Groundwater Age and Chemistry, and Future Nutrient Loads for Selected Rotorua Lakes Catchments

U Morgenstern, R Reeves, C Daughney, S Cameron and D Gordon

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U Morgenstern[1]
R Reeves[1]
C Daughney[1]
S Cameron[1]
D Gordon[2]

[1] Institute of Geological & Nuclear Sciences
[2] Environment Bay of Plenty, Whakatane

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U Morgenstern, Institute of Geological & Nuclear Sciences Limited, Wellington
R Reeves, Institute of Geological & Nuclear Sciences Limited, Taupo
C Daughney, Institute of Geological & Nuclear Sciences Limited, Wellington
S Cameron, Institute of Geological & Nuclear Sciences Limited, Taupo
D Gordon, Environment Bay of Plenty, Whakatane

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ABSTRACT

Hydrochemical analysis and age dating of groundwater and groundwater-fed streams were carried out in the Lake Rotorua and Okareka catchments to assess the past and current states, and future trends in groundwater chemistry. The study was undertaken because of declining lake water quality due to observed increases in nutrient loads entering these lakes (Rutherford 2003). This work was instigated by Environment Bay of Plenty and jointly funded by Environment Bay of Plenty and GNS.

The hydrogeology of the Rotorua Lakes area can be described as a permeable pumiceous surface tephra layer that allows easy penetration of rainwater recharge to deeper rhyolite and ignimbrite aquifers. These aquifers are essentially unconfined and yield high volumes of groundwater that discharges to spring fed streams or directly to the lake.

The hydrochemistry of groundwaters is characterised by much lower concentrations of Ca, Mg and SO_4, and much higher concentrations of PO_4-P and SiO_2 than other groundwaters in New Zealand. This chemical signature reflects the volcanic origin of the aquifer lithology.

Because the aquifers in the Rotorua area have large water storage capacity there is a long residence time for nutrient-laden groundwater. It takes decades for the water after being recharged to reach the spring fed streams and the lakes. The large groundwater bodies have therefore ‘silently’ been contaminated over decades, with the old pristine groundwater being progressively replaced by younger nutrient-laden water that will discharge to the spring-fed streams and finally to the lakes.

This study involved age dating of springs, wells, and groundwater-fed streams to assess how long it takes for nutrient-enriched groundwater to travel from pastoral land to springs and streams, and to the lakes. Most of the springs and wells in the Lake Rotorua and Okareka catchments contain relatively old groundwaters, with mean residence times between 40 and >170 years (only two wells have younger water of 26 and 31 years mean residence time). This corresponds to young water fractions (water recharged within the last 55 years since catchment development) of less then 80%. Significant fractions of these groundwaters were therefore recharged before land-use intensification, and these water discharges do not yet reflect the full effect of current landuse practices on the groundwater quality. Further deterioration of water quality must therefore be expected.

Age dating of the main groundwater-fed streams in the Lake Rotorua catchment revealed mostly mean residence times between 35 and 130 years. The streams with the oldest water are Waingaehe (127 years), Hamurana (110 years), Awahou (61 years), and Utuhina Streams (48 years). Only Ngongotaha Stream has younger water of 16 years mean residence time.

Total Phosphorus increases with groundwater age, concentration in young groundwater is <0.04 mg/L and about 0.13 mg/L in old groundwater. Absence of P in the young anthropogenically influenced waters demonstrates that P from land-use practices has not yet leached into the older groundwater but stayed absorbed in the soil. The occurrence of P in the investigated groundwaters is natural due to leaching from the volcanogenic aquifer material. For the naturally leached P in the groundwater, with equilibrium well established, no change in P loading to the lakes is expected. However, if in future P from landuse breaks through the soil as dissolved P, this would increase the P loading to the lakes. While the current data-set does not yet show elevated P in younger groundwater, such P breakthrough would not be visible if it had happened over the last 20 years because the data set includes only waters of mean residence time >20 years.

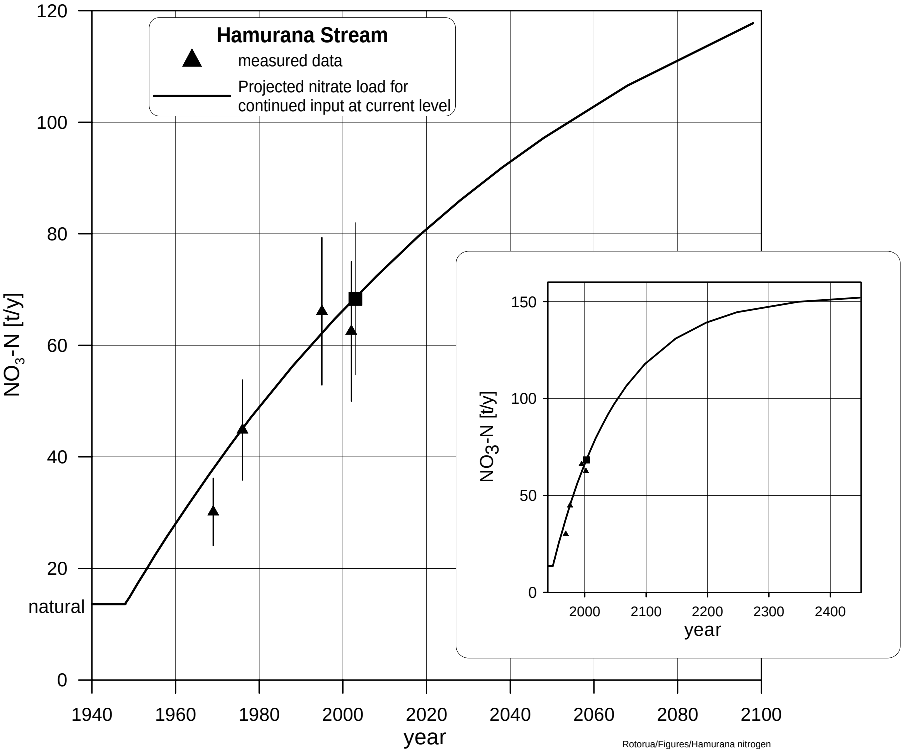
Trends for nitrate (NO_3), potassium (K) and sulphate (SO_4) indicate that these are increased in the young groundwaters as result of land-use intensification.

The natural background level of groundwater NO_3-N is determined from old groundwater (pre-landuse intensification) to 0.14 mg/L, and the current level is determined from young groundwater (post-landuse intensification) to 1.6 mg/L. Therefore, 9% of the current level can be attributed to the natural background, and 91% to land-use impacts. This is an increase in NO_3 by a factor 11.

Potassium concentrations indicate a natural background level of 0.6 mg/L and a current level of 3.8 mg/L. About 16% of the current K level is therefore natural background, and 84% is land-use impact, an increase by a factor 6. SO_4 shows a trend of elevated values of 3 mg/L in young waters compared to older water of 1.5 mg/L.

Nitrogen loading was calculated from a mass budget for the major streams to Lake Rotorua. Only NO_3-N, the main N component, was considered. Most of the nutrient flux via surface streams (ca. 90%) is contributed by the western catchment - Hamurana, Awahou, Puarenga, Waiteti, Ngongotaha and Utuhina Streams. The total load of NO_3-N is currently 376 t/year, and this is expected to increase to 577 t/year at steady state if the nitrate NO_3-N input in the catchment continues at the current level.

As an example, for Hamurana Stream 45% of the future steady-state NO_3 loading has been reached to-date, 90% will be reached in about 200 years.



Due to the groundwater-delayed impact, NO_3 would also decrease only slowly if NO_3 input were discontinued. Near natural background level (down to 10% of steady-state landuse NO_3) would be reached in about 250 years.

The significant increase in future nitrogen loading for the Lake Rotorua catchment is expected because the land-use impacted contaminated groundwater moves slowly through the large groundwater system and increasingly discharges to the lake via the spring fed streams or directly to the lake bed. Current medium nitrate concentrations found in the springs and streams still reflect the large dilution occurring from the old pristine groundwater. However, some of the major springs and streams are discharging already water with NO_3-N concentrations of 0.7-1.4 mg/L. Most of their NO_3-N concentrations are expected to increase to 1.5-2.5 mg/L if the current landuse patterns continue.

Keywords:

Groundwater contamination, Lake Rotorua, Nitrate loading, Groundwater dating, Mean residence time, Young water fraction, Tritium, CFCs, SF6, Hydrochemistry trends.

1.0 INTRODUCTION

Declining water quality in a number of the Rotorua lakes due to the delayed impact of land-use intensification has prompted this investigation of the chemistry and groundwater ages in the Lakes Rotorua and Okareka areas. Volcanic aquifers in this area are similar to those around Lake Taupo, in that large groundwater storage capacity has the potential to delay the impacts of land-use intensification that occurred 40 years ago (Vant & Huser 2000, Hadfield et al., 2001). Water from several springs in the Rotorua area has been estimated to have mean residence times of 50-100 years (Taylor & Stewart, 1987; Pang et al., 1996).

The lag time between land-use intensification (e.g. nitrate contamination from agriculture) and effects on the water quality of spring and groundwater reaching the lakes is therefore likely to be several decades. Consequently, the current surface water quality probably does not yet reflect the full extent of the current landuse (Fig. 1). Significant groundwater contamination from land-use can remain undetected for decades because of the time delays. Over time the pristine old water in the aquifer is progressively replaced with contaminated water, which then discharges to the lake. This means that further decline in lake water quality must be expected in the future, and remedial landuse action may take decades to take effect because of the time delays.

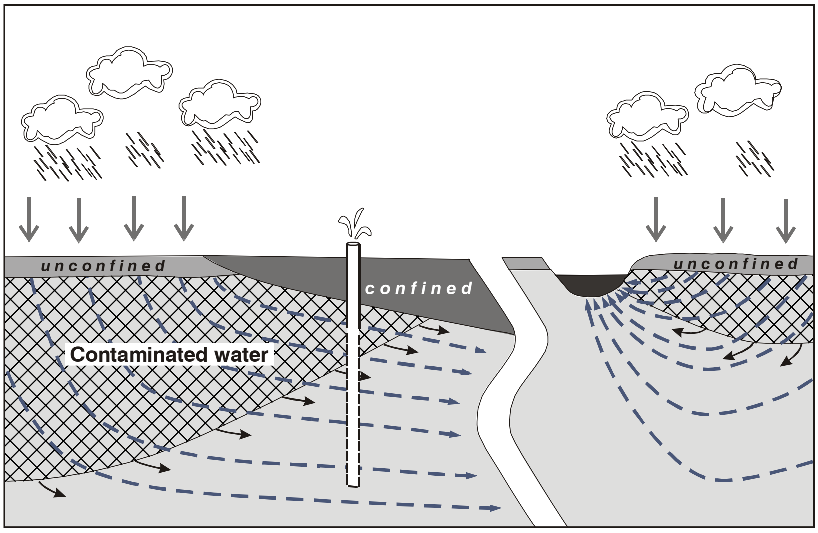


Figure 1. The tip of the iceberg. A water sample from a well or the stream or lake contains fractions of both young and old groundwater because long and short travel flowlines converge at the well or spring. For water mixtures with mean residence time >50 years, only a small fraction is young enough to show the contamination (hatched). The larger fraction is still uncontaminated old groundwater. But in time, the front of contaminated water moves forward (see arrows), and a higher fraction of contaminated water will discharge into the well/stream/lake. A large and so far unrecognised contamination is still to come.

This work was instigated by Environment Bay of Plenty and jointly funded by Environment Bay of Plenty and GNS. The objective of this study was to determine how long it takes for nutrient-enriched groundwater to travel from the catchment to springs and streams, and finally to Lake Rotorua, with the focus on:

1. Assessment of travel time of groundwater from springs in western Lake Rotorua catchment,
2. Assessment of the age of the water in the main streams that flow directly into Lake Rotorua, and
3. Assessment of a few groundwater ages in the Lake Okareka.

This involved measurement of chemical and age data for a representative number of groundwater wells, springs, and streams. The age distribution together with the chemical composition of the groundwater was then used to calculate the expected future nutrient loading to the lake assuming steady state conditions.

Hydrochemical data in conjunction with age dating are used to assess the past, present and future states of water quality. To identify the impact that land-use intensification has had on the water quality, the natural or un-impacted water chemistry was assessed from old groundwater that was recharged prior to land-use intensification in the lake catchments. The current water chemistry was assessed from young groundwater that was recharged after land-use intensification. Knowledge of effect and timeframes of the past and current land-use practices on the hydrology of the catchment will provide valuable information for proposed decisions on the management of landuse in the lakes catchments.

2.0 HYDROGEOLOGY IN THE ROTORUA LAKES AREA

Interpretation of the water dating results requires an understanding of the physical hydrogeology. In particular, knowledge of the geological units, the groundwater recharge mechanisms (such as from rainfall and/or river recharge), and the aquifer conditions (e.g. confined/unconfined) is helpful to constrain the groundwater flow models.

The geology of the Rotorua Lakes area is dominated by volcanic and fluvial deposits and is complex in nature because of the array of volcanic processes and volcanic material that has been erupted from a number of volcanic centres of the Taupo of Volcanic Zone that are located within a short distance from the Rotorua Lakes area (Fig. 2).

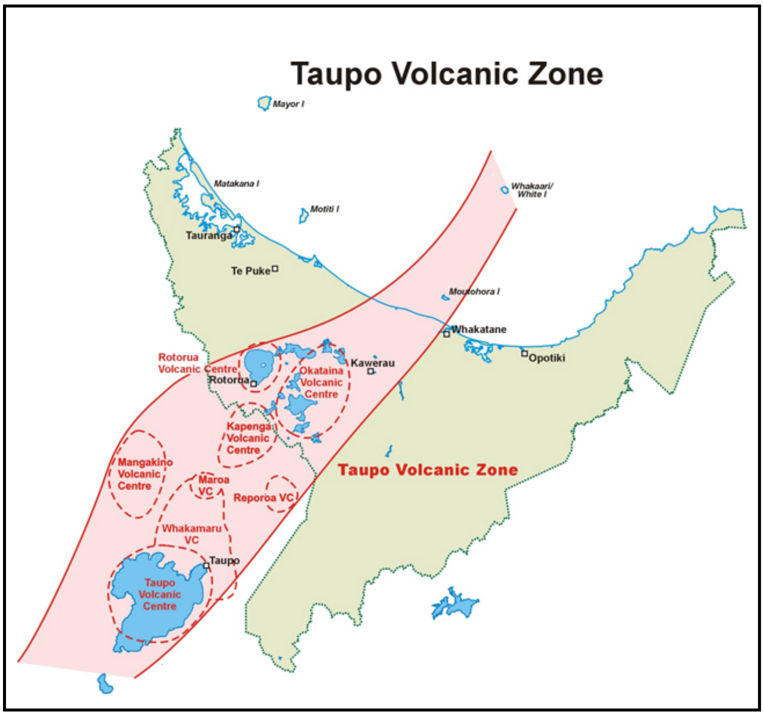


Figure 2. Location of the volcanic centres of Taupo Volcanic Zone (after Houghton et al., 1995).

Most of the lakes in the Rotorua area have been formed as a direct result of volcanic processes that have left large depressions that are now occupied by lakes. Large basins or explosion craters have formed as a result of catastrophic rhyolitic caldera eruptions from the Rotorua and Okataina volcanic centres. Some of the Rotorua lakes have also formed as result of historic damming of valleys by lava flows and volcanic deposits.

2.1 Geology of the Lake Rotorua catchment

The Lake Rotorua catchment has long been of interest to geologists, not only because of the volcanic processes, but also because of the geothermal activity of the Rotorua field at the southern end of Lake Rotorua and at the north and eastern margins of the Lake.

The Lake Rotorua basin was formed following the Mamaku rhyolitic eruption 220-230 ka ago (Wood, 1992). During this eruption over 145 km^3 of pyroclastic flow material known as the Mamaku Ignimbrite covered an area of 3200 km^2 (Milner et al., 2003). As result of the eruptive processes during the Mamaku eruption, collapse of the ground occurred, forming a ring-faulted depression known as the Rotorua caldera that is now occupied by the present lake Rotorua.

Soon after the Mamaku caldera eruptions a lake began to form in the ring-faulted depression. This resulted in the deposition of lake sediments known as the Huka Group that consists of reworked fine ash, pumiceous sands, and diatomaceous silts. Subsequent to this further effusive rhyolitic eruptions occurred, resulting in development of lava flow and dome complexes in and around the caldera. Rhyolitic domes within the caldera include Ngongotaha, Pukehangi, Kawaha Point and Mokoia Island. The caldera basin then started infilling with sediment and tephra that has been subsequently erupted from neighbouring Okataina Volcanic Centre. This process continues at present. Volcanic events in the neighbouring Okataina Volcanic Centre also caused the water level in Lake Rotorua to fluctuate by 100 m from present day level, resulting in a number of terraces to be formed in the caldera (Dravitzki 1999). The interpretation of the lake level history has been the subject of further investigations by Hodgson and Nairn (2004) and Marx (in prep.).

Thompson (1974) identified, mapped and described the major geological units in the Rotorua area. These units were later mapped on a regional scale by Healy (1975). Most geological investigations had been focused on the geothermal area of Rotorua, as summarised in International Geothermal Association (1992).

The main geological units of the Rotorua catchment are defined by a number of distinct ignimbrite sheets, rhyolite domes and sedimentary units. These units are described briefly here because they are considered to be the main geological units that influence the hydrology of the Rotorua catchment and are most likely to be the aquifer source for Lake Rotorua. A detailed summary of the stratigraphy of the main geological units is presented in the review of the Lake Rotorua catchment by White et al. (2004).

2.1.1 Ignimbrite and pyroclastics

The main underlying geological units are the Whakamaru Group pyroclastics, Pokai and Waikakairiri ignimbrites and younger Onuku-Pokopoko pyroclastics. The Whakamaru Group pyroclastics are considered the most basal units for groundwater aquifers in the Rotorua catchment. Drillholes have penetrated at least of 100 m of Rangitaiki ignimbrite, which is part of the Whakamaru Group Ignimbrites (Nairn, 2002). In general, the Whakamaru Group pyroclastics are non-welded to moderately welded with some jointing and they are distinguished by dark grey colour. Above the Whakamaru Group are younger Pokai and Waikakairiri ignimbrites. A recent study by Lynch-Blosse (in prep.) has identified that the Pokai was erupted from the Kapenga Caldera to the southwest of Rotorua City, whereas the Waimakariri was erupted from a newly identified caldera buried by the over lying Mamaku ignimbrite beneath the Mamaku plateau. These units are the basal units of the Mamaku Plateau. The Pokai Ignimbrite has been identified as dense, partially welded, grey to sandy grey ignimbrite.

The Waimakariri Ignimbrite is a moderately to densely welded sandy ignimbrite.

The Onuku-Pokopoko pyroclastics are considered to have been erupted from the Okataina Volcanic centre and are defined as a moderately compacted welded pyroclastic flow. This unit exceeds 120 m in thickness near Lakes Okareka and Okataina (Nairn, 2002) and has been identified in groundwater drillholes at Mamaku township where drilling has penetrated ca. 15 m of Pokopoko pyroclastics.

In general, all the aforementioned units have been buried by the overlying Mamaku Ignimbrite. However, old Taupo Volcanic Zone lava domes that predate the Mamaku ignimbrites do occur in the Rotorua Caldera. One such dome has been identified near Whakarewarewa. The groundwater potential in this formation is unknown, although groundwater flow is likely within fractures.

The Mamaku Ignimbrite is the most widespread geological unit of the Rotorua catchment, and it is likely to be the main unit that contains the aquifers in the catchment. The ignimbrite was erupted from the Rotorua caldera during large explosive rhyolitic pyroclastic eruptions 220 thousand years B.P. During the eruption, most of the flow was directed towards the west, north and southwest of the Rotorua caldera (Milner et al., 2003). The ignimbrite is characterised by its pinkish colour. Three main subunits are recognised within the Mamaku Ignimbrite (lower, middle and upper). The lower sheet (40-45 m thick) is a pale brown-creamy white, non-welded, predominantly fine grained, non-jointed ignimbrite. The middle section is a light brown, strongly welded ignimbrite with cooling joints that are 0.5 to 4 m wide (Milner et al., 2003). The upper sheet is a grey-pink-red, semi-welded, predominantly fine grained, non-jointed ignimbrite.

Following the Mamaku pyroclastic eruptions, ryholite lavas were extruded through the Mamaku Ignimbrite, forming lava dome complexes in and around the caldera. Groundwater is likely within the fractures, and the domes are the source of a number of springs.

2.1.2 Rotoiti pyroclastics and Earthquake Flat Breccia

Eruptions from the Okataina Volcanic Centres produced widespread airfall tephra and non-welded flow units 62 thousand years B.P. Material from these events is found to the north and northeast of the Rotorua catchment. Emplacement of these materials blocked the drainage of Lake Rotorua at the Ohau Channel. This caused the lake to fill to high stand that eventually resulted in overtopping of the pyroclastic dam in a dramatic breakout flood (Kennedy et al., 1978). This flood event rapidly drained the lake by about 50 m through the current Ohau channel.

The airfall tephra erupted from the Okataina volcanic centre is approximately 5 m thick on the east margins of Lake Rotorua. Reworked components of the Rotoiti pyroclastics are found through out the catchment. The earthquake flat breccia was erupted from the Kapenga caldera. Pumiceous flow deposits associated with this eruption are found widely across the Rotorua catchment.

2.1.3 Huka Group Sediments (220 to 20 year B.P) and Holocene Alluvium (20 thousand years B.P to present)

Lake sediments are distributed widely across the catchment and are associated with higher stand shorelines of the lake. These sediments consist of reworked volcanic ash and pumiceous materials associated with periodic eruptions from the Okataina Volcanic centres. Diatomaceous silts, some interbedded gravels, and in situ pyroclastic deposits are interspersed throughout the reworked ash and pumice layers. The Huka sediments have been found to be 80 m thick in some groundwater and geothermal bores. The most recent geological unit in the catchment is the Holocene alluvial deposit that infills the eroded gullies that formed in the Huka Group sediments after the lake level dropped about 20 000 years B.P. These Holocene alluvial deposits are localised in the catchment, occurring at the lake margins and in gully floors. These alluvial deposits consist of pumice gravels derived from erosion of pyroclastic sediment in the catchment (Nairn, 2002), and bring unconsolidated ash and reworked Huka Group sediments into Lake Rotorua.

2.2 Hydrogeology of the Lake Rotorua Catchment

White et al. (2004) identified the following eight geological units as the important groundwater-bearing formations in the Lake Rotorua catchment (in order of deposition and age):

- Pokai and Waimakariri pyroclastics
- Onuku-Pokopoko pyroclastics
- Old Taupo Volcanic Zone lava domes
- Mamaku Ignimbrite
- Rotorua caldera rhyolite domes
- Rotoiti pyroclastics
- Huka Group sediments
- Holocene alluvium

The major water contribution to Lake Rotorua is from the western catchment that drains the eastern flanks of the Mamaku Plateau (Fig. 3). A large area (~250 km^2) is drained by large springs emerging from the ignimbrite on the western side of Lake Rotorua (Hamurana Spring being the largest spring in the North Island). The springs are characterized by very constant water flow and temperature. Given the large extent of the ignimbrite aquifer, a large groundwater reservoir exists, with long water residence times in the aquifer. Taylor and Stewart (1987) estimated the water residence time of some of the springs to be 50-100 years.

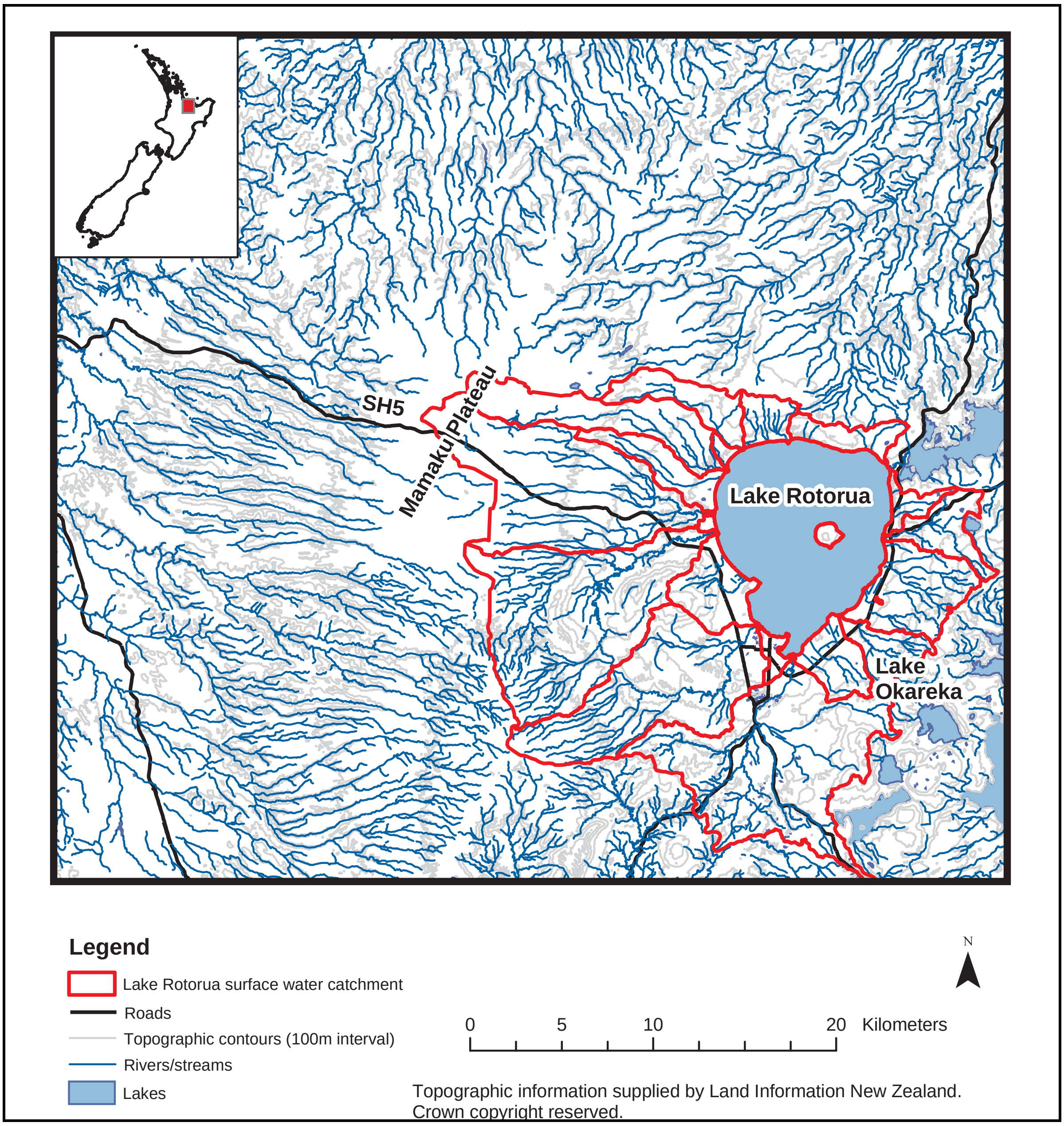
The water-bearing formations that predate the Mamaku Ignimbrite include both mid and upper Pleistocene rhyolitic domes. The rhyolite domes are likely to have fracture flow permeability based on spring discharges (e.g. Fairy Springs, U16, 795 358), although it is expected that permeability will vary significantly between rhyolite domes (Wood 1992) and will depend on fracture sizes and linkages. Faulting associated with the Rotorua caldera has offset several of the rhyolite domes, and groundwater is considered to flow through these faults from one formation to another (White et al. 2004). The rhyolite domes that have intruded into the older water-bearing formations may also influence the groundwater flow in the Rotorua caldera basin depending on the permeability of the rhyolite. If the rhyolite dome is impermeable or has lower permeability compared to the adjacent material, then groundwater will flow around the dome structure. However, if the dome has a similar or higher permeability compared to the adjacent formation, groundwater will flow through the dome structure.

The Mamaku Ignimbrite is an important water-bearing unit in the Lake Rotorua catchment. The lower and upper sheets are considered permeable by Rosen et al., (1998). The middle sheet is considered impermeable, but it is fractured and therefore considered to not act as an aquitard for the other two sheets. A tephra sequence at the base of the Mamaku Ignimbrite is thought to act as an aquitard and prevent water from flowing into the underlying deposits.

The sediments that post-date the Mamaku Ignimbrite are also important water-bearing units. For example, alluvium comprised of silt, sand, gravel (ignimbrite, obsidian and rhyolite pumice) is considered permeable (Rosen et al., 1998), although lenses of low permeability sediment occur. Generally these sedimentary units are considered to allow downward percolation of water (Rosen et al., 1998), although the alluvium and lacustrine sediments can also act as confining layers.

