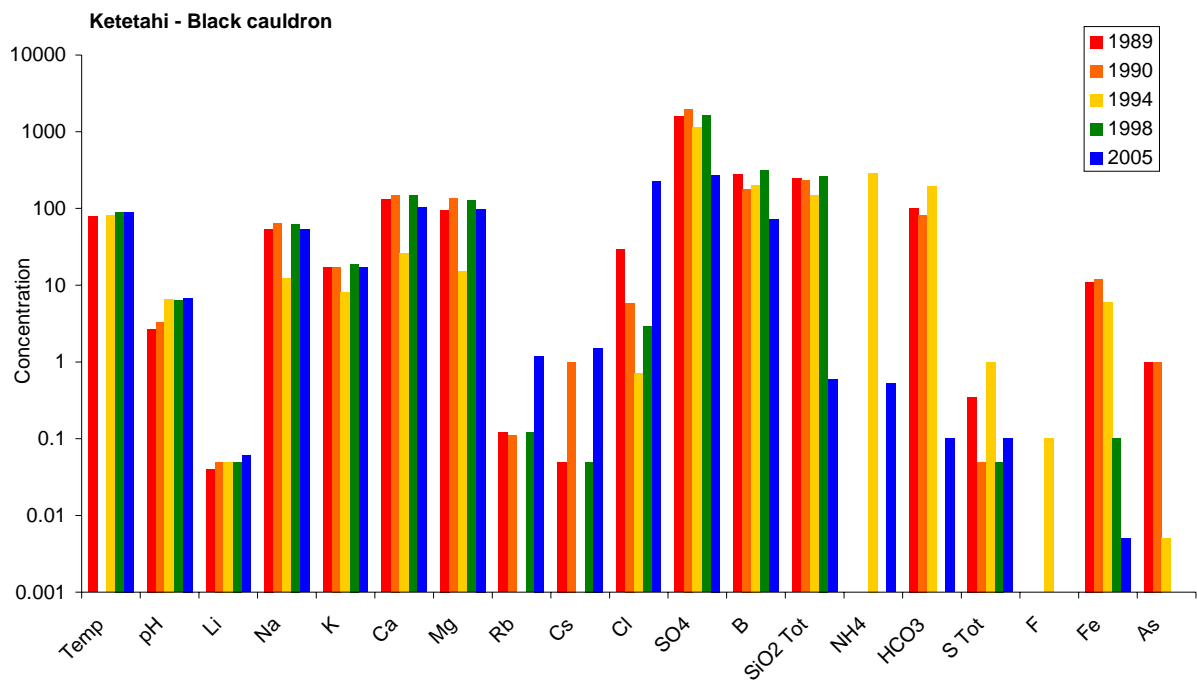
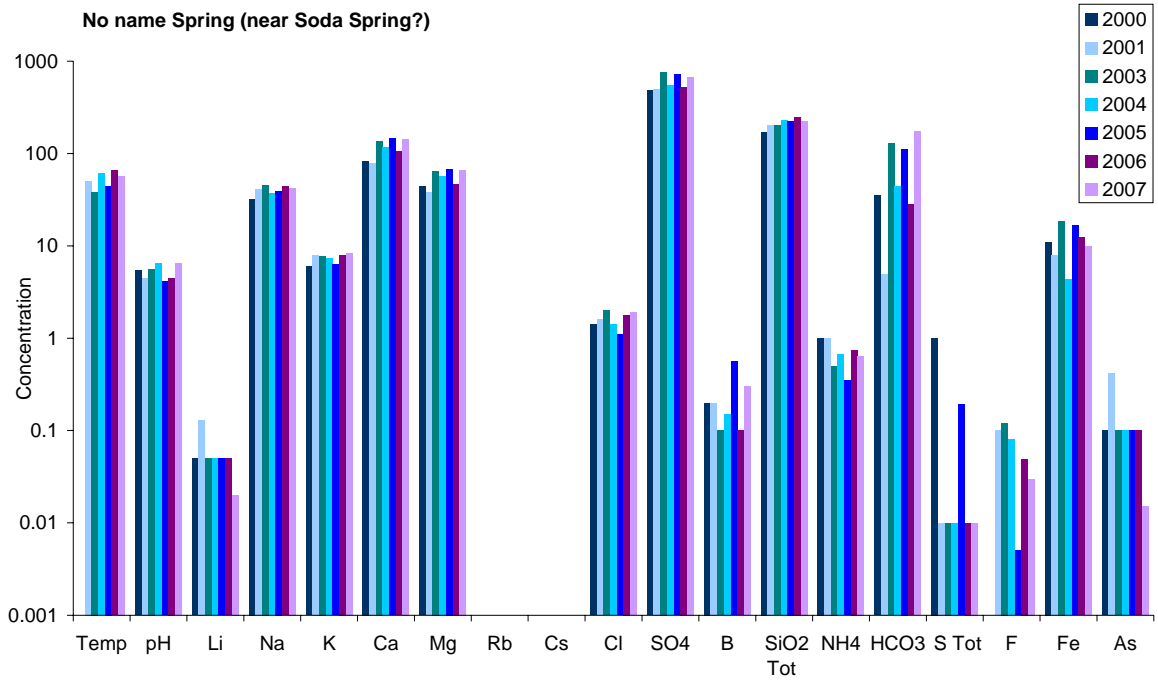


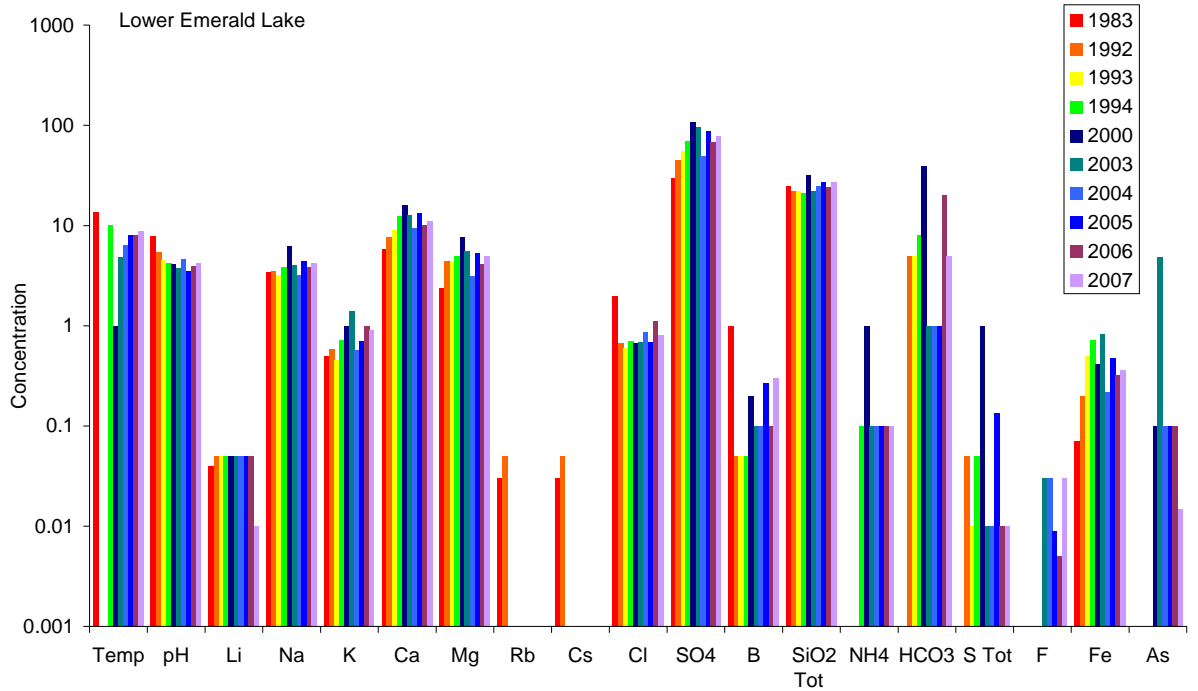
Figure 4 (continued)

(The concentration units are mg/L, the temperature unit is °C and the pH is in log units).

n)



o)



4 Data correlations

A correlation matrix compiled by Dr Nick Kim of Environment Waikato, on the 2005/06 data revealed the strongest correlations ($R^2 > 0.9$) between:

Li-Rb-Cs
Cs-As-Sb
Na-Cl-Br

Moderately strong correlations ($R^2 = 0.8-0.9$) were noted between:

Rb-Cs
(Li-Rb)-(As-Sb)
(Na-Cl-Br)-NH₄-B
(Cs-As-Sb) - temperature
K-Rb
A negative correlation occurred between: Mg-F

Weaker correlations ($R^2 = 0.7-0.8$) between:

Si-temperature
(Li-Rb-Cs) - temperature
(Na-Cl-Br) -Li
(Li-Rb-Cs) – (Na-Cl-Br)-B

These correlations arise as a consequence of the presence of these elements (except Mg and F) in the deep, high-temperature geothermal fluids.

4.1 Correlations in full dataset

When all data in Appendix 1 is plotted, the correlations noticed in the 2005/06 dataset are largely supported. A strong relationship between Li-Cs (Figure 5a) and Cs-As-Sb (Figure 5b) is shown, although the strong correlation proposed for Li-Rb does not appear to be shown in the more extensive dataset. Li-As-Sb correlations are stronger than evident in the 2005/06 dataset alone (Figure 5c).

Strong correlations are shown for Na-Cl and Cl-Br (Figures 5d and 5e), but the moderately strong relationship proposed for Cl-B is not evident (Figure 5f), nor is the 05/06 relationship between Si-temperature (Figure 5g).

There is no relationship between Cl and F (Figure 5f), although the negative correlation between Mg (and Ca) and F is evident, as they appear to have a mutually exclusive relationship (Figure 5h). This will be due to the formation of the fluoride salts of Ca and Mg (e.g, fluorite CaF₂) which are very insoluble.

