Environment Waikato Technical Report 2001/01

Hydrogeology Of Lake Taupo Catchment – Phase 1

Acknowledgements

The authors would like to thank the land-owners in the study area for providing access to their wells for sampling and testing. Well construction and geological information from Peter Booth of Landcorp was also much appreciated. The Institute of Geological and Nuclear Sciences have reported the geological setting and groundwater dating as well as providing more general comment. Rob Van der Raaij (GNS) is gratefully acknowledged for analysis and sampling of CFCs and tritium for groundwater dating.

Table Of Contents

List of Tables

List of Figures

List of Plates

Executive Summary

This report describes the geology, groundwater chemistry, flow and age of the northern and western Lake Taupo catchment. These areas have the greatest potential for intensification of agriculture which threatens lake water quality.

Geology is dominated by young (< 0.4 Ma), locally derived, rhyolitic pyroclastics. The sequence in the western catchment is relatively simple with surficial Oruanui ignimbrite overlying a large thickness of Whakamaru ignimbrite. The latter is sufficiently welded in places to have moderate vertical fracture development and to form impressive cliffs along the lake-front. East of Kawakawa Bay faulting is common and there is a more complex sequence of ignimbrites, fall deposits, localised lava extrusions and lacustrine sediments. Of most hydrogeologic relevance are the Oruanui ignimbrite and the underlying grouping of rhyolite pyroclastics. Although not fractured, they are likely to have moderate permeability. Occasional paleosols, which punctuate these formations, are expected to act as localised aquitards and to sometimes induce perching.

Small, non-irrigation, farm groundwater supplies were developed predominantly in the northern catchment. Large farms in the western catchment generally have stream or lesser spring supplies and hence hydrogeologic information in this area is sparse.

Groundwater flow in the area is consistent with topography although more subdued. There is no discrepancy evident between surface water and groundwater catchments. Some divergent flow away from headlands such as Kawakawa Rd area and toward valleys and bays e.g. Kinloch, is evident. A recharge regime generally exists in the catchment indicated by a strong relationship between the measured depths to static groundwater level and well depth. Vertical head gradients vary considerably with some large differentials (> 50 m) being observed. The lake is the sink for groundwater which is recharged from rainfall in the catchment.

Groundwater from a total of 44 wells within, and on the margin of, the catchment were sampled for the analysis of nutrients and major ion chemistry. Relatively uniform sodium bicarbonate dominated groundwater chemistry typical of rhyolitic formation was found. Although water quality was generally high, evidence of land use impacts was found at some sites with elevated nitrate, sulphate and chloride concentrations. Groundwater at one site exceeded the drinking water guideline for nitrate and five further sites were in excess of half the guideline. The mean nitrate-N concentration (2.28 ppm) is substantially higher than lake and surface water concentrations.

Anaerobic or poorly aerobic conditions are indicated at eight sites and manganese concentrations >0.25 ppm were found with similar frequency. These included one site with manganese in excess of the drinking water guideline.

Groundwater was sampled at 11 wells and one spring for age determination using CFCs and tritium. Results show that the mean residence time of groundwater sampled ranges from about 20 to 75 years. The percentage of young water in the samples was found to relate to the measured nitrate concentrations. Nitrate concentrations are expected to increase with the percentage of water recharged since 1965, unless land-use changes.

Groundwater is the primary link for the transport of nutrients derived from land use to the lake. Land-use impacts are clearly evident in groundwater and are expected to increase. The reported investigation is a first phase in the provision of information required as a basis for determining appropriate land management for lake-water quality protection. More detailed investigation into several aspects is planned.

1 Introduction

Lake Taupo is a very large oligotrophic lake (620 km^2) and an icon of national importance for aspects including recreation and tourism. The quality of water in the lake is affected by land use activities within its catchment. About half the catchment's native vegetation has been developed for forestry and sheep/beef farming (Leathwick, et al., 1995). Dairy farming, which generates relatively large loads of nitrogen, has recently been introduced.

Although lake water quality is currently excellent with low nutrient and phytoplankton levels, some degradation has been observed in recent years. Water clarity has declined by about one metre since the 1980s. The growth of phytoplankton in the lake is nitrogen limited and increasing nutrient load would be expected to cause a proportional decrease in water clarity (Vant and Huser, 2000). These effects are likely to be more pronounced in sheltered bays with a relatively plentiful nutrient supply. Nuisance weed growth in the lake margins is related primarily to groundwater and small stream inflow (Rae et al., 2000).

The most important pathway for nutrients generated from land use to enter the lake is via groundwater. Groundwater provides baseflow to streams as well as contributing directly to the lake. The relative rate of direct flow of groundwater to the lake is not well known but has been estimated by Schouten et al., (1981) at some 5%. The nitrogen contribution is likely to be much higher (possibly ~ 30%) as groundwater typically has nitrate concentrations that are much higher than surface waters.

It is important to characterise the local groundwater resource to enable the contribution of nutrient to the lake from this source to be estimated. Environment Waikato has responsibilities to manage land to protect water quality. Currently options for appropriate management are being considered (EW discussion paper, 2000). It is important to have sufficient information to allow policies for land management to be firmly based and most relevant.

2 Scope

The northern and western catchments of Lake Taupo (Figure 1) are studied in this first phase of hydrogeologic investigation. This is because these are the areas of greatest potential for agricultural intensification (MaF, 1997) and because there was little existing information.

The following four aspects are addressed in this report: geologic setting; piezometric surface and groundwater flow direction; water chemistry and groundwater age dating. These are fundamental to the consideration of groundwater influence on lake water quality and provide a basis for more detailed mass transport investigation.

3 Geologic Setting

3.1 Sources of information

Information from two main sources has been compiled to produce the map of surface geology presented in Figure 2. The first is unpublished mapping by E.F. Lloyd carried out under the auspices of the New Zealand Geological Survey in the 1980s at a scale of 1:25,000, with extensive ground control. This covers areas north of northing

6280000 and east of easting 2750000, with some reconnaissance work down to the northern edge of Lake Taupo in the Kinloch area. The second is interpretative photo-geological mapping supplemented by an extensive database of existing point observations by C.J.N. Wilson from studies of the Oruanui and Taupo ignimbrites. The map represents the main landscape-forming units and does not address deposits that drape the landscape (e.g. tephra fall deposits and interbedded paleosols between the 26.5 ka Oruanui and 1.8 ka Taupo ignimbrites), although these may influence groundwater flow on a local scale. In addition faults have not been included for clarity.

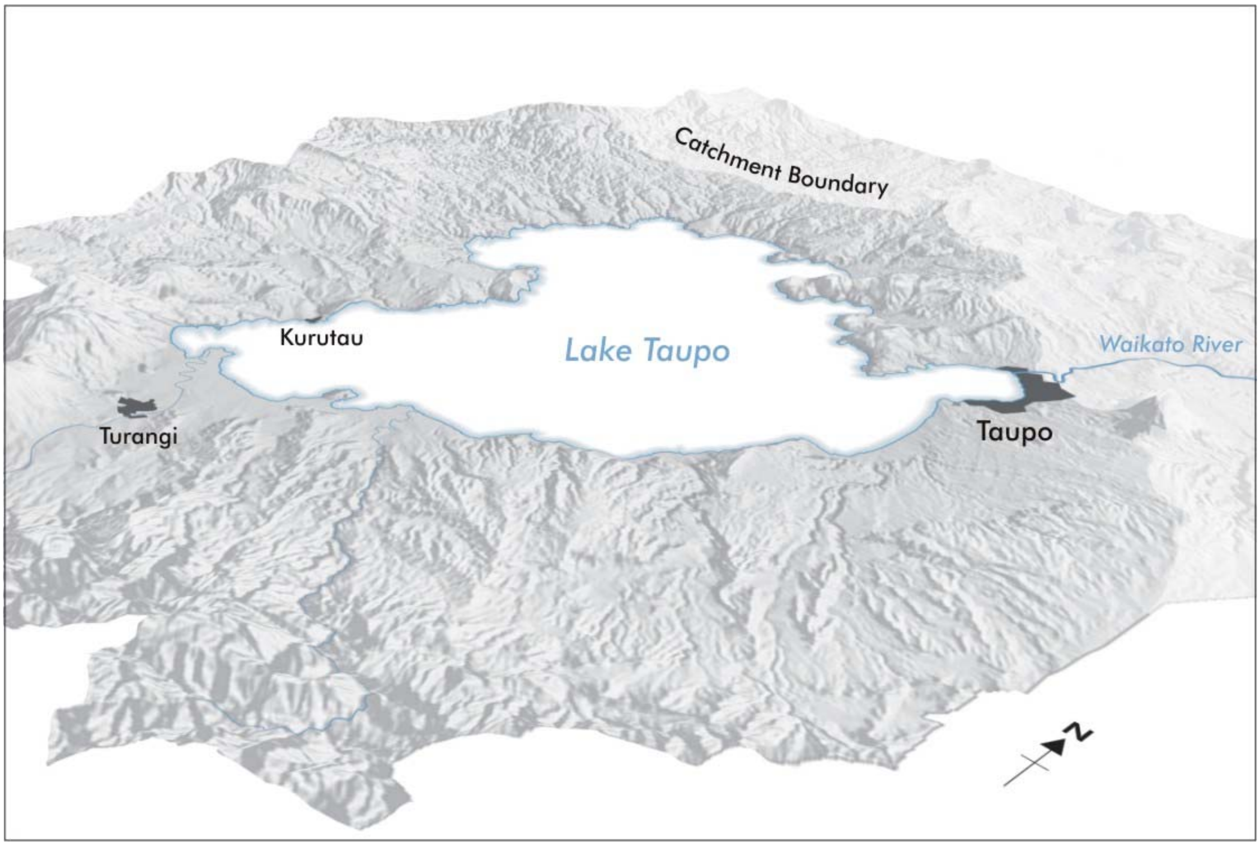

Figure 1: Study area location

The cross sections (Figures 3 and 4) have been compiled from interpreted extrapolations of surface geology, supplemented by unpublished information (held at the Institute of Geological & Nuclear Sciences Limited, Wairakei) from geothermal drillholes in the area of the Wairakei geothermal field, and by interpretations of the slope of the pre-Quaternary basement west of Lake Taupo by Hatherton (1974). In section b-b', only substantive faults that displace units of contrasting properties have been shown; others mapped (e.g. Grindley, 1961) have offsets that are too poorly defined or too small to be shown at the scale of the section.

3.2 Geological history of the area

Pre-Quaternary (>1.6 Ma)

The geological 'basement' to the area consists mostly of Mesozoic indurated sediments ('greywacke') that crop out extensively west of the mapped area to form the Hauhungaroa Ranges. Overlying the greywackes with a strong erosional break (unconformity) are local areas of Tertiary marine sediments and Pliocene andesite-derived debris flow deposits (Hauhungaroa Lahars)(Grindley, 1960), that are not separately delineated here.

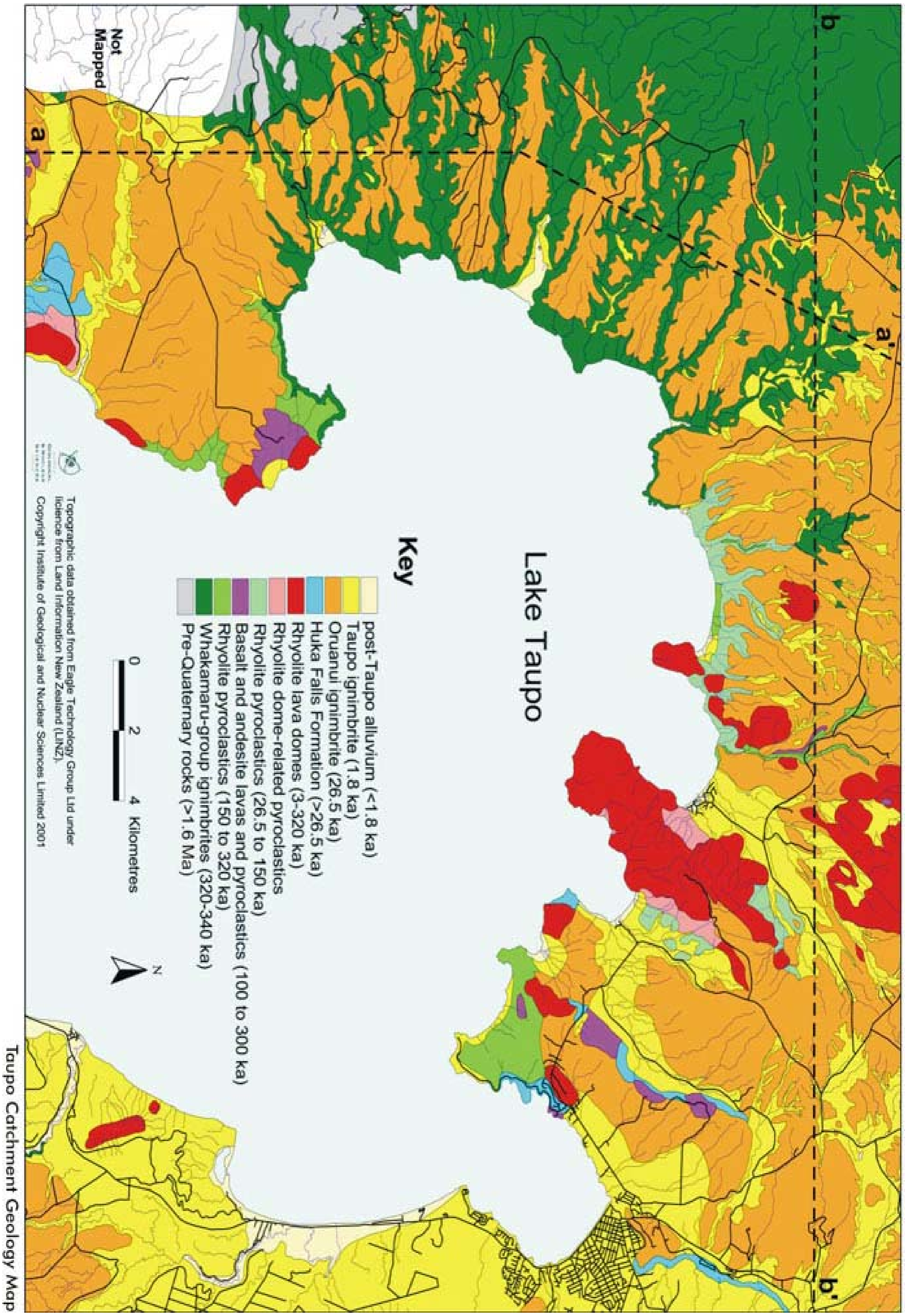

Figure 2: Geological map

Quaternary (10 ka to 1.6 Ma)

The earliest widespread volcanic rocks are welded ignimbrites inferred to have been erupted from sources in the Mangakino area between 1.6 and 0.9 Ma (Wilson, 1986; Houghton et al., 1995). These crop out at the surface N and W of the mapped area, may underlie the Whakamaru-group ignimbrites at depth, are likely to have very similar hydrological characteristics, and are thus not separately distinguished on the map or cross-sections.

The Whakamaru-group ignimbrites were erupted during one or more major eruptions at 320-340 ka from a large caldera source overlapping the northern part of the map area (Wilson et al., 1986). The Whakamaru ignimbrites crop out extensively in the west of the mapped area, and also in a small inlier at the Hinemaiaia B dam site in the SE corner of the map.

Across the northern half of the mapped area ignimbrites are down-faulted to the east by at least 800-1000 m across a north-south oriented lineament that marks the western margin of their source caldera (Wilson et al., 1986). They lie at depths well below sea level over the NE part of the map (see cross-section B-B'), while to the SW the ignimbrites appear to be downwarped to the south. Thicknesses of the Whakamaru-group ignimbrites in the map area range from a few tens of metres in the extreme NW of the mapped area to at least 200 m around Western Bay, and to 500-1000m where buried at depth in the Wairakei area (Grindley, 1965; Wilson et al., 1986).

