

**Interpretation of isotopic and chemical testing of  
groundwaters in the Takaka Valley (Envirolink grant  
1810-TSDC137)**

MK Stewart

**GNS Science Consultancy Report 2018/46  
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### **BIBLIOGRAPHIC REFERENCE**

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## EXECUTIVE SUMMARY

The results of isotopic and chemical sampling in September 2017 were examined in this Envirolink project to improve understanding of the recharge mechanisms to Arthur Marble and Te Waikoropupu Springs in the Takaka Valley. The samples represented a snapshot in time and built on the work of Stewart and Thomas (2008) by extending the record of isotopic and chemical measurements forward in time. The stable isotope measurements gave clear identifications of the water sources contributing to each sample based on the three recharge sources established by Stewart and Thomas (2008). Tritium ages for the Main Spring (7.9 years) and Fish Creek Spring (3.3 years) were as found earlier. Features sampled for the first time generally had young ages (0–2 years), except Dancing Sands Spring (5.8 years) which had age intermediate between the Main and Fish Creek Springs. The chemical results, which have been analysed more often than the isotopes, showed effects due to previously identified trends. These are (1) nutrients slightly higher in springs and bores in the upper valley (the higher value of nitrate-N of 4 mg/L for Savages Bore may be an anomaly), (2) input of small percentages of sea water to the Te Waikoropupu Springs and Balls Bore, and (3) input of carbonate-derived solutes to the Te Waikoropupu Springs and some other features.

## 1.0 INTRODUCTION

Tasman District Council (TDC) commissioned GNS Science to interpret water samples collected in the Takaka Valley for isotope and chemical analyses to inform the TDC as it develops its Takaka Water Management Plan and also contribute to information for the Water Conservation Order sought for the Te Waikoropupu Springs (TWS) and connected aquifers.

The TDC collected water samples from various sources in the Takaka Valley in September 2017, and had them analysed for isotopes and chemicals. The results of these measurements are combined with those from earlier studies (Stewart and Williams 1981; Stewart and Thomas 2008) and evaluated in this report to improve understanding of the recharge mechanisms to the Arthur Marble Aquifer and TWS. This study was funded by the Ministry for Business, Employment and Innovation Envirolink grant 1810-TSDC137.

## 2.0 METHODS

Samples were collected in September 2017 by TDC staff for this study. The study comprised environmental tracer and chemical measurements of one river, five springs and four boreholes with locations shown in Figures 1 and 2 (Thomas and Harvey 2013). Additional measurements from TWS Main Spring (MS) during 2017 were accessed from the National Groundwater Monitoring Project (NGMP) of GNS Science (2018). The environmental tracer analysis included stable isotopes (oxygen-18 and deuterium) and tritium. The chemistry analytical suite consists of alkalinity ( $\text{HCO}_3$  or T alk), sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), dissolved reactive phosphate (DRP), chloride (Cl), nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) and sulphate ( $\text{SO}_4$ ). Analytical method and laboratories are summarised in Table 1.

Water sample collection included field measurements (temperature, pH and conductivity) as these parameters are not stable and will change between in-situ and laboratory conditions. The three types of measurement provide different pieces of information about the system; stable isotope concentrations identify water sources, tritium concentrations enable estimation of water mean residence times and chemistry indicates chemical signature and evolution. Estimation of mean residence times from tritium are made by simulating the tritium concentrations using a lumped parameter model (in this case the exponential piston flow model (EPM)) to describe the hydrological system. The model has two parameters; mean residence time and exponential fraction (the fraction of the system that is described by the exponential - part of the model). This procedure is explained in Stewart and Thomas (2008).

Table 1: Analysis methods and laboratories.

