Lake Taupo Catchment Groundwater Age Distribution and Implications for Future Land-Use Impacts

Environment Waikato

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Lake Taupo catchment groundwater age distribution and implications for future land-use impacts

Uwe Morgenstern

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EXECUTIVE SUMMARY

The near pristine water of Lake Taupo is under threat, mainly as a result of delayed arrival of nitrate from farming. Nitrogen travels from farms to the lake mostly via groundwater, entering the lake via groundwater-fed streams, and directly by groundwater seepage via the lake bed. The age of the water was measured in all the larger streams in the northern and western parts of the Lake Taupo catchment, and in groundwater wells to estimate the time lag between landuse intensification and the arrival of landuse nitrogen in the lake via groundwater and groundwater fed streams. The northern and western sub-catchments contain the largest area of farming. The age distribution of the water can be used to estimate the future arrival of landuse-impacted water from current landuse practises, and predict future nitrogen mass loading to Lake Taupo.

The hydrogeology in the northern part of the catchment is dominated by relatively thick Oruanui ignimbrite (c. 26,500 years old) with areas of overlying Taupo ignimbrite (1,800 years old) overlying much older welded Whakamaru Group ignimbrites (also rhyolitic: c. 340,000-320,000 years old). The western part of the catchment is dominated by the old welded Whakamaru Group ignimbrites overlain by thinner Oruanui ignimbrite. The south-western part of the catchment is dominated by andesitic and basaltic lava, partially overlain by the Oruanui and Taupo ignimbrites.

While tritium data from northern streams clearly shows old (>50 years) water in streams, historic tritium data from the Kuratau River demonstrates that the major fraction of the stream water in the western catchment is very young (<1y). Therefore, the geohydraulic parameters are not uniform through the northern and western catchments. Northern unwelded ignimbrites have greater capacity to store water in the deep groundwater system than western welded Whakamaru Ignimbrites, which more rapidly contribute to surface flow. This is reflected by lower specific yields of northern stream sub-catchments.

Hydrochemistry results are mostly consistent over time. Only a few parameters of some wells vary considerably. About half of the samples have hydrochemistry indicative of anaerobic conditions, some of them up to the stage of methane fermentation. At anaerobic conditions nutrients (nitrate and sulphate) can be reduced, and the gas concentrations in the water can be disturbed causing difficulty in CFC and SF_6 age dating.

About half of the groundwaters have time series tritium data that enables unambiguous age interpretation. Most tritium time series give an excellent match to flow models with unusually high piston flow fraction. The remaining wells, except one, have been accurately dated using additional information.

A number of chemical species show a correlation with age of the water, indicating concentration increase due to progressive leaching from the volcanic aquifer. The best correlation with age in groundwater from Lake Taupo is observed for phosphorus, and to some extend for silica and fluoride, and pH in reduced groundwaters.

The groundwater system in the northern and western Lake Taupo catchment is very complex. The unusually high fraction of piston flow in most areas means that the groundwater system is not well mixed, with preferential flow paths likely to be important. The observed variability in groundwater chemistry, in space and time, reflects this.

Anoxic waters have lower nitrate concentrations by about a factor of two compared to oxic waters with similar fraction of landuse impacted water. This suggests that on average about half of the nitrate is being removed, where groundwaters are anoxic, by denitrification processes.

The groundwaters in the northern and western Lake Taupo catchment are relatively old with mean residence times between 20 and 180 years (only three shallow piezometers have very young water with age of about two years). Groundwater quality in general is not yet in equilibrium with current landuse and further increases in nitrogen load are expected as old pristine groundwater is progressively replaced by landuse impacted water. Nutrients show a clear landuse impact on groundwaters with the data indicating further increase in future for nitrate, sulphate, magnesium and calcium.

A significant increase in total nitrogen load via direct groundwater seepage of about 135 t/y is expected from the northern catchment area, in addition to an increase by 21 t/y increase from streams in the northern and western catchment. The groundwater nitrogen increase is only a rough estimate but it demonstrates that the most significant nitrogen load increase is expected from the northern catchment groundwater seepage.

KEYWORDS

Lake Taupo, groundwater dating, tritium, cfcs, SF_6, nitrate contamination

1.0   INTRODUCTION

The near pristine water of Lake Taupo is under threat, mainly as a result of delayed arrival of nitrate from farming. Large areas in the catchment were developed into pastoral agriculture 40 to 50 years ago (Vant & Smith, 2004). Nitrogen concentrations in streams draining pasture have slowly risen since the 1970s, and are still increasing, despite little change in the intensity of farming since then. This delay between pasture development and the associated nitrogen increase in streams and groundwater draining the catchment suggests that water residence times in the aquifer are several decades (Figure 1.1).
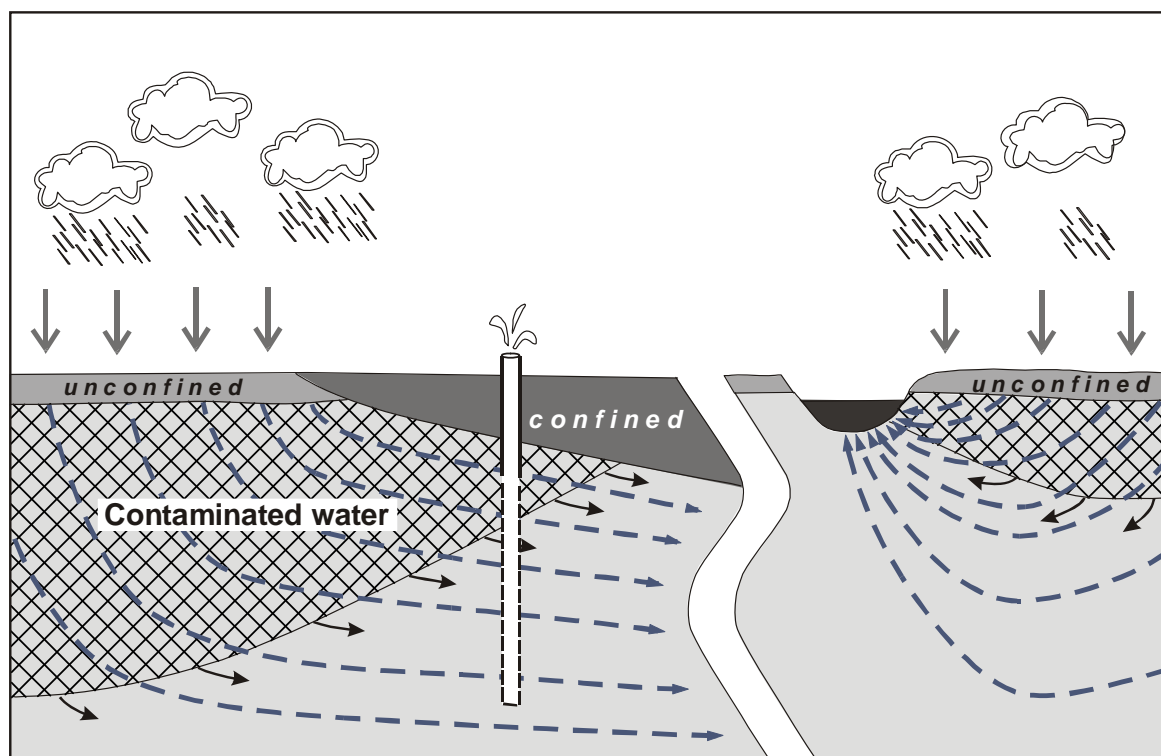
Figure 1.1   The tip of the iceberg. A water sample from a well or the stream or lake contains fractions of both young and old groundwater because long and short travel flowlines converge at the well or spring. For water mixtures with mean residence time >50 years, only a fraction of the water is young enough to show the contamination (hatched). Large fractions of the discharging water are still uncontaminated old groundwater. But in time, the front of contaminated water moves forward (see arrows), and a higher fraction of contaminated water will discharge into the well/stream/lake. A further increase in N loading is expected.

In areas with large groundwater reservoirs, the dissolved nitrogen concentrations of water discharging to the lake is still relatively low because of dilution with old pristine pre-landuse waters. These concentrations are expected to increase further in the future because of the progressive arrival of water recharged after catchment development which brings increased N loads. Large amounts of groundwater have insidiously become contaminated with nitrogen over the last 50 years in large groundwater reservoirs with related long groundwater travel times. The response time of the groundwater system to lake water mitigation action will be similar, it will also take decades until the nitrogen contaminated water is flushed out of the aquifers.

Groundwater is the conduit for most nitrogen travel from farms to the lake. Groundwater enters the lake via groundwater-fed streams, and directly by groundwater seepage via the lake bed.

The age of the water was measured to estimate the time lag between landuse intensification and the arrival of landuse nitrogen in the lake via groundwater and groundwater fed streams. This study was initiated by Environment Waikato (EW) in 2001 (Hadfield et al., 2001) and focused on groundwater wells in the northern and western parts of the Lake Taupo catchment which has the largest impact from land-use. The distribution of water ages enables estimation of the future arrival of post-landuse water and hence provides a basis for approximating future nitrogen mass loading to Lake Taupo from current landuse. This information is useful for groundwater flow and contaminant transport model calibration. The estimation of the lagged nitrogen input to the lake is critical for lake management.

Groundwater systems are usually very complex and difficult to understand. Therefore, multidisciplinary approaches are necessary, including hydrogeology, isotope signature and chemical characteristics of the groundwater. Groundwater flow in the northern and western catchment of Lake Taupo is complex due primarily to variations in terrain and geology.

Tritium dating is the most robust method for groundwater dating in the Lake Taupo area but for younger waters there is ambiguity in age interpretation due to the influence of bomb-tritium from the nuclear weapons testing in the 1960s. Complementary dating tools like chlorofluorocarbons (CFCs) and SF_6 can often resolve ambiguity. They are, however, of limited use in the Lake Taupo area because of gas exchange between the unconfined groundwater and the air, and because of CFC degradation due to reducing conditions found in many groundwaters, especially in the western catchment. From earlier measurements in the Mapara Stream it was known that water ages over 50 years can be expected allowing for identification of unambiguous pre-bomb tritium. For the younger waters, tritium time-series is expected to resolve remaining ambiguous results. Ambiguous results occur where high tritium concentrations could indicate very young water, or water with several decades residence time with remaining bomb-tritium. This is not resolved by CFCs in anoxic conditions or SF_6 with high gas exchange between the water and air in the unsaturated zone.

In 2001 and 2002, groundwater was sampled for tritium, CFC, and SF_6 analyses from wells in the northern and western catchment of Lake Taupo. The results gave reasonable estimates of age for the majority of samples. However, especially for shallow piezometric wells, a large degree of ambiguity remained. This was because of highly anoxic groundwater conditions with related alteration of CFCs and SF_6. The remaining ambiguity was hoped to be overcome with time-series data after a repeat sampling in 2007, 5 years after the first sampling.

In the initial study we found high tritium concentrations in a number of the wells which were explainable only by unusually high piston flow of groundwater. To test if these unusual piston flow conditions are realistic, four further samples were analysed in 2004 (GNS-funded). This was to obtain longer tritium time series from the wells with the most unusual groundwater flow conditions. The results confirmed the high piston flow fraction in these groundwaters, but with only two measurements only two years apart some uncertainty remained. In an additional EW initiative, about half of the wells were re-sampled in 2007. All data from between 2001 and 2007 form the basis of the age interpretation of this report.

The historic tritium data from the Kuratau River show that significant fractions of the surface water in the western catchment are very young (<1y) and therefore, that the geohydraulic parameters are not uniform through the northern and western catchment. This suggests the unwelded ignimbrites in the northern sub-catchments have very different water storage

capacities to the Whakamaru Ignimbrite. Detailed geological maps were available only for parts of the catchment. We now have a more detailed geological map available for the whole Lake Taupo catchment. This has helped to resolve the interpretation of age ambiguities and provide a better understanding of the groundwater flow processes around Lake Taupo.

2.0   HYDROGEOLOGY, SAMPLE LOCATION, AND BORE DATA

The geology of Lake Taupo catchment comprises predominantly rhyolitic volcanics (Figure 2.1, QMAP geological mapping, GNS Science). In the northern part of the catchment relatively thick Oruanui ignimbrite (c. 26,500 years old) with areas of overlying Taupo ignimbrite (1,800 years old) is overlying much older welded Whakamaru Group ignimbrites (also rhyolitic: c. 340,000-320,000 years old). The western part of the catchment is dominated by the old welded Whakamaru Group ignimbrites overlain by thinner Oruanui ignimbrite. The south-western part of the catchment is dominated by andesitic and basaltic lava, partially overlain by the Oruanui and Taupo ignimbrites. The tritium data (Morgenstern 2007) indicate that these geological units have very different hydraulic properties. Rain infiltrates readily into the groundwater system through Taupo and Oruanui Ignimbrites. Groundwater flow into the lake in the northern catchment with unwelded ignimbrites is mostly via lake bed seepage with long time delay in the groundwater system. Flow into the lake in the western catchment with welded fractured Whakamaru ignimbrite and andesite is mostly via much quicker near-surface runoff.

An indication of the different hydraulic properties between the northern and the western catchment can be obtained from the specific water yield which was investigated by Schouten et al. (1981). The specific water yields are summarised in Vant and Smith (2004) and the essential data listed in Table 2.1.

Table 2.1   Mean stream flow, specific water yield via stream, and stream runoff from the catchment. Details are described in Vant and Smith (2004). See text below for explanation of the colour code.

Stream	Mean flow L/s	Specific water yield L/s/km^2	Runoff mm/y
Mapara	85	4	125
Whangamata	110	3	110
Otaketake	135	7	220
Omoho	60	3	100
Waihora	1900	29	900
Waihaha	5530	42	1312
Whanganui	1230	39	1250
Whareroa	944	16	775
Kuratau	7000	36	1135
Omori	560	21	650

The streams from the northern catchments are characterised by flows, specific yields and runoff estimates which are low (yellow highlight, Table 2.1). This appears to reflect the occurrence of unwelded ignimbrites, allowing most rainwater to enter the deep groundwater system and to enter the lake through seepage on the lake bed. A relatively large groundwater storage reservoir with large mean residence time is supported by measured old water ages in this area. In this northern area (east of Waihora sub-catchment) about 70% of water reaches the lake directly by groundwater seepage via the lakebed.
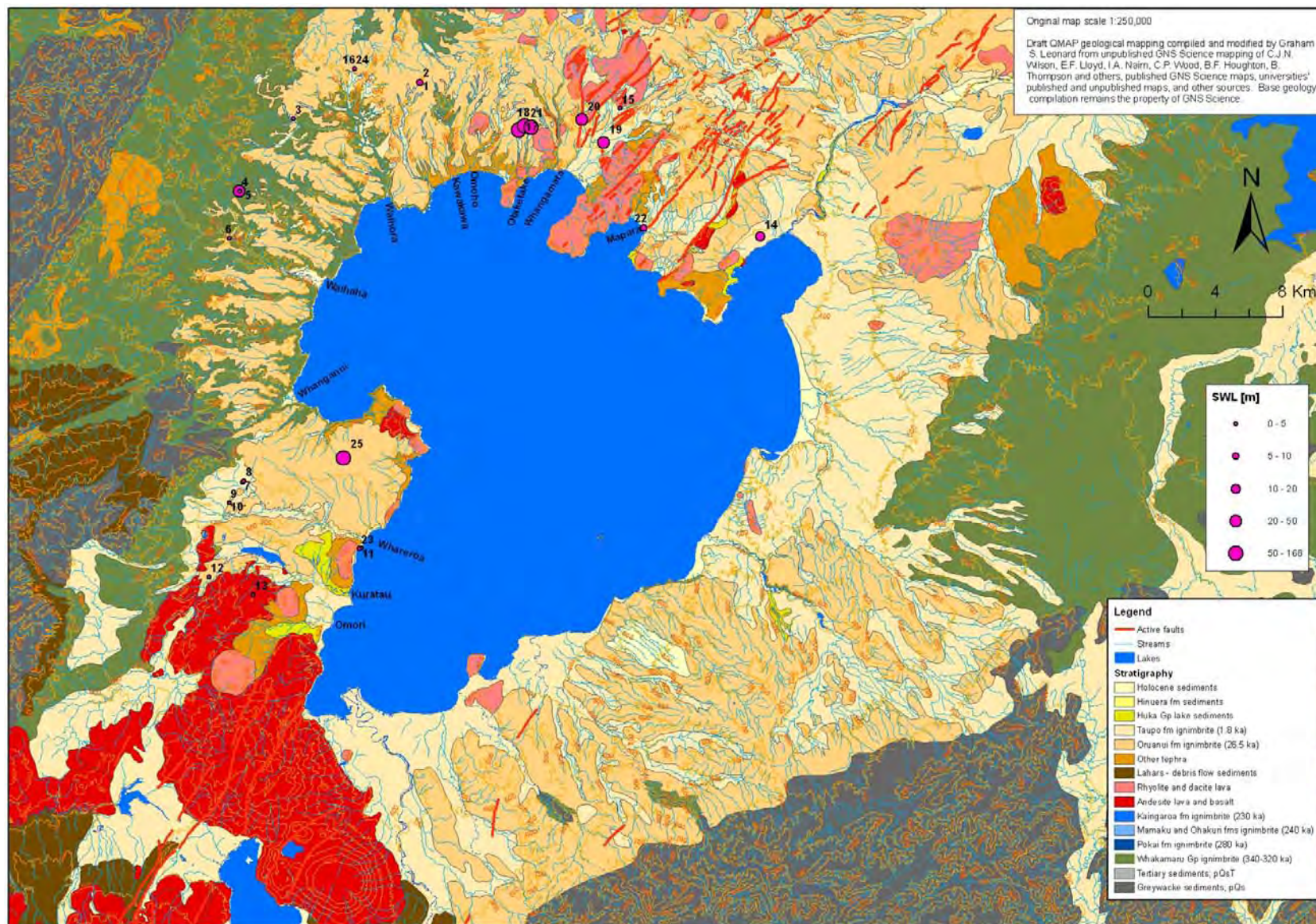
Figure 2.1   Geological map of Lake Taupo catchment and well location with depth to water table. See Table 2.2 for ID numbers.