The post-Whakamaru, pre-Oruanui history of the area is poorly constrained, but is here divided into two time slices, based on limited published (Houghton et al., 1991) and unpublished radiometric age data with a division at ~150 ka. During these periods, numerous individual rhyolite lava domes have been erupted, some with dome-related pyroclastic products of very limited extent. More-widespread rhyolitic pyroclastic units also occur, but are poorly constrained as to their sources and extents. During this time period also, there have been sporadic, small-scale accumulations of basaltic scoria and lava erupted, while the southwestern corner of the map includes andesite lavas that form the distal flank of Kakaramea volcano to the south.

In the area in the NE corner of the map, a large and long-lived lake developed (extending also to part of the area now occupied by Lake Taupo), in which volcaniclastic and background-lacustrine sediments of the Huka Falls Formation were emplaced. The sediments are highly variable in their properties, from sand- to gravel-grade pyroclastic or sedimentary units emplaced into the lake to extremely fine-grained diatomaceous mudstones. Although little exposed at the surface, these sediments have been penetrated at shallow depths beneath the Wairakei geothermal field (e.g. Grindley, 1965). Their transition westwards, however, into contemporaneous subaerial pyroclastic deposits has not been established. A small area in the south-west corner of the map is also mapped as Huka Falls Formation on the basis of limited exposures of pre-Oruanui lake sediments in this area.

At 26.5 ka, the enormous Oruanui eruption occurred (Self, 1983; Wilson, 2001), generating a widespread fall deposit (not separately delineated on the map) and a large non-welded ignimbrite that forms or underlies most of the modern landscape around the lake. In addition, large-scale caldera collapse associated with this eruption was responsible for creating the present shape of Lake Taupo (Davy & Caldwell, 1998). Originally the Oruanui ignimbrite was 50-240 m thick over most of the map area (Wilson, 1991), and remaining ignimbrite is still up to about 200 m thick in the Wairakei area, and 40-150 m thick west of Lake Taupo. This eruption occurred just prior to the climax of the last glaciation and extensive erosion has removed large amounts of the

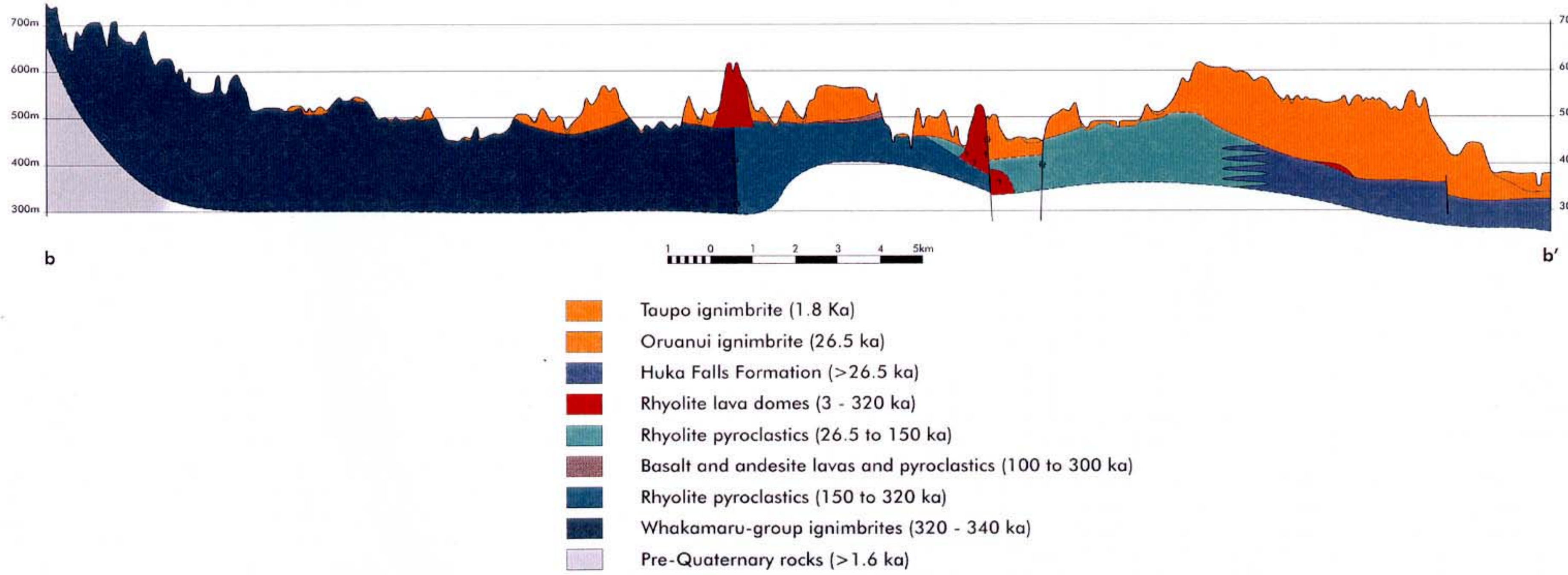

Figure 3: Geological cross-section of the northern catchment

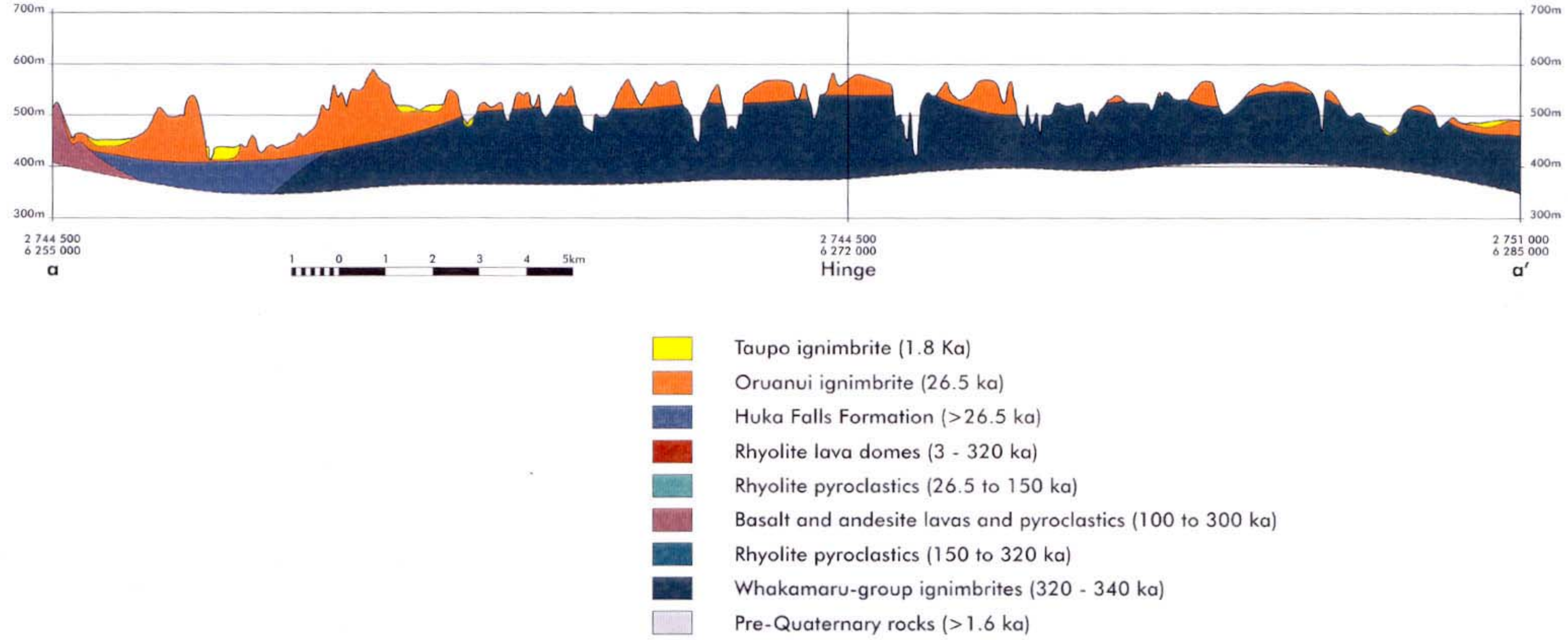

Figure 4: Geological cross-section of the western catchment

Oruanui ignimbrite and exposed the older, less permeable lithologies to give the outcrop pattern very much as seen at the present day. A thin (2-3 m maximum) skin of loess deposited between ~20 and ~13 ka drapes the erosion surface and is in turn overlain by the 'modern' (last 12 ka) sequence of pyroclastic deposits

Holocene (<10 ka)

Young eruptive activity at Taupo has generated numerous pyroclastic deposits, starting at around 12 ka but mostly during the Holocene (last 10 ka)(Wilson, 1993). All but 2 of these deposits are only dm to m-thickness and drape the landscape, and as such cannot be represented on a conventional map. Their collective thickness, together with interbedded palaeosols, is typically 3-5 m north and west of Lake Taupo. The two exceptions are the ignimbrites generated in eruptions at 3.5 and 1.8 ka. The former is exposed only in a very limited area in the extreme SE part of the map and not separately distinguished there, but the latter (the Taupo ignimbrite) is extremely widespread (Wilson, 1985). The Taupo ignimbrite consists of two contrasting geomorphological facies, a landscape-mantling veneer deposit that covers the entire map area to dm-m thicknesses, and a valley-ponded facies up to tens of m thick that occurs in low-lying areas. The latter is the unit that is represented on the map as it forms a distinct landscape element, and is thick enough (10-40 m) for its hydrological properties to be important.

Following the 1.8 ka eruption, large amounts of sediment were brought down the river entering Lake Taupo; much of this sediment is inferred to have been deposited on the floor of the lake, but locally significant shoreline aggradation occurred (most notably in the Waitahanui area).

3.3 Description of geological units

The geology of much of the area concerned has not been mapped at this level of detail before (cf. Grindley, 1960,1961). For the purposes of this report, the main landscape forming units have been identified and plotted, with the subdivisions being chosen to highlight units that are likely to be of contrasting hydrological properties.

Post-Taupo alluvium (<1.8 ka)

This term is applied only to mappable areas of fluvial and lacustrine sediments that post-date the 1.8 ka Taupo eruption, and are associated with progradation of the shoreline of Lake Taupo in response to enhanced sediment yields down tributary rivers in the immediate aftermath of the 1.8 ka eruption. All these sediments are unconsolidated, with high primary permeability.

Taupo ignimbrite (1.8 ka)

Non-welded pyroclastic flow deposit (ignimbrite) erupted during the 1.8 ka Taupo eruption. Note that the ignimbrite is mapped only where it represents a distinct landscape-forming element. In the extreme SE corner of the map, in the Hatepe area, deposits of the slightly older (3.5 ka) Waimihia ignimbrite also crop out but are not mapped separately because of their limited extent and similar physical properties to the Taupo ignimbrite. This material is characterised by a high primary permeability and a lack of jointing.

Oruanui ignimbrite (26.5 ka)

Non-welded ignimbrite from the 26.5 ka Oruanui eruption. Because of limitations of scale, the underlying Oruanui fall deposits and other overlying pyroclastic fall deposits, loess and palaeosols that mantle the eroded surface of the Oruanui ignimbrite (none exceeding ~5 m thickness at any locality) are included in the ignimbrite for mapping purposes. This unit is characterised by a high primary permeability and an almost-complete lack of jointing but, in comparison with the Taupo ignimbrite, is somewhat finer grained and somewhat less permeable (Plate 1).

Plate 1: Road cutting through Oruanui ignimbrite at T18:438-770

Huka Falls Formation (>26.5 ka)

Lacustrine sediments (in part volcaniclastic) that directly underlie the Oruanui eruption deposits in an area around and north of Taupo township. These sediments extensively underlie the Wairakei geothermal field, where they form a capping to the geothermal aquifer, due to their abundance of low permeability lacustrine silts. Primary permeability is likely to be highly variable but mostly low; jointing is sparsely present in the finer units, but not likely to contribute much to overall permeabilities.

Rhyolite lava domes (3-320 ka)

Rhyolite lavas mapped in the area range widely in age; 3 examples are known to post-date the Oruanui eruption, but most lie in the age range 100-300 ka. Some of the domes are flanked by co-eruptive pyroclastic materials and talus, and this has been recorded separately as **rhyolite dome-related pyroclastics** where mappable. Exposed material tends to have low intrinsic permeability, but abundant fracture permeability.

Rhyolite pyroclastics (26.5 to ~150 ka)

These are fall deposits and minor non-welded ignimbrites that are best exposed from Kawakawa Bay to Kinloch on the northern shores of Lake Taupo, and sporadically north of there. Pyroclastic deposits of this age also separate the Whakamaru and Oruanui ignimbrites west of the lake, but are too thin to be plotted as a distinct map unit. When compared with the Oruanui and younger units, these deposits are more weathered and often contain paleosols, and hence locally act as aquitards below the Oruanui ignimbrite. Thicker primary pyroclastic units, such as those cropping out on the shore of Lake Taupo west of Kinloch will have similar hydrologic properties to the Oruanui, i.e. moderately high intrinsic permeability but few or no fractures.

Basalt and andesite lavas and pyroclastics (~100 to 300 ka)

Mafic lavas and pyroclastic deposits form small isolated outcrops in the northern and south western parts of the map. Most examples represent small scoria cones or tuff sheets, the only exception being the andesite mapped on western parts of the southern margin of the map that represents the northernmost exposure of andesite lavas forming the northern flank of Kakaramea volcano. Scoria deposits almost entirely have a very high primary permeability; tuffs and lavas a low primary permeability but a high abundance of fractures.

Rhyolite pyroclastics (~150 to 320 ka)

These pyroclastic units are ignimbrites that post-date the Whakamaru, but appear from limited field and radiometric-age evidence to be older than ~150 ka. These deposits are generally more indurated, are occasionally welded, and hence have lower intrinsic permeabilities than the younger pyroclastics. With the onset of welding comes jointing, and the welded zones thus have a dominance of fracture permeability.

Whakamaru-group ignimbrites (320-340 ka)

The mapped area of Whakamaru-group ignimbrites encompasses mostly poorly to moderately welded lithologies that have a low intrinsic permeability and a range of fracture densities from ~1 m^{-1} to 0.2 m^{-1} when viewed on a cliff-or roadcut-face (Plate 2).

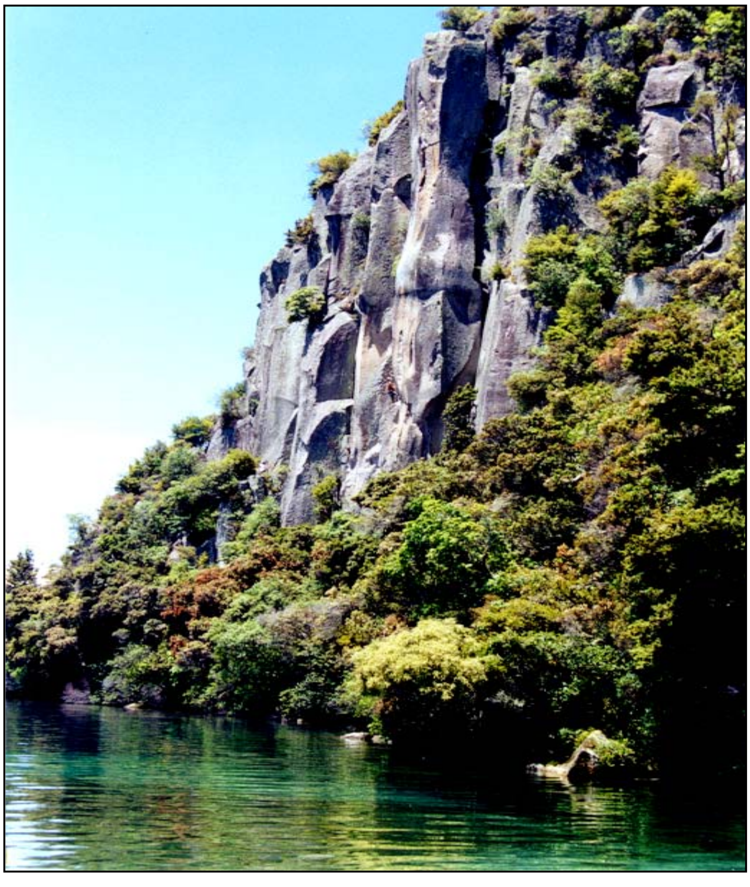

Plate 2: Whakamaru ignimbrite in cliffs at Whanganui Bay, T18:474-652

The upper contact of the Whakamaru-group ignimbrites is often a zone of low permeability due to the effects of weathering and the common presence of younger pyroclastic deposits that incorporate impermeable palaeosols, and seepages are common in road cuts that traverse this contact.

