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Attention: Peter Davidson

Dear Peter,

Mill Stream, Wairau and Rai valley water dating results

Groundwater age tracer results are listed below for the Mill Stream area and for the Wairau and Rai valleys. The notation of analytical and interpretation results is according to Morgenstern et al. 2008.

1. Mill Stream area samples

1.1 Aim

The aim of this study is to measure the age of the groundwater discharges in the Mill Stream area to identify a potential lag time between land-use activities in the Mill Steam catchment and impacts in the groundwater discharge area. Contaminants from land-use activities (for example nitrate) travelling with the groundwater can take a long time to reach groundwater discharge points under typical aquifer conditions. As a result of the large lag times between contaminant input and the time they reach sensitive points of use, groundwater systems can become contaminated before impacts are evident.

1.2 Rationale

Studies in a number of New Zealand catchments have shown that mean transit times on the order of several years to several decades are typical for groundwater before discharge as base flow to streams (Morgenstern et al. 2010; Stewart at al. 2010). To identify such long water transit times, it is necessary to measure the age of the water at the groundwater discharge point using such age tracers as tritium, and the complementary tracers chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6), to resolve potential age interpretation ambiguities. Only tritium dating is possible in the case of surface waters because the gases equilibrate quickly with the air. Therefore, in the Mill Stream catchment several wells and springs were sampled in addition to streams in order to derive groundwater age information from CFCs and SF_6. Wells were selected with potential to have a similar groundwater residence time to the groundwater discharging into the stream. The oldest water normally discharges into a

stream at the lowest flows near the end of the dry season, when most of the younger water has passed via near-surface flow paths. Therefore special emphasis was on collecting samples at the lowest flow. At such times, the highest age contrast is obtained. As the age of the water changes depending on the flow, water samples were collected for various baseflow scenarios.

1.3 Results

Sample site details, age tracer analytical results and age interpretation results are listed in Tables 1 and 2. Daily average flow at the MST-21 flow recorder on the day of sampling is also listed**.**

Sample collections cover scenarios for baseflows between 195 and 424 L/s, as measured at the flow recorder at MST-21 (Figure 1). The flow of 195 L/s is the lowest flow measured since 2007, and is therefore representative of minimum flow and driest conditions in the area.

1.4 Interpretation

All samples from the streams, springs, and monitoring wells have ambient tritium concentrations within the range of ambient Kaitoke rainfall tritium concentrations indicated by the blue curve (Figure 2).

Well O28W/0220 had been sampled previously in 2006, with a slight degree of ambiguity in age interpretation (Figure 3). It could have been either very young water of < 2 years age (blue line) or older water of 37 years age (red line). After re-sampling in 2011, the ambiguity in age interpretation could clearly be resolved. Only the age 0.5 ± 0.5 years can match the tritium time series data (Figure 3); the old age solution would not match the measure tritium concentration in 2011.

The time series data for well O28W/0015 and for Mill Stream all match an age distribution with a mean residence of 1.7 and 1.8 years. The CFC and SF_6 data for well O28W/0015 are consistent with these short transit times. The Mill Stream flows during February and May 2012 sampling were at the long-term low flows of 0.24 and 0.20 L/s, indicating the driest conditions at this time. If older groundwater were significantly contributing to the Mill Stream flow, it would be at these times. However, none of the samples taken at this low-flow condition indicates significantly older groundwater. All samples fit a mean residence time of 1.8 years.

At a number of sites tritium was measured only once. While in the past decades single tritium measurements at a site frequently resulted in ambiguous age interpretations which required re-sampling a few years later, for the single tritium data from 2011 and later there is very little ambiguity in age interpretation remaining because the bomb-tritium has now faded to below the level of interference (Morgenstern et al. 2010). Therefore all of the tritium data in Table 2 can be interpreted in terms of ages. All of these data indicate water with transit times of less than 2 years. The mean residence times (MRT) for all of the samples are listed in Table 2.

All stream and well water samples in the Mill Stream area have young water with mean residence times of less than 2 years, except well O28W/0219, which was

investigated earlier (see Morgenstern 2007). This well contains old, very evolved water. This water is likely to not be part of active recharge, as the well is probably screened in or below an aquiclude, indicated by the fact that the well runs dry after pumping for just a short time.

