

# Identifying leakage to groundwater from Lake Rerewhakaaitu using isotopic and water quality data

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## Abstract

Stable isotopes (<sup>18</sup>O, <sup>2</sup>H), water dating, and major anion and cation water chemistry of springs, groundwater bores, a stream and a lake have been used to identify areas of discharge from Lake Rerewhakaaitu. Groundwater aquifers and spring discharges to the north and west of Lake Rerewhakaaitu are found to contain up to 79% lake water.

Hierarchical cluster analysis is used to group sites into three clusters based on the major anion/cation water chemistry. Defining meaningful hierarchical clusters was difficult due to the similarity of the chemical compositions between sites. The three clusters defined in this study do not clearly identify the sites containing lake water. However, the hierarchical cluster analyses can be used to infer sites that are likely to contain proportions of lake water in the groundwater, and therefore provides a method to identify sites that may contain lake water.

The groundwater and spring discharges to the north and west of Lake Rerewhakaaitu flow into a different surface water catchment, thus providing a hydrological link between two different surface water catchments. This has implications for catchment management in the greater Rerewhakaaitu area.

## Introduction

The quality and quantity of recharge to a groundwater system can affect the sustainable use of groundwater resources, particularly where groundwater is used for domestic or public water supplies, because public health can be affected by contamination. Thus, identification and safe management of the source of groundwater recharge is essential for protection of groundwater resources. Natural sources of groundwater recharge to the groundwater aquifers include streams, rivers, lakes and rainfall.

Groundwater is used extensively in New Zealand for agricultural, horticultural, domestic and public water supplies. White (2001) estimates up to 26% of the New Zealand population depend totally on groundwater for drinking, and a further 24% are partially dependent on groundwater as a source of water.

Identifying the source of the water to a groundwater system commonly requires the use of chemical or isotopic tracers (Quast *et al.*, 2006), usually, in conjunction with other techniques such as water chemistry and/or physical hydrology. Chemical and isotopic tracers are particularly useful in areas where hydrological information important to

interpreting the data, such as bore geology, is missing.

Water chemistry, combined with the naturally occurring stable isotopes oxygen-18 and deuterium, have been used successfully to distinguish between rainfall, local groundwater and lake water as the source of water in geothermal systems (e.g., Stewart, 1978; Darling *et al.*, 1996; Ojiambo *et al.*, 2001) and groundwater systems (e.g., Stewart and Morgenstern, 2001; Ojiambo *et al.*, 2001; Chowdhury, 2004; Kristmannsdóttir and Ármannsson, 2004).

Determining the mean residence time of groundwater can significantly enhance the understanding of a groundwater system. The mean residence time can be taken as the average travel time for land-use effects to be observed and groundwater recharge times, and can be used to determine the percent age fractions of recharge water to a groundwater aquifer. Tritium and chlorofluorocarbons (CFCs) are two tracers that have been used extensively in New Zealand to understand groundwater systems (e.g., Taylor, 1994; Stewart *et al.*, 1999; Morgenstern and Gordon, 2006; Morgenstern *et al.*, 2004; Morgenstern and Stewart, 2004; Morgenstern, 2005).

Lake Rerewhakaaitu is one of twelve lakes in the Rotorua area (the 'Rotorua lakes') monitored regularly by Environment Bay of Plenty (EBOP). Regular cyanobacterial blooms in Lakes Rotorua and Rotoiti since 1997 have heightened public concerns about the declining water quality of these two lakes, and possibly in the other nine Rotorua Lakes (Lakes Water Quality Society, 2001). Nutrient inputs (nitrogen and phosphorus), their effects on the lakes, and how the lakes can be managed to maintain or improve their current water quality are issues requiring study. In response to the public concern, EBOP has been coordinating research programmes involving iwi, regional government, local government and scientific organizations to improve understanding of

the nutrient cycle in the Rotorua Lakes area. This will assist EBOP to form new policies and develop remediation programmes where necessary.

Nutrient levels, nutrient inputs, nutrient transport mechanisms, nutrient transport times, lake processes, and effects of land use are key scientific aspects that need to be better understood to solve the issues. To date, much scientific work in the Rotorua Lakes area has focused on Lakes Rotorua and Rotoiti (e.g., Lakes Water Quality Society Inc, 2003; Hamilton, 2003; Morgenstern and Gordon, 2006), in line with the priorities set by EBOP. The work reported in this paper may assist EBOP develop policies in the Lake Rerewhakaaitu area, where understanding of the groundwater system is more limited.

The objective of this study was to identify whether lake water is a source of recharge to the major aquifers around Lake Rerewhakaaitu and, if it is occurring, what the flow paths are. The study was carried out near Lake Rerewhakaaitu using a combination of water chemistry, stable isotopes and water dating techniques.

## Setting

Lake Rerewhakaaitu is situated approximately 26 km southeast of Rotorua, New Zealand and covers an area of approximately 630 ha. The surface water catchment is approximately 5300 ha in area, with elevations ranging from 435 m above sea level (asl) at the lake to approximately 1100 m asl on Mt Tarawera in the north of the catchment (Fig. 1). The elevation of the top of the surface water catchment to the east, south and west of Lake Rerewhakaaitu is between 420 m and 530 m asl. The surface water catchment is mainly to the south of the lake, with narrow catchment areas to the north, east and west. Mean rainfall is about 1600 mm per year.

Volcanic processes in the last 22 ka have moulded the landscape, resulting in the

formation of many of the lakes found in the region. Mt Tarawera is made up of several Okataina rhyolitic domes ranging in age from 0.7 ka to 21 ka. Three recent (<11 ka) deposits around Lake Rerewhakaaitu are attributed to eruptions from Mt Tarawera (Nairn, 2002): Waiohau pyroclastics (11 ka); Kaharoa pyroclastics (0.7 ka); and mud and ejecta from the 1886 eruption. The thickness of the Waiohau pyroclastic deposit is in excess of 30 m, while the thickness of the Kaharoa pyroclastic deposit is between 10 and 30 m thick in the area around Lake Rerewhakaaitu (White *et al.*, 2003). The thickness of ejecta from the 1886 eruption is too small to be mapped except near vent zones and the shores of Lake Rotomahana (Nairn, 2002).

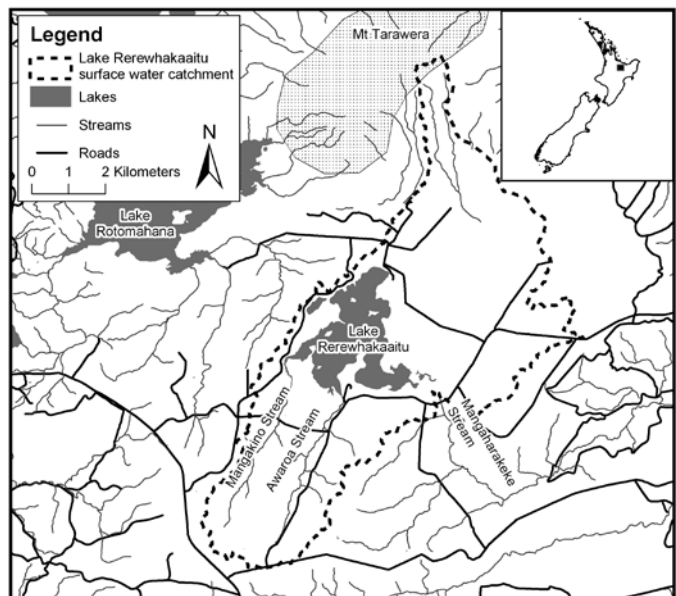
Lake Rerewhakaaitu is formed in an old deep narrow valley cut into the Rangitaiki Ignimbrite (White *et al.*, 2003). The valley is thought to have drained a large catchment to the south of the current lake, northwards to the Tarawera River. Infilling and damming of the valley probably occurred during the 11 ka eruption of Mt Tarawera (Waiohau pyroclastics) and probably caused a small lake to form. The lake reached its present form with further damming from the 0.7 ka Mt Tarawera eruption (Kaharoa pyroclastics).

The Rangitaiki Ignimbrite is considered to be the base unit in this study and is described by Nairn (2002) as a moderately welded, dark grey, crystal-rich tuff. The unit includes coarse tuffs, pumice breccias and air fall deposits. It is the oldest unit (0.34 Ma) mapped in the Rerewhakaaitu area. The unit outcrops to the east and in the steeply-incised valleys to the west of Lake Rerewhakaaitu.

Land use in the catchment is dominantly dairy farming.

