

# Groundwater Residence Times and Chemistry of the Pukekohe and Bombay Basalt Aquifers

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# Groundwater Residence Times and Chemistry of the Pukekohe and Bombay Basalt Aquifers

R W van der Raaij Institute of Geological and Nuclear Sciences Ltd

GNS Science Report, 2015/11

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# Abstract

A study of groundwater Mean Residence Time (MRT) and the relationship to groundwater chemistry has been carried out in the Bombay and Pukekohe volcanic aquifer systems in response to high nitrate concentrations observed in groundwater from these systems. Nitrate concentrations often exceed the drinking water standards for New Zealand (Ministry of Health, 2008) maximum acceptable value of 11.3mg/L NO<sub>3</sub>-N and also the national bottom line of 6.9mg/L NO<sub>3</sub>-N (annual median) for nitrate toxicity in rivers (Ministry for the Environment, 2014). This has implications for groundwater discharges to springs and streams.

MRT of groundwater from the sites tested in the Bombay and Pukekohe aquifer systems ranges between 16 years and 99 years. Groundwater in Bombay aquifers shows an increase in MRT both in the direction of groundwater flow and with depth. Groundwater from Pukekohe in the upper aquifer generally has MRT younger than 50 years; and the oldest ages are seen in the lower volcanic aquifer system.

Groundwater in both volcanic aquifers is predominantly of type Mg-Na-Ca-HCO<sub>3</sub>-NO<sub>3</sub>-Cl or Mg-Na-Ca-NO<sub>3</sub>-HCO<sub>3</sub>-Cl. The dominance of magnesium reflects the basalt mineralogy i.e., the presence of magnesium-rich olivines and pyroxenes. Nitrate is the dominant anion in younger groundwater, but is not present in older groundwater where bicarbonate concentrations are much higher.

Statistically significant positive relationships with MRT are observed for pH, bicarbonate, dissolved reactive phosphorus, potassium, and to a lesser extent, silica. These analytes have the potential to be used as proxies for groundwater age. To develop these as proxies, additional age-tracer data and chemistry should be collected to refine the groundwater residence time models. Iron, manganese, and ammonia also show relationships with groundwater age, which are primarily controlled by the groundwater redox state.

Nitrate concentrations show an inverse relationship with groundwater MRT. This is common for analytes associated with land use changes and intensification. The chemistry of younger waters reflects the impacts of recent land use, while older water retains the chemical signature of less-impacted recharge sources. However, it is difficult to use such a relationship as a groundwater age proxy as the variability in nitrate concentrations for young groundwaters is primarily a function of land use, not MRT. Although old groundwater at some wells is anoxic, there is no evidence of denitrification.

Changes in chemistry observed at two Auckland Council "State of the Environment" monitoring wells indicate that pumping-induced changes to the aquifer flow regimes may be occurring. This may have consequences on the groundwater age structure of the aquifer systems.

To refine the groundwater age models used in this study and to resolve age-tracer ambiguity, further age-tracer sampling should be carried out on the same wells after a three to five year interval. Wells which were sampled earlier than 2014 could be resampled sooner (i.e., within the next year). Additionally it is recommended extra wells and also spring / stream sites be sampled for chemistry and age-tracers to increase coverage both spatially and to cover a larger range of MRT.

# Keywords

Groundwater mean residence time, nitrate, groundwater age, groundwater age-tracers, groundwater chemistry, Bombay and Pukekohe basalt aquifers.

#### 1.0 Introduction

This report has been prepared in response to a request from the Auckland Council to investigate the age of groundwater in the shallow volcanic aquifers around the Bombay and Pukekohe areas. This is in response to high nitrate concentrations observed in groundwater from these aquifers (ARC, 2010). Market gardening has occurred in the areas for over 100 years; and with intensification of land use occurring since the 1950s (Murphy, 1991) has had a considerable impact on groundwater quality at Bombay and Pukekohe. High nitrate concentrations have been observed in groundwater from the basalt aquifers since the 1970s (Crush *et. al.,* 1997) with some concentrations in excess of the drinking water standards for New Zealand (Ministry of Health, 2008) maximum acceptable value of 11.3 mg/L NO<sub>3</sub>-N. Concentrations also exceed the national bottom line of 6.9 mg/L NO<sub>3</sub>-N (annual median) for nitrate toxicity in rivers, set in the National Policy Statement for Freshwater Management 2014 (Ministry for the Environment, 2014). This will have implications for groundwater discharges to springs and streams in the two areas.

Ten wells (five in each area) were selected for groundwater age-tracer sampling (Table 1). Sampling of groundwater chemistry was carried out concurrently. In addition to these ten wells, historic age tracer data was available for four other wells – two in the Bombay area (Wells BP, and BW) and two in the Pukekohe area (Wells PA, and PW). Well locations are shown in Figure 1 and Appendix 4.

The age-tracers tritium chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF<sub>6</sub>) have been used. These tracers have known input histories into groundwater systems, and can be used to calculate how long the water has been present in an aquifer system since recharge i.e. the groundwater residence time (Appendix 1). Establishment of relationships between groundwater residence time and groundwater chemistry could enable the use of chemistry measurements as proxies for groundwater age. This would allow fast, cheap and easy to analyse methods for assessment of groundwater age.

Sample ID	Auckland Council Well ID	Name	Easting <sup>1</sup>	Northing <sup>1</sup>	Well depth (m below ground level)	Depth to bottom of casing (m below ground level) <sup>2</sup>	Aquifer lithology <sup>3</sup>
B1	21950	Thich Phuoc An	1777097	5880392	26.5	15	Bombay Volcanic
B2	4315	H.A & H.C Braks	1776571	5882145	68	49.6	Bombay Volcanic
B3	4162	B.J & H.K Crowe	1774770	5883999	43	21	Bombay Volcanic
B4	4133	Martyn Farm Water	1774736	5884648	77	61.9	Bombay Volcanic
B5	4185	D.O & A.L Taylor	1774878	5884045	68	unknown	Bombay Volcanic
BP	965	BP Bombay	1775936	5881868	79.4	65.3	Bombay Volcanic
BW	4352 <sup>3</sup>	Wallabh	1777536	5883542	73	45.7	Bombay Volcanic
P1	3598	Ballance Agri-	1765891	5881153	37	24.8	Upper Pukekohe Volcanic
P2	3573	Plant & Food Research	1765286	5880737	40.4	22	Upper Pukekohe Volcanic
P3	3623	E A & J P Nicholls Ltd	1766630	5881015	72	49.7	Lower Pukekohe Volcanic
P4	3512	Gun Club Road	1764230	5880962	28	18.7	Upper Pukekohe Volcanic
P5	7428105	Rifle Range Rd Shallow	1766243	5880966	42	29.2	Upper Pukekohe Volcanic
PA	3506 <sup>4</sup>	Agrisystems	1764141	5880817	24.4	14	Upper Pukekohe Volcanic
PW	3610 <sup>5</sup>	A.S. Wilcox	1766180	5880280	78	46	Lower Pukekohe Volcanic

Table 1Summary of current and historic wells sampled for groundwater MRT and chemistry including IDs,<br/>location, well construction and aquifer lithology. Historic wells are in shaded rows.

<sup>1.</sup> Coordinates are NZTM.

<sup>2.</sup> Well depths and lithology supplied by Auckland Council (Auckland Council, 2014).

<sup>3.</sup> Wallabh well (Murphy, 1991) probably this well number.

<sup>4</sup> Well 3506 previously called Agrisystems (ARWB, 1989), now Bridge City Management.

<sup>5.</sup> Well 3610 previously called A.S Wilcox (ARWB, 1989) now S Clark Nurseries Ltd.



Figure 1 Map of well locations sampled for groundwater MRT and chemistry. Labels correspond to sample IDs presented in Table 1. Map background is simplified surface geology based on the QMap series (Edbrooke, 2001) with 20 m contour lines. Lines 1 – 2 and 3 – 4 are transects discussed further in Section 4. Wells marked in green were sampled for this study, whereas wells in red were previously sampled.

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# 2.0 Hydrogeologic setting

The geology of the study area has been described in detail in previous studies (ARWB, 1989; Murphy, 1991). The focus of the current study is the aquifer systems within the basaltic volcanic formations of the Pukekohe and Bombay areas. In these areas, two separate influxes of basalt are recorded which represent different periods of volcanism that occurred between 1.6 million (Bombay basalts) and 600,000 (Franklin basalts) years ago (Edbrooke, 2001; ARWB, 1989). The basalts vary from dense, fractured lava flows to fine scoria cones (ARWB, 1989). Lavas are fine to medium grained, vesicular and porphyritic (Edbrooke 2001). Basalts are spread widely at Pukekohe and thicknesses greater than 100 m may occur (ARWB, 1989). At Bombay basalt flows are smaller in areal extent, with layers isolated from one another by clay and silt-rich sediments (Murphy, 1991). The dominant rock types are basanite and hawaiite (Edbrooke, 2001). These rock types are rich in ferromagnesium silicates such as olivine and pyroxenes such as augite.

In Pukekohe the basalts generally overlie Seagrove Formation sediments (Figure 2), while in Bombay they may alternatively overlie the Jurassic greywacke or Waitemata Group sedimentary rocks depending on location (Figure 3). There is little material overlying the basalt formations. Where present this may include pumiceous sands, gravels, silty-clays, peats and basaltic tephras (ARWB, 1989). These materials are generally less than 10 m thick. Basalts at the surface are deeply weathered and form rich agricultural soils.

