Groundwater age, Time Trends in Water Chemistry, and Future Nutrient Load in the Lakes Rotorua and Okareka Area

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SUMMARY

Declining water quality due to delayed impact of land-use intensification has prompted this investigation by Environment Bay of Plenty (EBOP). Hydrochemical and age dating measurements were made in the western Rotorua and northern Okareka Lake catchments to assess the past and the current states, and future trends in water chemistry.

Volcanic aquifers in this area have large water storage capacity and therefore have the potential to delay impacts of land-use intensification. Because of the time delays, extensive groundwater contamination can remain undetected for decades. The old pristine groundwater is steadily being replaced by younger impacted water, which then recharges the streams and flows into the Lakes Rotorua and Okareka.

The hydrogeology of the Lake Rotorua 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. In the Lake Okareka study area, groundwater recharge is likely to be from rainfall infiltrating through the soil and into the aquifers of volcanogenic sediments and deeper rhyolite and ignimbrite aquifers.

The hydrochemistry 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 sampled through New Zealand. This chemical signature reflects the volcanic origin of the aquifer lithology.

This study involved age dating of five springs and seven groundwater wells to assess how long it takes for nutrient-enriched groundwater to travel from farms to springs and streams, and to the lakes. Most of these groundwaters are relatively old, 8 out of the 12 samples have mean residence times over 60 years. The corresponding young water fractions (i.e. water less than 40 years old) are between 1 and 44 %. These groundwaters were mainly recharged before land-use intensification and therefore do not yet show the full effect of the current landuse impact on the groundwaters quality.

Sample	MRT [yrs]	yf(40y) [%]
Hamurana Spring	145	18
Taniwha Spring	64	44
Trout Hatchery Spring	54	51
Te Waireka Spring	30	79
Barlows Spring	73	30
2116	135	1
1202	26	84
1561	112	8
3691	94	16
JROYAL	14	95
3901	170	1
10424	150	1

The four younger waters with mean residence times between 14 and 54 years have young water fractions of 51-95%. If there is contamination in the recharge area, this will already be reflected in the water quality. Therefore further significant deterioration of water quality would not be expected for these waters.

Trends in hydrochemistry indicate that only three analytes, nitrate (NO_3-N), potassium (K) and sulphate (SO_4) are impacted by land-use intensification. These analytes all have increased concentration in young groundwaters and are considered to be indicators of land use intensification.

Total Phosphorus is very low in young groundwater (<0.04 mg/L), but increases with age and with reducing young water fraction. Total phosphorus is considerably higher in the oldest groundwater (1.3 mg/L). This demonstrates that phosphorus does not originate from land-use practises but is naturally leached from the volcanogenic aquifer material. Therefore, no changes in phosphorus loading to the lakes can be expected.

The nitrate concentration is significantly higher for water recharged after land-use intensification. The natural background level of NO_3-N (before land-use intensification) is assessed to be 0.15 mg/L, and the current recharge level to be 2.7 mg/L. Therefore, 94 % of the NO_3-N in the young groundwater is derived from the land-use in the catchment. This is an increase by a factor 18 above natural background.

The following loads of phosphate and nitrate were calculated from a mass budget for the five springs: The current phosphate load is 13 t/yr, and this is expected to stay constant because it is natural occurring. However, the current load of nitrogen NO_3-N is 149 t/yr, and this is expected to increase to 476 t/yr once steady state is reached.

Dramatic increases in nutrient load are expected in the future for the large old water fractions. Land-use impacted water carrying high nitrogen loads (NO_3 is the major nitrogen component) will increasingly discharge into the lake as the old pristine water is depleted. The current total nitrogen concentration of Lake Rotorua is 0.45 mg/l. Some major springs already discharge water to the lake with 0.7-1.4 mg/L NO_3-N. These are expected to increase to about 3 mg/L. The nitrogen concentration in the lake is therefore expected to increase significantly.

RECOMMENDATIONS

1. Collecting nutrients, hydrochemistry and age data for the major surface water inflows to Lake Rotorua.
2. Verify the landuse change timeline for Lake Rotorua and Lake Okareka Catchments.
3. Establish a total mass budget of nutrients to the lakes via surface water flow.
4. Assess the contribution of nutrient load to the lakes via groundwater flowing directly into the lakes via the lake bed.
5. Establish a model to predict future nutrient loads for various scenarios of changes in land-use practises (various grades of reduction of nutrient input).
6. Investigate in-stream removal of spring sourced nutrients.

Additions:

7. Improve understanding of hydrogeology and recharge areas.
8. For the largest spring systems, monitoring of several sub-springs can verify if water age and chemistry are uniform. If they are not uniform, the more detailed data will ensure correct input data for the total nutrient mass budget to the lake.
9. Extend the understanding of the age structure of the old water using ^{32}Si dating of groundwater.
10. Improve the quality of the borehole data by educating drillers on local geology and data required by EBOP.

1.0 INTRODUCTION

Declining water quality in a number of the Rotorua lakes due to an assumed delayed impact of land-use intensification has prompted this investigation of hydrochemistry and groundwater ages in the Lakes Rotorua and Okareka area. Volcanic aquifers in this area are similar to those around Lake Taupo in that large water 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 had been estimated to have mean residence times of 50-100 years (Taylor & Stewart, 1987; Pang et al., 1996).

Therefore, the lag time between land-use intensification (e.g. nitrate contamination from agriculture) and effects on quality of spring and groundwater reaching the lakes could be several decades. Consequently, the current surface water quality is likely to not yet reflect the full extent of the current land-use practises (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 and increasingly, contaminated water discharges into the lake. A further decline in Lake water quality can be expected in the future, and any remedial action will take decades to take effect because of the time delays.

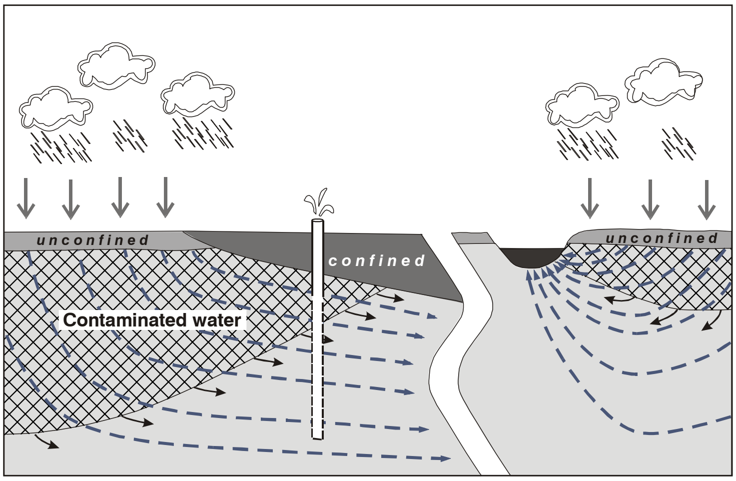


Figure 1. The tip of the iceberg. Only a fraction of contaminated water (hatched) has yet arrived at a groundwater well/stream/lake

The objective of this study was to assess how long it takes for nutrient-enriched groundwater to travel from farms to springs and streams, and to the lakes Rotorua and Okareka. The project involved measurement of hydrochemistry and age data for an array of groundwater wells and springs at lakes Rotorua and Okareka. A desktop evaluation of the hydrogeology was based on reviewing existing published literature and data supplied by Environment Bay of Plenty.

The age distribution together with the hydrochemistry of the groundwater can be used to calculate the future contaminant levels flowing into the lakes at steady state.

We measured hydrochemistry in conjunction with age dating to assess the past and current state, and future trends in water chemistry. We identified the natural pre-human level of groundwater chemistry from old groundwater that was recharged before land-use intensification. The impacts of land-use intensification on groundwater quality we identified from young groundwater that was recharged after land-use intensification. Finally, we estimated future nutrient loading to the lakes by scaling the land-use contribution of nutrients to 100% young water (when all water is recharged after land-use intensification).

2.0 HYDROGEOLOGY OF THE STUDY AREAS

Understanding the physical hydrogeology of the Lake Rotorua and Lake Okareka areas is necessary for improved interpretation of groundwater dating results. In particular, recharge mechanisms such as rainfall and/or river recharge to the groundwater aquifer, the type of aquifer and aquifer conditions e.g. confined/unconfined is necessary to narrow the number of possible groundwater flow models.

The geology of the Rotorua Lakes is dominated by volcanic and fluvial deposits. Most of the lakes in the area are the direct result of volcanic processes, including catastrophic caldera processes, explosion craters or historic damming of valleys due to volcanic deposits, and subsequent filling with water.

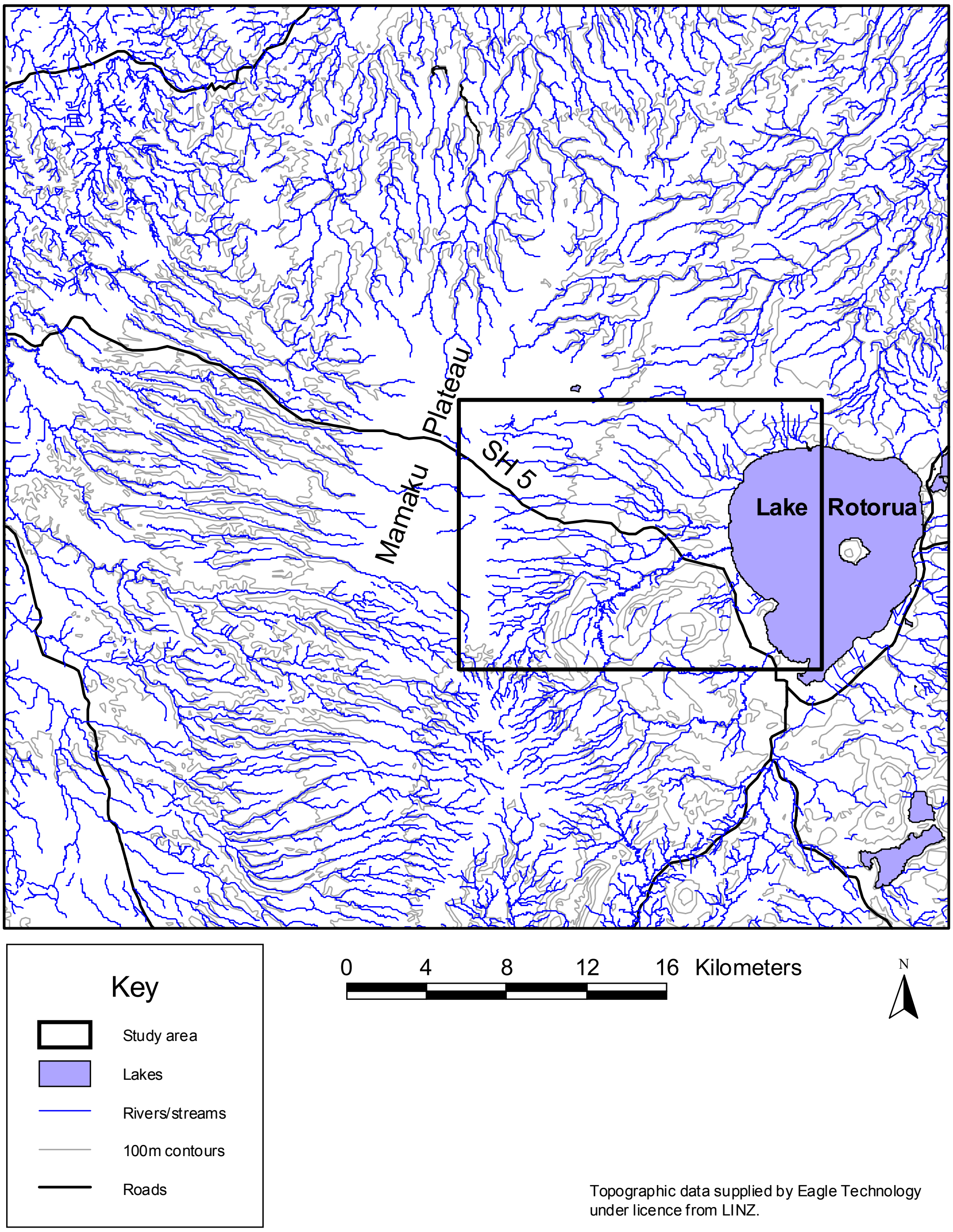
This section describes the geology and aquifer characteristics of the two study areas. These hydrogeologic interpretations are based on a desktop study of previous work, and data supplied by Environment Bay of Plenty (EBOP).

2.1 Rotorua

The Rotorua area has long been of interest to geologists, not only because of the volcanic processes, but also for the geothermal processes that exist at the southern end of Lake Rotorua. The Rotorua caldera is an infilled caldera that formed following the eruption of the Mamaku Ignimbrite about 220-230 ka ago (Wood, 1992). Subsequently, visible effusive rhyolitic eruptions built 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 (and still is) infilling with sediment and tephra. Volcanic events in the neighbouring Okataina Volcanic Centre have caused the water level in Lake Rotorua to vary by up to 100 m from its present day level (Dravitzki, 1999) resulting in a number of terraces to be formed in the caldera.

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). Much geological work has been focused on the geothermal area of Rotorua, summarised in International Geothermal Association (1992). Dravitzki (1999) investigated the stability of lake sediments in the Paradise Valley area and the petrographic geochemical variation of the Ngongotaha-Pukehangi dome complex. Milner (2001) focussed on the Rotorua caldera eruptions and suggested that the caldera was formed in one eruption. The caldera floor is cut by a number of faults complicating the caldera structure.

The western Rotorua study area (Fig. 2) is approximately 250 km^2 area on the eastern flanks of the Mamaku Plateau and ranges in elevation from about 500 masl in the west, down to about 280 masl at Lake Rotorua in the east.



Topographic data supplied by Eagle Technology under licence from LINZ.

Figure 2 **Western Rotorua study area**

Four geological units dominate the western side of Lake Rotorua (Fig. 3), and have been summarised by Rosen et al. (1998) as:

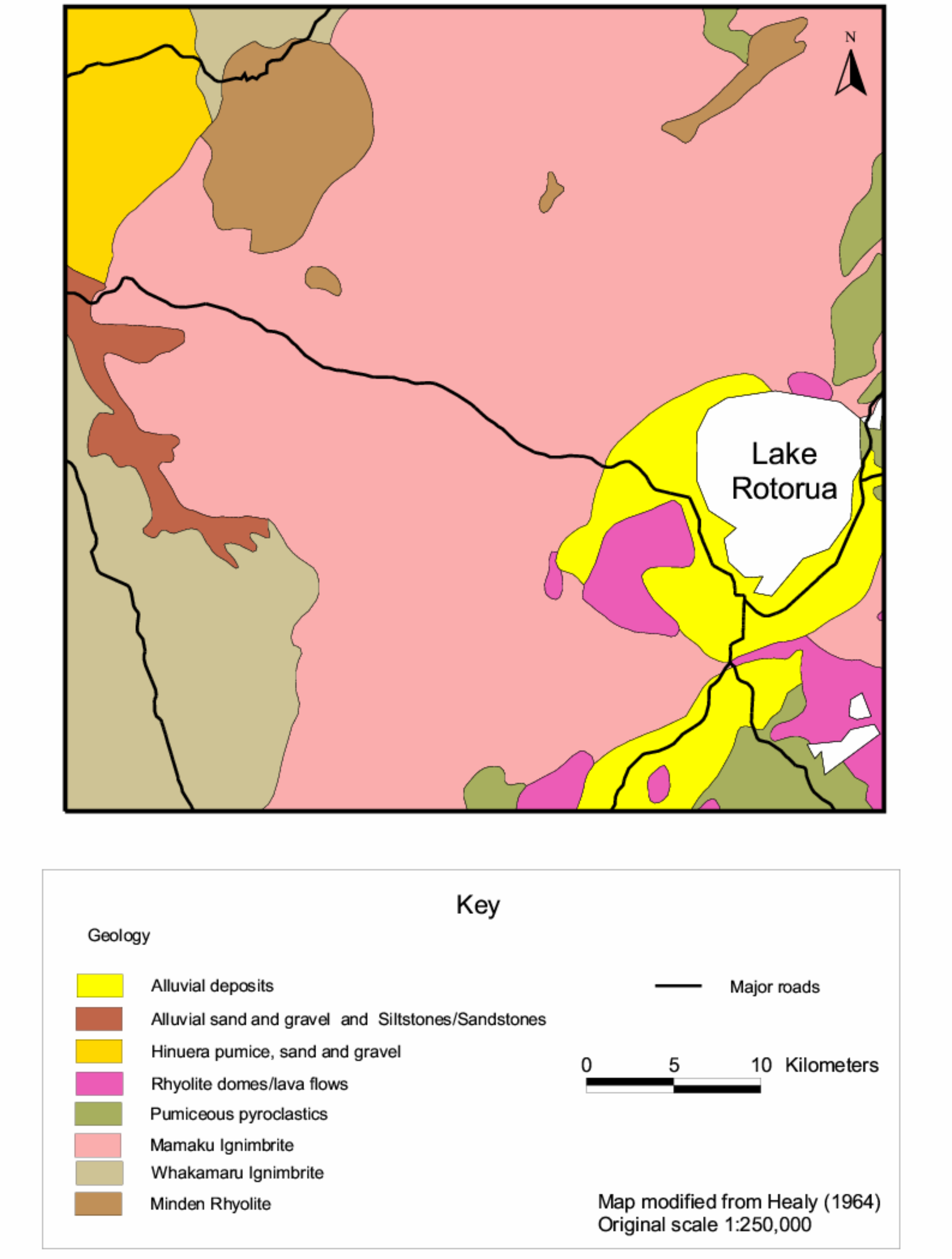


Figure 3. Geology of the Rotorua area

1. *Superficial tephra and loess:* This unit includes yellow, loosely consolidated air fall pumice, dark grey ash and wind-blown loess-sands. These sediments occur above the Mamaku Ignimbrite and are typically about 0.5-1.5 m thick. This unit is considered permeable and allows downward percolation of water (Rosen et al., 1998).

2. *Terrace and fan deposits:* Alluvium and fan deposits, which overlie the Mamaku Ignimbrite. The deposits are comprised of silt, sand, gravel (ignimbrite, obsidian and rhyolite pumice) and are considered permeable, but do contain lenses of low permeability sediment (Rosen et al., 1998).

3. *Mamaku Ignimbrite:* Three sheets have been identified in the Mamaku Ignimbrite based on welding, crystal content and vapour phase alteration (Milner, 2001). The lower sheet (40-45 m thick) is a pale brown-creamy white, non-welded, non-jointed ignimbrite. The middle section is a light brown, strongly welded ignimbrite with occasional jointing. The upper sheet is grey-pink-red, semi-welded, non-jointed ignimbrite. 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.

4. *Rhyolite:* These deposits include both the mid and upper Pleistocene rhyolitic domes. The deposits are light grey, vascular and well-jointed (Thompson, 1974). The units 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 and will depend on fracture sizes and linkages.

The rhyolite and ignimbrite aquifers have fractures that have formed as a result of faulting and contraction following deposition. The size and interconnectivity of fractures affects groundwater flow in these types of aquifers. Consequently, groundwater seepage and flow rates can vary significantly within small areas. Rosen et al. (1998) developed a schematic model for the Mamaku Ignimbrite near Taniwha Springs (Fig. 4), 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.

An attempt to measure direct groundwater flow into Lake Rotorua gave 698 L/day and 544 L/day (using ‘direct measurements’) for a 100 m x 1 m strip at two locations on the western shore of Lake Rotorua (John and Lock, 1977). Nothing is known about aquifers discharging groundwater directly to Lake Rotorua, but if this occurs it is likely to be from the terrace and fan deposits around the lake edge.

