Groundwater age and chemistry data report - Waingaehe and Ngongotaha Stream Calibration programme

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CONTENTS

FIGURES

TABLES

APPENDICES

EXECUTIVE SUMMARY

This study was initiated by Environment Bay of Plenty (EBOP) to understand groundwater - surface water interactions in the Lake Rotorua catchment as part of a larger study investigating nutrient loads to Lake Rotorua. The objective of this study is to sample groundwater and surface water in the Waingaehe Stream and Ngongataha Stream catchments for water quality and age dating to understand, in detail, interactions between the groundwater and the two streams. This report presents data collected to date within the stream calibration project. Detailed scientific interpretation of the data will be performed at a later stage after completion of data collection.

Sampling sites in the Waingaehe Stream catchment consist of recently drilled bores, springs that feed into the Waingaehe stream, and the Waingaehe Stream. Other sites sampled include two springs of Waitetahi Stream, and one sample from Ngongotaha Stream.

The age dating results at Waingaehe Stream indicate relatively young water (MRT 2-8 years) in the uppermost reaches of the stream, and old spring water (MRT 30 - several hundred years) lower down. This trend is in agreement with the old age (MRT 130 years) of the Waingaehe Stream water in its lower reaches at Te Ngae Road and indicates that the groundwater gained by Waingaehe Stream becomes older along its reach. This situation appears to be inverse to that of streams in the western catchment of Lake Rotorua that are related to the lava domes.

The Waingaehe Stream aquifer is very inhomogeneous. Cold and thermal, old and young water springs can be found very close to each other. The thermal waters are all old (MRT >100yrs). The mean residence time of the water in the studied bores also shows high diversity, from 6 years in WB-1 to 225 years in WB-3.

Waitetahi Springs have young water with mean residence times of 2-5 years. This is in agreement with other waters found in this area and indicates that Waitetahi springs are related to the lava dome hydrogeology.

The trends in regard to the nutrients are similar to the other parts of the Lake Rotorua catchment:

- Dissolved reactive phosphate is low in young water and elevated in old water
- Nitrate is high in younger water, low in old water, and completely absent in old anoxic water

However, nitrate concentrations in the young groundwater at Waingaehe catchment with up to 10 mg/L are much higher than the groundwater of the western Lake Rotorua catchment of about 2 mg/L. Much higher nitrate concentrations may be a result of the more recent land use intensification. Such high nitrate increases from recent land use intensification may not yet be observed in the western catchment because most investigated water samples have mean residence times > 20 years and therefore would not yet show this increase. The detailed Waingaehe catchment study may therefore be giving an early warning that more recent land use intensification in the western catchment of Lake Rotorua could also be increasing nitrate concentrations more significantly than delineated from the measured data so far. Because of the large water contributors in the western catchment, this could cause the ultimate nitrate loading to Lake Rotorua to be significantly higher than that predicted by the current nitrogen prediction model (Morgenstern and Gordon, 2006). The current prediction model has not yet taken into account more recent land use changes which may be more significant than originally thought.

It is recommended that a similar detailed study of groundwater ages be performed in the western catchment, in the area of the Mamaku ignimbrite where the largest water sources emerge. The study should involve young waters (<10 years) so that the effects of most recent land use changes become visible. It is important to assess the potential nitrate increase from recent landuse intensification in the Mamaku ignimbrite of the western catchment, because this has the potential for the most dramatic increases in nitrogen loading to Lake Rotorua.

At the same time, phosphate concentrations should be investigated with the availability of younger water in such a study, to see if land use phosphate has started to leach into the groundwater, or if it is still absorbed by the soil. Wells ‘Murphy’ and ‘site 31’ in Reeves et al. (2005), which have high dissolved reactive phosphate, might indicate that leaching of land use phosphate into the groundwater has occurred already.

KEYWORDS

Lake Rotorua catchment, Waingaehe Stream, groundwater dating, tritium, CFCs, SF_6, groundwater chemistry and nutrient concentration.

1. INTRODUCTION

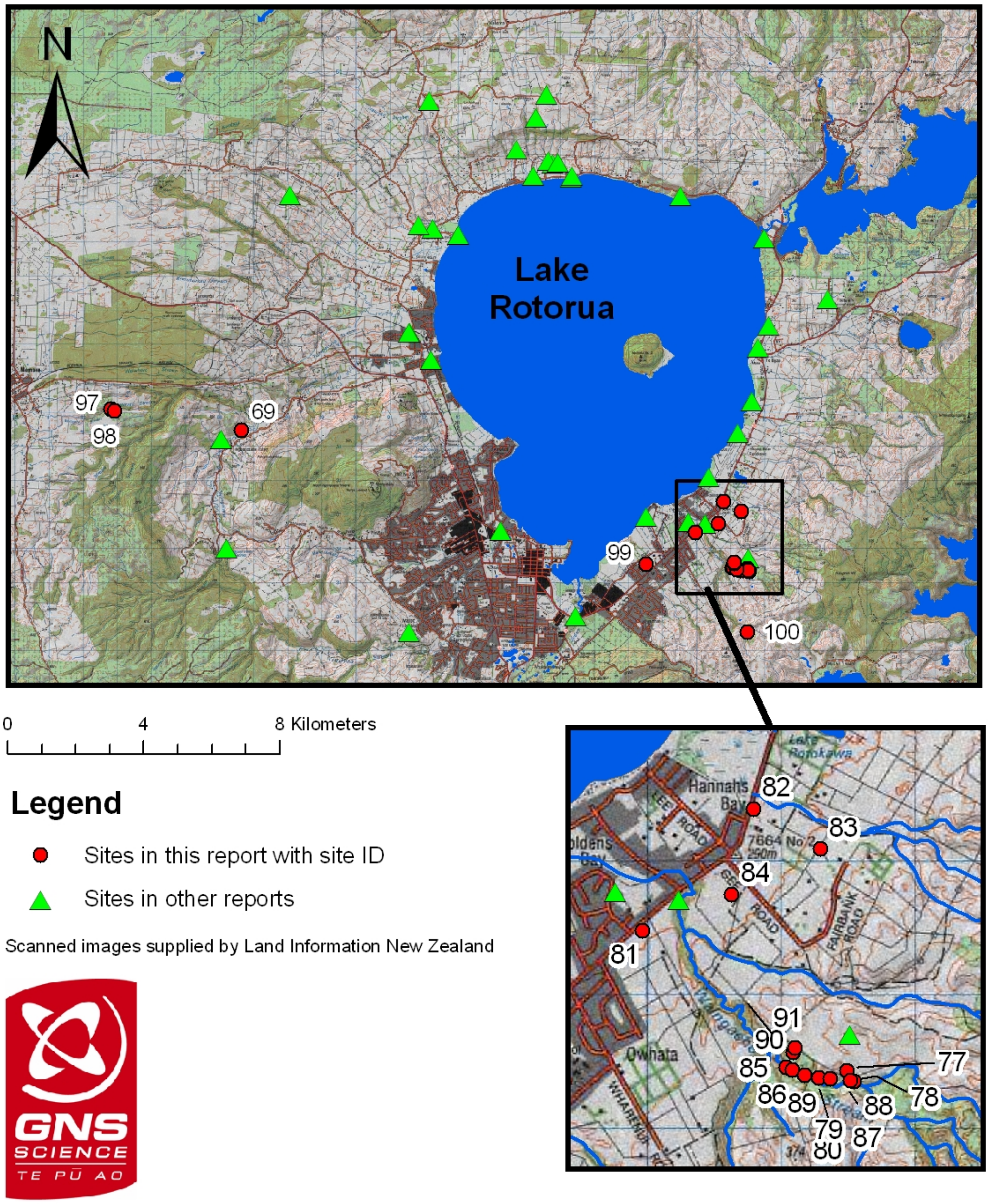
This study was initiated by Environment Bay of Plenty (EBOP) to understand groundwater - surface water interactions in the Lake Rotorua catchment as part of a larger study investigating nutrient loads to Lake Rotorua. The objective of this study is to sample groundwater and surface water in the Waingaehe Stream and Ngongataha Stream catchments for water quality and age dating to understand, in detail, interactions between the groundwater and the two streams. The data collected from this study will be used in conjunction with other EBOP data collection programmes to develop groundwater flow models, groundwater age models, and nutrient flux models to assist EBOP in managing nutrient inputs in the Lake Rotorua catchment. This report presents data collected to date within the stream calibration project. Detailed scientific interpretation of the data will be performed at a later stage after completion of data collection.

2. SAMPLING SITES AND BORE DATA

Sampling sites were selected by EBOP and GNS Science staff. Sampling sites in the Waingaehe Stream catchment consist of recently drilled bores, springs that feed into the Waingaehe stream, and the Waingaehe Stream. Other sites sampled include two springs of Waitetahi Stream, and one sample from Ngongotaha Stream. Geographic data and the descriptions of the sampling sites are summarized in Table 1. NZ map grid eastings and northings were measured by a Garmin handheld GPS in the field at the time of sampling except for data with grey highlight. Eastings and northings for the grey highlighted sites (Table 1) were located by EBOP using aerial photos because these sites could not be surveyed by GPS at the time of sampling due to limited GPS coverage in the steep gullies and thick bush cover. Sampling sites are shown in Figures 1 and 2 in relation to previous sampling sites (Morgenstern et al, 2004). Site photographs are listed in Appendix 1.

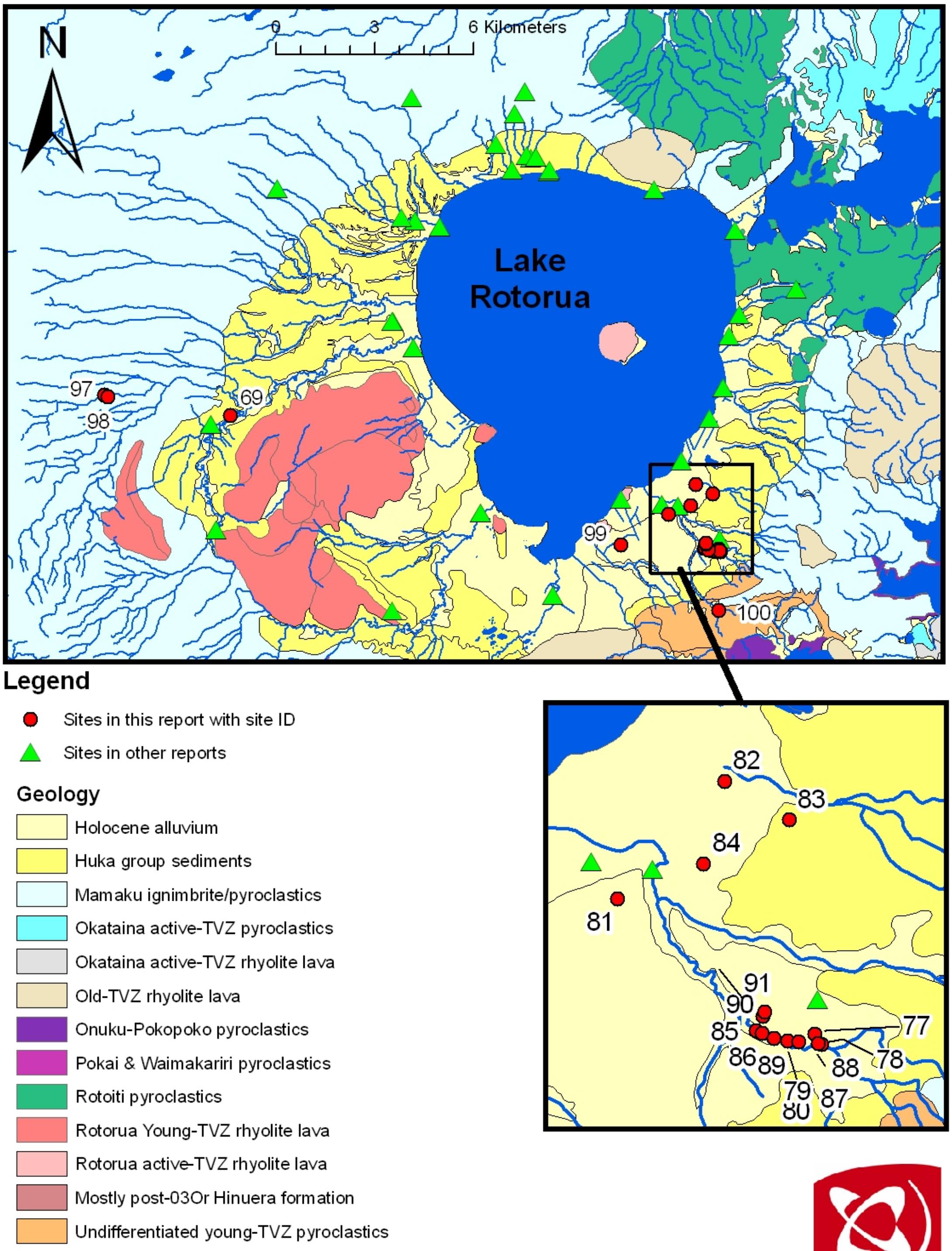
Table 1. Sampling site details. Eastings (E) and Northings (N) in grey highlight were supplied by Environment of Bay of Plenty.