Recharge to the unconfined aquifers is by direct infiltration of rainfall (Murphy, 1991; ARC, 1996), whereas recharge to the lower aquifers is by vertical leakage from the upper aquifers (ARC, 1996). Groundwater flow in the Bombay area is in a north-westerly direction. A steep piezometric gradient is defined by the topography and implies rapid groundwater flow (Murphy, 1991). The majority of water is discharged as springs at the base of Bombay Hill (Murphy, 1991). In the Pukekohe area the direction of groundwater flow is less consistent. However, there is a general pattern of flow outwards from the central recharge areas to the periphery of the area (ARC, 1996). Discharges from springs occur at the perimeter of the Pukekohe Plateau at elevations between 40 m and 80 m (ARC, 1996).

Aquifer properties in both areas are highly variable over small distances, with large variations in transmissivity both within and between aquifers. Transmissivity is generally higher in thicker basalt layers and lower in more weathered thinner layers (ARWB, 1989). In the Bombay area the basalts, while highly permeable, are limited in areal extent. North of Stephens Fault the basalts are surrounded by fine-grained sediments which act as a confining layer (Figure 3; Murphy, 1991). In the Pukekohe area the volcanic aquifers consist of a number of unconfined, confined, semiconfined and perched aquifers (ARWB, 1989). Separation into distinct aquifer systems is difficult, but static water levels show there to be two hydraulically distinct systems, an "upper aquifer" and a "lower aquifer" (ARWB, 1989).

Because of the prime loam soils formed by the weathered basalts, market gardening is the dominant land use in the Bombay area (~60%) accompanied by some orcharding (~20%) and minor use for other agricultural activities (Murphy, 1991). In the Pukekohe area land use is roughly half livestock farming (~50%), including dairying and drystock, and half market gardening with some orchards (Crush *et. al.*, 1997).



Figure 2 Geological cross-sections of the Pukekohe area from ARWB, (1989).
 a) W – E trending cross-section "L". b) N – S trending cross-section "D". c) N – S trending cross-section "E". Approximate locations of the wells from the present study are shown in red.



Figure 3 Geological cross-sections of the Bombay area from Murphy, (1991).
 a) N – S trending cross-section "2". b) W – E trending cross-section "C". Approximate locations and IDs of the wells from the present study are shown in red.

# 3.0 Methods

#### 3.1 Sampling and analytical methods

Age-tracer samples (tritium, CFCs, SF<sub>6</sub>) were collected at 10 sites in June 2014 using standard sampling protocols (Daughney *et al.*, 2006). Special care was taken to exclude air from the CFC and SF<sub>6</sub> samples. CFC samples were collected underwater in 125mL glass bottles and sealed using foil-lined caps to prevent gas exchange with the present day atmosphere. SF<sub>6</sub> samples were collected in 1L glass bottles with Polyseal caps which displace the headspace. Tritium samples were collected in 1L Nalgene plastic bottles.

CFCs and SF<sub>6</sub> were analysed at the GNS Science Water Dating Laboratory by gas chromatograph using an electron capture detector (GC ECD) with detection limits of approximately  $3 \times 10^{-15}$  mol/kg for CFCs and  $2 \times 10^{-17}$  mol/kg for SF<sub>6</sub>. The analytical system for CFCs is similar to that of Busenberg and Plummer, (1992). The analytical system for SF<sub>6</sub> is described in van der Raaij, (2003). CFC samples are analysed in duplicate for quality control. Dissolved argon, nitrogen and methane are measured simultaneously with CFCs by GC/thermal conductivity detector (TCD). Tritium was measured at the GNS Science Water Dating Laboratory by electrolytic enrichment and liquid scintillation counting using Quantulus low-level counters (Morgenstern and Taylor, 2009). The detection limit is approximately 0.03 tritium units (1TU is a <sup>3</sup>H/<sup>1</sup>H ratio of 1:1×10<sup>18</sup>).

Samples were taken simultaneously for routine major, minor ions and metals (Ca, Na, Cl, K, Mg, NO<sub>3</sub>-N, NH<sub>4</sub>-N, DRP, Fe, Mn, SiO<sub>2</sub>, HCO<sub>3</sub>). Procedures for collecting water chemistry samples were consistent with the Groundwater Sampling Protocol described by Daughney *et al.*, (2006). Samples were analysed by Watercare Laboratory Services, Auckland.

# 3.2 Groundwater age interpretation methodology

Groundwater sampled from a well or other discharge point (e.g., spring) is a mixture of water with variable residence times in the aquifer due to the convergence of different flow lines within the aquifer at the discharge point. Groundwater age-dating therefore yields a MRT of water from all converging flow lines. Lumped-parameter mixing models such as the exponential – piston flow model (EPM) are used to describe the distribution of groundwater residence time (Appendix 1). The mixing of different flow lines occurs at the sampling point and the extent to which this occurs is specific to the well. It depends on several factors including well construction, screen length, well depth and pumping rates. Mixing is also dependent on the hydrogeologic attributes of the aquifer surrounding the well as this affects the variety of possible flow paths that may be intersected by the well. MRT has been calculated for all wells in this study using the EPM. This model has been applied successfully to groundwaters from many areas of New Zealand (Morgenstern and Daughney, 2012). An explanation of the model theory and tracer characteristics is given in Appendix 1 including a discussion of the assumptions and uncertainties involved. The derivation of model parameters is described in Section 5.0.

For the interpretation of groundwater age, CFCs and  $SF_6$  concentrations must be converted to atmospheric equivalents. This is accomplished via Henry's law for dissolved gases using an estimated recharge temperature and excess air correction derived from dissolved Ar and N<sub>2</sub> measurements (Busenberg and Plummer, 1992; Heaton and Vogel, 1981). Dissolved Ar and N<sub>2</sub> may also be used to provide insight into groundwater recharge mechanisms (Section 5.1).

#### 4.0 Analytical results

The analytical results of tritium, CFC, SF<sub>6</sub>, Ar and N<sub>2</sub> measurements for samples taken in 2014 are presented in Table 2 and Table 3. Equivalent atmospheric partial pressures of CFCs and SF<sub>6</sub> have been calculated from the analytical results and are presented in Table 4 along with the recharge temperatures and excess air concentrations used in these calculations. The derivation of recharge temperature and excess air from dissolved argon and nitrogen measurements is discussed in section 5.1. Chemistry results are presented in Table 5.

Well ID	Ar mL(STP)/kg <sup>1</sup>	± Ar mL(STP)/kg <sup>1</sup>	N <sub>2</sub> mL(STP)/kg <sup>1</sup>	± N <sub>2</sub> mL(STP)/kg <sup>1</sup>	CH₄ µmol/kg	± CH₄ μmol/kg
B1	0.399	0.010	15.62	0.13	<0.2	-
B2	0.385	0.006	15.74	0.15	<0.2	-
B3	0.421	0.008	16.52	0.14	<0.2	-
B4	0.413	0.007	16.41	0.15	17.2	3.0
B5	0.416	0.007	16.19	0.32	<0.2	-
P1	0.432	0.007	18.03	0.18	<0.2	-
P2	0.389	0.006	15.22	0.17	<0.2	-
P3	0.430	0.007	17.84	0.15	0.8	0.3
P4	0.328	0.008	11.87	0.18	<0.2	
P5	0.456	0.007	19.29	0.30	<0.2	-

Table 2 Dissolved argon, nitrogen and methane concentrations for wells sampled in this study.

Dissolved Ar and  $N_2$  concentrations are expressed in mL of gas at standard temperature and pressure (STP =273.15K, 101.325kPa) per kg of water.

Well ID	Sampling Date	CFC-11 pmol/kg <sup>1</sup>	± CFC-11 <sup>4</sup> pmol/kg <sup>1</sup>	CFC-12 pmol/kg <sup>1</sup>	± CFC-12 <sup>4</sup> pmol/kg <sup>1</sup>	CFC-113 pmol/kg <sup>1</sup>	± CFC-113 <sup>4</sup> pmol/kg <sup>1</sup>	SF <sub>6</sub> fmol/kg <sup>2</sup>	± SF <sub>6</sub> <sup>4</sup> fmol/kg <sup>2</sup>	Tritium TR <sup>3</sup>	± Tritium <sup>4</sup> TR <sup>3</sup>
B1	11/06/2014	5.26	0.30	5.03	0.20	0.17	5.26	1.55	0.03	0.593	0.021
B2	11/06/2014	2.87	0.16	2.87	0.12	0.20	2.87	1.15	0.03	0.689	0.022
B3	11/06/2014	1.13	0.06	0.95	0.05	0.06	1.13	1.85	0.04	0.277	0.016
B4	11/06/2014	0.00	0.01	0.00	0.06	0.00	0.00	0.31	0.02	-0.009	0.015
B5	11/06/2014	5.00	0.46	4.54	0.51	0.00	5.00	34000	1000	0.043	0.013
P1	12/06/2014	4.70	0.26	2.41	0.10	0.37	0.04	2.56	0.05	0.74	0.023
P2	12/06/2014	5.11	0.28	3.37	0.13	0.44	0.05	2.28	0.05	0.882	0.024
P3	12/06/2014	0.03	0.01	0.08	0.02	0.00	0.01	0.18	0.01	0.018	0.017
P4	25/07/2014	5.39	0.32	2.99	0.12	0.47	0.03	0.51	0.02	0.885	0.027
P5	12/06/2014	3.29	0.18	2.22	0.09	0.39	0.05	2.92	0.06	0.862	0.025

Table 3 Measured CFC,  $SF_6$  and tritium concentrations for groundwaters sampled in this study.