McIntosh *et al.* (2001) estimate 77% of the catchment is pasture, 15% exotic forest, 6% indigenous forest/scrub and 2% 'other'. Of the 77% pasture, 70% is used for dairy cows and 7% for sheep/cattle. Dairying and use of fertilizers has intensified between 1990 and 2000, with relatively high application rates (>300 kg/ha/year) of nitrogen-based fertilizers (McIntosh *et al.*, 2001).

Lake Rerewhakaaitu is shallow, having a mean depth of 6.3 m and a maximum depth of 15 m. The lake receives water from rainfall, streams and shallow groundwater systems (White *et al.*, 2003). The lake is described as a mesotrophic lake in average condition (Scholes and Bloxham, 2005). Mean total nitrogen and mean total phosphorus (as P) are 0.38 g m<sup>-3</sup> and 0.008 g m<sup>-3</sup> respectively for the period 1991–2001. No net trend is observed in the total nitrogen and total phosphorus data over this period. However, an increase in nitrogen and phosphorus occurred between 1995 and 1997. McIntosh *et al.* (2001) suggest that this increase could be due to an increased lake level mobilizing nutrients in the sediment of the lake margin.



**Figure 1** – Map of the Lake Rerewhakaaitu area.

Mangakino Stream and Awaroa Stream are the only two streams that flow into Lake Rerewhakaaitu. Both streams flow into a wetland at the southern end of the lake, and both streams have a shallow groundwater aquifer as their source. Mangakino Stream has a mean flow of  $24 \text{ l s}^{-1}$  (from measurements between 1995 and 2001) measured approximately 1 km upstream from the lake. Total nitrogen concentrations have increased from a median of  $1.21 \text{ g m}^{-3}$  in the 1970's to  $2.36 \text{ g m}^{-3}$  in 2000 (McIntosh *et al.*, 2001). Total phosphorus concentrations have remained at about  $0.045 \text{ g m}^{-3}$  over this period. Awaroa Stream is commonly dry. Water samples collected from Awaroa Stream in the 1970s and the 1990s show both total nitrogen and total phosphorus have approximately tripled (median total nitrogen to  $8.43 \text{ g m}^{-3}$  and median total phosphorus to  $0.681 \text{ g m}^{-3}$ ) over this period (McIntosh *et al.*, 2001).

The only surface water outlet to Lake Rerewhakaaitu is an upper tributary of Mangaharakeke Stream that flows from the southeast corner of the lake to the Rangitaiki River. This tributary only flows when the lake level is high.

All major geological units in the Lake Rerewhakaaitu catchment, except the Okataina Rhyolites, are identified as having groundwater aquifers. The Rangitaiki Ignimbrite is the main groundwater aquifer that is used to supply water for domestic and farming purposes. Lake Rerewhakaaitu is a possible source of recharge to the Rangitaiki Ignimbrite aquifer because groundwater levels in the Rangitaiki Ignimbrite aquifer are generally lower than the level in Lake Rerewhakaaitu (White *et al.*, 2003).

Groundwater flow directions are variable in the Rangitaiki Ignimbrite aquifer near Lake Rerewhakaaitu. Lake Rerewhakaaitu is situated on a groundwater divide, with groundwater flowing to the west on the west side of the lake and to the east on the

east side of the lake (White *et al.*, 2003). A small groundwater flow from the Rangitaiki Ignimbrite aquifer could be entering Lake Rerewhakaaitu from the northeast. An assessment of groundwater flow directions for the other aquifers is difficult to determine due to a lack of data. Lake Rerewhakaaitu is estimated to be losing water at a rate of  $556 \text{ l s}^{-1}$  to groundwater aquifers (White *et al.*, 2003). Most of this is probably going into the Rangitaiki Ignimbrite aquifer; however, other smaller aquifers need to be considered.

A number of small seeps and springs are observed near the base of gullies and depressions near the northern and northwestern parts of Lake Rerewhakaaitu. One of these springs (Te Kaue Spring) contains significant amounts of lake water (Taylor *et al.*, 1977) based on stable isotope measurements. White *et al.* (2003) speculates that Lake Rerewhakaaitu may also be losing water through a subsurface flow along the pyroclastic buried valley cut into the Rangitaiki Ignimbrite flowing under the lake to the north.

## Methods

GNS collected water samples from existing groundwater bores, springs, streams and the lake from the Lake Rerewhakaaitu study area in January-February 2006. Grab samples were obtained for spring, stream and lake samples. Groundwater bores were purged until the field parameters temperature, conductivity, pH, and turbidity were stable prior to sampling. Bore samples were collected as close to the bore-head as possible. The field parameters were recorded immediately prior to sampling. Water samples were collected in bottles appropriate for the required analyses using appropriate methods (Rosen *et al.*, 1999; van der Raaij, 2004 *pers. comm.*). Water samples were filtered (0.45 micrometer pore size), acidified and chilled in the field where required.

Water samples were analysed for alkalinity ( $\text{HCO}_3$ ) and pH measured on a Metrohm autotitrator, magnesium (Mg), Calcium (Ca), iron (Fe), manganese (Mn), potassium (K), silica as  $\text{SiO}_2$  ( $\text{SiO}_2$ ) and sodium (Na) using a Thermo Jarrell Ash inductively-coupled plasma optical emission spectrometer, chloride (Cl), sulphate ( $\text{SO}_4$ ), nitrate as nitrogen ( $\text{NO}_3\text{-N}$ ), bromide (Br), fluoride (F) and dissolved reactive phosphate as phosphorus (DRP) using a Dionex ion exchange chromatograph, ammonia as nitrogen ( $\text{NH}_3\text{-N}$ ) using an auto analyzer, oxygen 18 ( $^{18}\text{O}$ ) and deuterium ( $^2\text{H}$ ) using a mass spectrometer, tritium using low-level liquid scintillation spectrometry, and chlorofluorocarbons (CFCs) using a gas chromatograph.

Data collected by GNS were augmented with data collected by EBOP in the Lake Rerewhakaaitu area over the last three years. Not all water samples collected by EBOP were analysed for the major cations/anions above as some surveys were designed to investigate nutrient levels only. The sampling methodology or methods of the EBOP analyses were not known. Data supplied by EBOP has been modified to be consistent with the GNS chemical parameters to enable the data to be used for statistical processing. The modifications were:

- Alkalinity as  $\text{HCO}_3$  has been calculated from Alkalinity (as  $\text{CaCO}_3$ ).
- Soluble iron is used as an indicator for iron.
- Soluble manganese is used as an indicator for manganese.
- Dissolved reactive phosphorus (DRP) is used as an indicator for phosphorus.

Ion balances were calculated for all water samples to ensure data quality. Only samples with ion balances (Freeze and Cherry, 1979) within  $\pm 10\%$  were retained for hierarchical cluster analysis. This reduced the number of samples that could be used from the dataset. It also restricted samples that could be used to those that contained major cations and major

anions. In general, this left between one and three samples that could be used to calculate a median at a site. Censored data is given the value of zero in the ion balance calculation.

Medians of the samples at each site were calculated with Microsoft Excel to analyse the spatial distributions of the water chemistry and to use in the hierarchical cluster analyses. Several data processing steps were required to obtain medians. Firstly, censored data was converted into values by using half the detection limit. Where multiple detection limits existed (e.g., Br,  $\text{NO}_3\text{-N}$ ), the highest detection limit was used. Results were changed to half the highest detection limit for samples with results less than half the highest detection limit. This was done to ensure data all had the same lower limit.

#### **Hierarchical cluster analysis**

Differences in water chemistry within an aquifer and from different aquifers can be used to identify the factors above using hierarchical cluster analysis (Daughney and Reeves, 2005; Guler *et al.*, 2002). Hierarchical cluster analysis is a multi-variate statistical technique used to 'group' samples based on any number of variables (Back, 1961, 1966; Morgan and Winner, 1962; Seaber, 1962). The groups are called hydrochemical facies, and represent groundwaters with similar chemical composition.

Water quality data was processed for the hierarchical cluster analyses as described by Daughney and Reeves (2003) using the Statgraphics software package. Medians for each analyte were transformed (where required) and tested for normality and homoscedasticity using the Kolmogorov-Smirnov test ( $p=0.1$ ). Once a suitable transformation had been selected, all medians were scaled according to their z-scores to ensure that each analyte imparted a similar degree of influence to the clustering algorithm (Helsel and Hirsch, 1992; Guler *et al.*, 2002).