1.5 Conclusion

All age tracer data from single and time series tritium analyses, and from CFC and SF_6 analyses, indicate consistently very young water with a mean residence time of < 2 years for all medium and extremely low baseflow scenarios. The hydrogeologic system of the Mill Stream area is such that the water passes through the groundwater system very quickly, with a mean residence time of less than two years. Any impact from land-use activities will be reflected in the Mill Stream discharges within one or two years.

2.0 Wairau and Rai Valley samples

2.1 Results

Six samples were collected for age tracer analysis during 2012 from the Wairau and Rai valleys. Site details, well data, and field parameters are listed in Table 3. Hydrochemistry data are listed in Table 4.

2.2 Age interpretation

Age tracer data for the various samples are listed in Table 5, including the mean residence times (MRT).

Well P28W/3667:

Only tritium is available for this site, but the low tritium concentration indicates, without ambiguity, older water of with a MRT of c. 215 years.

Well P28W/3390:

This water does not contain tritium (MRT > 240 years) and has an extremely low ^{14}C concentration. Using the ^{14}C correction from Morgenstern et al. 2008, the calculated ^{14}C age is 32,500 years. This water originates from a previous glacial period. Also the hydrochemistry data indicate highly evolved water. Therefore, the high concentrations of arsenic, phosphate, and boron are deduced to be from geogenic sources. This water is too old to indicate contamination by the landfill upstream.

Well O28W/4476:

The age parameters are based on a fit to the tritium and SF_6 data. This is very young water with a MRT of 1 year. The water is oxic, and hydrochemistry parameters are compatible with young water. The high nitrate indicates impact by land-use activities.

Well P27W/0542:

This well also contains young water with a MRT of 4 years, based on tritium and SF_6 data. The CFCs are likely to be degraded. Marginal iron elevation may also indicate

an anoxic history, even though the water was slightly oxic at the sampling point. Low nitrate may be a result of absence of nitrate contamination in the capture zone, or of denitrification. Elevated Na, Cl, and Br indicate influence by seawater for this well, which is situated close to the coast.

Well O27W/0119:

This well contains old water with a MRT of 155 years, as indicated by low tritium. SF_6 and CFC11 are low in relation to the present atmospheric equilibrium concentration, but too high for this old age, indicating possible slight contamination. CFC12 is highly contaminated. The water is anoxic, and slightly elevated Na, Cl, and Br also indicate seawater influence, even though the water is not close to the coast.

Well 10323:

This water has a MRT of 7.5 years, based on tritium only. Elevated nitrate indicates impact by land-use activities.

3.0 References

Davidson, P. (2012 *pers. comm.*) Marlborough District Council, Blenheim, mdc@marlboroughlgovt.nz.

Morgenstern, U. (2007) GNS Letter Report 2007/334LR

Morgenstern, U.; van der Raaij, R.W.; Trompetter, V.; McBeth, K. (2008) The Marlborough Deep Wairau Aquifer sustainability review 2008: isotopic indicators. Lower Hutt: GNS Science. GNS Science report 2008/33, 23p.

Morgenstern, U.; Stewart, M.K.; and Stenger, R. (2010) Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit time with streamflow, Hydrol. Earth Syst. Sci. 14, 2289-2301

Stewart, M.K.; Morgenstern, U.; McDonnell, J.J. (2010) Truncation of stream residence time: how the use of stable isotopes has skewed our concept of streamwater age and origin, Hydrol. Process. ,24, 1646-1659, DOI: 10.1002/hyp.7576, 2010