Analytical test	GNS Science facility
Mass spectrometry (Oxygen-18, deuterium)	Stable Isotope Laboratory
Radiometric detection, electrolytic enrichment and low level scintillation detectors (Tritium)	Water Dating Laboratory
Anions by Ion Chromatography (Cl, $\text{NO}_3\text{-N}$ , $\text{SO}_4$ ), APHA 4110B	New Zealand Geothermal Analytical Laboratory services
Cations by Inductively-Coupled Plasma Optical Emission Spectrometry (Ca, Mg, Na, K), APHA 3120B	
Flow Injection Analysis with electrochemical detection (DRP), APHA 4500-P G (modified)	
Basic Water Chemistry (pH, conductivity, T alk)	

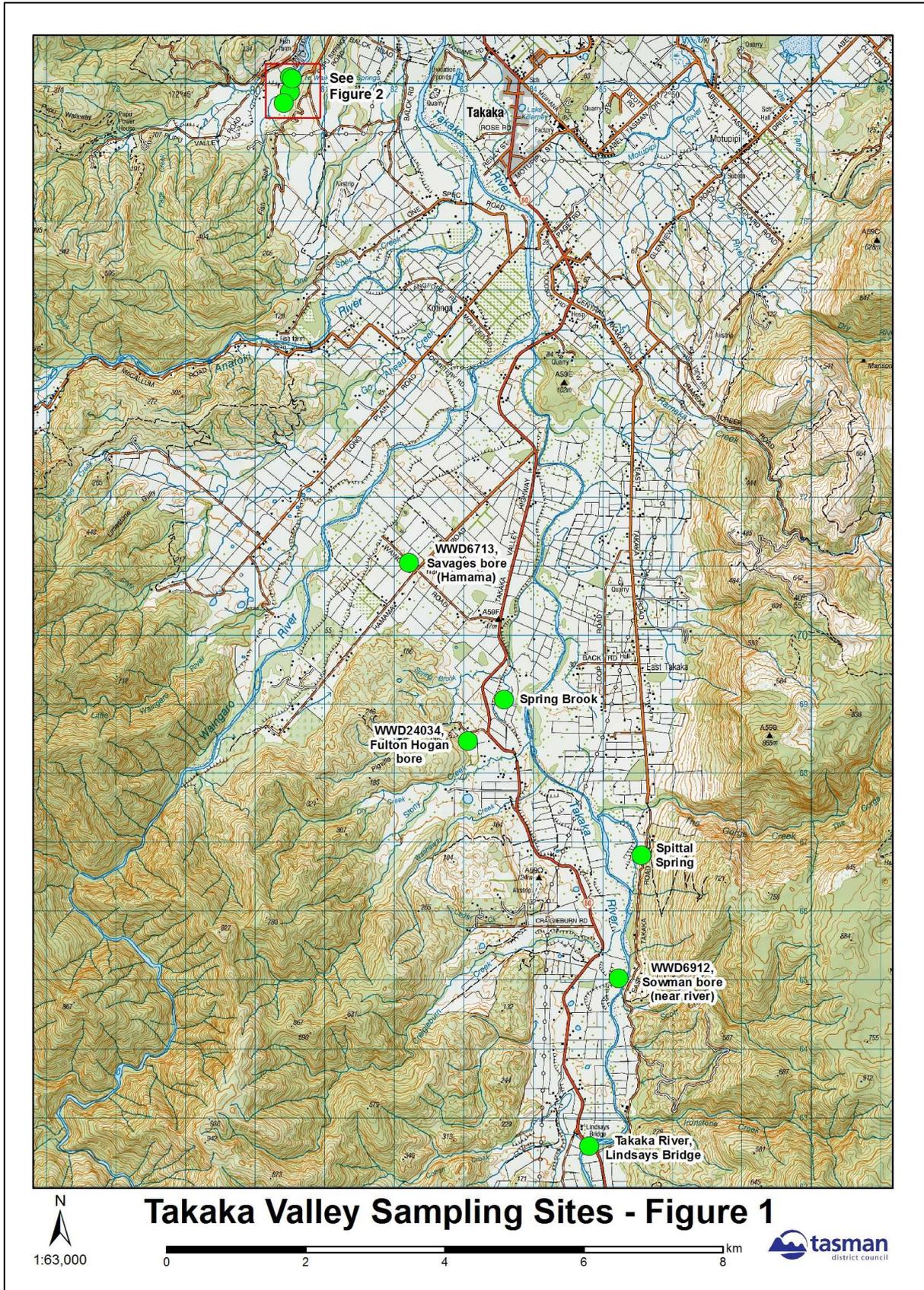


Figure 1: Takaka Valley sampling sites.