<sup>1.</sup> Dissolved CFC concentrations are expressed in pmol/kg where 1 pmol =  $1 \times 10^{-12}$  mol.

<sup>2.</sup> Dissolved SF<sub>6</sub> concentrations are expressed in fmol/kg where 1 fmol =  $1 \times 10^{15}$  mol.

<sup>3.</sup> Tritium concentrations are expressed as  ${}^{3}H:{}^{1}H$  ratios where 1 tritium unit (TR) signifies a ratio of  $1:1 \times 10^{18}$ .

<sup>4.</sup> The measurement error is the combined standard uncertainty (Eurachem/Citac, 2000).

Well	Rech Temp °C	± Rech Temp °C	Excess Air <sup>1</sup>	± Excess Air <sup>1</sup>	CFC-11	± CFC-11 ppt <sup>2</sup>	CFC-12	± CFC-12	CFC-113	± CFC-113	SF <sub>6</sub>	± SF <sub>6</sub>
B1	9.0	2.0	1.4	0.9	244	30	895	96	24.6	4.4	3.30	0.37
B2	12.2	1.5	2.7	0.6	158	15	589	47	35.1	5.1	2.39	0.18
B3	7.5	1.5	1.6	0.7	47.4	4.8	154	14	8.6	2.6	3.58	0.31
B4	8.8	1.3	2.0	0.6	0.0	0.5	0.0	11.2	0.1	2.8	0.60	0.05
B5	7.6	1.4	1.3	0.9	211	26	743	99	0.1	2.3	69000	7000
P1	8.9	1.4	4.1	0.7	212	20	412	33	52.7	7.7	4.25	0.31
P2	10.7	1.3	1.3	0.6	256	23	643	49	71.2	9.4	5.13	0.42
P3	8.8	1.3	3.9	0.6	1.3	0.4	13.6	2.9	0.0	1.9	0.31	0.03
P4	14.9	2.2	-1.7	0.9	341.1	42.4	718.2	76.2	99.1	13.8	1.92	0.41
P5	7.3	1.4	5.1	0.9	135	13	348	29	50.1	7.5	4.33	0.34

Table 4 Recharge temperatures, excess air concentrations and calculated atmospheric partial pressures of CFCs and SF<sub>6</sub> for groundwater samples collected in this study.

<sup>1.</sup> Excess air concentrations are expressed in mL of gas at standard temperature and pressure per kg of water.

<sup>2.</sup> CFC and SF<sub>6</sub> partial pressures are expressed in parts per trillion (ppt) where 1ppt signifies a volumetric ratio of  $1 \times 10^{-12}$ .

Well	EC μS/cm	pH (field)	DO (field) mg/L	Temp (field) °C	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	HCO₃ mg/L	CI mg/L	DRP mg/L	NO <sub>3</sub> -N mg/L	NH₄-N mg/L	Fe mg/L	Mn mg/L	SiO₂ mg/L
B1	218.2	- 1	8.08	15.1	10	14	10	1.4	57	17	0.051	8.4	<0.005	0.0058	<0.0005	40
B2	356	-	5.09	15.1	19	23	14	2.3	78	22	0.069	19	<0.005	0.0031	<0.0005	43
B3	279	-	2.59	15.4	14	21	12	3.4	110	27	0.15	0.39	0.005	0.47	0.01	43
B4	315	-	0.06	16.1	15	25	15	4.1	160	21	0.22	0.0077	0.14	0.10	0.067	49
B5	286	-	1.9	15.8	15	21	13	4	130	22	0.21	0.27	<0.005	0.19	0.012	45
P1	311	6.45	5.26	16.2	13	22	12	2.1	56	29	0.056	13	0.006	0.025	0.00062	30
P2	344	6.21	7.66	15.7	15	22	14	1.8	39	25	0.014	22	<0.005	0.0083	<0.0005	34
P3	269	8.03	0.83	14.0	13	17	14	3	120	22	0.3	0.041	0.048	0.041	0.034	46
P4	378	6.43	7.43	15.45	17	24	16	1.7	37	28	0.02	28	<0.005	0.019	0.00072	35
P5	234	6.57	7.47	16.1	11	19	7.6	1.1	39	16	0.071	13	0.013	0.67	0.031	39
1.		ourod of o	itoo D1 DE													

Table 5 Summary of chemistry datasets for groundwater samples collected in this study.

pH not measured at sites B1 – B5.

#### 5.0 Age-tracer interpretation

MRT results for the 14 wells are presented in Table 6, and primarily reflect the tritium concentrations from each well. The model parameters for each well were estimated by the following methods. A summary of the model methodology is presented in Appendix 1. Alternative MRT interpretations from ambiguous tracer data are presented in Appendix 2.

For the five wells with MRT greater than 70 years, the percentage of exponential mixed flow was set to minimise the proportion of water less than 60 years old in the resulting groundwater age distribution. This is based on the assumption that water recharged after 1955 contains elevated nitrate levels due to land use intensification (Murphy, 1991) and these five wells have very low nitrate concentrations. This assumption is discussed further in Section 5.1.

Groundwaters with relatively high tritium concentrations may result in ambiguous age interpretations, especially if only one data point is available (See Appendix 1). For these wells, comparison to CFC and  $SF_6$  ages can often resolve the ambiguity by indicating which tritium age is more likely. This commonly also indicates the appropriate percentage of exponential mixed flow. In this study the ambiguity in age was resolved in this way for four wells (B1, B2, P4 and P5). For these wells, the groundwater was less than 60 years old. Groundwater with MRT greater than 60 years old is unambiguously old.

Matching exponential – piston flow model outputs to a time-series of tritium data allows better estimation of the model parameters. The best-fit model output is found by minimising the differences between modelled and observed tritium concentrations. Only one well (P5) had sufficient data for model fitting in this way and is discussed further in Section 5.3.

Well ID	Depth of sampled interval (m)	% Exponential	MRT (years)
B1	15 – 26.5	30	27 (24 – 30) <sup>1</sup>
B2	49.6 - 58	30	35 (33 – 39)
В3	21 – 43	30	70 (69 – 71)
B4	61.9 – 77	35	> 91
B5	? - 68	30	80 (77 – 91)
BP	65.3 - 79.4	30	63 (62 - 64)
BW	45.7 – 73	30	37 (36 – 38)
P1	24.8 - 37	70	23 (20 – 27)
P2	22 - 40.4	70	16 (14 – 19)
P3	49.7 – 72	40	99 (> 89)
P4	18.7 – 28	30	52 (47 – 56)
P5	29.2 - 42	90	38 (36 – 40)
PA	14 - 24.4	30	28 (27 – 29)
PW	46 – 78	30	89 (> 66)

Table 6	Groundwater mean residence time (MRT). % Exponential defines the spread of the residence time
	distribution – a low percentage gives a narrow distribution and a high percentage a wide distribution
	(See Section 5.1).

<sup>1.</sup>The stated model age ranges for all wells (in brackets) result from the 95% confidence interval based on the uncertainty in tracer concentrations only and do not account for the uncertainty in ascertaining the model parameters.

The MRT for all samples ranges between 16 years and 99 years. Groundwater in the Bombay aquifers shows an increase in MRT both in the direction of groundwater flow

(south-east to north-west) and with depth (Figure 4). However, it is unclear if the sampling points are hydraulically connected or whether they represent small individual disconnected aquifers (Figure 3). In the Pukekohe upper aquifer, groundwater ages also change in the assumed direction of groundwater flow (Figure 5). Upper aquifer groundwater generally has a MRT younger than 50 years (Table 6). However, there is more ambiguity in the age-tracer results for the Pukekohe upper aquifer samples and these should be refined further by future sampling in three to five years. At Pukekohe the oldest ages are seen in the "lower" volcanic aquifer system which is not directly hydraulically connected to the "upper" volcanic aquifer system (See Section 2).









approximate surface elevation. The arrows indicate the direction of groundwater flow as implied by piezometric contours (ARC, 1996). Note that the vertical scale is exaggerated for figure clarity.

#### 5.1 Implications of MRT and Residence Time Distribution.

Both the MRT and the residence time distribution have implications for future trends in nitrate concentrations within the aquifer. A water sample from a well or spring contains a mixture of younger to older groundwater because long and short flowlines converge at the well or spring. For water mixtures with relatively old MRT, only a fraction of the water is young enough to show nitrate contamination from recent land use (Figure 6) and large fractions of the discharging water are still uncontaminated. In time the front of the contaminated water moves forward and a higher fraction of contaminated water will discharge into the well or spring; with a resultant increase in nitrate concentrations.



Figure 6 Distribution of contaminated water in a groundwater system. Contaminated water is illustrated by the hatched shading. Figure from Morgenstern & Gordon, 2006.

Figure 7 shows the residence time distribution for three wells from this study (wells P5, BP and B2). The Rifle Range shallow well (P5) has a high proportion of exponential mixed flow with a resulting wide distribution of residence times. The fraction of water recharged post-1955 for this well is 80%. Wells BP and B2 have low proportions of exponential mixed flow with narrower distribution of residence times. These two wells differ in MRT; Well BP has a MRT of 63 years and well B2 a MRT of 35 years. The proportions of post-1955 water reaching these wells are 55% and 96% respectively.

If only water recharged after 1955 contains elevated nitrate levels due to land use intensification (Murphy, 1991), then the residence time distributions imply that the nitrate concentrations in groundwater from the wells P5 and BP will continue to rise in the future, assuming constant land use contributions of nitrate to the system. Nearly all the water reaching well B2 is recharged after 1955, and the nitrate concentration at this well would therefore not be expected to rise greatly in the future.



