

**ENVIRONMENT WAIKATO
TECHNICAL REPORT 1993/7**

**GROUNDWATER CHEMISTRY
OF THE PIAKO CATCHMENT,
HAURAKI PLAINS**

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ABSTRACT

This report discusses the groundwater chemistry of the Piako catchment in the Hauraki Plains. The investigation described is part of a larger study to characterise the groundwater resources of the catchment. This information is required to support resource management policies. These policies promote groundwater resource development and land disposal of waste in preference to reliance upon already stressed and limited surface waters. Results of a synoptic survey are primarily described and other collated information is also discussed.

Groundwater chemistry in the Piako catchment reflects the highly variable nature of the predominantly sedimentary aquifers. A number of strong spatial trends are however apparent. Redox conditions become progressively more reducing northwards and strongly influence groundwater chemistry. This is evident from reductions in dissolved oxygen, nitrate and sulphate in this direction. Also increases in iron, manganese and ammonia are associated with anaerobic conditions and peat development in the northern catchment. Other parameters such as total dissolved solids, bicarbonate and salts were also found to generally increase in concentration northward. This may be attributed to a number of factors including: greater organic and microbial influences; longer residence times in finer sediments; location further along the flowpath; and hydrothermal and seawater influences.

These trends in groundwater chemistry are consistent with hydrogeologic trends along the catchment. These include changes from coarser, sands and gravels of the southern catchment to finer, more estuarine, sediments in the north. The low-lying, flood plain of the lower catchment also has more extensive peat development. Slower flow rates and therefore greater opportunity for dissolution and ion exchange, occur toward the north as a result of low gradients and less permeable sediments.

Changes in groundwater chemistry with depth were also noted. High nitrate and sulphate concentrations tend to be limited to shallow aerobic conditions. Regression of sample temperature with depth also indicates an enhanced geothermal gradient in the study area.

Groundwater quality generally ranges from moderately high in the cleaner, shallow, southern aquifers to poor in much of the northern catchment. Excessive iron concentration is currently the most important groundwater quality limitation to resource development. This problem restricts groundwater use for domestic and industrial supply in much of the northern plains where anaerobic conditions dominate.

Nitrate contamination of shallow, southern aquifers, from agricultural land use is, however, a potentially important problem. Concentrations of nitrate are currently predominantly below the World Health Organisation recommended drinking water limit of 10 ppm but may be increasing. Nitrate contamination and excessive iron concentrations occur independently.

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CONTENTS

	Page
ABSTRACT	(i)
ACKNOWLEDGEMENTS	(ii)
TABLE OF CONTENTS	(iii)
LIST OF TABLES	(v)
LIST OF FIGURES	(vi)
1 INTRODUCTION	1
2 HYDROGEOLOGIC SETTING	3
2.1 Structure and geomorphology	3
2.2 Stratigraphy and formation distribution	3
2.2.1 Tauranga Group	3
2.2.2 Ignimbrites	6
2.2.3 Kiwitahi Volcanics	7
2.3 Groundwater flow regime	7
3 SAMPLING AND DATA ANALYSIS	9
3.1 Sampling	9
3.2 Data Analysis	9
4 GROUNDWATER CHEMISTRY CHARACTERISTICS	13
4.1 Introduction	13
4.2 Groundwater chemical characteristics of geologic groupings	15
4.2.1 Hinuera Formation	15
4.2.2 Non-Hinuera Formation Tauranga Group Sediments	18
4.2.3 Ignimbrites	19
4.2.4 Kiwitahi Volcanics	20
4.3 Spatial distribution of chemical characteristics	20
4.3.1 Lateral distribution	20
4.3.2 Vertical distribution	22

	Page
5 DISCUSSION AND REVIEW OF FACTORS INFLUENCING GROUNDWATER CHEMISTRY	29
5.1 Introduction	29
5.2 Chemical influence of rainwater	29
5.3 Chemical influence of formation	30
5.3.1 Reduction and oxidation processes	31
5.4 Organic and microbial influences	32
5.5 Saltwater influence	33
5.6 Geothermal influence	34
5.7 Chemical influence on streams	36
5.8 Human influence	36
6 ENVIRONMENTAL ISOTOPES	37
6.1 Introduction	37
6.2 Tritium	37
6.3 Oxygen and deuterium	38
7 GROUNDWATER QUALITY AND IMPLICATIONS FOR USE	39
7.1 Introduction	39
7.2 Nitrate contamination	39
7.3 Excessive iron problem	40
7.4 Domestic use	41
7.5 Agricultural use	43
7.6 Industrial use	44
7.7 Land disposal practices	45
8 SUMMARY AND CONCLUSIONS	47
REFERENCES	49
APPENDIX I GROUNDWATER CHEMICAL ANALYSES	53
APPENDIX II IONIC RATIOS	59
APPENDIX III COMPARATIVE BOX PLOTS	61
APPENDIX IV CHEMISTRY OF HAURAKI PLAINS THERMAL WATERS	65

LIST OF TABLES

		Page
1	Stratigraphic table	5
2	List of synoptic survey chemical parameters and detection limits	11
3	Mean and standard deviations of chemical parameters for the geologic sub-groupings of the Tauranga Group Sediments	14
4	Comparison of analyses of variance between geologic and spatial groupings	21
5	Some redox reactions that consume organic matter and reduce inorganic compounds	32
6	Comparison between various ionic ratios for seawater and geothermal water	33
7	Selected ionic ratios from high chloride samples	33
8	Selected chemistry of geothermally influenced survey sites	35
9	Environmental isotope results	37
10	Drinking water standards (Department of Health, 1984).	42
11	Water quality classifications and important dissolved constituents (Victoria Environmental Protection Agency)	43

LIST OF FIGURES

	Page	
1	Location map of the Piako catchment	2
2	Geology map of the Hauraki Plains	4
3	Location map of bores sampled for the synoptic survey	10
4	Hinuera Formation piper tri-linear plot	16
5	Non-Hinuera Formation sediments piper tri-linear plot	16
6	Stiff diagrams for geologic groups	17
7	Plot of chloride ion concentration versus northing	22
8	Distribution of measured nitrate concentrations	23
9	Distribution of measured ammonia concentrations	24
10	Plot of sample temperature versus well depth	25
11	Plot of nitrate concentration versus well depth	26
12	Plot of sulphate concentration versus well depth	26
13	Plot of total iron concentration versus well depth	26
14	Schoeller plot of rainwater, Hinuera Formation and other Tauranga Group sediments	29
15	Plot of the isotopic ratios of oxygen and deuterium for groundwater samples in the Piako catchment.	38

INTRODUCTION

This study is part of a larger investigation of the Piako catchment groundwater resources. The Piako catchment comprises an area of approximately 1435 km² of predominantly dairy farmland in the Hauraki Plains (figure 1). Surface water resources in the catchment are limited. Groundwater supplies some 80% of farms and about half of the total water supply to the area.

A need to improve the degraded surface water quality of the catchment has been recognised by Environment Waikato. Dairy industry waste discharge is the major cause of degradation in surface water quality (Van Rossem, 1990). Land disposal of waste and associated utilisation of nutrient resources is increasingly attractive. It is now the preferred policy option rather than discharge to surface water. This has highlighted the need for information regarding groundwater resources in the catchment and potential impacts upon groundwater quality.

The major content of this report is a presentation of the results from a groundwater chemistry survey undertaken in December 1992. Time series analyses are not included but are recommended for future state of environment monitoring. Such analyses would enable potential impacts of land use upon groundwater quality to be predicted. This is however beyond the scope of this investigation, which is to provide baseline synoptic data.

Previous groundwater chemistry work undertaken in the area generally comprised ad-hoc investigations carried out by the Hauraki Catchment Board (Dewhurst, 1981). Such information and a large number of other analyses collated from consent holders and local water chemistry laboratories, are used to support data obtained during this investigation.

2 HYDROGEOLOGIC SETTING

2.1 Structure and geomorphology

The Piako catchment extends from Hinuera in the south, to the Firth of Thames in the north (figure 1). It occupies a large portion of the Hauraki Plains, which form part of a young continental rift structure. The plains are bounded to the west by Jurassic greywackes of the Hapuakohe Range, Hangawera and Pakaroa Hills near Morrinsville and the three Kiuwitihi Volcanic cones of Ruru, Mangakawa and Te Tapui. The Tertiary to Quaternary volcanic Kaimai and Coromandel Ranges rise some 500 to 800 m to the east, forming an impressive youthful fault scarp.

The cross-sectional structure of the Hauraki Plains from west to east consists of a fault angle depression, a horst and a graben. These tectonic units are delineated by major NNW-SSE striking, west dipping, normal faults. The Hauraki and Kerepehi Faults form the eastern boundaries of the graben and fault angle depression respectively. The Firth of Thames Fault is a minor fault on the western side of the rift (Hochstein and Nixon, 1979; Davidge, 1982; Hochstein *et al.*, 1986).

The Piako River and its major tributary, the Waitoa River, drain essentially northward to discharge into the Firth of Thames. In the south, they are entrenched within underfit channels in the volcanoclastic sediments of an alluvial fan. Toward the north the river channels meander along a very low lying and shallow gradient, floodplain. The Waihou River, which drains the eastern side of the Hauraki Plains, is not included in the Piako catchment study area. The entire Hauraki Lowland, however, may be addressed in this study, where it is considered more appropriate as a hydrogeologic unit.

2.2 Stratigraphy and formation distribution

This section describes the general stratigraphy, formation distribution and trends of relevance to the following discussion of groundwater chemistry. A map of surface geology is illustrated in figure 2 and a stratigraphic summary presented in table 1.

2.2.1 Tauranga Group

Surface geology in the Hauraki Plains is dominated by the Tauranga Group of sediments. This highly variable group includes essentially all the infilling sand, silt, clay, gravel and peat sediments in the study area. By the broadest definition it includes the mainly pumiceous terrestrial, estuarine and marine sediments deposited since the beginning of the Pleistocene (Kear and Schofield, 1978).

The Tauranga Group is generally subdivided into the Piako, Walton and Frankton Sub-groups. The Hinuera Formation is the major member of the shallow Piako Sub-group (Schofield, 1972). In the southern Hauraki Lowland, it is described by Cuthbertson (1981), as late Pleistocene, cross-bedded, fluvial, pumiceous, rhyolitic and ignimbritic sands and gravels. The rapid deposition of this formation was characterised by frequent

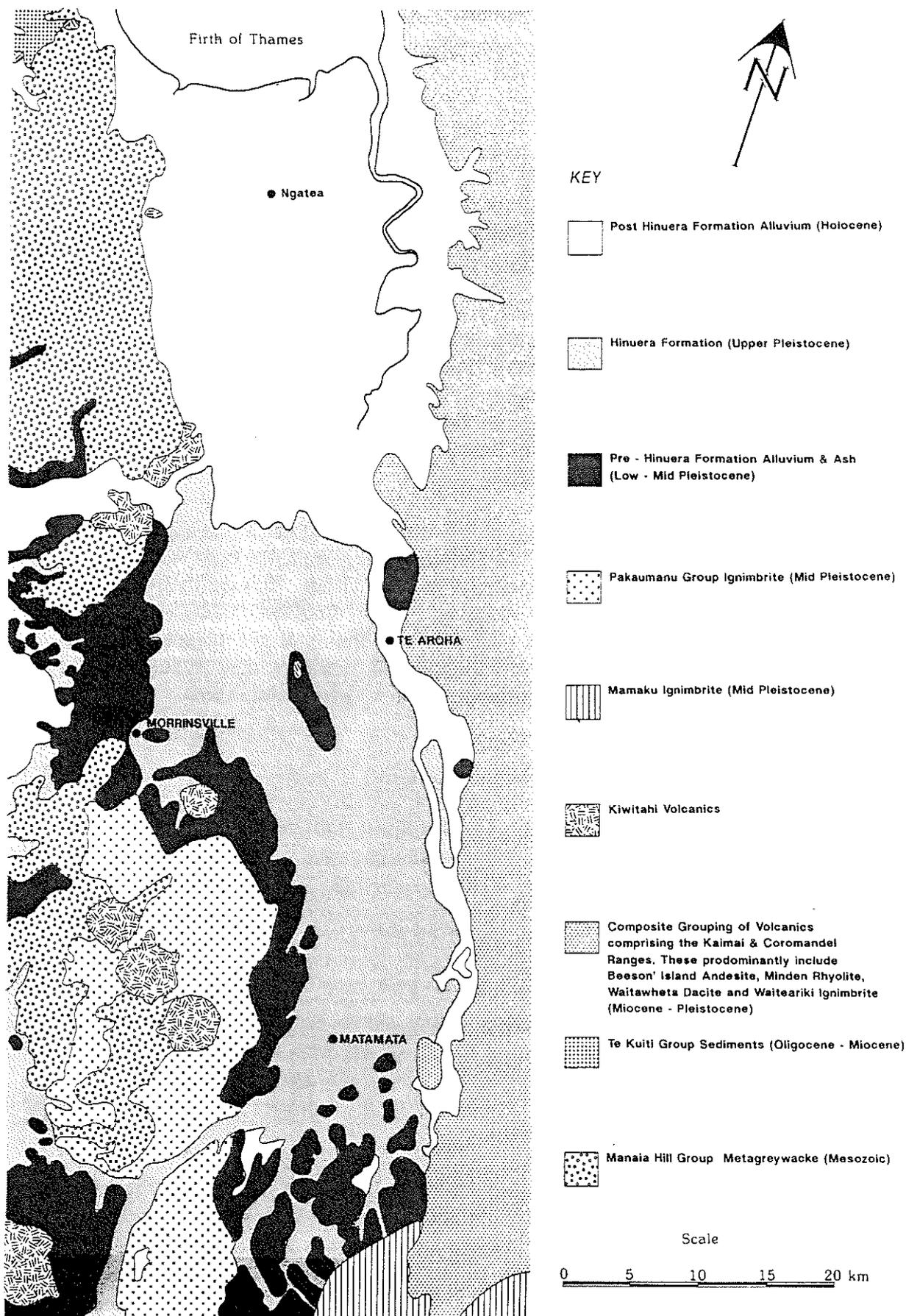


Figure 2 : Geology map of the Hauraki Plains

Era	Period	Epoch	Stratigraphy	Age m.y.B.P
Cenozoic	Quaternary	Holocene	Tirau Ash	0.01
		Pleistocene	Hinuera Formation	0.02
			Mangaone Lapilli	0.03
			Rotoehu Ash	0.04
			Mamaku Ignimbrite	0.1
		Pleistocene	Non-marine sediment and interbedded tuffs	0.2
			Rocky Hill Ig.	0.4
			Pakaumanu Group	0.5
			Ahuroa Ig.	0.6
			Ongatiti Ig.	0.7
			-Waiteariki Ignimbrite-	0.8
		Pliocene	Minden Rhyolite	1.0
Hydrothermal alteration of Beeson's Island Volcanics	3.0			
Pliocene	Omaha Andesite	3.0		
	Waitawheta Dacite	4.0		
Miocene	-Kiwitahi-volcanics	6.0		
	Minden Rhyolite	8.0		
Miocene	Beeson's Island Volcanics	10.0		
	Beeson's Island Volcanics	12.0		
Miocene	Beeson's Island Volcanics	14.0		
	Beeson's Island Volcanics	16.0		
Mesozoic	Jurassic		Manaia Hill Group	137.0
				195.0

Table 1 : Stratigraphic table

lateral migration of river channels. Thicknesses of up to 70 m have been identified in the southern Hauraki Plains. The Hinuera Formation is not extensively exposed north of Morrinsville and Te Aroha.

Deeper (pre-Hinuera Formation) sediments include current-bedded, volcanic grits and massive, poorly sorted, pumiceous and rhyolitic, gravelly sands and silts of the Karapiro Formation. These, and the sub-aerial and alluvial channel deposits of the Puketoka Formation tend to be similar to, but more weathered and often finer than, the Hinuera Formation.

Extensive peat deposits are interbedded with, and overlie, the Hinuera Formation sediments in the northern catchment. A holocene marine transgression (5 to 6.5 ka), resulted in the widespread deposition of deltaic muds and fine estuarine sediments in the low-lying, broad, northern Hauraki floodplain (de Lange, 1989). A general trend toward finer sediment and the intercalation of estuarine facies northward was noted from investigative drilling (Dewhurst, 1985).

Aquifers of the Tauranga Group sediments comprise the bulk of the developed and potential groundwater resources within the Hauraki Lowland. A division is made between the Hinuera Formation and other Tauranga Group sediments for the sake of groundwater chemistry comparison in chapter 4. For this purpose the Hinuera Formation is defined as shallow, fluviatile, volcanoclastic, sands and gravels which occur predominantly in the southern plains. It thereby tends to be coarser and less organic than other Tauranga Group sediments and exclusive of estuarine materials.

2.2.2 Ignimbrites

The deposition of the Tauranga Group sediments is strongly influenced by the eruption of a series of Quaternary ignimbrites. These include the Pakaumanu Group, which outcrops along the western margin of the southern Hauraki Lowland (figure 2). This group is generally densely welded near Tirau and becomes progressively softer and less welded toward Morrinsville. It includes the Ongatiti, Ahuroa and Rocky Hill ignimbrites.

Other ignimbrites include the Waiteariki, which is generally a grey coloured, highly welded, lenticulite occurring predominantly toward the southern end of the Kaimai Ranges. A large plateau immediately southeast of the study area is formed by Mamaku Ignimbrite, which is a poorly welded, crystal rich, ignimbrite.

Ignimbrites are likely to be more widespread throughout the southern plains than is apparent from existing bore log information. This is suggested by the recent confirmation of the occurrence of Rocky Hill Ignimbrite at shallow depth at Matamata Airfield and other ignimbrite occurrences at Waharoa and Okauia (Hadfield, 1992).

Ignimbrites generally form fractured rock aquifers. The ignimbrites occurring within the study area are commonly poorly welded, distal ignimbrites and thus produce generally poor to moderate groundwater yields. Although varied, ignimbrites are considered as a group for water chemistry analyses purposes.

2.2.3 Kiwitahi Volcanics

Kiwitahi Volcanics consist of porphyritic, hypersthene, andesite and basaltic andesite. Characteristically this formation occurs as residual volcanic cones such as Ruru, Maungakawa and Te Tapui, which form a line from NW to SE, west of Matamata. Kiwitahi Volcanics also occur as the remnant cones of Maungakawa near Morrinsville, Pukekaraka between Waitoa and Waihou, and occasional expressions along the western hills north of Tahuna.

2.2.4 Groundwater flow regime

The spatial variation in piezometric levels indicates that groundwater flows is generally northwards along the Hauraki Plains. Recharge occurs predominantly in the southern lowland and groundwater discharges in the low-lying, northern plains. The water table has a slope of about 1.5 to 2 m km^{-1} in the southern Hauraki Plains and reduces to less than 0.2 m km^{-1} north of Te Aroha. Hydraulic heads which increase with depth and common flowing artesian bores in the northern plains are indicative of a groundwater discharge regime.

3 SAMPLING AND DATA ANALYSIS

3.1 Sampling

Groundwater samples were recovered from water bores and piezometers throughout the study area by Environment Waikato staff using standard sampling methods, as described by Hem (1985). Sample sites were selected to include a range of hydrogeologic situations and to ensure an appropriate spatial distribution (figure 3). Groundwater was primarily sampled from the predominant Tauranga Group alluvial aquifers. The groundwater chemistry of other locally less important aquifers received only cursory investigation.

Sampled bores and piezometers were pumped until a minimum of three bore volumes of groundwater had been displaced before sampling was undertaken. In situations where piezometers are constructed in poorly permeable formation, this required substantial time and effort.

Filtered and unfiltered samples were collected in glass or polypropylene bottles as appropriate, in accordance with standard procedures (A.H.P.A. 1989). Parameters which were measured in the field included dissolved oxygen, pH, conductivity and temperature.