Figure 5: Chemical correlations

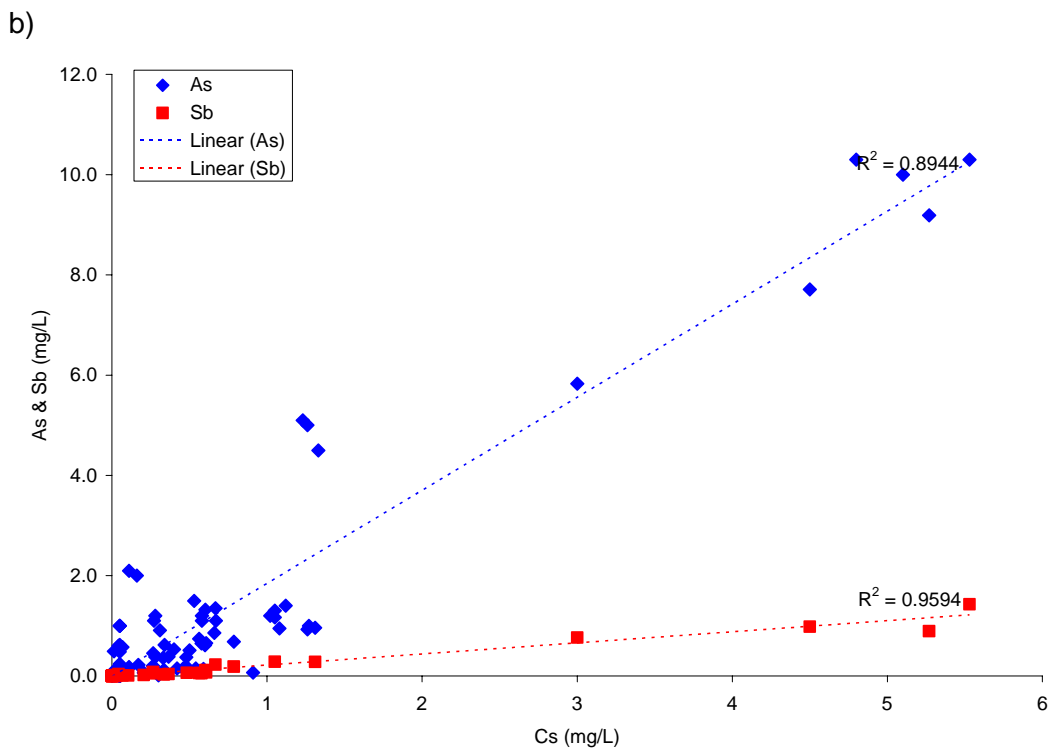
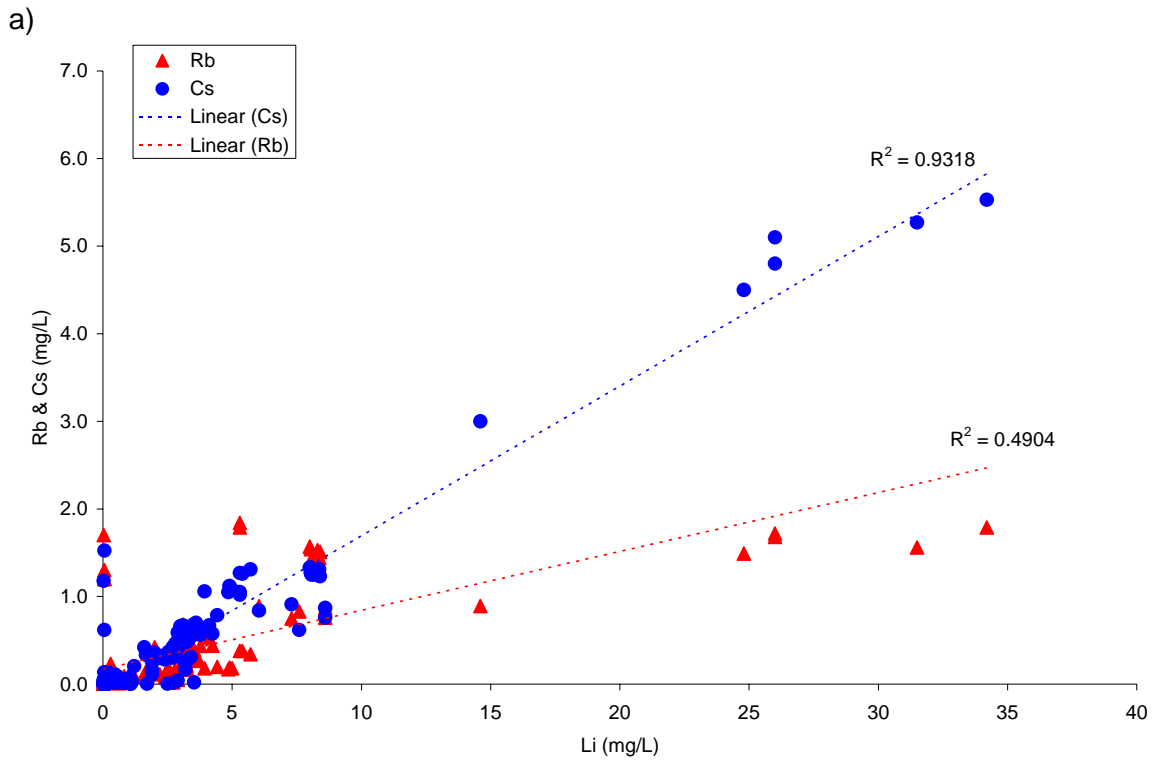
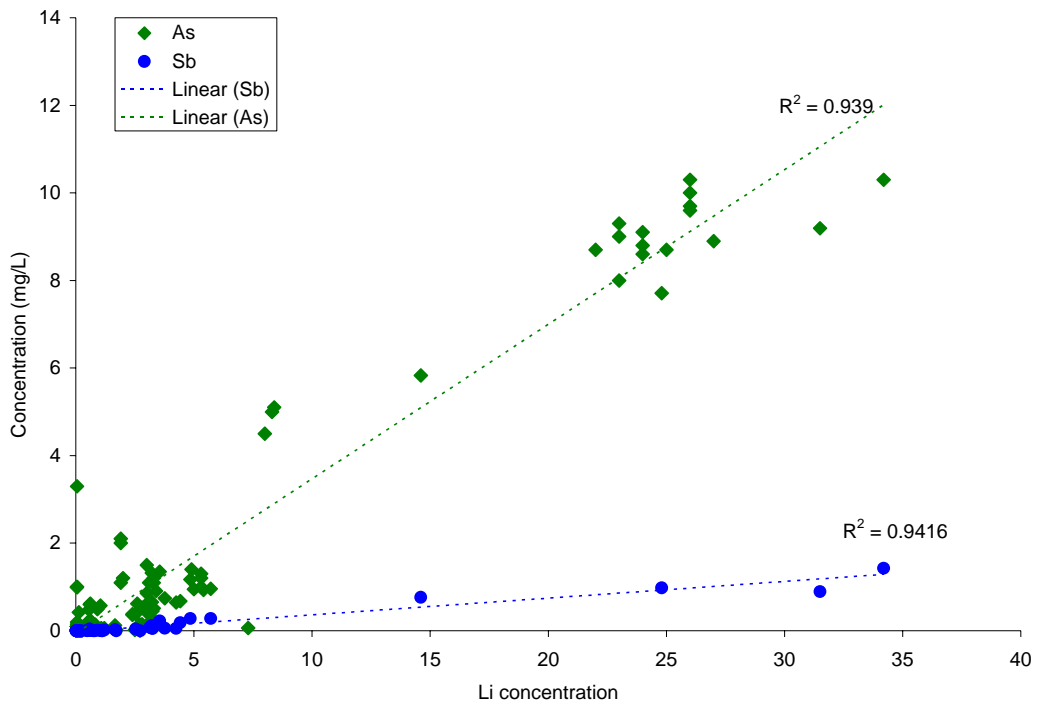


Figure 5 (continued)

c)



d)

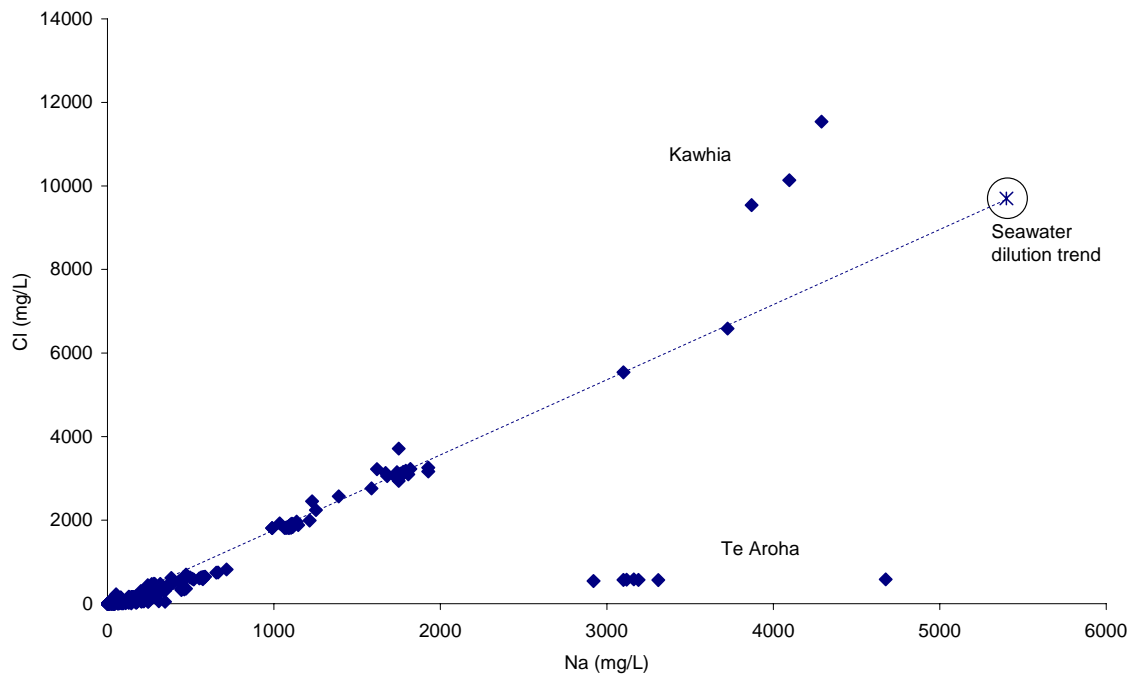
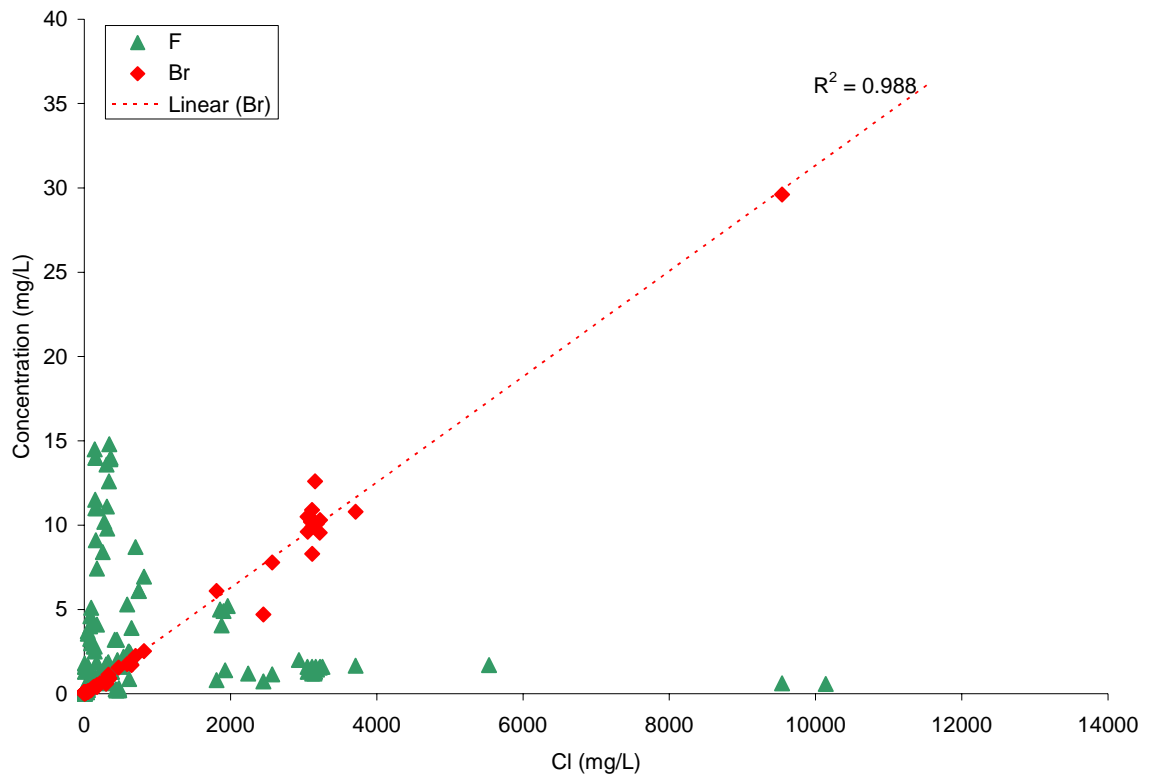


