

Hydrochemical interpretation of groundwater-surface water interactions at catchment and local scales, Lake Rotorua catchment, New Zealand

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Abstract

Due to land-use intensification, deteriorating water quality has threatened the cultural and environmental values of Lake Rotorua, which is located in a circular caldera basin, central North Island, New Zealand. The objective of this study was to employ hydrochemical and multivariate statistical methods to elucidate groundwater-surface water interaction in the lake catchment and, in particular, in the Ngongotaha Stream subcatchment. Sampling took place under baseflow conditions in winter/spring 2003 and winter 2012 in the catchment and subcatchment-scale studies, respectively. Hierarchical cluster analysis (HCA) and principal components analysis (PCA) were independently applied to different sets of parameters comprising major and minor ions and hydrochemical field parameters. PCA showed that hydrochemical variation at both scales was largely related to the concentration of total dissolved solids and hence to natural water-rock interaction and, to a lesser degree, to redox potential. HCA at both scales suggested that hydrochemistry was driven by interaction between water and the major lithologies in the study area, with human and geothermal influence being important in

some areas. This study has shown that PCA and HCA are complementary techniques that can be usefully applied across catchment and subcatchment scales to increase our understanding of groundwater-surface water interactions in order to improve land and water management around Lake Rotorua.

Keywords

Lake Rotorua, New Zealand; groundwater/surface-water relations; hydrochemistry; groundwater statistics; scale effects

Introduction

Deteriorating water quality has threatened the cultural and environmental values of Lake Rotorua since the 1960s (Rutherford *et al.*, 1989). Land use in the catchment has intensified significantly over the past 50 years and is now predominantly agriculture (48%) and plantation forestry (23%) (Burger *et al.*, 2008; Rutherford *et al.*, 2009). Increasing nitrate concentrations were observed in nearly all of the major streams flowing into the lake during the period 1968-2003 (Hoare, 1987; White *et al.*, 2004; Rutherford *et al.*, 2009), strongly suggesting that, in addition to a small number of identified point sources, nutrient

inputs to the streams are derived from diffuse sources throughout the catchment.

The groundwater system plays an important role in the transport of nutrients from the land surface into streams and ultimately into Lake Rotorua. Groundwater-derived baseflow typically accounts for approximately 90% of the average flow in streams in the Lake Rotorua catchment (Hoare, 1987). Groundwater also supplies many springs and seeps that contribute to stream flows or feed directly into the lake (White *et al.*, 2007). Under baseflow conditions, mean residence times in the major streams are in the range of ca. 10–200 years (Morgenstern *et al.*, 2004). This implies that much of the nitrate emerging from aquifers into streams today was introduced to the groundwater system over the past several decades as a result of historic land use practices. The corollary is that nitrate loads to the lake can be expected to increase in the future as nutrients from historic and present land use transit through the groundwater system and ultimately enter the streams, springs and the lake. This trend will be exacerbated by any further intensification of land use within the catchment.

The objective of this study is to employ hydrochemical data and multivariate statistical methods to elucidate groundwater-surface water interaction in the Lake Rotorua catchment. Numerous studies indicate that hydrochemical data, such as major ion ratios or the concentration of total dissolved solids, can be used to qualitatively or statistically identify the locations where groundwater-surface water interaction is occurring (e.g., Burden, 1982; Taylor *et al.*, 1989; Woocay and Walton, 2008; Kumar *et al.*, 2009; Guggenmos *et al.*, 2011). Quantitative evaluation of groundwater-surface water exchange is possible with hydrochemical data if water flux data are also available (Schmidt *et al.*, 2010; Vásquez-Suñé *et al.*, 2010; de Louw *et al.*, 2011). Multivariate statistical

techniques such as hierarchical cluster analysis and principal components analysis have also proven to be useful for characterising groundwater-surface water interactions at various scales on the basis of hydrochemical data (Güler and Thyne, 2004; Thyne *et al.*, 2004; Lautz and Fanelli, 2008; Kumar *et al.*, 2009; Guggenmos *et al.*, 2011).

This study makes its main contributions with regard to the scale of multivariate statistical methods used to evaluate groundwater-surface water interaction. Evaluation of scaling effects is achieved by independently applying the same multivariate statistical methods to hydrochemical data at the catchment scale, the subcatchment scale and at the scale of an individual stream reach. The intention is to identify catchment-wide hydrochemical facies that are indicative of interaction between water and the various lithologies in the study area and then determine whether these same facies are identifiable at more localised scales. It is expected that the findings from the broader investigation will be applicable to the many other New Zealand catchments for which hydrochemical data are available (Stewart and Morgenstern, 2001; Daughney *et al.*, 2010, 2012).

Study area

Geology

Lake Rotorua is located in a circular caldera basin in the central North Island, New Zealand (Fig. 1). The study area is situated in the Taupo Volcanic Zone, an area of NW-SE extension and geothermal activity roughly 60 km wide by 300 km long that is related to subduction of the Pacific plate beneath the Australian plate off New Zealand's east coast (Wilson *et al.*, 1995). Figure 2 displays the surficial geology based on the 1:250,000 geological map of Leonard *et al.* (2010). Mesozoic greywacke, which outcrops to the east and west of the Taupo Volcanic Zone,

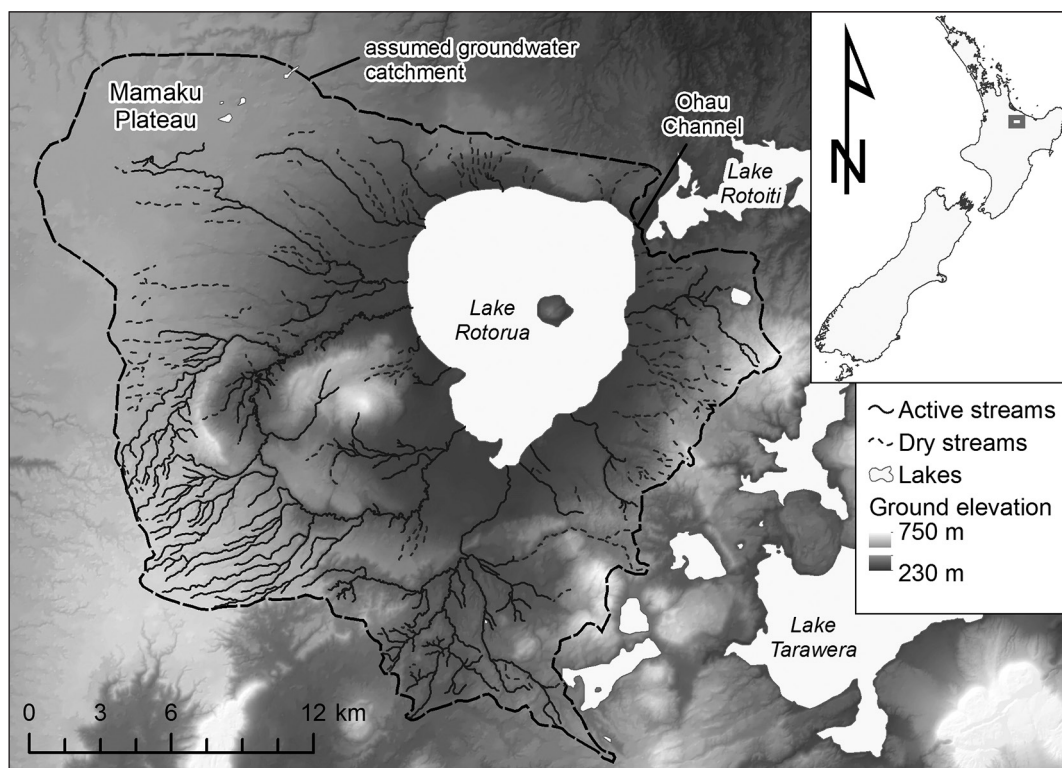


Figure 1 – Location of the study area. Grey scale represents ground surface elevation based on a 20 m digital terrain model. Assumed groundwater catchment is from White and Rutherford (2009).

forms the basement rocks in the study area. Younger formations are predominantly ignimbrites, rhyolite and dacite domes, and lacustrine and alluvial sediments. The geological formations and processes of greatest relevance to the hydrology and hydrogeology of the study area are depicted in the three dimensional geological model of White *et al.* (2007) (Fig. 3) and summarised in the following paragraphs, based on White *et al.* (2007) and Leonard *et al.* (2010).