3.2 DATA ANALYSIS

A list of all parameters for which analyses were undertaken and their relevant methods and detection limits is presented in table 2. The suite of analyses was selected to characterise the groundwater chemistry and to maximise information regarding relationships spatially and between geologic groups.

Random repeat samples were utilised to ensure that the accuracy of analyses was within acceptable limits. Ionic balances were also calculated to check the accuracy of analyses. This resulted in the rechecking of one stored sample for one determinant.

Groundwater chemistry analyses results are presented in appendix I. These have been separated on the basis of aquifer geology. The majority of samples are from Tauranga Group aquifers. This group has been subdivided into the Hinuera Formation and remaining Tauranga Group units. Minor representation of other geologic formations is also included. Results are also analysed in respect to spatial distribution.

Ionic ratios of major ions have been calculated and presented in appendix II. Results are also compared with water quality standards and other published data in order to describe relative character and potential water quality limitations to use (chapter 5).

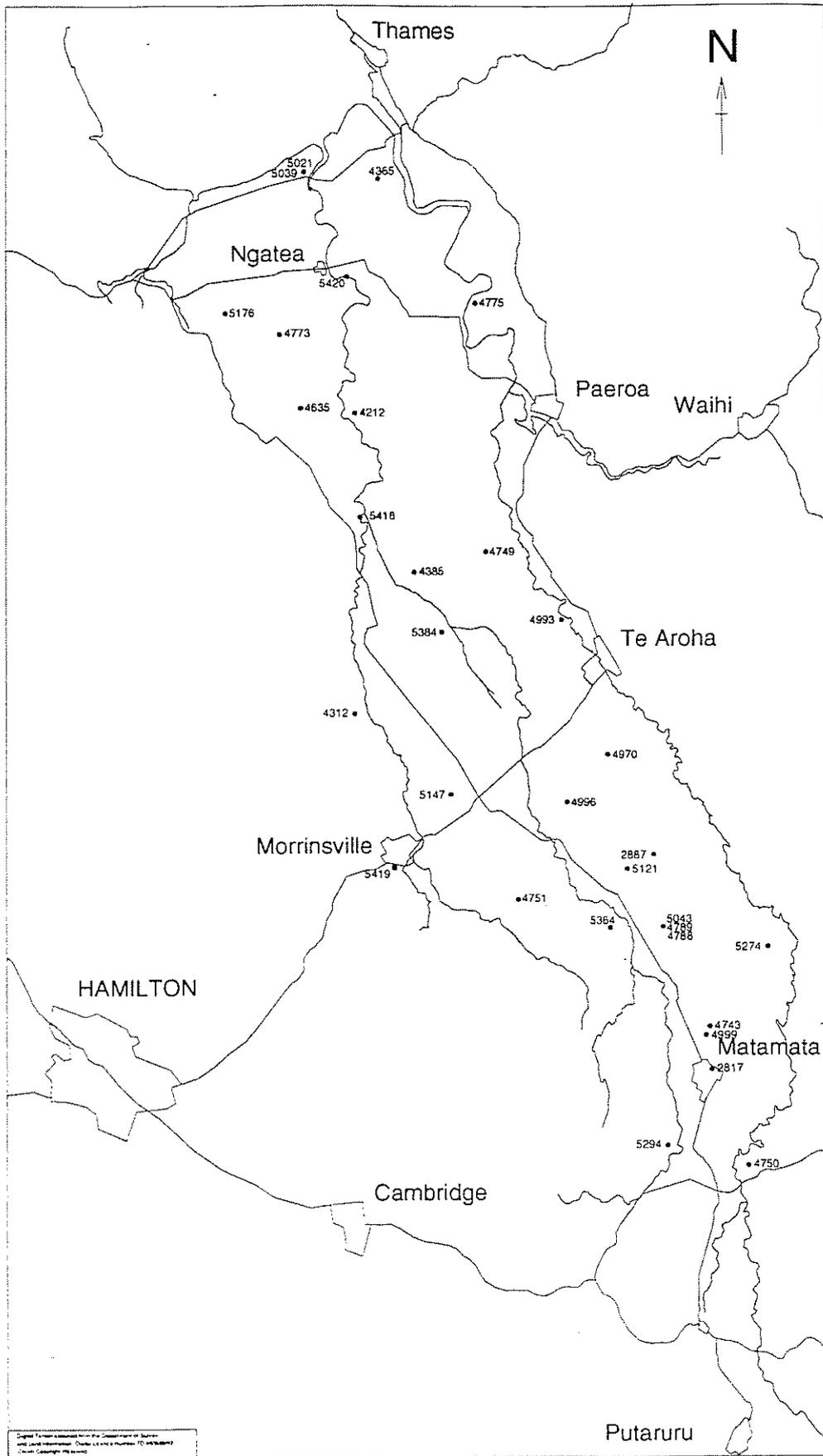


Figure 3 : Location map of bores sampled for the synoptic survey

Table 2 : List of synoptic survey chemical parameters and detection limits

ANALYSIS	METHOD	DETECTION LIMIT
Absorbance @ 270 nm Unfiltered	Spectrophotometer	0.000 cm ⁻¹
Absorbance @ 270 nm Filtered	Spectrophotometer	0.000 cm ⁻¹
Absorbance @ 400 nm Unfiltered	Spectrophotometer	0.000 cm ⁻¹
Absorbance @ 400 nm Filtered	Spectrophotometer	0.000 cm ⁻¹
Alkalinity Total	Titration with 0.02N HCl to pH 4.5	2 ppm
Ammoniacal Nitrogen	Colorimetry, Phenolhypochlorite	0.01 ppm
Bicarbonate	Bicarbonate, calculation (APHA)	1 ppm
Boron	Colorimetry, Azomethine-H	0.03 ppm
Bromide	Ion exchange chromatography	0.05 ppm
Calcium	AAS	0.05 ppm
Chloride	Colorimetry	0.1 ppm
Conductivity	Measured in Lab by Meter	0.1 mS/m
Dissolved Oxygen	Meter with temp. compensation	0.0 ppm
Fluoride	Specific ion electrode (APHA)	0.05 ppm
Total Hardness	EDTA titrimetric method	2 ppm
Iodide	Colorimetric determination	0.005 ppm
Iron Acid Soluble	Direct aspiration AAS	0.04 ppm
Iron Total	AAS, acid digestion	0.04 ppm
Lithium	AAS	0.002 ppm
Manganese Total	AAS, acid digestion	0.02 ppm
Magnesium	AAS	0.02 ppm
Nitrite/Nitrate Nitrogen	Cadmium reduction	0.002 ppm
pH	Meter (temp. comp.) Lab & Field	0.01 pH
Dissolved Reactive Phosphorous	Ascorbic acid reduction	0.003 ppm
Phosphorus, Total	Persulphate digestion	0.005 ppm
Potassium	AAS	0.02 ppm
Silica Dissolved Reactive	Modified molybdosilicate	0.1 ppm
Sodium	AAS	0.02 ppm
Sulphate	Turbidimetric	0.5 ppm
Suspended Solids	Sampled directly	2 ppm
Temperature	Calibrated glass thermometer	0.05 °C
Total Dissolved Solids	Filt, evaporated, dried 180°C	1 ppm
Zinc (total)	AAS, acid digestion	0.01 ppm

4 GROUNDWATER CHEMISTRY CHARACTERISTICS

4.1 Introduction

The groundwater chemistry characteristics of aquifer groupings are considered in this chapter. It will be shown that there are significant trends in groundwater chemistry within the Piako catchment and that these are consistent with hydrogeologic trends. Groundwater chemistry characteristics are considered both in respect to groups and spatial distribution.

The aquifers of the predominant Tauranga Group sediments are highly variable (section 2.2.1). In order to investigate differences within this group two geologic sub-groups are considered. The sub-groups comprise the Hinuera Formation and the remaining Tauranga Group sediments (referred to simply as Tauranga Group or T.G.). The mean and standard deviations of chemical parameters for both groups are presented in table 3.

Piper trilinear plots of ionic milli-equivalent ratios for the Hinuera Formation and other Tauranga Group aquifer samples are presented (figures 4 and 5). These figures indicate the relatively highly variable, mixed sodium bicarbonate character of Piako catchment groundwater. The mean results for each of these groups are denoted by asterisks. The range and shifts in the means are discussed in following sections.

Groundwater chemistry characteristics are also considered in respect to their spatial distribution. This is achieved by comparing the groundwater chemistry of sample sites in the southern or upper catchment with those from the northern or lower catchment. The relationship of chemical parameters with depth is also considered.

Mass balance calculations have not been attempted in this study due to the variable nature of the formations considered. Data from two sample sites (well numbers 4773 and 5039), have not been included in statistical analysis. Site number 4773 is in the Torehape peat dome. Analyses indicate that the sample was very turbid and atypical. The other site 5039, is located adjacent to the Piako River and exhibits strong tidal and saline influence. Both sites are considered to have undue influence on the groups considered in this chapter.

The water chemistry results generally reflect the water quality of completed water supply bores. Many bores are abandoned if the groundwater encountered is considered to be of insufficient quality. Strata likely to produce higher quality groundwater tend to be preferentially developed, while other layers, particularly peat, are commonly excluded (e.g. cased off). This deliberate work practice of the water well industry tends to skew groundwater chemistry results to reflect useable aquifers rather than total formation.

Table 3 : Mean and standard deviations of chemical parameters for the geologic sub-groupings of the Tauranga Group Sediments.

Parameter	Hinuera Formation		Tauranga Group (non-Hinuera)	
	Mean	Standard Deviation	Mean	Standard Deviation
pH	6.46	0.22	6.62	0.40
conductivity	18.4	4.0	47.4	33.2
temperature	16.3	1.1	19.4	4.2
suspended solids	3.05	4.19	97.47	209.98
T.D.S	178.4	32.7	350.1	207.2
NO ₃	2.94	2.93	0.03	0.04
NH ₄	0.292	0.560	1.477	1.621
P (sol.)	0.025	0.027	0.297	0.872
P (tot.)	0.102	0.067	0.558	0.794
alkalinity	38	17	187	166
HCO ₃	46	21	227	201
F	0.05	0.04	0.24	0.23
SiO ₂	77.8	18.1	84.4	20.2
SO ₄	17.8	13.3	9.1	13.8
Ca	8.26	1.99	9.55	6.90
Mg	5.03	0.93	9.57	10.00
Na	14.69	3.04	71.69	68.96
hardness	40	7	63	55
Cl	15.9	6.0	49.5	61.7
Fe (sol.)	4.26	7.06	10.25	12.24
Fe (tot.)	5.23	9.01	14.13	16.33
Li	0.009	0.006	0.090	0.131
Mn (tot.)	0.13	0.17	0.53	0.54
K	5.02	1.44	7.50	5.60
Zn	0.08	0.10	0.04	0.05
B	0.04	0.08	0.67	0.88
dissolved oxygen	6.3	2.5	3.3	1.8
absorption 270f	0.163	0.328	0.486	0.485

n = 12 for Hinuera Formation samples
n = 16 for other Tauranga Group samples
T.D.S. = total dissolved solids.
refer to appendix 1 for parameter units

4.2 Groundwater chemistry characteristics of geologic groupings

4.2.1 Hinuera Formation

The Hinuera Formation is defined for the purposes of analysis in this report as shallow, fluvial, volcanoclastic, sands and gravels which occur predominantly in the southern plains (section 2.2.1). Important shallow aquifers of the southern catchment are comprised of this formation. The mean depth of wells in the Hinuera Formation in the survey is about 16 m.

The piper trilinear plot of Hinuera Formation analyses (figure 4), indicates a moderate range in chemical character. This reflects the range of sediments which comprise the formation. The ratio of anions exhibit greater variation than is apparent in the ratio of cations. The anionic character is likely to be more strongly effected by a range in redox conditions. Mean values for the Hinuera Formation indicate a less pronounced sodium and bicarbonate character than is exhibited by the remaining Tauranga Group. This is particularly apparent in the central rhombic plot where the respective means diverge, predominantly due to the lower concentrations of bicarbonate in the Hinuera group.

The mean dissolved silica concentration of 77.8 ppm is high for sedimentary aquifers (Mandel and Shiftan, 1981). Although the dissolution of silica is a very gradual process, this concentration may be attributed to the mildly acid pH and rhyolitic volcanoclastic sediments which characterise this group.

Conductivity and total dissolved solids concentrations may be used as indicators of general groundwater quality and are generally moderate in the Hinuera Formation. The stiff diagram (figure 6), shows that most major anions and cations, (with the exception of carbonate) are well represented. The Hinuera Formation groundwater may be described as "soft" due to the low magnesium and calcium concentrations (calculated mean hardness of about 40 ppm).

The ionic ratios of selected determinants (appendix II), may be used to make inferences about the evolution of groundwater chemistry characteristics and aquifer conditions (Mandel and Shiftan, 1981). The high Na/Cl ratios may be attributed to ion exchange, which is commonly encountered in groundwater from formations of volcanic origin. A mean ratio of about 1 for Mg/Ca is consistent with waters from silicate aquifers. The Na/K ratios are, by contrast, relatively very low and combined with the $(Ca+Mg)/(Na+K)$ ratios suggest a recharge regime with some ion exchange of Na occurring.

High iron concentrations are evident but are not consistent within the Hinuera Formation. Nearly half of the bores sampled have iron concentrations in excess of desirable drinking water standards (sections 7.3 & 7.4). Excessive iron concentrations are generally associated anaerobic conditions and organic layers e.g. peat.

Nitrate is the predominant form of nitrogen in the Hinuera Formation and is generally indicative of oxidising conditions. Concentrations generally do not exceed the World Health Organisation recommended limit of 10 ppm -N (sections 7.2 & 7.4). Other aspects of Hinuera Formation groundwater chemistry will be considered in the next section by means of comparison.

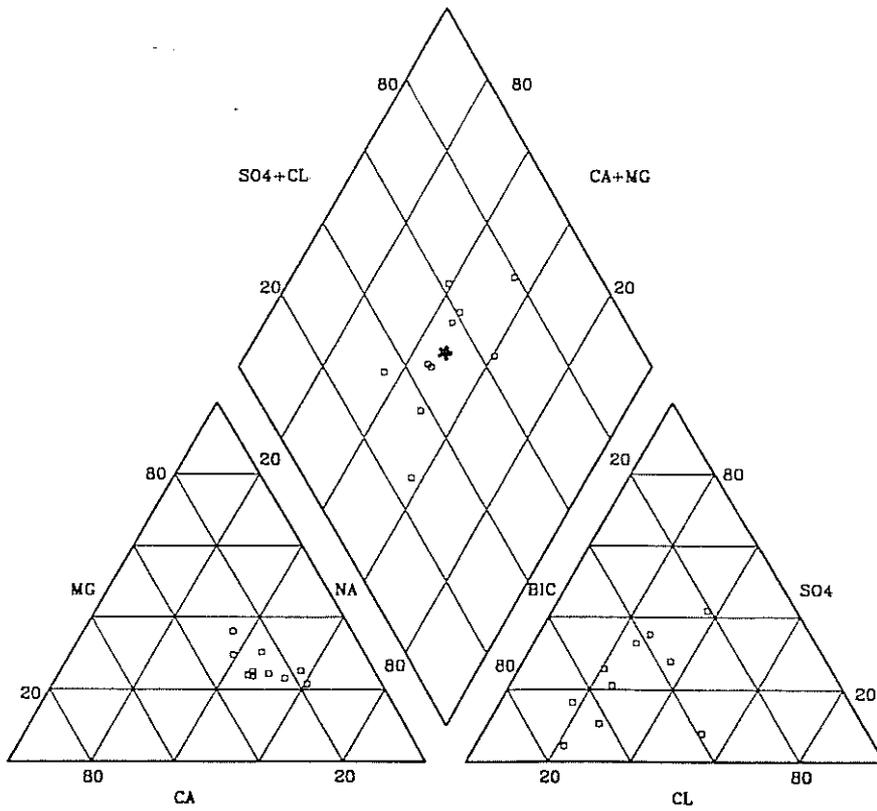


Figure 4 : Hinuera Formation piper tri-linear plot

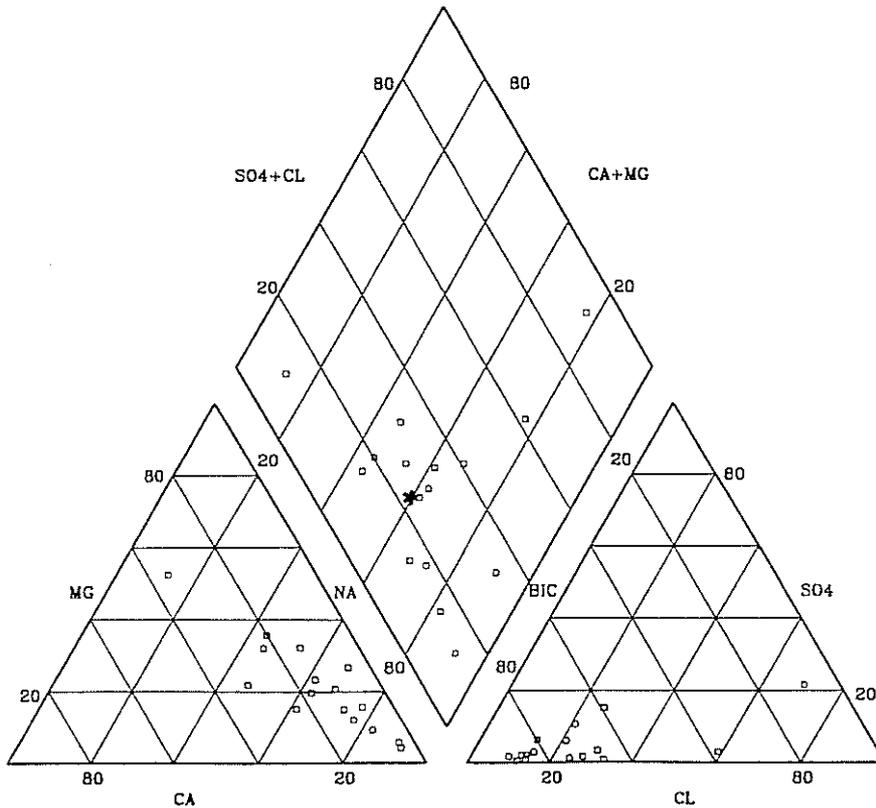
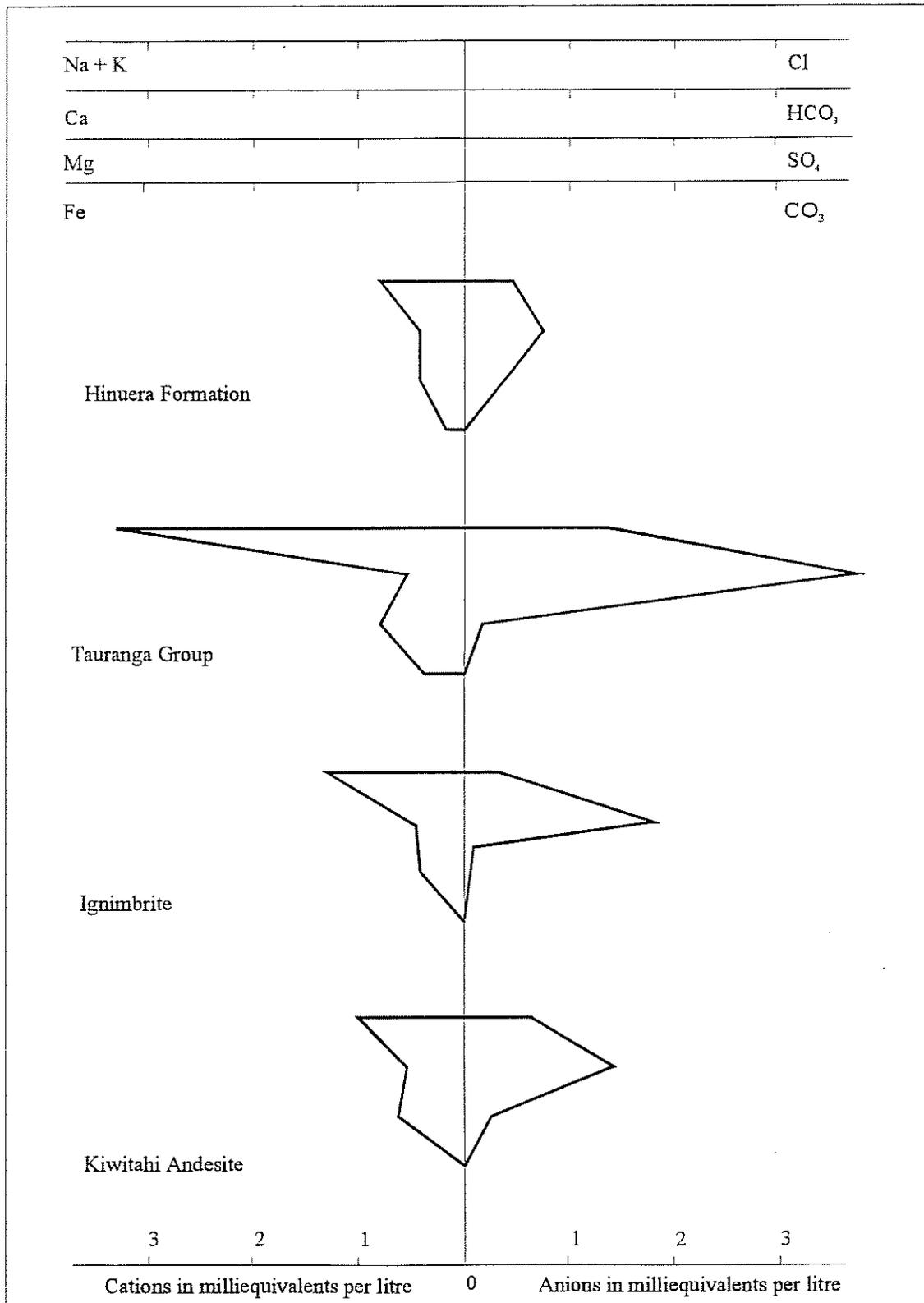


