Identifying Pollutant Sources within the Waimea Catchment:

Applying Hydrochemical Tracers to Surface Water Time Series Data

Clint Rissmann and Lisa Pearson

Land and Water Science Report 2018/15
Envirolink 1807-ESRC285
July 2018

Identifying Pollutant Sources within the Waimea Catchment:

Applying Hydrochemical Tracers to Surface Water Time Series Data

Prepared by
Rissmann, C[1,2]. and Pearson, L.[1]

[1]Land and Water Science Ltd.
www.landwaterscience.co.nz
61c Leet Street
Invercargill, 9810

[2]Waterways Centre for Freshwater Management
University of Canterbury
Private Bag 4800
Christchurch

Corresponding Author
Clint Rissmann
Contact number: 03 214 3003
Email: clint@landwatersci.net

Document Information
Land and Water Science Report No: 2018/15
Report Date: 02.07.2018
Project Number: 18008

Reviewed By: Karen Wilson
Organisation: Environment Southland
Position: Team Leader – Science, Strategy, and Design
Review Date: 29.06.2018

Document Status: Final

Citation Advice
Rissmann, C. and Pearson, L. (2018). Identifying Pollutant Sources within the Waimea Catchment: Applying hydrochemical tracers to surface water time series data. Land and Water Science Report 2018/15. p54.

Disclaimer: This report has been prepared by Waterways Centre for Freshwater Management and Land and Water Science Ltd. exclusively for, and under contract to Southland Regional Council (Environment Southland). Waterways Centre for Freshwater Management and Land and Water Science accepts no responsibility for any use of, or reliance on any contents of this report by any person or organisation other than Environment Southland, on any ground, for any loss, damage, or expense arising from such use or reliance. Information presented in this report is available to Environment Southland for use from June 2018.

Table of Contents

List of Figures

List of Tables

1 Introduction

Water quality outcomes vary in both space and time. For a broadly equivalent land use pressure, spatial and temporal variation in water quality reflects the role of the landscape and climatic drivers over hydrological pathway and biogeochemical processes that influence water quality outcomes (Inamdar, 2012). If water quality is to be managed in an efficient manner, identification of both the spatial and temporal controls over water quality outcomes is necessary. Ideally, such an approach would enable the location and timing of likely contaminant loss to the surface water network to be elucidated and subsequently used to inform a more targeted approach to resource management.

Environment Southland is interested in assessing the value of a hydrochemical hydrograph separation method to determining the source of water and contaminants supplying streams for surface water sites within the Waimea Valley, Southland. The work presented here aims to increase temporal resolution and understanding of water source and contaminant supply to the Waimea Stream. It is hoped that this work will contribute to a larger body of work looking at directing the selection of mitigations for improving the health of degraded freshwater ecosystems as mandated by the Ministry for the Environment (MfE), National Policy Statement for Freshwater Management (NPSFM; MfE, 2014).

We therefore apply a novel hydrogrpagh separation method to time series water quality data for surface water sites within the Waimea Valley, Southland, New Zealand. This work exemplifies the need to consider both spatial and temporal variation in catchment properties when considering the source and attenuation of land use contaminants along the main hydrological pathways to the stream channel.

1.1 Objectives

In the following, we apply a new method for hydrograph separation designed for application to lower resolution temporal data sets, such as Environment Southland's State of the Environment (SOE) surface water quality monitoring which is undertaken monthly. Key objectives include:

1. Resolve the temporal variation in water source and associated end-member water quality concentrations

2. Provide a measure of the water quality signatures associated with each water source and associated hydrological pathway

3. Identify the indicies of catchment wetness that govern variation in water source and attendant water quality

4. Provide evidence for spatiotmeporal linkage between climatic drivers and key water source compartments.

1.2 Waimea Catchment

The Waimea stream is located on the northern plains in the Southland Region (Figure 1). The stream originates in hill country and is a tributary of the Mataura River. The Physiographic setting of each site is provided in Table 1.

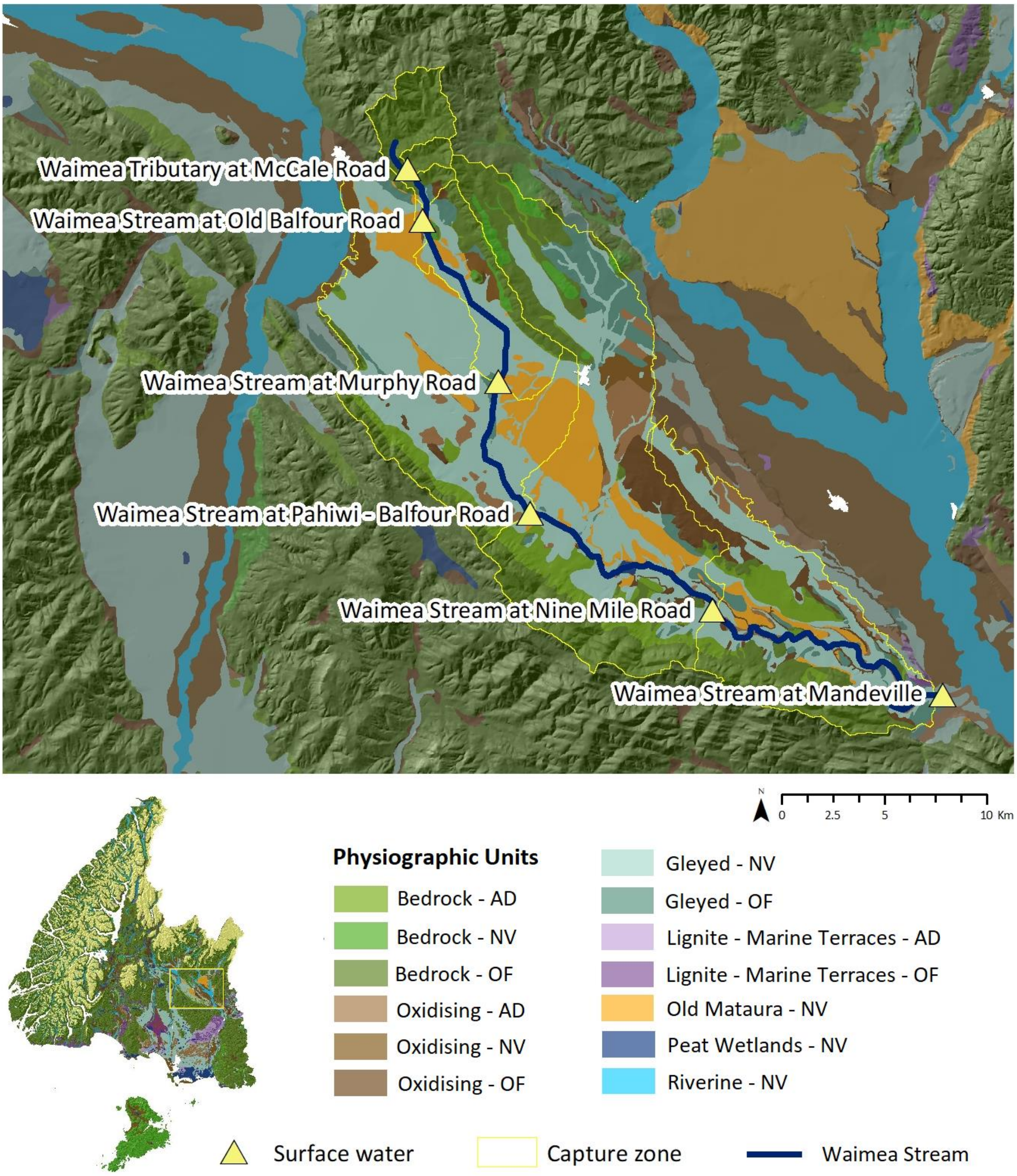

Figure 1: Physiographic setting of the Waimea Valley and location of water quality sites on the Waimea Stream, Southland. NV- no variant, AD – artificial drainage variant, OF – overland flow variant (after Hughes et al., 2016).