Most streams from the western sub-catchments are characterised by relatively high flow, specific water yield, and runoff (pink highlight, Table 2.1). The geology in these catchments comprises predominantly Whakamaru Group ignimbrites, with lesser andesitic and basaltic lava. The high specific yield and runoff via streams indicate that relatively little water from these sub-catchments reaches the lake directly via seepage. This probably reflects the low permeability fractured nature of the formation and higher rainfall. A smaller portion of water migrates directly to the lake via old groundwater. The majority of the water from the western sub-catchment reaches the lake via much quicker near-surface runoff.

Streams not highlighted in Table 2.1 have intermediate flow, specific water yield and runoff, and are from the boundary zone between the two geologic formations with different hydraulic conductivity. Waihora is from a boundary zone between the Oruanui and Whakamaru Group ignimbrites. In the Whareroa catchment a significant layer of Oruanui and Taupo ignimbrites overlie the Whakamaru Group ignimbrites. In the Omori catchment andesite lava and basalt are overlain by tephra and, closer to the lake, by Taupo Ignimbrite. The relatively low surface runoff is probably a result of the easily draining Taupo Ignimbrite close to the lake and subsequent groundwater seepage via the lake bed.

The specific water yields of the catchments demonstrate qualitatively the general surface-groundwater interaction.

Well location and construction details, aquifer geology, and static water levels are listed in Table 2.2 from data supplied by EW. Wells were selected to provide a good spatial distribution and representation of hydrogeologic conditions throughout the investigated area. The shallow wells were generally specifically constructed for monitoring and where possible paired with deeper wells.

Table 2.2   Well location and construction details, aquifer geology, and static water levels. Data provided by Environment Waikato.

#	Site	E	N	Bore Depth m	Depth Screen Top m	Depth Screen Bottom m	Aquifer Geology	Aquifer confinem	SWL [m bgl]
1	72.383	2754701	6283922	38.4	32.6	38.4	Whakamaru Ignimbrite	leaky	8.6
2	72.1009	2754704	6283920	9	3.65	9	Oruanui Ignimbrite	unconf	6.62
3	72.1006	2747200	6281800	5.43	2.43	5.43	Sand & pumice	conf	1.12
4	72.1069	2744054	6277500	11.7	2.7	11.7	Oruanui Ignimbrite	unconf	4.21
5	72.1089	2744000	6277500	50	?50	50	Oruanui Ignimbrite ?	unconf?	20.6
6	72.1071	2743433	6274670	7.5	1.5	7.5	Oruanui Ignimbrite	unconf	2.34
7	72.1072	2744200	6260200	21	14.5	20.5	Oruanui Ignimbrite	conf	1.77
8	72.1087	2744272	6260257	6.6	0.6	6.6	Taupo Ignimbrite	unconf	1.53
9	72.1078	2743405	6258989	58	6.7	58	Whakamaru Ignimbrite	unconf	3.6
10	72.1079	2743407	6258991	3.5	1.5	3.5	Oruanui Ignimbrite	unconf	1.82
11	72.1075	2751217	6256277	5.5	0.5	5.5	Gravel Sand	unconf	1.52
12	72.1081	2742204	6254577	4.6	0.45	4.6	Sands	unconf	1.69
13	72.1076	2744830	6253517	7.9	1.9	7.9	Ignimbrite	unconf	4.64
14	68.32	2774906	6274794	62	43	62	Oruanui Ignimbrite	unconf	14.07
15	72.364	2766590	6282404	0	NA	NA	Rhyolite lava	na/conf	0
16	72.377	2750827	6284765	50.3	45.4	50.3	Whakamaru Ignimbrite	conf	4.51
17	68.317	2760588	6281128	104	73	104	Rhyolite pyroclastic	leaky	54.24
18	72.392	2760912	6281337	93	65.2	93	Rhyolite pyroclastic	leaky	51.4
19	68.301	2765622	6280392	53.6	49	53.6	Rhyolite pyroclastic	leaky	38.4
20	68.66	2764338	6281753	37.7	19.5	37.7	Rhyolite	leaky	20.35
21	72.158	2761325	6281271	277.7	169.8	277.7	Rhyolite pyroclastic	leaky	167.5
22	72.332	2767985	6275286	5.7	2.7	5.7	Taupo Ignimbrite	unconf	5.12
23	72.399	2751127	6256230	6	3	6	Post Taupo lacustrine seds	unconf	0.39
24	72.331	2750827	6284765	5.8	2.8	5.8	Oruanui Ignimbrite	unconf	3.71
25	72.397	2750170	6261617	?	NA	NA	Whakamaru Ignimbrite	unconf	59.05

Well location and static water levels are shown in the geological map Figure 2.1. Only wells #17-21 in the northern catchment and well #25 in the west tap into significant Oruanui ignimbrite formations as indicated by deep static water levels. Most of the wells in the northern catchment contain oxic waters (Section 4.1) as expected for ignimbrite dominated aquifers containing little organic material. Only wells #14 and 22 near the lake shore indicate reducing conditions which indicates that these waters are from aquifers that contain organic matter - paleolake sediments or paleosoils. Toward the west, higher static water levels in wells #1, 2, 16 and 24 indicate thinning Oruanui ignimbrite cover or occurrence of aquitards e.g. paleosols as indicated by shallow springs in this area, and hydrochemistry indicates onset of reducing conditions.

The wells in the western catchment of Whakamaru ignimbrite with thin or no Oruanui ignimbrite cover have mostly highly reduced waters, including well #25 penetrating through thicker Oruanui ignimbrite into Whakamaru ignimbrite . The wells furthest to the south in and near the andesite indicate extremely high reducing conditions up to methane fermentation, with wells #9, 12 and 13 containing traces of methane. These highly anaerobic conditions suggest that some wells in this area may be influenced by localised slightly swampy conditions. Low water drainage of this geologic formation compared to the ignimbrite can be considered favourable for the formation of swamp-like conditions. Oxic water is found in the west in wells near the lake shore (#11, 23) and in the Taupo ignimbrite (#8, 10), and in well #5 which is a deep well in the Whakamaru ignimbrite.

3.0   AGE AMBIGUITY – YOUNG COSMOGENIC TRITIUM VERSUS OLD BOMB TRITIUM

The tritium time-series alone are still ambiguous for several wells (#12, 13, 24, 25). Old ages of mean residence time (MRT) of c.50 y and very young ages of MRT 2-9 y are possible. It was hoped that tritium time series over 5 years would resolve this ambiguity. This is because the old bomb-tritium shows a decline over that period, while the young cosmogenic tritium should remain constant over that time. However, over the last 10 years the concentration of tritium in New Zealand rain has coincidently dropped considerably (Figure 3.1, blue line). This drop is similar to the expected drop in bomb-tritium in old water. Therefore, the young and old age water have identical tritium outputs at the present time and the ambiguity cannot be resolved on the basis of tritium data only. However, other evidence can be used to resolve ambiguous ages such as CFCs, SF_6, hydrochemistry, and hydrogeologic information.

We assume that the further drop in tritium over the last 10 years is a result of reduced production of cosmogenic tritium due to modulation by the solar field. The wash-out of bomb-tritium from the atmosphere essentially concluded in 1990 (Figure 3.1) and would not account for any further decline in tritium. The solar field shields the earth from the cosmic rays that produce the tritium, therefore there is low tritium production at high solar activity. We expect this process to reverse over the next few years according to the solar cycle. If so, then there will be a slight increase in tritium in rain over the next years (as seen between 1993 and 1998). This will allow old bomb tritium (declining over time) to be easier distinguished from young cosmogenic tritium (increasing over time).

Hydrochemistry data can give additional information for distinguishing between the very young and old age solutions. Several chemical parameters, particularly Si, F and P, have shown relatively strong correlation with age in other catchments of New Zealand. These ions may be progressively leached from aquifer material with time leading to increasing

concentrations (Morgenstern et al., 2005). Those trends are discussed in Chapter 8, and are used where possible to assist in resolving remaining ambiguity.
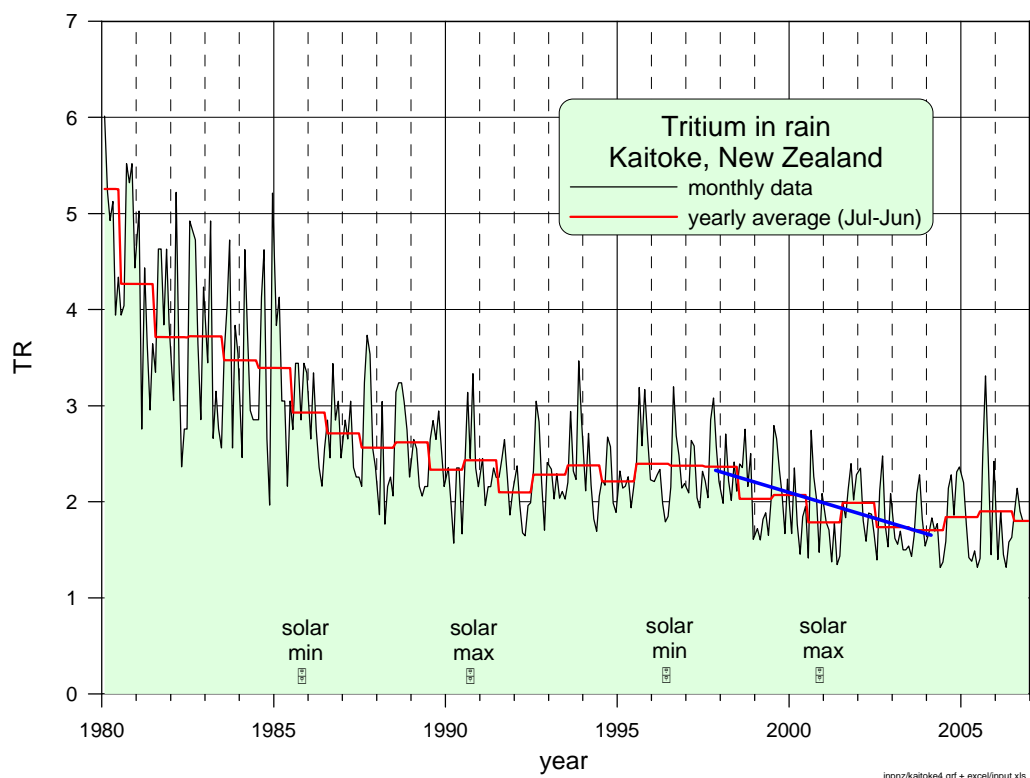
Figure 3.1   Tritium in recent rain in Kaitoke. Note the drop in tritium over the last decade (blue line).

4.0   RESULTS

4.1   HYDROCHEMISTRY

The phase 1 groundwater chemistry results and the series of redox reactions are summarised in Hadfield et al., 2001. Hydrochemistry results of those samples selected for age dating are summarised in Table 4.1, together with hydrochemistry results from 2002 and 2007 (data supplied by EW). Most chemistry parameters are consistent over time. Only a few parameters of some wells vary considerably, these are highlighted in orange.

Total Fe and Mn vary considerably in about half of the wells and may be related to suspended solids from purging. Shallow piezometer wells 4 and 13 show high variability in several parameters most of which can be related to landuse. This high variability supports the finding that these are very young groundwaters (Chapter 6). Varying point source input and/or seasonal changes in young rainwater contribution with little smoothing due to the young age is likely to cause this high variability. The old groundwater from deep well 14 had significantly different hydrochemistry in 2001. This water is highly impacted by landuse (Hadfield and Barkle, 2004) as indicated by extremely high nitrate. The reason for the high variability may be related to differences in pumping as indicated by the significantly lower static water level in 2001.

Table 4.1   Groundwater hydrochemistry in the northern and western Lake Taupo catchment. Samples with name highlighted in red have hydrochemistry indicative of reducing conditions indicative of potential CFC degradation. High variation in hydrochemistry is highlighted in orange.

