Groundwater residence time assessment of Hastings District Council water supply wells in the context of the Drinking-water Standards for New Zealand

R.W van der Raaij
U. Morgenstern
J. Begg

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EXECUTIVE SUMMARY

This report provides the results of age-tracer analyses and modelled mean residence times of groundwater from fifteen Hastings District Council water supply wells. These results are interpreted with respect to Section 4.5.2.1 of the Drinking-water Standards for New Zealand: 2005 (Ministry of Health, 2008). Available data from previous age-tracer measurements of groundwater from the same wells has been incorporated in the analysis. Incorporation of such historical time-series data improves the robustness of the age interpretation.

Eleven wells (Waipatiki, Whirinaki, Portsmouth Road, Pakipaki, Parkhill, Beach Road, Tucker Lane, Ferry Road, Whakatu, Waipatu and Eastbourne No.5) draw groundwater with modelled mean residence times ranging from 2 years to more than 115 years. These eleven wells are all interpreted to draw groundwater with less than 0.005% of water under one year old, and therefore satisfy the residence time criterion (Section 4.5.2.1) of the Drinking-water Standards for New Zealand: 2005 at the present time.

The modelled groundwater ages indicate that three wells (Omahu, Wilson Road and Brookvale No.1) have potential to draw water younger than one year and therefore do not satisfy the residence time criterion (Section 4.5.2.1) of the Drinking-water Standards for New Zealand: 2005 at the present time.

For the remaining well (Lyndhurst No.5), there are two age solutions, one of which satisfies the residence time criterion and the other which does not. It is not possible to exclude either solution with the data to date, and collection of additional data is recommended.

Both the Portsmouth Road and Lyndhurst No.5 wells are close to the criterion threshold and collection of additional data may enable exclusion of a young water component through improved robustness of parameter estimation. If this can be demonstrated, age interpretations made in the future may indicate that these wells satisfy the residence time criterion.

It is recommended that two-monthly or three-monthly sampling be undertaken for all of the active wells at the Portsmouth Rd. and Lyndhurst well fields. The samples should be analysed for all age tracers and also for a full suite of chemistry parameters. These samples should be collected for at least one year to capture any possible seasonal effects that might influence the age distribution of water drawn by these wells.

It may be desirable to undertake additional samples for all of the Hastings District wells at a higher frequency than required by the DWSNZ:2005. This should be at intervals of at most two years, to enable further refinement of model parameters as well as identification of possible temporal changes in the age distributions. For wells with minimum residence times of the order of only a few years, more frequent sampling (three-monthly intervals) may be useful to identify possible seasonal changes in groundwater age distributions.

1.0 INTRODUCTION

Hastings District Council (HDC) commissioned GNS Science to assess groundwater security at fifteen HDC water supply wells, using groundwater dating methods based on measurement of the concentrations of tritium, chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6). The measured concentrations of tritium, CFCs, and SF_6 are used to estimate the component of groundwater that is less than one year old, according to Section 4.5.2.1 of the Drinking-water Standards for New Zealand: 2005 (DWSNZ:2005) (Ministry of Health 2008). Samples for CFC, SF_6 and tritium analysis were collected in May 2016. Details of the wells are given in Table 1.1 and well locations are shown in Figure 1.1. All fifteen wells have been previously assessed for groundwater security (Cameron and Morgenstern 2001; Trompetter et al., 2011; van der Raaij 2014).

Table 1.1 Well details.

Well name	HBRC Well ID number	Easting [1]	Northing [2]	Total well depth [m below ground level]	Screen depth (m below ground level) [2]	Aquifer confinement condition [2]
Waipatiki	3516	1942704	5642678	37.5	23.7 - 28.0 31.3 - 34.3	confined
Whirinaki	5033	1933186	5632652	10.2	7.2 - 10.2	unconfined
Omahu	10334	1923223	5611906	12.2	Not specified	confined
Portsmouth Rd	3253	1924038	5606956	48	37.0 - 40.0 40.9 - 43.9 45.0 - 48.0	confined
Wilson Rd	897	1925802	5606559	46	38.5 - 46	confined
Pakipaki	1905	1925137	5599411	30	21.95 - 28.96	confined
Parkhill	5830	1938931	5606995	37	32.5 - 36.5	confined
Beach Rd, Haumoana	1187	1939107	5608137	51.3	22.0 - 28.1	confined
Tucker Lane, Clive	542	1936402	5610725	47.55	41.45 - 47.55	confined
Ferry Rd, Clive	1658	1936643	5611357	48.2	41.0 - 47.0	confined
Whakatu	473	1934545	5608832	38.4	32.3 - 38.4	confined
Waipatu	15415	1932395	5606254	36.57	Not specified	confined
Brookvale No.1	1329	1935195	5603353	22	11.4 - 17.4 19.0 - 22.0	confined
Lyndhurst No.5	130	1929225	5607179	63.4	51.7 - 54.1 56.0 - 58.4 60.3 - 62.7	confined
Eastbourne No.5	1302	1929853	5604651	85.5	69.4 - 76.4	confined

1. Coordinates are NZTM and were measured at the time of sampling by handheld GPS.
2. Screen depths and aquifer confinement condition provided by the Hastings District Council.

Figure 1.1 Map showing location and well name of sampled wells.

2.0 METHODOLOGY

2.1 ANALYTICAL METHODOLOGY

Samples were collected by GNS Science staff using standard New Zealand-specific, internationally reviewed sampling protocols (Daughney et al., 2006; 2007). Care was taken to exclude air from the CFC and SF_6 samples. CFC samples were collected underwater in 125 mL glass bottles and sealed using foil-lined caps to prevent contact with the present-day atmosphere. SF_6 samples were collected in 1 L glass bottles with Polyseal caps which displace the headspace. Tritium samples were collected in 1 L Nalgene plastic bottles. Localised tritium sources such as luminous watches were avoided.

CFCs and SF_6 were analysed by gas chromatograph using an electron capture detector (GC ECD) with detection limits of approximately 3 x 10^{-15} mol.kg^{-1} for CFCs and 2 x 10^{-17} mol.kg^{-1} for SF_6. The analytical system for CFCs is similar to that of Busenberg and Plummer (1992). The analytical system for SF_6 is described in van der Raaij (2003). CFC samples were analysed in duplicate. Dissolved argon, nitrogen and methane were measured simultaneously with CFCs by GC/thermal conductivity detector (TCD). CFCs and SF_6 concentrations were subsequently converted to atmospheric equivalents using Ar / N_2 derived temperatures and corrected for excess air.

Tritium was measured by electrolytic enrichment and liquid scintillation counting using Quantulus low-level counters (Morgenstern and Taylor 2009). The detection limit is approximately 0.025 tritium units (1 TU is a 3H/1H ratio of $1{:}1\times10^{18}$).

2.2 GROUNDWATER AGE INTERPRETATION METHODOLOGY

Groundwater sampled from a groundwater outflow such as a well or spring is a mixture of water from various flow lines, and therefore of different residence times. This age distribution can be described by lumped parameter mixing models that provide a system response function. Convolution of known tracer inputs into the system using the chosen system response function and matching to the measured tracer concentrations allows calculation of the mean residence time (MRT) of the groundwater, along with the associated distribution of groundwater residence times.

MRTs have been calculated for all fifteen HDC sites considered in this report using either the exponential-piston flow model (EPM) or a binary model combining two separate EPMs. The EPM has been applied successfully to groundwaters from many areas of New Zealand (Daughney et al., 2010; Morgenstern and Daughney 2012). An explanation of the model methodology and tracer characteristics is given in Appendix 1, including a discussion of the assumptions and uncertainties involved.

3.0 ANALYTICAL RESULTS

Analytical results for tritium, CFCs and SF_6 concentrations in samples taken in May 2016 are presented in Table 3.1 and Table 3.2. Equivalent atmospheric partial pressures of CFCs and SF_6 have been calculated from the analytical results and are presented in Table 3.3, along with the recharge temperatures and excess air concentrations used in these calculations, which are derived from dissolved argon and nitrogen concentrations (Table 3.4). Analytical methods are described in Section 2.1.

Table 3.1 Tritium (^3H) concentrations in groundwater samples.

Well name	Sampling date	Tritium Lab no.	^3H [TR] [1]	$\pm^3H$ [TR] [2]
Waipatiki	04/05/2016	THB293	0.027	0.013
Whirinaki	04/05/2016	THB294	1.079	0.026
Omahu	04/05/2016	THB295	1.538	0.031
Portsmouth Rd	04/05/2016	THB296	1.38	0.032
Wilson Rd	04/05/2016	THB297	1.514	0.033
Pakipaki	04/05/2016	THB298	0.164	0.016
Parkhill	04/05/2016	THB299	1.033	0.026
Beach Rd, Haumoana	04/05/2016	THB300	0.546	0.020
Tucker Lane, Clive	04/05/2016	THB301	0.979	0.025
Ferry Rd, Clive	04/05/2016	THB302	0.944	0.024
Whakatu	05/05/2016	THB303	0.934	0.024
Waipatu	05/05/2016	THB304	0.918	0.025
Brookvale No.1	05/05/2016	THB305	1.562	0.036
Lyndhurst No.5	05/05/2016	THB306	1.403	0.030
Eastbourne No.5	05/05/2016	THB307	0.833	0.026

1. Tritium concentrations are expressed as ^3H:^1H ratios with a Tritium Ratio (TR) of one equal to a ratio of $1:1\times10^{18}$.
2. The quoted measurement error is the combined statistical standard uncertainty from all processes contributing to the measurement uncertainty, expressed as one-sigma standard deviation (Eurachem/Citac 2000).

Table 3.2 Measured CFC and SF_6 concentrations in groundwater samples.

Well name	CFC no.	CFC-11 [pmol/kg] [1]	± CFC-11 [pmol/kg] [3]	CFC-12 [pmol/kg] [1]	± CFC-12 [pmol/kg] [3]	CFC-113 [pmol/kg] [1]	± CFC-113 [pmol/kg] [3]	SF_6 no.	SF_6 [fmol/kg] [2]	± SF_6 [fmol/kg] [3]
Waipatiki	FHB127	0.01	0.03	0.02	0.01	0.00	0.01	SHB114	0.09	0.06
Whirinaki	FHB128	1.76	0.03	1.78	0.05	0.16	0.01	SHB115	3.01	0.08
Omahu	FHB129	4.08	0.06	2.21	0.06	0.43	0.02	SHB116	2.61	0.08
Portsmouth Rd	FHB130	2.97	0.05	2.31	0.06	0.21	0.02	SHB117	5.25	0.13
Wilson Rd	FHB131	3.17	0.05	2.4	0.06	0.23	0.02	SHB118	3.52	0.09
Pakipaki	FHB132	0.00	0.06	0.01	0.01	0.00	0.05	SHB119	0.37	0.06
Parkhill	FHB133	0.41	0.05	1.21	0.03	0.02	0.02	SHB120	1.70	0.06
Beach Rd, Haumoana	FHB134	0.01	0.05	0.01	0.03	0.01	0.03	SHB121	0.26	0.06
Tucker Lane, Clive	FHB135	0.02	0.05	3.40	0.08	0.00	0.03	SHB122	1.23	0.06
Ferry Rd, Clive	FHB136	0.01	0.05	2.23	0.06	0.01	0.03	SHB123	1.06	0.06
Whakatu	FHB137	0.01	0.05	8.61	0.19	0.00	0.04	SHB124	1.26	0.06
Waipatu	FHB138	0.01	0.05	0.83	0.03	0.00	0.03	SHB125	1.59	0.06
Brookvale No.1	FHB139	3.21	0.05	2.34	0.06	0.26	0.02	SHB126	2.82	0.08
Lyndhurst No.5	FHB140	1.09	0.05	2.22	0.05	0.02	0.03	SHB127	2.41	0.07
Eastbourne No.5	FHB141	0.01	0.05	0.48	0.02	0.00	0.02	SHB128	1.45	0.06

1. Dissolved CFC concentrations are expressed in pmol/kg where 1 pmol = 1×10^{-12} mol.
2. Dissolved SF_6 concentrations are expressed in fmol/kg where 1 fmol = 1×10^{-15} mol.
3. The quoted measurement error is the combined statistical standard uncertainty from all processes contributing to the measurement uncertainty, expressed as one standard deviation (Eurachem/Citac 2000).

Table 3.3 Calculated atmospheric partial pressures of CFCs and SF_6. Partial pressures are calculated from the measured concentrations via Henry's Law using recharge temperatures after correction for excess air, as given in Table 3.4.

Well name	CFC-11 [ppt] [1]	± CFC-11 [ppt] [2]	CFC-12 [ppt] [1]	± CFC-12 [ppt] [2]	CFC-113 [ppt] [1]	± CFC-113 [ppt] [2]	SF_6 [ppt] [1]	± SF_6 [ppt] [2]
Waipatiki	0.4	1.4	3.6	2.2	0.1	0.7	0.13	0.09
Whirinaki	93.8	8.4	353	30	27.2	3.1	5.90	0.57
Omahu	269	22	541	42	93.8	9.7	7.73	0.86
Portsmouth Rd	155	13	458	35	35.2	5.2	12.78	1.16
Wilson Rd	169	15	483	40	40.6	5.6	8.58	0.86
Pakipaki	0.2	3.1	1.9	2.5	0.4	9.7	0.87	0.16
Parkhill	23.3	3.7	255	25	4.3	4.4	3.64	0.45
Beach Rd, Haumoana	0.6	2.8	1.4	5.9	0.9	5.1	0.58	0.13
Tucker Lane, Clive	0.9	2.9	695	54	0.5	6.1	2.62	0.24
Ferry Rd, Clive	0.6	2.7	453	36	1.3	5.4	2.37	0.24
Whakatu	0.6	2.6	1650	140	0	6.8	3.27	0.39
Waipatu	0.7	2.9	175	13	0	5	3.72	0.32
Brookvale No.1	185	14	505	35	49.7	5.9	6.95	0.56
Lyndhurst No.5	54.2	5	422	33	3.9	4.1	5.92	0.69
Eastbourne No.5	0.7	2.7	95.3	9	0	4.2	3.04	0.36

1. CFC and SF_6 partial pressures are expressed in parts per trillion (ppt) where 1ppt signifies a volumetric ratio of 1×10^{-12}.

2. The quoted measurement error is the combined statistical standard uncertainty from all processes contributing to the measurement uncertainty, expressed as one standard deviation (Eurachem/Citac 2000).

Table 3.4 Dissolved argon, nitrogen and methane concentrations and the derived variables recharge temperature and excess air.

Well name	Ar [mL(STP)/kg] [1]	± Ar [2]	N_2 [mL(STP)/kg] [1]	± N_2 [2]	CH_4 [µmol/kg]	± CH_4 [2]	Temp. [°C]	± Temp. [°C] [2]	Excess Air [mL(STP)/kg] [1]	± Excess Air [mL(STP)/kg] [2]
Waipatiki	0.446	0.008	19.26	0.62	284.8	20.4	9.3	2.1	5.7	1.5
Whirinaki	0.398	0.006	16.43	0.37	<0.1		12	1.7	3.1	1
Omahu	0.342	0.006	13.27	0.24	<0.1		16.1	1.7	0.5	0.7
Portsmouth Rd	0.38	0.007	14.71	0.13	<0.1		11.6	1.5	0.8	0.6
Wilson Rd	0.378	0.007	14.69	0.22	<0.1		12	1.6	0.9	0.7
Pakipaki	0.423	0.009	22.8	0.48	0.8	0.2	25.3	3.6	15.1	1.3
Parkhill	0.383	0.007	15.62	0.48	<0.1		13.2	2	2.5	1.2
Beach Rd, Haumoana	0.386	0.007	15.41	0.21	<0.1		12.1	1.6	1.9	0.7
Tucker Lane, Clive	0.387	0.007	15.68	0.15	<0.1		12.5	1.6	2.4	0.6
Ferry Rd, Clive	0.384	0.007	15.34	0.18	<0.1		12.3	1.6	1.8	0.7
Whakatu	0.379	0.008	14.27	0.17	<0.1		10.7	1.7	-0.1	0.8
Waipatu	0.376	0.006	14.95	0.16	<0.1		13	1.4	1.6	0.6
Brookvale No.1	0.369	0.006	14.55	0.13	<0.1		13.5	1.4	1.3	0.6
Lyndhurst No.5	0.384	0.007	14.65	0.14	<0.1		10.7	1.5	0.3	0.9
Eastbourne No.5	0.391	0.007	15.87	0.42	<0.1		12.2	1.9	2.5	1.1

1. Ar, N_2 and excess air concentrations are expressed in mL of gas at standard temperature and pressure (STP) per kg of water. Negative values indicate degassing has occurred.

2. The quoted measurement error is the combined statistical standard uncertainty from all processes contributing to the measurement uncertainty, expressed as one standard deviation (Eurachem/Citac 2000).

4.0 GROUNDWATER RESIDENCE TIME DETERMINATION

Calculated groundwater model ages (Table 4.1) are based on lumped-parameter flow models (Maloszewski and Zuber 1982). The model outputs are matched to the measured age tracer concentrations presented in Table 3.1 and Table 3.3, as well as previous data held by GNS Science available for the wells (Appendix 2). Models have been fitted to the data using the Microsoft Excel-based TracerLPM software from the United States Geological Survey (Jurgens et al., 2012). This software finds the best fitting model for the data by minimising the total error between model tracer output concentrations and measured concentrations.

Table 4.1 Groundwater mean residence time (MRT) and young fraction (i.e., water less than one year old).

Well name	Exponential mixed flow %	MRT [years]	Minimum residence time [years] [2]	Young Fraction <0.005%
Waipatiki	50	115	58	Yes
Whirinaki	72	10	2.8	Yes
Omahu	50	0.2	0.1	No
Portsmouth Road	19	2.1	1.7	Yes
Wilson Road	56	2.1	0.9	No
Pakipaki	71	149	43	Yes
Parkhill	BMM [1]	20.8	3.3	Yes
Beach Rd, Haumoana	53	73	34	Yes
Tucker Lane, Clive	BMM [1]	26.6	5.4	Yes
Ferry Road, Clive	BMM [1]	34.1	5.0	Yes
Whakatu	BMM [1]	29.9	2.0	Yes
Waipatu	BMM [1]	29.9	2.0	Yes
Brookvale No.1	BMM [1]	4.3	0.1	No
Lyndhurst No.5	50 BMM [1]	5 9.0	2.5 1.0	Yes No
Eastbourne No.5	BMM [1]	25.0	2.4	Yes

1. BMM denotes a binary mixing model.
2. Minimum residence time is the age of the youngest water present in the well outflow. Values in red indicate non-compliance with the DWSNZ:2005 residence time criterion.

The age tracer data from the seven Waipatiki, Whirinaki, Omahu, Portsmouth Road, Wilson Road, Pakipaki, and Beach Road wells can be matched to an exponential piston flow model (EPM) with parameters as given in Table 4.1

For the remaining eight wells, the currently available time series tracer data cannot be matched to a single EPM. Therefore, for these wells a binary mixing model (BMM) has been applied (Plummer et al., 2006; Jurgens et al., 2012). The BMM is a combination of two EPM models, each with a distinct MRT and residence time distribution (Figure 4.1). The parameters for each EPM, as well as the proportion of each EPM contributing to the BMM, are specific to each individual well. This type of residence time distribution could be expected for wells with multiple (or continuous) screens that intersect several discrete vertical layers of a heterogeneous aquifer, and is in keeping with the complex geology of the Heretaunga Plains aquifer system, for example the inter-fingering of the Tukituki fan gravels at various levels with Holocene fine-grained silts (see Appendix 4 for bore logs and Appendix 5 for geological cross-sections).

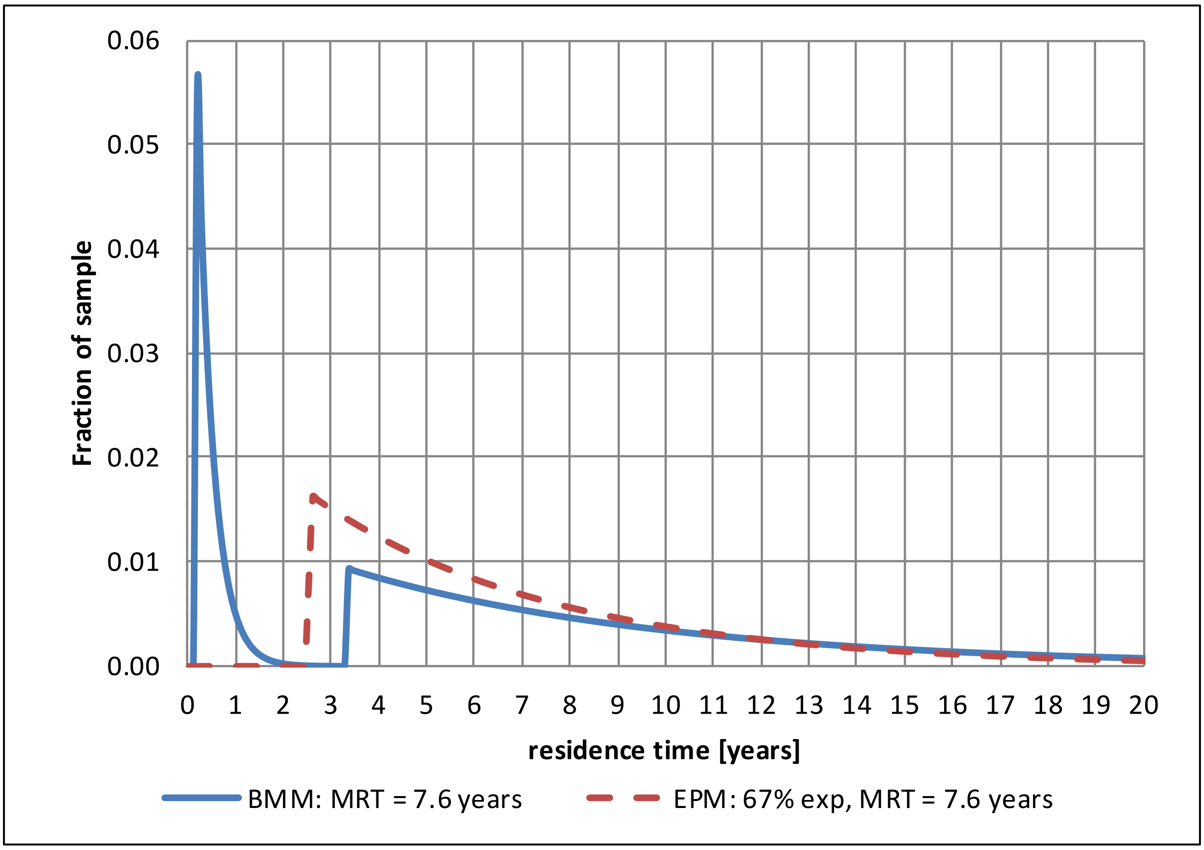


Figure 4.1 Residence time distribution for a binary mixing model (BMM). This BMM is a combination of two EPMs, both with 67% exponential mixing, one with MRT of 0.5 year, and one with MRT of 10 years. The resulting MRT for the BMM is 7.6 years. A single EPM with MRT of 7.6 years, also with 67% exponential mixing, is shown for comparison. The graph shows the fraction of the total flow at the sample point having a particular residence time per month.