A hierarchical cluster analysis algorithm using the nearest neighbour linkage rule, with the square of the Euclidean distance as a measure of similarity, was used to identify residual samples. Residual samples were identified and removed from the dataset. The cluster analysis algorithm using Ward's linkage with the square of the Euclidean distance as a measure of similarity was then used on the data without the residuals. The hierarchical cluster analysis produces a membership list (site and cluster), a dendrogram (graphical method of visualising cluster memberships), and centroid values (averages) for each cluster. Centroid values are reduced back to 'real' values by using the opposite function used to transform the data and compared to the water dating, stable isotope, geology and hydrological data.

## Results

### Stable Isotopes

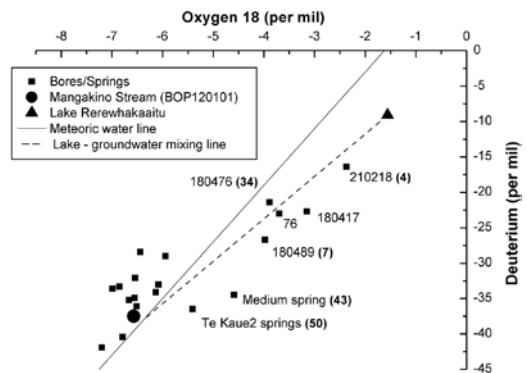
Oxygen-18 and deuterium results range from  $-1.56\text{‰}$  to  $-7.2\text{‰}$  and  $-9.1\text{‰}$  to  $-41.9\text{‰}$  respectively (Table 1, Table 2). Groundwater sourced from infiltrating rainfall is expected to fall on the meteoric water line (Fig. 2) appropriate for the district (given by the equation  $\delta^2\text{D} = 8 \times \delta^{18}\text{O} + 13$ , Stewart and Morgenstern, 2001).

The isotope data clearly indicate that water from Lake Rerewhakaaitu is different from most of the groundwater collected from around the lake (Fig. 2). The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  ratio is consistent with isotopic enrichment caused by evaporation from the lake surface. This gives the water a unique isotopic signature and allows the water to be used as a groundwater recharge 'tracer'. Stewart and Taylor (1981) demonstrate good vertical mixing of  $\delta^{18}\text{O}$  in Lake Rerewhakaaitu, making the lake water a homogeneous source of  $\delta^{18}\text{O}$  to the groundwater recharge. The isotopic concentration of the lake represents the first end member of a simple rainfall – lake water mixing model.

The isotopic composition of the water sample from Mangakino Stream (site BOP120101) plots close to the meteoric water line, suggesting the stream source is either rainwater or a shallow groundwater aquifer with an isotopic ratio similar to rainfall. The isotopic concentration at this site is considered to represent the second end member in a simple rainfall – lake water mixing model.

Sites Lake Rerewhakaaitu, BOP210218, BOP180476, BOP180417, 76, BOP180489, Medium Spring and Te Kauae2 Springs all show enriched isotopic concentrations relative to the meteoric water line. All these sites occur on the western side of Lake Rerewhakaaitu. The isotopic ratio of Site BOP210218 is the closest to Lake Rerewhakaaitu (Fig. 2). This site is probably the most strongly influenced by the lake water as a source of recharge. Site BOP210218 is a spring situated near the northwest corner of Lake Rerewhakaaitu.

All sites with enriched isotopic concentrations relative to the meteoric water line plot close to a mixing line (Fig. 2) between water from Mangakino Stream and water from Lake Rerewhakaaitu. This suggests a lake component of water in the groundwater at these sites. A simple mixing model using isotope mass balances (Cook and Herczeg, 1999) can be used to estimate the percentage



**Figure 2** – Oxygen-18 verses deuterium with the mean residence times (MRT) of samples in brackets.

of the lake water that contributes to the groundwater at each site (Table 3). Average contributions of lake water are estimated to range from 79% at site BOP210218 to 13% at site Te Kaue2 Springs.

All other sites have similar isotopic concentrations and plot close to the meteoric water line (Fig. 2). These sites probably have rainfall recharge as their main source of groundwater recharge, with little or no input from the lake.

### Water age dating

Eleven sites were sampled for tritium and/or CFCs. Mean residence times were calculated for each sample (Table 1). Residence times range from 1 year at site BOP120101 (Mangakino Stream) to 145 years at site BOP180486. The majority of the mean residence times are greater than 30 years.

Sites BOP210218 and BOP180489 have ambiguous mean residence times of 4/44 years and 7/40 years respectively. Ambiguous residence times can occur due to tritium concentrations falling within a specific range, coinciding with duplicate atmospheric tritium concentrations occurring either side of the 'tritium bomb peak' (Stewart and Morgenstern, 2001). CFC data cannot be used reliably to identify the 'correct' mean residence time, as both sites have strongly anaerobic waters. Anaerobic water can degrade CFC concentrations, making a residence time interpretation based on CFCs at these sites impossible. The youngest mean residence times at sites BOP210218 and BOP180489 have been used in this paper based on hydrological and chemical conditions (e.g., hierarchical cluster analyses) at these sites.

### Major anion and cation chemistry

Major anion and cation concentrations used in this work have been collated using data from three sampling rounds sampled and analysed by EBOP, and one sampling round

collected and analysed by GNS. Data was sampled between March 2003 and February 2006. Not all sites were sampled in each sampling round, and the suite of parameters analysed differed between sampling rounds.

In general, median water quality of the groundwater and streams in this study is good compared to the New Zealand Drinking Water Standards (NZDWS) (Ministry of Health, 2005) (Table 1). Median manganese (both total and dissolved) is the only parameter above the Drinking Water Standards maximum allowable value ( $0.4 \text{ g m}^{-3}$ ). This occurs at sites BOP180451, BOP180489 and BOP210218. All three sites occur to the northwest of Lake Rerewhakaaitu and also contain high median concentrations of both total and dissolved iron, and trace amounts of ammonia. This demonstrates that anaerobic conditions are present in the groundwater aquifer in this area.

Median dissolved iron concentrations range from below the detection limit ( $<0.02 \text{ g m}^{-3}$ ) to  $13.2 \text{ g m}^{-3}$ . In most of these cases, a high median dissolved iron concentration is associated with a high median dissolved manganese concentration.

Median  $\text{NH}_3\text{-N}$  concentrations range from below the detection limit ( $<0.01 \text{ g m}^{-3}$ ) to  $62.5 \text{ g m}^{-3}$ . Only nine of the 52 sites with  $\text{NH}_3\text{-N}$  data have median  $\text{NH}_3\text{-N}$  concentrations above the detection limit. Site 76 has the highest median  $\text{NH}_3\text{-N}$  concentration of  $62.5 \text{ g m}^{-3}$ . The median  $\text{NO}_3\text{-N}$  concentration at this site is  $0.052 \text{ g m}^{-3}$ . Low dissolved oxygen, low oxidation-reduction potential, high median ammonia, high median iron, high median manganese and low median nitrate are conditions indicating a reducing groundwater environment at this site (Table 1).

Median nitrate-nitrogen concentrations range from below detection ( $0.02 \text{ g m}^{-3}$ ) to  $10.17 \text{ g m}^{-3}$ . The six sites with median nitrate concentrations below the detection limit can be divided into three areas: 1) sites

**Table 1** – Chemical and isotopic results for waters from the Lake Rewhakaaitu catchment and environs

Notes EC – Electrical Conductivity (uS/cm @ 25°C)  
 D – Dissolved Fraction  
 T – Total Fraction  
 ORP – Oxidation reduction potential  
 DO – Dissolved Oxygen  
 $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  and Mean Residence times are from a single sample