#	Code	ID	remark	E	N
100	WST 1	Waingaehe stream, upper	stream near Wharenui station	2801464	6333547
77	WSP 1	Waingaehe spring 1 WQ 120142	start of true right stream branch, in rubbish dump gully surrounded by willows	2801480	6335430
78	WSP 2	Waingaehe spring 2 WQ 120143	start of visible flow in main stream bed	2801530	6335350
88	WSP 7	Waingaehe spring 7	main stream channel, true left bank	2801505	6335359
87	WSP 6	Waingaehe spring 6 WQ 120146	main stream channel, true left bank, spring opposite WSP-3	2801353	6335372
79	WSP 3	Waingaehe spring 3 WQ 120140	main stream channel, seeps from true right bank	2801270	6335380
80	WSP 3	Waingaehe spring 3 WQ 120140	main stream, seeps from true right bank, individual spring emerging from confining layer	2801270	6335380
89	WSP 8	Waingaehe spring 8 WQ 120148	main stream channel, true right, warm	2801163	6335396
86	WSP 5	Waingaehe spring 5 WQ 120138	warm stream from cave, true right	2801070	6335440
85	WSP 4	Waingaehe spring 4 WQ 120136	spring in main channel 30m downstream of WSP-2, true left	2801026	6335455
90	WSP 9	Waingaehe spring 9 WQ 120149	bog with twin blackberry springs, cold spring in gully, true right	2801080	6335570
91	WSP 10	Waingaehe spring 10 WQ 120150	above WSP9 bog, true right	2801090	6335600
81	WB 1	Waingaehe, EBOP bore 10746	bore ran dry	2799950	6336480
82	WB 2	Waingaehe, EBOP bore 10750		2800780	6337390
83	WB 3	Waingaehe, EBOP bore 10745		2801280	6337090
84	WB 4	Waingaehe, EBOP bore 10961	water was still pink from ESR dye-experiments, foaming	2800620	6336750
99	WB 5	Waingaehe, EBOP bore 10748	Rugby league grounds	2798500	6335549
97	Wait W	Waitetahi Spring west	691 Dansey road, main water supply spring, in gully next to deer fence	2782807	6340099
98	Wait E	Waitetahi Spring east	691 Dansey road, spring in west gully that supplies farm	2782900	6340042
69	Ngst Eg	Ngongotaha Stream at Egger	865 Paradise Valley road, site on bend in stream approx 200m NW of house	2786637	6339473



Scanned images supplied by Land Information New Zealand

Figure 1. Sampling site locations.



Original map scale 1:250,000

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

Topographic data supplied by Eagle Technology under licence by LINZ.

Figure 2. Geological map of sampling site locations.

3. METHODS OF SAMPLING AND ANALYSIS

3.1 WATER DATING

Water samples for tritium analysis were collected in 1.1 litre Nalgen bottles. Samples for CFC and SF_6 measurements were collected in such a way as to strictly prevent contact of the water with air. Glass bottles with 0.2 litre volume were used for CFCs, and 1.1 litre bottles for SF_6. All springs and bores were sampled using a Bennet pump that is free of plastic material, and nylon tubing. Bottles were quickly screw-sealed while submerged below the water surface to eliminate air contamination. SF_6 bottles were capped with nylon seals, and CFC bottles were sealed with aluminium washers. The bores were purged prior to sampling using a Grundfos pump.

The tritium samples were analysed using the GNS Science state-of-the-art tritium measurement system with extremely high detection sensitivity for the low tritium concentrations prevailing in New Zealand's waters (Morgenstern and Taylor, 2005). The detection limit is 0.03 TR, using ultra low-level liquid scintillation spectrometry and electrolytic enrichment prior to detection. One litre of water is required for analysis. Reproducibility of a standard enrichment is 2%, and an accuracy of 1% can be achieved via deuterium calibrated enrichment (Taylor 1994). Gas concentrations (CFCs, SF_6, Ar, N_2) were analyzed at GNS Science by gas chromatography.

3.2 WATER CHEMISTRY

Eleven springs, five bores, and two stream sites were sampled for water quality parameters between 9 and 14 May 2005. Sampling methodology and the bottles collected at each site varied depending on the analyses required (Appendix 5) and type of site. In most cases, the field parameters electric conductivity, pH, water temperature, dissolved oxygen, turbidity and oxidation – reduction potential were measured in the field with a portable Yeo-Kal 611 multiparameter meter prior to collecting the sample.

Spring samples were collected at the point they emerge from the aquifer using a Bennet pump. Stream samples were collected from the middle of the stream using a grab technique. Water samples from bores were collected by purging the bore of at least three casing volumes using a portable Grundfos MP1 submersible pump, and then using a Bennet pump to collect the water sample. Water samples that required filtering were filtered in the field using 0.45μm filter paper. The bottles for nutrients (Table 2) were supplied by R. J. Hill laboratories with the H_2SO_4 preserve already in the appropriate bottle. Three drops of HNO_3 was added to the appropriate GNS Science supplied bottle for anions/cations (Table 2). All samples were chilled to less than 4 ^{o}C during transport.

Water samples were sent to their respective laboratories as soon as possible after the sampling. Two laboratories were used to analyse the water depending on the analyses suite.

Table 2. Bottles collected for analyses.

Analyses	**Bottles collected**
Nutrients	100 ml filtered, 100 ml raw, 250 ml raw with H_2SO_4 , all chilled
Anions/cations	100 ml filtered, 100 ml filtered + HNO_3, 250 ml raw, all chilled

- **Nutrients**

Total ammoniacal-N, total kjeldahl Nitrogen (TKN), nitrate-N + nitrite-N (TON), nitrate-N, nitrite-N, dissolved reactive phosphorus and total phosphorus were analysed at R.J. Hill labs.

- **Anions/cations**

Alkalinity (as HCO_3), pH, sodium, potassium, calcium, magnesium, iron (dissolved), manganese (dissolved), silica (as SiO_2), fluoride, chloride, bromide, sulphate, and conductivity were analysed at GNS Science, Wairakei.

4. RESULTS

4.1 AGE DATING

Table 3 summarizes the measured field parameters, and the tritium, CFC and SF_6 analysis results together with the calculated recharge temperatures, excess air concentrations and age distribution results. Raw CFC and SF_6 data are given in Appendix 3.

None of the samples from the upper Waingaehe Stream and Springs are contaminated in CFC or SF_6. Slight CFC contamination occurs only at some bores within the farming area.

Recharge temperatures and excess air concentrations are shown in Figure 3. Excellent agreement between the repeat samples indicates good sampling performance. All recharge temperatures are within the expected narrow range 11-15 °C. The results indicate highly negative excess air concentration for bore WB-3. This is the only water sample indicative of strong anaerobic conditions in the aquifer. Therefore, the calculated negative excess air concentration can be related to gas losses from the water due to excessive microbial gas production. Gas losses can occur in the aquifer, or during sampling (excessive gas bubbles in the water were observed during sampling). Significant denitrification in the aquifer is considered unlikely as such a process, this would have increased the N_2 concentration.

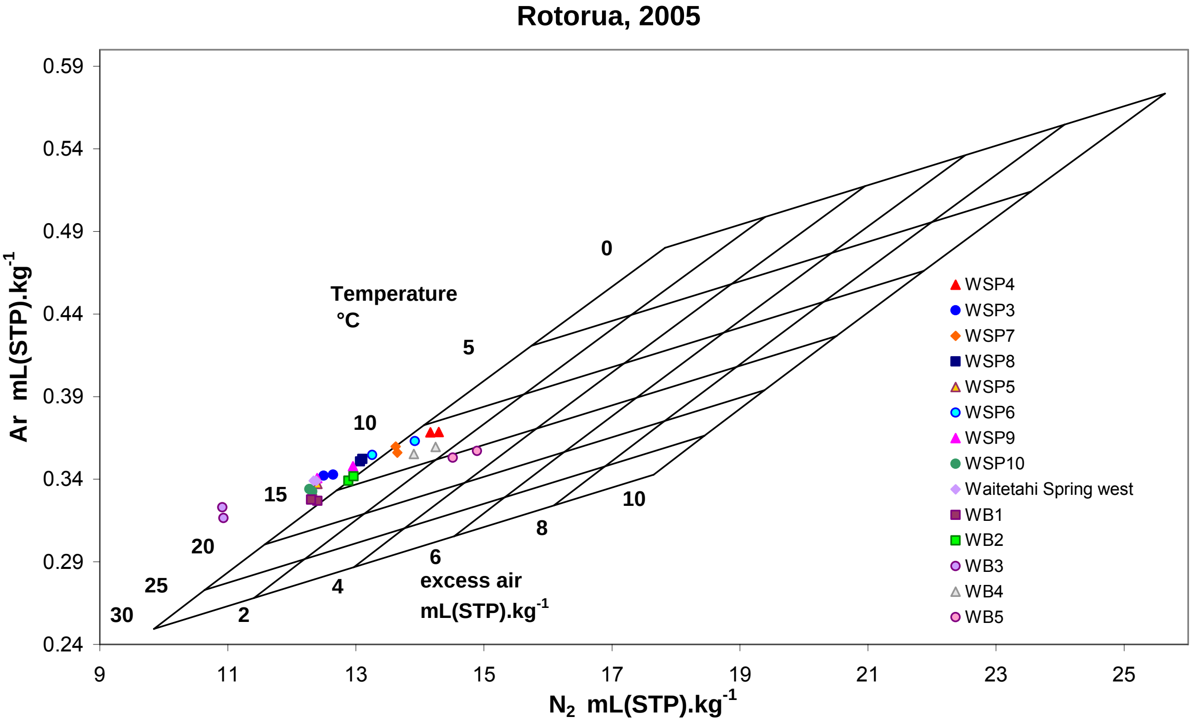


Figure 3. Calculated recharge temperatures and excess air concentrations.

Table 3. Field parameters and water dating results with age interpretations. Orange highlighted temperatures indicate raised temperature due to geothermal water. For dissolved oxygen (DO), brown highlights indicate low DO but without onset of anaerobic condition (absence of Fe and Mn), and red highlight indicates anaerobic condition (Fe and Mn present) with the possibility of CFC degradation in the aquifer (see Appendix 1). TROT are the tritium laboratory code numbers. TR (tritium ratio) corresponds to one tritium atom per 10^{18} hydrogen atoms. The radioactivity equivalent for one TR in one kg of water is 0.118 Bq. ±TR is the one sigma standard measurement error. pptv is one part per trillion by volume or 10^{-12}. For CFCs, red highlight indicates high contamination above natural equilibrium (Fig. 4). For age interpretation, the Exponential Piston Flow model was used (see Appendix 2). E%PM is the fraction of mixed flow within the total flow volume. MRT is the mean residence time in years.