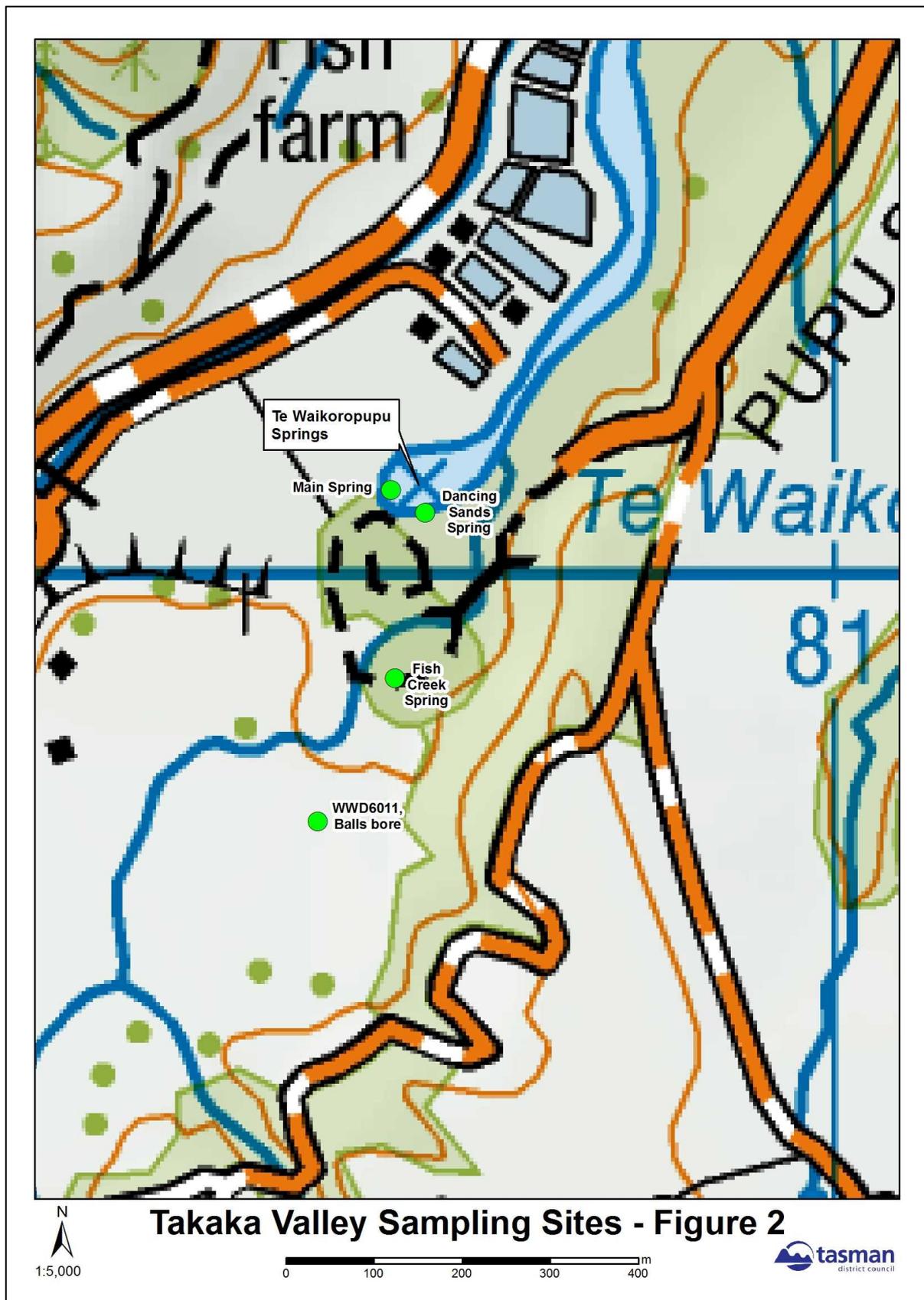


Figure 2: Te Waikoropupu Springs sampling sites and Balls Bore.