Grinsled and Wilson (1978) showed nitrate concentrations in the groundwater around the western side of Lake Rotorua to be below 5 mg/L, but suggested there is enough nitrogen mass entering the lake from groundwater to influence any nutrient balance calculation. Hoare (1987) estimates that Lake Rotorua retains approximately 36 tonnes of phosphorus and 363 tonnes of nitrogen (with some nitrogen lost to the air) in his nutrient balance calculations.

Apart from major springs, no nitrogen and phosphorus data from groundwater is used in the nutrient balance.

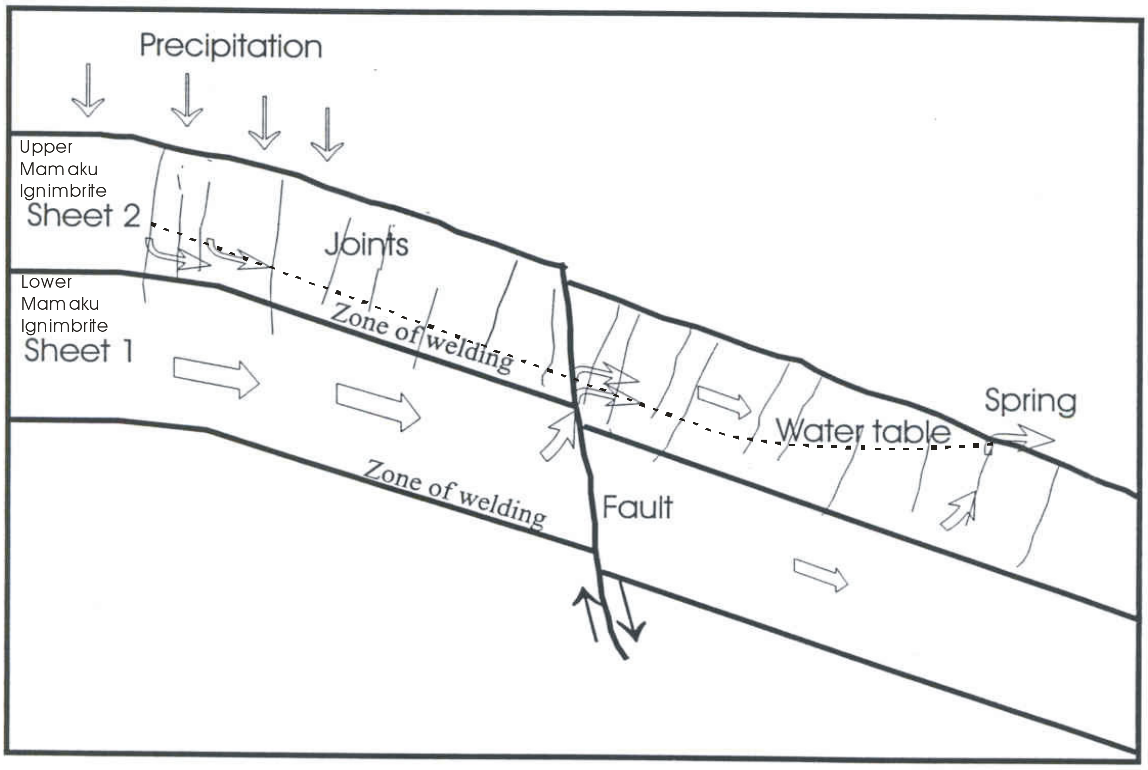


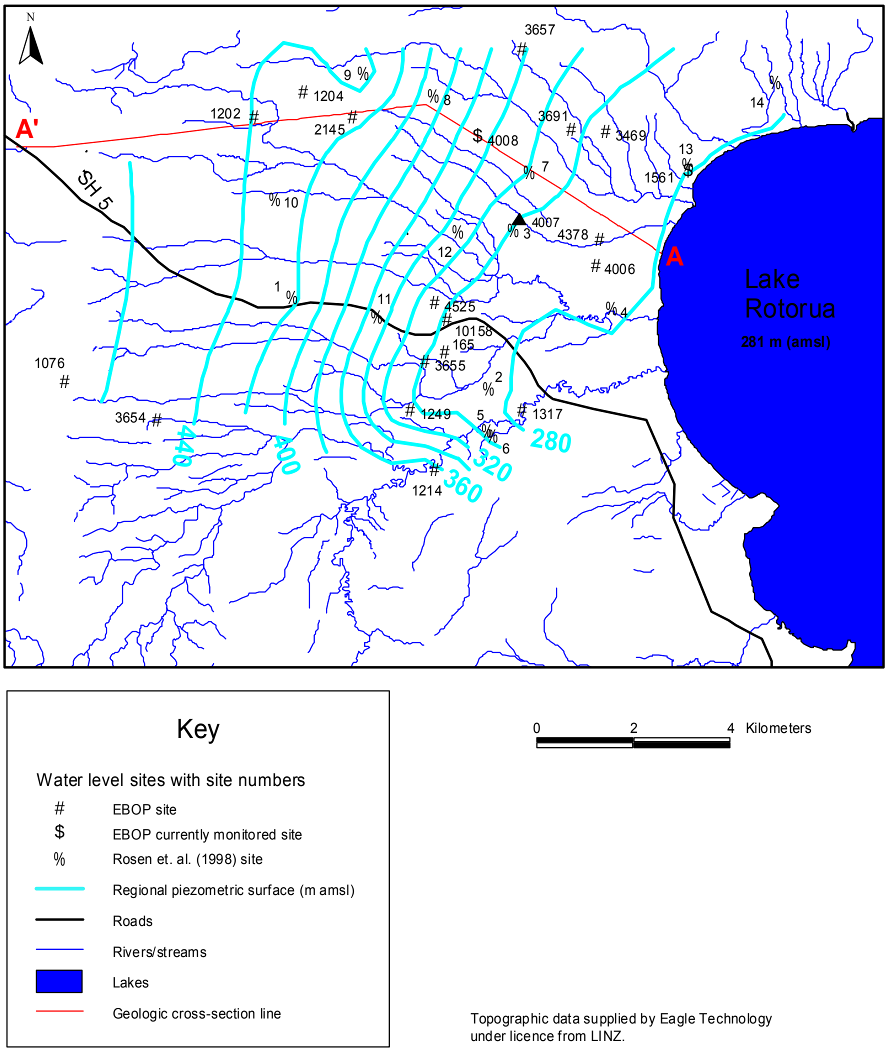
Figure 4 Schematic diagram of water movement in the Mamaku Ignimbrite. 1) Water falls on the ignimbrite's surface, and permeates downward mainly along joints. 2) Once a zone of welding is reached, water is forced to flow down the dip direction of the ignimbrite. 3) Water accesses sheet 2 (from sheet 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).

Ngongotaha Village sources its municipal water supply from springs on the western side of Lake Rotorua. Faecal contamination of the Ngongotaha water supply prompted a number of studies to investigate the source of the contamination (Dewhurst 1992, Dewhurst 1993, Dewhurst 1996 and Rosen et al., 1998) for the Rotorua District Council. The contamination events also prompted Environment Bay of Plenty (EBOP) and Rotorua District Council to investigate groundwater protection areas for major springs in the Lake Rotorua catchment, in particular, those that are or could be, used as a public drinking water supply (Pang, 1996). Pang (1996) only focused on protection zones for bacterial contamination, and did not consider dissolved (e.g. nitrates) or particulate matter. Most of the large freshwater springs discharge from western catchment of Lake Rotorua and appear to emerge from both the rhyolite and ignimbrite deposits (Pang, 1996).

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 fresh water 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.

A piezometric map of the study area (Fig. 5) has been constructed using data from Rosen et al. (1998) and data from EBOP (Appendix 1). The piezometric map is constructed from three data sets:

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



Topographic data supplied by Eagle Technology under licence from LINZ.

Figure 5 **Piezometric map of the Western Rotorua area.**

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. 6) for the period 1994-2002. A range in level of 3m is considered insignificant for interpretation of groundwater flow direction (Fig. 5).

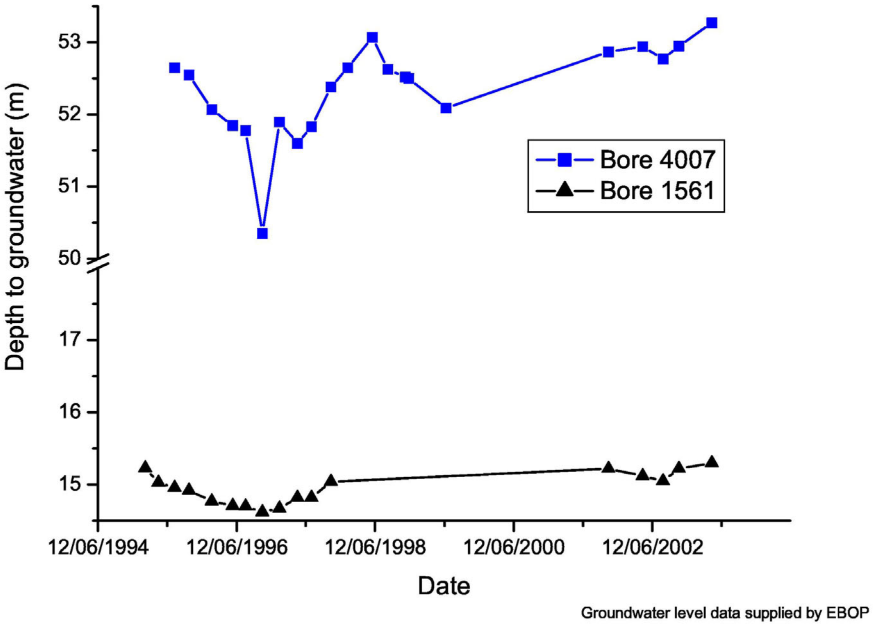


Figure 6 Water levels in bores 4007 and 1561.

The piezometric map (Fig. 5) shows groundwater flows towards Lake Rotorua. The groundwater gradient is steeper on the higher flanks of the Mamaku Plateau than it is close to Lake Rotorua.

Borehole data collected by drillers and supplied by EBOP is used to identify and correlate aquifer units. However borehole data is often not of sufficient quality to identify aquifer units and is used with caution. This is because the geology is 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. 3). In some cases, the borehole data correctly describes the lithology as ignimbrite, but no distinction is made between upper or lower Mamaku Ignimbrite units.

Figure 7 shows a cross-section based on drill hole data supplied by EBOP (Appendix 2). 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.

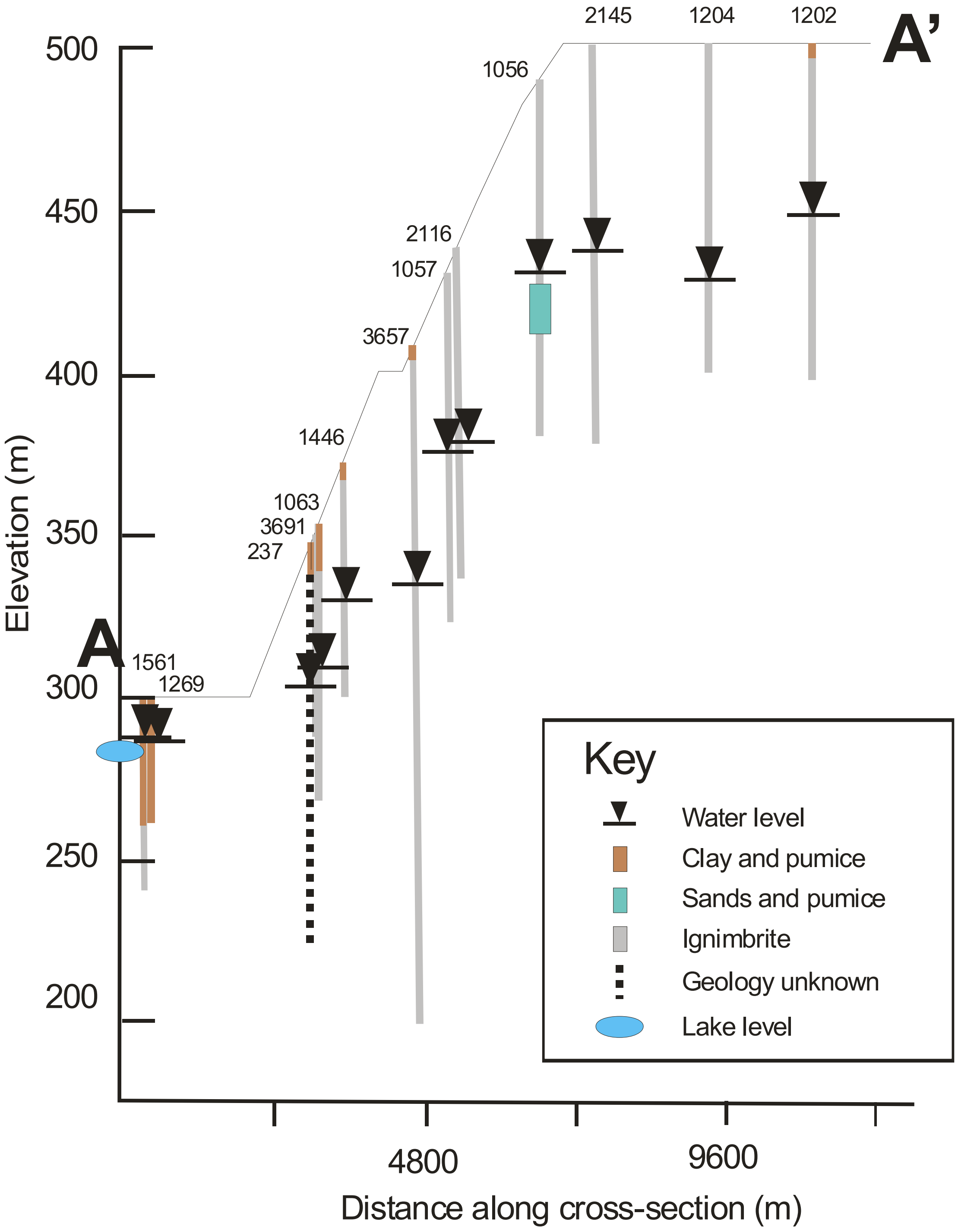
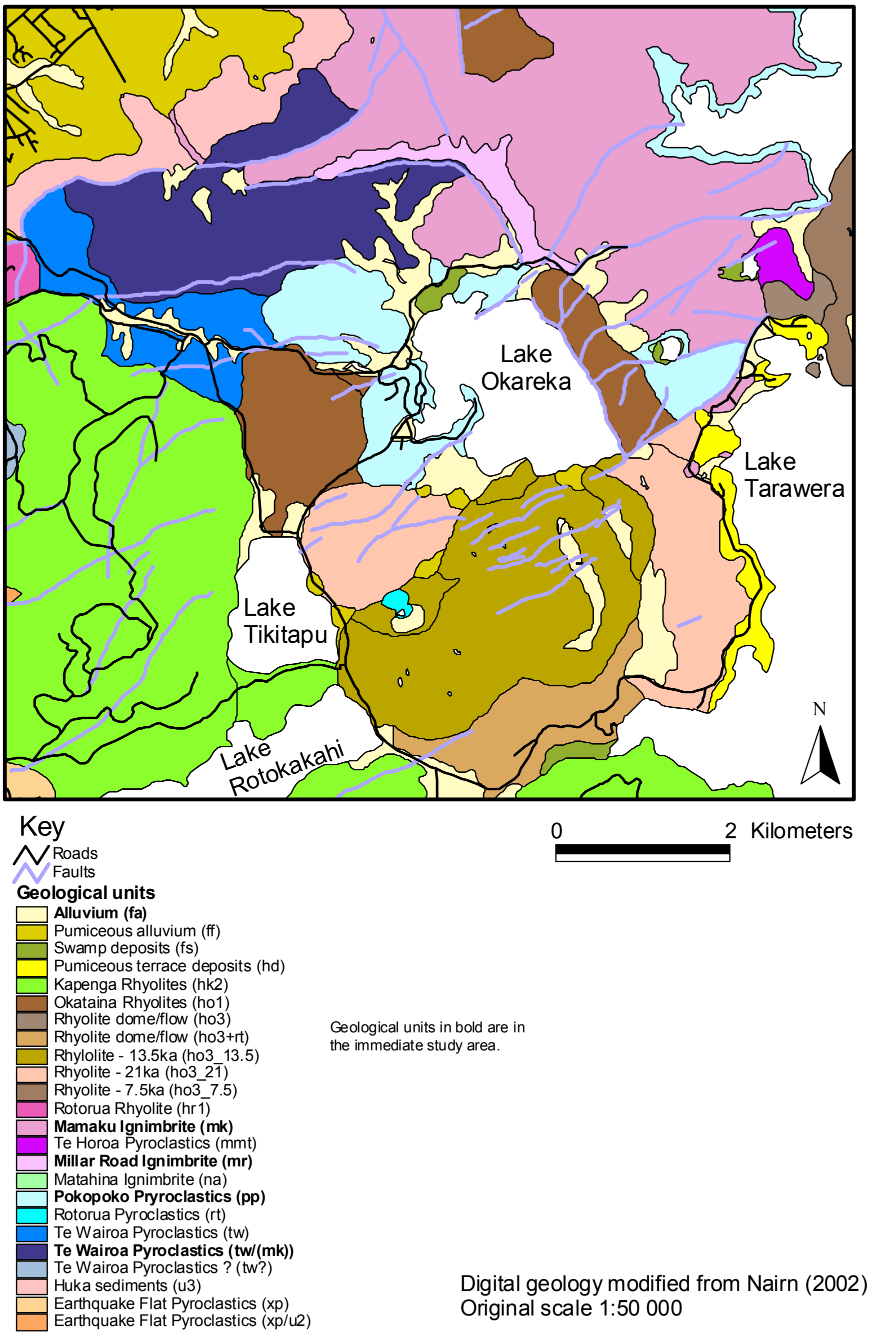


Figure 7 Cross-section A-A’ (Fig. 5) across the western Rotorua study area.

2.2 Okareka

Geology in the Okareka area consists mainly of volcanic and sedimentary deposits (Healy, 1964). Detailed geological mapping (Fig. 8) has been done at the 1:50 000 scale by Nairn

(2002). Geological mapping shows a series of rhyolitic domes/lava flows flanking the west, south and east of Lake Okareka.



Digital geology modified from Nairn (2002)
Original scale 1:50 000

Figure 8 Geology of the Okareka area.

The depositional history of the area is complex but suffice to say 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 the 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 to the 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 Lake Okareka groundwater study area is an approximately 4 km^2 area on the north-western shore of Lake Okareka (Fig. 9). The study area is dominated by farming and forestry land use. Two small streams drain the catchment into Lake Okareka.

It is not clear which geological units are water bearing based on the geological descriptions obtained. Characteristics about each unit (Nairn, 2002) with an 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 vesculated pumiceous lavas. Rhyolite flow bending and jointing is common.