Figure 7 Residence time distributions for example wells. a) Rifle Range Shallow (well P5); b) BP Bombay (well BP); c) well B2. The total area under each distribution is equal to one and the shaded areas show the fraction of water recharged between 1955 and 2014 reaching these wells.

Based on the assumptions given above and the present nitrate concentrations of these wells, we can make predictions of the maximum concentrations that may be reached in these wells. Wells P5, BP and B2 have current NO<sub>3</sub>-N concentrations of 9.9mg/L, 11mg/L and 19mg/L respectively, with predicted maximum NO<sub>3</sub>-N concentrations of 12.3mg/L, 20.1mg/L and 19.7mg/L respectively. These predictions rely heavily on the proportion of exponential mixed flow used in the models; therefore future work should include further sampling of these wells to allow refinement of the model parameters. Refinement of the predictions could also involve more detailed information of nitrate inputs into the system.

# 5.2 Recharge Temperature and Excess Air

Groundwater age determination using CFCs and SF<sub>6</sub> requires dissolved tracer concentrations to be converted to the equivalent atmospheric concentrations. This is achieved with Henry's Law for dissolved gases, using an estimated recharge temperature and making a correction for excess air (See Appendix 1 for an explanation of excess air). For this study the recharge temperatures and excess air concentrations have been determined by measuring dissolved argon and dissolved nitrogen concentrations (Table 4). Plotting the concentrations of argon and nitrogen against each other indicates the recharge temperature as well as the amount of excess air in the samples (Figure 8). Concentrations of these gases in equilibrium with the atmosphere would plot along the bold black line on the left of the grid depending on the temperature during dissolution. The presence of excess air will shift the plotted points upwards and to the right in a parallel direction to the grid which is determined by the ratio of argon to nitrogen in air. Sample degassing, which can occur within the aquifer or during sampling, will shift the points towards the bottom left.

Comparison of dissolved argon and dissolved nitrogen concentrations can also allow for identification of "excess" dissolved nitrogen caused by denitrification (Figure 8). This process increases the nitrogen concentration but leaves the argon concentration unaltered and thus can be identified distinctly from excess air. Based on this analysis, there is no evidence of considerable denitrification occurring in groundwater from the sampled wells.





Groundwater recharge temperatures are often expected to be similar to the mean annual air temperature of the recharge area (Busenberg and Plummer, 1992; Heaton and Vogel, 1981). This is dependent on the depth of the unsaturated zone, as dissolved gases are continuously equilibrating with unsaturated zone air until isolated from air in the saturated zone. The mean annual air temperature over the period 1981 – 2010 was 14.5°C at Pukekohe, (NIWA National Climate Database, 2015) while the derived recharge temperatures ranged from 7.3°C to 14.9°C (Table 4). Seasonal recharge might also be expected to affect the recharge temperature, especially in areas with shallow unsaturated zones. For example if most recharge occurs in the winter months then the recharge temperature could be lower compared to the mean annual air temperature.

Excess air concentrations ranged from -1.7 to 5.1mL of gas at standard temperature and pressure (STP = 273.15K, 101.325kPa) per kg of water (denoted as mL(STP)/kg). The negative excess air concentration from well P4 indicates that the gas tracers at this well have been influenced by degassing which most likely occurred during the sampling process due to the high pumping rate. For the remaining wells, excess air concentrations can be separated in to two distinct groups. The first group has relatively low excess air ranging from 1.2 to 2.7 mL(STP)/kg and includes all of the Bombay wells plus well P2 from Pukekohe. The second group of three wells from Pukekohe has higher excess air concentrations between 3.9 and 6.5 mL(STP)/kg. The cause of the difference between the two groups is currently unknown.

# 5.3 Rifle Range Shallow Well

The Auckland Council SOE monitoring well Rifle Range Shallow (Site 7428105; P5) was sampled for this project. This well has also been sampled for groundwater age-tracers

(Figure 9) as part of the National Groundwater Monitoring Programme (NGMP) administered by GNS Science, as well as being sampled quarterly for general chemistry.

In 2010 an abrupt change in water chemistry indicated that surface water or shallower groundwater was leaking down the bore casing (Figure 10). As a result the well was decommissioned in 2013 and a new well was installed in 2014. The new well was located several metres away and screened at the same depth as the old well. The new well had just been completed when the age-tracer samples were taken in 2014. Unfortunately, as shown by further SOE sampling, the well at this time was not purged sufficiently, and the age-tracer data from this sampling has been disregarded. The groundwater MRT presented for this well is therefore based on old data collected prior to 2010 (sample size n= 3).

Despite having longer term age-tracer data for this well, several possible model age solutions exist. The best-fit model solution with MRT of 13 years did not agree well with the gas-tracer data for this well, which indicated an older MRT. Therefore the preferred solution is a MRT of 38 years at 90% exponential mixed flow. Further age-tracer sampling at this well would be beneficial and allow refinement of the groundwater age model. Using the same proportion of exponential mixed flow (90%), the MRT of the water that was leaking into the well from 2010 to 2014 was 9 years. This may be a composite MRT of younger water leaking down and the older volcanic aquifer water.



Figure 9 Time-series tritium data for the Rifle Range Shallow Well (P5) with fitted exponential – piston flow models. The model output lines show the changes in tritium concentrations that would be expected in groundwater from these wells over time, given the stated model parameters (fraction of exponential mixed flow in %, MRT (T) in years). The tritium input is shown for comparison and is tritium in rainfall at Kaitoke, Wellington, averaged by year and scaled to Auckland. The three points in blue were used for model-fitting, while the two points collected after 2012 are affected by shallower water. The orange point was collected while the casing was leaking and is not representative of the aquifer groundwater. The hollow data point is the sample collected in 2014 for this study.



Figure 10 Concentration of bicarbonate, silica and nitrate concentrations from 1998 – 2015 for the Rifle Range Shallow Well (P5). The hollow data points are from the samples collected in 2014 for this study.

#### 6.0 Chemistry

Groundwater sampled from the volcanic aquifers was predominantly of type Mg-Na-Ca- $HCO_3$ -NO\_3-Cl or Mg-Na-Ca-NO\_3-HCO\_3-Cl (Figure 11, Table 7). The dominance of magnesium reflects the basalt mineralogy i.e., the presence of magnesium-rich olivines and pyroxenes. Nitrate is the dominant anion in younger groundwater, but not in older groundwater where bicarbonate concentrations are much higher and nitrate is not present.



Figure 11 Piper diagram showing the variation of major ion chemistry. The left and right triangles show the major cation and anion ratios on an equivalence basis respectively, and the centre diamond plots projections based on the two triangular plots. Wells P5 and RR are the same site. Well P5 (in red) is the sample from June 2014 which was insufficiently purged. RR is median chemistry from the old well at the same site. Sulphate concentrations were not measured for most wells and have been estimated except for wells BP, BW, P4, PW and RR where data was available.

Table 7Groundwater chemistry types.

Well ID	Cations	Anions
B1	Mg-Na-Ca	HCO <sub>3</sub> -NO <sub>3</sub> -CI
B2	Mg-Na-Ca	NO <sub>3</sub> -HCO <sub>3</sub> -CI
B3	Mg-Na-Ca	HCO <sub>3</sub> -CI
B4	Mg-Na-Ca	HCO <sub>3</sub> -CI
B5	Mg-Na-Ca	HCO <sub>3</sub> -CI
BP	Mg-Ca-Na	HCO <sub>3</sub> -NO <sub>3</sub> -CI
BW	Mg-Na-Ca	NO <sub>3</sub> -HCO <sub>3</sub> -CI
P1	Mg-Na-Ca	NO <sub>3</sub> -HCO <sub>3</sub> -CI
P2	Mg-Na-Ca	NO <sub>3</sub> -HCO <sub>3</sub> -CI
P3	Mg-Na-Ca	HCO <sub>3</sub> -CI
P4	Mg-Na-Ca	NO <sub>3</sub> -HCO <sub>3</sub> -CI
P5	Na-Mg-Ca	HCO <sub>3</sub> -NO <sub>3</sub> -CI
PA	ND	ND
PW	Na-Ca-Mg	HCO <sub>3</sub> -CI

Previous studies indicated that groundwater of the volcanic aquifers can be separated into two distinct types (Murphy, 1991; ARC, 1996). The first type has low alkalinity and high nitrate concentrations, while the second type has high alkalinity and low nitrate concentrations. In general the first type occurs in the shallower volcanic aquifer systems, with the second type of groundwater present in the deeper volcanic aquifers. Figure 12 shows the bicarbonate and nitrate concentrations from wells in this study. All but five wells have groundwater which falls into the low alkalinity – high nitrate group. In addition, the two groups can be distinguished by MRT, with type 1 (low alkalinity – high nitrate) having a MRT less than 70 years, and type 2 (high alkalinity - low nitrate) types having a MRT greater than 70 years.





Bicarbonate alkalinity arises from dissolution of rock minerals by carbonic acid. Alternatively, calcium in the groundwater is derived primarily from weathering of plagioclase and other minerals, as well as from surface inputs such as fertilisers and animal wastes (Murphy, 1991). Plotting calcium against bicarbonate shows that all calcium in the sampled groundwaters could potentially be derived from mineral dissolution (Figure 13). Similarly, while magnesium could also come from surface inputs, plotting against silica shows that most magnesium is derived from dissolution of ferromagnesium minerals (Figure 14; Murphy, 1991).