Figure 5 : Non-Hinuera Formation sediments piper tri-linear plot



NB: CO₃ not measured but assumed

Figure 6 : Stiff diagrams for geologic groups

4.2.2 Non-Hinuera Formation Tauranga Group Sediments

The non-Hinuera Formation sediments are described for convenience in this section and in figures simply as Tauranga Group (T.G). This widespread, extremely variable group comprises terrestrial sediments such as sand, gravel, silt, clay and peat (section 2.2.1). It differs from the Hinuera Formation by including deeper (mean survey depth about 55 m), more frequently organic and often finer sediments. Also included are sediments of estuarine origin toward the north of the Hauraki Plains. This somewhat arbitrary differentiation of sediments allows the exploration of results on the basis of hydrogeology, as well as spatial distribution.

Parameter statistics are graphically presented for comparative purposes in box plots in appendix III. There are substantial apparent chemical differences between the Tauranga Group and the Hinuera Formation. Analysis of variance was used to test the significance of these differences (log transformation was required for most parameters).

The wide range of sediments comprising the Tauranga Group is reflected in the spread of water chemistry characteristics (figure 5). The Tauranga Group has a more pronounced sodium bicarbonate character (figure 6). The significantly ($p=.001$) increased bicarbonate concentration and associated increased alkalinity ($p=.001$), is probably due to a greater organic content and micro-biological activity.

There is also a significantly ($p=.021$) greater total dissolved solids concentration. This may be attributed to a number of factors. Longer residence time of groundwater (in finer and deeper sediments); increased organic content and associated microbial activity; location further along the flow path and in a discharge groundwater regime; as well as geothermal (section 5.5) and possible seawater (section 5.6) influences may all contribute to the observed increased ionic activity.

Evidence for a greater hydrothermal influence in the Tauranga Group sampled includes a minor but significant increase ($p=.019$) in mean sample temperature. Significant increases were also found in the concentrations of the hydrothermally associated parameters of fluoride ($p=.006$), lithium ($p=.004$) and boron ($p=.003$).

A substantial and important change in redox conditions between the Hinuera Formation and the remaining Tauranga Group is also indicated by differences in several determinants. The mean dissolved oxygen concentration is significantly lower ($p=.006$) in the Tauranga Group. Dissolved oxygen is influenced by the pumping required to obtain a sample, which tends to elevate the measured value. The trend, however, rather than the absolute value is nevertheless consistent with the differences in redox conditions indicated by other parameters.

The predominant form of nitrogen in the Tauranga Group is ammonia, which is also indicative of anaerobic conditions. Nitrate was detected only at very low concentrations in this group. Analysis of variance between the Tauranga Group and the Hinuera Formation in respect to differences between nitrate and ammonia concentrations indicate that they are highly significant ($p<.001$). A significantly reduced concentration of sulphate ($p=.017$) was also measured in the Tauranga Group samples. This is also consistent with more anaerobic

conditions, in which sulphate tends to be reduced to HS^- and then to H_2S . The pungent odour of H_2S is often encountered during drilling in the northern Hauraki Plains.

A significantly increased concentration of total phosphorous ($p=.001$) and filtered absorbance (A270f $p=.008$), in the Tauranga Group indicate a greater organic content. Silica content may also be expected to increase with longer residence time and increased hydrothermal influence. This may explain the marginally higher mean silica content of 84.4 ppm measured in the Tauranga Group.

Although there are increases in sodium, chloride and magnesium concentrations in the Tauranga Group, which may reflect a greater seawater influence, they are not statistically significant (table 3).

Soluble iron concentrations are also greater in the Tauranga Group (mean of about 10 ppm), than in the Hinuera Formation but are not statistically significantly different. Anaerobic conditions and a supply of soluble organic carbon for microbial activity more prevalent in the Tauranga Group, are favourable to high iron concentrations. Excessive iron is the primary water quality problem identified in this group (section 7.3).

Considerable variation in ionic ratios from the Tauranga Group is apparent in appendix III. The mean Na/Cl ratio for the Tauranga Group is high (about 2.5), which implies substantial sodium ion exchange. The mean Mg/Ca ratio is also high (1.68), which may be indicative of a combination of siliceous aquifer materials and some estuarine influence. A substantially higher Na/K ratio than that derived from the Hinuera Formation is probably associated with movement away from the zones of recharge. A decrease in the ratio of $(\text{Ca}+\text{Mg})/(\text{Na}+\text{K})$ may be attributed to the increase in alkali metals along the flowpath by ion exchange.

4.2.3 Ignimbrites

Several different ignimbrite flows are represented in the study area (section 2.2.2). Ignimbrite aquifers are however locally less important than alluvial aquifers and thus only three samples were collected. An investigation of the groundwater chemistry of the ignimbrite units is beyond the scope of this investigation. Only brief discussion will therefore be offered in this section. The measured chemical parameter concentrations are presented in appendix I and data are illustrated in box plots in appendix III.

The average measured temperature of the samples recovered from ignimbrite formations was relatively high (19.8 °C) and probably reflects the greatest average depth for the groups (about 113 m). The relationship of the major anions and cations is similar to the alluvial aquifers, with a predominantly sodium and bicarbonate character (figure 6). The most obvious difference between the ignimbrite and alluvial aquifers, is the low concentrations of iron and nitrogen in the former. This is largely an indication of the lack of organic components to these formations and greater depth. A higher mean pH of 7.2 is apparent and is probably a function of ion exchange and relative isolation from organic processes and relatively acid rainwater.

4.2.4 Kiwitahi Volcanics

The sparse occurrence of Kiwitahi Volcanics in the study area tends to be limited to relic volcanic cones (figure 2). Only one site was found from which a groundwater chemistry sample could be reliably recovered. The relative concentrations of the major anions and cations is graphically presented in figure 6. This sample is also dominated by sodium and bicarbonate and has a similar character to the ignimbrite samples analysed.

Anecdotal evidence suggests that Kiwitahi Volcanic groundwater quality is generally high. This is consistent with the fractured volcanic rock nature of these aquifers, particularly where they are not overlain by other formations. The single sample analysed is of high quality, with low iron and nitrate concentrations.

4.3 Spatial distribution of chemical characteristics

4.3.1 Lateral distribution

Lateral trends in groundwater chemistry within the alluvial aquifers of the Hauraki Lowland were examined by considering two groups of sample sites. The upper catchment group refers to sites on the southern side of the Morrinsville - Te Aroha road and the lower catchment group comprises sites to the northern side.

Box plots illustrating parameter concentrations of respective groups are presented in appendix III to enable comparison. Analyses of variance (involving log transformation), were undertaken to determine the significance of the apparent differences between the two groups.

In general more significant differences were found between these two groups than was the case between the Hinuera Formation and the remaining Tauranga Group. The results of this analysis are summarised in table 4. It is apparent that significant differences are reported for sodium, chloride and magnesium. Also differences in the concentrations of iron and manganese are now significant. The only parameter for which the difference in concentration was significant between geologic groups but is not in the spatial grouping is sulphate.

The changes in the listed relationships are primarily the consequence of transferring southern sites of the non-Hinuera Formation Tauranga Group to the upper catchment group. These sites generally have relatively low iron, manganese, sodium, magnesium and chloride. Spatial differences in the first two of these parameters are indicative of less common organics (peat) in the southern sediments. The greater difference in the other three parameters implies less saltwater influence on the non-Hinuera Formation samples from the south, relative to the mean of the total group. An increase in chloride ions toward the north is illustrated in figure 7. Despite this strong trend, there is little specific evidence of seawater influence (section 5.5). The lesser difference between sulphate concentrations in the spatial groupings is also influenced by depth relationships (section 4.3.2).

Table 4 : Comparison of analyses of variance between geological and spatial groupings.

Analyses of variance results for respective groupings (p-values)		
Parameter	Geologic	Spatial
dissolved oxygen	0.006	0.009
pH	n.s.	n.s.
SiO ₂	n.s.	n.s.
conductivity	0.019	<0.001
temperature	0.019	0.026
TDS	0.021	<0.001
NO ₃	<0.001	<0.001
NH ₄	0.007	<0.001
DRP	n.s.	n.s.
TP	<0.001	0.006
alkalinity	0.001	0.001
HCO ₃	0.001	0.001
B	0.003	0.001
Cl	n.s.	<0.001
F	0.006	0.002
SO ₄	0.017	n.s.
Ca	n.s.	n.s.
Mg	n.s.	0.042
Na	n.s.	0.023
hardness	n.s.	n.s.
Fe (total)	n.s.	0.002
Fe (soluble)	n.s.	0.003
Li	0.004	<0.001
Mn	n.s.	0.002
K	n.s.	n.s.
Zn	n.s.	n.s.
absorbance 270F	0.008	<0.001

n.s. = not significant

The results of table 4 suggest that differentiation of groundwater chemistry in the study area is better achieved on the basis of linear trends and location, than in respect to the previous geologic groups. Groundwater chemistry variation down the length of the plains is, however, consistent with physical trends (chapter 2). These trends include decreasing particle size, increasing organic content, decreased flow rates in association with decreased hydraulic gradient and permeability and thus increased residence time. Also the location along the flowpath and with respect to flow regimes, as well as geothermal and seawater influences, as mentioned previously are also important.

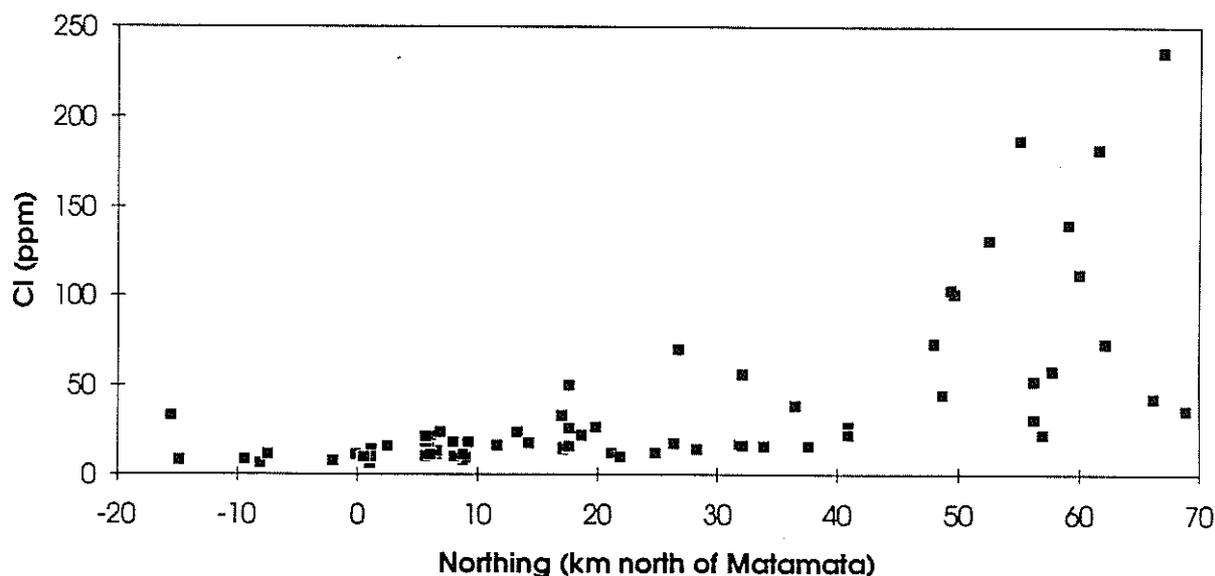


Figure 7 : Plot of chloride ion concentration versus northing

The division of sample sites into only two spatial groups was undertaken for statistical expedience. A general trend in groundwater chemistry along the plains is suggested by maps of sampled sites on which parameter concentrations are presented. Two such maps (figures 8 and 9), illustrate the distribution of measured nitrate and ammonia concentrations respectively. The distributions of the nitrogen forms in these maps are indicative of a strong spatial trend in redox conditions. Aerobic conditions are more prevalent in the upper catchment, whereas essentially anaerobic environments are ubiquitous in the lower or northern catchment.

Variations in groundwater chemistry with depth have not been filtered from the above analyses but will be addressed in the following section.

4.3.2 Vertical distribution

The vertical distribution of chemical parameter concentration was initially examined by correlation of concentration versus depth. Only two parameters were shown to have significant correlations with depth. A significant positive relationship between sample temperature and depth was found ($p < .001$) and is illustrated in figure 10. Regression analysis of 39 sites produced an intercept of 15.8°C and a coefficient of about 0.06°C per meter. The intercept is representative of mean shallow groundwater temperature. The coefficient indicates that the mean geothermal gradient of the study area is estimated to be about three times the normal gradient.