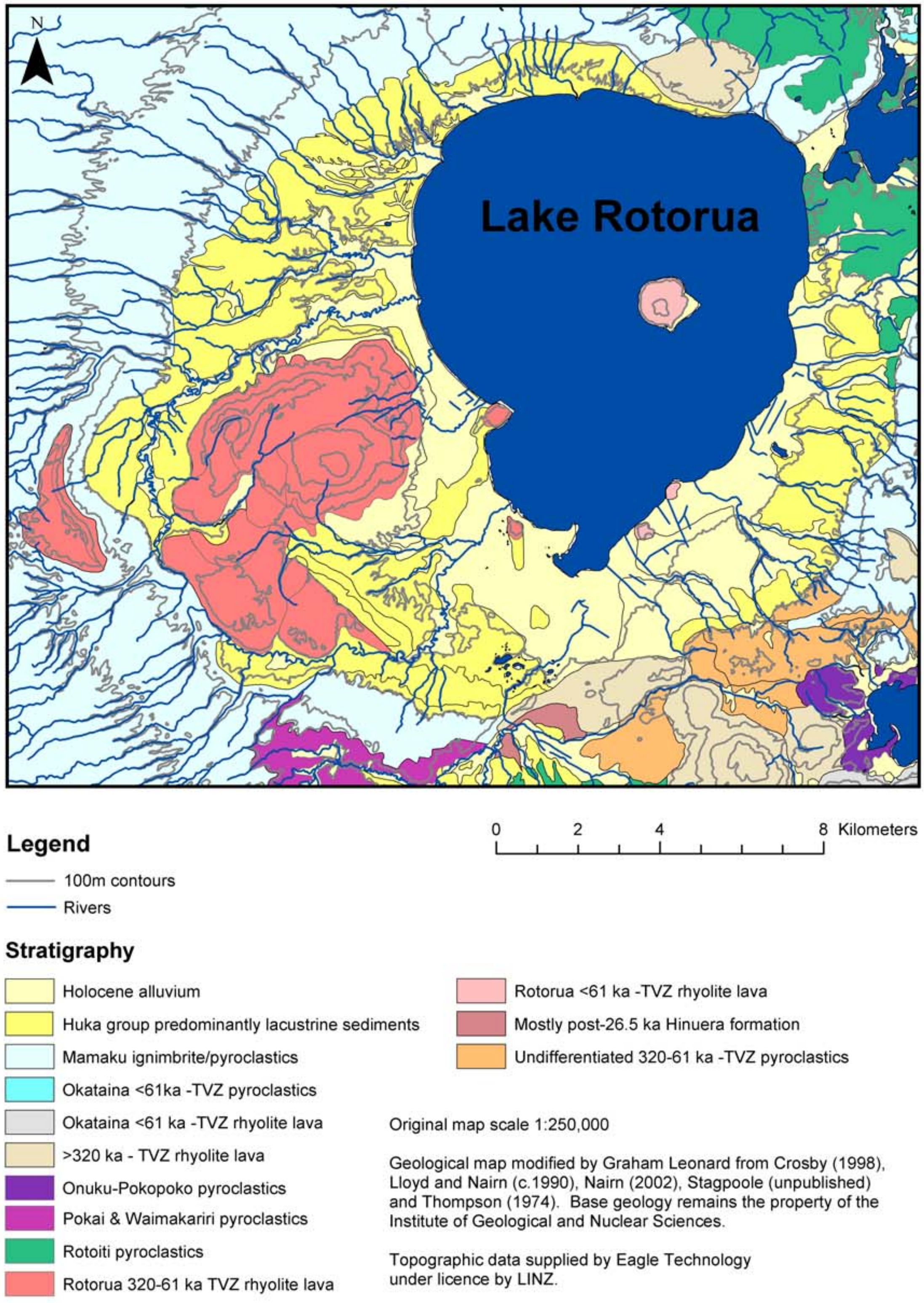
The surficial geology in the vicinity of Lake Rotorua is displayed in Fig. 4. Alluvium and lacustrine sediments (Huka Group) dominate the surface geology within 2 km of the edge of Lake Rotorua, except for the north east corner where ignimbrite and pyroclastic deposits are evident (Nairn, 2002). Mamaku ignimbrite is mapped beyond the alluvial deposits to the north and west of Lake Rotorua. Rhyolite domes (320 – 61 ka) have intruded through the surface deposits to the west, with smaller, older, rhyolite domes near the lake shore in the south east corner of Lake Rotorua. Geology on the eastern side of Lake Rotorua is complex and is a result of much volcanism from the Rotorua and Okataina volcanic centres. Mamaku ignimbrite, Okataina pyroclastic deposits, and rhyolite domes boarder the edge of the Huka

Group sediments from the south of Lake Rotorua, around to the east, and to the north of Lake Rotorua.



Topographic information supplied by Land Information New Zealand. Crown copyright reserved.

Figure 3. Lake Rotorua water catchment.



Original map scale 1:250,000

Geological map modified by Graham Leonard from Crosby (1998), Lloyd and Nairn (c.1990), Nairn (2002), Stagpoole (unpublished) and Thompson (1974). Base geology remains the property of the Institute of Geological and Nuclear Sciences.

Topographic data supplied by Eagle Technology under licence by LINZ.

Figure 4. Geology at Lakes Rotorua and Okareka.

Groundwater seepage and flow rates can vary significantly within small areas of the Lake Rotorua catchment. This is because of the fractures within the rhyolite and ignimbrite aquifers that formed as a result of faulting and contraction following deposition. The size and interconnectivity of these fractures affects groundwater flow in these types of aquifers. Rosen et al. (1998) developed a schematic model for the Mamaku Ignimbrite near Taniwha Springs (Fig. 5), which describes water percolating down to the groundwater table and then flowing through fractures in the upper ignimbrite sheet. There is potential for groundwater to flow from the lower sheet into the upper sheet (and vice-versa) via faults and fractures through the zone of welding.

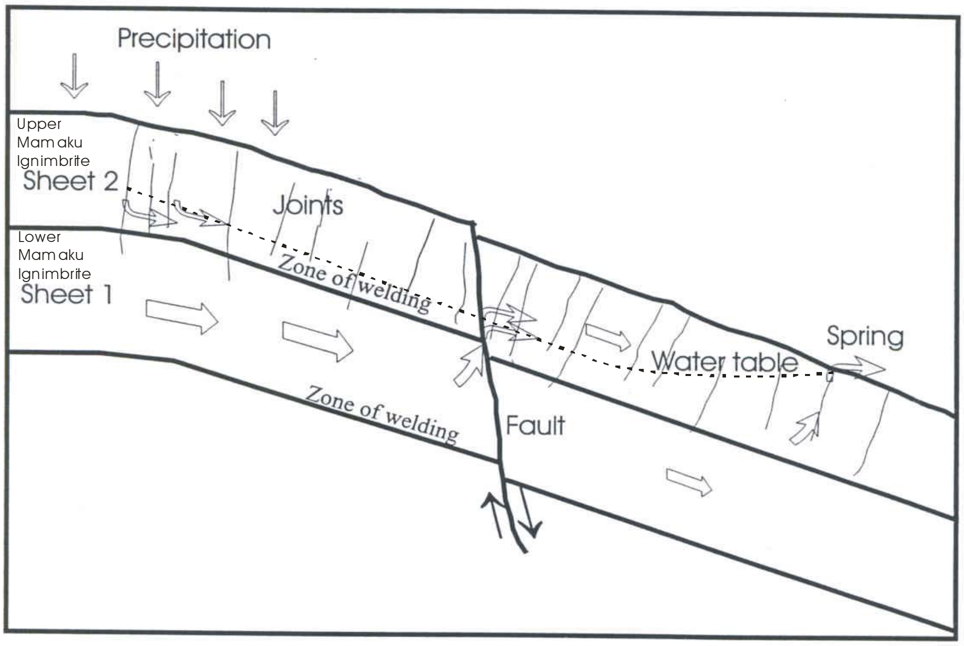


Figure 5. Schematic diagram of water movement in the Mamaku Ignimbrite. 1) Water falls on the ignimbrite's surface, and permeates downward mainly along joints. 2) Once a zone of welding is reached, water is forced to flow down the dip direction of the ignimbrite. 3) Water accesses sheet 2 (from sheet 1) along faults or joints, finally emerging from sheet 2 at a joint controlled spring. Open arrows represent water movement. Filled arrows indicate fault movement. Dip and paleotopography of underlying layers is unknown and therefore not included (modified from Rosen et al., 1998).

Numerous streams drain from the Mamaku Plateau into Lake Rotorua. Most of the streams have baseflow that is either groundwater spring-sourced or have a major groundwater spring contribution. The major freshwater springs of the northern and western Lake catchment occur in the Hamurana, Ngongotaha, Waiteti and Awahou streams (Pang, 1996). Rosen et al. (1998) suggests that faulting, in combination with jointing, allows water from the lower Mamaku Ignimbrite aquifer (separated from the upper Mamaku Ignimbrite aquifer by the zone of welding) to flow into the upper Mamaku Ignimbrite aquifer, and may be responsible for some large springs.

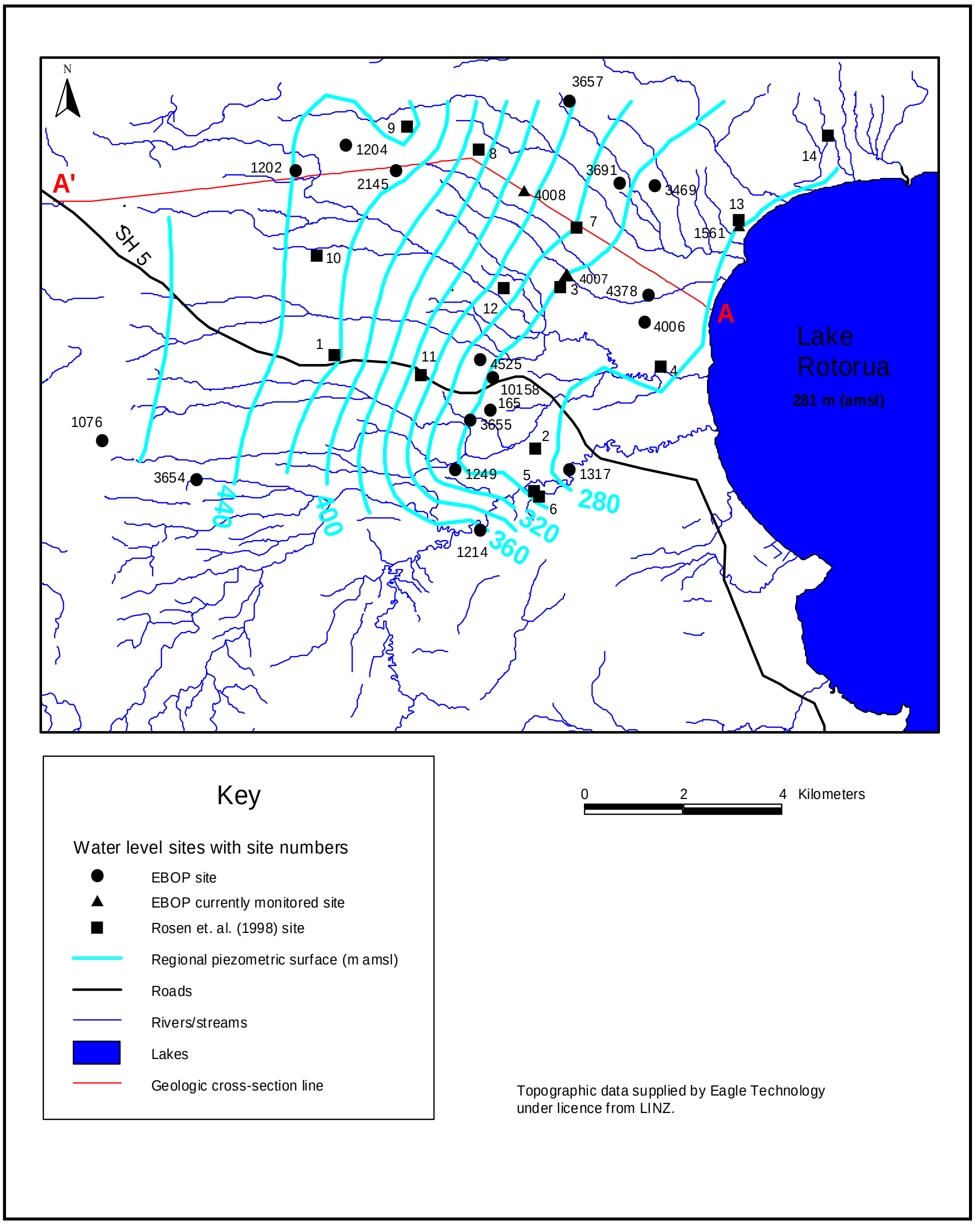
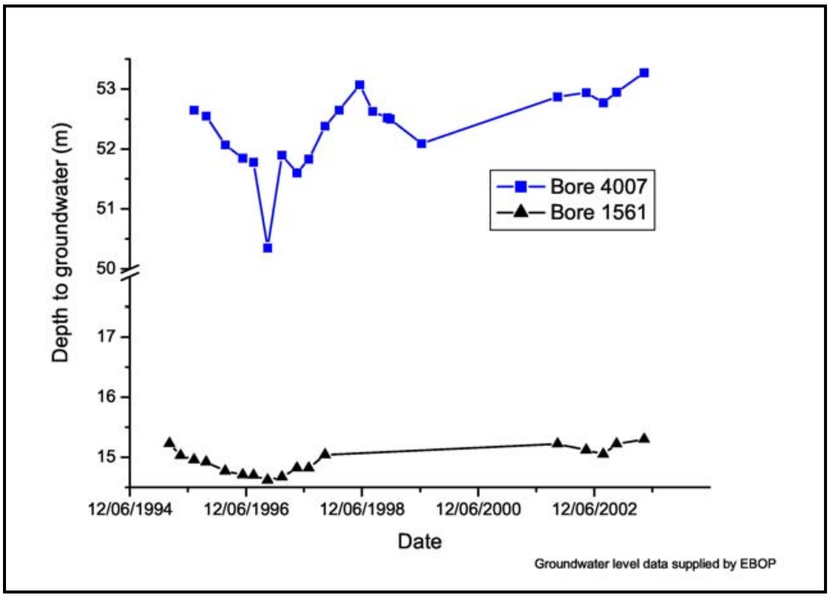


Figure 6. Piezometric map of the Western Rotorua area.

A piezometric map of the study area (Fig. 6) has been constructed using data from Rosen et al. (1998) and data from Environment Bay of Plenty (Morgenstern et al., 2004). The piezometric map is constructed from three data sets:

- water level and ground surface elevations from Rosen et al. (1998)
- water level data from drillers logs at the time bores were drilled (supplied by Environment Bay of Plenty)
- water level data obtained as part of an Environment Bay of Plenty monitoring programme (supplied by Environment Bay of Plenty)

Data from Rosen et al. (1998) form the basis of the map. Bore positions and ground surface elevations were measured at the time of water level measurements. Ground surface elevations at the bores were estimated from the 1:50 000 topographic map series, so the likely error could be up to ± 20 m. This is considered acceptable for obtaining an indication of regional groundwater flow directions. The ranges in groundwater levels in bores 4007 and 1561 have been less than 3 m (Fig. 7) for the period 1994-2002. A range in level of 3 m is considered insignificant for interpretation of groundwater flow direction. The piezometric map (Fig. 6) shows groundwater flows towards Lake Rotorua. The groundwater gradient is steeper on the higher flanks of the Mamaku Plateau (500 masl) closer to Lake Rotorua (280 masl).



Groundwater level data supplied by EBOP

Figure 7. Water levels in bores 4007 and 1561.

Borehole data collected by drillers and supplied by Environment Bay of Plenty is used to identify and correlate aquifer units. However, borehole data is often not of sufficient quality to identify aquifer units and thus must be used with caution. This is because geological units are often incorrectly identified. In many logs, 'rhyolite' is identified as the major unit underlying the surface deposits. We have interpreted 'rhyolitic' units in the borehole data as 'ignimbrite' units where drill holes have not been located near a mapped rhyolitic deposit (Fig. 4). In some cases, the borehole data correctly describe the lithology as ignimbrite, but no distinction is made between upper or lower Mamaku Ignimbrite units.

Figure 8 shows a cross-section based on Environment Bay of Plenty drill hole data (Morgenstern et al., 2004). Mamaku Ignimbrite dominates all drill holes, except near Lake Rotorua, where clay and pumice sediments dominate. No distinction can be made between the two Mamaku Ignimbrite aquifers based on drill hole data. A sand and pumice layer in hole 1056 may represent a localised deposit.

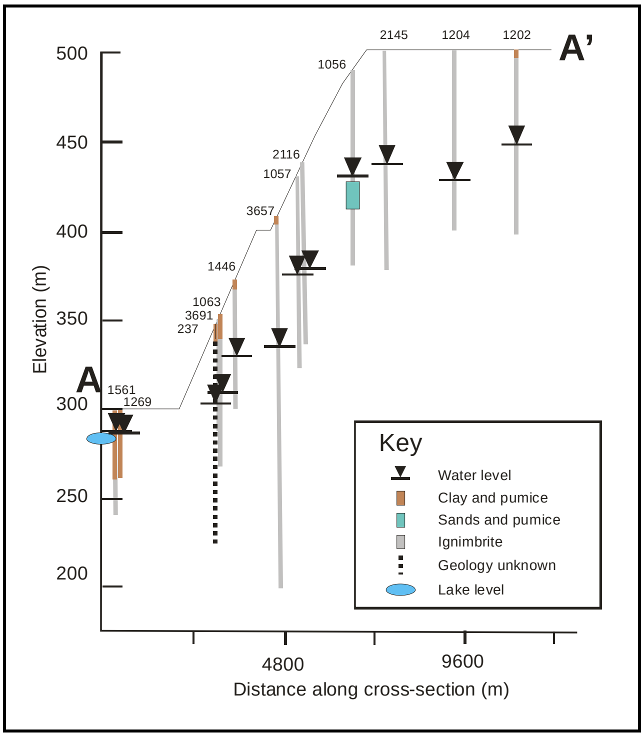


Figure 8. Cross-section A-A’ (Fig. 5) across the western Rotorua study area.

2.3 Hydrogeology of Lake Okareka catchment

Geology in the Okareka area consists mainly of volcanic and sedimentary deposits (Healy, 1964). Detailed geological mapping at the 1:50 000 scale was carried out by Nairn (2002). A simplified geological map is shown in Figure 4. Geological mapping shows a series of rhyolitic domes/lava flows flanking the west, south and east of Lake Okareka.

The depositional history of the area is complex, but the geology of the area is dominated by dome-building events. Lake Okareka is probably a result of a natural depression filled with water, later domed by 21 ka and 13.5 ka rhyolitic lavas between Lake Okareka and Lake Tarawera (Nairn, 2002).

Pokopoko Pyroclastics are present to the west and north of Lake Okareka, with the Mamaku Ignimbrite present to the north. Swamp and alluvium deposits occur near the lake shore and near water courses. The Okareka Fault is mapped running down the eastern edge of the lake, with other smaller NE/SW trending faults to the south and west (Nairn, 2002).

The ground around the lake is steep, ranging from about 560m to 355m (Lake Okareka level). Several small streams (some of which are groundwater sourced) flow into Lake Okareka. The only known outflow for Lake Okareka is into Lake Tarawera through Waitangi Springs. The north-western shore of Lake Okareka area is dominated by farming and forestry.

It is not clear which geological units are water-bearing based on the geological descriptions obtained. Bore logs are not of sufficient quality to make detailed interpretations of the geology. The characteristics of each unit (Nairn, 2002), with its interpreted ability to conduct groundwater, are:

Alluvium: Reworked volcanic deposits. They are potentially water-bearing in coarser grained deposits. Finer-grained deposits have less potential to be aquifers.

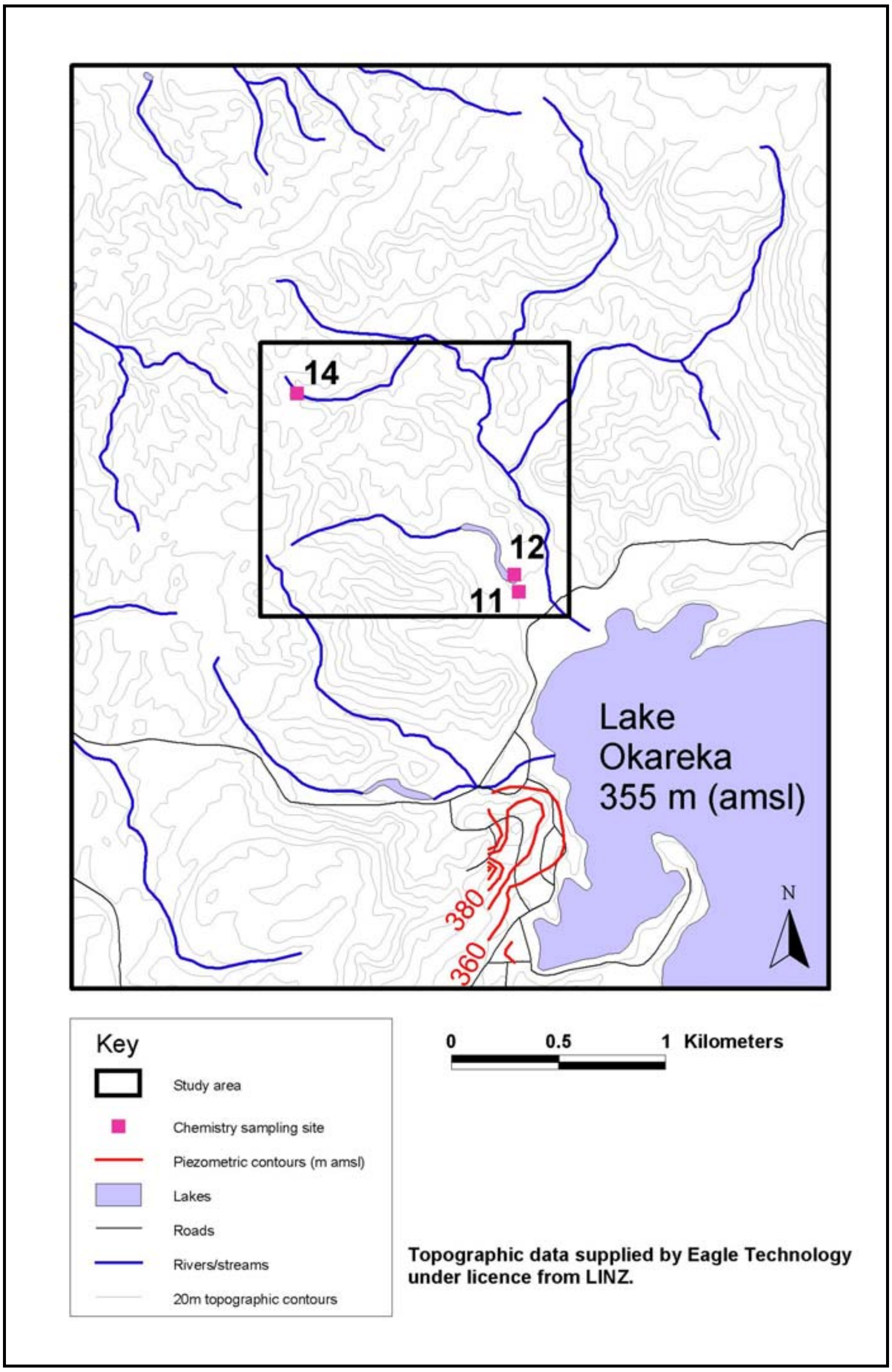
Rhyolite: Obsidian or vesiculated pumiceous lavas. Rhyolite flow banding and jointing is common.

Ignimbrite: The Mamaku Ignimbrite as described in section 2.1.

Pyroclastics: Generally consists of pumice, ash and lapilli with varying degrees of compaction and welding. The coarser-grained pumice material is likely to be water-bearing. The finer grained ash and lapilli are likely to have poor water-bearing potential and act as aquitards.

Nutrient transport via groundwater has been identified as a potential source of nitrogen and phosphorous input to Lake Okareka. Ray and Timpany (2002) estimated 4.0 tonnes of inorganic nitrogen per year enters the lake via groundwater based on sampling shallow (0.5 m deep) groundwater at the lake edge. Septic tanks were estimated to contribute between 16-44% of all nitrogen input to the lake (Ray and Timpany, 2002).

Bore logs in Okareka township suggest that a layer of pumice/sand overlies the unit considered to be Pokopoko Pyroclastics. Interpretation of the bore logs suggests that the Pokopoko Pyroclastics are described as rhyolite/ignimbrite in the driller's logs. The surface pumice/sand layer probably supports localised aquifers, from which groundwater is likely to flow into the deeper fractured aquifer system (the pyroclastics). It is unclear from the drill logs whether units other than volcanic sediment were encountered in the north of the study area.



Topographic data supplied by Eagle Technology under licence from LINZ.

Figure 9. Piezometric map and sample locations at Lake Okareka.

Defining groundwater flow patterns around Lake Okareka is essential to understand the interaction between the groundwater and the lake (i.e. whether or not groundwater flows into the lake). A piezometric map (Fig. 9) is constructed from the limited available groundwater level data (from Morgenstern et al. 2004). Water levels were obtained from driller's records and elevations were estimated from the 1:50,000 map series. The accuracy of the elevations estimated from these maps is ± 20 m. The depths of the bores range from 17 m (bore 173) to 92 m (bore 220), with most bores about 35 m deep.

The piezometric map of the Lake Okareka township area (Fig. 9), approximately 1 km south of the study area, shows that the direction of groundwater flow is towards Lake Okareka. In general, groundwater flow follows local topography, with groundwater levels high on the ridge, and low groundwater levels in the valleys. Given the complex geology of the lake area, these observations are only considered to be valid in this area of the lake. Due to the lack of groundwater data in this area, it is impossible to rule out hydraulic influence from Lake Tikitapu and Lake Rotokakahi on Lake Okareka, which have lake levels higher than Lake Okareka (419 m and 396 m respectively). The higher lake levels in Lake Tikitapu and Lake Rotokakahi compared to Lake Okareka suggest possible leakage from these lakes to groundwater. The groundwater leakage may possibly flow into Lake Okareka.

The groundwater flow directions are consistent with the regional flow direction, which is assumed to be towards Lake Tarawera (lake level approximately 55 m lower than Lake Okareka).

Water levels measured on 24/07/03 at site 12 (bore 3901, 43 m deep) and the nearby site 11 (well 10963, 1.6 m deep) show similar static water levels (Morgenstern et al., 2004), suggesting a hydraulic connection between these aquifers.

Springs emerge from high up in the catchment (e.g. Site 14, Fig. 9) and contribute flow to the streams through the study area. These springs flow from pumiceous sediment overlying the major geological units, and probably represent groundwater from perched aquifers.

A piezometric map of the study area could not be constructed due to the lack of data. Water levels measured at sites 11 and 12 are higher than the lake level so it is likely that groundwater flows toward the lake.

2.4 Summary of aquifer characteristics

The hydrogeology of the area around Rotorua Lakes can be described as a permeable surface pumiceous tephra layer that allows easy penetration of rainwater recharge to deep rhyolite and ignimbrite aquifers that form essentially unconfined aquifers yielding high volumes of groundwater. The water table near the Mamaku Plateau is fairly deep (~70m). Most sites sampled in the Rotorua area are in unconfined aquifers and probably tap aquifers that are recharged by rainfall. The aquifer status and recharge mechanism for sites #9 (well 10964) and #13 (well 10424) cannot be established due to a lack of geological data.

3.0 GROUNDWATER AGE DATING

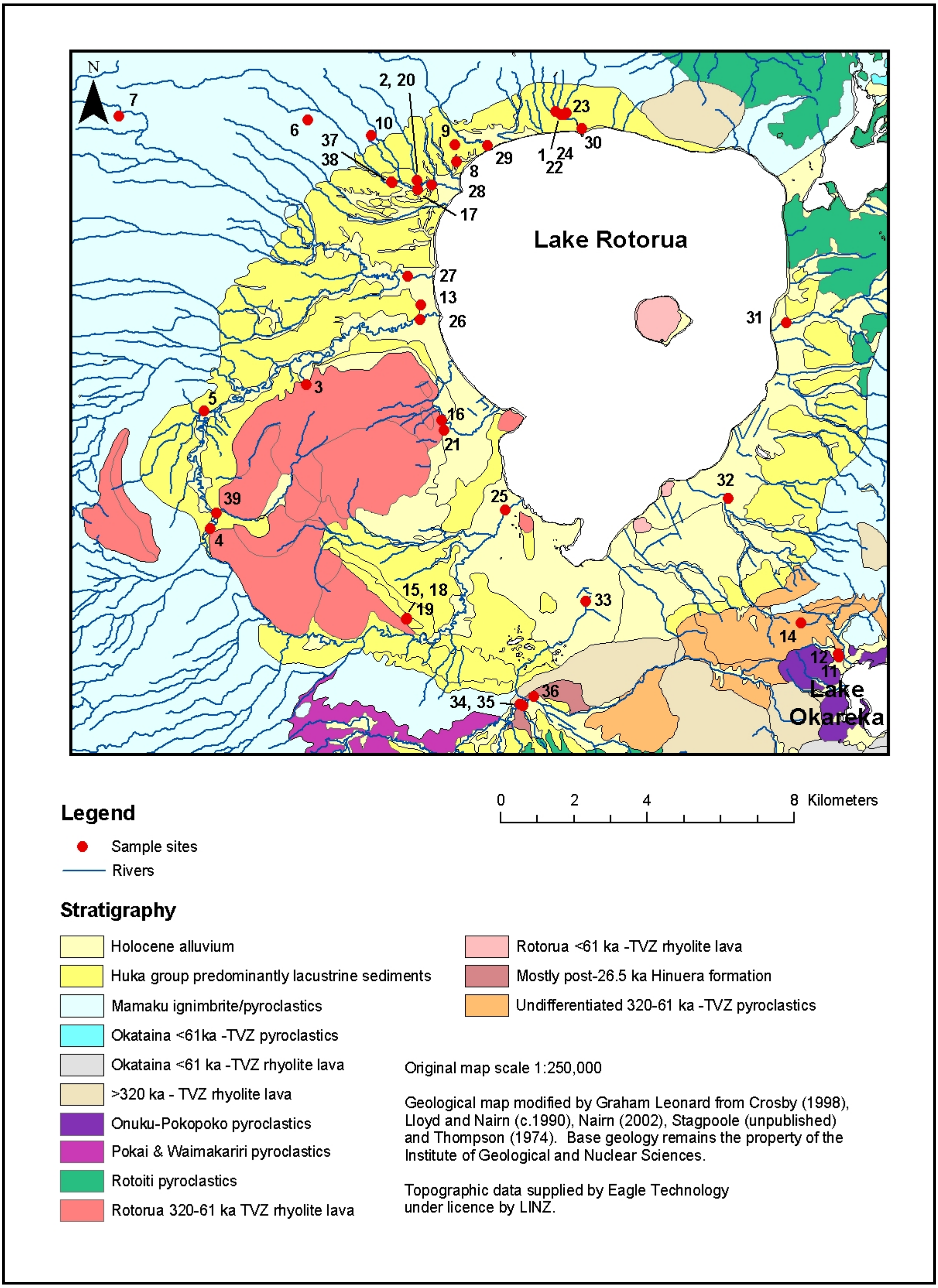
The methodology for age dating of groundwater is described in Appendix 1.