From 2 million years ago to 200 thousand years (ka) ago, a number of rhyolite domes were emplaced and volcanic activity from Taupo Volcanic Zone calderas resulted in pyroclastic deposits across the study area, including the highly welded Waitapu Ignimbrite (ca. 710 ka) and the variably welded, jointed ignimbrites of

the Whakamaru Group (ca. 350 ka). The period from 240 to 200 ka is defined by the eruption that deposited the Mamaku Plateau Formation (240 ka) and formed the Rotorua Caldera. The Mamaku Plateau Formation, commonly referred to as Mamaku Ignimbrite, is variably welded, variably jointed and very permeable. Several rhyolite domes began to develop soon after the caldera collapse. Also soon after the eruption, a lake began to form in the ring-faulted depression, leading to the deposition of lacustrine fine ash and pumice, commonly referred to as Huka Group sediments (Leonard *et al.*, 2010).

From 200 to 61 ka, volcanic activity in the vicinity of the study area was relatively subdued. A number of eruptions from the Okataina Volcanic Centre, located to the east of the Rotorua caldera, produced widely

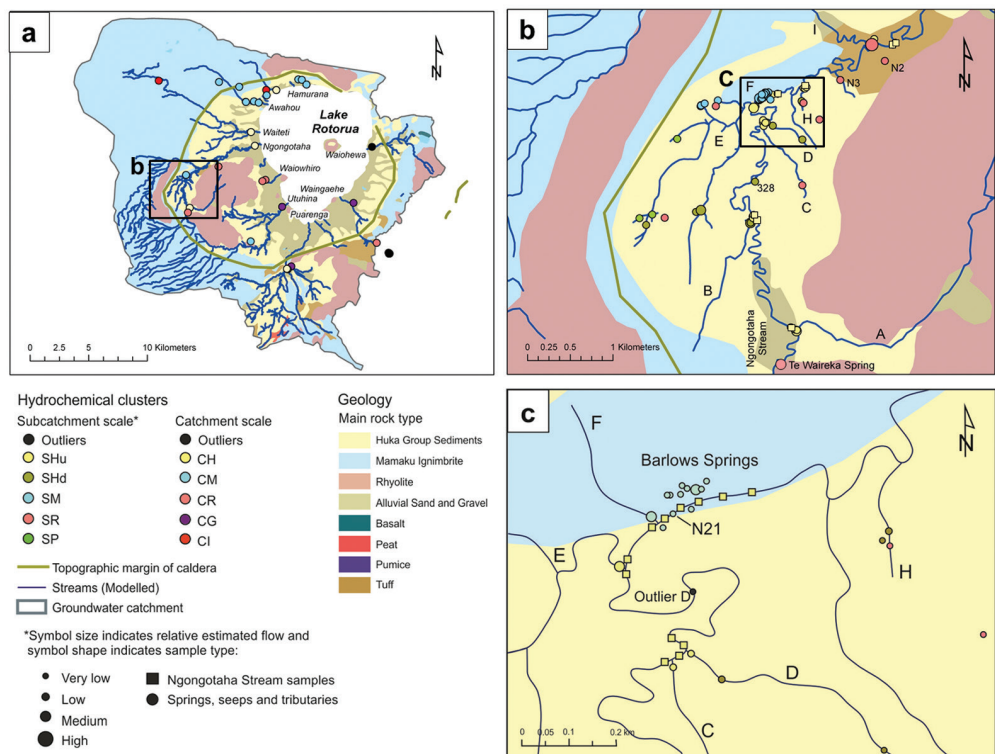


Figure 2 – Sampling locations, cluster assignments and surficial geology based on the 1:250,000 map of Leonard *et al.* (2010) at a) catchment scale and b) and c) subcatchment scale. Panel a) shows approximate caldera trace; cross-section A–A' is shown on the cut-away face of Figure 3.

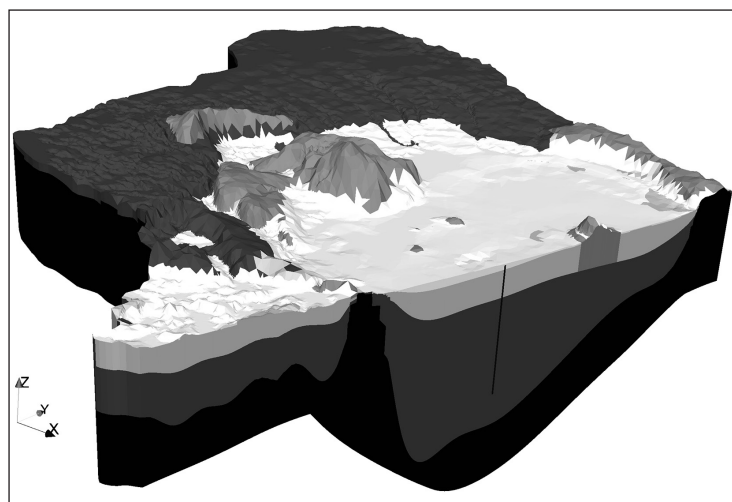


Figure 3 – Three dimensional geological model of the study area from White *et al.* (2007). The location of the vertical cut-away face is shown in Figure 2. The vertical exaggeration is 5× with a 1 km vertical scale bar shown in the centre. The five shades from dark to light (bottom to top) represent: Pre-Mamaku formations, Mamaku Plateau Formation, Huka Formation, rhyolite and Holocene alluvial deposits.

dispersed but relatively thin pyroclastic fall deposits. These pyroclastic materials caused periodic damming of drainage pathways and led to fluctuations in lake level that in turn resulted in widespread and variably thick Huka Group sediments being deposited in the Rotorua Caldera. This period of relatively quiet volcanic activity ended with the Rotoiti eruption from the Okataina Volcanic Centre, which produced the widespread pyroclastic deposits, including non-welded ignimbrites of the Rotoiti Formation and the Earthquake Flat Formation.

From 61 ka to the present, numerous eruptions from the Okataina Volcanic Centre (the most recent of which was in 1886) deposited tephra layers in the study area. Numerous rhyolite lava units were also emplaced during this period. The periodic deposition of pyroclastic materials presumably caused fluctuations in the lake level, with current lake level being reached sometime within the last few thousand years (White *et al.*, 2004). Due to the decline in lake level, Holocene alluvial sand and gravel deposits are found in stream channels and around the current lake shoreline.

There are several geological characteristics of the study area that should be highlighted in the context of the present study. The pre-Mamaku ignimbrites are not substantial sources for groundwater and are expected to be the basal units for aquifers in the study area (White *et al.*, 2004). In contrast, the Mamaku Ignimbrite serves as a major source of groundwater in the study area and is known to support several major springs (> 20 L/s) (Gordon, 2001). The Mamaku Ignimbrite is known to be variably welded and jointed, which may lead to preferential flow paths that could cause hydrochemistry to vary substantially, even within a localised area. In addition, the Mamaku Ignimbrite is assumed to be more than 1 km thick in the centre of the caldera depression (Fig. 3),

which may lead to hydrochemical signatures that reflect long groundwater transit times. Like the Mamaku Ignimbrite, the rhyolite units in the catchment are known to transmit groundwater and support several major springs. Finally, the ring faults associated with the caldera margin (Fig. 2) constitute a major structural feature that may affect the direction and rate of groundwater flow within the catchment.

Hydrology

Lake Rotorua has a surface area of 79 km² and a mean depth of 10.8 m (Burger *et al.*, 2008). The total catchment area is ca. 475 km² (White and Rutherford, 2009) (Fig. 1). Inflow to the lake occurs from nine major and several minor streams (Figs. 1 and 2), as well as direct inputs of rainfall and groundwater. The only surface outflow from the catchment occurs through Ohau Channel (Fig. 1). Water balance calculations indicate that the total catchment area exceeds the surface water catchment area; in other words, groundwater from outside the surface water catchment flows through the aquifer system and enters Lake Rotorua (White and Rutherford, 2009).