Table 1: Physiographic setting of the Waimea Valley, Southland. NV- no variant, AD – artificial drainage variant, OF – overland flow variant.

	McCale Rd	Old Balfour Rd	Murphy Rd	Pahiwi - Balfour Rd	Nine Mile Rd	Mandeville
Bedrock (NV)	0.3	0.7	127.4	128.1	583.3	587.1
Bedrock (AD)	0.3	14.9	54.2	724.3	2,174.5	2,997.0
Bedrock (OF)	293.9	1,755.7	2,385.5	3,213.4	7,093.4	9,245.3
Oxidising (NV)		2.8	165.6	560.9	894.6	1,002.4
Oxidising (AD)		0.5	0.6	382.2	1,183.7	1,831.0
Oxidising (OF)		27.4	58.0	143.3	1,158.1	1,970.4
Gleyed (NV)		38.5	1,527.5	7,765.2	11,932.1	14,713.6
Gleyed (OF)		30.0	162.3	400.8	1,706.1	2,146.8
Lignite - Marine Terraces (AD)						6.9
Lignite - Marine Terraces (OF)						27.4
Old Mataura (NV)		4.1	437.4	2,194.2	3,823.4	4,222.4
Peat Wetlands (NV)					42.9	42.9
Riverine (NV)				6.8	6.8	6.8

2 Background and Literature Review

2.1 Compartmental and geographical water sources

There is a long history of exploiting differences in the hydrochemical composition of water to separate stream flow hydrographs into individual source components and/or hydrological flow paths (Pinder and Jones, 1969; Sklash et al., 1979; O'Brien and Hendershot, 1993; Bazemore et al., 1994; Buttle, 1994; Hooper et al., 1990; Hooper, 2003). All such studies are founded upon a common assumption that water flowing through various watershed compartments (or geographic sources) acquired unique signatures representative of the characteristics of those compartments and that these distinct signatures could be used to determine the contributions from each (Inamdar, 2012).

In most geographical settings there are 3-main 'compartments' that supply stream flow: (i) the land surface and upper ~300 mm of the regolith/soil zone, hereafter 'surficial' compartment; (ii) the soil zone and 'C' horizon, 'soil,' compartment, and; (iii) the aquifer(s)/saturated zone connected to stream, 'aquifer' compartment (Figure 2; Ogunkoya and Jenkins, 1993; Katsuyama et al., 2001, 2009; Inamdar, 2012 and references therein). These main compartments may be naturally subdivided into two or more compartments, for example in areas of stratified aquifers supplying stream.

Separations into the 3-main compartments are simplest when streamflow is derived from a single recharge domain (e.g. Bedrock/Hill Country or Lowland only) or 'geographical source'. However, where stream flow is the product of volumetric inputs from two or more recharge domains separation of the hydrograph becomes more challenging. In this instance, a simple 3-compartment separation, on its own, may not adequately discriminate the compartmental contributions from different geographical sources. Here, varying the number of compartments can aid in better constraining the number of important compartments for multiple recharge domains. For example, a 4-compartment separation may further subdivide an aquifer or soil water compartment identified in a 3-compartment separation.

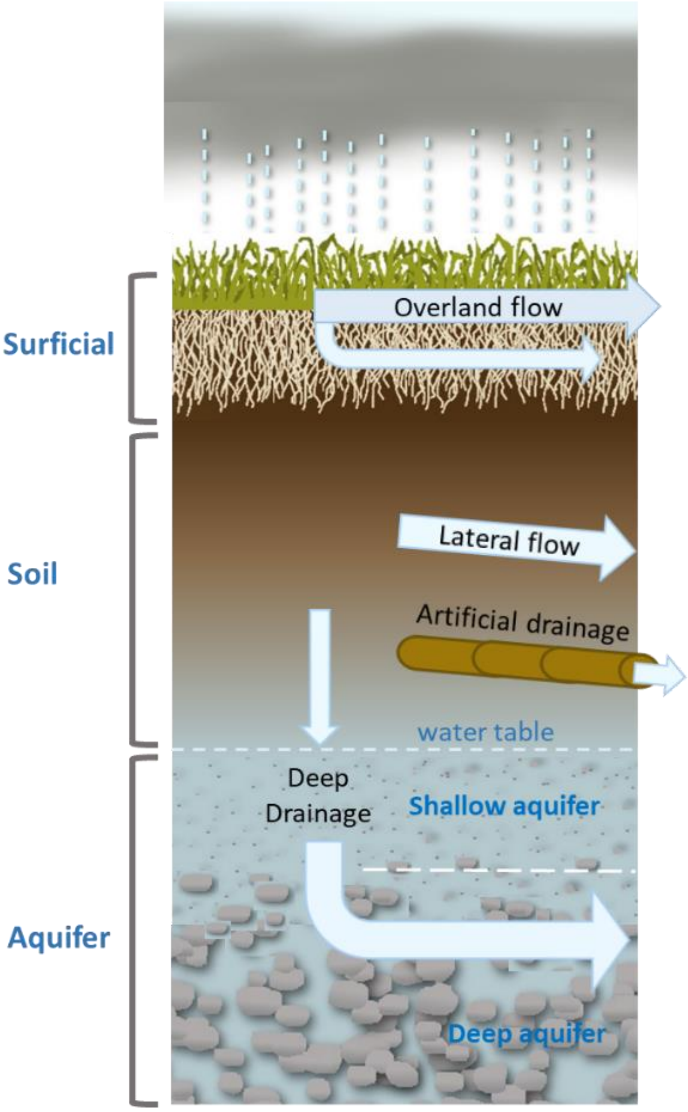

Figure 2: Example of compartments contributing to stream flow and the associated flow paths water takes to the stream (Hughes et al., 2016; Rissmann and Beyer, 2018).

2.2 Hydrograph separation methods

Historically, two main methods have been applied to hydrograph separation: (i) the chemical/isotopic mixing model approach (CIMM; Pinder and Jones, 1969), and; (ii) the more recent Endmember Mixing Model (EMMA) approach of Hooper (Hooper et al., 1990). EMMA was developed in response to limitations associated with the common problem of over-determination associated with the traditional geochemical mixing model approach. Specifically, the inability to use multiple tracers simultaneously to separate the hydrograph into the number of compartments supplying stream flow (Hooper et al., 1990). To overcome this limitation, EMMA employs a multivariate approach to identify the number of 'endmembers' (compartments) supplying stream flow. Despite being able to specify the likely number of end-members, for EMMA to work samples of each end-member are required to validate hydrograph separation. Most commonly these approaches have been applied to 'research datasets' that employ high temporal resolution sampling of stream flows, often under event flow conditions and have not routinely been applied to lower resolution (i.e. monthly) water quality monitoring datasets including long-term monitoring data that characterises State of the Environment (SOE) monitoring (Hooper, 2003; Inamdar, 2012). These research datasets require intensive sampling of both the stream and the inferred source waters or ‘endmembers’ in order to constrain the water source.