Figure 5 (continued)

e)



f)

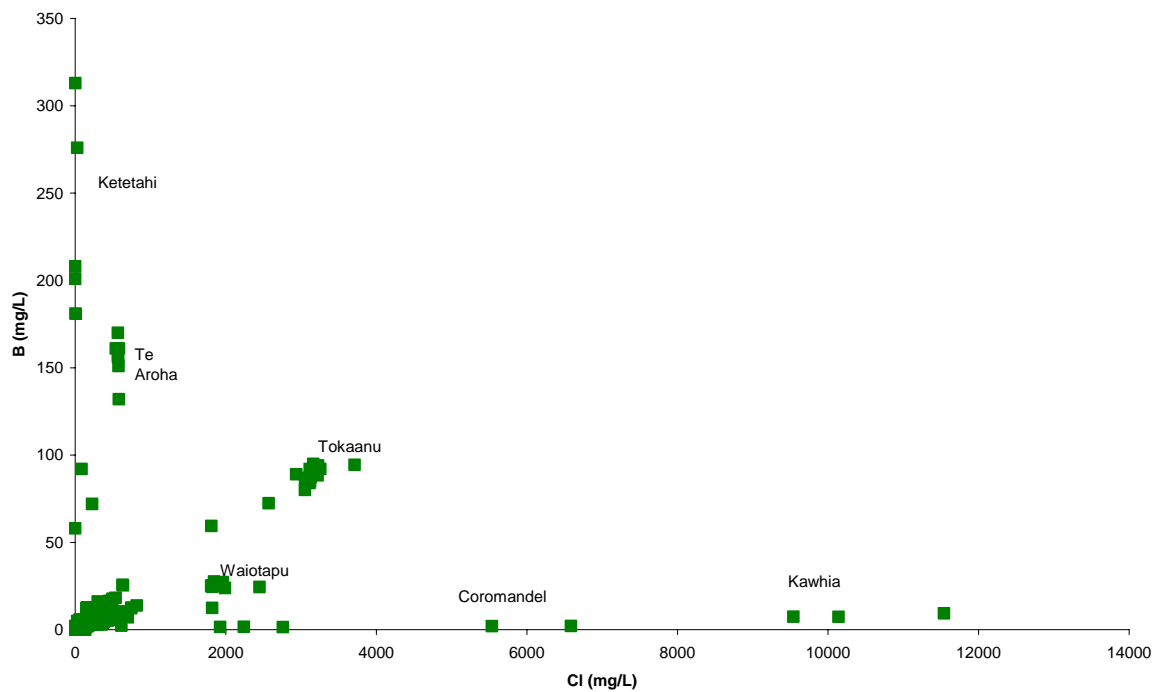
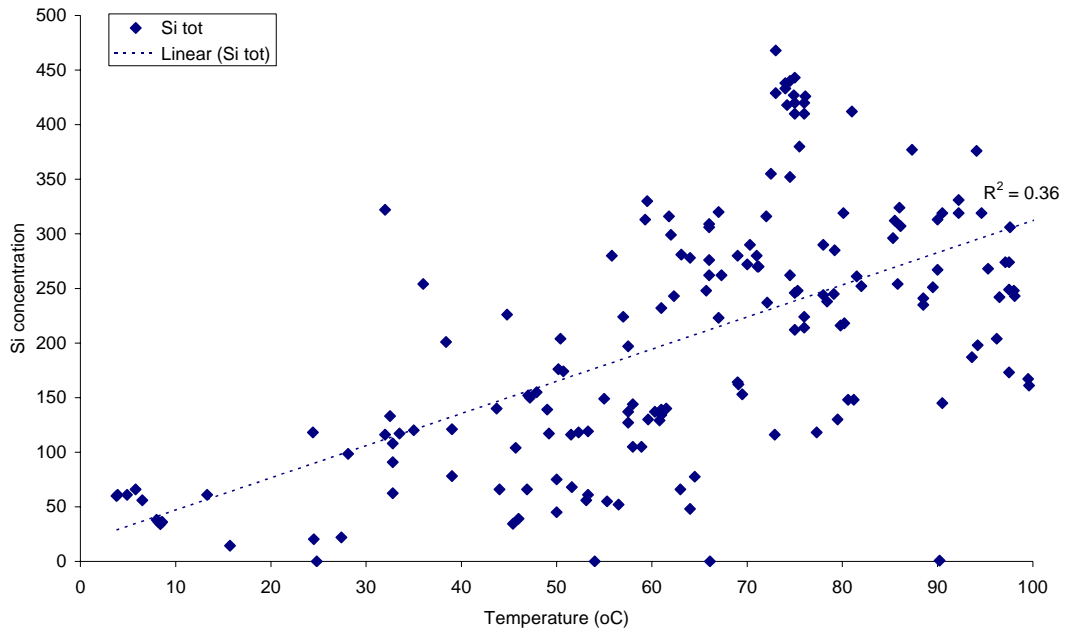
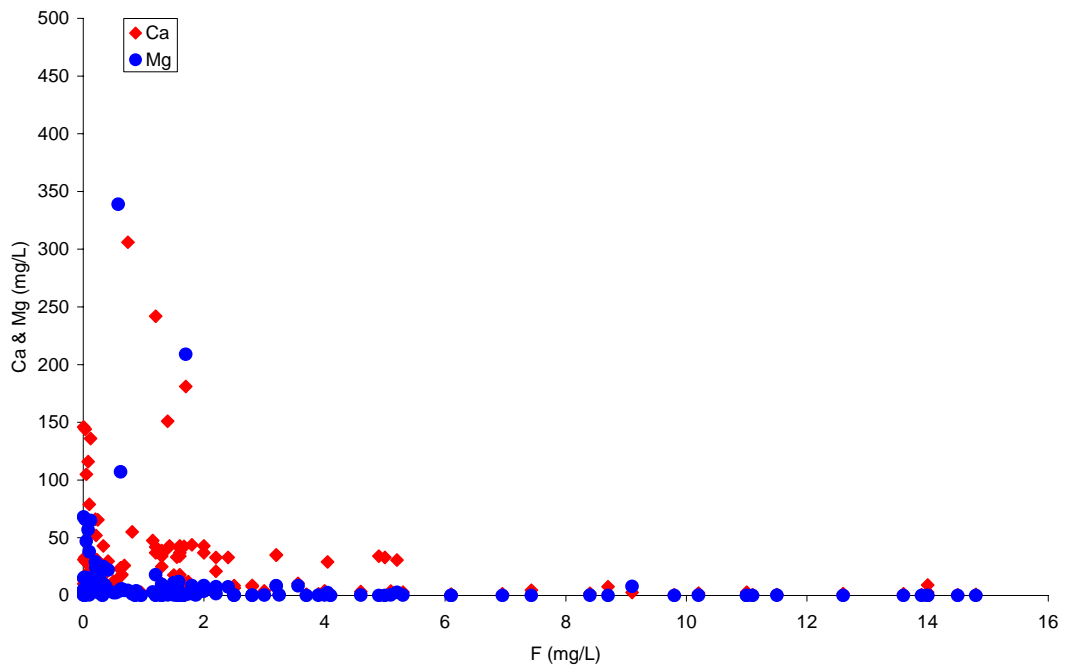


Figure 5 (continued)

g)



h)



A search for correlations among steam-heated components of the fluid was largely in vain. Although an apparent relationship is shown in a plot of pH (which is a log parameter) vs log SO₄ (Figure 6), this is not strong. Similarly no strong correlations were evident in SO₄-Fe or K-SO₄ relationships.

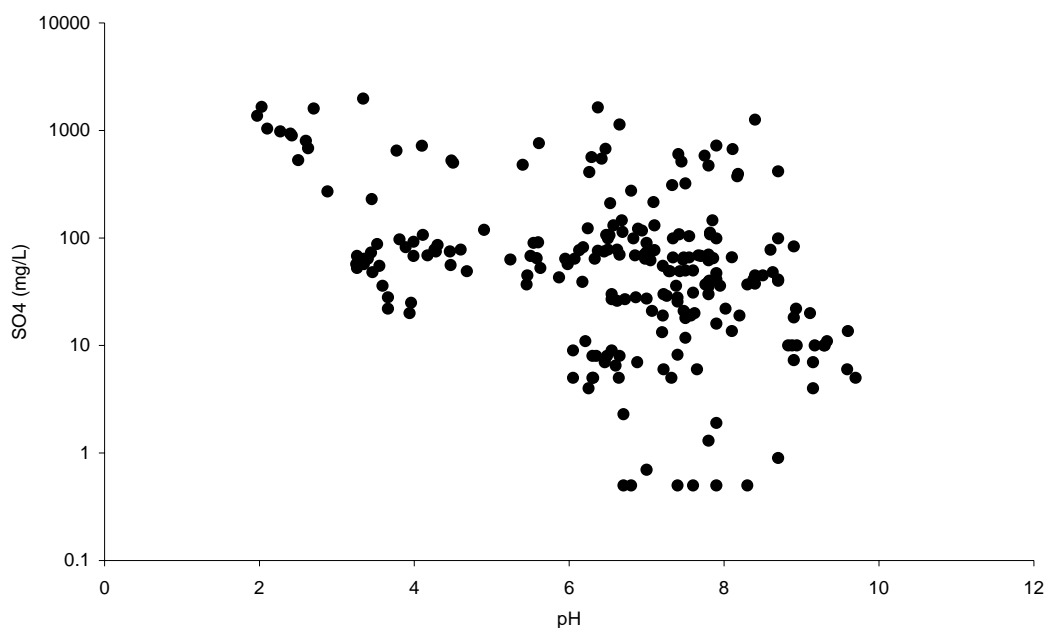


Figure 6: Sulphate vs pH

In summary: The strongest correlations, over the entire dataset (Appendix 1) are the following:

Li-Cs-As-Sb
Na-Cl-Br

The major ions which are probably the most conservative are Li, B and Cl. When plotted on a trilinear diagram (Figure 7a), some trends are noted. The data are divided, as in Appendix 1, into the North Waikato, Taupo Volcanic zone and Ketatahi/Tongariro National Park. The data for the North Waikato springs show no obvious correlation. However, the data for the volcanic and geothermal regions do show linear trends. The dark lines represent constant Cl/B ratio, with varying lithium content. Most geothermal fields would be expected to show a constant Cl/B ratio within the field, and this is borne out in the data.

The Na/Li/K trilinear diagram is shown in Figure 7b. This diagram seems to indicate a change in the Na/Li ratio from high to low from North to South. A Li/Cs/As diagram showed no obvious trends. A Na/Cl/Br also showed no obvious trends.