3.1 Sampling and analysis

Sampling locations are shown in Fig. 10 and bore details listed in Table 1. Five springs and six privately owned groundwater wells in the north-western Lake Rotorua area, and two privately owned wells in the north-western Lake Okareka area were sampled in July/August 2003 for tritium, CFCs, and SF_6 to obtain initial estimates of groundwater residence times and time trends in hydrochemistry. More tritium and chemistry samples were collected from some springs and from all significant stream flows to Lake Rotorua in November 2003. This was to confirm the tritium time trends for robust age dating, and to extend the study to 10 more springs and to the 12 major stream water inflows to Lake Rotorua. In 2005, another major sampling campaign was carried out on springs and groundwater wells to (i) establish seasonal water age and nutrient variations in major springs and streams, (ii) establish a representative spatial coverage of the hydrochemistry trends, and (iii) obtain detailed age-chemistry information in one catchment (Waingaehe Stream). Age interpretation of the new data (ii and iii) will be given in a separate report.

Water samples for tritium analysis were collected in clean 1.1 litre Nalgen bottles. Samples for CFC and SF_6 concentration measurements were collected in such a way as to strictly prevent contact of the water with air. In 2003, glass bottles with 0.5 or 1 litre volume were used for CFCs, and 2.5 litre bottles for $SF_{6.}$ Springs were sampled by placing the glass bottle in the spring outlet and, using nylon tubing attached to a vacuum pump, to allow the flow of fresh uncontaminated water through the bottle until the water in the bottle had been displaced 3-5 times. Bottles were then quickly screw-sealed while still submerged below the water surface. Wells were sampled by connecting a nylon tube directly to the wellhead to avoid contact with plastic parts in the piping system. After the well had been flushed for 20-100 minutes, the sample bottle was filled from the bottom via the nylon tube. The bottle was allowed to overflow, replacing the water more than 5 times, before the bottle was sealed with a screw cap. Two bottles were collected for each of CFCs and SF_6. All bottles were capped with nylon seals.

The tritium samples were analysed using the Institute of Geological & Nuclear Sciences Ltd. (GNS) state-of-the-art tritium measurement system that has an extremely high detection sensitivity for the low tritium concentrations prevailing in New Zealand's waters. The detection limit is 0.03 TU, using ultra low-level liquid scintillation spectrometry and electrolytic enrichment prior to detection. One litre of water is required for analysis. Reproducibility of a standard enrichment is 2%, and an accuracy of 1% can be achieved via deuterium calibrated enrichment (Taylor 1994). Water gas (CFCs and SF_6) concentrations were analyzed at GNS by gas chromatography.



Original map scale 1:250,000

Geological map modified by Graham Leonard from Crosby (1998), Lloyd and Nairn (c.1990), Nairn (2002), Stagpoole (unpublished) and Thompson (1974). Base geology remains the property of the Institute of Geological and Nuclear Sciences.

Topographic data supplied by Eagle Technology under licence by LINZ.

Figure 10. Lakes Rotorua water sampling sites.

Table 1. Sampling location and well characteristics for samples from the Lake Rotorua and Lake Okareka area.

#	Sample	collected at:	Catch-ment	E	N	Depth to Water (m)	Bore depth (m)	Screened interval (m)
1	**Hamurana Spring**	beside water intake	ROT	2795621	6347367	n/a	n/a	n/a
2	**Taniwha Spring**	old well	ROT	2791832	6345487	n/a	n/a	n/a
3	**Trout Hatchery Spring**	weir	ROT	2788810	6339920	n/a	n/a	n/a
4	**Te Waireka Spring**	bottling plant intake	ROT	2786200	6336000	n/a	n/a	n/a
5	**Barlows Spring**	water supply intake	ROT	2786036	6339206	n/a	n/a	n/a
6	**2116**		ROT	2788852	6347137	72	124	90 - 124
7	**1202**		ROT	2783712	6347247	63	124	91 - 124
8	**1561**		ROT	2792917	6346011	15	73.1	63 - 73.1
9	**10964**		ROT	2792871	6346460	16	45	39 - 45
10	**3691**		ROT	2790581	6346727	60	118.5	78 - 118.5
11	**10963**		OKA	2803342	6332487	1.15*	1.6	open hole
12	**3901**		OKA	2803320	6332567	3.63*	43	30 -43
13	**10424**		ROT	2802307	6333413	2.74	21	14.5 - 21
14	**Spring 2**		OKA	2802307	6333413	n/a	n/a	n/a
15	**Utuhina Spring**	main	ROT	2791553	6333538	n/a	n/a	n/a
16	**Te Waiowhero**	(Fairy Spring)	ROT	2792512	6338948	n/a	n/a	n/a
17	**Awahou Stream**	Central Rd. bridge	ROT	2791850	6345240	n/a	n/a	n/a
18	**Utuhina Spring**	#1	ROT	2791550	6333528	n/a	n/a	n/a
19	**Utuhina Spring**	#2	ROT	2791546	6333531	n/a	n/a	n/a
20	**Taniwha Spring**	water intake	ROT	2791832	6345487	n/a	n/a	n/a
21	**Rainbow Spring**		ROT	2792562	6338681	n/a	n/a	n/a
22	**Hamurana Spring**	#1	ROT	2795763	6347294	n/a	n/a	n/a
23	**Hamurana Spring**	Head spring	ROT	2795914	6347325	n/a	n/a	n/a
24	**Hamurana Spring**	#3	ROT	2795836	6347293	n/a	n/a	n/a
25	**Utuhina Stream**	Lake Rd	ROT	2794235	6336495	n/a	n/a	n/a
26	**Ngongotaha Stream**	Ngongotaha Rd	ROT	2791915	6341700	n/a	n/a	n/a
27	**Waiteti Stream**	Ngongotaha Rd	ROT	2791582	6342872	n/a	n/a	n/a
28	**Awahou Stream**	Hamurana Rd	ROT	2792233	6345372	n/a	n/a	n/a
29	**Hauraki Stream**	Hamurana Rd	ROT	2793747	6346449	n/a	n/a	n/a
30	**Hamurana Stream**	Hamurana Rd	ROT	2796323	6346919	n/a	n/a	n/a
31	**Waiohewa Stream**	Te Ngae Rd (geoth.)	ROT	2801911	6341607	n/a	n/a	n/a
32	**Waingaehe Stream**	Te Ngae Rd	ROT	2800327	6336820	n/a	n/a	n/a
33	**Puarenga Stream**	Te Ngae Rd (geoth.)	ROT	2796442	6334000	n/a	n/a	n/a
34	**Kauaka Stream**	Waipa State Mill Rd	ROT	2794716	6331155	n/a	n/a	n/a
35	**Upper Puarenga Stream**	SH5-HemoGorge	ROT	2794645	6331200	n/a	n/a	n/a
36	**Waipa Stream**	Hemo Gorge	ROT	2795024	6331402	n/a	n/a	n/a
37	**Awahou Spring**	#1	ROT	2791151	6345435	n/a	n/a	n/a
38	**Awahou**	upstream	ROT	2791131	6345455	n/a	n/a	n/a
39	**Ngongataha stream**	Paradise springs	ROT	2786362	6336406	n/a	n/a	n/a

* Water levels measured prior to sampling

3.2 Analysis results

Tritium, CFC, and SF_6 results are listed in Table 2.

Table 2. Tritium, CFC, and SF_6 results of spring water and groundwater well samples from the Lake Rotorua and Lake Okareka area. TROT and FBP are the laboratory codes. TR (tritium ratio) corresponds to one tritium atom per 10^{18} hydrogen atoms. The radioactivity equivalent for one TR in one kg of water is 0.118 Bq. ±TR is the one sigma standard measurement error. pptv is one part per trillion by volume or 10^{-12}.

#	Sample	Date	Tritium			Equil. temp. [oC]		Atm.part.press.[pptv]		
			TROT	TR	±TR		FBP	CFC11	CFC12	SF_6
1	**Hamurana Spring**	10/07/2003	332	0.407	0.026	12.8	3	152	196	0.595
2	**Taniwha Spring**	10/07/2003	333	0.831	0.029	12.8	4	180	423	1.91
3	**Trout Hatchery Spring**	10/07/2003	334	1.35	0.04	12.8	5	171	990	3.13
4	**Te Waireka Spring**	10/07/2003	335	1.35	0.04	12.8	6	203	477	3.21
5	**Barlows Spring**	10/07/2003	337	0.807	0.027	12.8	7	60	135	0.88
6	**2116**	11/07/2003	338	0.076	0.02	12.8	8	3.9	7.7	0.11
7	**1202**	11/07/2003	339	1.28	0.04	12.8	9	248	601	3.64
8	**1561**	11/07/2003	340	0.385	0.022	12.8	10	36.7	96	0.42
9	**10964**	11/07/2003	341	1.24	0.04	12.8	11	433	6950	0.81
10	**3691**	11/07/2003	342	0.605	0.025	12.8	12	178	463	1.96
11	**10963**	21/08/2003	354	1.51	0.05	12.8	13	213	461	4.86
12	**3901**	21/08/2003	355	0.014	0.02	12.8	14	2.9	2.5	0.19
13	**10424**	21/08/2003	356	0.035	0.019	12.8	15	4.4	7.1	0.62
15	**Utuhina Spring**	21/08/2003	357	0.508	0.027	na	na	na	na	na
16	**Te Waiowhero**	21/08/2003	358	1.06	0.04	na	na	na	na	na
17	**Awahou Stream**	21/08/2003	359	0.854	0.032	na	na	na	na	na
18	**Utuhina Spring #1**	22/11/2003	360	0.585	0.027	na	na	na	na	na
19	**Utuhina Spring #2**	22/11/2003	361	0.547	0.026	na	na	na	na	na
20	**Taniwha Spring**	22/11/2003	362	0.813	0.032	na	na	na	na	na
21	**Rainbow Spring**	22/11/2003	366	1.21	0.04	na	na	na	na	na
22	**Hamurana Spring #1**	22/11/2003	368	0.537	0.031	na	na	na	na	na
23	**Hamurana Spring**	22/11/2003	369	0.636	0.025	na	na	na	na	na
24	**Hamurana Spring #3**	22/11/2003	370	0.614	0.028	na	na	na	na	na
25	**Utuhina Stream**	22/11/2003	371	0.830	0.029	na	na	na	na	na
26	**Ngongotaha Stream**	22/11/2003	372	1.14	0.04	na	na	na	na	na
27	**Waiteti Stream**	22/11/2003	373	1.03	0.03	na	na	na	na	na
28	**Awahou Stream**	22/11/2003	374	0.726	0.030	na	na	na	na	na
29	**Hauraki Stream**	22/11/2003	375	1.39	0.04	na	na	na	na	na
30	**Hamurana Stream**	22/11/2003	376	0.551	0.026	na	na	na	na	na
31	**Waiohewa Stream**	22/11/2003	377	1.07	0.03	na	na	na	na	na
32	**Waingaehe Stream**	22/11/2003	378	0.480	0.026	na	na	na	na	na
33	**Puarenga Stream**	22/11/2003	379	0.973	0.036	na	na	na	na	na
34	**Kauaka Stream**	22/11/2003	380	1.39	0.04	na	na	na	na	na
35	**Upper Puarenga Stream**	22/11/2003	381	0.751	0.031	na	na	na	na	na
36	**Waipa Stream**	22/11/2003	382	0.978	0.034	na	na	na	na	na
37	**Awahou Spring**	16/12/2003	383	0.887	0.030	na	na	na	na	na
38	**Awahou**	16/12/2003	384	1.17	0.04	na	na	na	na	na
39	**Ngongataha stream**	10/07/2003	336	1.41	0.04	na	na	na	na	na
3	**Trout Hatchery Spring**	22/11/2003	363	1.44	0.04	na	na	na	na	na
4	**Te Waireka Spring**	22/11/2003	364	1.50	0.04	na	na	na	na	na
5	**Barlows Spring**	22/11/2003	365	0.751	0.030	na	na	na	na	na
16	**Te Waiowhero**	22/11/2003	367	1.04	0.04	na	na	na	na	na

Most of the water samples have tritium ratios below 1.3 TR, indicating that the groundwater was mainly recharged before atmospheric nuclear weapons testing occurred in the 1960s (i.e. they have pre-bomb tritium concentrations). Unique ages can be determined for these samples. Most of the CFC and SF_6 concentrations are less than the equilibrium values with respect to current atmospheric levels. This means that there is no obvious large artificial CFC and SF_6 contamination. However, CFCs and SF_6 concentrations are too high for water recharged before the 1960s. This indicates slight contamination or possible gas exchange processes in the unconfined aquifers or in the unsaturated zone (see 3.3.). The CFC and SF_6 data therefore have only restricted use for dating in this case. Three of the waters have atmospheric CFC partial pressures above current air levels and are clearly contaminated with artificial CFC in the aquifer. These cannot be used for dating. Trout Hatchery spring and well 1202 are slightly contaminated with CFC-12, while well 10964 is highly contaminated with CFC-12 and slightly contaminated with CFC-11.

3.3 Groundwater age interpretation

A combined exponential and piston-flow model (EPM) was applied to calculate the mean residence times (MRT) and young water fractions (yf) of the samples. This model represents a partly-mixed flow regime (see Appendix 1). The fraction of mixed flow is represented by E%PM, where the percentage is the fraction of mixed flow within the total flow volume. This model produces good matches to long-term tritium data in the Rotorua area (unpublished data) and therefore describes realistically the groundwater flow regime.

Of the springs emerging from the Mamaku ignimbrite aquifer, Hamurana, Taniwha and Trout Hatchery yield high fractions of mixed flow of 90-96%. A well-mixed groundwater reservoir is expected for this aquifer because of the large extent and the unconfined nature of the Mamaku ignimbrite aquifer. Barlows Spring with 85% fraction of mixed flow is slightly lower with the likely reason that the groundwater seems to emerge directly from a deep-leading semi-confined fracture (a more confined flow regime which is represented by higher fraction of piston flow is also indicated by the smaller age difference between tritium and CFCs - SF_6). The springs emerging from the rhyolite lava dome aquifers (Trout Hatchery, Te Waireka, Fairy, Rainbow) yield lower fractions of mixed flow of 50-80%. This seems to be related to the lower permeability of these aquifers, or to semi-confined conditions.

No long-term tritium data are available for the groundwater wells that tap into the ignimbrite aquifer. The results from the springs show that a high fraction of mixed flow has to be applied to the aquifers in this area (about 90% for springs). However, a slightly lower fraction of 70% was chosen for the deep wells because springs are likely to have higher fractions of mixed flow due to flow lines converging at the spring. For the very shallow (1.6 m) well 10963 at Okareka the flow situation is unclear. Tritium and CFC ages disagree, and 45% mixed flow was used to give the smallest disagreement.

For several Lake Rotorua streams long-term tritium data were available for assessment of the fraction of mixed flow. In most cases the data indicated mixed flow fraction of >90%. This is in agreement with the high values obtained from the springs. The streams which are a mix of several springs are therefore expected to have mixed flow fraction of near 100%. Only Waipa Stream resulted in a lower mixed fraction of 75%.

The mean residence time of the water can be obtained by matching the model output to the measured data. Most of the water samples were old enough to give unique tritium age solutions (pre-bomb water), or long-term data were available for resolving ambiguity. However, two of the streams that have no long-term tritium data available (Hauraki and Kauaka) resulted in tritium concentrations with ambiguous mean residence times. Higher tritium concentrations in these streams indicate shorter residence time compared to other streams. However, high iron and manganese in these streams indicate reduced groundwater conditions (these streams may not follow the general groundwater flow pattern). Of the possible mean residence times, the older (35 years) was chosen because the very young residence times are unlikely in this geological unit.

Three of the waters that were sampled for tritium, CFCs and SF_6 (well 10963, 10964, and 1202) resulted also in tritium concentrations with ambiguous residence times. Ambiguity could be resolved using the CFC and SF_6 results. Full details of age interpretation for these springs and wells are listed in Table 3.

The mean residence times derived from the CFC and SF_6 concentrations are significantly younger than those derived from the tritium data in almost all cases (Fig. 11, Table 3). Likely reasons for this are:

1. ***Gas exchange between the water and the soil air.***
   Gas exchange does occur during travel of the water through the unsaturated zone (~ 50m thick). However, water travel through the unsaturated zone does not explain the age differences even though the unsaturated zone is very thick. These large age differences may indicate that there is additional gas exchange at unconfined aquifer conditions after passage through the unsaturated zone between the soil air and the water table. Unconfined aquifer conditions are indicated by the large fractions of mixed flow. The fact that very old waters are also affected does indicate that this excess air pick-up is not only related to water passage through the unsaturated zone.

2. ***CFC/SF_6 contamination.***
   The excess gas concentrations are lowest (several percent) for the oldest waters, but increase to 20-80% for younger water (Fig. 11). This could also suggest contamination of the younger water. But this is unlikely because all 3 species show the same effect.

Samples #7 and #11 are excluded from this consideration because they do not have unique tritium ages.

Table 3. Age results for Rotorua springs and groundwater wells based on **tritium, CFC and SF_6. E%PM** is the percentage of piston flow within the combined exponential-piston flow model (see 3.1). **MRT tritium** is the mean residence time deduced from tritium data, for the **unique** solution (where the result is not ambiguous), the **sec**ond solution (where the result is ambiguous), and for the solution with ambiguity resolved (**Amb.res.**). For the CFC and SF6 results, **pptvc** is the atmospheric partial pressure corrected to the mean residence time deduced from tritium, **diff pptv** is the difference between expected and observed pptv, and **% exc** is the percentage of excess CFC or SF6 compared to recent partial pressure in air (the excess is likely due to gas exchange between the groundwater and air in the soil in unconfined aquifers). For age interpretation the tritium input from Kaitoke (near Wellington) scaled by a factor of 0.9 was used, with integration steps of one year.

#	Sample	E%PM	MRT tritium			MRT				MRT				MRT			
			unique	sec	Amb.res.	CFC11	CFC11	diff	% exc	CFC12	CFC12	diff	% exc	SF6	SF6	diff	% exc
			[yrs]	[yrs]	[yrs]	[yrs]	pptvc	pptv		[yrs]	pptvc	pptv	exc	[yrs]	pptvc	pptv	
1	**Hamurana Spring**	90	**145**			28	22	130	50	47	43	153	28	63	0.115	0.48	9
2	**Taniwha Spring**	90	**64**			21	75	105	40	15	141	282	51	22	0.57	1.34	25
3	**Trout Hatchery Spring**	90	**54**			23	87	84	32	0	168	822	149	10	0.72	2.41	45
4	**Te Waireka Spring**	60	**30**			18	153	50	19	11	246	231	42	9	0.83	2.38	44
5	**Barlows Spring**	70	**73**			55	29	31	12	50	57	78	14	34	0.11	0.77	14
6	**2116**	70	**135**			110	1	2.9	1	115	5	2.7	0	71	0	0.11	2
7	**1202**	70		8-30	**26**	8.5	156	92	35	0	298	303	55	7	1.26	2.38	44
8	**1561**	70	**112**			66	4	32.7	13	58	10	86	16	47	0.01	0.41	8
9	**10964**	70			**31**	cont.				cont				23	0.5	0.31	6
10	**3691**	70	**94**			22	9.5	169	65	12	21	442	80	18	0.03	1.93	36
11	**10963**	45		2,40	**40**	15	25	188	75	12	75	386	70	2	0.3	4.56	83
12	**3901**	70	**170**			115	1	1.9	1	135	2	0.5	0	62	0	0.19	4
13	**10424**	70	**150**			108	1	3.4	1	117	4	3.1	1	40	0	0.62	11

As a quantitative measure of the gas exchange in the unsaturated zone, the 'excess' CFC and SF_6 concentration was calculated that would be necessary to account for the difference in the mean residence time deduced from tritium and dissolved gases. Compared to present atmospheric levels, an 'excess' of up to 80% would be necessary to account for these differences. In general, SF_6 shows the biggest discrepancy to the tritium data.

If gas exchange between groundwater and soil air occurs, the CFC and SF_6 clock will be partially reset toward zero, and CFC and SF_6 derived ages therefore indicate only a minimum mean residence time.

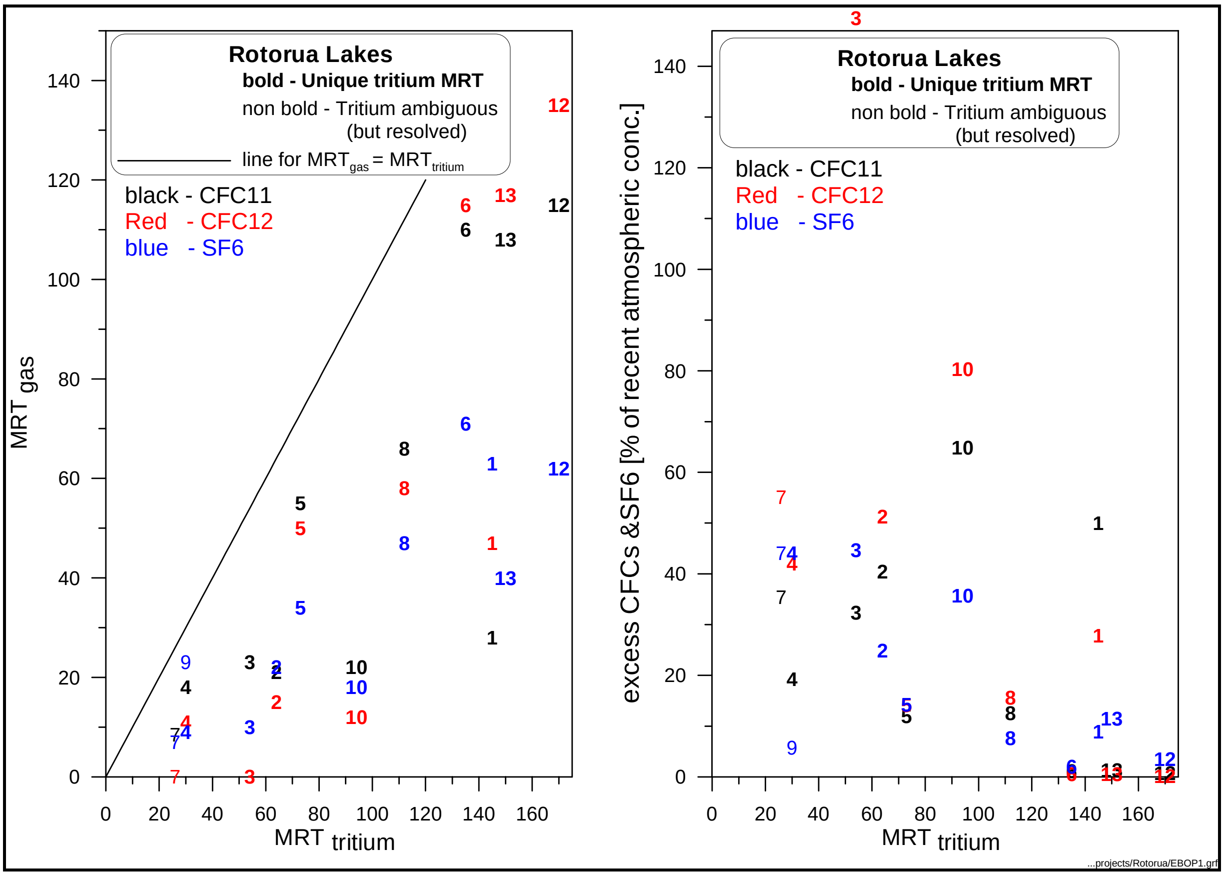


Figure 11. Comparison of tritium and CFC - SF_6 results. Mean residence times at left, and excess gas that would be necessary to account for the difference in tritium and gas MRT at right. Mean residence times deduced from CFCs and SF_6 are generally too low (see text), with the likely reason of gas exchange in the thick unsaturated zone and in the unconfined aquifer.

Tritium is an ideal conservative tracer for groundwater flow, and for age interpretation highest emphasis was given to the tritium results with unique age solution (which in most cases gave pre-bomb recharge) for the following reasons:

- The gas results were inconsistent between one another (potential gas exchange), and
- CFCs are prone to contamination (which was observed in several cases).
- Tritium is inert to chemical alterations,
- Tritium is also not affected by gas exchange process in the unsaturated zone,
- No tritium contamination has ever been observed in New Zealand because there are no nearby nuclear facilities, and
- Some of the tritium age interpretations are based on tritium time series data that shows good agreement with the decay and mixing models.

If available, the unique tritium mean residence times are used. For the ambiguous tritium results, CFCs and SF_6 could be used to resolve the ambiguity despite the differences in ages obtained by the tritium and gas methods. The second tritium age interpretation for these cases is also listed in Table 3, but this solution is considered unlikely.

3.4 Groundwater age dating results

Mean residence times (MRT) and the percentage of young water calculated for the Rotorua springs and groundwater wells are listed in Table 4. The ‘percentage of young water’ is the fraction of the groundwater mixture (in %) that was recharged within the last 55 years. This is the assumed time since land-use intensification in the Rotorua area started. The date of land-use intensification of 55 years ago is based on new data collected by Environment Bay of Plenty and supersedes the 40 year ago assumption used in Morgenstern et al (2004).

Most of these groundwaters are relatively old (mean residence time >30 years). The corresponding young water fractions are therefore significantly below 100%. Significant fractions of these waters were recharged before land-use intensification, and therefore do not yet reflect the full effect of current land-use practices. Even if the recharging groundwater is contaminated, contaminant levels in these waters would still be low because the contaminant has not yet arrived in full extent in these groundwater discharges. However, over time the pristine old water in the aquifer will be progressively replaced and increasingly contaminated water will be discharged into the lakes. A further decline in water quality must therefore be expected in the future. Any potential remedial action undertaken now will require decades to take effect because of the time delays.

Only four water samples with mean residence times between 14 and 31 years have young water fractions of >90%. If there is contamination in the recharge area, it will mostly be reflected already in the quality of the discharging water. Further deterioration of water quality would therefore not be expected for these waters (assuming constant contaminant input at the current level).

Table 4. Age results for Rotorua springs and groundwater wells. E%PM is the percentage of piston flow within the total flow volume of the combined exponential-piston flow (Appendix 1). The unique solution was deduced from long-term tritium data, while the applied numbers are chosen from comparison with similar hydrogeologic situation. MRT is the mean residence time of the water, deduced mostly from unique tritium age solutions (or solutions with ambiguity resolved). Yf(55y) is the fraction of water recharged after land-use intensification 55 years ago. The tritium input from Kaitoke (near Wellington) scaled by a factor of 0.9 was used for age interpretation. Hauraki and Kauaka Streams have ambiguous age interpretations, the more likely age is printed in bold.