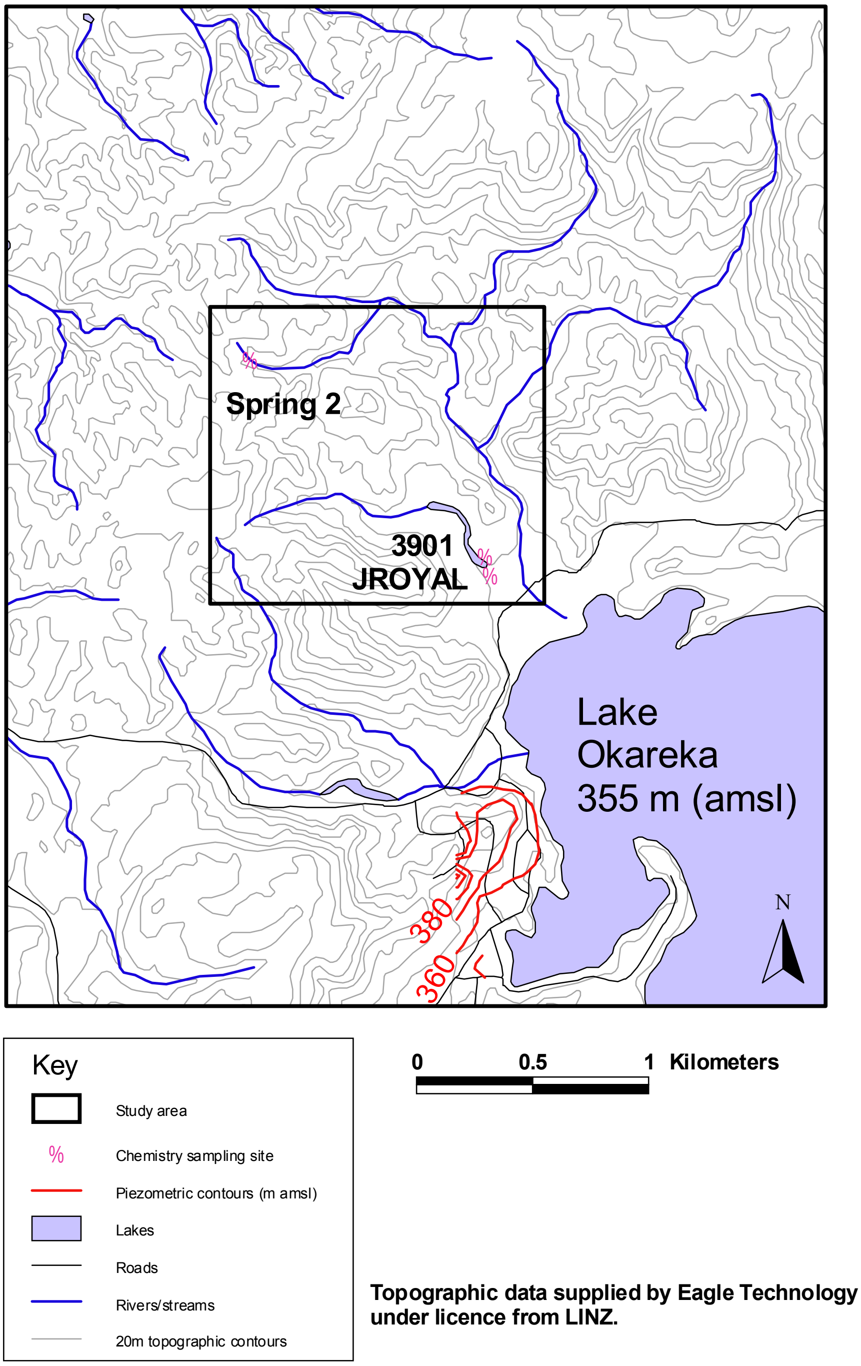
Ignimbrite: The Mamaku Ignimbrite as described in section 2.1.

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.

Only one bore in the study area has a geological log available (bore 3901), although logs for other bores do exist outside of the study area, near Okareka Township (Appendix 2). All bore logs are of insufficient quality to make detailed interpretations of the geology.

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 of the Okareka area.**

Defining groundwater flow patterns around Lake Okareka is essential to understand the interaction between groundwater and the lake i.e. does groundwater flow into the lake? A piezometric map is constructed from the limited available groundwater level data supplied by

EBOP (Fig. 9, Appendix 1). The water levels are obtained from drillers 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, which is approximately 1 km south of the study area, shows that the direction of groundwater flow is towards Lake Okareka (Fig. 9, Appendix 1). In general, groundwater flow follows local topography, with groundwater levels high on the ridge, and low groundwater levels in the valleys. The groundwater level at bore 220 causes a steep groundwater gradient at this site. It is suspected that this site may either be located incorrectly, or tap a deeper aquifer that has a lower groundwater level.

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 the 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 infer 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 in bore 3901 (43 m deep) and the nearby JROYAL (1.6 m deep) show similar static water levels (Appendix 1), suggesting a hydraulic connection between these aquifers.

Springs emerge from high up in the catchment (e.g. Spring 2, Fig. 9) and contribute flow to the streams through the study area. The springs high up in the catchment 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 in bores 3901 and JROYAL are higher than the lake level so it is likely that groundwater flows toward the lake.

2.3 Summary of aquifer characteristics

Table 1 summarises aquifer characteristics and likely groundwater recharge source for the sites sampled in the Lake Rotorua and Okareka study areas.

The hydrogeology of the Lake Rotorua study area 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 which yield high volumes of groundwater. 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 Dr Irvin and 10424 cannot be established due to a lack of geological and isotopic data.

In the Lake Okareka study area, groundwater recharge is likely to be from rainfall infiltrating through the soil and into the aquifers of volcanogenic sediments and deeper rhyolite and ignimbrite aquifers. The aquifer is likely to be unconfined around site 3901.

Table 1. Aquifer characteristics.

Catch-ment	Date sampled	Well ID	Easting	Northing	Depth to Water (m)	Bore depth (m)	Screened interval (m)	Chemical Analyses	Aquifer type	Probable recharge source
Rotorua	10/07/2003	Hamurana Spring	2795621	6347367	n/a	n/a	n/a	C, I	Unconfined	Rainfall
Rotorua	10/07/2003	Taniwha Spring	2791832	6345487	n/a	n/a	n/a	C, I	Unconfined	Rainfall
Rotorua	10/07/2003	Hatchery Spring	2788810	6339920	n/a	n/a	n/a	C, I	Unconfined	Rainfall
Rotorua	10/07/2003	Te Waireka Spring	2786200	6336000	n/a	n/a	n/a	C, I	Unconfined	Rainfall
Rotorua	10/07/2003	Barlows Spring	2786036	6339206	n/a	n/a	n/a	C, I	Unconfined	Rainfall
Rotorua	11/07/2003	2116	2788852	6347137	72	124	90 - 124	C, I	Unconfined	Rainfall
Rotorua	11/07/2003	1202	2783712	6347247	63	124	91 - 124	C, I	Unconfined	Rainfall
Rotorua	11/07/2003	1561	2792917	6346011	15	73.1	63 - 73.1	C, I	Unconfined	Rainfall
Rotorua	11/07/2003	Dr. Irvin	2792871	6346460	16	45	39 - 45	C, I	??	Rainfall/stream/lake
Rotorua	11/07/2003	3691	2790581	6346727	60	118.5	78 - 118.5	C, I	Unconfined	Rainfall
Rotorua	20/08/2003	10424	2791945	6342100	2.74	21	14.5 - 21	C, I	Unconfined	Rainfall/stream/lake
Okareka	24/07/2003	JROYAL	2803342	6332487	1.15[*1]	1.6	open hole	C, I	Unconfined	Rainfall
Okareka	24/07/2003	3901	2803320	6332567	3.63[*1]	43	30 -43	C, I	Unconfined	Rainfall
Okareka	24/07/2003	Spring 2	2802307	6333413	n/a	n/a	n/a	C	Unconfined	Rainfall

Water levels taken from drillers log
[*1] Water level measured prior to sampling
C = full chemistry analyses
I = SF_6, Tritium and CFC

3.0 GROUNDWATER AGE DATING

The methodology for age dating of groundwater is described in Appendix 3.

3.1. Sampling and Analysis

Five springs and six privately owned groundwater wells in the north-western Lake Rotorua area (Fig. 10), and two privately owned wells in the north-western Lake Okareka area (Fig. 9) were sampled for tritium, CFCs, and SF_6. Location and bore details are listed in Table 1.

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. Glass 0.5 or 1 litre bottles were used for CFCs, and 2.5 litre bottles for $SF_{6.}$ All bottles were caped with nylon seals. For sampling springs, the bottle was placed in the spring outlet and fresh uncontaminated water was sucked through the bottle until the water was displaced 3-5 times using nylon tubing attached to a vacuum pump. Bottles were then quickly screw-sealed 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.

The tritium samples were analysed using the Institute of Geological & Nuclear Sciences Ltd. (GNS) state-of-the-art tritium measurement system with 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 SF6) concentrations were analyzed at GNS by gas chromatography.

3.2. Results

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

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 air levels (no obvious large artificial contamination), but they are too high for recharge before the 1960s (only restricted use for dating). Three of the waters have corresponding atmospheric CFC partial pressures above current air levels and are clearly contaminated with artificial CFC in the aquifer (cannot be used for dating). Trout Hatchery spring and well 1202 are slightly contaminated with CFC-12, while Dr. Irvin well is highly contaminated with CFC-12 and slightly contaminated with CFC-11.

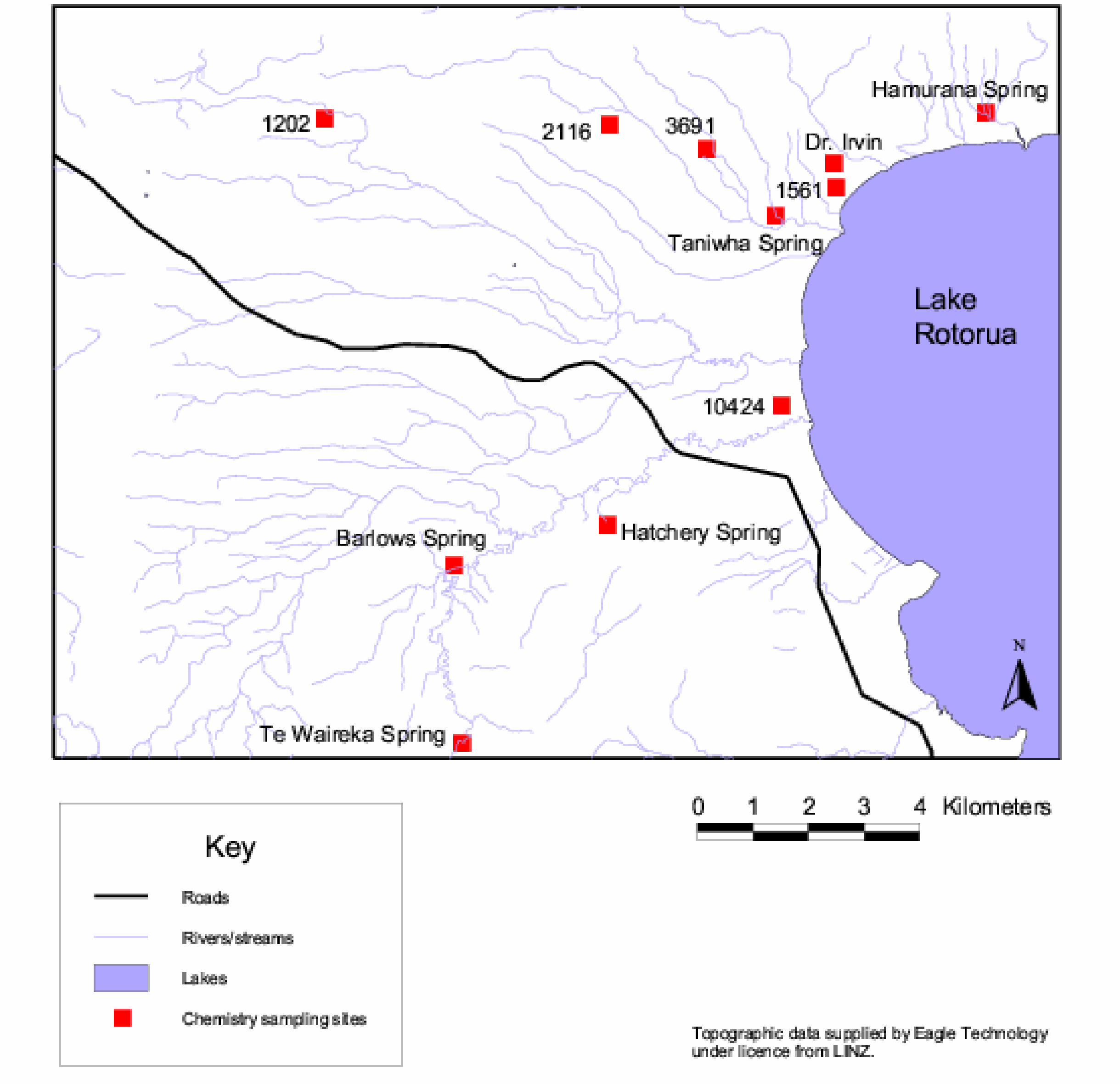


Figure 10 Western Rotorua water sampling sites. The springs were sampled at the following locations: Hamurana @ the spring beside the water supply intake, Taniwha @ the old well beside the water supply intake, Hatchery @ weir, Barlows @ water supply intake, and Te Waireka @ the upper pool at the water intake for the bottling plant.

Table 2. Tritium, CFC, and SF_6 results of spring water and groundwater well samples from the Lake Rotorua and Lake Okareka area. Locations are listed in Table 1. **TROT** and **FBP** are the laboratory codes for the samples. **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. **SigTR** is the one sigma standard measurement error. **pptv** is one part per trillion by volume or 10^{-18}. * To be analysed.

#	Sample	date	Tritium			Equil.		Atm.part.press.[pptv]		
			TROT	TR	sigTR	Temp	FBP	CFC11	CFC12	SF_6
						oC				
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	**Dr. Irvin**	11/07/2003	341	*		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	**JROYAL**	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

3.3 Resolving ambiguity and age interpretation

A combined exponential and piston-flow model (EPM) was applied to calculate the mean residence time (MRT) and the young water fraction (yf). This model represents a partly-mixed flow regime (Appendix 3). 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 very good matches to long-term tritium data in the Rotorua area (unpublished data) and therefore describes realistically the groundwater flow regime. Best matches are obtained with 90% mixed flow for Hamurana, Taniwha, and Trout Hatchery Springs. Slightly lower fractions of 60% and 70% of mixed flow match Te Waireka and Barlows Spring. A lower fraction of mixed flow (and consequently higher fraction of piston flow) at Barlows Spring is also indicated from two independent observations:

1. the groundwater seems to emerge directly from a deep-leading confined fracture, and
2. the smaller age difference between tritium and CFCs/SF_6 indicates a more confined flow regime which is represented by higher fraction of piston flow.

No long-term tritium data is available for the groundwater wells that were sampled in this study. 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 well JROYAL at Okareka 80% mixed flow was used because the well is very shallow (1.6m).

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). Only two samples (JROYAL and 1202) resulted in ambiguous residence times. However, ambiguity could be resolved using the CFC and SF_6 results. Full details of age interpretation are listed in Appendix 4.

The mean residence times derived from CFC and SF_6 are in almost all cases significantly younger than those derived from the tritium data (Appendix 4, Fig. 11). There are several reasons that can be attributed to this:

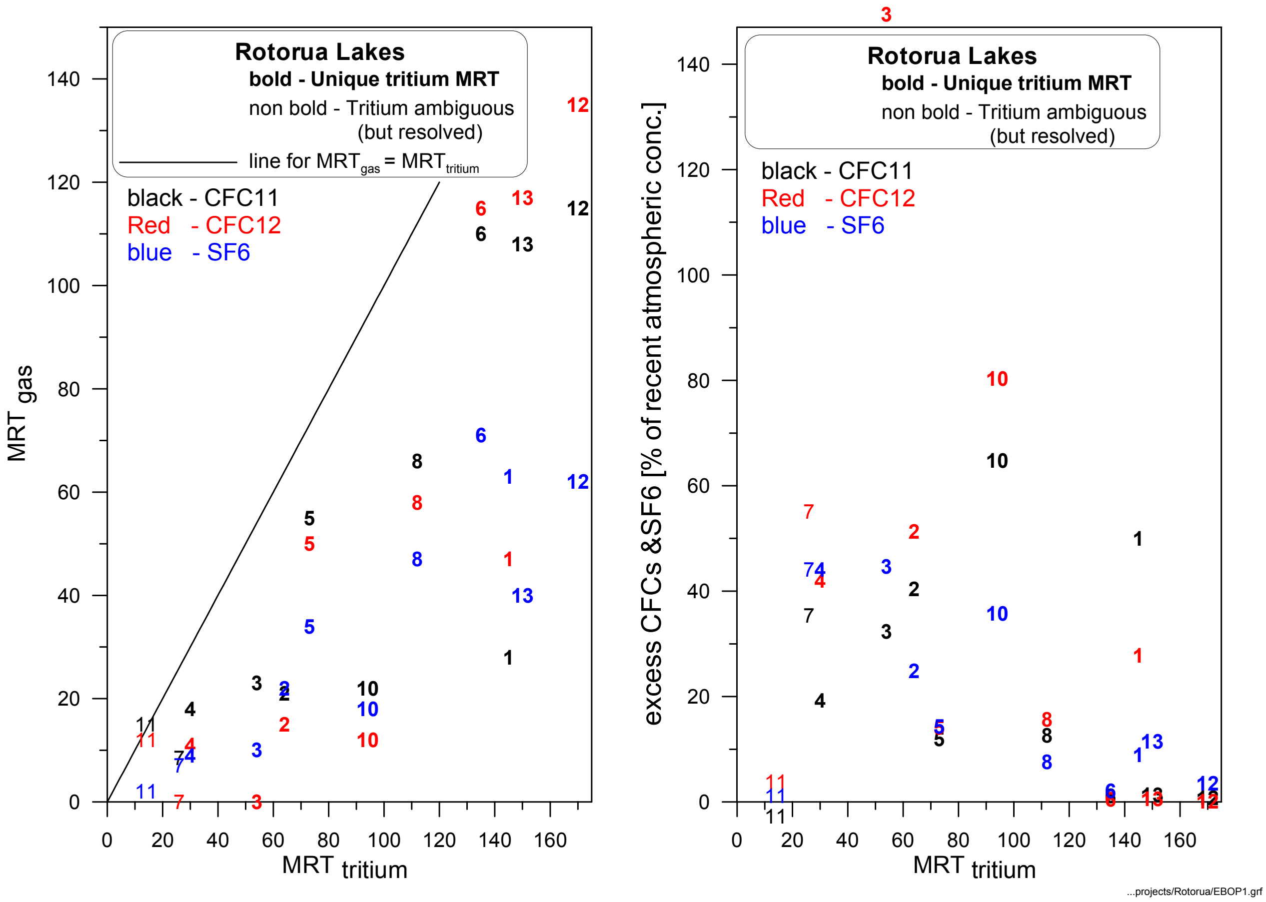


Figure 11 Comparison of tritium and CFC&SF_6 results. Mean residence times at left, and excess gas that would be necessary to account for the difference in tritium and gas MRT at right. Mean residence times deduced from CFC's and SF_6 are generally too low (see text), with the likely reason of gas exchange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

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, groundwater travel through the unsaturated zone does not explain the age differences even though 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.

As a quantitative measure for 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. 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 the groundwater and soil air occurs the CFC and SF$_6$ clock is partially reset toward zero, and CFC and SF$_6$ therefore indicate only a minimum mean residence time.

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 excessively 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 in this study are based on tritium time series data that shows good agreement with the decay- and mixing model.

Despite the differences in the tritium and gas methods the results indicate that the groundwater in the Lake Rotorua and Okareka area is at least several decades old. The unique tritium mean residence times are used, and for the ambiguous tritium results, CFCs and SF$_6$ could be used to resolve the ambiguity. The second tritium age interpretation for these cases is also listed in Appendix 4, but this solution is considered unlikely.

The age dating results for Rotorua springs and groundwater wells are summarised in Table 3. To identify the fraction of water that was recharged after land-use intensification (assumed to have started 40 years ago), the fraction younger than 40 years was calculated for each sample.