### 3.0 RESULTS

#### 3.1 Stable Isotopes

The results of the isotope measurements are given in Table 2.

The stable isotope compositions of the samples are plotted in Figure 3. The 2017 samples represent a snapshot of the Takaka Valley system in time. The stable isotope compositions fit a line (called the local meteoric water line) given by

$$\delta^2H = 8.0 \delta^{18}O + 12.4 \quad (1)$$

which is like that observed in the earlier work (Stewart and Williams 1981); i.e.

$$\delta^2H = 8.0 \delta^{18}O + 13.0 \quad (2)$$

showing that consistent results were obtained for both  $\delta^{18}O$  and  $\delta^2H$  in 2017.

The three TWS springs MS, Dancing Sands Spring (DS) and Fish Creek Spring (FS) plot near the middle of the line indicating they have a mixture of sources (Karst Uplands, Takaka River and Valley Rainfall), consistent with the previous interpretation (Stewart and Thomas 2008). Spring Brook (SB) has an isotopic composition similar to the TWS springs. The sample from Takaka River (TR) has the most negative  $\delta$  values as expected from previous results. The Sowman Bore (SO) plots near TR indicating input of a large fraction of river water. The Balls Bore (BB), Spittal Spring (SS) and the Savages Bore (SA) have increasing inputs of Valley Rainfall. The Fulton Hogan Bore (FH) has the least negative  $\delta$  values, showing it contains a large fraction of Valley Rainfall.

Sampling in 1976–1979 had shown considerable variations in the  $\delta^{18}O$  values of the TWS springs (from -7.0 to -7.6‰ for MS and -7.3 to -8.0‰ for FS). The variations were short-term (month to month), seasonal and longer term (with steady trends over the four years of sampling). The average values are plotted in Figure 4. However, the 2017 samples have values outside the range of those seen in 1976–1979. This is apparent from the plot of  $\delta^{18}O$  values versus chloride concentrations (Figure 4), where the 2017 mixing line (blue) is strongly displaced to the right (i.e. to less negative  $\delta^{18}O$  values) of the 1976–1979 mixing line (orange). Single samples are expected to show variations because they represent only a snapshot in time, so a consistent period of regular sampling would be needed to identify longer-term average changes in the system.

Table 2: Tritium and stable isotope concentrations of Takaka Valley samples.

Symbol	Feature	Date	Tritium (TU)	sd (TU)	$\delta^2H$ (‰)	$\delta^{18}O$ (‰)
MS	TWS - Main Spring	19/09/2017	1.289	0.033	-41.5	-6.77
DS	TWS - Dancing Sands Spring	19/09/2017	1.367	0.034	-42.8	-6.85
FS	TWS - Fish Creek Spring	19/09/2017	1.433	0.036	-43.0	-6.99
BB	Balls Bore, TDC well ID WWD6011	19/09/2017	0.935	0.028	-40.5	-6.47
TR	Takaka River @ Lindsays Bridge	19/09/2017	2.213	0.046	-49.5	-7.84
SO	Sowman Bore, TDC well ID WD6912	27/09/2017	2.072	0.043	-48.6	-7.61
SA	Savages Bore, TDC well ID WD6713	27/09/2017	1.768	0.040	-37.2	-6.09
SB	Spring Brook	27/09/2017	1.604	0.037	-41.8	-6.80
SS	Spittal Spring	27/09/2017	1.892	0.041	-38.8	-6.59
FH	Fulton Hogan Bore, TDC well ID WWD24034	27/09/2017	1.628	0.037	-31.5	-5.41