#	Code	Date	pH	cond	temp	ORP	turb	DO	TROT	TR	±TR	SF6	±	CFC11	±	CFC12	±	Recharge	±	excess air	±	E%PM	E%PM	MRT
				uS/cm	°C	mV	NTU	mg/l				pptv		pptv		pptv		temp [oC]		mL(STP)/kg		estimate	determin	yrs
100	WST 1	14/05/05	6.87	88	10.4	110	20	8.5	428	1.53	0.04											100		**2**
77	WSP 1	11/05/05	na	109	11.1	278	1.2	na	418	1.39	0.04											80		2.5
78	WSP 2	11/05/05	6.18	91	10.2	282	4.2	5.5	419	1.25	0.05											90		8
88	WSP 7	12/05/05	6.21	96	10	46	3.3	5.6	424	0.967	0.030	2.17		113	2.6	248	4.9	12	0.6	0.2	0.3		**80**	**42**
87	WSP 6	12/05/05	6.31	75	10.5	86	1.9	5.9	423	0.159	0.021	0.07		5.5	0.2	13.7	0.4	11.7	0.1	0	0.6		**90**	**285**
79	WSP 3	11/05/05	6.52	104	11.1	277	1.7	6.4																
80	WSP 3	12/05/05	na	na	na	na	na	na	420	1.26	0.04	2.88		158	0.2	341	1.0	12.6	0.1	-1	0.2		**35**	**28**
89	WSP 8	12/05/05	5.58	178	20.3	7	3.1	1.5	425	0.008	0.017	0.24		3.3	0.0	10.3	0.5	12	0.2	-0.5	0	80		**250**
86	WSP 5	12/05/05	6.68	180	19.8	107	10.7	3.1	422	0.136	0.019	0.9		35.6	0.1	85.4	1.2	13.6	0.5	-0.9	0.1	80		**190**
85	WSP 4	12/05/05	6.22	116	13.9	134	1.8	4.5	421	0.116	0.021	0.13		8.5	0.9	18.7	2.1	11.3	0.2	0.7	0.2		**100**	**600**
90	WSP 9	12/05/05	6.51	206	23.6	-28	1.4	1.1	426	0.085	0.021	0.07		11.7	0.0	20.7	0.6	12.5	0.1	-0.9	0.5		**100**	**700**
91	WSP 10	12/05/05	6.06	143	14.1	213	4.4	6.7	427	1.43	0.05	3.54		248	2.6	521	0.2	13.9	0.3	-0.9	0.1		40	42
81	WB 1	11/05/05	6.1	145	12.2	250	>600	8.1	430	1.28	0.04	5.91		265	3.5	591	4.5	15.4	0.3	-0.3	0.2		45	**6**
82	WB 2	11/05/05	6.11	235	13.4	263	10.1	5.1	431	1.44	0.04	5.01		237	2.1	569	3.5	14	0.3	0	0		40	42
83	WB 3	11/05/05	6.51	139	12.6	257	7.3	1.1	432	0.025	0.022	0.19		2.2	1.1	6.4	3.2	13.3	1	-2.8	0.4		80	225
84	WB 4	11/05/05	5.72	536	16.4	254	11.2	2.5	433	1.19	0.04	foaming		194	0.4	502	0.6	13.3	0	1.2	0.3		50	30
99	WB 5	14/05/05	6.08	117	14.8	151	>600	2.1	434	1.38	0.06	4.07		181	1.5	617	4.6	15.5	0.1	2.7	0.4		40	37
97	Wait W	14/05/05	5.57	72	9.6	149	1.6	6.5	435	1.27	0.04	5.55		441	2.8	811	2.5	12.8	0.1	-1.2	0.1	70		5
98	Wait E	14/05/05	5.66	72	9.8	146	0.9	5.6	436	1.37	0.04													2.5
69	Ngst Eg	15/05/05	6.51	48	8.23	334	3.9	10.7	437	1.13	0.05												70	12 - 32

The methodology for age dating of groundwater is described in Appendix 2 and 4. The fraction of mixed (exponential) flow within the total flow could in some cases be determined from the measurement results. In all other cases, it was estimated according to information from similar hydrogeologic settings.

The age dating results at Waingaehe Stream indicate relatively young water (MRT 2-8 years) in the uppermost reaches of the stream, and old spring water (MRT 30 - several hundred years) lower down. This trend is in agreement with the old age (MRT 130 years) of the Waingaehe Stream water in its lower reaches at Te Ngae Road (Morgenstern et al. 2004) and indicates that the groundwater gained by Waingaehe Stream becomes older along its reach. This situation appears to be the inverse to that of streams in the western catchment of Lake Rotorua that are related to the lava domes. For example for Utuhina Stream, the uppermost springs supply the oldest water while the stream gains significantly younger water in its lower reaches.

The Waingaehe Stream aquifer is very inhomogeneous. Cold and thermal, old and young water springs can be found very close to each other. The thermal waters are all old (MRT >100yrs).

The mean residence times of the water in the studied bores also shows high diversity, from 6 years in WB-1 to 225 years in WB-3.

Waitetahi Springs have young waters with mean residence times of 2-5 years. This is in agreement with other waters found in this area and indicates that Waitetahi springs are related to the lava dome hydrogeology.

The information for the single sample from Ngongotaha Stream is too sparse to resolve ambiguity. This stream water has a mean residence time of 12-32 years.

4.2 NUTRIENTS AND CHEMISTRY

Nutrient and chemical results are summarized in Table 4 with raw results and methods in Appendix 5. Detailed interpretation of the results will be given in a separate report.

The trends in regard to the nutrients are similar to the other parts of the Lake Rotorua catchment:

- Dissolved reactive phosphate is low in young water and elevated in old water
- Nitrate is high in younger water, low in old water, and completely absent in old anoxic water

However, nitrate concentrations in the young groundwater at Waingaehe catchment with up to 10 mg/L are much higher than the groundwater of the western Lake Rotorua catchment of about 2 mg/L. Much higher nitrate concentrations may be a result of the more recent land use intensification. Such high nitrate increases from recent land use intensification may not yet be observed in the western catchment because most investigated water samples have mean residence times > 20 years and therefore would not yet show this increase. The detailed Waingaehe catchment study may therefore be giving an early warning that more recent land use intensification in the western catchment of Lake Rotorua could also be

Table 4. Chemistry results. Original reports and analysis methods are listed in Appendix 5.

#	Code	Date	NH_4-N	TKN	TON	NO_3-N	NO_2-N	DRP	TP	Alkalinity	pH	temp [°C]	Na	K	Ca	Mg	Fe	Mn	SiO2	F	Cl	Br	SO4
			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L (HCO3)	at analysis		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			RJ Hill laboratory results							GNS water/gas laboratory results													
100	WST 1	14/05/05	< 0.01	0.4	2.48	2.48	< 0.002	0.02	0.077	20	7.07	17	9.5	5.5	3.3	1.5	0.02	<0.005	72	0.05	5.4	<0.04	11.3
77	WSP 1	11/05/05	0.02	< 0.1	4.59	4.59	< 0.002	0.018	0.018	23	6.63	15	8.4	5.7	6.5	2.3	<0.02	<0.005	68	0.043	4.4	<0.04	12.8
78	WSP 2	11/05/05	< 0.01	0.1	1.92	1.92	< 0.002	0.048	0.061	28	6.4	16	9.9	4.3	4.1	2.3	<0.02	0.035	73	0.067	5.7	<0.04	10
88	WSP 7	12/05/05	< 0.01	0.2	2.39	2.39	< 0.002	0.071	0.068	28	6.41	18	10.1	3.9	3.6	2.8	<0.02	<0.005	70	0.1	5.6	<0.04	10.2
87	WSP 6	12/05/05	< 0.01	< 0.1	0.653	0.653	< 0.002	0.102	0.104	27	6.65	20	9.6	2.3	2.6	2.1	<0.02	<0.005	71	0.16	4.6	<0.04	10.2
79	WSP 3	11/05/05	< 0.01	0.1	3.3	3.3	< 0.002	0.09	0.095	25	6.37	16	11.2	3.8	3.9	2.7	<0.02	<0.005	77	0.085	6.5	<0.04	9.8
80	WSP 3	12/05/05																					
89	WSP 8	12/05/05	< 0.01	< 0.1	0.114	0.113	< 0.002	0.125	0.123	72	6.72	19	23	5.1	4.7	4.4	<0.02	<0.005	95	0.42	14	<0.04	9.4
86	WSP 5	12/05/05	< 0.01	< 0.1	0.403	0.402	< 0.002	0.2	0.204	71	6.7	19	27	4.4	3.8	4.3	<0.02	<0.005	100	0.54	15.6	<0.04	8.8
85	WSP 4	12/05/05	< 0.01	< 0.1	0.569	0.569	< 0.002	0.127	0.122														
90	WSP 9	12/05/05	< 0.01	0.2	0.296	0.296	< 0.002	0.173	0.168	84	6.67	18	30	3.9	4.2	5	<0.02	<0.005	103	0.65	17.9	<0.04	9
91	WSP 10	12/05/05	< 0.01	< 0.1	7.5	7.49	< 0.002	0.045	0.043	23	6.3	19	11.4	6.9	7.2	3	<0.02	<0.005	78	0.047	9.2	<0.04	11.2
81	WB 1	11/05/05	< 0.01	0.6	5.87	5.86	0.003	< 0.004	0.104	23	6.22	15	10.2	4.8	8.7	3.8	0.04	0.035	66	0.11	8.6	<0.04	16.5
82	WB 2	11/05/05	0.07	< 0.1	9.35	9.35	0.002	< 0.004	0.008	22	6.04	15	8.4	4.6	23	4.4	<0.02	<0.005	49	0.054	19.5	<0.04	25
83	WB 3	11/05/05	0.1	0.3	0.024	0.003	0.021	< 0.004	0.136	44	6.24	14	12.4	1.3	3.9	1.6	14.2	0.54	81	0.14	7.7	<0.04	22
84	WB 4	11/05/05	< 0.01	< 0.1	10	10	0.005	0.013	0.018	28	5.96	14	29	15.1	31	15.9	0.03	0.036	61	0.022	92	0.76	38
99	WB 5	14/05/05	0.73	1.2	4.95	4.9	0.046	0.016	0.339	22	6.11	17	17.5	3.6	6	2.6	0.36	0.25	79	0.45	9.9	<0.04	16.9
97	Wait W	14/05/05	< 0.01	< 0.1	2.24	2.24	< 0.002	0.026	0.022	21	5.78	18	8.8	2.7	3.4	1.2	<0.02	<0.005	34	0.013	6.9	<0.04	4
98	Wait E	14/05/05	< 0.01	< 0.1	2.16	2.16	< 0.002	0.024	0.021	21	5.8	18	8.8	2.7	3.4	1.3	<0.02	<0.005	34	0.013	6.9	<0.04	4
69	Ngst Eg	9/05/05	0.03	0.2	0.611	0.608	0.002	0.043	0.057	23	6.71	16	7	2.8	2	1.1	0.06	0.013	50	0.042	4.4	<0.04	1.6

increasing nitrate concentrations more significantly than delineated from the measured data so far. Because of the large water contributors in the western catchment, this could cause the ultimate nitrate loading to Lake Rotorua to be significantly higher than that predicted by the current nitrogen prediction model (Morgenstern and Gordon, 2006). The current prediction model has not yet taken into account more recent land use changes which may be more significant than originally thought.

5. RECOMMENDATIONS

It is recommended that a similar detailed study of groundwater ages be performed in the western catchment, in the area of the Mamaku ignimbrite where the largest water sources emerge. The study should involve young waters (<10 years) so that the effects of most recent land use changes become visible. It is important to assess the potential nitrate increase from recent landuse intensification in the Mamaku ignimbrite of the western catchment, because this has the potential for the most dramatic increases in nitrogen loading to Lake Rotorua.

At the same time, phosphate concentrations should be investigated with the availability of younger water in such a study, to see if land use phosphate has started to leach into the groundwater, or if it is still absorbed by the soil. Wells ‘Murphy’ and ‘site 31’ in Reeves et al. (2005), which have high dissolved reactive phosphate, might indicate that leaching of land use phosphate into the groundwater has occurred already.

6. CONCLUSIONS

Age dating results in the Waingaehe Stream catchment indicate a pattern of young water contribution in the upper reaches, and old water contribution in the lower reaches of the stream. This is an inverse situation compared to the western catchment. The age dating results also indicate a very inhomogeneous aquifer. Old and young, cold and thermal water springs can be found very close to each other.