Table 3. Age dating 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 (see 3.1). MRT is the mean residence time of the water, deduced mostly from unique tritium age solutions (or solutions with ambiguity resolved). Full dating details are listed in Appendix 4. Yf(40y) is the fraction of water recharged after land-use intensification 40 years ago.

#	Sample	E%PM [%]	MRT [yrs]	yf(40y) [%]
1	Hamurana Spring	90	145	18
2	Taniwha Spring	90	64	44
3	Trout Hatchery Spring	90	54	51
4	Te Waireka Spring	60	30	79
5	Barlows Spring	70	73	30
6	2116	70	135	1
7	1202	70	26	84
8	1561	70	112	8
9	Dr. Irvin	70	in progress	
10	3691	70	94	16
11	JROYAL	80	14	95
12	3901	70	170	1
13	10424	70	150	1

Most of these groundwaters are relatively old with 8 out of the 12 samples having a mean residence time over 60 years. The corresponding young water fractions are between 1 and 44 %. These waters were recharged mainly before land-use intensification and therefore do not yet show the full effect of current land-use practices. Even if there is currently contamination in the recharge area, contaminant levels in these waters would still be low because the contaminants have not yet arrived at the springs and wells. However, over time the pristine old water in the aquifer is progressively replaced and increasingly contaminated water discharges into the lakes. Therefore, a further decline in water quality must be expected in the future. Any remedial action now will take decades to take effect because of the time delays.

The four younger waters with mean residence times between 14 and 54 years have young water fractions of 51-95%. If there is contamination in the recharge area, this will be reflected in the water quality already. Therefore further significant deterioration of water quality would not be expected for these waters.

4.0 HYDROCHEMISTRY

This hydrochemistry investigation involved collection and analysis of groundwater samples from eleven sites in the Rotorua catchment (Fig. 10) and from three sites in the Okareka catchment (Fig. 9). One sample was collected from each site between July and August of 2003 using standard sampling guidelines (Rosen et al., 1999). The samples were analysed by GNS for alkalinity, pH, Na, K, Ca, Mg, SiO_2, F, Cl, Br and SO_4. Further analysis was conduced by Hill Laboratories for NO_3-N, NO_2-N, NH_4-N, total oxidised nitrogen (TON), total kjeldahl nitrogen (TKN), dissolved reactive phosphorus (PO_4-P), total phosphorus (TP), dissolved Fe, and dissolved Mn. Laboratory reports of sample hydrochemistry are present in Appendix 5. A summary of results is presented in Table 4.

The composition of the Rotorua and Okareka groundwaters can be compared to groundwaters from other parts of New Zealand using the categories defined by Daughney and Reeves (2003). Six categories are based on the median compositions of fifteen analytes from 110 sites across New Zealand, sampled quarterly through the National Groundwater Monitoring Programme (NGMP). These categories reflect differences in hydrochemistry associated with oxidation-reduction potential, aquifer lithology and confinement, extent of water-rock interaction, and degree of human impact (Table 5). 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 6). These categories provide a useful framework for comparing the Rotorua and Okareka groundwaters to other groundwaters in New Zealand.

In the context described above, eleven of the fourteen sites investigated here fall into category 1B-2 (Table 4). This category is characterised by oxidised groundwaters, because there is little or no dissolved Fe or Mn, and nitrogen is in the form of nitrate-nitrogen (NO_3-N) rather than ammonium (NH_4-N). Groundwaters in this category typically show little evidence of anthropogenic impact from human or agricultural runoff, which is reflected by the relatively low chloride (Cl) & potassium (K) levels. Nitrate NO_3-N levels are generally found to be below a threshold value of 3.5 mg/L.

Finally, groundwaters in category 1B-2 are often hosted by volcanic or volcaniclastic aquifers, rather than by carbonate or siliciclastic aquifers. Two of the remaining sites (Dr. Irvin and JROYAL) fall into category 1A-2. Groundwaters in this category are similar to those in group 1B-2 because they are typically oxidised and hosted by volcanic or volcaniclastic aquifers; however, they show significant human impact in the form of elevated Cl and K and NO_3-N in excess of 3.5 mg/L. The remaining site (10424) falls into category 2A, indicating that it is reduced (without oxygen), and also indicated by measurable dissolved iron (Fe) and/or manganese (Mn), and nitrogen present in ammonium (NH_4-N) form.

Although the Rotorua and Okareka groundwaters can be meaningfully compared to one another and to other sites around New Zealand using the categories defined above, it is important to note that as a group, the Rotorua and Okareka groundwaters show some unusual chemical features. To identify these chemical features, the concentration of each analyte at each Rotorua and Okareka site can be compared to the range of ‘normal’ (i.e. background) concentrations expected for each of the six groundwater categories. The range of background concentrations were based on the 5th and 95th percentiles in concentration for each analyte in each of the six groundwater categories as defined by Daughney and Reeves (2003). In making this comparison it is important to note that the background concentrations defined by Daughney and Reeves (2003) was based on 110 National Groundwater Monitoring Programme (NGMP) sites. Only one of the NGMP sites penetrates an ignimbrite aquifer, Bay of Plenty site Pemberton.

Rotorua and Okareka groundwaters often show much lower concentrations of Ca, Mg and SO_4 and much higher concentrations of PO_4 and SiO_2 compared to other groundwaters sampled through the NGMP at the 90% confidence interval (Table 4). These hydrochemical features reflect the aquifer lithology. Ignimbrites are typically depleted in calcium (Ca), magnesium (Mg) and sulphate SO_4, and enriched in phosphorus and silicates relative to other rock types (Cox et al., 1979; Faure, 1998, Langmuir, 1997). Therefore a similar chemical pattern is expected in the Rotorua and Okareka groundwaters. They should also have relatively high concentrations of Na, K and F. Several sites do indeed show anomalously high concentrations of Na, K and/or F (relative to the NGMP sites), but this pattern cannot be considered universally representative of the Rotorua and Okareka catchments.

Table 4. Groundwater age and chemistry in the Rotorua and Okareka catchements. Water type calculated from major element composition. Category pertains to definitions given by Daughney and Reeves (2003) and summarised in Tables 5 and 6. MRT is the mean residence time (years), E%PM is the fraction (in percent) of mixed flow in the exponential piston flow model. Analytes measured in the field are highlighted in grey. 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.

	Hamurana Spring	Taniwha Spring	Hatchery Spring	Te Waireka Spring	Barlows Spring	2116	1202	1561	Dr. Irvin	3691	10424	JROYAL	3901	Spring 2
Date sampled	11/07/2003	11/07/2003	11/07/2003	11/07/2003	11/07/2003	11/07/2003	11/07/2003	11/07/2003	11/07/2003	11/07/2003	20/08/2003	24/07/2003	24/07/2003	24/07/2003
Water type	Na-Mg-HCO3	Na-Mg-Ca-HCO3	Na-HCO3-Cl	Na-HCO3	Na-Mg-HCO3-Cl	Na-HCO3	Na-Ca-HCO3	Na-Mg-HCO3	Ca-Mg-Na-HCO3-Cl	Na-HCO3	Na-HCO3	Ca-Na-Mg-HCO3	Na-HCO3-Cl	Na-HCO3-SO4
Category	1B-2	1B-2	1B-2	1B-2	1B-2	1B-2	1B-2	1B-2	1A-2	1B-2	2A	1A-2	1B-2	1B-2
MRT (years)	145	64	54	30	73	135	26	112		94	150	14	170	
E%PM	90	90	90	60	70	70	70	70	70	70	70	80	70	
Br (mg/L)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Ca (mg/L)	3.1	3.5	2	2.4	2.3	2.3	2.9	3.2	12.5	3.9	2.5	7	0.33	2.5
Cl (mg/L)	4.7	5.3	5.3	4.3	4.4	4.4	4.3	4.7	13	4.6	3.6	5.3	5.4	2.2
F (mg/L)	0.06	0.05	0.13	0.06	0.06	0.08	0.03	0.05	0.05	0.05	0.14	0.03	0.1	0.03
Fe (mg/L)	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	<0.02	0.07	< 0.02	< 0.02	3.78	< 0.02	0.43	< 0.02
HCO3 (mg/L)	39	35	21	26	27	34	25	39	26	58	49	31	27	21
K (mg/L)	2.5	1.9	3.3	4.4	2.7	0.21	1.9	2.6	5.5	0.49	2.7	6	0.7	5.9
Mg (mg/L)	2.1	2.2	1.2	1.2	1.5	1.3	1.4	2.2	6.6	2.7	1	2.6	0.17	1.4
Mn (mg/L)	< 0.0005	< 0.0005	0.0007	< 0.0005	< 0.0005	< 0.0005	<0.0005	0.0019	0.0007	0.009	0.162	< 0.0005	0.0008	0.0021
Na (mg/L)	9.7	9.6	7.1	8.2	6.9	10.4	7.9	10.2	10.6	15.8	11.4	7.5	14.5	9.6
NH4-N (mg/L)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	<0.01	< 0.01	< 0.01	< 0.01	0.32	< 0.01	0.02	0.02
NO2-N (mg/L)	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	<0.002	< 0.002	< 0.002	< 0.002	<0.002	< 0.002	< 0.002	< 0.002
NO3-N (mg/L)	0.735	1.41	0.945	1.75	0.567	0.223	1.4	0.606	13.7	0.847	0.012	3.84	0.1	1.8
TKN (mg/L)	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	1.3	0.1	< 0.1	1.6
PO4-P (mg/L)	0.096	0.067	0.045	0.033	0.083	0.081	0.029	0.091	0.048	0.045	0.021	0.015	0.585	0.041
TP (mg/L)	0.094	0.127	0.042	0.024	0.084	0.074	0.025	0.203	0.033	0.065	1.32	< 0.004	0.587	0.093
SiO2 (mg/L)	68	55	63	66	60	77	42	70	54	62	74	60	75	81
SO4 (mg/L)	1.4	1.6	3	2.3	1.4	1.4	3	1.3	1.4	1.4	0.13	5.7	4.7	14.6
DO (mg/L)	6.6	7.6	9.7	9.3	10.1	9.9	7.4	6.4	5.2	5.6	0.2	6.8	9	10
ORP (mV)	312	328	336	333	344	355	371	286	346	287	32	384	300	410
Turb (NTU)	25	<0	25	50	<0	147	84.2	21.1	52.6	255	>600	210	>600	>600
Cond (uS)	67	72	51	61	46	50	56	72	199	104	64	99	55	70
Temp (deg. C)	11.67	12.04	10.96	11.85	10.77	11.48	11.88	12.26	13.63	12.53	13.6	12.7	12.6	10.2
pH	6.97	6.85	7.17	7.09	6.98	7.04	6.51	6.86	6.33	6.78	7.09	6.16	6.88	6.75

Table 5. 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	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	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 6. 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

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 3). The MRT values range from 14 to 170 years. A direct comparison between samples using the MRT is usually not useful because MRT has a different meaning for different fraction of mixed flow. However, the mixing fraction of all these waters is considered to be in a narrow range from 70% to 90% of mixed flow (section 3.3). Therefore, comparison using MRT is meaningful, and the hydrochemical data can be plotted versus MRT as shown in Figures 12-15. Some very clear relationships between hydrochemistry and mean residence time can be identified.

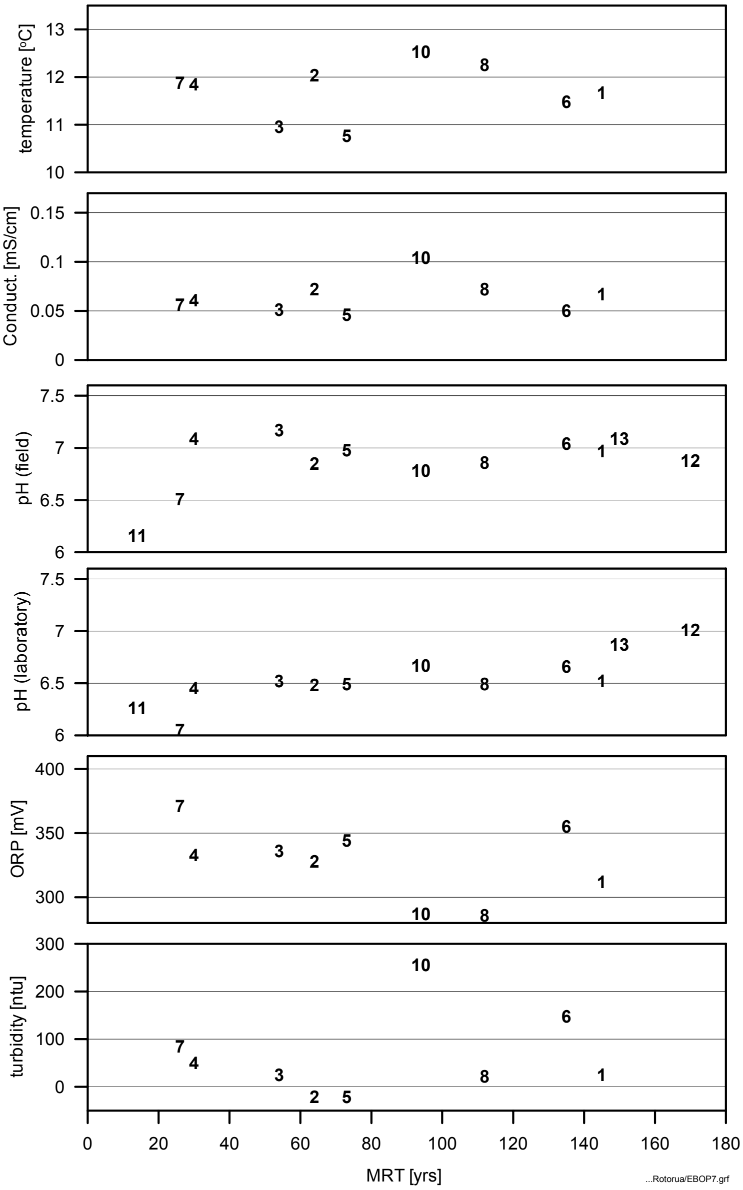


Figure 12 **Water parameters versus mean residence time (sample codes in Tab. 2 & 3).**

Water temperature, conductivity, and turbidity are relatively constant over MRT. These parameters do not depend on the time the water has been in contact with the aquifer. For the pH of the water there is a trend of increase over time. With longer contact time between the water and the aquifer minerals, the hydrochemistry changes with the result of increasing pH. The likely explanation is that the hydrogeochemical reactions during water-rock interaction result in higher pH, and these reactions come closer to equilibrium with increasing contact time. The oxygen-reduction potential (ORP) shows only a slight trend, with higher values for younger waters.

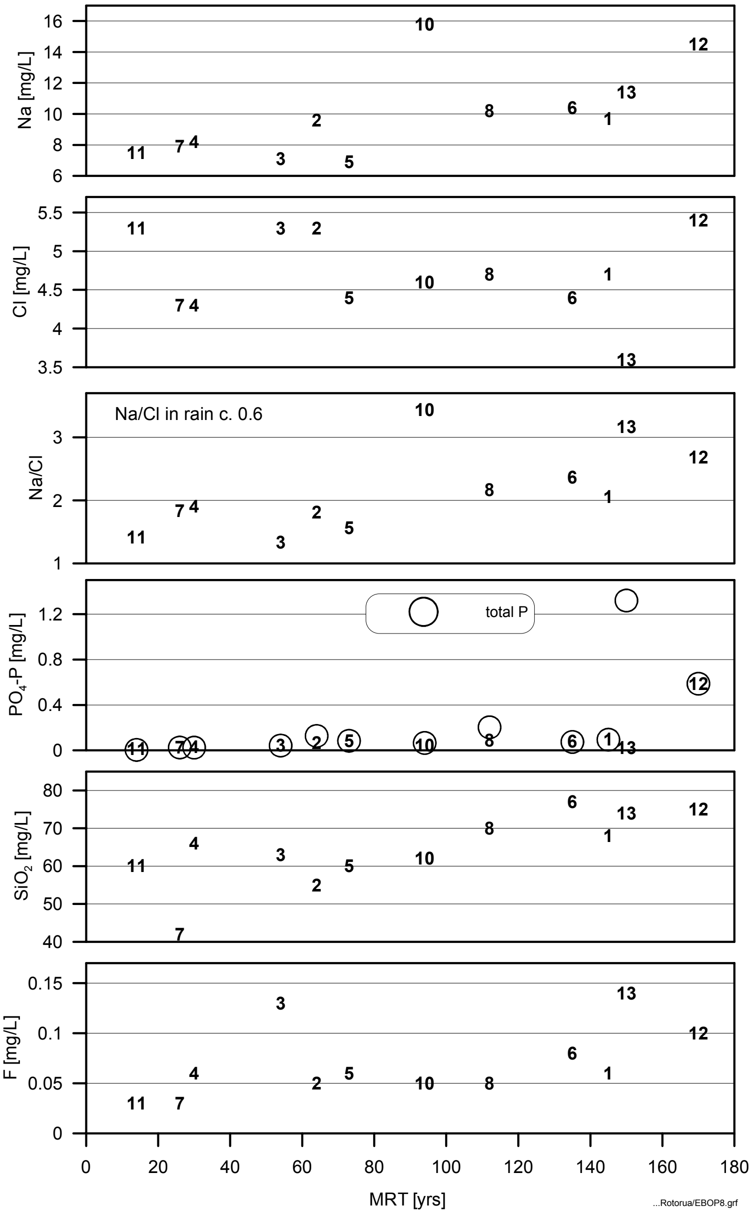


Figure 13 Hydrochemistry versus mean residence time

For several chemical species the relationship between concentration and age indicates progressive water-rock interaction (Fig.13). 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 these ignimbrite aquifers due to the dissolution of silicate minerals. Langmuir (1997) also found 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 is also progressively leached from the aquifer medium, while chloride (Cl) concentrations do not change and are relatively constant at 4.5 mg/L, reflecting the NaCl input by rain (Cl is about 10 mg/L in coastal rain and expected to be about 5 mg/L in the central North Island). It is expected that Cl is not being altered in the aquifer because Cl is generally a conservative tracer in groundwater. Progressive leaching of sodium is also indicated by the increasing sodium to chloride ratios, and by the excessive ratios compared to that of rain water which is about 0.6. Sodium and fluoride trends indicate that saturation concentration is not yet reached after MRT 170 years.

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. 13. Most of the PO_4-P and total P values agree, indicating that most of the present phosphorus is in the reactive dissolved PO_4-P form. Only well 10424 (#13) has high total P but little reactive dissolved PO_4-P. The likely reason for this is that the water in this well has reducing or anoxic conditions (Section 4.0).