#	Sample	collected at:	E%PM unique	E%PM applied	MRT Trit. [yrs]	yf(55y) [%]
1	**Hamurana Spring**	beside water intake	**93**		**151**	**27**
2	**Taniwha Spring**	old well	**96**		**46**	**70**
3	**Trout Hatchery Spring**	weir	**80**		**45**	**72**
4	**Te Waireka Spring**	bottling plant intake	**50**		**38.5**	**84**
5	**Barlows Spring**	water supply intake		**75**/100	**76**	**49**
6	**2116**			70	**135**	**19**
7	**1202**			70	**26**	**95**
8	**1561**			70	**112**	**29**
9	**10964**			70	**31**	**90**
10	**3691**			70	**94**	**38**
11	**10963**			45	**40**	**84**
12	**3901**			70	**>170**	**<3**
13	**10424**			70	**150**	**7**
15	**Utuhina Spring**	main	**90**		**115**	**34**
16	**Te Waiowhero**	(Fairy Spring)	**73**		**57**	**61**
17	**Awahou Stream**	Central Rd. bridge	**100**		**62**	**59**
18	**Utuhina Spring #1**	#1	**90**		**115**	**34**
19	**Utuhina Spring #2**	#2	**90**		**115**	**34**
20	**Taniwha Spring**	water intake	**96**		**46**	**70**
21	**Rainbow Spring**		**65**		**41.5**	**78**
22	**Hamurana Spring #1**	#1	**93**		**108**	**38**
23	**Hamurana Spring**	Head spring	**93**		**88**	**45**
24	**Hamurana Spring #3**	#3	**93**		**97**	**41**
25	**Utuhina Stream**	Lake Rd	**100**		**48**	**68**
26	**Ngongotaha Stream**	Ngongotaha Rd		80	**15.5**	**99**
27	**Waiteti Stream**	Ngongotaha Rd		95	**40**	**75**
28	**Awahou Stream**	Hamurana Rd	**100**		**61**	**59**
29	**Hauraki Stream**	Hamurana Rd		100/**50**	4/**35**	100/**88**
30	**Hamurana Stream**	Hamurana Rd	**100**		**110**	**39**
31	**Waiohewa Stream**	Te Ngae Rd (geoth.)		95	**40**	**75**
32	**Waingaehe Stream**	Te Ngae Rd	**100**		**127**	**35**
33	**Puarenga Stream**	Te Ngae Rd (geoth.)	**100**		**37**	**77**
34	**Kauaka Stream**	Waipa State Mill Rd		100/**50**	4/**35**	100/**88**
35	**Upper Puarenga Stream**	SH5-HemoGorge	**90**		**53**	**65**
36	**Waipa Stream**	Hemo Gorge	**75**		**45**	**73**
37	**Awahou Spring**	#1	**96**		**46**	**70**
38	**Awahou**	upstream	**96**		**32**	**83**
39	**Ngongataha stream**	Paradise springs		70	**13.5**	**100**

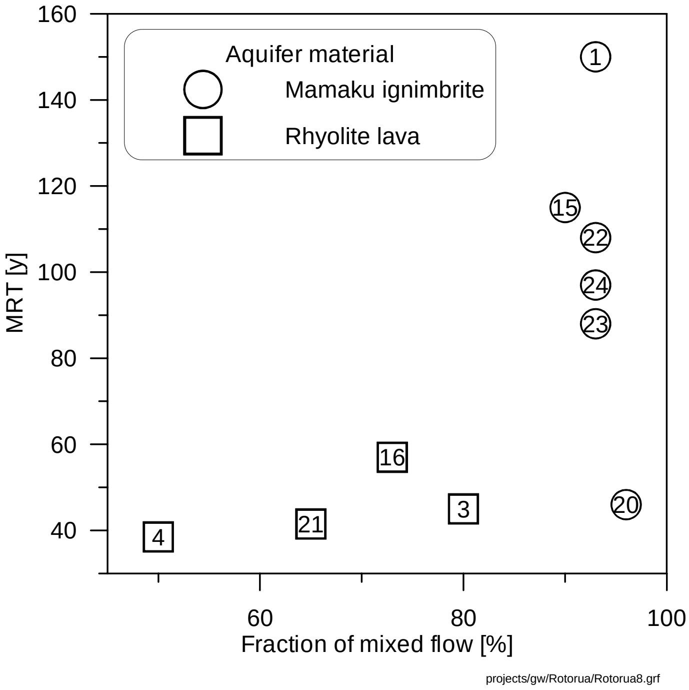


Figure 12. Mean residence time versus fraction of mixed flow for the springs emerging from ignimbrite and rhyolite aquifers.

The mixed flow fraction for the natural springs versus mean residence time, deduced from long-term tritium data, is shown in Fig. 12. The Mamaku ignimbrite aquifers yield significantly higher mixing fractions and mean residence times compared to the water in the rhyolite dome aquifers.

4.0 HYDROCHEMISTRY

The hydrochemical component of this investigation involved the collection and analysis of samples from 39 sites in the Rotorua area (8 bores, 17 springs, and 14 streams). One sample was collected from each site between July and November of 2003 using standard sampling guidelines (Rosen et al., 1999). Unfiltered samples were analysed by GNS for alkalinity, pH and conductivity, filtered (0.45 µm pore size) unpreserved samples were analysed for Br, F, Cl and SO_4, and filtered preserved (nitric acid) samples were analysed for Na, K, Ca, Mg, Fe, Mn and SiO_2. Filtered unpreserved samples were analysed by Hill Laboratories for NO_3-N, NO_2-N, NH_4-N, Nitrate-nitrite nitrogen (NNN) and dissolved reactive phosphorus (PO_4-P). An unfiltered preserved (sulphuric acid) was analysed by Hill Laboratories for Total Kjeldahl Nitrogen (TKN). Finally, an unfiltered unpreserved sample was analysed by Hill Laboratories for total phosphorus (TP). Note that TP and PO_4-P are analysed in different samples, and thus the analytical results can on occasion show higher concentrations of the latter simply due to analytical uncertainties. A summary of the chemistry results is presented in Table 5.

4.1 Initial Assessment of Hydrochemistry using a National Context

An initial attempt to compare the hydrochemistry of the samples collected in this investigation can be made using the categories defined by Daughney and Reeves (2003). These authors defined six categories of groundwater, based on the median concentrations of fifteen analytes from 110 sites in the National Groundwater Monitoring Programme (NGMP). These categories reflect differences in chemical composition associated with oxidation-reduction potential, aquifer lithology and confinement, extent of water-rock interaction, and degree of human impact (Table 6). Four of the six categories are representative of oxidised, surface-dominated systems and have compositions similar to the global average for river water. The other two categories are representative of reduced, subsurface-dominated systems with compositions similar to the global average for groundwater (Table 7). These categories provide a useful framework for comparing the samples collected in this investigation to one another, and to groundwaters from other parts of New Zealand.

Table 5. Hydrochemistry results for bore, spring and stream samples from the Rotorua area. Water type was calculated from major element composition using AquaChem. 'Cat' pertains to category definitions given by Daughney and Reeves (2003) and summarised in Tables 6 and 7. 'Clust' pertains to the four distinct hydrochemical groups (clusters) relevant to the Rotorua area. Pink and green highlights indicate analyte concentrations that are anomalously low or high, respectively, relative to other National Groundwater Monitoring Programme sites in the same category (95% confidence limits).

#	Sample	Date	Water Type	Cat.	Clust.	Br	Ca	Cl	F	Fe	HCO_3	K	Mg	Mn	Na	NH_4-N	NO_2-N	NO_3-N	NNN	TKN	PO_4-P	TP	SiO_2	SO_4	Cond	pH	O_2	Temp
1	Hamurana Spring @ water intake	10/07/2003	Na-Mg-HCO3	1B-2	1	<0.10	3.1	4.7	0.06	<0.02	39	2.5	2.1	<0.0005	9.7	<0.01	<0.002	0.735	ND	<0.1	0.096	0.094	68	1.4	67	6.97	6.6	11.67
2	Taniwha Spring @ old well	10/07/2003	Na-Mg-Ca-HCO3	1B-2	1	<0.10	3.5	5.3	0.05	<0.02	35	1.9	2.2	<0.0005	9.6	<0.01	<0.002	1.41	ND	0.1	0.067	0.127	55	1.6	72	6.85	7.6	12.04
3	Trout Hatchery Spring @ weir	10/07/2003	Na-HCO3-Cl	1B-2	2	<0.10	2	5.3	0.13	<0.02	21	3.3	1.2	<0.0005	7.1	<0.01	<0.002	0.945	ND	<0.1	0.045	0.042	63	3	51	7.17	9.7	10.96
4	Te Waireka @ bottling plant intake	10/07/2003	Na-HCO3	1B-2	2	<0.10	2.4	4.3	0.06	<0.02	26	4.4	1.2	<0.0005	8.2	<0.01	<0.002	1.75	ND	<0.1	0.033	0.024	66	2.3	61	7.09	9.3	11.85
5	Barlows Spring @ water intake	10/07/2003	Na-Mg-HCO3-Cl	1B-2	1	<0.10	2.3	4.4	0.06	<0.02	27	2.7	1.5	<0.0005	6.9	<0.01	<0.002	0.567	ND	<0.1	0.083	0.084	60	1.4	46	6.98	10.1	10.77
6	2116	11/07/2003	Na-HCO3	1B-2	1	<0.10	2.3	4.4	0.08	<0.02	34	0.21	1.3	<0.0005	10.4	<0.01	<0.002	0.223	ND	<0.1	0.081	0.074	77	1.4	50	7.04	9.9	11.48
7	1202	11/07/2003	Na-Ca-HCO3	1B-2	1	<0.10	2.9	4.3	0.03	<0.02	25	1.9	1.4	<0.0005	7.9	<0.01	<0.002	1.4	ND	0.1	0.029	0.025	42	3	56	6.51	7.4	11.88
8	1561	11/07/2003	Na-Mg-HCO3	1B-2	1	<0.10	3.2	4.7	0.05	0.07	39	2.6	2.2	0.0019	10.2	<0.01	<0.002	0.606	ND	<0.1	0.091	0.203	70	1.3	72	6.86	6.4	12.26
9	10964	11/07/2003	Ca-Mg-Na-HCO3-Cl	1A-2	1	<0.10	12.5	13	0.05	<0.02	26	5.5	6.6	0.0007	10.6	<0.01	<0.002	13.7	ND	<0.1	0.048	0.033	54	1.4	199	6.33	5.2	13.63
10	3691	11/07/2003	Na-HCO3	1B-2	1	<0.10	3.9	4.6	0.05	<0.02	58	0.49	2.7	0.009	15.8	<0.01	<0.002	0.847	ND	<0.1	0.045	0.065	62	1.4	104	6.78	5.6	12.53
11	10963	21/08/2003	Ca-Na-Mg-HCO3	1A-2	1	<0.10	7	5.3	0.03	<0.02	31	6	2.6	<0.0005	7.5	<0.01	<0.002	3.84	ND	0.1	0.015	<0.004	60	5.7	99	6.16	6.8	12.7
12	3901	21/08/2003	Na-HCO3-Cl	1B-2	3	<0.10	0.33	5.4	0.1	0.43	27	0.7	0.17	0.0008	14.5	0.02	<0.002	0.1	ND	<0.1	0.585	0.587	75	4.7	55	6.88	9	12.6
13	10424	21/08/2003	Na-HCO3	2A	3	<0.10	2.5	3.6	0.14	3.78	49	2.7	1	0.162	11.4	0.32	<0.002	0.012	ND	1.3	0.021	1.32	74	0.13	64	7.09	0.2	13.6
14	Spring 2	21/08/2003	Na-HCO3-SO4	1B-2	2	<0.10	2.5	2.2	0.03	<0.02	21	5.9	1.4	0.0021	9.6	0.02	<0.002	1.8	ND	1.6	0.041	0.093	81	14.6	70	6.75	10	10.2
15	Utuhina Spring (main)	21/08/2003	Na-HCO3	1B-2	1	<0.10	2.5	4	0.06	<0.02	32	2.1	1.5	<0.005	8.9	< 0.01	< 0.002	0.405	0.405	< 0.1	0.08	0.079	73	2.3	57	7.25	10.7	12.2
16	Fairy Spring (Te Waiowhero)	22/11/2003	Na-HCO3-Cl	1B-2	2	<0.10	2	4.9	0.11	<0.02	18.7	2.7	0.87	<0.005	6.6	< 0.01	< 0.002	0.83	0.83	< 0.1	<0.05	0.038	61	2.6	46	7.15	10.3	11.8
17	Awahou Stream @ Central Rd bridge	21/08/2003				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
18	Utuhina Spring #1	22/11/2003				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
19	Utuhina Spring #2	22/11/2003				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
20	Taniwha Spring @ water intake	22/11/2003	Na-Ca-Mg-HCO3	1B-2	1	<0.10	4	5.3	0.04	<0.02	33	2.1	1.9	<0.005	9.1	< 0.01	< 0.002	1.39	1.39	< 0.1	0.06	0.061	59	1.9	63	7.27	9.3	12
21	Rainbow Spring	22/11/2003	Na-Ca-HCO3-Cl	1B-2	2	<0.10	2.2	4.9	0.08	<0.02	19.7	2.8	0.9	<0.005	6.6	0.05	< 0.002	0.867	0.867	0.1	0.05	0.048	57	2.7	45	7.02	10.1	12.8
22	Hamurana Spring #1	22/11/2003				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
23	Hamurana head spring	22/11/2003	Na-Ca-HCO3	1B-2	1	<0.10	2.9	4.7	0.05	<0.02	32	2.2	1.6	<0.005	8.5	< 0.01	< 0.002	0.775	0.776	< 0.1	0.07	0.074	60	1.7	63	6.77	9.4	11.5
24	Hamurana Spring #3	22/11/2003				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
25	Utuhina Stream @ Lake Rd	22/11/2003	Na-HCO3-Cl	1B-2	4	<0.10	3.4	14	0.41	0.23	35	3.7	1.1	0.04	17.3	0.06	0.003	0.685	0.688	0.2	<0.05	0.051	68	7.6	119	6.87	7	16.2
26	Ngongotaha Stream @ Ngongotaha Rd	22/11/2003	Na-Ca-HCO3-Cl	1B-2	2	<0.10	2.6	4.7	0.06	0.21	22	3	1.1	0.02	6.3	0.02	< 0.002	0.736	0.738	0.2	<0.05	0.051	46	2.3	52	6.97	9	15.6
27	Waiteti Stream @ Ngongotaha Rd	22/11/2003	Na-Ca-HCO3-Cl	1B-2	2	<0.10	3.3	5.3	0.04	0.17	28	2.6	1.4	0.02	8	< 0.01	< 0.002	1.22	1.22	< 0.1	<0.05	0.043	50	2.2	64	7.07	10.2	14.9
28	Awahou Stream @ Hamurana Rd	22/11/2003	Na-Ca-HCO3	1B-2	1	<0.10	3.6	5.2	0.05	<0.02	35	2	1.8	<0.005	9.4	< 0.01	< 0.002	1.21	1.21	0.4	0.07	0.065	58	1.6	73	6.78	8.9	12.7
29	Hauraki Stream @ Hamurana Rd	22/11/2003	Ca-Na-HCO3	1B-2	2	<0.10	5.5	5	0.04	1.2	37	3.9	1.6	0.09	6.2	0.02	0.004	0.193	0.197	0.2	<0.05	0.019	52	1.9	71	6.66	6	17
30	Hamurana Stream @ Hamurana Rd	22/11/2003	Na-Ca-HCO3	1B-2	1	<0.10	3	4.6	0.05	<0.02	34	2.3	1.6	<0.005	9	0.02	0.002	0.703	0.705	< 0.1	0.08	0.082	62	1.7	62	7.01	11.1	12.3
31	Waiohewa Stream @ Te Ngae Rd	22/11/2003	Na-Ca-Mg-SO4	2A	4	<0.10	7.4	7.2	0.11	0.2	14.5	3.5	3.5	0.22	14.1	1.8	0.03	1.16	1.19	1.9	<0.05	0.061	65	40	166	7.08	8.9	14.9
32	Waingaehe Stream @ Te Ngae Rd	22/11/2003	Na-Mg-HCO3	1B-2	4	<0.10	4.2	7.7	0.21	<0.02	40	3.1	3.4	0.007	13.5	< 0.01	< 0.002	1.31	1.31	0.1	0.1	0.1	81	10.3	111	7.24	10.2	15.3
33	Puarenga Stream @ Te Ngae Rd	22/11/2003	Na-Cl-SO4	1A-2	4	0.13	4.5	43	0.41	0.44	19.2	6.9	1.7	0.12	42	0.1	0.004	0.987	0.991	0.3	<0.05	0.061	83	37	276	6.39		18.8
34	Kauaka Stream @ Waipa State Mill Rd	22/11/2003	Na-Ca-HCO3-Cl	1B-2	2	<0.10	3.6	6.9	0.05	0.49	30	3.3	1.5	0.08	8.9	0.03	0.002	0.695	0.697	0.3	<0.05	0.05	64	2.8	68	7.48	10.6	12.4
35	Upper Puarenga Stream @ SH5 - Hemo Gorge	22/11/2003	Na-Ca-HCO3	1B-2	2	<0.10	3.1	4.3	0.12	0.52	30	2.6	1.5	0.09	8.5	0.02	0.003	0.56	0.563	0.2	<0.05	0.074	65	3.7	60	7.71	10.2	13.5
36	Waipa Stream @ Hemo Gorge	22/11/2003	Na-HCO3-Cl-SO4	1A-2	4	<0.10	4.6	19.5	0.13	0.32	38	5.3	2.3	0.07	24	0.04	0.006	1.92	1.93	0.2	<0.05	0.043	58	16.5	170	7.3	10.6	12.4
37	Awahou spring #1	16/12/2003	Na-Ca-HCO3	1B-2	1	<0.10	3.9	5.3	0.04	<0.02	35	1.8	1.8	<0.005	9.6	0.01	< 0.002	1.37	1.37	< 0.1	0.06	0.054	55	1.3	73	7.04	7.5	12.4
38	Awahou upstream	16/12/2003	Na-Ca-HCO3-Cl	1B-2	1	<0.10	3.7	5.4	0.05	0.02	30	2.3	1.6	0.009	8.2	0.01	0.003	1.56	1.56	0.1	0.05	0.054	45	1.6	66	6.76	7.7	13.3
39	Ngongataha stream @ Paradise springs	10/07/2003	Na-Ca-HCO3-Cl	1B-2	2	<0.10	2.3	4.5	0.08	0.1	22	4.2	0.83	0.03	6.5	< 0.01	< 0.002	0.777	0.779	< 0.1	<0.05	0.012	58	2.6	52	6.85	9.8	15.5

Note: NNN is Nitrate-Nitrite Nitrogen, TKN is Total Kjeldahl Nitrogen, TP is Total Phosphorus. Concentrations for all analytes in mg/L, except for conductivity in µS cm^{-1}, pH in pH units and temperature in ºC.

Table 6. General characteristics of groundwater hydrochemical categories defined by Daughney and Reeves (2003).

Category	Description	Category	Description	Category	Description
1	Surface-dominated Oxidised Unconfined aquifer Low to moderate TDS Ca-Na-Mg-HCO_3 water	1A	Signs of human impact Moderate TDS Na-Ca-Mg-HCO_3-Cl water Rainfall recharge?	1A-1	Moderate human impact Carbonate or clastic aquifer Ca-Na-Mg-HCO_3-Cl water
				1A-2	Most human impact Volcanic or volcaniclastic aquifer Na-Ca-Mg-HCO_3-Cl water
		1B	Little human impact Low TDS Ca-Na-HCO_3 water River recharge?	1B-1	Carbonate or clastic aquifer Ca-HCO_3 water
				1B-2	Volcanic or volcaniclastic aquifer Na-Ca-Mg-HCO_3-Cl
2	Groundwater-dominated Reduced Confined aquifer Higher TDS Ca-Na-HCO_3 water			2A	Moderately reduced High TDS
				2B	Highly reduced Highest TDS

Table 7. Median concentrations (mg/L) for groundwater categories listed in Table 5 (Daughney and Reeves, 2003).

Category	Median Concentration (mg/L)													
	Br	Ca	Cl	F	Fe	HCO_3	K	Mg	Mn	Na	NH_4	NO_3	PO_4	SiO_2	SO_4
1A-1	0.07	15.54	16.92	0.07	0.01	69.71	1.36	7.08	0.01	15.6	0.01	1.51	0	19.15	11.57
1A-2	0.1	13.09	24.71	0.03	0.02	51.32	3.1	7.84	0	20.83	0.01	4.68	0.02	47.03	8.62
1B-1	0.02	18.7	3.11	0.07	0.01	70.6	1.06	2.66	0	5.6	0	0.62	0	11.73	5.18
1B-2	0.04	6.39	7.29	0.04	0.02	34.15	1.46	2.27	0	8.36	0.02	0.73	0.02	23.01	3.86
2A	0.07	25.98	17.95	0.13	0.22	153.04	2.36	7.46	0.07	26.84	1.8	0.02	0.03	27.59	5.75
2B	0.2	57.57	46.3	0.21	1.25	344.99	5.91	13.34	0.44	60.29	12.28	0	0.05	38.38	0.28

Aerobic uncontaminated waters:
In the context described above, Category 1B-2 accounts for 28 of the 34 samples from this investigation for which a category can be assigned. This category is characteristic of oxidised groundwaters, because there is typically little or no dissolved Fe or Mn, and nitrogen is in the form of nitrate (NO_3-N) rather than ammonium (NH_4-N). Groundwaters in this category usually show little evidence of anthropogenic impact from human or agricultural runoff, which is reflected by relatively low levels of Cl and K. Most groundwaters in Category 1B-2 have less than 2.7 g m^{-3} NO_3-N. Finally, groundwaters in Category 1B-2 are usually hosted by volcanic or volcaniclastic aquifers, rather than by carbonate or siliciclastic aquifers.

Aerobic contaminated waters:
Four of the sites (for which a label can be assigned) fall into Category 1A-2. Groundwaters in this category are similar to those in Category 1B-2, in that they are usually hosted by volcanic or volcaniclastic aquifers. However, most groundwaters in Category 1A-2 show significant signs of human impact in the form of elevated K, Cl, and NO_3-N. These substances can be introduced to groundwaters via direct discharge of sewage, or via leaching of K, Cl and NO_3-N through the soil zone during rainfall recharge.

Anaerobic contaminated waters:
The remaining two sites that can be categorised fall into Category 2A. Waters in this category are moderately reduced (oxygen removed), and as a result typically contain measurable concentrations of dissolved Fe and/or Mn, and NH_4-N often exceeds NO_3-N.

Although the samples collected in this investigation can be meaningfully compared to one another and to other sites around New Zealand using the categories defined by Daughney and Reeves (2003), it is important to note that, as a group, waters from the Rotorua area display some unusual chemical features. To identify these features, the concentration of each analyte at each site can be compared to the range of ‘normal’ (i.e. baseline) concentrations expected for each of the six categories. Here, baseline is defined as a range, based on the 5th and 95th percentiles in concentration of each analyte in each of the six categories defined by Daughney and Reeves (2003). In making this comparison, note that the baseline concentration range defined in this manner is based on 110 NGMP sites, only one of which penetrates an ignimbrite aquifer (Pemberton site in the Bay of Plenty region).

The samples collected in this investigation often show much lower concentrations of Ca, Mg and SO_4 and much higher concentrations of F, PO_4 and SiO_2, compared to groundwaters in the same categories but from other parts of New Zealand (Table 5). These hydrochemical features reflect the aquifer lithologies common to the Rotorua area. Ignimbrites are typically depleted in calcium, magnesium and sulfate and enriched in sodium, fluoride, potassium, phosphorus and silicates relative to other rock types (Cox et al., 1979; Faure, 1988; Langmuir, 1997). Therefore a similar chemical pattern is expected in the waters of the Rotorua area, with the pattern becoming more pronounced with increased time of water-rock interaction. Several of the sites sampled in this investigation do indeed show anomalous concentrations of one or more of the above-listed analytes (relative to the NGMP sites), but this pattern should not be considered universally representative of the Rotorua area.

4.2 Refinement of Hydrochemical Assessment for the Rotorua Area

Although the general character of the chemical composition of the waters in the Rotorua area can be assessed using a national perspective as discussed above, refinement of the hydrochemical interpretation requires consideration of the samples from the Rotorua area in isolation.

In this investigation, Hierarchical Cluster Analysis (HCA) was used to further analyse the hydrochemistry of the samples collected in the Rotorua area. HCA is a multivariate statistical method that can be used to assign water samples to a limited number of groups based on any or all aspects of their chemistry (Jaquet et al., 1975; Alther, 1979; Williams, 1982; Farnham et al., 2002 Güler et al., 2002). Each group represents a *facies*, as conceptualised by Back (1961, 1966), Morgan and Winner (1962) and Seaber (1962). By definition, each hydrochemical facies would describe a group of water samples with similar compositions, and each facies would have a unique origin and/or pattern of evolution (Freeze and Cherry, 1979).

After z-scaling of all medians (Helsel and Hirsch, 1992; Daughney and Reeves, 2003), HCA was performed using Br, Ca, Cl, F, Fe, HCO_3, K, Mg, Mn, Na, NH_4-N, NO_3-N, PO_4-P, SiO_2 and SO_4 and all expressed in log molar concentration. After a comparison of different similarity measures, Ward's method and the square of the Euclidean distance were selected as the best linkage rule and the similarity measure, respectively. Ward's method is based on an analysis of variance, and produces smaller distinct clusters than other linkage rules, such that each sample in a cluster is more similar to other samples in the same cluster than to any sample from a different cluster. The combination of Ward's linkage rule and the Euclidean distance similarity measure was also selected by Güler et al (2002) in a comparison of multivariate methods for classification of hydrochemical data.

The output of the HCA is shown in the form of a dendrogram in Figure 13. Using a separation threshold of roughly 250 permits the definition of four clusters relevant to the Rotorua area. These four clusters, simply named 1, 2, 3 and 4, contain 16, 11, 2 and 5 water samples, respectively. Site 33 could be classed as a fifth cluster at this separation threshold, but for the purpose of this investigation, it is included as part of the cluster 4. The cluster to which each sample is assigned is listed in Table 5 and shown by location on Figure 14. Bubble plots showing analyte variation by location are compiled in Appendix 2. Note that for clarity, the sample groups defined for the Rotorua area are called ‘clusters’, whereas the groups defined by Daughney and Reeves, based on data from the entire NGMP, are called ‘categories’. The significance of variation of each analyte between the four Rotorua clusters was assessed using the (non-parametric) Kruskal-Wallis test (α = 0.1) (Helsel and Hirsch, 1992). The results of the Kruskal-Wallis tests are summarised in Table 8, and presented as a set of Box-Whisker plots in Figure 15.

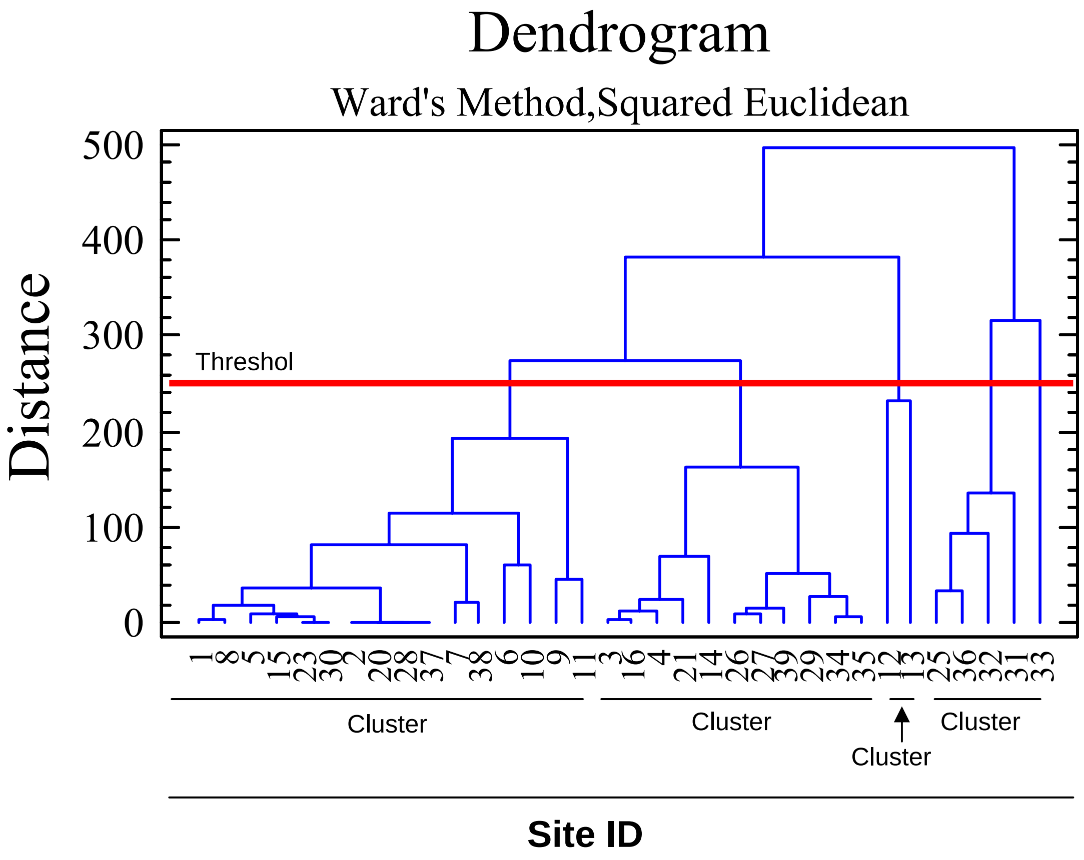
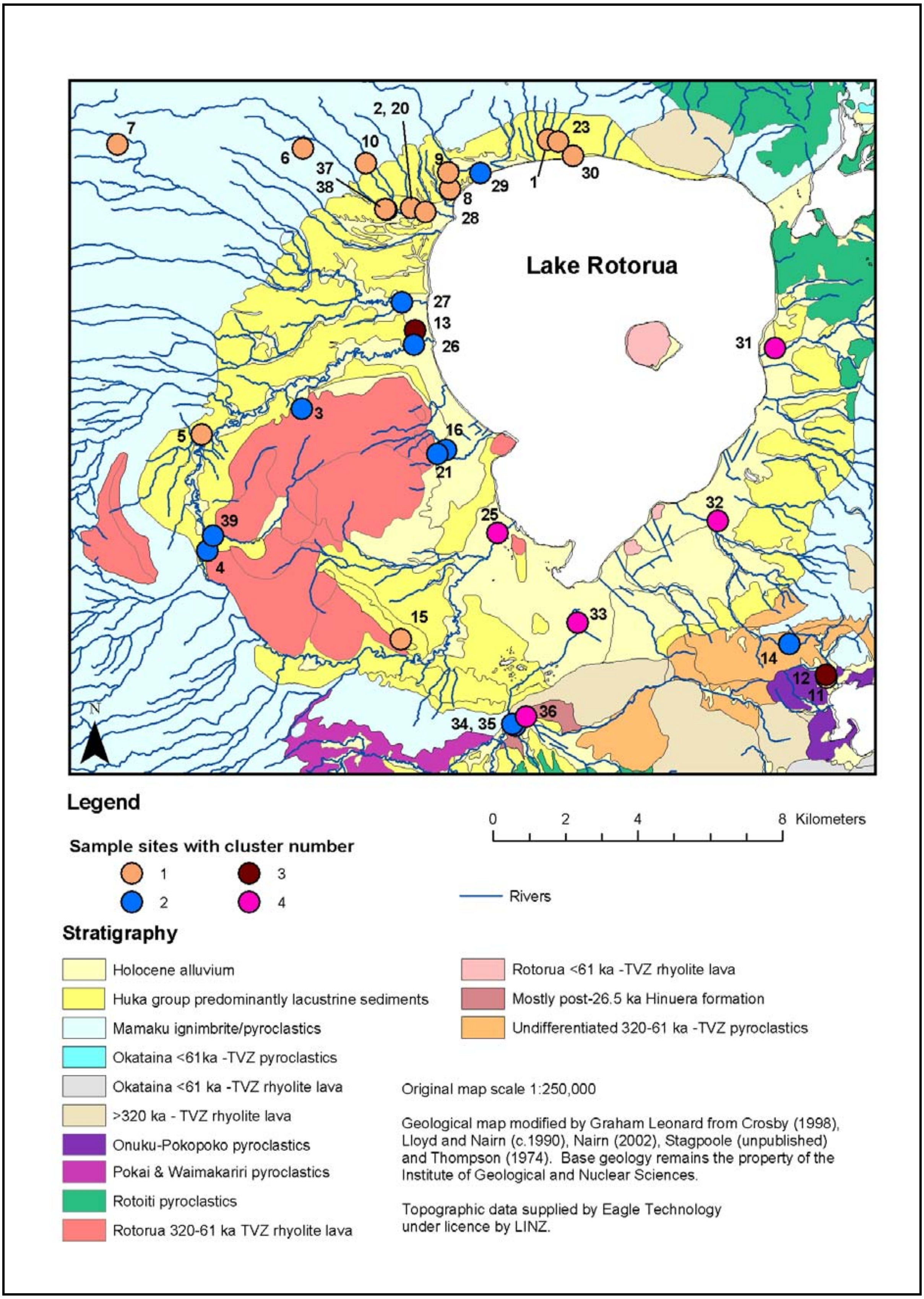


Figure 13. Dendrogram for water samples collected from the Rotorua area, based on log transformed and scaled concentrations of Br, Ca, Cl, F, Fe, HCO_3, K. Mg, Mn, Na, NH_4, NO_3, PO_4, SiO_2 and SO_4. Samples or groups of samples that are the most hydrochemically similar are joined by horizontal lines at the lowest levels on the Distance axis. The red horizontal line shows the level of separation of the four clusters relevant to the Rotorua area.