Annual rainfall in the catchment is strongly affected by topography and varies from less than 1,400 mm southeast of the lake to more than 2,200 mm northwest of the lake (Hoare, 1980; White *et al.*, 2007; Rutherford *et al.*, 2008). It is estimated that approximately 50% of rainfall infiltrates into the groundwater system, as shown by: 1) comparisons of rainfall and actual evapotranspiration for various parts of the catchment (Hoare, 1980; Dell, 1982; White *et al.*, 2004; White *et al.*, 2007; Rutherford *et al.*, 2008); 2) data from paired lysimeters, a standard rain gauge and a ground level rain gauge installed near the northern boundary of the catchment (White *et al.*, 2007); and 3) a numerical groundwater model relevant to baseflow conditions (White *et al.*, 2007).

Total rainfall infiltration into the groundwater system is estimated to be $4.57 \times 10^8 \text{ m}^3/\text{year}$, based on the catchment shown in Figure 1 and excluding rainfall inputs direct to the lake (White *et al.*, 2007). The rainfall recharge supports stream flows and direct groundwater inflow to the lake. During baseflow conditions, the streams and springs entering Lake Rotorua have a combined flow of about $3.78 \times 10^8 \text{ m}^3/\text{year}$ and direct groundwater inflow to the lake is estimated to be $0.78 \times 10^8 \text{ m}^3/\text{year}$ L/s (White *et al.*, 2007; Hoare, 1980). Overland flow is generally observed to be minor (Dell, 1982).

Methods

Sample collection and analysis

The catchment-scale component of this investigation involved the collection and analysis of samples from 33 sites: 8 wells, 13 springs and 12 streams (Fig. 2a). Sampling locations were selected with the intention of representing all major subcatchments and important hydrological features. Samples were collected between July and November 2003 under baseflow conditions using standard sampling techniques (Standards New Zealand, 1998; Rosen *et al.*, 1999, later replaced by Ministry for the Environment, 2006).

The subcatchment-scale component of this investigation involved the collection and analysis of samples from 74 sites in the Ngongotaha subcatchment: 7 seeps, 25 springs, 28 sites on the Ngongotaha Stream and 14 sites on its tributaries (Fig. 2b and c). The Ngongotaha Stream subcatchment was chosen for the localised study because it contains all of the major lithologies that had been shown through the catchment-scale study to influence hydrochemistry (see discussion below). Sampling locations were selected based on a preliminary visual inspection of the subcatchment, again with the intention of representing dominant

flows, tributary inputs to the Ngongotaha Stream and potential areas of groundwater-surface water interaction. Sampling took place between May and July 2012 during baseflow conditions, as indicated by data from the Ngongotaha Stream gauging station (www.niwa.co.nz). Comparability of the hydrochemical results between the dates of the catchment and subcatchment-scale components of this study is addressed in the Results and Discussion section.

The site names used in this study were official location names (e.g., Te Waireka Spring) or were based on names used in Kovacova and White (2009) (e.g., N21); previously unnamed tributaries were referred to as A to H from upstream to downstream (Fig. 2b and c).

Table 1 lists the hydrochemical parameters, their units, and the abbreviations used in this study. Electrical conductivity (EC), pH, dissolved oxygen (O_2) and temperature (T) were measured in the field using portable meters. Four different samples were collected at each site and then split for analysis at GNS Science (Wairakei, New Zealand) or Hill Laboratories (Hamilton, New Zealand). Unfiltered unpreserved samples were analysed for HCO_3^- using an autotitrator (Metrohm) and for total phosphorus (TP) using a colorimetric analyser (Konelab). Filtered ($0.45 \mu\text{m}$ pore size) unpreserved samples were analysed for Br, F, Cl and SO_4 using ion chromatography (Dionnex) and for $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NH}_4\text{-N}$ and dissolved reactive phosphorus ($\text{PO}_4\text{-P}$) using colorimetric methods (Konelab). Unfiltered H_2SO_4 -preserved samples were analysed for Total Kjeldahl Nitrogen (TKN) using a colorimetric method (Konelab). Filtered HNO_3 -preserved samples were analysed for Ca, Mg, Na, K, Fe, Mn and SiO_2 using inductively coupled plasma optical emission spectrometry (Thermo Jarrell Ash). All analyses were conducted in accordance with APHA (2012).

Table 1 – Hydrochemical parameters considered in this study and their abbreviations.

	Parameter	Units	Abbreviation
Major Elements	Calcium	mg/L	Ca
	Magnesium	mg/L	Mg
	Sodium	mg/L	Na
	Potassium	mg/L	K
	Bicarbonate	mg/L	HCO ₃
	Chloride	mg/L	Cl
	Sulphate	mg/L	SO ₄
	Silica	mg/L	SiO ₂
Minor Elements	Bromide ¹	mg/L	Br
	Fluoride	mg/L	F
	Iron	mg/L	Fe
	Manganese	mg/L	Mn
	Nitrate-nitrogen	mg/L	NO ₃ -N
	Nitrite-nitrogen ¹	mg/L	NO ₂ -N
	Ammoniacal nitrogen	mg/L	NH ₄ -N
	Total Kjeldahl Nitrogen ¹	mg/L	TKN
	Dissolved Reactive Phosphorus	mg/L	PO ₄ -P
	Total Phosphorus ¹	mg/L	TP
Field Parameters	Dissolved Oxygen ²	mg/L	O ₂
	Electrical Conductivity	uS/cm	EC
	pH	pH units	pH
	Temperature	°C	T

Notes:

¹ Not analysed in the subcatchment-scale study. ² Not analysed in all subcatchment samples.

Note that in the subcatchment-scale study Br, NO₂-N, NH₄-N, TKN, and TP were not analysed due to budgetary constraints and O₂ was not analysed at some sites due to unavailability of appropriate equipment. All hydrochemical data from this study can be accessed through the GNS Science Geothermal-Groundwater database (<http://ggw.gns.cri.nz/ggwdata/>).

Statistical methods

Analytical results from each sample were screened based on charge balance error (CBE), calculated as described by Freeze and Cherry (1979):

$$CBE = \frac{\sum vm_c - \sum vm_a}{\sum vm_c + \sum vm_a} \times 100\% \quad (1)$$

Here, v is the absolute value of the ionic valance, m_c is the molarity of the cationic species and m_a is the molarity of the anionic species. Censored analytical results were replaced with the detection limit for calculation of CBE and for all subsequent statistical procedures described below. It is acknowledged that some studies have replaced censored values with a fraction of the detection limit or with a zero, but in this study the replacement operation is

simply performed to allow calculations to be made, and the results are insensitive to which approach is used: the censored results are replaced with a numeric concentration that is too low to affect the CBE results, and for multivariate statistical approaches all of the replacement approaches cause the censored results to be treated as indistinguishable. Samples that yielded CBE greater than 5% or less than -5% were considered to be affected by sampling or analytical errors and were therefore excluded from subsequent statistical analyses. This threshold for CBE is recommended by Freeze and Cherry (1979) and is more stringent than the threshold of $\pm 10\%$ employed by Güler *et al.* (2002) and Guggenmos *et al.* (2011).

Hierarchical cluster analysis (HCA) and principal components analysis (PCA) were conducted using the statistical software package STATGRAPHICS Centurion (Version 15.2.12). The analytical results were first log-transformed (except for pH and temperature) to meet the assumptions of homoscedasticity and normality (Güler *et al.*, 2002; Guggenmos *et al.*, 2011). Log-transformed results were then standardised according to their z-scores (Güler *et al.*, 2002; Woocay and Walton, 2008):

$$z_{ij} = \frac{x_{ij} - \bar{x}_i}{s_i} \quad (2)$$

Here, z_{ij} represents the standardised result for analyte i at site j , x_{ij} represents the unstandardised result for analyte i at site j , and \bar{x}_i and s_i represent the average and standard deviation, respectively, of the unstandardised results for analyte i across all sites. The z-scores were calculated separately for 1) the group of 34 samples collected at the catchment scale and 2) the group of 74 samples collected at the subcatchment scale.

PCA was used to identify the components that explain the variance in the original data. PCA was conducted using analytical

results that were log-transformed then z-scored according to Equation 2. PCA was performed using all available analytes but was conducted separately for the data obtained from the catchment-scale and subcatchment-scale components of this study. In both cases a varimax rotation was conducted in order to produce highly positive, highly negative or near-zero weightings for the analytes in each of the components identified by PCA (Davis, 1986). Following the established Kaiser criterion, only those components with an eigenvalue greater than one were retained.