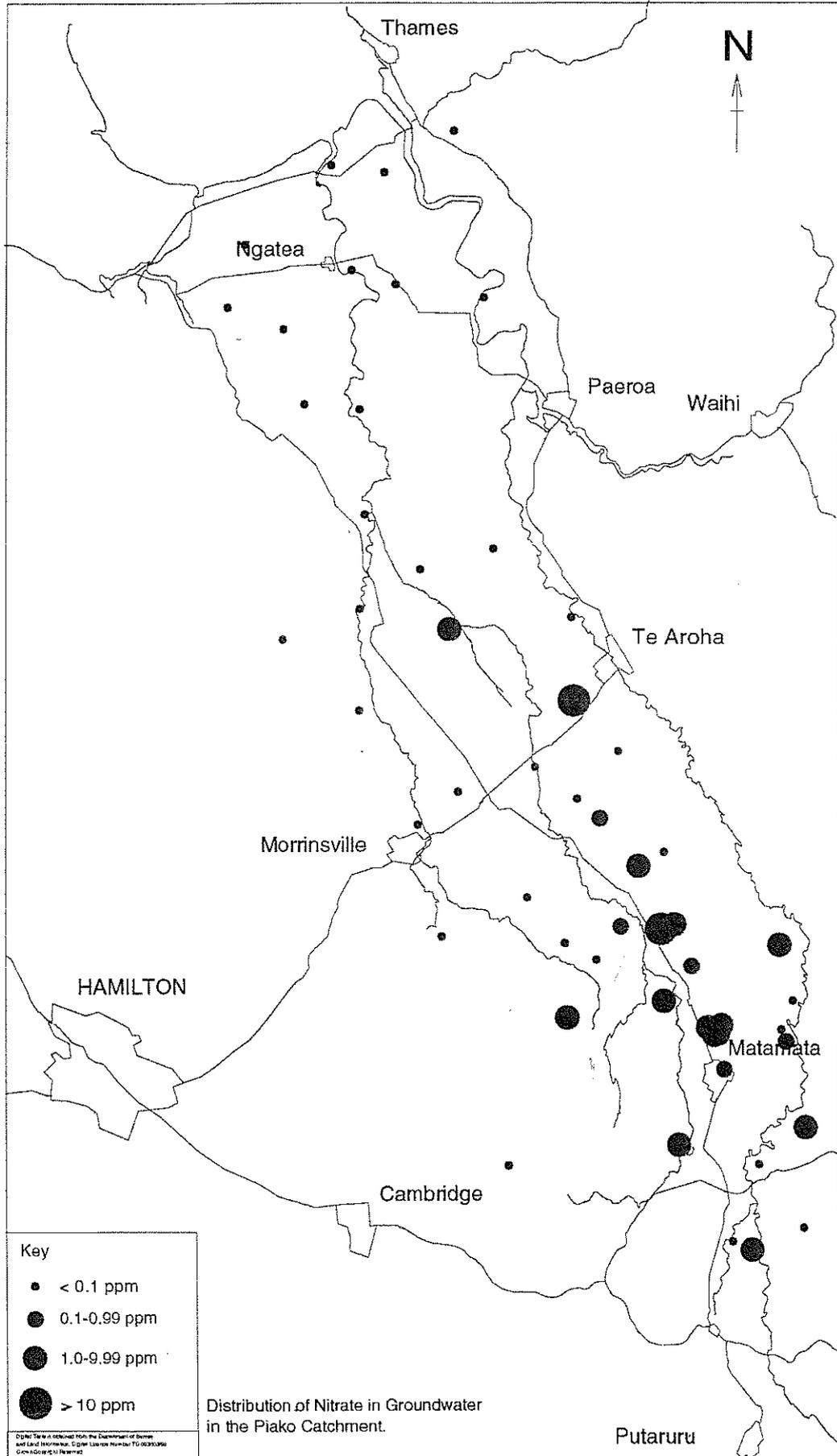


Figure 8 : Distribution of measured nitrate concentrations

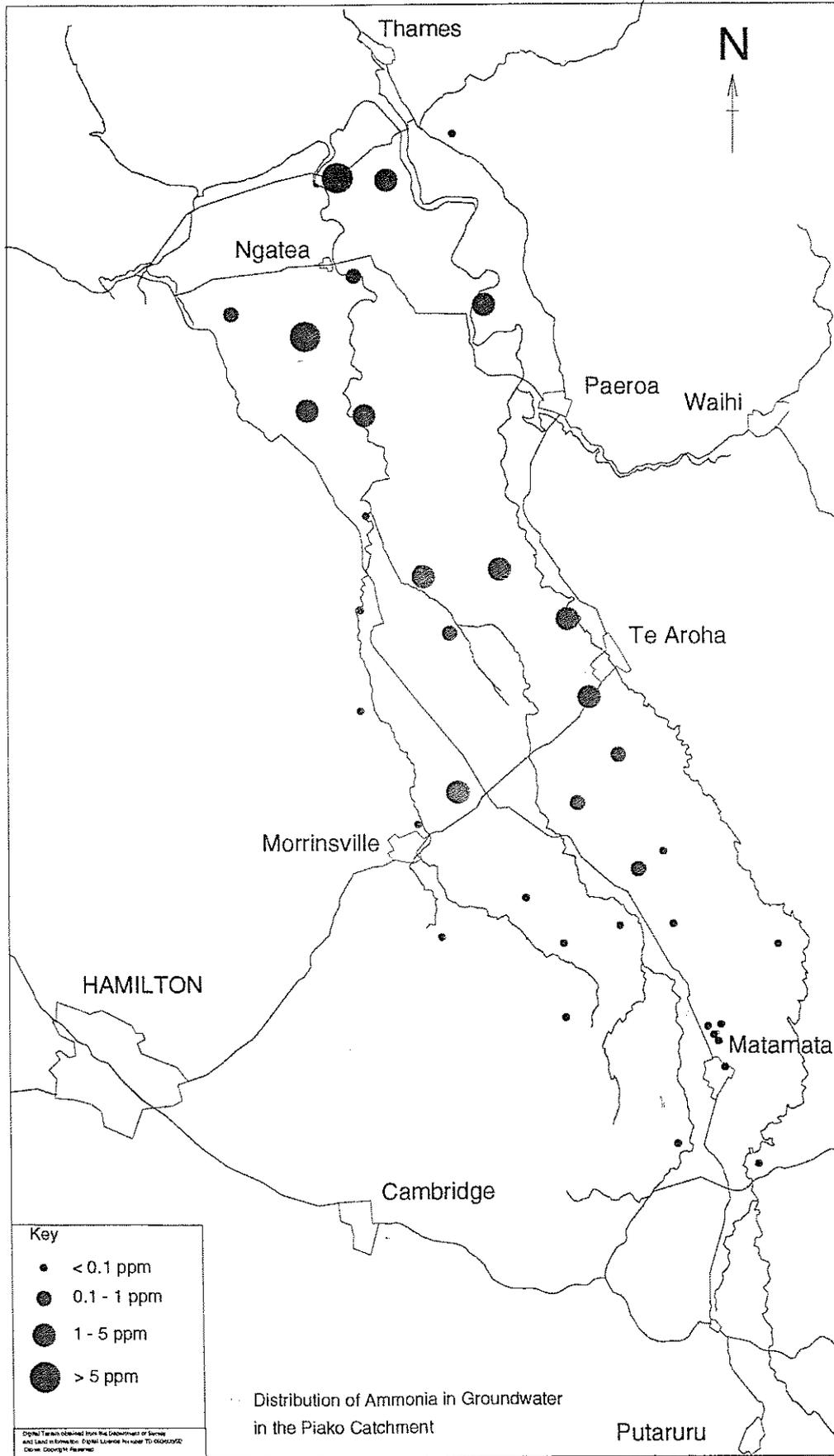


Figure 9 : Distribution of measured ammonia concentrations

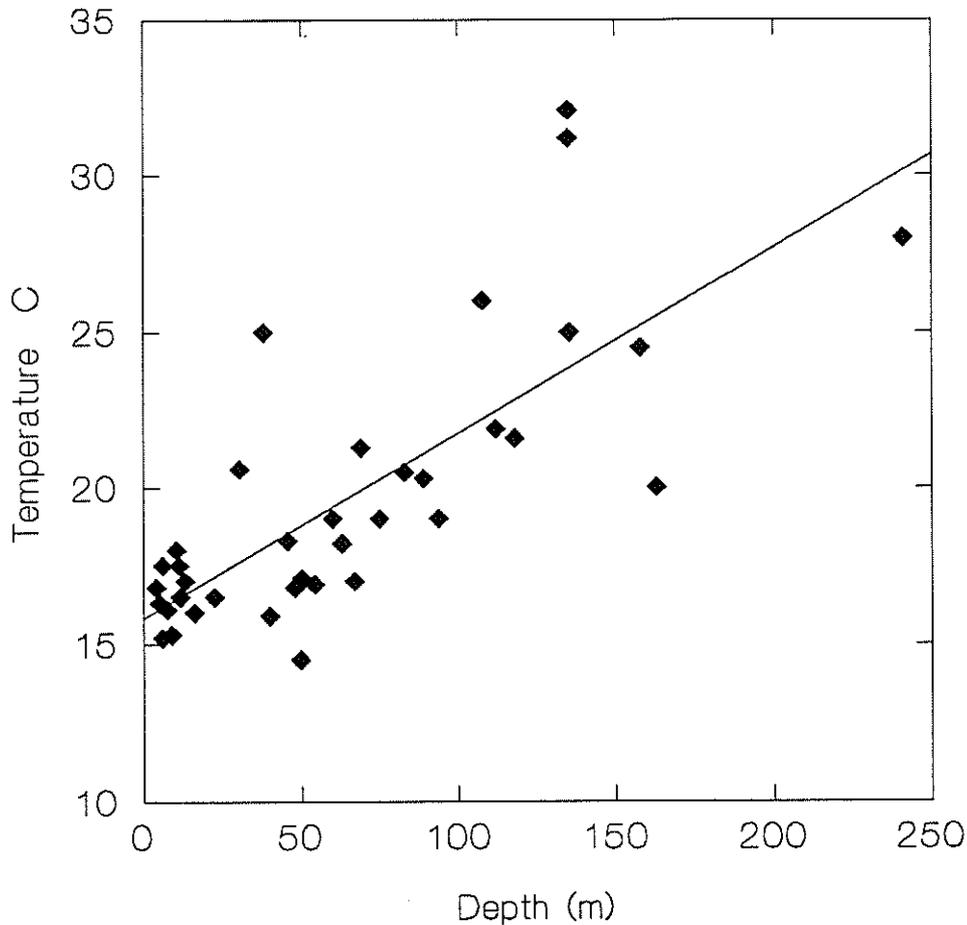


Figure 10 : Plot of sample temperature versus well depth

A less significant positive relationship ($p=0.0017$) was also found between pH and depth. This relationship may be attributed to longer residence times and isolation from mildly acidic rainfall and the generally shallow, acidic, organic influence.

Depth distributions of nitrate, sulphate and iron concentrations are also presented (figures 11, 12 and 13). Although these parameters do not have correlatable relationships with depth, their vertical distributions warrant further discussion.

High nitrate concentrations in groundwater are related to land use practices e.g. dairy farming (Burden, 1982, Hoare, 1986). Such concentrations tend to be limited to shallow unconfined aquifers (section 7.2). This trend is supported by the distribution of nitrate in figure 11. The deepest occurrences of nitrate in concentrations above 1 ppm are about 60 m. Unconfined aquifers of this depth do occur rarely in the Piako catchment, however some leakage of recent waters may account for some of these measurements. Deeper groundwater is generally anaerobic and therefore denitrification by eventual volatilisation or conversion to ammonia may be expected from deeper aquifers.

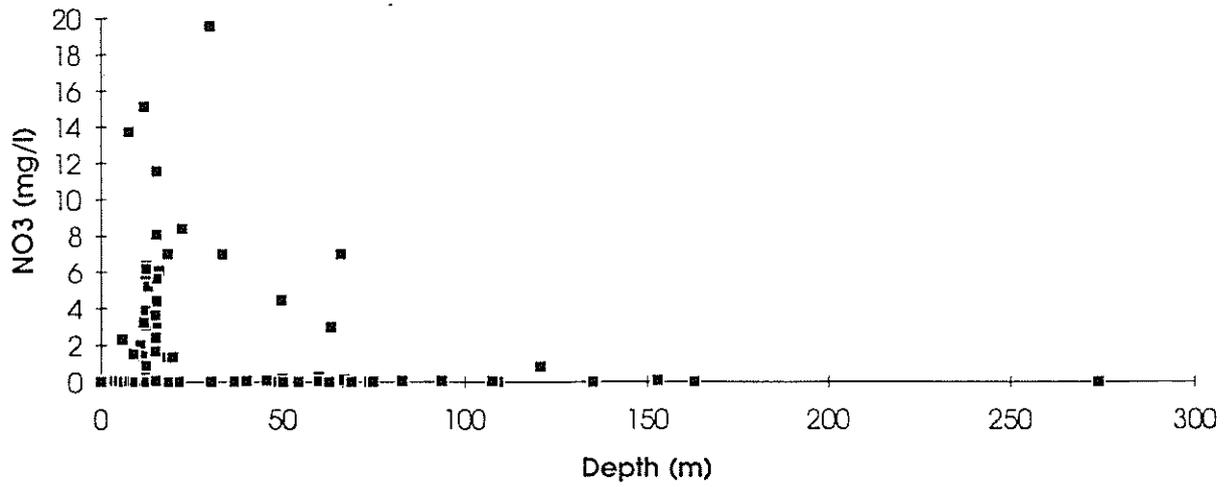


Figure 11 : Plot of nitrate concentration versus well depth

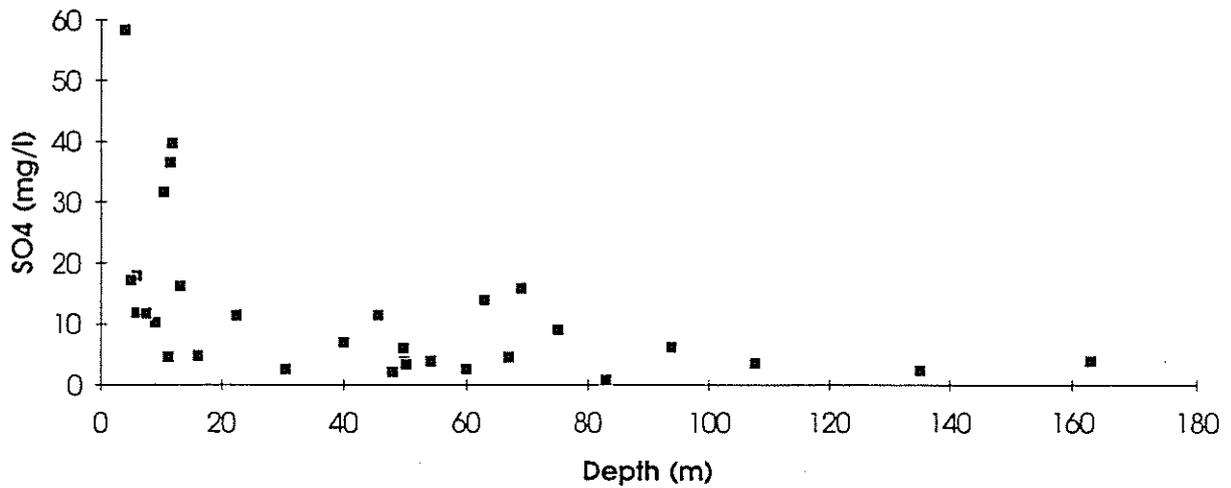


Figure 12 : Plot of sulphate concentration versus well depth

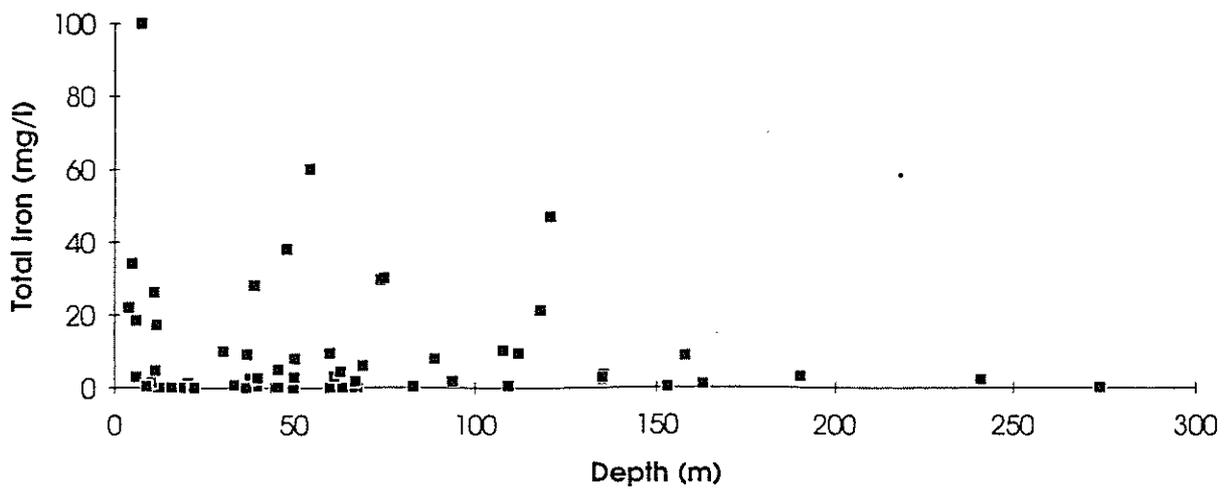


Figure 13 : Plot of total iron concentration versus well depth

The highest concentrations of sulphate also occur at shallow depths (figure 12). This is primarily a function of redox conditions. Sulphate is stable in aerobic conditions which occur predominantly in shallow, unconfined, (southern) aquifers. Progressive reduction of sulphate to hydrogen sulphide may be expected with depth providing there is sufficient microbial activity.

A general decrease of iron (figure 13), and ammonia in deeper wells may be related to decreasing organic content. The apparent distribution trends indicate a more gradual decline than occurs for nitrate and sulphate. This suggests that deeper anaerobic conditions do not limit the occurrence of iron. Shallow anaerobic conditions with high organic content and microbial activity are however apparently conducive to high concentrations (section 7.3). The more careful design of deeper wells may also be a factor.

A multi-piezometer installed at Matamata Airfield (T14:519-818) offers the opportunity to compare groundwater chemistry from three different depth intervals at the same location. The three piezometers 5043, 4789 and 4788 are at depths of 9 m, 40 m and 163 m respectively. The shallow piezometer is constructed in Hinuera Formation, the middle piezometer in deeper Tauranga Group sediments and the deepest in Rocky Hill Ignimbrite. There are a number of apparent chemical trends with depth at this site which are in general agreement with previous observations. The following parameters increase with depth: pH; temperature; alkalinity; total dissolved solids and associated conductivity. Several ions also increase in concentration with depth, as expected with increased residence time and temperature, these include; sodium, calcium, chloride, bicarbonate, fluoride and boron. In contrast, nitrate and sulphate concentrations decrease with depth as noted previously.

5 DISCUSSION AND REVIEW OF FACTORS INFLUENCING GROUNDWATER CHEMISTRY

5.1 Introduction

There are a large number of influences on the chemical character of groundwater. These include rainwater chemistry, aquifer geology, soil type, saltwater and geothermal influences and modifying factors such as climate and geomorphology. Some of these influences and associated processes are discussed in the following sections.

5.2 Chemical influence of rainwater

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 which may increase some ion concentrations e.g. sodium and chloride. Such an effect is, however, unlikely to be pronounced in the Hauraki Plains due to predominant westerly winds and would probably be masked by other possible saltwater influences upon groundwater (section 5.5).

The chemical composition of rainwater has been investigated by a number of workers including Miller (1961), and Phipps (1982). The concentration of major ions of the Hinuera Group and the remaining Tauranga Group are compared with rainwater composition at Taita (Miller, 1961), in figure 14.

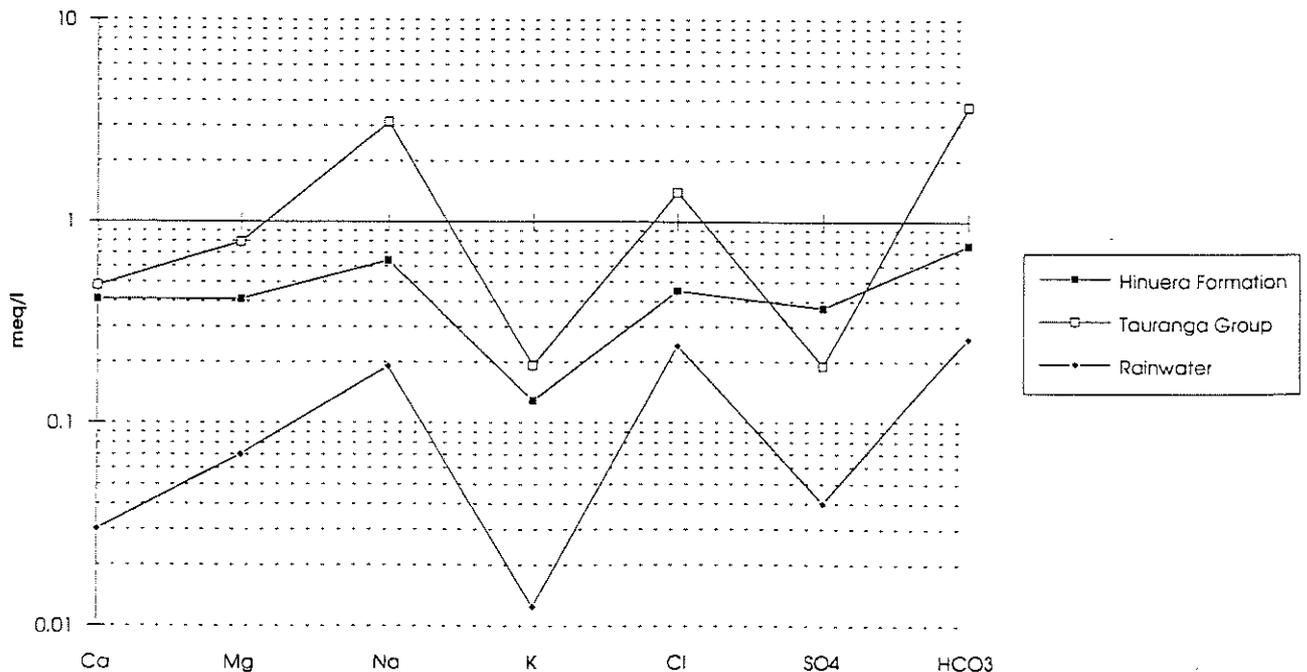
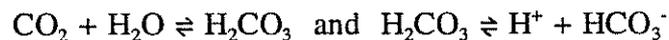


Figure 14 : Schoeller plot of rainwater, Hinuera Formation and other Tauranga Group sediments

This figure illustrates that the Hinuera Formation has a chemical character closer to rainwater. This is consistent with this group being shallower and predominantly located within recharge areas. The sub-parallel relationship exhibited in the Schoeller plot (figure 14), implies that the waters are of a generally similar character although some modification of ionic ratios is evident (Zaporozec, 1972).

5.3 Chemical influence of formation

Water infiltrating into the ground is altered chemically even before it reaches the water table. Uptake of CO₂ by water to form HCO₃⁻ is one of the major alterations processes within soil and may be expressed as follows:



CO₂ 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 toward the north in the Piako catchment is largely in response to progressive dissolution. The end products of this process are insoluble clay minerals.

Ion exchange primarily involves the clay minerals which adsorb 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, observed in the last chapter, indicates substantial cation exchange is occurring. This is accentuated by the more common occurrence of finer sediments with greater cation exchange capacities toward the north.

Groundwater undergoes a complex series of chemical reactions with the formations through which it migrates. In the Piako catchment, groundwater predominantly flows through sediments of the Tauranga Group which are highly variable. Reconstruction of the sequence of chemical reactions responsible for the observed groundwater chemistry, by way of mass balance calculations, is not practical within this study.

5.3.1 Reduction and oxidation processes

The importance of redox conditions to groundwater chemistry trends within the study area has already been noted (chapter 4). 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 generally organic matter, catalysed by bacteria (section 5.4). The trends noted in chapter 4, involved progressive oxygen depletion and reducing conditions along the flow path toward the north and with depth.

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, typical in the northern catchment, may readily reduce recharging groundwater to an anaerobic condition. The common, relatively recent, peat content in much of the catchment provides abundant reactive or readily metabolised organic matter. The finer sediments and reduced water table gradients in the northern catchment also result in reduced groundwater circulation and sufficient time for bacterial decomposition reactions to proceed along the flowpath.