Yours sincerely

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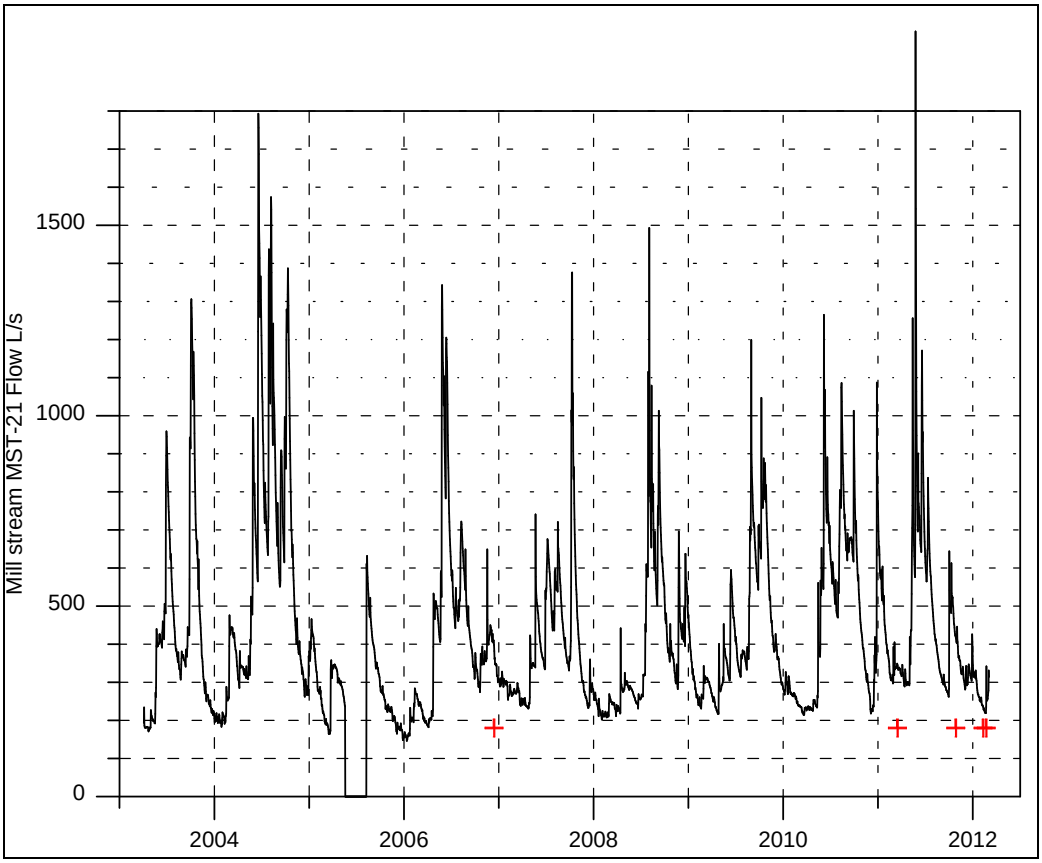

Figure 1: Measured flow at Mill Stream MST-21 recording site. Red crosses indicate sampling times. Flow data from Davidson (2012).

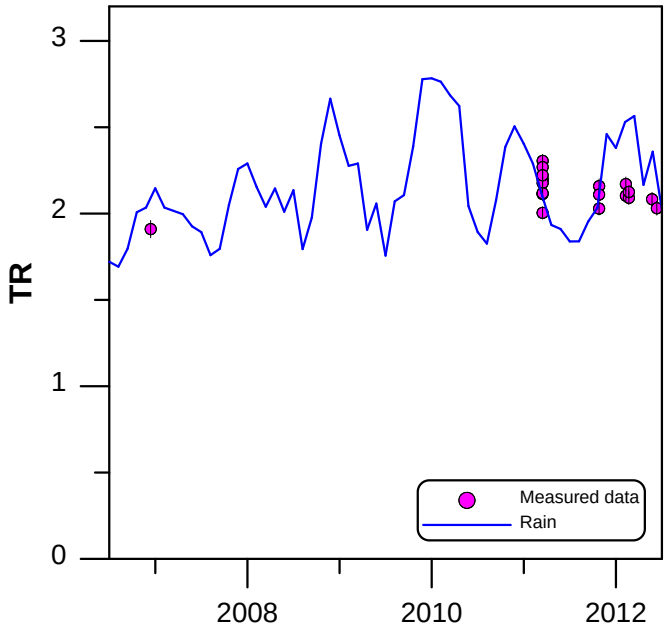

Figure 2: Measured tritium concentrations in the Mill Stream groundwater discharges (red dots), together with Kaitoke rain data (blue curved line), scaled by factor 1.1 and smoothed by an exponential piston flow model with 0.3 years mean residence time and 50% exponential flow.