To separate a hydrograph chemically a key requirement is the identification of the most suitable tracers. Specifically, suitable tracers are those that are conserved during transit to the stream along a given flow path and during mixing within the stream channel (Pinder and Jones, 1969; O’Brien and Hendershot, 1993; Hooper, 2003; Inamdar, 2012). The most suited tracers are characterised by significant contrasts in concentrations between the compartments supplying stream and should retain a relatively constant concentration over time. Evaluating which tracers meet the above criteria can be challenging given evidence for considerable between-site variation in tracer suitability. Specifically, James and Roulet (2006) noted that the suitability of tracers for hydrograph separation varied between 8 nested catchments within the 1.47 km^2 Westcreek Watershed, Mont Saint-Hilaire, Quebec. Hooper and Shoemaker (1986) found that silica was conserved in the Hubbard Brook Experimental Forest, whereas Christopherson et al. (1990) found silica to be non-conservative at the Birkenes and Plynlimon catchments of Southern Norway. O’Brien and Hendershot (1993) noted that dissolved silica (Si) in upwelling groundwater was not conserved during passage to the stream due to retention by exchange sites within the subsoil. Collectively, these papers cite variability in topographic, soil and/or geological assemblages as the likely cause of variation in tracer suitability between sites, hereafter ‘physiographic setting.’ Accordingly, it is erroneous to assume that a tracer suited for hydrograph separation at one location is suited at another, especially when the compartments supplying stream are associated with distinctly different biogeochemical and hydrological characteristics.

3 TRaCS: Chemical Hydrograph Separation Model

The steps for applying and testing the Tracer and Compartment-Specific Hydrograph Separation (TRaCS) application to long-term data sets for the Waimea Valley is summarised in Figure 3.

Apart from the assessment of tracer suitability and application of multivariate methods, the information underpinning the method, either simple data processing or in the instances of physiographic science, is published elsewhere (Rissmann et al., 2016; Rissmann et al., 2018). Accordingly, here we focus on the technical aspects of assessing tracer suitability and subsequent hydrograph separation using multivariate methods.

Our model assesses the suitability of a wide range of water quality and hydrochemical tracers for separation of stream flow hydrographs into component sources i.e., surficial, soil zone and aquifer (Table 2). We base our approach on the seminal work of Pinder and Jones (1969) and O’Brien and Hendershot (1993) who applied correlation analysis to assess the suitability of tracers for the separation of stream flow hydrographs into source components for sites across North America. These and other works (see also Hooper, 2003; Inamdar, 2012) note that a high degree of correlation, linear or non-linear, with flow is indicative of: (i) strongly contrasting concentrations of a given tracer between the compartments that supply stream flow; (ii) the conservation of the tracer along the hydrological pathway to the stream, and; (iii) conservation of the tracer during mixing within the stream channel. Specifically, our model hypothesises that flow conservative tracers maintain the concentrations characteristic of the compartment (source) they are derived from making them most suited to hydrograph separation and that tracers with a correlation coefficient close to 1 are most likely to meet the assumptions listed above (O’Brien and Hendershot, 1993; Hooper, 2003). Here we use the term ‘conservative’ to denote conservation with flow and not to refer to whether or not a given tracer is ‘chemically ideal.’ Although chemically ideal tracers, such as Cl or $\delta^{18}O\text{-}H_2O$, are widely considered be conservative from a reactivity perspective, this does not mean they will necessarily meet the criteria for conservation with flow, making it erroneous to automatically assume they are suited for hydrograph separation.

DATA PREPERATION

1. QA/QC of long term chemical, flow and meteorological (including soil moisture, temperature and ground water level if available), data for relevant surface water monitoring sites
    a. Each water sample must have flow appended along with available soil moisture, soil temperature, 24Hr/48Hr rainfall, and if available relevant ground water level data
2. Assess representativeness of individual analytes relative to flow data
3. Pre-processing of long-term data for multivariate analysis – RIN transformation

TRACER SUITABILITY

1. Tracer suitability assessment using a correlation matrix – conservation with flow
2. Ranking of tracer suitability according to tier-I through III thresholds for each site

GEOSPATIAL DATA

1. Delineate SW capture zones for each site to be assessed
2. Quantify the relative area of 'physiographic units,' within a capture zone

HYPOTHESIS BUILDING

1. Hypothesise as to the likely number of geographical and compartmental sources supplying streamflow using the number of distinct geographical domains (Recharge Domains) and physiographic units

APPLICATION

1. Apply fuzzy c-means (FCM) to hypothesised number of water sources, vary number of compartments (# of clusters) for testing and refinement of hypotheses
2. Summarise chemical, metrological and climatic statistics for winner clusters for each FCM run
3. Interpret key hydrochemical signatures in terms of maturity and likely source within the context provided by physiographic, climatic and hydrological data
4. Produce a summary of the controls and sources of water and contaminants to stream

Use best model to constrain end-member composition and contaminant concentrations by isolating samples with an FCM proportion >0.9

Figure 3: Tracer and Compartment-Specific Hydrograph Separation method (Rissmann et al., in prep).

Table 2: Hydrograph separation suitability criteria (Rissmann et al., in prep.). The coefficient of correlation, r, may be negative (-) or positive (+) with flow. α is the level of significance (0.01 – 0.05). *It is likely that tier-I-III thresholds would be further refined by application to a larger number of sites (e.g. regional surface water monitoring network).*

Tracer	Correlation coefficient (r)	Probability (p, 2-tailed)	Description	Tracer suitability
Tier-I	≥ ±0.85	$p < \alpha$	Tracers exhibit strong co-linearity with the mixing space	Highly likely to meet the assumptions of conservative mixing and constant end-member mixing
Tier-II	≥ 0.75 <0.85	$p < \alpha$	Tracers exhibit moderately strong co-linearity within the mixing space	Mostly meets general assumptions of conservative mixing and constant end-member composition and able to produce a similar separation to Tier-I tracers
Tier-III	≥ 0.70 <0.75	$p < \alpha$	Tracers exhibit moderate co-linearity within the mixing space	Some failure to meet the assumptions of conservative mixing and constant end-member composition but still able to produce a comparative separation with Tier-I and Tier-II
Hydrological flow path tracer	<0.7	$p < \alpha$	Tracers exhibit weak co-linearity within the mixing space or are only correlated across a restricted flow range	Unsuited for identifying water source but may be a useful tracer of hydrological flow path
Potential tracer of climatically decoupled land use signals	-	$p > \alpha$	Not statistically significant with flow	Unsuited for identifying water source but may still provide useful ancillary data as to potential land use signals that may be decoupled from the general climatic drivers of water source and hydrological flow path

Few if any tracers exhibit a perfect conservation correlation with flow. This may reflect the failure of one or more of the key assumptions listed above and/or poor hydrological estimates of flow (e.g. simulated flow records), a small number of analytes (e.g., water quality only measures) and a lack of representative sampling across the flow range. Therefore, for practical purposes, we propose a 3-tier classification system for assessing the suitability of a tracer for hydrograph separation at surface water monitoring sites characterised by monthly sampling. Our classification system is based on our experience of correlation ranges for streams within the Waimutuku, Waituna and Waimea catchments of Southland. A less subjective classification of correlation thresholds for assigning tracers to tier-I – III classes may be derived mathematically via comparative analysis of streamflow separation of a larger dataset. However, this was not applied here.