Waitetahi Springs in the western catchment have young water with mean residence times of 2-5 years. This agrees with other waters found in this area and indicates the water is related to the lava dome hydrogeology.

The chemistry data can only be fully understood in term of impacts of landuse on ground- and lake water quality in combination with the age data. Measured currently-low nutrient concentrations could be misleading if the investigated water is too old to reflect landuse impacts. High nitrate concentrations in the young groundwater at Waingaehe catchment may be a result of the more recent land use intensification, and may be an early warning for much higher nitrate increases than currently predicted occurring also in the western Lake Rotorua catchment. Most investigated water samples in the western catchment have mean residence times > 20 years and therefore would not yet show nitrate increases from recent landuse changes.

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8. ACKNOWLEDMENTS

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APPENDIX 1

PHOTOGRAPHS OF SAMPLING SITES.

WST-1: Upper Waingaehe stream near Wharenui station.

WSP-1: Start of true right stream branch, in rubbish dump gully surrounded by willows.

WSP-2: Start of visible flow in main stream bed.

WSP-3: Main stream, seeps from true right bank, individual spring emerging from confining layer.

WSP-4: Spring in main channel 30m downstream of WSP-2, true left.

WSP-5: Warm stream from cave, true right.

WSP-6: Main stream channel, true left bank, spring opposite WSP-3.

WSP-7: Main stream channel, true left bank.

WSP-8: Main stream channel, true right, warm.

WSP-9: Bog with twin blackberry springs, cold spring in gully, true right.

WB-2

WB-3

WB-4: Water was still pink from ESR dye-experiments, foaming.

WB-5: Rugby league grounds.

Waitetahi Spring West: Main water supply spring, in gully next to deer fence.

Waitehahi Spring East: Spring in west gully that supplies farm.

Ngongotaha Stream at Egger: Site on bend in stream approx 200m NW of house

APPENDIX 2

METHODOLOGY OF GROUNDWATER AGE DATING

TRITIUM, CFC AND SF_6 METHOD

Tritium is produced naturally in the atmosphere by cosmic rays, but large amounts were also released into the atmosphere in the early 1960s during nuclear bomb tests, giving rain and surface water high tritium concentration at this time (Figure 4). Surface water becomes separated from the atmospheric tritium source when it infiltrates into the ground, and the tritium concentration in the groundwater then decreases over time due to radioactive decay. The tritium concentration in the groundwater is therefore a function of the time the water has been underground. Additionally, detection of superimposed bomb tritium can identify water recharged between 1960 and 1975. Groundwater dating using tritium is described in more detail in Cook & Herczeg (1999) and Stewart & Morgenstern (2001).

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

Chlorofluorocarbons (CFCs) are entirely man-made contaminants. They were used for refrigeration and pressurising aerosol cans, and their concentrations in the atmosphere have gradually increased (Figure 4). CFCs are relatively long-lived and slightly soluble in water and therefore enter the groundwater systems with groundwater recharge. Their concentrations in groundwater record the atmospheric concentrations when the water was recharged, allowing determination of the recharge date of the water. CFCs are now being phased out of industrial use because of their destructive effects on the ozone layer. Thus rates of increase of atmospheric CFC concentrations slowed greatly in the 1990s, meaning that CFCs are not as effective for dating water recharged after 1990.

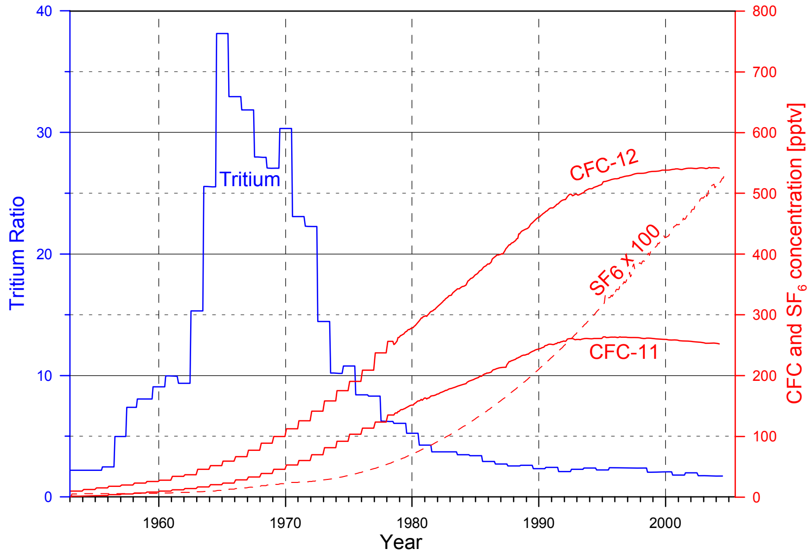

Figure 4. Tritium, CFC and SF_6 input for New Zealand rain. Tritium concentrations are in rain at Kaitoke, 40km north of Wellington (yearly averages), and CFC and SF_6 concentrations are for southern hemispheric air. TR=1 represents a 3H/1H ratio of 10-18, and 1 pptv is one part per trillion by volume of CFC or SF_6 in air, or 10^{-12}. Pre-1978 CFC data are reconstructed according to Plummer and Busenberg (1999), and scaled to southern hemisphere by factor 0.83 (CFC-11) and factor 0.9 (CFC-12). Post-1978 CFC data are from Tasmania. Pre-1970 SF_6 data are reconstructed (USGS Reston), 1970-1995 data are from Maiss and Brenninkmeijer (1998), and post-1995 data was measured in Tasmania.

Sulphur hexafluoride (SF_6) is primarily anthropogenic in origin, but can also occur in some volcanic and igneous fluids. Significant production of SF_6 began in the 1960s for use in high-voltage electrical switches, leading to increasing atmospheric concentrations (Figure 4). The residence time of SF_6 in the atmosphere is extremely long (800-3200 years). It holds considerable promise as a dating tool for post-1990s groundwater because, unlike CFCs, atmospheric concentrations of SF_6 are expected to continue increasing for some time (Busenberg and Plummer, 1997).

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

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

GROUNDWATER MIXING MODELS

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

Schematic groundwater flow situations are shown in Figure 5. The unconfined aquifer situation is described by the exponential model (EM). Flow lines of different length containing water of different age converge in the well or the stream, and the abstracted water has a wide range of ages with an exponential age distribution. The confined aquifer situation is described by the piston flow model (PM) with a narrow range of ages. The partly confined aquifer situation is described by the exponential-piston flow model (EPM). The free parameter is the fraction of exponential flow within the total flow volume (represented by E%PM, where the fraction is given in %), or the ratio η of the total flow volume to the volume of the exponential part. The water has a wide range of ages, but because part of the flow is piston flow, the age distribution has a minimum age (no water can be younger than the time necessary to pass through the piston flow part). The piston flow part can be represented by a partly confined flow with no vertical input of young water from the surface, or it can be represented by a significant unsaturated zone with vertical piston flow toward the water table and mixing of different ages below the water table.

As an example, the age distribution for the exponential-piston flow model for different fractions of mixed flow is shown in Figure 6 for water with a mean residence time of 50 years. Water with a high fraction of exponential flow of 90% has a wide range of ages, starting at 5 years and still significant contributions of old water with ages over 150 years. Despite the mean residence time of 50 years, the major part of the water is younger than 50 years. The water can therefore partly be contaminated before the mean residence time of 50 years has elapsed. About 2% of the water can already be contaminated after 5 years. With each further year, these young fractions accumulate, and increasingly contaminated water arrives at the spring or well. The total fraction of water within a certain age range can be obtained by integrating the age distribution over the specified age range. This is equal to the area below that part of the curve, with the total area below the whole curve being 100% water fraction. The fraction of water that is younger than a specified age is called the young water fraction (yf). The young water fraction younger than 55 years is about 80% in the example in Fig. 7 (hatched area).

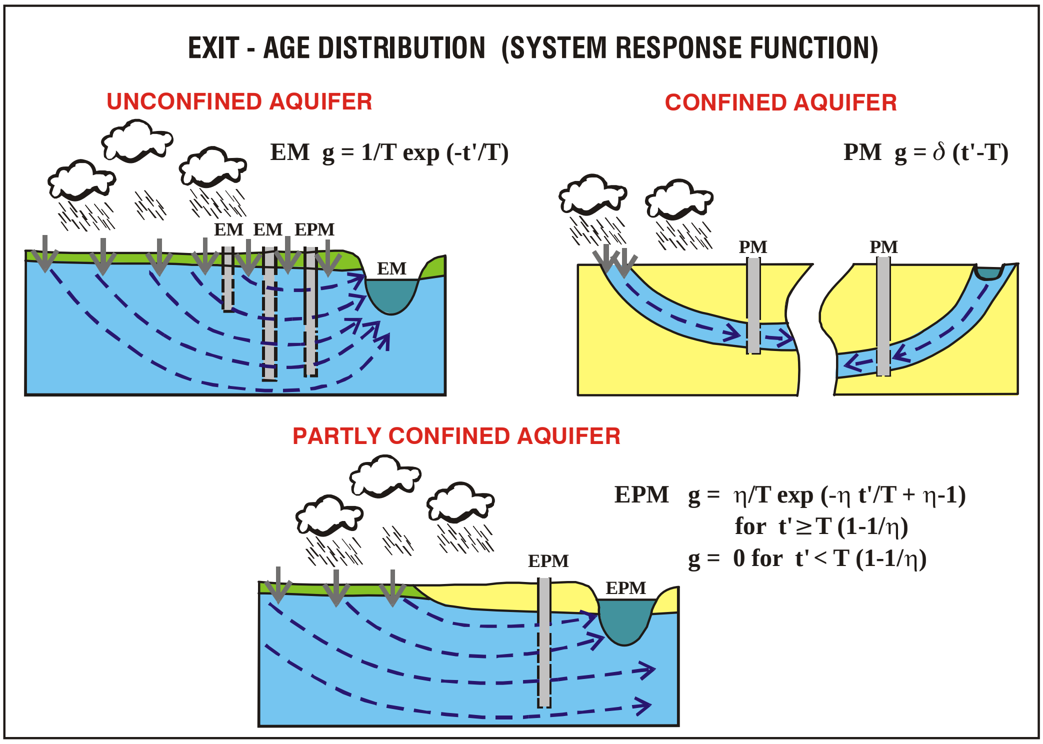

Figure 5. Schematic groundwater flow situations and corresponding age distribution functions (see Maloszewski and Zuber (1982) for theoretical background).

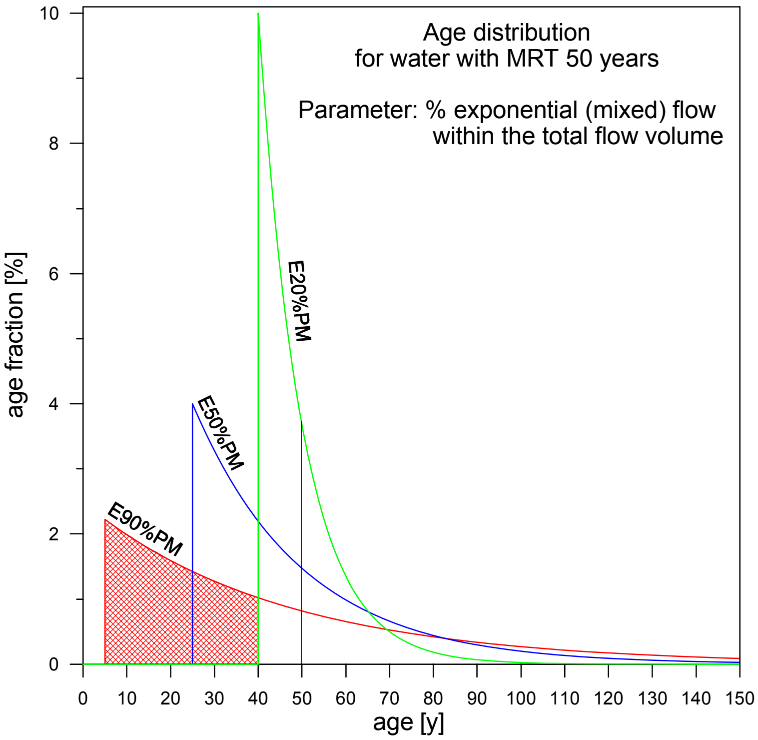

Figure 6. Age distribution for the exponential-piston flow model.