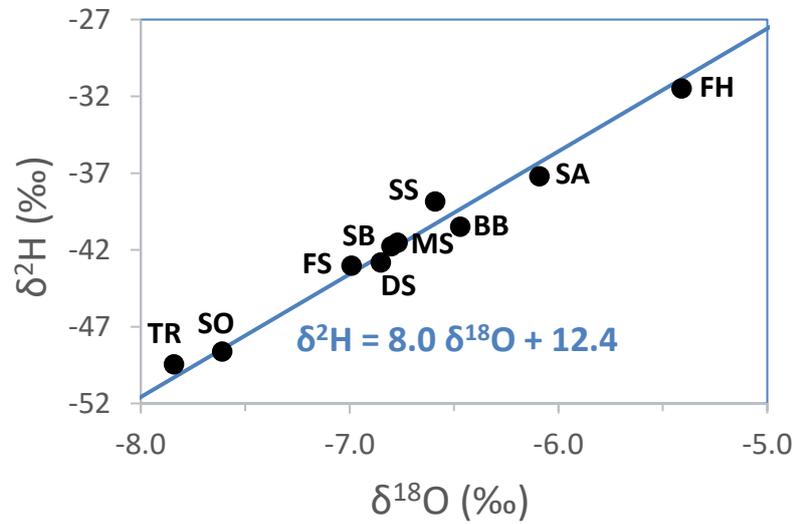


Figure 3: Stable isotope compositions of 2017 samples.

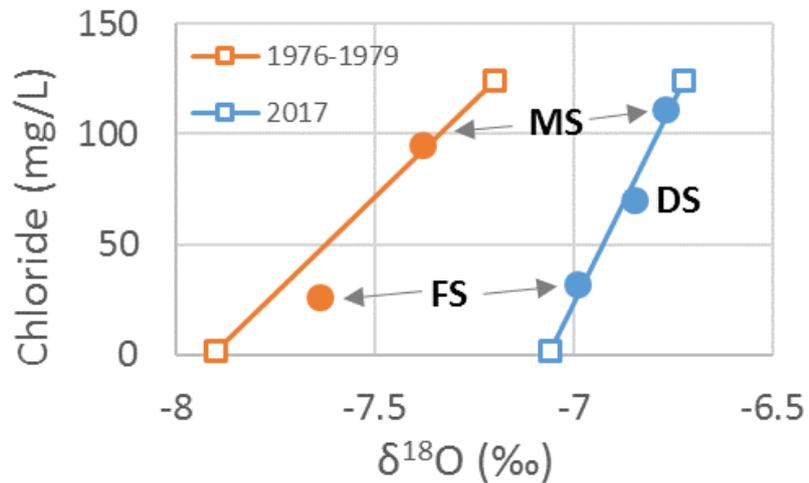


Figure 4:  $\delta^{18}\text{O}$  values versus chloride concentrations for 1976–1979 and 2017 samples. The squares represent the deep and shallow systems (end members) identified by Stewart and Thomas (2008). (The deep end member has relatively high chloride and the shallow end member near-zero chloride concentrations.)

### 3.2 Tritium

Tritium concentrations are given in Table 2 and mean residence times (water age) determined from them are given in Table 3. The MS result confirms previously reported results (with overall age of 8 years, and two water components with ages of 1 and 10 years; Stewart and Thomas 2008). DS has a water age of 5.8 years, intermediate between the MS and FS ages, the latter being 3.3 years. BB has an EPM water age of 46 years and applying a model with two water components gives two very different age components with 63% of 4.5 year-old water and 37% of 155 year-old water (and an overall age of 60 years). TR has a very young water age (0.2 year), as do the groundwaters in bores SO, SA and spring SS (0.6, 0.3, and 0.1 years, respectively). SB (1.8 years) and FH (1.7 years) have water ages a little older than the other groundwaters.