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 , $\text{Fe}(\text{OH})_3$, 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 5 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. Strongly reducing environments in the northern Piako are also indicated by the occasional noted presence of H_2S gas.

Table 5 Some redox reactions that consume organic matter and reduce inorganic compounds (from Freeze and Cherry, 1979).

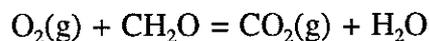
Process	Equation
Denitrification	$\text{CH}_2\text{O} + 4/5\text{NO}_3^- = 2/5\text{N}_2(\text{g}) + \text{HCO}_3^- + 1/5\text{H}^+ + 2/5\text{H}_2\text{O}$
Manganese reduction	$\text{CH}_2\text{O} + 2\text{MnO}_2(\text{s}) + 3\text{H}^+ = 2\text{Mn}^{2+} + \text{HCO}_3^- + 2\text{H}_2\text{O}$
Iron reduction	$\text{CH}_2\text{O} + 4\text{Fe}(\text{OH})_3(\text{s}) + 7\text{H}^+ = 4\text{Fe}^{2+} + \text{HCO}_3^- + 10\text{H}_2\text{O}$
Sulfate reduction	$\text{CH}_2\text{O} + 1/2\text{SO}_4^{2-} = 1/2\text{HS}^- + \text{HCO}_3^- + 1/2\text{H}^+$
Methane fermentation	$\text{CH}_2\text{O} + 1/2\text{H}_2\text{O} = 1/2\text{CH}_4 + 1/2\text{HCO}_3^- + 1/2\text{H}^+$

5.4 Organic and microbial influences

The substantial occurrence of peat domes, organic matter and associated microbial activity in the northern catchment strongly influences groundwater chemistry.

The addition of dissolved and to a lesser extent solid-phase organic carbon along the groundwater flowpath, provides 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.



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. High ammonium-N concentrations relative to nitrate-N were measured in shallow groundwater derived from the Torehape peat dome in the Piako catchment by McLay (1986) indicating a strongly reducing environment.

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.

5.5 Saltwater influence

Seawater may influence groundwater chemistry as a result of saltwater intrusion, entrapment of connate water in fine grained sediments or aerosol salts in rainfall. The occurrence of some relatively elevated chloride concentrations apparent in the synoptic survey may also, however, result from geothermal influences.

The mixing of seawater with other groundwaters results in rapid cation exchange. By contrast, the major anion chloride is conservative. The ratios of the concentrations of chloride and several other anions may be used to differentiate between waters influenced by seawater and geothermal waters. Tabulated below are comparisons between seawater and New Zealand geothermal waters for various ionic ratios (Ellis and Mahon, 1977).

Table 6 : Comparison between various ionic ratios for seawater and geothermal water.

Ratio	Seawater	Geothermal
Cl : Br	290	200 to 350
Cl : F	14900	50 to 1000
Br : I	1117	1 to 20

The ratio between chloride and magnesium in seawater is 14 and is generally substantially lower in geothermal waters. This ratio, however, varies dependent upon geology and is therefore less dependable. Ionic ratios from sample sites with relatively high chloride ion concentrations are tabulated below.

Table 7 : Selected ionic ratios for high chloride samples.

Well No	Cl	Cl : Br	Cl : F	Br : I	Cl : Mg
4775	52.1	144.7	137	4.5	1.5
4212	44.7	-	45.6	-	9.1
4635	103	-	202	-	18
5021	236	347	2,622	22.7	20.5
4365	42.8	-	305	-	1.3
5419	16	64	133	>25	3.3
5420	140	200	700	17.5	10.4
4773	187	-	645	-	8.1
5039	5500	88.7	7,746	75.6	20.4

* (Included because of available Br and I data).

The most useful ionic ratio used for distinguishing seawater from geothermal influences above was found to be the CL : F ratio. The use of several ratios together is however more dependable.

Only two samples have ionic ratios which indicate that they are influenced by seawater. These were obtained from well numbers 5039 and 5021. These samples are from a dual piezometer at the same site adjacent to the Piako River (T12:312-400). The river at this point is tidal and brackish. Monitoring has also indicated that there is a tidal impact on water levels in these piezometers. The deeper piezometer also has some minor geothermal influence indicated by a measured temperature of 21.3°C and lower than expected Br : I ratio.

Sample wells 4775, 4212, 4635 and 4365 have ionic ratios which suggest that their relatively high chloride concentrations may be attributed to a geothermal influence. The first is shallow (6 m) but overlies known deeper thermal water. The latter three have slightly elevated measured temperatures. These will be discussed further in the next section.

The remaining three wells; 5419, 5420 and 4773 are not obviously influenced by seawater or geothermal waters. The relatively high chloride concentrations of the last two appear to be an artifact of high suspended and total dissolved solids.

A strong trend of increasing chloride ion concentration northward was previously noted (figure 7). It was possible that this could result from a seawater influence, either as a result of connate seawater in sediments deposited during a holocene marine transgression; from aerosol salts in rainfall or less likely from seawater intrusion. There is, however, little evidence of seawater influence in the above data. On the contrary the only obvious chemical impacts from seawater are very close to the tidal Piako River.

5.6 Geothermal influence

Numerous hydrothermal springs associated with faulting occur in the Hauraki Lowland. Water chemistry analyses of a number of hot springs in the area have been published by Petty (1972) and Hochstein and Nixon (1979). It is generally accepted that thermal waters are derived from deep circulation and conductive heating of waters of meteoric origin. Isotopic studies suggest that thermal waters result from tectonic fracture flow with fault zones acting as preferential flow pathways (Lyon and Giggenbach, 1992).

Springs associated with the median horst were found to have significantly higher mineralisation than the springs discharging along the boundary faults. A stoichiometric imbalance noted between sodium and chloride, in the more mineralised waters, is characteristic of fluids which have interacted with hot greywacke rocks (Ellis and Mahon, 1967).

More recent and ongoing work by Jenkinson (in prep.), addresses the geothermometry of numerous hydrothermal springs and the geothermal influence upon groundwater chemistry in the Hauraki Lowland. A compilation of information provided from this current

investigation is presented in appendix IV. Included are ion chemistry, measured temperatures and reservoir temperatures estimated from geothermometers.

Thermal springs in the Hauraki Lowland generally have low surface temperatures of $< 60^{\circ}\text{C}$, with the exception of Te Aroha (88°C). Geothermometry suggests reservoir temperatures averaging 110°C (and up to 144°C). Thermal spring discharges are typically low ($< 4 \text{ l sec}^{-1}$) and warm groundwater bores are commonly flowing artesian with pressures $< 12 \text{ kpa}$ (Jenkinson, in prep.).

The thermal waters sampled are generally dominated by sodium and bicarbonate ions. An increasing sodium chloride character toward the north, however, is attributed to the influence of intrusive or relic seawater in formation. The total dissolved solids concentration of thermal waters is generally greater than other groundwater. Substantial mixing and horizontal migration of geothermal waters is reported to be common (Jenkinson, in prep.).

Elevated concentrations of silicon, fluoride, lithium and boron are indicative of geothermal influence. The ratio of chloride to fluoride, found to be particularly useful in separating geothermal from seawater influences in the preceding section, is also included in appendix IV. All the tabulated samples have Cl : F ratios less than 310.

Lithium concentrations are generally significantly greater in the listed thermal samples (0.1-0.7 ppm), than in non-thermal groundwaters ($< 0.1 \text{ ppm}$). Boron to chloride ratios were also found to be significantly higher, for thermal waters ($< 0.02 \text{ ppm}$) in the Hauraki Lowland, than in non-thermal waters ($< 0.02 \text{ ppm}$). About 50% of samples also have silicon concentrations greater than 100 ppm (Jenkinson, in prep.).

Several bores sampled in the synoptic survey have chemical characteristics which suggest they are geothermally influenced. The following table lists five such bores with indicative parameters.

Table 8 : Selected chemistry of geothermally influenced survey sites.

Well Number	Location	Depth (m)	Temp $^{\circ}\text{C}$	B ppm	Li ppm	F ppm	SiO ₂ ppm	Cl ppm	Cl:F
4385	T13:354-095	107.7	26.0	1.80	0.280	0.33	108.0	38.9	118
4212	T13:319-217	135	31.2	2.48	0.390	0.98	127.0	44.7	45.6
4635	S13:279-224	30.5	20.6	2.53	0.090	0.51	89.3	103.0	202
5021	T12:312-400	69	21.3	1.00	0.059	0.09	39.4	236.0	236
4751	T14:413-846	83	20.5	0.79	0.027	0.46	69.0	16.3	35.4
4365	T12:350-392	75	19.0	0.88	0.033	0.14	85.4	42.8	305

Despite substantial mixing with non-thermal waters, the geothermal influence on the above parameters is apparent. Bore number 4749 also has a relatively high lithium concentration at 0.37 ppm but little other indication of geothermal character. Also site 4775 has some very minor geothermal character (section 5.5).

All the geothermally influenced bores from the synoptic survey occur in non-Hinuera Formation sediments and ignimbrite, predominantly in the northern catchment. It should be reiterated that the sampled bores were randomly selected and thus it may be hypothesised that geothermally influenced groundwaters may be more widespread in the northern catchment. It is recognised that higher mean temperatures for the northern and non-Hinuera Formation groups is a factor in analyses of variance.

5.7 Chemical influence on streams

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 discharge areas of the northern catchment is influenced by groundwater chemistry. Lowered dissolved oxygen and high colour are noted as effects from drainage of peat influenced groundwater (van Rossem, 1990). 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.

5.8 Human influence

Human activities 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 human influence in the Piako catchment results from intensive agricultural landuse activities, particularly dairy farming.

Nitrate contamination of shallow aquifers is the most obvious impact associated with farming. Evidence suggests that nitrate in groundwater is primarily derived from farm animals (section 7.2), and is an example of diffuse contamination.

Contamination from point sources such as leachate from landfills, offal holes, septic tanks and oxidation ponds may also be locally important. Despite activity in the Piako catchment being predominantly agricultural, it has also nevertheless experienced recent minor incidents of hydrocarbon spills and leakage from underground petrol tanks. Although these examples had very localised impact they are nevertheless reminders of the potential for such occurrences even in non-industrial areas. It is important to recognise the potential for human impacts generally and develop appropriate resource management strategies to avoid difficult and costly remediation.

6.0 ENVIRONMENTAL ISOTOPES

6.1 Introduction

A minor investigation using environmental isotopes was undertaken in association with chemical sampling. The occurrence of the stable isotopes of oxygen and deuterium and the radioactive isotope of tritium were measured as an independent means of determining the age and origin of groundwater. Carbon 14 isotopes will also be used to date some older groundwater in the study area when facilities are available.

A total of seven samples were collected from sites representing a range of depths, ages and hydrogeologic situations. Samples were collected using standard methods (Hulston *et al.*, 1981), and analysed by the Institute of Geological and Nuclear Sciences. The results of analyses and site information are provided in table 9.

Table 9 : Environmental isotope results

Well No.	Map ref.	Depth (m)	Sampling date	TR $\pm \sigma$	$\delta^{18}\text{O} \pm \sigma$	$\delta \text{D} \pm \sigma$
5043	T14:519-818	9	17.12.92	2.12 \pm 0.07	-5.36	-29.3
4789	T14:519-818	40	17.12.92	.079 \pm .014	-5.88	-32.1
4788	T14:519-818	163.5	17.12.92	.037 \pm .013	-5.60	-31.9
4212	T13:319-217	135	15.12.92	.029 \pm .013	-5.82	-34.4
5039	T12:312-400	5	15.12.92	-	-3.78	-23.9
5021	T12:312-400	69	15.12.92	1.63 \pm .06	-5.31	-28.7
5294	T15:510-655	49.8	15.12.92	2.32 \pm .13	-5.78	-34.6

6.2 Tritium

Tritium (^3H), is a radioactive isotope of hydrogen with a half life of 12.43 years. Tritium data are reported as a tritium ratio (TR), where 1 TR equates to 1 part tritium to 1018 hydrogen. Tritium concentrations in rainfall increased markedly with the atmospheric testing of nuclear weapons from the early 1950's to 1980 (when atmospheric testing ceased). As a result, a large pulse of tritium was measured with a peak of 40 TR in 1965 (Stewart and Taylor, 1981). Tritium ratios before 1955 were about 1 to 1.5 and the TR of recent rainfall in the study area is about 2.5 (Taylor, 1993).

Measured tritium ratios of close to 2.5 suggest that groundwater samples have received recharge during the period of elevated tritium concentrations. A tritium level of about one or less suggests that the groundwater is older than 1955. Two of the samples listed in table 9, have tritium ratios which suggest recent groundwater recharge. Bores 5043 and

5294 are representative of water table situations. The latter is constructed in a large thickness of Hinuera Formation sediments and despite the total completion depth of 49.8 m, was nevertheless shown to be unconfined. The result for site 5021 suggest some recent leakage from the adjacent tidal Piako River. The remaining three sites have tritium measurements suggestive of older waters. Carbon 14 measurement of samples from two of these, 4788 and 4212, will also be undertaken for age determination.

The first three samples (5043, 4789 and 4788), were recovered from a multi piezometer at Matamata Airfield. The measured tritium ratio is shown to decrease with depth at this site. This is the general trend expected in the study area and implies that deeper groundwater is substantially older and less rapidly recharged. These results are consistent with a similar study in the Hamilton Basin (Marshall and Petch, 1985).

6.3 Oxygen and deuterium

The ratios of the main isotopes that comprise the water molecule may be used to make inferences in regard to the origin and recharge of groundwater. The isotopic ratios of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ are expressed in delta units δ , which are parts per thousand differences from an arbitrary standard mean ocean water. Variation in isotopic ratios, known as isotopic fractionation, can occur as a result of evaporation, condensation, chemical reactions and biological processes. The isotopic composition of rainfall is also temperature dependent.

Oxygen and deuterium concentrations correlate according to the relationship $\delta\text{D} = 8 \delta^{18}\text{O} + 13$, which is the local meteoric line for the study area (Stewart and Taylor, 1983). All the samples with the exception of one, plot within experimental error of this line (figure 15). This suggests that all groundwater recharge to these aquifers is from a similar rainfall source with little evidence of isotopic fractionation. Sample 5039 has an oxygen deuterium ratio suggestive of evaporation during recharge, although there is no obvious reason for this. Although this sample is brackish, the seawater content is not expected to significantly alter the the oxygen deuterium result (Taylor, pers com.).

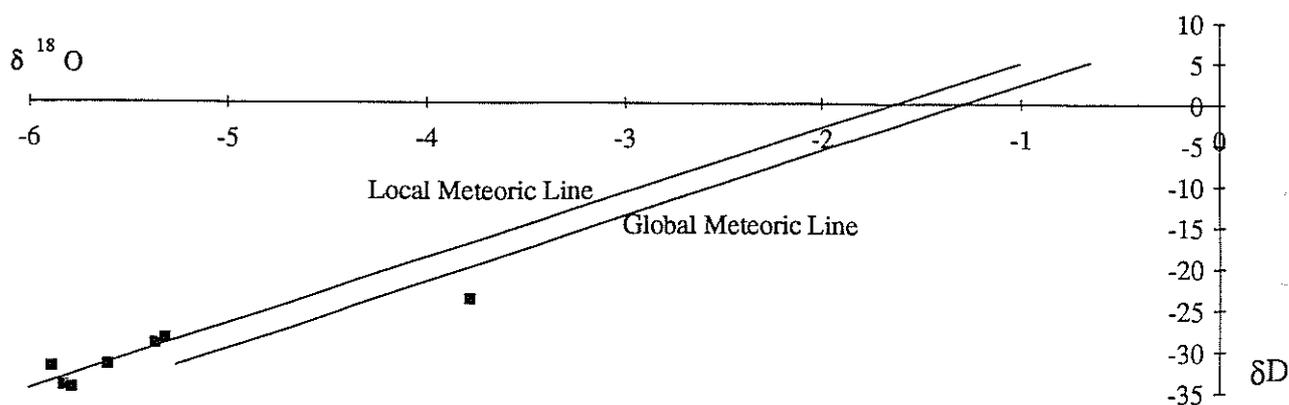


Figure 15 : Plot of isotopic ratios of oxygen and deuterium for groundwater samples in the Piako catchment

7.0 GROUNDWATER QUALITY AND IMPLICATIONS FOR USE

7.1 Introduction

Groundwater quality in the Piako catchment is assessed in this chapter, to determine its suitability for domestic, agricultural and industrial use. The two most common groundwater quality problems of nitrate contamination and excessive iron are initially discussed in some detail. Implications for groundwater resource development and land disposal practices are also considered.

7.2 Nitrate contamination

Nitrate contamination is the primary potential threat to groundwater quality in the Piako catchment. High nitrate concentrations are linked to a blood disorder known as methaemoglobinaemia, to which infants are particularly sensitive. The World Health Organisation (W.H.O.) recommended drinking water limit for nitrate is 10 ppm.

A mean nitrate concentration of 1.94 ppm, was calculated from collated data from 95 sites in the Piako catchment. Five samples had concentrations above the W.H.O. recommended limit. All of these were below 20 ppm except one, at 38 ppm, which is probably the result of localised contamination.

The origin of nitrate in groundwater relates to landuse practices and particularly dairy farming in the Piako catchment. Excreta and particularly urine from farm animals is the main source of groundwater nitrate (Baber, 1972; Burden, 1982). The increasing use of nitrogenous fertilisers and sewage disposal, e.g. septic tanks, can also result in leaching of nitrate to groundwater.

Nitrate generally enters groundwater from the ground surface and thus has the greatest impact on shallow, unconfined aquifers. Nitrification, the process whereby ammoniacal-N is converted to nitrate, generally occurs above the water table in the soil zone, where organic matter and oxygen are abundant (Freeze and Cherry, 1979).

Nitrate is very mobile and conservative in groundwater, largely because of its anionic form, high solubility and reluctance to adsorb onto fine sediments. Nitrate concentration has been shown to correlate with water table fluctuations. This is attributed to the washing of excess soil nitrate into groundwater (Baber and Wilson, 1972; Marshall, 1986).

Strong spatial trends in nitrate distribution are apparent (chapter 4). Nitrate concentrations decrease northwards along the plains and with depth. It is very uncommon to encounter concentrations above 2 ppm at depths greater than 30 m.

Mineral nitrogen in groundwater is strongly affected by redox conditions. Nitrate is the stable form of nitrogen in aerobic environments. Under anaerobic conditions in an aqueous environment, nitrate is reduced predominantly to nitrogen gas. Ammonium

formed by the mineralisation of organic nitrogen is the dominant form of nitrogen in anaerobic conditions (Burden, 1982).

In general, nitrates are introduced into shallow groundwater, predominantly in the recharging areas of the southern catchment, where aerobic conditions are more prevalent. Nitrate removal or denitrification dominates in the lower lying, more organic, finer and anaerobic northern plains. The ample supply of soluble carbon from organic matter is important for microbial activity which accelerates these processes.

Intensive dairy farming throughout the Piako catchment provides considerable organic nitrogen, which is initially converted to ammonia through the ammonification process. There is unlikely to be any short-term prospect of a major change in pastoral farm management in the catchment that will result in a marked decrease in the leaching of nitrate to groundwater. On the contrary, nitrate concentrations in shallow groundwater are likely to increase in future, as a result of high stocking rates and increased nitrogen fertiliser application. Approximately 8% of excreta from dairy cows is generated in the milking shed (Selvarajah, pers. com.). Well managed land disposal of this waste, when soils are not saturated, is preferable to disposal to surface waters.

There is no current practical remediation option for groundwater contaminated by nitrates. Rather an alternative water supply must be sought or dilution carried out by mixing. It is therefore important that time series monitoring of nitrate concentrations in groundwater is undertaken to determine trends. One possible management option is to establish groundwater protection zones up-gradient of important water supply wells (e.g. municipal supplies). The mobile character of nitrate in groundwater, however, is likely to make this option prohibitive.