Original map scale 1:250,000

Geological map modified by Graham Leonard from Crosby (1998), Lloyd and Nairn (c.1990), Nairn (2002), Stagpoole (unpublished) and Thompson (1974). Base geology remains the property of the Institute of Geological and Nuclear Sciences.

Topographic data supplied by Eagle Technology under licence by LINZ.

Figure 14. Sampling sites categorised by cluster types relevant to the Rotorua area.

Table 8. Summary of Kruskal-Wallis tests to determine whether or not median analyte concentrations differ significantly (95% confidence level) between clusters relevant to the Rotorua area. H, M and L indicate clusters for which analyte concentrations are highest, moderate or lowest, respectively. These H, M and L descriptors are only relative, and do not imply that analyte concentrations are anomalously high or low.

	Cluster			
	1	**2**	**3**	**4**
Br	No difference			
Ca	M	M	L	H
Cl	L	L	L	H
F	L	H	H	H
Fe	L	M	H	M
HCO3	No difference			
K	M	H	L	H
Mg	H	M	L	H
Mn	L	H	H	H
Na	M	L	H	H
NH4	L	L	H	H
NO2	L	M	L	H
NO3	No difference			
NNN	Not considered			
TKN	Not considered			
PO4	H	M	H	L
TP	Not considered			
SiO2	No difference			
SO4	L	L	L	H
Cond	L	L	L	H
pH	No difference			
O2	No difference			
Temp	L	L	L	H

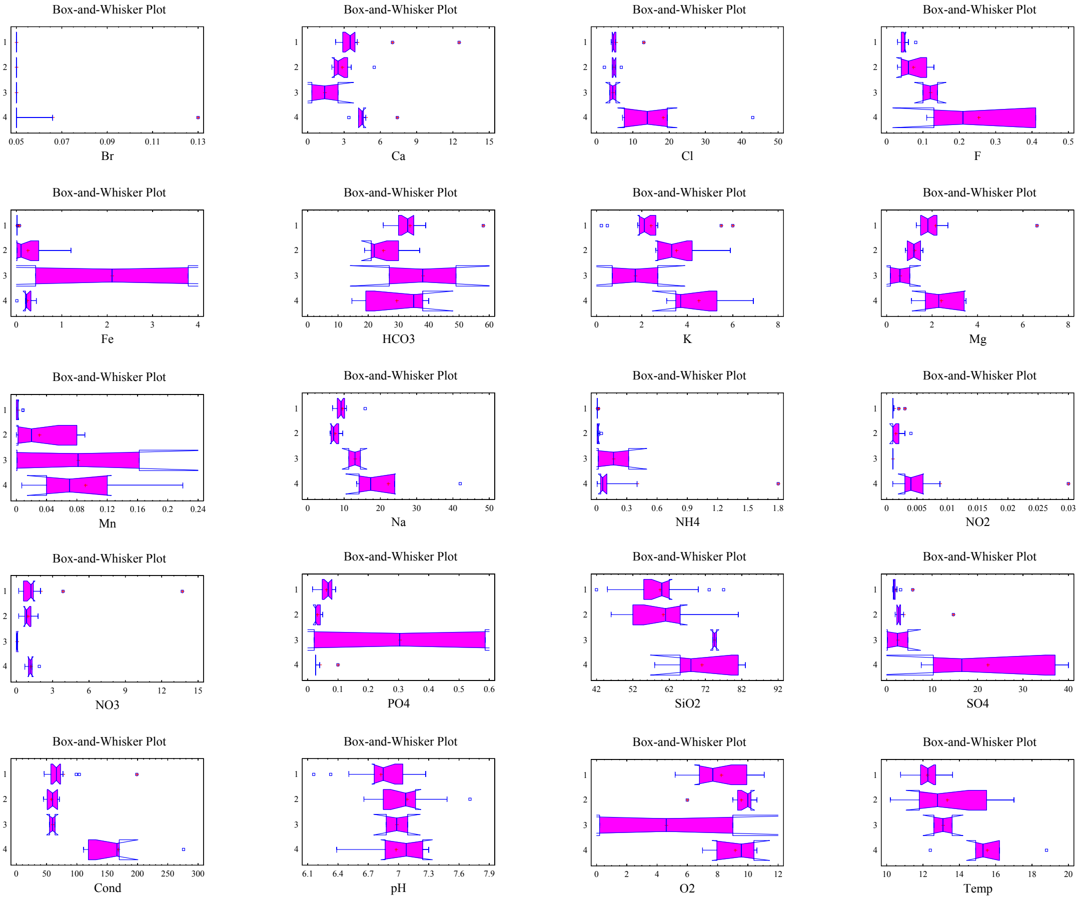


Figure 15. Box-Whisker plots showing differences in analyte concentrations between the four hydrochemical clusters relevant to the Rotorua area. The rectangular part of each box extends from the lower quartile to the upper quartile (i.e. the interquartile range, IQR). The centre line in each box shows the location of the median. The whiskers extend from the box to the minimum and maximum values for each cluster, except for any outside (more than 1.5 times the IQR above or below the box) or far outside points (more than 3 times the IQR above or below the box), which are plotted as squares or squares with plus signs, respectively. Each box also shows notches extending above and below the median value. If the median notches for any two boxes do not overlap, then there is a statistically significant difference between the median values at the 95% confidence level.

The results of the HCA clearly show that water samples from the Rotorua area can be placed into one of at least four different hydrochemical clusters. Based on Figures 14 and 15 and Tables 5 and 8, the following generalisations can be made:

- *Cluster 1* waters are distinguished by having among the lowest concentrations of F, K, and SO_4 found in the Rotorua area, and among the highest concentrations of Mg and PO_4.

Geographically, sites in Cluster 1 are found in the northern and western parts of the Lake Rotorua catchment, and appear to be predominantly associated with the Mamaku Ignimbrite.

- *Cluster 2* waters are distinguished by having low concentrations of Na and HCO_3 and high concentrations of K, relative to other waters in the Rotorua area. Cluster 2 waters may also display higher concentrations of Fe and Mn than waters from Cluster 1. Geographically, most sites in Cluster 2 are located in the west to southwest portion of the Lake Rotorua catchment, and appear to be associated with the rhyolite domes found there.
- There are only two water samples falling into *Cluster 3*. These waters are clearly reduced (low oxygen concentration), as evidenced by measurable concentrations of Fe and Mn, and in one case with NH_4-N in excess of NO_3-N. Cluster 3 waters are also distinguished by very low concentrations of K, Ca and Mg and high concentrations of Na, relative to other water samples from the Rotorua area. Geographically, these two sites are situated on opposite sides of Lake Rotorua. However, both sites are shallow bores, one of which is known to tap alluvial material. It is possible that the aquifers at these two sites contain some organic carbon, which is often required for the onset of reducing conditions.
- *Cluster 4* waters show a range of chemistries, but in general have among the highest conductivities, highest concentrations of Cl and SO_4, and lowest concentrations of PO_4, compared to other waters from the Rotorua area. Waters in Cluster 4 may also show measurable concentrations of Mn and NH_4. These chemical characteristics suggest some geothermal influence and/or influence by agricultural runoff, sewage or septic tank effluent. Geographically, sites in Cluster 4 are located in the southern and eastern parts of the Lake Rotorua catchment and may be associated with alluvial deposits.

There are two caveats that must be listed in regard to the categorisation of water samples based on the four clusters described above. First, it is not clear whether or not the clusters defined in this investigation are equally appropriate for bores, streams and springs. For example, both Cluster 3 waters were collected from bores (Figure 16). The latter is reasonable, since waters in Cluster 3 show characteristics of oxygen depletion, which could occur in an aquifer but would not be expected in a stream. All Cluster 2 and 4 waters were collected from springs or streams, but Cluster 1 waters were collected at bores, streams and springs in almost equal proportion, and so the importance of site ‘type’ is not clear. A second caveat is that the age of a water sample probably affects the extent to which the characteristics of any given cluster are developed. Most of the recharge in the Rotorua Lake catchment originates as rainfall, which would have similar chemistry across the entire catchment. Infiltration of the rainfall into different geological units around the catchment appears to cause the water chemistry to evolve in different directions. For example, waters that equilibrate with the Mamaku Ignimbrite (Cluster 1) appear to develop relatively low concentrations of F, K, and SO_4, and relatively high concentrations of Mg and PO_4. However, for young water that hasn't equilibrated with the rock for an appreciable period of time, this hydrochemistry might not be apparent.

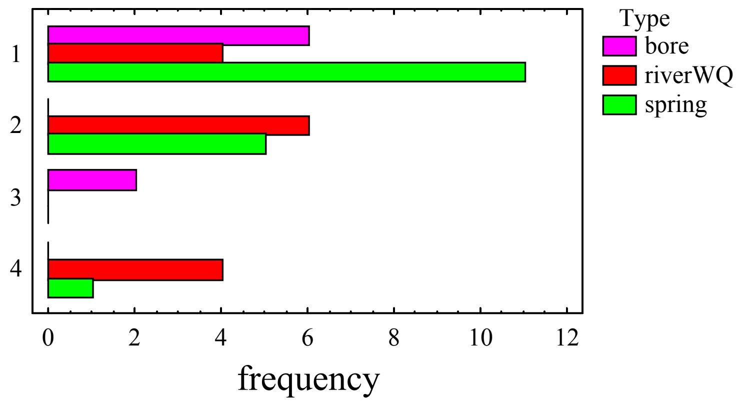


Figure 16. Bar chart of the clusters relevant to the Rotorua area, categorised by feature type.

5.0 TIME TRENDS IN THE CHEMICAL COMPOSITION OF THE GROUNDWATER

The groundwater age distribution is represented by the mean residence time (MRT, years), and the ratio between exponential (mixed) and piston flow (Table 4). The MRT values range from 14 to >170 years. A direct comparison between the samples using the MRT is usually not useful because MRT has a different meaning for different fraction of mixed flow. However, the fraction of exponential (mixed) flow of all these waters (except for well 10963) is in a narrow range between 70% and 100% (section 3.4). Therefore, comparison using MRT is meaningful, and the hydrochemical data are plotted versus MRT in Figures 17-20. The chemical composition of groundwater is altered over time due to increasing contact between the water and the aquifer matrix. This is reflected in some very clear relationships between chemistry and mean residence time.

Water temperature, conductivity, and turbidity are relatively independent of MRT. These parameters do not depend on the time the water has been in contact with the aquifer. For the temperature, this trend can be seen clearly for the Mamaku Ignimbrite samples. Raised temperatures are mostly associated with geothermal inputs or stream waters with raised summer temperatures. Raised conductivities are associated with higher mineralization in geothermal water. Only well 10964 (#9) has unusual high conductivity.

There is a slight trend of pH increase with time for the Mamaku Ignimbrite water. The chemistry changes with increasing contact time between the water and the aquifer minerals, with the result of increasing pH. The pH is 6.5 at MRT 20 yrs, increasing to an equilibration value of 7 which is reached at MRT 50 yrs. The likely explanation is that the chemical reactions during water-rock interaction result in higher pH, and these reactions come closer to equilibrium with increasing contact time. The rhyolite water shows a stronger increase in pH from 6.7 to 7.7 within 50 years of mean residence time. The geothermal samples also reach equilibrium after 50 years of mean residence time, just above pH 7. The oxygen-reduction potential (ORP) is constant over time, with slightly higher spread at younger ages (sample #13 is reducing environment). Mamaku Ignimbrite waters have the highest values, and geothermal waters the lowest.

The relationship between concentration and age indicates progressive water-rock interaction for several chemical species (Fig. 18). In particular, SiO_2, PO_4-P, Na and F concentrations increase with groundwater age due to leaching from the aquifer minerals. SiO_2 concentrations reach high values of about 75 mg/L in the ignimbrite aquifers due to the dissolution of silicate minerals. The highest SiO_2 concentrations are associated with geothermal waters. Langmuir (1997) also reports SiO_2 concentrations of 85 ppm in pyroclastic volcanics. Our dating results indicate that SiO_2 saturation concentration is reached after a mean residence time (time of water-rock interaction) of 130 years. Sodium (Na) is also progressively leached from the aquifer medium, while chloride (Cl) concentrations do not change and are relatively constant at 4.5 mg/L (except the geothermal waters with much higher concentrations), reflecting the NaCl input by rain (about 10 mg/L of Cl in coastal rain and expected to be about 5 mg/L in the central North Island). It is expected that Cl is not being gained in the aquifer, because Cl is generally a conservative tracer in groundwater. Progressive leaching of sodium is indicated by the increasing sodium to chloride ratios, and by ratios higher than that of rain water (about 0.6). Also the geothermal waters, with much higher NaCl concentrations, match the Na/Cl trend of the other groundwaters. Sodium and fluoride trends indicate that saturation is not reached after MRT 170 years. Raised F concentrations are associated with geothermal waters.

Phosphorus shows a clear trend of increasing concentration with age, with highly increased concentrations for the oldest water. In addition to the dissolved PO_4-P, the total phosphorus concentrations (open circles) are plotted in Fig. 18. Most of the PO_4-P and total P values agree, indicating that most of the phosphorus in the groundwater is present in the reactive dissolved PO_4-P form. Only sample #13 has high total P (1.3 mg/L, value not plotted) but little reactive dissolved PO_4-P. The likely reason for this is that the water in this well has anoxic conditions (Section 4.0).

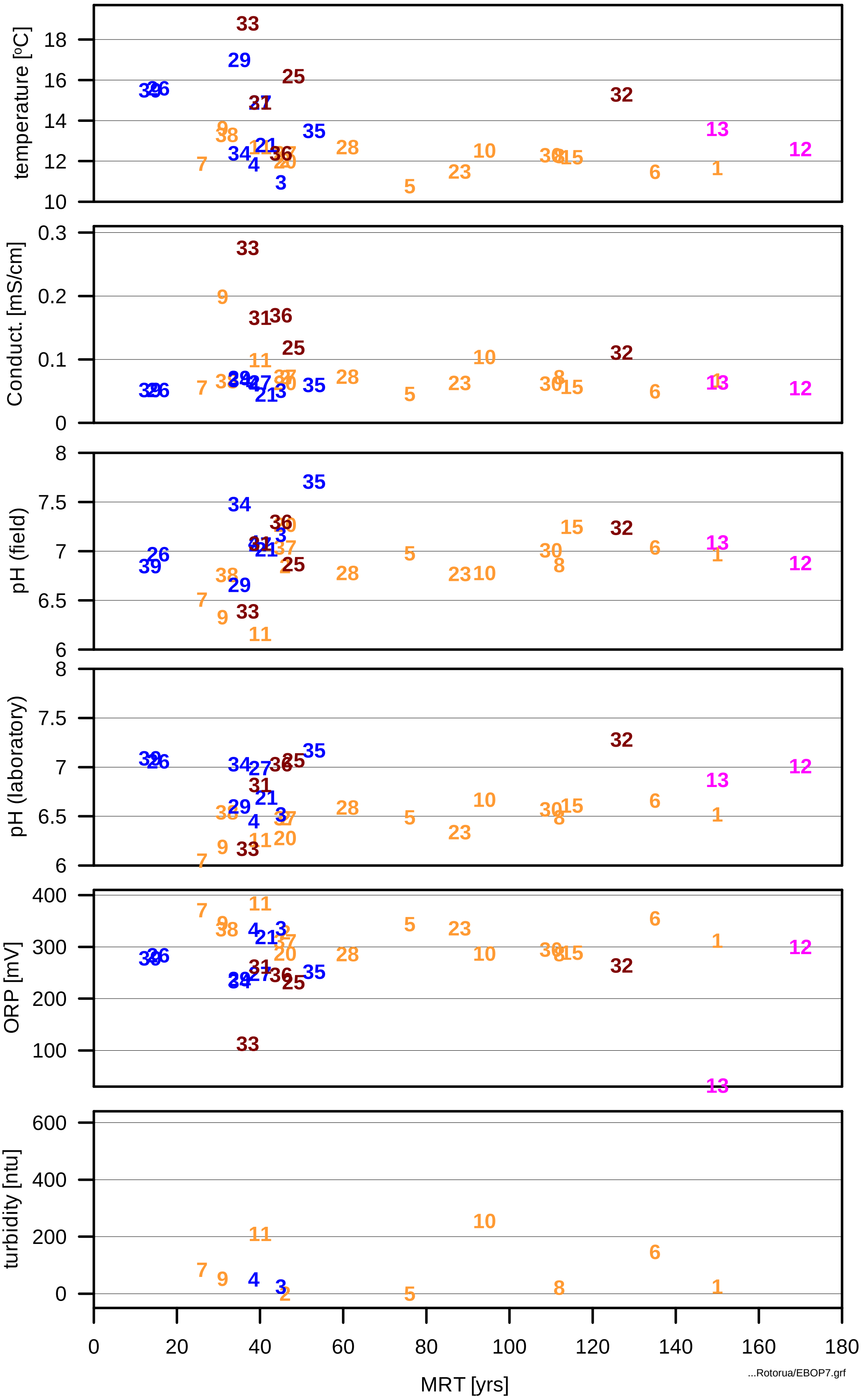


Figure 17. Water parameters versus mean residence time (sample codes in Tab. 1-3). Color code: orange – Mamaku ignimbrite, blue – rhyolite, brown – geothermal, red – cluster 3.

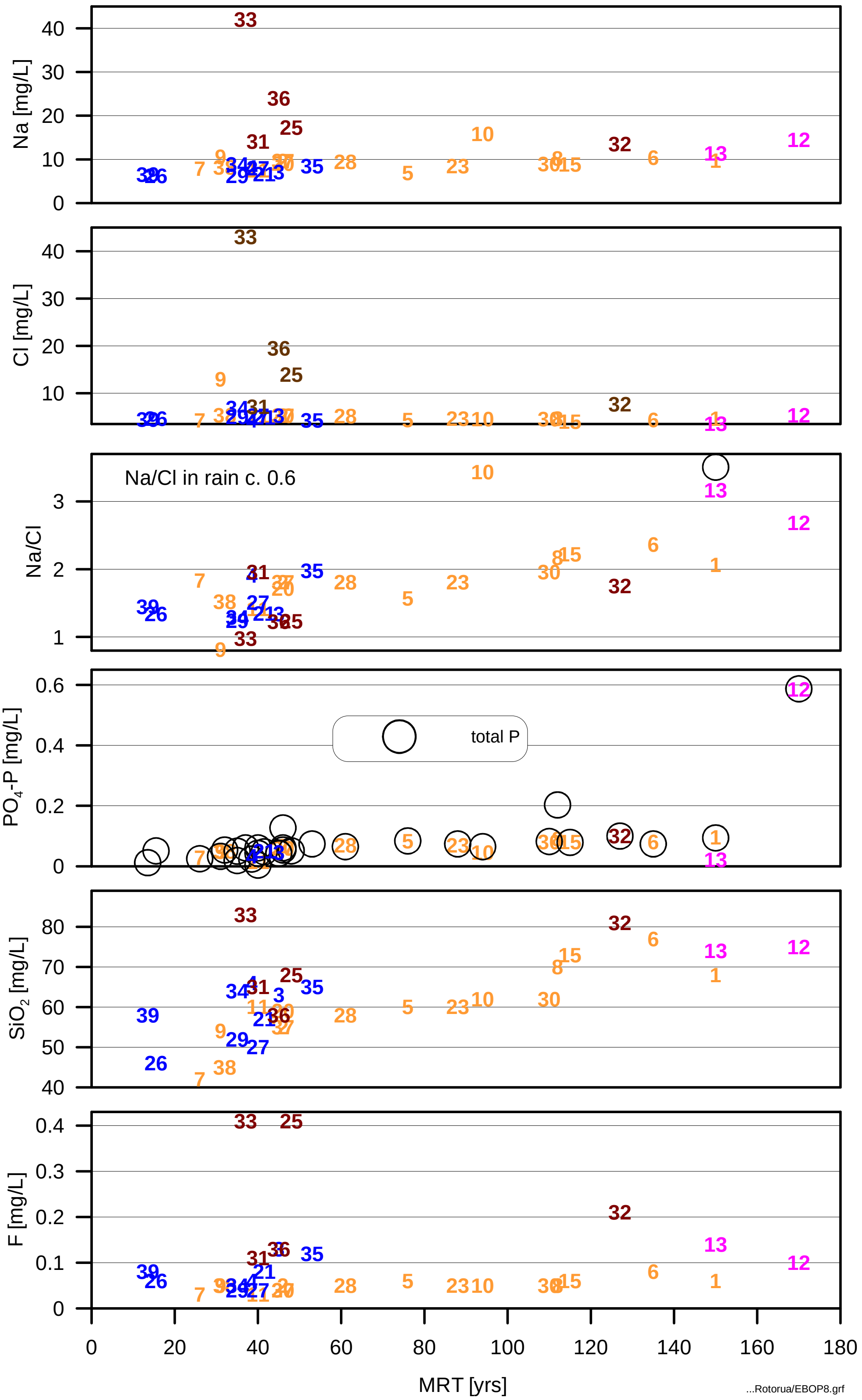


Figure 18. Hydrochemistry versus mean residence time. Color code: orange – Mamaku ignimbrite, blue – rhyolite, brown – geothermal, red – cluster 3.

Some analytes do not increase or decrease significantly with groundwater age (Fig. 19). Concentration of Mg increases only slightly. Ca is constant over time, probably due to the absence of readily-soluble carbonate minerals in the aquifers. On the other hand, there is a trend of increasing concentration with groundwater age for bicarbonate (HCO_3). This increase in HCO_3 cannot be attributed to the dissolution of carbonate minerals because of the likely absence of carbonates in the ignimbrite aquifer, but it could be caused by conversion of CO_2 into HCO_3 by interaction with silicates, or by microbial respiration of organic carbon introduced during recharge. Raised HCO_3 levels in anoxic waters #13, 29 and 36 indicate that microbial respiration of organic matter may be involved in HCO_3 occurrence.

Well 10964 (#9) shows abnormally high concentrations in Mg, Ca, K, and $NO_{3,}$ and has CFC contamination. This indicates clearly anthropogenic impact.

The bulk of the water samples show aerobic conditions. However, increased concentrations in Fe and Mn and depletion of dissolved oxygen clearly indicate anoxic groundwater conditions for well 10424 (#13). Lower dissolved oxygen in stream water #29, and raised Mn and Fe levels in stream waters #29 and #33-36 indicate that these streams are fed from reducing aquifer conditions. Raised Mn levels of streams #25, #31 and #32 may indicate onset of anoxic conditions. Anoxic groundwater conditions are associated with geothermal and rhyolite aquifers, and occur mainly in the southern part of Lake Rotorua.

NO_3-N, K and SO_4 show highest concentration in young groundwater (Fig. 20), in contrast to SiO_2, PO_4, Na, F and HCO_3. This trend strongly suggests that these species are impacted by land-use activities.

Apart from high SO_4 concentrations associated with geothermal groundwaters (excluded in plot), SO_4 shows a trend of elevated values (3 mg/L) in young waters compared to older water (1.5 mg/L). The abnormally low SO_4 concentration in well 10424 (#13) indicates SO_4 reduction in this anoxic aquifer, and well 3901 (#12) is an outlier.

The NO_3 component is clearly the major component of nitrogen in this aquifer (Fig. 20). NO_2, NH_4 and TKN are negligible, except for the anoxic water. For that reason, the trends for nitrogen loading were established on the basis of nitrate only.

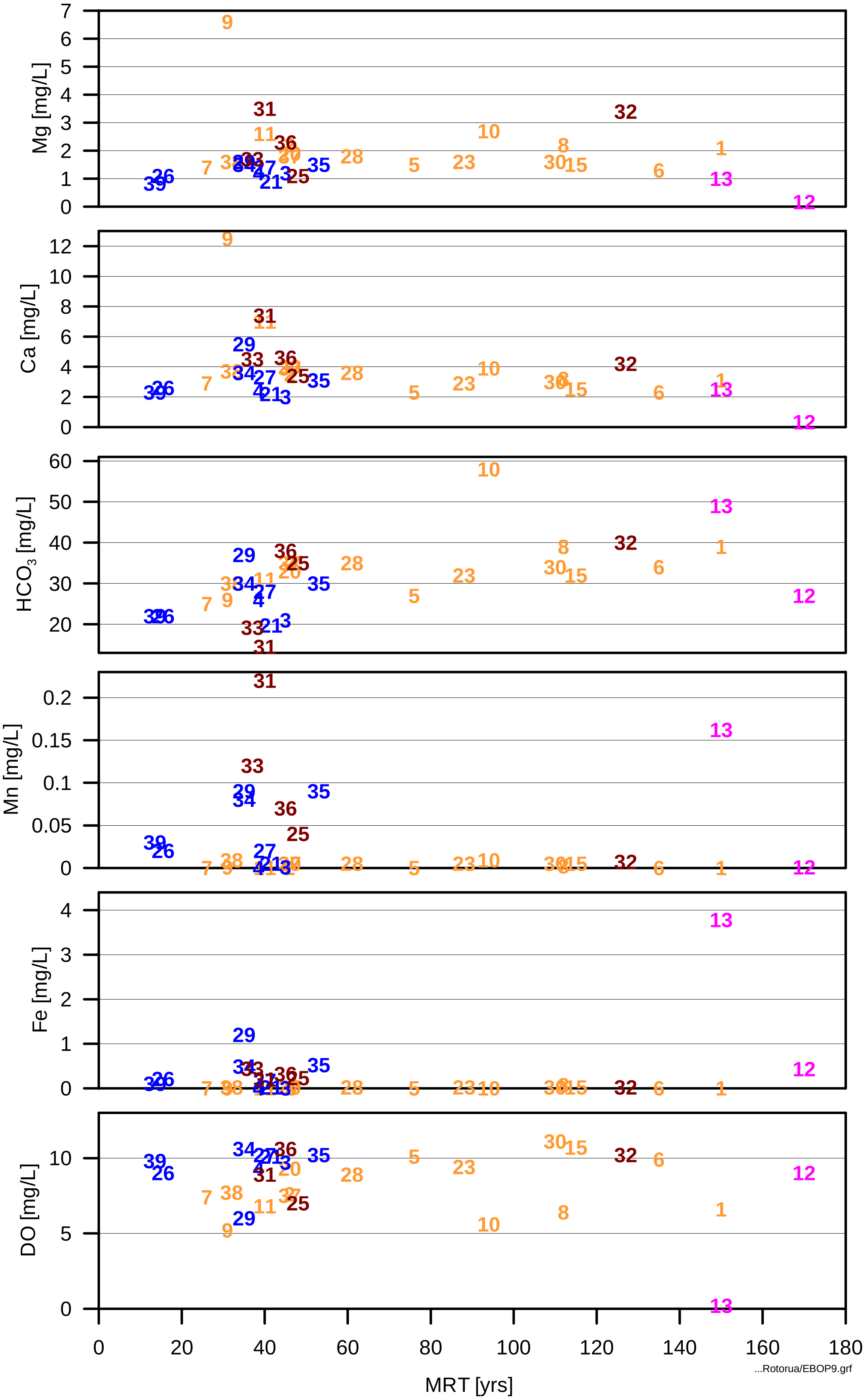


Figure 19. Hydrochemistry versus mean residence time. Color code: orange – Mamaku ignimbrite, blue – rhyolite, brown – geothermal, red – cluster 3.