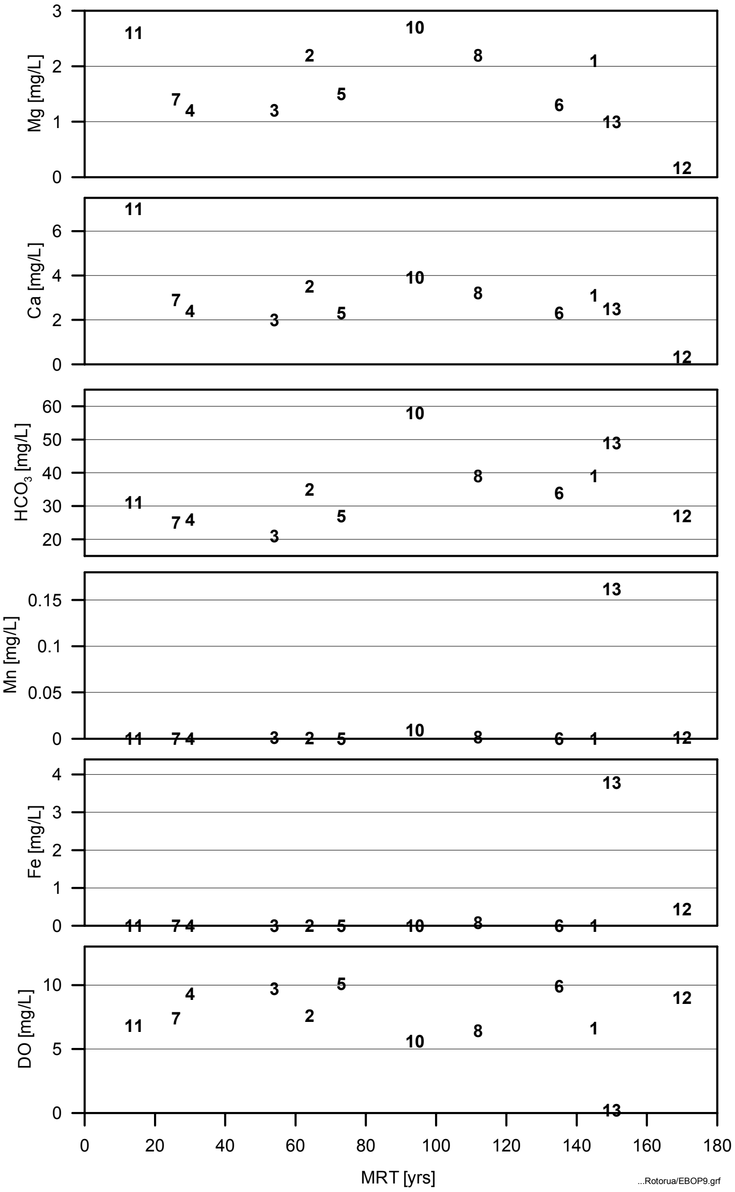


Figure 14 **Hydrochemistry versus mean residence time**

Some analytes do not increase or decrease much with groundwater age (Fig.14). Concentrations of Ca and Mg show little change with time, probably due to the absence of readily-soluble carbonate minerals in the aquifers. The trend is slightly decreasing concentration with increasing age. For bicarbonate (HCO_3), the trend indicates increasing concentration with groundwater age. This increase in HCO_3 cannot be attributed to the dissolution of carbonate minerals because of 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.

Increased concentrations in Fe and Mn and depletion of dissolved oxygen indicate anoxic groundwater conditions. This is observed only in well 10424 (#13). All other water samples show aerobic conditions.

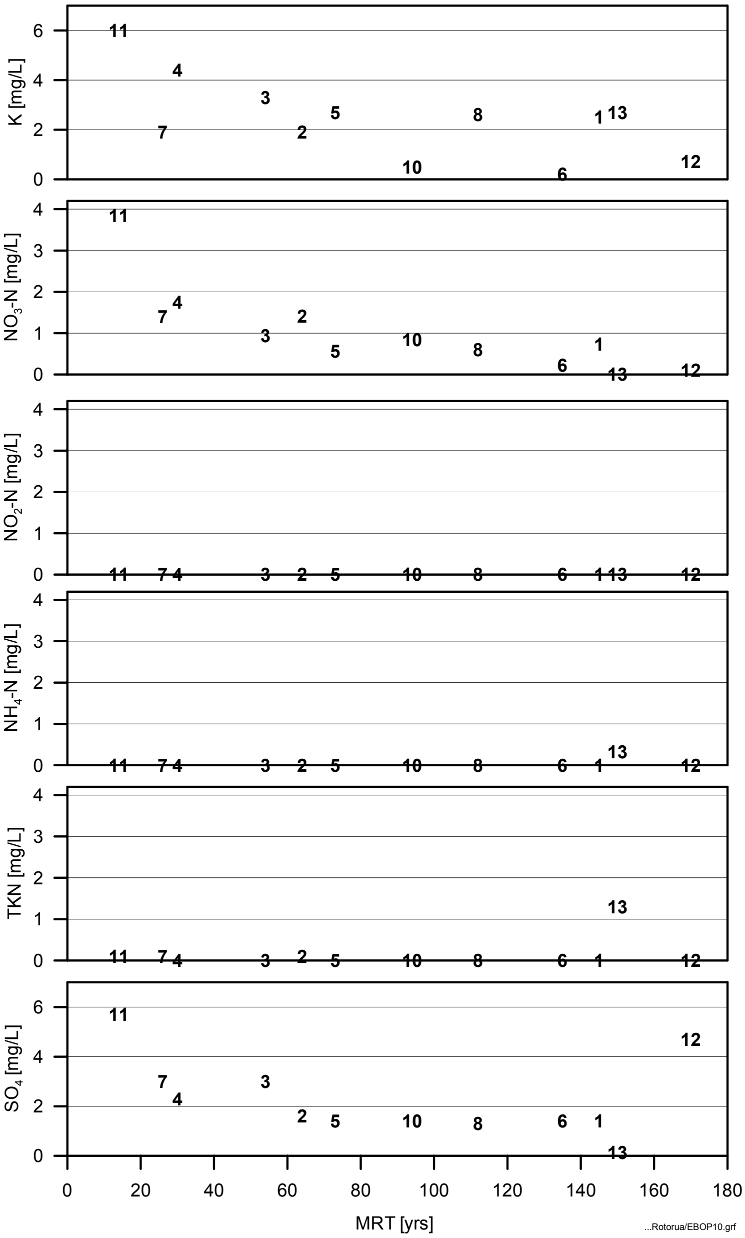


Figure 15 **Hydrochemistry versus mean residence time**

NO_3-N, K and SO_4 show highest concentration in young groundwater (Fig. 15), in contrast to SiO_2, PO_4-P, Na, F and HCO_3. This strongly suggests that these species are impacted by land-use intensification.

SO_4 concentrations are highest in young waters, and lower in older water (despite an outlier, #12, well 3901). The trend of increasing SO_4 and K concentrations in younger waters suggests a significant contribution from land-use activities.

A decrease in NO_3 concentration over time could be caused by microbial denitrification in reducing conditions where older groundwaters can become anoxic, such that NO_3 is converted to NH_4. However, only one of the oldest groundwaters is anoxic. Therefore, the NO_3 component in these groundwaters is expected to be stable (except for #13), and time trends in NO_3 concentration will indicate changes in NO_3 input to the groundwater system. The NO_3 component is clearly the major component of nitrogen in this aquifer (Fig. 15). NO_2, NH_4 and TKN are negligible, except for the anoxic water. For that reason, the trends for nitrogen loading are deduced from nitrate only.

Nitrate, the main concern of nutrient loading to the lakes, shows a clear trend versus age. The oldest waters contain nearly no nitrate, while concentration increases with increasing contribution of water recharged after land-use intensification. Therefore it can be concluded that most of the nitrate originates from land-use activities. The youngest waters contain about 4 mg/L nitrate-N (for comparison the NZ drinking water standard is 11.3 mg/L), while the oldest waters contain 0.1 mg/L.

6.0 CURRENT AND FUTURE NUTRIENT LOAD

The groundwater system of the Rotorua Lakes area generally has old groundwater so it is likely that contamination can go unrecognised for some time because of the long residence time of the water in the ground. Contaminant levels in surface water are likely to increase because of the progressive arrival of contaminated groundwater discharging to surface water. In future, the old pristine groundwater in the aquifers will be replaced by contaminated water, which will then discharge back to the surface through springs and through the lake beds.

The hydrochemistry was measured in conjunction with age dating to assess the past and current state, and future trends in water chemistry:

- *Background hydrochemistry – undeveloped catchment*
  The natural background groundwater chemistry that is not influenced by human land-use change can be identified from the old groundwater that is still travelling in the groundwater system. Old water with low young water fraction (recharged prior to land-use change) cannot be influenced by land-use intensification and must reflect natural conditions. The natural level of water chemistry depends on the atmospheric, soil, and aquifer conditions, and the time the water has been in contact with the aquifer rocks. Establishment of the natural pre-landuse level without age data is not trivial. Even if there is an undeveloped area available with the same hydrogeology for comparison, different residence times of the water in the aquifer can cause 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 is recharged after land-use intensification), the contaminant levels that will occur in the future can be estimated for the current contaminant input in the recharge area.

The major nutrient loading to Lakes Rotorua and Okareka are nitrate, phosphorus, and potassium. Figure 16 shows the concentrations of these nutrients in the water versus young water fraction. The young water fractions of the samples range between 0 and 100%. Therefore, excellent time trends of hydrochemical composition 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 is a linear function of the fraction of contaminated water. Therefore, in plots of the NO_3 and K concentration versus young water fraction, the intercept of linear fits to the data at 0% defines the natural background concentration level, and the intercept at 100% young water defines the current contamination level after land-use intensification.

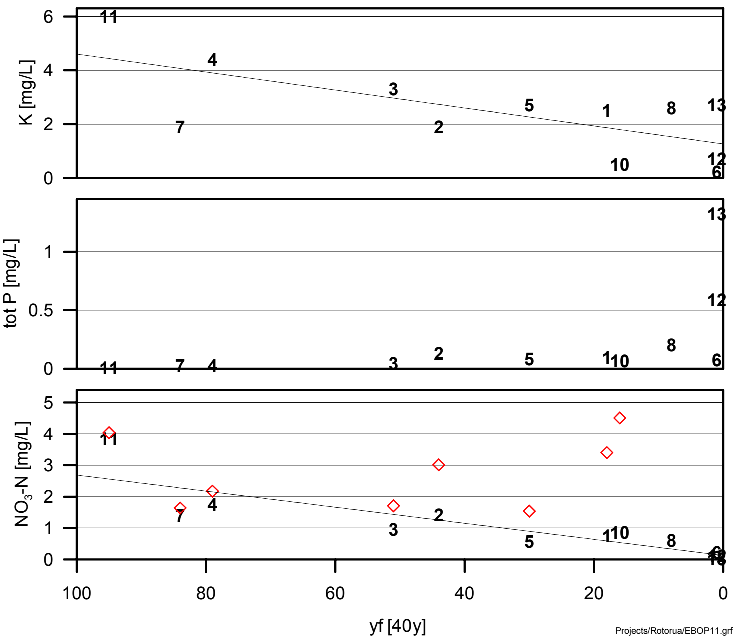


Figure 16 Nutrient concentrations versus young water fraction. Yf(40y) is the fraction of water recharged after land-use intensification 40 years ago. The diamonds are the expected future NO_3 concentrations. For the oldest waters the future concentrations are not plotted because erroneous errors due to extrapolation from near zero.

The nitrate concentration is significantly higher for water with high fraction recharged after land-use intensification. The data follow a clear trend over the whole range of young water fraction, allowing for good estimates of background and current contamination level.

The natural background level of NO_3-N (before land-use intensification) can be calculated from the linear regression to be 0.15 mg/L. Sample #13 (bore 10424) in the western Rotorua study area was not included because it's low NO_3-N concentration could be caused by denitrification due to anoxic conditions. The low background level of 0.15 mg/L from the linear regression is in good agreement with the data of samples #6 (bore 2116- Rotorua catchment) and #12 (bore 3901-Okareka catchment) that have 99% pre-land-use 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).

For the present water recharge, a NO_3-N level of 2.7 mg/L can be deduced from the linear fit to the data. With the low natural background, the major contribution of the current NO_3-N level consequently is from land-use. From the current NO_3-N level, only 6% can be attributed to natural background, and 94% is from land-use impacts. This is an increase by a factor 18. There is little variation of the data along the time trend, which indicates that the nitrate contamination is relatively uniform in the catchment, and/or that the groundwater systems are relatively well mixed (suggested also by the tritium results).

A similar fit to the potassium data indicates a natural background level of 1.3 mg/L and a current level of 4.6 mg/L. Therefore, about 30% of the current K level is natural background, and 70% is from land-use change impact. This is an increase by a factor 3.5. 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. This would reduce the projected future increase. Potassium is not of major concern as contaminant because it is not a limiting nutrient.

Total Phosphorus is very low in young water (<0.04 mg/L), but increases with decreasing young water fraction, and is considerably higher in the oldest water (1.3 mg/L). This clearly suggests that the phosphorus in the groundwater does not originate from land-use practises, but is leached from the aquifer material of volcanic deposits. This is consistent with observations by Vant & Smith, (2002) in the Lake Taupo catchment (which has similar ignimbrite geology and landuse change chronology). The current total phosphorus levels represent natural conditions, and no changes in P concentration are expected over time.

SO_4 does show anthropogenic influence but no time trend was done because it has high levels in the lakes from geothermal influence and would not be a limiting nutrient.

			mean	current	bkg	current NO_3-N load				future NO_3-N load			
			flow	NO_3-N	NO_3-N	bkg	land-use	total	total	land-use	total	total	add.
site	spring	yf (40y)	[m^3/s]	[g/m^3]	[g/m^3]	[t/y]	[t/y]	[t/y]	%	[t/y]	[t/y]	%	[t/y]
1	Hamurana	18	2.75	0.735	0.15	13.0	51	64	43	282	295	62	231
2	Taniwha (Awahou)	44	1.67	1.41	0.15	7.9	66	74	50	151	159	33	85
3	Trout Hatchery	51	0.12	0.945	0.15	0.6	3.0	3.6	2	5.9	6.5	1	2.9
4	Te Waireka	79	0.06	1.75	0.15	0.3	3.0	3.3	2	3.8	4.1	1	0.8
5	Barlows	30	0.24	0.567	0.15	1.14	3.2	4.3	3	10.5	11.7	2	7.4
						23	126	149	100	453	476	100	327

			mean	current	bkg	current K load				future K load			
			flow	K	K	bkg	land-use	total	total	land-use	total	total	add.
site	spring	yf (40y)	[m^3/s]	[g/m^3]	[g/m^3]	[t/y]	[t/y]	[t/y]	%	[t/y]	[t/y]	%	[t/y]
1	Hamurana	18	2.75	2.5	1.3	113	104	217	61	579	691	76	474
2	Taniwha (Awahou)	44	1.67	1.9	1.3	69	32	100	28	72	140	15	40
3	Trout Hatchery	51	0.12	3.3	1.3	4.9	7.6	12.5	3	14.9	19.8	2.2	7.3
4	Te Waireka	79	0.06	4.4	1.3	2.5	5.9	8.3	2	7.4	9.9	1.1	1.6
5	Barlows	30	0.24	2.7	1.3	9.85	10.6	20.4	6	35.3	45.2	5.0	24.7
						199	160	358	100	708	907	100	548

		mean	current	PO_4-P	
		flow	PO_4-P	load	
site	spring	[m^3/s]	[g/m^3]	[t/y]	%
1	Hamurana	2.75	0.096	8	65
2	Taniwha (Awahou)	1.67	0.067	4	28
3	Trout Hatchery	0.12	0.045	0.2	1
4	Te Waireka	0.06	0.033	0.1	0
5	Barlows	0.24	0.083	0.6	5
				13	100

Table 7. Estimates of the current and future loads (t/yr) of NO_3-N, PO_4-P and K for the springs. Data for mean flow are from Pang et al. (1996), and supplied by EBOP. The calculations 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 40 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 draining water is post-1965 (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 the five springs.

Table 7 summarises the nutrient loads for the springs calculated from the mean flows. Of the five investigated springs, the Hamurana and Awahou-Taniwha spring systems contribute most of the nutrient load to Lake Rotorua (about 90%) because of their large flow regimes. The total loads of NO_3-N, K, and PO_4-P are currently 149, 358, and 13 t/year, respectively. However this is based on one sub-spring sample for age dating and chemical analysis for

Hamurana and Awahou-Taniwha springs systems which are multispring systems. In absence of more detailed data we have applied the total flow of the spring system to the age and chemistry data of the sub-spring, assuming that these measured data is representative for the whole spring system. This may need to be verified because these springs are critical for the total nutrient load to the lake. Sampling and analysis of several sub-springs would provide verification if the whole spring system is uniform.

The current NO_3-N loads are relatively high for the Hamurana and Taniwha spring system, but the future load is likely to increase dramatically to 454 t/year. The current concentrations are still relatively low due to the old age of the water, and 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-N concentrations (scaled to 100% young water) for the individual springs are plotted in Fig. 16. These will reach values close to current NO_3-N level of young water (1.7-4.5 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 outlines also indicates that the model assumptions are realistic.

In conclusion some major springs already discharge water to the lake with NO_3-N of 0.7-1.4 mg/L. These are expected to increase to about 3 mg/L while the current total nitrogen concentration of Lake Rotorua is 0.45 mg/l. Therefore dramatic increases in nutrient load to the lake must be expected in the future decades especially for the large old groundwater bodies. The nitrate concentration in the lake must therefore be expected to increase significantly.

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APPENDIX 1 - WATER LEVEL DATA.

Study Area	Well Number	Easting	Northing	Static Level (m)	Elevation (m)	Data source	Relative water level (m)	Method of obtaining elevation
Rotorua	165	2787900	6342200	45.7	342	EBOP	296.3	Estimated
Rotorua	1076	2780100	6341600	39.6	504	EBOP	464.4	Estimated
Rotorua	1202	2784000	6347000	63	503	EBOP	440	Estimated
Rotorua	1204	2785000	6347500	78	503	EBOP	425	Estimated
Rotorua	1214	2787700	6339800	24	400	EBOP	376	Estimated
Rotorua	1249	2787200	6341000	88	380	EBOP	292	Estimated
Rotorua	1317	2789500	6341000	20.1	290	EBOP	269.9	Estimated
Rotorua	2145	2786000	6347000	74	500	EBOP	426	Estimated
Rotorua	3469	2791220	6346700	54	345	EBOP	291	Estimated
Rotorua	3654	2782000	6340800	52	504	EBOP	452	Estimated
Rotorua	3655	2787500	6342000	58.5	357	EBOP	298.5	Estimated
Rotorua	3657	2789500	6348400	88	430	EBOP	342	Estimated
Rotorua	4006	2791010	6343970	18.3	300	EBOP	281.7	Estimated
Rotorua	4007	2789360	6344720	unknown	346	EBOP	unknown	Estimated
Rotorua	4378	2791100	6344500	13	300	EBOP	287	Estimated
Rotorua	4525	2787700	6343200	65	370	EBOP	305	Estimated
Rotorua	10158	2787950	6342860	56	350	EBOP	294	Estimated
Rotorua	3691	2790510	6346760	60	365	EBOP	305	Estimated
Rotorua	1	2784777.897	6343301	47.57	472.934	Rosen (1998)	424.894	Surveyed
Rotorua	2	2788826.843	6341451	45.82	336.606	Rosen (1998)	290.386	Surveyed
Rotorua	3	2789325.189	6344683	51.75	346.812	Rosen (1998)	294.152	Surveyed
Rotorua	4	2791338.036	6343090	2.32	288.38	Rosen (1998)	284.13	Surveyed
Rotorua	5	2788781.195	6340580	2.61	297.394	Rosen (1998)	294.164	Surveyed
Rotorua	6	2788902.279	6340489	2.63	296.065	Rosen (1998)	293.435	Surveyed
Rotorua	7	2789659.053	6345860	47.03	367.617	Rosen (1998)	319.897	Surveyed
Rotorua	8	2787677.576	6347433	72.71	461.652	Rosen (1998)	387.882	Surveyed
Rotorua	9	2786236.886	6347882	89.97	541.981	Rosen (1998)	451.461	Surveyed
Rotorua	10	2784409.807	6345315	76.32	508.711	Rosen (1998)	431.461	Surveyed
Rotorua	11	2786527.919	6342902	68.11	419.256	Rosen (1998)	350.706	Surveyed
Rotorua	12	2788183.698	6344643	52.48	385.751	Rosen (1998)	332.311	Surveyed
Rotorua	13	2792912.422	6346015	15.1	300.801	Rosen (1998)	285.701	Surveyed
Rotorua	14	2794702.418	6347715	56.16	338.96	Rosen (1998)	282.8	Surveyed
Rotorua	1561	2792910	6345900	15.3	295	EBOP	279.7	Estimated
Rotorua	4008	2788600	6346600	63.93	410	EBOP	346.07	Estimated
Okaraka	110	2803300	6330700	3.05	358	EBOP	354.95	Estimated
Okaraka	133	2803500	6331500	7.62	370	EBOP	362.38	Estimated
Okaraka	145	2803500	6331600	3.66	358	EBOP	354.34	Estimated
Okaraka	153	2803400	6331500	16	390	EBOP	374	Estimated
Okaraka	172	2803400	6331600	10.7	365	EBOP	354.3	Estimated

Study Area	Well Number	Easting	Northing	Static Level (m)	Elevation (m)	Data source	Relative water level (m)	Method of obtaining elevation
Okaraka	173	2803500	6331700	3	356	EBOP	353	Estimated
Okaraka	220	2803200	6331300	66	420	EBOP	354	Estimated
Okaraka	225	2803300	6330800	7.3	357	EBOP	349.7	Estimated
Okaraka	1251	2803500	6331400	6	372	EBOP	366	Estimated
Okaraka	1276	2803300	6331100	10	368	EBOP	358	Estimated
Okaraka	3728	2803200	6331200	7.23	410	EBOP	402.77	Estimated
Okaraka	3730	2803200	6331000	10.87	380	EBOP	369.13	Estimated
Okaraka	JROYAL	2803342	6332487	1.15	358	GNS	356.85	Estimated
Okaraka	3901	2803320	6332567	3.63	360	GNS	356.37	Estimated

APPENDIX 2 - GEOLOGICAL DATA.