7.3 Excessive iron problem

Excessive iron concentration is the major current water quality limitation to development of the groundwater resource in the Piako catchment. This problem seriously effects the suitability of groundwater particularly for domestic and industrial use. It commonly results in the staining of plumbing fixtures, encrustation of well screens, blocking of pipes and tainting of water supplies.

The mean and standard deviations of iron concentrations for the various hydrogeologic groupings are listed in table 3, and indicate that excessive iron concentration problems are common in the Piako catchment. The iron concentrations tend to be highest in the northern catchment and in the non-Hinuera Formation sediments (appendix III). The mean concentration of soluble iron from all the survey samples is very high at 8.4 ppm. A considerable concentration range is, however, apparent and about 30% of samples had concentrations of less than 1 ppm. An iron concentration of greater than 0.3 ppm in groundwater is aesthetically undesirable and may impart discolouration and staining.

The solubility and chemical behaviour of iron in water is strongly dependent on redox conditions and also pH (Barnes and Back, 1964). The highest iron concentrations are generally associated with peat layers which have strong reducing conditions conducive to

iron dissolution. Iron is present in organic material and its occurrence in water is also strongly influenced by microbial activity (Hem, 1985). Micro-organisms, particularly bacteria, are commonly involved in oxidation and reduction processes of iron (section 5.3.1).

Strongly reducing conditions permit a considerable ferrous ion concentration. Small changes in redox conditions, however, can cause a significant change in iron solubility. The distribution of iron in groundwater in the Piako Catchment is often erratic over a small area. This is attributed to variations in redox conditions at different depths and the discontinuous channel deposit nature of the aquifers. The selection of screen intervals for well design is therefore important. Peat layers and green coloured sediments indicative of reducing environments are generally excluded behind casing, where possible. Corrosion of steel casings in acid environments also adds iron to water in the reticulation system.

Excessive iron problems may be accentuated by the growth of iron bacteria. Filamentous species such as *Crenothrix*, *Gallionella* and *Leptothrix* may be so abundant that marked clogging of reticulation systems may result (Driscoll, 1987).

Groundwater containing high ferrous iron concentrations may be initially clear but on exposure to air will turn a cloudy rust colour and form a precipitate of ferric hydroxides. This rapid precipitation of Fe^{2+} ions on exposure to air is the basis of the iron treatment method most commonly used i.e. aeration followed by sand filtering. This method is substantially effective but does not remove all iron from solution.

There is a good correlation between iron and ammonium concentrations in the Piako catchment. More importantly, high iron and nitrate concentrations are mutually exclusive. They do not occur together because they require opposite redox conditions.

7.4 Domestic use

The suitability of groundwater quality for domestic use may be assessed by comparison with the drinking water standards for New Zealand. These standards are set by the Health Department (1984), based on World Health Organisation standards. Included are standards for constituents with health significance as well as measurements of aesthetic quality.

Parameters of concern for public health include nitrate, boron, heavy metals, organic chemicals, toxins and microbial content. The first two of these parameters and other aesthetic measurements, included in the synoptic survey, are listed in table 10. Comparison of these guidelines with the mean and standard deviations of chemical parameters for the hydrogeologic groupings in table 3, enables an assessment of groundwater suitability for domestic use.

The only parameter of concern in respect to public health is nitrate. All of the survey samples had nitrate concentrations less than the recommended limit of 10 ppm. A larger collated sample of 95 analyses, however, produced 5 sites that had concentrations in excess of the recommended limit (section 7.2). It is important that alternative water supplies are used at these sites, particularly for infants.

Table 10 : Drinking water standards (Department of Health, 1984)

Property	Highest Desirable	Maximum Acceptable	Effects
pH	7.4 to 8.5	7.0 to 8.5	corrosion (<7.0) scaling (>8.5)
Total Dissolved Solids (ppm)	500	1000	taste
Turbidity	1	5	discolouration
Nitrate (ppm)	10	10	higher levels can be toxic
Boron (ppm)	0.5	5	higher levels can be toxic
Chloride (ppm)	100	250	corrosion; taste threshold 200-300
Sulphate (ppm)	50	400	corrosion; laxative effect when magnesium is present
Calcium (ppm)	75	250	scaling; hard water
Magnesium (ppm)	<50	50	scaling; hard water
Sodium (ppm)	100	200	taste
Hardness (ppm)	80	200	scaling; hard water
Iron (ppm)	<0.1	1.0	'metal' taste; discolouration; iron deposits
Manganese (ppm)	0.05	0.5	taste; deposits; discolouration
Zinc (ppm)	5	5	taste; deposits; discolouration

Note : Hardness is a measure of magnesium and calcium concentrations such that :

$$\text{Hardness} = 2.5 (\text{Ca}^{2+}) + 4.1(\text{Mg}^{2+}).$$

The most obvious aesthetic parameter which exceeds acceptable limits is iron (section 7.3). Excessive iron commonly results in staining, well screen and pipe blockage and tainting of water supplies. Associated manganese levels are also frequently in excess of desirable limits

and have similar objectionable effects as iron. The common treatment for these constituents is aeration and sand filtering.

The pH measured in the survey is generally acid and thus corrosive. The conditions in the low-lying northern plains are particularly conducive to corrosion as attested by the short life of many well casings. Low pH, high total dissolved solids, frequent thermal influence and occasionally free CO₂ and H₂S gases contribute to corrosion.

Conductivity and the associated total dissolved solids (TDS) concentration may be used as a general indicator of water quality. The mean conductivities and TDS concentrations of the hydrogeologic groupings (table 3), are generally well below the recommended limits. The occasional sample wells which have TDS concentrations in excess of drinking water standards are not used for water supply (appendix I). It is apparent that the general water quality is generally higher in Hinuera and ignimbrite formations, than in the remaining Tauranga Group sediments. An exception to this assertion, however, is the nitrate contamination in the Hinuera Formation. Kiwitahi Volcanic aquifers have potentially the highest groundwater quality but insufficient information is available to confirm this.

7.5 Agricultural use

Groundwater supplies some 80% of farms in the Piako catchment, most of which are involved in pastoral farming with minor market gardening. It is therefore important to consider the suitability of groundwater quality for agriculture. New Zealand has no current water quality guidelines for agricultural use. Water quality classifications from the Environmental Protection Agency of Victoria (1983), are therefore presented in table 11.

Table 11 : Water quality classifications and important dissolved constituents (Victoria Environmental Protection Agency, 1983)

Water Classification	Criteria (ppm)	
Stock watering	boron	5.0
	calcium	1000
	iron	50
	nitrate	30
	chloride	1400 - 5,600
	TDS	3500 - 14,000
Irrigation	boron	0.75
	iron	5.0
	chloride	355 - 1,775
	TDS	500 - 3,500

Note: TDS = total dissolved solids

Groundwater quality in the Piako catchment is suitable for stock supply according to Victorian EPA criteria. Both iron and nitrate levels, however, rarely approach the recommended limits.

Boron concentrations measured during the survey were occasionally in excess (up to 2.5 ppm), of the levels recommended for the irrigation water (appendix I). High boron concentrations in the Piako catchment relate to geothermal rather than seawater influences. Such groundwater may be unsuitable for the irrigation of boron sensitive plants.

The sodium adsorption ratio (SAR) gives an indication of the degree to which irrigation water tends to enter into cation-exchange reactions in the soil. High values of SAR imply a hazard of sodium replacing calcium and magnesium and ultimately damaging the soil structure (Hem, 1985). It is defined as:

$$\text{SAR} = \frac{\text{Na}}{\sqrt{(\text{Ca} + \text{Mg}) / 2}}$$

High SAR values (18 or above), indicate that sodium will accumulate in soils from irrigation. Values below 10 indicate little danger of a sodium problem. The SAR values of the groundwater sampled in the Piako catchment were generally very low and averaged 3.88 (appendix II). Only three sites had values above 10. These were sites 4212 (13.9), 4635 (11.8) and 5039 (30). All of these are located in the northern plains. The first two are geothermally influenced and the last is effected by saline water from the lower, tidal, Piako River. There is in general no concern regarding potential damage to the soil structure via sodium exchange from irrigation waters in the Piako catchment.

Groundwater in the study area may be described as moderately soft i.e. hardness commonly less than 60 (table 3). It therefore tends to lather readily and not require large amounts of detergent in wash-down water.

7.6 Industrial use

Groundwater quality requirements for industrial supply vary widely dependent on the respective use. The major industrial users in the Piako catchment are dairy factories but food processing plants, fertiliser and chemical plants, as well as quarries are also included. Significantly higher water quality is required for activities such as food processing than for cooling or quarrying. Increasingly stringent limits are being placed on water used for dairy export products. Sanitary requirements for water used for milk processing exceed drinking water standards. There are also very stringent quality limits for water used in boilers.

It is often difficult to obtain groundwater of sufficient quality to meet the requirements of the more sensitive industries in the Piako catchment. Excessive iron and manganese concentrations, are the most common problems, particularly toward the north of the catchment. The corrosive nature of much of the groundwater is also a costly problem. Other problems of water supply include staining, scaling, erosion, foaming and sludge

formation. Some of these problems can be improved with careful well design but should be considered when siting a plant.

7.7 Land disposal practices

It is generally accepted that land disposal of waste is preferable to its discharge to surface waters. Unless carefully managed, however, it may lead to significant nitrate contamination of groundwater. Nitrates are more likely to be introduced to groundwater through free-draining soils in recharge areas where aerobic conditions are prevalent i.e. the southern catchment. Nitrates tend to be removed by natural processes of denitrification in the more anaerobic northern catchment. Although this natural attenuation of nitrate along the flow path is convenient, it does not protect the southern plains from increasing nitrate contamination.

By contrast, anaerobic conditions and groundwater discharge would tend to protect aquifers in the northern plains from contamination. However, poorly draining soils and water-logged conditions for a significant part of the year, render this area less suitable for land disposal practices. Relatively less use of groundwater in the northern catchment also decreases the associated risk to water supplies.

It is apparent from overseas experience that increased land disposal of wastes as well as increased stocking rates, tend to increase nitrate contamination of shallow groundwater (Burden, 1982). These effects can however be mitigated by careful waste disposal management aided by appropriate resource management policies.

8.0 SUMMARY AND CONCLUSIONS

The highly variable nature of sedimentary aquifers within the Piako catchment is reflected in a substantial range of groundwater chemistry. There are, however, strong spatial trends in chemical character.

Trends include progressively reducing conditions down the catchment. Evidence for this includes reduced measured dissolved oxygen toward the north. This change in redox conditions along the plains strongly influences groundwater chemistry. Nitrate concentrations decrease and ammonia concentrations increase northwards. Sulphate reduction is also marked in the lower catchment. Increases in iron and manganese toward the north are attributed to the greater abundance of organic matter (peat) and anaerobic conditions in the lower catchment.

A general increase in total dissolved solids, bicarbonate and salt concentrations may be attributed to a number of factors. These include longer residence times in finer sediments; location further along the flowpath, which allows greater dissolution and ion exchange; higher organic content and greater seawater and hydrothermal influences. The latter is substantiated by higher concentrations of boron, lithium and fluoride as well as higher average temperatures in the northern catchment. The influence of seawater, however, although implied by a strong spatial trend in chloride ion concentration, is rarely substantiated by ionic ratios in specific samples.

The only substantial correlatable trend with depth is in regard to temperature. This indicates a higher than normal geothermal gradient in the study area. Distributions of ionic concentrations with depth also indicate that nitrate and sulphate ions, which are stable in aerobic conditions, tend to be limited to shallow and probably unconfined aquifers.

The noted groundwater chemistry trends are consistent with a number of hydrogeological trends down the catchment. These include a change from relatively coarse, clean, alluvial sand and gravel sediments in the south to finer, estuarine, sediments in the north. An increasing organic content and peat dome development in the low-lying, northern, swampy, floodplain; slower flow rates associated with lower gradients and lower permeability formation; and a change from recharge to discharge groundwater flow regimes, also strongly influence groundwater chemistry in the Piako catchment.

Statistical analyses indicate that spatial differences in chemical character are more pronounced than chemical differences between geologically subdivided groups. In general, however, groundwater quality is higher in the Hinuera Formation than in the remaining Tauranga Group sediments.

Environmental isotopes, oxygen and deuterium, indicate that groundwater recharge is from a similar rainfall source with little evidence of isotopic fractionation. Increasing groundwater age with depth is indicated by tritium isotope measurement with recent recharge apparent in shallow, unconfined aquifers.

Groundwater quality within the Piako catchment is highly variable and ranges from moderately high in some of the cleaner, shallow, southern, aquifers to very poor quality waters, which restrict resource development, in much of the northern plains.

The two most common groundwater quality problems in the Piako catchment are excessive iron concentrations and nitrate contamination. High iron and nitrate concentrations occur in opposite redox conditions and thus do not occur together. The highest iron concentrations are associated with reducing conditions and particularly with peat layers, and occur predominantly in the northern catchment. Excessive iron concentrations result in staining, encrustation, pipe blockage and tainted water supplies. Such problems often render groundwater supplies unsuitable for industrial and domestic use.

Nitrate concentrations are predominantly well below the World Health Organisation recommended drinking water limit of 10 ppm. Contamination of groundwater by nitrate originating from agricultural land-use is, however, a potentially serious problem. Further investigation is warranted to determine temporal trends in nitrate concentration. The effects of nitrate contamination can be mitigated by careful waste disposal management supported by appropriate resource management policies.

- American Public Health Association, (1989). Standard Methods for the examination of Water and Wastewater (16th Edition). John Wiley & Sons, New York.
- Baber, H.L.; Wilson, A.T., (1972). Nitrate Pollution of Groundwater in the Waikato Region. Journal of the New Zealand Institute of Chemistry 36.
- Barnes, I. & Back, W. (1964). In: Hem, J.D., (1985). Study and interpretation of the chemical characteristics of natural water. US Geological Survey Water Supply Paper, 2254.
- Burden, R.J., (1982). Nitrate contamination of New Zealand aquifers: a review. New Zealand Journal of Science 25: 205-220.
- Cuthbertson, A.S., (1981). The Hinuera Formation in the Southern Hauraki Lowland, central North Island. Unpublished M.Sc Thesis, University of Waikato.
- Davidge, S.C., (1982). A geophysical study of the South Hauraki Lowlands. Unpublished M.Sc. Thesis, University of Auckland.
- de Lange, P.J., (1989). Late Quaternary development of the Kopouatai Peat Bog, Hauraki Lowlands, and some paleoenvironmental inferences. Unpublished M.Sc. Thesis, University of Waikato.
- de Lange, P.J.; Lowe, D.J., (1990). History of the vertical displacement of Kerepehi Fault at Kopouatai bog, Hauraki Lowlands, New Zealand, since c. 10,700 years ago. New Zealand Journal of Geology and Geophysics, 1990, Vol.33: 277-283
- Dewhurst, R.H., (1981). Thames Valley groundwater investigation (chemistry). Hauraki Catchment Board Report 106.
- Dewhurst, R.H. (1985). Report on groundwater investigation drilling in the Ngatea-Patetonga area of the northwest Hauraki Plains. Hauraki Catchment Board Report 177.
- 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
- Driscoll, F.G., (1987). Groundwater and Wells. 2nd Edition. Johnston Division, St. Paul, Minnesota
- Ellis, A.J.; Mahon, W.A., (1967). in Hochstein, M.P., and Nixon, I.M., 1979. Geophysical study of the Hauraki Depression, North Island, New Zealand. New Zealand Journal of Geology and Geophysics 22: 1-19.

- Ellis, A.J.; Mahon, W.A.J. (1977). Chemistry and Geothermal Systems. Academic Press, New York
- Environmental Protection Agency of Victoria, (1983). Recommended Water Quality Criteria. Environmental Protection Authority of Victoria Publication 165.
- Freeze, R.A.; Cherry, J.A., (1979). Groundwater. Prentice-Hall, Englewood Cliffs.
- Hadfield, J.C., (1992). A report on exploratory drilling and piezometer construction in the Hauraki Lowland. Waikato Regional Council Technical Report 1992/9
- Hem, J.D., (1985). Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water Supply Paper, 2254.
- Hoare, R.J., (1986). Groundwater nitrate in the Hamilton Basin. Waikato Valley Authority Technical Report 1986/12.
- Hochstein, M.P.; Nixon, I.M. (1979). Geophysical study of the Hauraki depression, North Island, New Zealand. New Zealand Journal of Geology and Geophysics 22: 1-19
- Hochstein M.P.; Tearney, K.; Rawson, S.; Davey, F.J.; Davidge, S.; Henrys, S.; Backshall, D. 1986. Structure of the Hauraki rift (New Zealand). The Royal Society of New Zealand Bulletin 24: 333-348
- Hulston, J.R., et al., (1981). Environmental isotopes in New Zealand Hydrology, 2. Standards, measurement techniques and reporting of measurements of Oxygen-18, Deuterium and Tritium in water. New Zealand Journal of Science 24: 313-322.
- Jenkinson, D.G., (in prep) Studies of thermal waters and thermal wells in the Hauraki Depression. Unpublished M.Sc. Thesis. University of Auckland.
- Kear, D.; Schofield, J.C., (1978). Geology of the Ngaruawahia Subdivision. New Zealand Geological Survey Bulletin 88.
- Lyon, G.L.; Giggenbach, W.F., (1992). The isotope geochemistry of hot spring gases and waters from Coromandel and Hauraki. Proceedings of the 14th New Zealand Workshop, 1992.
- New Zealand Department of Health, (1984). Drinking water standards for New Zealand. New Zealand Board of Health, Wellington.
- McLay, C.D. The management of organic substrates for agriculture: An investigation of peat hydrology and chemistry at Torehape, Hauraki Plains. Unpublished MSc. Thesis. University of Waikato.
- Mandel, S.; Shiftan, Z.L., (1981). Groundwater Resources Investigation and Development. Academic Press, New York.

- Marshall, T.W.; Petch, R.A., (1985). A study of groundwater and surface water resources in the Hamilton Basin. Waikato Valley Authority Technical Publication 30.
- Marshall, T.W. (1986). Groundwater chemistry characteristics of the Mangaonua-Mangaone Catchments. Waikato Valley Authority Technical Report 86/2.
- Miller, R.B., (1961). The chemical composition of rainwater at Taita, New Zealand, 1956-1958. New Zealand Journal of Science 4: 844-853.
- Palmer, C.D.; Cherry, J.A., (1984). Geochemical evolution of ground water in sequences of sedimentary rocks. Journal of Hydrology 75: 27-65
- Petty, D.R., (1972). Springs of the Auckland Region. New Zealand Geological Survey Report 1957.
- Phipps, A.G., (1982). Solute movement in a steep-land catchment, South Auckland, New Zealand. Unpublished M.Sc. Thesis, University of Waikato.
- Schofield, J.C., (1972). Groundwater of the Hamilton Lowland. New Zealand Geological Survey Bulletin 89. D.S.I.R.
- Selvarajah, N. Personal communication. Scientist. Environment Waikato.
- Stewart, M.K.; Taylor, C.B., (1983). Environmental Isotopes in New Zealand Hydrology, 1. Introduction: the role of Oxygen-18, Deuterium and Tritium in Hydrology. New Zealand Journal of Science, 24: 295-311.
- Taylor, C.B., (1993). Report on Tritium, Oxygen-18 and Deuterium measurements, Piako Area. Unpublished Report of the Institute of Geological & Nuclear Sciences, Wellington for Environment Waikato.
- Taylor, C.B., (1993). Personal communication. Scientist . Institute of Geological and Nuclear Sciences.
- Van Rossem, J.E. (1990). A review of surface water quality issues in the Piako/Waitoa Catchment. Waikato Regional Council Technical Report 1990/27.
- Zaporozec, A., (1972). Graphical interpretation of water quality data. Groundwater 10: 32-43.

Chemical Analyses of groundwater from the Piako catchment.