Groundwater flow conditions represented by the BMM are more complex than for the EPM and may represent preferential flow paths along shallow aquifers, in addition to discharge from the main aquifer system. Such shallow flow paths in a multi-aquifer system have a potential to contribute young water in a larger fraction when compared to the continuous age distribution of a simple EPM, and therefore are more likely to result in a well not satisfying the residence time criterion (Section 4.5.2.1) of the DWSNZ:2005.

In theory the BMM could also be applied to a situation in which young surface water is entering a well due to poor well head protection and mixes with the older aquifer water. However, in practice the amount of water entering the well from this type of process is expected to be small, and unlikely to be detectable. In contrast, the BMMs used for this assessment have substantial contributions of the younger water component, which are between 15 and 50% of the total flow volume from the wells. Well head protection is assessed under a separate criterion of the DWSNZ:2005 (Section 4.5.2.2).

Eleven wells (Waipatiki, Whirinaki, Portsmouth Road, Pakipaki, Parkhill, Beach Road, Tucker Lane, Ferry Road, Whakatu, Waipatu and Eastbourne No.5) all draw groundwater with less than 0.005% of water younger than one year old and therefore satisfy the residence time criterion (Section 4.5.2.1) of the Drinking-water Standards for New Zealand: 2005 (Ministry of Health 2008) at the present time.

Three wells (Omahu, Wilson Road and Brookvale No.1) potentially draw groundwater with greater than 0.005% of water younger than one year old, and therefore do not satisfy the residence time criterion (Section 4.5.2.1) of the Drinking-water Standards: 2005 (Ministry of Health 2008) at the present time. These three wells which do not meet the residence time criterion all appear to be associated with the Holocene river fans of the Tukituki and Ngaruroro Rivers (see Appendix 5).

For the Lyndhurst No.5 well, there are two possible age solutions, one of which satisfies the residence time criterion and one which does not. It is not possible to exclude either solution with the data to date, and collection of additional data is recommended to verify one or the other solution (see Section 5.0).

The Portsmouth Road well draws groundwater with a minimum residence time of just over one year (Table 4.1). However, this well is also located on the Ngaruroro River fan, and given the complexity of the aquifer structure with potential for shallow flow paths at certain climatic conditions, it is recommended that this well should be tested quarterly for at least one year to cover all four seasons to ensure shallow flow contribution is unlikely under all climatic conditions.

4.1 DISCUSSION

The drinking water assessment utilises three age tracer techniques. All tracer techniques have ambiguities which are specific to each tracer. These include several alternative age solutions, tracer degradation and contamination (see Appendix 1). Thus to increase the robustness of the interpretation it is best to apply all three tracer techniques (tritium, CFCs and SF_6). However, recent studies have indicated that CFCs are not particularly conservative tracers when compared to tritium and SF_6 (Beyer et al., 2016). Recently a fourth tracer technique, Halon-1301, that is more robust than the CFC technique, has been developed within GNS Science’s Smart Aquifer Characterisation programme (Beyer et al., 2015; 2016). This tracer may have potential to replace the use of CFCs for future DWSNZ assessments.

Previous DWSNZ studies of HDC wells have been undertaken in 2001, 2007, 2011 and 2014 (Cameron and Morgenstern 2001; van der Raaij 2008; Trompetter et al., 2011; van der Raaij 2014). The first water age assessment of the Hastings District Council wells was undertaken in 2001, at which time only the tritium and CFC techniques were available. At this time the ambiguity around the interpretation of the results was much higher than now: tritium results could be fitted to several age solutions; the limitations of CFC tracers were not well understood and CFC results were not corrected for recharge temperature and excess air by dissolved gas data (Ar, N_2), which would increase the reliability of the age interpretations based on these data. The SF_6 age tracer technique was not available until 2003.

All three water age tracer techniques are significantly more robust now than they were at the times of previous assessments due to improved calibration of CFCs and SF_6 measurements. Sensitivity of the SF_6 analytical procedure has increased due to higher atmospheric concentrations (Appendix 1), and due to the ongoing radioactive decay of the “bomb” tritium, the tritium data no longer have several age possibilities. High tritium concentrations now directly indicate young water - in 2016 all non-compliant wells have tritium concentrations close to the concentrations observed in rainfall (Figure 4.2). Ten years ago groundwater with a mean residence time between 20 and 60 years could also have had tritium concentrations close to those of current rain, due to the presence of bomb-tritium.

The 2016 HDC age tracer results show that the tritium and SF_6 methods are now so robust that more complex groundwater age distributions can be indicated, and binary mixing models can be calibrated.

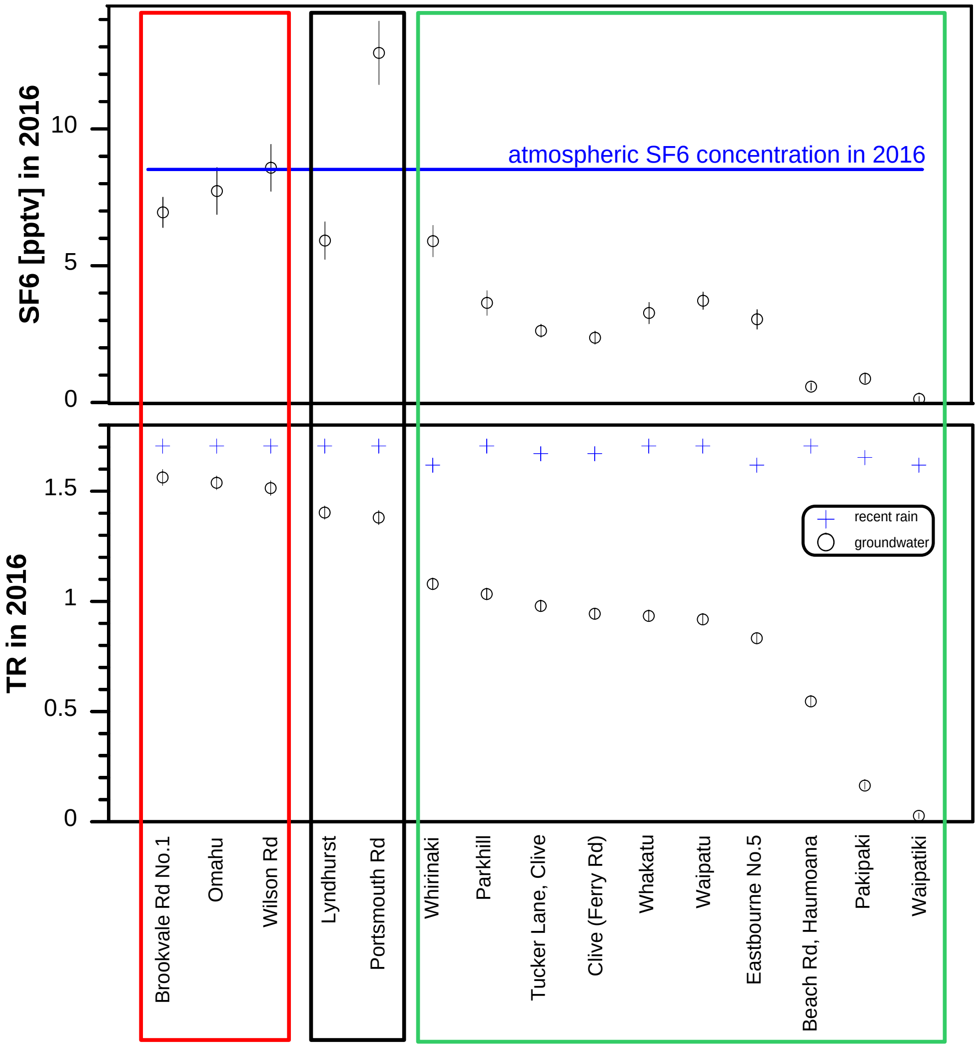


Figure 4.2 Tritium and SF_6 concentrations measured in 2016 in the drinking water wells, in relation to the concentrations in rain. For the tritium rain input, the tritium record from Kaitoke Regional Park (Tararuas) was scaled by a factor of between 0.93 and 0.98, depending on the source of the groundwater recharge. Refer to App.1 for further information on the tracer input concentrations. The raw age tracer data clearly indicate the presence of very young water for the wells Brookvale No.1, Omahu and Wilson Rd, with age tracer concentrations close to those of recent rain. The tritium concentrations are only 8-11% below those of rain, and SF_6 concentrations overlap those of recent rain (red box). Wells Lyndhurst and Portsmouth Rd. have intermediate age tracer concentrations (black box), with tritium concentrations 18-19% below those of rain. SF_6 at Portsmouth Rd. is elevated, likely due to local sources. The age tracer data for wells Whirinaki, Parkhill, Tucker Lane, Ferry Rd, Whakatu, Waipatu, Eastborne No.5, Haumoana, Pakipaki, and Waipatiki indicate the presence of older water with tritium concentrations 33-98% below those of rain, and SF_6 concentrations 30-98% below those of recent rain (green box).

In addition to the improvement in the precision of the tracer age interpretations and scientific understanding of the behaviour of the CFCs and SF_6 in the groundwater systems as outlined above, collection of long term data for the individual wells now allows for revision of the residence time model. This may lead to minor refinement of the model parameters, whereby the MRT may not change significantly, or to rejection of the previous model, in which case both the modelled residence time distribution and MRT may change significantly. The residence time model has not changed significantly for the Waipatiki, Omahu, Pakipaki and Beach Road wells. For the other wells, the recently acquired data has led to revision of the model, in some cases requiring a change from use of the EPM to a BMM.

Significant changes observed in tracer data not predicted by a previous model may be an indicator of changing flow conditions within the aquifer system, such as those induced by ongoing and/or increased extraction, through aquifer leakage, or through climatic and/or seasonal influences. Changes in flow conditions could result in groundwater with different residence time distributions reaching the well at different times. It is not currently possible to determine whether changes in aquifer flow regime are responsible for the observed changes in tracer concentrations. Tracer data are available on average only with time resolution of 5 years or more, but higher resolution data (at three monthly to two yearly intervals) would be required to detect any such changes in flow conditions. In addition, statistical analysis of major ion chemistry data from this same time period, if available, could assist with determination of whether any such changes in flow regime are occurring at individual wells.

The following section discusses three HDC wells as examples to illustrate the concepts described above.

4.2 Example Cases

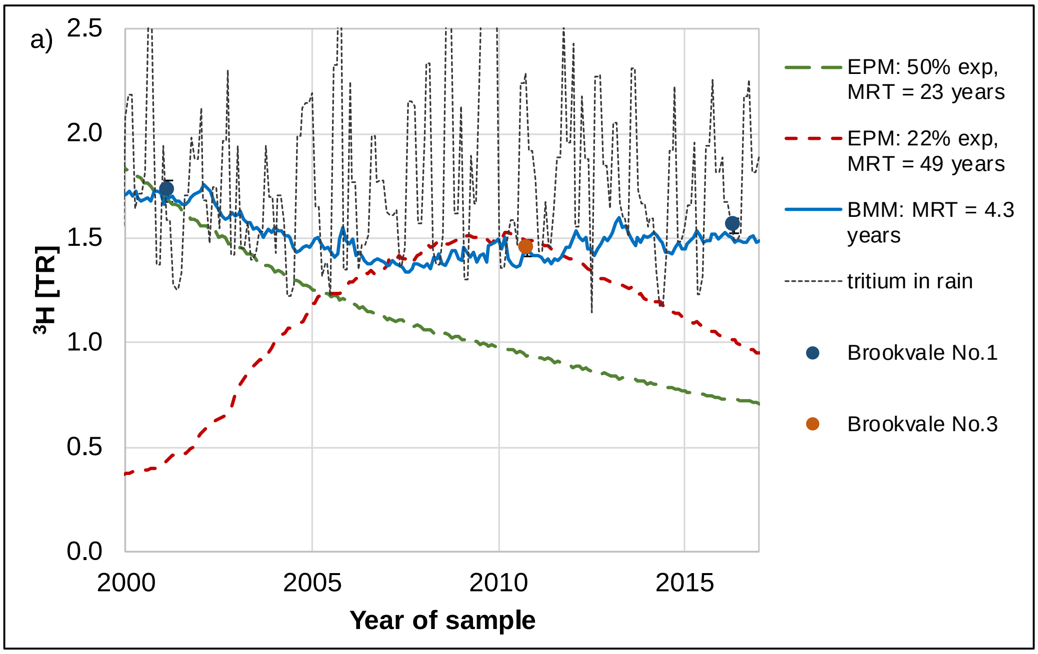
4.2.1 Brookvale

The initial assessment in 2001 was performed for Brookvale No.1 well, at which time the well was assessed as having MRT of c. 20 years, based on complementary interpretation of tritium and CFCs (Cameron and Morgenstern 2001). Tritium alone indicated two possible age solutions, one for young water with MRT of 4 years, and one for older water with MRT of 23 years. The 4 year MRT model solution does not satisfy the DWSNZ residence time criterion, whereas the 23 year MRT model solution does satisfy this criterion. The initial assessment in 2001 ruled out the young age solution due to disagreement with the CFC results, and hence it was concluded that the water was older than 12 years.

In 2011 the assessment was carried out on Brookvale No.3 well (Trompetter et al., 2011). At this time the tritium data were still ambiguous, indicating MRT of either 4 years or 49 years. The old age solution, caused by the bomb-tritium, was now considerably older as more time had elapsed since the input of the bomb tritium from the atmospheric thermonuclear tests in the early 1960s. The young age solution was again ruled out due to the disagreement with the CFC and SF_6 tracer data. In particular, the SF_6 data indicated a minimum MRT of at least 12 years. The Brookvale No.3 well is screened slightly deeper than the Brookvale No.1 well (from 15.5 m to 26.5 m, compared with 11.4 m to 22 m for Brookvale No.1).

With the availability of the 2016 data for Brookvale No.1, the older age solution now clearly needs to be ruled out: the green and red curves in Figure 4.3 do not match the 2016 data. However, the SF_6 data are also not consistent with the young age as indicated by tritium (blue curve). It is now apparent that the wells draw water with a more complex age distribution, interpreted to be caused by the geological complexity, i.e., the inter-fingering of the Tukituki fan gravels at various levels with the Holocene fine-grained silts. Note that Brookvale 1 and 3 are spatially separated and therefore likely to have different groundwater age tracer time series data and MRT.

Due to the complexity of the age distribution of the Brookvale well waters, a Binary Mixing Model (BMM) was developed to include shallower short flow paths. The best-fitting model was a BMM with MRT of 4.3 years (green curve Figure 4.3). This model fits both the old tritium data as well as the current tritium and SF_6 data. The interpreted age of the youngest water present in the well outflow (i.e., the minimum residence time of groundwater from this well) is 0.1 years, with a substantial fraction of water less than one year old present (Figure 4.4 and Figure 4.5). The Brookvale No.1 well therefore does not satisfy the residence time criterion (Section 4.5.2.1) of the DWSNZ:2005 (Ministry of Health 2008).



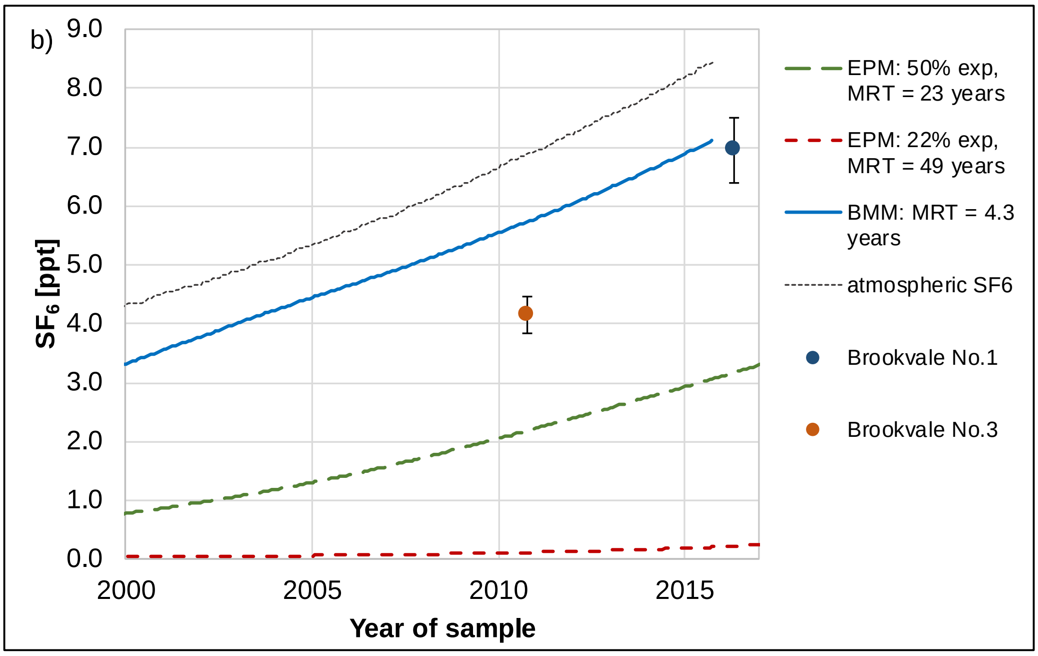


Figure 4.3 Time-series data ((a) tritium, (b) SF_6) for the Brookvale wells, with fitted lumped parameter models. The model output lines show the changes in tracer concentrations that would be expected in groundwater from these wells over time, given the stated model parameters (fraction of exponential mixed flow in %, MRT in years). The green curve is a fitted EPM age model presented in the 2001 report, the red curve is the EPM age model presented in the 2011 report, and the blue curve is the BMM from the current interpretation. (a) The tritium input from rain is shown for comparison and is monthly tritium in rainfall at Kaitoke, Wellington, scaled to the Hawke's Bay. (b) The SF_6 atmospheric record for the Southern Hemisphere is rain is shown for comparison.

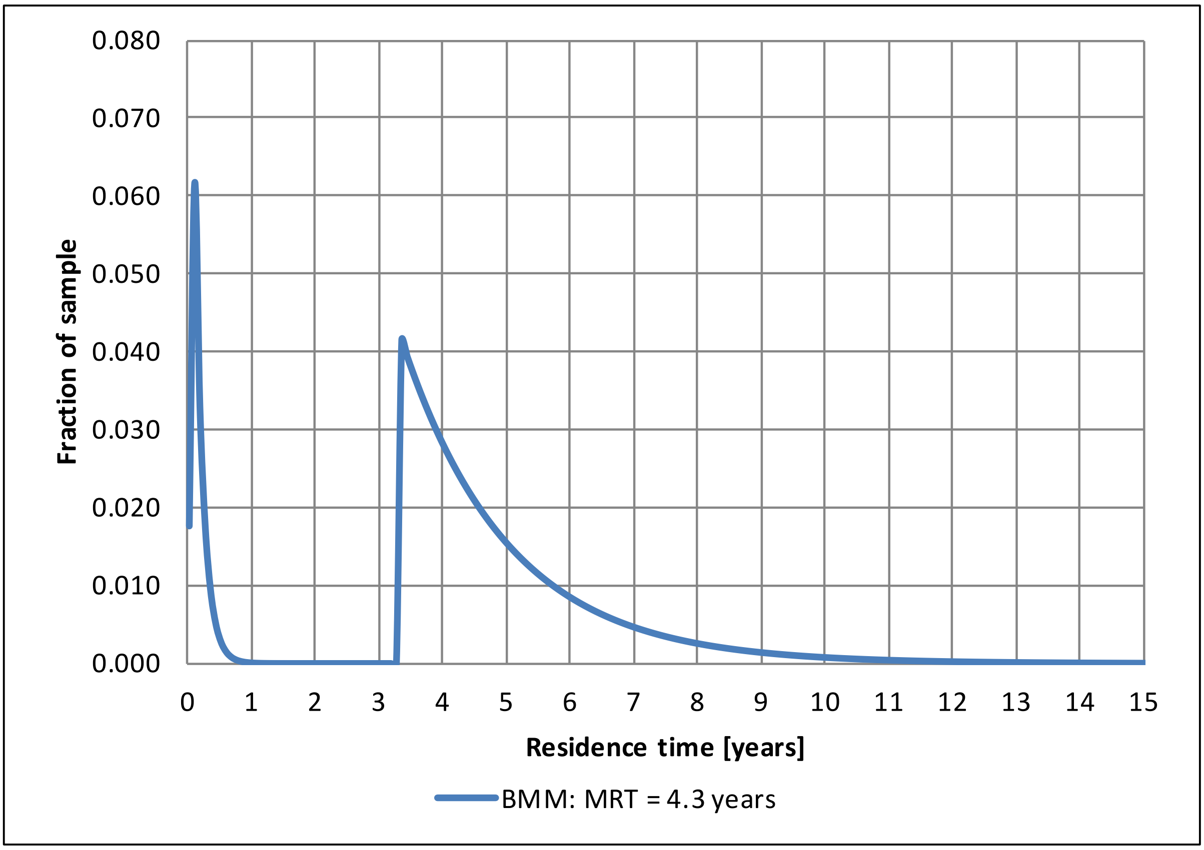


Figure 4.4 Residence time distribution of the binary mixing model fitted to the age tracer data of the Brookvale No.1 well.