HCA was conducted according to previously published methods. The square of the Euclidean distance (E^2) between the z-scored results was used as the similarity metric, which has been found in previous hydrochemical studies to produce the most distinctive sample groupings (e.g., Adar *et al.*, 1992; Güler *et al.*, 2002; Daughney and Reeves, 2005, 2006; Cloutier *et al.*, 2008; Guggenmos *et al.*, 2011; Daughney *et al.*, 2012):

$$E^2(j, k) = \sum_{i=1}^n (z_{ij} - z_{ik})^2 \quad (3)$$

Here, j and k represent the two samples (or clusters) for which E^2 is being calculated, and the summation is performed for all analytes i . Two agglomerative linkage rules were applied in this study to group the samples into clusters based on E^2 . First, the nearest-neighbour linkage rule was applied to identify samples with unusual hydrochemistry. Such samples, referred to in this study as outliers, were identified by a sharp change in slope on the agglomeration-distance plot (Timm, 2002). Outliers were excluded to prevent potential biasing of results and then HCA was repeated using Ward's linkage rule. Ward's method performs agglomerative clustering using an analysis of variance procedure that has been shown in previous studies to produce smaller and

more distinct clusters than other linkage rules (Güler *et al.*, 2002; Cloutier *et al.*, 2008). The above-listed steps in HCA were performed using several different combinations of analytes as input.

Several complementary statistical and graphical methods were employed to assist with the interpretation of results from PCA and HCA. Box-whisker plots were used to visualise the hydrochemical differences between the clusters identified by HCA. Multiple range tests ($\alpha = 0.05$) were used to evaluate differences in the distributions of analytical results amongst the clusters (Helsel and Hirsch, 1992). Piper diagrams were used to compare the major ion ratios of samples (Freeze and Cherry, 1979).

Results and discussion

Several observations can be made from a high-level overview of the analytical data. All samples had CBE within the acceptable range from -5% to $+5\%$. Concentrations of Br and $\text{NO}_2\text{-N}$, which were only analysed in the catchment-scale component of this study, were below the analytical detection limit for the majority of samples. These two parameters thus offered no insight into hydrochemistry and were therefore excluded from the interpretation of the catchment-scale data and were not analysed at all in the subcatchment-scale component of this study. Concentrations of TP and $\text{PO}_4\text{-P}$ were similar for most samples collected in the catchment-scale component of this study: the mean difference between them was 1% across all samples (95% confidence intervals for mean difference were $\pm 19\%$). Given that $\text{PO}_4\text{-P}$ concentration has been previously recognised as an indicator of water-rock interaction in New Zealand groundwater (Daughney and Reeves, 2005; Morgenstern and Daughney, 2012), TP was considered redundant and was excluded from the interpretation of the catchment scale-data and was not analysed at

all in the subcatchment-scale component of this study. TKN followed the concentration of $\text{NH}_4\text{-N}$ and hence TKN was also considered redundant and excluded from the subcatchment-scale component of this study.

It is important to determine whether the samples collected in 2003 and 2012 can be meaningfully compared. Support is provided in a recent paper by Morgenstern *et al.* (2015), in which time-series measurements of tritium concentration were used to determine water age at several sites across the Lake Rotorua catchment. The investigation concluded that the catchment's flow regime has been in steady state for many years; i.e., the age of water at a particular location does not vary over the long term. If major ion hydrochemistry is controlled primarily by water-rock interaction (and not by human influence), as we demonstrate below to be the case for the Lake Rotorua catchment, then temporal trends in major ion hydrochemistry should be slow, allowing for meaningful comparison of samples collected several years apart. This hypothesis could be confirmed in our study because there were six sites that were sampled during both campaigns, i.e., in 2003 and then again in 2012. For these sites, no major ion concentration differed by more than 10% between these two dates, and for most ions at most sites the difference was less than 5%. We therefore conclude that it is valid to compare hydrochemistry of the samples collected in the catchment and subcatchment-scale components of this study.

Principal components analysis

For the catchment-scale dataset, PCA was conducted with the 18 parameters that had not been excluded (as outlined above): Ca, Mg, Na, K, HCO_3 , Cl, SO_4 , SiO_2 , F, Fe, Mn, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, $\text{PO}_4\text{-P}$, O_2 , EC, pH and temperature. PCA for the subcatchment-scale dataset was performed with the same parameters except for O_2 and

NH₄-N, which had not been analysed in some or all of the samples. Five components, referred to hereafter as components C1 to C5, were identified in the catchment-scale dataset (Table 2). Four components, referred to hereafter as components S1 to S4, were identified in the subcatchment-scale dataset. These principal components were cumulatively able to describe 79.4% and 77.2% of the variance in the catchment and subcatchment-scale datasets, respectively. The following paragraphs interpret the results of PCA in terms of the main hydrochemical variations detected and their potential causes.

Hydrochemical variation at both scales was largely related to the concentration of total dissolved solids (TDS). At the catchment scale, the importance of TDS was illustrated by component C1, which had positive weightings for EC and all other parameters except for O₂ and PO₄-P. Similarly, component S1 identified at the subcatchment scale also had positive weightings for EC and all other parameters except SO₄, Fe, Mn and pH. Thus, the first component identified at both scales suggested a distinction between dilute waters with low TDS and more concentrated waters with higher TDS. This

Table 2 – Eigenvalues, variance explained and parameter weightings for principal components C1 to C5 identified at the catchment scale and principal components S1 to S5 identified at the subcatchment scale. NA indicates parameters that were not available for the analysis.

Component		Catchment Scale					Subcatchment Scale			
		C1	C2	C3	C4	C5	S1	S2	S3	S4
Eigenvalue		4.35	4.02	2.52	2.16	1.23	6.33	2.97	1.64	1.42
Component variance (%)		24.2	22.3	14.0	12.0	6.9	39.5	18.6	10.2	8.9
Cumulative variance (%)		24.2	46.5	60.5	72.5	79.4	39.5	58.1	68.4	77.2
Parameter weightings	Ca	0.32	-0.29	-0.20	-0.09	-0.07	0.20	0.32	0.22	-0.08
	Mg	0.26	-0.31	-0.09	-0.23	-0.16	0.35	0.00	-0.08	0.14
	Na	0.26	0.15	0.28	-0.37	-0.03	0.34	0.07	0.17	-0.15
	K	0.23	-0.15	-0.11	0.32	-0.22	0.31	0.25	-0.01	0.07
	HCO ₃	0.03	0.10	-0.15	-0.56	0.18	0.33	-0.15	0.21	0.02
	Cl	0.35	-0.04	0.22	-0.09	0.32	0.12	0.44	0.11	0.12
	SO ₄	0.21	-0.08	0.42	0.27	-0.12	-0.06	0.48	-0.22	0.01
	SiO ₂	-0.01	0.23	0.25	-0.22	-0.51	0.35	-0.14	0.10	0.00
	F	0.19	0.30	0.23	0.02	-0.03	0.22	0.04	0.19	-0.44
	Fe	0.20	0.36	-0.18	0.14	0.15	-0.23	0.12	0.52	0.26
	Mn	0.30	0.25	-0.15	0.20	0.08	-0.15	0.18	0.49	0.41
	NO ₃ -N	0.12	-0.45	0.18	0.06	0.03	0.14	0.03	-0.38	0.56
	NH ₄ -N	0.28	0.25	-0.06	0.16	-0.30	NA	NA	NA	NA
	PO ₄ -P	-0.16	0.17	0.39	-0.11	0.32	0.14	-0.33	0.01	0.38
	O ₂	-0.08	-0.22	0.43	0.23	0.20	NA	NA	NA	NA
	EC	0.42	-0.11	0.11	-0.22	-0.01	0.34	0.25	-0.08	0.02
	pH	0.01	0.26	0.18	0.12	-0.17	-0.09	0.32	-0.31	0.04
	T	0.28	0.12	-0.14	0.19	0.47	0.31	-0.21	0.00	0.18

pattern of hydrochemical variation is inferred to result from natural water-rock interaction. The parameters with positive weights in components C1 and S1 were those expected to accumulate over time in groundwater as a result of mineral dissolution, such as Ca, Mg, Na, K, and SiO_2 (Freeze and Cherry, 1979). Evaporation would also contribute to an increase in the concentration of such substances, but evaporation rates are relatively low in the study area.