According to our criteria, a suitable tracer must be both statistically significant with flow ($p < 0.05$) and exhibit an r value ≥0.85 to achieve tier-I status; such a tracer is most likely to meet the assumptions of conservation with flow. Although tier-II and especially tier-III tracers are less likely to satisfy all of these assumptions they are still considered of value for separating the hydrograph. For example, Rice and Hornberger (1998) concluded that the although the results of a three-compartment separation varied widely between 7 pairs of different tracers (i.e., deuterium and oxygen 18, deuterium and chloride, deuterium and sodium, deuterium and silica, chloride and silica, chloride and sodium, and sodium and silica) broadly consistent patterns in the relative contribution from each compartment were observed. Other works have noted similar variation between tracers although they do not always specify the degree of correlation with flow. Rather they firstly assess co-linearity between tracers as a basis for testing suitability (Hooper, 2003; Inamdar, 2012 and references therein). The later does not provide a basis for ranking tracer suitability although we do note from this work that those tracers that are strongly correlated with flow are also strongly correlated with each other. Specifically, our model hypothesises that flow conservative tracers maintain the concentrations characteristic of the compartment (source) they are derived from making them most suited to hydrograph separation.

Tracers that are statistically significant and yet fail to meet the tier-III correlation criteria (i.e., <0.7) may still provide meaningful information about the hydrological flow path, biogeochemical processes and contaminant source (O'Brien and Hendershot, 1993). For example, although a given species may not be strongly correlated across the flow range it may still be statistically significant and in some instances a useful indicator of when a hydrological pathway is activated. For example, the silica to potassium (Si/K) mass ratio has been used to identify the activation of overland flow with a steep decline in Si/K as the surficial overland flow path is activated (Elsenbeer et al., 1995; 1996). However, once again, it would be incorrect to assume that the Si/K ratio is a useful hydrological pathway tracer in all settings.

Those species that are not statistically significant with flow are considered unsuited for hydrograph separation and inferring hydrological flow path. However, these species may still provide useful ancillary data as to potential land use signals that may be decoupled from the general climatic drivers of water source. For example, E. coli may not achieve significance with flow and yet show elevated numbers under low flow during the drier months of the year in association with Farm Dairy Effluent (FDE) irrigation over artificially drained soils (see Section 6.2).

Importantly, the criteria listed in Table 1 assumes that the sample population provides a reasonable estimate of the actual population variance. Assessment of the representativeness of samples can be undertaken by plotting samples against the flow range for a site and 'eye-balling' the distribution of data. Statistical assessments of the adequacy of sample representation can also be performed (see Ramsey and Hewitt, 2005). Our subjective experience, for a restricted number of locations (i.e. Waimutuku, Waituna and Waimea catchments) suggests a minimum of 30 repeat samples, that are well distributed across the flow range are needed for any meaningful hydrograph separation to better understand the temporal variation in surface water quality at regional monitoring sites. In general, the larger the number of samples the better, although 5 – 10 years of data is easier to manage and less likely to be significantly impacted by changes in land use intensity. In terms of utility for surface water State of the Environment (SOE) monitoring networks, it is ideal if a well-represented, 'standard,' water quality measure(s) attains tier-I – III status as it is more likely to be representative of the flow range and attendant water source signals.

Following an assessment of both the suitability and representativeness of water quality measures for hydrograph separation, tier-I-III tracers provide the input for Fuzzy C-Means clustering (FCM; Güler et al., 2004). We prefer FCM as it is a soft clustering method that allows for the potential transitional composition of stream samples. For example, FCM recognises that a stream sample for a given flow may not be a 100% member of a single cluster or compartment; rather, FCM apportions the membership of samples between groups (compartments) as a gradient ranging between 0 and 1, where the greater the certainty of a sample belonging to a cluster, the closer is its membership degree to 1. During FCM, the number of compartments supplying stream can be specified and varied in order to evaluate the suitability of an nth-compartment solution. A more detailed discussion of FCM is given by Güler et al. (2004).

The plausibility of the TRaCS approach is assessed in terms of the fit with: (i) the climatic drivers of streamflow as recorded by time-series variation in percent saturation of soil pores, soil temperature, precipitation volume; (ii) comparison against hydrological measures of streamflow (i.e., recorder flow or simulated flow), and; (iii) hydrochemical signals of water source and hydrochemical evolution.

4 Data and Processing

4.1 Raw Data

Environment Southland supplied data for continuous flow, soil moisture, soil temperature, and rainfall data for sites close to or within the Waimea Stream catchment for the 2008 – 2017 time period. The data supplied included soil moisture, soil temperature and rainfall at the 'Balfour at Glenure St Patricks Rd' site and 'Riversdale Aquifer at York Road' metrological sites. Rainfall only data was also supplied for the 'Waimea at Mandeville' and the 'Oreti at Lumsden Cableway' sites. All sites have a simulated flow record, but only the 'Waimea at Mandeville' has recorded flow.

Discrete water quality samples (n = 641) taken between 2008 – 2016 were supplied for 6 long-term monitoring sites along the Waimea Stream (Table 3). Soil moisture, soil temperature, flow (simulated or recorded) and rainfall was assigned to each sample according to the sample timestamp.

Table 3: Site details. Number of samples is for water quality measures only; a smaller subset contains hydrochemical measures.

Site Name	Easting	Northing	No. of samples
Waimea Tributary at McCale Road	1248787	4924372	78
Waimea Stream at Old Balfour Road	1249506	4921879	79
Waimea Stream at Murphy Road	1253192	4914018	79
Waimea Stream at Pahiwi - Balfour Road	1254753	4907611	78
Waimea Stream at Nine Mile Road	1263616	4902923	80
Waimea Stream at Mandeville	1274804	4898793	122

4.2 Data QA and QC

Environment Southland undertakes quality assurance assessments of all data prior to archiving. This includes checking of all hydrological and water quality data according to national protocols.

Censored values were removed from the dataset and the method detection limit was retained. Following the removal of censored data, additional evaluation of the water quality data set for outliers was undertaken by comparing water quality measures against flow. No obvious outliers were observed, although we noted that on occasion dissolved oxygen (DO) saturation had been entered into the field for DO concentration, these minor issues were rectified.

4.3 Data Processing

A rank-based inverse normal transformation (RIN) was then applied to all discrete water quality data and associated hydrological information (Bishara and Hittner, 2012):

$$f(x) = \phi^{-1}\left(\frac{x_r - 1/2}{n}\right) \qquad \text{(Equation 1)}$$

Where x_r is the ascending rank of x, such that $x_r = 1$ for the lowest value of x, ϕ^{-1} is the inverse normal cumulative distribution function and *n* is the sample size. RIN transformation was preferred due to its ability to approximate normality regardless of the original distribution shape, reducing the chances of Type I and Type II errors (Bishara and Hittner, 2012). Application of a RIN transformation is particularly useful when dealing with a wide range of measures, many of which may have different distributions with respect to flow.

Following transformation, a correlation matrix utilising the three most commonly used correlation coefficients (Pearson, Spearman, Kendall) is applied to the time series data set for each site. For each measure, the correlation coefficient with the strongest r value is retained for use. All statistically significant ($p < 0.05$) correlations between flow and water chemical measures, soil moisture, soil temperature and rainfall were identified. Correlation coefficients for all significant results were ordered into tier-I, tier-II and tier-III tracers according to the criteria presented in Table 1.

Tracers meeting tier- I-III criteria form the input for Fuzzy c-means (FCM) clustering using the KNIME Analytics, Visual Modelling Software Platform (v. 3.5.2.). Here tier-I tracers are the preferred input to FCM as they are considered most suited to hydrograph separation. However, not all sites have tracers that meet the tier-I criteria, in which case tier-II or tier-III tracers are used. Within the KNIME Visual Modelling Platform, the number of clusters must be specified before running FCM. As noted above, the hypothetical number of clusters are assigned according to the number of recharge domains (i.e., geographical sources) and the proportional area of physiographic units. Separate runs using a variable number of clusters aids in testing and refining the hypothesised number of geographical and compartmental sources supplying stream.