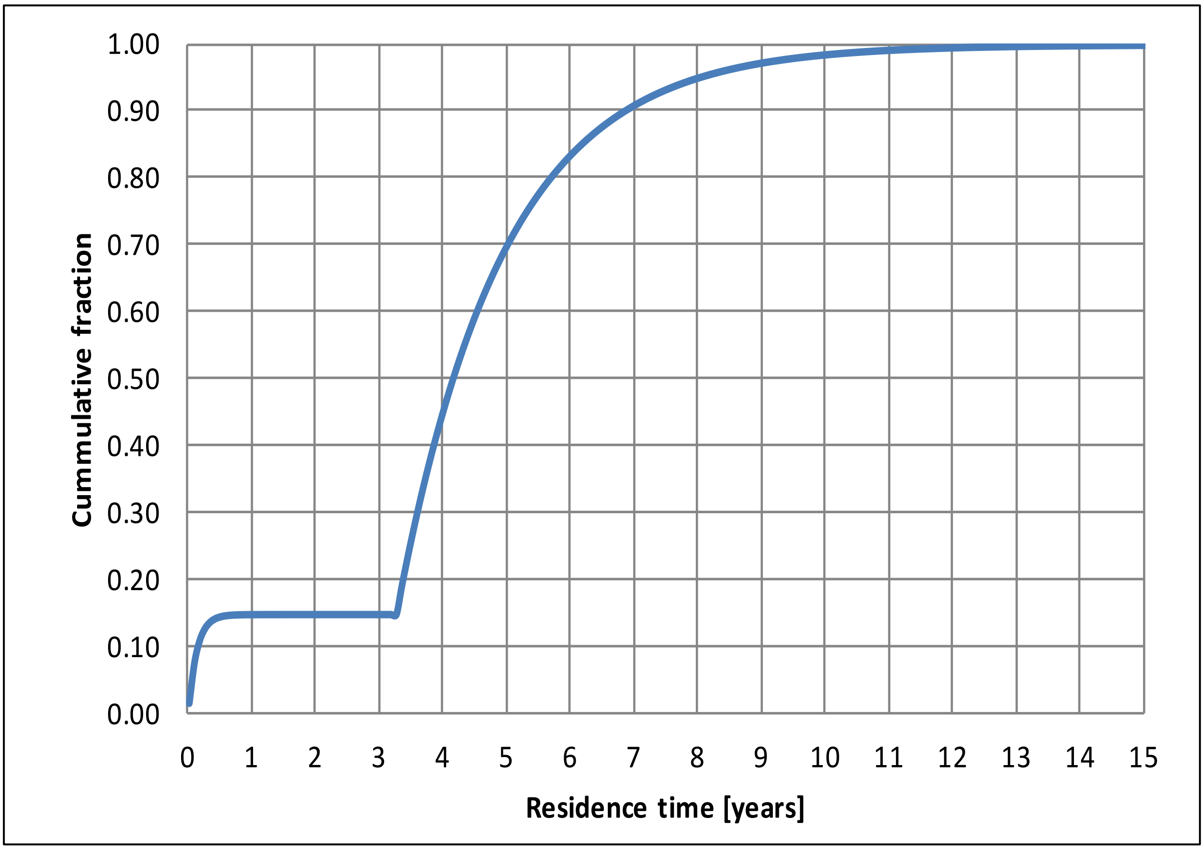


Figure 4.5 Cumulative residence time distribution of the binary mixing model fitted to the age tracer data of the Brookvale No.1 well.

4.2.2 Lyndhurst

The initial assessment in 2001 was performed for Lyndhurst No.3 well (Figure 4.6; Cameron and Morgenstern 2001). Subsequently additional tritium data were collected for this well in 2004. In 2001, Lyndhurst No.3 was assessed as having MRT of 43 years, based on agreement between tritium and CFCs. Tritium alone indicated two possible age solutions of either 27 years or 45 years. Measurements in 2004 confirmed the MRT of 43 years for this well (red curve in Figure 4.7).

Figure 4.6 Aerial view of the Lyndhurst wellfield.

The current assessment, as well as that performed in 2011, was performed on Lyndhurst No.5 well (Trompetter et al., 2011). In 2011, this well was assessed as having MRT of 41.5 years, in keeping with the MRT of the previously assessed Lyndhurst No.3 well. This assessment does not fit the 2016 tracer measurements (Figure 4.7). There are two alternative models that fit the data for the Lyndhurst No.5 well. The first is an EPM with 50% exponential mixed flow and MRT of 5 years. The second is a BMM with MRT of 9 years. Neither of these models fit the data from the Lyndhurst No.3 well, indicating either the groundwater flow across this well field is not spatially uniform or that the flow patterns of the well field have changed considerably since 2004.

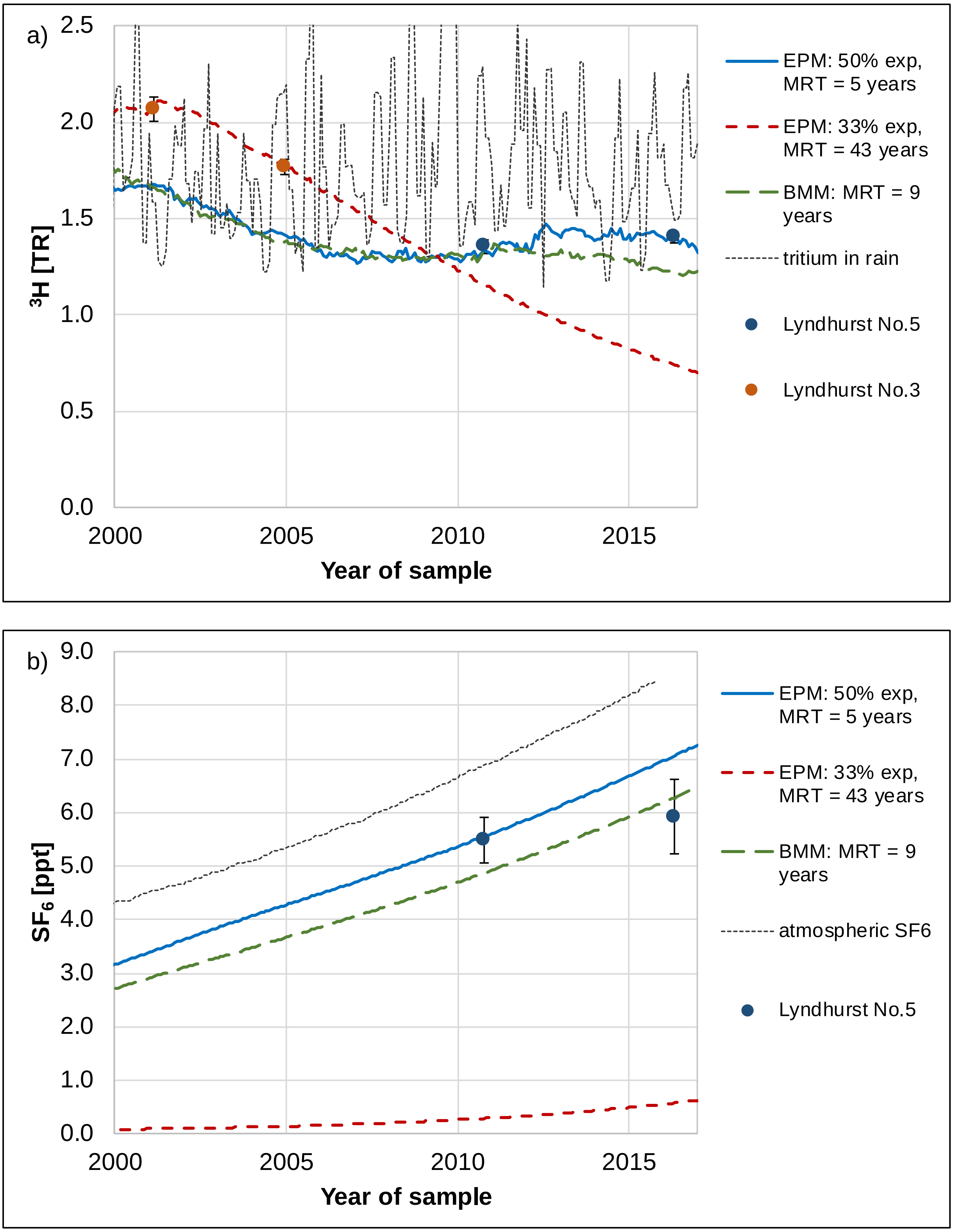


Figure 4.7 Time-series data ((a) tritium, (b) SF_6) for the Lyndhurst wells, with fitted lumped parameter models. The model output lines show the changes in tracer concentrations that would be expected in groundwater from these wells over time, given the stated model parameters (fraction of exponential mixed flow in %, MRT in years). The red curve is a fitted EPM age model for the 2001 and 2004 data; the blue and green curves are the fitted EPM and the BMM from the current interpretation respectively. (a) The tritium input from rain is shown for comparison and is monthly tritium in rainfall at Kaitoke, Wellington, scaled to the Hawke's Bay. (b) The SF_6 atmospheric record for the Southern Hemisphere rain is shown for comparison.

With respect to the DWSNZ:2005, the percentage of water less than one year old present in the groundwater from the Lyndhurst No.5 well depends on which of the two alternative models is used (Figure 4.8 and Figure 4.9). Under the EPM, this percentage is effectively zero and the Lyndhurst No.5 would satisfy the residence time criterion (Section 4.5.2.1) of the DWSNZ:2005 (Ministry of Health 2008). However, under the BMM this well would not satisfy the residence time criterion. It is not possible to exclude either model with the data to date, and collection of additional data is recommended (see Section 5.0).

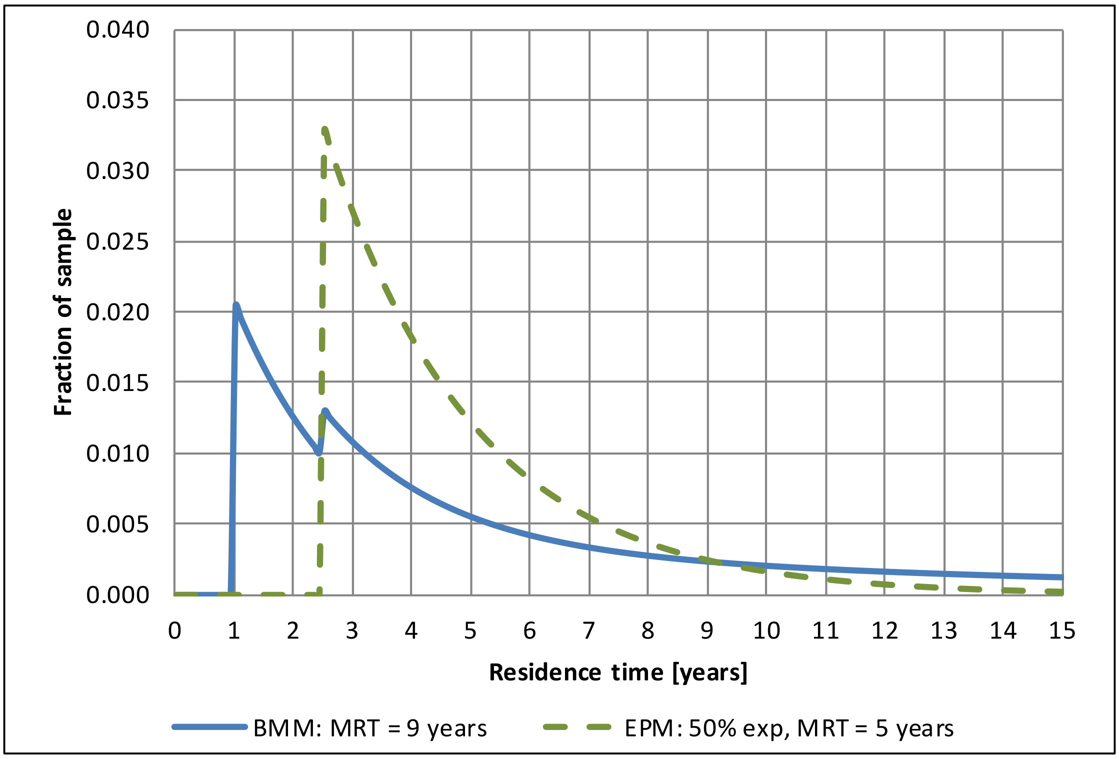


Figure 4.8 Residence time distribution of the BMM and alternative EPM for the Lyndhurst No.5 well.

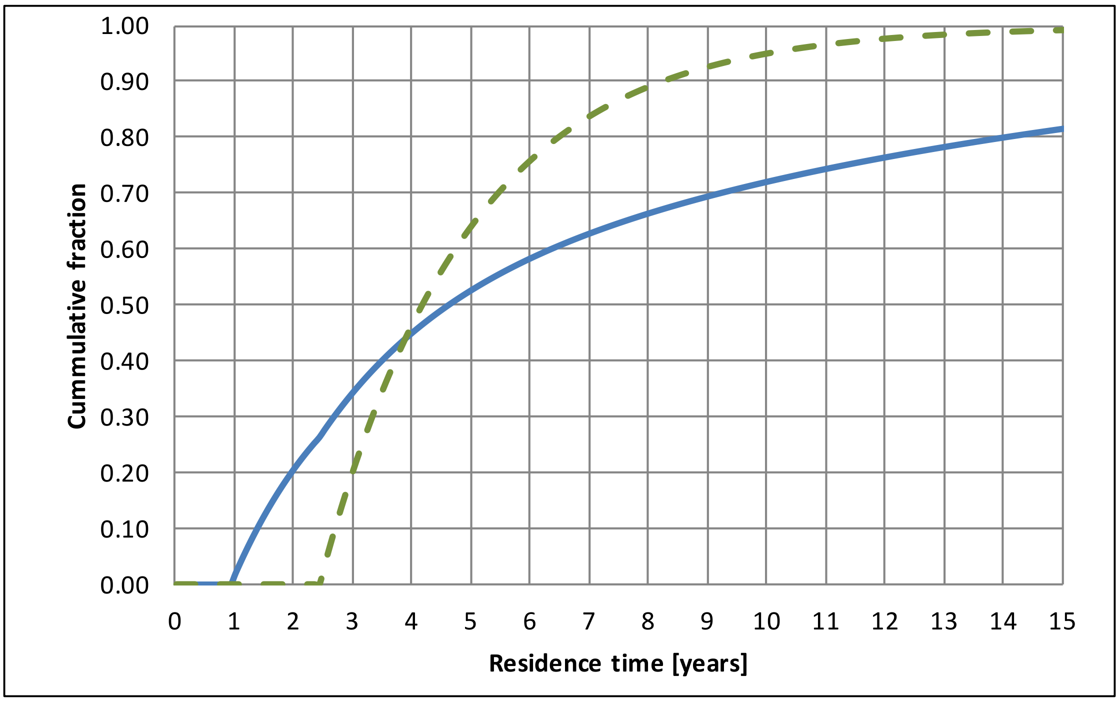


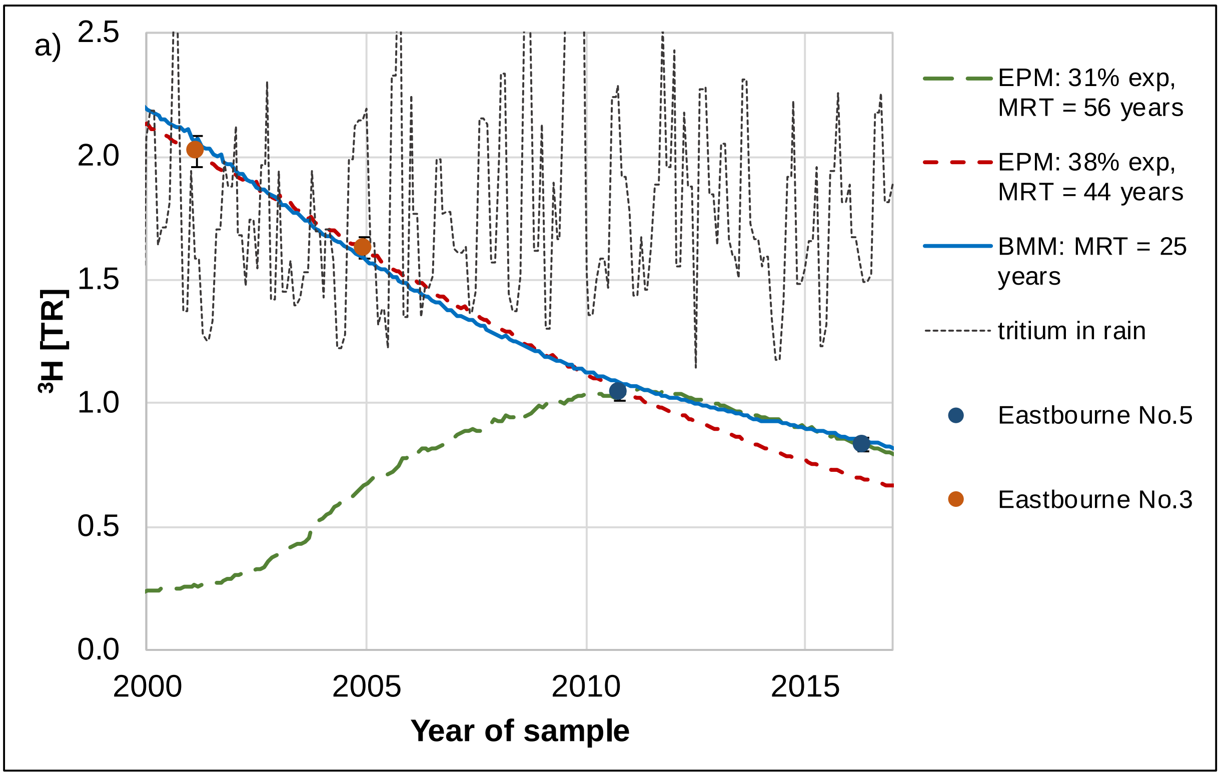
Figure 4.9 Cumulative residence time distribution of the BMM and alternative EPM for the Lyndhurst No.5 well.

4.2.3 Eastbourne

The initial assessment in 2001 was performed for Eastbourne No.3 well (Cameron and Morgenstern 2001). Subsequently, additional tritium data were collected for this well in 2004. In 2001 Eastbourne No.3 was assessed as having MRT of 47 years, based on agreement between tritium and CFCs. Tritium alone indicated two possible age solutions of either 26 years or 45 years. Measurements in 2004 resulted in an interpreted MRT of 43.5 years for this well (red curve in Figure 4.10).

The current assessment, as well as that performed in 2011, was performed on Eastbourne No.5 well. In 2011 this well was assessed as having MRT of 43 years (Trompetter et al., 2011). However, this age interpretation is not consistent with the 2016 tritium measurement (Figure 4.10). The best-fit EPM for the current and 2011 tritium data is an MRT of 57 years at 31 % exponential mixed flow (green curves in Figure 4.10). However, this model does not fit the gas tracer data for this well. The overall best-fit model for both tritium and gas-tracer data from the Eastbourne No.5 well is a BMM with MRT of 25 years. This model also fits the data from the Eastbourne No.3 well, indicating groundwater flow at this well field may be reasonably spatially uniform and consistent over time.

All of the above-mentioned models for this well field result in the wells satisfying the residence time criterion (Section 4.5.2.1) of the DWSNZ:2005 (Ministry of Health 2008), both for Eastbourne No.3 well and Eastbourne No.5 well (Figure 4.11 and Figure 4.12).



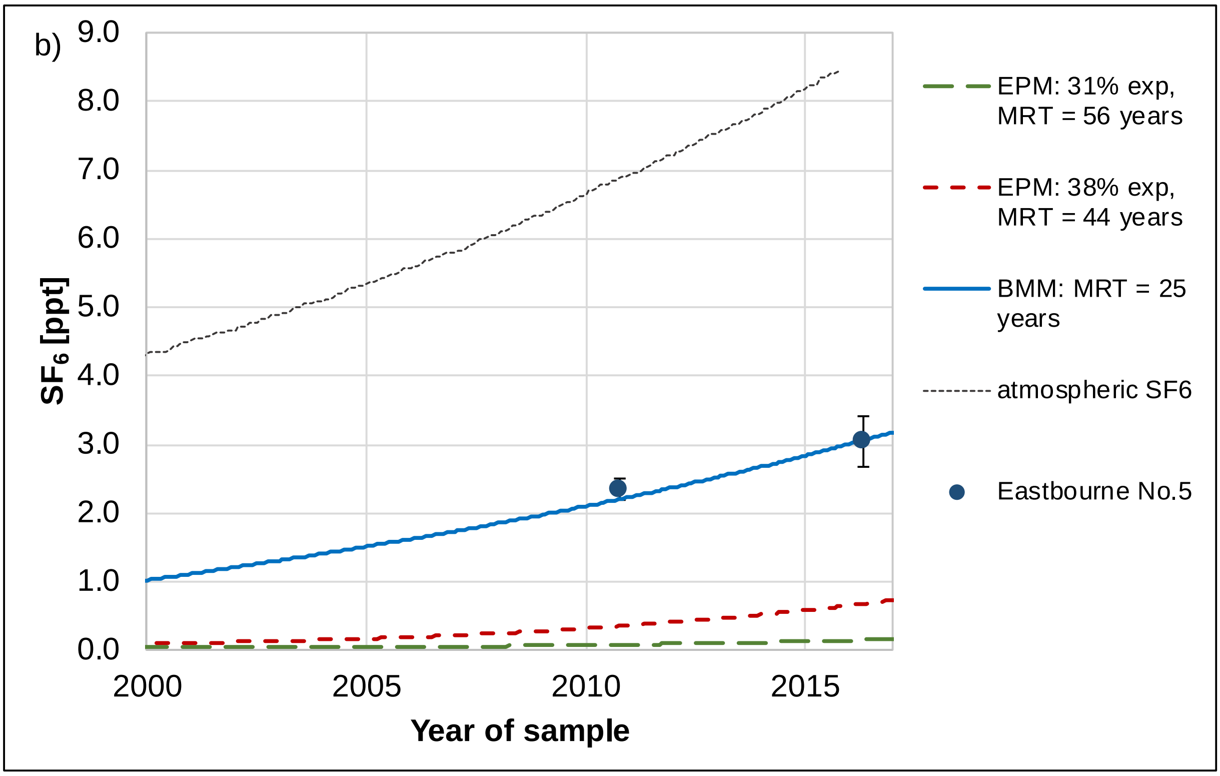


Figure 4.10 Time-series data ((a) tritium, (b) SF_6) for the Eastbourne wells, with fitted lumped parameter models. The model output lines show the changes in tracer concentrations that would be expected in groundwater from these wells over time, given the stated model parameters (fraction of exponential mixed flow in %, MRT in years). The red curve is a fitted EPM age model for the 2001 and 2004 data; the green curve is a fitted EPM age model for the 2010 and 2016 data; and the blue curve is the BMM from the current interpretation. (a) The tritium input from rain is shown for comparison and is monthly tritium in rainfall at Kaitoke, Wellington, scaled to the Hawke's Bay. (b) The SF_6 atmospheric record for the Southern Hemisphere rain is shown for comparison.