A decrease in NO_3 concentration with time can be caused by microbial denitrification in reducing conditions where groundwaters become anoxic, such that NO_3 is converted to NH_4. Anoxic sample #13 indicates this, with abnormal low NO_3-N, while the 'missing' NO_3-N appears as NH_4-N. Denitrification is also indicated in anoxic sample #29, with abnormal low NO_3 (NH_4 is not elevated, probably due to degassing in the stream), and in anoxic sample #31, with elevated NH_4. Denitrification processes are indicated in young (#29, 31) and old (#13) water.

All aerobic samples show a clear time trend in NO_3 concentration. The samples span a wide range of sources (springs, streams, wells and geothermal) and cover both major geologic units (ignimbrite and rhyolite). The oldest water has a mean residence time of >170 years which is too old to be affected by land-use, and contains only 0.1 mg/L NO_3-N. The younger waters (MRT <60 yrs) have high fraction of water recharged after land-use intensification, and the nitrate concentrations are high, typically 1-2 mg/l NO_3-N.

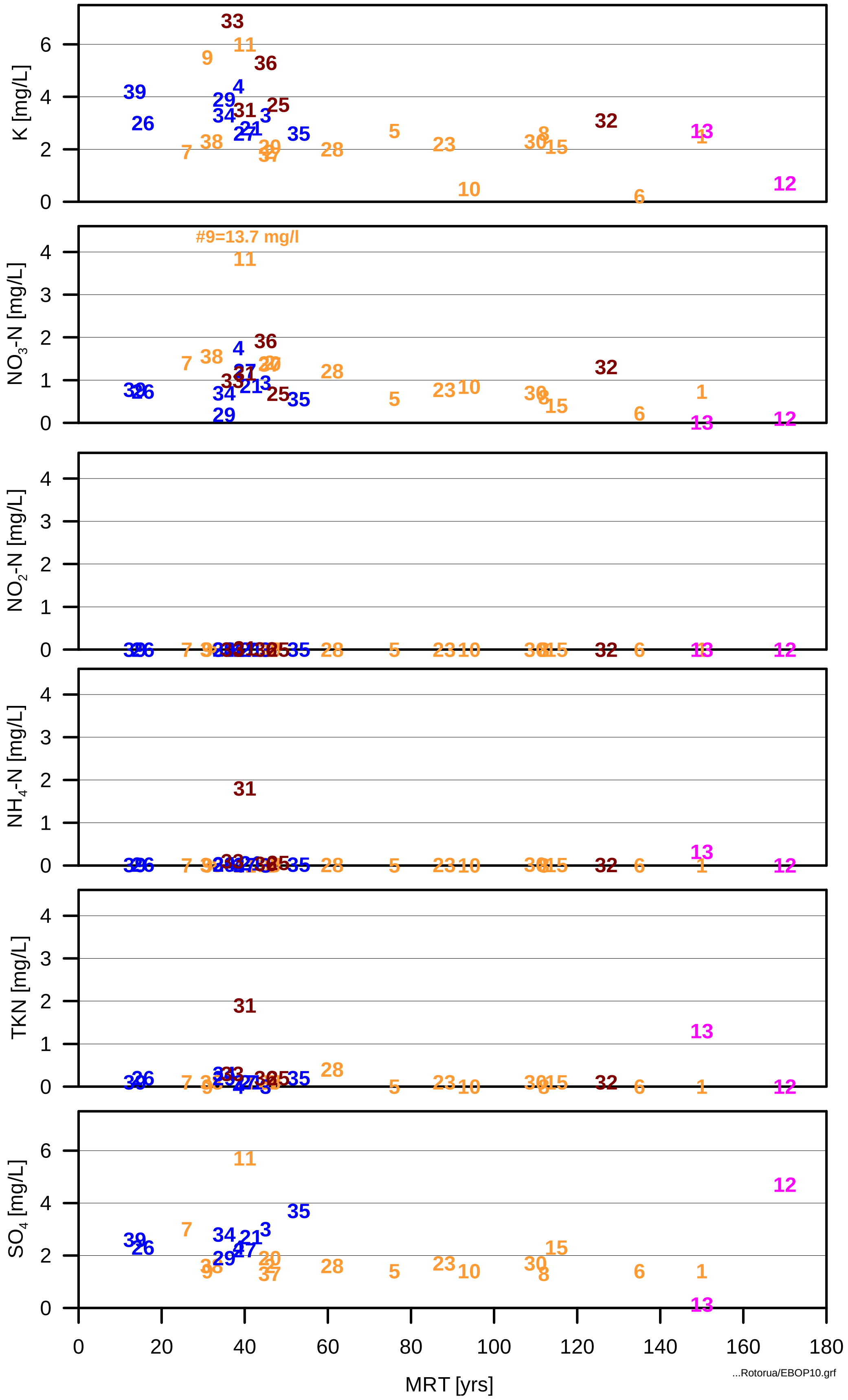


Figure 20. Hydrochemistry versus mean residence time. Color code: orange – Mamaku ignimbrite, blue – rhyolite, brown – geothermal, red – cluster 3.

6.0 CURRENT AND FUTURE NUTRIENT LOADS

Water discharges into the Rotorua Lakes generally are old groundwater (mean residence time 10 to >100 yrs). Therefore increasing contamination can go unrecognised for long periods of time because of the long delay of water moving through the aquifer. In the Mamaku ignimbrite aquifers, it takes many decades for contaminants to work their way through the large aquifer systems, and steady-state for contaminant discharge from landuse intensification since the 1940s has not yet been reached. Contaminant levels are expected to continue to increase in surface water for some time, because of the progressive arrival of contaminated groundwater. Old pristine groundwater in the aquifers is gradually replaced by contaminated water, which discharges back to the surface through springs and directly to lake beds.

Chemical compositions were measured in conjunction with ages to assess the past and current state, and future trends in water chemistry:

- *Background hydrochemistry – undeveloped catchment*
  The natural background water chemistry before land-use intensification can be identified from the old groundwater that is still travelling through the groundwater system. Old water with low young water fraction (recharged prior to land-use change) reflects natural conditions. The natural level of water chemistry depends on the atmospheric, soil, and aquifer conditions, and contact time with the aquifer material. Establishing the natural pre-landuse level water quality without age data is difficult. Even if there is an undeveloped area available with the same hydrogeology for comparison, different residence times of the water in the aquifer can result in different chemical compositions.

- *Impacts of land-use intensification on groundwater quality*
  Water with a high fraction of young water will reflect the hydrochemistry of the current land-use conditions. By subtracting the natural from the current level, the contribution from land-use can be established.

- *Prediction of future trends in groundwater quality*
  By scaling the land-use contribution to 100% young water (when all water fractions are recharged after land-use intensification), future water chemistry concentrations can be estimated for the current contaminant input, or for various scenarios of contaminant inputs.

Major nutrients in Lake Rotorua are nitrate, phosphorus, and potassium. Figure 21 shows the concentrations of these nutrients versus the young water fraction. The young water fractions of the samples range between 0 and 100%, so excellent time trends of water chemistry can be established. With the assumption of constant contaminant input to the groundwater from a certain point in time, it is expected that the groundwater contamination from landuse change will be a linear function of the fraction of contaminated water. The plots of NO_3 and K versus young water fraction therefore show the natural background (intercept at 0% young water) and the current contamination level after land-use intensification (intercept at 100% young water).

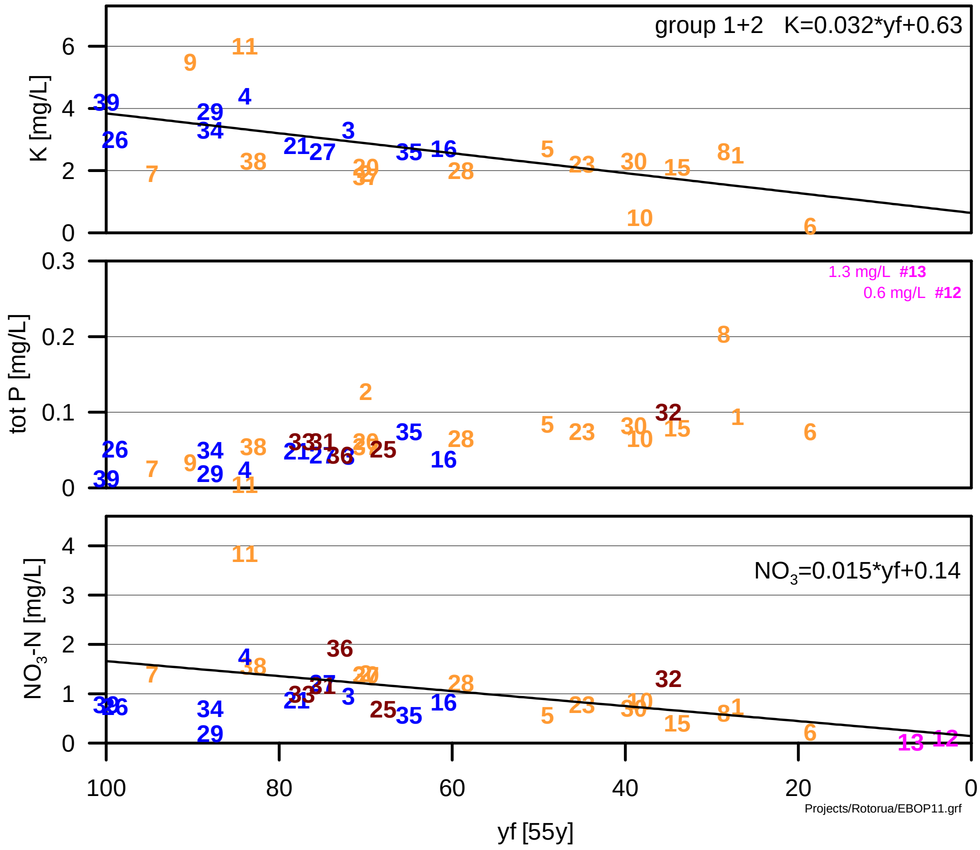


Figure 21, Nutrient concentrations versus young water fraction. Yf(55y) is the fraction of water recharged after land-use intensification 55 years ago. For the K linear fit, only the samples from clusters 1 and 2 are considered (anaerobic and geothermal waters excluded). For the NO_3 linear fit, the anoxic samples #13, 25, 29, 31-36, and the highly contaminated sample #9 are excluded. The anaerobic samples #12,13 have unusual high tot P concentration.

The NO_3 concentration is significantly higher for water with high young fraction (recharged after land-use intensification). The data follow a clear trend over the whole range of young water fractions, allowing for a reasonably accurate estimate of background and current contamination levels.

The natural background level of NO_3-N determined is 0.14 mg/L. The anoxic samples were not included in the regression because their low NO_3 concentrations are likely to be caused by denitrification. The low background level of 0.14 mg/L from the linear regression is in good agreement with the data of well 2116 (#6 - Rotorua catchment) and well 3901 (#12 - Okareka catchment) that have 81% and 97% pre-landuse water and associated NO_3-N concentrations of 0.10 and 0.22 mg/L, and is also in good agreement with stream waters in undeveloped catchments of Lake Taupo that have total nitrogen concentrations of 0.1-0.2 mg/L (Vant & Smith, 2002).

NO_3 shows little scatter around the linear trend suggesting that the nitrate contamination is relatively uniform in the catchment, and/or that the groundwater systems in the Rotorua volcanic aquifer system are relatively well-mixed. This is confirmed by the tritium data which show 70-100% mixed flow (section 3.4).

The linear correlation between NO_3 and young water fraction is an independent indication that no denitrification processes occur in the aerobic Rotorua volcanic aquifers. NO_3 is a stable component in the water even after 50 years and more. The nitrate is still present in the water even after decades of residing in the aquifer, and it returns to the surface with the water after passing through the aquifer.

Elevated NO_3 in the young groundwater is clearly anthropogenic. The current NO_3-N contamination level is determined to 1.6 mg/L. 9% of this can be attributed to the natural background, and 91% to land-use impacts. This is an increase in NO_3-N by a factor 11.

A similar fit to the potassium data indicates a natural background level of 0.6 mg/L and a current level of 3.8 mg/L. About 16% of the current K level is therefore natural background, and 84% is land-use impact. This is an increase by a factor 6. Higher variation of this data along the time trend indicates that the K input to the groundwater is not as uniform as the NO_3 input in the catchment and/or the variation of the natural background is higher. However, it is not clear if the higher anthropogenic K levels will remain constant in the water during passage of the aquifer because K may equilibrate with the aquifer rocks and therefore could be removed from the water, for example through ion exchange. This would reduce the projected future increase. Potassium is not a nutrient of major concern as a contaminant, because it is not a limiting nutrient for algae growth.

Total Phosphorus increases with groundwater age, concentration in young groundwater is <0.04 mg/L and about 0.13 mg/L in old groundwater (higher concentrations in #12 and 13 are related to anaerobic aquifer conditions). Absence of P in the young anthropogenically influenced waters demonstrates that P from land-use practices has not yet leached into the older groundwater but stayed absorbed in the soil. The occurrence of P in the investigated groundwaters is natural due to leaching from the volcanogenic aquifer material because only the old groundwaters contain P, and the concentration increases with time (water-rock interaction). This is consistent with observations by Vant & Smith, (2002) in the Lake Taupo catchment with similar ignimbrite geology and landuse change history. For the naturally leached P in the groundwater, with equilibrium well established, no change in P loading to the lakes is expected. However, if in future P from landuse breaks through the soil as dissolved P, this would increase the P loading to the lakes. Ghani et al. (2004) have found evidence that P has moved down below 1 m depth. While the current data-set does not yet show elevated P in younger groundwater, such P breakthrough would not be visible if it had happened over the last 20 years because the data set includes only waters of mean residence time >20 years.

SO_4 does show anthropogenic influence (higher concentrations in young water), but no time trend was performed because SO_4 has high levels in the lakes from geothermal influence and would not be a limiting nutrient for cyanobacteria growth.

Table 9 summarises the NO_3 and K loads for the streams calculated from the mean flow rates. Most of the nutrient flux via surface streams (ca. 90%) is contributed by the western catchment (Hamurana, Awahou, Puarenga, Waiteti, Ngongotaha and Utuhina Streams) because of the large water flow from the western catchment. The total loads of NO_3-N and K are currently 376 and 1,422 t/year, and are expected to increase to 577 and 2,033 t/year, respectively. An assessment of PO_4 loading is not possible at this stage because the phosphorus samples of the stream waters were not analysed with sufficient detection sensitivity. For some of the streams which originate as multi-spring systems, several sub-springs were sampled for age dating and chemical analysis to verify uniformity and that the measured data are representative of the whole spring system.

Note that the nitrogen projections are now lower than in the previous report [Morgenstern et al. 2004] because of the following reasons: (i) The young water fraction is now calculated for 55 years instead of 40 years (the need for this correction was identified in Morgenstern et al. [2004]), and (ii) Hamurana Spring was previously age dated only at the water intake spring. This spring was now found to be significantly older then the others, and is not representative for the whole Hamurana Spring system (although the chemistry is uniform for all of the Hamurana Springs).

Due to the higher young water fractions, streams are estimated to be closer to steady-state than was originally considered. This means that the nitrate increase expected will not be as dramatic as initially stated, and equilibrium times for reaching steady-state will be about 200 years. This means that reductions in nutrient loading due to potential landuse change would start improving lake water quality sooner (10 instead of 20 years).

Of the major NO_3 contributors, Hamurana and Awahou Streams are expected to have the highest increases in future because they have high flows, and mean residence times considerably older than 55 years and are therefore not yet close to steady-state in regard to

NO_3 from landuse intensification. Therefore, their NO_3 loading is expected to continue to increase. At steady-state, Hamurana Stream is expected to increase its NO_3-N loading from 68 to 154 t/y, and Awahou Stream from 63 to 102 t/y.

Table 9. Estimates of the current and future loads (t/yr) of NO_3-N and K for the Lake Rotorua streams. Mean flow data from Hoare 1976 in Rutherford (2003). The projections of future nutrient loads are based on the assumptions that (i) the input to groundwater from land use remains at the current level, and (ii) water that is younger than 55 years is affected by land-use. Background load is the natural load (product of mean flow and background (bkg) concentration), total load is the current load (product of mean flow and mean concentration), and land-use is the load caused by land-use (difference between total and bkg). The future load is the expected load at steady state, when all of the discharge water is post-1950 (recharged after land-use intensification). Future load land-use is the load resulting from land-use change (current load from land-use change divided by the current fraction of young water). Total future load (the total predicted nutrient load) is the sum of future land-use change load and the background load. Add future load is the additional load at steady state. Total % is the percentage of the individual stream load to the sum of all streams. *Waiowhiro stream was not sampled, yf and NO_3 and K concentrations are averages between Fairy and Rainbow Springs.

						current NO_3-N load				future NO_3-N load			
#	Streams at Lake Rotorua	yf (55y)	mean flow [m^3/s]	current NO_3-N [g/m^3]	bkg NO_3-N [g/m^3]	bkg [t/y]	land-use [t/y]	total [t/y]	total %	land-use [t/y]	total [t/y]	total %	add. [t/y]
25	Utuhina	68	2.04	0.685	0.14	9.0	35	44	12	52	61	11	17
26	Ngongotaha	99	1.98	0.736	0.14	8.7	37	46	12	38	46	8	0
27	Waiteti	75	1.39	1.22	0.14	6.1	47.4	53.5	14	63.2	69.3	12	15.8
28	Awahou	59	1.66	1.21	0.14	7.3	56.1	63.4	17	95.0	102	18	39.0
29	Hauraki	88	0.002	0.193	0.14	0.0	0.0	0.0	0	0.0	0.0	0	0.0
30	Hamurana	39	3.08	0.703	0.14	13.6	54.7	68.3	18	140	154	27	85.6
31	Waiohewa	75	0.41	1.16	0.14	1.8	13.2	15.0	4	17.6	19.4	3	4.4
32	Waingaehe	35	0.27	1.31	0.14	1.2	10.0	11.2	3	28.5	29.7	5	18.5
33	Puarenga	77	2.05	0.987	0.14	9.1	54.8	63.9	17	71.2	80.2	14	16.4
16/21	Waiowhiro*	70	0.41	0.85	0.14	1.8	9.2	11.0	3	13.1	14.9	3	3.9
						59	318	**376**	100	518	**577**	100	200

						current K load				future K load			
#	Streams at Lake Rotorua	yf (55y)	mean flow [m^3/s]	current K [g/m^3]	bkg K [g/m^3]	bkg [t/y]	land-use [t/y]	total [t/y]	total %	land-use [t/y]	total [t/y]	total %	add. [t/y]
25	Utuhina	68	2.04	3.7	0.63	40.6	198	238	17	291	331	16	93
26	Ngongotaha	99	1.98	3	0.63	39.4	148	187	13	150	189	9	1
27	Waiteti	75	1.39	2.6	0.63	27.6	86	114	8	115	143	7	28.8
28	Awahou	59	1.66	2	0.63	33.0	71.8	105	7	122	155	8	49.9
29	Hauraki	88	0.002	3.9	0.63	0.0	0.2	0.3	0	0.3	0.3	0	0.0
30	Hamurana	39	3.08	2.3	0.63	61.2	162	224	16	416	477	23	254
31	Waiohewa	75	0.41	3.5	0.63	8.2	37.1	45.3	3	49.5	57.7	3	12.4
32	Waingaehe	35	0.27	3.1	0.63	5.4	21.0	26.4	2	60.1	65.5	3	39.1
33	Puarenga	77	2.05	6.9	0.63	40.8	406	446	31	527	568	28	121
16/21	Waiowhiro*	70	0.41	2.8	0.63	8.2	27	36	3	39	47	2	12
						264	1158	**1422**	100	1769	**2033**	100	611

The current NO_3 concentrations are still relatively low for the older waters, but these concentrations must be expected to increase in the future because of the progressive arrival of water recharged after land-use intensification. The expected future NO_3 concentrations at steady-state (current concentrations scaled to 100% young water) for the individual springs are plotted in Fig. 22. These will reach values close to the current NO_3 level of young water (1.5 - 4.5 mg/L), which seems plausible. There are no outliers in the dataset, which indicates that there is a large well-mixed groundwater reservoir. The absence of outliers also suggests that the flow-model assumptions are realistic. The highest increase in NO_3 concentration is expected for Waingaehe Stream (#32) due to its old age, and its already high NO_3 concentration.

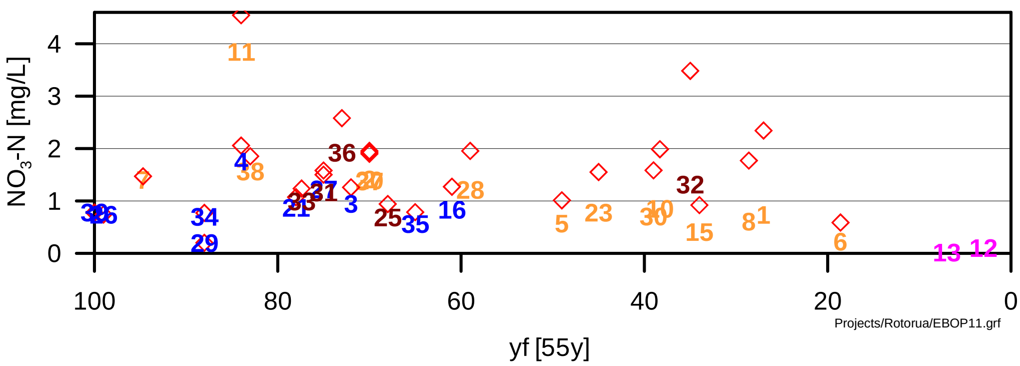
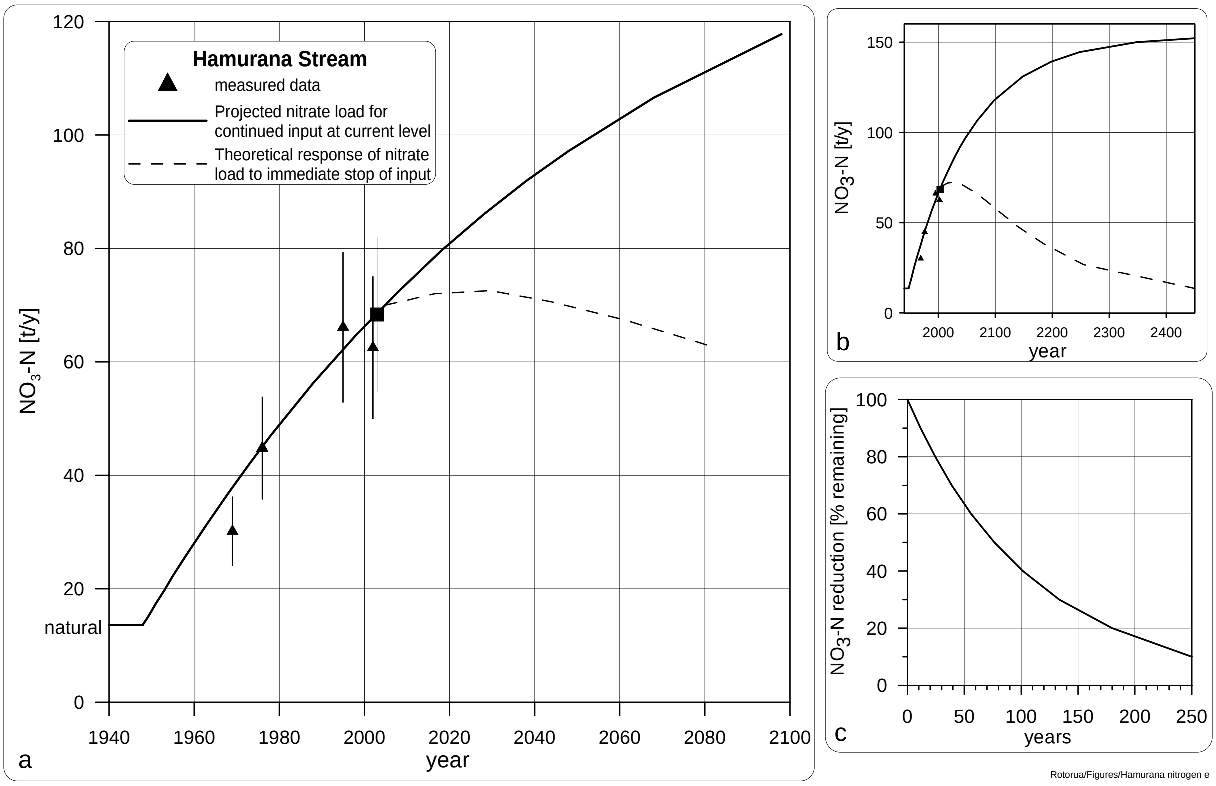


Figure 22. Projected NO_3 concentrations (diamonds), in comparison to their current concentration (numbers). Projected values are not plotted for the oldest waters (yf<10%) because errors due to scaling from near zero to 100% would become excessive.

As an example of how the NO_3 load to Lake Rotorua will respond in future due to the delayed impacts, the projected NO_3 load of Hamurana Springs, the main contributor (27% at steady state), is shown in Figure 23a. The good match between the projected curve and the measured NO_3 data (Fig. 23a) indicates that (i) the assumption of catchment development 55 years ago, and (ii) the flow model used for the calculation of young water fraction, are realistic.

The NO_3 loading in the long-term at steady state is shown in Fig. 23b for continued NO_3 input at the current level. 45% of the future steady-state NO_3 loading has been reached to-date, 90% will be reached in about 200 years. Fig. 23c shows the average response to nitrate reduction, i.e. how NO_3 would decrease in future if the NO_3 input were stopped. This is an average response, landuse changes high up in the valley would have a slower response, and changes near the lake would have a quicker response. For comparison, the theoretical response of NO_3 reduction for Hamurana Stream is shown in Figs. 23a+b (dashed lines) for the case that NO_3 input were stopped immediately in the whole catchment. Due to the delayed impact, NO_3 would decrease only slowly over decades, and would reach near natural background level (down to 10% of steady-state landuse NO_3) in about 250 years.



Rotorua/Figures/Hamurana nitrogen e

Figure 23. **a)** Projected nitrogen loading to Lake Rotorua through Hamurana Springs. **b)** Nitrate loading in the long-term at steady-state. Measured data shown as triangle are from Rutherford 2003. Measured value shown as square is from this report, and this was used for the projection. **c)** Medium response of nitrate reduction to discontinuation of nitrate input.

7.0 CONCLUSIONS

The hydrogeology of the Rotorua Lakes area can be described as a permeable volcanogenic pumiceous surface tephra layer that allows easy penetration of rainwater recharge to deeper volcanic rhyolite and ignimbrite aquifers. These aquifers are essentially unconfined and yield high volumes of groundwater.

The hydrochemistry of groundwater is characterised by much lower concentrations of Ca, Mg and SO_4, and much higher concentrations of PO_4-P and SiO_2 than other groundwaters in New Zealand. This chemical signature reflects the volcanic origin of the aquifer lithology.

Because the aquifers in the Rotorua area have large water storage capacity there is a long residence time for nutrient-laden groundwater. It takes decades for the water after being recharged to reach the spring fed streams and the lakes. The large groundwater bodies have therefore ‘silently’ been contaminated over decades, with the old pristine groundwater being progressively replaced by younger nutrient-laden water that will discharge to the spring-fed streams and finally to the lakes.

Age dating of springs and wells revealed that groundwaters of the Lake Rotorua and Okareka catchments are relatively old, with mean residence times mostly between 40 and >170 years, with only two wells having younger water of 26 and 31 years mean residence time. This corresponds to young water fractions (water recharged within the last 55 years since catchment development) of less then 80%. Therefore significant fractions of these groundwaters were recharged before land-use intensification and these water discharges do not yet show the full effect of the current landuse on the groundwater quality. Further deterioration of water quality must therefore be expected for these water discharges.

Age dating of the main groundwater-fed streams in the Lake Rotorua catchment revealed mostly mean residence times between 35 and 130 years. The streams with the oldest water are Waingaehe (127 years), Hamurana (110 years), Awahou (61 years), and Utuhina Streams (48 years). Only Ngongotaha Stream has younger water of 16 years mean residence time.

Total Phosphorus increases with groundwater age, concentration in young groundwater is <0.04 mg/L and about 0.13 mg/L in old groundwater. Absence of P in the young anthropogenically influenced waters demonstrates that P from land-use practices has not yet leached into the older groundwater but stayed absorbed in the soil. For the naturally leached P in the groundwater, with equilibrium well established, no change in P loading to the lakes is expected. However, if in future P from landuse breaks through the soil as dissolved P, this would increase the P loading to the lakes. While the current data-set does not yet show elevated P in younger groundwater, such P breakthrough would not be visible if it had happened over the last 20 years because the data set includes only waters of mean residence time >20 years. Surface runoff of phosphorus is the subject of other studies.