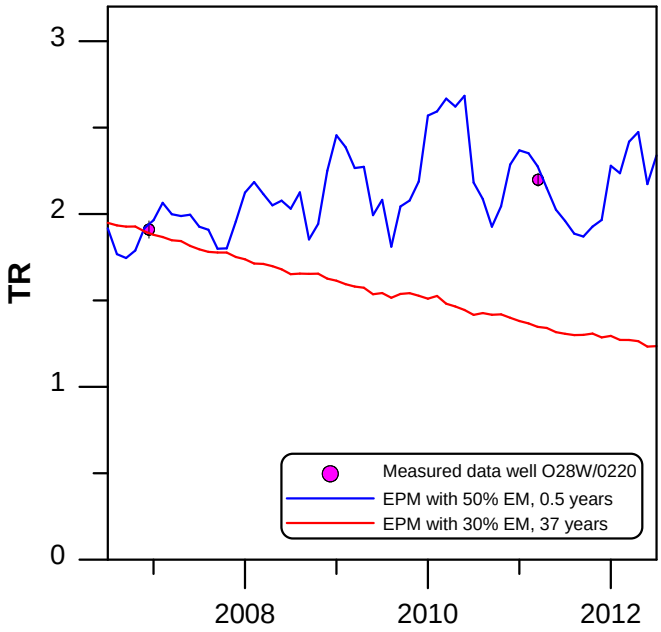

Figure 3: Measured tritium concentration and calculated tritium output for Well O28W/0220. EPM – exponential piston flow model; EM – exponential flow model.

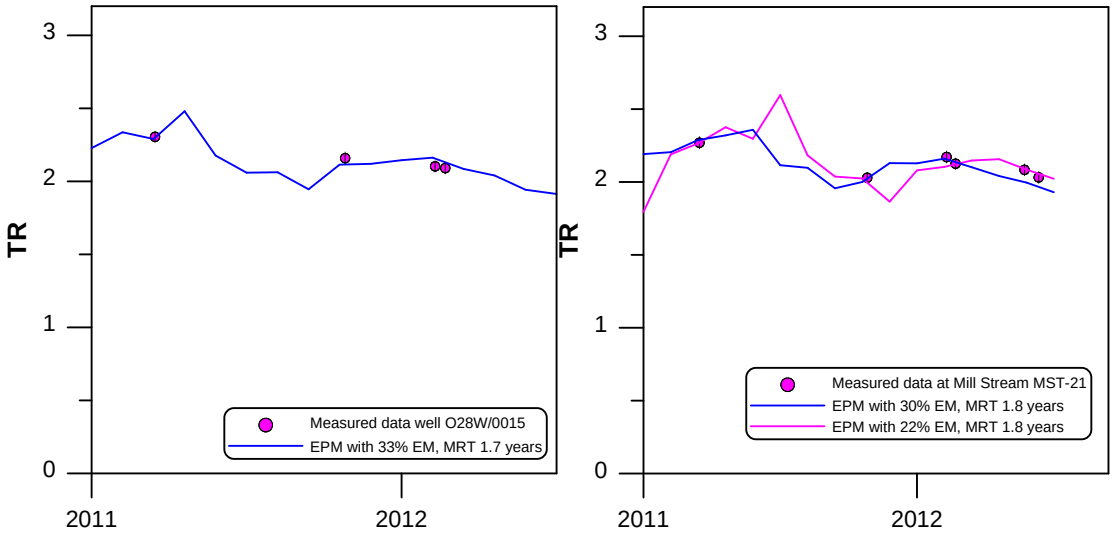

Figure 4: Measured tritium concentrations and calculated tritium outputs for Well O28W/0015 nd for Mill Stream at flow recorder site MST-21. EPM – exponential piston flow model; EM – exponential flow model; MRT – mean residence time.

Table 1: Site information for the Mill Stream area.