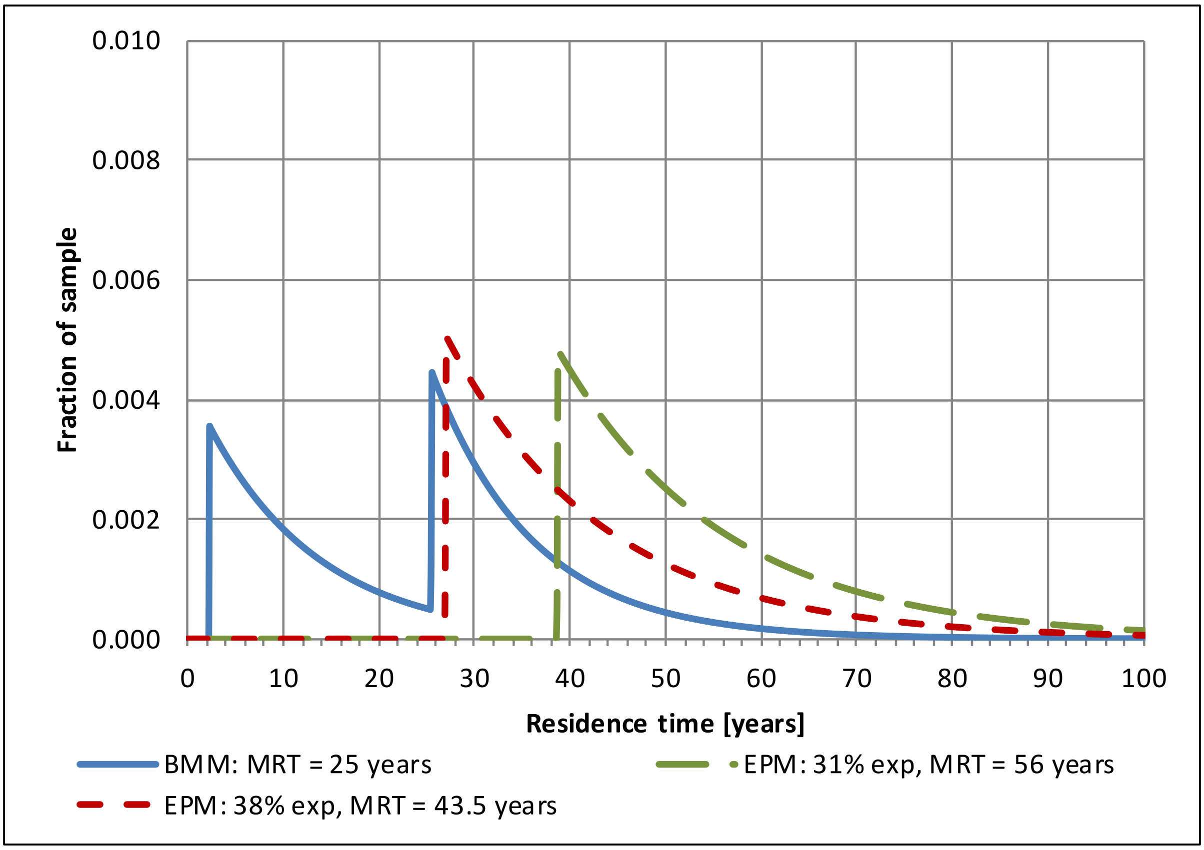


Figure 4.11 Residence time distributions for lumped parameter models fitting the Eastbourne well data.

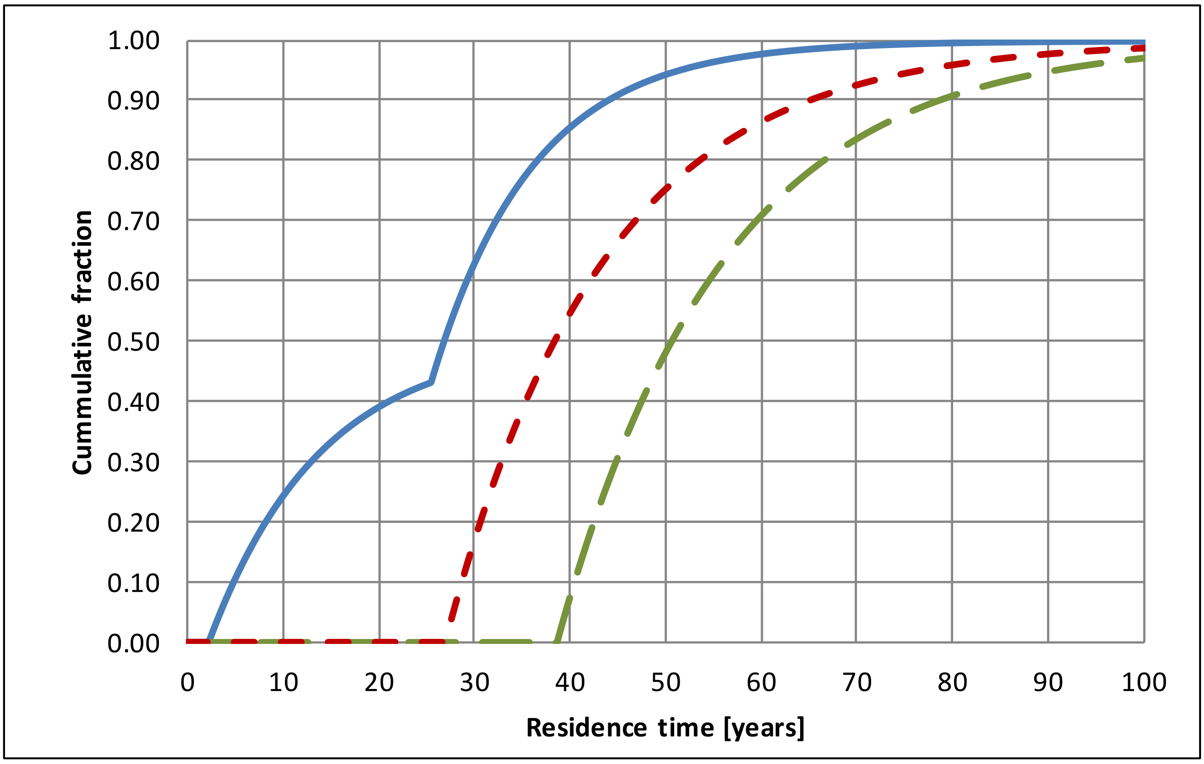


Figure 4.12 Cumulative residence time distributions for lumped parameter models fitting the Eastbourne well data.

5.0 SUMMARY AND RECOMMENDATIONS

Modelled groundwater ages indicate that eleven wells (Waipatiki, Whirinaki, Portsmouth, Pakipaki, Parkhill, Beach Road, Tucker Lane, Ferry Road, Whakatu, Waipatu and Eastbourne No.5) draw relatively old groundwater with modelled mean residence times ranging from 10 years to more than 115 years. These eleven wells are all interpreted to draw groundwater with less than 0.005% of water under one year old, and therefore satisfy the residence time criterion (Section 4.5.2.1) of the Drinking-water Standards for New Zealand: 2005 (Ministry of Health 2008) at the present time.

Age models for three wells at Omahu, Wilson Road and Brookvale No.1 indicate groundwater with significant fractions of water younger than one year old. These wells are therefore interpreted to not satisfy the residence time criterion (Section 4.5.2.1) of the Drinking-water Standards for New Zealand: 2005 (Ministry of Health, 2008) at the present time.

For the Lyndhurst No.5 well, there are two separate age models that are consistent with the available data, one of which satisfies the residence time criterion and one of which does not. It is not possible to exclude either age model with the data to date, and collection of additional data is recommended. Under the BMM model, the age distribution at the Lyndhurst well is interpreted to be close to the criterion threshold, and collection of additional data may enable exclusion of a young water component through improved parameter estimation. If this can be demonstrated, a future refinement of the age interpretation for this well may indicate satisfaction of the residence time criterion.

While the water in the Portsmouth Rd. well has a minimum residence time of just over one year, given the complexity of the aquifer structure with potential for shallow flow paths at certain climatic conditions, it is recommended that this well should be tested quarterly for at least one year. This sampling over all four seasons would allow assessment of the shallow flow contribution to this well under a range of climatic conditions.

The additional data required for the Lyndhurst No.5 well and the Portsmouth Rd. well would include two-monthly or three-monthly sampling of the active wells for all age tracers, plus additional samples collected for a full suite of chemistry parameters. Samples should be collected for at least one year to capture any possible seasonal effects.

Significant changes observed in the tracer data, not predicted by previous models for some wells, may be an indicator of changing flow conditions within the aquifer system. This could result in groundwater with different residence time distributions reaching the well at different times. It is not currently possible to determine whether changes in aquifer flow regime are responsible for the observed changes in tracer data. Higher resolution tracer data (at three monthly to two yearly intervals) would be required to detect such changes in flow conditions. In addition, statistical analysis of major ion chemistry data from this same time period, if available, could assist identification of changes in flow regime.

In this light, it may be desirable to undertake additional samples for all of the Hastings District wells at a higher frequency than required by the DWSNZ:2005. This should be at intervals of at most two years, to enable further refinement of model parameters as well as identification of possible temporal changes in the age distributions. For wells with minimum residence times of the order of only a few years, more frequent sampling (three monthly intervals) may be useful to identify possible seasonal changes in groundwater age distributions.

While the flow models used for this assessment are primarily based on the tracer data, it is important to hold background information on the wells so that models can be assessed and/or rejected. For future assessments we recommend that information such as basic hydrogeologic information including artesian status, well construction, geologic model if available, a summary of well performance (e.g., problems, repairs, screen changes, contamination, increased pumping) and chemistry monitoring data be supplied to GNS Science at the time the sample is submitted. Ideally GNS Science should also be involved in the sampling planning process to optimise the data set.

6.0 REFERENCES

Beyer, M.; van der Raaij, R.; Morgenstern,U.; Jackson, B. 2015. Assessment of Halon-1301 as a groundwater age tracer, Hydrol. Earth Syst. Sci., 19, 2775-2789, doi:10.5194/hess-19-2775-2015, 2015.

Beyer, M.; Morgenstern, U.; van der Raaij, R.; Martindale, H. 2016. Halon-1301 - A new groundwater age tracer – further evidence of its performance as an age tracer in New Zealand Groundwater (in prep.).

Busenberg, E.; Plummer, L.N. 1992. Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age dating tools: the alluvium and terrace system of Central Oklahoma. *Water Resources Research.* 28 (9), 2257-2283.

Cameron, S.G.; Morgenstern, U. 2001. Groundwater security at Hastings District Council municipal supply wells based on CFC and tritium dating and on hydrogeological data. Institute of Geological and Nuclear Sciences client report 2001/73. 22 p., appendices.

Daughney, C.J.; Jones, A.; Baker, T.; Hanson, C.; Davidson, P.; Zemansky, G.M.; Reeves, R.R.; Thompson, M. 2006. A national protocol for state of the environment groundwater sampling in New Zealand. Wellington, NZ: Ministry for the Environment. GNS Science miscellaneous series 5; ME / Ministry for the Environment 781. 54 p.

Daughney, C.J.; Baker, T.; Jones, A.; Hanson, C.; Davidson, P.; Thompson, M.; Reeves, R.R.; Zemansky, G.M. 2007. Comparison of sampling methods for state of the environment monitoring in New Zealand. *Journal of Hydrology NZ*. 46, 19-31.

Daughney, C.J.; Morgenstern, U.; van der Raaij, R.; Reeves, R.R. 2010. Discriminant analysis for estimation of groundwater age from hydrochemistry and well construction: application to New Zealand aquifers. *Hydrogeology J.* 18, 417-428.

Eurachem/CITAC 2000. Quantifying uncertainty in analytical measurement. EURACHEM / CITAC Guide CG4, Second edition QUAM:2000.1. Available at:

http://www.measurementuncertainty.org/mu/QUAM2000-1.pdf

Jurgens, B.C.; Böhlke, J.K.; Eberts, S.M. 2012. TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data: U.S. Geological Survey Techniques and Methods. Report 4-F3, 60 p.

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

Ministry of Health 2008. Drinking-water Standards for New Zealand 2005 (Revised 2008). Ministry of Health, Wellington, New Zealand. 163 p. Available online at: http://www.moh.govt.nz.

Morgenstern, U. ; Daughney, C.J. 2012. Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification – The National Groundwater Monitoring Programme of New Zealand. *Journal of Hydrology* (2012) http://dx.doi.org/10.1016/j.jhydrol.2012.06.010

Morgenstern, U.; Taylor, C.B. 2009. Ultra low-level tritium measurement using electrolytic enrichment and LSC. Isotopes in Environmental and Health Studies. 45(2), 96-117.

Plummer. L.N.; Busenberg E.; Han, L.F. 2006. CFCs in binary mixtures of young and old Groundwater. In: *Use of chlorofluorocarbons in hydrology: a guidebook.* International Atomic Energy Agency, Vienna.Ch. 54. 59-72.

Trompetter, V.; van der Raaij, R.W.; Morgenstern, U. 2011. Mean residence time determination for Hastings District Council municipal water supply wells. GNS Science consultancy report 2011/75. 15 p.

van der Raaij, R.W. 2003. Age dating of New Zealand groundwaters using sulphur hexafluoride. MSc thesis, School of Earth Sciences, Victoria University of Wellington.122 p.

van der Raaij, R.W. 2008. Groundwater residence time determination of Hastings District Council groundwater supplies. GNS Science consultancy report 2007/390LR. 5 p.

van der Raaij, R.W. 2014. Groundwater residence time determination for the Parkhill Road well. GNS Science consultancy report 2014/296LR. 6 p.

APPENDICES

APPENDIX 1: ASSESSMENT OF GROUNDWATER RESIDENCE TIME USING TRITIUM, CFCS AND SF6

A1.1 TRACER CHARACTERISITICS

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 A1.1). 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 $^3H^1HO$. These water molecules follow the same pathways as water molecules not containing tritium (^1H_2O) 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 exiting 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:

$$C(t) = C_o \exp(-\lambda t') \qquad (1)$$

where $C(t)$ = tritium ratio in groundwater after time t
C_o = initial tritium ratio in rainwater
λ= 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 A1.1). 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_6 (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).

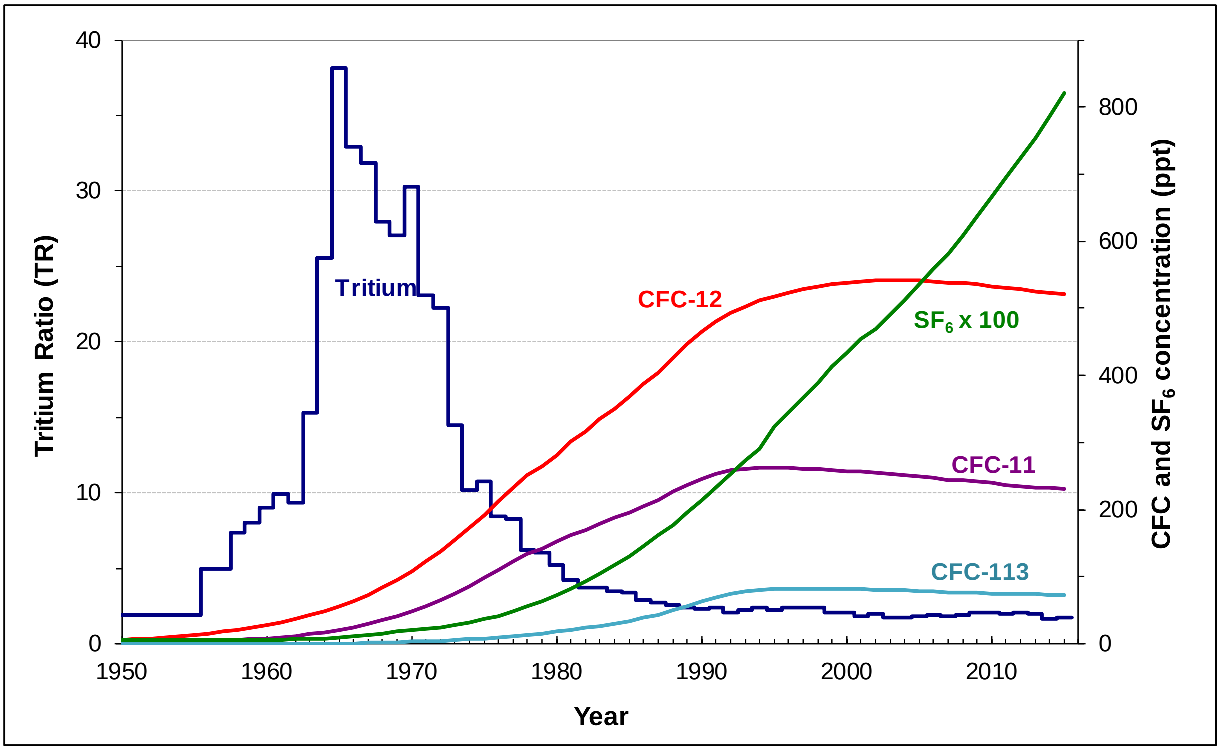


Figure A 1.1 Tracer input curves. The tritium concentrations are from rainfall at Kaitoke, New Zealand, and have been measured monthly since the 1960s. CFC and SF_6 concentrations are for southern hemispheric air (IAEA 2006). Annual values are means of monthly samples running from July to June each year, expressed in tritium ratios (TR) where 1TR = $^3H/^1H$ ratio of $1{:}1\times10^{-18}$. CFC and SF_6 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 SF6

Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) 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 by dissolved CFC and SF_6 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_6 is mainly anthropogenic in origin. However, a small amount of SF_6 is also produced in certain volcanic minerals and fluids.

CFCs and SF_6 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 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 ppt for CFC-11 (Figure A1.1). 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_6 atmospheric concentrations have risen steadily since the 1970s to the present level of around 8.5 ppt.

The CFC or SF_6 ‘recharge age’ relates to the time elapsed since of 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_6 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.

Recharge temperature

The solubility of CFCs and SF_6 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.

Thickness of the unsaturated zone

CFC and SF_6 recharge ages relate to the time these tracers are isolated from unsaturated zone air and enter the groundwater zone. Therefore CFC and SF_6 concentrations in groundwater will be affected by gas transport processes in the unsaturated zone air. Cook and Solomon (1995) found that for unsaturated zones less than ten metres in thickness CFC derived recharge ages may be overestimated by up to few years due to a diffusive time-lag. In unsaturated zones less than five metres thick, the over-estimation is negligible. For unsaturated zones around 30 metres thick, this time lag can be considerable. The effect on SF_6 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 bore, and are generally in the order SF_6 < 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. SF_6 is much less susceptible to contamination.

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^{-1} 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_6 appears unaffected by these processes (Wilson and Mackay 1996; Busenberg and Plummer 2000).

Excess air

Groundwaters often contain “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_6 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_6 is much greater and corrections need to be applied when interpreting SF_6 data.

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 complementary to the more robust tracer tritium and help resolve ambiguity in age interpretation.

A1.2 INTERPRETATION OF GROUNDWATER AGES USING LUMPED PARAMETER FLOW MODELS

The Drinking-water Standards for New Zealand: 2005 (DWSNZ:2005) states that bore water is considered secure when it can be demonstrated that contamination by pathogenic organisms is unlikely because the bore water is:

- not directly affected by surface or climate influences, as demonstrated by compliance with bore water security criteria 1 (section 4.5.2.1) and 3 (section 4.5.2.3), and
- abstracted from a bore head that provides satisfactory protection, bore water security criterion 2 (section 4.5.2.2).

  (Ministry of Health 2008).

Establishing how long water has been underground (i.e., the residence time) using tritium, CFCs and SF_6 is one method of assessing security criterion 1 (section 4.5.2.1). The DWSNZ specifies that the fraction of groundwater with a residence time of less than one year must be less than 0.005 percent of the water present in the aquifer (Ministry of Health 2008). To determine this fraction, the distribution of groundwater residence times must be determined. This distribution can be described using lumped-parameter mixing models (Maloszewski and Zuber 1982).

Groundwater extracted from a bore 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 A1.2). Groundwater age-dating therefore yields the mean age of water from all converging flow lines. The mixing of different flow lines occurs at the sampling point and the extent to which this occurs is specific to the bore. It depends on several factors including bore construction, screen length, bore depth and pumping rates; and also the hydrogeologic attributes of the aquifer around the bore (which affect the variety of possible flow paths that may be intersected by the bore).