Study Area	Well Number	easting	Northing	Unit Top	Unit Bottom	Description
Rotorua	237	2789800	6345600	6	15	PUMICE SANDS and SILT
Rotorua	237	2789800	6345600	0	6	
Rotorua	1056	2786500	6347500	0	4.6	CLAY and yellow PUMICE
Rotorua	1056	2786500	6347500	4.6	76.2	RHYOLITE
Rotorua	1056	2786500	6347500	76.2	94.5	soft SANDS and PUMICE
Rotorua	1056	2786500	6347500	94.5	134.1	pumiceous IGNIMBRITE with layered GRAVELS and SANDS
Rotorua	1057	2788000	6347000	0	3	CLAY
Rotorua	1057	2788000	6347000	3	85.3	RHYOLITE
Rotorua	1057	2788000	6347000	85.3	103.6	soft IGNIMBRITE
Rotorua	1057	2788000	6347000	103.6	134.1	firm IGNIMBRITE with fine layered white grey brown Undiff. S
Rotorua	1063	2789300	6344700			
Rotorua	1063	2789300	6344700	0	9.1	yellow PUMICE CLAY
Rotorua	1063	2789300	6344700	9.1	97.5	brown and grey RHYOLITE becoming hard
Rotorua	1063	2789300	6344700	97.5	103.6	soft fractured RHYOLITE
Rotorua	1202	2784000	6347000	2	124	Rhyolite
Rotorua	1202	2784000	6347000	0	2	Clay, pumice
Rotorua	1204	2785000	6347500	0	137	Rhyolite
Rotorua	1269	2792900	6345800	0	45	PUMICE fine and silty SANDS
Rotorua	1446	2788700	6344600			
Rotorua	1446	2788700	6344600	0	10	Clay and pumice
Rotorua	1446	2788700	6344600	10	87	Mamaku ignimbrite soft but becoming firm with depth. Fractured.
Rotorua	1561	2792910	6345900	42.7	68.6	pink RHYOLITE
Rotorua	1561	2792910	6345900	68.6	73.1	brown RHYOLITE
Rotorua	1561	2792910	6345900	0	42.7	layered CLAY PUMICE SANDS and SILT
Rotorua	2116	2788000	6347200	0	124	Rhyolite
Rotorua	2145	2786000	6347000			
Rotorua	2145	2786000	6347000	0	147.5	Rhyolite
Rotorua	3657	2789500	6348400	0	4	Clay and pumice
Rotorua	3657	2789500	6348400	4	250	Rhyolite
Rotorua	3691	2790510	6346760	6	118.5	Rhyolite pink – some fractured
Rotorua	3691	2790510	6346760	0	6	Pumice
Okaraka	110	2803300	6330700	0	18.3	hard compacted SANDS and PUMICE
Okaraka	133	2803500	6331500	0	42.7	PUMICE and SANDS
Okaraka	145	2803500	6331600	0	29.1	Unknown
Okaraka	153	2803400	6331500	0	67.1	PUMICE SILT and SANDS over RHYOLITE
Okaraka	154	2803300	6331200	0	19.5	PUMICE SANDS and GRAVELS
Okaraka	172	2803400	6331600	0	15.3	PUMICE SANDS and GRAVELS
Okaraka	173	2803500	6331700	0	17.1	PUMICE SANDS and GRAVELS

Study Area	Well Number	easting	northing	Unit Top	Unit Bottom	Description
Okaraka	220	2803200	6331300	0	9	PUMICE and SANDS
Okaraka	220	2803200	6331300	9	92	RHYOLITE
Okaraka	222	2803300	6331800	0	19.5	SANDS
Okaraka	225	2803300	6330800	0	19.5	PUMICE and SANDS
Okaraka	1251	2803500	6331400	0	31	PUMICE and SANDS over RHYOLITE
Okaraka	1254	2803300	6331100	0	31	PUMICE and SANDS over RHYOLITE
Okaraka	1276	2803300	6331100	0	20	SANDS and fine SILT
Okaraka	1276	2803300	6331100	20	32	RHYOLITE
Okaraka	3728	2803200	6331200	0	0.3	Rock and fill
Okaraka	3728	2803200	6331200	0.3	6.15	Pumice
Okaraka	3728	2803200	6331200	6.15	34.65	Ignimbrite
Okaraka	3729	2803400	6331400	0	0.3	Road
Okaraka	3729	2803400	6331400	0.3	2.1	Soft pumice and silt
Okaraka	3729	2803400	6331400	2.1	46.6	Ignimbrite
Okaraka	3730	2803200	6331000	0	0.25	Road
Okaraka	3730	2803200	6331000	0.25	14	Loose pumice
Okaraka	3730	2803200	6331000	14	25.23	Ignimbrite
Okaraka	3731	2803500	6331200	0	0.2	Top soil
Okaraka	3731	2803500	6331200	0.2	14.42	Loose sand and pumice
Okaraka	3731	2803500	6331200	14.92	19.12	Ignimbrite
Okaraka	3901	2803320	6332567	0	13	Pumice and sand
Okaraka	3901	2803320	6332567	13	30	White and brown pumice
Okaraka	3901	2803320	6332567	30	31	Sand and clay
Okaraka	3901	2803320	6332567	31	36.5	Sand pumice
Okaraka	3901	2803320	6332567	36.5	43	Pumice and gravel

APPENDIX 3 - METHOD OF TRITIUM AND CFC/SF_6 AGE DATING OF GROUNDWATER

Groundwater Age Dating

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). 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).

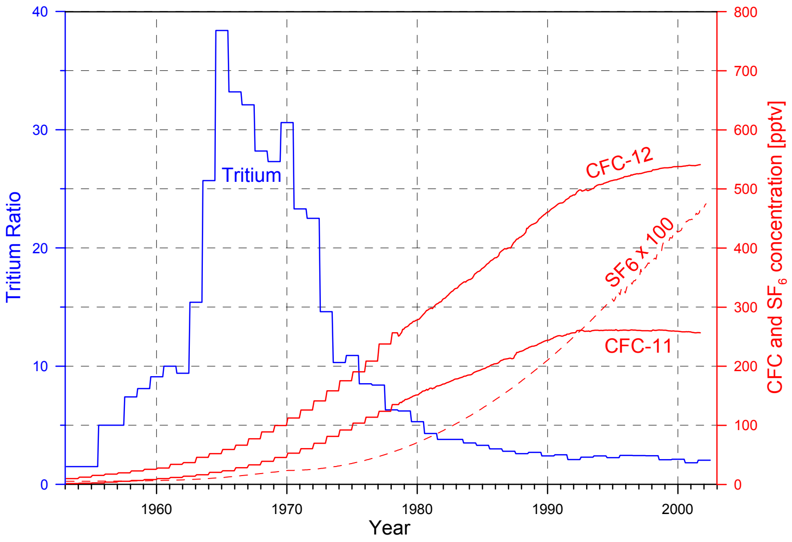


Figure 17 Tritium and CFC/SF_6 input. Tritium concentrations in rain at Kaitoke, 40km north of Wellington (yearly averages), and CFC and SF6 concentrations in southern hemispheric air. TR=1 represents a 3H/1H ratio of 10-18, and 1 pptv is one part per trillion by volume of CFC or SF6 in air, or 10-12. Pre-1978 CFC data are reconstructed according to Plummer and Busenberg (1999), and scaling to southern hemisphere by factor 0.83 (CFC-11) and factor 0.9 (CFC-12). Post-1978 CFC data are from Tasmania. Pre 1970 SF6 data are reconstructed (USGS Reston), 1970-1995 data are from Maiss and Brenninkmeijer (1998), and post 1995 data measured in Tasmania.

As a result of the superimposed atmospheric tritium "bomb" peak in the 60s, 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 concentrations in the atmosphere have gradually increased (Fig.). 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.). 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 relatively well with tritium data. Note that CFC and SF_6 ages do not take into account of travel time through unsaturated zones.

Due to the large tritium input during 1965-1975 the tritium method is very sensitive to the flow (mixing) model. If time series of tritium data, or additional CFC and SF_6 data are available, age ambiguity can be resolved. Therefore, both groundwater age and age distribution can be obtained.

Groundwater mixing models

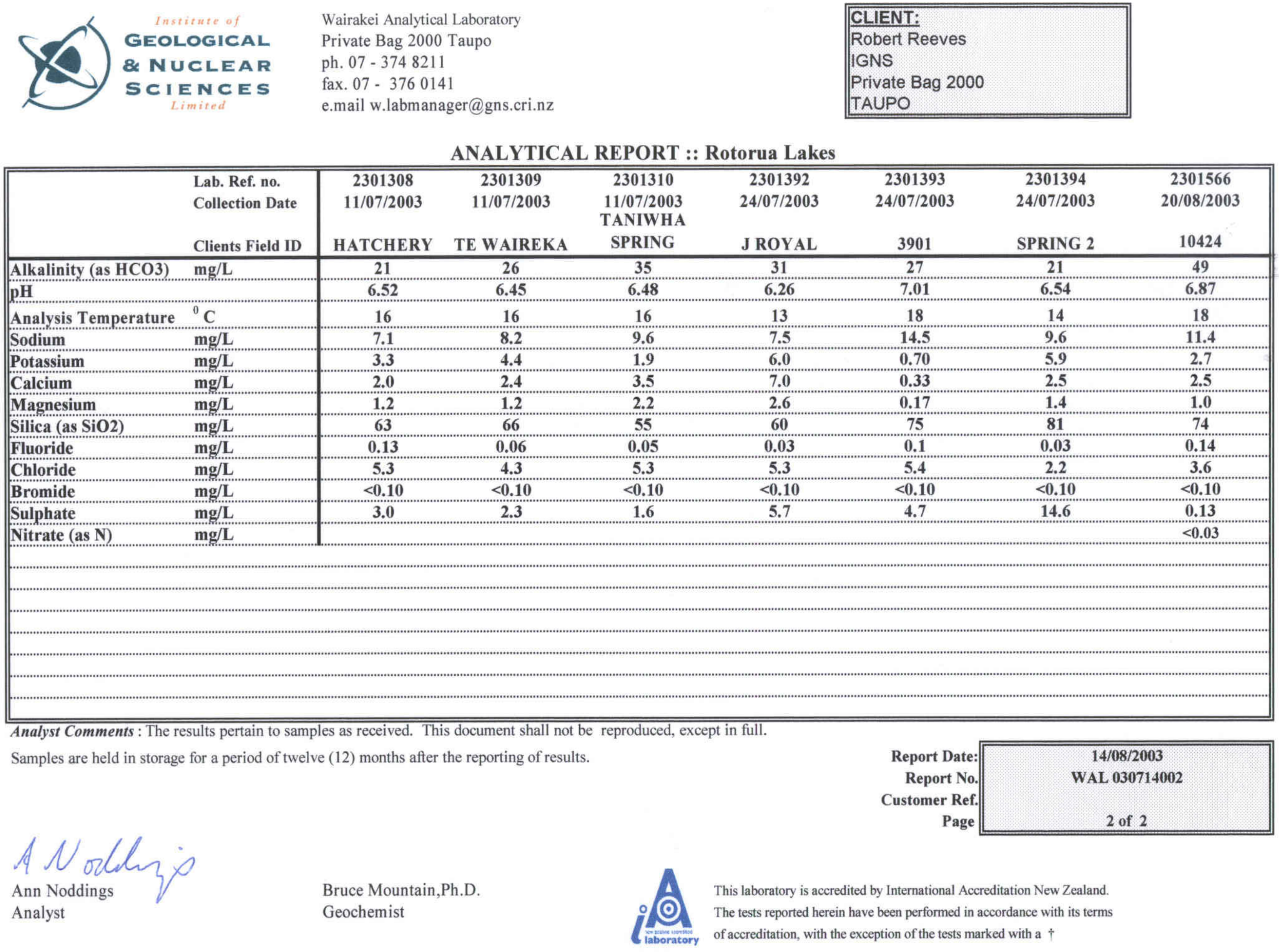
Groundwater comprises a mixture of water of different ages due to mixing processes underground. Therefore, the groundwater doesn't have a discrete age but has an age distribution or spectrum. Various mixing models with different age distributions describe different hydrogeological situations (Maloszewski 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) or two measurements over time are necessary

APPENDIX 4 - AGE DATING RESULTS FOR ROTORUA SPRINGS AND GROUNDWATER WELLS.

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). **Yf(40y)** is the fraction of water younger than 40 years. For age interpretation the tritium input from Kaitoke scaled by a factor of 0.9 was used, with integration steps of one year.

#	Sample	E%PM	MRT tritium			MRT				MRT				MRT				yf(40y)
			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	**18**
2	**Taniwha Spring**	90	**64**			21	75	105	40	15	141	282	51	22	0.57	1.34	25	**44**
3	**Trout Hatchery Spring**	90	**54**			23	87	84	32	0	168	822	149	10	0.72	2.41	45	**51**
4	**Te Waireka Spring**	60	**30**			18	153	50	19	11	246	231	42	9	0.83	2.38	44	**79**
5	**Barlows Spring**	70	**73**			55	29	31	12	50	57	78	14	34	0.11	0.77	14	**30**
6	**2116**	70	**135**			110	1	2.9	1	115	5	2.7	0	71	0	0.11	2	**1**
7	**1202**	70		8-30	**26**	8.5	156	92	35	0	298	303	55	7	1.26	2.38	44	**84**
8	**1561**	70	**112**			66	4	32.7	13	58	10	86	16	47	0.01	0.41	8	**8**
9	**Dr. Irvin**	70																
10	**3691**	70	**94**			22	9.5	169	65	12	21	442	80	18	0.03	1.93	36	**16**
11	**JROYAL**	80		0-4	**14**	15	220	-7	-3	12	440	21	4	2	4.8	0.06	1	**95**
12	**3901**	70	**170**			115	1	1.9	1	135	2	0.5	0	62	0	0.19	4	**1**
13	**10424**	70	**150**			108	1	3.4	1	117	4	3.1	1	40	0	0.62	11	**1**

APPENDIX 5 - ORIGINAL WATER CHEMISTRY REPORTS.



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ANALYTICAL REPORT :: Rotorua Lakes

	Lab. Ref. no. Collection Date Clients Field ID	2301308 11/07/2003 HATCHERY	2301309 11/07/2003 TE WAIREKA	2301310 11/07/2003 TANIWHA SPRING	2301392 24/07/2003 J ROYAL	2301393 24/07/2003 3901	2301394 24/07/2003 SPRING 2	2301566 20/08/2003 10424
Alkalinity (as HCO3)	mg/L	21	26	35	31	27	21	49
pH		6.52	6.45	6.48	6.26	7.01	6.54	6.87
Analysis Temperature	°C	16	16	16	13	18	14	18
Sodium	mg/L	7.1	8.2	9.6	7.5	14.5	9.6	11.4
Potassium	mg/L	3.3	4.4	1.9	6.0	0.70	5.9	2.7
Calcium	mg/L	2.0	2.4	3.5	7.0	0.33	2.5	2.5
Magnesium	mg/L	1.2	1.2	2.2	2.6	0.17	1.4	1.0
Silica (as SiO2)	mg/L	63	66	55	60	75	81	74
Fluoride	mg/L	0.13	0.06	0.05	0.03	0.1	0.03	0.14
Chloride	mg/L	5.3	4.3	5.3	5.3	5.4	2.2	3.6
Bromide	mg/L	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Sulphate	mg/L	3.0	2.3	1.6	5.7	4.7	14.6	0.13
Nitrate (as N)	mg/L							<0.03

Analyst Comments : The results pertain to samples as received. This document shall not be reproduced, except in full.

Samples are held in storage for a period of twelve (12) months after the reporting of results.