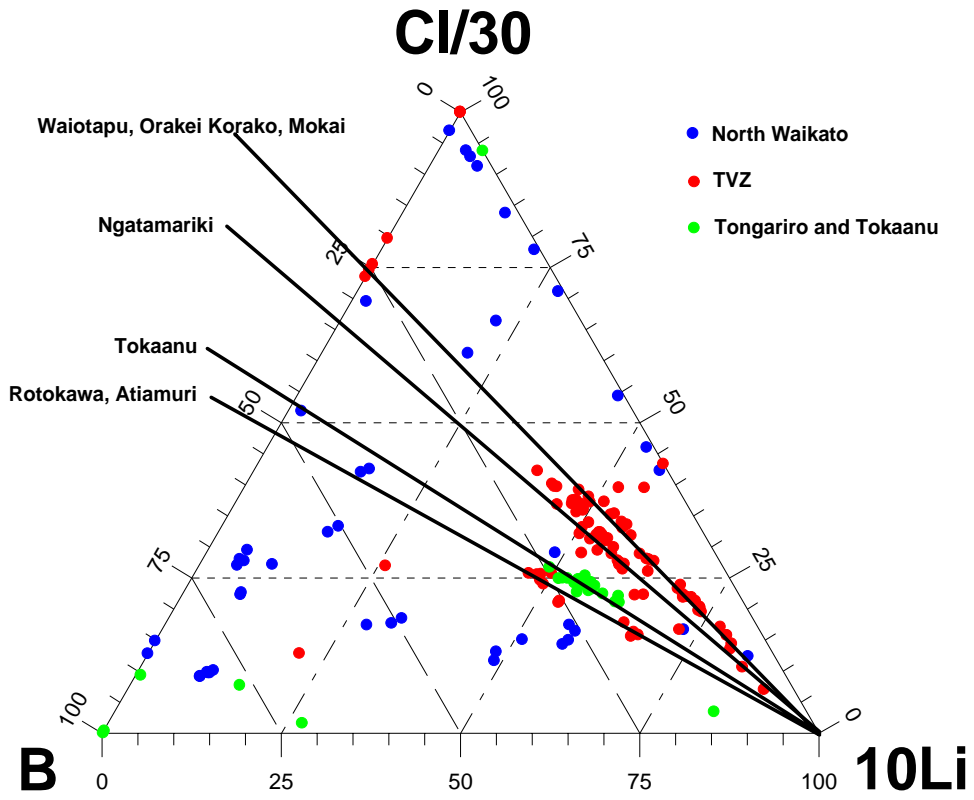


Figure 7a: Trilinear Cl/Li/B plot

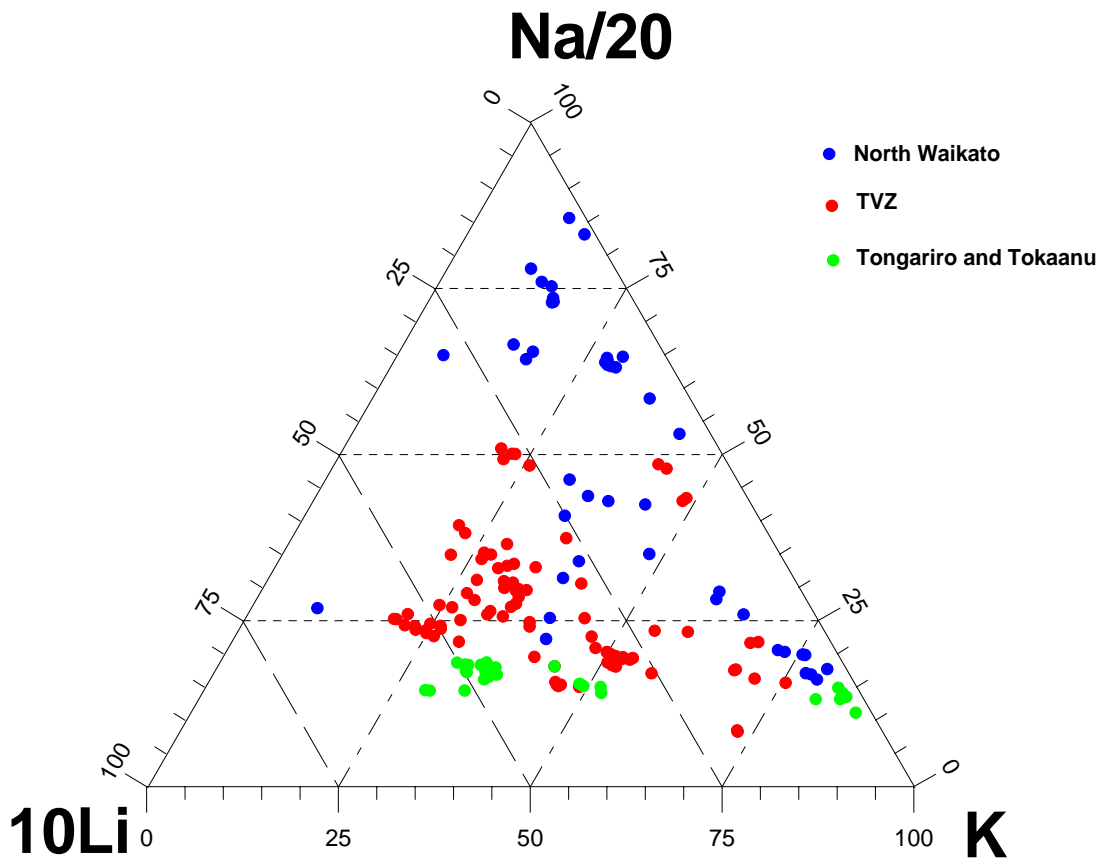


Figure 7b: Trilinear Na/Li/K plot

5 Stable isotopes

The total stable isotope data available is shown in Figure 8 on a $\delta^2\text{H} / \delta^{18}\text{O}$ plot.

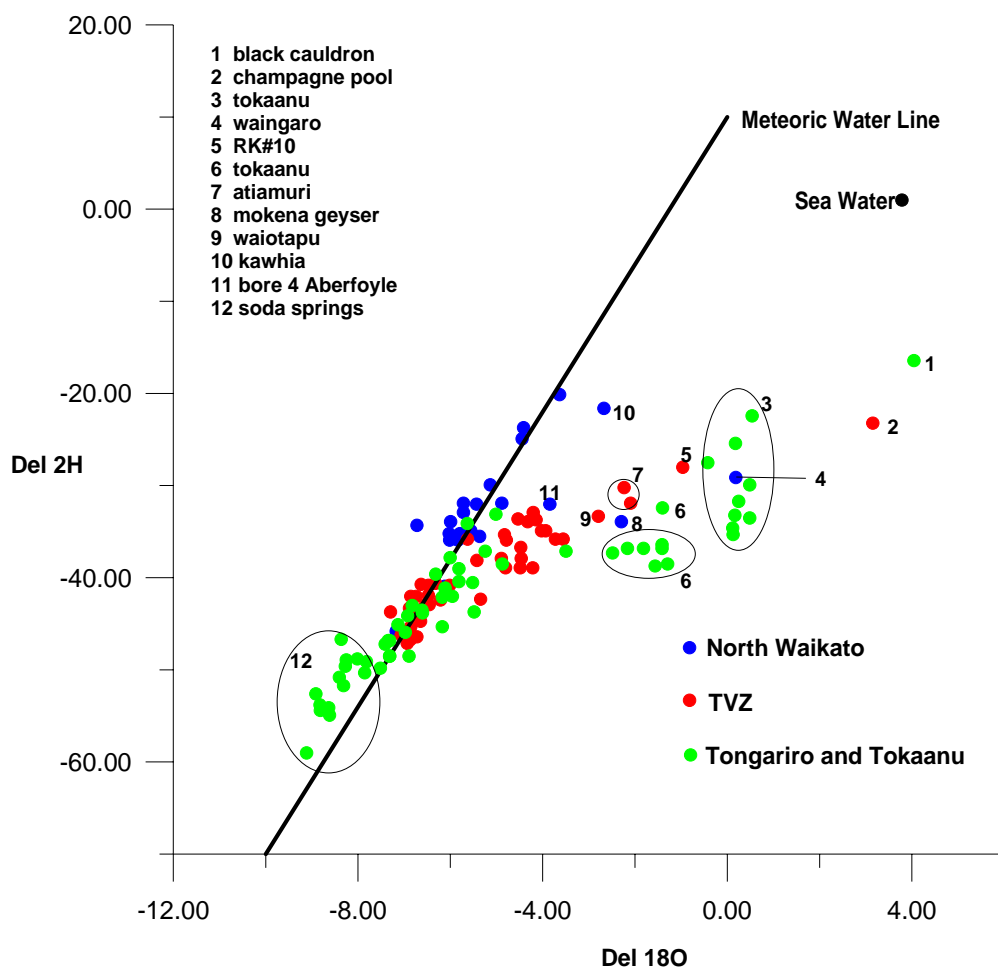


Figure 8: Isotope data for all available analyses

Stable isotopes are a unique tracer signature of the water. They can indicate mixing of waters of different origins, reaction of the water with country rock, and boiling or vapour separation in the water. The very heavy isotopes for Black Cauldron and Champagne Pool (1 and 2) are probably due to evaporation in these features as the lighter isotopes are preferentially distributed into the vapour phase. The Tokaanu features (3 and 6) display a dilution trend between those features with the heaviest isotopes and meteoric water, probably indicating dilution of rock interacted water by meteoric water. However, this could also indicate varying evaporation of an essentially meteoric-derived geothermal water. Most of the northern Waikato features fall close to the meteoric water line as expected, indicating probably deep circulation of meteoric waters for these features. The glaring exception is the Waingaro springs (4). The sample was collected from the Waingaro bore and would not be expected to be affected by evaporation. It is unclear why this water has such heavy isotopes.

The Mokena geyser at Te Aroha (8) erupts and an amount of the water flows back into the well. Consequently, these heavy isotopes observed could be due to evaporation. The sample from Kawhia Te Puia (10) lies on a dilution line between meteoric water and seawater indicating that it is a mixture of these two end members. Samples from Atiamuri (7) probably indicate dilution of deep geothermal waters with meteoric waters. Samples from Waitapu spring #24 (9) indicate evaporation since this is mainly an acid sulphate spring. Analysis of the samples from Soda Springs, with their lighter isotopes, suggests that they are fed from snow melt/rain water from a higher altitude on the Tongariro system.

6 Geochemical geothermometers

There are a number of geochemical geothermometers that can be applied to calculate the temperature of the geothermal waters at depth. These geothermometers arise as geothermal water equilibrates with minerals in the country rock. They are more useful where the original geothermal water was at high-temperature ($>250^{\circ}\text{C}$) as this ensures a reasonable chance of reaching chemical equilibrium.

The two principal geothermometers are the silica geothermometers and the cation geothermometers. The silica geothermometer arises due to equilibrium of water with quartz, or in some cases chalcedony. These geothermometers equilibrate relatively quickly (days to months) at temperatures $>250^{\circ}\text{C}$. At lower temperatures, they can take a longer time to equilibrate. The geothermometers are calculated simply from the measured concentration of silica. In hot springs, the silica concentration can be altered by deposition of silica, and previous loss of steam, introducing uncertainty into the geothermometer calculation.

The cation geothermometers arise due to the exchange of cations (Na, K, Ca, Li) in alkali feldspars. These geothermometers utilise *ratios* of the cations, and are therefore not affected by steam separation. As well, the components are usually very soluble and not likely to change by deposition of minerals at the surface. However, the cation geothermometers are very slow to come to equilibrium (years at temperatures $<300^{\circ}\text{C}$). Consequently, in large, high-temperature geothermal systems, they are usually used to characterise fluids from the deep reservoir recharge fluid.

Quartz and chalcedony geothermometers have been calculated (Fournier (1973)) from the silica concentrations and Na/K (Fournier (1983)) and Na K Ca (NKC) (Fournier and Truesdell (1973)) geothermometers have been calculated from the Na, K and Ca concentrations. The correlation between these geothermometers is shown in Figure 9.