Site	Points	Turbidity NTU	EC mV	ORP mV	Temp °C	DO g m <sup>-3</sup>	HCO <sub>3</sub> g m <sup>-3</sup>	pH	NH <sub>3</sub> -N g m <sup>-3</sup>	Br g m <sup>-3</sup>	Ca g m <sup>-3</sup>	Cl g m <sup>-3</sup>	DRP g m <sup>-3</sup>	TP g m <sup>-3</sup>	F g m <sup>-3</sup>
70	1	0.9	169	540	7.4	6.6	40	6.25	<0.01	<0.1	6.6	4.9	0.044		0.095
76	1	71	584	-2	9.2	1.1	333	7.58	62.5	<0.1	5.4	8.4	0.079		0.025
BOP120101	4	3	129	480	9.7	9.5	28	7.11	<0.01	<0.1	5.92	11.5	0.022	0.052	0.032
BOP180417	4	10.1	121	477	13.9	2.1	66	6.52	<0.01	<0.1	6.65	3.7	0.073	0.0535	0.16
BOP180445	3	5.5	140	538	7	8.8	24	5.95	<0.01	0.36	5.3	8.3			0.03
BOP180448	1	79	79	514	14.4	10	23.9	6.3	<0.01	2.43	4.5	0.039	0.046		0.18
BOP180449	4	1.7	96	514	7.8	33	33	6.28	<0.01	<0.1	3.4	6.3	0.054		0.11
BOP180451	2	90	90	514	15	2.1	42.8	6.8	0.13	4.11	9.1	0.007	0.022		0.16
BOP180454	2	145.5	145.5	514	14.15	8.05	23.6	6.075	<0.01	6.39	10.3	0.006	0.022		0.09
BOP180456	3	100	100	514	13.2	7.5	29.3	6.2	<0.01	3.49	6.5	0.081	0.076		0.14
BOP180457	2	66.5	66.5	514	14.85	6.8	28.25	6.65	<0.01	2.395	2.7	0.264	0.257		0.175
BOP180458	2	186	186	514	14	8.5	30.3	5.875	<0.01	9.27	8.9	0.026	0.0205		0.08
BOP180459	2	236	236	514	17.6	7.25	26.1	5.7	<0.01	10.045	7.9	0.0155	0.015		0.075
BOP180460	2	136.5	136.5	514	13.3	5.4	31.55	6.1	<0.01	10.75	13.6	0.011	0.0095		0.075
BOP180462	3	4.5	180	492	6.9	6.9	32	6.07	<0.01	<0.1	7.8	12.3	0.022		0.035
BOP180463	2	79	79	514	15	8.8	38	6.8	<0.01	3.25	2.9	0.197	0.194		0.13
BOP180464	2	123.5	123.5	514	13.35	9.9	28.35	6.2	<0.01	5.975	6.7	0.0245	0.026		0.085



Site	Fe <sub>p</sub> g m <sup>-3</sup>	Fe <sub>T</sub> g m <sup>-3</sup>	Mg g m <sup>-3</sup>	Mn <sub>D</sub> g m <sup>-3</sup>	Mn <sub>T</sub> g m <sup>-3</sup>	NO <sub>3</sub> -N g m <sup>-3</sup>	K g m <sup>-3</sup>	SiO <sub>2</sub> g m <sup>-3</sup>	Na g m <sup>-3</sup>	SO <sub>4</sub> g m <sup>-3</sup>	B g m <sup>-3</sup>	δ <sup>2</sup> H ‰	δ <sup>18</sup> O ‰	MRT Years
70	<0.02		3.5	<0.005		1.8	5.6	73	13.1	19.6		-28.4	-6.44	81
76	13.2		3.9	0.12		0.052	16.6	5.2	7.6	0.18		-23	-3.7	
BOP120101	0.11	0.185	2.28	0.0101	0.0132	2.78	7.13	63.4	10.1	7.6	0.0165	-37.5	-6.57	1
BOP180417	0.39	0.565	4.12	0.0545	0.0806	<0.03	5.4	71.75	9.4	0.92		-22.7	-3.15	
BOP180445	<0.02		2	0.006		3.4	6.9	73	11.8	13.2		-34.1	-6.13	
BOP180448	0.12	0.14	1.3	<0.005	0.0019	2.33	4.63	84.3	8.81	2.4	0.009			
BOP180449	<0.02		2	0.01		<0.03	4.9	73	9.7	6.5		-29	-5.94	
BOP180451	2.43	3.25	2	1.43	1.47	0.467	3.61	49.2	8.97	0.9	0.023			
BOP180454	<0.02	<0.02	2.35	0.01275	0.0019	6.225	8.34	73.8	12.45	9.4	0.0165			
BOP180456	<0.02	<0.02	1.79	<0.005	0.0005	3.02	4.77	74.4	10.3	5.6	0.032			
BOP180457	<0.02	<0.02	2.11	<0.005	0.000525	0.1975	2.73	84.7	6.125	3.9	0.0195			
BOP180458	<0.02	<0.02	3.885	<0.005	0.000425	7.17	7.69	70.9	13.65	16.55	0.027			
BOP180459	<0.02	<0.02	3.56	0.0032	0.0032	3.23	10.25	93	22.25	56.05	0.022			
BOP180460	<0.02	0.05	3.68	0.0117	0.01245	8.185	9.705	80.6	13	10.4	0.047			
BOP180462	0.02		4	<0.005		8	6.7	74	12.9	2.9		-35.2	-6.66	5
BOP180463	<0.02	<0.02	2.56	<0.005	0.0006	0.373	3.56	83	6.97	2.1	0.03			
BOP180464	<0.02	<0.02	1.98	<0.005	0.000675	6	6.505	80.6	11.1	1.55	0.006			

Site	Points	Turbidity NTU	EC	ORP mV	Temp °C	DO g m <sup>-3</sup>	HCO <sub>3</sub> g m <sup>-3</sup>	pH	NH <sub>3</sub> -N g m <sup>-3</sup>	Br g m <sup>-3</sup>	Ca g m <sup>-3</sup>	Cl g m <sup>-3</sup>	DRP g m <sup>-3</sup>	TP g m <sup>-3</sup>	F g m <sup>-3</sup>
BOP180465	2		280		13.9	10.9	46.2	5.775	<0.01		15.95	10.7	0.025	0.036	0.085
BOP180466	2		170		22.35	3.9	31.55	6.25	0.085		10.03	4.1	0.022	0.0475	0.11
BOP180467	2		167		14.55	6.5	41.05	6.525	<0.01		7.825	13.2	0.1015	0.097	0.16
BOP180469	3	0.9	105	506	13.8	6	28.2	6.14	<0.01	<0.1	2.48	6.5	0.058	0.059	0.14
BOP180470	3	2.1	128	522	10.65	3.1	25.35	6.06	<0.01	<0.1	3.6	9.1	0.067	0.074	0.1045
BOP180471	3	8.2	78.5	580	11.45	9.4	23.4	6.33	0.0075	<0.1	2.845	4.85	0.016	0.029	0.0845
BOP180473	2		63		13.5	8.9	29.3	6.65	<0.01		2.295	3	0.1025	0.106	0.14
BOP180474	2		79		12.3	6.8	30	6.4	<0.01		2.69	4.8	0.092	0.09	0.1
BOP180476	3	0	139	387	13.4	3.6	48	6.3	<0.01	<0.1	7.43	5.95	0.074	0.076	0.14
BOP180477	3	1.1	122	564	13.3	6.2	28	6.25	<0.01	<0.1	5	6	0.044	0.0465	0.12
BOP180478	2		84		16	6.9	38.1	6.8	<0.01		3.45	3.8	0.177	0.183	0.17
BOP180480	3	1.1	143	498	13.2	7.1	24.2	6.05	<0.01	<0.1	6.71	9.3	0.039	0.044	0.11
BOP180481	2		95		13.6	9.8	31.2	6.45	<0.01		3.77	6	0.058	0.064	0.16
BOP180483	2		154		14.25	8.65	22.8	6.075	0.0075		7.375	10.5	0.0085	0.0115	0.08
BOP180484	3	0.9	90	452	13.6	9	26	6.2	<0.01	<0.1	3.3	5.35	0.062	0.0625	0.12
BOP180486	3	0.7	87	457	13.6	3.4	39.1	6.5	<0.01	<0.1	3.1	4.2	0.118	0.113	0.21
BOP180488	2		89		12.8	10.1	25	6.2	<0.01		3.07	4.6	0.062	0.062	0.16