The flanks of the Hauhungaroa Range west and north of the mapped area also have outcropping older Quaternary ignimbrites. These have not been separately mapped, in part due to poor exposure and lack of knowledge of their detailed distribution, and in part because their hydrologic properties are likely to be very similar to the Whakamaru-group ignimbrites.

Pre-Quaternary rocks (>1.6 Ma)

There are small areas in the western portion of the map where pre-Quaternary rocks crop out, the best exposed being the ~Ma Hauhungaroa Lahars along Western Bay Road. All lithologies included in this grouping (see Section 3.2) are likely to be of lower permeability than any of the younger formations, with the possible exception of the Huka Falls Formation mudstones.

4 Well Distribution and Characteristics

4.1 Groundwater development and well distribution

In total, 135 bores have been identified in the northern and western catchments of Lake Taupo as illustrated in Figures 5 and 6. Well construction and other information relating to supplies is summarised in Appendix I. The information is variable with 57% of sites identified having detailed bore construction and geological log information. One of the two primary sources of information is logs provided to Environment Waikato since the late 1980’s as a requirement of land use consenting for well construction. The other main source of information is Lands & Survey documentation of groundwater supply wells constructed during development of the area in the 1960’s and 1970’s into large farm stations. Very good records of both bore construction and aquifer geology have been kept for the northern catchment. Subsequent to this initial development, a large number of bores were constructed, particularly in the 1990’s, as blocks were subdivided and other land uses e.g. lifestyle blocks were introduced.

The distribution of groundwater bores on the western side of Lake Taupo is particularly sparse (Figure 6). This reflects both the small population and availability of alternative water supplies. Most farm supplies in the western catchment are derived from streams rising in the Hauhungaroa Ranges including a number of scheme supplies. Numerous springs on the lower slopes have also been tapped for farm supply. Wells were sampled and monitored wherever possible, for example a lifting rig was used to gain access for water level and quality monitoring to some wells (Plate 3).

In the northern catchment wells are more regularly distributed and are commonly located adjacent to roadways. Farm blocks in this area are generally smaller and lifestyle properties are becoming more common, particularly in the Kinloch area.

Plate 3: Lifting rig providing access to site 72.397

4.2 Well construction and usage

Well depths in the study area range from 3.0 m to about 280 m in depth. The majority of wells (82%) are deeper than 40 m and nearly half of these (41%) are deeper than 100m. The preponderance of deep wells in the area reflects high elevation, deep static water levels (Section 5) and need to expose sufficient open saturated formation for well yield. Only 7% of wells are shallower than 10 m. They include four shallow piezometers which were constructed as part of this investigation to gather water chemistry and water level information.

Groundwater supplies in the area are generally small and commonly flow tested at less than 50 m^3 d^{-1}. Supplies are predominantly for stock and domestic use with no known current irrigation use.

Older water supply wells typically have 75 mm diameter casings and deep well cylinder pumps. These pumps provide only small supplies, generally < 50 m^3 d^{-1}. Newer wells are generally 100 mm in diameter and have submersible pumps installed which are capable of higher flow rates. Deep well cylinder pumps in older wells with sufficient yield and casing diameter are progressively being replaced with the higher capacity and less management intensive submersible pumps. Many of the wells in the western catchment originally drilled for the Lands & Survey are no longer used. They generally have very deep water levels and were low yielding. Difficulty in maintaining older deep well cylinder pumping equipment where static water levels are very deep encouraged alternative supply. The hydraulic characteristics of aquifers in the study area will be addressed in a subsequent investigation.

5 Piezometric Surface and Groundwater Flow Directions

5.1 General

Static water level was measured in most wells documented in the study area using electric probes. The relative height of these was obtained by surveying a reference point for each well, usually the casing head flange, by global positioning (GPS). An accuracy of 2 cm was achieved using real time kinematic (RTK) GPS. This involved establishing a series of known height base stations and relaying differential information by radio to a rover.

Measured static water levels ranged from 0.39 m to 167.5 m. The deepest levels are exceptionally deep for the region. The mean depth is just under 40 m. The distribution is however skewed toward shallower levels with a median about 26 m. Just under half (44%) the wells measured have static water levels less than 20 m deep.

5.2 Piezometric surface and flow directions

The piezometric surfaces illustrated in Figure 5 and Figure 6 represent a composite of water levels from available wells including shallow phreatic expression of the water table and deeper wells with static water levels which are generally lower than the water table. Wherever possible shallower wells were used in preference to deeper wells to better represent the water table. There is insufficient data available to provide detailed surface definition. In areas of sparse information such as the western catchment note is particularly taken of spring and stream elevation. The contours illustrated are inferred with account taken of likely topographic influence.

Lake level during the three month summer period of January to March 2001 varied from 356.31 to 356.74 m above mean sea level. The mean for this period was 356.57 m. The lake is the local groundwater sink for groundwater within the catchment. Although fluctuation in lake level can influence static water level in nearby shallow wells in permeable formation (Hadfield, 1995) this is less likely in apparently lower permeability formation in the study area.

Figure 5 shows that piezometric contours are generally consistent with topography although more subdued. Equipotential contours generally cross streams at right angles indicating consistency between groundwater and surface water flow directions. The available data show no indication of any significant departure in catchment divide between groundwater and surface water catchments. Measured relative water levels range up to about 195 m above lake level. Wells within about 2 kms of the lake at Kawakawa Rd are still about 150 m above the lake.

Groundwater flow is toward the lake. Where there is sufficient information it can be seen that there is some flow from areas of headland such as Kawakawa Rd toward valley areas such as Kinloch. Gradients range from some 0.075 in this area to 0.004 near Kinloch.

Groundwater flow in the western catchment is not well defined due to the paucity of available monitoring wells. It is however clear that flow is toward the lake. Wells on Karangahape Rd show a substantial difference in elevation. Static levels measured in wells near the end of the road were only about 9 m above lake level whereas wells about 2 kms further west were found to have levels about 124 m higher. It is likely in such cases that there is some aquitard separation between these aquifers.

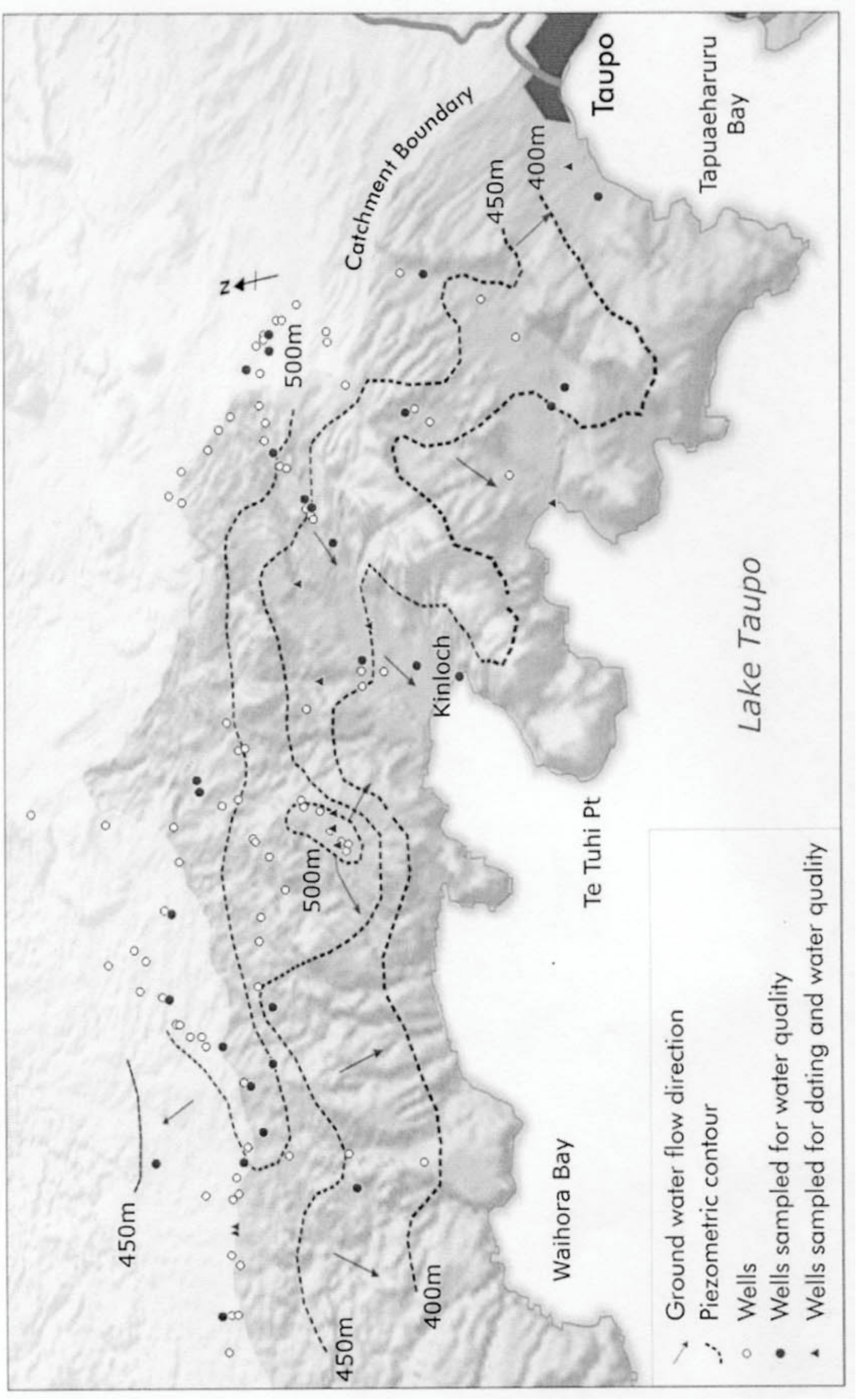

Figure 5: Piezometric surface and groundwater flow of the northern catchment

5.3 Vertical piezometric gradients

Vertical piezometric gradients were measured at two locations (Table 1). Shallow piezometers were installed adjacent to existing deeper wells at these sites. Static water levels were measured at each of these locations to determine the hydraulic head difference. The shallow formation at both sites is Oruanui ignimbrite. The deeper aquifer at site 72.377 is Whakamaru ignimbrite whereas the other site (72.352) is underlain by the mapped rhyolitic pyroclastic grouping.

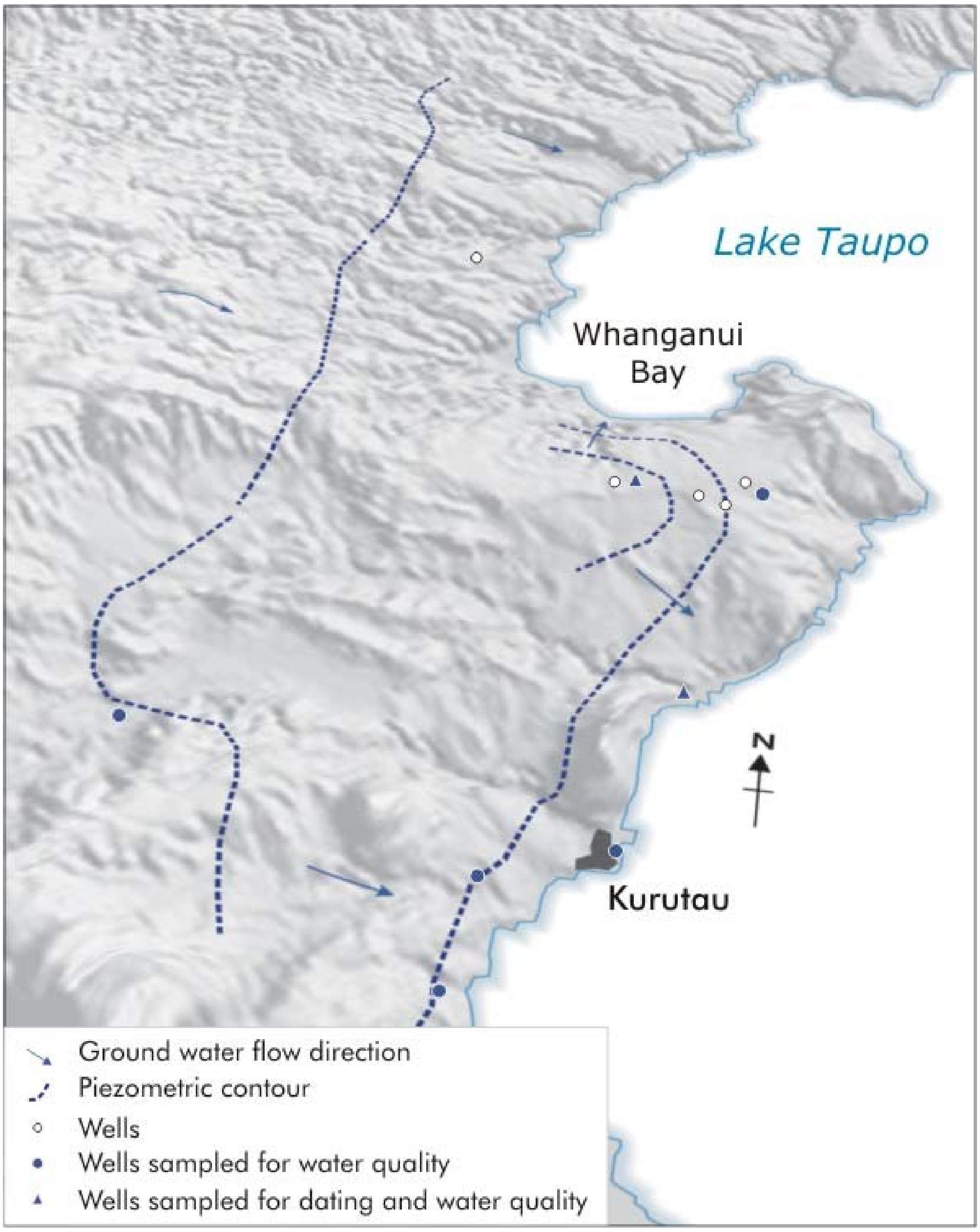

Figure 6: Piezometric surface of the western catchment and sampling sites

It can be seen that there is a substantial recharge gradient between the piezometer 72.354 and adjacent deeper well 72.352 of about 45 m. This Otake Rd site is located at the head of the Otaketake Stream. A seepage or spring zone is located within about 100 m to the east of this site. A seepage zone occurs at a similar distance at the other site on Whangamata Rd. The hydraulic gradient is however much smaller. Despite the common occurrence of such springs in the Oruanui formation these sites show that there may be substantial differences in vertical hydraulic gradients.