5 Results and Discussion

5.1 Tracer Suitability and Representativeness

The correlation of tracers with flow for each site is summarised in Table 4 and those suitable for hydrograph separation are identified in Table 5 according to the three levels of suitability (i.e., tier I – III). As anticipated the suitability of tracers varies between sites reflecting different physiographic settings (i.e. atmospheric, hydrological, redox, and weathering ‘driver layers’; Rissmann et al., 2016).

Table 4. Correlation of hydrological and water quality measures with flow (Q) for surface water monitoring sites on the Waimea Stream, Southland. All units in mg/L, unless otherwise indicated. Tier-I tracers ≥ 0.85; tier-II ≥0.75<0.85; tier-III ≥0.7<0.75. n.s. = not statistically significant with flow.

	McCale Rd	Old Balfour Rd	Murphy Rd	Pahiwi – Balfour Rd	Nine Mile Rd	Mandeville
Soil Moisture (water filled pores, %)	0.88	0.87	0.88	0.89	0.91	0.89
Soil Temp. (◦C)	-0.83	-0.84	-0.72	-0.69	-0.69	-0.74
Rain (mm/24 - 48 Hr)	n.s.	0.23	0.31	0.27	0.47	0.44
Water Temp (◦C)	-0.67	-0.72	-0.71	-0.62	-0.65	-0.72
Conductivity (mS/cm)	-0.70	-0.42	n.s.	-0.45	-0.41	n.s.
pH	-0.59	-0.61	-0.58	-0.70	-0.54	-0.74
Total Alk.	-0.67	-0.57	-0.62	-0.68	-0.67	-0.79
B	-0.54	-0.63	-0.54	0.75	0.77	0.65
Br	n.s.	n.s.	-0.21	n.s.	n.s.	-0.40
Cl	n.s.	-0.43	-0.45	-0.42	-0.40	-0.41
F	-0.77	-0.85	-0.79	n.s.	n.s.	n.s.
I	-0.78	n.s.	-0.61	n.s.	n.s.	-0.25
Ca	-0.65	-0.48	n.s.	0.59	0.72	0.71
Mg	-0.58	-0.57	-0.45	-0.54	-0.29	-0.55
Na	-0.66	-0.71	-0.58	-0.71	-0.83	-0.85
K	-0.52	-0.71	n.s.	0.63	0.61	0.64
Si	n.s.	0.86	n.s.	-0.65	n.s.	0.28
DO	0.68	0.51	0.59	n.s.	0.23	0.19
NNN	0.62	0.86	0.85	0.28	0.42	0.54
Mn	n.s.	0.61	n.s.	0.74	n.s.	n.s.
Fe	-0.76	0.58	-0.50	0.43	n.s.	n.s.
SO_4	n.s.	0.64	0.81	0.86	0.88	0.86
DOC	n.s.	n.s.	n.s.	0.73	n.s.	n.s.
TKN	n.s.	n.s.	0.55	0.52	0.51	0.47
TN	0.53	0.81	0.86	0.37	0.53	0.64
TAM	n.s.	n.s.	n.s.	n.s.	n.s.	0.30
TP	-0.30	0.23	n.s.	0.52	0.26	0.45
DRP	-0.64	n.s.	-0.43	0.23	n.s.	0.28
TSS	0.32	0.40	0.33	0.51	0.39	0.56
VSS	n.s.	n.s.	n.s.	n.s.	0.49	n.s.
Turbidity (NTU)	n.s.	0.74	0.51	0.80	0.65	0.83
Clarity (black disk)	-0.43	-0.53	-0.39	-0.67	-0.57	-0.78

Metrological measures are for the Balfour-Glenure-St Patricks meteorological site (Environment Southland data).

Table 5: Tracer suitability by tier (I – III) for hydrograph separation. Analytes that have a sufficient sample size to be representative are classified into tiers with tier I tracers are identified in red, tier II traces in orange and tier III tracers in blue. Tracers that meet tier-I through III suitability but are associated with too small a sample size to be considered representative of the larger flow population are in black. Additional measures of these tracers over a longer time period will probably add additional value to hydrograph separation at these sites.

	McCale Rd	Old Balfour Rd	Murphy Rd	Pahiwi – Balfour Rd	Nine Mile Rd	Mandeville
Water Temp (◦C)		**-0.72**	**-0.71**			**-0.72**
Conductivity (mS/cm)	**-0.70**					
pH				**-0.70**		**-0.74**
Total Alk.						**-0.79**
B				0.75	0.77	
F	-0.77	-0.85	-0.79			
I	-0.78					
Ca					0.72	**0.71**
Na		-0.71		-0.71	-0.83	**-0.85**
K		-0.71				
Si		0.86				
NNN		**0.86**	**0.85**			
Mn				0.74		
Fe	-0.76					
SO_4			0.81	0.86	0.88	**0.86**
DOC				0.73		
TN		**0.81**	**0.86**			
Turbidity (NTU)		**0.74**		**0.80**		**0.83**
Clarity (black disk)						**-0.78**
Tracer(s) selected for TRaCS analysis	Condy	NNN, TN	NNN, TN	Turbidity, pH	Nil.	Turbidity, pH, Water Temp

With the exception of McCale Rd, all sites have at least one tracer that meets the tier-I (i.e., ≥0.85) criteria, however, not all have sufficient sample size to be representative. At McCale Rd, only conductivity attains tier-III status and is sufficiently well represented (n = 74) for flow separation. At Old Balfour Rd, only NNN is both sufficiently well represented (n = 78) and achieves tier-I status. Fluoride (F) and Si achieve tier-I status but due to a small sample number (n = 12) fail the test of representativeness. Total Nitrogen achieves tier-II status, and water temperature and turbidity achieve tier-III status - as standard water measures these tracers are well represented (n = 78). At Murphy Rd, both TN and NNN achieve tier-I status, whilst water temperature achieves tier-III status. Sulphate and F achieve tier-II status but fail the test of representativeness with only 22 and 17 repeat measures, respectively.

At the Pahiwi-Balfour Rd site, only turbidity and pH, both tier-II tracers, are sufficiently well represented for hydrograph separation. All other tracers are of too small a sample size to be considered suited for hydrograph separation. At the Nine Mile site, none of the tier- I-III tracers are sufficiently well represented (n ≤23) to be used for hydrograph separation. If considered valuable, the addition of Na and SO_4 to the long-term measurement data set at Nine-Mile Rd would likely enable a tier-I separation. At Mandeville, SO_4 and Na achieve tier-I status and are sufficiently well represented (n = 68) across the flow range to be used to separate the hydrograph. Total alkalinity (n = 68), clarity (n = 122), and turbidity (n=122) achieve tier-II status and are also well represented. pH, water temperature and Ca achieve tier-III status and as they are standard water quality measures they are well represented. For Mandeville we ran multiple separations using all tier-I tracers and a mix of tier-I through II tracers. However, we settled on the use of turbidity, pH and water temperature as these three tracers are both standard water quality measures and provided the largest sub-sample of the actual population. For the Mandeville site, the greater accuracy of the flow record (i.e., recorded vs simulated flow) lends extra confidence to the separation.

Finally, flow at all sites exhibits a high degree of correlation with soil moisture at the Balfour-Glenure-St Patricks meteorological site. Flow at each site is also correlated with soil temperature at 10 cm but was weakly or not correlated (i.e., McCale Rd) with 24 – 48 Hr rainfall. There was a poorer correlation between flow, soil moisture, soil temperature and rainfall at the York Rd meteorological site. There was little correlation between flow and rainfall for the Lumsden metrological site. Accordingly, data for the York Rd and Lumsden metrological sites were not retained for subsequent assessment.