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

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APPENDIX 3

CFC AND SF_6 RAW DATA

Table 5. Raw data of CFC and SF_6 results. See appendix 2 for explanation.

				Measured concentration in solution					Calculated Atmospheric Partial Pressure in pptv					Piston Flow Model Recharge Dates			Concentration in solutio				calculated variables			
Sample	CFC	SF_6	Sampling	$fmolkg^{-1}$	$pmolkg^{-1}$		$pmolkg^{-1}$										$mL(STP).kg^{-1}$				temp		excess air	
Details	No.	No.	Date	SF_6	CFC-11	±	CFC-12	±	SF_6	CFC-11	±	CFC-12	±	SF_6	CFC-11	CFC-12	Ar	±	N_2	±	°C	±	$mL(STP).kg^{-1}$	±
WSP-3	FBP33	SBP27	12.05.05	0.88	2.75	0.02	1.56	0.00	2.88	158	0.15	341	1.05	1993.5	1980	1983	0.342	0.001	12.57	0.11	12.6	0.1	-1.0	0.2
WSP-4	FBP33	SBP26	12.05.05	0.05	0.16	0.02	0.09	0.01	0.13	8.52	0.93	18.74	2.14	1965.5	1960	1957	0.368	0.000	14.23	0.09	11.3	0.2	0.7	0.2
WSP-5	FBP36	SBP30	12.05.05	0.26	0.59	0.01	0.37	0.00	0.90	35.61	0.10	85.39	1.19	1981.5	1968.0	1968.0	0.335	0.003	12.36	0.06	13.6	0.5	-0.9	0.1
WSP-6	FBP37	SBP31	12.05.05	0.03	0.10	0.00	0.07	0.00	0.07	5.51	0.20	13.66	0.36	1961.0	1957.5	1955.0	0.359	0.006	13.59	0.47	11.7	0.1	0.0	0.6
WSP-7	FBP34	SBP28	12.05.05	0.79	2.04	0.02	1.18	0.01	2.17	113	2.56	248	4.88	1990.0	1976	1977.5	0.358	0.003	13.63	0.02	12.0	0.6	0.2	0.3
WSP-8	FBP35	SBP29	12.05.05	0.08	0.06	0.00	0.05	0.00	0.24	3.32	0.02	10.25	0.49	1971.0	1955.5	1953	0.352	0.001	13.08	0.03	12.0	0.2	-0.5	0.0
WSP-9	FBP38	SBP32	12.05.05	0.02	0.20	0.00	0.10	0.00	0.07	11.66	0.03	20.75	0.58	1960.0	1961.5	1957.5	0.344	0.005	12.68	0.39	12.5	0.1	-0.9	0.5
WSP-10	FBP39	SBP33	12.05.05	1.04	4.04	0.02	2.24	0.03	3.54	248	2.59	521	0.21	1996.5	1990.0	1995.5	0.333	0.001	12.30	0.03	13.9	0.3	-0.9	0.1
WB-1	FBP41	SBP35	11.05.05	1.77	4.00	0.01	2.38	0.01	5.91	265	3.54	591	4.54	Modern	1994-1997	Contam. (>5%)	0.327	0.000	12.35	0.07	15.4	0.3	-0.3	0.2
WB-2	FBP42	SBP36	11.05.05	1.65	3.86	0.03	2.45	0.02	5.01	237	2.10	569	3.46	2003.0	1989.0	Modern	0.340	0.002	12.92	0.06	14.0	0.3	0.0	0.0
WB-3	FBP43	SBP37	11.05.05	0.04	0.04	0.02	0.03	0.01	0.19	2.19	1.09	6.41	3.21	1968.5	1954.0	1950.5	0.320	0.005	10.92	0.01	13.3	1.0	-2.8	0.4
WB-4	FBP44	SBP38	11.05.05	--	3.28	0.01	2.27	0.00	--	194	0.38	502	0.59	--	1984.5	1992.5	0.357	0.003	14.08	0.24	13.3	0.0	1.2	0.3
WB-5	FBP45	SBP39	14.05.05	1.76	2.74	0.01	2.56	0.02	4.07	181	1.46	617	4.59	1998.5	1983.0	Contam. (>5%)	0.355	0.003	14.70	0.27	15.5	0.1	2.7	0.4
Waitet Spr W	FBP40	SBP34	14.05.05	1.63	7.60	0.01	3.65	0.03	5.55	441	2.75	810	2.50	2005.0	Hi Cont. (>25%)	Hi Cont. (>25%)	0.339	0.000	12.36	0.03	12.8	0.1	-1.2	0.1

APPENDIX 4

CFC AND SF_6 CONTAMINATION

Several of the water samples have unambiguous old tritium ages, and in most cases the CFC and SF_6 concentrations are too high for water of such old age. This indicates a small contamination or possible gas exchange processes in the unconfined aquifers or in the unsaturated zone.

Gas exchange does occur during travel of the water through the unsaturated zone. However, groundwater travel through the unsaturated zone cannot completely explain the large age differences even though unsaturated zone is very thick in some cases. These large age differences may indicate that there is additional gas exchange at semi- or unconfined aquifer conditions after passage through the unsaturated zone between the soil air and the water table.

If gas exchange between the groundwater and soil air occurs, the CFC and SF_6 clock is partially reset toward zero, and CFC and SF_6 therefore indicate only a minimum mean residence time. This was also found in other areas throughout New Zealand.

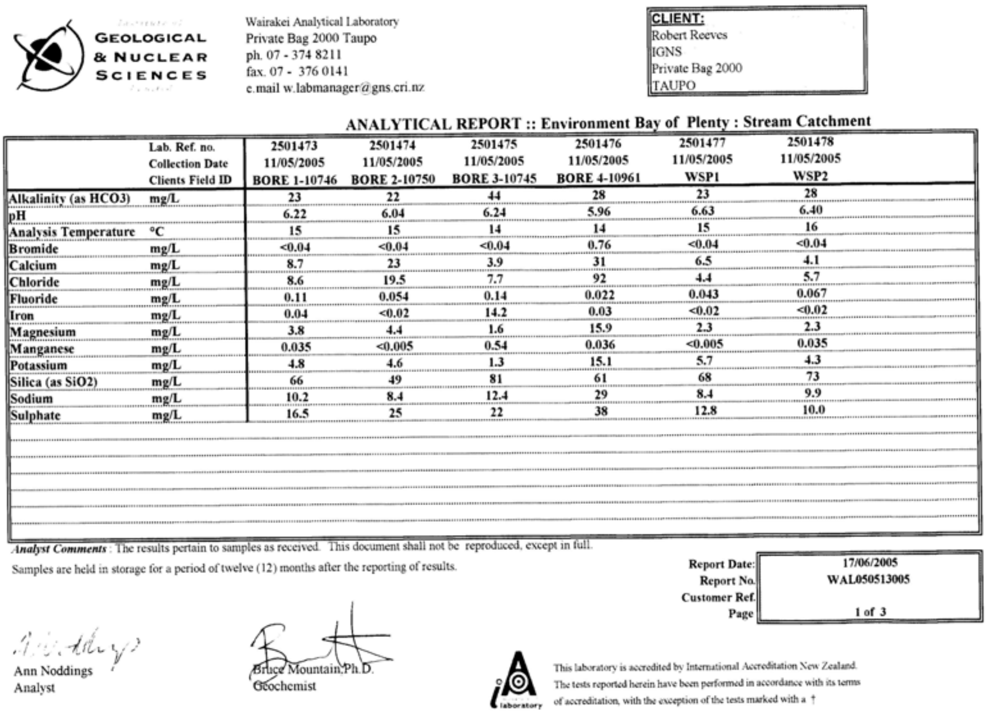
Tritium is an ideal conservative tracer for groundwater flow, and for age interpretation highest emphasis was given to the tritium results with unique age solution (which in most cases gave pre-bomb recharge) for the following reasons:

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

The unique tritium mean residence times were used, and for the ambiguous tritium results, CFCs and SF_6 could be used in most cases to resolve the ambiguity despite the differences between the tritium and gas methods.

APPENDIX 5

CHEMISTRY ANALYSIS RESULTS AND METHODS



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ANALYTICAL REPORT :: Environment Bay of Plenty : Stream Catchment

	Lab. Ref. no.	2501473	2501474	2501475	2501476	2501477	2501478
	Collection Date	11/05/2005	11/05/2005	11/05/2005	11/05/2005	11/05/2005	11/05/2005
	Clients Field ID	BORE 1-10746	BORE 2-10750	BORE 3-10745	BORE 4-10961	WSP1	WSP2
Alkalinity (as HCO3)	mg/L	23	22	44	28	23	28
pH		6.22	6.04	6.24	5.96	6.63	6.40
Analysis Temperature	°C	15	15	14	14	15	16
Bromide	mg/L	<0.04	<0.04	<0.04	0.76	<0.04	<0.04
Calcium	mg/L	8.7	23	3.9	31	6.5	4.1
Chloride	mg/L	8.6	19.5	7.7	92	4.4	5.7
Fluoride	mg/L	0.11	0.054	0.14	0.022	0.043	0.067
Iron	mg/L	0.04	<0.02	14.2	0.03	<0.02	<0.02
Magnesium	mg/L	3.8	4.4	1.6	15.9	2.3	2.3
Manganese	mg/L	0.035	<0.005	0.54	0.036	<0.005	0.035
Potassium	mg/L	4.8	4.6	1.3	15.1	5.7	4.3
Silica (as SiO2)	mg/L	66	49	81	61	68	73
Sodium	mg/L	10.2	8.4	12.4	29	8.4	9.9
Sulphate	mg/L	16.5	25	22	38	12.8	10.0

Analyst Comments : The results pertain to samples as received. This document shall not be reproduced, except in full.
Samples are held in storage for a period of twelve (12) months after the reporting of results.

Report Date:	17/06/2005
Report No.	WAL050513005
Customer Ref.	
Page	1 of 3

Ann Noddings
Analyst

Bruce Mountain, Ph.D.
Geochemist

laboratory

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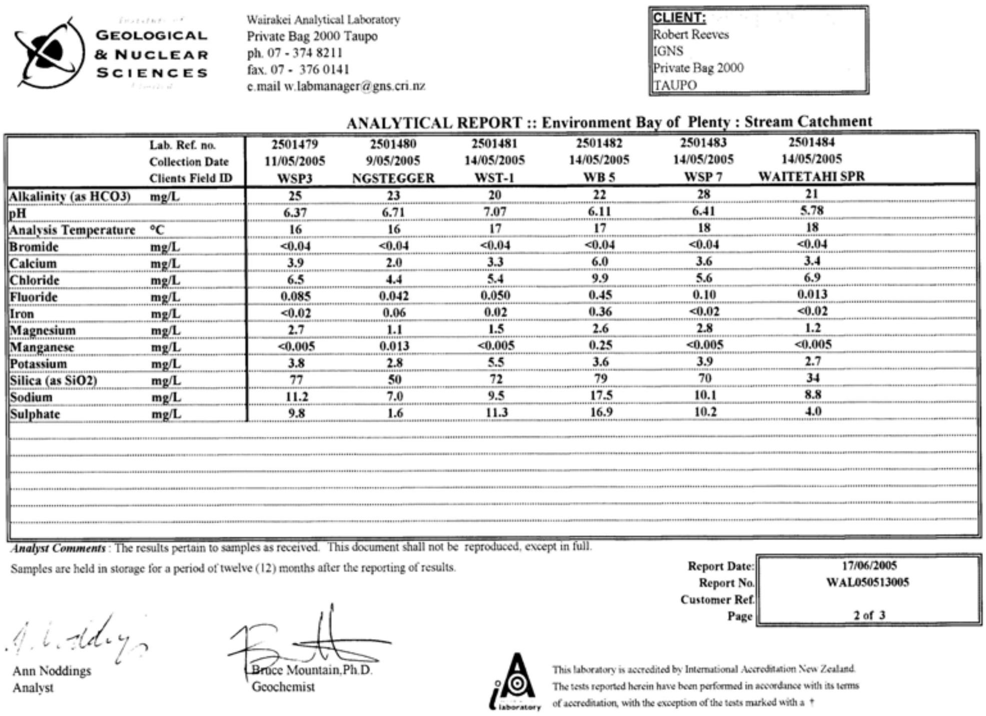