Table 1: Comparison of water levels at two pairs of shallow piezometers and adjacent wells

Site number	Map ref.	Well depth (m)	Casing depth (m)	Water level (m bgl)	Water level (m asl)
72.352	U17: 617-855	152.4	121.9	48.80	504.30
72.354	"	4.16	1.16	2.52	550.68
72.377	U17:508-848	50.3	45.4	4.51	489.92
72.331	"	5.8	2.8	3.71	490.66

There is a strong overall relationship between well depth and depth to water level (Figure 7). This indicates a strong recharge regime occurs generally in the area studied. It also shows that depth to water level generally increases substantially with drilling depth. Care must therefore be taken in monitoring well design if the water table is to be effectively represented.

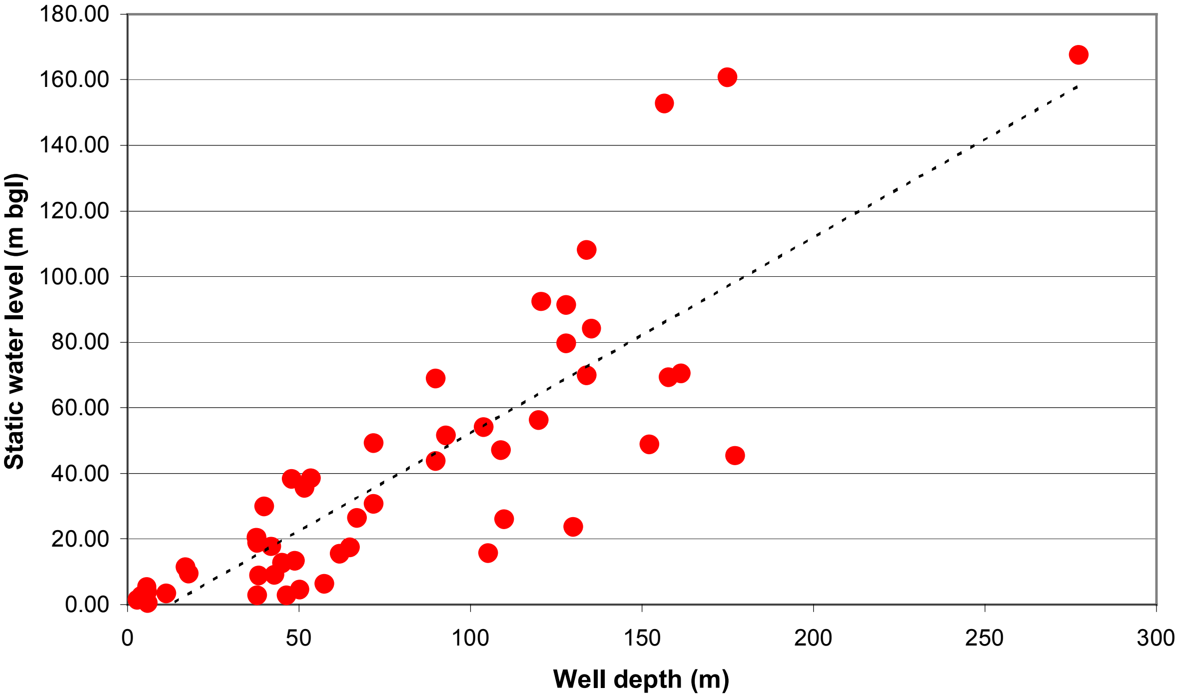

Figure 7: Well depth versus depth to static water level

6 Water Quality

6.1 Introduction and site selection

The chemical characteristics of groundwater sampled in and on the margins of the western and northern Lake Taupo catchment are described in this chapter. Groundwater quality was investigated to determine nitrogen nutrient content in particular, as well as general chemical characterisation

A total of 44 wells were sampled for groundwater quality in a single synoptic survey during February and March, 2000. Sites were selected, where possible, to represent a broad range of hydrogeologic conditions and to provide a well distributed network. The latter proved difficult on the western side of the lake where few wells were found and only seven sites sampled. Preference was given to sites with documented geological logs and construction details to aid interpretation. One site (72.394) listed in Appendix I has not been included in statistical analyses. Insufficient purging of this well was possible to provide dependable results. The locations of sites sampled are indicated in Figures 5 and 6. Both spatial variation and geological influence in results were investigated.

6.2 Sampling methods

Samples were collected from each of the wells using the groundwater sampling protocol developed by the Institute of Geological and Nuclear Sciences (Rosen et al., 1999). Care was taken to obtain samples which were as representative as possible. This involved sampling as close as possible to the well-head before water passed through any treatment process, or sat stagnant in pressure cylinders or storage tanks. At least three annular volumes of water were pumped to purge the wells and piezometers sampled. Existing pumps were used for sampling wherever possible. These were predominantly deep well cylinder and submersible pumps. Samples were cooled and sent promptly to the laboratory for analyses.

6.3 Analytical methods

Samples were analysed at Hill Laboratories for nitrate, ammonia, dissolved reactive phosphorous (DRP), dissolved iron and other ‘routine’ water quality analyses parameters. Routine parameters comprise pH; conductivity total dissolved solids; alkalinity; CO_2; calcium; magnesium; hardness; sodium; potassium; chloride, sulphate, boron, total iron, manganese copper and zinc. Detection limits and methods are listed in Table 2.

6.4 Chemical characteristics

A Piper trilinear plot of ionic milli-equivalents for all results is presented in Figure 8. This indicates a sodium and bicarbonate dominated chemistry typical of rhyolitic aquifers (Hounslow, 1995). The relatively uniform distribution is consistent with the predominantly siliceous (~ 70 %), acid volcanic formation which, although physically variable, is generally chemically similar.

The most notable outliers in the Piper diagram are sites A (68.320), B (72.331), C (72.401) and D (68.387). Site 68.320 has a nitrate concentration of 16.5 ppm as well as high chloride and sulphate concentrations. It is clearly influenced by land use, which in this case is probably a point source. Site 72.331 is a shallow piezometer constructed to investigate vertical variations in water quality and level. It also has relatively high chloride and nitrate concentrations consistent with land use impacts.

Well 72.401 is relatively deep (>100 m) with water chemistry indicative of alkali carbonate waters. It has a relatively high pH (7.7) whilst the calcium concentration is low (1.27 ppm). Groundwater sampled at the remaining site D (68.387) is anaerobic, as indicated by iron and ammonia concentrations and has temporary hardness. The geology of this south-western site includes deep alluvial sediments and peat layers which is different from all the other sites sampled.

Table 2: Groundwater chemical parameters analysed, methods and detection limits (Hill Laboratories, Routine Water Methods).

Parameter	Method Used	Detection Limit
pH (7.0-8.5)	pH meter APHA $4500\text{-}H^+$ B 20thed. 1998	0.1 pH Units
Electrical Conductivity	Conductivity meter, 25C APHA 2510 B 20thed. 1998	1 μS/cm
Total Dissolved Salts (1000)	Calculation: from Electrical Conductivity	2 $g.m^{-3}$
Alkalinity	Titration to pH 4.5 APHA 2320 B (Modified for alk <20) 20thed. 1998	1 $g.m^{-3}$ as $CaCO_3$
Free carbon dioxide	Calculation: from alkalinity and pH APHA $4500\text{-}CO_2$ D 20thed. 1998	1 $g.m^{-3}$
Calcium	Boiling nitric acid digestion. ICP-OES or ICP-MS APHA 3125 B 20thed. 1998	0.02 $g.m^{-3}$
Magnesium	Boiling nitric acid digestion. ICP-OES or ICP-MS APHA 3125 B 20thed. 1998	0.005 $g.m^{-3}$
Total Hardness (200)	Calculation: from Ca and Mg	1 $g.m^{-3}$ as $CaCO_3$
Sodium (200)	Boiling nitric acid digestion. ICP-OES or ICP-MS APHA 3125 B 20thed. 1998	0.5 $g.m^{-3}$
Potassium	Boiling nitric acid digestion. ICP-OES or ICP-MS APHA 3125 B 20thed. 1998	0.1 $g.m^{-3}$
Nitrate-N [11.3]	Filtered sample. Ion Chromatography. APHA 4110 B 20thed. 1998	0.02 $g.m^{-3}$
Chloride (250)	Filtered sample. Ion Chromatography. APHA 4110 B 20thed. 1998	0.5 $g.m^{-3}$
Sulphate (250)	Filtered sample. Ion Chromatography. APHA 4110 B 20thed. 1998	0.2 $g.m^{-3}$
Boron [1.4]	Boiling nitric acid digestion. ICP-OES or ICP-MS APHA 3125 B 20thed. 1998	0.005 $g.m^{-3}$
Total Iron	Boiling nitric acid digestion. ICP-OES or ICP-MS APHA 3125 B 20thed. 1998	0.02 $g.m^{-3}$
Total Manganese [0.5] (0.05)	Boiling nitric acid digestion. ICP-OES or ICP-MS APHA 3125 B 20thed. 1998	0.005 $g.m^{-3}$
Total Copper [2] (1)	Boiling nitric acid digestion. ICP-OES or ICP-MS APHA 3125 B 20thed. 1998	0.01 $g.m^{-3}$
Total Zinc (3)	Boiling nitric acid digestion. ICP-OES or ICP-MS APHA 3125 B 20thed. 1998	0.005 $g.m^{-3}$
Total Ammoniacal-N (1.17)	Phenol/hypochlorite colorimetry. Flow injection analyser. (NH4-N = NH4+-N + NH3-N) APHA 4500-NH3 G 20thed. 1998	0.01 $g.m^{-3}$
Dissolved Reactive Phosphorus	Molybdenum blue colorimetry. Flow injection analyser. APHA 4500-P G (Proposed) 20thed. 1998	0.004 $g.m^{-3}$
Dissolved Iron (0.2)	Filtered sample, ICP-OES or ICP-MS. APHA 3125 B 20thed. 1998	0.02 $g.m^{-3}$

Note. Values given in square brackets are maximum acceptable values for drinking water (MoH, 2000). Rounded brackets provide maximum acceptable aesthestic values.

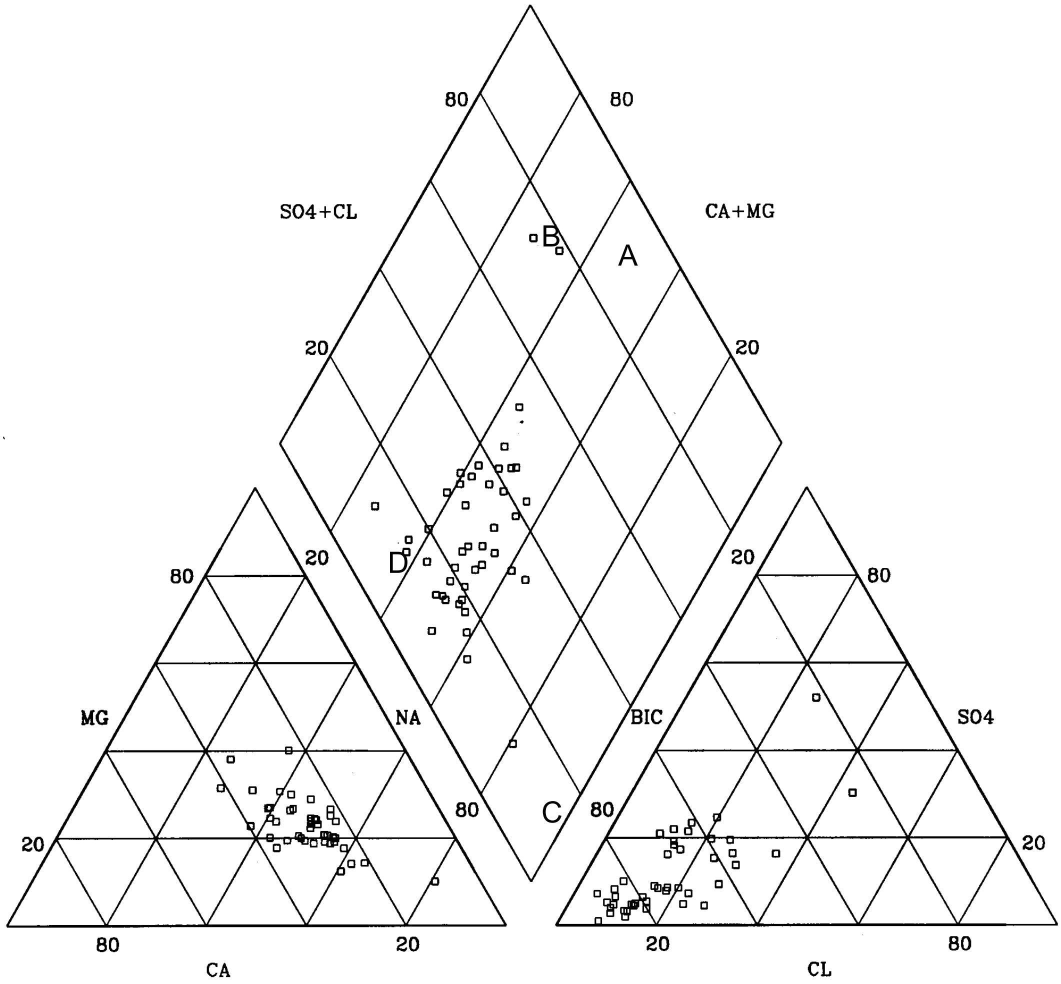

Figure 8: Piper trilinear plot of sample ionic chemistry

Variations in bicarbonate and to a lesser extent sodium concentration account for the most significant spread in the Piper plot. Bicarbonate concentrations in groundwater commonly relate to residence time and migration path-length. A significantly higher mean bicarbonate concentration ($p=0.004$) was found in groundwater from Whakamaru ignimbrite (33.5 ppm) than from shallow groundwater (23 ppm).

Mean sodium concentration (8.1 ppm) in Whakamaru ignimbrite aquifers is significantly lower ($p=0.002$) than in other rhyolitic pyroclastic formation (11.4 ppm). This is however the only discernible difference between these groups and suggests some difference in ion exchange capacity. Groundwater chemistry from a composite grouping ($n=7$) of relatively shallow wells (< 20m) can, by contrast, be significantly differentiated by higher mean concentrations of the following major ions: sodium; calcium; magnesium; potassium and chloride. The shallower groundwater is also slightly harder and has a slightly higher mean boron concentration.

Nitrate-N exceeded the maximum acceptable value for drinking water (MoH, 2000) of 11.3 ppm (or 50 ppm as NO_3) at one of the wells (68.320) sampled, probably as a result of point source contamination. Groundwater at five further sites exceeded half the drinking water standard. The mean and median nitrate-N concentrations of samples were 2.28 ppm and 1.45 ppm respectively (st dev. of 3.14). Nitrate-N was found to exceed 2 ppm in 25% of samples and was below detection levels at 16 % (7)

of sites. The nitrate concentration distribution is illustrated in a histogram in Figure 9. Excluding sites on the outside margin of the catchment the mean and median nitrate concentrations are 2.1 ppm and 1.12 ppm respectively.