Figure 13 Plot of calcium against bicarbonate. The dashed lines depict ratios of bicarbonate and calcium that would be expected for the dissolution of augite and anorthite (or calcite).



Figure 14 Plot of silica against magnesium. The dashed lines depict ratios of silica and magnesium that would be expected for the dissolution of augite and olivene.

Comparison of chloride to sodium concentrations shows that roughly 30 to 50% of sodium is not derived from marine-origin sodium chloride (Figure 15). This "excess" sodium may be derived from dissolution of sodium feldspars (Figure 16), and/or ion exchange processes within the aquifer which result in sodium replacing calcium in the presence of clays. Inputs from fertiliser use may also be possible.



Figure 15 Plot of chloride against sodium. The dashed line is the seawater concentration dilution line.



Figure 16 Plot of silica against sodium concentrations corrected for sodium derived from marine sources. The dashed line depicts ratios of silica and sodium that would be expected for the dissolution of the sodium plagioclase albite.

#### 6.1 Trends in aquifer chemistry

Three wells from this study are part of the Auckland Council State of the Environment (SOE) monitoring network, and/or the NGMP (BP, P4, P5). Two of these wells (BP and P5) have sufficient long-term chemistry data to undertake statistical trend analysis. Long-term monotonic trends over time are identified using the non-parametric Mann-Kendall test (Daughney, 2007; 2010). This test indicates whether a change in parameter generally follows the same direction over time (either increasing or decreasing trend), or if there is no statistically significant change over time. Once a trend is identified, the magnitude is calculated using Sen's Slope Estimator and a linear regression method (Daughney, 2007; 2010). The two estimations of magnitude often yield similar results, although linear regression is more sensitive to outliers in the data. The results of the tests are presented in Table 8.

Statistically significant trends of increasing concentration have occurred for the major cations including calcium, magnesium and sodium at both wells BP and P5 over the period 1998 to 2014 (Figure 17a, Figure 18a). At well BP nitrate, sulphate and silica concentrations also show increasing trends (Figure 17b). Nitrate concentrations are increasing at well P5, while chloride and sulphate concentrations show decreasing trends at this well (Figure 18b). Potassium, bicarbonate and dissolved phosphorus do not show any trends for either well.

Table 8 Results of trend analysis for chemistry from wells BP and P5 over the time period 1998 to 2014. The top row shows whether a trend was detected (p = 0.05), at well BP and if so whether it was increasing (INCR) or decreasing (DECR) (NT = no trend); and the second row shows the magnitude of the trends for this well (Sen's Slope Estimator) in mg/L/year. The bottom two rows show the same information for well P5.

ID	Ca	Mg	Na	К	CI	SO <sub>4</sub>	NO <sub>3</sub> -N	HCO <sub>3</sub>	SiO <sub>2</sub>	DRP
BP	INCR	INCR	INCR	NT	NT	INCR	INCR	NT	INCR	NT
BP	0.090	0.040	0.060	0.001	0.010	0.022	0.195	-0.115	0.200	0.000
P5	INCR	INCR	INCR	NT	DECR	DECR	INCR	NT	NT	NT
P5	0.178	0.160	0.079	-0.002	-0.038	-0.056	0.479	-0.074	0.000	0.000



Figure 17 Changes in chemistry over time for the BP Bombay well (BP) including a) calcium, sodium and magnesium concentrations; and b) chloride, nitrate and sulphate concentrations. The solid lines are trend lines from linear regression, showing increasing trends for all six analytes.

Trends in chemistry over time can result from several different processes. For example, changes in the flow regime due to groundwater abstraction may cause either older or younger water to begin reaching the well with accompanying changes in water quality. Alternatively, changes in land use in the recharge area over time could affect the quality of groundwater recharged to the well. For nutrients such as nitrate, land use activities are more likely, although the observed increasing trends could result from a combination of both processes. For analytes thought to come primarily from rock dissolution, such as magnesium (Murphy, 1991), the first process is more likely. This may indicate that the groundwater age structure of the aquifer systems is changing due to groundwater abstraction.



Figure 18 Changes in chemistry over time for the Rifle Range Shallow (P5) well. a) calcium, sodium and magnesium; b) chloride, nitrate and sulphate. The solid lines are trend lines from linear regression, showing increasing trends for calcium, sodium, magnesium and nitrate-nitrogen and a decreasing trend for sulphate. Note that bad data from 2010 to 2013 have been removed (See Section 5.2).

#### 6.2 Variation in chemistry with groundwater age

In the following section, the relationship of hydrochemistry to groundwater MRT is examined. These relationships rely somewhat on the particular flow models used to calculate ages and therefore should be treated as generalisations of any actual relationships. The groundwater MRT have some ambiguity and/or uncertainty, and many of the MRTs are calculated using arbitrarily selected model parameters. Older groundwaters have minimum MRTs defined by tritium which could actually be much older, thus the observed relationships may not necessarily be as linear as depicted. R<sup>2</sup> values, which are presented in the following graphs as an indication of statistical significance, should therefore be treated as illustrative only. Due to the small number of data points the analyses were carried out on the combined data from both areas.

Relationships with MRT can potentially allow identification of chemical parameters that could be used as groundwater age-proxies. With such proxies a more expansive survey of groundwater age could be obtained at lower cost. The origin, fate and predicted future changes in nutrient concentrations associated with land use change may also be obtained through examination of relationships between chemistry and MRT. The pH of groundwater increases with MRT (Figure 19a), and pH is near 6 for young groundwater and gradually increases up to around pH 8 for old groundwater. Dissolved oxygen decreases with MRT, with very old water becoming anoxic (Figure 19c). While it might be expected that conductivity would increase with MRT due to the increased time for water-rock interaction and subsequent dissolution of minerals in the aquifer matrix, this is not the case in the Bombay and Pukekohe aquifers (Figure 19b). This result is probably due to the higher solute loading in younger groundwater due to land use intensification.



Figure 19 Plots of the relationship between chemistry and MRT a) pH, b) electrical conductivity, and c) dissolved oxygen. Error bars are the age ranges defined in Table 6. R<sup>2</sup> values show significant relationships for pH and dissolved oxygen at the 95% confidence level.

Dissolved silica in groundwater shows only a slight positive relationship with groundwater MRT (Figure 20a). Concentrations rise from around 30mg/L to between 40 and 50mg/L. MRT above 40 years are fairly constant. This implies that equilibrium concentrations of silica with respect to mineral dissolution are reached reasonably quickly. Further variations in concentrations are probably due to differences in mineral assemblages in the catchments of each individual well. Bicarbonate shows a positive relationship with MRT (Figure 20b). Concentrations change little for MRT less than 50 years then rise dramatically as water gets older. The somewhat abrupt change reflects the change in redox state as groundwater evolves as well as changes in lithology as the groundwater penetrates to the deeper aquifers. This may indicate that the chemistry changes are driven by water interaction with the fine sediment layers between the volcanic aquifer systems.



Figure 20 Plots of the relationships between chemistry and MRT including a) silica, b) bicarbonate, c) dissolved reactive phosphorus, and d) potassium. Error bars are the age ranges defined in Table 6. R<sup>2</sup> values show significant relationships for all four analytes at the 95% confidence level.

Both dissolved reactive phosphorus and potassium concentrations increase with MRT (Figure 20c & d). In a similar fashion to bicarbonate, concentrations of these two analytes in groundwater with MRT less than 50 years are varied but do not increase over time. This indicates that any land-surface inputs of these two analytes have not reached the shallower young groundwater, and are probably unlikely to do so. The increase in potassium in older groundwater shows a lack of sinks, which would tend to decrease potassium concentrations over time, within the aquifer matrix.

Magnesium and calcium concentrations show no relationship to MRT (Figure 21a & b). This could mean either equilibrium concentrations of these analytes with respect to mineral dissolution are reached quickly with little change there-on, or that these analytes may also be

derived from surface inputs resulting from land use activities. In the younger groundwater, both calcium and magnesium are under-saturated with respect to bicarbonate; therefore the first reason is unlikely. Alternatively, these cations may be replaced in solution over time by ion-exchange processes which release sodium ions. However, sodium concentrations do not increase over time (Figure 21c), therefore surface inputs resulting from land use activities seems the most likely explanation for the lack of relationship to MRT.



Figure 21 Chemistry relationships with MRT a) magnesium; b) calcium; c) sodium; d) chloride. Error bars are the age ranges defined in Table 6. R<sup>2</sup> values show no significant relationships for all four analytes at the 95% confidence level.

Chloride, which does not come from mineral dissolution, does not increase with groundwater MRT (Figure 21d), indicating a lack of sources of chloride within the aquifer matrices such as

marine deposits and / or saline connate water. It is therefore likely that the chloride is predominantly derived from surface inputs such as seaspray deposition, fertilisers and effluent. An examination of CI:Br ratios may further delineate these sources (Rosen, 2001).

Nitrate has an inverse relationship with MRT (Figure 22a). Groundwater with a MRT greater than 70 years has no significant nitrate. This is not uncommon for analytes which are generally associated with land use changes and intensification. The chemistry of younger waters (<60 - 70 years) reflects the impacts of recent land use, while older water retains the chemical signature of less-impacted recharge sources.

Low nitrate concentrations in old groundwater might also be caused by denitrification, as dissolved ammonia is present in the oldest groundwaters while nitrate is not (Figure 22b). High concentrations of ammonia and nitrate are mutually exclusive as ammonia is usually only present in reduced groundwaters while nitrate is not (Figure 23). This implies that the older groundwater is in a redox state where denitrification would occur. However, evidence for substantial denitrification is not seen in dissolved nitrogen concentrations (Section 5.1) and it would seem the primary reason for low nitrate concentrations in the old groundwaters is that land use effects have not reached them yet. However, dissolved oxygen levels decrease with MRT and the oldest water is anoxic (Figure 19c). Therefore when nitrate contamination does reach these parts of the aquifer systems it is likely to be, at least in part, denitrified.