Report Date:	14/08/2003
Report No.	WAL 030714002
Customer Ref.	
Page	2 of 2

A Noddings
Ann Noddings
Analyst

Bruce Mountain,Ph.D.
Geochemist

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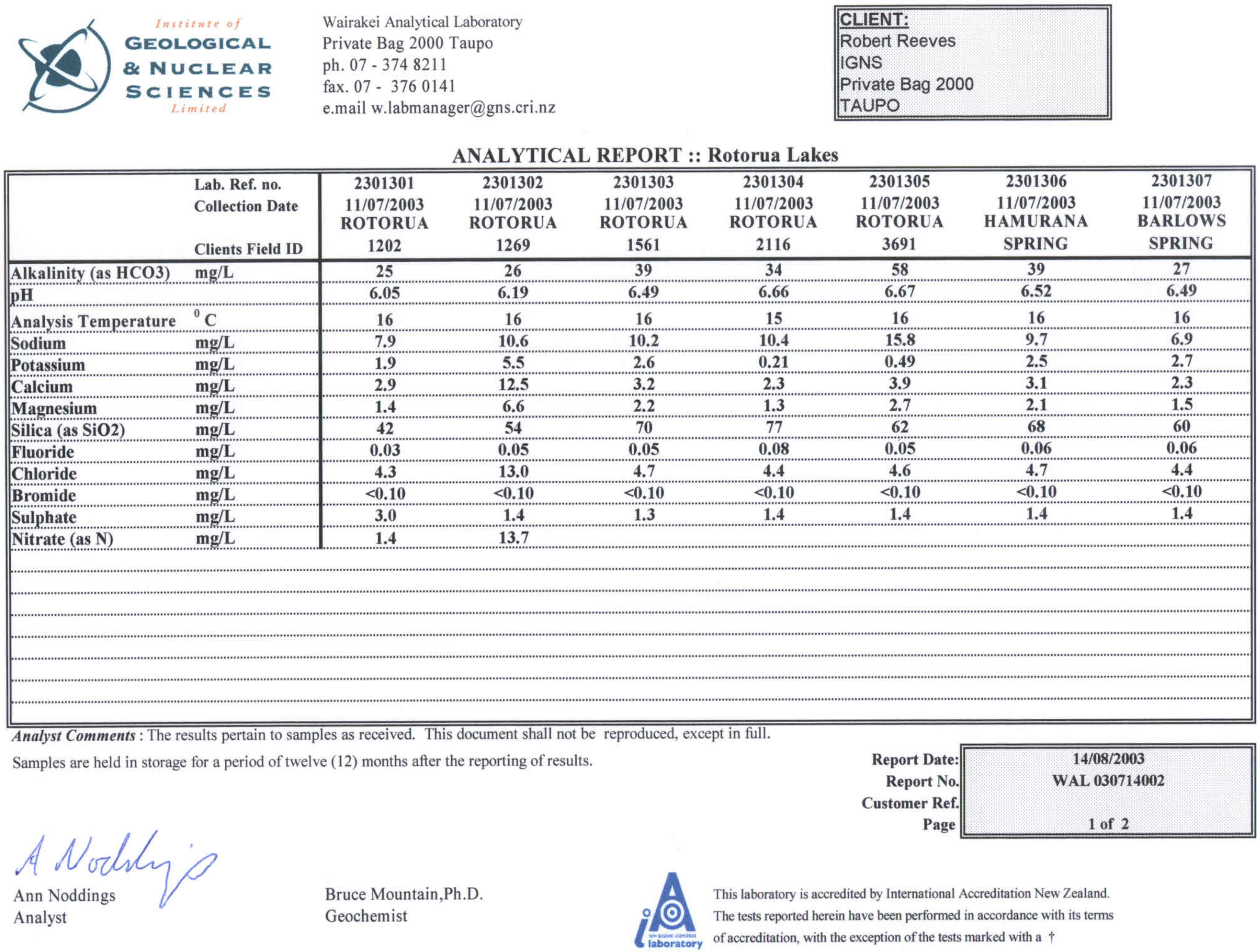

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ANALYTICAL REPORT :: Rotorua Lakes

	Lab. Ref. no. Collection Date Clients Field ID	2301301 11/07/2003 ROTORUA 1202	2301302 11/07/2003 ROTORUA 1269	2301303 11/07/2003 ROTORUA 1561	2301304 11/07/2003 ROTORUA 2116	2301305 11/07/2003 ROTORUA 3691	2301306 11/07/2003 HAMURANA SPRING	2301307 11/07/2003 BARLOWS SPRING
Alkalinity (as HCO3)	mg/L	25	26	39	34	58	39	27
pH		6.05	6.19	6.49	6.66	6.67	6.52	6.49
Analysis Temperature	°C	16	16	16	15	16	16	16
Sodium	mg/L	7.9	10.6	10.2	10.4	15.8	9.7	6.9
Potassium	mg/L	1.9	5.5	2.6	0.21	0.49	2.5	2.7
Calcium	mg/L	2.9	12.5	3.2	2.3	3.9	3.1	2.3
Magnesium	mg/L	1.4	6.6	2.2	1.3	2.7	2.1	1.5
Silica (as SiO2)	mg/L	42	54	70	77	62	68	60
Fluoride	mg/L	0.03	0.05	0.05	0.08	0.05	0.06	0.06
Chloride	mg/L	4.3	13.0	4.7	4.4	4.6	4.7	4.4
Bromide	mg/L	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Sulphate	mg/L	3.0	1.4	1.3	1.4	1.4	1.4	1.4
Nitrate (as N)	mg/L	1.4	13.7					

Analyst Comments : The results pertain to samples as received. This document shall not be reproduced, except in full.

Samples are held in storage for a period of twelve (12) months after the reporting of results.

Report Date:	**14/08/2003**
Report No.	**WAL 030714002**
Customer Ref.	
Page	**1 of 2**

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Ann Noddings
Analyst

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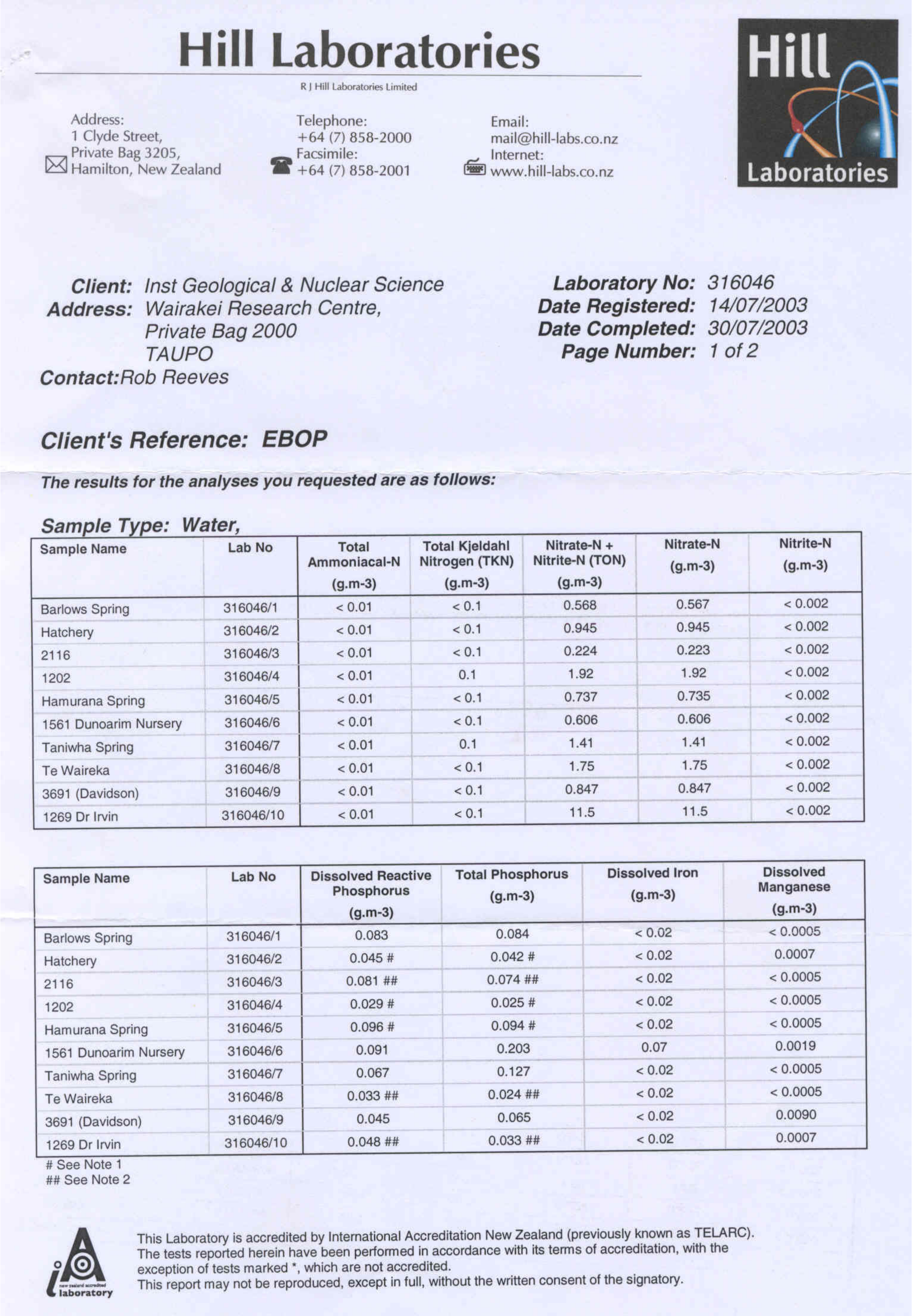

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Laboratory No: *316046*
Date Registered: *14/07/2003*
Date Completed: *30/07/2003*
Page Number: *1 of 2*

Client's Reference: EBOP

The results for the analyses you requested are as follows:

Sample Type: Water,

Sample Name	Lab No	Total Ammoniacal-N (g.m-3)	Total Kjeldahl Nitrogen (TKN) (g.m-3)	Nitrate-N + Nitrite-N (TON) (g.m-3)	Nitrate-N (g.m-3)	Nitrite-N (g.m-3)
Barlows Spring	316046/1	< 0.01	< 0.1	0.568	0.567	< 0.002
Hatchery	316046/2	< 0.01	< 0.1	0.945	0.945	< 0.002
2116	316046/3	< 0.01	< 0.1	0.224	0.223	< 0.002
1202	316046/4	< 0.01	0.1	1.92	1.92	< 0.002
Hamurana Spring	316046/5	< 0.01	< 0.1	0.737	0.735	< 0.002
1561 Dunoarim Nursery	316046/6	< 0.01	< 0.1	0.606	0.606	< 0.002
Taniwha Spring	316046/7	< 0.01	0.1	1.41	1.41	< 0.002
Te Waireka	316046/8	< 0.01	< 0.1	1.75	1.75	< 0.002
3691 (Davidson)	316046/9	< 0.01	< 0.1	0.847	0.847	< 0.002
1269 Dr Irvin	316046/10	< 0.01	< 0.1	11.5	11.5	< 0.002

Sample Name	Lab No	Dissolved Reactive Phosphorus (g.m-3)	Total Phosphorus (g.m-3)	Dissolved Iron (g.m-3)	Dissolved Manganese (g.m-3)
Barlows Spring	316046/1	0.083	0.084	< 0.02	< 0.0005
Hatchery	316046/2	0.045 #	0.042 #	< 0.02	0.0007
2116	316046/3	0.081 ##	0.074 ##	< 0.02	< 0.0005
1202	316046/4	0.029 #	0.025 #	< 0.02	< 0.0005
Hamurana Spring	316046/5	0.096 #	0.094 #	< 0.02	< 0.0005
1561 Dunoarim Nursery	316046/6	0.091	0.203	0.07	0.0019
Taniwha Spring	316046/7	0.067	0.127	< 0.02	< 0.0005
Te Waireka	316046/8	0.033 ##	0.024 ##	< 0.02	< 0.0005
3691 (Davidson)	316046/9	0.045	0.065	< 0.02	0.0090
1269 Dr Irvin	316046/10	0.048 ##	0.033 ##	< 0.02	0.0007

See Note 1
See Note 2

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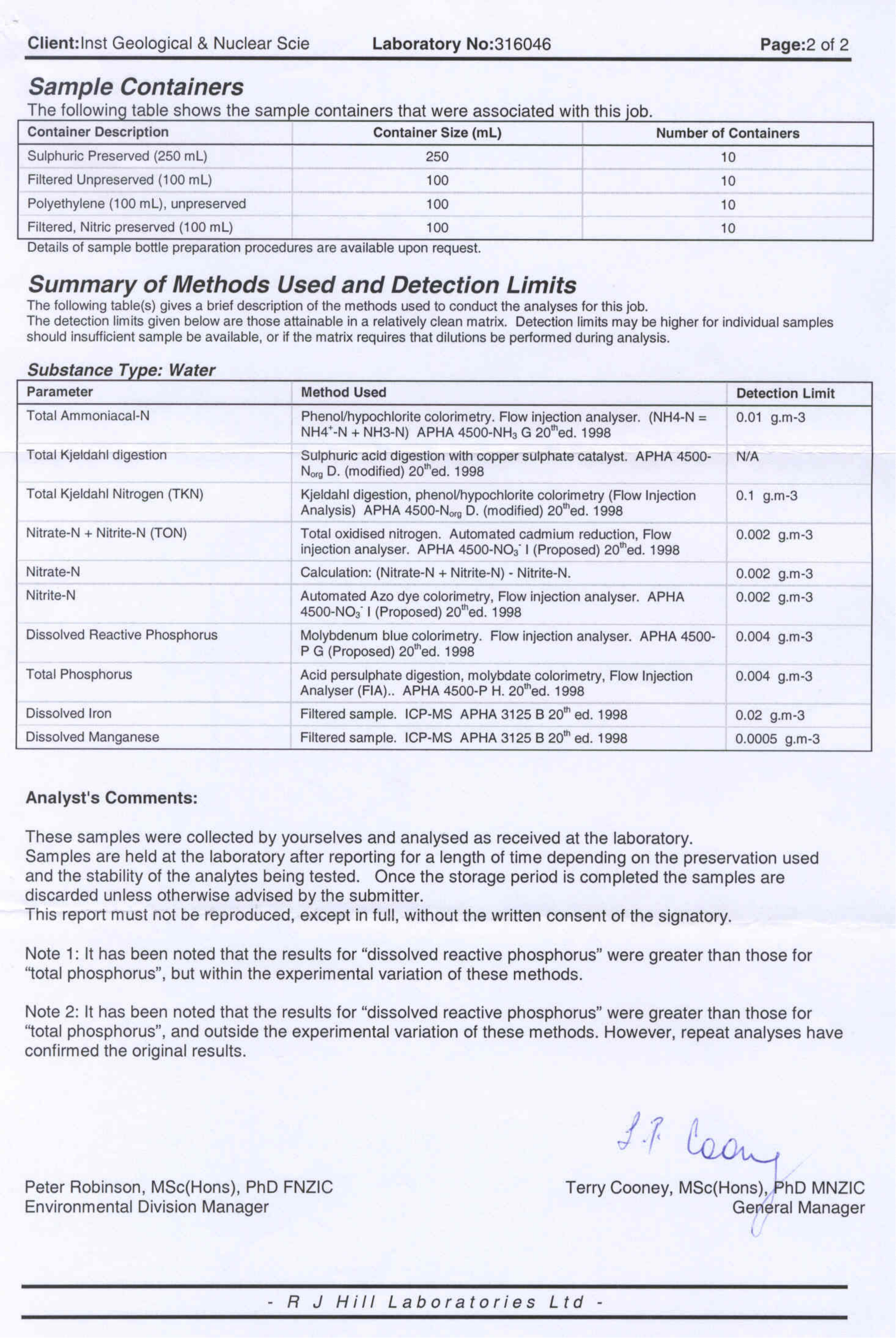

Client: Inst Geological & Nuclear Scie **Laboratory No:** 316046 **Page:** 2 of 2

Sample Containers

The following table shows the sample containers that were associated with this job.

Container Description	Container Size (mL)	Number of Containers
Sulphuric Preserved (250 mL)	250	10
Filtered Unpreserved (100 mL)	100	10
Polyethylene (100 mL), unpreserved	100	10
Filtered, Nitric preserved (100 mL)	100	10

Details of sample bottle preparation procedures are available upon request.

Summary of Methods Used and Detection Limits

The following table(s) gives a brief description of the methods used to conduct the analyses for this job.
The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Substance Type: Water

Parameter	Method Used	Detection Limit
Total Ammoniacal-N	Phenol/hypochlorite colorimetry. Flow injection analyser. (NH4-N = NH4$^+$-N + NH3-N) APHA 4500-NH_3 G 20th ed. 1998	0.01 g.m-3
Total Kjeldahl digestion	Sulphuric acid digestion with copper sulphate catalyst. APHA 4500-N_{org} D. (modified) 20th ed. 1998	N/A
Total Kjeldahl Nitrogen (TKN)	Kjeldahl digestion, phenol/hypochlorite colorimetry (Flow Injection Analysis) APHA 4500-N_{org} D. (modified) 20th ed. 1998	0.1 g.m-3
Nitrate-N + Nitrite-N (TON)	Total oxidised nitrogen. Automated cadmium reduction, Flow injection analyser. APHA 4500-NO_3^- I (Proposed) 20th ed. 1998	0.002 g.m-3
Nitrate-N	Calculation: (Nitrate-N + Nitrite-N) - Nitrite-N.	0.002 g.m-3
Nitrite-N	Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO_3^- I (Proposed) 20th ed. 1998	0.002 g.m-3
Dissolved Reactive Phosphorus	Molybdenum blue colorimetry. Flow injection analyser. APHA 4500-P G (Proposed) 20th ed. 1998	0.004 g.m-3
Total Phosphorus	Acid persulphate digestion, molybdate colorimetry, Flow Injection Analyser (FIA).. APHA 4500-P H. 20th ed. 1998	0.004 g.m-3
Dissolved Iron	Filtered sample. ICP-MS APHA 3125 B 20th ed. 1998	0.02 g.m-3
Dissolved Manganese	Filtered sample. ICP-MS APHA 3125 B 20th ed. 1998	0.0005 g.m-3

Analyst's Comments:

These samples were collected by yourselves and analysed as received at the laboratory.
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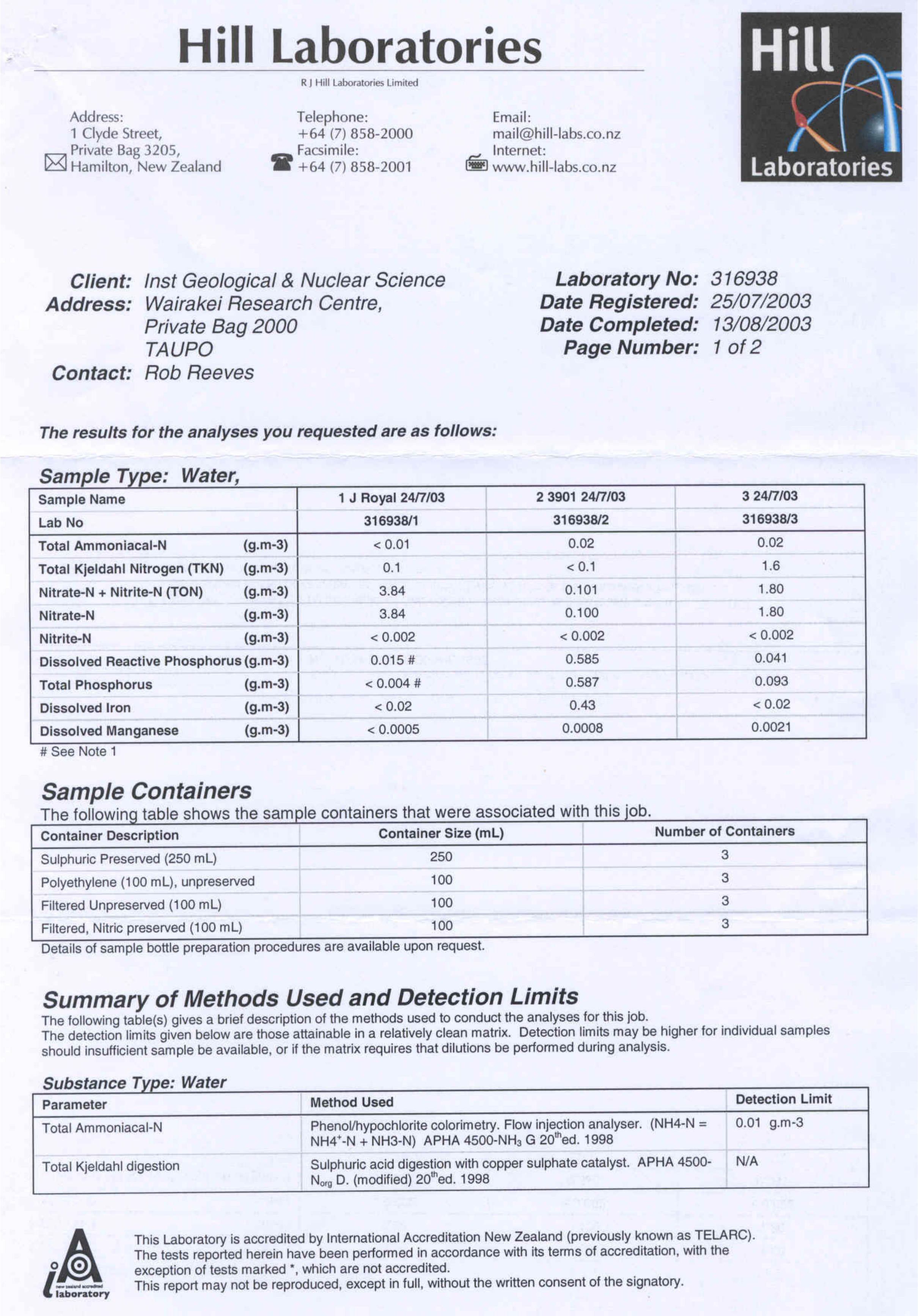
Note 1: It has been noted that the results for "dissolved reactive phosphorus" were greater than those for "total phosphorus", but within the experimental variation of these methods.