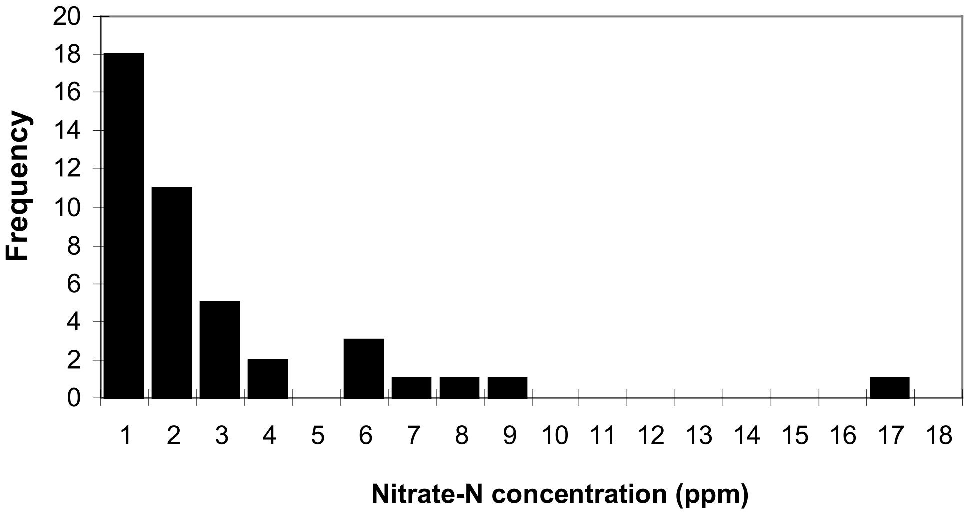

Figure 9: Histogram of sampled nitrate-N concentrations

Analysis of nitrate variance based on land use is limited by available sites and complicated by other factors including well depth and redox conditions. For example, groundwater wells were only able to be sampled at three dairy farm sites. Higher mean nitrate concentration apparent for areas of sheep and beef farming than in forest and residential land use areas was found to be statistically insignificant. Similarly no significant difference was found between mean nitrate concentrations on the basis of geologic groupings (Whakamaru ignimbrite, rhyolitic pyroclastics and a shallow formations grouping).

Although nitrate concentrations are generally low relative to levels in many other parts of the Waikato region (Environment Waikato, 1998), they are commonly substantially higher than lake and surface waters in the area (total nitrogen in the lake is typically 0.08 ppm). The likely mass contribution of nitrogen from groundwater to the lake will be addressed in later investigation reporting.

There is a substantial difference between the total and dissolved iron concentrations measured in the samples. This indicates that iron is in a particulate form or rapidly precipitates before analysis. Although there was no direct measure of redox condition, high iron concentrations and the presence of ammonia are indications of reducing conditions. Such conditions are indicated at sites 72.407, 72.435 and 68.387. Several other sites (~5) have water chemistry indicative of low dissolved oxygen status.

Manganese is common in the samples analysed with groundwater from eight wells having concentrations of more than 0.25 ppm. One of these (72.390), has a concentration of 1.61 ppm being well in excess of the drinking water guideline of 0.5 ppm. A black powdery precipitate collected from pipework at well 68.801 was found to be predominantly manganese. There was also evidence of a black 'manganese pan' at shallow depth (~2m) during construction of a piezometer at Kinloch (72.363). Manganese is generally found in reducing environments and associated with much higher iron concentrations. This association is however not apparent at some of the sites sampled.

Groundwater in the area investigated is generally soft, having hardness of less than 60 ppm as $CaCO_3$. The sodium adsorption ratios for these waters are also low (generally less 2) indicating there is little risk of soil damage from irrigation through cation exchange. Boron concentrations are also low (<0.25 ppm) and well below the MAV of 1.4 ppm. A strong correlation between copper, zinc and total iron is indicative of the likely influence of corrosion products. High metal concentrations were found at well 72.394, probably due to insufficient purging.

Ionic ratios (milli-equivalents) can provide useful information about aquifer characteristics. These ratios can indicate the degree of mixing of waters, whether minerals are dissolving or precipitating, if ion exchange is occurring and if there is active recharge (Mandel and Shiftan, 1981). The ratio of Ca+Mg/Na+K is generally close to one, indicating active recharge is common (Table 3). The Mg/Ca ratio is predominantly in the range 0.6 to 1.2 and average 0.8. Ratios above 0.9 are more typical of silicate waters. 'Normal' waters have Na/Cl ratios close to that of seawater (0.876 +/- 10%). Ratios above this were commonly found and indicate sodium exchange for calcium and magnesium in solution. Na/K ratios of 15-25 generally indicate recharge conditions in most aquifers and ratios generally increase downstream due to ion exchange.

Table 3: Mean, minimum and maximum ionic ratios - (milli-equivalent) for groundwater sites sampled

	Mg/Ca	Na/Cl	Na/K	Ca+Mg/Na+K
mean	0.81	3.56	10.71	1.11
max	1.22	8.01	107.98	2.83
min	0.46	0.51	1.93	0.24

6.5 Spatial distribution of chemical characteristics

Changes in water chemistry with depth may be indicative of changes such as aquifer geology or redox conditions and land-use impacts. As previously discussed there is relatively little variation in major ion chemistry. There is also no significant correlation between any of the chemical parameters measured and well depth. There is nevertheless a tendency for higher concentrations of parameters such as nitrate, sulphate and chloride to occur at shallower depths (Figure 10). All of these parameters are commonly influenced by land-use. The poor correlation with depth is mainly due to low concentrations at shallow depth where sources may be absent.

Two shallow piezometers were constructed beside deeper wells to enable water chemistry and levels to be compared at these locations (Table 1). Nitrate, sulphate and chloride concentrations were higher in the shallow piezometers at both locations (Appendix I).

No lateral trends in chemical character across the catchment are obvious from the analytical results. Available data are however from wells of varying depth and redox conditions.

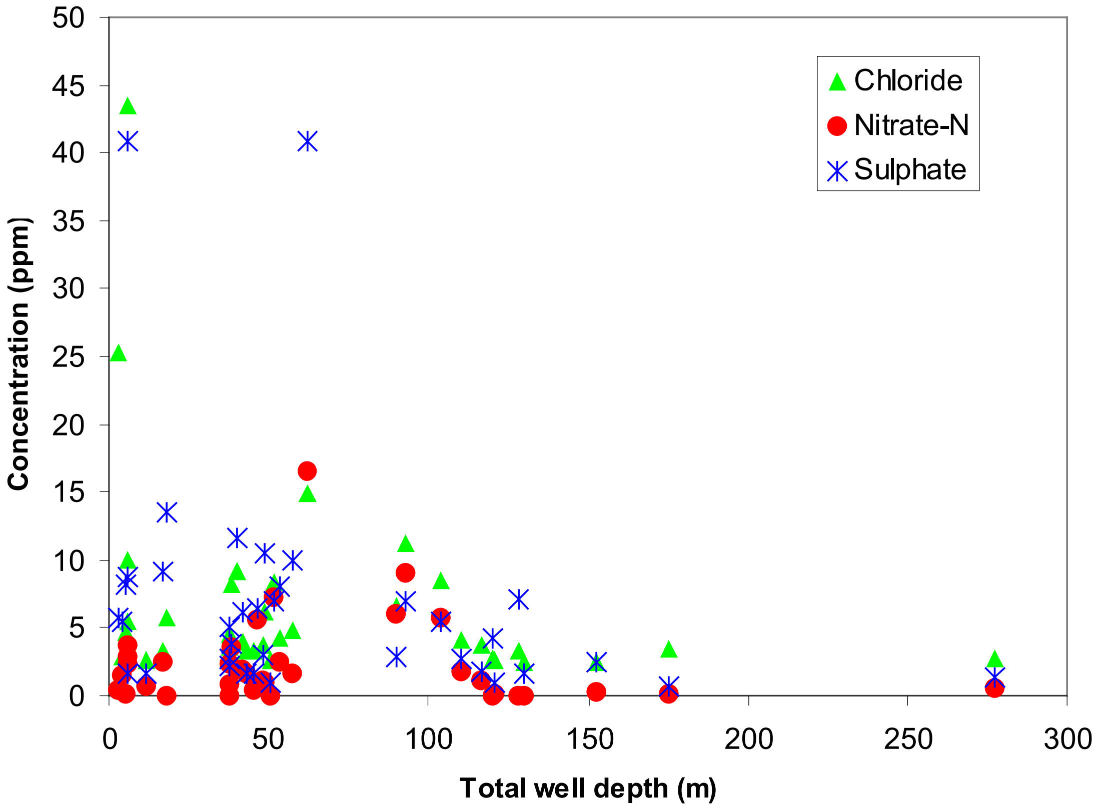

Figure 10: Variation of nitrate-N, sulphate and chloride concentrations with depth.

6.6 Discussion of groundwater chemistry

There are a large number of influences on the chemical character of groundwater. These include rainwater chemistry, aquifer geology, soil type and geothermal influences and modifying factors such as climate and geomorphology.

Groundwater recharge in the study area is derived originally from rainfall. The chemistry of local rainwater thus influences groundwater chemistry, particularly of shallow aquifers in recharge areas. Rainwater chemistry may be modified spatially by factors such as proximity to the ocean. The chemical composition of rainwater in the Taupo area was investigated by Timperley and Vigor-Brown, (1986). The concentrations of major ions in rainwater represented in Figure 11 are flow-weighted mean annual averages from a site on the eastern side of the lake. The mean concentrations of major ions for selected groundwater groupings are compared with rainwater composition in Figure 11.

This figure illustrates that groundwater in the Whakamaru ignimbrite and rhyolitic pyroclastic groups have chemical character closer to rainwater than the grouping of shallow aquifers. This implies that although the latter may have received most recent recharge, on average it is most modified. The sub-parallel relationship exhibited in the Schoeller plot implies that the waters are of a generally similar character (Zaporozec, 1972). The divergence in relative bicarbonate concentration between rainwater and groundwater reflects normal carbonic acid leaching of rhyolitic formation.

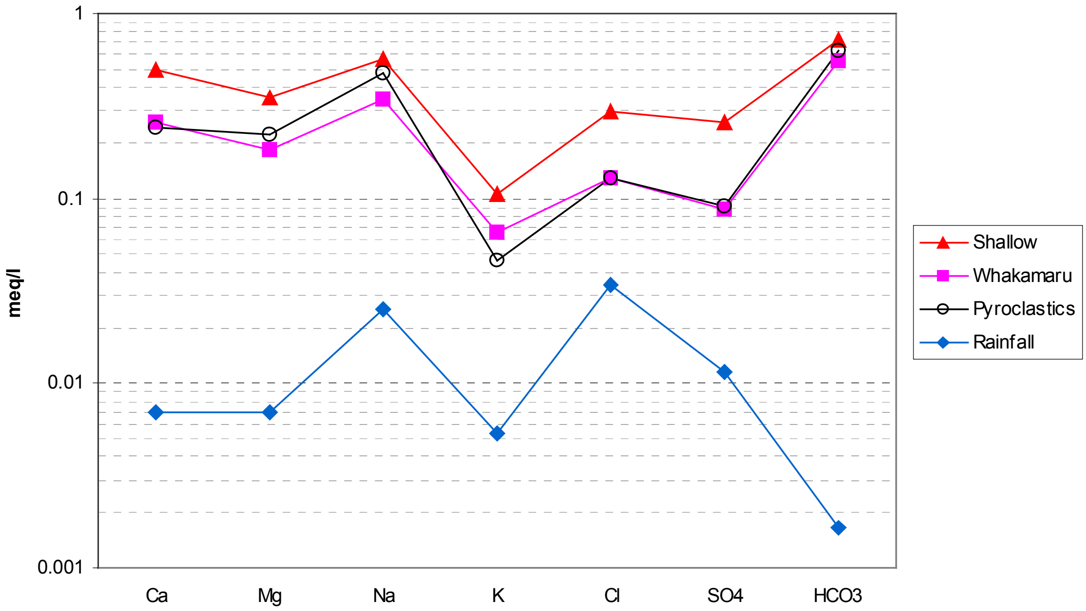

Figure 11: Schoeller plot of rainfall and mean chemistry for groundwater groupings.

Water infiltrating into the ground is altered chemically even before it reaches the water table. Uptake of CO_2 by water to form HCO_3 is one of the major alterations processes within soil and may be expressed as follows:

$$CO_2 + H_2O = H_2CO_3 \text{ and } H_2CO_3 = H^+ + HCO_3^-$$

CO_2 is brought into solution in the soil, where it has a higher partial pressure than in the atmosphere, caused primarily by root and microbial respiration. The soil exerts a strong influence on the chemistry of infiltrating water and is capable of generating relatively large amounts of acid (Palmer and Cherry, 1984).

After recharge at the water table, groundwater migrates through a sequence of formations and mineral assemblages. The composition of these formations and the order in which they are encountered control the groundwater chemistry. The length of the flowpath and the groundwater velocity are also strong influences on chemical character. The most important reactions in the evolution of groundwater chemistry are mineral dissolution and precipitation, redox reactions and cation exchange (Freeze and Cherry, 1979).

Dissolution results in the progressive weathering of minerals releasing cations and dissolved silica in the process. Mineral dissolution generally proceeds in several steps each releasing cations into solution. The increase in bicarbonate concentrations observed in the deeper Whakamaru ignimbrite is largely in response to progressive dissolution.

Ion exchange primarily involves clay minerals which absorb cations such as calcium, magnesium, and potassium, in preference to sodium, which is released into solution (Downes, 1985). A progressive increase in sodium ratios along the groundwater flowpath indicates substantial cation exchange is occurring.

Groundwater undergoes a complex series of chemical reactions with the formations through which it migrates. Reconstruction of the sequence of chemical reactions responsible for the observed groundwater chemistry, by way of mass balance calculations requires detailed information and is not addressed in this study.

Redox conditions are important in respect to nitrogen transformation and hence its contribution from groundwater to the lake. It is therefore worth considering in more detail the processes involved. Redox reactions effectively involve the transfer of electrons between dissolved, gaseous or solid constituents. In the natural system considered, every oxidation (electron loss) is balanced by reduction (electron gain). In order for the reduction of inorganic constituents to occur some other component must be oxidised. The constituent oxidised is often organic matter, catalysed by bacteria.

Groundwater redox levels are essentially determined by the relative rates of introduction and consumption of dissolved oxygen. Oxygen is introduced by circulation but is not readily replenished due to isolation from the atmosphere. Consumption of oxygen is primarily by bacterially mediated decomposition of organic matter and to a lesser extent by other hydrochemical reactions. There are four factors identified by Drever (1988), as being most important in determining redox conditions:

(i) the oxygen content of recharge water;
(ii) the availability and reactivity of organic matter and other potential reductants,
(iii) the existence of potential redox buffers in the aquifer and
(iv) groundwater circulation rate.

The percolation of water infiltrating through organic rich soils may readily reduce recharging groundwater to an anaerobic condition. However sources of readily metabolised organic matter are very limited in the catchment and hence also available organic carbon.

Oxidation of organic matter can still occur once dissolved oxygen has been consumed. In the absence of dissolved oxygen, the oxidising agents which are progressively reduced are; NO_3, MnO_2, $Fe(OH)_3$, SO_4 and others. The groundwater environment becomes progressively more reduced as these oxidising agents are consumed. Organic constituents may be anaerobically degraded should conditions become sufficiently reduced.

Table 4 lists a sequence of redox reactions which progress downwards from aerobic oxidation to methane fermentation. These reactions proceed at a significant rate provided there is a supply of consumable organic matter and bacteria have sufficient nutrients.

Table 4: Some redox reactions that consume organic matter and reduce inorganic compounds (from Freeze and Cherry, 1979).

Process	Equation
Denitrification	$CH_2O + 4/5NO_3^- = 2/5N_2(g) + HCO_3^- + 1/5H^+ + 2/5H_2O$
Manganese reduction	$CH_2O + 2MnO_2(s) + 3H^+ = 2Mn^{2+} + HCO_3^- + 2H_2O$
Iron reduction	$CH_2O + 4Fe(OH)_3(s) + 7H^+ = 4Fe^{2+} + HCO_3^- + 10H_2O$
Sulfate reduction	$CH_2O + ½SO_4^{2-} = ½HS^- + HCO_3^- + ½H^+$
Methane fermentation	$CH_2O + ½H_2O = ½CH_4 + ½HCO_3^- + ½H^+$

The addition of dissolved and to a lesser extent solid-phase organic carbon along the groundwater flowpath can provide reactants for such processes as sulphate reduction.

Dissolved organic matter participating in metal oxide reduction largely explains increases in iron and manganese in groundwater from wells near organic-carbon sources (Freeze and Cherry, 1979).