#	Site	date	Temp field	Cond field	pH field	DO field	Cond lab	pH lab	TDS	Alkal as CaCO3	Free CO2	Tot Hardn CaCO3	K	DRP	SO4	NO3-N	NH4-N	Fe tot	Mn tot	B	Na	Cl	Na/Cl	F	SiO2	As	Ca
			oC	µS/cm		ppm	µS/cm		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm		ppm	ppm	ppm	ppm
1	72.383	25/06/02		c.110	6.5		125	6.8	84	26	8	28	3.4	0.052	3.8	3.55	0.01		0.54	0.005	0.005	9.3	8.2	1.13			0.005	7.21
1	72.383	07/03/07	12.8	110.2	6.47	10.2	110	7.1	74	26	4	26	3.5		5.6	3.03	0.01		0.07	0.005	0.05	9.4	7.1	1.32				6.89
1	72.383	16/08/07					107	6.6	71	25	12	26	3.5	0.057	5.5	2.74	0.01		0.1	0.005	0.05	9.2	6.8	1.35	0.05	79.5		6.79
2	72.1009	25/06/02		c.100	6.4											2.3											0.048	
2	72.1009	07/03/07	13.6	116	6	8.18	112	6.8	75	34	12	32	5.3		4.2	3.13	0.01	2.31	0.099	0.05	8.9	3.9	2.28				8.58
2	72.1009	16/08/07					112	6.3	75	32	32	29	5.1	0.004	4.2	3.3	0.01	0.75	0.017	0.05	8.4	3.9	2.15	0.05	73.4		7.93
3	72.1006	07/03/07		58	6.6	7	55	7.2	37	25	3	13	1.3		1.1	0.07	0.01	3.41	0.066	0.05	7	2.4	2.92			0.002	2.67
3	72.1006	16/08/07				7.1	61	6.7	41	26	11	15	1.5	0.096	1	0.19	0.01	0.12	0.005	0.05	6.9	2.8	2.46	0.06	68.9		3.1
4	72.1069	25/06/02		160	6.9	9										3.53			0.02	0.001							0.003	
4	72.1069	07/03/07	13.6	169.3	6.21	8.38	163	6.5	109	40	23	30	37.5		16.3	3.15	0.01	13.4	0.14	0.11	3.7	2.5	1.48				6.35
4	72.1069	16/08/07					129	6.4	86	32	26	15	27.7	0.004	14.4	1.91	0.01	0.8	0.007	0.07	3.5	2.2	1.59	0.05	43.3		3.8
5	72.1089	07/03/07		215	6.5		219	7	147	48	11	63	5.6		22.4	7.11	0.01	0.29	0.054	0.1	16.4	5.6	2.93			0.004	14.7
5	72.1089	16/08/07					207	6.6	139	47	26	60	5.5	0.035	19.4	7.21	0.01	0.21	0.01	0.09	15.9	6.1	2.61	0.05	73		14.3
6	72.1071	12/06/02		68	6.1	3.4										0.27			1.06	0.055							0.003	
6	72.1071	07/03/07	12.9	66	6.01	3.4	71	6.8	47	30	10	19	1.6		1.2	0.57	0.04	2.39	0.037	0.05	7.8	3.1	2.52				4.2
6	72.1071	16/08/07					66	6.2	44	26	32	17	1.7	0.004	1.3	0.8	0.04	1.16	0.051	0.05	6.7	2.9	2.31	0.05	58		3.91
7	72.1072	07/03/07		82	7	0.8	84	7.2	56	40	5	20	2.5		0.5	0.05	0.24	3.36	0.673	0.05	8.8	3.4	2.59			0.007	5.42
7	72.1072	15/08/07				9.11	84	6.8	56	40	12	21	2.4	0.073	0.5	0.14	0.22	4.13	0.834	0.05	9.2	3.5	2.63	0.26	64.6		5.3
8	72.1087	20/06/02		74	6.5	8.4										1.64			0.02	0.005							0.001	
8	72.1087	07/03/07	16.7	74	6.45	8.93	74	7.1	50	21	4	15	3.5	0.009	4.2	1.6	0.01	0.24	0.008	0.05	7.4	3.6	2.06				4.1
8	72.1087	15/08/07					71	6.7	48	21	8	15	3.8		4.5	1.67	0.01	0.83	0.021	0.05	7.3	3.5	2.09	0.05	54.9		4.26
9	72.1078	20/06/02		91	6.5											0.05			high	high							0.002	
9	72.1078	07/03/07	13	101	6.62	0.05	93	7	63	37	8	26	2		2.8	0.05	0.11	2.06	1.44	0.05	7.6	5.7	1.33				5.64
9	72.1078	15/08/07					102	6.6	63	38	19	27	2.1	0.004	2.9	0.05	0.09	2.73	1.45	0.05	7.4	5.8	1.28	0.08	44.7		5.76
10	72.1079	20/06/02		78	6.5	2.4										0.38			0.02	0.064							0.001	
10	72.1079	07/03/07	14.7	66	6.05	2.39	65	6.8	44	22	7	11	4.4		3.3	0.29	0.01	0.61	0.016	0.05	6.9	4.2	1.64				2.75
10	72.1079	15/08/07					64	6.4	43	17	14	12	3.7	0.004	3.6	0.99	0.01	0.08	0.005	0.05	6.3	4.6	1.37	0.05	49.1		3.09
11	72.1075	12/06/02		100	6.7	3.9										0.77			0.02	0.01							0.003	
11	72.1075	07/03/07	19	95	6.36	1.52	90	7	60	28	6	22	2.2		5	0.62	0.04	0.28	0.013	0.09	9	6.3	1.43				5.21
11	72.1075	15/08/07					90	6.6	61	26	12	22	1.8	0.004	6.3	0.38	0.01	0.07	0.007	0.1	9.6	7.5	1.28	0.13	32.1		5.05
12	72.1081	12/06/02		69	6.3	1.4										0.05			2.93	0.167							0.001	
12	72.1081	07/03/07	15.2	88	6.17	0.76	78	6.6	52	37	17	16	3.1		0.5	0.05	0.01	6.19	0.157	0.05	6.9	4.1	1.68				4.34
12	72.1081	14/08/07					76	6.4	51	51	44	18	3.6	0.004	1	0.12	0.01	11.4	0.146	0.05	7.3	8.2	0.89	0.05	39.4		5.13
13	72.1076	12/06/02		310	6.4	1.2										17.2			0.02	0.083							0.003	
13	72.1076	07/03/07	13.7	385	6.13	1.16	377	6.8	253	125	39	127	33.5		6.3	5.3	0.06	0.93	0.535	0.05	7.6	21.5	0.35				38.7
13	72.1076	14/08/07					252	6.4	169	112	92	105	21.4	0.328	9.7	0.07	0.02	0.84	0.17	0.05	4.9	3.3	1.48	0.05	24.4		32.8
14	68.32	05/03/01					317	6.8	212	18	6	91	2.7	0.014	40.9	16.5	0.02	2.61	0.337	0.023	19.9	14.9	1.34				19.4
14	68.32	07/03/07	15.1	365	6.6	1.89	367	6.9	246	13	3	116	3.4		40.6	21.2	0.21	1.06	0.021	0.05	19.5		1.18				25.2
14	68.32	18/08/07					343	6.6	232	13	6	104	3.1	0.042	39.8	18.7	0.11	1.66	0.017	0.05	21.1	17.1	1.23	0.16	67.3		22.8
15	72.364	06/03/01					85	7	57	25	5	17	2.2	0.105	2.7	1.58	0.01	0.01	0.005	0.006	7.7	3.7	2.08				3.8
15	72.364	17/08/07					84	6.9	56	27	7	20	2.3	0.066	3.1	1.93	0.01	0.01	0.005	0.05	8.3	3.8	2.18	0.11	69		4.56
16	72.377	06/03/01					66	6.9	44	26	6	15	0.6	0.23	1	0	0.01	0.2	0.005	0.005	6.8	2.6	2.62				3.19
16n	72.513	07/03/07					83	7.4	55	40	3	26	1.1		1.5	0.05	0.01	0.04	0.362	0.05	7.2	2.2	3.27				5.45
16n	72.513	16/08/07					79	7.1	53	39	7	26	1.1	0.132	1.2	0.05	0.02	0.16	0.344	0.05	7	2.3	3.04	0.08	69.5		5.41
17	68.317	05/03/01					139	6.8	93	24	8	27	2.9	0.09	5.5	5.69	0.01	0.01	0.005	0.005	14.3	8.5	1.68				6.01
17	68.317	07/03/07	14.4	149	6.57	10.2	151	7.2	101	27	3	32	3.2		7.2	4.88	0.01	0.02	0.005	0.05	15.1	9.1	1.66				7.28
17	68.317	16/08/07					149	6.7	100	26	9	31	3	0.073	11.1	5.18	0.01	0.01	0.005	0.05	14.2	8.9	1.6	0.09	76.9		6.91
18	72.392	06/03/01					175	6.9	117	21	5	41	2.4	0.041	7	9	0.01	0.09	0.005	0.005	13.3	11.2	1.19				8.76
18	72.392	07/03/07	11.5	186	6.5	11.2	188	7.1	126	24	4	50	2.8		18.1	5.91	0.04	0.02	0.005	0.05	16.3	11.4	1.43				10.5
18	72.392	16/08/07					189	6.8	126	24	8	49	2.7	0.042	19.7	6.19	0.01	0.03	0.005	0.05	15.3	12.2	1.25	0.12	79.7		10.6
19	68.301	06/03/01					117	7	78	29	6	25	1.5	0.125	8	2.48	0.01	0.09	0.005	0.005	12	4.2	2.86				4.82
19	68.301	07/03/07					108	7.3	72	31	3	25	1.5		8.5	2.15	0.01	0.01	0.005	0.05	12	3.8	0				4.88
19	68.301	17/08/07				6.66	104	6.9	70	31	7	24	1.4	0.131	8.1	2.21	0.01	0.01	0.005	0.05	11.2	3.8	3.16	0.12	70.6		4.67
20	68.66	05/03/01					83	6.8	56	28	9	17	2	0.101	2.2	0.85	0.01	0.09	0.005	0.006	7.9	3.5	2.26				3.87
20	68.66	10/06/04				9																						
21	72.158	06/03/01					74	7	50	25	5	14	2	0.103	1.3	0.48	0.01	0.04	0.005	0.005	7.1	2.8	2.54				3.18
21	72.158	16/08/07					67	6.8	45	27	9	15	1.9	0.084	1.5	0.59	0.01	0.05	0.005	0.05	7.4	2.9	2.55	0.1	70.1		3.49
22	72.332	06/03/01					154	6.7	103	36	14	37	3.6	0.065	8.8	2.91	0.01	2.72	0.132	0.007	15.2	10	1.52				9.18
23	72.399	06/03/01					131	6.9	88	38	10	35	3.1	0.053	1.7	2.39	0.01	0.02	0.005	0.009	8.8	5.4	1.63				7.89
23	72.399	15/08/07					109	6.8	73	37	11	33	2.9	0.041	2.4	2.03	0.01	0.01	0.005	0.05	8.4	5.5	1.53	0.28	67		7.48
24	72.331	06/03/01					380	6.7	255	36	14	119	10.2	0.007	40.8	3.64	0.07	1.31	0.294	0.008	14.5	43.5	0.33				27
25	72.397	06/03/01					159	6.8	107	37	12	45	2.6	0.051	2.4	6.85	0.03	9.59	0.085	0.005	11.7	8.3	1.41				10.1
25	72.397	15/08/07				9.98	127	6.6	85	40	18	36	2.1	0.033	1.7	3.72	0.01	2	0.026	0.05	11	5.8	1.9	0.07	73.1		7.87

Samples with name highlighted in red have hydrochemistry indicative of reducing conditions (based on DO, Fe, Mn and NH_4). Samples #9, 12 and 13 contain traces of methane (Table 4.1) and indicate extremely strong reducing conditions up to methane fermentation. However, the indicators for reducing conditions are not always conclusive. Manganese for example is not preferentially associated with much higher iron (Figure 4.1).
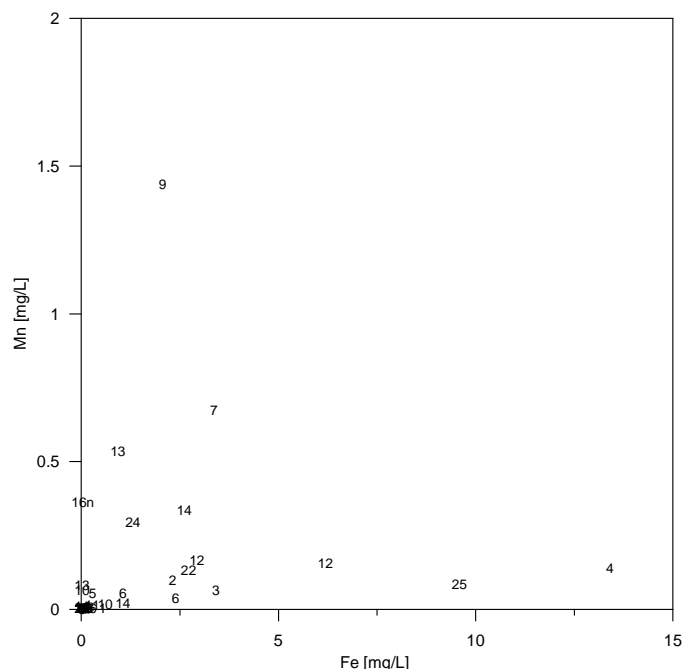

Figure 4.1   Manganese versus iron.

Redox reactions in the aquifer alter the chemistry and gas concentrations of the water. Therefore, different colours are used for oxic (green) and reduced (red) waters for most figures through this report.

4.2   TRITIUM AND GASES

Half of the wells (#14-25) were sampled first in 2001, including tritium and CFCs. The other half of the wells (#1-13) were sampled in 2002, with SF_6 added. The age results for about 10 samples were still ambiguous, so another sampling campaign was performed in 2007 to obtain time series of tritium, CFC, and SF_6. Special focus was on the wells with ambiguous results and unusual mixing flow fractions. In 2007 the gas samples were also analysed for argon and nitrogen as indicators for gas alteration in the groundwater, and methane as an indicator for strong reducing conditions with related CFC degradation. Also dissolved oxygen as an indicator of oxic/anoxic conditions was measured in 2007 with a robust non-membrane probe (Haach HQ40d). The analysis results are listed in Tables 4.2 and 4.3. Dissolved oxygen results are included in the field parameters of Table 4.1.

Table 4.2   Tritium, SF$_6$, and CFC results for the northern and western Lake Taupo catchment.

#	Site	Tritium No.	Tritium sampling date	TR (2005 scale)	±TR	Gas sampling date	SF6 No.	CFC No.	SF6	CFC-11	±	CFC-12	±
									Atm. Part. Press. pptv				
1	72.383	TT562	25/06/02	2.54	0.05	17/10/02		FT36	3.50	93		204	
1	72.383	TT705	8/03/07	1.84	0.05								
2	72.1009	TT564	25/06/02	1.72	0.04	13/08/02		FT34	4.33	238		473	
2	72.1009	TT706	8/03/07	1.51	0.04	8/03/07	ST26	FT65	6.23	231	0.7	501	1
3	72.1006	TT563	12/06/02	0.305	0.023	12/06/02		FT31	1.39	30.7		89	
4	72.1069	TT565	25/06/02	1.72	0.05	25/06/02		FT24	5.13	244		499	
4	72.1069	TT707	8/03/07	1.71	0.04	8/03/07	ST27	FT66	5.31	204	0.7	468	1.8
5	72.1089	TT574	25/06/02	1.48	0.04	3/10/02		FT35	1.98	190		354	
6	72.1071	TT566	12/06/02	1.99	0.05	12/06/02		FT29	3.02	24.2		131	
6	72.1071	TT708	8/03/07	1.77	0.05	8/03/07	ST28	FT67	3.95	33.5	0	153	1.5
7	72.1072	TT567	20/06/02	0.556	0.026	20/06/02		FT26	0.26	1.6		3.9	
8	72.1087	TT573	20/06/02	1.96	0.05	20/06/02		FT25	4.12	218		496	
8	72.1087	TT709	8/03/07	1.71	0.04	8/03/07	ST29	FT68	5.08	200	2.4	459	3.5
9	72.1078	TT570	20/06/02	1.74	0.05	20/06/02		FT32	2.47	1.5		46	
9	72.1078	TT710	7/03/07	1.42	0.04	7/03/07		FT69	broke	-0.1	0.2	13.4	2
10	72.1079	TT571	20/06/02	1.8	0.05	20/06/02		FT33	4.80	109		333	
10	72.1079	TT711	7/03/07	1.56	0.04	7/03/07	ST31	FT70	4.70	93	0.1	296	0.6
11	72.1075	TT568	12/06/02	1.88	0.07	12/06/02		FT30	4.80	118		376	
11	72.1075	TT712	7/03/07	1.52	0.04	7/03/07	ST32	FT71	4.68	140	2.1	457	7.5
12	72.1081	TT572	12/06/02	1.74	0.04	12/06/02		FT27	5.24	46		145	
12	72.1081	TT713	7/03/07	1.51	0.04	7/03/07	ST33	FT72	4.14	39		166	
13	72.1076	TT569	12/06/02	1.74	0.05	12/06/02		FT28	4.85	173		433	
13	72.1076	TT714	7/03/07	1.49	0.05	7/03/07	ST34	FT73	3.10	50	3	387	32
14	68.32	TT486	5/03/01	2.07	0.06	5/03/01		13		91		255	
14	68.32	TT715	8/03/07	1.21	0.04								
15	72.364	TT497	6/03/01	0.956	0.036								
16	72.377	TT493	6/03/01	0.136	0.023	6/03/01		19		0.6		3.7	
17	68.317	TT487	5/03/01	2.72	0.08	5/03/01		14		79		198	
17	68.317	TT716	8/03/07	2.1	0.05								
18	72.392	TT491	6/03/01	3.33	0.09	6/03/01		18		81		221	
18	72.392	TT717	8/03/07	1.71	0.04								
19	68.301	TT489	6/03/01	0.92	0.037	6/03/01		16		24.6		56	
20	68.66	TT488	5/03/01	0.886	0.036	5/03/01		15		84		180	
21	72.158	TT490	6/03/01	0.64	0.031	6/03/01		17		24.0		66	
21	72.158	TT730	16/08/07	0.566	0.029								
22	72.332	TT496	6/03/01	1.31	0.04	6/03/01		23		95.6		294	
23	72.399	TT494	6/03/01	1.51	0.05	6/03/01		21		175		391	
24	72.331	TT492	6/03/01	1.77	0.06	6/03/01		20		164		345	
25	72.397	TT495	6/03/01	1.79	0.06	6/03/01		22		59.7		177	
25	72.397	TT735	15/08/07	2.30	0.05								

Table 4.3   Argon, nitrogen, and methane results with calculated recharge temperature and excess air. Highlighted in red are results indicative of strongly reducing groundwater conditions with related potential gas alteration.