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ANALYTICAL REPORT :: Environment Bay of Plenty : Stream Catchment

	Lab. Ref. no.	2501479	2501480	2501481	2501482	2501483	2501484
	Collection Date	11/05/2005	9/05/2005	14/05/2005	14/05/2005	14/05/2005	14/05/2005
	Clients Field ID	WSP3	NGSTEGGER	WST-1	WB 5	WSP 7	WAITETAHI SPR
Alkalinity (as HCO3)	mg/L	25	23	20	22	28	21
pH		6.37	6.71	7.07	6.11	6.41	5.78
Analysis Temperature	°C	16	16	17	17	18	18
Bromide	mg/L	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Calcium	mg/L	3.9	2.0	3.3	6.0	3.6	3.4
Chloride	mg/L	6.5	4.4	5.4	9.9	5.6	6.9
Fluoride	mg/L	0.085	0.042	0.050	0.45	0.10	0.013
Iron	mg/L	<0.02	0.06	0.02	0.36	<0.02	<0.02
Magnesium	mg/L	2.7	1.1	1.5	2.6	2.8	1.2
Manganese	mg/L	<0.005	0.013	<0.005	0.25	<0.005	<0.005
Potassium	mg/L	3.8	2.8	5.5	3.6	3.9	2.7
Silica (as SiO2)	mg/L	77	50	72	79	70	34
Sodium	mg/L	11.2	7.0	9.5	17.5	10.1	8.8
Sulphate	mg/L	9.8	1.6	11.3	16.9	10.2	4.0

Analyst Comments : The results pertain to samples as received. This document shall not be reproduced, except in full.
Samples are held in storage for a period of twelve (12) months after the reporting of results.

Report Date:	17/06/2005
Report No.	WAL050513005
Customer Ref.	
Page	2 of 3

Ann Noddings
Analyst

Bruce Mountain, Ph.D.
Geochemist

laboratory

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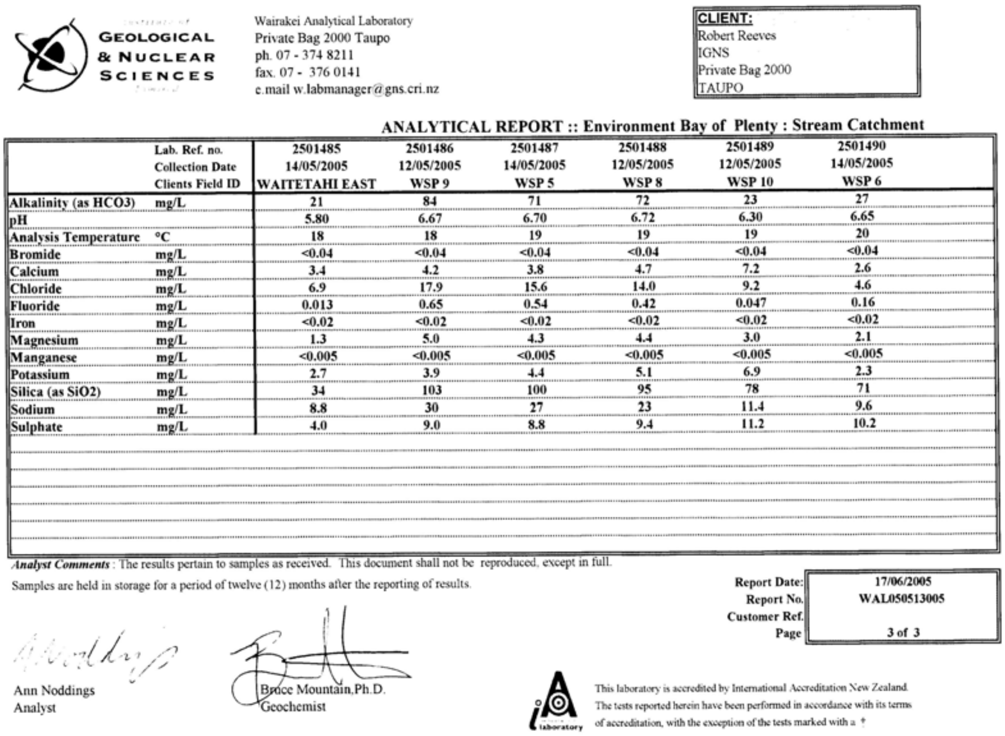

GEOLOGICAL & NUCLEAR SCIENCES

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Robert Reeves
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ANALYTICAL REPORT :: Environment Bay of Plenty : Stream Catchment

	Lab. Ref. no. **Collection Date** **Clients Field ID**	**2501485** **14/05/2005** **WAITETAHI EAST**	**2501486** **12/05/2005** **WSP 9**	**2501487** **14/05/2005** **WSP 5**	**2501488** **12/05/2005** **WSP 8**	**2501489** **12/05/2005** **WSP 10**	**2501490** **14/05/2005** **WSP 6**
Alkalinity (as HCO3)	**mg/L**	21	84	71	72	23	27
pH		5.80	6.67	6.70	6.72	6.30	6.65
Analysis Temperature	**°C**	18	18	19	19	19	20
Bromide	**mg/L**	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Calcium	**mg/L**	3.4	4.2	3.8	4.7	7.2	2.6
Chloride	**mg/L**	6.9	17.9	15.6	14.0	9.2	4.6
Fluoride	**mg/L**	0.013	0.65	0.54	0.42	0.047	0.16
Iron	**mg/L**	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Magnesium	**mg/L**	1.3	5.0	4.3	4.4	3.0	2.1
Manganese	**mg/L**	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Potassium	**mg/L**	2.7	3.9	4.4	5.1	6.9	2.3
Silica (as SiO2)	**mg/L**	34	103	100	95	78	71
Sodium	**mg/L**	8.8	30	27	23	11.4	9.6
Sulphate	**mg/L**	4.0	9.0	8.8	9.4	11.2	10.2

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

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

Report Date:	**17/06/2005**
Report No.	**WAL050513005**
Customer Ref.	
Page	**3 of 3**

Ann Noddings
Analyst

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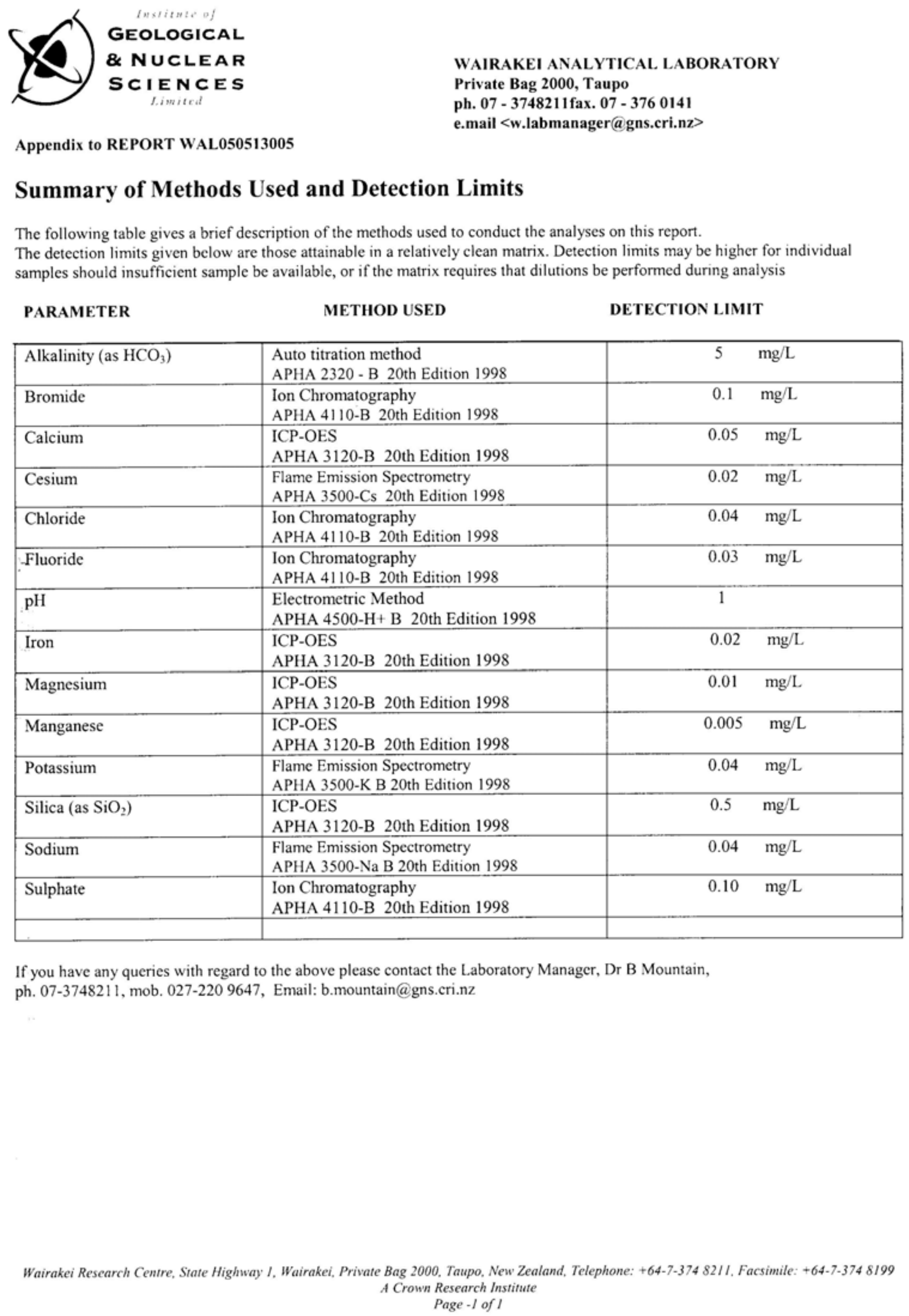

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Appendix to REPORT WAL050513005

Summary of Methods Used and Detection Limits

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

PARAMETER	METHOD USED	DETECTION LIMIT
Alkalinity (as HCO_3)	Auto titration method APHA 2320 - B 20th Edition 1998	5 mg/L
Bromide	Ion Chromatography APHA 4110-B 20th Edition 1998	0.1 mg/L
Calcium	ICP-OES APHA 3120-B 20th Edition 1998	0.05 mg/L
Cesium	Flame Emission Spectrometry APHA 3500-Cs 20th Edition 1998	0.02 mg/L
Chloride	Ion Chromatography APHA 4110-B 20th Edition 1998	0.04 mg/L
Fluoride	Ion Chromatography APHA 4110-B 20th Edition 1998	0.03 mg/L
pH	Electrometric Method APHA 4500-H+ B 20th Edition 1998	1
Iron	ICP-OES APHA 3120-B 20th Edition 1998	0.02 mg/L
Magnesium	ICP-OES APHA 3120-B 20th Edition 1998	0.01 mg/L
Manganese	ICP-OES APHA 3120-B 20th Edition 1998	0.005 mg/L
Potassium	Flame Emission Spectrometry APHA 3500-K B 20th Edition 1998	0.04 mg/L
Silica (as SiO_2)	ICP-OES APHA 3120-B 20th Edition 1998	0.5 mg/L
Sodium	Flame Emission Spectrometry APHA 3500-Na B 20th Edition 1998	0.04 mg/L
Sulphate	Ion Chromatography APHA 4110-B 20th Edition 1998	0.10 mg/L

If you have any queries with regard to the above please contact the Laboratory Manager, Dr B Mountain, ph. 07-3748211, mob. 027-220 9647, Email: b.mountain@gns.cri.nz