Figure 22 Plots showing the relationship between chemistry and MRT including a) nitrate, and b) ammonia. Error bars are the age ranges defined in Table 6. R<sup>2</sup> values show significant relationships for both analytes at the 95% confidence level.



Figure 23 Plot showing the relationship between ammonia and nitrate.

Iron and manganese have negligible concentrations in young groundwater and higher concentrations in older groundwater (Figure 24a & b). This reflects the increased availability of these analytes due to prolonged water rock interaction and mineral dissolution in the older groundwater, as well as the changing redox state of the groundwater towards an anoxic state (Figure 25a & b). Old groundwater in the Bombay aquifers has higher iron and manganese concentrations than in old groundwater from the Pukekohe aquifers, likely reflecting small differences in mineralogy.



Figure 24 Plot showing the relationships between chemistry and MRT including a) iron, and b) manganese. Error bars are the age ranges defined in Table 6. R<sup>2</sup> values show a significant relationship for manganese at the 95% confidence level.



Figure 25 Plot showing the relationships dissolved oxygen and chemistry including a) iron, and b) manganese. Error bars are the age ranges defined in Table 6.

### 7.0 Summary and recommendations

MRTs of groundwater from the Bombay and Pukekohe volcanic aquifer systems range between 16 years and 99 years. Groundwater in the Bombay aquifers show an increase in MRT both in the direction of groundwater flow and with depth, while at Pukekohe the upper aquifer groundwater generally has MRT younger than 50 years and the oldest ages are seen in the lower aquifer system.

Groundwater in the volcanic aquifers is predominantly of type Mg-Na-Ca-HCO<sub>3</sub>-NO<sub>3</sub>-Cl or Mg-Na-Ca-NO<sub>3</sub>-HCO<sub>3</sub>-Cl. The dominance of magnesium reflects the basalt mineralogy i.e., the presence of magnesium-rich olivines and pyroxenes. Nitrate is the dominant anion in younger groundwater. However, in older groundwater bicarbonate concentrations are much higher and nitrate is not present.

Positive relationships with MRT are observed for pH, bicarbonate, dissolved reactive phosphorus, potassium, and to a lesser extent, silica. These analytes have the potential to be used as proxies for groundwater age. To develop these as proxies, additional age-tracer and chemistry data should be collected to refine the model. Iron, manganese and ammonia also show relationships with groundwater age, which are primarily controlled by the groundwater redox state. Sodium and chloride concentrations do not increase with age. This could be due to land use changes and warrants further investigation.

Nitrate shows an inverse relationship with groundwater MRT. This is common for analytes associated with land use changes and intensification. The chemistry of younger waters reflects the impacts of recent land use, while older water retains the chemical signature of less-impacted recharge sources. However, it is difficult to use such a relationship as a groundwater age proxy as the variability in concentrations for young groundwaters is primarily a function of land use rather than MRT. Although old groundwater at some wells is anoxic, there is no evidence of denitrification.

Changes in chemistry observed at SOE monitoring wells indicate that pumping-induced changes to the aquifer flow regimes may be occurring. This may have consequences on the groundwater age structure of the aquifer systems.

The MRT determined in this study are somewhat preliminary due to there being only one sampling round for most wells. To refine the groundwater age models and resolve age-tracer ambiguity as well as to better understand the chemical evolution of the system we make the following recommendations:

- Further age-tracer sampling should be carried out on the same wells after a three to five year interval allowing refinement of the groundwater age models, establishment of more robust groundwater age-chemistry relationships and development of a groundwater chemistry age-proxy model.
- Wells which were sampled earlier than 2014 (BP, BW, P5, and BA); especially the Rifle Range Shallow well (P5); could be resampled sooner (i.e., within the next year).
- Additional wells in both shallow and deep aquifers should be sampled for chemistry and age-tracers to increase coverage both spatially and over a wider range of MRT.
- Springs and streams fed by groundwater discharges should be sampled for agetracers and chemistry to determine the fate of nitrate in the aquifer systems, and to

allow modelled predictions of future nitrogen loadings to these springs and streams to aid management of the "national bottom line" for nitrate toxicity.

- Predictions of future nitrogen loadings can be refined by incorporation into the model of known historical nitrate inputs to the aquifer systems.
- The origin of surface inputs of analytes such as sodium and chloride could be further investigated through geochemical analyses such as CI:Br ratios.

#### 8.0 Acknowledgements

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# **Appendices**

# Appendix 1: Determination of groundwater age for "young" groundwaters

## A1.1 Tracer characteristics

#### A1.1.1 Tritium

Tritium is a naturally occurring radioisotope of hydrogen, produced by cosmic radiation induced spallation of nitrogen in the upper atmosphere. Prior to the 1950s this resulted in a total global inventory of 3.6 kg (Solomon and Cook, 2000). From 1952 to 1963, substantially greater amounts of tritium were released to the upper atmosphere via atmospheric nuclear bomb testing. About 5 percent of this nuclear fallout reached the Southern Hemisphere (Stewart and Taylor, 1981), resulting in a marked peak in tritium concentrations in rainfall in New Zealand (Figure A 1). This 'bomb peak' defines the input function into the hydrologic system. Tritium levels in New Zealand rainfall have subsequently returned to almost background natural levels since atmospheric tests were banned by treaty in 1963 (McGlynn *et al.*, 2003).

Tritium is part of water molecules as  ${}^{3}H^{1}HO$ . These water molecules follow the same pathways as water molecules not containing tritium ( ${}^{1}H_{2}O$ ) and are not affected by chemical and microbial processes that could alter their concentrations (unlike for example CFCs) (Plummer *et al.*, 1993; Stewart and Morgenstern, 2001). Thus tritium is nearly an ideal hydrologic tracer. However, where zones of immobile water exist within the aquifer system, for example water in aquitards or bound water in clay matrices then diffusional loss of tritium into these zones may occur resulting in an apparent tritium age which is greater than the actual age of the mobile water existing the system (Zuber *et al.*, 2010).

Once surface water infiltrates it is separated from the atmospheric source of tritium and its tritium concentration will begin to decrease due to radioactive decay. Tritium concentrations in groundwater are therefore a function of the time spent underground, such that:

$$C(t) = C_0 \exp(-\lambda t) \tag{1}$$

where

C(t) = tritium ratio in groundwater after time t Co = initial tritium ratio in rainwater  $\lambda$  = the tritium radioactive decay constant

Tritium has a half-life of 12.32 years and thus is useful for studying processes over the last 100 years or so (Lucas and Unterweger, 2000).

The tritium groundwater age derived from a single tritium measurement for water originating in the 'bomb peak' era is often ambiguous, as the tritium value could correspond either to the rising limb or the falling limb of the peak (Figure A 1). This can often be resolved by further tritium measurements separated by a reasonable period of time (usually a few years), or by using a complementary dating technique such as CFCs or SF<sub>6</sub> (Stewart and Morgenstern, 2001). Interpretation of groundwater ages from the naturally produced low levels of tritium on either side of the bomb peak can be more straight-forward, but requires measurements with extremely high detection sensitivity (Morgenstern and Taylor, 2009).



Figure A 1 Tracer input curves. Mean annual tritium concentrations in rainfall at Kaitoke, New Zealand. Monthly rainfall concentrations at Kaitoke have been measured continuously since 1960. Annual values are means of monthly samples running from July to June each year, expressed in tritium units (TU) or tritium ratio (TR) where 1TU = 1TR = <sup>3</sup>H/<sup>1</sup>H ratio of 1:1×10-18. CFC and SF<sub>6</sub> concentrations (in parts per trillion or ppt) are for Southern Hemispheric air and consist of measured and reconstructed data (IAEA, 2006; Cunnold *et al.*, 1997; Prinn *et al.*, 2000; Walker *et al.*, 2000; Thompson *et al.*, 2004; Maiss and Brenninkmeijer, 1998).

#### A1.1.2 CFCs and SF<sub>6</sub>

Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF<sub>6</sub>) are relatively conservative tracers in groundwater environments, and can be used to estimate recharge dates for aquifers (Busenberg and Plummer, 1992; Busenberg and Plummer, 2000). Groundwater age information can be obtained from dissolved CFC and SF<sub>6</sub> concentrations due to the steady increase of these compounds in the atmosphere since the start of their manufacture in the 1930s and 1950s respectively. CFCs are entirely synthetic and do not occur naturally, therefore the presence of CFCs in groundwater is predominantly the result of these rising atmospheric levels (Lovelock, 1971). SF<sub>6</sub> is also mainly anthropogenic in origin. However, a small amount of SF<sub>6</sub> is also produced in certain volcanic minerals and fluids.

CFCs and SF<sub>6</sub> dissolved in recharge water entering the groundwater zone are in equilibrium with unsaturated zone air concentrations at the time of recharge. Once in the groundwater zone they are isolated from the unsaturated zone air so that the dissolved concentrations can be matched back to this recharge date (Plummer and Busenberg, 2000). In the Southern Hemisphere, atmospheric CFC levels have increased from zero in the 1940s to maximum levels of 545 parts per trillion (ppt) for CFC-12 and 262 pptv for CFC-11 (Figure A 1). However, since the banning of CFC production following the Montreal Protocol in 1987, CFC concentrations have begun to decrease in the atmosphere meaning groundwater dating using CFCs in this period is much less effective (Cunnold *et al.*, 1997). SF<sub>6</sub> atmospheric concentrations have risen steadily since the 1970s to the present level of around 8 ppt.