Site	Fe <sub>D</sub> g m <sup>-3</sup>	Fe <sub>T</sub> g m <sup>-3</sup>	Mg gm <sup>-3</sup>	Mn <sub>D</sub> g m <sup>-3</sup>	Mn <sub>T</sub> g m <sup>-3</sup>	NO <sub>3</sub> g m <sup>-3</sup>	K g m <sup>-3</sup>	SiO <sub>2</sub> g m <sup>-3</sup>	Na g m <sup>-3</sup>	SO <sub>4</sub> g m <sup>-3</sup>	B g m <sup>-3</sup>	δ <sup>2</sup> H ‰	δ <sup>18</sup> O ‰	MRT Years
BOP180465	<0.02	<0.02	6.28	<0.005	0.0014	10.17	9.845	60.4	20.1	35.6	0.028			
BOP180466	1.895	3.3	2.78	0.266	0.2655	0.1	5.945	108.85	11.65	41.85	0.021			
BOP180467	<0.02	<0.02	6.155	<0.005	0.00075	1.1	4.745	77.5	11.3	32.55	0.0295			
BOP180469	<0.02	<0.02	1.05	<0.005	0.0017	1.81	4.19	75.3	15	9.3	0.0235	-32.1	-6.54	
BOP180470	0.03	0.1	1.825	0.04705	0.0912	2.015	4.7	78	15.85	16.25	0.036v	-36.1	-6.51	
BOP180471	0.55	1.36	1.32	0.0153	0.0204	2.735	4.41	75.85	8.84	1.6	0.015	-41.9	-7.2	
BOP180473	<0.02	<0.02	1.02	<0.005	0.000375	0.5875	2.305	81.6	7.455	1.75	0.009			
BOP180474	<0.02	<0.02	1.46	<0.005	<0.005	1.5	3.98	82.7	8.15	1.2	0.009			
BOP180476	<0.02	0.035	3.57	0.101	0.1034	2.42	5.6	58.7	10.2	9.7	0.0135	-21.4	-3.89	34
BOP180477	<0.02	<0.02	2.5	<0.005	0.000525	3.9	5.7	74.6	9.2	4.5	0.0135	-33	-6.08	76
BOP180478	<0.02	<0.02	2.39	<0.005	0.0006	0.613	3.5		6.9	3.3	0.011			
BOP180480	<0.02	<0.02	2.68	<0.005	0.000875	4.8	6.92	79.55	11.3	12.2	0.022	-33.3	-6.85	
BOP180481	<0.02	<0.02	1.54	<0.005	<0.005	2.95	5.19	85.1	9.89	1.8	0.008			
BOP180483	<0.02	0.025	2.47	<0.005	0.0011	5.635	9.195	80.1	12.4	16.05	0.049			
BOP180484	<0.02	<0.02	1.47	<0.005	<0.005	2.6	4.3	81.8	10.2	2.2	0.018	-33.6	-6.99	
BOP180486	0.22	0.41	1.96	0.258	0.3095	<0.03	4.3	78.85	10.6	2.7	0.016	-40.4	-6.79	145
BOP180488	<0.02	<0.02	1.2	<0.005	<0.005	2.21	4.56	81.7	8.13	2.1	0.008			

Site	Points	Turbidity NTU	EC	ORP mV	Temp °C	DO g m <sup>-3</sup>	HCO <sub>3</sub> g m <sup>-3</sup>	pH	NH <sub>3</sub> -N g m <sup>-3</sup>	Br g m <sup>-3</sup>	Ca g m <sup>-3</sup>	Cl g m <sup>-3</sup>	DRP g m <sup>-3</sup>	TP g m <sup>-3</sup>	F g m <sup>-3</sup>
BOP180489	3	0	126	343	13.7	1.5	64.9	6.62	0.08	<0.1	3.6	5.3	0.096	0.095	0.18
BOP180490	2		95		13.8	8.4	27.3	6.1	<0.01		3.34	6.6	0.016	0.02	0.1
BOP180491	1		118		15.3	6.8	22.3	6.05	<0.01		6.05	7.8	0.01	0.008	0.09
BOP180493	2		98		14.7	7.7	20.7	5.9	0.08		3.53	9	0.009	0.051	0.08
BOP180494	2		82		16.8	6.3	30	6.2	0.2		2.87	7.7	0.069	0.118	0.11
BOP180495	2		110		14.3	7.95	20.15	6.35	<0.01		6.045	12.75	<0.004	0.004	0.0575
BOP180496	2		77		13.7	8.1	18.3	6.3	<0.01		2.22	5.2	0.035	0.034	0.12
BOP180502	1		76		15.3	2.8	20.1	6.1	0.09		2.16	6.8	0.021	0.21	0.2
BOP180512	2	2.3	105	485	7.3	9.1	22	6.14	<0.01	<0.1	3.6	5.1	0.101		0.066
BOP210218	3	5.3	106.5	378	10.3	3.45	52.1	6.68	0.12	<0.1	4.255	5.25	0.056	0.046	0.125
BOP210219	2		106		14.9	7	54.2	7.1	<0.01		5.78	4.6	0.037	0.042	0.12
BOP210249	1		101		15.1	6.2	28.9	6.5	<0.01		4.25	4.3	0.045	0.045	0.11
BOP210250	1		89		15.6	7.7	28.1	7.4	<0.01		3.72	5	0.033	0.041	0.12
BOP210251	1		90		18.6	10.3	16.5	7.5	<0.01		2.88	3.2	<0.004	0.045	0.16
Lake	1	0.3	57	490	17.3	9	23	7.49	<0.01	<0.1	2.2	5.2	<0.004		0.051
Medium spring	1	0	172	440	6.8	7.1	42	6.43	<0.01	<0.1	7.6	5.6	0.05		0.067
Te Kauae2 Springs	1	0.1	183	469	11.9	4.3	50	6.23	<0.01	<0.1	10.5	5.8	0.071		0.06

Site	Fe <sub>p</sub> g m <sup>-3</sup>	Fe <sub>T</sub> g m <sup>-3</sup>	Mg g m <sup>-3</sup>	Mn <sub>p</sub> g m <sup>-3</sup>	Mn <sub>T</sub> g m <sup>-3</sup>	NO <sub>3</sub> -N g m <sup>-3</sup>	K g m <sup>-3</sup>	SiO <sub>2</sub> g m <sup>-3</sup>	Na g m <sup>-3</sup>	SO <sub>4</sub> g m <sup>-3</sup>	B g m <sup>-3</sup>	δ <sup>2</sup> H ‰	δ <sup>18</sup> O ‰	MRT Years
BOP180489	5.7	6.505	1.48	<b>0.449</b>	<b>0.4675</b>	<0.03	1.99	70.8	16.7	2	0.0195	-26.7	-3.98	7 or 40
BOP180490	<0.02	<0.02	1.43	<0.005	0.0017	2.32	4.99		9.54	3.9	0.014			
BOP180491	<0.02	0.04	2.37	0.0107	0.0127	2.54	4.35	68.5	10.4	14.4	0.044			
BOP180493	<0.02	<b>0.41</b>	1.33	0.0047	0.0172	2.73	5.83		9.68	5.5	0.044			
BOP180494	0.06	0.08	1.03	0.007	0.0095	0.355	5.43		8.6	3.2	0.016			
BOP180495	<0.02	<0.02	2.04	<0.005	0.0009	4.44	6.615	64.3	8.955	6.95	0.0125			
BOP180496	<0.02	<0.02	0.85	<0.005	<0.005	2.24	3.7		8.21	5.1	0.017			
BOP180502	<b>4.45</b>	<b>12.7</b>	0.86	<b>0.168</b>	<b>0.174</b>	1.45	4.14		8.51	4.3	0.014			
BOP180512	<0.02		1.8	<0.005		2.7	4.5	67	8.6	4.7		-34.9	-6.55	59
BOP210218	<b>2.715</b>	<b>2.29</b>	2.49	<b>1.865</b>	<b>1.75</b>	<0.03	3.235	42	8.26	1.585	0.015	-16.4	-2.37	4 or 44
BOP210219	0.08	0.25	2.73	0.028	0.0549	0.247	5.17		9.02	3.2	0.011			
BOP210249	<0.02	0.08	1.68	<0.005	0.0168	1.68	4.57		9.33	10.7	0.011			
BOP210250	<b>0.25</b>	<b>0.38</b>	1.78	0.0372	0.0349	0.106	4.28		7.79	9.7	0.009			
BOP210251	0.05	0.09	1.6	0.0061	0.0088	2.36	4.39		8.68	13.2	0.016			
Lake	0.05		2.4	<0.005		<0.03	1.1	1	6.5	2.6		-9.1	-1.56	
Medium spring	<0.02		3.6	<0.005		2.9	5.5	61	11.1	14.9		-34.5	-4.59	43
Te Kauae2 Springs	<0.02		4.9	<0.005		2	5.3	70	14.5	25		-36.5	-5.409	50