There is perfect correlation between the quartz and chalcedony as expected. There is a loose correlation between the quartz geothermometer and the Na K Ca geothermometer above $\sim 125^{\circ}\text{C}$. However, there is little or no correlation between the quartz geothermometer and the Na/K geothermometer. For these data, the silica geothermometer is probably the most useful.

For the low-temperature, small geothermal hot springs in North Waikato, the silica temperature is always greater than the measured temperature, indicating a hotter temperature at depth. Except for Kaiawa, Aberfoyle St and Kawhia, the silica geothermometer predicts deep temperatures greater than 100°C . The highest calculated silica geotemperatures in the north Waikato region are from Waitoa ($160\text{--}170^{\circ}\text{C}$), Te Aroha ($145\text{--}155^{\circ}\text{C}$) and Matamata (148°C). For the north Waikato features, silica geotemperatures have remained fairly constant with time.

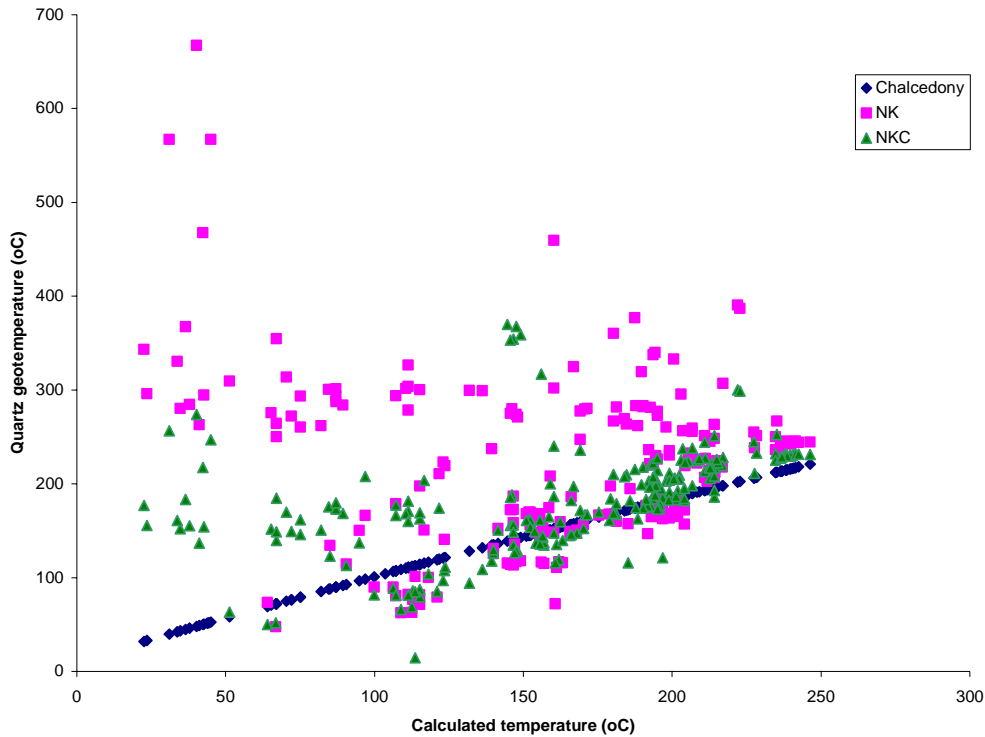


Figure 9: Correlation between the different geothermometers

For the TVZ data, nearly all of the silica geotemperatures are less than the known temperature of the geothermal resource. This probably indicates deposition of silica from the deep geothermal fluid as it rises to the surface and equilibrates at a lower temperature. Silica geothermometers from production wells in these TVZ geothermal systems normally agree very well with measured downhole temperatures where they are available. In general, cation geothermometers are also predicting temperatures considerably lower than known reservoir temperatures. Within the accuracy of the quartz geothermometer, there appear to be no temporal trends in the TVZ geothermometer data.

For all of the Tokaanu data, there is reasonable agreement between the quartz geotemperature and the NKC geotemperature. The Tokaanu data show no significant geothermometer trends with time.

7 Recommendations for future REGEMP design

If this is to be a viable, ongoing monitoring programme it is recommended that the programme become more focused, using consistent sites, methodology and parameter sets from year to year. Our interpretation of the objectives of this programme is to:

- understand the nature and vulnerability of the regions warm water resources, in order to sustainably manage these resources
- determine likely changes in environmental impacts of these features/systems.

Recommendations for adjustments in data collection

- Return to measuring HCO_3 rather than alkalinity.
- Remove Al and salinity (measure conductivity only) from the monitoring data, as well as parameters unrelated to the objectives of the programme (for example, nutrients).
- For the **full suite**, monitor the parameters shown in Appendix 1 once every four years.
- Isotopes should be only included in the full suite every four years.
- Every two years, monitor a **minimum suite** of: Temp, pH, Li, Na, Cl, Mg, SO_4 , F, B and HCO_3 . This is based on the **minimum suite** recommended in Huser and Jenkinson, but includes Li (as an indicator of correlated parameters Cs, As and Sb), B and F (independent variables of environmental interest).

Recommended adjustments to sites sampled

- The following sites are not necessary for the purpose of monitoring geothermal activity: Hahei (monitor instead at Hot Water Beach), Lake Waikare surface waters and Tama Lakes.
- Select only a small number of significant features to be sampled in the larger geothermal systems; the features should be chosen with a view to longevity, ease of access and be representative of both deep geothermal fluid and steam-heated fluids where possible.
- Accurate GPS coordinates should be measured and recorded, and used to confirm the same feature is sampled each time. If the next sampling includes samples from the 1993/94 survey that were not sampled in 2005/06, then the grid coordinates listed in Appendix I should be checked with the newer measured GPS coordinates.

References

Fournier, R.O. 1973: Silica in thermal waters: Laboratory and field investigations. *Proceedings of the International Symposium on Hydrogeochemistry and Biochemistry 1970*, Tokyo. 122-139.

Fournier, R.O. 1983: A method of calculating quartz solubilities in aqueous sodium chloride solutions. *Geochim et Cosmochim Acta* 47:579–586.

Fournier, R.O. and Truesdell, A.H. 1973: An empirical Na-K-Ca geothermometer for natural waters. *Geochim et Cosmochim Acta* 52:2749–2765.

Huser, B.A. and Jenkinson, D. 1996: *Regional geothermal features monitoring programme*. Environment Waikato Technical Report 96/18, Environment Waikato, Hamilton.

GEONET data was provided by the New Zealand GEONET project, which is sponsored by EQC, GNS Science and FRST.

Luketina, K. 2007: *Regional geothermal features monitoring programme (REGEMP II)*. Environment Waikato Technical Report 2007/36, Environment Waikato, Hamilton.

Dissolved concentration unless noted as TR (Total Recoverable)																																							
Area:	Eastings	Northing	GRID REF:	Site description	LOC KEY	Date Sampled	Temp	pH	Li	Na	K	Ca	Mg	Rb	Cs	Cl	SO4	B	SiO2 (Tot)	NH4	Alk	HCO3	S Tot	F	Fe	As	$\delta^{18}O_{VSMOW}$	δ^2H_{VSMOW}	Cond	Br	Hg TR	Sb	Tl						
TVZ: HOROHORO (14)	2787600	6327700	U16:876-277	Horohoro	1291	6/11/1963	47	8.7	0.5	186	4.3	9				155	40	9	152				0.3	14															
	2787600	6327700			4674	4/02/1980	55	8.5		209	1.9	0.07	0.26			168	45		149			285																	
	2787600	6327700			5717	17/04/1984	49.9	8.38	0.6	224	6	2	0.12	0.04	0.06	169	41	2.4				244																	
	2787600	6327700		Horohoro Hot Spring	5981/2/m	4/02/1985	52	8.32								172	42		152																				
	2787600	6327700			7169/1	8/07/1993	43.7	8.3	0.55	188	4.2	0.86	0.17	<0.05	<0.05	150	37	2.1	140	0.37		159	<1	11.5	<0.25	0.48								91					
	2787600	6327700			7323/18	11/05/1994	47.2	8.39	0.61	219	4.5	0.65	0.07	<0.05	<0.05	168	41	2.4	150	0.46		177	<1	11	<0.3	0.62	-4.81	-35.4						100					
	2788379	6323150	U16:883-231*	Waipupumahana	72-3006	4/10/2005	47.9	8.4	0.584	214	4.85	0.63	0.06	0.0425	0.0432	143	37.6	2.34	155	0.37	141	85	<0.002	14.5	0.04	0.603	-4.77	-36						90	0.427	0.00011	0.0397	< 5.E-05	
WAIOTAPU (15)	2804500	6310200	U16:045-102	Waiotapu #24	7323/8	27/04/1994	92.2	1.97	1.9	318	28	18	2.2	0.36	0.11	475	1370	5.6	319	27			1.3	0.34	11	2.1	-2.78	-33.4						70					
	2804500	6310200			7169/5	8/07/1993	90.5	2.03	1.9	279	29	17.7	1.9	0.34	0.16	428	1659	5.1	319	24.9			1.8	0.27	12.7	2								7.8					
	2804500	6310200				1978			81	2.5	2.9	384	65	2.5	4.1		0.59	614	530	2.35					0.88														
	2804491	6310255	U16:044-102*	Waiotapu Geyser S70	72-3007	30/09/2005	87.3	7	1.04	272	34.6	9.17	0.22	0.128	0.0682	332	89.9	4.75	377	3.68	89	54	8.16	1.65	<0.02	0.574	-4.47	-39						142	1.13	0.00014	0.0094	< 5.E-05	
	2803781	6311228	U16:037-112*	Post Mistress S20	72-3008	30/09/2005	96.2	8.6	3.55	472	22.2	7.6	0.01	0.266	0.668	699	77.5	7.13	204	0.48	65	39	3.22	8.7	<0.02	1.350	-4.45	-38						192	2.25	< 8.E-05	0.224	0.00045	
	2804600	6310500	U16:046-105	Champagne Pool WT	7323/7	27/04/1994	76.1	5.54	8.3	1115	153	34	0.05	1.53	1.26	1905	90	26	426	34			237	11	4.9	<0.3	5	3.17	-23.3						616				
	2804600	6310500			7289/1	21/01/1994	75.5	5.72	8.4							1929																							
	2804600	6310500			7169/6	8/07/1993	74.9	5.6	8.4	1090	148	33	0.05	1.51	1.23	1858	91	26	427	31.8			220	8.8	5	<0.25	5.1								680				
	2804600	6310500			6317/m	7/06/1986	74	5.5	8.3	1065	144	33	0.55	1.42	1.27	1814	68	25.2	438																				
	2804600	6310500			5716/2	14/04/1984	75.5	6.07	8.2	990	144	36	0.04	1.41	1.25	1807	64	25.1	380					424	18.1														
	2804600	6310500			5720	3/04/1984	75	5.98	8.2	990	142	36	0.05	1.45	1.28	1813	57	25	410					290	11.1														
	2804600	6310500			5679/2	31/01/1984	74	6.17	8.33	1109	150	34.2	0.06	1.41	1.28	1839	39	25	433				188.9	5.51															
	2804600	6310500			5672/1	10/01/1984	76	5.87	8.23	1113	138	34.7			1.4	1.3	1835	43	25.3	410					344	18													
	2804600	6310500			5670/1	15/12/1983	74.2	5.95	8.19	1103	141	33.7	0.05	1.4	1.27	1817	64	25.2	418																				
	2804600	6310500			5653/1	8/12/1983	74.5	5.45	8.37	1091	149	32.3	0.04	1.44	1.31	1845	37	27.6	440																				
	2804600	6310500			5638/1	23/11/1983	76	7.05	8.07	1088	143	32.4	0.03	1.41	1.25	1825	62	25.3	420						28.7														
	2804600	6310500			5626	27/10/1983		5.58	8.04	1079	143	32.6	0.04	1.41	1.27	1820	65	12.5	435						170	23													
	2804600	6310500			5538/1	3/08/1983	73	5.24	8	1072	143	33.6	0.05	1.57	1.33	1816	63	24.6	429								4.5												
	2804600	6310500			5428/11	19/05/1983	75			1078	141	33.8	0.06			1820	54		420																				
	2804600	6310500			5383/7	17/03/1983	75	5.63	8.25	1102	151	35.1	0.048			1898	52.5	25.4	443																				
2804600	6310500			5126	18/05/1982	73	7.82	8.04	1109	150	33.8	0.06	1.54	1.33	1912	108	25.6	468																					
2804600	6310500				24/07/1958			8.2	1137	160	30.7	2.8			1961	143	27.2																						
2804600	6310500				27/06/1955			6.5	8	1146	160	29	2.4			1879	99	27	170	4.5																			
2804600	6310500				1926			4.9		1215	164	38.6	0.3			1990	119	23.9	448	37																			
WAIKITE (16)	2799100	6314300	U16:991-143	Waikite WE1031	6914/32	21/01/1992	99.5	7.8	2.2	215	8.8	7.8	0.22	0.11	0.31	145	39	1.46	167																				
	2799100	6314300			7136	21/05/1993	99.6	7.76	2.4	219	8.6	8.8	0.2	0.08	0.33	143	37	1.5	161	0.19																			
	2799100	6314300			7323/19	11/05/1994	101.2	7.38	2.4	220	8.8	8.5	0.18	0.11	0.28	143	36	1.5	162	0.3																			
	2799811	6315010	U16:998-150*	HT Geyser	72-2993	21/09/2005	97.5	7.9	3.25	292	20.1	0.95	0.03	0.167	0.266	174	41.2	1.99	249	0.17	373	225	0.006	4.1	<0.02	0.454	-5.41	-38.2							124	0.509	0.00072	0.0517	0.00024
	2799028	6314264	U16:990-142*	Manuroa	72-2994	21/09/2005	97.5	7.8	2.53	226	10.1	7.83	0.17	0.121	0.365	127	35.3	1.73	173	0.32	280	169	0.012	2.8	<0.02	0.383	-6.00	-40.9							104	0.403	< 8.E-05	0.0398	9.00E-05
ATIAMURI (17)	2776600	6311100	U16:766-111	Atiamuri Large Spring	3937	15/03/1978	69	8.7	3.93	445	20.1	1	0.01	0.18	1.06	328	41	11.2	280																				
	2776600	6311100		Atiamuri	7169/2	8/07/1993	66	7.43	5	443	22	0.64	0.01	0.18	1.08	354	49	12.9	262	1.6																			
	2776600	6311100			7323/17	11/05/1994	70	7.29	4.9	472	24	0.73	0.02	0.19	1.12	362	49	13.1	272	2.4																			
	2776588	6311132	U16:765-111*	Whangapoua West	72-3004	4/10/2005	55.8	8.4	4.85	462	25.9	0.98	<0.02	0.17	1.05	343	44.9	13.5	280	1.62	442	267	<0.002	14.8	<0.02	1.170													