The decomposition or oxidation of only a small amount of organic matter in groundwater can result in the consumption of all available dissolved oxygen. The decomposition of organic matter may be represented by the following reaction in the presence of bacteria and free oxygen.

$$O_2(g) + CH_2O = CO_2(g) + H_2O$$

As a consequence of the limited replenishment and solubility of oxygen in the subsurface environment anaerobic conditions are readily produced where there is significant organic content.

Micro-organisms are the catalysts for nearly all the important redox reactions that occur in groundwater. Microbial involvement, particularly bacteria, substantially increases the rates of such reactions. Bacteria, including both aerobic and anaerobic varieties, derive energy in the process. They are also small enough to migrate through most porous formations. The lack of an essential nutrient for microbial activity, such as carbon, nitrogen, sulphur and phosphorous, however, may result in substantially slowed reaction rates. The general lack of organic matter and associated microbial activity in much of the catchment strongly limits the extent of denitrification. Occasional paleosols provide one of the few likely sources of significant organic carbon in the catchment apart from localised wetland development.

Streams gain or lose water to the ground depending on the local flow regime. The interaction between groundwater and streams has some influence on the water chemistry of both. The water quality of streams in the lower discharge areas is likely to be influenced by groundwater chemistry. Such effects are likely to be more pronounced during periods of low flow. The influence of streams upon groundwater chemistry in the recharge areas is, by contrast, likely to be localised and therefore less significant.

Human activities can have an important influence on the environmental factors influencing the composition of water. These impacts predominantly occur as contamination from the disposal of waste either into or onto the ground. The most pronounced anthropogenic influence in the catchment is from agricultural land use activities. Nitrate contamination of shallow aquifers is the most obvious impact associated with farming. There is evidence of diffuse contamination of groundwater resulting in elevated nitrate concentrations. The introduction of more intensive agriculture e.g. dairying, into the catchment can be expected to result in higher nitrogen loading (Vant and Huser, 2000).

Contamination from point sources such as wastewater discharge may also be of localised importance. It is important to recognise the potential for further anthropogenic impacts and develop appropriate resource management strategies particularly in respect to lake water quality protection. Groundwater quality in the catchment is relatively very high. Apart from isolated incidences of drinking water guidelines being exceeded in respect to nitrate and manganese concentrations, these waters are suitable for all likely uses. Constraints in respect to lake water quality protection are however much higher and require very careful land use management.

7 Groundwater Age Dating

7.1 CFC and tritium dating techniques

Tritium is naturally produced 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 a high tritium concentration (Figure 12). 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.

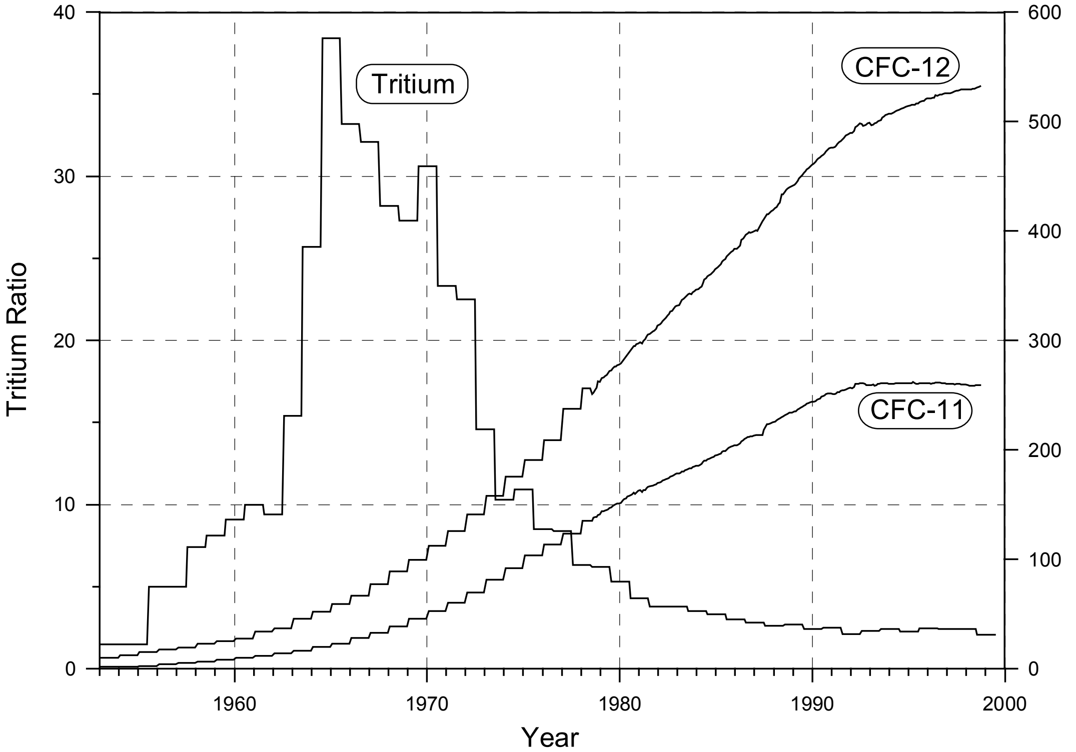

Figure 12: Tritium in rain from Kaitoke, 40km North of Wellington (yearly averages) and CFC concentrations in Southern Hemispheric air. Tritium Ratio TR=1 represents T/H ratio 10^{-18}, 1 pptv is one part per trillion by volume of CFC in air, or 10^{-12}.

As a result of the 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 combining the tritium data with CFC data. CFC concentrations in the atmosphere have risen linearly over that time.

Chlorofluorocarbons (CFCs) are entirely man-made contaminants. They were used for refrigeration and pressurising aerosol cans, and concentrations in the atmosphere have gradually increased (Figure 1). CFCs are relatively long-lived and slightly soluble in water and therefore enter the groundwater systems during 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.

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. In CFC age interpretation, however, care has to be taken. A number of factors can modify CFC 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). See Plummer and Busenburg (1999) for more information. CFC-11 has been found in New Zealand to be less susceptible to local contamination and agrees relatively well with tritium data. Note that CFC ages do not take into account of travel time through unsaturated zones.

Due to the large tritium input during 1960-1970 the tritium method is very sensitive to the flow model, but such cases are ambiguous in the dating range 15-40 years. CFC input concentrations are steadily increasing over that time range. Therefore, by combining both methods, both groundwater age and age distribution can be obtained.

7.2 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 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 and flow 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, can not be estimated from hydrogeologic information, two independent tracers (tritium and CFC) or two measurements over time are necessary.

For contaminant input since 1965 (for example nitrates from stock farming since 1965) determining the fraction of water younger than 35 years is useful to establish how much of the groundwater could be carrying the contaminant load already. The fraction of young water (yf) can be calculated by integrating the appropriate age distribution function over the time 0 to 35 years. yf = 100% means that all of the water has been underground for less than 35 years, and yf = 0% means that none of the water has been underground for less than 35 years.

7.3 Sampling methods

Samples for tritium analysis were collected in clean 1.1 L Nalgen bottles. Concentrations of ^{3}H are reported as Tritium Ratios (TR) at the date of sample collection ± 1 standard measurement error, using the scale recommended by Taylor and Roether (1982). TR = 1 corresponds to a T/H ratio of 10^{-18}.

Sufficient sensitivity and accuracy for detection of tritium is necessary to make use of low-level natural tritium as a tracer of the hydrologic cycle. Because of the low tritium concentrations prevailing in New Zealand's surface waters we have established at the

Institute of Geological & Nuclear Sciences Ltd. (GNS) a tritium measurement system with extremely high detection sensitivity. The lower 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 samples for CFC concentration measurements were collected in such a way as to prevent contact with the atmosphere or with plastic materials, either of which could contaminate the sample with CFCs. The samples are preserved in the field by sealing them into 62 mL borosilicate glass ampoules at the well site. The sampling apparatus is connected to the well outlet by copper tubing. All other tubing in contact with the water during sampling is stainless steel. The ampoule is attached to the sampling apparatus and flushed with ultra-high-purity nitrogen gas. The well water is then allowed to flow through the tubing and valves and into the bottom of the ampoule displacing the nitrogen. The ampoule is rinsed with several hundred ml of water, then nitrogen is forced into the neck to displace some of the water. The ampoule is then fused shut about 1-2 cm above the water level with an oxy/acetylene gas torch. Nitrogen flows continually across the union to prevent any contamination with air. Five ampoules are normally collected at each sampling site. The CFC samples were analysed at GNS by gas chromatography.

Plate 4: Water sampling for CFC dating

7.4 Results and interpretation of CFC ages

CFC and tritium samples were collected in March, 2001 from wells detailed in Table 5. Tritium and CFC data are listed in Table 6.

Table 5: Sampled well location and construction details

Well	Map reference	Total depth (m)	Casing depth (m)	Geology	Aquifer confinement	Static water level (m bgl)
68.320	U18:749-747	62.0	43	Oruanui Ignimbrite	unconfined	15.34
72.364	U17:665-824	spring	spring	Rhyolite Lava	spring	spring
72.377	T17:508-847	50.3	45.4	Whakamaru Ignimbrite	confined	4.51
68.317	T17:605-811	104.0	73	Rhyolite pyroclastic	leaky	54.00
72.392	T17:609-813	93	65.2	Rhyolite pyroclastic	leaky	51.40
68.301	T17:656-803	53.6	49	Rhyolite pyroclastic	leaky	38.40
68.660	T17:643-817	37.7	19.5	Rhyolite	leaky	20.35
72.158	T17:613-812	277.7	169.8	Rhyolite Pyroclastic	leaky	167.5
72.397	T18:501-616	NA	NA	Whakamaru Ignimbrite	unconfined	59.05
72.332	T18:679-752	5.7	2.7	Taupo Ignimbrite	unconfined	5.12
72.399	T18:511-562	6.0	~3	Lake sediments	unconfined	0.39
72.331	T17:508-847	5.8	2.8	Oruanui Ignimbrite	unconfined	3.71

A combined exponential and piston flow model was used to calculate the mean residence time (MRT) and young water fraction (yf). The input function from Kaitoke was used for tritium interpretation.

The fraction of mixed flow (Table 7) was estimated from the best match of tritium and CFC dates, and from the aquifer condition in Table 5. As an example, E%PM = 0% means there is no mixing of water in the aquifer (pure piston flow), and E%PM = 100% means that there is complete mixing. Real groundwaters are somewhere between 0 and 100%.

The recommended mean residence times of the combined methods, with ambiguous ages resolved, are listed in Table 6. The best matching mean residence times for the individual methods are listed in bold.

CFC-11 and CFC-12 data lay relatively close to the atmospheric equilibrium ratio. This indicates that in this area local contamination or loss by degradation or sorption in the subsurface has less affect than found in other areas. Such processes would have had different effects on the two CFCs, shifting the CFC-11/CFC-12 ratios away from the atmospheric equilibrium. The CFC-12 dates are, however, slightly younger than the CFC-11 dates. Previous work comparing CFC and tritium dates on Canterbury Plains groundwater has shown better agreement between CFC-11 and tritium dates than between CFC-12 and tritium dates (Stewart et al., 1999; Stewart and White, 2000). CFC-11 dates are therefore preferred except for very old samples (older than 1950) or very young samples (younger than 1990).

Table 6: CFC and tritium analysis results. PPTV is one part per trillion by volume or 10^{-12}. One 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.

Well	**CFC-11 [pptv]**	**CFC-12 [pptv]**	**TR**	**sigTR**
68.320	91.2	255.4	2.12	0.06
72.364			0.98	0.036
72.377	0.6	3.7	0.139	0.023
68.317	78.5	197.5	2.79	0.08
72.392	81.2	221.4	3.41	0.09
68.301	24.6	56.1	0.943	0.037
68.660	83.9	179.6	0.908	0.036
72.158	24.0	65.7	0.656	0.031
72.397	59.7	176.6	1.83	0.06
72.332	95.6	293.5	1.34	0.04
72.399	175.1	390.5	1.55	0.05
72.331	163.8	345.4	1.81	0.06

The mean residence time is strongly dependent on the flow model and therefore not a good term to compare the different wells with different flow situations. A better age-term to compare the different wells in regard to a surface contaminant is the fraction of water younger than a certain age (usually the age when the contamination started).

The fraction of water younger than 35 years is listed in Table 7. The age 35 years was chosen because stock farming increased significantly between 1960-70. As an example, yf = 10% means that only 10% of the water is young enough to carry nitrate from increased stock farming in the 60s, while 90% of the water is too old to reflect that change yet. In time more and more of the water recharged after 1965 will arrive at the well. Consequently, if there is additional nitrate in the recharge area, an increase in nitrate level is likely as more contaminated water arrives at the well. In contrast, yf = 95% means that nearly all the water is younger than 35 years and therefore, is already carrying the contaminant load. Assuming no change in land use, the nitrate level is likely to remain constant at the present level for wells with high yf.

Table 7: Flow model, mean residence time and young water fraction. E%PM is the fraction of mixed flow in the total flow as a percentage. Recd is the recommended mean residence time of the combined methods. 'yf' is the fraction of water younger than 35 years.

Well	**E%PM**	**Mean residence time [yrs]**				**yf [%]**	**NO_3-N [ppm]**	
		Tritium	**CFC-11**	**CFC-12**	**Recd.**	**(35y)**	**current**	**100%yf**
68.320	35	**30**	**30**	24	**30**	**80**	16.5	21
72.364	50	**64**			**64**	**10**	1.58	16
72.377	35	**65**	**68**	**68**	**65**	**0**	0.00	
68.317	20	**30**/40	**30**	27	**30**	**85**	5.69	7
72.392	10	**31**	**29**	26	**30**	**95**	9.00	9
68.301	75	**75**	79	75	**75**	**25**	2.48	10
68.660	50	65	34	32	**60**	**40**	0.85	2
72.158	35	56	44	42	**50**	**15**	0.48	3
72.397	50	<4 / **34**	**40**	**33**	**35**	**65**	6.85	11
72.332	80	**41**	**41**	25	**40**	**55**	2.91	5
72.399	80	**27**	**21**	16	**25**	**80**	2.39	3
72.331	50	<4 / 40	**22**	**19**	**20**	**90**	3.64	4

Nitrate levels scaled from the present level to yf = 100% are listed in the last column of Table 7. These are forecast nitrate levels that may be reached in future when all age fractions in the water carry nitrate from post 1965 land-use. Nitrate travelling from further away would also have reached the well. In wells with high fractions of water recharged before 1965, low nitrate concentrations are often due to nitrate from recent land-use not having arrived at the well. The forecast values were calculated with the assumption that nitrate input in the recharge area remains at post 1965 levels and the nitrate inputs are the same in the recharge areas of the older and the younger waters.

7.5 Interpretation

Consistent results between the dating techniques were obtained for most of the wells, and ambiguities could be resolved by applying both tritium and CFC methods. The best matches between tritium and CFC ages were obtained for wells in deep and confined aquifers with 35-50% mixed flow. This is in good agreement with findings in other areas in New Zealand. The high tritium ratios in wells 68.317 and 72.392 can be explained only with a high proportion of piston flow. Wells 68.660, 72.158 and 72.331 do not show good matches between tritium and CFC data, indicating that the flow situation is more complicated than can be described with a combination of piston and mixed flows. Well 72.399 shows little agreement between all three methods, indicating a more complicated flow situation due to possible water recharge from the lake.

The data are the first indication of the age of groundwater in the Western Bays area. The data are consistent with other age dating results that has been done in the Waitahanui and Waimarino areas (GNS, unpublished data).

Nitrate-N concentration versus fraction of young water (younger than 35 years) are plotted in Figure 13. A good correlation is obvious. Wells with high young water fraction show high nitrate-N levels, while wells with little young water fraction show only little nitrate-N. Note that wells with a high fraction of young water do not necessarily have high nitrate-N concentrations, as a source of contamination is required in the recharge area. In contrast, wells with no fraction of water younger than 35 years should necessarily have low nitrate-N as the water is too old to carry the contaminant already.