**Table 2** – Summary of water sample sites  
 NGMP facies is as defined by Daughney and Reeves (2005)

Site	Type	Points	Cluster	Facies	Aquifer
70	Bore	1	1	1A-2	Rangitiki Ignimbrite
76	Bore	1	outlier	2B	Rangitiki Ignimbrite
BOP120101	Stream	4	1	1A-2	
BOP180417	Bore	4	2	2A	Rangitiki Ignimbrite
BOP180445	Bore	3	1	1A-2	Rangitiki Ignimbrite
BOP180448	Bore	1	2	1B-2	Rangitiki Ignimbrite
BOP180449	Bore	4	2	1B-2	Rangitiki Ignimbrite
BOP180451	Bore	2	3	2A	Rangitiki Ignimbrite
BOP180454	Bore	2	1	1A-2	Rangitiki Ignimbrite
BOP180456	Bore	3	2	1A-2	Rangitiki Ignimbrite
BOP180457	Bore	2	2	1B-2	Rangitiki Ignimbrite /Onuku ?
BOP180458	Bore	2	1	1A-2	Onuku Pyroclastic
BOP180459	Bore	2	1	1A-2	Onuku Pyroclastic ?
BOP180460	Bore	2	1	1A-2	Alluvial ?
BOP180462	Bore	3	1	1A-2	Perched
BOP180463	Bore	2	2	1B-2	Rangitiki Ignimbrite/Onuku ?
BOP180464	Bore	2	2	1A-2	Rangitiki Ignimbrite
BOP180465	Bore	2	1	1A-2	Onuku Pyroclastic ?
BOP180466	Bore	2	outlier	2A	Rangitiki Ignimbrite /Onuku ?
BOP180467	Bore	2	1	1A-2	Rangitiki Ignimbrite
BOP180469	Bore	3	2	1B-2	Rangitiki Ignimbrite
BOP180470	Bore	3	2	1A-2	Rangitiki Ignimbrite
BOP180471	Bore	3	2	1B-2	Onuku Pyroclastic
BOP180473	Bore	2	2	1B-2	Rangitiki Ignimbrite ?
BOP180474	Bore	2	2	1B-2	Rangitiki Ignimbrite ?
BOP180476	Bore	3	1	1A-2	Rangitiki Ignimbrite
BOP180477	Bore	3	2	1A-2	Onuku Pyroclastic
BOP180478	Bore	2	N/A	1B-2	Rangitiki Ignimbrite ?
BOP180480	Bore	3	1	1A-2	Rangitiki Ignimbrite
BOP180481	Bore	2	2	1B-2	Rangitiki Ignimbrite ?
BOP180483	Bore	2	1	1A-2	Rangitiki Ignimbrite
BOP180484	Bore	3	2	1B-2	Rangitiki Ignimbrite
BOP180486	Bore	3	2	2A	Rangitiki Ignimbrite
BOP180488	Bore	2	2	1B-2	Onuku Pyroclastic ?
BOP180489	Bore	3	3	2A	Kaharoa/Waiohau/Rerewhakaaitu
BOP180490	Bore	2	N/A	1B-2	Rangitiki Ignimbrite
BOP180491	Spring	1	1	1A-2	Onuku Pyroclastic ?
BOP180493	Spring	2	N/A	1B-2	Kaingaroa Ignimbrite ?
BOP180494	Spring	2	N/A	1B-2	Kaingaroa Ignimbrite
BOP180495	Spring	2	1	1A-2	Kaingaroa Ignimbrite ?
BOP180496	Spring	2	N/A	1B-2	Kaingaroa Ignimbrite ?
BOP180502	Bore	1	N/A	1B-2	Rangitiki Ignimbrite
BOP180512	Bore	2	2	1B-2	Rangitiki Ignimbrite
BOP210218	Spring	3	3	2A	Rangitiki Ignimbrite
BOP210219	Spring	2	N/A	1B-2	Rangitiki Ignimbrite/Onuku ?
BOP210249	Spring	1	N/A	1B-2	Rangitiki Ignimbrite/Onuku ?
BOP210250	Spring	1	N/A	1B-2	Rangitiki Ignimbrite/Onuku ?
BOP210251	Spring	1	N/A	1B-2	Rangitiki Ignimbrite
Lake	Lake	1	2	1B-1	
Medium spring	Spring	1	1	1A-2	Rangitiki Ignimbrite
Te Kaue2 Springs	Spring	1	1	1A-2	Rangitiki Ignimbrite

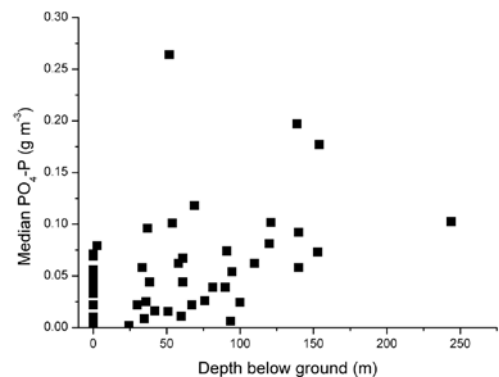
**Table 3** – Estimated percentage of lake water contribution to the groundwater.

Site	$\delta^2\text{H}$ (‰)	$\delta^{18}\text{O}$ (‰)	% Lake water
BOP210218	-16.4	-2.37	79
BOP180476	-21.4	-3.89	55
BOP180417	-22.7	-3.15	60
76	-23	-3.7	54
BOP180489	-26.7	-3.98	45
Medium Spring	-34.5	-4.59	25
Te Kauae2 Springs	-36.5	-5.409	13

Lake, BOP210218 and BOP180489 in the northwest, 2) site BOP180417 located close to the western shore of Lake Rerewhakaaitu, and 3) sites BOP180486 and BOP180449 located close together to the southeast of, and close to, Lake Rerewhakaaitu. Forty-two sites have median nitrate-nitrogen concentrations greater than  $0.14 \text{ g m}^{-3}$ , suggesting groundwater in the area has been affected by anthropogenic sources. This assumes background (pre-development) nitrate-nitrogen concentrations calculated for the Rotorua aquifers (Morgenstern *et al.*, 2004) are the same for the Rerewhakaaitu aquifers.

Median dissolved reactive phosphorus (DRP) concentrations range from below the detection limit ( $<0.002 \text{ g m}^{-3}$ ) to  $0.264 \text{ g m}^{-3}$ . High ( $>0.1 \text{ g m}^{-3}$ ) median dissolved reactive phosphorus levels were measured at five sites (BOP180457, BOP180478, BOP180463, BOP180473 and BOP180467) south of Lake Rerewhakaaitu, and two sites (BOP180512 and BOP180486) to the east of Lake Rerewhakaaitu. Median dissolved reactive phosphorus concentrations generally increase with depth (Fig. 3). Fish (1978) suggested that dissolved phosphate entering Lake Rerewhakaaitu is rapidly adsorbed by colloidal allophanic clays in the Rotomahana mud deposits, reducing dissolved phosphorus concentrations in the lake and limiting algae growth.

All sites were classified into the six hydrochemical facies (Table 2) developed by Daughney and Reeves (2005) to observe how data collected in this study compared to data collected in the National Groundwater Monitoring Programme (NGMP). Sites in this study fall into five of the six hydrochemical facies defined by Daughney and Reeves (2005). Namely, seventeen sites fall into category 1A-2, one site (Lake) into category 1B-1, twenty-two sites into category 1B-2, six sites into category 2A and one site (site 76) into category 2B. Most sites fall into the threshold 1 (clusters prefixed by a '1') category. This category represents 'Surface-dominated, oxidised, unconfined aquifers with a low to moderate TDS (total dissolved

**Figure 3** – Median dissolved reactive phosphorus (DRP) versus depth.

solids)'. From within this category, seventeen of the sites (category 1A-2) have been classified as most probably having human impact on the aquifer. The 1B-1 classification (surface waters from a carbonate or clastic aquifer) for the Lake water sample is marginal, based on the five censored parameters in the water analyses. The NGMP hydrochemical facies classifications assigned to the Lake Rerewhakaaitu data are mostly consistent with what would be expected, e.g., thirty-nine of the forty-seven sites have been identified as coming from a volcanic or volcanoclastic aquifer (categories 1A-2 and 1B-2).

### Hierarchical cluster analysis

Median concentrations of 14 analytes (SiO<sub>2</sub>, K, Mg, Mn, Na, NH<sub>3</sub>-N, NO<sub>3</sub>-N, SO<sub>4</sub>, Ca, Cl, DRP, F, Fe and HCO<sub>3</sub>) were calculated for 41 sites. Only sites where the full list of analytes was available were used for the analysis (Table 1, Table 2). Twelve sites were not used because the SiO<sub>2</sub> analyses were missing. Other analytes such as boron and bromide were not used due to the limited number of sites that contained this data.