Hydrochemical variation at both scales was also related to redox potential. At the catchment scale, the importance of redox potential was indicated by component C2, for which O_2 and $\text{NO}_3\text{-N}$ were oppositely weighted from $\text{NH}_4\text{-N}$, Fe and Mn. This suggested a distinction between oxic waters, in which O_2 and $\text{NO}_3\text{-N}$ were present but $\text{NH}_4\text{-N}$, Fe and Mn were absent, and anoxic waters, which displayed the opposite pattern. SO_4 was weighted similarly to $\text{NO}_3\text{-N}$, which suggested that sulphate reduction was not widespread within the catchment. A similar pattern of weights for $\text{NO}_3\text{-N}$, SO_4 , Fe and Mn was observed for component S3, which suggested that redox potential was also an important variable at the subcatchment scale. Redox potential is known to be driven by the natural process of microbial respiration, which in turn influences the concentration of substances such as $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, Fe and Mn in groundwater systems (Langmuir, 1997). Notably, redox potential did not appear to be strongly correlated to TDS at either scale, as indicated by low weightings of EC in components C2 and S3.

Hydrochemical variation at both scales was also related to ion concentration ratios. At the catchment scale, this type of variation was indicated in components C2 to C4, as shown by the weightings of Ca, Mg, Na, K, $\text{PO}_4\text{-P}$, F, SO_4 and SiO_2 . The subcatchment-scale dataset had similar variations in the weights for these parameters in components S2 to S4. These hydrochemical distinctions

were inferred to result from interaction between water and the different lithologies within the catchment. This inference was further tested through HCA, which allows evaluation of the specific ratios of the major ions (see discussion below).

Finally, variation in the two datasets suggested the importance of water temperature, as indicated by its weighting in several components at both scales. Temperature was observed to be correlated to EC (and hence TDS) at both scales, as observed for components C1, C5 and S1. The relationship between temperature and TDS could have arisen from two different processes. First, geothermal activity is known to occur in the study area (e.g., White *et al.*, 2007) and would be expected to produce a correlation between temperature and EC because geothermal fluids are typically more mineralised than shallow groundwaters. Secondly, temperature variations in the dataset may indicate different degrees of solar heating. Groundwater samples would typically have temperatures near the mean annual air temperature, particularly where residence times were long, whereas surface water samples would have been more similar to the air temperature on the day of sampling. The sampling in this study was undertaken during the New Zealand winter and spring at the catchment scale and solely during the winter at the subcatchment scale, when groundwater would have probably had a higher temperature than recent precipitation. The groundwater would have also likely had higher TDS than recent precipitation, which could give rise to the observed correlation between temperature and EC. The following sections revisit the question of whether variations in temperature are related to geothermal influence or to the extent of solar radiation.

Overall, the inferences made on the basis of PCA were consistent with previous investigations. Several studies of groundwater

quality have reported that the dominant hydrochemical variations were related to TDS, redox potential and major ion ratios (e.g., Freeze and Cherry, 1979; Güler *et al.*, 2002; Cloutier *et al.*, 2008; Daughney *et al.*, 2012).

Hierarchical cluster analysis at catchment scale

HCA was conducted on the catchment-scale dataset using the same 18 parameters that were considered in PCA. The selection of parameters was informed by the results of PCA, which indicated that all parameters had weightings greater than ± 0.1 in at least one of the five identified components. The selection of parameters was further supported by previous applications of HCA in New Zealand that have shown that the major cations and anions, SiO_2 and $\text{PO}_4\text{-P}$ are useful for understanding water-rock interaction, analytes such as $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, SO_4 , Fe and Mn assist with understanding redox status, and analytes such as $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, Cl and K can be useful for identifying recharge sources and human influence (Daughney and Reeves, 2005; Guggenmos *et al.*, 2011; Daughney and Reeves, 2012; Morgenstern and Daughney, 2012).

HCA conducted on the catchment-scale dataset using the nearest neighbour linkage rule revealed three outlier samples with unusual hydrochemistry, hereafter referred to as samples A, B and C in order of degree of difference from the remainder of the samples. Sample A, the most hydrochemically unusual sample, was distinguished by anomalously high concentrations of HCO_3 , Fe, Mn and $\text{NH}_4\text{-N}$ and a low concentration of SO_4 compared to all other samples. This was a highly anoxic sample, indicative of sulphate-reducing conditions, collected from a well screened in pyroclastic material. As noted above, sulphate reduction was not widespread in the study area, leading Sample A to be classified as an outlier. Sample B, the second-

most hydrochemically unusual sample, was distinguished by anomalously low concentrations of Ca and Mg and an anomalously high concentration of $\text{PO}_4\text{-P}$ compared to other samples. This sample, also from a well screened in pyroclastic material, had hydrochemistry suggesting an exceptional degree of ion exchange. Sample C, collected from a stream, had anomalously high concentrations of Ca, Mg, SO_4 , $\text{NH}_4\text{-N}$ and F, suggesting a substantial degree of geothermal influence.

HCA conducted with Ward's linkage rule allowed the remaining 30 samples to be partitioned into five clusters (Fig. 4). These are referred to as clusters CM, CR, CH, CI and CG, where the first letter indicates derivation from the catchment-scale component of this study and the second letter relates to the main inferred driver of hydrochemistry (see discussion below). While higher or lower thresholds would result in a different number of clusters, the threshold $E^2 = 250$ was selected to identify a practical number of clusters for interpretation (see discussions in Güler *et al.*, 2002 and Guggenmos *et al.*, 2011). The following paragraphs describe the hydrochemical characteristics of each cluster, based on their centroids (Table 3), the spatial arrangement of samples assigned to each cluster relative to the main rock types in the catchment (Fig. 2), box-whisker plots (Fig. 5), a Piper diagram to compare ion ratios (Fig. 6), and the Multiple Range test applied to individual parameters (Table 4).

Samples assigned to cluster CM had hydrochemistry inferred to indicate interaction between water and the Mamaku Ignimbrite. Accordingly, these samples were predominantly collected in the northern and western parts of the Lake Rotorua catchment. These samples had Na and HCO_3 as the dominant cation and anion, respectively, and were distinguished from other samples by having among the highest concentrations of Mg, $\text{PO}_4\text{-P}$ and SiO_2 and

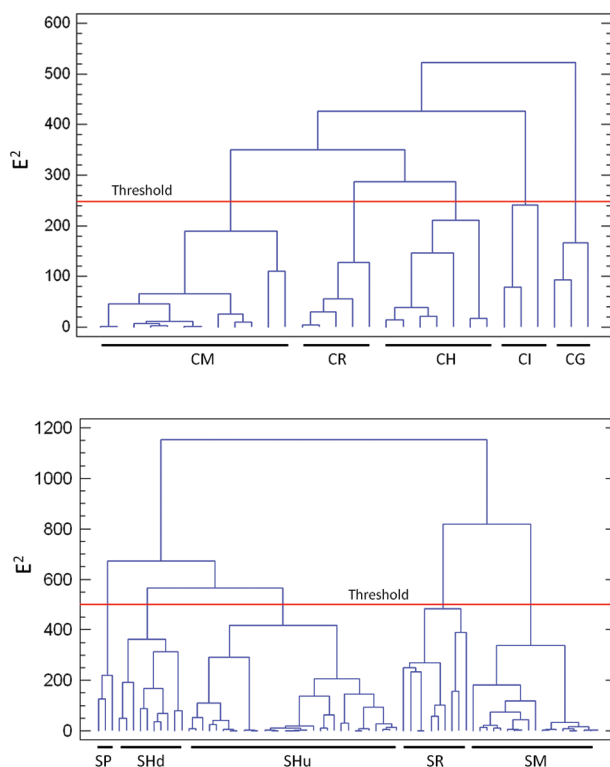


Figure 4 – HCA dendrograms for water samples collected at catchment scale (upper panel) and subcatchment scale (lower panel). Subcatchment-scale results based the parameters Ca, Mg, Na, K, HCO_3 , Cl, SO_4 , SiO_2 , F, Fe, Mn, $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$, EC, pH and temperature. Catchment-scale results based on the same parameters with addition of $\text{NH}_4\text{-N}$ and O_2 .

among the lowest concentrations of F, K and SO_4 . Samples assigned to cluster CM were generally oxalic, as indicated by low but measurable concentrations of $\text{NO}_3\text{-N}$ and concentrations of $\text{NH}_4\text{-N}$, Fe and Mn near or below the detection limit.