Geology	Location	Well number	Depth (m)	pH	Cond. mS/m	Temp. Deg.C
<u>Hinuera Formation</u>						
	T15 : 510-655	5294	49.8	6.5	13.8	14.5
	T14 : 548-741	4743	22.4	6.4	17.9	16.5
	T14 : 545-735	4999	13.1	6.4	19.0	17.0
	T14 : 595-797	5274	16.1	6.5	21.9	16.0
	T14 : 496-863	5121	11.5	6.5	15.3	16.5
	T14 : 516-872	2887	10.4	6.6	21.1	18.0
	T14 : 455-916	4996	11.8	6.6	24.2	16.5
	T13 : 371-049	5384	6.0	5.9	16.5	15.2
	T13 : 461-051	4993	11.2	6.5	22.2	17.5
	T14 : 519-818	5043	9.0	6.7	11.9	15.3
<u>Tauranga Group</u>						
	T14 : 548-709	2817	67.0	7.4	17.3	17.0
	T14 : 480-820	5364	50.0	6.6	11.7	17.0
	T14 : 488-949	4970	60.0	6.9	16.8	19.0
	T14 : 369-928	5147	48.0	6.6	20.8	16.8
	T14 : 302-994	4312	63.0	6.3	16.5	18.2
	T13 : 354-095	4385	107.7	6.7	73.0	26.0
	T13 : 408-106	4749	54.3	7	58.0	16.9
	T13 : 415-293	4775	6.0	6.5	98.0	17.5
	T13 : 319-217	4212	135.0	6.9	93.0	31.2
	S13 : 279-224	4635	30.5	6.6	87.0	20.6
	T12 : 312-400	5021	69.0	6.5	80.0	21.3
	T12 : 350-392	4365	75.0	6.3	71.0	19.0
	T14 : 519-818	4789	40.0	6.8	11.3	15.9
	T14 : 338-906	5419	114.0	6.6	18.1	.
	S12 : 229-300	5176	50.2	6.7	20.5	17.1
	S13 : 321-321	5420	4.0	5.5	65.0	16.8
	S13 : 268-281	4773	7.5	6.3	145.0	16.1
	T12 : 312-400	5039	5.0	6.9	1580.0	16.3
<u>Ignimbrite</u>						
	T15 : 568-636	4750	93.8	6.6	15.7	19.0
	T14 : 413-846	4751	83.0	7.8	22.1	20.5
	T14 : 519-818	4788	163.0	7.4	25.0	20.0
<u>Kiwitahi Andesite</u>						
	T13 : 317-139	5418	45.7	6.6	20.5	18.3

Geology	T.D.S. ppm	NO ₃ ppm-N	NH ₄ ppm-N	P (sol) ppm-P	P (tot) ppm-P	Alkalinity ppm	HCO ₃ ppm
<u>Hinuera Formation</u>							
	153	4.460	0.038	0.029	0.064	37	45
	199	8.390	0.048	0.033	0.063	30	37
	170	5.200	0.035	0.050	0.084	35	43
	177	6.070	0.032	0.024	0.066	24	30
	179	1.420	0.104	<0.003	0.114	19	23
	180	0.077	0.030	0.084	0.149	36	43
	232	0.003	0.771	<0.003	0.139	53	65
	168	2.300	0.104	<0.003	0.028	25	30
	213	0.002	1.740	0.003	0.256	78	96
	113	1.530	0.017	0.029	0.052	43	52
<u>Tauranga Group</u>							
	111	0.102	0.069	0.126	0.137	60	73
	149	0.141	0.067	0.084	0.214	47	57
	182	0.026	0.934	<0.003	0.306	78	95
	223	0.005	2.520	<0.003	0.104	99	120
	182	0.002	0.065	0.029	0.188	56	69
	549	0.025	2.490	0.008	0.303	343	418
	272	0.006	4.420	0.003	0.380	216	264
	656	0.009	4.020	3.550	3.320	518	632
	685	0.004	1.630	0.324	0.615	466	569
	601	0.004	3.020	0.045	0.730	295	360
	541	0.010	0.266	0.037	0.160	214	261
	466	0.002	3.640	0.074	0.728	385	470
	148	0.031	0.080	0.096	0.144	47	57
	210	<0.02	<0.01	0.158	0.166	70	85
	161	0.004	0.217	0.004	0.251	70	86
	466	0.043	0.186	0.210	1.180	24	29
	1060	0.042	8.590	4.190	7.500	627	765
	7810	0.016	10.500	0.004	1.750	1020	1240
<u>Ignimbrite</u>							
	111	0.016	0.039	0.221	0.447	47	57
	166	0.015	0.047	0.150	0.182	90	110
	221	0.004	0.058	0.182	0.232	132	161
<u>Kiwitahi Andesite</u>							
	175	0.083	0.056	0.110	0.099	71	87

Geology	F ppm	SiO ₂ ppm	SO ₄ ppm	Ca ppm	Mg ppm	Na ppm	Hardness ppm
<u>Hinuera Formation</u>							
	<0.05	99.4	6.0	7.0	4.0	13.1	38
	<0.05	72.1	11.4	10.9	5.1	14.4	46
	<0.05	85.0	16.2	9.4	4.5	13.0	43
	0.05	82.2	4.7	9.4	4.8	13.2	43
	0.06	64.6	36.4	7.8	4.8	18.5	39
	0.08	86.5	31.5	10.8	6.1	12.6	51
	0.08	97.9	39.6	9.1	6.8	17.6	48
	0.06	78.3	17.9	5.3	3.8	17.2	31
	0.12	76.2	4.5	5.5	4.7	18.1	31
	0.06	36.2	10.2	7.4	5.7	9.2	40
<u>Tauranga Group</u>							
	0.09	78.8	4.5	6.5	5.5	12.4	39
	0.06	93.4	3.7	3.4	4.7	12.2	27
	0.15	79.0	2.6	4.1	3.0	26.0	24
	0.15	84.9	2.1	6.1	4.1	23.0	31
	0.09	101.0	13.9	3.3	3.6	20.0	24
	0.33	108.0	3.5	12.7	8.6	142.0	67
	0.20	65.1	3.9	9.2	8.3	0.6	59
	0.38	88.3	11.8	11.6	35.0	156.0	180
	0.98	127.0	2.4	7.6	4.9	200.0	40
	0.51	89.3	2.6	6.0	5.7	168.0	41
	0.09	39.4	15.8	18.0	11.5	134.0	90
	0.14	85.4	9.0	31.0	33.0	72.0	213
	0.08	76.0	6.9	7.7	3.2	10.9	34
	0.12	94.0	1.0	5.2	4.9	22.0	33
	0.33	57.1	3.3	9.6	3.7	28.0	44
	0.20	84.4	58.3	10.8	13.5	120.0	68
	0.29	53.0	11.7	22.0	23.0	270.0	193
	0.71	45.3	17.1	158.0	270.0	2700.0	1690
<u>Ignimbrite</u>							
	0.15	105.0	6.1	2.8	2.5	15.2	18
	0.46	69.0	0.8	8.4	2.4	36.0	31
	0.13	76.0	3.9	15.4	9.8	31.0	77
<u>Kiwitahi Andesite</u>							
	0.05	79.3	11.5	10.8	7.5	23.0	59

Geology	Cl ppm	Fe (sol) ppm	Fe (tot.) ppm	Li ppm	Mn (tot.) ppm	K ppm	Zn (tot.) ppm
<u>Hinuera Formation</u>							
	11.3	<0.04	<0.04	0.006	<0.02	4.5	0.03
	9.9	<0.04	<0.04	0.004	<0.02	7.0	0.15
	9.6	<0.04	0.05	0.006	<0.02	6.6	0.30
	23.7	<0.04	<0.04	0.006	<0.02	6.4	0.05
	23.9	4.30	4.60	0.011	0.07	5.4	0.19
	17.8	1.11	1.19	0.007	0.05	4.9	0.02
	22.1	14.20	17.20	0.014	0.33	3.2	0.01
	16.9	2.90	2.90	0.021	0.42	5.5	0.09
	16.3	20.00	26.00	0.010	0.38	4.0	<0.01
	8.1	0.11	0.32	<0.002	0.02	2.7	<0.01
<u>Tauranga Group</u>							
	7.4	1.47	1.55	0.017	0.21	4.2	0.14
	9.5	2.70	2.80	0.006	0.05	4.8	0.03
	9.8	8.90	9.40	0.016	0.26	3.4	0.03
	26.7	29.00	38.00	0.012	0.45	3.5	0.02
	17.4	4.20	4.30	0.013	0.18	4.4	0.01
	38.9	10.10	10.10	0.280	0.38	8.2	0.01
	15.8	46.00	60.00	0.370	0.81	5.5	0.15
	52.1	6.90	18.30	0.063	1.58	25.0	0.08
	44.7	3.10	2.90	0.390	0.14	8.7	<0.01
	103.0	8.80	10.00	0.090	0.34	9.4	0.01
	236.0	4.20	5.90	0.059	0.46	10.4	0.08
	42.8	22.00	30.00	0.033	1.98	10.7	0.01
	10.1	0.67	2.70	0.006	0.83	3.8	0.02
	16.0	0.11	0.17	0.019	0.04	4.9	<0.01
	22.5	8.00	8.00	0.022	0.30	1.4	0.07
	140.0	7.90	22.00	0.039	0.49	11.7	0.06
	187.0	47.00	100.00	0.018	2.70	19.5	0.21
	5500.0	14.80	34.00	0.030	14.80	88.0	0.10
<u>Ignimbrite</u>							
	8.4	1.71	1.75	0.012	0.18	5.9	0.15
	16.3	<0.04	0.09	0.027	0.12	2.9	0.31
	11.3	0.40	0.93	0.058	1.13	3.4	<0.01
<u>Kiwitahi Andesite</u>							
	22.2	0.07	0.09	0.006	0.02	2.4	0.01

Geology	B ppm	Br ppm	I ppm	D.O ppm	Susp. Solids ppm	Abs. 270u.f /cm	Abs. 270 f /cm
<u>Hinuera Formation</u>							
	<0.03	.	.	.	<2	0.000	0.001
	0.03	.	.	8.9	<2	0.012	0.005
	0.28	.	.	7.9	<2	0.012	0.003
	<0.03	.	.	8.8	<2	0.009	0.005
	0.03	.	.	8.2	10	0.084	0.041
	<0.03	.	.	5.4	<2	0.018	0.012
	<0.03	.	.	2.6	<2	0.249	0.460
	<0.03	.	.	5.4	5	0.121	0.075
	0.05	.	.	3.0	6	0.866	1.007
	0.03	.	.	.	9	0.066	0.019
<u>Tauranga Group</u>							
	<0.03	.	.	8.2	<2	0.099	0.083
	<0.03	.	.	2.5	4	0.127	0.036
	0.10	.	.	1.9	<2	0.549	0.674
	0.30	.	.	4.4	12	0.929	1.380
	<0.03	.	.	.	<2	0.019	0.047
	1.80	.	.	3.2	<2	0.803	0.920
	0.37	.	.	2.7	101	1.095	1.220
	0.95	0.36	0.08	1.7	659	1.736	0.493
	2.48	.	.	2.9	<2	0.709	0.689
	2.53	.	.	2.1	<2	1.263	1.277
	1.00	0.68	0.03	2.8	78	1.046	0.432
	0.88	.	.	2.4	28	0.495	0.122
	0.05	.	.	.	63	0.547	0.068
	<0.05	0.25	<0.01	.	<2	.	0.012
	<0.03	.	.	4.7	17	0.295	0.205
	0.25	0.70	0.04	.	598	1.564	0.133
	0.86	.	.	0.9	4440	1.771	1.561
	1.31	62.00	0.82	1.8	1060	1.803	1.603
<u>Ignimbrite</u>							
	0.03	.	.	3.0	7	0.081	0.014
	0.79	.	.	7.8	<2	0.010	0.005
	0.21	.	.	.	43	0.133	0.043
<u>Kiwitahi Andesite</u>							
	<0.030	.	.	8.0	<2	0.008	0.007

Abs.400uf /cm	Abs.400f /cm
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0.001	0.001
0.003	0.001
0.003	0.000
0.003	0.001
0.067	0.005
0.009	0.002
0.036	0.074
0.029	0.009
0.163	0.189
0.043	0.001

0.031	0.012
0.100	0.010
0.080	0.098
0.182	0.269
0.004	0.008
0.157	0.168
1.148	1.329
1.486	0.084
0.078	0.074
0.135	0.138
0.373	0.065
0.408	0.008
0.353	0.017