The dating results suggest that most of the wells have high fractions of water recharged before the increased land use. Therefore, the water is too old to reflect that change yet. However, in time, more and more of the water recharged after 1965 will arrive at the wells and Lake Taupo. Therefore, land use will have an impact on nitrogen concentrations entering Lake Taupo for some time to come in the future, even if no further intensification of land use proceeds.

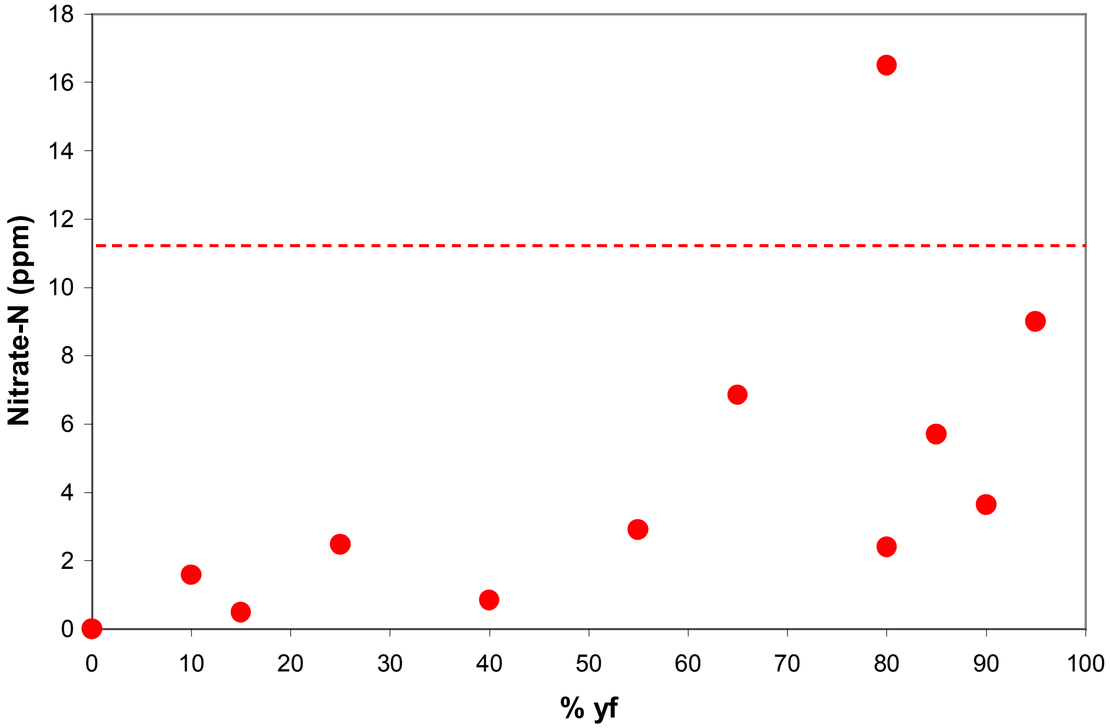

Figure 13: Nitrate-N versus young water fraction. %yf is the fraction of water younger than 35 years. The New Zealand Drinking Water Standard is 11.3 ppm for NO_3-N

.

8 Summary

This first phase of hydrogeological investigation focused on the geological setting, supply distribution, flow regime, groundwater quality and age in the northern and western Lake Taupo catchments.

The geology comprises predominantly young (< 0.4 Ma), rhyolitic pyroclastic formation. The stratigraphic sequence in the western catchment is generally simple with Oruanui ignimbrite overlying a large thickness of Whakamaru ignimbrite. The Whakamaru ignimbrite is sufficiently welded in places to form imposing lakefront bluffs.

A more complex series of ignimbrites, fall deposits, localised lava extrusions and lacustrine sediments occurs east of Kawakawa Bay. Faulting in this northern catchment area is also more common. The unwelded Oruanui ignimbrite thickens toward the east and overlies a composite grouping of rhyolite pyroclastics. Although likely to be moderately permeable, they also have occasional paleosols which are likely to act as aquitards and cause localised perching. Huka Formation lacustrine sediments are evident towards Taupo township east of Kinloch.

There are very few wells in the western catchment where farms instead generally take water from streams rising from the ranges to the west. Hydrogeologic information in this area is therefore sparse. Groundwater wells are more prevalent in the northern catchment and have been developed predominantly as small, non-irrigation, farm supplies.

The surveyed level data available does not indicate any discrepancy between surface water and groundwater catchments. Groundwater flow in the area studied is consistent with topography although more subdued. There is a strong relationship between groundwater levels and well depth indicating a recharge regime generally exists in the catchment. Groundwater is recharged from rainfall in the catchment and drains toward the lake, which is the local sink.

Groundwater quality samples were collected from a total of 44 wells within and on the margins of the lake catchment. They were analysed for nutrients and major ion chemistry. The sodium bicarbonate dominated chemical character of the waters is relatively uniform and typical of normal weathering of rhyolitic formations. Water quality is generally high although there is some evidence of land use impacts. These effects have resulted in elevated nitrate, sulphate and chloride at some sites. The drinking water guideline for nitrate is exceeded at one site and another five sites exceed half the guideline value. The mean nitrate-N concentration (2.28 ppm) is substantially higher than lake and surface water concentrations.

Water quality results from eight wells infer that anaerobic or poorly aerobic conditions occur at these sites. Manganese concentrations >0.25 ppm were found with similar frequency including one site with manganese in excess of the drinking water guideline.

A total of 11 wells and one spring were sampled for age determination using CFCs and tritium. The results of CFC and tritium analyses show the mean residence time of groundwater sampled ranges from about 20 to 75 years. Nitrate concentrations increase with the percentage of young water in the samples. Concentrations are expected to increase as the percentage of water recharged since 1965 increases unless land-use changes.

In summary, groundwater flows through predominantly young rhyolitic pyroclastic formation towards the lake. Although groundwater quality is generally high there is clear evidence of land-use impacts. These impacts are greatest in younger waters and the nitrogen load from groundwater entering the lake is expected to increase. Further phased hydrogeologic investigation is planned to provide more detailed information relevant to the management of land-use for lake water quality protection.

References

Davy, B.W., and Caldwell, T.G. (1998) Gravity, magnetic and seismic surveys of the caldera complex, Lake Taupo, North Island, New Zealand. Journal of Volcanology and Geothermal Research, 81, 69-89.

Downes, C.J., (1985) Redox reactions, mineral equilibria and groundwater quality in New Zealand aquifers. In: Ward, C.H.; Giger, W.; McCarthy, P.L., (eds.) *Groundwater Quality*. Wiley Interscience, New York.

Drever,J.I., (1988). *The Geochemistry of Natural Waters.* 2nd Edition. Prentice Hall Inc. New Jersey, 435 p.

Environment Waikato (1998) Waikato state of the environment report, 244 p.

Environment Waikato (2000) Issues and options for managing water quality in Lake Taupo. A discussion paper, 23 p.

Freeze, R.A.; Cherry, J.A., (1979). *Groundwater.* Prentice-Hall, Englewood Cliffs. 604 p.

Grindley, G.W. (1960) Sheet 8 Taupo. Geological Map of New Zealand 1:250,000. Department of Scientific and Industrial Research, Wellington.

Grindley, G.W. (1961) Sheet N94 Taupo. Geological Map of New Zealand 1:63,360. Department of Scientific and Industrial Research, Wellington.

Grindley, G.W. (1965) The Geology, Structure, and Exploitation of the Wairakei Geothermal Field, Taupo New Zealand. New Zealand Geological Survey Bulletin 75.

Hadfield, J.C., 1995: A groundwater contaminant tracer study at Waitahanui, Taupo. Unpublished University of Waikato MPhil thesis, 289 p.

Hatherton, T. (1974) Basement surface west of Lake Taupo. Report 90, Geophysics Division, DSIR, Wellington, New Zealand.

Houghton, B.F., Lloyd, E.F., Wilson, C.J.N., and Lanphere, M.A. (1991) K-Ar ages from the Western Dome Belt and associated rhyolitic lavas in the Maroa-Taupo area, Taupo Volcanic Zone, New Zealand. New Zealand Journal of Geology and Geophysics, 34, 99-101.

Houghton, B.F., Wilson, C.J.N., McWilliams, M.O., Lanphere, M.A., Weaver, S.D., Briggs, R.M., and Pringle, M.S. (1995) Chronology and dynamics of a large silicic magmatic system: central Taupo Volcanic Zone, New Zealand. Geology 23, 13-16.

Hounslow, A.W., (1995) *Water quality data: analysis and interpretation*, CRC Press Inc, New York, 397 p.

Leathwick, J., Clarkson, B., Whaley, P., (1995) Vegetation of the Waikato region: Current and historic perspectives. Landcare research, Hamilton.

Maloszewski P, Zuber A, 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers: I.: Models and their applicability, J. Hydrology., 57 p.

Mandel, S. and Shiftan, Z.L., (1981) Groundwater resources investigation and development. Academic Press, New York.

Ministry of Agriculture (1997) Impacts of dairy conversions in the Lake Taupo District. MAF Policy Technical Paper 1997/9. Ministry of Agriculture, Wellington.

Ministry of Health, 2000: Drinking water standards for New Zealand, 2000. Wellington, 130 p.

Palmer, C.D. and Cherry, J.A., (1984) Geochemical evolution of groundwater in sequences of sedimentary rocks. *Journal of Hydrology*, 75: 27-65.

Plummer, L.N., Busenburg, E. 1999: Chlorofluorocarbons. Chapter 15 *in* Environmental Tracers in Subsurface Hydrology. Eds: P. Cook and A.L. Herczeg. Kluwer Academic Publishers. Pp. 441-478.

Rae, R., Hawes, I., Chague-Goff, C., Gibbs, M., 2000: Nuisance plant growths in the shallow littoral zone of Lake Taupo. NIWA report CHC00/75 for Environment Waikato , 34p.

Rosen, M.R., Cameron, S.G., Reeves, R.R., Taylor, C.B., (1999) New Zealand guidelines for the collection of groundwater samples for chemical and isotopic analysis. Institute of Geological and Nuclear Sciences Limited , Wairakei. 80 p.

Schouten, C.J., Terzaghi, W., Gordon, Y., (1981) Summaries of water quality and mass transport data for the Lake Taupo catchment, New Zealand. Water and Soil Miscellaneous Publication 24, Ministry of Works, and Development, Wellington.

Self, S. (1983) Large-scale phreatomagmatic silicic volcanism: a case study from New Zealand. Journal of Volcanology and Geothermal Research, 17, 433-469.

Stewart, M.K., Trompetter, V., Van der Raaij, R. 1999: Conceptual model of the groundwater resource between the Ashley and Rakaia rivers, Canterbury, using the CFC dating technique. *New Zealand Hydrological Society 1999 Symposium Proceedings*, p 76. Napier, 23-26 November.

Stewart, M.K., White, P.A. 2000: Geochemical indicators of groundwater recharge. *New Zealand Hydrological Society 2000 Symposium Proceedings*, p 160. Christchurch, 21-24 November.

Taylor, C.B., (1994) The relationship between electrolytic deuterium and tritium separation factors, and attainment of improved accuracy in radiometric low-level tritium measurement. *Applied Radiation and Isotopes*, 45, 683-692.

Taylor, C.B. and Roether, W., (1982) A uniform scale for reporting low-level tritium measurements in water. *International Journal of Applied Radiation and Isotopes*, 33: 377-382.

Timperley, M,H., and Vigor-Brown, R.J., (1986) Water chemistry of lakes in the Taupo volcanic zone, New Zealand . New Zealand Journal of Marine and Freshwater Research, 1986, vol. 20: 173:183.

Wilson, C.J.N. (1985) The Taupo eruption, New Zealand II. The Taupo ignimbrite. Philosophical Transactions of the Royal Society of London, A314, 229-310.

Wilson, C.J.N. (1986) Reconnaissance stratigraphy and volcanology of ignimbrites from Mangakino volcano. In I.E.M. Smith, Ed. Late Cenozoic Volcanism in New Zealand, Bulletin 23, p. 179-193. Royal Society of New Zealand, Wellington.

Wilson, C.J.N. (1991) Ignimbrite morphology and the effects of erosion: a New Zealand case study. Bulletin of Volcanology, 53, 635-644.

Wilson, C.J.N. (1993) Stratigraphy, chronology, styles and dynamics of late Quaternary eruptions from Taupo volcano, New Zealand. Philosophical Transactions of the Royal Society of London, 343, 205-306.

Wilson, C.J.N. (2000) The 26.5 ka Oruanui eruption, New Zealand: an introduction and overview. Journal of Volcanology and Geothermal Research, (under review).

Wilson, C.J.N., Houghton, B.F., and Lloyd, E.F. (1986) Volcanic history and evolution of the Maroa-Taupo area, central North Island. In I.E.M. Smith, Ed. Late Cenozoic Volcanism in New Zealand, Bulletin 23, p. 194-223. Royal Society of New Zealand, Wellington.

Vant, B and Huser, B., (2000) Effects of intensifying land-use on the water quality of Lake Taupo. Proceedings of the New Zealand Society of Animal Production 60: 261-264.

Zaporozec, A., (1972) Graphical interpretation of water quality data. *Ground Water*, 10: 32-43.

Appendix I: Site Details

Hydrol Number	Map Reference	Well depth (m)	Casing depth (m)	WL (m)	RWL (m)	Geology
68.82	T18:699-752	38.0	32.5	18.68	398.32	Rhyolite pyroclastic
68.244	U17:724-833	90.0	58.0	43.72	513.58	Rhyolite pyroclastic
68.264	T17:647-806	45.1	39.3	12.40	400.56	Rhyolite pyroclastic
68.301	T17:656-803	53.6	49.0	38.40	365.03	Rhyolite pyroclastic
68.317	T17:605-811	104.0	73.0	54.00	506.37	Rhyolite pyroclastic
68.320	U18:749-747	62.0	43.0	15.34	369.18	Oruanui Ignimbrite
68.364	U17:706-843	161.5	97.5	70.47	521.17	Rhyolite pyroclastic
68.377	U17:717-838	90.0	84.0	68.75	519.58	Oruanui Ignimbrite
68.387	T19:482-497	128.0	96.0	79.41	418.75	Huka Formation
68.423	T17:586-866	120.7	76.2	92.34	509.05	Whakamaru Ignimbrite
68.430	T17:613-848	134.1	73.4	69.80	479.71	Rhyolite pyroclastic
68.446	T17:601-834	135.4	80.0	84.00	488.30	Rhyolite pyroclastic
68.656	T17:675-812	40.0	32.5	29.84	420.98	Rhyolite pyroclastic
68.660	T17:643-817	37.7	19.5	20.35	420.90	Rhyolite
68.718	T17:642-806	67.1	58.5	26.32	389.17	Rhyolite pyroclastic
68.801	T17:488-850	130.0	65.1	23.50	489.56	Whakamaru Ignimbrite
68.872	T17:645-800	72.0	39.0	30.55	362.61	Rhyolite pyroclastic
68.915	T17:697-829	43.0	33.5	9.00	500.40	Oruanui Ignimbrite
68.964	T18:506-533	5.0	2.0	2.76	356.50	Post Taupo lacustrine
68.981	T17:479-849	109.0	65.2	47.00	452.13	Whakamaru Ignimbrite
68.1000	T18:420-547	spring	spring	spring	spring	Whakamaru Ignimbrite
72.158	T17:613-812	277.6	169.8	167.50	396.52	Rhyolite pyroclastics
72.172	T17:681-819	148.0	98.5	40.10	437.66	Rhyolite pyroclastic
72.173	T17:682-820	148.0	97.5	44.55	437.97	Rhyolite pyroclastic
72.174	T17:683-821	148.0	97.5	55.67	426.58	Rhyolite pyroclastic
72.331	T17:508-847	5.8	2.8	3.71	490.66	Oruanui Ignimbrite
72.332	T18:679-752	5.7	2.7	5.12	356.39	Taupo Ignimbrite
72.334	U18:741-741	18.0	NA	9.30	367.20	Taupo Ignimbrite
72.335	T18:494-615	NA	NA	61.45	478.59	Whakamaru Ignimbrite
72.338	U17:723-835	72.0	64.0	49.13	513.62	Rhyolite pyroclastic
72.341	T17:566-833	116.7	36.3			Whakamaru Ignimbrite
72.343	T17:606-808	177.3	95.7	45.32	507.54	Whakamaru Ignimbrite
72.348	T17:570-836	97.5	NA	83.24	446.99	Rhyolite pyroclastic
72.349	T17:700-831	65.0	59.0	17.25	500.98	Rhyolite pyroclastic
72.351	T17:633-845	NA	NA	*25.20*	504.71	Rhyolite pyroclastic?