Samples assigned to cluster CR had hydrochemistry that appeared to indicate interaction between water and rhyolite. These samples were collected in the vicinity of Mount Ngongotaha, a rhyolite dome in the southwest portion of the catchment. These samples had Na and HCO_3 as the dominant cation and anion, respectively, but had lower concentrations of $\text{PO}_4\text{-P}$ compared to samples assigned to cluster CM and had among the

highest concentrations of K in the study area. Samples assigned to cluster CR were generally oxalic, as indicated by the concentrations of O_2 , $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, Fe and Mn.

Samples assigned to cluster CH had hydrochemistry inferred to indicate interaction between groundwater and Huka Group and/or alluvial sediments. These samples were collected on the western side of the catchment, typically from sites close to the lake. The majority had Na-Ca- $\text{HCO}_3\text{-Cl}$ water type and had lower SiO_2 and higher temperatures than samples assigned to clusters CM and CR. The latter characteristic may indicate shorter residence times and/or less groundwater influence

Table 3 – Centroids for clusters identified at the catchment and subcatchment scales. NA indicates parameters that were not available for the analysis.

Parameter	Units	Catchment Scale					Subcatchment Scale				
		CM	CR	CH	CI	CG	SM	SR	SHu	SHd	SP
Ca	mg/L	3.1	2.2	3.3	6.3	4.0	2.5	2.8	2.1	2.9	1.4
Mg	mg/L	1.8	1.1	1.3	2.9	2.0	1.5	1.2	0.9	1.0	0.6
Na	mg/L	9.6	7.5	7.4	8.6	17.8	7.5	6.9	6.0	5.3	3.9
K	mg/L	1.6	3.6	3.1	4.0	3.9	2.8	3.3	2.3	2.4	1.4
HCO ₃	mg/L	35.5	21.1	28.0	27.2	37.6	27.0	18.5	18.2	18.1	12.1
Cl	mg/L	4.7	4.1	5.1	6.7	12.8	4.4	5.4	4.6	5.1	3.7
SO ₄	mg/L	1.6	3.7	2.4	2.9	10.9	1.3	3.3	2.0	2.2	1.9
SiO ₂	mg/L	62.9	65.1	53.8	51.4	68.4	63.1	50.1	43.5	39.7	35.8
F	mg/L	0.05	0.07	0.06	0.04	0.22	0.04	0.04	0.03	0.04	0.04
Fe	mg/L	0.02	0.02	0.22	0.02	0.11	0.02	0.03	0.09	0.26	0.23
Mn	mg/L	<0.01	<0.01	0.04	<0.01	0.03	0.01	0.01	0.02	0.04	0.02
NO ₃ -N	mg/L	0.8	1.2	0.7	4.2	1.2	0.7	1.0	0.7	0.3	0.3
NH ₄ -N	mg/L	0.01	0.02	0.02	0.01	0.03	NA	NA	NA	NA	NA
PO ₄ -P	mg/L	0.07	0.04	0.05	0.03	0.06	0.06	0.01	0.03	<0.01	<0.01
O ₂	mg/L	8.4	9.9	8.9	6.4	9.1	NA	NA	NA	NA	NA
EC	uS/cm	65.5	53.8	61.4	103.3	131.0	66.2	69.3	53.4	56.0	33.7
pH	pH units	7.0	7.0	7.1	6.3	7.1	6.8	7.0	7.1	6.9	6.7
T	°C	12.0	11.5	14.6	12.7	14.6	11.1	8.9	8.8	7.1	5.9

(hence water temperatures that were closer to air temperature on the day of sampling than to average annual air temperature). Some samples assigned to cluster CH had concentrations of NH₄-N, Mn and/or Fe significantly above the detection limit, suggesting anoxic conditions.

Samples assigned to cluster CI had hydrochemistry inferred to indicate some degree of impact by human activities (incorporating the possible effect of agriculture). The inferred impact was based on concentrations of K, NO₃-N, Cl and/or SO₄, which were relatively high compared to samples from clusters CM, CR and CH (see Daughney and Reeves, 2005; Guggenmos *et al.*, 2011). In addition, these samples had relatively higher proportions of Ca and Mg

compared to the samples assigned to other clusters, still with HCO₃ as the dominant anion. Concentrations of NH₄-N, Mn and Fe were low in all samples assigned to cluster CI, implying oxic conditions.

Samples assigned to cluster CG had hydrochemistry that suggested some degree of geothermal influence. These samples had relatively high temperatures and EC and elevated concentrations of Na, Cl, SO₄, SiO₂ and NH₄-N. These samples were collected in the southern portion of the catchment, where geothermal influence has been previously recognised (White *et al.*, 2007).

In summary, HCA conducted using the catchment-scale dataset suggested that hydrochemistry was driven by interaction between water and the different major lithologies in

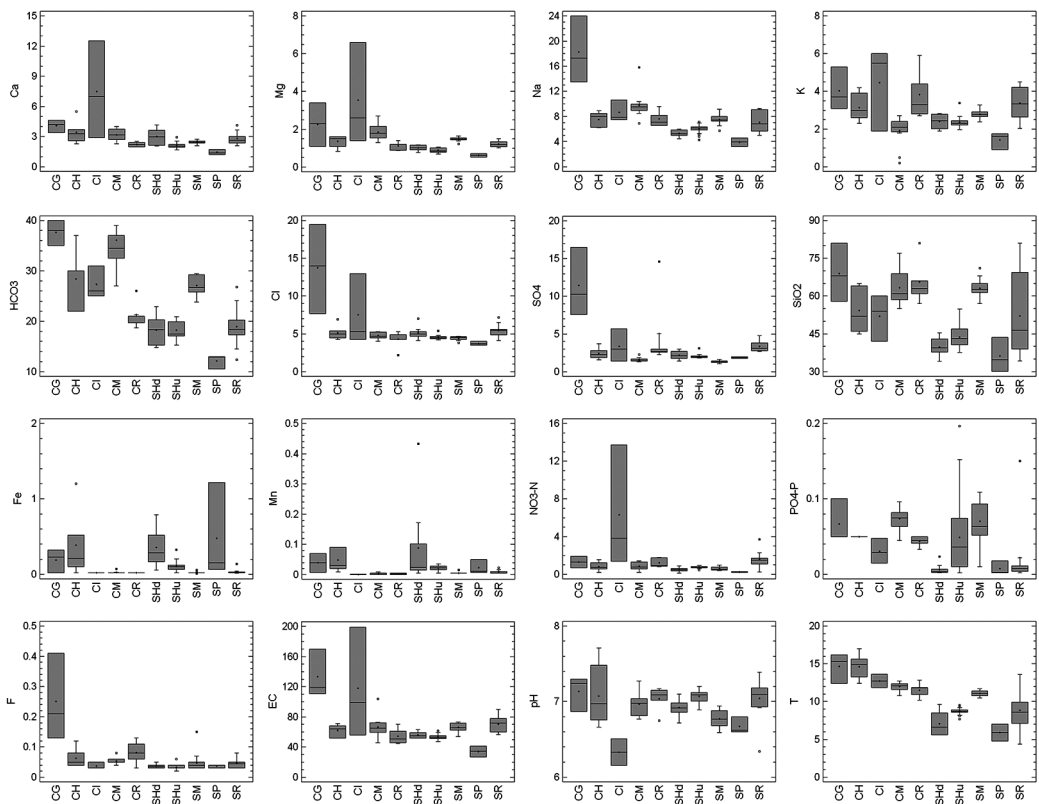


Figure 5 – Box-whisker plots showing differences among selected parameters for the clusters defined by HCA.