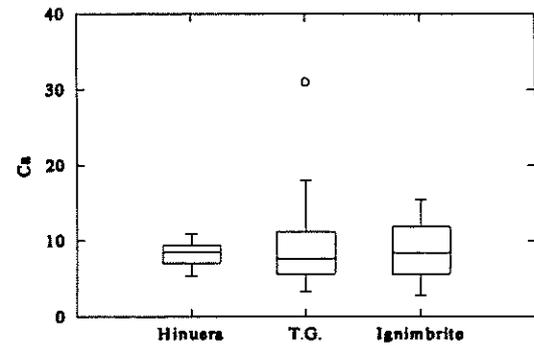
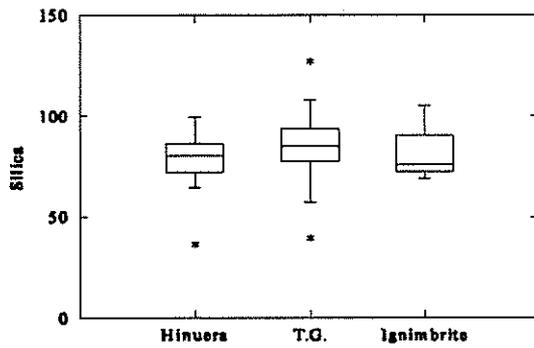
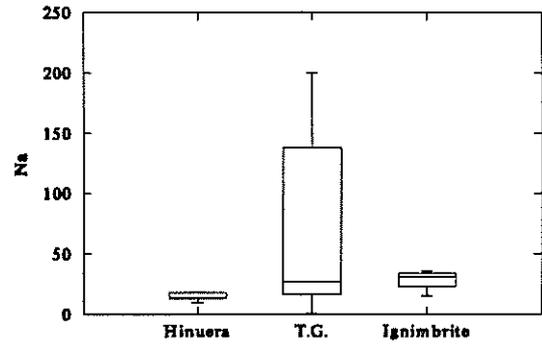
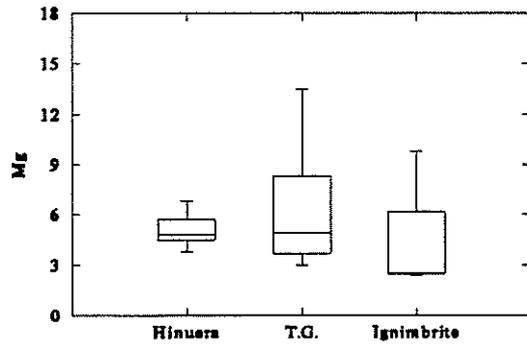
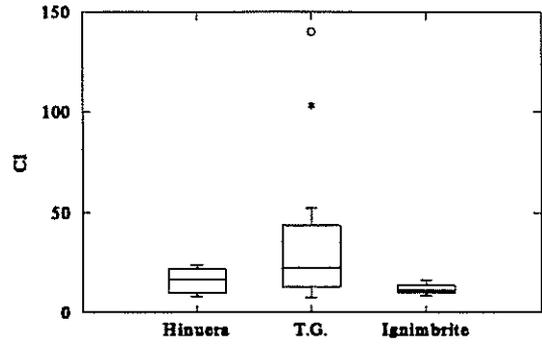
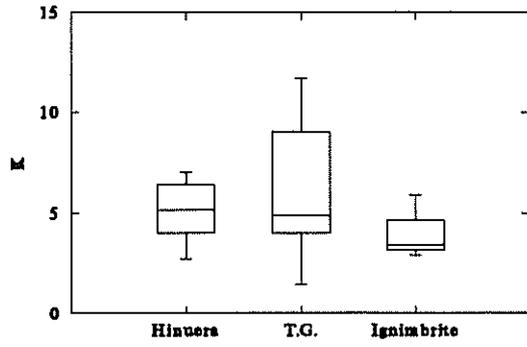
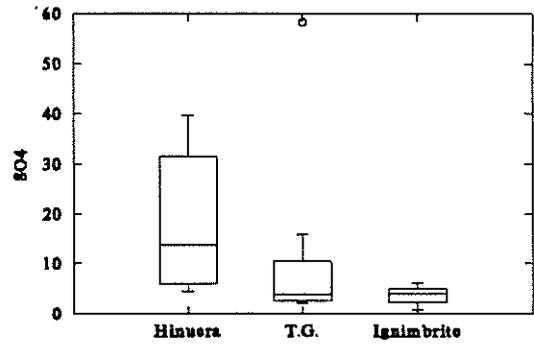
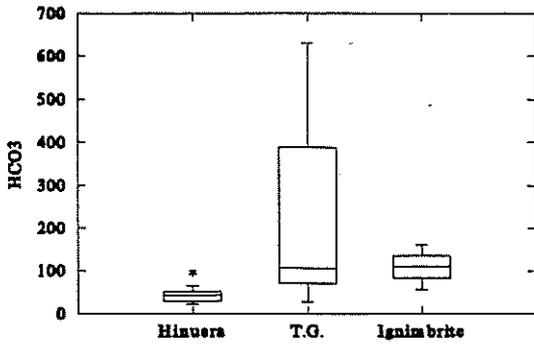
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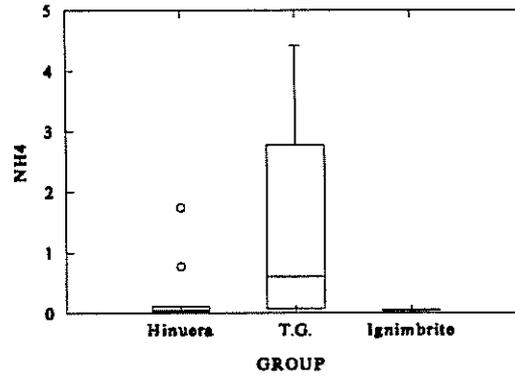
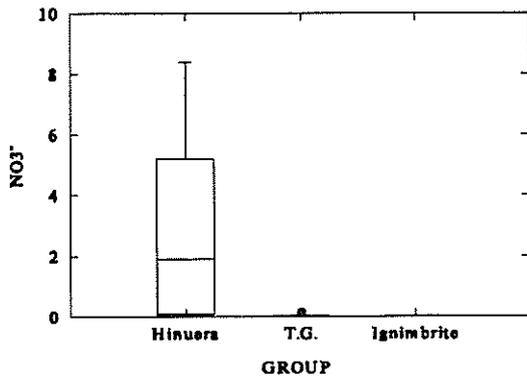
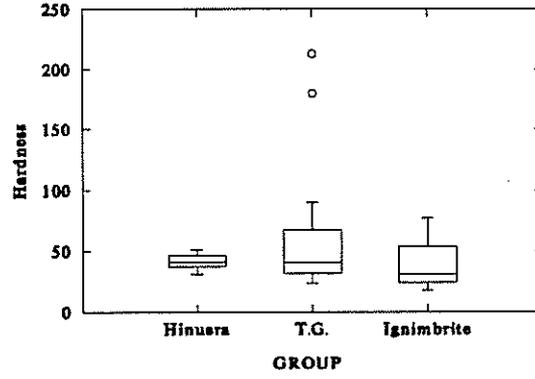
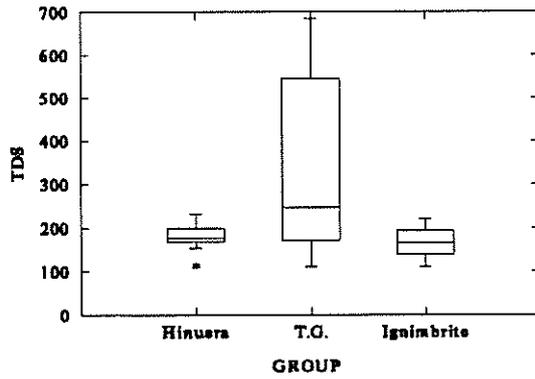
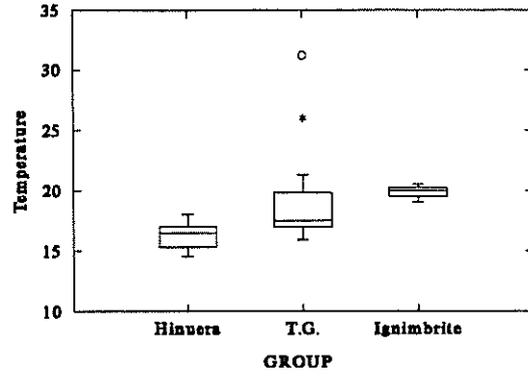
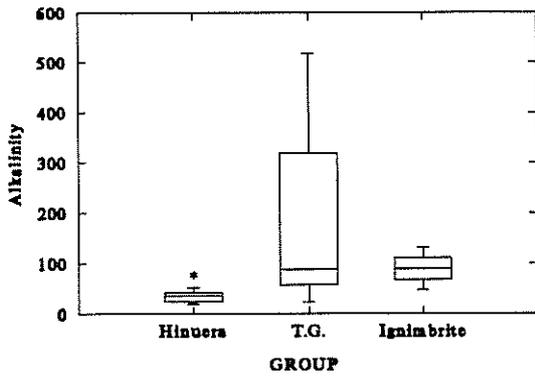
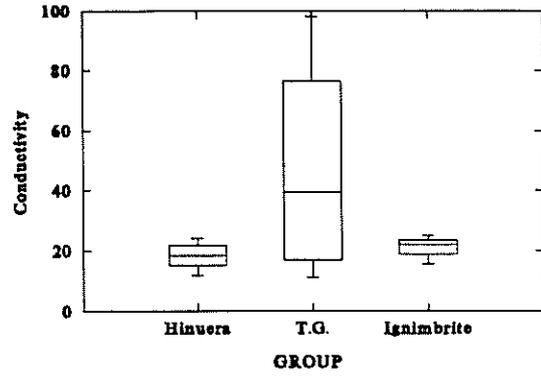
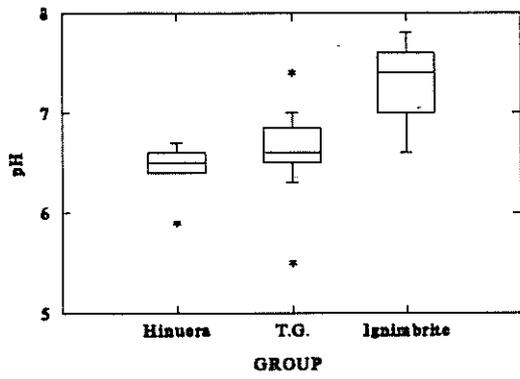
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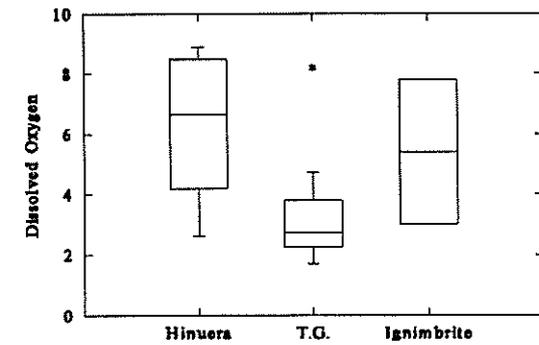
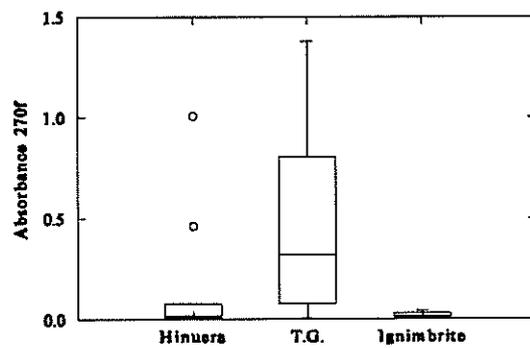
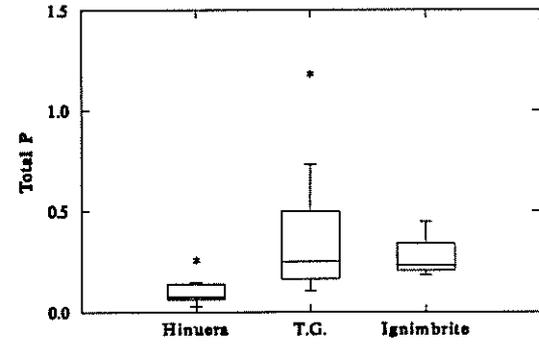
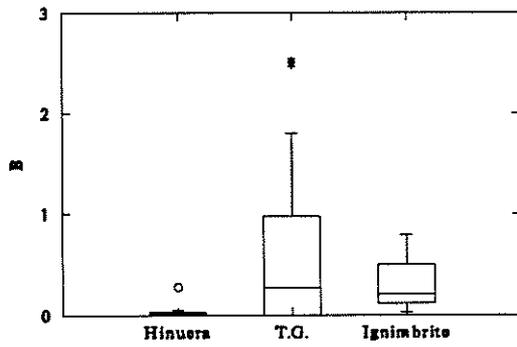
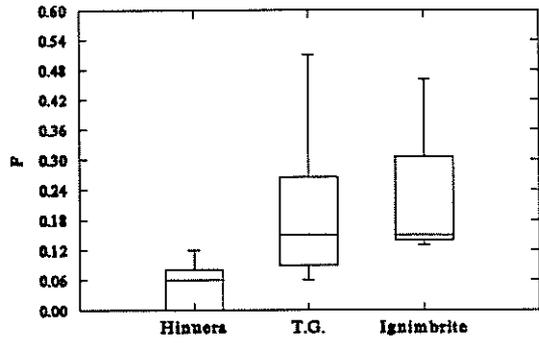
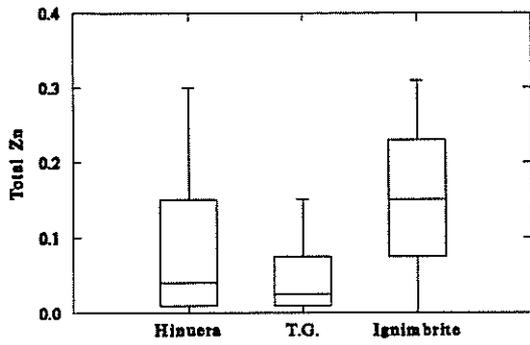
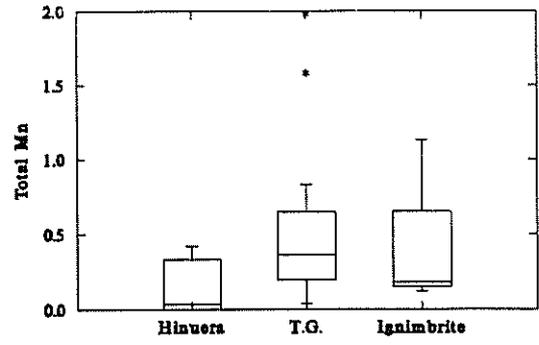
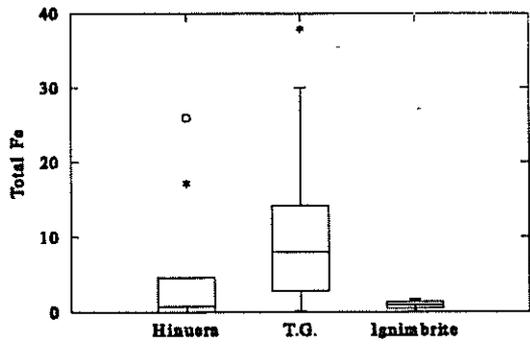
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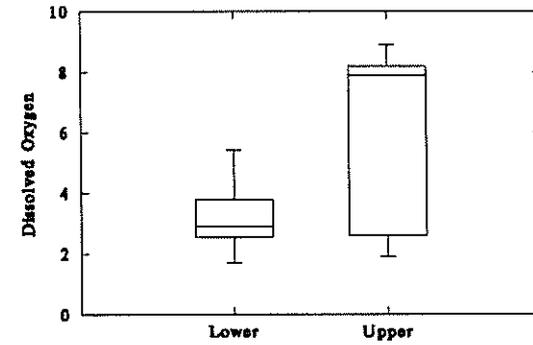
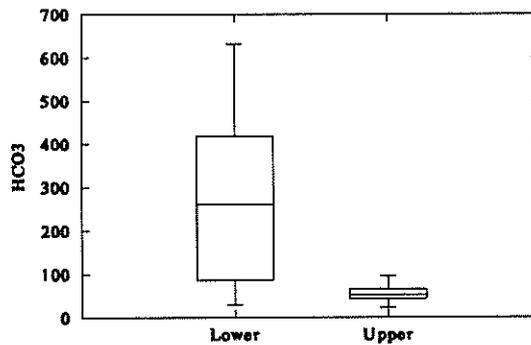
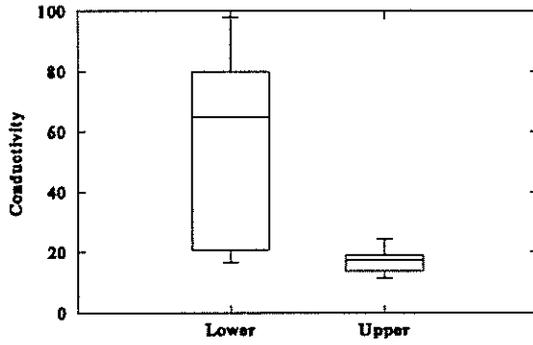
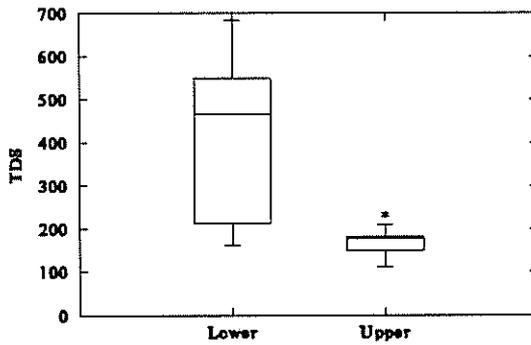
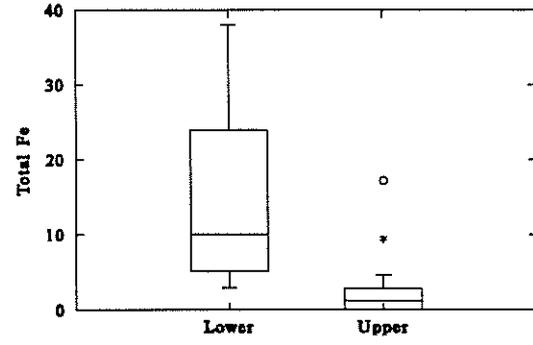
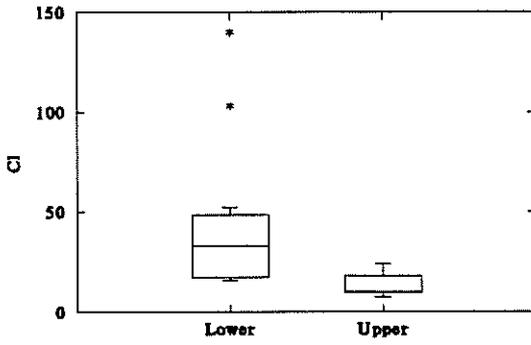
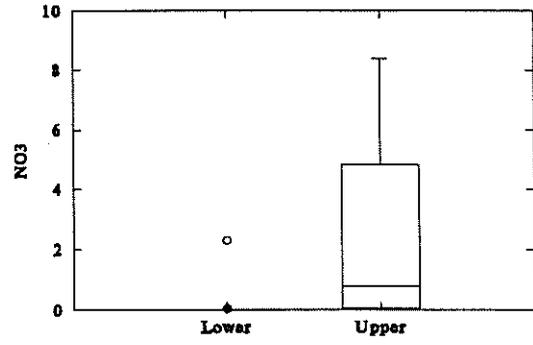
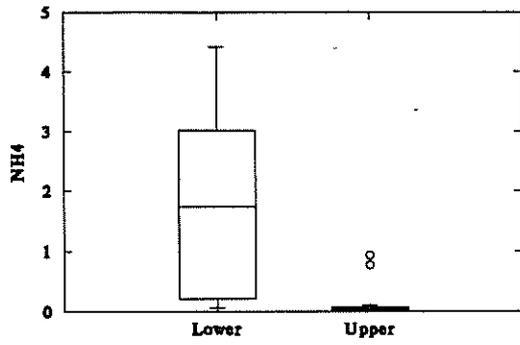
Ionic ratios of groundwater from the Piako catchment.

GEOLOGY	WELL NUMBER	Na : Cl	Mg : Ca	Na : K	(Ca+Mg) : (Na+K)
<u>Hinuera Formation</u>					
	5294	1.788	0.942	4.950	0.991
	4743	2.252	0.772	3.498	1.196
	4999	2.097	0.789	3.350	1.143
	5274	0.859	0.842	3.507	1.171
	5121	1.194	1.015	5.826	0.832
	2887	1.092	0.931	4.373	1.546
	4996	1.228	1.232	9.353	1.196
	5384	1.569	1.182	5.318	0.649
	4993	1.712	1.409	7.695	0.743
	5043	1.758	1.270	5.794	1.786
	mean	1.555	1.039	5.366	1.125
<u>Tauranga Group</u>					
	2817	2.594	1.395	5.021	1.201
	5364	1.984	2.280	4.322	0.851
	4970	4.074	1.207	13.004	0.371
	5147	1.328	1.108	11.175	0.589
	4312	1.772	1.799	7.730	0.469
	4385	5.629	1.117	29.449	0.210
	4749	0.057	1.488	0.179	6.883
	4775	4.617	4.976	10.611	0.466
	4212	6.899	1.063	39.093	0.088
	4635	2.515	1.567	30.393	0.102
	5021	0.876	1.054	21.911	0.303
	4365	2.594	1.755	11.443	1.252
	4789	1.664	0.685	4.878	1.133
	5419	2.120	1.554	7.635	0.612
	5176	1.919	0.636	33.066	0.624
	5420	1.322	2.061	17.442	0.299
	4773	2.226	1.724	23.546	0.244
	5039	0.757	2.818	52.176	0.251
	mean	2.497	1.683	17.949	0.886
<u>Ignimbrite</u>					
	4750	2.787	1.472	4.381	0.425
	4751	3.406	0.471	21.110	0.376
	4788	4.230	1.049	15.505	1.097
<u>Kiwitahi Andesite</u>					
	5418	1.598	1.145	16.297	1.089









NB: Lower refers to the lower catchment on the northern side of the Morrinsville - Te Aroha road. Upper refers to the catchment south of this road.

Site	Map Ref.	Na ppm	K ppm	Ca ppm	Mg ppm	HCO ₃ ppm	Cl ppm	SO ₄ ppm	NO ₃ ppm
Miranda 1	S12:173-411	137	1.9	3.1	0.1	80	162.8	10	trace
Miranda 2	S12:174-410	152	0.3	3.3	0	79	190.2	7.5	0
Beck	T12:352-338	330	39.5	39.8	19.2	810	195.6	<2	12
Ngatea	T12:318-333	306	22.1	34.5	22.8	1060	62.7	<2	0
Netherton	T13:415-293	186	8.1	33	28.8	720	29.1	<2	16
Patetonga	T13:319-217	200	8.7	7.6	4.9	569	44.7	2.4	0
Chatfield 1	T13:354-095	142	8.2	12.7	8.6	418	38.9	3.5	0
Te Bogt 2	T13:389-084	203	29.9	21.5	11.1	640	36.5	<2	16
Chatfield 2	T13:358-079	67	3.9	13.6	8.9	250	16.5	<2	trace
Te Bogt 1	T13:386-076	222	27.2	19.9	11.8	700	43.7	<2	16
Suisted 1	T13:387-073	239	47	30.7	15.3	830	48.4	<2	16
Suisted 2	T13:388-072	234	46.7	29.1	14.9	790	46.1	<2	16
McLeod	T14:428-810	20	4.1	7	4.1	82	9.4	3	0
Parker	T14:594-756	43	2.9	2	1.2	100	8.8	<2	0
Crystal Spr	T14:601-756	110	11.9	16.3	8.6	360	17.2	<2	trace
Opal Spr	T14:601-756	110	11	17	12	372	19	1	trace
Totara Spr	T14:592-734	85	15.1	10.8	8.9	310	12.1	<2	0
Matamata	T14:545-729	63	7.6	13	9.2	240	13	<2	0
Wilson	T15:561-669	136	16.7	25.1	12.9	500	19	<2	0
Okoroire	T15:565-574	91	13.6	8.2	8.3	310	15.2	<2	0
Goodwin	T15:608-625	19	3.1	3.7	2.6	58	6.8	2	trace
Sommerville1	T15:571-561	88	12.7	7.9	7.1	320	12.7	<2	0
Sommerville2	T15:567-564	105	15.3	9.2	9.2	350	15.8	<2	trace

(from Jenkinson in prep.)

Site	SiO ₂ ppm	Li ppm	F ppm	B ppm	Cl:F	pH ppm	Cond. mS/m	Sample temp.	Na-K-Ca temp.	Si temp.
Miranda 1	53	0.2	0.53	4.32	307.2	8.7	103	56	102	75
Miranda 2	49	0.06	0.71	4.5	267.9	8.8	85	57	41.5	71
Beck	128	0.42	0.84	26.92	232.9	6.3	173	31.3	197	126
Ngatea	101	0.65	0.97	5.63	64.6	6.7	154	24.9	169	111
Netherton	111	0.42	1.01	1.29	28.8	6.8	107	31.1	137	117
Patetonga	127	0.39	0.98	2.48	45.6	7	94.3	33	150	126
Chatfield 1	108	0.28	0.33	1.8	117.9	6.8	78.7	26	153	115
Te Bogt 2	129	0.3	0.34	1.66	124.9	6.8	11.8	38.8	205	127
Chatfield 2	90	0.15	0.34	0.45	48.5	6.7	4.1	23	142	104
Te Bogt 1	116	0.29	0.35	1.92	124.9	6.7	12.4	37.6	196	120
Suisted 1	162	0.3	0.28	4.38	172.9	7.3	16.2	50.3	223	142
Suisted 2	165	0.29	0.3	4.08	153.7	6.9	14.8	43.9	224	144
McLeod	80	0.03	0.16	0.03	58.7	7	14.2	18.8	190	97
Parker	92	0.08	0.53	0.12	16.6	7.4	16	34	157	105
Crystal Spr	74	0.19	0.31	0.87	55.5	7.3	50.5	37.3	209	93
Opal Spr	48	n.d.	0.26	n.d.	73.1	7	53	-	174	70
Totara Spr	106	0.16	0.47	0.62	25.7	7.6	41.5	34	206	114
Matamata	98	0.12	0.36	0.56	36.1	7.4	33.8	32	177	109
Wilson	95	0.25	0.41	1.69	46.3	7.4	66.1	44.5	185	107
Okoroire	133	0.15	0.26	0.42	58.5	7.1	50.3	36.9	200	129
Goodwin	90	0.03	0.58	0.07	26.2	7.5	n.d.	22.9	182	104
Sommerville1	102	0.13	0.27	0.4	47	7.1	49.1	28.8	197	112
Sommerville2	135	0.18	0.24	0.52	65.8	7.1	56.6	34	200	130