ID	Date	site	East	North	Screen [m]		Flow at MST21	Temp	Cond	pH	DO
					upper	lower	L/s	°C	uS/cm		mg/L
O28w/0219	9/05/07	MDC Test well @ Mill Rd									
O28w/0219	4/07/07	MDC Test well @ Mill Rd									
O28W/0220	14/12/06	MDC Wairau Vly shallow test well	2551547	5959435	9.73	12	398				
O28W/0220	17/03/11	MDC Wairau Vly shallow test well	2551547	5959435	9.73	12	347				8.62
O28W/0015	17/03/11	Wairau Valley	1643550	5399624	8.1	10	347				
O28W/0015	27/10/11	Wairau Valley	1643550	5399624	8.1	10	424	12.5	159.7	6.51	
O28W/0015	10/02/12	Wairau Valley	1643550	5399624	8.1	10	237				
O28W/0015	22/02/12	Wairau Valley	1643550	5399624	8.1	10	235				
O28W/0144	17/03/11	Webb irrigation well			7	11	347				8.37
MST-6		Mill Stream @ Ken Anderson									
MST-21	17/03/11	Mill strm at flow recorder	1642825	5398669			347				
MST-21	27/10/11	Mill strm at flow recorder	1642825	5398669			424	13.5	147.3	7.23	
MST-21	10/02/12	Mill strm at flow recorder	1642825	5398669			237				
MST-21	22/02/12	Mill strm at flow recorder	1642825	5398669			235				
MST-21	24/05/12	Mill strm at flow recorder	1642825	5398669			195				
MST-21	12/06/12	Mill strm at flow recorder	1642825	5398669			490				
MST-26	17/03/11	Stm Tributary at Mill Rd	1641651	5397519			347				
MST-26	27/10/11	Stm Tributary at Mill Rd	1641651	5397519			424	13.2	145.9	6.64	
MST-28	17/03/11	Excell at well pump, the terraces					347				
WST-7	17/03/11	Walkers Stream at Parsons					347				
WVL-10	17/03/11	Spring seep feeding upper Walker Stm					347				

Table 2: Age tracer analysis and age interpretation results for the Mill Stream area.

ID	Date	Lab ID	TR	±	CFCs	CFC-11	±	CFC-12	±	SF_6		±	Kait	EM%	MRT	±MRT
						pptv		pptv			pptv			estim		
O28w/0219	9/05/07	TMB85	0.014	0.021												
O28w/0219	4/07/07	TMB87	0.003	0.026		1.9		29000			1.08					
O28W/0220	14/12/06	TMB83	1.91	0.05		166		442			5.26		1.1		**0.5**	**0.5**
O28W/0220	17/03/11	TMB114	2.198	0.038												
O28W/0015	17/03/11	TMB115	2.305	0.038												
O28W/0015	27/10/11	TMB123	2.159	0.042	FMB81	252	22	471	43	SMB75	7.02	0.69	1.1	33	**1.7**	**0.7**
O28W/0015	10/02/12	TMB130	2.103	0.038												
O28W/0015	22/02/12	TMB132	2.091	0.039												
O28W/0144	17/03/11	TMB111	2.177	0.038									1.1		1	1
MST-6																
MST-21	17/03/11	TMB112	2.269	0.041									1.1	30	**1.8**	**0.7**
MST-21	27/10/11	TMB122	2.029	0.037									or			
MST-21	10/02/12	TMB129	2.171	0.041									1.1	22	**1.8**	
MST-21	22/02/12	TMB131	2.125	0.039												
MST-21	24/05/12	TMB138	2.083	0.04												
MST-21	12/06/12	TMB140	2.031	0.04												
MST-26	17/03/11	TMB110	2.222	0.039									1.1	40	1.9	0.7
MST-26	27/10/11	TMB121	2.11	0.038												
MST-28	17/03/11	TMB113	2.113	0.038									1.1		1	1
WST-7	17/03/11	TMB109	2.004	0.036									1.1		1	1
WVL-10	17/03/11	TMB116	2.118	0.037									1.1		1	1

TR = 1 corresponds to a ratio T/H = 10^{-18}; Kait – scaling factor to Kaitoke tritium record; EM% - percent of exponential flow volume within the exponential piston flow model; MRT – mean residence time; red font indicates contamination.