#	Site	Gas sampling date	Ar	±	N2	±	Rech. Temp	±	excess air	±	CH4	±
			mL(STP)/kg				oC	0	mL(STP)/kg		μmol/L	
2	72.1009	8/03/07	0.357	0.003	13.4	0.23	11.3	0.1	-0.2	0.3	0	0
4	72.1069	8/03/07	0.382	0.003	14.88	0.32	9.8	0.2	1.1	0.5	0	0
6	72.1071	8/03/07	0.389	0.001	14.73	0.01	8.1	0.1	0.2	0.1	0	0
8	72.1087	8/03/07	0.361	0.002	13.69	0.24	11.2	0.1	0.1	0.4	0	0
9	72.1078	7/03/07	0.379	0.002	15.55	0.31	12.1	0.3	2.8	0.5	3.48	0.06
10	72.1079	7/03/07	0.373	0.001	15.05	0.02	12.1	0.3	2.2	0.1	0	0
11	72.1075	7/03/07	0.365	0.006	15.42	0.38	14.7	0.5	3.5	0.3	0	0
12	72.1081	7/03/07	0.395	0.02	16.21	1.14	10.4	1.3	3	1	6.05	3.8
13	72.1076	7/03/07	0.325	0.005	18.32	0.36	39.1	0.2	12.1	0.4	0.2	0

5.0   GASES IN GROUNDWATER

The situation with dissolved gases in the groundwater of the western and northern catchment of Lake Taupo is extremely difficult. All gases (CFCs, SF_6, Ar, N) give inconclusive results which is most likely related to air exchange between the groundwater and the atmosphere, and degradation and degassing due to anaerobic groundwater conditions. Particularly in the western catchment the majority of groundwaters indicate highly reducing conditions up to the methane fermentation stage in the southwest. Age interpretation of CFC and SF_6 results is therefore very limited.

5.1   ARGON AND NITROGEN

Measured argon and nitrogen concentrations with related recharge temperature and excess air are listed in Table 4.3 and shown in Figure 5.1. Two repeat samples are collected from each well and measured for a reproducibility check, which was found to be good for most of the analysed samples. Only the gases of sample 12 are not reproducible. This water is highly reduced up to the stage of methane fermentation and it is likely that gas loss in one of the bottles has caused that concentration drift.

Most calculated recharge temperatures are in the expected range between 10 and 13°C. Excess air, however, is relatively high for most of the samples. The gases in sample 13 are completely out of the expected range. This sample has an unusual chemistry with high Ca, Mg, Cl, K, NO_3, CO_2 and total hardness, and traces of methane and ammonia indicate highly reducing conditions (while not associated with high Fe and Mn levels). Denitrification with associated degassing is a possible process to have caused these unusual concentrations. Reducing conditions are found in many of these water samples with potential alteration of the gas concentrations. Therefore, excess air is not used for fingerprinting the origin of the water.
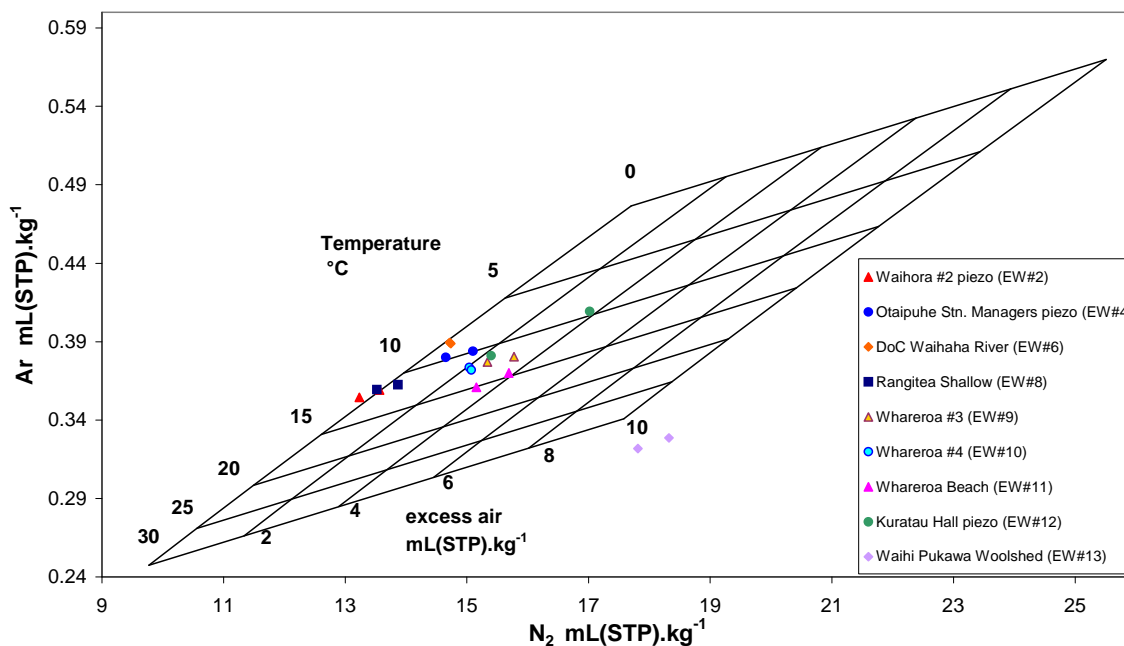
Figure 5.1   Ar and N_2 concentrations and calculated recharge temperature and excess air.

5.2 CFCs

CFC concentrations, listed in Table 4.2, are extremely difficult to interpret into ages in the Lake Taupo catchment groundwaters due to strongly reducing conditions in about half of the wells with related potential CFC degradation and degassing. Most CFC data are inconclusive between CFC11 and CFC12 (giving different ages) and indicate that CFCs are modified in the groundwater system. Most data indicate too low CFC11 or too high CFC12 which can be related to CFC contamination which affects usually more CFC-12, and CFC degradation which affects more CFC-11. No extremely high CFC concentrations are observed in the northern and western Lake Taupo catchment. Highly CFC contaminated groundwaters are often found near horticulture areas and are most likely related to herbicide and pesticide sprays.

Several sites were re-sampled after five or six years. While results for most samples reproduce well, for several wells (#2, 4, 10, 11, 13) the repeat results do not match the CFC-11 or CFC-12 trend. A reason for this may be that the measurements are very sensitive to sampling conditions (e.g., water level, location of pump, pump rate) which will affect gas exchange and degassing in this area.

The oxic groundwaters are expected to have little CFC degradation and therefore CFC-11 and CFC-12 should be close to the ratio of atmospheric equilibrium. Only a few samples are close to the equilibrium ratio but these are oxic waters. The samples that are not close to the equilibrium ratio have no trend between oxic and reduced waters. Particularly oxic samples 8, 10, and 11 are shifted away from the equilibrium ratio similarly to reduced waters 6, 12-14, and 22. This indicates that also a slight CFC-12 contamination occurs in the groundwater of Lake Taupo catchment. The CFC data of the waters indicative of the highest reduced stage 9, 12 and 13 are furthest away from the equilibrium ratio, and are most unreproducible. Sample 13 is also highly disturbed in Ar and N_2 concentrations.

CFC dating does not take into account water travel time through the unsaturated zone (which can be over 50m thick), and the CFC clock can be re-set by air exchange between the groundwater and the atmosphere. To test for air exchange, CFC and tritium ages of the samples with unambiguous tritium ages were compared. For all oxic waters the CFC ages are significantly younger than the unambiguous tritium ages. CFC ages are therefore significantly disturbed by the unsaturated zone and/or gas exchange processes and can give only minimum ages. However, for most oxic waters these minimum ages can resolve the ambiguity in tritium age interpretation. For reduced waters, CFC degradation can lead to CFC ages being interpreted as too old. This is observed only in one of the unambiguous samples, sample 14. Samples 3 and 6 indicate that despite clearly reduced conditions, CFC degradation is of lesser influence than gas exchange processes with atmospheric air.

To test for the reliability of CFC ages in the younger age range, with its necessary corrections for excess air and recharge temperature, CFCs in the young groundwaters were compared to CFCs in stream waters that have been in equilibrium with air. CFCs in stream water are expected to quickly equilibrate to atmospheric levels and ratios due to exchange between the water and the air. In a previous test on how quickly this exchange occurs and if any age information (low CFC concentration) is retained in stream water, CFCs were measured at 5 sites along the course of two streams (Mapara and Whangamata) which have clearly old water with pre-bomb tritium ratios (recharged before 1960). The CFC concentrations according to the recharge year would be near zero. However, all samples showed CFC concentrations and ratios very close to equilibrium with the atmosphere. Gas

exchange between the water and the atmosphere re-sets the CFC clock quickly to zero in open waters. CFC dating can therefore only be applied at springs and in groundwater where the water has not been in contact with air. The CFC data in the streams, however, confirm the assumptions for CFC equilibrium that are used for groundwater dating. Most stream water data were close to the atmospheric concentration and ratio at this time. Two samples, however, had slightly lower concentrations, similar to samples 2 and 4, demonstrating that samples 2 and 4 are at the boundary of current equilibrium concentration and within the limitation of the CFC method and therefore can be interpreted as very young.

In summary, air exchange between the water and the atmosphere, and anaerobic degradation are two competing processes that alter the CFC concentrations particularly in the western Lake Taupo catchment groundwaters. However, there are trends that make it possible to use the CFCs for resolving ambiguity in tritium dating. Particularly for the oxic waters minimum groundwater ages can be established with the CFCs with the true water ages being significantly older.

5.3   SF$_6$

SF$_6$ data, analysed according to Van der Raaij (2003), are listed in Table 4.2. To test how SF$_6$ data are affected by gas exchange processes, the calculated SF$_6$ ages according to the flow model are plotted versus the tritium ages in Figure 5.2 for the samples with unambiguous tritium ages. Clearly, the SF$_6$ ages are too young by decades, confirming the high degree of gas exchange processes in the northern and western Lake Taupo catchment that is also suggested by the CFC data. Similar age differences were observed in the ignimbrites of Lake Rotorua catchment (Morgenstern et al., 2004). Due to these gas exchange processes SF$_6$ data also can only give minimum ages, with the true ages being decades older. But for several samples SF$_6$ data can be used for distinguishing between the young (<4y) and the old (~40y) tritium age.
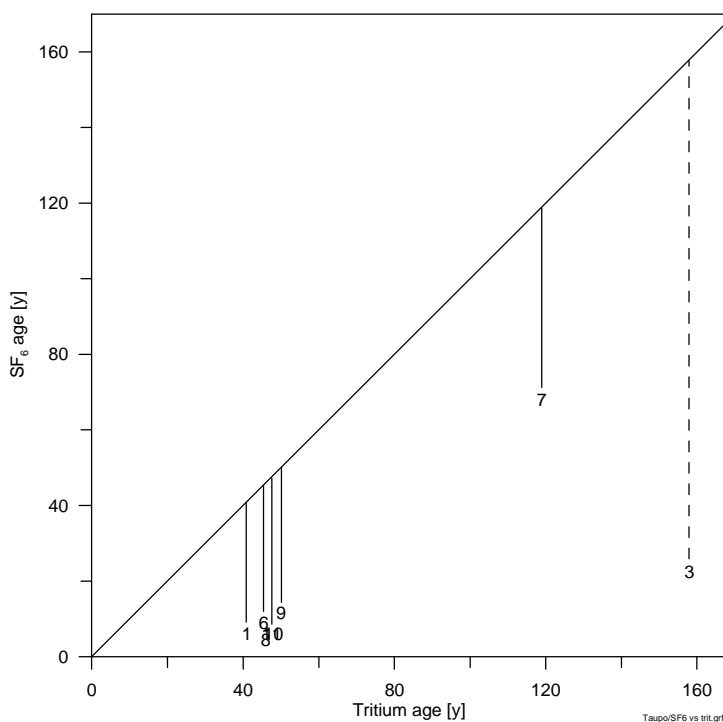
Figure 5.2   Age difference between unambiguous tritium ages and SF$_6$ ages. Sample #3 is near the detection limit of the SF$_6$ method.

6.0   TRITIUM AND AGE INTERPRETATION

The tritium data are listed in Table 4.2. All analysed waters contain detectable tritium and are therefore datable with tritium (none of the water is too old for the tritium method).

Figure 6.1 shows the tritium results that are non-ambiguous in age interpretation. These tritium results are either below the ambiguous range (indicated by the black line in the centre of the figure), or have non-ambiguous time series. The model that was used is the Exponential Piston Flow model (Appendix 1), with E_% the fraction of exponential (mixed) flow, and y the mean residence time (MRT) in years.

In 2001 and 2002 several wells (1, 17, and 18) and also some streams (Morgenstern 2007) had relatively high tritium concentrations in the water that are explainable by an unusually high fraction of piston flow in the groundwater system (as indicated by the low fraction of exponential flow). Even 40 years after the bomb-tritium, higher than current rain tritium concentrations in the groundwater can still have remained in groundwater systems with high piston flow and therefore little mixing of waters of different ages. To confirm such unusual high piston flow fractions, several wells were re-sampled in 2004 and in 2007. The tritium time series give an excellent match to the flow models with high piston flow fraction, confirming these unusual flow models with high confidence.

All tritium results >1 TR are post-bomb level, with the water containing significant bomb-tritium. The flow models for those groundwaters were established using the time-series tritium data. The steeply declining bomb-tritium allows for high confidence in model establishment. MRT ranges between 27 and 50 years, and the fraction of exponential flow ranges between 20 and 40%, which is very low compared to other groundwaters throughout New Zealand.

For the older waters with tritium <1 TR, only 19, 20, and 21 have tritium time series for establishing the flow model. Wells 19 and 20 match an age distribution of MRT 80 years and 85% exponential flow, and well 21 matches MRT 96 years and 69% exponential flow. Such old ages and high exponential flow fractions are also typical of waters in the Mamaku ignimbrite (Morgenstern et al., 2004). For all the other wells/springs with old water (tritium <1TR) no tritium time series were available for establishing the flow model. For consistency, 80% mixed flow was used for all of these sample sites except Kinloch Spring (15) with 85% mixed flow fraction (springs usually have higher mixed flow due to convergence of flow lines). Mean residence times for these older waters range between 72 and 180 years. All mean residence times and mixing flow fraction are listed in Figure 6.1 and in Table 7.1.
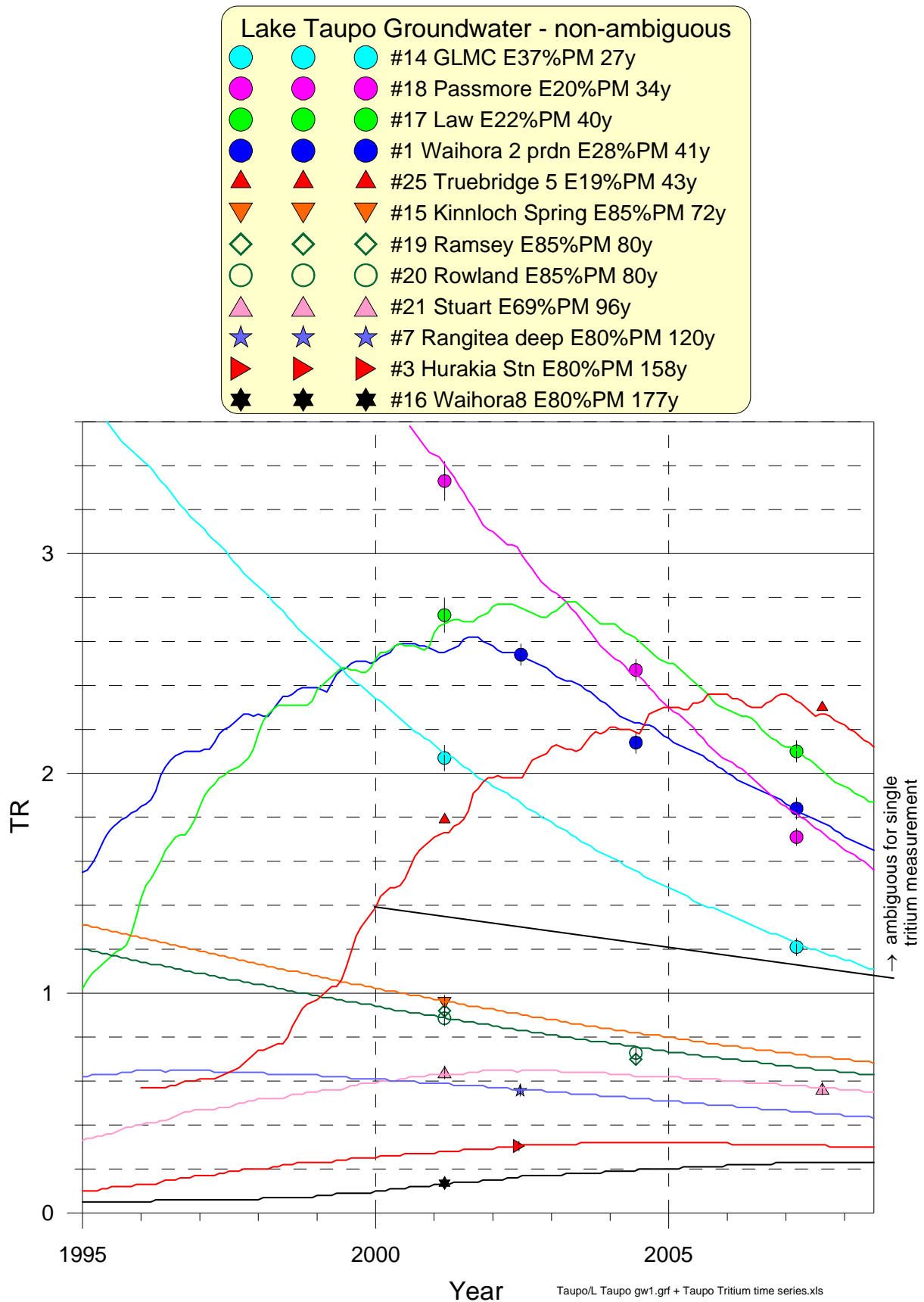
Figure 6.1   Non-ambiguous tritium time series and best fit flow model outputs.