Dissolved concentration unless noted as TR (Total Recoverable)

Area:	Eastings	Northing	GRID REF:	Site description	LOC KEY	Date Sampled	Temp	pH	Li	Na	K	Ca	Mg	Rb	Cs	Cl	SO4	B	SiO2 (Tot)	NH4	Alk	HCO3	S Tot	F	Fe	As	¹⁸ O _{VS} MOW	² H _{VS} MOW	Cond	Br	Hg TR	Sb	Tl			
TVZ cont ...																																				
ORAKEIKORAKO (21)	2785500	6300800	U17:855-008	Waihunuhunu - 674		18/05/1905	79.5	7.9	1.2	180	8	4	2			106	16	1.09	130			271														
	2785500	6300800			7169/4	8/07/1993	58	7.62	0.58	115	3.1	3.3	0.51	<0.05	<0.05	54.2	20	0.66	105	<0.10		196	<1	1.6	<0.25	0.22										
	2785500	6300800			7323/9	27/04/1994	58.9	7.07	0.61	118	3.5	3.7	0.47	<0.05	<0.05	57	21	0.65	105	<0.10		237	<1	1.5	<0.3	0.24	-6.84	-42.1								
	2785500	6300800			7582/4/M	18/10/1995	52.3	7.21	0.62	113	5.2	3.8	0.53	0.01	<0.05	57	19	0.59	118			229	<1													
	2785381	6300493	U17:853-004*	Waihunuhunu S674	72-2995	21/09/2005	80.6	7.4	0.918	170	6.72	3.96	0.31	0.0381	0.0127	93.2	27.9	1.07	148	0.41		207	< 0.002	3	< 0.02	0.493	-6.46	-40.9								
	2785300	6300400		OK Guest House Pool	7323/10	27/04/1994	85.8	7.86	3	346	17	0.7	0.01	0.2	0.6	312	65	3.2	254	0.26		317	<1	9.8	<0.3	0.61	-4.13	-33.8								
	2784265	6298542	U17:842-985*	Map Of Australia S25	72-2998	29/09/2005	82	8.1	3.22	346	19.7	0.64	<0.02	0.189	0.608	309	66.3	3.58	252	0.07	245	148	0.004	11.1	< 0.02	0.656	-3.92	-35								
	2784653	6298512	U17:846-985 *	Sapphire S106	72-2999	29/09/2005	97.6	8.9	4.24	342	49.7	1.55	<0.02	0.438	0.577	336	83.3	3.79	306	0.08	229	138	0.627	12.6	< 0.02	0.647	-4.19	-33								
	2784750	6298522	U17:847-986*	OK Manganese Pool - 120	5352/8	9/02/1983	94.1	8.7	4.11	322	48.6	1.7	0.05	0.53	0.67	339	99	3.6	376			207														
	2784700	6298600			7169/3	8/07/1993	64	7.42	3.1	241	37	2	0.23	0.38	0.48	254	108	2.8	278	<0.10		146	<1	8.4	<0.25	0.37										
	2784700	6298600			7323/21	11/05/1994	70.3	7.55	3.3	263	40	2.1	0.23	0.41	0.5	275	104	2.9	290	0.14		152	<1	10.2	<0.3	0.51	-4.52	-33.7								
	2784700	6298500	U17:847-985	Manganese S120	72-3000	29/09/2005	94.6	7.9	3.77	312	51.2	1.53	0.06	0.436	0.562	304	99.2	3.54	319	0.15	176	106	0.74	13.6	< 0.02	0.740	-4.31	-34								
NGATAMARIKI (22)	2786700	6291800	U17:867-918	New Spring	7137	21/05/1993	88.5	7.3	3.4	553	28	6.4	0.3	0.27	0.54	605	49	9	241	1.16		479	<1	2.5	<0.25	0.15										
	2787097	6290463	U17:870-904*	New North Spring	7323/22	11/05/1994	89.5	7.21	3.4	565	30	6.8	0.35	0.31	0.59	613	55	9.6	251	1.2		496	<1	2.5	<0.3	0.14	-4.88	-38								
	2787313	6292575	U17:873-925*	North Stream Source	72-2990	20/09/2005	93.6	7.5	1.66	334	17.4	5.13	0.53	0.15	0.335	327	11.8	5.4	187	0.82	269	162	3.23	1.87	< 0.02	0.121	-6.20	-42.5								
	2787933	6293431	U17:879-934 *	Waikato River	72-2991	20/09/2005	69.5	7.2	1.21	229	10.7	4.35	1.07	0.0889	0.206	216	13.3	3.74	153	0.52	188	114	0.134	1.28	< 0.02	0.061	-6.52	-43								
	2786621	6291710	U17:866-917*	Southern Spring	72-2992	20/09/2005	74.5	7	1.12	238	27.8	4.13	0.77	0.0727	0.0285	171	0.7	2.85	262	0.26	318	192	0.154	1.85	0.12	0.019	-6.64	-43.6								
	2786600	6291700		Ngatamariki Main Pool	72-2997	29/09/2005	72.1	7.6	3.24	587	22.6	1.28	0.17	0.211	0.482	646	49.8	9.6	237	0.56	367	222	0.036	3.9	< 0.02	0.180	-4.20	-39								
	2786600	6291700			3371/4	1/10/1974	88.5	7.95	3.38	518	31.2	6.44	0.2	0.31	0.56	579	36	8.45	235			343														
	2786600	6291700			W/215	1/03/1960		7.34	2.9	450	24	7.5	0.96	0.05	<0.04	461	99	7	250	0.3																
	2786600	6291700		Blue Pool	6424/2/m	9/01/1987	71.1	7.8	3.6	583	33.2	6	0.23	0.29	0.67	639	65	9.9	270																	
	2786600	6291700			6356/a	16/07/1986	71.2	7.8	3.5	579	34.2	5.1	0.23	0.31	0.68	638	70	9.5	270																	
	2786600	6291700			6311/a	28/05/1986	71	7.7	3.6	571	32.5	5.1	0.25	0.31	0.7	634	68	9.6	280																	
	2786600	6291700			5960/1	18/12/1984	78	7.67	3.6	498	31.5	4.21	0.16	0.33	0.69	628	69	9.5	244																	
	2786600	6291700			4412	24/07/1979		7.81	3.53	510	32	5.1	0.19	0.39	0.02	597	40	9.1	245																	
	2786600	6291700		Flowing Spring (Blue)	5444/1	7/06/1983	81.5	8.63	3.47	563	29.8	3.9	0.16	0.33	0.66	630	48	9.3	261																	
OHAAKI (23)	2798300	6296400	U17:983-964	Ohaaki	7323/11	27/04/1994	32.5	6.64	0.78	219	10.6	17.8	11	<0.05	<0.05	54	<5	1.2	133	1.3		847	<1	1.5	0.97	0.12										
ROKAWA (24)	2787900	6281300	U17:879-813	Rotokawa #4	7341/3	14/06/1994	94.2	6.83	3.4	430	34	21	1.6	0.35	0.31	538	99	18.2	198	3.6		155	<1	2.2	0.3	0.91	-5.33	-42.4								
	2787900	6281300			7291/1	28/01/1994	80.2	7.82	3	393	30	18	1	0.38	0.53	496	112	17.7	218	3.6		115	<1	1.6	<0.3	1.5										
	2787900	6281400	U17:879-814	Rotokawa #4A	7341/1	14/06/1994	78.4	2.63	2.8	379	47	35	8.3	0.5	0.46	447	685	15.5	238	10			27.1	3.2	6.3	0.15	-3.54	-35.9								
	2787900	6281400			7291/2	28/01/1994	75	2.4	2.7	362	42	35	8.4	0.47	0.42	418	932	13.2	246	9.5			20.8	3.2	9.6	0.15										
	2788600	6281600	U17:886-816	Rotokawa #22	7341/4	14/06/1994	90	2.27	3	366	50	43	8.5	0.64	0.66	454	980	16.3	313	20			<1	2	14	0.86	-3.71	-35.9								
	2788600	6281600			7291/4	28/01/1994	80.1	2.1	3.1	375	53	44	8.5	0.68	0.67	450	1038	16.5	319	17			<1	1.8	15	1.1										
	2788400	6282100	U17:884-821	Rotokawa #10	7341/5	14/06/1994	74.5	2.6	5.3	462	206	33	7.4	1.79	1.02	629	803	25.7	352	36		290	<1	2.4	0.46	1.2	-0.95	-28.1								
	2788400	6282100			7291/5	1/02/1994	72.5	2.42	5.3	473	206	33	7.6	1.84	1.05	635	898	25.4	355	33		110	<1	2.2	0.68	1.3										
WAIRAKEI (25)	2779000	6280200	U17:790-802	WK Totara Gut	7323/14	4/05/1994	33.5	6.62	<0.05	25	4.8	9.4	3.7	<0.05	<0.05	8.5	26	0.1	117	<0.1		94	<1	0.18	<0.3	0.012	-6.87	-43.4								
	2779000	6280200			7178/3	15/07/1993	32	6.72	<0.05	24	4.4	9	3.7	<0.05	<0.05	9.2	27	0.1	116	<0.10		64	<1	0.17	<0.25	0.008										
TAUPO/TAUHARA (26)	2778331	6273570	U18:783-735*	Taharepa	7323/26	9/06/1994																														