5.2 'TRaCS' application

5.2.1 McCale Tributary, Waimea Stream

The capture zone associated with the McCale Rd site is characterised by a small Bedrock/Hill Country drainage basin of 294 Ha (Figure 1, Table 1). Discharge from this small area contributes to the larger Waimea Stream, upgradient of the Old Balfour Rd monitoring site. There are no other physiographic units within this drainage basin, although it is of lower elevation and steepness when contrast with the larger (1,580 Ha) and more northern Waimea Stream headwater catchment. Soils within the McCale Rd capture zone are defined as silty and shallow (<0.3 – 0.6 m), overlying fractured bedrock with moderate over slow permeability. Aquifer storage is considered minor with thin soils and steep slopes favouring lateral soil zone flow at the contact with bedrock and a quick flow response during periods of wet soils and/or in response to high-intensity rainfall.

On the basis of a single recharge domain, a 3-compartment separation was run using electrical conductivity (tier-III). The separation reveals a pattern of decreasing hydrochemical evolution from cluster I – III (Table 6). Specifically, the most evolved signatures are associated with the driest and warmest soil conditions and the lowest flow values (Figure 4). Cluster II is associated with colder and wetter soils and higher flows, with cluster III associated with the coldest and wettest conditions and peak flow values.

Cluster III waters are associated with a slightly higher median soil moisture value, the highest median flow, lowest soil temperature and by far the highest mean 48 Hr rainfall. Overall these waters are the least evolved with the lowest median Na, alkalinity, Ca, Mg, Fe^{II}, Mn^{II}, K and conductivity and yet similar Cl and Br to cluster II waters. These geochemical signatures indicate a larger component of water that has had little interaction with the soil matrix along with limited residence time for regulation of ion concentrations or for redox evolution to occur. Importantly, signatures of surficial overland flow such as TSS, Turbidity and E. coli peak in association with cluster III supporting a predominantly shallow flow path. DRP concentration peaks in the deeper compartment (cluster I) whilst NNN/TN is at its lowest. Sediment (as TSS) and median *E. coli* peak in association with the surficial compartment (cluster III), although *E. coli* is also elevated under low flow conditions (cluster I). Despite occurring in small numbers, it is likely that repeat measures of dissolved Fe would aid in refining the separation of the hydrograph at the McCale Rd site as would some greater confidence in the simulated flow record[1].

---

[1] F and I may also help but are more expensive to measure and the controls over their variability are less well understood.

Table 6. Summary statistics by dominant ('winner') cluster for a 3-compartment separation at McCale Rd, Tributary.

	Flow (simulated)	Soil moisture (%)	Soil temp at 10 cm (deg. C)	48 hr rain. (mm)	Water Temperature	pH	Conductivity (us/cm)	DO
Bedrock (Cluster I)								
n	28	13	13	13	28	28	19	27
Mean	0.009	43.3	13.2	1.4	10.3	7.4	116.7	10.22
Median	0.0049	42.3	14.8	0.0	11.1	7.4	111.0	10.20
C.V.	1.59	0.1	0.2	1.4	0.3	0.0	0.1	0.26
Min.	0.0029	39.6	7.1	0.0	2.1	6.9	97.0	3.58
Max.	0.0649	50.0	16.0	5.3	14.5	7.8	155.0	15.30
Soil (Cluster II)								
n	33	17	17	17	32	31	21	27
Mean	0.030	47.5	10.2	1.2	8.0	7.3	97.3	12.36
Median	0.013	47.9	10.1	0.5	7.1	7.3	92.0	11.90
C.V.	1.6	0.1	0.4	1.5	0.5	0.0	0.2	0.19
Min.	0.002	40.9	4.2	0.0	1.4	6.8	84.0	8.92
Max.	0.26	50.9	16.7	6.0	14.1	7.8	145.0	18.40
Surficial (Cluster III)								
n	17	13	13	13	16	17	17	16
Mean	0.04	47.5	9.9	5.2	7.4	7.3	80.1	11.89
Median	0.02	48.6	10.1	0.5	7.5	7.3	79.0	11.70
C.V.	1.7	0.1	0.3	1.5	0.4	0.0	0.1	0.12
Min.	0.004	43.3	5.9	0.0	1.4	6.9	70.0	9.18
Max.	0.3	50.9	14.3	20.5	12.5	7.6	99.0	13.80

Table 6 Continued: Summary statistics by dominant ('winner') cluster for a 3-compartment separation at McCale Rd, Tributary.

	Talk	Ca	Mg	Si	Na	K	Cl	SO_4	Fe	Mn	NNN	TKN	TN	DRP	TP	TSS	VSS	Turb.	E.Coli
Bedrock (Cluster I)																			
n	6	6	6	3	6	6	6	6	6	6	28	13	28	28	28	28	6	22	28
Mean	51.5	10.5	3.55	9.27	11.33	1.07	7.5	3.65	0.53	0.04	0.51	0.39	1.05	0.013	0.045	7.7	2.7	6.7	8911
Median	52.0	10.1	3.65	8.80	11.80	1.28	7.8	3.50	0.42	0.03	0.40	0.37	0.93	0.011	0.030	3.3	3.0	4.3	245
C.V.	0.2	0.2	0.18	0.11	0.15	0.58	0.4	0.32	0.48	0.67	0.99	0.34	0.54	0.601	0.774	1.4	0.3	1.2	3
Min.	40.0	8.1	2.60	8.60	9.00	0.24	3.9	2.40	0.31	0.02	0.07	0.24	0.41	0.004	0.014	2.5	1.1	2.0	10
Max.	61.0	13.7	4.30	10.40	13.50	1.75	11.5	5.70	0.97	0.08	2.60	0.71	2.90	0.040	0.160	47.0	3.0	40.0	140000
Soil (Cluster II)																			
n	8	8	8	5	8	8	8	8	8	8	30	17	31	31	31	32	7	23	31
Mean	30.0	7.6	2.40	10.52	8.84	0.56	7.0	4.35	0.33	0.02	0.85	0.37	1.30	0.009	0.032	6.6	1.9	5.0	492
Median	30.0	6.8	2.25	10.60	8.50	0.54	6.8	4.10	0.30	0.03	0.84	0.36	1.25	0.006	0.026	3.3	2.4	4.1	160
C.V.	0.5	0.3	0.29	0.12	0.14	0.26	0.3	0.25	0.59	0.37	0.56	0.29	0.38	0.732	0.631	1.4	0.6	0.6	2
Min.	13.0	5.6	1.89	9.20	8.10	0.34	4.9	3.20	0.08	0.01	0.10	0.20	0.50	0.004	0.007	1.8	0.6	2.2	10
Max.	62.0	12.9	4.00	11.80	11.80	0.77	10.1	6.00	0.63	0.04	1.75	0.62	2.50	0.031	0.090	50.0	3.0	13.4	4900
Surficial (Cluster III)																			
n	9	9	9	4	9	9	9	9	9	9	17	13	16	16	16	16	4	16	16
Mean	24.8	5.9	1.96	10.98	7.84	0.47	5.9	4.51	0.22	0.02	0.68	0.37	1.08	0.007	0.026	6.4	1.9	6.3	609
Median	21.0	5.8	1.92	11.10	7.60	0.50	6.7	4.20	0.18	0.02	0.46	0.32	1.00	0.006	0.022	5.0	2.0	4.5	285
C.V.	0.3	0.3	0.25	0.13	0.09	0.28	0.2	0.20	0.45	0.38	0.66	0.33	0.44	0.426	0.522	0.8	0.6	0.6	1
Min.	18.4	4.1	1.34	9.10	7.20	0.29	4.3	3.50	0.12	0.00	0.22	0.22	0.53	0.004	0.011	2.9	0.8	2.6	50
Max.	44.0	9.5	3.10	12.60	9.70	0.70	7.3	5.70	0.42	0.03	1.48	0.66	1.91	0.011	0.054	21.0	3.0	14.8	3100