Figure 6.2 shows tritium results that have tritium time-series for establishing the flow model, and ambiguity resolved via CFCs or SF_6. Mean residence times and mixing flow fraction are listed in Figure 6.2 and in Table 7.1.
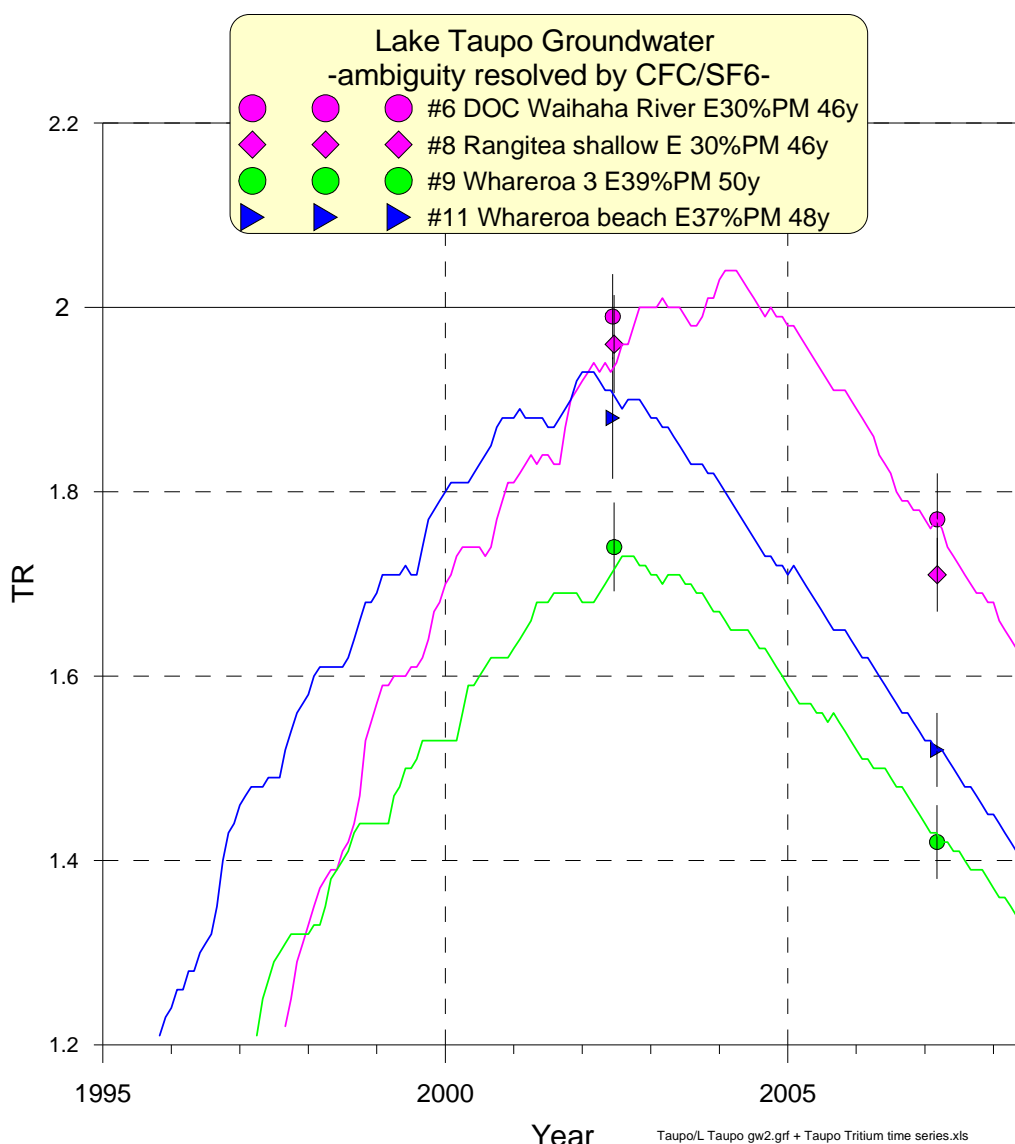

Figure 6.2   Ambiguity-resolved tritium time series and best fit flow model outputs.

The remaining samples 2, 4, 5, 10, 12, 13, and 22-24 have tritium data that are ambiguous (indicative for very young water of c. 2 years, or 30-50 years). The tritium time series for those wells are insufficient for resolving ambiguity. The main reason is the decline in tritium in rain over the last decade (Chapter 3). This causes similar tritium output for very young waters and older waters with declining bomb tritium. The trend of declining tritium in rain is expected to reverse in the next few years according to the solar activity cycle that modulates tritium production in the stratosphere. Therefore, tritium data in a few years can probably resolve all tritium ambiguities and constrain the flow model for most of the samples. CFC, SF_6 and hydrochemistry data were used to help resolving ambiguity.

For wells **2** and **4**, old water is unlikely as indicated by the CFC and SF_6 data. These waters are identified as very young with MRT around two years. Both of these are shallow piezometer wells. They ran dry when pumping even at low pump rate of c. 1.5 L/min. This indicates that these formations have low transmissivity and the wells contain only water from

the top of the water table of locally recharged groundwater. Highly variable hydrochemistry also supports the young water age for well 4.

For sample **5** the tritium result is highly ambiguous. However, this is the only water with consistent CFC-11 and CFC-12 ages, indicating that CFC alteration in this aquifer does not occur. This may be related to the Whakamaru ignimbrite aquifer without organic material. It is the only sample from a deep well in the Whakamaru ignimbrite that is not reduced. The tritium age distribution was chosen that matches the CFC age, MRT 22 years, and an assumed fraction of exponential flow of 50%. DRP (Chapter 8) confirms this age.

The water of well **10** is oxic and therefore CFCs and SF_6 reliably indicate an old age of >30 years with a tritium age distribution of MRT 48 years and exponential flow of 33%. This result is unusual because the nearby but significantly deeper well 9 has a very similar age.

The waters from wells **12** and **13** remain ambiguous in age interpretation. However, ambiguity can be resolved with some certainty. Both these wells contain highly reduced water (traces of methane, Table 4.3). The CFCs have therefore the potential to be degraded significantly. The water in well 13 is most likely very young (c. 2 years) because CFCs indicate relatively young age and the chemistry is highly variable (Table 4.1). Low and highly variable SF_6 is most likely a result of degassing as indicated by low argon (Figure 5.1). In contrast, Sample 12 is most likely old (48 years). CFCs indicate significantly older age than 13. Also SF_6 indicates an old age because degassing in the water of well 12 seems insignificant as indicated by normal argon concentration (Figure 5.1). SiO_2 (Chapter 8) does support the significantly older age of 12 compared to 13.

The water from wells **22** and **23** are not very young. An age of >8 years is indicated by the tritium, and CFC data indicate even older age. Age distributions were chosen that match the tritium data and are in agreement with the CFC data. Also dissolved reactive phosphate (Chapter 8) support these ages.

For the water of well **24** there remains a high degree of age ambiguity. This well was marked for tritium re-sampling in 2007 but the well could not be found (probably buried under a concrete platform). So the limited data for this well leave a high ambiguity. As a rough estimate for #24, the very young age of < 5 years is less likely as indicated by the CFC data. The MRT is likely to be in the range of 24-50 years.

7.0   GROUNDWATER AGE DISTRIBUTION

The mean residence times and fractions of mixed flow for all groundwaters are summarised in Table 7.1. MRT data in bold are well established non-ambiguous tritium results. Data in normal font have ambiguity for the tritium data alone but this could be resolved with CFCs, SF_6, and hydrochemistry trends. Sample 24 remains highly ambiguous in age interpretation. E%PM is the % fraction of Exponential Flow within the total flow, determined from tritium time-series or estimated according to the hydrogeologic situation.

Table 7.1   Age distribution, young water fraction, and extrapolated nitrate concentrations. Nitrate is also extrapolated for the anoxic waters which may be questionable because of changing denitrification rates with changing N input. However, all anoxic waters have either low nitrate or high young water fraction and therefore non-linear denitrification processes have insignificant impact on the NO_3 extrapolation.

#	Site	E%PM estimate	E%PM determed	MRT	Post-1955 water fraction	NO3 in 2007	NO3 at steady-state
		%	%	y	%	ppm	ppm
1	72.383		28	**41**	86	3.1	3.6
2	72.1009	50		2	100	3.2	3.2
3	72.1006	80		**158**	15	0.2	1.3
4	72.1069	50		2	100	2.9	2.9
5	72.1089	50		22	98	7.2	7.3
6	72.1071		30	**46**	77	0.7	0.9
7	72.1072	80		**119**	26	0.1	0.5
8	72.1087		31	**46**	76	1.6	2.2
9	72.1078		39	50	67	0.0	
10	72.1079		33	48	71	0.6	0.8
11	72.1075		37	48	72	0.6	0.8
12	72.1081		33	48	71	0.1	0.1
13	72.1076	50		2	100	0.1	0.1
14	68.32		37	**27**	97	18.8	19.4
15	72.364	85		**72**	49	1.8	3.6
16	72.377	80		177	11	0.0	
17	68.317		22	**40**	91	5.3	5.8
18	72.392		20	**34**	97	6.1	6.3
19	68.301		85	**80**	45	2.3	5.1
20	68.66		85	**81**	44	0.9	1.9
21	72.158		69	**96**	29	0.5	1.9
22	72.332	50		46	72	2.9	4.1
23	72.399	70		30	87	2.2	2.5
24	72.331	40		24	98	3.6	3.7
25	72.397		19	**43**	88	4.0	4.6

Figure 7.1 shows the MRT versus depth. Poor correlation is observed between MRT and depth. Old water occurs in shallow and deep wells. However, deep wells do not contain very young water. The weak correlation between age and bore depth suggests that this groundwater system is inhomogeneous implying preferred flow paths. These preferred flow paths could be along aquicludes like interbedded paleosols and paleo lake beds, through deposits with higher permeability, and along fractures. Such groundwater flow dominated by preferential flow paths may be the reason for the observed unusually high fraction of piston flow in this area.

Figure 7.2 shows the mean residence time of groundwater in the northern and western catchment of Lake Taupo. Most of the groundwater in this area of Lake Taupo is relatively old. Only some shallow piezo wells indicate very young water of < 5 years. The remaining groundwater has mean residence times of > 20 years. The groundwater in the northern, thick Oruanui ignimbrite, has MRT typically around 40-80 years. The oldest groundwater ages are observed in the western Whakamaru ignimbrite.

The old groundwater ages in the northern Oruanui ignimbrite are consistent with the old water ages in the northern streams (Whangamata 84y, Mapara 75y, Kawakawa 60y) which are mostly groundwater sourced (Morgenstern, 2007). The older groundwater ages in the western Whakamaru ignimbrite contrast to the younger stream ages indicating relatively little water flux through the groundwater system.
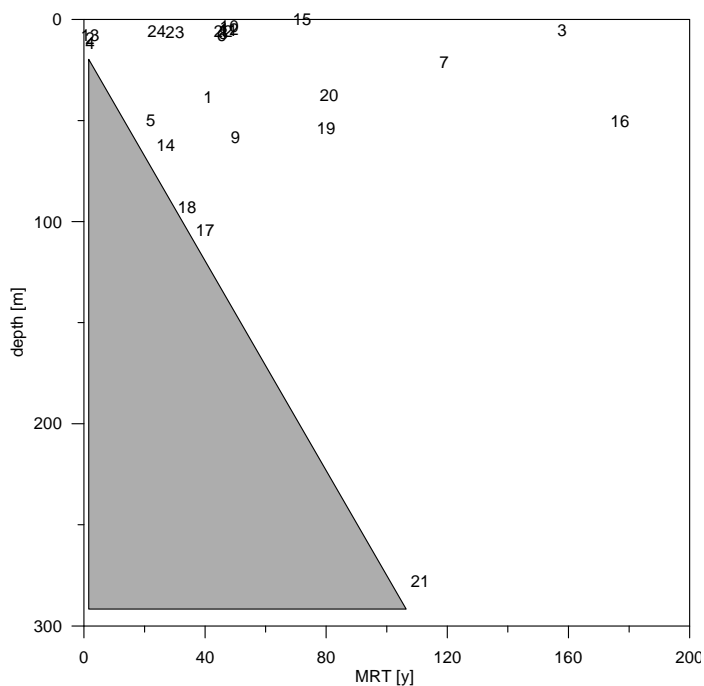
Figure 7.1   Mean residence time versus depth.

High exponential (mixed) flow fractions are found only in the northern catchment in the thick Oruanui ignimbrite. These exponential flow fractions are similar to those of the Mamaku Ignimbrite (Morgenstern et al., 2004), a comparable hydrogeological unit. All other groundwater in the northern and western catchment of Lake Taupo (with established flow model) have a high fraction of Piston Flow, between 60 and 80 % (exponential flow between 20 and 40%). These high piston flow fractions are observed through the whole northern and western catchment. The highest fractions of piston flow are observed in the north western part of the catchment. The high fractions of piston flow in the groundwater are consistent with high piston flow fractions found in some stream waters, and with the observed heterogeneous aquifer (preferential flow paths).