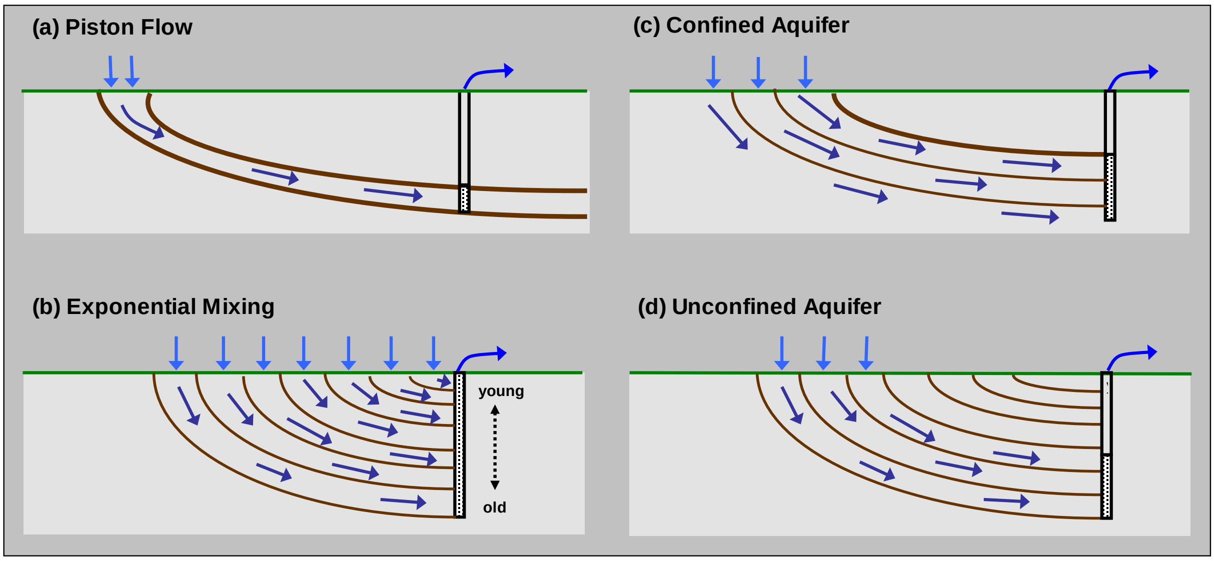


Figure A 1.2 Examples of conceptual groundwater flow situations which can be described by lumped parameter mixing models (Maloszewski and Zuber 1982). a) The piston flow model is a reasonable approximation for aquifers in which the recharge zone is narrow with respect to the overall distance from recharge 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

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.:

$$t_w = V_m / Q \qquad (3)$$

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

$$t_t = \int_0^\infty t' C_I(t')\mathrm{d}t' \,/ \int_0^\infty C_I(t')dt' \qquad (4)$$

where $C_I(t')$ 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 relationship between variable tracer input concentrations C_{in} and output concentrations C_{out} is given by the convolution integral:

$$C_{out}(t) = \int_0^\infty C_{in}(t - t').g(t').\exp(-\lambda t')\,\mathrm{d}t' \qquad (5)$$

where t = time of observation, t' = the transit time, exp(-λt') 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 Małoszewski 2001).

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.

$$g(t') = \delta\,(t' - t_t) \qquad (6)$$

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

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

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_t), modified by radioactive decay if applicable. Hence, the only parameter for this model is the transit time t_t (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 example, aquifers in which the recharge zone is narrow with respect to the overall distance from the recharge zone to the sampling point (Figure A1.2 a), and where there is little longitudinal dispersion, all of the water sampled at a bore or discharge point will have nearly the same age (Cook and Böhlke 2000). Thus the PFM may be a reasonable approximation for aquifers of this type. More complicated models are required for other cases. For example, in heterogeneous aquifers with preferential flow lines which lead to significant dispersion, or where substantial mixing 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 model

The exponential model (EM) is characterised by the system response function:

$$g(t') = t_t^{-1}\, e^{-t/t_t} \qquad (2.7)$$

This model assumes there is an exponential distribution of transit times, corresponding to the situation in an aquifer of decreasing permeability with increasing depth (Zuber 1986). The shortest flow line has a transit time equal to zero, with transit times for longer flow lines stretching to infinity (Figure A1.2 b). The EM is equivalent to the well-mixed model which is applicable to some hydrological reservoirs such as lakes and the ocean mixed layer (Stewart and Taylor 1981).

The EM is applicable to aquifers where the shortest flow lines are able to occur at the sampling point, for example unconfined aquifers where the bore screen begins at the water table or from a river or spring comprising the sole aquifer outflow (Cook and Böhlke 2000). The model cannot be applied to aquifers where these short flow lines do not exist, for example in confined aquifers or where the bore screen begins at some depth from the water table (Figure A1.2 c and d).

A1.2.3 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:

$$g(t') = 0 \qquad \text{for } t' < t_t\,(1\text{- f}) \qquad (8)$$

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

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 Małoszewski 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 A1.3).

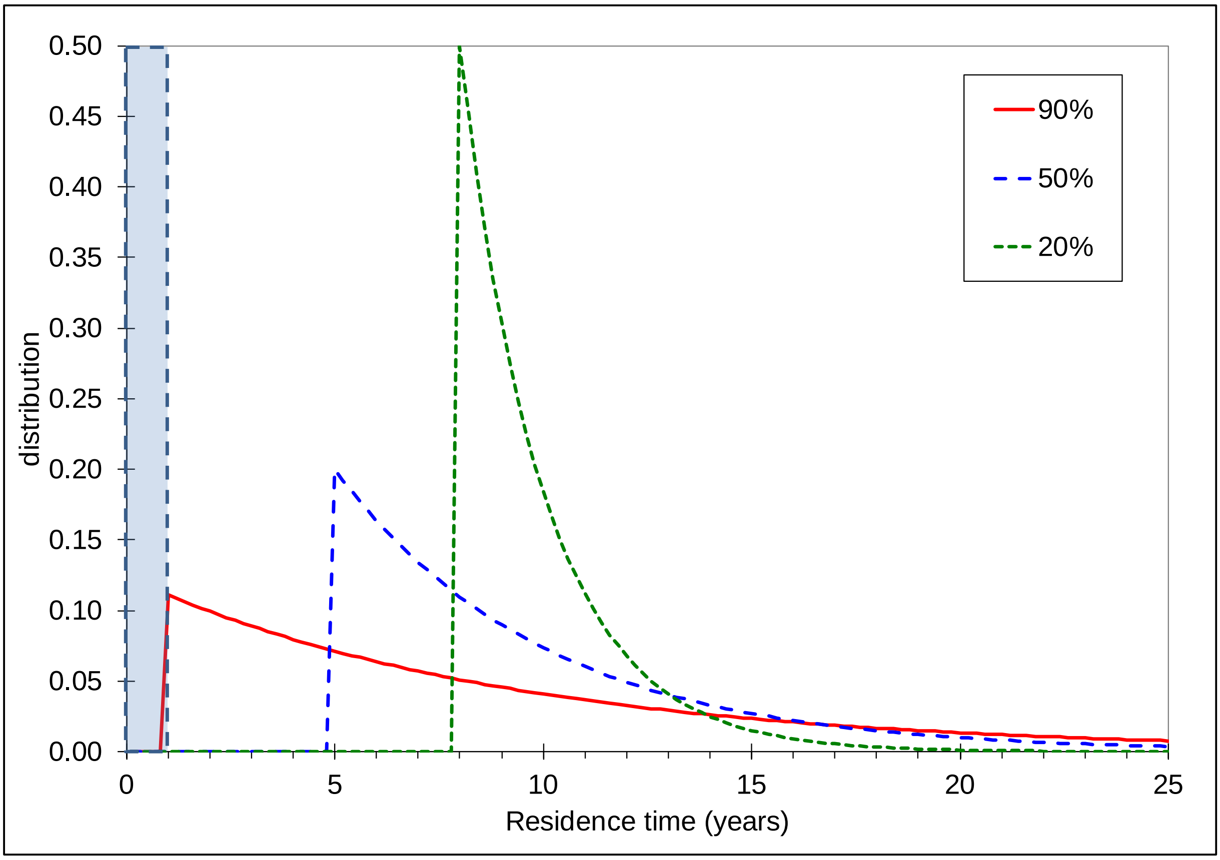


Figure A 1.3 Residence time distributions for the exponential piston flow model for MRT = 10 years, with typical parameter values (20%, 50% and 90% of the flow is exponential mixed flow). The shaded area to the left is the area of interest for the drinking water assessment. Integration of the residence time distribution curve which intersects this area yields the fraction of water less than one year old.

A1.2.4 Use of models to interpret age-tracer data

Solving the convolution integral 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 model to observed tracer concentrations by a trial and error procedure. The goodness of fit can be described by statistical tests such as the χ^2 test (Stewart and McDonnell 1991) or SIGMA test (Figure A1.4; Maloszewski and Zuber 2002).

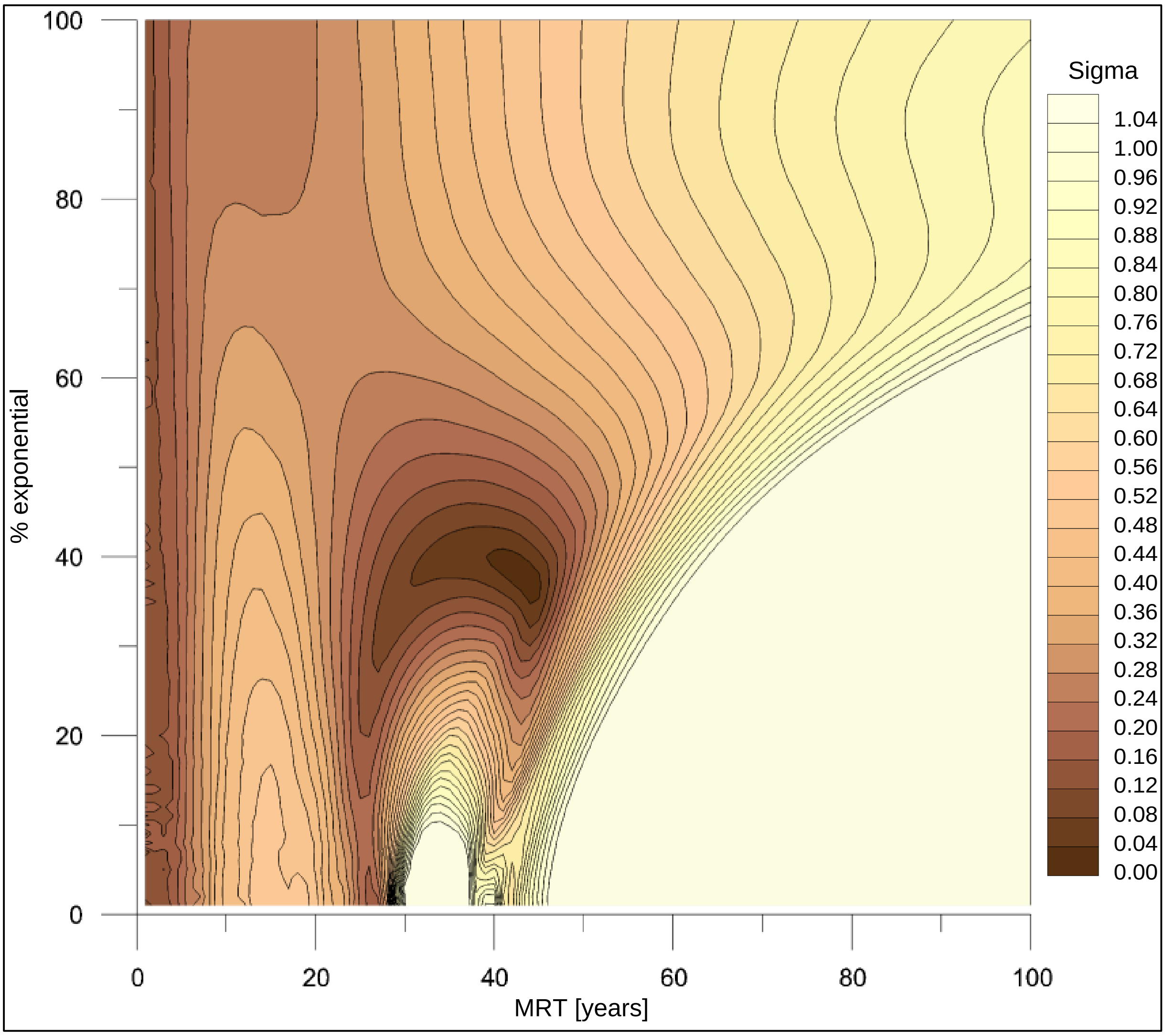


Figure A 1.4 Goodness of fit values (SIGMA) for the EPM as a function of the fitting parameters (%exponential and MRT) for a representative well, based on tritium data. Better fits are associated with lower SIGMA values (dark colours), while light colours indicate poor fits and large SIGMA values

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 satisfactory 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, bore depth and bore 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. Model parameters may give unique results for long-term 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 A1.5). For the majority of groundwaters, however, fractions of exponential mixed flow greater than 50% are more probable. These fractions above 50% will now yield unambiguous age data for all naturally observed tritium levels, as the bomb-tritium has decayed below natural tritium concentrations.

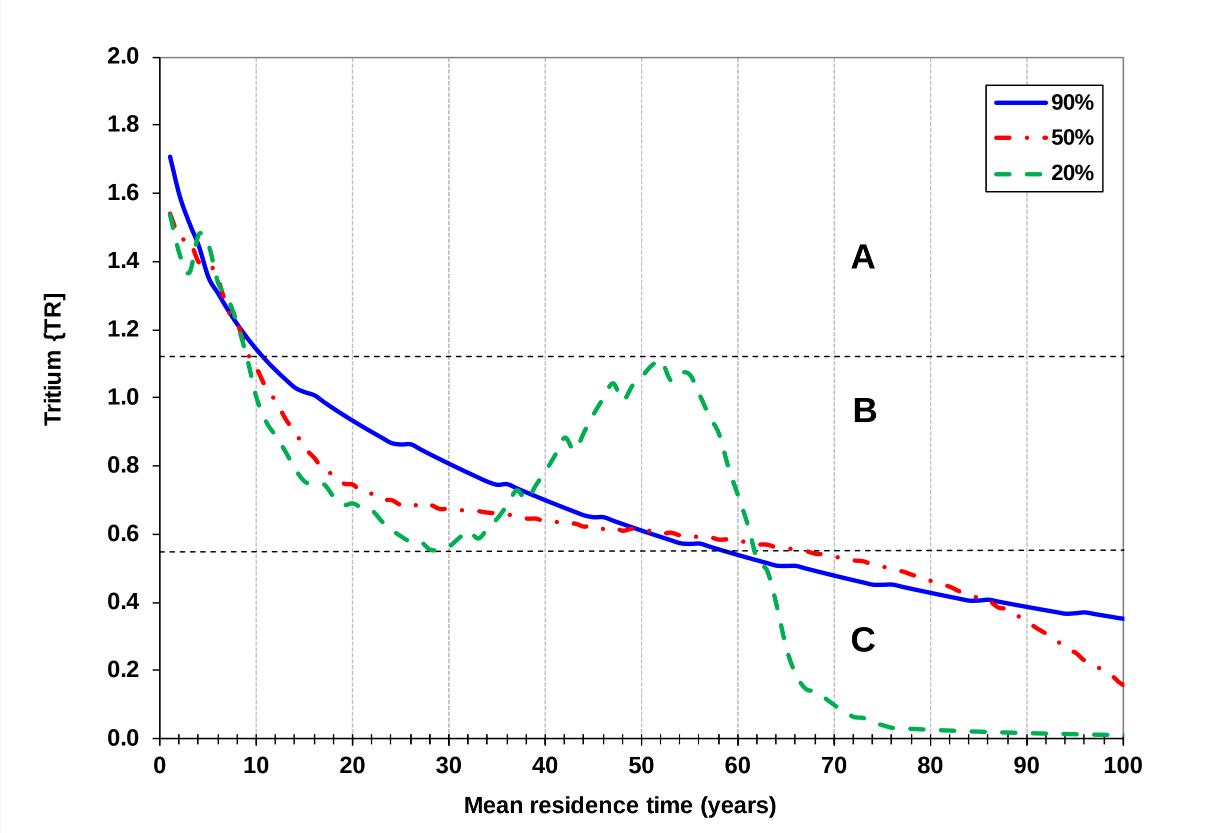


Figure A 1.5 Concentration of tritium in groundwater discharge as a function of mean residence time for different exponential-piston flow parameters, calculated for 2016. Measured tritium values falling in area B may yield ambiguous age data when low fractions of exponential mixed flow are indicated. Fractions of exponential mixed flow greater than 50%,will yield unambiguous age data.

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 to 25 years ago (Figure A1.6). 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 model parameters used and can help constrain the mean age but not the fraction of mixing. Similarly, SF_6 yields unambiguous ages but is insensitive for mean ages of less than 18 years.

Uncertainties in modelled groundwater ages reflect the different contributing factors. These include (1) the choice of model, which should adequately represent the system being modelled (constraining relevant models can be improved by the amount of tracer data available, and knowledge of aquifer lithology); (2) how adequately processes that may modify tracer concentrations can be accounted for, including degradation in the groundwater system and local contamination (3) accounting for the difference in age from tritium (time since infiltration into the ground) and the gases (time since reaching the water table, (4). how well the input function into the system is known for any particular tracer, (5) sufficient measurement accuracy (extremely sensitive methods are necessary for tritium; Morgenstern and Taylor 2009).

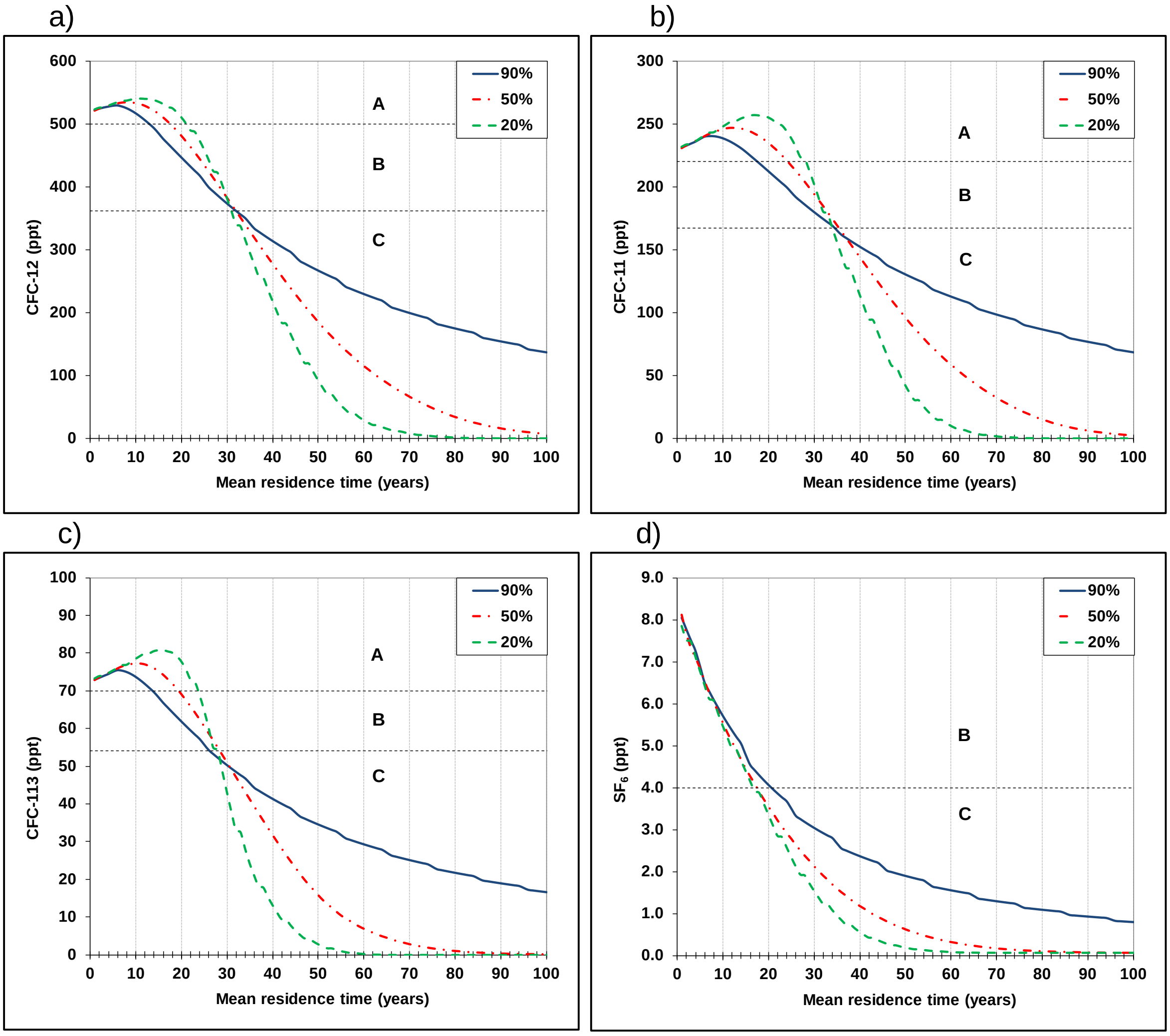


Figure A 1.6 Concentration of CFC-11, CFC12, CFC-113 and SF_6 in groundwater discharge expressed as the equivalent atmospheric concentration, as a function of mean residence time for different exponential-piston flow parameters. a b) Since the phasing out of CFCs in 1988, atmospheric concentrations of these tracers have declined and CFCs are not as effective for groundwater dating over the last 20 to 25 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, SF6ROB concentrations are also insensitive to the model parameters used (Area B).

The uncertainty cannot be accounted for by a single number. Each contributing factor must be accounted for individually. Use of the dispersion or exponential-piston-flow models has been demonstrated to be adequate for many aquifers in New Zealand (Morgenstern and Taylor 2009; Daughney et al., 2010; Morgenstern and Daughney 2012). The tritium input functions for New Zealand are well known from monthly tritium monitoring in Kaitoke since 1960 and scaling according to latitude (Stewart and Taylor 1981), and the input functions for the gases are very accurately known from the atmospheric observations (e.g., Prinn et al., 2000; Thompson et al., 2004). As to how well the data fit the model, and how well modifications to tracer concentrations are accounted for, this must be examined on a well-by-well basis.

A1.3 REFERENCES PERTAINING TO THE APPENDICES

Busenberg, E.; Plummer, L.N. 1992. Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age dating tools: the alluvium and terrace system of Central Oklahoma. *Water Resources Research.* 28 (9), 2257-2283.