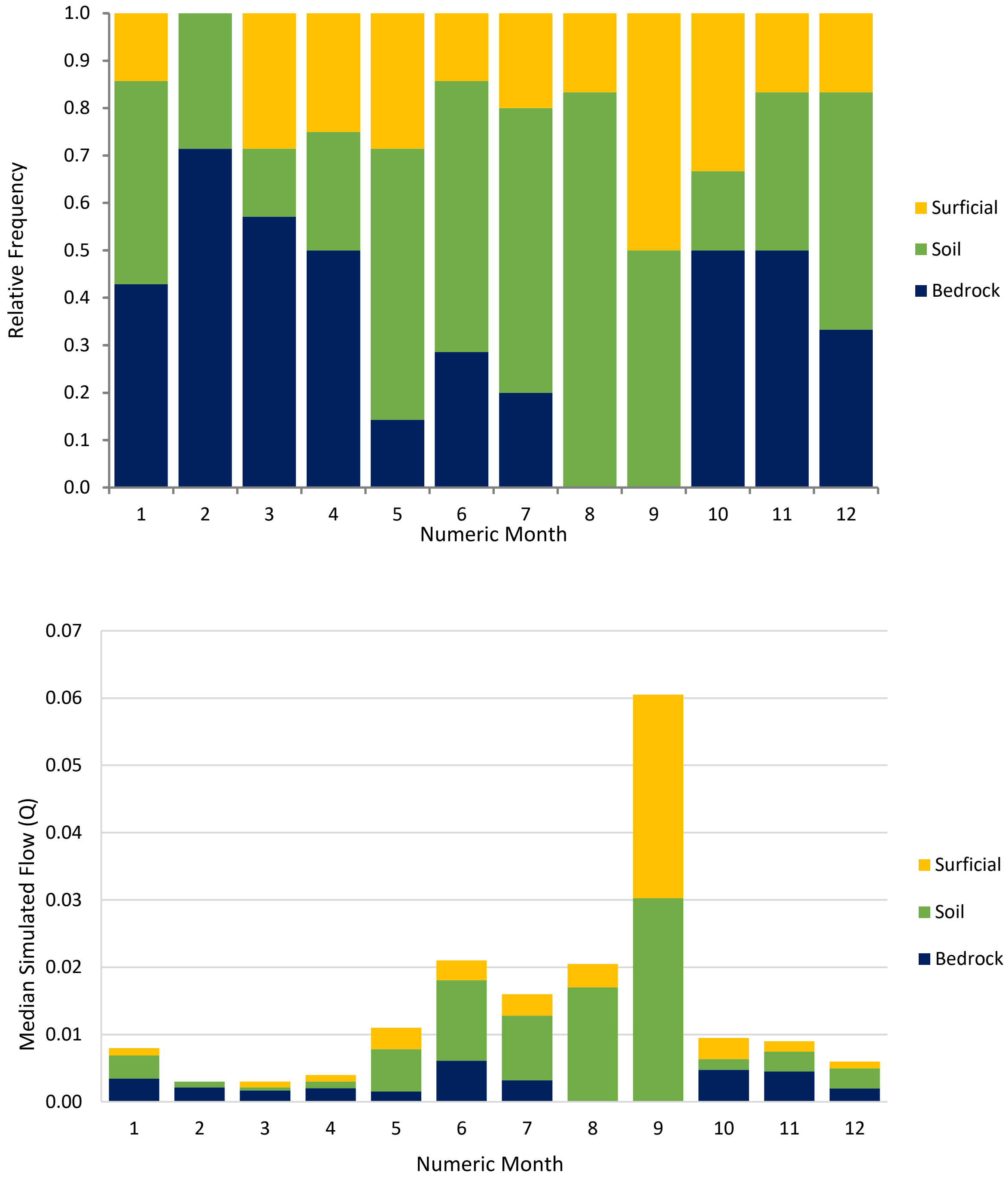

Figure 4: a) Relative frequency and b) proportion of simulated flow by compartmental source water (Cluster) for a 3-compartment separation by month for the McCale Rd Tributary monitoring site, Waimea Valley, Southland (Environment Southland data).

Given some overlap between cluster I and II, within a bivariate plot of flow versus proportional cluster membership, a two-compartment solution was also run. The two-compartment solution exhibits less overlap and separates the hydrograph into ‘warm-dry’ and ‘cold-wet’ groupings. Once again, the ‘warm-dry’ cluster is associated with the most hydrochemically evolved signatures consistent with a somewhat deeper and likely older water source. The ‘cold-wet’ cluster is associated with higher DO and NNN and lower dissolved Fe and DRP that suggest shallower flows that have had less time to evolve (e.g., reduction and water-soil-rock type interactions).

On the basis of both the 3 and 2 compartment separations, hydrological and hydrochemical signals we propose 3 storage compartments associated with waters of different residence times: (i) a slower more evolved source that predominates under low flows and dominates during the warmer/drier months and shows evidence of strongly reducing conditions. This water source is thought to be associated with residual water storage derived from seepage of water stored in shallow fractured bedrock and/or at the contact between valley infill and basement rock; (ii) and a more rapid, wetter soil water signature (cluster II) that dominates during ‘cool-wet’ conditions that is perched above or at the contact with the fractured basement rock and travels laterally to stream. The soil water signature compartment (cluster II) is dominant during the cooler months and appears to be gradually exhausted as soils dry up over the warmer months of the year, and; (iii) a shallow or Surficial compartment (cluster III) associated with quick flow during periods of high soil moisture content. These waters are hydrochemically the least evolved (most dilute and least reduced). A 4-compartment separation further subdivides the surficial compartment into cool-wet and warm-dry runoff events, respectively.

The general noise between cluster 1 (slow-dry soil/bedrock compartment) and cluster II (rapid-wet soil/bedrock compartment) suggests relatively poor differentiation and/or some spatial and temporal overlap of these compartments. This is not unexpected for this setting where storage of so-called ‘deeper’ water supplying stream is thought to occur at relatively shallow levels. As such it is perhaps better to define the deeper compartment as ‘slow stored water’ that constitutes a residual fraction that dominates the water source following the drying up of the intermediate soil zone reservoir. Notably, NNN, and as such TN, concentrations peak in association with drainage of the intermediate soil zone compartment (cluster II) in this setting. The latter is consistent with low NNN concentrations associated with a reducing (cluster I) compartment and the dominance of a shallow overland flow water source for cluster III.

Table 7: Table of Endmember Hydrological and Water Quality Signatures at McCale Rd Tributary. Endmembers statistics are derived for samples with a cluster membership of ≥0.9 and differ from summary statistics by the 'winner' cluster.