All but six analytes were normalised using a log-normal distribution. F and Na required no transformation as the data was already normally distributed. HCO<sub>3</sub>, DRP, NO<sub>3</sub>-N and SiO<sub>2</sub> were power transformed by the exponents -2, 0.5, 0.5 and 3 respectively. Fe, Mn and NH<sub>3</sub>-N have poor log-normal distributions so other transformations were investigated, but could not improve the results of the Kolmogorov-Smirnov test for these three analytes. The inability to obtain a normal distribution using some transformation for these

analytes is probably due to large number of samples that contain censored data for these analytes.

Sites 76 and BOP180466 were identified as outliers using the nearest neighbour linkage rule in the hierarchical cluster analysis algorithm. The water chemistry of Site 76 is clearly different from all the other sites, having a HCO<sub>3</sub> concentration an order of magnitude higher than any other site, and very high NH<sub>3</sub>-N, Fe and K concentrations compared to all the other sites. Site BOP180466 abstracts water from a reducing environment, based on the median dissolved oxygen, median Fe (total and dissolved), median Mn (total and dissolved) and median NH<sub>3</sub>-N concentrations. This site has significantly higher median SO<sub>4</sub>, SiO<sub>2</sub> and Ca concentrations compared to the other sites in the study extracting water from reducing environments. This may be caused by effects of local land use, and therefore makes this site an outlier. Both of these sites were taken out for the remaining hierarchical cluster analysis clustering process.

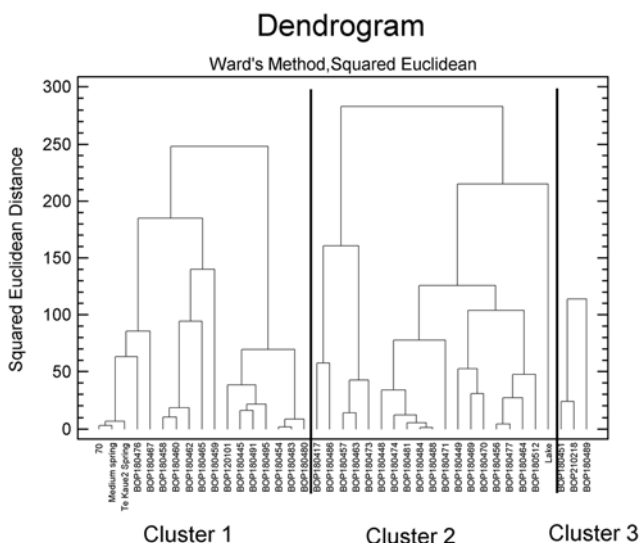


Figure 4 – Dendrogram from the hierarchical cluster analysis clustering algorithm showing the 3 clusters.



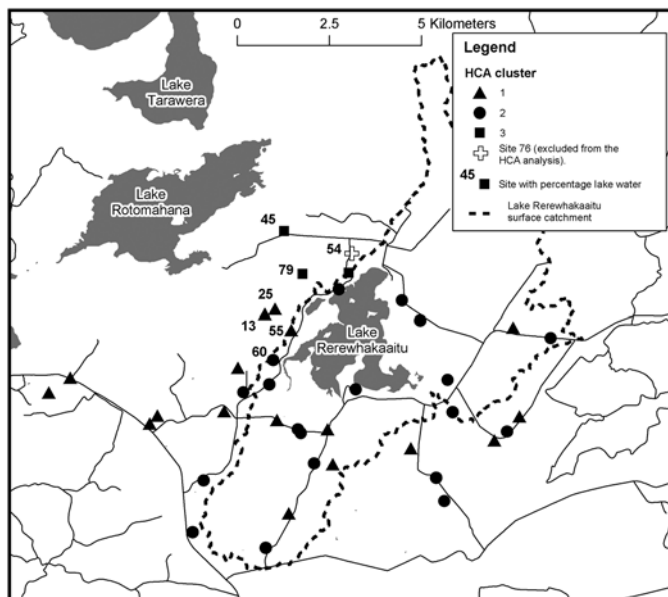
Three clusters were determined by the authors to be the optimum number of meaningful clusters that could be interpreted from the hierarchical cluster analyses for the 39 sites (Fig. 4). A large geographic spread of sites classified as cluster 1 or 2, both inside and outside of the surface water catchment, is observed (Fig. 5). This suggests that the surface water catchment has little to do with the groundwater catchments and that groundwater is moving from/to the Lake Rerewhakaaitu surface water catchment, and similar chemical processes are occurring in groundwater aquifers inside and outside of the Lake Rerewhakaaitu catchment. No link between bore elevation or bore depth to the clusters was observed.

Cluster 1 includes four springs, one stream and twelve bores, and geographically covers the whole study area. All sites in this cluster, except sites BOP180483 and BOP180462, have median  $\text{NH}_3\text{-N}$  and Fe concentrations below the detection limit ( $0.01 \text{ g m}^{-3}$  for  $\text{NH}_3\text{-N}$  and  $0.02 \text{ g m}^{-3}$  for

Fe). Sites BOP180483 and BOP180462 have negligible concentrations of  $\text{NH}_3\text{-N}$  and Fe, with either a median  $\text{NH}_3\text{-N}$  or median Fe concentration equal to the detection limit. Water from this cluster is oxidized. Cluster 1 has the highest centroid median of Cl, Mg,  $\text{NO}_3\text{-N}$  and  $\text{SO}_4$  concentrations (Table 4) compared to the centroid medians from the other clusters. This suggests that these waters may be affected by land-use activities. Nitrate is the dominant nutrient leaching into the water around these sites given that this cluster has the highest median concentration of  $\text{NO}_3\text{-N}$ , but the lowest median DRP concentration compared to the other clusters.

Cluster 2 includes 18 bores and the Lake Rerewhakaaitu site. Sites with this classification (excluding the lake site) occur to the east and the south of Lake Rerewhakaaitu. This cluster has the highest centroid median DRP and  $\text{SiO}_2$  concentrations and lowest centroid medians of Ca, Cl,  $\text{HCO}_3$ , Mg and Na compared to the centroid medians from the other clusters (Table 4). All sites except for BOP180471 have no  $\text{NH}_3\text{-N}$  (site

BOP180471 has a median  $\text{NH}_3\text{-N}$  concentration equal to the detection limit). Five sites in this cluster (BOP180448, BOP180470, BOP180417, BOP180471 and BOP180486) contain Fe and Mn, with the Lake site containing Fe. All these six sites are close (within 1.5 km) to the Lake. Sites BOP180448, BOP180474, BOP180481, BOP180484, BOP180488 and BOP180471 are more like each other than like other sites (Figure 4), given that they plot together in one sub-cluster of cluster 2. These sites are located to the south of Lake Rerewhakaaitu. No other obvious geographic



**Figure 5** – Map showing the geographical distribution of sites, with their assigned cluster and percentage lake water component.

**Table 4** – Centroid median concentrations of hierarchical cluster analysis clusters.

Cluster	Ca	Cl	DRP	F	Fe	HCO <sub>3</sub>	K	Mg	Mn	Na	NH <sub>3</sub> -N	NO <sub>3</sub> -N	SiO <sub>2</sub>	SO <sub>4</sub>
1	7.77	8.94	0.025	0.080	<0.02	28.8	6.86	3.28	0.0047	12.91	0.005	4.16	72.9	14.3
2	3.29	4.93	0.069	0.128	0.02	28.0	4.06	1.76	0.0052	9.52	0.005	1.35	77.4	2.9
3	3.98	6.33	0.044	0.155	3.35	51.0	2.85	1.95	1.0619	11.31	0.108	0.10	56.7	1.4

All concentrations are in g m<sup>-3</sup>

distributions for sites in sub-clusters of cluster 2 are observed.

Cluster 3 includes two bores and one spring, all located to the northwest part of the study area. These three sites are more like each other than the other sites sampled. Cluster 3 has the highest median centroid concentrations of F, Fe, HCO<sub>3</sub>, Mn and NH<sub>3</sub>-N and the lowest centroid median concentrations of NO<sub>3</sub>-N and SiO<sub>2</sub> than the other clusters (Table 4). This cluster represents anaerobic waters from a reducing environment.

Cluster 2 includes the lake site. Interestingly, the lake site is chemically more like groundwater that occurs to the southwest and to the northeast than to groundwater to the northwest of Lake Rerewhakaaitu. Sites in cluster 3 plot closer to the lake site than sites Te Kauae2 Springs, Medium Springs and site 70 (all from cluster 1) (Fig. 4). Different sources of water for the groundwater (including springs) in the northwest part of the study area may explain this. Also, sites BOP180454, BOP180483 and BOP180480 are grouped (Cluster 1) together and represent the cluster 1 sites to the southeast of Lake Rerewhakaaitu.