The CFC or  $SF_6$  'recharge age' relates to the time elapsed since introduction of the tracer to the water as it enters the saturated zone and not to the age of the water itself. This means

the CFC and SF<sub>6</sub> clock starts at the groundwater zone and does not account for travel time through the unsaturated zone. The accuracy with which the two ages match is dependent on how well the tracer is transported in the aqueous phase and the nature of the groundwater zone. There are a number of factors that can affect this transport and the subsequent calculation of the tracer age. The major factors are summarised below but more comprehensive reviews can be found in Plummer and Busenberg, (2000), Busenberg and Plummer, (2000) and Cook *et al.*, (2006).

• Recharge temperature

The solubility of CFCs and SF<sub>6</sub> in water is dependent on temperature. Therefore, errors in the estimated recharge temperature will affect the model ages; if estimated recharge temperatures are too low older apparent ages will result, while temperatures that are too high result in younger apparent ages. For CFCs, an error in estimated recharge temperature of  $\pm 2^{\circ}$ C will result in model age errors of  $\pm 1$  year for water recharged before 1970,  $\pm 1$ -3 years for water recharged between 1970 and 1990, and > $\pm 3$  years for water recharged after 1990 (Stewart *et al.*, 2002).

• Thickness of the unsaturated zone

CFC and SF<sub>6</sub> recharge ages relate to the time these tracers are isolated from unsaturated zone air and enter the groundwater zone. Therefore CFC and SF<sub>6</sub> concentrations in groundwater will be affected by gas transport processes in the unsaturated zone air. Cook and Solomon, (1995), found that there is a diffusion related time-lag for CFC-derived recharge ages which can be considerable for thick unsaturated zones. The effect on SF<sub>6</sub> concentrations is similar to that of CFC-12 (Busenberg and Plummer, 2000). However, even though there may be a time lag due to gaseous diffusion, these tracers still reach the groundwater zone faster than tritium, for which the recharge age includes travel time through the unsaturated zone and thus begins once the tritium in water enters the ground surface and begins to percolate downwards (Schwientek *et al.*, 2009). Thus in general these processes often cause the gas tracer ages to be younger than the tritium-derived groundwater model age for a respective well, and are generally in the order SF<sub>6</sub> < CFC-12 < CFC-11 < tritium.

• Local CFC sources (contamination)

Elevated CFC levels may occasionally occur from localised anthropogenic sources in urban and industrialised areas, and less often in rural areas, which can cause excess CFCs to be present in the water. These concentrations can be higher than possible for water in equilibrium with the atmosphere, thus no model ages will be calculable. If slight contamination occurs then the tracer-derived ages will be too young. In the Canterbury region, CFC-12 contamination occurs more often than CFC-11 contamination (Stewart *et al.*, 2002). SF<sub>6</sub> is much less susceptible to contamination, although elevated concentrations above that possible for water in equilibrium with modern air have been observed in Canterbury groundwaters (van der Raaij, 2003).

Loss of tracer

Chemical processes such as microbial degradation and sorption can affect CFC concentrations. Degradation occurs in anaerobic environments and affects CFC-11 more than CFC-12 (Lovley and Woodward, 1992). If the dissolved oxygen concentration is below 0.5 mgL<sup>-1</sup> then some degradation in CFC concentration is likely to occur. Adsorption of CFCs may also occur under certain conditions. Experiments have shown that adsorption of CFCs, in particular CFC-11, onto dry organic soil material can occur (Russell and Thompson, 1983). Loss of CFCs through these

processes will result in overestimated groundwater ages. SF<sub>6</sub> appears unaffected by these processes (Wilson and Mackay, 1996; Busenberg and Plummer, 2000).

• Excess air

Groundwater often contains "excess air". Excess air is dissolved air in excess of the equilibrium-soluble amount at the given recharge temperature and is thought to originate by processes such as bubble entrapment occurring during recharge (Heaton and Vogel, 1981). This introduces extra CFCs and SF<sub>6</sub> to the groundwater, leading to underestimated model ages. The effect is small for CFCs and can generally be ignored for waters recharged before 1990 (Stewart *et al.*, 2002). The effect on SF<sub>6</sub> is much greater and corrections need to be applied when interpreting SF<sub>6</sub> data (Figure A 2). The size of the correction is usually estimated by analysis of dissolved argon and nitrogen which allows calculation of the volume of dissolved excess air (Heaton and Vogel, 1981).





Because of these processes with the potential to modify CFC and  $SF_6$  concentrations in groundwater, studies should not rely on these tracers alone. Rather, these tracers should be used complementarily to the more robust tracer tritium to help resolve ambiguity in age interpretation.

# A1.2 Interpretation of groundwater ages using lumped parameter flow models

Groundwater extracted from a well or other discharge point is a mixture of water with different ages due to the convergence of different flow lines within the aquifer at the discharge point (Figure A 3). Groundwater age-dating therefore yields the mean age (or mean residence time: MRT) of water from all converging flow lines. Lumped-parameter mixing models are used to describe the distribution of groundwater age. The mixing of different flow lines occurs at the sampling point and the extent to which this occurs is specific to the well. It depends on several factors including well construction, screen length, well

depth and pumping rates; and also the hydrogeologic attributes of the aquifer around the well (which affect the variety of possible flow paths that may be intersected by the well).

The age of water leaving a groundwater system, usually called the turnover time  $t_w$  or mean residence time of the water, is defined as the ratio of the volume of mobile water in the system  $V_m$  to the volumetric flow rate Q (Zuber and Maloszewski, 2001). i.e.:

$$t_w = V_m / Q \tag{3}$$

The mean tracer age  $t_t$  (mean travel time of tracer, mean residence time (MRT) of tracer) is defined as:

$$t_t = \int_0^\infty t^* C_I(t') dt' / \int_0^\infty C_I(t') dt'$$
(4)

where  $C_{l}(t)$  is the tracer concentration observed at the sampling site after time t' resulting from an instantaneous injection at the entrance of the system at time t'=0 (Zuber and Maloszewski, 2001).

The mean tracer age  $t_t$  is equal to the turnover time  $t_w$  of the water in the system only if there are no zones containing immobile water in the system and the tracer is injected and measured in flux, that is, the amount of tracer entering or exiting the system is proportional to the volumetric flow rate (Zuber and Maloszewski, 2001). If there is immobile water in the system then the transport of the tracer through the system may be delayed due to diffusive exchange between the mobile and immobile zones. The second condition of flux injection and measurement is often fulfilled naturally for tracers entering the system with infiltrating water and measured in outflowing water (Zuber and Maloszewski, 2001).

The relationship between variable tracer input concentrations  $C_{in}$  and output concentrations  $C_{out}$  is given by the convolution integral:

$$C_{\text{out}}(t_{obs}) = \int_{0}^{\infty} C_{\text{in}}(t_{obs} - t') g(t') \exp(-\lambda t') dt'$$
 (5)

where  $t_{obs} = time$  of observation,  $t' = the transit time, exp(-\lambda t')$  accounts for radioactive decay and g(t') is the system response function which describes the transit time distribution of water within the system (Zuber and Maloszewski, 2001).



Figure A 3 Examples of conceptual groundwater flow situations which can be described by lumped parameter mixing models (Maloszewski and Zuber, 1982). a) The piston flow model is a reasonable approximation for aquifers in which the recharge zone is narrow with respect to the overall distance from recharge zone to sampling point when there is little dispersion. b) The exponential model - the shortest flow line has a transit time equal to zero, with transit times for longer flow lines stretching to infinity. The mixing of different flow lines occurs at the sampling point. For cases in between these two scenarios the exponential - piston flow model or dispersion model should be applied, for example: c) a partly confined aquifer with constant thickness and depth. d) an unconfined aquifer where the sampling well is screened over part of the aquifer at depth.

#### A1.2.1 The Piston Flow Model

The piston flow model (PFM) is a widely used approximation of groundwater flow. This model assumes all flow lines have the same transit time and that there is negligible hydrodynamic dispersion or molecular diffusion (Zuber and Maloszewski, 2001). The system response function for this model is the Dirac delta function, which is a function describing approximately a pulse of unbounded height and zero width.

$$g(t') = \delta \left( t' - t_t \right) \tag{6}$$

Integration of the Dirac delta function reduces the convolution integral for the PFM to:

$$C_{\text{out}}(t) = C_{\text{in}}(t - t') \exp(-\lambda t_t)$$
(7)

This means the tracer moves through the system in an unchanged 'parcel', such that the output concentration  $C_{out}$  at a specified time *t* is equal to the input concentration  $C_{in}$  at an earlier time (*t* - *t<sub>i</sub>*), modified by radioactive decay if applicable. Hence, the only parameter for this model is the transit time t<sub>t</sub> (Zuber and Maloszewski, 2001).

Piston flow is the simplest approximation of groundwater flow and thus is widely used in tracer studies. However, its use is only appropriate under certain conditions. For aquifers in which the recharge zone is narrow with respect to the overall distance from recharge zone to sampling point (Figure A 3(a)), and where there is little longitudinal dispersion, all of the water sampled at a well or discharge point will have nearly the same age (Cook and Böhlke, 2000). Thus the PFM is a reasonable approximation for aquifers of this type. More complicated models may be required in other cases. For example, in heterogeneous aquifers with preferential flow lines which lead to significant dispersion, or where substantial mixing

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occurs at the sampling point such as groundwater wells which draw from an extensive open interval or across different water bearing zones (Plummer and Busenberg, 2000).