72.352	T17:616-855	152.4	121.9	48.80	504.30	Rhyolite pyroclastic
72.354	T17:616-855	4.2	1.2	2.52	550.68	Oruanui Ignimbrite
72.356	T17:685-821	42.0	37.0	17.60	465.61	Rhyolite pyroclastic
72.358	U18:702-786	101.2	94.8	95.24	428.64	Rhyolite pyroclastic
72.359	T18:686-763	157.9	43.6	69.27	362.69	Rhyolite pyroclastic
72.361	T17:693-826	NA	NA	8.12	488.65	Rhyolite pyroclastic
72.362	T17:645-807	NA	NA	6.00	412.20	Rhyolite pyroclastic
72.363	T18:644-778	3.0	1.0	1.32		Post Taupo lacustrine
72.364	U17:665-824	spring	spring	spring	spring	Rhyolite lava
72.369	T17:520-876	46.5	1.2	2.67	469.02	Whakamaru Ignimbrite
72.370	U17:716-833	NA	NA	41.59	518.44	Rhyolite pyroclastic?
72.371	T17:615-843	128.0	25.0	91.30	447.74	Rhyolite pyroclastic
72.374	U17:721-831	51.8	39.0	35.47	516.10	Oruanui Ignimbrite
72.377	T17:508-847	50.3	45.4	4.51	489.92	Whakamaru Ignimbrite
72.379	T17:527-843	38.0	32.6	2.61	507.40	Whakamaru Ignimbrite
72.381	T17:535-836	49.0	32.6	13.29	519.29	Whakamaru Ignimbrite
72.383	T17:546-839	38.4	32.6	8.80	539.23	Whakamaru Ignimbrite
72.384	T17:555-847	110.0	35.0	25.91	531.02	Whakamaru Ignimbrite
72.389	T17:564-868	57.5	12.8	6.23	528.78	Whakamaru Ignimbrite
72.390	T17:552-833	120.0	38.4	56.22	479.63	Whakamaru Ignimbrite
72.391	T17:608-814	93.0	47.2	51.80	512.60	Rhyolite pyroclastic
72.392	T17:609-813	93.0	65.2	51.40	513.22	Rhyolite pyroclastic
72.394	T18:527-612	175.1	NA	160.65	365.07	Whakamaru Ignimbrite
72.395	T18:524-616	156.7	NA	152.69	365.05	Whakamaru Ignimbrite
72.397	T18:501-616	NA	NA	59.05	488.70	Whakamaru Ignimbrite
72.398	U17:720-812	NA	NA	66.29	477.90	Whakamaru Ignimbrite
72.399	T18:511-562	6.0	NA	0.39	358.06	Post Taupo lacustrine seds
72.400	U17:728-827	NA	NA	40.82	513.70	Rhyolite pyroclastic?
72.401	U18:702-788	NA	NA	106.30	431.42	Rhyolite pyroclastic
72.402	T17:642-806	NA	NA	18.65	397.51	Rhyolite pyroclastic
72.403	T17:572-876	NA	NA	40.00	522.59	Whakamaru Ignimbrite?
72.407	U18:702-747	NA	NA	3.58	408.69	Rhyolite pyroclastic?
72.408	T17:694-828	NA	NA	10.67	489.12	Rhyolite pyroclastic
72.412	T17:522-846	45.1	NA	12.55	494.56	Whakamaru Ignimbrite
72.413	T17:516-857	NA	NA	23.31	467.98	Whakamaru Ignimbrite
72.414	U17:725-831	NA	NA	41.04	514.06	Rhyolite pyroclastic?
72.415	T17:614-823	NA	NA	72.27	511.80	Rhyolite pyroclastic?
72.424	T18:482-522	11.5	4.8	3.28	429.74	Post Oruanui lacustrine seds
72.426	T17:607-888	134.0	19.5	108.02	512.23	Whakamaru Ignimbrite

72.431	T17:528-806	48.0	45.7	38.19	428.37	Whakamaru Ignimbrite
72.434	T18:646-790	17.0	11.3	11.29	359.38	Post-Oruanui pyroclastics
72.435	U18:732-784	NA	NA	39.48	481.27	Rhyolite pyroclastic?
72.466	T17:605-811	100.0	58.6	48.80	511.19	Rhyolite pyroclastics

Appendix II: Water Quality Results

Hydrol Number	pH pH Units	EC uS/cm	TDS g.m-3	Alkalinity g.m-3 as CaCO3	CO2 g.m-3	Ca g.m-3	Mg g.m-3	Hardness g.m-3 as CaCO3	Na g.m-3	K g.m-3	Ammoniacal-N g.m-3
68.264	7	81	54	30	6	3.81	1.86	17	8.3	1.7	< 0.01
68.301	7	117	78	29	6	4.82	3.24	25	12	1.5	< 0.01
68.317	6.8	139	93	24	8	6.01	3.01	27	14.3	2.9	< 0.01
68.320	6.8	317	212	18	6	19.4	10.3	91	19.9	2.7	0.02
68.377	7	138	92	29	6	7.13	3.94	34	11.8	1	< 0.01
68.387	7.1	206	138	89	14	14.4	9.16	74	9.9	3.5	0.15
68.423	6.9	64	43	25	6	2.59	1.17	11	5.6	3.1	< 0.01
68.656	6.5	152	102	36	23	7.04	4.98	38	13.8	2.6	< 0.01
68.660	6.8	83	56	28	9	3.87	1.86	17	7.9	2	0.01
68.801	7	77	52	32	6	4.34	1.71	18	7	1.2	< 0.01
68.915	7	89	60	29	6	4.27	2.41	21	8.3	1.8	< 0.01
68.964	6.5	108	72	31	19	5.65	3.5	29	7	2.7	0.02
68.1000	6.7	69	46	18	7	3.34	1.3	14	5.4	2.5	< 0.01
72.158	7	74	50	25	5	3.18	1.48	14	7.1	2	< 0.01
72.331	6.7	380	255	36	14	27	12.4	119	14.5	10.2	0.07
72.332	6.7	154	103	36	14	9.18	3.51	37	15.2	3.6	0.01
72.334	7.3	141	94	42	4	8.18	5.3	42	13.3	1.5	< 0.01
72.341	6.7	84	56	27	11	3.93	2.1	18	6.9	2.2	< 0.01
72.352	6.8	92	62	34	11	4.53	2.17	20	8.2	1.8	< 0.01
72.354	6.5	72	48	16	10	4.61	1.94	19	4.5	3.5	< 0.01
72.356	6.6	105	70	27	14	4.84	2.41	22	11.3	2.2	< 0.01
72.363	6.8	270	178	89	28	15	4.2	55	35.3	6.4	0.02
72.364	7	85	57	25	5	3.8	1.83	17	7.7	2.2	< 0.01
72.369	6.2	128	86	19	23	7.23	2.1	27	6.7	5.9	< 0.01
72.374	6.6	157	105	25	13	8.74	3.41	36	13.8	3.6	< 0.01
72.377	6.9	66	44	26	6	3.19	1.71	15	6.8	0.6	< 0.01
72.379	6.9	97	65	26	6	4.85	2.49	22	9.5	0.9	< 0.01
72.381	6.5	108	72	25	16	4.88	2.74	23	9.7	1.9	0.02
72.383	6.8	125	84	26	8	7.21	2.48	28	9.3	3.4	< 0.01
72.384	6.6	87	58	24	12	4.16	1.79	18	8.1	2.7	< 0.01
72.389	6.6	114	76	27	14	4.66	2.04	20	8.6	4.9	0.01
72.390	7.1	112	75	44	7	7.45	2.43	29	8.5	2.3	< 0.01
72.392	6.9	175	117	21	5	8.76	4.65	41	13.3	2.4	< 0.01
72.394	7.3	82	55	32	3	7.12	7.34	48	11.4	2.4	< 0.01
72.397	6.8	159	107	37	12	10.1	4.78	45	11.7	2.6	0.03

Hydrol Number	pH	EC	TDS	Alkalinity	CO2	Ca	Mg	Hardness	Na	K	Ammoniacal-N
	pH Units	uS/cm	g.m-3	g.m-3 as CaCO3	g.m-3	g.m-3	g.m-3	g.m-3 as CaCO3	g.m-3	g.m-3	g.m-3
72.399	6.9	131	88	38	10	7.89	3.82	35	8.8	3.1	< 0.01
72.401	7.6	77	52	33	2	1.27	0.844	7	12.7	0.2	< 0.01
72.407	7.6	121	81	50	3	5.31	3.92	29	13.9	1	0.09
72.414	6.8	105	70	26	8	4.01	1.64	17	12.8	2.2	< 0.01
72.422	7.1	117	78	43	7	4.69	3.05	24	12.5	1.2	< 0.01
72.424	6.7	93	62	36	14	8.4	2.9	33	7	3.6	<0.01
72.431	6.9	85	57	26	7	4.15	2.29	20	7.8	1.5	< 0.01
72.434	6.6	123	82	31	16	10.2	4.33	43	10.7	5	<0.01
72.435	7.4	107	72	43	3	4.99	1.79	20	13.5	2.4	0.03

Hydrol Number	Chloride g.m-3	Nitrate-N g.m-3	DRP g.m-3	Sulphate g.m-3	Boron g.m-3	Total Iron g.m-3	Dis Iron g.m-3	Mn g.m-3	Cu g.m-3	Zn g.m-3
68.264	3.3	0.41	0.091	1.7	0.006	0.04	< 0.01	< 0.005	< 0.005	0.144
68.301	4.2	2.48	0.125	8	< 0.005	0.09	< 0.01	< 0.005	< 0.005	< 0.005
68.317	8.5	5.69	0.09	5.5	< 0.005	0.01	< 0.01	< 0.005	< 0.005	< 0.005
68.320	14.9	16.5	0.014	40.9	0.023	2.61	0.04	0.337	< 0.005	0.018
68.377	6.6	5.99	0.065	2.9	< 0.005	0.19	< 0.01	< 0.005	< 0.005	0.724
68.387	3.3	0	0.013	7.1	0.014	8.69	0.5	0.27	< 0.005	0.494
68.423	2.6	0.15	0.154	0.9	0.006	0.04	< 0.01	< 0.005	< 0.005	0.028
68.656	9.1	1.92	0.088	11.6	< 0.005	1.22	< 0.01	< 0.005	< 0.005	0.016
68.660	3.5	0.85	0.101	2.2	0.006	0.09	< 0.01	< 0.005	< 0.005	0.022
68.801	2.4	0.04	0.164	1.7	0.007	< 0.01	< 0.01	0.317	< 0.005	0.009
68.915	3.3	1.59	0.099	1.7	< 0.005	0.03	< 0.01	< 0.005	< 0.005	< 0.005
68.964	4.7	0.09	0.032	8.2	0.015	0.7	0.42	0.013	0.005	0.005
68.1000	3.6	1.04	0.014	2.1	<0.005	<0.01	<0.02	<0.005	<0.005	<0.005
72.158	2.8	0.48	0.103	1.3	0.005	0.04	< 0.02	< 0.005	< 0.005	0.187
72.331	43.5	3.64	0.007	40.8	0.008	1.31	< 0.02	0.294	0.05	0.024
72.332	10	2.91	0.065	8.8	0.007	2.72	0.02	0.132	< 0.005	0.026
72.334	5.7	0	0.225	13.5	0.006	1.52	< 0.01	0.02	< 0.005	0.009
72.341	3.7	1.15	0.126	1.8	< 0.005	< 0.01	< 0.01	0.025	< 0.005	< 0.005
72.352	2.4	0.27	0.093	2.5	0.006	0.36	0.03	< 0.005	< 0.005	0.171
72.354	2.9	1.45	0.006	5.4	0.007	9.23	< 0.02	0.172	< 0.005	0.031
72.356	3.9	1.94	0.051	6.1	0.008	0.38	< 0.01	0.013	< 0.005	0.099
72.363	25.3	0.42	0.048	5.7	0.249	6.86	0.14	0.266	< 0.005	0.057
72.364	3.7	1.58	0.105	2.7	0.006	< 0.01	< 0.01	< 0.005	< 0.005	< 0.005
72.369	6	5.56	0.007	6.4	0.021	0.47	< 0.01	0.02	0.03	0.221
72.374	8.3	7.18	0.088	6.9	< 0.005	0.01	< 0.01	< 0.005	< 0.005	< 0.005
72.377	2.6	0	0.23	1	< 0.005	0.2	0.04	< 0.005	< 0.005	0.078
72.379	4.5	2.39	0.084	2.7	< 0.005	1.1	0.05	0.01	0.101	0.108
72.381	6.2	0.99	0.048	10.5	< 0.005	3.37	0.13	0.037	< 0.005	0.04
72.383	8.2	3.55	0.052	3.8	< 0.005	0.54	0.02	< 0.005	< 0.005	0.408
72.384	4.1	1.71	0.116	2.7	< 0.005	< 0.01	< 0.01	< 0.005	< 0.005	< 0.005
72.389	4.8	1.6	0.056	10	0.007	0.07	< 0.01	0.008	< 0.005	2.98
72.390	2.8	0	0.078	4.2	0.009	0.13	0.01	1.61	< 0.005	0.155
72.392	11.2	9	0.041	7	< 0.005	0.09	< 0.02	< 0.005	< 0.005	0.074
72.394	3.4	0.08	0.088	0.7	< 0.005	52.5	< 0.02	0.403	0.403	17.7
72.397	8.3	6.85	0.051	2.4	< 0.005	9.59	0.2	0.085	0.074	1.51
72.399	5.4	2.39	0.053	1.7	0.009	0.02	< 0.02	< 0.005	0.025	< 0.005
72.401	2.5	0.18	0.08	1	< 0.005	2.09	0.05	0.006	0.007	1.98
72.407	3.1	0	0.283	< 0.5	0.012	1.36	0.35	0.175	0.015	0.12

Hydrol Number	Chloride	Nitrate-N	DRP	Sulphate	Boron	Total Iron	Dis Iron	Mn	Cu	Zn
	g.m-3	g.m-3	g.m-3	g.m-3	g.m-3	g.m-3	g.m-3	g.m-3	g.m-3	g.m-3
72.414	4.5	1.87	0.134	6.6	< 0.005	0.01	< 0.01	< 0.005	< 0.005	0.021
72.422	3.1	0	0.144	5.1	< 0.005	0.13	0.07	0.028	< 0.005	0.007
72.424	2.6	0.63	0.041	1.6	< 0.005	5.96	0.029	0.112	< 0.005	0.021
72.431	3.7	1.09	0.114	3	< 0.005	< 0.01	< 0.01	< 0.005	< 0.005	< 0.005
72.434	3.3	2.41	0.039	9.2	0.02	12.5	<0.02	0.312	0.005	0.021
72.435	2.6	0	0.477	2.5	0.008	2.55	1.26	0.343	< 0.005	0.182