## Discussion

Oxygen 18 and deuterium data show that Lake Rerewhakaaitu contributes water to the springs and groundwater to the north and west of Lake Rerewhakaaitu. The contribution of lake water to the groundwater at sites on the northwestern side of the lake increases to the northwest. Sites close to the lake typically have larger proportions of lake water than

sites further away. The mean residence time of the groundwater gets older as the proportion of the lake water gets smaller at sites (except Site BOP180476) on the west and north of the lake.

Bores BOP180417 (153 m deep) and BOP180476 (91 m deep) have large proportions of lake water (60% and 55% respectively) (Table 2), considering their depths. Bore BOP180476 is cased to 39 m, therefore has a 52 m water inlet into the bore. Further work is required to determine the depth range at which recharge is occurring from the lake. No casing data exists for bore BOP180417. Both bores are regularly used to supply water to dairy farms. The increased groundwater recharge required to account for drawdown and recovery may affect the naturally occurring ratio of lake water to the native aquifer water.

A significant reduction in the proportion of lake water can be seen between sites BOP180476, Medium Springs and Te Kauae2 Spring (Table 3). All these sites are in the Rangitaiki Ignimbrite aquifer. This suggests that:

- 1) Lake water is been diluted by native groundwater or rainwater between sites BOP180476 and the springs.
- 2) The springs represent typical mixing proportions in the Rangitaiki Ignimbrite aquifer in this area, whereas site BOP180476 has increased proportions of lake water, due to pumping causing water from the lake to preferentially recharge the aquifer.

3) Mixing of lake water in the aquifer is variable with depth. This is difficult to determine given the large water intake at the bore.

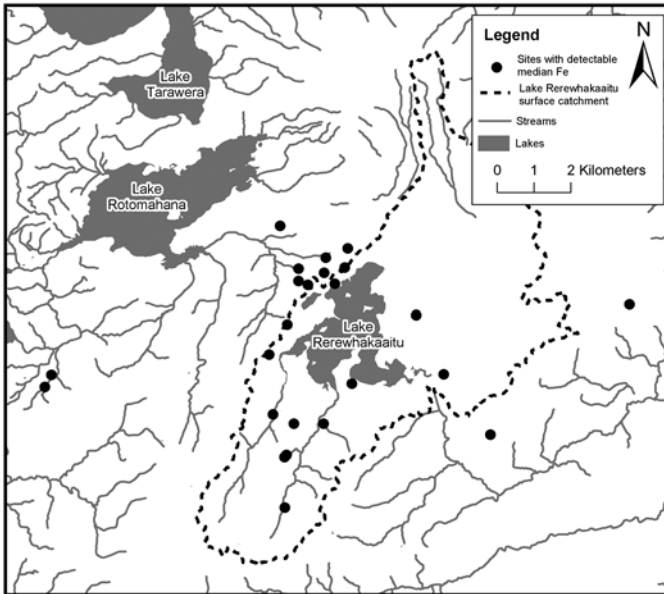
The large number of springs and seeps that are observed in the area around site BOP210218 to site 76 (northwest side of the lake) probably contain high proportions of lake water. The high proportion of lake water at these sites (79% and 54% at sites BOP210218 and site 76 respectively) suggests significant lake leakage in this area. Also, the three sites included in the hierarchical cluster analyses in this area (BOP180451, BOP210218 and BOP180489) form their own cluster (Cluster 3). This cluster is partially characterized by high concentrations of Fe, Mn and  $\text{NH}_3\text{-N}$ . The high Fe, Mn and  $\text{NH}_3\text{-N}$  concentrations are also measured at site 76, not included in the hierarchical cluster analyses. Water flow from the lake to the springs is probably rapid, given that the mean residence time of water from site BOP210218 is young (mean residence time of 4 or 44 years). The series of blast vents along the western edge of Lake Rerewhakaaitu (Nairn, 2002) may have increased permeability in the volcanic material, enabling lake water to leak in this area. This also suggests that water leaking from Lake Rerewhakaaitu is a significant contributor to the groundwater recharge of the Kaharoa/Waiohau/Rerewhakaaitu aquifer. The groundwater of this aquifer flows to the west into Lake Rotomahana (White *et al.*, 2003).

Hierarchical cluster analyses of the water quality data has not produced clusters that clearly identify groundwater that has been recharged from the lake. This is because there is not a large variation in water chemistry in the study area, making meaningful clustering difficult. Overall, there is little difference between the median centroid concentrations for clusters 1 and 2, which contain all but three sites used in this analyses. However,

some clustering of sites with suspected lake water contributions does occur, namely, the cluster 1 and cluster 3 sites mentioned above. Significant differences in aquifer conditions between these clusters are evident. The cluster 3 sites (BOP210218 and BOP180489) are in strongly reducing environments and have very young mean residence times (4 and 7 years respectively), whereas the cluster 1 sites (Medium Spring, Te Kauae Spring and BOP180476) are in an oxidizing environment and have older mean residence times (43, 50 and 34 years respectively). The older mean residence times at these sites suggest either lake water is mixing with older groundwater, or, that the groundwater flow is slower from the lake to these sample points. These possibilities enable the groundwater to be altered via contaminants in the older groundwater or from increased water-rock interaction.

Water in the Rangitaiki Ignimbrite aquifer on the eastern side of the lake is interpreted to be recharged by rainfall and/or other rainfall-recharged groundwater aquifers, based on the available data. Oxygen-18 and deuterium isotope data for sites plot in a group close to the meteoric water line, suggesting no lake water signature. No distinctive pattern is observed in the hierarchical cluster analyses of major anions and cations. The oldest mean residence time (145 years) is measured at site BOP180486, approximately 700 m east from the eastern edge of Lake Rerewhakaaitu. The site is a bore that draws water from approximately 26–69 m below ground. Water having a long mean residence time would be expected with slow-moving groundwater on the top of a groundwater divide, as mapped by White *et al.* (2003).

Elevated iron concentrations in the groundwater in the Lake Rerewhakaaitu area may be due to the leaching of iron from material erupted from the 1886 Mt Tarawera eruption. Nairn (2002) shows that basaltic material erupted from this event has the



**Figure 6** – Location of sites where the median iron (dissolved or total) concentration is above the detection limit.

highest concentrations of hematite ( $\text{Fe}_2\text{O}_3$ ) of any volcanic material tested in this area, approximately 5–50 times higher in hematite than the representative ignimbrites and pyroclastic formations in the area. Iron could be leaching out of this material (and eroded sediment) as water passes through this layer of sediment. It would be expected that this sediment would be abundant near the vents (e.g., Mt Tarawera, along the west side of Lake Rerewhakaaitu) and in low-lying areas where sediment has been moved due to erosion (e.g., Lake Rerewhakaaitu, stream valleys). Sites with detectable median iron (total or dissolved) concentrations tend to follow this trend (Fig. 6). More work is required to confirm that this material is the main source of iron in these groundwater aquifers.

## Summary

Oxygen-18, deuterium, tritium, chloro-fluorocarbon and major water chemistry data have been successfully used to identify areas of lake leakage from Lake Rerewhakaaitu. The data suggest that rainwater infiltration

is the dominant form of aquifer recharge in the Lake Rerewhakaaitu catchment; however, aquifers to the west and north of Lake Rerewhakaaitu also have a lake water contribution. This may have environmental catchment management implications for both the Lake Rerewhakaaitu and Lake Rotomahana catchments.

An area of anaerobic groundwater is identified in the northwest part of the study area, containing elevated levels of iron, manganese and ammonium. Recent volcanic deposits may be the source of iron in the groundwater. Nutrient levels in most aquifers

are above the expected background levels, suggesting some effect of land use on the water quality in the study area.

Defining meaningful hierarchical cluster analysis clusters based on the major anion/cation water chemistry was difficult due to the similarity of water chemistry between the sites. Similarities in major anion and cation water chemistry are probably due to groundwater not having time for significant water-rock interactions (based on the low mean residence times) in aquifers of similar material. The three clusters defined in this study do not show clear ‘clustering’ between sites that contain lake water and those that don’t. However, the hierarchical cluster analyses can be used to infer sites that may have lake water components in the groundwater, and therefore provide a method to identify sites that may require further study.

## Acknowledgements

The authors would like to thank the bore owners who allowed us to sample their

bores/springs. This project was funded by EBOP and the Foundation of Research and Technology, non-specific output funding contract.

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