Despite the unusually high piston flow fraction, a large degree of gas exchange is observed in these groundwaters. This may indicate that flow along aquicludes like paleosoils and paleo lakebeds may be the controlling influence for the high degree of piston flow rather than fracture flow (fractures would be expected to be mostly separated from air).
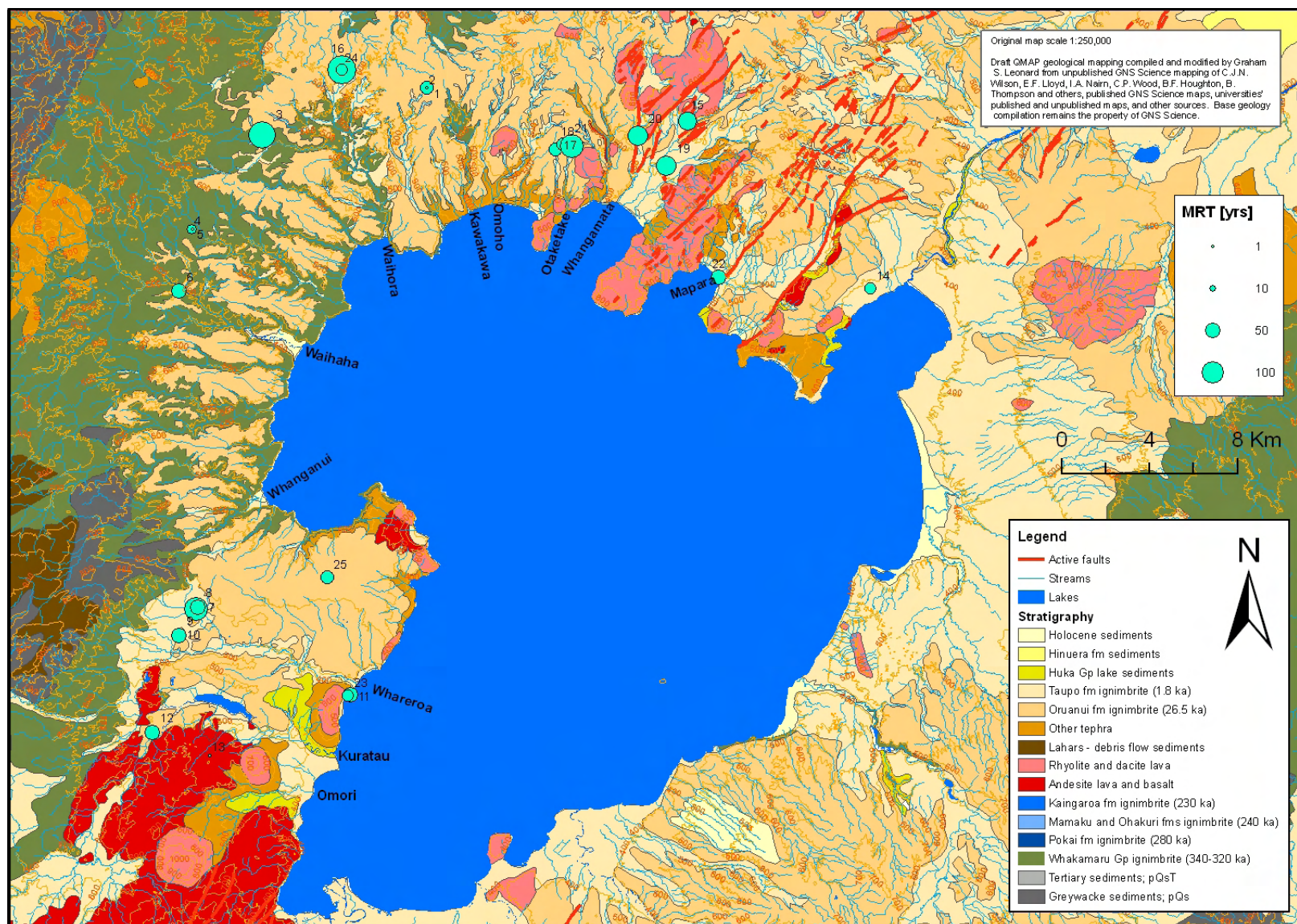
Figure 7.2   Mean residence times (MRT) in the northern and western catchment of Lake Taupo.

8.0   LANDUSE IMPACTS ON GROUNDWATER QUALITY

Relating groundwater quality to the recharge age assists to distinguish between geogenic and anthropogenic impacts on groundwater quality. Geogenic origin is indicated where concentrations of elements increase with age (leaching). The landuse origin is likely when only young water has high concentrations given that farming is a recent development. The age of landuse impacted water can give information about the timing of landuse impacts on groundwater quality. If the age distribution of groundwater is known, the fraction of landuse impacted water can be calculated. Relating it to groundwater quality can indicate current contaminant levels and likely pre-landuse levels. Future contaminant levels can be estimated by extrapolating to the time when pre-landuse water is completely flushed out of the groundwater system. Then only undiluted post-landuse water will discharge to the lake.

Several hydrochemistry parameters show a strong correlation to groundwater age. If such trends can be established with non-ambiguous age data, then these chemistry parameters can help resolve the ambiguous age data.

The following colour code is used in the Figures to distinguish between oxic (green) and reduced (red) water because redox reactions can cause different trends. Large font bold is used for data where ages are well established.

Non ambiguous age - oxic
Ambiguous age - oxic

Non ambiguous age - reduced
Ambiguous age - reduced

Figure 8.1 shows the field parameters versus MRT. Water **temperature** does not show a marked trend with age. **Conductivity** is relatively constant for the older water (>60yrs MRT), independent of geologic formation and of oxic/reducing conditions. Only young water shows elevated conductivities which are likely to be related to landuse impacts. The **pH** of oxic water is nearly constant at about pH 7 (green line). However, the pH of reduced water shows a more significant increase with age from 6.6 to 7.2 (red line) due to evolving bio-geochemical reactions.

Figure 8.2 shows Hardness, free CO_2, and Alkalinity. **Alkalinity** and **free CO_2** are relatively constant over mean residence time. Only wells 12 and 13 from the andesite have significantly elevated values. This water also shows a large distortion in the gas concentrations. **Hardness** also shows little variation with age except that some young groundwater (mostly anoxic) has elevated hardness.

Figure 8.3 shows that there is little trend in **reducing conditions** with age. Old and young water can be reduced as indicated by elevated Fe and Mn. The data indicate a higher level of reducing conditions in younger water but this is probably biased because most old water occurs in the northern Oruanui Ignimbrite containing little organic matter. Samples 9, 12, and 13 are highly reduced as indicated by traces of methane. High **dissolved oxygen** in reduced samples 2 and 4 is likely to be a result of air contact of the water prior to sampling. These two bores ran dry during sampling and recharged with only a few litres per hour. Due to this slow flow rate the water has enough air contact to significantly equilibrate with air prior to sampling. It is unclear why reduced water #7 had high dissolved oxygen at the last sampling in August 07.
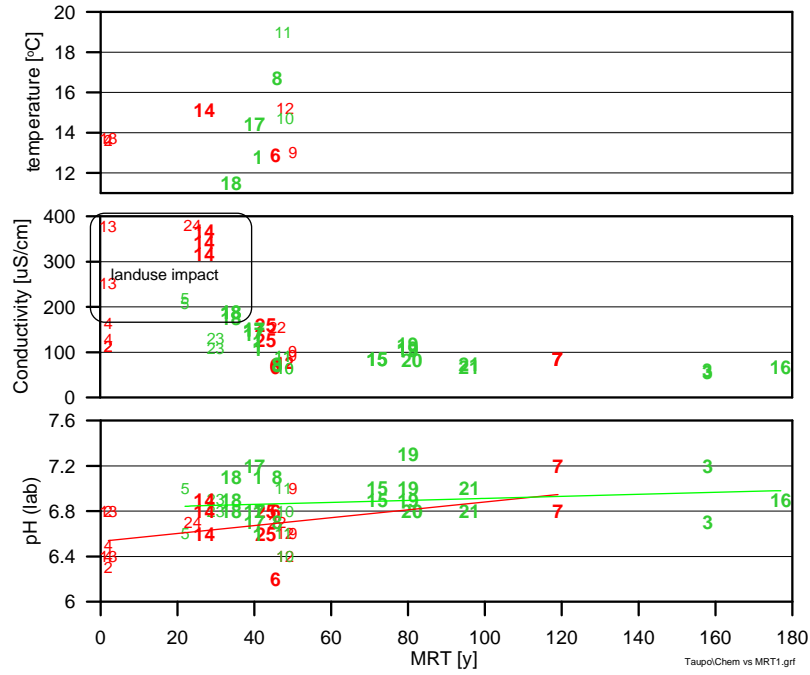
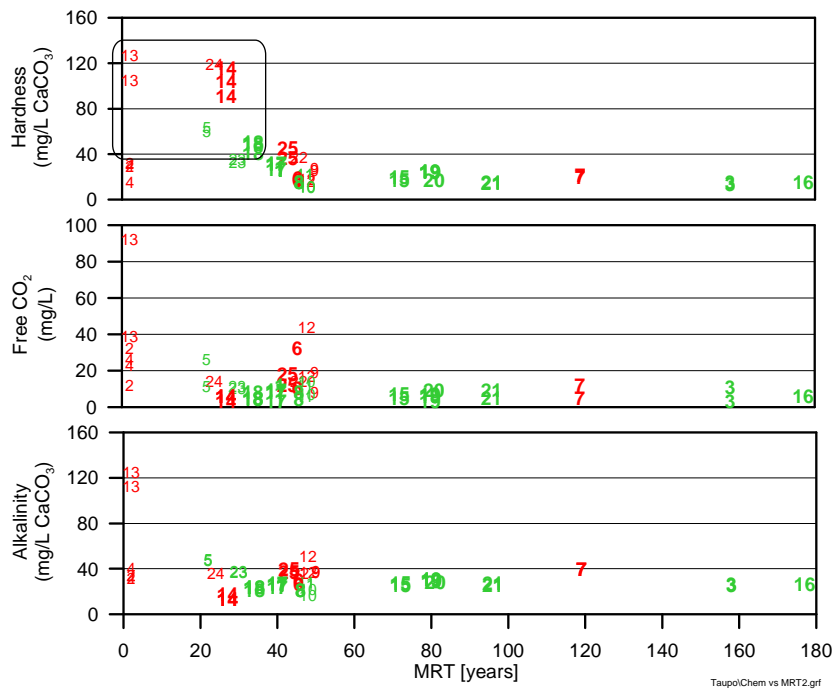Figure 8.1   Field parameters versus mean residence time.

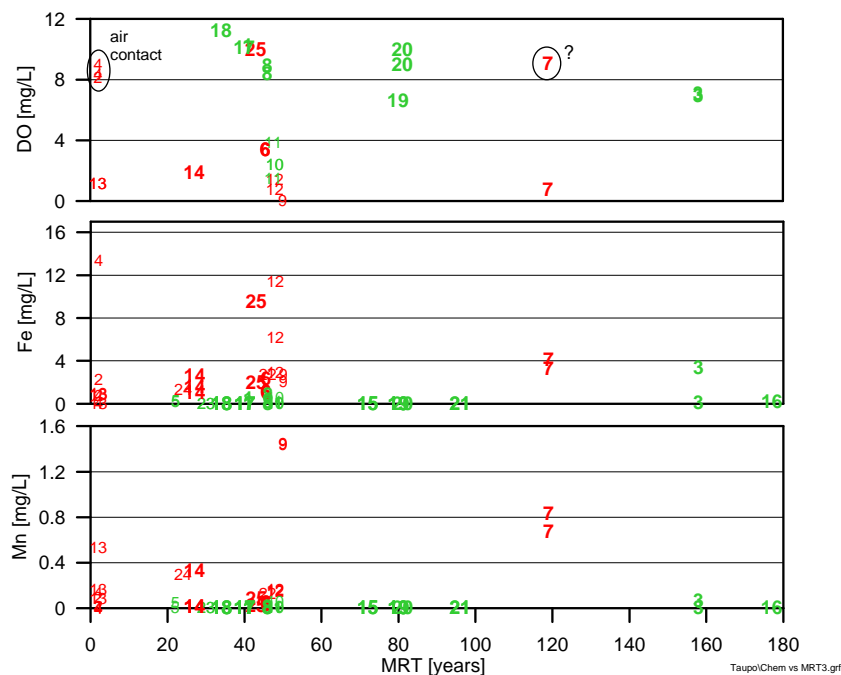Figure 8.2   Hardness, free CO$_2$, and Alkalinity versus mean residence time.

Figure 8.3   Dissolved Oxygen, Fe, and Mn versus mean residence time.

Figure 8.4 shows silica, fluoride, boron, calcium, magnesium, and arsenic. SiO$_2$ and F concentrations were found in several areas in New Zealand to correlate relatively well with the residence time of the water in the aquifer. Concentrations increased over time due to increased leaching from the aquifer material. Also the aquifers around Lake Taupo show a correlation between hydrochemistry and age.

Most **SiO$_2$** concentrations are high (except the wells near and in the andesite/rhyolite) as expected for pyroclastic volcanics. However, in the Mamaku ignimbrite near Rotorua we found that it takes more than 100 years for the groundwater to reach equilibrium concentration of about 75 mg/L SiO$_2$. In contrast, the ignimbrite north of Lake Taupo seems more readily soluble and equilibrium concentrations are reached quickly within a few years. SiO$_2$ equilibrium concentration of about 70 mg/L appears to be reached slower in the Whakamaru ignimbrite (wells 3-8), with a trend similar to that of the Mamaku ignimbrite. The low SiO$_2$ concentration of sample 4 matches the trend and indicates that this water is very young (<2 yrs). SiO$_2$ concentrations in and near the andesite/rhyolite (9-13) are considerably lower (20-50 mg/L). Again, the low SiO$_2$ concentration of sample 13 matches the trend and indicates that this water is very young (<2 yrs). On the other hand, the high SiO$_2$ concentration of 12 supports an old tritium age (about 50 years mean residence time).

F data shows only little correlation between hydrochemistry and age, possibly due to additional sources like geothermal. Similar concentrations but better correlations were found in the Mamaku and Rangitiki ignimbrite (Morgenstern et al., 2004, Reeves at al., 2007). Samples #7 and #23 in the southern part of the Lake Taupo catchment have extremely high F concentrations of 0.26-0.28 mg/L. In general older water tends to have higher F concentration but low F concentration is found in the youngest and the oldest water. However, low F in the ambiguous samples #2, #4, and #13 supports their young age.

B was measured in samples from the different sampling campaigns with variable detection sensitivity. Most of the samples are below the detection limit of 0.05 mg/L. Only 3 younger groundwaters from the western catchment have elevated B, not necessarily associated with

reducing groundwater conditions. **Ca** and **Mg** do not increase over time. Most young water has elevated concentrations which is likely to be caused by fertilisers and lime. These elevated concentrations are mostly associated with reduced water. Elevated **As** was found in only one young water.
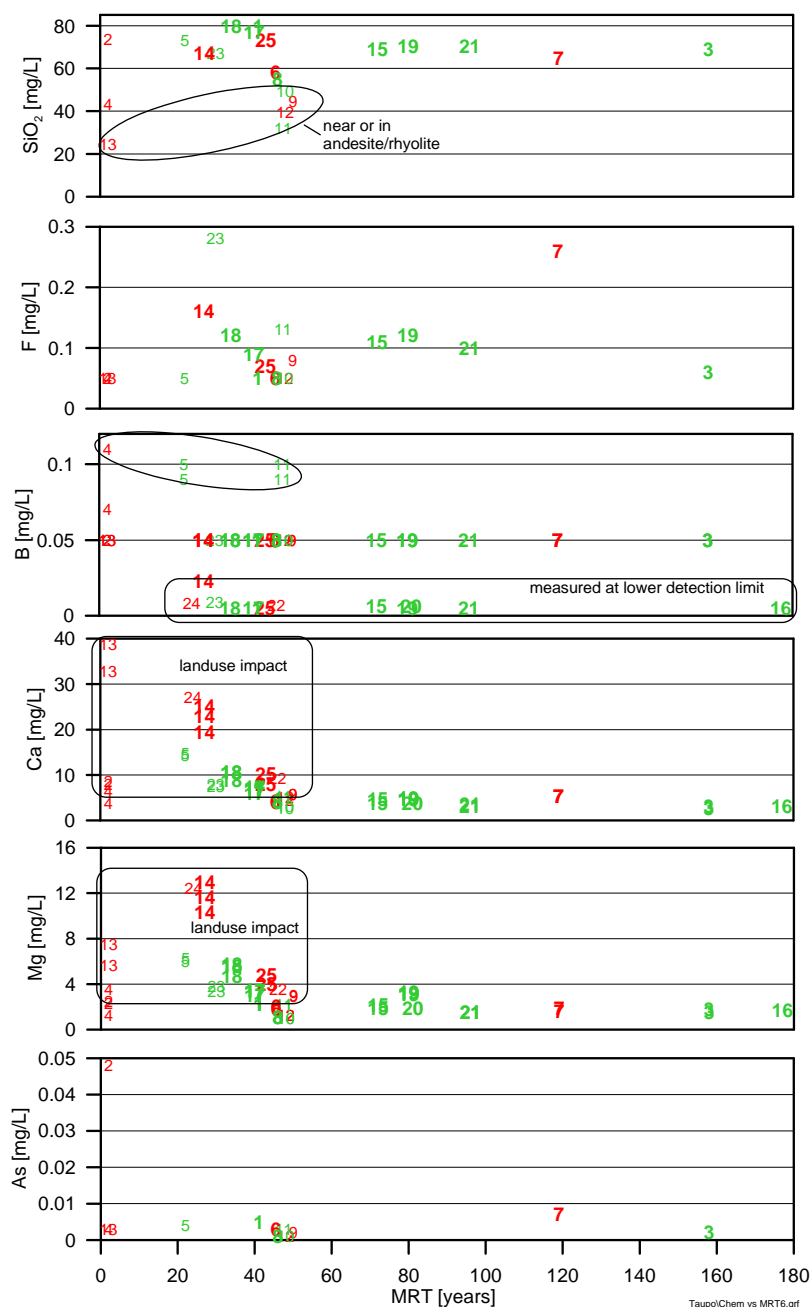

Figure 8.4 SiO_2, F, B, Ca, Mg, and As versus mean residence time.