Dissolved concentration unless noted as TR (Total Recoverable)

Area:	Easting	Northing	GRID REF:	Site description	LOC KEY	Date Sampled	Temp	pH	Li	Na	K	Ca	Mg	Rb	Cs	Cl	SO4	B	SiO2 (Tot)	NH4	Alk	HCO3	S Tot	F	Fe	As	$\delta^{18}O_{VSMOW}$	δ^2H_{VSMOW}	Cond	Br	Hg TR	Sb	Tl	
TNP & VICINITY WAIHI (27)	2747861	6246796	T19479-468*	Waihi #47 Whakatara	7323/29	9/06/1994										469						551					-6.16	-42.2						
	2747861	6246796			7323/15	4/05/1994	76	6.86	3.3	284	45		24	0.33	0.58	470	28	14.2	224	3		455	<1	0.21	<0.01	1.2	5.94	-42.1	203					
	2747861	6246796			7242/1	18/10/1993	76	6.55	3.3	280	46	52	24	0.32	0.58	477	30	14.8	214	3.1		539	<1	0.21	<0.01	1.1								
	2747861	6246796	T19:478-467*	Whakatara S47	72-2982	16/09/2005	75.3	7	3.21	267	49.9	65.6	25	0.326	0.603	467	27.3	14.9	248	2.54	257	155	< 0.002	0.24	< 0.02	1.320	-5.80	-40.5	186	1.55	0.0003	0.118	0.00066	
	2747861	6246796			1939/14	19/04/1966	75	6.55	2.7	242	42	66	29	0.1	0.3	440	27	13.3	212	2		468		0.2	0.01	0.01								
TOKAANU (28)	2749400	6244900	T19:494-449	Bathroom Spg Tokaanu	7323/16	4/05/1994	66	6.37	26	1927	162		0.18	1.68	4.8	3165	76	95	309	4.9		132	<1	1.6	<0.3	10.3	0.18	-33.3	961					
	2749400	6244900			7242/2	18/10/1993	66	6.18	26	1927	171	43	0.22	1.72	5.1	3258	82	92	306	4.78		134	<1	1.6		10								
	2749692	6244929	T19:496-449*	Tuwhare	72-2983	16/09/2005	79.2	7.5	24.8	1390	166	47.7	3	1.49	4.5	2570	49.9	72.4	285	2.56	168	101	< 0.002	1.15	< 0.1	7.710	-2.15	-36.9	586	7.78	0.00208	0.982	0.0086	
	2749633	6244866	T19:496-448*	Taumatapuhipuhi	72-2984	16/09/2005	98.1	7.8	31.5	1620	168	33.2	0.1	1.56	5.27	3220	62	88.3	243	2.56	56	34	< 0.002	1.55	< 0.1	9.190	-2.47	-37.4	635	9.55	0.00083	0.896	0.008	
	2749636	6244799		Taumatapuhipuhi geyser	2201857	28/11/2002	98	7.47	23	1680	187	34	0.11			3056	63	86	248	3.6		64	<0.01	1.3	0.06	8.0	-1.8	-36.9		9.6				
	2749459	6244729	T19:494-447*	Takarea No.5	72-2985	16/09/2005	59.5	6.5	34.2	1750	177	42.4	0.2	1.79	5.53	3710	77.8	94.5	330	3.87	40	24	0.004	1.67	< 0.1	10.300	0.26	-31.8	768	10.8	0.00389	1.43	0.0079	
	2749211	6244703	T19:492-447*	Healy Bore No.2	72-2986	16/09/2005	90.5	7.9	14.6	1090	98.2	55	1.5	0.893	3	1810	47.2	59.4	145	4.41	40	24	< 0.002	0.81	< 0.1	5.830	-3.48	-37.2	427	6.09	8.00E-05	0.765	0.0038	
	2749211	6244703			1939/45	3/05/1966	67	6.85	21.8	1750	165	37				2936	69	89	320	1.7		22		2										
	2749589	6244772	6244772 N	#31D Spring(Teretere)	2201858	28/11/2002	72.0	7.10	24	1760	183	42	0.21			3117	77	92	316	3.4		60	0.21	1.2	0.06	8.8	0.5	-30		8.3				
	2749589	6244772			2302417	1/12/2003	86	7.55	23	1671	174	36.0	0.43			3128	66.0	87	324	2.7		67	<0.02	1.3	0.4	9.0	-1.4	-36.5		10.2				
	2749589	6244772			2402704	22/12/2004	85.3	7.34	24	1779	189	37	0.56			3116	66	84	296	2.7		102	<0.01	1.6	<0.02	9.1	-1.28	-38.6		10.9				
	2749589	6244772			2503635	19/12/2005	86.1	7.48	27	1808	203	41	0.56			3099	66	87	307	2.9		107	<0.01	1.4	<0.02	8.9	-1.39	-32.5		10.2				
	2749589	6244772			2700753	17/04/2006	85.5	6.98	26	1793	174	43	0.9			3182	64	92	312	3.1		128	<0.01	1.4	<0.08	9.6	-1.55	-38.8		10.1				
	2749456	6244722	6244722 N	#5 Pool	2201859	28/11/2002	32.0	6.33	24	1740	190	37	0.26			3147	64	91	322	3.3		74	<0.01	1.2	0.05	8.6	-1.4	-36.9		10.2				
	2749456	6244722			2302416	1/12/2003	61.8	6.62	23	1777	168	39	0.16			3157	78	90	316	3.9		47	<0.02	1.3	<0.02	9.3	0.5	-33.6		12.6				
	2749456	6244722			2402705	22/12/2004	63.1	6.65	22	1726	177	34	0.18			3053	70	80	281	3.0		44	<0.01	1.6	<0.02	8.7	0.14	-35.4		10.5				
	2749456	6244722			2503634	19/12/2005	62.0	6.45	25	1740	193	38	0.09			3121	75	85	299	4.2		50	<0.01	1.3	<0.02	8.7	0.19	-25.5		9.9				
2749456	6244722			2700754	17/04/2006	59.3	6.13	26	1820	173	41	0.18			3226	77	94	313	4.5		86	0.017	1.6	<0.08	9.7	0.13	-34.7		10.3					
KETATAHI (29)	2738982	6229752	6229752 N	Ketatahi Stream	8075/2/M	11/06/1998	67	3.77	<0.05	25	10.2	56	25	<0.05	<0.05	1.27	648	58	223				1.6		15.5									
	2738982	6229752		Ketatahi Stream Lower)	2503346	1/12/2005	54	3.45	<0.05	28	12.1	41	20	1.2	619	84	230	92	0.01	5.7		10.4	<0.1		0.01	-0.41	-27.6							
	2738994	6229561	6229561 N	Ket Stream Headwaters	2503345	1/12/2005	66.1	7.09	<0.05	20	8.9	40	24	1.3	136	1.1	216	208	0.024	0.77		<0.1	<0.1		0.10	-6.91	-44.2							
	2739023	6229712	6229712 N	Black Cauldron	9800443	27/11/1998	90	6.37	0.05	63	18.8	147	128	0.12	<0.05	2.9	1638	313	267				0.05		<0.1									
	2739023	6229712			2503344	1/12/2005	90.2	6.80	0.06	53	17.0	104	99	1.2	1524	224	275	72	0.59	0.52		<0.1	<0.1		<0.005		4.06	-16.5						
	2739100	6229500	T19:391-295		7377/2	14/09/1994	81.2	6.65	<0.05	12.2	8.1	26	15			0.71	1135	201	148	290		192	<1	<0.1	6	0.005								
	2739100	6229500			6853/2	30/08/1990		3.34	<0.05	64	17.2	150	135	0.11	>0.05	5.85	1980	181	230			82	<0.05		12	<1								
	2739100	6229500			6680/5	4/04/1989	79.1	2.7	0.04	54	17	130	96	0.12	<0.05	29	1600	276	245			102	0.35		11	<1								
	2739000	6229400	T19:390-294	Iron Spring	7377/1	14/09/1994	62.3	6.29	0.08	34	10.5	43	25			1.4	564	2.1	243	17.4		225	0.33		4.6	0.005								
	2739000	6229400			6853/1	28/08/1990		7.33	<0.05	28	10.2	60	36	0.05	<0.05	1.17	310	<0.05	201			63	<0.05		4.8	<1								
	2739000	6229400			6675/1/m	23/04/1989	69		0.02	25	7	36	22	0.04	<0.03	3	141	1	164															
	2739020	6230057	6230057 N	Ketatahi Stream at track crossing	2700940	22/05/2007	24.8	2.88	0.03	34	13.4	77	40	1.7	1180	135	271		<0.01	15.8			30	<0.015		0.36	0.55	-22.5						

Dissolved concentration unless noted as TR (Total Recoverable)