Trends for nitrate (NO_3), potassium (K) and sulphate (SO_4) indicate that these are increased in the young groundwaters as result of land-use intensification.

The natural background level of groundwater NO_3-N is determined from old groundwater (pre-landuse intensification) to 0.14 mg/L, and the current level is determined from young groundwater (post-landuse intensification) to 1.6 mg/L. Therefore, 9% of the current level can be attributed to the natural background, and 91% to land-use impacts. This is an increase in NO_3 by a factor 11.

Potassium concentrations indicate a natural background level of 0.6 mg/L and a current level of 3.8 mg/L. About 16% of the current K level is therefore natural background, and 84% is land-use impact, an increase by a factor 6. SO_4 shows a trend of elevated values of 3 mg/L in young waters compared to older water of 1.5 mg/L.

Nitrogen loading was calculated from a mass budget for the major streams to Lake Rotorua. Only NO_3-N, the main N component, was considered. Most of the nutrient flux via surface streams (ca. 90%) is contributed by the western catchment - Hamurana, Awahou, Puarenga, Waiteti, Ngongotaha and Utuhina Streams. The total load of NO_3-N is currently 376 t/year, and this is expected to increase to 577 t/year at steady state if the nitrate NO_3-N input in the catchment continues at the current level. 45% of the future steady-state NO_3 loading has been reached to-date, 90% will be reached in about 200 years. Due to the groundwater-delayed impact, NO_3 would also decrease only slowly if the NO_3 input were stopped immediately. Near natural background level (down to 10% of steady-state landuse NO_3) would be reached in about 250 years.

The significant increase in future nitrogen loading for the Lake Rotorua catchment is expected because the land-use impacted contaminated groundwater moves slowly through the large groundwater system and increasingly discharges to the lake via the spring fed streams or directly to the lake bed. Current medium nitrate concentrations found in the springs and streams still reflect the large dilution occurring from the old pristine groundwater. However, some of the major springs and streams are discharging already water with NO_3-N concentrations of 0.7-1.4 mg/L. Most of these concentrations are expected to increase to 1.5-2.5 mg/L if the current landuse patterns continue.

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Appendix 1: Methodology of groundwater Age dating.

Tritium, CFC and SF_6 method

Tritium is produced naturally in the atmosphere by cosmic rays, but large amounts were also released into the atmosphere in the early 1960s during nuclear bomb tests, giving rain and surface water high tritium concentration at this time (Figure 24). Surface water becomes separated from the atmospheric tritium source when it infiltrates into the ground, and the tritium concentration in the groundwater then decreases over time due to radioactive decay. The tritium concentration in the groundwater is therefore a function of the time the water has been underground. Additionally, detection of superimposed bomb tritium can identify water recharged between 1960 and 1975. Groundwater dating using tritium is described in more detail in Cook & Herczeg (1999) and Stewart & Morgenstern (2001).

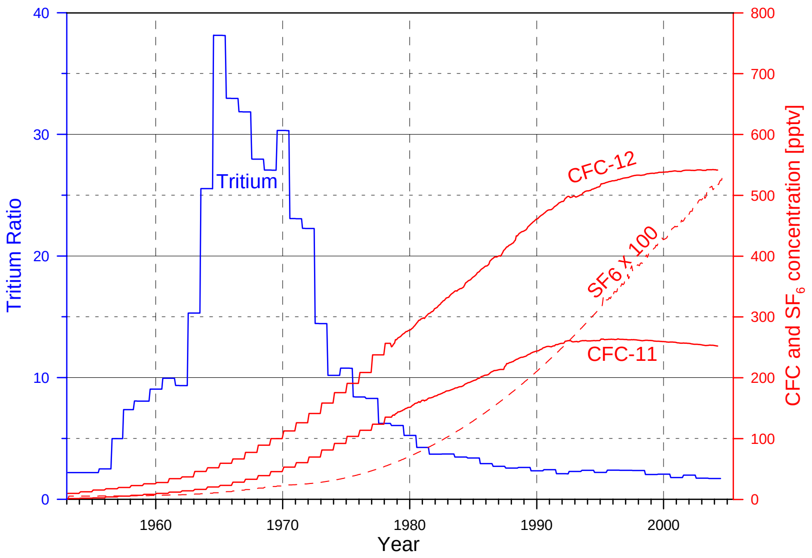


Figure 24. Tritium, CFC and SF_6 input for New Zealand rain. Tritium concentrations are in rain at Kaitoke, 40km north of Wellington (yearly averages), and CFC and SF_6 concentrations are for southern hemispheric air. TR=1 represents a $^3H/^1H$ ratio of 10^{-18}, and 1 pptv is one part per trillion by volume of CFC or SF_6 in air, or 10^{-12}. Pre-1978 CFC data are reconstructed according to Plummer and Busenberg (1999), and scaled to southern hemisphere by factor 0.83 (CFC-11) and factor 0.9 (CFC-12). Post-1978 CFC data are from Tasmania. Pre-1970 SF_6 data are reconstructed (USGS Reston), 1970-1995 data are from Maiss and Brenninkmeijer (1998), and post-1995 data was measured in Tasmania.

As a result of the superimposed atmospheric tritium "bomb" peak in the 1960s, ambiguous ages can occur with single tritium determinations in the age range 15-40 years (i.e. the tritium concentration can indicate any of several possible groundwater ages). This ambiguity can be overcome by using a second tritium determination after about 2-3 years, or combined age interpretation of tritium data and data from an independent dating method, for example CFCs or SF_6. CFC and SF_6 concentrations in the atmosphere have risen monotonously over that time and therefore can resolve tritium ambiguity if they are not altered in the aquifer.

Chlorofluorocarbons (CFCs) are entirely man-made contaminants. They were used for refrigeration and pressurising aerosol cans, and their concentrations in the atmosphere have gradually increased (Fig. 24). CFCs are relatively long-lived and slightly soluble in water and therefore enter the groundwater systems with groundwater recharge. Their concentrations in groundwater record the atmospheric concentrations when the water was recharged, allowing determination of the recharge date of the water. CFCs are now being phased out of industrial use because of their destructive effects on the ozone layer. Thus rates of increase of atmospheric CFC concentrations slowed greatly in the 1990s, meaning that CFCs are not as effective for dating water recharged after 1990.

Sulphur hexafluoride (SF_6) is primarily anthropogenic in origin, but can also occur in some volcanic and igneous fluids. Significant production of SF_6 began in the 1960s for use in high-voltage electrical switches, leading to increasing atmospheric concentrations (Fig. 24). The residence time of SF_6 in the atmosphere is extremely long (800-3200 years). It holds considerable promise as a dating tool for post-1990s groundwater because, unlike CFCs, atmospheric concentrations of SF_6 are expected to continue increasing for some time (Busenberg and Plummer, 1997).

Tritium is a conservative tracer in groundwater. It is not affected by chemical or microbial processes, or by reactions between the groundwater, soil sediment and aquifer material. Tritium is a component of the water molecule, and age information is therefore not distorted by any processes occurring underground. For CFCs, a number of factors can modify the concentrations in the aquifer, including microbial degradation of CFCs in anaerobic environments (CFC-11 is more susceptible then CFC-12), and CFC contamination from local anthropogenic sources (CFC-12 is more susceptible to this), Plummer and Busenburg (1999). CFC-11 has been found in New Zealand to be less susceptible to local contamination and age estimates agree better with tritium data. Note that CFC and SF_6 ages do not take into account travel time through unsaturated zones.

The tritium method is very sensitive to the flow model (distribution of residence times in the sample) due to the large pulse-shaped tritium input during 1965-1975. With a series of tritium measurements, and/or additional CFC and SF_6 measurements, age ambiguity can usually be resolved. In that case, both the mean groundwater age and the age distribution can be obtained.

Groundwater mixing models

Groundwater comprises a mixture of water of different ages due to mixing processes underground. Therefore, the groundwater doesn't have a discrete age but has an age distribution or spectrum. Various mixing models with different age distributions describe different hydrogeological situations (Maloszewski and Zuber, 1982). The piston-flow model describes systems with little mixing (such as confined aquifers and river recharge), while the exponential model describes fully mixed systems (more like unconfined aquifers and local rain recharge). Real groundwater systems, which are partially mixed, lie between these two extremes. They can be described by a combination of the exponential and piston-flow models representing the recharge, flow and discharge parts of a groundwater system respectively. The output tracer concentration can be calculated by solving the convolution integral, and the mean residence time (MRT) can be obtained from the tracer output that gives the best match to the measured data. If the second parameter in the age distribution function, the fraction of mixed flow, cannot be estimated from hydrogeologic information, then two independent tracers (tritium and CFC/SF_6) or two tritium measurements over time are necessary.

Schematic groundwater flow situations are shown in Fig. 25. The unconfined aquifer situation is described by the exponential model (EM). Flow lines of different length containing water of different age converge in the well or the stream, and the abstracted water has a wide range of ages with an exponential age distribution. The confined aquifer situation is described by the piston flow model (PM) with a narrow range of ages. The partly confined aquifer situation is described by the exponential-piston flow model (EPM). The free parameter is the fraction of exponential flow within the total flow volume (represented by E%PM, where the fraction is given in %), or the ratio η of the total flow volume to the volume of the exponential part. The water has a wide range of ages, but because part of the flow is piston flow, the age distribution has a minimum age (no water can be younger than the time necessary to pass through the piston flow part). The piston flow part can be represented by a partly confined flow with no vertical input of young water from the surface, or it can be represented by a significant unsaturated zone with vertical piston flow toward the water table and mixing of different ages below the water table.

As an example, the age distribution for the exponential-piston flow model for different fractions of mixed flow is shown in Fig. 26 for water with a mean residence time of 50 years. Water with a high fraction of exponential flow of 90% has a wide range of ages, starting at 5 years and still significant contributions of old water with ages over 150 years. Despite the mean residence time of 50 years, the major part of the water is younger than 50 years. The water can therefore partly be contaminated before the mean residence time of 50 years has elapsed. About 2% of the water can already be contaminated after 5 years. With each further year, these young fractions accumulate, and increasingly contaminated water arrives at the spring or well. The total fraction of water within a certain age range can be obtained by integrating the age distribution over the specified age range. This is equal to the area below that part of the curve, with the total area below the whole curve being 100% water fraction. The fraction of water that is younger than a specified age is called the young water fraction (yf). The young water fraction younger than 55 years is about 80% in the example in Fig. 26 (hatched area).

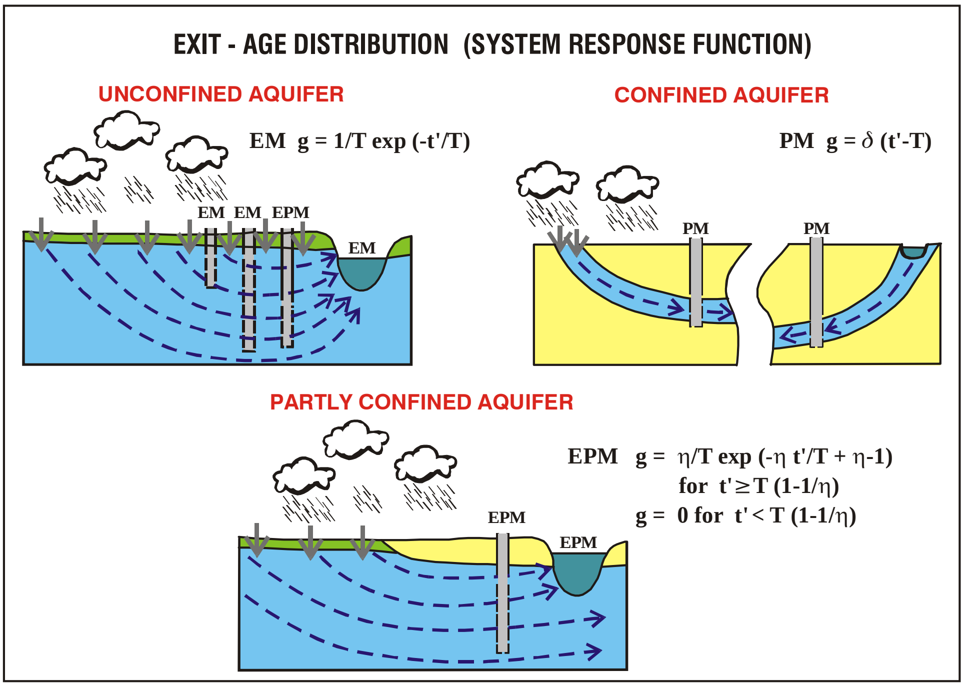


Figure 25. Schematic groundwater flow situations and corresponding age distribution functions (see Maloszewski and Zuber (1982) for theoretical background).

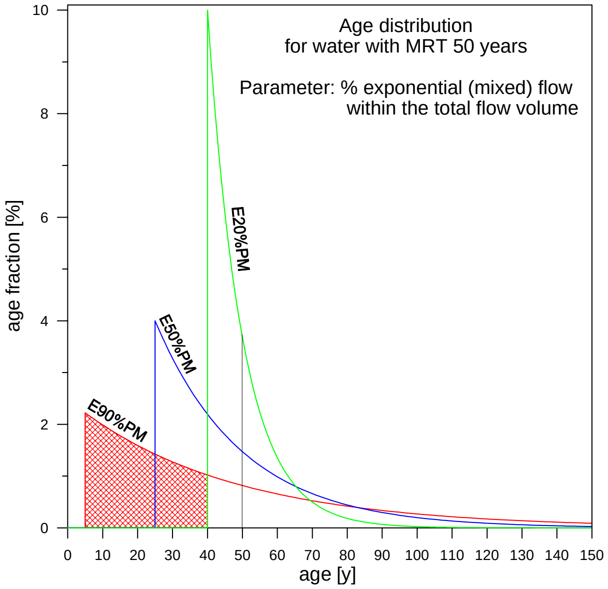
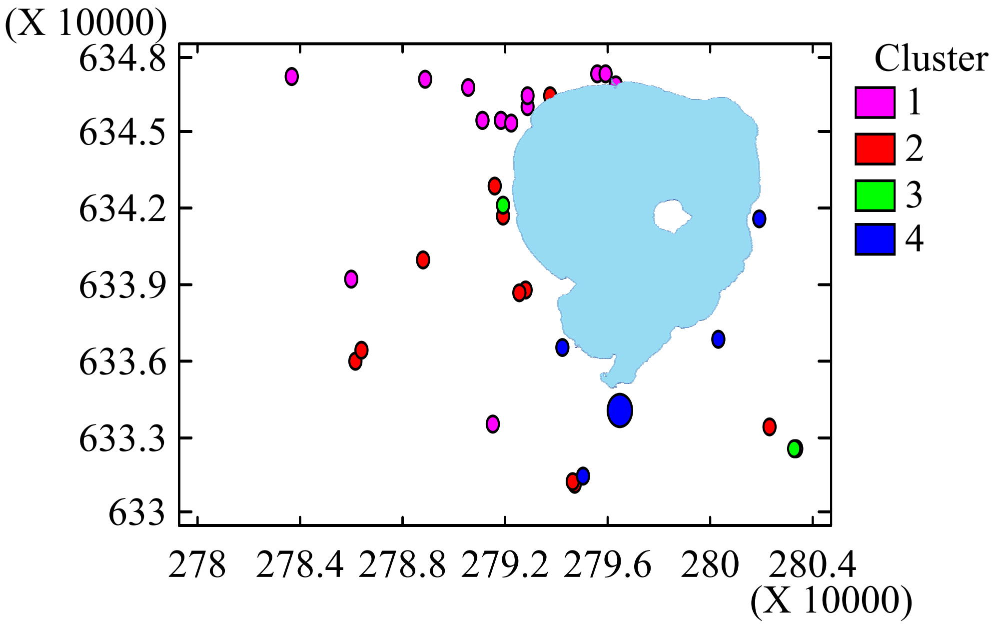


Figure 26. Age distribution for the exponential-piston flow model.

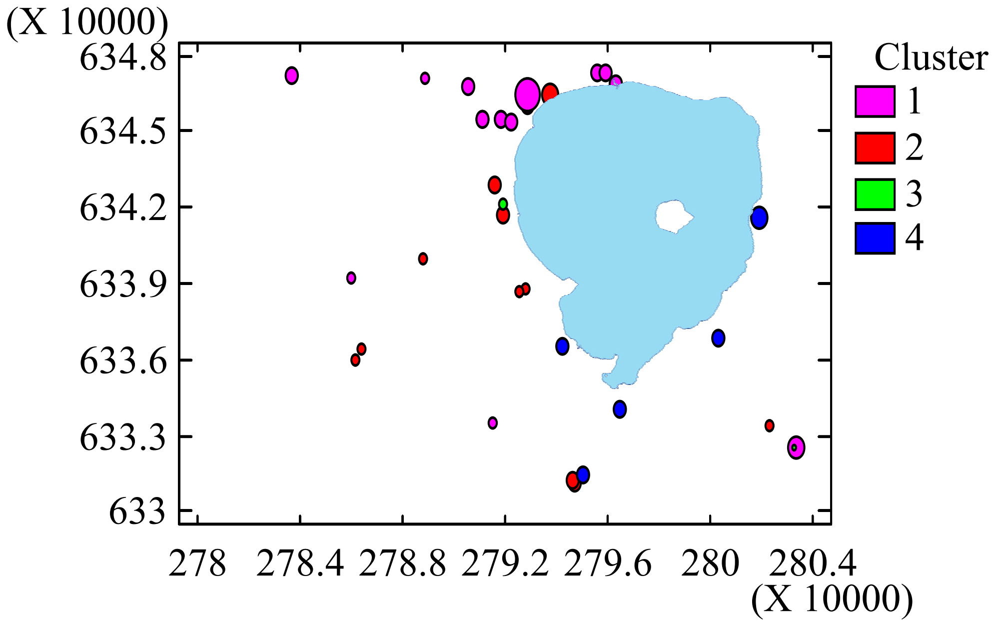
In a flow situation with less exponential flow, the age distribution of the water is less wide-spread. At 50% exponential flow, the minimum age is 25 years, and the water does not contain significant fractions older than 150 years. At only 20% exponential flow, the age distribution is relatively peaked around the mean residence time. The minimum age is 40 years, and there is an insignificant amount of water older than 100 years. This water would just start to show a contaminant introduced 40 years ago, but this contaminant would arrive in a relatively sharp front, with 10% contribution in the first year of arrival after 40 years time.

Appendix 2. Bubble plots showing variation in analyte concentrations as a function of sample location. X and Y axes on all plots represent easting and northing, respectively. Point size represents analyte concentration using a generalised linear scale in which smaller point sizes indicate lower concentrations (see Table 5 for actual values of each analyte). Point colours correspond to clusters defined in Section 4.



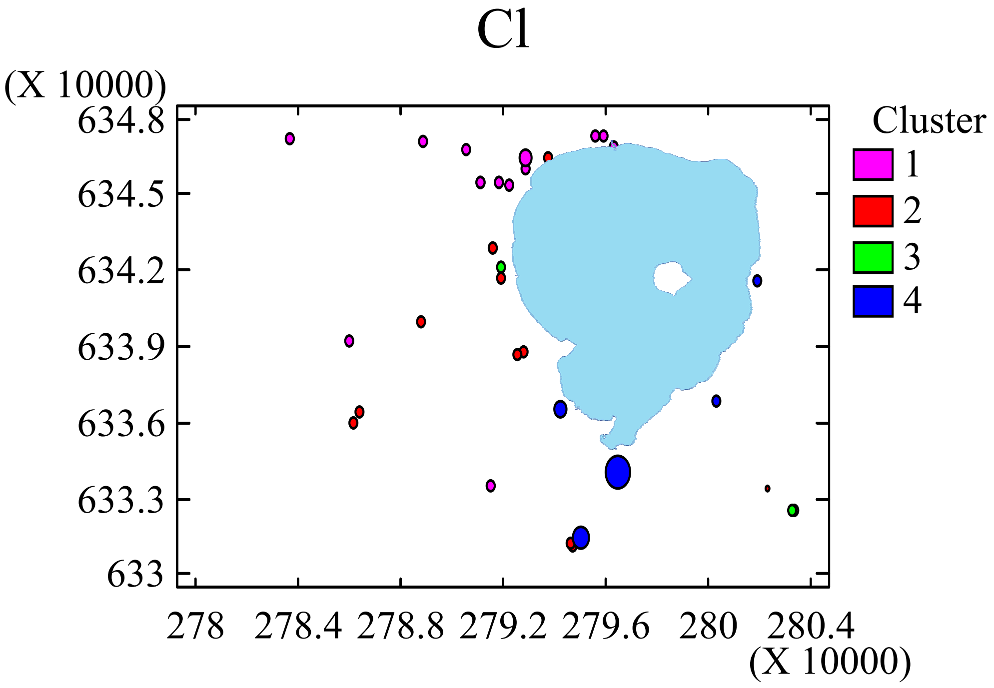
Br

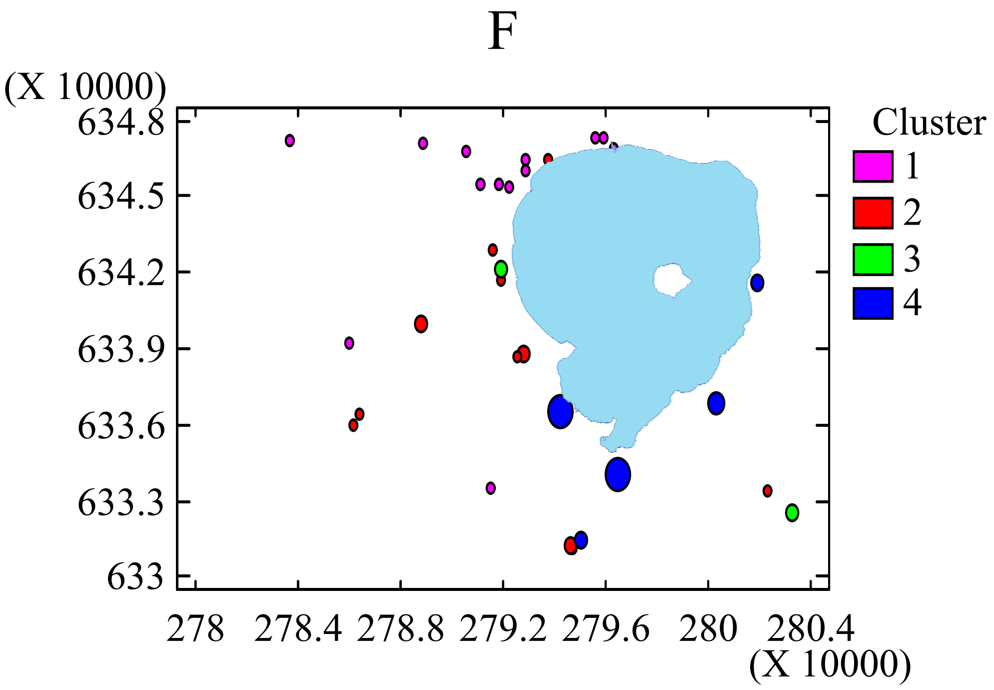
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4

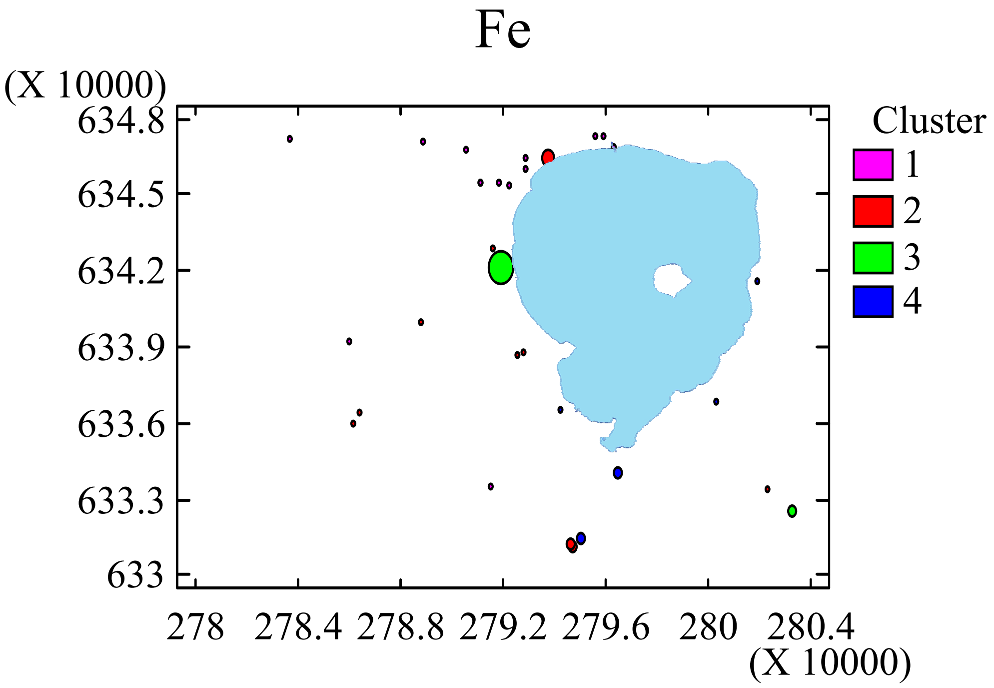


Ca

(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4

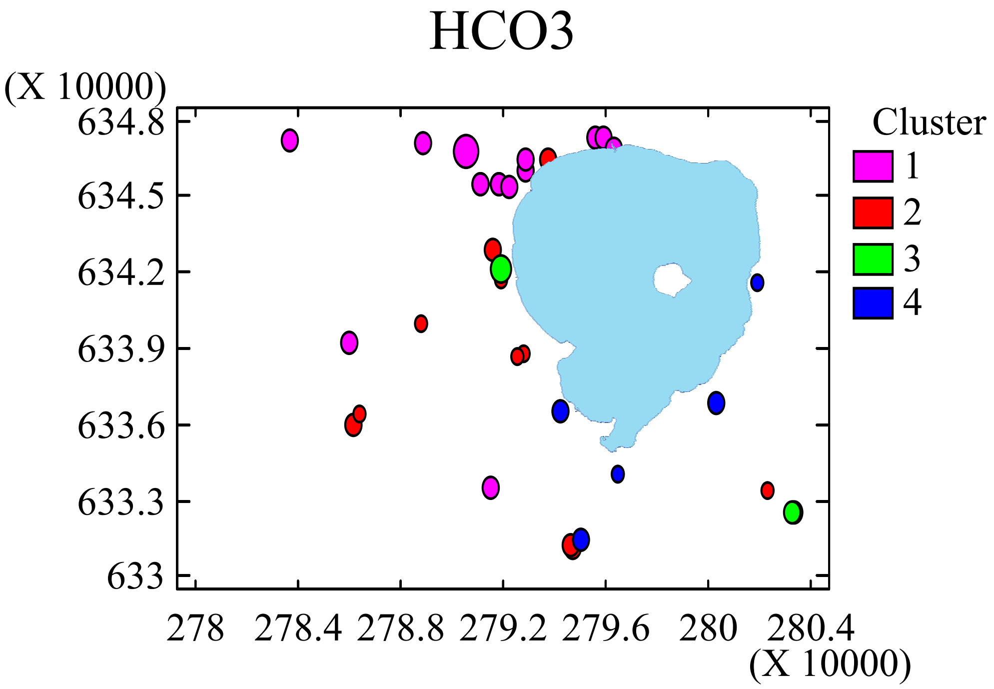

Cl
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


F
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4



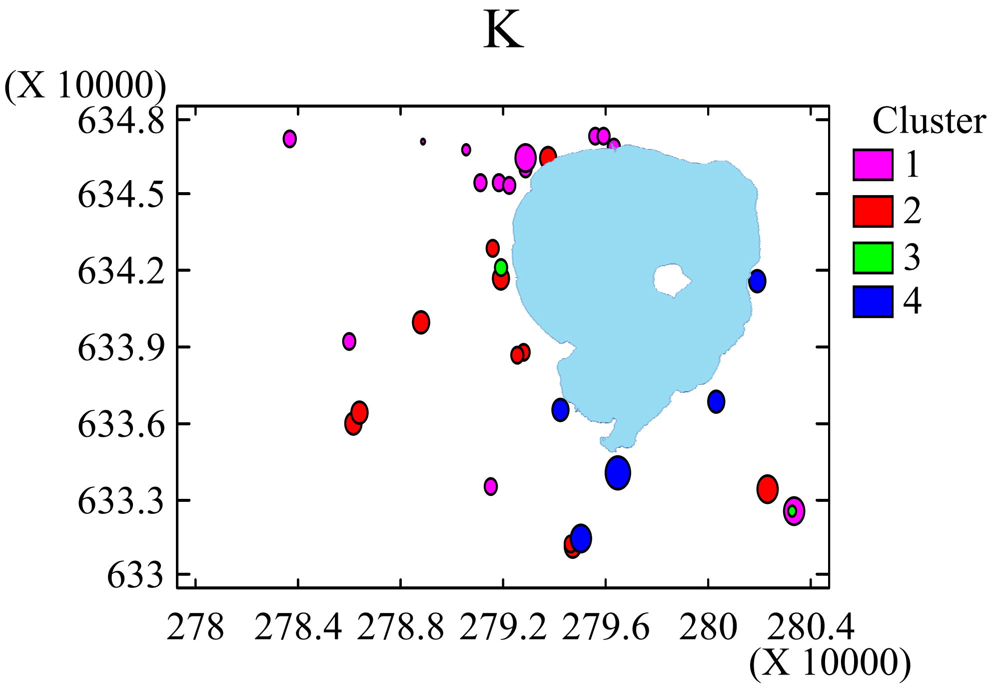
Fe

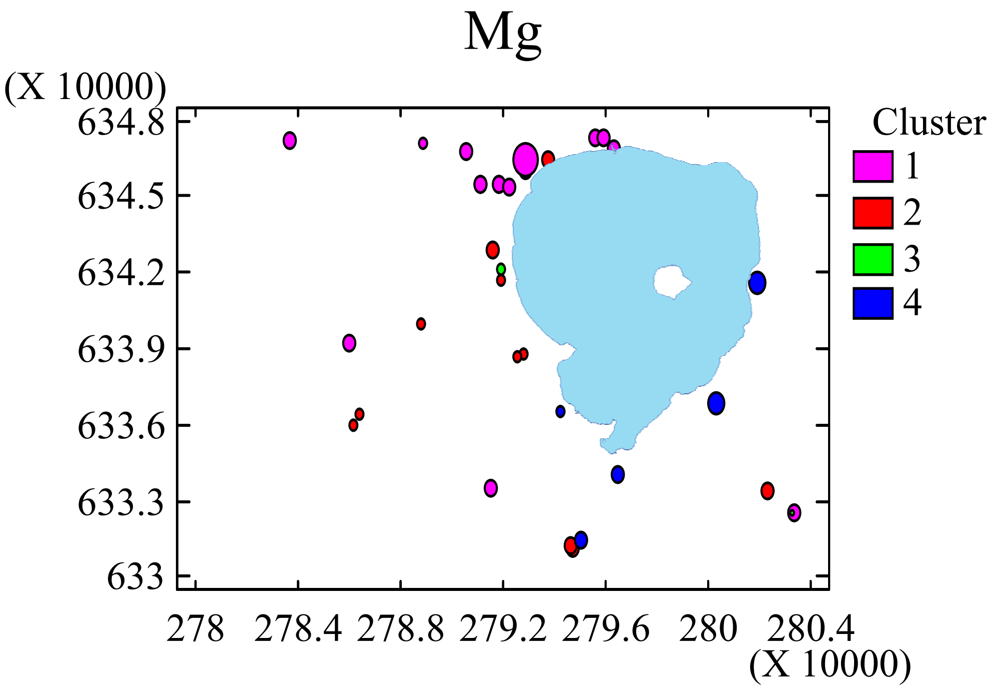
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4