Table 3: Mean residence times based on the tritium concentrations. The exponential piston flow model (EPM) with exponential fraction = 70% was used for features where there was only one measurement. Previous tritium measurements from each feature have been included where available.

Symbol	No. of samples	Mean residence time estimated using EPM model (years)	Exponential fraction (%)
MS	10	7.9	94
DS	1	5.8	70
FS	2	3.3	100
BB	2	46	100
TR	5	0.2	100
SO	2	0.6	100
SA	1	0.3	70
SB	1	1.8	70
SS	1	0.1	70
FH	1	1.7	70

### 3.3 Chemistry

The chemical compositions of the samples are given in Table 4. Here the first two columns are nutrients (NO<sub>3</sub>-N and DRP), the next five are solutes given to TWS by addition of sea water (Cl, SO<sub>4</sub>, Na, K and Mg) and the final two are solutes contributed by interaction with carbonate rocks (T Alk and Ca). NO<sub>3</sub>-N concentrations are low but variable among the groundwaters. The TWS springs (MS, DS and FS) have constant values around 0.4–0.5 mg/L and BB has a value around half of that, but has the highest DRP. SA and FH have the highest NO<sub>3</sub>-N concentrations at 4.0 and 1.1 mg/L respectively; the SA value is anomalous and not consistent with other marble bores in the vicinity. There may have been issues with this sample because of difficulty in pumping the bore. Retesting of this and the nearby two bores is recommended. Sea water solutes are seen in the TWS springs and to a lesser but still significant extent in BB. Carbonate-derived solutes are seen in the TWS springs and several of the other groundwaters.

Several samples were collected from MS for chemical analysis in 2017 (Table 5) and the flow versus chloride concentrations from these are plotted in Figure 5. The trend line for the 2017 samples differs from the line for the 1976–1979 samples (from Stewart and Thomas 2008), suggesting that there may be longer term (40 year) changes in the relationship between flow and sea water input. Although the flow was measured differently in 1976–1979 (the flow was the total of MS flow plus FS flow, whereas in 2017 it was just the MS flow), an attempt was made to correct for this in the Stewart and Thomas (2008) paper by putting the line on the left edge of the points. So, it remains an intriguing possibility that the relationship with sea water input has changed over the 40 years between samplings.

Table 4: Chemical compositions of samples in mg/L.

Symbol	NO <sub>3</sub> -N	DRP	Cl	SO <sub>4</sub>	Na	K	Mg	T Alk	Ca
MS	0.43	0.004	111	19	65.0	4.9	9.2	203	64.0
DS	0.53	0.004	70	13.1	40.0	3.9	6.7	158	58.7
FS	0.44	0.004	32	7.8	21.0	2.5	4.4	143	52.3
BB	0.26	0.260	12.1	4.3	8.9	2.2	3.2	137	49.7
TR	0.11	0.001	2.5	2.0	2.3	0.3	2.3	40	13.2
SO	0.52	0.008	2.5	2.4	2.4	0.3	2.8	45	15.2
SA	4.00	0.008	2.9	5.9	4.0	0.6	1.8	24	11.3
SB	0.48	0.005	5.9	3.5	5.2	0.7	2.7	97	38.0
SS	0.19	0.007	2.0	1.1	2.0	0.3	1.2	94	36.4
FH	1.11	0.003	4.8	2.0	3.0	0.7	2.6	195	77.0

Table 5: Flow and chloride concentrations of samples from MS.