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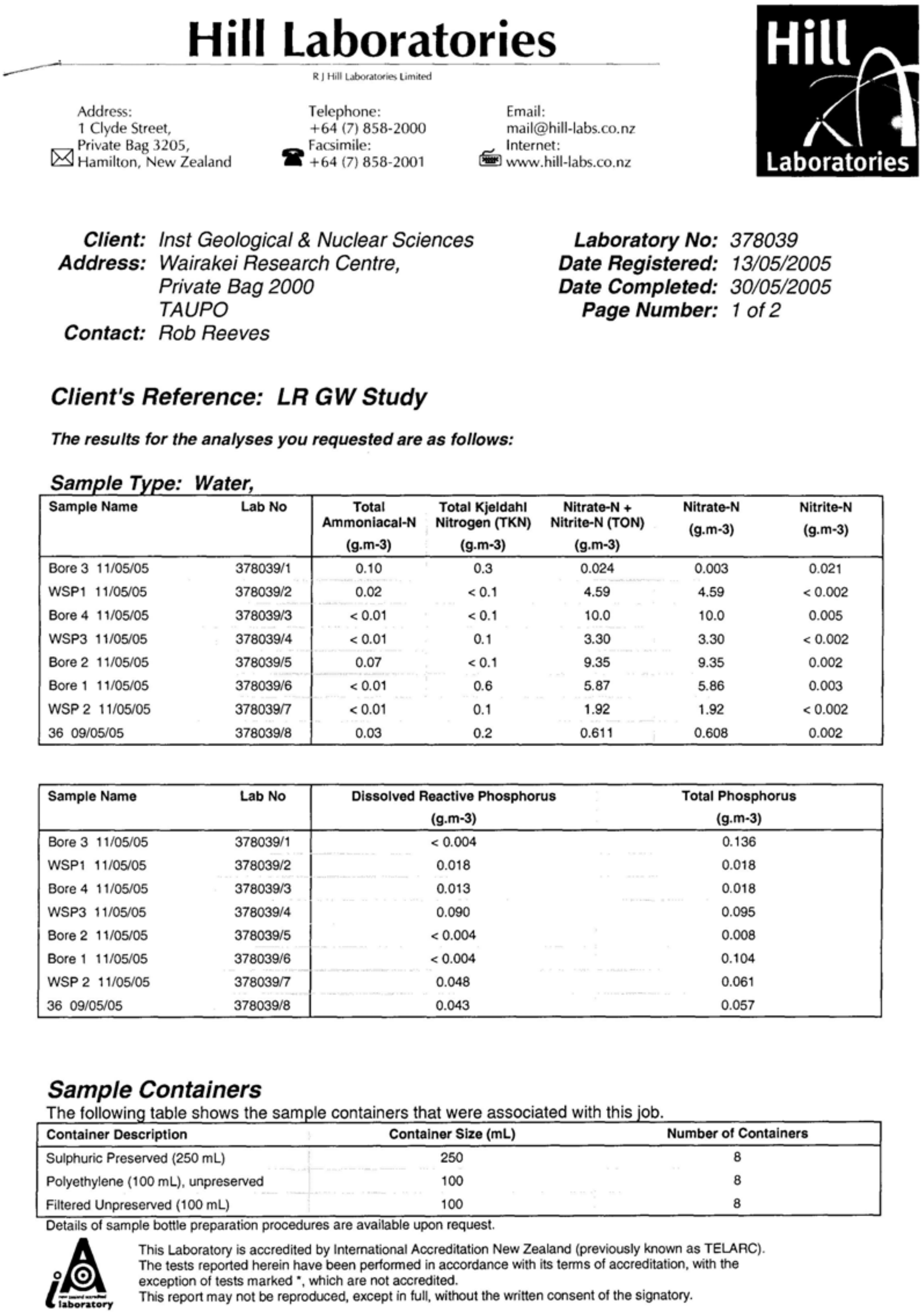
Page -1 of 1



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Private Bag 2000
TAUPO
Contact: Rob Reeves

Laboratory No: 378039
Date Registered: 13/05/2005
Date Completed: 30/05/2005
Page Number: 1 of 2

Client's Reference: LR GW Study

The results for the analyses you requested are as follows:

Sample Type: Water,

Sample Name	Lab No	Total Ammoniacal-N (g.m-3)	Total Kjeldahl Nitrogen (TKN) (g.m-3)	Nitrate-N + Nitrite-N (TON) (g.m-3)	Nitrate-N (g.m-3)	Nitrite-N (g.m-3)
Bore 3 11/05/05	378039/1	0.10	0.3	0.024	0.003	0.021
WSP1 11/05/05	378039/2	0.02	< 0.1	4.59	4.59	< 0.002
Bore 4 11/05/05	378039/3	< 0.01	< 0.1	10.0	10.0	0.005
WSP3 11/05/05	378039/4	< 0.01	0.1	3.30	3.30	< 0.002
Bore 2 11/05/05	378039/5	0.07	< 0.1	9.35	9.35	0.002
Bore 1 11/05/05	378039/6	< 0.01	0.6	5.87	5.86	0.003
WSP 2 11/05/05	378039/7	< 0.01	0.1	1.92	1.92	< 0.002
36 09/05/05	378039/8	0.03	0.2	0.611	0.608	0.002

Sample Name	Lab No	Dissolved Reactive Phosphorus (g.m-3)	Total Phosphorus (g.m-3)
Bore 3 11/05/05	378039/1	< 0.004	0.136
WSP1 11/05/05	378039/2	0.018	0.018
Bore 4 11/05/05	378039/3	0.013	0.018
WSP3 11/05/05	378039/4	0.090	0.095
Bore 2 11/05/05	378039/5	< 0.004	0.008
Bore 1 11/05/05	378039/6	< 0.004	0.104
WSP 2 11/05/05	378039/7	0.048	0.061
36 09/05/05	378039/8	0.043	0.057

Sample Containers

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

Container Description	Container Size (mL)	Number of Containers
Sulphuric Preserved (250 mL)	250	8
Polyethylene (100 mL), unpreserved	100	8
Filtered Unpreserved (100 mL)	100	8

Details of sample bottle preparation procedures are available upon request.

laboratory

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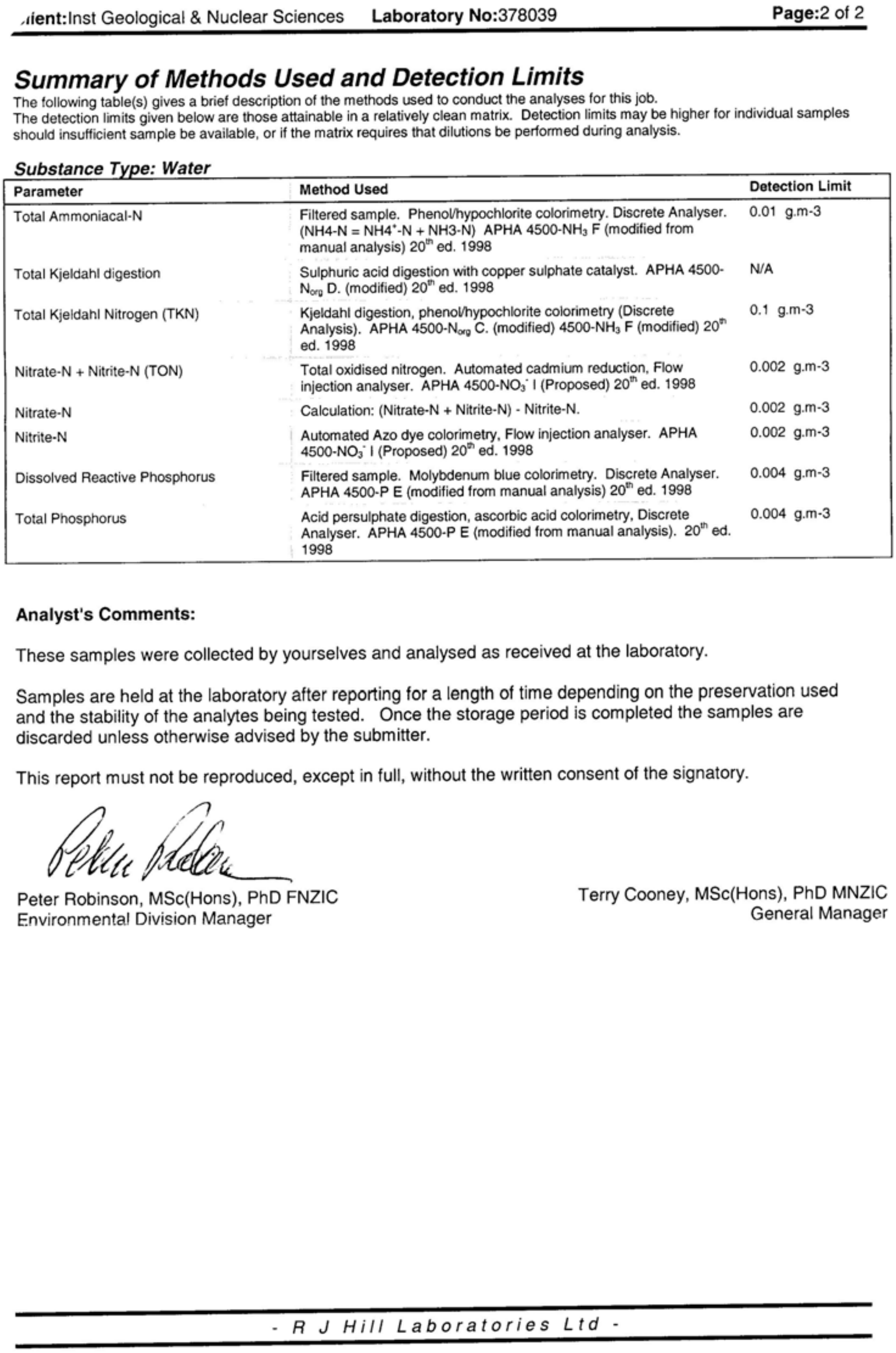

ient: Inst Geological & Nuclear Sciences **Laboratory No:**378039 **Page:**2 of 2

Summary of Methods Used and Detection Limits

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

Substance Type: Water

Parameter	Method Used	Detection Limit
Total Ammoniacal-N	Filtered sample. Phenol/hypochlorite colorimetry. Discrete Analyser. (NH4-N = NH4$^+$-N + NH3-N) APHA 4500-NH$_3$ F (modified from manual analysis) 20th ed. 1998	0.01 g.m-3
Total Kjeldahl digestion	Sulphuric acid digestion with copper sulphate catalyst. APHA 4500-N$_{org}$ D. (modified) 20th ed. 1998	N/A
Total Kjeldahl Nitrogen (TKN)	Kjeldahl digestion, phenol/hypochlorite colorimetry (Discrete Analysis). APHA 4500-N$_{org}$ C. (modified) 4500-NH$_3$ F (modified) 20th ed. 1998	0.1 g.m-3
Nitrate-N + Nitrite-N (TON)	Total oxidised nitrogen. Automated cadmium reduction, Flow injection analyser. APHA 4500-NO$_3^-$ I (Proposed) 20th ed. 1998	0.002 g.m-3
Nitrate-N	Calculation: (Nitrate-N + Nitrite-N) - Nitrite-N.	0.002 g.m-3
Nitrite-N	Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO$_3^-$ I (Proposed) 20th ed. 1998	0.002 g.m-3
Dissolved Reactive Phosphorus	Filtered sample. Molybdenum blue colorimetry. Discrete Analyser. APHA 4500-P E (modified from manual analysis) 20th ed. 1998	0.004 g.m-3
Total Phosphorus	Acid persulphate digestion, ascorbic acid colorimetry, Discrete Analyser. APHA 4500-P E (modified from manual analysis). 20th ed. 1998	0.004 g.m-3

Analyst's Comments:

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

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

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

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

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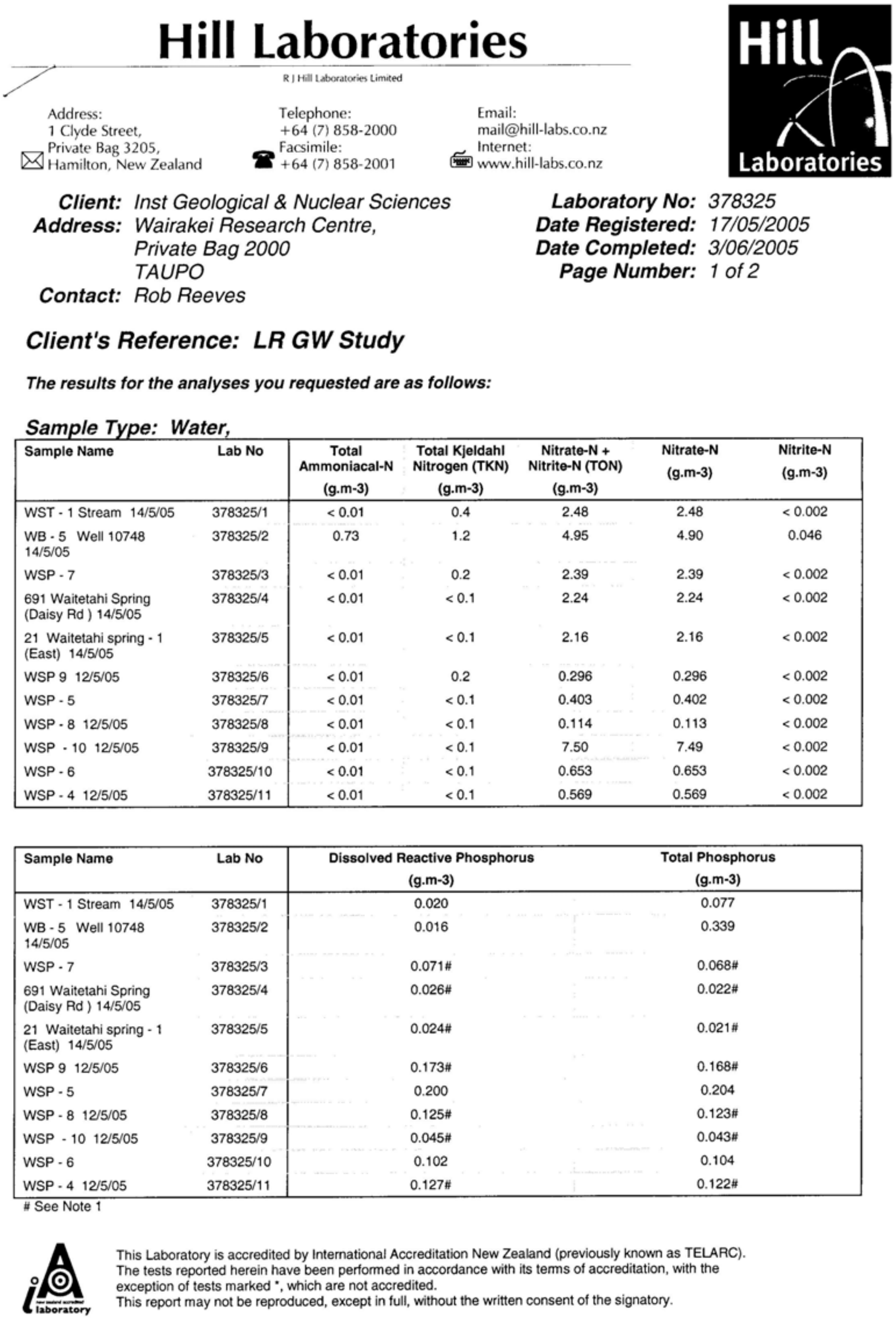

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Private Bag 2000
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Contact: *Rob Reeves*

Laboratory No: *378325*
Date Registered: *17/05/2005*
Date Completed: *3/06/2005*
Page Number: *1 of 2*

Client's Reference: LR GW Study

The results for the analyses you requested are as follows:

Sample Type: Water,

Sample Name	Lab No	Total Ammoniacal-N (g.m-3)	Total Kjeldahl Nitrogen (TKN) (g.m-3)	Nitrate-N + Nitrite-N (TON) (g.m-3)	Nitrate-N (g.m-3)	Nitrite-N (g.m-3)
WST - 1 Stream 14/5/05	378325/1	< 0.01	0.4	2.48	2.48	< 0.002
WB - 5 Well 10748 14/5/05	378325/2	0.73	1.2	4.95	4.90	0.046
WSP - 7	378325/3	< 0.01	0.2	2.39	2.39	< 0.002
691 Waitetahi Spring (Daisy Rd) 14/5/05	378325/4	< 0.01	< 0.1	2.24	2.24	< 0.002
21 Waitetahi spring - 1 (East) 14/5/05	378325/5	< 0.01	< 0.1	2.16	2.16	< 0.002
WSP 9 12/5/05	378325/6	< 0.01	0.2	0.296	0.296	< 0.002
WSP - 5	378325/7	< 0.01	< 0.1	0.403	0.402	< 0.002
WSP - 8 12/5/05	378325/8	< 0.01	< 0.1	0.114	0.113	< 0.002
WSP - 10 12/5/05	378325/9	< 0.01	< 0.1	7.50	7.49	< 0.002
WSP - 6	378325/10	< 0.01	< 0.1	0.653	0.653	< 0.002
WSP - 4 12/5/05	378325/11	< 0.01	< 0.1	0.569	0.569	< 0.002

Sample Name	Lab No	Dissolved Reactive Phosphorus (g.m-3)	Total Phosphorus (g.m-3)
WST - 1 Stream 14/5/05	378325/1	0.020	0.077
WB - 5 Well 10748 14/5/05	378325/2	0.016	0.339
WSP - 7	378325/3	0.071#	0.068#
691 Waitetahi Spring (Daisy Rd) 14/5/05	378325/4	0.026#	0.022#
21 Waitetahi spring - 1 (East) 14/5/05	378325/5	0.024#	0.021#
WSP 9 12/5/05	378325/6	0.173#	0.168#
WSP - 5	378325/7	0.200	0.204
WSP - 8 12/5/05	378325/8	0.125#	0.123#
WSP - 10 12/5/05	378325/9	0.045#	0.043#
WSP - 6	378325/10	0.102	0.104
WSP - 4 12/5/05	378325/11	0.127#	0.122#

See Note 1

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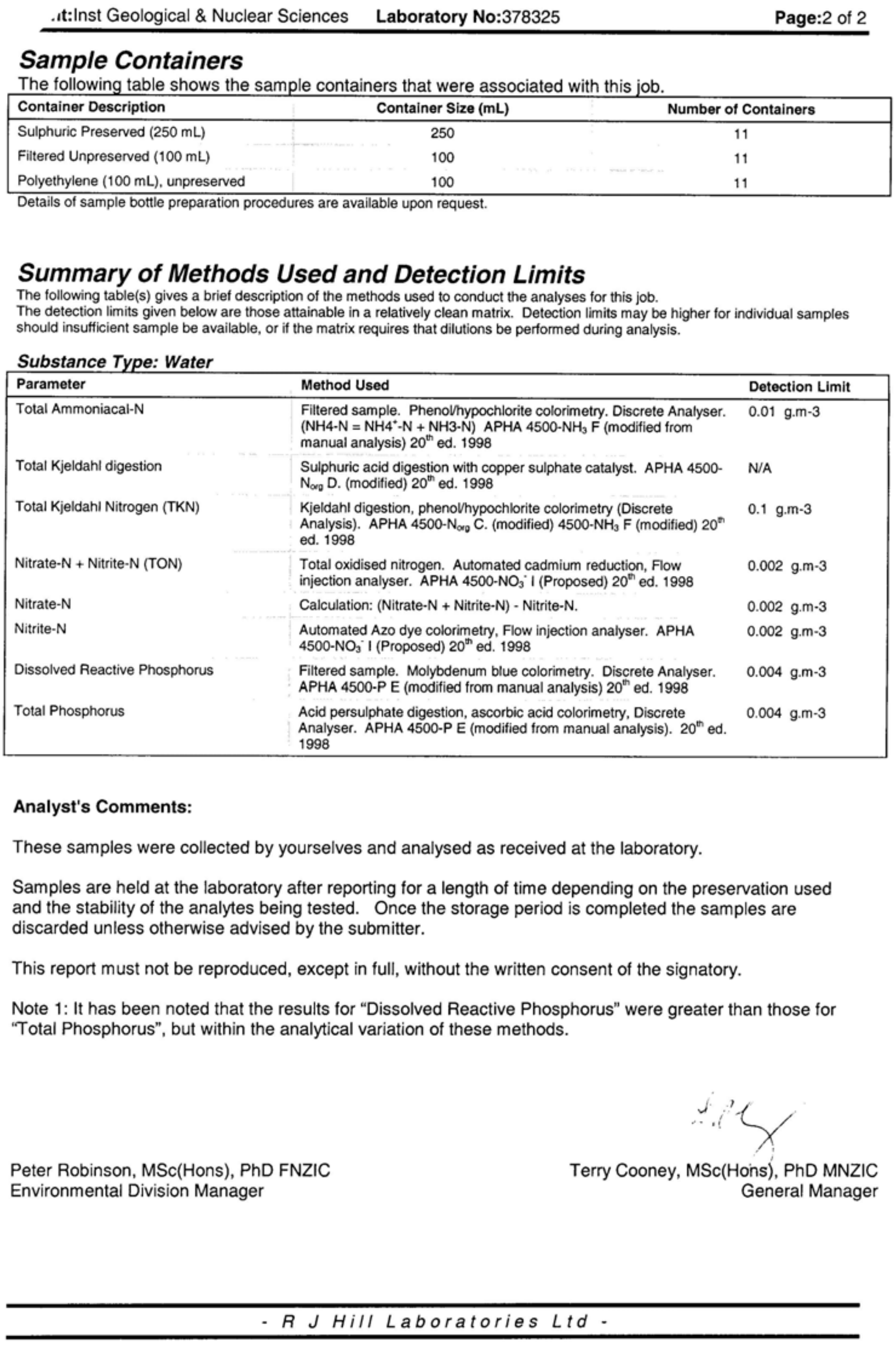

.ıt:Inst Geological & Nuclear Sciences **Laboratory No:**378325 **Page:**2 of 2

Sample Containers

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

Container Description	Container Size (mL)	Number of Containers
Sulphuric Preserved (250 mL)	250	11
Filtered Unpreserved (100 mL)	100	11
Polyethylene (100 mL), unpreserved	100	11

Details of sample bottle preparation procedures are available upon request.

Summary of Methods Used and Detection Limits

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

Substance Type: Water

Parameter	Method Used	Detection Limit
Total Ammoniacal-N	Filtered sample. Phenol/hypochlorite colorimetry. Discrete Analyser. (NH4-N = NH_4^+-N + NH3-N) APHA 4500-NH_3 F (modified from manual analysis) 20th ed. 1998	0.01 g.m-3
Total Kjeldahl digestion	Sulphuric acid digestion with copper sulphate catalyst. APHA 4500-N_{org} D. (modified) 20th ed. 1998	N/A
Total Kjeldahl Nitrogen (TKN)	Kjeldahl digestion, phenol/hypochlorite colorimetry (Discrete Analysis). APHA 4500-N_{org} C. (modified) 4500-NH_3 F (modified) 20th ed. 1998	0.1 g.m-3
Nitrate-N + Nitrite-N (TON)	Total oxidised nitrogen. Automated cadmium reduction, Flow injection analyser. APHA 4500-NO_3^- I (Proposed) 20th ed. 1998	0.002 g.m-3
Nitrate-N	Calculation: (Nitrate-N + Nitrite-N) - Nitrite-N.	0.002 g.m-3
Nitrite-N	Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO_3^- I (Proposed) 20th ed. 1998	0.002 g.m-3
Dissolved Reactive Phosphorus	Filtered sample. Molybdenum blue colorimetry. Discrete Analyser. APHA 4500-P E (modified from manual analysis) 20th ed. 1998	0.004 g.m-3
Total Phosphorus	Acid persulphate digestion, ascorbic acid colorimetry, Discrete Analyser. APHA 4500-P E (modified from manual analysis). 20th ed. 1998	0.004 g.m-3

Analyst's Comments:

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

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

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Note 1: It has been noted that the results for "Dissolved Reactive Phosphorus" were greater than those for "Total Phosphorus", but within the analytical variation of these methods.

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