Area:	Easting	Northing	GRID REF:	Site description	LOC KEY	Date Sampled	Temp	pH	Li	Na	K	Ca	Mg	Rb	Cs	Cl	SO4	B	SiO2 (Tot)	NH4	Alk	HCO3	S Tot	F	Fe	As	$\delta^{18}O_{VSMOW}$	δ^2H_{VSMOW}	Cond	Br	Hg TR	Sb	Tl
TNP cont...																																	
SILICA RAPIDS (30)	2728305	6217075	6217075 N		2300752	23/04/2003	8.5	6.24	<0.05	13.8	3.0	30	14.9			10.1	123	<0.1	36			58	0.01	0.05	0.06	0.2	-8.8	-54.5			<0.1		
	2728305	6217075			2400967	24/05/2004	8.4	6.52	<0.05	12.6	2.9	29	13.4			9.3	106	0.38	34			48	<0.01	0.04	<0.02	0.15	-8.62	-54.2			<0.10		
	2728305	6217075			2501264	24/05/2005	8.0	6.94	<0.05	14.1	2.8	33	15.9			9.2	117	0.42	38			49	0.222	0.027	0.11	<0.1	-8.9	-52.7			<0.04		
	2728305	6217075			2601572	16/05/2006	8.2	6.89	<0.05	16.1	3.3	31	15.4			9.5	122	0.34	36			42	<0.01	0.01	<0.02	<0.1	-8.6	-55.0			<0.04		
	2728305	6217075			2700755	17/04/2007	8.6	6.69	<0.01	16.0	3.7	29	14.7			9.2	114	<0.3	36			43	<0.01	<0.1	<0.08	<0.015	-9.1	-59.1			<0.04		
SODA SPRINGS (31)	2736949	6226138	6226138		2300751	23/04/2003	4.9	3.89	<0.05	7.2	1.7	18.7	3.5			1.2	82	<0.1	61			12	<0.01	0.13	<0.02	3.3	-8.3	51.8			<0.10		
	2736948	6226136	6226136		2400968	24/05/2004	3.8	4.46	<0.05	6.9	1.6	21	2.9			1.1	75	<0.1	60			<5	<0.01	0.12	<0.02	0.1	-7.5	-49.9			<0.10		
	2736954	6226142	6226142		2501565	24/05/2005	6.5	4.28	<0.05	6.9	1.5	18	3.2			1.2	75	<0.1	56			<5	0.195	0.075	<0.02	<0.1	-8.39	-50.9			<0.04		
	2736951	6226135	6226135		2601571	16/05/2006	3.9	4.60	<0.05	7.4	1.4	19.2	3.4			1.2	78	<0.1	61			<5	<0.01	0.06	0.03	<0.1	-8.0	-48.9			<0.04		
	2737025.2	6226106.3	6226106.3		2700057	17/01/2007	13.3	3.99	<0.05	8.1	2.3	21	3.8			1.3	92	0.29	61			11.1	<0.01	0.13	0.27	<0.1	-8.24	-49.0			<0.04		
	2737102.5	6226144.6	6226144.6		2700058	17/01/2007	5.8	4.30	<0.05	7.4	1.7	20	3.5			1.2	86	0.15	66			28	<0.01	0.14	0.14	<0.1	-8.26	-49.7			<0.04		
	2739662	6226652	6226652 N	No Name Spring	2000890	25/05/2000		5.4	<0.05	32	6.0	83	44			1.4	480	<0.2	170			35			11.1	<0.1	-6.96	-46			<0.03		
	2739662	6226652			2101068	7/07/2001	50.4	4.5	0.13	41	8.0	79	38			1.6	501	0.2	204	1.0		<5	<0.01	<0.1	7.9	0.42	-6.16	-45.4			<0.03		
	2739662	6226652			2300785	7/05/2003	38.4	5.61	<0.05	46	7.8	136	65			2.0	761	<0.1	201	0.5		129	<0.01	0.12	18.6	<0.1	-6.1	-41.2			<0.10		
	2739662	6226652			2400932	17/05/2004	61.0	6.42	<0.05	37	7.3	116	57			1.4	546	0.15	232	0.67		44	<0.01	0.08	4.3	<0.1	-4.86	-38.6			<0.10		
	2739662	6226652			2501562	25/05/2005	44.8	4.1	<0.05	39	6.3	146	68			1.1	721	0.56	226	0.35		112	0.19	<0.005	16.6	<0.1	-6.59	-43.9			<0.04		
	2739662	6226652			2601370	27/04/2006	65.7	4.48	<0.05	44	7.9	105	47			1.8	525	<0.1	248	0.74		28	<0.01	0.049	12.3	<0.1	-5.5	-40.6			<0.04		
	2739662	6226652			2700860	8/05/2007	57	6.47	0.02	42	8.3	144	66			1.9	677	<0.3	224	0.64		173	<0.01	<0.03	9.9	<0.015	-5.47	-43.8			<0.10		
EMERALD LAKES (32)	2739504	6226621	6226621 N	Upper Emerald	2000886	25/05/2000	NA	3.40	<0.05	0.81	<0.04	2.0	1.8			0.69	64	<0.2	11.5	NA		NA	NA		2.2	<0.1	-5.23	-37.2			<0.03		
	2739504	6226621			2101066	7/07/2001	0	3.46	<0.1	1.4	0.28	1.7	1.2			1.5	48	<0.2	9.6	1.0		NA	0.013	<0.1	0.96	0.16	-7.12	-45.2			<0.03		
	2739504	6226621			2300782	7/05/2003	4.6	3.35	<0.05	1.1	1.7	2.2	1.5			0.81	57	<0.1	10.3	0.86		ND	<0.01	<0.03	1.1	1.7	-5.0	-33.2			<0.10		
	2739504	6226621			2400929	17/05/2004	6.2	3.26	<0.05	1.1	0.24	2.0	1.5			0.74	52.5	<0.1	11.1	0.46		ND	<0.01	<0.03	1.4	<0.1	-5.62	-34.2			<0.10		
	2739504	6226621			2501561	25/05/2005	6.6	3.26	<0.05	0.98	0.16	2.6	1.6			0.75	68	0.2	10.6	1.1		ND	0.024	<0.005	1.5	0.25	-5.99	-37.9			<0.04		
	2739504	6226621			2601369	27/04/2006	6.9	3.25	<0.05	1.2	0.46	2.3	1.4			0.95	57	<0.1	9.2	0.91		<20	<0.01	<0.005	0.98	<0.1	-6.3	-39.7			<0.04		
	2739504	6226621			2700857	8/05/2007	9.9	3.35	<0.01	1.2	0.83	2.5	1.9			0.78	64	<0.3	11	0.78		15.1	<0.01	<0.03	1.6	<0.015	-5.8	-39.1			<0.10		
	2739510	6226635	6226635 N	Middle Emerald	2000887	25/05/2000	NA	3.44	<0.05	1.1	<0.4	2.9	1.0			0.58	73	<0.2	11.7	NA		NA	NA		1.0	<0.1	-6.88	-48.6			<0.03		
	2739510	6226635			2101067	7/07/2001	0	3.59	0.11	1.3	0.25	1.7	0.54			0.92	36	<0.2	8.7	0.19		NA	0.012	<0.1	0.32	<0.1	-8.81	-53.9			0.03		
	2739510	6226635			2300783	7/05/2003	3.9	3.55	<0.05	1.2	1.3	2.7	0.85			0.54	55	<0.1	11.9	0.25		ND	<0.01	<0.03	0.65	1.0	-6.6	-43.6			<0.10		
	2739510	6226635			2400930	17/05/2004	5.7	3.66	<0.05	0.86	0.19	1.1	0.35			0.82	22	<0.1	6.0	<0.1		ND	<0.01	<0.03	0.13	<0.1	-6.81	-43.1			<0.10		
	2739510	6226635			2501560	25/05/2005	6.2	3.66	<0.05	0.58	0.17	1.4	0.42			0.48	28	0.3	8.4	<0.1		ND	0.032	<0.005	0.17	0.19	-7.33	-46.9			<0.04		
	2739510	6226635			2601368	27/04/2006	5.9	3.94	<0.05	0.96	0.31	1.1	0.36			1.2	20	<0.1	5.8	0.12		<20	<0.01	<0.005	0.14	<0.1	-7.3	-46.9			<0.04		
	2739510	6226635			2700858	8/05/2007	7.2	3.96	<0.01	1.2	1.3	1.2	0.5			0.88	25	<0.3	7.7	<0.1		<5	<0.01	<0.03	0.2	<0.015	-7.3	-48.6			<0.10		
	2739699	6226680	6226680 N	Lower Emerald	2000888	25/05/2000	NA	4.11	<0.05	6.2	1.0	16.1	7.6			0.68	107	<0.2	32	NA		39	NA		0.42	<0.1					<0.10		
	2739699	6226680			2300784	7/05/2003	4.8	3.81	<0.05	4.0	1.4	12.8	5.6			0.69	97	<0.1	22	<0.1		ND	<0.01	0.03	0.82	4.8	-7.4	-47.3			<0.10		
	2739699	6226680			2400931	17/05/2004	6.4	4.68	<0.05	3.2	0.57	9.4	3.1			0.86	49	<0.1	25	<0.1		ND	<0.01	0.03	0.22	<0.1	-8.35	-46.77			<0.10		
	2739699	6226680			2501559	25/05/2005	8.0	3.52	<0.05	4.4	0.7	13.3	5.3			0.69	88	0.27	27	<0.1		ND	0.136	0.009	0.48	<0.1	-7.84	-50.4			<0.04		
	2739699	6226680			2601367	27/04/2006	8.1	3.99	<0.05	3.9	1.0	10.2	4.1			1.1	68	<0.1	24	<0.10		<20	<0.01	<0.005	0.32	<0.1	-7.8	-49.2			<0.04		
	2739699	6226680			2700859	8/05/2007	8.7	4.26	<0.01	4.2	0.91	11.2	5.0			0.81	78	<0.3	27	<0.1		<5	<0.01	<0.03	0.36	<0.015	-7.3	-48.6			<0.10		
	2739699	6226680																															

Appendix II

Correlation matrix compiled by Dr Nick Kim (Environment Waikato) using only the 2005/06 REGEMP II data.

	WTP	pH	Cnd	ALK	SiT	Ca	Mg	Na	K	Li	Rb	Cs	NH4	SO4	ST	Cl	F	Br	B	As
WTP	1.000																			
pH	0.069	1.000																		
Cnd	0.518	0.017	1.000																	
ALK	0.207	-0.082	0.119	1.000																
SiT	0.739	-0.431	0.479	0.414	1.000															
Ca	-0.297	-0.183	0.321	-0.356	-0.430	1.000														
Mg	-0.559	-0.341	-0.221	-0.039	-0.449	0.714	1.000													
Na	0.538	0.087	0.748	0.131	0.268	0.360	-0.194	1.000												
K	0.510	-0.220	0.661	0.125	0.493	0.335	-0.023	0.714	1.000											
Li	0.691	-0.153	0.691	0.136	0.560	0.100	-0.336	0.853	0.787	1.000										
Rb	0.720	-0.204	0.664	0.065	0.675	0.055	-0.337	0.714	0.886	0.907	1.000									
Cs	0.811	-0.069	0.627	0.089	0.666	-0.139	-0.532	0.695	0.645	0.912	0.880	1.000								
NH4	0.510	-0.097	0.662	0.092	0.350	0.340	-0.103	0.807	0.590	0.700	0.569	0.646	1.000							
SO4	0.576	0.126	0.321	-0.247	0.369	-0.051	-0.459	0.443	0.444	0.477	0.548	0.581	0.470	1.000						
ST	0.411	0.172	0.143	-0.021	0.156	-0.061	-0.286	0.287	0.100	0.156	0.122	0.231	0.354	0.289	1.000					
Cl	0.546	0.108	0.659	-0.200	0.197	0.325	-0.287	0.900	0.644	0.786	0.686	0.718	0.773	0.633	0.365	1.000				
F	0.568	0.347	0.269	0.219	0.447	-0.596	-0.817	0.388	0.031	0.449	0.320	0.558	0.230	0.440	0.383	0.367	1.000			
Br	0.509	0.119	0.622	-0.397	0.135	0.340	-0.258	0.918	0.657	0.790	0.711	0.713	0.770	0.672	0.367	0.997	0.310	1.000		
B	0.530	0.013	0.687	-0.074	0.340	0.274	-0.224	0.842	0.607	0.800	0.709	0.786	0.836	0.389	0.252	0.831	0.335	0.829	1.000	
As	0.742	-0.119	0.661	0.027	0.678	-0.125	-0.498	0.625	0.680	0.874	0.887	0.903	0.588	0.640	0.060	0.642	0.507	0.659	0.647	1.000
Sb	0.805	-0.008	0.588	0.001	0.664	-0.256	-0.603	0.561	0.594	0.825	0.851	0.921	0.548	0.655	0.118	0.642	0.533	0.646	0.672	0.925