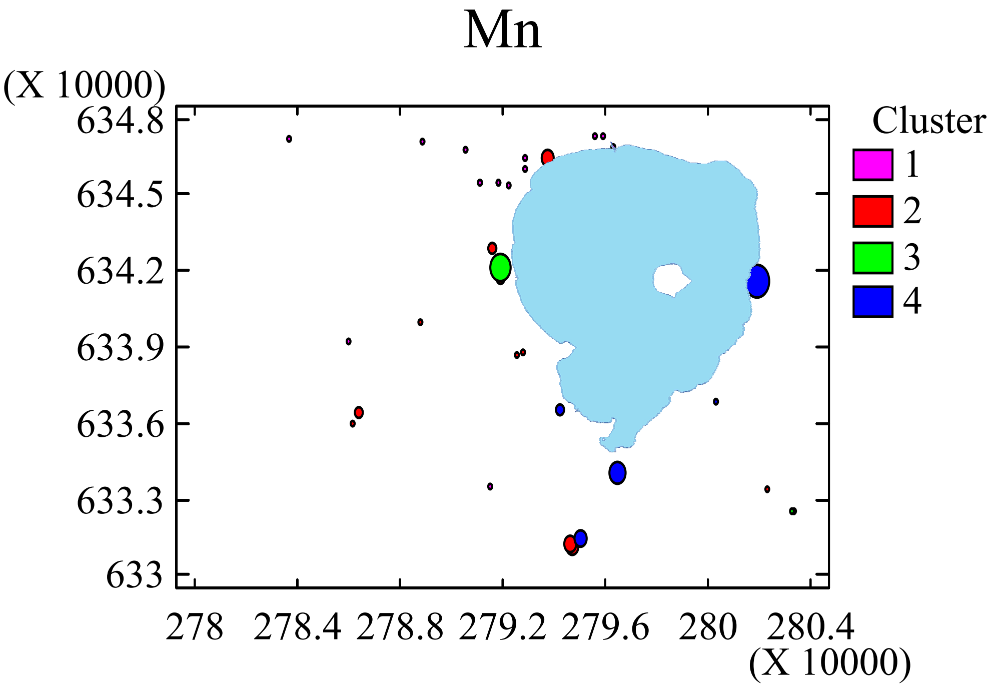


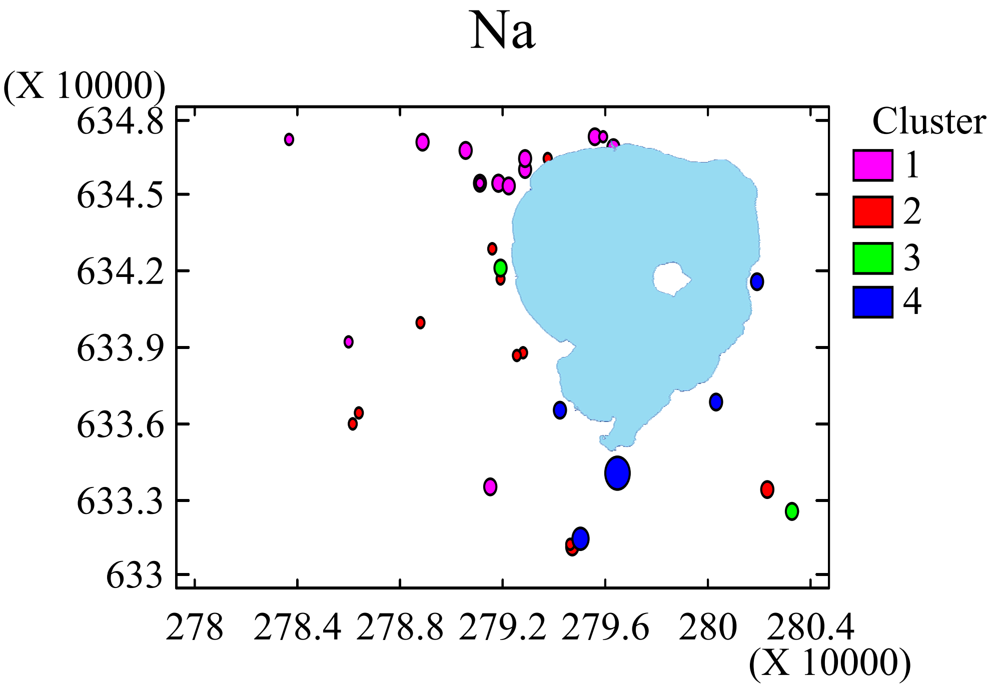
HCO3

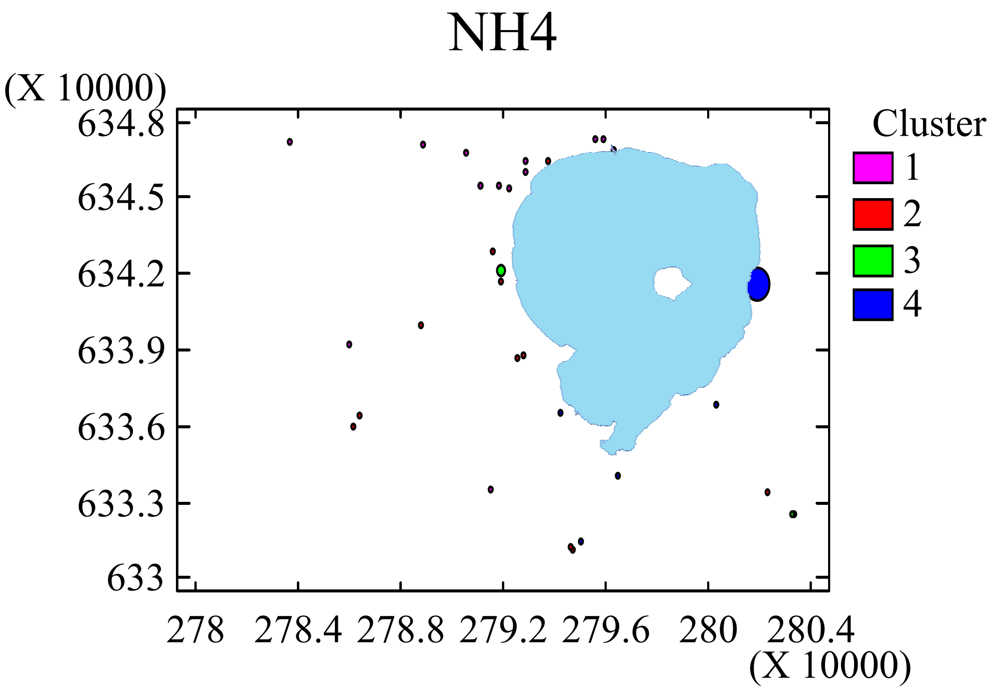
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


K
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


Mg
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


Mn
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


Na
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


NH4
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
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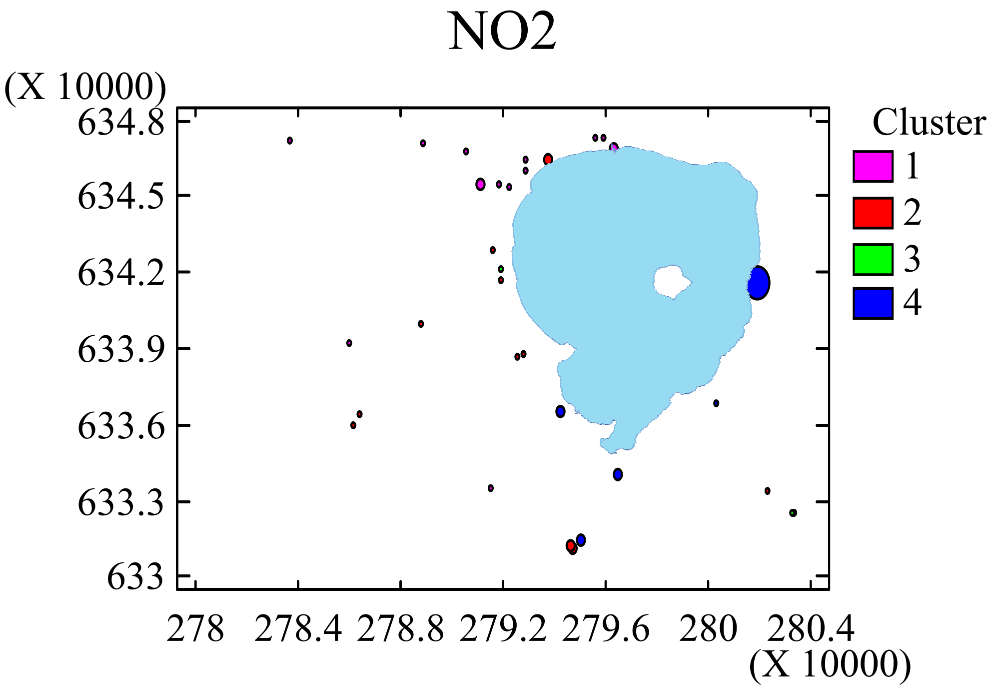
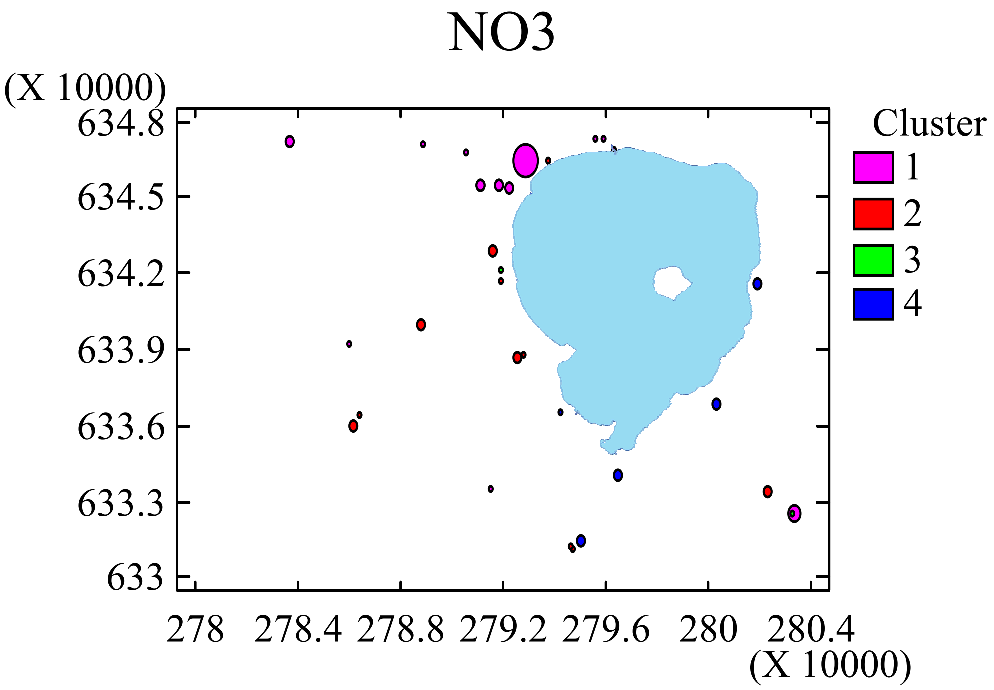
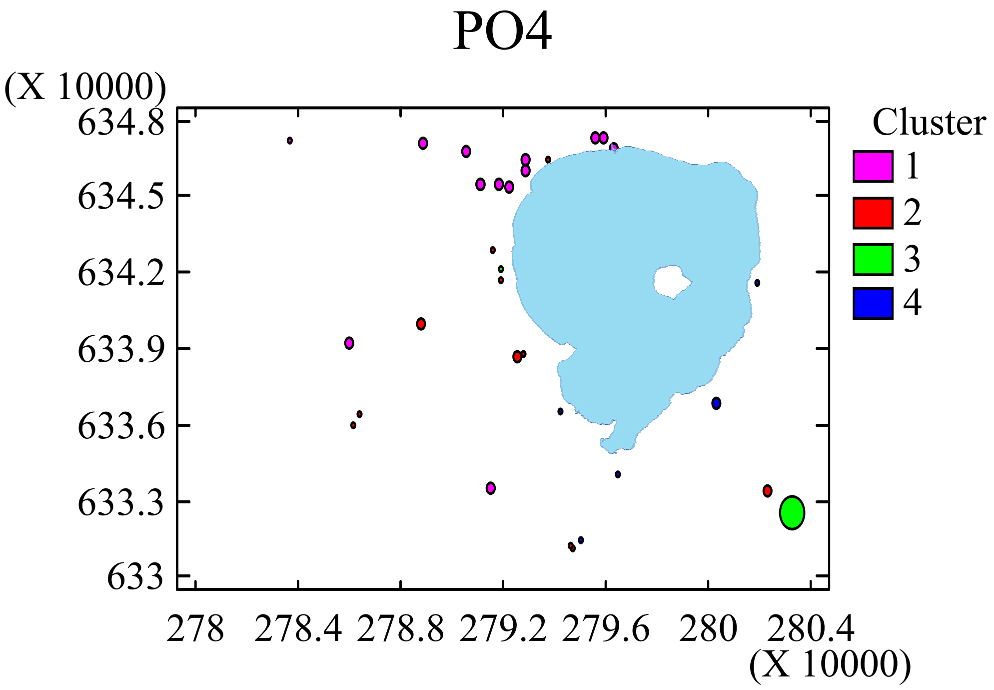
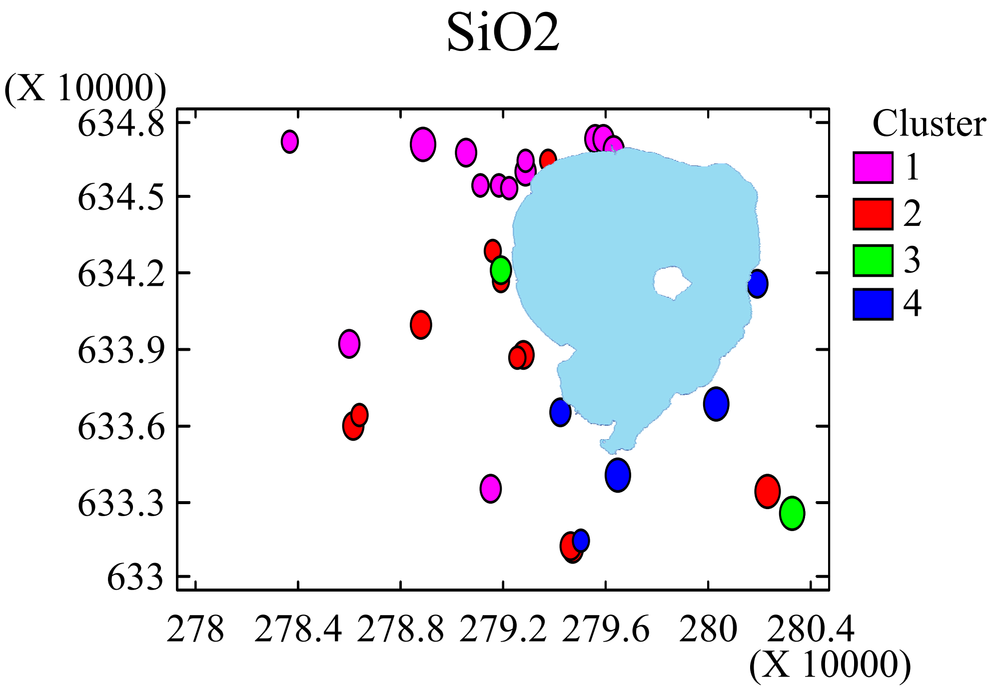
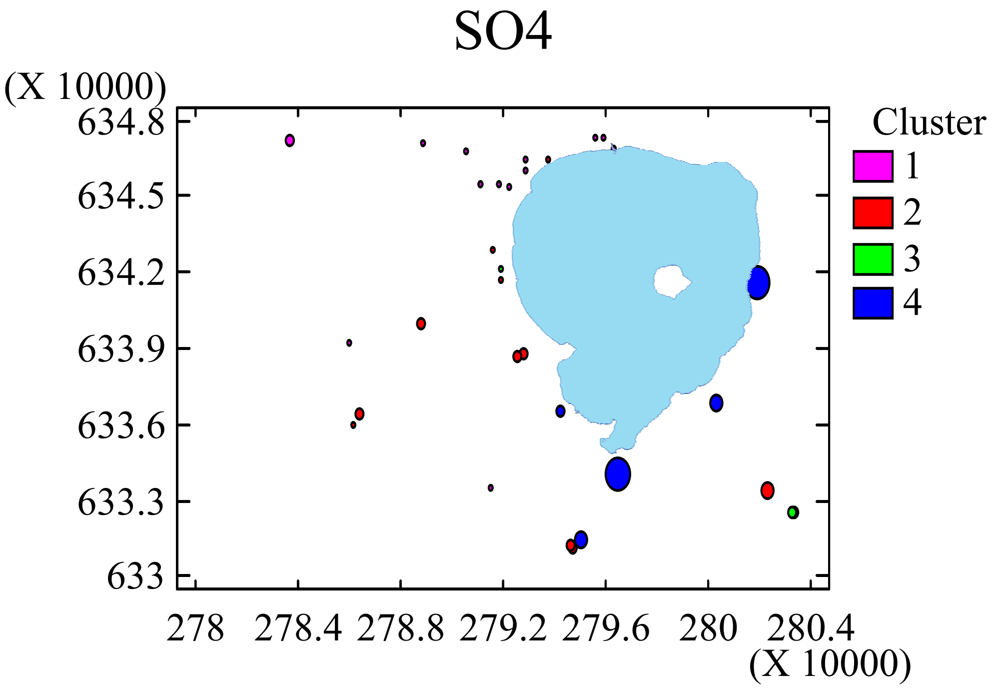
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4

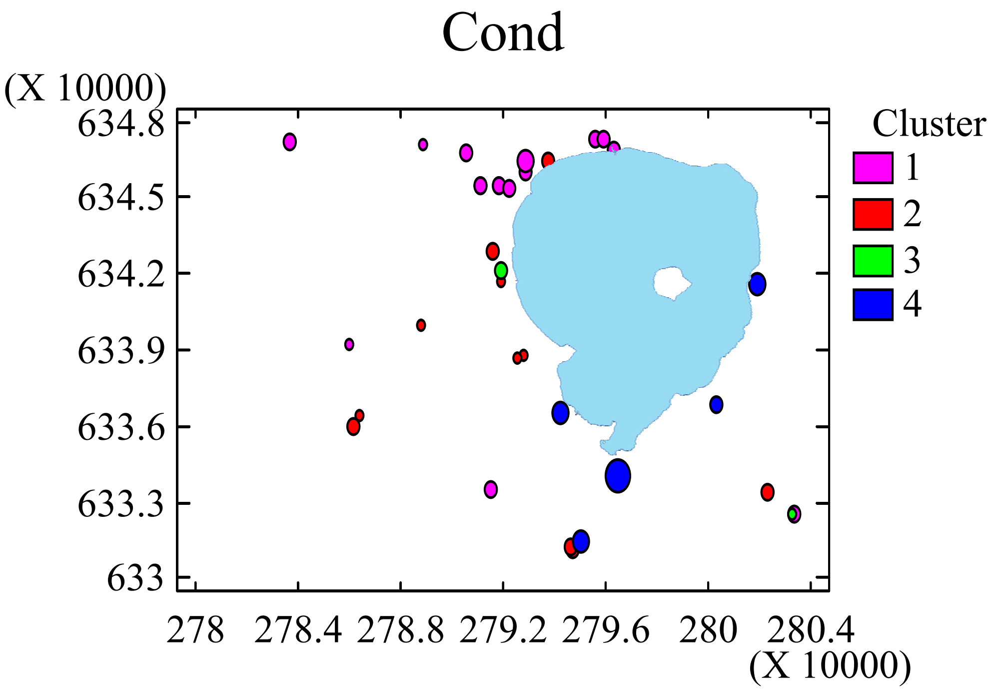

NO2
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


NO3
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


PO4
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


SiO2
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


SO4
(X 10000)
634.8
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


Cond
(X 10000)
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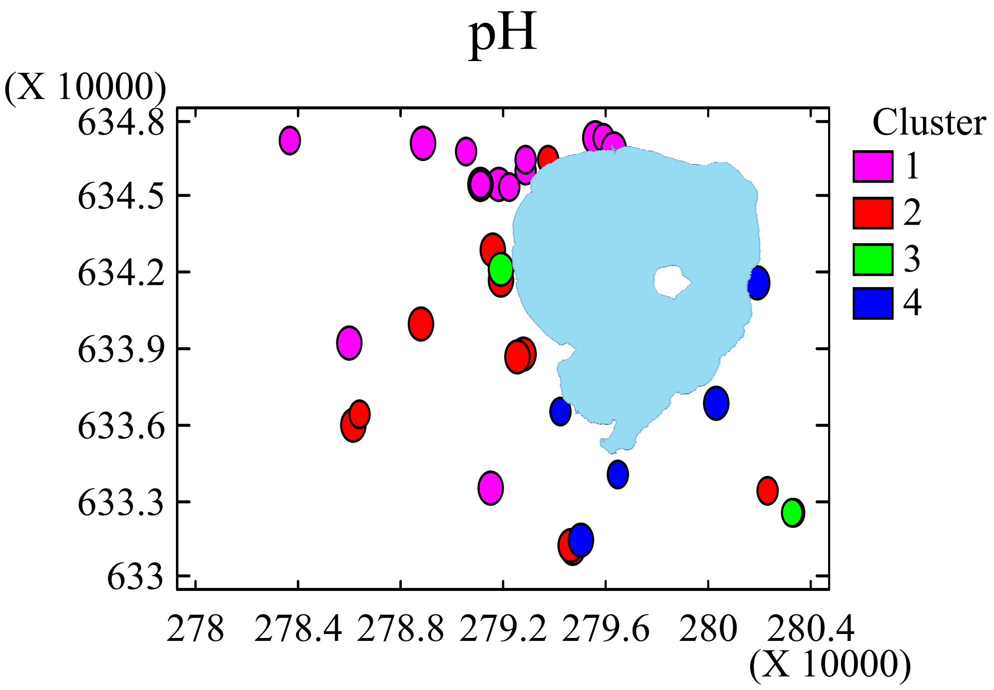
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


pH
(X 10000)
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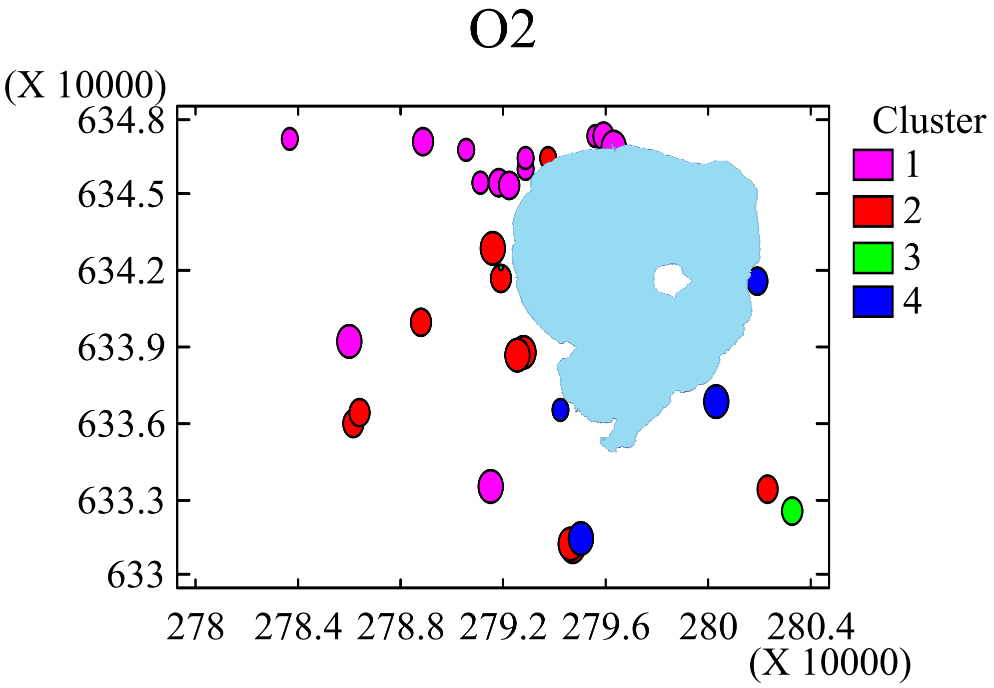
634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


O2
(X 10000)
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634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
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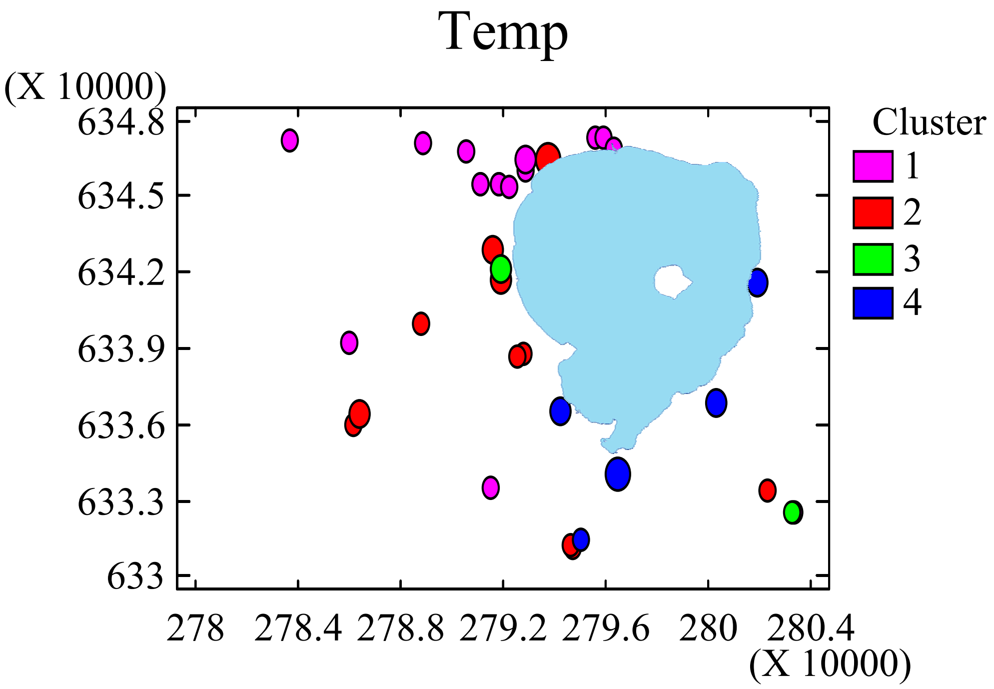
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4


Temp
(X 10000)
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634.5
634.2
633.9
633.6
633.3
633
278
278.4
278.8
279.2
279.6
280
280.4
(X 10000)
Cluster
1
2
3
4