#### A1.2.2 The Exponential-Piston Flow Model

The exponential - piston flow model (EPM) is a combination of models in which the aquifer is assumed to consist of two sequential parts, one with an exponential distribution of transit times and one with a piston flow approximation (Zuber, 1986) This results in a water age distribution resembling a translated form of the exponential distribution where younger aged water is not present. The response function is given by:

$$g(t') = 0$$
 for  $t < t_t (1 - f)$  (8)

$$g(t') = (1 / ft_t) \exp(-ft' / ft_t + 1/f - 1) \text{ for } t' > t_t (1 - f)$$
(9)

where  $t_t$  is the mean transit time, f is the fraction of exponential mixed flow; i.e., the ratio of the volume with an exponential distribution of transit times to the total volume in the aquifer; and  $t_t$  (1- f) is the period of time water flows through the piston flow section (Zuber and Maloszewski, 2001). A high proportion of exponential flow in the model results in a wider age distribution than for a low proportion of exponential flow (Figure A 4).



Figure A 4 Age frequency distributions for the exponential - piston flow model, with examples of model solutions (fraction of exponential mixed flow; MRT) for a hypothetical well with a tritium concentration of 0.5 TU at 01.01.10. The piston flow model age is also shown.

Models such as the EPM which have a broad distribution of transit times may often describe situations where only the shorter flow lines supply the tracer to the sampling point. In these situations no information can be gained through the use of the model about the flow lines that do not contain tracer and these flow lines may therefore be distributed differently than implied by the model (Zuber and Maloszewski, 2001).

#### A1.2.3 Use of models to interpret age-tracer data

Solving the convolution integral (equation 5) gives the modelled output of tracer concentrations at specified times. The model output can then be matched to the measured tracer concentrations to obtain the model parameters. Calibration of these parameters involves varying the parameters to fit the observed tracer concentrations by a trial and error procedure. The goodness of fit can be described by statistical tests such as the  $\chi^2$  test (Stewart and McDonnell, 1991) or SIGMA test (Maloszewski and Zuber, 1996).

Observation of tracer concentrations over a period of time allows a proper fit of the model parameters. With just one observation, it is possible that a number of different combinations of parameters will give close fits to the data points thereby yielding ambiguous age data. In these situations, parameters must be estimated based on other information, including the hydrogeologic situation, well depth and well screen length. Less precise estimates of the model parameters may also be obtained using multiple tracers.

Tritium is a good tracer for model calibration due to the pulse-shape of the input function curve. Unique model parameters may be gained with long sequences of observations. Even for single observations in some cases, model parameters can be constrained by the tritium concentration. For example, high tritium values associated with the bomb peak may dictate the maximum amount of exponential mixing allowed in the model to achieve a fit to the observed value (Figure A 5). For the majority of groundwaters, however, fractions of exponential mixed flow greater than 50% are more probable. Fractions above 50% now yield unambiguous age data for all naturally observed tritium levels as the bomb-tritium has decayed below natural tritium concentrations.



Figure A 5 Concentration of tritium in groundwater discharge as a function of mean residence time for different exponential - piston flow parameters, calculated for January 2010. Measured tritium values falling in area A or B may yield ambiguous age data when low fractions of exponential mixed flow are indicated. Fractions of exponential mixed flow greater than 50% will yield unambiguous age data. In area A, comparison with other age-tracers such as CFCs or SF<sub>6</sub> may help constrain the model parameters, e.g., if these tracers indicate an older age which is only possible for very low fractions of exponential mixed flow.

On the other hand, for tritium measurements which yield ambiguous age interpretations, additionally using other tracers such as CFCs or  $SF_6$  may be useful. For CFCs single measurements of these tracers can yield unambiguous ages due to the monotonic shape of the input function up to about 20 years ago (Figure A 6). For groundwaters younger than this, CFCs may not be appropriate due to the flattening of the input curve subsequent to the phasing out of these substances since 1988. For mean ages between 20 and 35 years CFC concentrations are relatively insensitive to the exponential fraction used and can help constrain the mean age but not the fraction of mixing. Similarly, SF<sub>6</sub> yields unambiguous ages but is insensitive to exponential fraction for mean ages less than 18 years.



Figure A 6 Concentration of CFC-11, CFC-12 and  $SF_6$  in groundwater discharge expressed as the equivalent atmospheric concentration, as a function of mean residence time for different exponential - piston flow parameters (a,b). Since the phasing out of CFCs in 1988, atmospheric concentrations of these tracers have declined and CFCs are not as effective for groundwater dating over the last 20 years (marked area A on graphs). For mean ages between 20 and 35 years CFC concentrations are relatively insensitive to the model parameters used (Area B). c) For mean ages less than 18 years,  $SF_6$  concentrations are also insensitive to the model parameters used (Area B).

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#### Appendix 2: Groundwater Mean Residence Time

Table A2.1

Groundwater mean residence times. Where tracer concentrations allow alternative MRT these are presented in the "Alternative MRT" column. The most likely MRT is presented in the "preferred MRT" column, with reasoning given in the "Comments" column. "Unambiguous" MRT can still vary depending on the % exponential used.

Well ID	Alternative MRT (years)	% Exponential	Preferred MRT (years)	Comments		
B1	27, 64	30	27 (24 – 30) <sup>1</sup>	best fit <sup>3</sup> H/gases		
B2	18, 35, 62	30	35 (33 – 39)	best fit <sup>3</sup> H/gases		
B3	70	30	70 (69 – 71)	unambiguous		
B4	> 91	35	> 91	unambiguous		
B5	80	30	80 (77 – 91)	unambiguous		
BP	63	30	63 (62 – 64)	unambiguous		
BW	37	30	37 (36 – 38)	unambiguous		
P1	14, 38, 60	70	23 (20 – 27)	best fit <sup>3</sup> H/gases		
P2	10 – 20, 47 – 58	70	16 (14 – 19)	best fit <sup>3</sup> H/gases		
P3	99	40	99 (> 89)	unambiguous		
P4	10 – 20, 47 – 56	30	52 (47 – 56)	$SF_6$ says > 27y		
P5	13, 38, 52	90	38 (36 – 40)	pre-2010 data, SF <sub>6</sub> indicates > 22y		
PA	5, 28	30	28 (27 – 29)	consistency with P4		
PW	89	30	89 (> 66)	unambiguous		

<sup>1.</sup> The stated model age ranges (in brackets) result from the 95% confidence interval based on the uncertainty in tracer concentrations only and do not account for the uncertainty in ascertaining the model parameters.

# Appendix 3: Historical data

Table A3.1Chemistry dataset

Well	EC µS/cm	рН	DO mg/L	Temp °C	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	HCO₃ mg/L	CI mg/L	SO4 mg/L	DRP mg/L	NO <sub>3</sub> -N mg/L	NH₄-N mg/L	Fe mg/L	Mn mg/L	SiO <sub>2</sub> mg/L
BP <sup>1</sup>	266	6.9	7.5	14.5	15	16.5	12	2.11	78	20	2.3	0.100	9.2	<0.01	<0.005	0.001	44.1
BW <sup>2</sup>	NA	NA	NA	NA	13.3	16.4	11.1	1.45	46.4	20	1.9	0.042	12.8	<0.01	0.09	0.03	43
PA <sup>3</sup>	NA	NA	NA	NA	NA	NA	NA	NA	43.9	NA	NA	NA	20	NA	NA	NA	NA
P5 <sup>4</sup>	212	6.62	6.68	15.2	10.4	15.7	8.2	0.97	55	17.2	2.3	0.06	7.5	<0.01	<0.02	<0.005	48
PW <sup>5</sup>	NA	8.2	NA	15.5	17.2	20	10	3.7	124	19.8	<0.5	.317	0.013	0.08	0.02	NA	42.6

<sup>1.</sup> Median values of SOE quarterly sampling 1998-2015.

<sup>2.</sup> Data from Murphy (1991).

<sup>3.</sup> Data from ARWB (1989).

<sup>4.</sup> Median values of NGMP quarterly sampling 1997-2010.

<sup>5.</sup> Data from ARWB (1989).

Table A3.2	GNS Science age-tracer dataset
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Well	Sampling Date	Tritium TR <sup>3</sup>	± Tritium TR <sup>3</sup>	CFC- 11 ppt	± CFC- 11 ppt	CFC- 12 ppt	± CFC- 12 ppt	SF₀ ppt	± SF <sub>6</sub> ppt	Ar mL(STP)/kg	± Ar mL(STP)/kg	N₂ mL(STP)/kg	± N <sub>2</sub> mL(STP)/kg
BP	08/12/2011	0.512	0.020	1187	84	304	30	1.76	0.17	0.487	0.009	23.74	0.49
BW	25/05/1990	1.47	0.10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
PA	06/11/1985	3.16	0.21	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
P5	20/07/1998	1.25	0.040	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
P5	20/07/2005	0.948	0.034	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
P5	10/04/2007	NA	NA	117	10	315	30	NA	NA	0.441	0.007	19.14	0.29
P5	23/07/2007	NA	NA	175	22	399	53	1.86	0.22	0.416	0.009	18.59	0.45
P5	20/01/2009	0.897	0.034	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
P5	08/01/2013	1.096	0.029	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
PW	24/06/1998	0.019	0.018	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

### Appendix 4: Maps

Table A4.1Close up map of Pukekohe wells