Figure 8.5 shows sodium and chloride versus MRT. **Cl** is usually a conservative tracer and this is also observed in the old Taupo groundwater with generally constant Cl concentrations of about 5mg/L, which is about the Cl concentration of central North Island rain. However, some younger water has significantly elevated Cl concentrations, indicating likely landuse impact. Also **Na** is relatively constant over time, but again elevated in many young groundwaters. Na and Cl concentrations and therefore the Na/Cl ratios are constant in the old groundwater.

The lower Na/Cl ratios in the young landuse impacted groundwater indicate excessive input of Cl, which has increased over time because the lowest Na/Cl ratios are found in the youngest water.
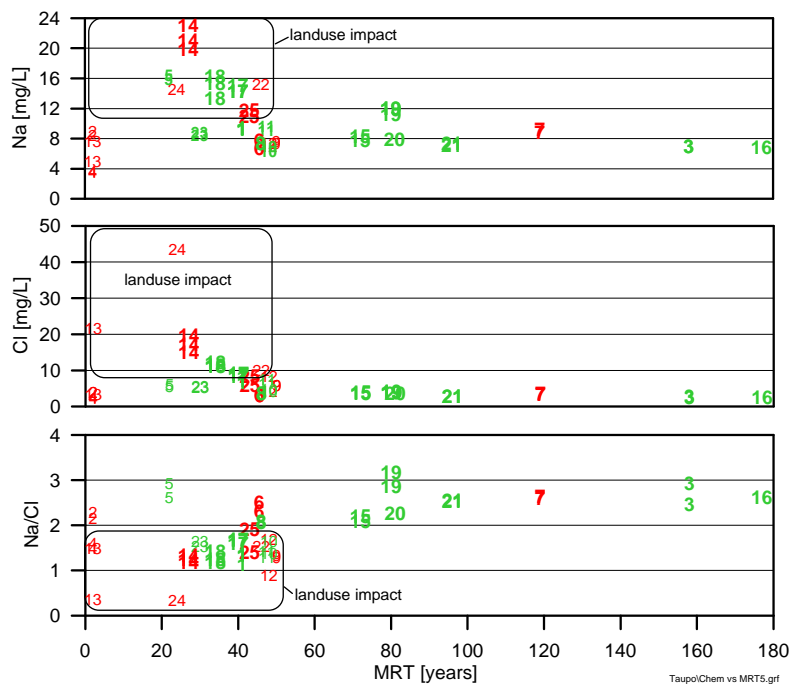
Figure 8.5   Na, Cl, and Na/Cl versus mean residence time.

Nutrients versus MRT are shown in Figure 8.6. Potassium, sulphate, and nitrate show the highest concentrations in young groundwater indicating impact by landuse activities, in contrast to dissolved reactive phosphate which has the lowest concentrations in young water.

Two reduced groundwaters, wells 4 and 13 in the western catchment, have very high **K** concentrations indicating a nearby point source contamination. Also the other samples show a trend of decreasing K concentration over the whole age range. This indicates that K is being progressively removed from the groundwater by ion exchange, and indicates that water samples 4, and 13 are very young.

DRP shows a good correlation with age (black line, correlation given in figure). With increasing contact time of the water with the aquifer material, phosphorus is progressively being leached from the volcanic material causing increasing DRP. Only wells 6 and 8-12 have unusually low DRP with respect to their water age, which for wells #8-12 is likely to be related to difference in aquifer material near the andesite/rhyolite. No elevated DRP is observed in young water, indicating that phosphorus from fertiliser has not yet broken through into the groundwater but is absorbed in the soil (except in well 13 which is likely to be caused by a nearby point source). Phosphorus in the groundwater is mostly geogenic and P discharge from the groundwater can therefore not be controlled.

SO$_4$ is elevated only in young water indicating landuse origin. **NH$_4$** is associated with reduced water and does not show a trend with age. **NO$_3$** is low in old groundwater (<1 mg/L), for both oxic and reduced water. This indicates that prior to landuse there was no significant NO$_3$ source in the catchment. Most young water has elevated NO$_3$ and shows that most young groundwater is impacted by landuse NO$_3$.
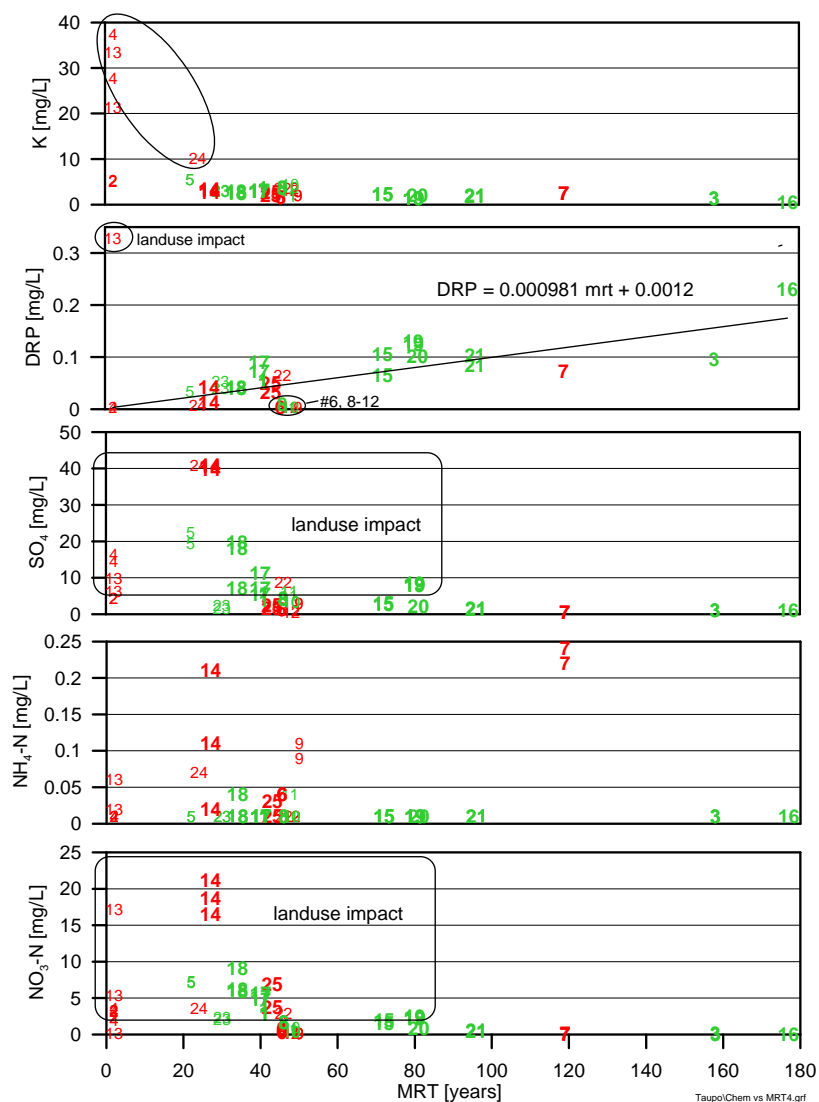
Figure 8.6   K, DRP, SO$_4$, NH$_4$ and NO$_3$ versus mean residence time. For the DRP correlation line well #13 was excluded because this is most likely an out-layer due to nearby point source contamination.

A number of chemical species show a correlation with age of the water, indicating concentration increase due to progressive leaching from the volcanic aquifer. The best correlation with age in groundwater from Lake Taupo is observed for phosphorus, and to some extend for silica and fluoride, and pH in reduced groundwaters. These correlations can assist in resolving the age ambiguity of the water, because these parameters normally vary significantly between very young (<3 yrs) and old (c. 40 yrs) water. Other groundwaters throughout New Zealand also correlate in DRP, Si and F with age (Morgenstern, 2005; Morgenstern et al., 2004, 2007; Reeves et al., 2007), with generally increasing concentrations relative to water age. In the northern and western Lake Taupo catchment, none of the chemistry results contradict the observed general trends, which support the dating results despite ambiguities in some cases. Using the trends of DRP, Si and F versus MRT may resolve remaining ambiguities for the surface stream waters (Morgenstern 2007).

9.0 PREDICTION OF FUTURE NUTRIENT CONCENTRATION AND NITROGEN LOAD

Groundwater around Lake Taupo is sometimes over 100 years old. Therefore it still contains significant fractions of old pre-landuse water, and nutrients from farming may still have low concentrations in the groundwater because of dilution of young post-landuse water with old pristine water. With time, old pristine water will progressively be replaced by landuse impacted water. Further increases in nutrient loading can be expected as more landuse impacted water discharges from the groundwater system.

To assess the future nutrient load from past and current landuse activities, the fraction of landuse impacted water needs to be established. The fraction of landuse impacted water can be calculated by integrating over the relevant age fractions of the age distribution of the water given in Table 7.1. The parameters of the age distribution are the mean residence time (MRT) and the fraction of exponential flow (E%PM). In the northern and western catchment of Lake Taupo the landuse intensification is assumed to have started in 1955 (Vant and Smith 2004). Therefore the fraction of water younger than 52 years (2007-1955) was calculated (Table 7.1). The nutrients N predominantly from animals, P, K, S, and Mg applied with fertilisers, and Ca applied with lime, are plotted versus fraction of post-landuse water in Figure 9.1. The fraction of post-landuse water is the fraction of water that fell as rain since 1955. 0% means all water is old pre-landuse water, 100% means all water is young post-landuse water. On the left side are the pristine old groundwaters, and toward the right the groundwaters have increasing fractions of post-landuse water. By extrapolating to 100% post-1955 water, landuse impacted nutrient concentrations can be estimated that will be reached in the future when all old pre-landuse water is replaced by post-landuse water.

Nitrate concentrations in pre-landuse water in Lake Taupo catchment are extremely small. Old oxic water with less than 20% post-1955 water (3 and 16) has nitrate-N concentration of about 0.1 mg/L. Therefore, the nitrate input into the groundwater was extremely small prior to landuse intensification, and the high levels of nitrate-N in the young waters (2-20 ppm) are caused mostly by landuse activities. Two samples (wells 13 and 14) have extremely high nitrate-N concentration between 16 and 23 mg/L. These waters have high concentration for most nutrients and are relatively young. Well 14 was demonstrated to be influenced by a nearby point source (Hadfield and Barkle, 2004), and it is likely that this is also the case for well 13. Apart from these two samples, most samples follow a trend of increasing nitrate with increasing fraction of landuse water. This indicates that the nitrate contamination is spread relatively evenly throughout the area. The anoxic waters have lower nitrate concentration than the oxic waters as a result of partial nitrate removal due to denitrification processes. Extrapolation of the nitrate data (excluding the highly contaminated samples) to 100% landuse water results in 3.8 mg/L nitrate-N for purely landuse impacted water. This would be the approximate nitrate concentration reached at steady-state for all groundwaters if the nitrate input continues at the current level. Anoxic waters would reach between 0 and 5 mg/L, and oxic waters between 5 and 10 mg/L nitrate-N.

Steady-state nitrate concentrations were calculated for individual wells (Table 7.1). Estimates are not included for the oldest waters where the error would be erroneous due to extrapolation from near detection limit. The current 2007 nitrate concentrations were deduced from up to 3 repeat measurements over the last 6 years (Table 4.1). The estimated steady-state nitrate concentrations for the waters with significant fraction of pre-1955 water are in the same range as reached in young waters already. The anoxic samples have a larger uncertainty because denitrification rates might change with increasing N concentration.
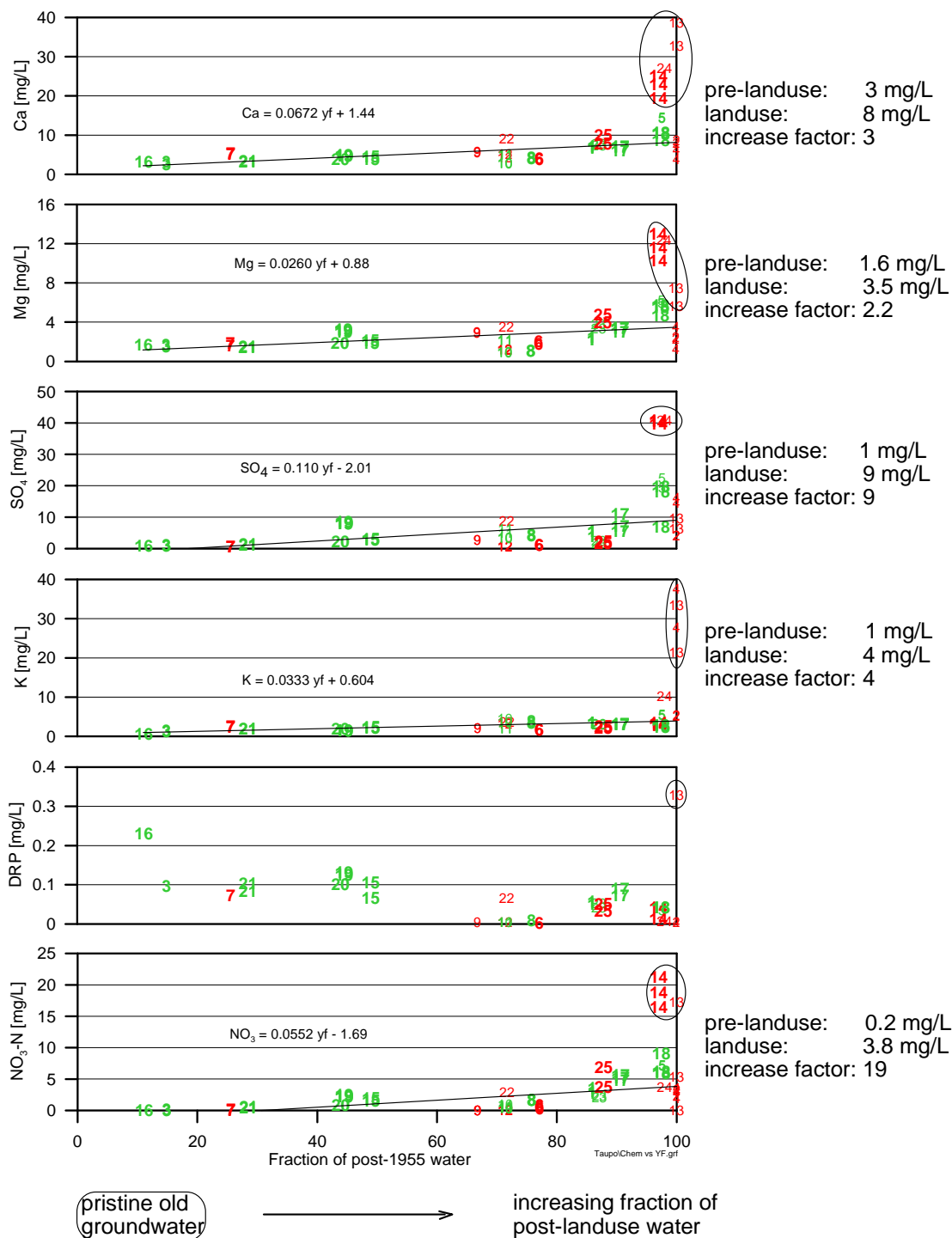
Figure 9.1   NO$_3$, DRP, K, SO$_4$, Mg and Ca versus fraction of landuse impacted water. The circled data are not included in the statistical calculation because they are most likely out-layers due to nearby point source contamination.

Phosphorus is relatively low (<0.05 mg/L) in the young landuse impacted groundwater, compared to high concentrations (>0.05 mg/L) of old waters due to leaching from the volcanic aquifer material. Fertiliser P has not yet broken through the soil into the groundwater (apart from well 13 which is probably related to a nearby point source). Landuse P is still absorbed in the soil. However, Ghani et al. (2004) have found evidence that P has moved down below 1 m depth. If in future fertiliser P breaks through the soil into the groundwater,

the already high P concentrations in groundwater due to leaching from the volcanic aquifers would then increase further.