Busenberg, E.; Plummer, L.N. 2000. Dating young groundwater with sulfur hexafluoride; natural and anthropogenic sources of sulfur hexafluoride. *Water Resources Research.* 36 (10), 3011-3030.

Cook, P.G.; Böhlke, J.K. 2000. Determining timescales for groundwater flow and solute transport. In: Cook, P.G., Herczeg, A.L. (Eds.) *Environmental tracers in subsurface hydrology*. Kluwer Academic, Boston. Ch1, 1-30.

Cook, P.G.; Solomon, D.K. 1995. The transport of atmospheric trace gases to the water table: Implications for groundwater dating with chlorofluorocarbons and Krypton-85. Water Resources Research. 31 (2), 263-270.

Cunnold, D.; Weiss, R.; Prinn, R.; Hartley, D.; Simmonds, P.; Fraser, P.; Miller, B.; Alyea, F.; Porter, L. 1997. GAGE/AGAGE measurements indicating reductions in global emissions of CCl3F and CCl2F2 in 1992-1994. Journal of Geophysical Research. 102, 1259-1269.

Daughney, C.J.; Morgenstern, U.; van der Raaij, R.; Reeves, R.R. 2010. Discriminant analysis for estimation of groundwater age from hydrochemistry and well construction: application to New Zealand aquifers. Hydrogeology J. 18, 417-428.

Heaton, T.H.E.; Vogel, J.C. 1981. "Excess air" in groundwater. Journal of Hydrology. 50, 201-216.

IAEA 2006. Use of chlorofluorocarbons in hydrology: a guidebook. International Atomic Energy Agency, Vienna. 277 p.

Lovelock, J.E. 1971. Atmospheric fluorine compounds as indicators of air movements. Nature. 230, 379.

Lovley, D.R.; Woodward, J.C. 1992. Consumption of freons CFC-11 and CFC-12 by anaerobic sediments and soils. Environ. Sci. Technol. 26, 925-929.

Lucas, L.L.; Unterweger, M.P. 2000. Comprehensive Review and Critical Evaluation of the Half-Life of Tritium. Journal of Research of the National Institute of Standards and Technology. 105 (4), 541-549.

Maiss, M.; Brenninkmeijer, C.A.M. 1998. Atmospheric SF_6: Trends, sources and prospects. Environmental Science and Technology. 32, 3077-3086.

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

Maloszewski, P.; Zuber, A. 2002. Manual on lumped parameter models used for the interpretation of environmental tracer data in groundwaters.In: *Use of Isotopes for Analyses of Flow and Transport Dynamics in Groundwater System*s IAE A-UIAGS/CD, 2002.

McGlynn, B.; McDonnell, J.; Stewart, M.; Seibert, J. 2003. On the relationships between catchment scale and streamwater mean residence time. Hydrological Processes. 17, 175-181.

Ministry of Health 2008. Drinking-water Standards for New Zealand 2005 (Revised 2008). Ministry of Health, Wellington, New Zealand. 163 p. Available online at: http://www.moh.govt.nz.

Morgenstern, U.; Daughney, C.J. 2012. Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification – The National Groundwater Monitoring Programme of New Zealand. Journal of Hydrology (2012) http://dx.doi.org/10.1016/j.jhydrol.2012.06.010

Morgenstern, U.; Taylor, C.B. 2009 Ultra low-level tritium measurement using electrolytic enrichment and LSC*. Isotopes in Environmental and Health Studies.* 45(2), 96-117.

Plummer, L.N.; Busenberg, E. 2000. Chlorofluorocarbons. In: Cook, P.G., Herczeg, A.L. (Eds.) Environmental tracers in subsurface hydrology. Kluwer Academic, Boston. Ch15, 441-478.

Prinn, R.G.; Weiss, R.F.; Fraser, P.J.; Simmonds, P.G.; Cunnold, D.M.; Alyea, F.N.; O'Doherty, S.; Salameh, P.; Miller, B.R.; Huang, J.; Wang, R.H.J.; Hartley, D.E.; Harth, C.; Steele, L.P.; Sturrock, G.; Midgely, P.M.; McCulloch, A. 2000. A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. Journal of Geophysical Research. 105 (D14), 17751-17792.

Russell, A.D.; Thompson, G.M. 1983. Mechanisms leading to enrichment of atmospheric fluorocarbons CCl_3F and CCl_2F_2 in groundwater. *Water Resources Research.* 19, 57-60.

Schwientek, M.; Maloszewski, P.; Einsiedl, F. 2009. Effect of the unsaturated zone thickness on the distribution of water mean transit times in a porous aquifer. *Journal of Hydrology* 373 (2009) 516-526.

Solomon, D.K.; Cook, P.G. 2000. ^3H and ^3He. In: Cook, P.G., Herczeg, A.L. (Eds.) *Environmental tracers in subsurface hydrology*. Kluwer Academic, Boston. Ch13, 397-424.

Stewart, M.K.; Taylor, C.B. 1981. Environmental isotopes in New Zealand hydrology: 1. Introduction: The role of oxygen-18, deuterium, and tritium in hydrology. *New Zealand Journal of Science.* 24, 295-311.

Stewart, M.K.; Morgenstern, U. 2001. Age and source of groundwater from isotope tracers. In Groundwaters of New Zealand, Rosen, M.R. and White, P.A. (Eds.). New Zealand Hydrological Society Inc., Wellington. Pp. 161-183.

Stewart, M.; Trompetter, V.; van der Raaij, R. 2002. Age and source of Canterbury plains groundwater. *Environment Canterbury Report No*. U02/30, Christchurch, New Zealand.

Thompson T.M.; Butler J.H.; Daube B.C.; Dutton G.S.; Elkins J.W.; Hall B.D.; Hurst., D.F.; King D.B.; Kline E.S.; Lafleur B.G.; Lind J.; Lovitz, S.; Mondeel D.J.; Montzka S.A.; Moore F.L.; Nance J.D.; Neu J.L.; Romashkin P.A.; Scheffer A.; Snible W.J. 2004. Halocarbons and other Atmospheric Trace Species. Climate Monitoring and Diagnostics Laboratory Summary Report No. 27. Ch 5.

Walker, S.J.; Weiss, R.F.; Salameh, P.K. 2000. Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11, CFC-12, CFC-113 and carbon tetrachloride. J Geophys Res 105: 14285-14296

Wilson, R.D.; Mackay, D.M. 1996. SF_6 as a conservative tracer in saturated media with high intragranular porosity or high organic carbon content. *Ground Water*. 34 (2), 241-249.

Zuber, A. 1986. Mathematical models for the interpretation of environmental radioisotopes in groundwater systems. *Handbook of Environmental Isotope Geochemistry, Vol. 2, Part B.* Fritz P., Fontes J.Ch. (Eds.), Elsevier, Amsterdam: 1-59.

Zuber, A.; Maloszewski, P. 2001. Lumped Parameter Models. *Environmental Isotopes in the Hydrological Cycle – Principles and Applications. Volume VI: Modelling.* Mook, W.G. (Ed.). UNESCO/IAEA series 1998-2001. Ch.2, 5-35. Available online at: http://www.iaea.org/programmes/ripc/ih/volumes/volumes.htm

Zuber, A.; Różański, K.; Kania, J.; Purtschert, R. 2010. On some methodological problems in the use of environmental tracers to estimate hydrogeologic parameters and to calibrate flow and transport models. Hydrogeology Journal. DOI 10.1007/s10040-010-0655-4.

APPENDIX 2: HISTORIC AGE-TRACER DATA

Well name	Sampling date	^3H [TR]	$\pm^3H$ [TR]	CFC-11 [ppt]	± CFC-11 [ppt]	CFC-12 [ppt]	± CFC-12 [ppt]	CFC- 113 [ppt]	± CFC- 113 [ppt]	SF_6 [ppt]	± SF_6 [ppt]
Waipatiki	27/03/07	-0.006	0.023	0.3	0.1	0.7	0.5			0.00	
Waipatiki	18/10/10	-0.048	0.022	4.7	0.2	4.6	0.1			0.11	0.03
Whirinaki	27/03/07	1.120	0.040	133.9	5.6	417	10			5.64	
Whirinaki	18/10/10	1.454	0.038	81.5	0.0	338	0.1			5.41	0.47
Omahu	20/02/01	2.009	0.061	247.7	0.4	513	1				
Omahu	24/06/03	1.851	0.061	205.6	0.0	494	0			5.1	0.0
Omahu	16/12/04	1.99	0.04								
Omahu	27/03/07	1.83	0.05								
Omahu	19/10/10	2.148	0.048	173.2	12.3	476	33			6.8	0.6
Portsmouth Rd	20/02/01	1.970	0.061	121.8	1.1	436	6				
Portsmouth Rd	19/10/10	1.626	0.041	148.6	12.7	472	39			6.3	0.8
Wilson Rd	20/02/01	1.912	0.061	138.4	1.7	482	8				
Wilson Rd	19/10/10	1.898	0.069	159.8	10.6	496	33			6.0	0.5
Pakipaki	20/02/01	0.020	0.019	0.3	0.1	0	0				
Pakipaki	19/10/10	0.164	0.023	0.7	17.5	6	16			0.8	0.1
Parkhill	25/06/14	1.07	0.026	21	2	245	19	0	2	4.2	0.3
Beach Rd, Haumoana	20/02/01	0.577	0.028	0.1	0.1	2	1				
Beach Rd, Haumoana	25/06/03	0.734	0.033								
Beach Rd, Haumoana	16/12/04	0.386	0.021								
Beach Rd, Haumoana	27/03/07	0.659	0.032								
Beach Rd, Haumoana	19/10/10	0.684	0.029	0.9	3.9	2	13			0.6	0.1
Tucker Lane, Clive	20/02/01	2.263	0.061								

Well name	Sampling date	^{3}H [TR]	$\pm^{3}H$ [TR]	CFC-11 [ppt]	± CFC-11 [ppt]	CFC-12 [ppt]	± CFC-12 [ppt]	CFC- 113 [ppt]	± CFC- 113 [ppt]	SF_6 [ppt]	± SF_6 [ppt]
Tucker Lane, Clive	24/06/03	1.978	0.051								
Tucker Lane, Clive	16/12/04	1.75	0.04								
Tucker Lane, Clive	27/03/07	1.55	0.04								
Tucker Lane, Clive	18/10/10	1.21	0.034	4.6	5.7	274	22			2.2	0.2
Ferry Rd, Clive	20/02/01	2.263	0.061	0.1	0.1	18	0				
Ferry Rd, Clive	18/10/10	1.259	0.039	0.5	5.2	164	17			2.0	0.1
Whakatu	20/02/01	2.175	0.061	0.2	0.2	159	3				
Whakatu	16/12/04	1.760	0.040								
Whakatu	18/10/10	1.203	0.036	0.4	5.4	1004	57			2.5	0.3
Waipatu	20/02/01	1.970	0.061	0.1	0.1	40	1				
Waipatu	16/12/04	1.660	0.040								
Waipatu	19/10/10	1.192	0.042	0.5	3.7	130	40			2.8	1.5
Brookvale No.1	20/02/01	1.727	0.051	184.5	0.2	446	4				
Brookvale No.3	18/10/10	1.455	0.039	120.0	8.6	390	27			4.2	0.3
Lyndhurst No.3	20/02/01	2.068	0.061	32.8	0.1	439	2				
Lyndhurst No.3	16/12/04	1.770	0.040								
Lyndhurst No.5	18/10/10	1.356	0.035	45.4	6.7	390	26			5.5	0.4
Eastbourne No.3	20/02/01	2.019	0.061	0.4	0.4	17	16				
Eastbourne No.3	16/12/04	1.63	0.04								
Eastbourne No.5	18/10/10	1.039	0.031	8.3	6.8	76	19			2.3	0.2

APPENDIX 3: PHOTOS OF THE WELLS SAMPLED IN MAY 2016

Figure A 3.1 Waipatiki.

Figure A 3.2 Whirinaki.

Figure A 3.3 Omahu.

Figure A 3.4 Portsmouth.

Figure A 3.5 Wilson Road.

Figure A 3.6 Parkhill.

Figure A 3.7 Beach Rd, Haumoana.

Figure A 3.8 Tucker Lane, Clive.

Figure A 3.9 Ferry Rd, Clive.

Figure A 3.10 Whakatu.

Figure A 3.11 Waipatu.

Figure A 3.12 Brookvale No.1.

Figure A 3.13 Lyndhurst No.5.

Figure A 3.14	Eastbourne No.5.

APPENDIX 4: BORE LOGS

Well 3516

IDENTIFICATION

WQ site:

Easting: 2852700
Northing: 6204202
Method:

Owner: HASTINGS DISTRICT COUNCIL

Address: WAIPATIKI RD, WAIPATIKI

WELL INFORMATION

Drill date: 09-Sep-94
Driller:
Casing diameter (mm): 150 mm
Bore depth (m): 37.5 **Water level access**
Well depth (m):
Casing top elevation (m):
Method:
Land surface elevation (m):
Method:
Screen top (m): 23.7 31.3
Screen bottom (m): 28 34.3

Comment: Replacement public water supply well for 2726.
Confirmed drilled by Peter Free (HDC).
Drill date is consent date.

CONSENT INFORMATION

Bore consent:

Consent	Use 1	Use 2
LU940295B	Public Water Supply	Potable Supply

Ground-water consent:

AQUIFER INFORMATION

Aquifer lithology: **Aquifer condition:** **Initial water level (m):** +0.2

Depth interval (m)		Lithology
0.00	0.30	top SOIL
0.30	19.50	SILT and SAND and some wood (casing pre driven over this distance)
19.50	23.50	grey coarse SAND and wood with some clay layers
23.50	28.50	blue LIMESTONE with a layer of wood at 24.2 m
28.50	31.80	grey SILTS
31.80	32.50	blue LIMESTONE
32.50	33.00	grey SANDY CLAY
33.00	34.20	blue LIMESTONE
34.20	37.00	grey SILTY CLAYS (firm)

Figure A 4.1 Bore log from the Waipatiki well 3516.

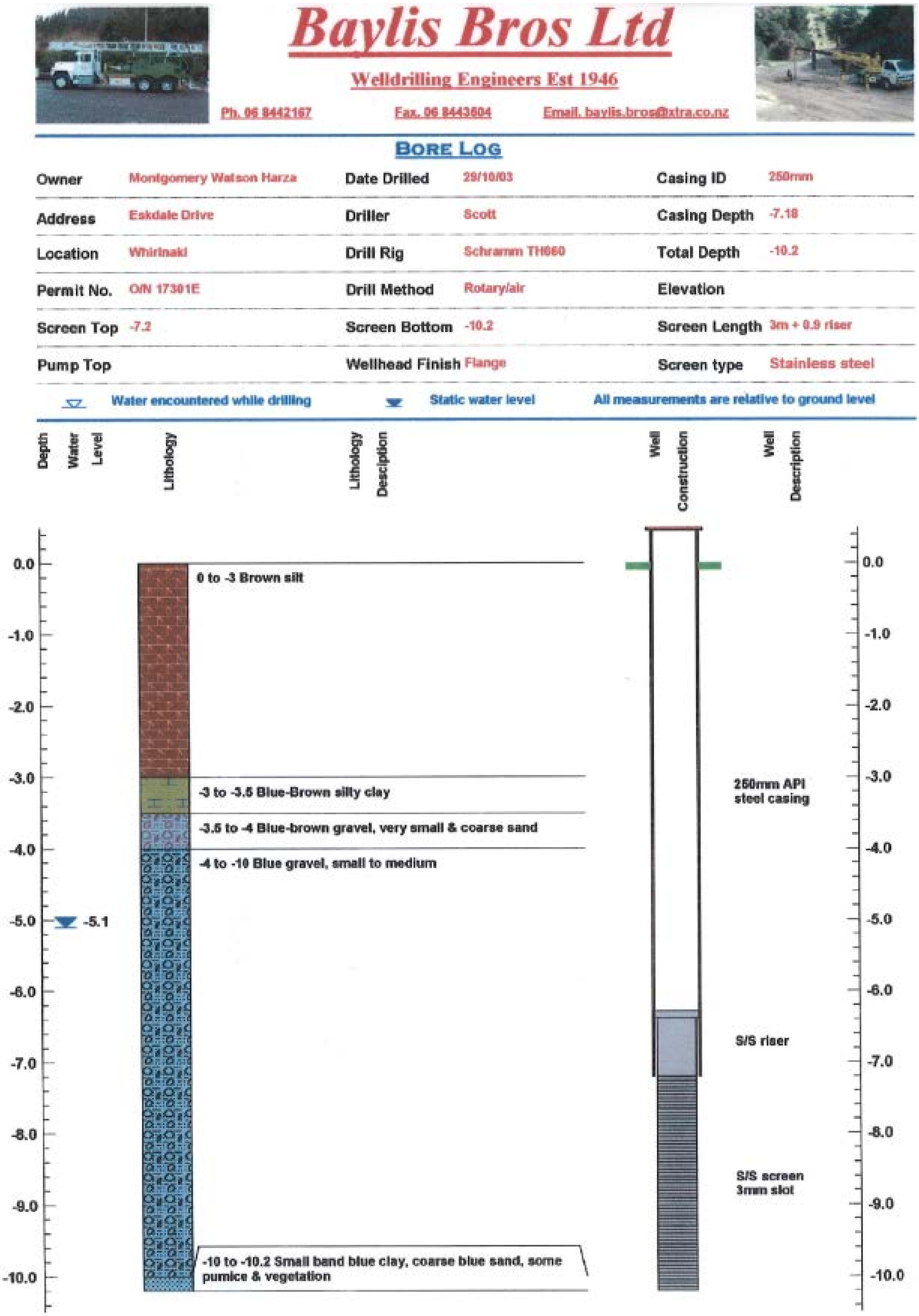


Figure A 4.2 Bore log from the Whirinaki well 5033.

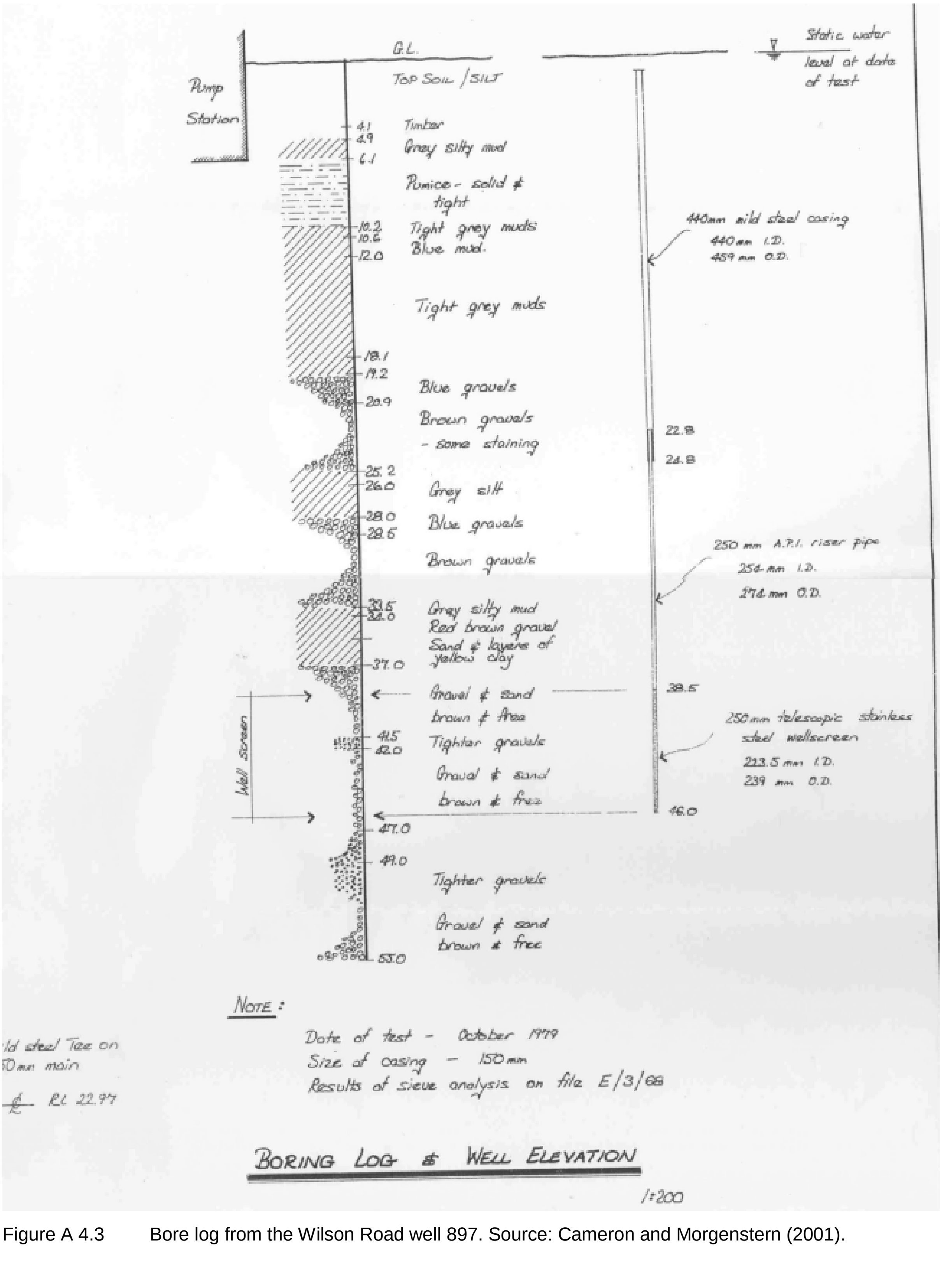


Figure A 4.3 Bore log from the Wilson Road well 897. Source: Cameron and Morgenstern (2001).