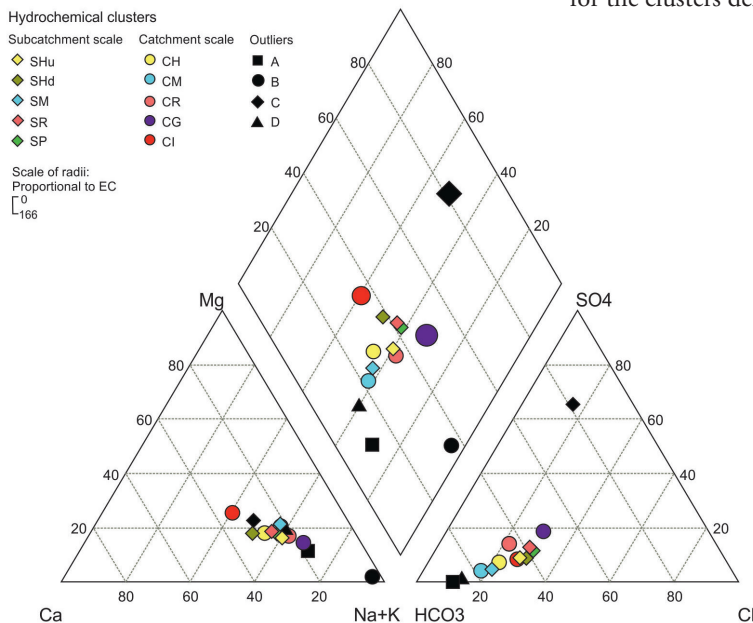


Figure 6 – Piper diagram for the centroids of the clusters defined by HCA. Ion proportion ratios in meq/L.

Table 4 – Results of Multiple Range tests to evaluate differences amongst mean parameter values in the clusters defined by HCA*.

Cluster	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄	SiO ₂	F	Fe	Mn	NO ₃ -N	NH ₄ -N	PO ₄ -P	O ₂	EC	pH	T
CM	00XX0	000X0	000X0	XX0000	000X	XX00	X0000	000X	0XX0	X00	X00	XX0	X0	0000X	0X	00XX0	00XX	000X0
CG	000X0	000X0	0000X	0000XX	000X	000X	0000X	000X	000X	XX0	XXX	XX0	0X	00XXX	0X	0000X	00XX	0000X
CH	00XX0	0XX00	00X00	000XX0	00X0	XX00	XXXX00	00X0	0XX0	0XX	0XX	XX0	X0	0XXXX	0X	0XXXX0	00XX	0000X
CI	0000X	0000X	00XX0	00000X	00X0	00X0	0XXXX0	0XX0	XX00	X00	XX0	00X	X0	XXXXXX	X0	0000X	X000	000X0
CR	XX000	XXXX0	00X00	0000XX	0X00	XX00	000X0	000X	00X0	X00	XX0	XX0	X0	0XXXX	0X	0XX00	00XX	00XX0
SHd	0XXXX0	XX000	XXXX0	0XX000	0X00	XX00	XXXX00	X000	XX00	0XX	00X	X00		X0000		0XX00	00X0	X0000
SHu	X0000	X0000	0X000	0X0000	0X00	XX00	X0X00	XX00	X000	X00	XX0	X00		000X0		0X000	000X	0X000
SM	XX000	00X00	00X00	00XX00	00X0	X000	X0000	000X	XX00	X00	X00	X00		0000X		00XX	0X00	00X00
SP	X0000	X0000	X0000	X00000	X000	X000	XXXX0	X000	XX00	00X	XX0	X00		XX000		X0000	0X00	X0000
SR	0XX00	XXXX00	00X00	0000X0	0X00	0X00	0X000	00X0	XX00	X00	XX0	0X0		XXXX00		000X0	00XX	0X000

* For each parameter, the Xs within each column indicate the clusters for which means that were not statistically different ($\alpha = 0.05$). For example, mean Ca did not differ between clusters SM and SP (both have Xs in the first column) or between clusters SM and SR (both have Xs in the second column) but did differ significantly between clusters SP and SR (the former has an X in the first column but the latter does not). Some parameters, such as Fe and Mn, had few homogenous groups and therefore required few columns of Xs and 0s, whereas other parameters, such as K and SO₄, had more homogenous groups and therefore required more columns of Xs and 0s. NH₄-N and O₂ were not analysed in the subcatchment-scale component of this study.

the study area, with human and geothermal influence being important in some areas. The clustering appeared to be controlled primarily by the concentrations of major ions, SiO_2 , F and $\text{PO}_4\text{-P}$. HCA was affected to a lesser degree than PCA by O_2 , $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, Fe and Mn. This was possibly because most of the samples collected in the catchment-scale component of this study were oxic, meaning that redox-sensitive substances exerted a lesser influence on the clustering. For context, the Lake Rotorua catchment is dominated by volcanic materials such as ignimbrites and rhyolites, and hence the samples collected in this study had lower concentrations of Ca, Mg and SO_4 and higher concentrations of F, $\text{PO}_4\text{-P}$ and SiO_2 compared to most other aquifer systems in New Zealand (compare to Daughney and Reeves, 2005; Daughney *et al.*, 2012).

Hierarchical cluster analysis at subcatchment scale

HCA was performed using the same parameters that were considered in the catchment-scale study, with the exception of O_2 and $\text{NH}_4\text{-N}$, which were not analysed at the subcatchment scale. HCA conducted with the nearest neighbour linkage rule revealed one sample with unusual chemistry, referred to here as sample D. Compared to other samples collected in the subcatchment, sample D had anomalously high concentrations of HCO_3 , Fe, Mn, F, SiO_2 and $\text{PO}_4\text{-P}$ and anomalously low concentrations of K, SO_4 and $\text{NO}_3\text{-N}$. Sample D was collected from a small spring on the bank of the Ngongotaha Stream. Yellow-brown staining was clearly visible on the surrounding rock, inferred to originate from the precipitation of iron and manganese oxide minerals from the anoxic spring water upon exposure to air. Sample D was excluded from subsequent statistical analysis to avoid potential biasing influence.

HCA conducted with Ward's linkage rule allowed the remaining 73 samples to be

partitioned into five clusters at a threshold of $E^2 = 500$ (Fig. 4). These are referred to as clusters SP, SHd, SHu, SR and SM, where the first letter indicates the subcatchment-scale component of this study and the following letters relate to the main inferred driver of hydrochemistry. A higher E^2 threshold was used for the subcatchment scale compared to the catchment scale in order to generate the same number of clusters in each case (the subcatchment scale included a larger number of samples having higher hydrochemical diversity, necessitating a slightly higher E^2 threshold). The following paragraphs compare the characteristics of the clusters defined in the subcatchment-scale and catchment-scale components of this study in terms of their centroids (Table 3), the spatial arrangement of samples assigned to each cluster relative to the main rock types in the catchment (Fig. 2), box-whisker plots (Fig. 5), a Piper diagram to compare ion ratios (Fig. 6), and the Multiple Range test applied to individual parameters (Table 4).

Of the five clusters identified at the subcatchment scale, none were comparable to cluster CG or cluster CI identified at the catchment scale (most evident in Figs. 5 and 6). This result indicated that geothermal influence and human impact, inferred to drive the hydrochemistry of clusters CG and CI, were not strong factors affecting hydrochemistry in the Ngongotaha subcatchment.

Just as some clusters were identified at the catchment scale but not at the subcatchment scale, the opposite was also true: cluster SP was not analogous to any of the clusters identified at the catchment scale. Samples assigned to cluster SP were collected in the upper headwater tributaries of the Ngongotaha Stream and had hydrochemistry inferred to indicate relatively recent precipitation. EC and major ion concentrations were substantially lower in samples from cluster SP compared to any other cluster identified

in this study. Temperatures were also low, reflecting the air temperature on the day of sampling, which suggested shallow flow paths with relatively short residence times.

The clusters SM and SR identified at the subcatchment scale were very similar to the clusters CM (Mamaku Ignimbrite) and CR (Rhyolite) identified at the catchment scale. Clusters SM and CM had statistically equivalent values of all parameters except Ca, Mg, Na, K, HCO_3 , pH and temperature, and even for these parameters the differences were small and major ion ratios were highly comparable. Most sites assigned to cluster SM were springs located along a relatively short reach of Ngongotaha Stream. Given their location and chemistry it was inferred that these sites were fed by groundwater that had

interacted with Mamaku Ignimbrite. Clusters SR and CR were also very similar, differing only in the values of SO_4 , SiO_2 , F, EC and temperature. Most sites assigned to cluster SR were collected from streams that drained from Mount Ngongotaha and, similarly to samples in cluster CR, the hydrochemistry was inferred to indicate interaction between water and rhyolite. Overall, these results showed that the hydrochemistry indicative of interaction with Mamaku Ignimbrite or rhyolite was evident at both catchment and subcatchment scales.