Note 2: It has been noted that the results for "dissolved reactive phosphorus" were greater than those for "total phosphorus", and outside the experimental variation of these methods. However, repeat analyses have confirmed the original results.

Peter Robinson, MSc(Hons), PhD FNZIC
Environmental Division Manager

Terry Cooney, MSc(Hons), PhD MNZIC
General Manager

- R J Hill Laboratories Ltd -



Hill Laboratories

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Client: *Inst Geological & Nuclear Science*
Address: *Wairakei Research Centre,*
Private Bag 2000
TAUPO
Contact: *Rob Reeves*

Laboratory No: *316938*
Date Registered: *25/07/2003*
Date Completed: *13/08/2003*
Page Number: *1 of 2*

The results for the analyses you requested are as follows:

Sample Type: Water,

Sample Name		**1 J Royal 24/7/03**	**2 3901 24/7/03**	**3 24/7/03**
Lab No		**316938/1**	**316938/2**	**316938/3**
Total Ammoniacal-N	**(g.m-3)**	< 0.01	0.02	0.02
Total Kjeldahl Nitrogen (TKN)	**(g.m-3)**	0.1	< 0.1	1.6
Nitrate-N + Nitrite-N (TON)	**(g.m-3)**	3.84	0.101	1.80
Nitrate-N	**(g.m-3)**	3.84	0.100	1.80
Nitrite-N	**(g.m-3)**	< 0.002	< 0.002	< 0.002
Dissolved Reactive Phosphorus	**(g.m-3)**	0.015 #	0.585	0.041
Total Phosphorus	**(g.m-3)**	< 0.004 #	0.587	0.093
Dissolved Iron	**(g.m-3)**	< 0.02	0.43	< 0.02
Dissolved Manganese	**(g.m-3)**	< 0.0005	0.0008	0.0021

See Note 1

Sample Containers

The following table shows the sample containers that were associated with this job.

Container Description	**Container Size (mL)**	**Number of Containers**
Sulphuric Preserved (250 mL)	250	3
Polyethylene (100 mL), unpreserved	100	3
Filtered Unpreserved (100 mL)	100	3
Filtered, Nitric preserved (100 mL)	100	3

Details of sample bottle preparation procedures are available upon request.

Summary of Methods Used and Detection Limits

The following table(s) gives a brief description of the methods used to conduct the analyses for this job.
The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Substance Type: Water

Parameter	**Method Used**	**Detection Limit**
Total Ammoniacal-N	Phenol/hypochlorite colorimetry. Flow injection analyser. (NH4-N = $NH4^+$-N + NH3-N) APHA 4500-NH_3 G 20th ed. 1998	0.01 g.m-3
Total Kjeldahl digestion	Sulphuric acid digestion with copper sulphate catalyst. APHA 4500-N_{org} D. (modified) 20th ed. 1998	N/A

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The tests reported herein have been performed in accordance with its terms of accreditation, with the exception of tests marked *, which are not accredited.
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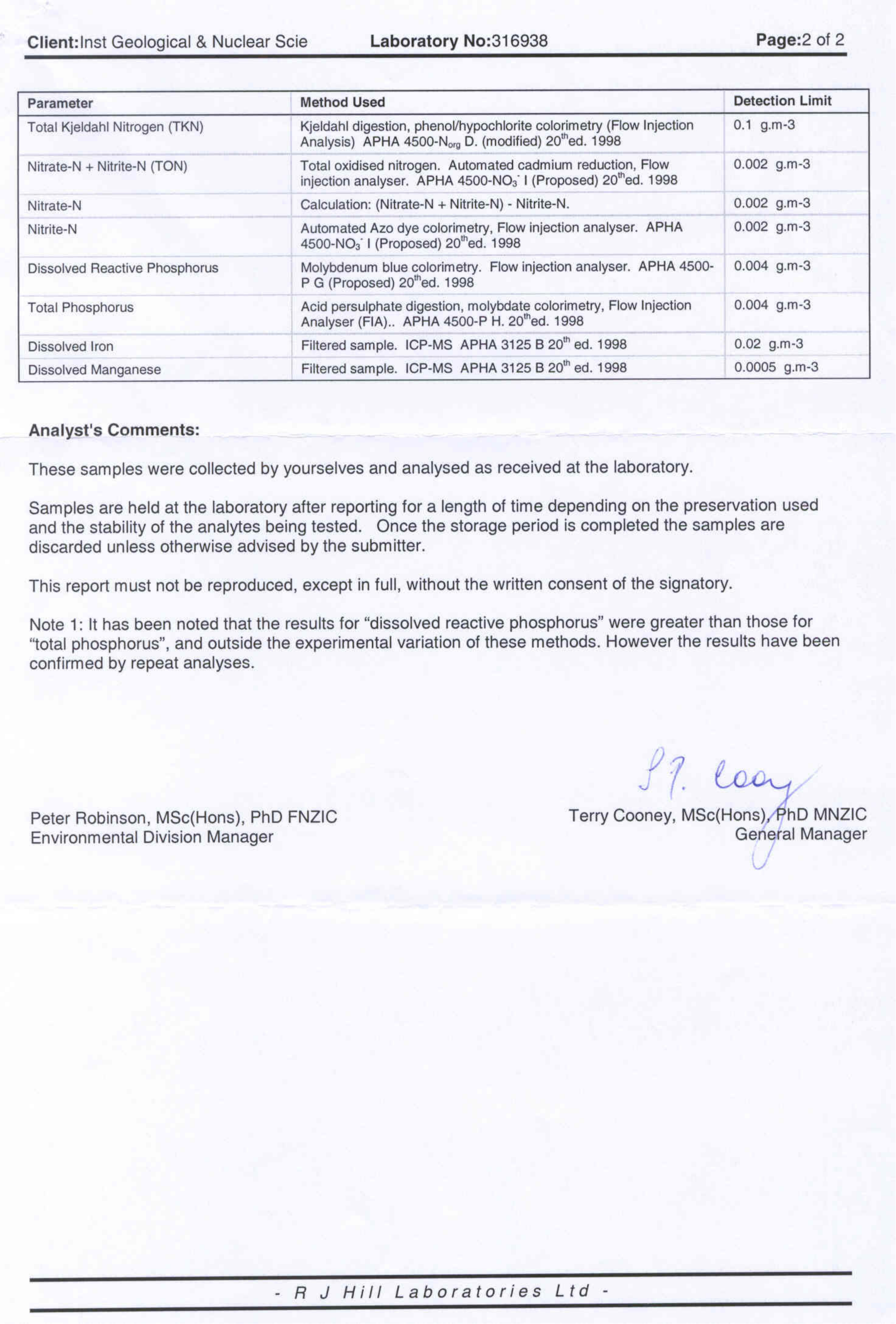

Client: Inst Geological & Nuclear Scie **Laboratory No:**316938 **Page:**2 of 2

Parameter	Method Used	Detection Limit
Total Kjeldahl Nitrogen (TKN)	Kjeldahl digestion, phenol/hypochlorite colorimetry (Flow Injection Analysis) APHA 4500-N_{org} D. (modified) 20thed. 1998	0.1 g.m-3
Nitrate-N + Nitrite-N (TON)	Total oxidised nitrogen. Automated cadmium reduction, Flow injection analyser. APHA 4500-NO_3^- I (Proposed) 20thed. 1998	0.002 g.m-3
Nitrate-N	Calculation: (Nitrate-N + Nitrite-N) - Nitrite-N.	0.002 g.m-3
Nitrite-N	Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO_3^- I (Proposed) 20thed. 1998	0.002 g.m-3
Dissolved Reactive Phosphorus	Molybdenum blue colorimetry. Flow injection analyser. APHA 4500-P G (Proposed) 20thed. 1998	0.004 g.m-3
Total Phosphorus	Acid persulphate digestion, molybdate colorimetry, Flow Injection Analyser (FIA).. APHA 4500-P H. 20thed. 1998	0.004 g.m-3
Dissolved Iron	Filtered sample. ICP-MS APHA 3125 B 20th ed. 1998	0.02 g.m-3
Dissolved Manganese	Filtered sample. ICP-MS APHA 3125 B 20th ed. 1998	0.0005 g.m-3

Analyst's Comments:

These samples were collected by yourselves and analysed as received at the laboratory.

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Note 1: It has been noted that the results for "dissolved reactive phosphorus" were greater than those for "total phosphorus", and outside the experimental variation of these methods. However the results have been confirmed by repeat analyses.

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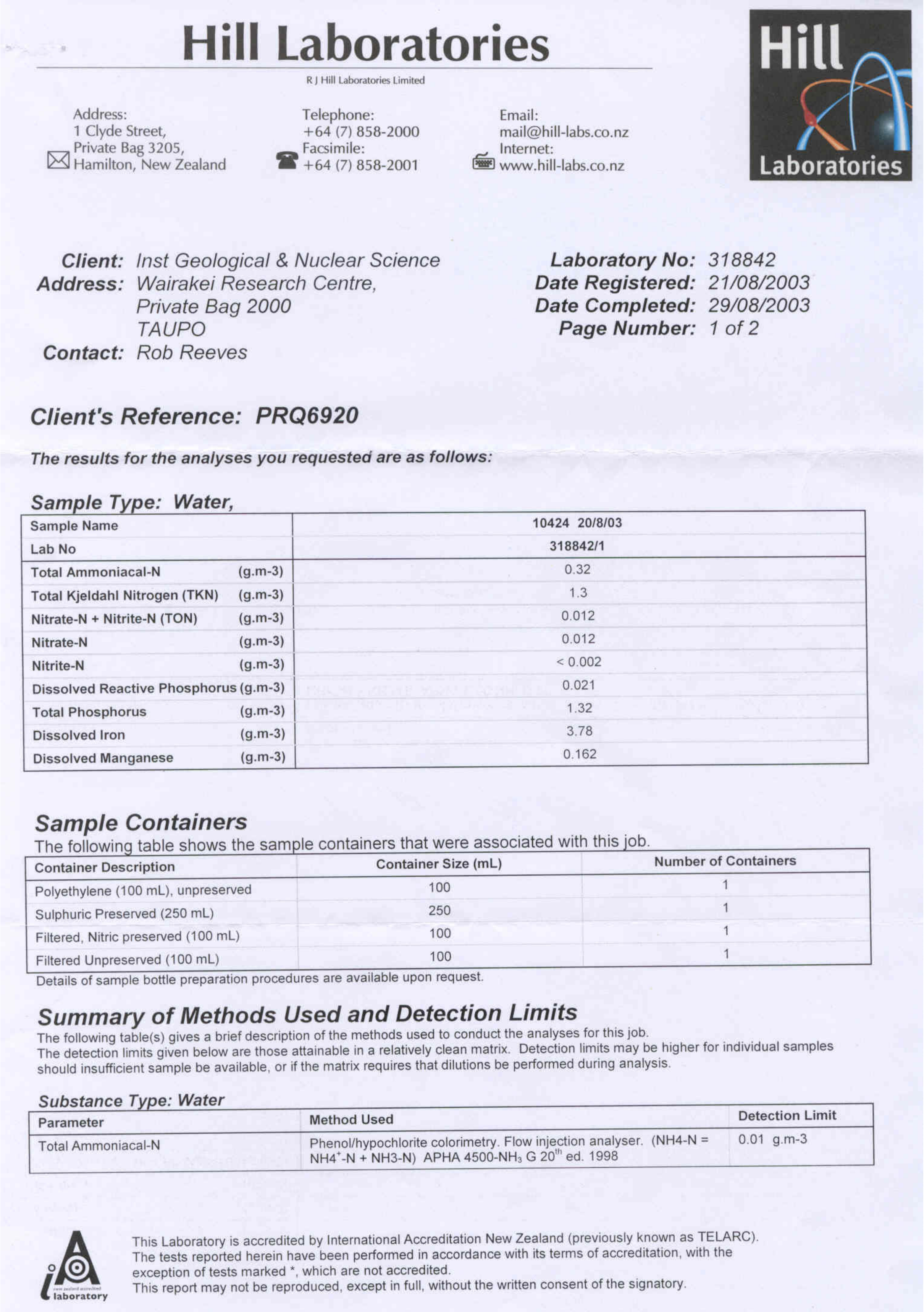

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Client: *Inst Geological & Nuclear Science*
Address: *Wairakei Research Centre,*
Private Bag 2000
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Contact: *Rob Reeves*

Laboratory No: *318842*
Date Registered: *21/08/2003*
Date Completed: *29/08/2003*
Page Number: *1 of 2*

Client's Reference: PRQ6920

The results for the analyses you requested are as follows:

Sample Type: Water,

Sample Name		**10424 20/8/03**
Lab No		**318842/1**
Total Ammoniacal-N	**(g.m-3)**	0.32
Total Kjeldahl Nitrogen (TKN)	**(g.m-3)**	1.3
Nitrate-N + Nitrite-N (TON)	**(g.m-3)**	0.012
Nitrate-N	**(g.m-3)**	0.012
Nitrite-N	**(g.m-3)**	< 0.002
Dissolved Reactive Phosphorus	**(g.m-3)**	0.021
Total Phosphorus	**(g.m-3)**	1.32
Dissolved Iron	**(g.m-3)**	3.78
Dissolved Manganese	**(g.m-3)**	0.162

Sample Containers

The following table shows the sample containers that were associated with this job.

Container Description	Container Size (mL)	Number of Containers
Polyethylene (100 mL), unpreserved	100	1
Sulphuric Preserved (250 mL)	250	1
Filtered, Nitric preserved (100 mL)	100	1
Filtered Unpreserved (100 mL)	100	1

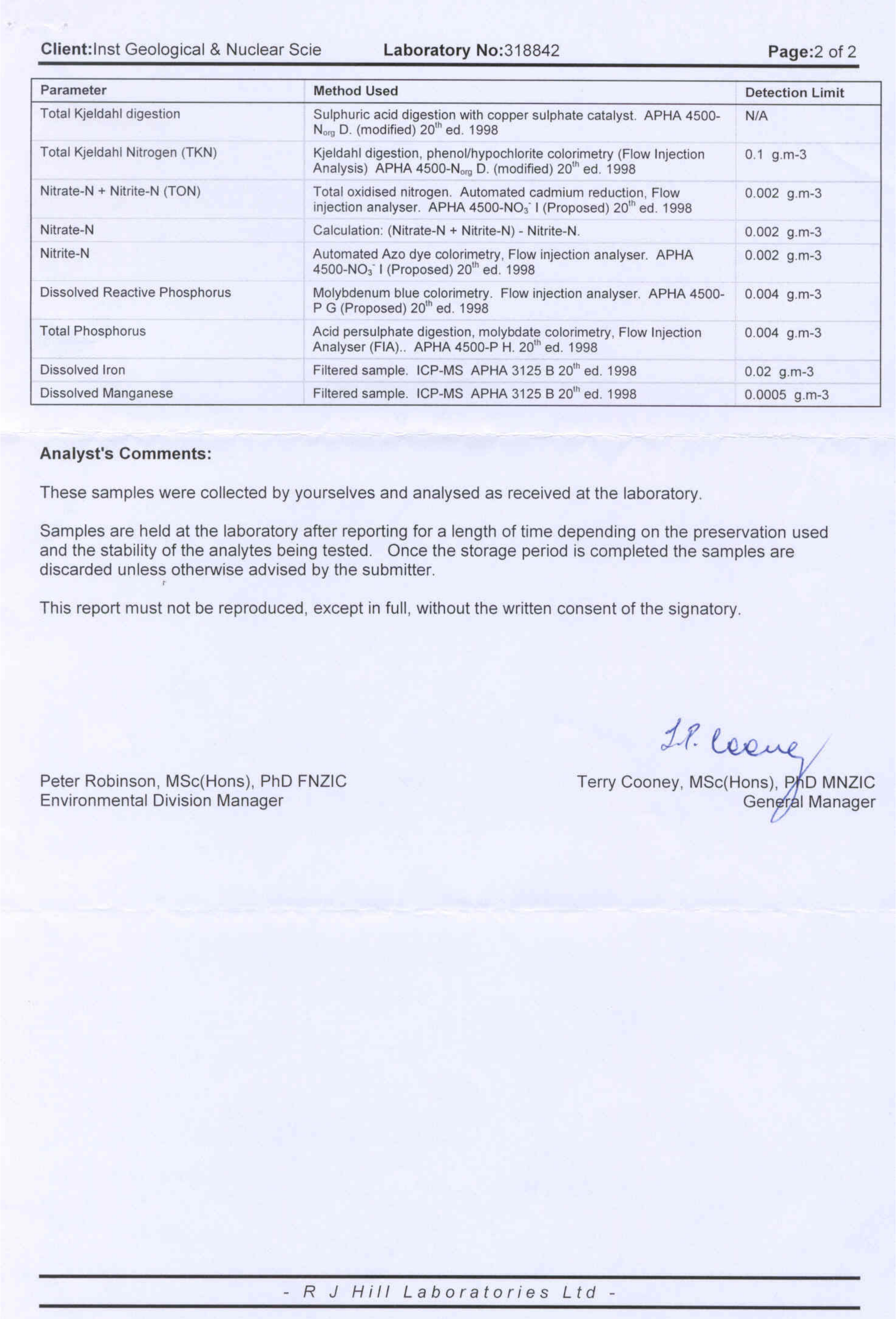
Details of sample bottle preparation procedures are available upon request.

Summary of Methods Used and Detection Limits

The following table(s) gives a brief description of the methods used to conduct the analyses for this job.
The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Substance Type: Water

Parameter	Method Used	Detection Limit
Total Ammoniacal-N	Phenol/hypochlorite colorimetry. Flow injection analyser. (NH4-N = NH4$^+$-N + NH3-N) APHA 4500-NH_3 G 20th ed. 1998	0.01 g.m-3



Client: Inst Geological & Nuclear Scie **Laboratory No:**318842 **Page:**2 of 2

Parameter	Method Used	Detection Limit
Total Kjeldahl digestion	Sulphuric acid digestion with copper sulphate catalyst. APHA 4500-N_{org} D. (modified) 20th ed. 1998	N/A
Total Kjeldahl Nitrogen (TKN)	Kjeldahl digestion, phenol/hypochlorite colorimetry (Flow Injection Analysis) APHA 4500-N_{org} D. (modified) 20th ed. 1998	0.1 g.m-3
Nitrate-N + Nitrite-N (TON)	Total oxidised nitrogen. Automated cadmium reduction, Flow injection analyser. APHA 4500-NO_3^- I (Proposed) 20th ed. 1998	0.002 g.m-3
Nitrate-N	Calculation: (Nitrate-N + Nitrite-N) - Nitrite-N.	0.002 g.m-3
Nitrite-N	Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO_3^- I (Proposed) 20th ed. 1998	0.002 g.m-3
Dissolved Reactive Phosphorus	Molybdenum blue colorimetry. Flow injection analyser. APHA 4500-P G (Proposed) 20th ed. 1998	0.004 g.m-3
Total Phosphorus	Acid persulphate digestion, molybdate colorimetry, Flow Injection Analyser (FIA).. APHA 4500-P H. 20th ed. 1998	0.004 g.m-3
Dissolved Iron	Filtered sample. ICP-MS APHA 3125 B 20th ed. 1998	0.02 g.m-3
Dissolved Manganese	Filtered sample. ICP-MS APHA 3125 B 20th ed. 1998	0.0005 g.m-3

Analyst's Comments:

These samples were collected by yourselves and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the submitter.

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