Potassium is highly elevated only in some of the youngest, purely post-1955 anoxic waters. Much smaller K concentrations in slightly older water indicate that the majority of highly elevated K is being removed quickly from the groundwater by exchange with the aquifer, and the steady decrease toward older water indicates continued K removal with a slower ion exchange rate at low concentration. K concentration of about 1 mg/L is observed in the oldest groundwater.

Sulphate is elevated in younger landuse impacted water. In general, the highest concentration is expected for oxic water, because SO_4 can be reduced in anoxic conditions. However, the highest concentrations are observed in two anoxic waters (14 and 24) which may be related to nearby point sources as indicated by high concentrations of other nutrients. Water that has a high fraction of post-1955 water has SO_4 concentration of about 9 mg/L, while the old pre-landuse waters have about 1 mg/L. This is an increase by a factor of about 9 due to landuse intensification.

Magnesium is also elevated in young landuse impacted water, with the highest concentrations in anoxic water. Water that has a high fraction of post-1955 water has Mg concentration of about 3.5 mg/L m, while the old pre-landuse water has about 1.6 mg/L. This is an increase by about a factor 2 due to landuse intensification.

Calcium is also elevated in young landuse impacted water, with the highest concentrations in anoxic waters. Water that has a high fraction of post-1955 water has Ca concentration of about 8 mg/L, while the old pre-landuse water has about 3 mg/L. This is an increase by about a factor 3 due to landuse intensification.

With progressive arrival of landuse impacted groundwater, the concentrations of nitrate, sulphate, magnesium and calcium are expected to increase. These compounds are relatively stable in the groundwater over time frames of decades.

An estimate of future total nitrogen (TN) load to Lake Taupo from the western and northern catchment was made in Morgenstern (2007). The age distribution of surface waters in the western catchment, being dominated by young water, indicates streams are almost in steady-state with current landuse. Only small increases in nitrogen load are expected from the western catchment. The majority of water flux to the lake in the northern catchment is much more delayed and not yet in steady state with current landuse. However, because the surface streams form only a minor fraction of the total water flux in the north, the nitrogen load increase in northern streams is also only moderate. A total nitrogen load increase via surface streams of only 21 t/y was estimated, in addition to 289 t/y current load.

A much larger nitrogen load increase, however, is expected from direct seepage of groundwater into the lake in the north. The surface stream flows sampled in the northern catchment comprise the minority of the total discharge with about 80% discharging directly via groundwater to the lake. Based on the current nitrogen load of 28.3 t/y from the northern streams and assuming a nitrogen attenuation during stream transport (depleted due to uptake by plants) of factor two, a total future nitrogen load directly from groundwater of about 225 t/y may be inferred. Significant fractions of that may be still to come. With a landuse water fraction (post-1955) of about 50% in the surface streams, the landuse fraction of the

deeper groundwater seepage is estimated to about 40%. According to the total nitrogen load and the landuse fraction of the groundwater seepage, the expected nitrogen load increase via direct groundwater seepage is some 135 t/y. This is only a rough estimate because nitrogen and age data are not yet available from groundwater seepage at the lakebed. It does, however, show that the most significant nitrogen load increase is expected from northern catchment direct groundwater seepage to the lake.

These results are in the same order of numerical groundwater modelling predictions (Hadfield, 2007). Estimated annual nitrogen load to come for the northern catchment (including Waihora) from this work is about 125 tonnes. Also about 90 tonnes of this is estimated to come from direct groundwater seepage.

10.0   CONCLUSION

The groundwaters in the northern and western Lake Taupo catchment are relatively old with mean residence times between 20 and 180 years (only three shallow piezometers have very young water of about two years). Groundwater quality in general is not yet in equilibrium with current landuse and further increases in nitrogen load are expected as old pristine groundwater is progressively replaced by landuse impacted water. Nutrients and additives show a clear landuse impact on groundwaters with the data indicating further increase in future for nitrate, sulphate, magnesium and calcium.

A major TN load increase via direct groundwater seepage of about 135 t/y is expected from the northern catchment. This is only a rough estimate because TN and age data are not yet available from groundwater seeping directly into the lake. It does, however, demonstrate that the most significant TN load increase is expected from the northern catchment groundwater seepage.

Anoxic water has lower nitrate concentrations compared to oxic water of comparable fraction of post-1955 (landuse impacted) water. Despite the data being scarce, it suggests that on average about half of the nitrate is being removed in anoxic groundwater by denitrification processes. Nitrogen loads generated from land-use in recharge areas where the water passes through anoxic groundwater systems is more readily attenuated. While anoxic conditions normally occur in the poor draining geologic formations where large fractions of the rain water drain via surface run-off over short wet periods, the majority of nitrate over time still passes through the groundwater system and would be subject to denitrification processes.

The groundwater system in the northern and western Lake Taupo catchment is very complex. We have been able to derive robust groundwater ages and flow models, by tracing how the pulse-shaped bomb-tritium from the nuclear weapons testing period (1960s) has moved through the groundwater system. An unusually high fraction of piston flow is indicated in most areas, meaning that the groundwater system is not well mixed, with generally preferential flow paths likely to be important. The observed variability in groundwater chemistry, in space and time, is a result of this. Most groundwater wells have old water which may reflect localised landuse conditions far away from the well, or from before landuse intensification. This needs consideration in groundwater monitoring programmes.

11.0   RECOMMENDATION

Age distribution depends on the groundwater flow model (see Appendix 1). Flow models for old water is based on only 2 sites with tritium time series 3 years apart (Ramsey and Rowlands). The high mixed flow found in these two wells is in agreement with flow models found in similar aquifers through New Zealand. However, these flow models are distinctly different to those of younger water in the Lake Taupo catchment. Therefore, it is recommended they be re-measured for tritium. Such tritium time series over 6-7 years now would allow for very robust flow models of the old waters. The samples have already been collected.

A large increase in nitrogen load from groundwater seepage through the lakebed is expected in the northern catchment. While this is the largest component of expected nitrogen increase, little is known about it. It is recommended that a representative number of samples from direct groundwater seepage is obtained for chemistry and age distribution analysis. Using the current nitrogen signature and age distribution would allow for a more reliable estimate of nitrogen load increase from the northern catchment groundwater seepage.

Further investigation is recommended into the extent of nitrate load reduction by denitrification processes in anoxic groundwater systems. Further detailed study of hydrogeology, hydrochemistry, and isotopes should be performed. With better understanding of groundwater flow paths, and the relation between landuse and denitrification processes in anaerobic groundwater systems, it is hoped to identify areas of the catchment that are subject to active denitrification of the groundwater system. These areas would be less sensitive to landuse activities than areas where the nitrate is not being reduced before migrating to the lake.

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APPENDIX 1: METHODOLOGY OF GROUNDWATER AGE DATING

1.1 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 concentrations (Figure 1). 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 in the groundwater allows for establishment of groundwater mixing models and age distribution of the groundwater (Morgenstern 2004). Groundwater dating using tritium is described in more detail in Cook & Herczeg (1999), Stewart & Morgenstern (2001), and Morgenstern and Taylor 2005. The low-level tritium analysis procedure used at GNS Science is described in detail in Morgenstern and Taylor, 2005.

As a result of the superimposed atmospheric tritium "bomb" peak in the 1960s, ambiguous ages can occur with single tritium determinations (i.e., the tritium concentration can indicate any of several possible groundwater ages between 0 and 40 years). This ambiguity can be overcome by using a second tritium determination after about three or more years, or combined age interpretation of tritium data and data from an independent dating method for example CFCs or SF6. CFC and SF6 concentrations in the atmosphere have risen monotonously during that time and therefore can resolve tritium ambiguity if they are not altered in the aquifer.
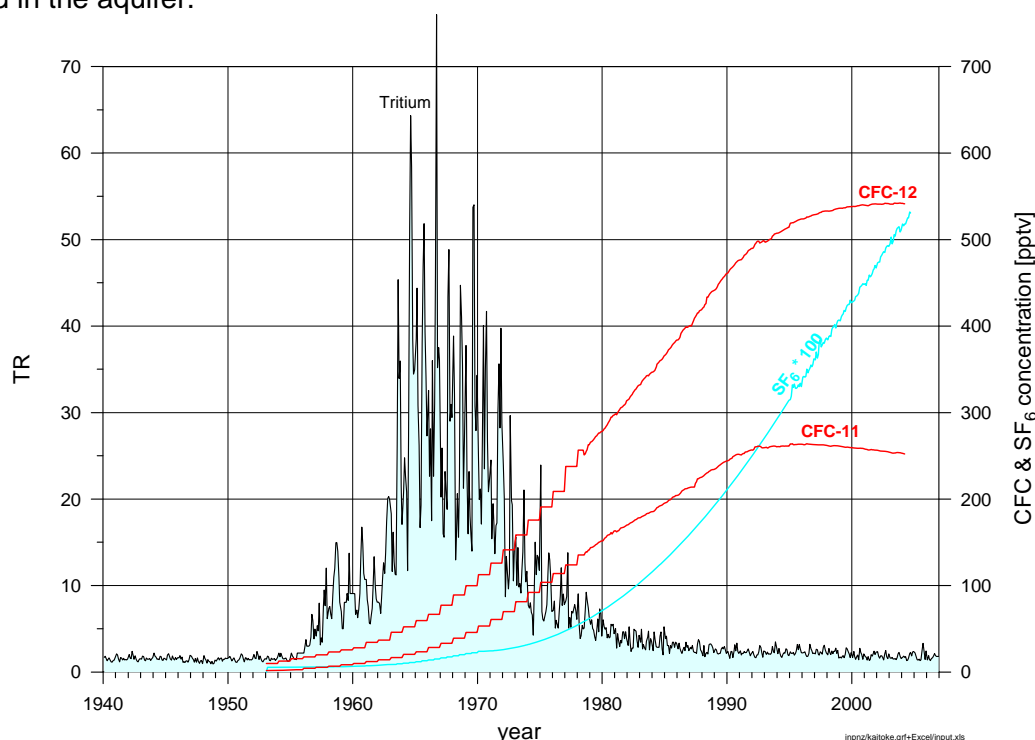

Figure A1 Tritium, CFC and SF$_6$ input for New Zealand rain. Tritium concentrations are from rain at Kaitoke, 40km north of Wellington (monthly data), and CFC and SF$_6$ concentrations are for southern hemispheric air. TR=1 represents a ^{3}H/^{1}H ratio of 10^{-18}, and 1 pptv is one part per trillion by volume of CFC or SF$_6$ in air, or 10^{-12}. Tritium data from before 1960 are reconstructed from Antarctic ice cores. 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.

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 A1). CFCs are relatively long-lived in the atmosphere 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 have been phased out of industrial use in the 1990s because of their destructive effects on the ozone layer. Thus rates of increase of atmospheric CFC concentrations slowed greatly in the 1990s, meaning that CFCs are not as effective for dating water recharged after 1990.

Sulphur hexafluoride (SF$_6$) is primarily anthropogenic in origin, but can also occur in some volcanic and igneous fluids. Significant production of SF$_6$ began in the 1960s for use in high-voltage electrical switches, leading to increasing atmospheric concentrations (Figure A1). The residence time of SF$_6$ in the atmosphere is relatively long (800-3200 years). It holds considerable promise as a dating tool for post-1970s 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 and aquifer material. Tritium is an isotope of hydrogen and therefore is a component of the water molecule. Therefore, age information is not distorted by any bio- or geo-chemical reaction 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 than 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 SF6 ages do not take into account travel time through unsaturated zones.

Tritium with its pulse-shaped input into groundwater systems (Figure A1) is very sensitive to the flow model (distribution of residence times in the sample). 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.

1.2   GROUNDWATER MIXING MODELS

Groundwater comprises a mixture of water of different ages due to mixing processes underground. Therefore, the groundwater doesn't have a discrete age but has an age distribution. 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 lie between these two extremes can often be described by a combination of the exponential and piston-flow models representing the recharge, flow and discharge parts of a groundwater system. 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 several independent tracers (tritium and CFC/SF$_6$) or several tritium measurements over time are necessary.

Schematic groundwater flow situations are shown in Figure A2. 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 mixed (exponential) flow within the total flow volume (represented by E_%PM, with the fraction 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 A3 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, significant fractions of the water are younger than 50 years. The discharging 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 five years. With each further year, 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 40 years is 54% in the example in Figure A3 (hatched area).
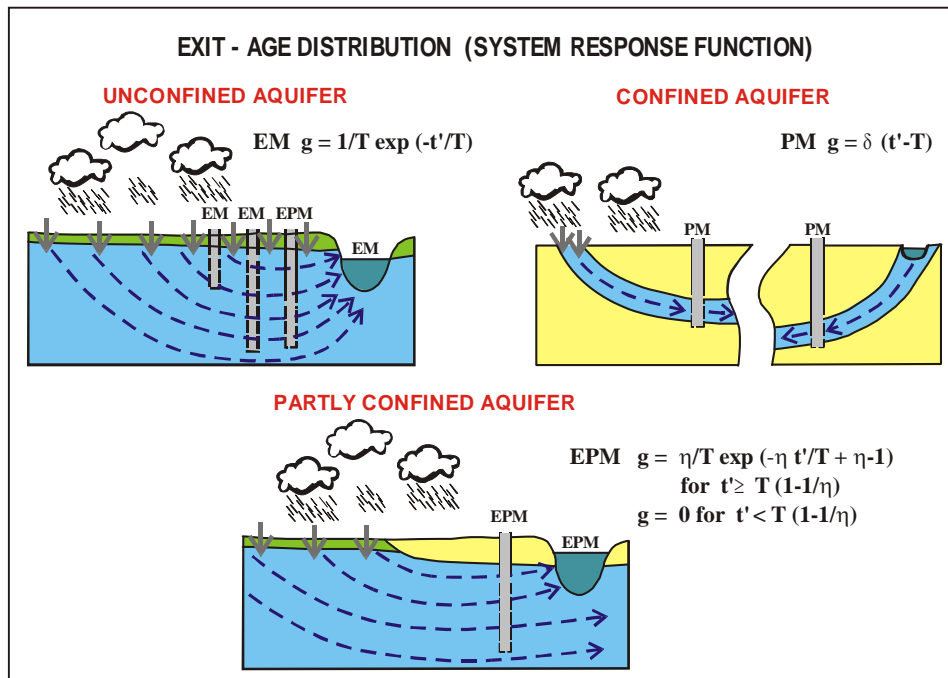
Figure A2   Schematic groundwater flow situations and corresponding age distribution functions (see Maloszewski and Zuber (1982) for theoretical background).
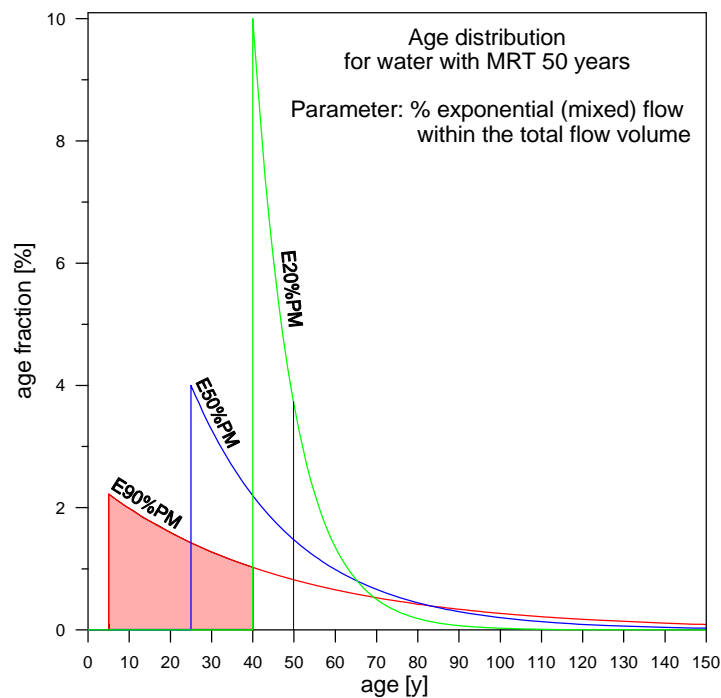

Figure A3   Age distribution for the exponential-piston flow model.

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