Table 3: Site details, well data, and field parameters for Wairau and Rai valley wells

Well_ID	Name	East	North	well depth [m]	Screen [m] top	Screen [m] bottom	water level (m)	confined aquifer?	Temp °C	Cond uS/cm	pH	DO mg/L
P28W/3667	Hinepango Deep							highly confined	15.6	261	8.22	0.13
P28W/3390	Aerodrome Rd	2587426	5962889	19.4	14.4	19.4	9.801		15.2	1027	7.59	0.11
O28W/4476	MacKenzie	2533428	5950481	16.36	13.6	16.36		unconf.	13.9	163	5.5	6.71
P27W/0542	Twidle Island farm	2571167	5992319	13.1	12.2	13.1	2.957		14.2	419	6.15	1.57
O27W/0119	Rai Valley Merryn Prattley Farm	2559091	5996151	16.6	11	14	3.663	unconf. Rai-Pe	14.8	324	7.46	0.41
10323	Rai Valley Merryn Prattley Farm			16	6.5	8.5		unconf. Rai-Pe	14.6	148	6.22	33%

Table 4: Hydrochemistry data for Wairau and Rai valley wells

Well ID	chem date	Bicarbonate (as HCO_3)	Alkalinity (as $CaCO_3$)	NO_3-N	NH_4-N	Br	F	Cl	SO_4	Mn	Fe	B	K	Ca	Na	Mg	Silica	DRP	As
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
P28W/3667								25							54				
P28W/3390	7/03/12	198	162	0.003	0.79	0.54	0.07	220	0.5	0.48	0.38	1.08	0.5	32	143	3.3	24	1.39	0.103
O28W/4476	6/03/12	41	34	4.8	0.01	0.05	0.05	14	9.6	0.0102	0.01	0.07	1.3	10	11.1	3.4	16.7	0	0.001
P27W/0542	7/03/12	69	57	0.2	0.01	0.28	0.05	84	17	0.0053	0.1	0.06	2.5	5	60	7.1	17.5	0.05	0.001
O27W/0119	7/03/12	114	94	0.3	0.01	0.12	0.05	58	3.1	0.2	0.01	0.08	0.9	18.3	39	7.2	19.2	0.01	0.001
10323		51		2.8	0.01	0.05	0.07	7.8	7.6	0.001	0.01	0.04	0.7	9.9	6.2	7.6	17.7	0.01	0.001

Table 5: Age tracer data for Wairau and Rai valley wells. MRT - mean residence time. E%PM estim - estimated % of exponential flow within an exponential piston flow model. Data in red indicate contamination or gas exchange.

Well ID	Tritium sampl date	Code TMB	TR	sigTR	gas sampl date	#SF_6	SF_6 pptv	±	CFC11 pptv	±	CFC12 pptv	±	Concentration in solution mL(STP)/kg Ar	±	N_2	±	rech temp °C	±	exc air ml(STP)	±	CH_4 µmol/L	±	^{14}C ID	pmc	±	^{13}C	q	^{14}C age y	E%PM estim	MRT
P28W/3667	24/02/12	133	0.105	0.016																									80	215
P28W/3390	7/03/12	134	0.027	0.014	7/03/12	SMB76	0.19	0.04	19	4	95	31	0.37	0.01	16.89	0.15	21.2	1.9	6.6	0.6	1132	54	CMB 10	1.17	0.05	-14.2	0.6	32500	80	>240
O28W/4476	6/03/12	135	2.101	0.036	6/03/12	SMB77	6.13	0.46	188	14	524	42	0.38	0.01	15.15	0.14	11.6	1.3	2.0	0.6	<1								70	1
P27W/0542	7/03/12	136	1.695	0.031	7/03/12	SMB78	5.44	0.40	108	8	328	30	0.40	0.01	16.11	0.14	10.3	1.3	2.1	0.6	<1		CMB 11	101.9	0.22	-18.2	0.8		40	4
O27W/0119	7/03/12	137	0.132	0.016	7/03/12	SMB79	1.53	0.12	32	3	762	61	0.44	0.01	18.81	0.23	8.8	1.4	5.0	0.8	<1								70	150
10323	28/05/12	139	1.512	0.035																									70	7.5