Hawke's Bay Regional Council
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Bore Log Report

Bore No: 10334

Easting	2833000		
Northing	6173700		
MapRef	V21:330-737		
Owner	HAWKE'S BAY COUNTY COUNCIL		
Address	OMAHU PA		
Diameter		WaterConsentID	
Depth	12.2	LandConsentID	
DrillDate	28/12/63 00:00:14	DrillerID	BABR
WellHeadElevation	0	Accuracy	2
GroundElevation	0	ElevAccuracyID	
AquiferTypeID	FAG	ConstructionID	DS
AquiferAreaID		PumpTypeID	
HighWaterLevel	2.4	LegacyPropID	
LowWaterLevel	2.4	FarmID	HB0796
TopScreen	0	Use1ID	UNKN
BtmScreen	0	Use2ID	UNKN

Depth	Strata
0.9	SILT
4.8	GRAVEL
6.1	blue CLAY
12.2	red GRAVEL

Figure A 4.4 Bore log from the Omahu well 10334. Source: Cameron and Morgenstern (2001).

Hawke's Bay Regional Council
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Bore Log Report

Bore No: 1905

Easting	2835100		
Northing	6161071		
MapRef	V21:361-610		
Owner	HAWKE'S BAY COUNTY COUNCIL		
Address	PAKIPAKI (L/C)		
Diameter	150	WaterConsentID	
Depth	28.96	LandConsentID	
DrillDate	18/05/85 00:00:29	DrillerID	HOW
WellHeadElevation	0	Accuracy	2
GroundElevation	0	ElevAccuracyID	
AquiferTypeID	FAG	ConstructionID	DPS
AquiferAreaID		PumpTypeID	
HighWaterLevel	3.30	LegacyPropID	
LowWaterLevel	0	FormID	
TopScreen1	21.95	Use1ID	UNKN
BtmScreen1	28.96	Use2ID	UNKN

Depth	Strata
0.3	GRAVEL (very soft)
0.61	TOPSOIL with clay
7.93	ASH/PUMICE
21.03	blue CLAY
22.25	blue GRAVEL
28.96	blue/brown GRAVEL

Figure A 4.5 Bore log from the Pakipaki well 1905. Source: Cameron and Morgenstern (2001).

Honnor Well Drillers Limited

Detailed summary of Well Details

7/08/2009 4:34:12 p.m.

Well ID: PARKHILL
Client ID: PARKHILL
Map Reference: E:2848886 N:6[illegible]866
Log Book Ref : BK 12 : PG 2509
Drill Date: 07/08/2008

Consent Number: LU080218B
Permit Number: 5830

Client Details

Name: Parkhill Ltd
Contact: Lynn Willims
Address: Cnr Parkhill & East Roads
Haumoana
Telephone: 021 875 117
FAX:
Notes: Postal: PO Box 11014, Hastings

Bore Depth:	37.00	M
Casing Diameter:	150.00	M
Wellhead Elevation:	-999.99	M
Ground Elevation:	-999.99	M
Screen Length 1:	6.00	M
Bottom of Screen 1:	36.50	M
Screen Length 2:	-999.99	M
Bottom of Screen 2:	-999.99	M
Static Water Level:	2.30	M

Well Log Details :

Depth	Description
1.00M	TOP SOIL
4.00M	BROWN CLAY
12.00M	BLUE GRAVEL
28.00M	BLUE CLAY
31.00M	BLUE CLAY, SAND AND SHELL
38.00M	BROWN GRAVEL
42.00M	BROWN GRAVEL WITH SOME CLAY
45.00M	BROWN GRAVEL
46.00M	BROWN GRAVL WITH SOME CLAY
48.00M	BLUE CLAY
48.50M	BROWN GRAVEL
55.00M	BLUE CLAY
57.00M	SANDY BROWN GRAVEL
60.00M	BLUE CLAY

Pump Test Details :

Test date: 07-Aug-08 **SWL prior:** 2.300 M **Drawdown:** -999.999 M
Conducted by:

Time since start of test	Water level	Flow rate or Pumping Rate	Water level in observation bore	Water level during recovery	Remarks
60.00	2.3	20400	-999.999 M	-999.999	Free Flow 4" jet

Figure A 4.6 Bore log from the Parkhill well 5830.

Hawke's Bay Regional Council

Safeguarding Your Environment

Bore Log Report

Bore No: 1187

Easting	2849024		
Northing	6169796		
MapRef	V21:490-697		
Owner	HAWKE'S BAY COUNTY COUNCIL		
Address	BEACH RD HAUMOANA (L/C)		
Diameter	200	WaterConsentID	
Depth	64.6	LandConsentID	
DrillDate	26/01/82 00:00:27	DrillerID	HIWE
WellHeadElevation	0	Accuracy	2
GroundElevation	0	ElevAccuracyID	
AquiferTypeID	FAG	ConstructionID	OPOE
AquiferAreaID		PumpTypeID	
HighWaterLevel	2.5	LegacyPropID	
LowWaterLevel	0	FarmID	
TopScreen1	22	Use1ID	UNKN
BtmScreen1	28.1	Use2ID	UNKN

Depth	Strata
2.5	TOPSOIL
12.9	blue CLAY with shell
15.5	blue/brown GRAVEL
17	brown GRAVEL with limestone
17.8	brown CLAY
19.5	brown GRAVEL
21	brown CLAY
28.7	brown GRAVEL
29.1	brown CLAY with gravel (very soft)
32.4	brown GRAVEL with sand
33.2	blue/grey CLAY with gravel
36	blue CLAY with gravel
44	blue CLAY with gravel
47.2	GRAVEL with clay/sand
51.3	grey CLAY with gravel
64.6	blue CLAY with sand

Figure A 4.7 Bore log from the Beach Road well 1187. Source: Cameron and Morgenstern (2001).

Hawke's Bay Regional Council
Safeguarding Your Environment

Bore Log Report

Bore No: 542

Easting	2846363		
Northing	6172370		
MapRef	V21:463-723		
Owner	HB COUNTY COUNCIL		
Address	TUCKER LANE		
Diameter	150	WaterConsentID	HKB1535
Depth	47.55	LandConsentID	
DrillDate	31/05/75	DrillerID	BOHI
WellHeadElevation		Accuracy	2
GroundElevation		ElevAccuracyID	
AquiferTypeID	FAG	ConstructionID	DPOE
AquiferAreaID		PumpTypeID	
HighWaterLevel	6.1	LegacyPropID	542
LowWaterLevel	0	FarmID	H50189
TopScreen1	41.45	UseID	PUWA
BtmScreen1	47.55	Use2ID	UNKN

Depth	Strata
6.4	SILT with clay
6.71	SAND
14.63	blue CLAY
17.68	SAND with shell
37.18	blue CLAY
47.55	GRAVEL with sand

Figure A 4.8 Bore log from the Tucker Lane well 542. Source: Cameron and Morgenstern (2001).

Hawke's Bay Regional Council
Safeguarding Your Environment

Bore Log Report

Bore No: 1658

Easting	2846535		
Northing	6173024		
MapRef	V21:465-730		
Owner	HAWKE'S BAY COUNTY COUNCIL		
Address	FERRY RD CLIVE (L/C)		
Diameter	150	WaterConsentID	
Depth	47	LandConsentID	
DrillDate	20/03/64 00:00:10	DrillerID	HIWE
WellBaseElevation	0	Accuracy	2
GroundElevation	0	ElevAccuracyID	
AquiferTypeID	FAG	ConstructionID	DPOE
AquiferAreaID		PumpTypeID	
HighWaterLevel	7.5	LegacyPropID	
LowWaterLevel	0	FarmID	
TopScreen1	41	Use1ID	UNKN
BtmScreen1	47	Use2ID	UNKN

Depth	Strata
2.8	brown TOPSOIL with silt
3.2	blue CLAY
8.5	blue GRAVEL
16.2	blue CLAY with silt
17.3	SHELL with gravel
32	blue CLAY with silt
39.5	blue CLAY (soft)
41	blue GRAVEL
47	brown GRAVEL

Figure A 4.9 Bore log from the Ferry Road well 1658. Source: Cameron and Morgenstern (2001).

Hawke's Bay Regional Council
Safeguarding Your Environment

Bore Log Report

Bore No: 1329

Easting	2845141		
Northing	6165015		
MapRef	V21:451-650		
Owner	HAVELOCK NORTH BOROUGH COUNCIL		
Address	BROOKVALE RD (L/C)		
Diameter	320	WaterConsentID	
Depth	24	LandConsentID	
DrillDate	10/12/62 00:00:41	DrillerID	HWE
WellheadElevation	0	Accuracy	2
GroundElevation	0	ElevAccuracyID	
AquiferTypeID	NFAG	ConstructionID	DPOE
AquiferAreaID		PumpTypeID	
HighWaterLevel	-2.35	LegacyPropID	
LowWaterLevel	0	FormID	
TopScreen1	~~0.00~~ 11.4 to 12.4 and 14.0 to 22.0	UseID	UNKN
BtmScreen1	~~11.73~~	Use2ID	UNKN

Depth	Strata
2.6	TOPSOIL with silt
9.8	brown GRAVEL
10	brown/red GRAVEL (stained)
24	GRAVEL

Figure A 4.10 Bore log from the Brookvale No.1 well1329. Source: Cameron and Morgenstern (2001).

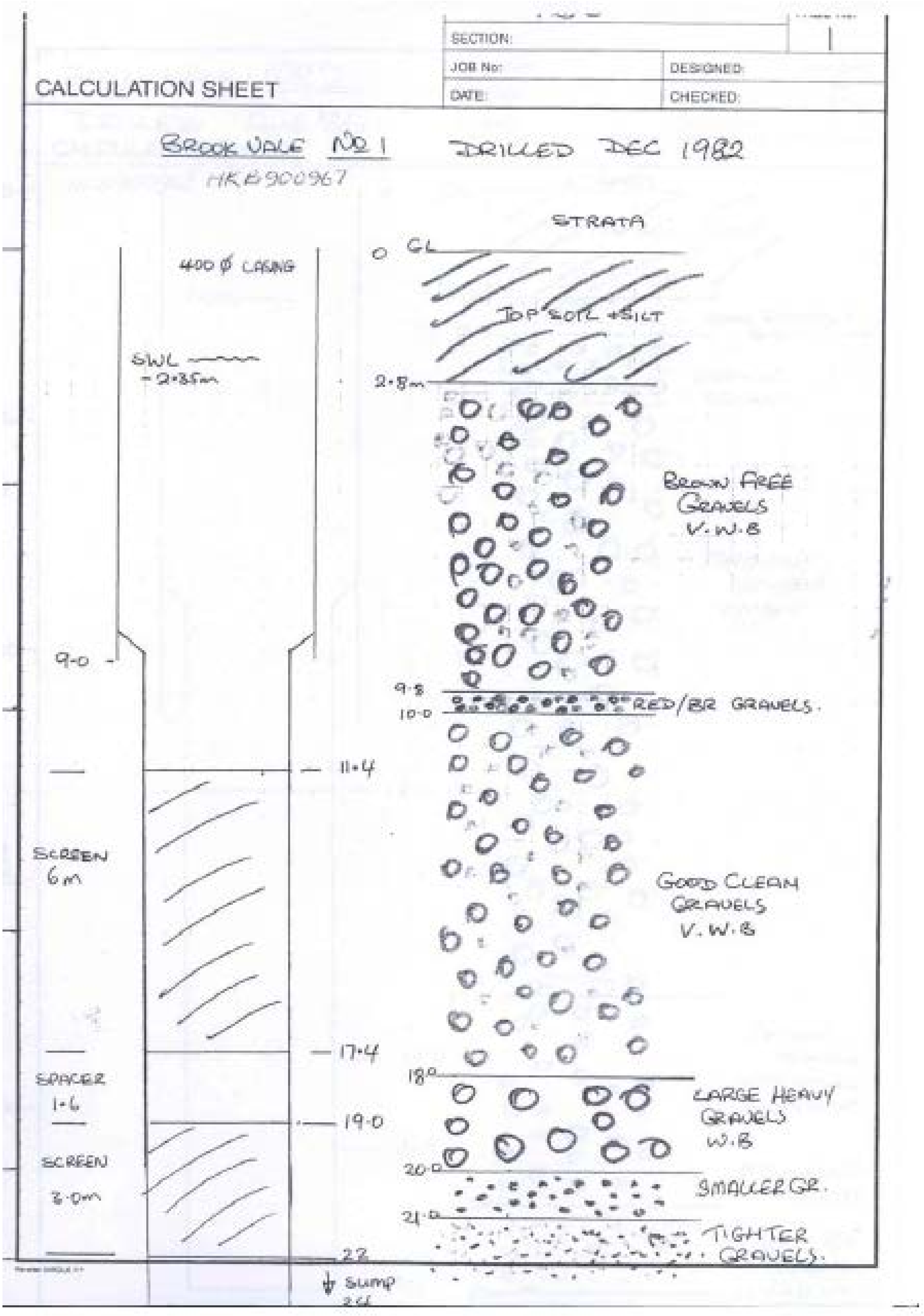

Figure A 4.11 Bore log from the Brookvale No.1 well1329. Source: Cameron and Morgenstern (2001).

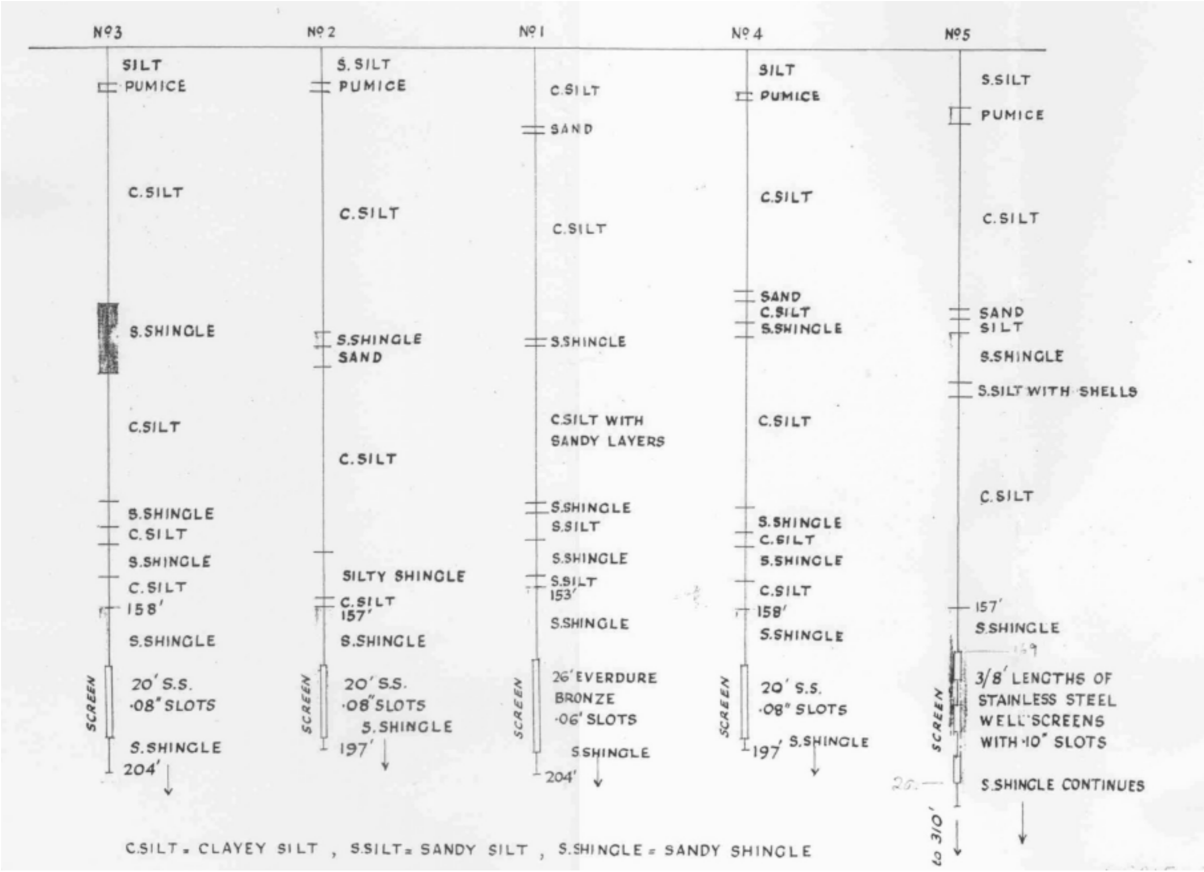

Figure A 4.12 Bore logs from the Lyndhurst wells. Source: Cameron and Morgenstern (2001).

Hawke's Bay Regional Council

Safeguarding Your Environment

Bore Log Report

Bore No: 1302

Easting	2839800		
Northing	6165300		
MapRef	V21:398-653		
Owner	HASTINGS CITY COUNCIL		
Address	LEGAL RD EASTBOURNE STREET HASTINGS (L/C		
Diameter	260	WaterConsentID	
Depth	85.5	LandConsentID	
DrillDate	09/12/62 00:00:26	DrillerID	HIWE
WellHeadElevation	0	Accuracy	2
GroundElevation	0	ElevAccuracyID	
AquiferTypeID	FAG	ConstructionID	DPOE
AquiferAreaID		PumpTypeID	
HighWaterLevel	1	LegacyPropID	
LowWaterLevel	0	FarmID	HU0000
TopScreen1	69.4	Use1ID	UNKN
BtmScreen1	76.4	Use2ID	UNKN

Depth	Strata
2.8	GRAVEL
6.5	blue CLAY (loose)
9	brown PEAT/VEG/WOOD
12.2	SAND with ash/pumice
18	blue CLAY
30.8	blue CLAY with sand
41.5	blue/brown CLAY with peat/veg/wood
44.2	brown GRAVEL (cemented, stained)
50	brown GRAVEL with clay/silt
51.5	GRAVEL
52	GRAVEL (cemented)
55.8	GRAVEL (cemented)
55.9	brown CLAY with sand (mud)
58.5	blue CLAY (mud)
61.2	brown GRAVEL (stained)
61.6	brown CLAY
64.35	blue CLAY
66.2	GRAVEL
68.75	blue CLAY
74.5	GRAVEL
75.5	brown CLAY with gravel (mud)
76	GRAVEL
76.4	GRAVEL with sand (very sandy)
78.7	brown CLAY (mud)
78.14	blue CLAY (mud)
84.77	brown GRAVEL
85.5	blue CLAY

Figure A 4.13 Bore log from the Eastbourne No.5 well 1302. Source: Cameron and Morgenstern (2001).

APPENDIX 5: GEOLOGICAL CROSS-SECTIONS OF THE HERETAUNGA PLAINS AQUIFER SYSTEM

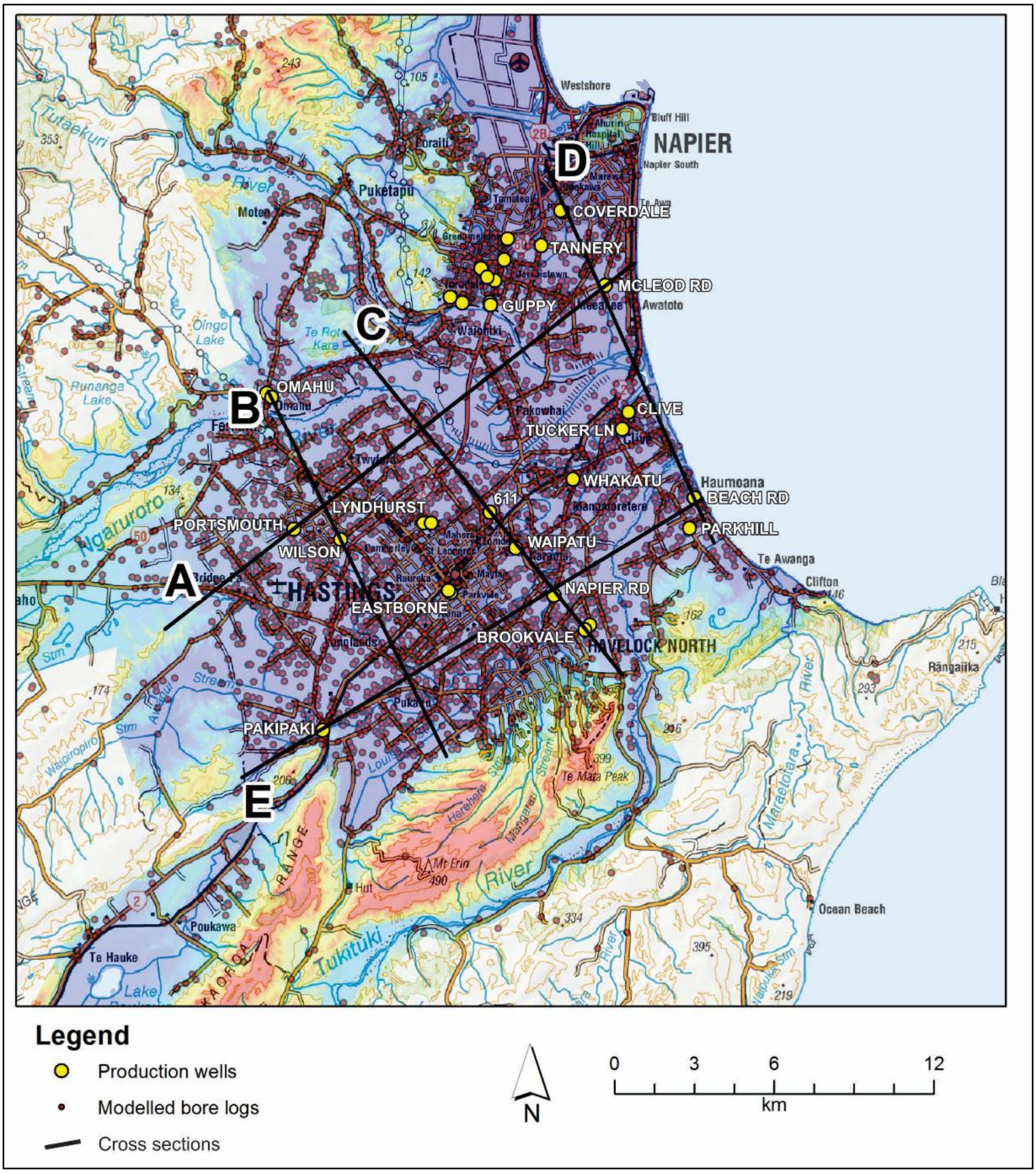

Figure A 5.1 Location of borehole collars and production bores constraining the Heretaunga Plains geological model. The base map is the LINZ Topo250 map, underlain by the lidar-derived 1 m digital elevation model, colour-ramped to indicate relative elevation. The annotated lines represent the location of cross sections depicted in Figures A5.2 - 5.6 and production bores are named.