Date	Flow (m <sup>3</sup> /sec)	Cl (mg/L)
22/03/2017	9.78	92
28/06/2017	10.3	96
19/09/2017	11.58	111
24/11/2017	10.5	105
13/12/2017	9.85	91

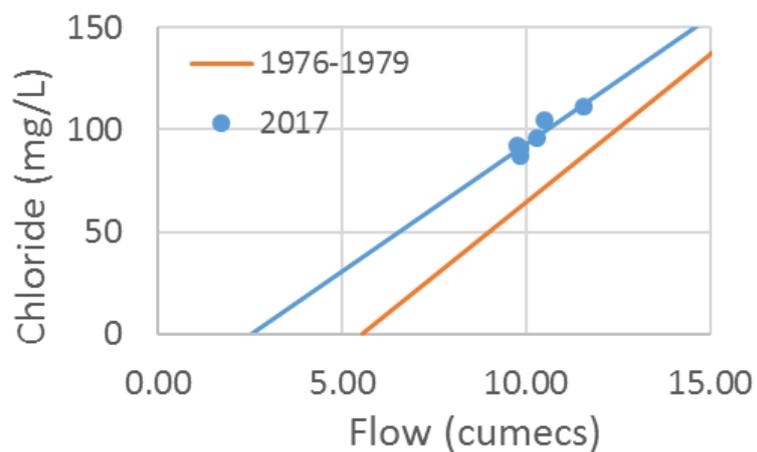


Figure 5: Flow versus chloride concentrations for MS.

## 4.0 DISCUSSION

This report has compared results collected in 2017 with those collected 40 years earlier (reported in Stewart and Thomas 2008). However, many of the 2017 isotopic results were for bores that had not been sampled for isotopes before.

The stable isotopes gave a clear pattern (Figure 3). Three water types (the Karst Uplands, Takaka River and Valley Rainfall recharge waters) were identified by Stewart and Thomas (2008) to be feeding the Takaka Valley groundwaters. The average  $\delta^{18}\text{O}$  values of the recharge waters were -7.2‰ for Karst Uplands, -8.67‰ for Takaka River and -6.0‰ for Valley Rainfall, so Takaka River water plots at the lower left end of the meteoric water line, Valley Rainfall water plots at the upper right end of the line, and Karst Uplands water plots in between.

The new stable isotopic results for the TWS (MS, DS and FS) all plot near the middle of the meteoric water line with isotopic compositions similar to that expected for Karst Uplands water, although they are actually mixtures of all three of the recharge water types with Karst Uplands contributing strongly. Their tritium mean residence times are as previously observed, with DS having a water age (5.8 years) between those of MS (7.9 years) and FS (3.3 years). SB (1.8 years) flows from marble just on the unconfined aquifer side of the boundary with confined marble and plots with this group. Its  $\text{NO}_3\text{-N}$  is like that of the TWS springs, it contains little sea water solutes as expected, and has carbonate-derived solutes.

TR plots in the position expected (lower left in Figure 3) given that the isotopic compositions of individual samples can vary considerably. SO plots very close to it showing strong Takaka River water input. Both TR and SO samples have young water ages and similar chemistries, although  $\text{NO}_3\text{-N}$  and DRP are slightly higher in the SO sample.

FH plots on the upper right end of the line in Figure 3 showing that it is dominated by Valley rainfall, i.e. local rainfall in this part of the valley. The water is drawn from marble at 30 m depth and has an age of about 1.7 years. The water contains some  $\text{NO}_3\text{-N}$ , shows no sea water solutes and has carbonate-derived solutes.

BB, SS and SA all show higher proportions of Valley Rainfall than the TWS springs group (Figure 3). BB draws from a 114 m depth borehole below 33 m of cover (Motupipi Coal Measures) and has a younger component (4.5 years) and a much older component (155 years) probably from depth. The water has a small amount of  $\text{NO}_3\text{-N}$  probably from the shallow component and a higher amount of DRP probably from the deep old component. There is a trace of sea water and carbonate-derived solutes are present. SS draws from marble on the east side of the valley near Rameka Creek. Its age is very young and it has low concentrations of solutes except for some carbonate-derived solutes. SA in Hamama draws from the top of the marble but discharges mainly local rainfall-derived very young (0.3 year) water. Its  $\text{NO}_3\text{-N}$  concentration is the highest of the group at 4 mg/L, but this result is thought to be anomalous. No sea water or carbonate influence is seen.

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[www.gns.cri.nz](http://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