The subcatchment-scale clusters SHu and SHd were similar to the catchment-scale cluster CH, which suggested interaction between groundwater and Huka Group and/or alluvial sediments. Samples assigned

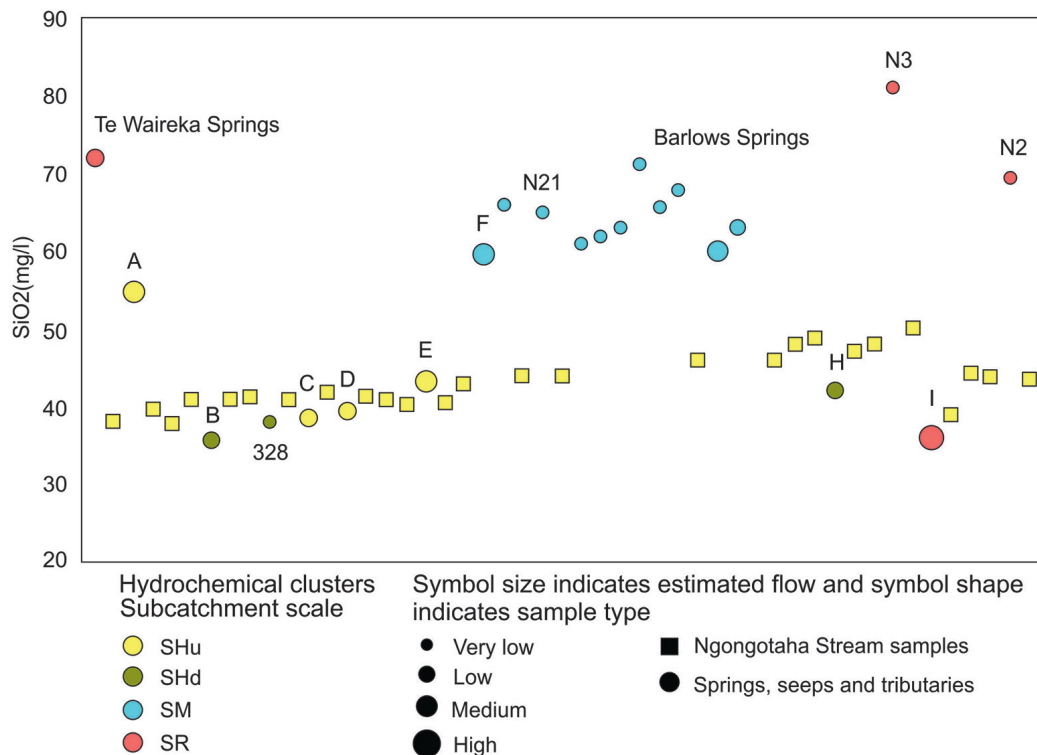


Figure 7 – Relative downstream profile of SiO_2 concentration in samples collected from Ngongotaha Stream (squares) compared to samples from tributaries and bank-side springs and seeps (circles). Symbol colour, shape and size relate to site cluster, source of flow and relative flow, respectively. Letters refer to sampling points, see Figure 2.

to cluster SHu were collected in upstream locations. In contrast, samples assigned to cluster SHd were collected from locations further downstream, in the area between samples assigned to clusters SR and SHu. This spatial pattern and some aspects of the hydrochemistry suggested that SHd waters may have arisen from mixing of SR and SHu waters. However, concentrations of some substances in SHd samples, such as Ca, Na and SiO₂, could not be explained by such mixing. This implied that SHd samples were also affected by hydrochemical processes that were not occurring elsewhere in the subcatchment, possibly as a result of interaction between water and locally distinctive aquifer materials.

The results of subcatchment-scale HCA provided useful context for interpretation of hydrochemical changes along the length of Ngongotaha Stream. Figure 7 illustrates this concept for SiO₂, a parameter that had a strong influence on the results of PCA and HCA, but this approach could be equally applied to any other variable. Te Waireka Spring (cluster SR) and tributary A (cluster SHu) had relatively high flows and high concentrations of SiO₂, which probably caused the increase in SiO₂ concentration observed in the upstream portion of Ngongotaha Stream. SiO₂ concentrations in Ngongotaha Stream were fairly constant at ca. 40 mg/L between tributaries B and E, presumably because the volumetric inflows from tributaries and springs were small, and their SiO₂ concentrations were not markedly different from the stream. The concentration of SiO₂ in Ngongotaha Stream increased from ca. 40 mg/L at the confluence with tributary E to ca. 50 mg/L just upstream of the confluence with tributary H. This pattern was inferred to result from inflows of cluster SM-type waters from tributary F, the streambed spring N21 and nearby springs (e.g., Barlows Springs), all of which had relatively high concentrations of SiO₂. Tributaries H and I, both with relatively low concentrations

of SiO₂, caused corresponding decreases in the concentration of SiO₂ in Ngongotaha Stream. Despite the observed changes in SiO₂ concentration along Ngongotaha Stream, all samples taken from it were assigned to cluster SHu, with the exception of one sample assigned to cluster SR that was collected immediately downstream of the confluence with tributary I (tributary I was also assigned to cluster SR). This analysis suggested that SiO₂ concentrations along Ngongotaha Stream were mostly affected by inflows from Te Waireka Spring, the SM-type springs including N21 and the Barlows Springs, and tributaries A, F and I.

Summary

The application of PCA in this study revealed that hydrochemical variations at both catchment and subcatchment scales were largely related to natural water-rock interaction involving the different major lithologies in the study area. Five principal components were identified at the catchment scale (C1 to C5) whereas four principal components were identified at the subcatchment scale (S1 to S4). At both scales, the first principal components indicated that hydrochemical variations largely depended on the TDS concentration. Redox potential played a lesser role at both scales as indicated by principal components C2 and S3. Water temperature was found to be correlated to EC (and hence TDS) at both scales, as observed for components C1, C5 and S1. Given that geothermal activity is known to occur at some areas in the catchment, this relationship could be explained by geothermal influence for some samples of the catchment-scale study. However, at the subcatchment scale no geothermally-influenced water could be identified (see below), suggesting that the observed temperature variations were caused by solar radiation.

HCA conducted using Ward's linkage rule produced five clusters at both scales,

which could be assigned to the different major lithologies or to other hydrochemical driving forces such as geothermal or human influence. Notably, highly comparable clusters were identified at the catchment and subcatchment scales, inferred to indicate interaction of water with Mamaku Ignimbrite (clusters CM and SM), rhyolite (clusters CR and SR) and Huka Group and/or alluvial sediments (clusters CH, SHu and SHd). At the catchment scale, geothermal influence and human impact were also identifiable in the HCA results (clusters CG and CI respectively). These drivers of hydrochemistry were not identifiable at the subcatchment scale, but some samples appeared to be influenced by recent precipitation (cluster SP).

The hydrochemical data and the interpretation based on PCA and HCA proved to be useful for evaluating groundwater-surface water interaction at the subcatchment scale. Using SiO₂ as an example, groundwater-surface water interaction could be visualised by evaluating hydrochemical changes along the length of Ngongotaha Stream. The analysis suggested that the SiO₂ concentrations along Ngongotaha Stream were mostly affected by inflows from Te Waireka Spring, the SM-type springs including N21 and the Barlows Springs, and tributaries A, F and I.

By explaining hydrochemical variation at catchment and subcatchment scales and assigning the samples to clusters representing the influence of different lithologies or other processes, this study provides useful context to the broader aim of water management within the Lake Rotorua catchment. For example, this investigation provides a dataset and associated interpretations that may assist with future calibration of hydrogeological models using hydrochemical data. In particular, this study has shown that PCA and HCA are complementary techniques that can be usefully scaled to interpret hydrochemical data at the catchment scale, subcatchment scale and even for individual stream reaches.

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