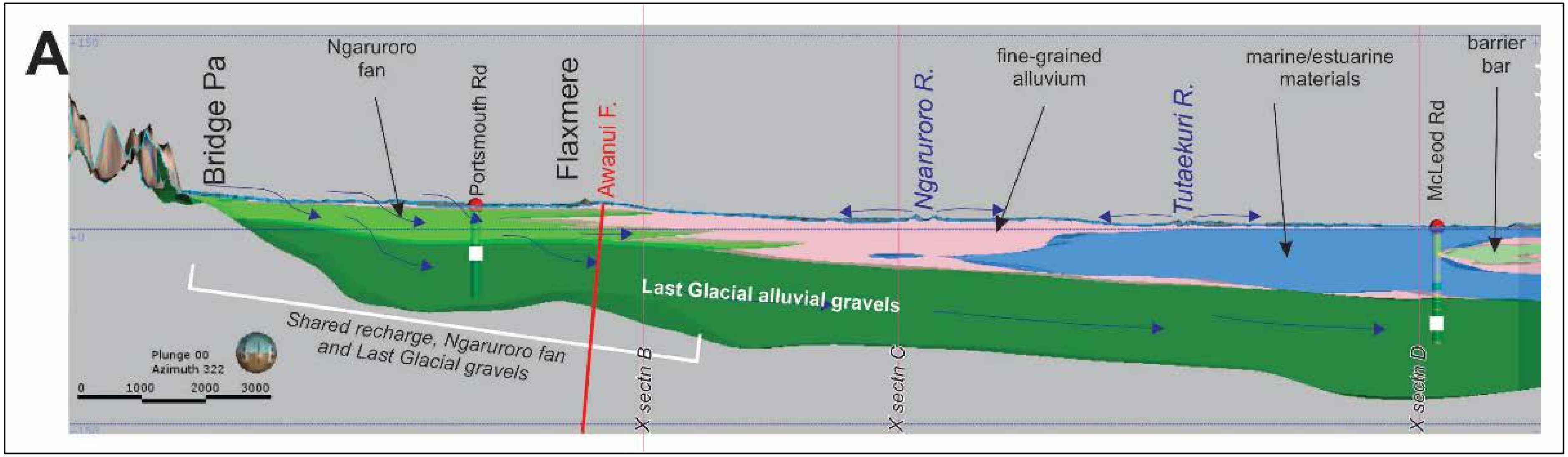

Figure A 5.2 Geological cross-section A: Bridge Pa (left) to Awatoto (right). The sections show the geological units above the top of the Last Glacial alluvial gravels (dark green). Colours representing primary lithologies within borehole logs are identified. Representation shows the base of the last Glacial gravels. The primary groundwater aquifer for the Heretaunga Plains, due to sparsity of borehole input data, is approximate only. Light green units represent Holocene alluvial fan gravels (of the Ngaruroro and Tukituki rivers) and barrier bar gravels at Napier and Haumoana; the blue unit represents the modelled Holocene marine/estuarine materials and the pink unit represents dominantly fine-grained Holocene overbank alluvial deposits. Red balls at the surface mark production well sites and white squares on those logs represent the upper extent of screening. Thin dark blue arrows represent likely water flow paths on the plane represented. No attempt is made to represent flow at angles to the section planes. Sub-vertical red lines represent the approximate location of active faults. Crimson vertical lines represent intersections with the other cross-sections. All sections are to the same indicated horizontal scale with a vertical exaggeration 20 x.

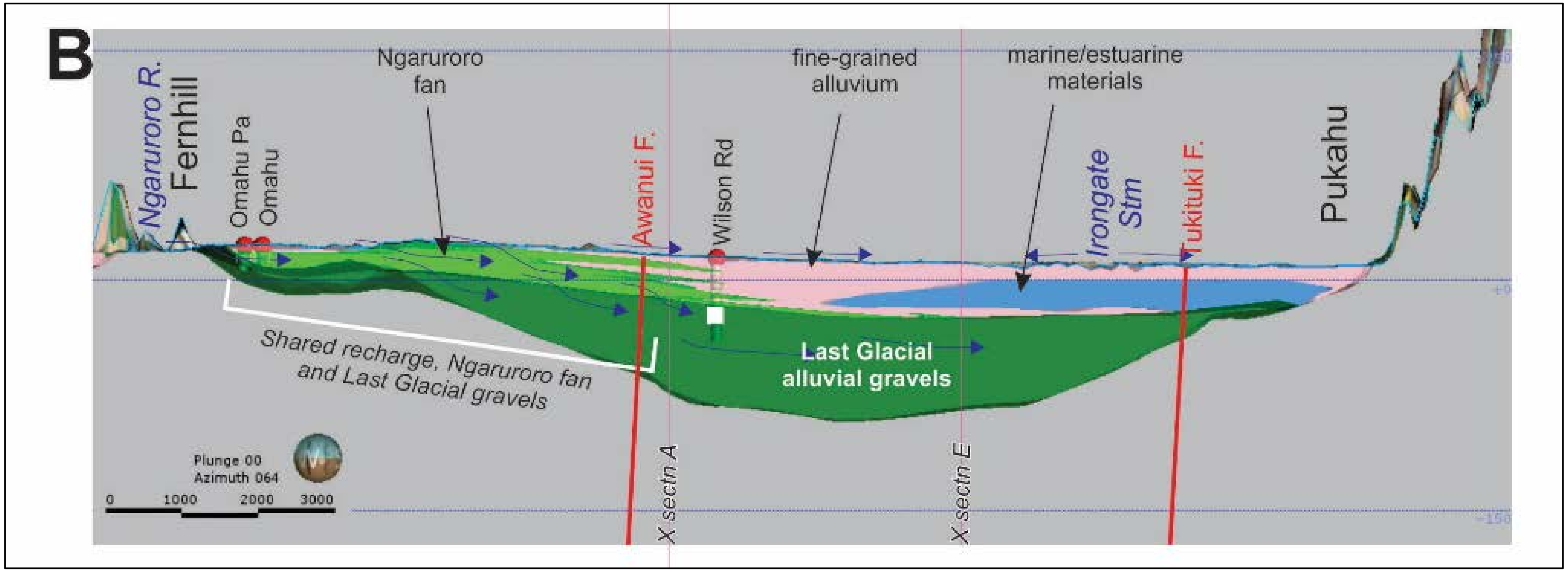

Figure A 5.3 Geological cross-section: B: Fernhill (left) to Pukahu (right). The sections show the geological units above the top of the Last Glacial alluvial gravels (dark green). Colours representing primary lithologies within borehole logs are identified. Representation shows the base of the last Glacial gravels. The primary groundwater aquifer for the Heretaunga Plains, due to sparsity of borehole input data, is approximate only. Light green units represent Holocene alluvial fan gravels (of the Ngaruroro and Tukituki rivers) and barrier bar gravels at Napier and Haumoana; the blue unit represents the modelled Holocene marine/estuarine materials and the pink unit represents dominantly fine-grained Holocene overbank alluvial deposits. Red balls at the surface mark production well sites and white squares on those logs represent the upper extent of screening. Thin dark blue arrows represent likely water flow paths on the plane represented. No attempt is made to represent flow at angles to the section planes. Sub-vertical red lines represent the approximate location of active faults. Crimson vertical lines represent intersections with the other cross-sections. All sections are to the same indicated horizontal scale with a vertical exaggeration 20 x.

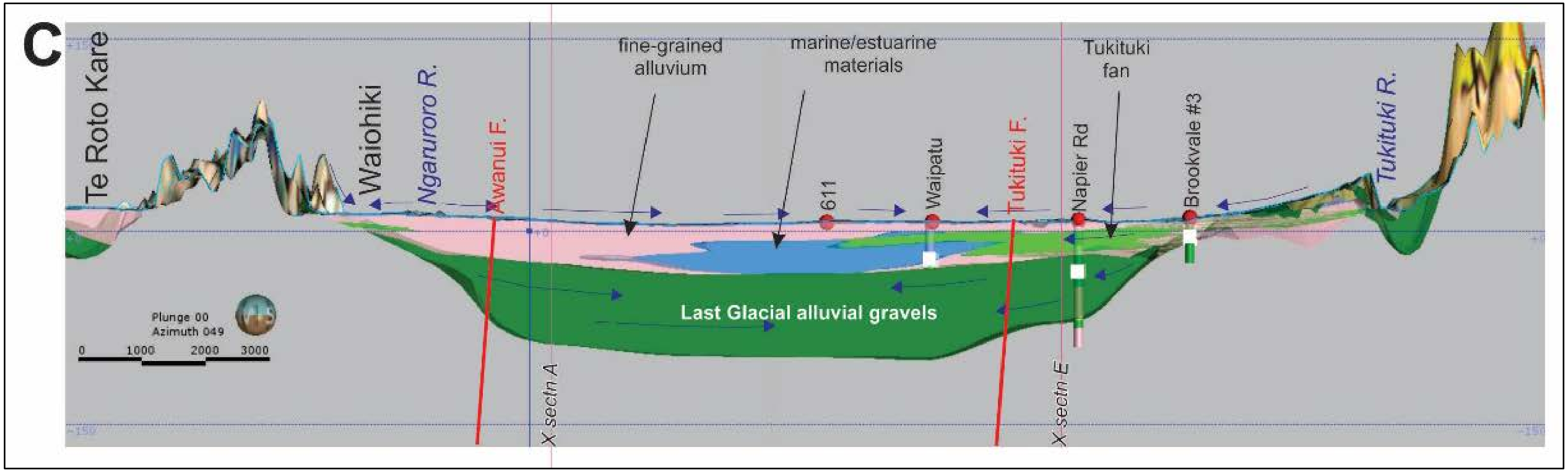

Figure A 5.4 Geological cross-section C: Te Roto Kare (left) to Tukituki River (right). The sections show the geological units above the top of the Last Glacial alluvial gravels (dark green). Colours representing primary lithologies within borehole logs are identified. Representation shows the base of the last Glacial gravels. The primary groundwater aquifer for the Heretaunga Plains, due to sparsity of borehole input data, is approximate only. Light green units represent Holocene alluvial fan gravels (of the Ngaruroro and Tukituki rivers) and barrier bar gravels at Napier and Haumoana; the blue unit represents the modelled Holocene marine/estuarine materials and the pink unit represents dominantly fine-grained Holocene overbank alluvial deposits. Red balls at the surface mark production well sites and white squares on those logs represent the upper extent of screening. Thin dark blue arrows represent likely water flow paths on the plane represented. No attempt is made to represent flow at angles to the section planes. Sub-vertical red lines represent the approximate location of active faults. Crimson vertical lines represent intersections with the other cross-sections. All sections are to the same indicated horizontal scale with a vertical exaggeration 20 x.

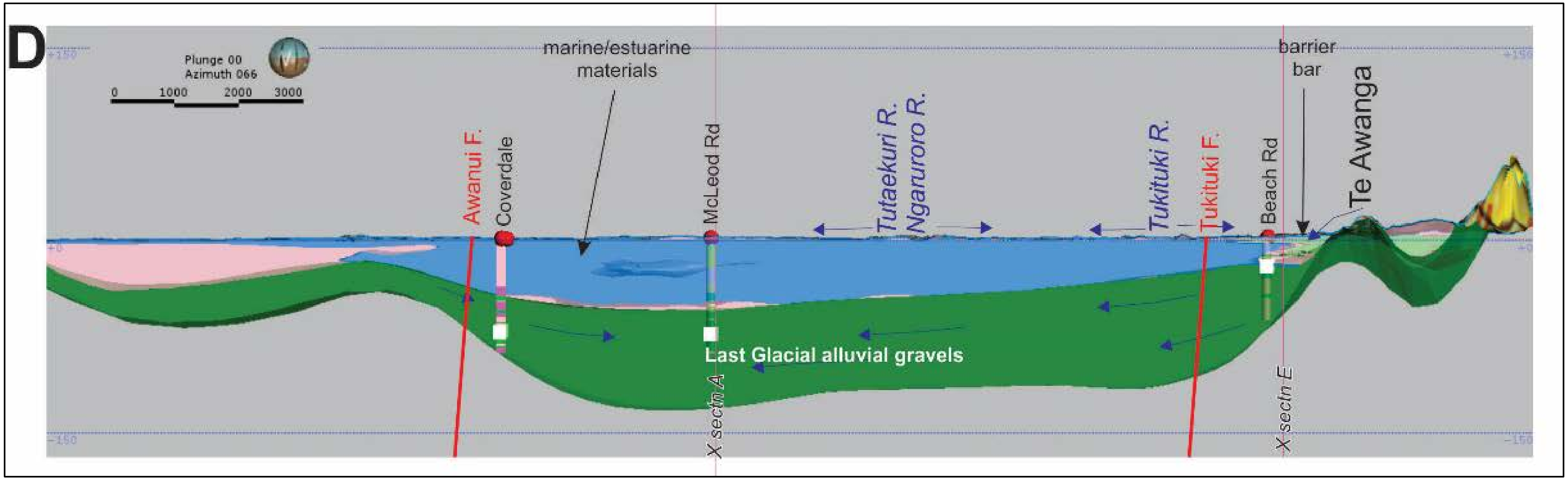

Figure A 5.5 Geological cross section D: Napier CBD (left) to Haumoana (right). The sections show the geological units above the top of the Last Glacial alluvial gravels (dark green). Colours representing primary lithologies within borehole logs are identified. Representation shows the base of the last Glacial gravels The primary groundwater aquifer for the Heretaunga Plains, due to sparsity of borehole input data, is approximate only. Light green units represent Holocene alluvial fan gravels (of the Ngaruroro and Tukituki rivers) and barrier bar gravels at Napier and Haumoana; the blue unit represents the modelled Holocene marine/estuarine materials and the pink unit represents dominantly fine-grained Holocene overbank alluvial deposits. Red balls at the surface mark production well sites and white squares on those logs represent the upper extent of screening. Thin dark blue arrows represent likely water flow paths on the plane represented. No attempt is made to represent flow at angles to the section planes. Sub-vertical red lines represent the approximate location of active faults. Crimson vertical lines represent intersections with the other cross-sections. All sections are to the same indicated horizontal scale with a vertical exaggeration 20 x.

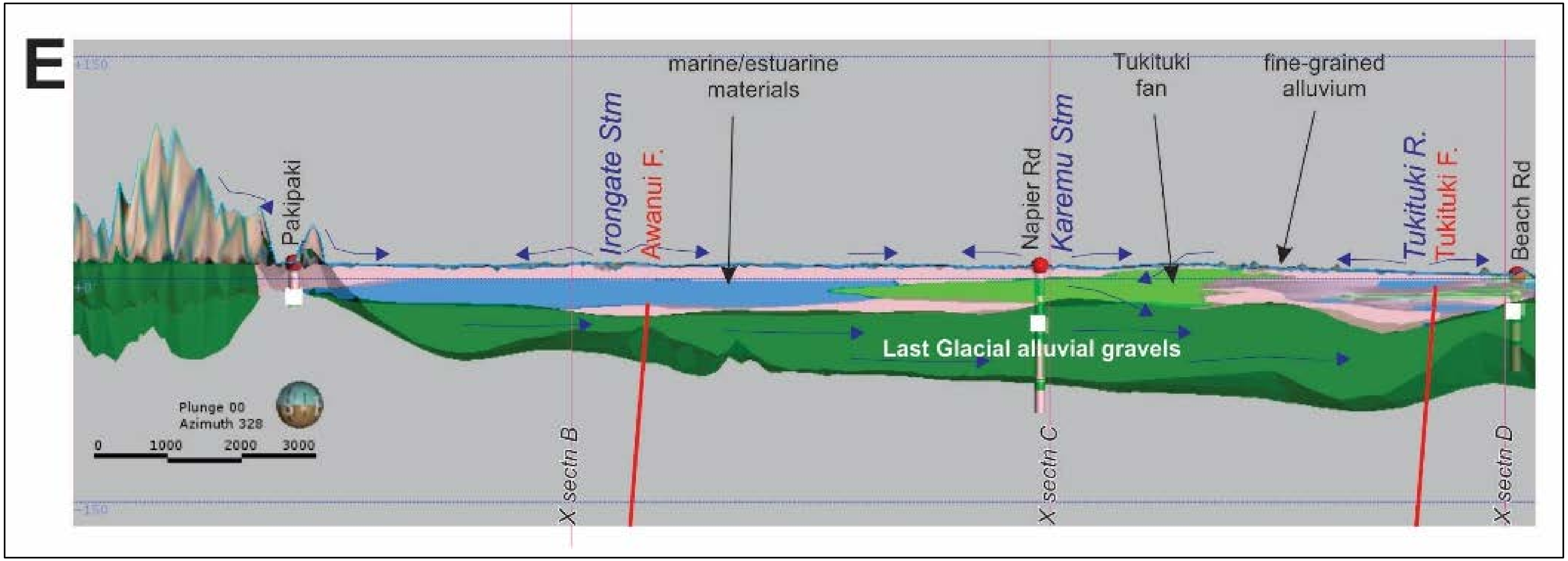

Figure A 5.6 Geological cross sections E: Pakipaki (left) to Haumoana (right). The sections show the geological units above the top of the Last Glacial alluvial gravels (dark green). Colours representing primary lithologies within borehole logs are identified. Representation shows the base of the last Glacial gravels. The primary groundwater aquifer for the Heretaunga Plains, due to sparsity of borehole input data, is approximate only. Light green units represent Holocene alluvial fan gravels (of the Ngaruroro and Tukituki rivers) and barrier bar gravels at Napier and Haumoana; the blue unit represents the modelled Holocene marine/estuarine materials and the pink unit represents dominantly fine-grained Holocene overbank alluvial deposits. Red balls at the surface mark production well sites and white squares on those logs represent the upper extent of screening. Thin dark blue arrows represent likely water flow paths on the plane represented. No attempt is made to represent flow at angles to the section planes. Sub-vertical red lines represent the approximate location of active faults. Crimson vertical lines represent intersections with the other cross-sections. All sections are to the same indicated horizontal scale with a vertical exaggeration 20 x.

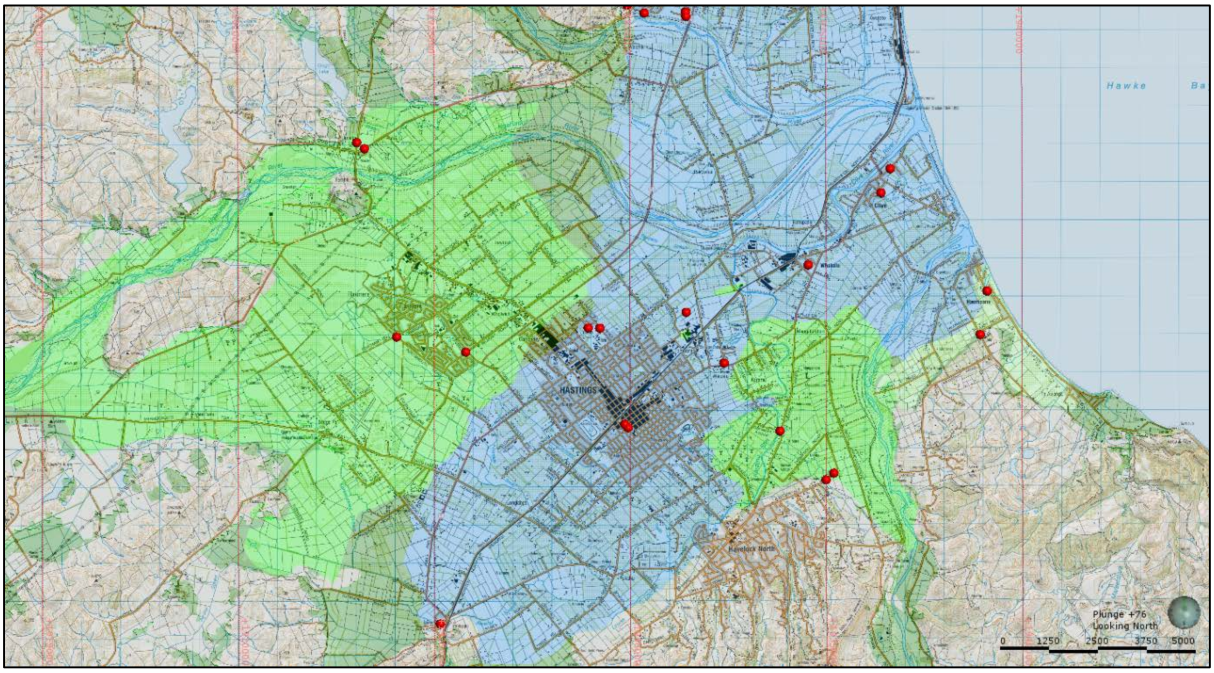

Figure A 5.7 The extent of subsurface Holocene alluvial fans from the Ngaruroro and Tukituki rivers is shown in this map image. The area coloured blue indicates the extent of the Holocene marine incursion, and the light green colour (with a solid line border) the lateral extent of the loose gravel fans from these two rivers. The slightly darker green areas (with dotted line borders) show the extent of Holocene fan gravels older than c. 6500 years. The named red points represent production water bore sites.

www.gns.cri.nz

Principal Location

1 Fairway Drive
Avalon
PO Box 30368
Lower Hutt
New Zealand
T +64-4-570 1444
F +64-4-570 4600

Other Locations

Dunedin Research Centre
764 Cumberland Street
Private Bag 1930
Dunedin
New Zealand
T +64-3-477 4050
F +64-3-477 5232

Wairakei Research Centre
114 Karetoto Road
Wairakei
Private Bag 2000, Taupo
New Zealand
T +64-7-374 8211
F +64-7-374 8199

National Isotope Centre
30 Gracefield Road
PO Box 31312
Lower Hutt
New Zealand
T +64-4-570 1444
F +64-4-570 4657