	Q (simulated)	Soil Moisture (%)	Soil Temp at 10 cm	48 Hr Rainfall	NNN	TKN	TN	DRP	TP	TSS	VSS	Turbidity	E.Coli
Bedrock (Cluster I)													
n	14	8	8	8	14	8	14	14	14	14	3	12	14
Mean	0.004	43.0	14.0	1.3	0.4	0.4	0.9	0.010	0.050	6.8	3.0	7.1	6342
Median	0.004	42.9	15.0	0.3	0.4	0.4	0.8	0.010	0.040	3.0	3.0	4.3	260
C.V.	0.420	0.1	0.2	1.5	0.5	0.3	0.5	0.360	0.780	1.5	0.0	1.5	3
Min.	0.002	39.6	9.9	0.0	0.1	0.2	0.4	0.010	0.020	2.5	3.0	2.0	10
Max.	0.009	46.5	15.9	5.3	0.6	0.6	2.1	0.020	0.160	39.0	3.0	40.0	83000
Soil (Cluster II)													
n	5	2	2	2	5	2	5	5	5	5	1	4	5
Mean	0.030	50.3	5.8	0.5	1.0	0.3	1.4	0.010	0.030	4.7	3.0	4.8	192
Median	0.013	50.3	5.8	0.5	1.1	0.3	1.5	0.010	0.020	5.0	3.0	4.6	130
C.V.	0.988	0.0	0.2	1.4	0.7	0.0	0.5	0.420	0.530	0.4	0.0	0.4	1
Min.	0.012	49.9	5.0	0.0	0.2	0.3	0.7	0.000	0.020	2.6	3.0	2.5	10
Max.	0.082	50.7	6.6	1.0	1.8	0.3	2.1	0.0	0.1	7.8	3.0	7.6	600
Surficial (Cluster III)													
n	7	5	5	5	7	5	7	7	7	7	1	7	7
Mean	0.07	47.1	9.1	12.6	0.7	0.4	1.1	0.010	0.040	8.6	3.0	8.5	1013
Median	0.04	46.5	9.7	15.5	0.5	0.3	0.9	0.010	0.030	7.0	3.0	8.4	410
C.V.	1.36	0.1	0.3	0.7	0.7	0.3	0.5	0.450	0.400	0.7	0.0	0.4	1
Min.	0.01	43.3	5.9	0.0	0.2	0.2	0.6	0.000	0.020	3.0	3.0	3.0	100
Max.	0.27	50.5	13.1	20.5	1.5	0.5	1.9	0.010	0.050	21.0	3.0	14.8	3100

5.2.2 Old Balfour Road

The capture zone associated with the Old Balfour site encompasses an area of 1,874 Ha with an assemblage of 95% Bedrock/Hill Country and 5% Lowland type physiographic units (Figure 1, Table 1). The small Lowland component of the capture zone is comprised of 3.7% Gleyed and 1.3% Oxidising and Old Mataura physiographic units. Given the dominance by single geographical source and evidence for 2 – 3 compartments at McCale Rd, we hypothesise that stream flow can be separated into 2 or 3-compartments. Accordingly, two 3-compartment separations were run using NNN on its own (tier-I) and another using both NNN and TN (tier-II) (Table 8). There was little apparent difference in the proportional separation between NNN only and both NNN and TN so we proceeded with the latter.

As with the McCale Rd Tributary, the 3-compartment separation identified a pattern of decreasing hydrochemical evolution from cluster I – III (Table 8). Specifically, the most evolved signatures (cluster I Bedrock) are associated with the driest and warmest soil conditions and the lowest flow values. Cluster II (Soil) is associated with colder and wetter soils and higher flows and cluster III (Surficial) with the coldest and wettest conditions and peak flow values (Figure 5). Volumetrically, flow at Old Balfour Rd is dominated by water sourced from the Surficial compartment with median flow values that are at least 15 and 5 times larger than flows associated with the Bedrock/Soil compartments, respectively (Table 8, Figure 5).

Notably, NNN and as such TN, TSS and TP concentrations all peak in association with runoff from the Surficial compartment (cluster III), reflecting greater flushing of both intermediate soil zone and surficial compartments under saturated to near saturated soil conditions. This differs from the McCale Rd site where NNN and TN concentrations peaked in the waters derived from cluster II and the rapid-wet soil compartment. However, mean and median *E. coli* concentrations (not load) are once again highest under low flow conditions. A 4-compartment separation further subdivides the Surficial compartment into cool-wet and warm-dry runoff events, or saturation excess and infiltration excess events respectively.

As with McCale Rd, the two-compartment solution separates out the hydrograph into 'warm-dry' and 'cold-wet' groupings. The 'warm-dry' cluster is associated with the most hydrochemically evolved signatures and what is inferred to be an older water source. The 'cold-wet' cluster is associated with higher DO and NNN but lower dissolved Fe and DRP indicative of shallower flows that have had less time to evolve (i.e., reduction and water-soil-rock type interactions). However, at a monthly time step, a 2-compartment separation does not adequately capture the seasonality of water composition derived from the dominantly Bedrock/Hill Country capture zone supplying the Old Balfour Rd site.

The general overlap between cluster I and cluster II in the 3-compartment separation again suggest relatively poor differentiation and/or some spatial and temporal overlap of these compartments. This is not unexpected when soil overlies fractured rock. Specifically, soil matrix potentials are likely to strongly influence fracture flow with higher/faster drainage rates under wet soil conditions (cluster II) and lower and slower rates of more evolved waters associated with residual storage or displacement of older more evolved waters from secondary storage (cluster I). Temporally, cluster I waters are most common across the shoulders of the seasons (Autumn and Spring) and as such it is perhaps better to define these waters as 'slow stored water' that constitutes an older and subsequently more evolved water source - hereafter slow-dry soil/bedrock compartment waters.

Table 8: Summary statistics by dominant ('winner') cluster for a 3-compartment separation at Old Balfour Rd.

	Flow (simulated)	Soil moisture (%)	Soil temp at 10 cm (deg. C)	48 hr rain. (mm)	Water Temperature	pH	Conductivity (us/cm)	DO
Bedrock (Cluster I)								
n	20	11	11	11	19	20	11	16
Mean	0.0070	42.6	13.6	1.0	12.5	7.6	107.2	10.31
Median	0.0000	42.3	14.5	0.5	12.8	7.6	96.0	10.25
C.V.	1.5612	0.1	0.2	1.5	0.2	0.0	0.3	0.27
Min.	0.0000	39.6	9.7	0.0	8.4	7.0	75.0	3.19
Max.	0.0300	46.3	15.6	4.0	18.2	7.9	205.0	16.80
Soil (Cluster II)								
n	36	22	22	22	36	35	24	33
Mean	0.0716	46.4	11.6	2.3	10.0	7.5	92.6	11.49
Median	0.0570	46.4	12.0	0.5	9.8	7.5	93.0	11.50
C.V.	1.1941	0.1	0.3	1.9	0.3	0.0	0.1	0.13
Min.	0.0010	41.1	4.2	0.0	3.8	7.0	75.0	9.06
Max.	0.4690	50.7	16.7	19.0	15.2	7.7	131.0	15.10
Surficial (Cluster III)								
n	23	11	11	11	23	23	11	21
Mean	0.4484	50.1	6.7	4.4	5.4	7.2	92.3	13.39
Median	0.2650	50.4	6.4	0.5	4.7	7.2	92.0	13.10
C.V.	1.1754	0.0	0.4	1.6	0.5	0.0	0.1	0.13
Min.	0.0600	47.4	3.9	0.0	1.7	6.9	84.0	10.60
Max.	1.9970	50.9	12.1	20.5	12.1	7.6	100.0	18.40

Table 8 continued: Summary statistics by dominant ('winner') cluster for a 3-compartment separation at Old Balfour Rd.

	Talk	Ca	Mg	Si	Na	K	Cl	SO$_4$	Fe	Mn	NNN	TKN	TN	DRP	TP	TSS	VSS	Turb.	E.Coli
Bedrock (Cluster I)																			
n	9	9	9	5	9	9	9	9	9	9	20	9	19	18	18	15	7	18	19
Mean	38.2	8.7	2.98	8.42	9.46	0.81	9.4	4.08	0.09	0.01	0.06	0.28	0.36	0.007	0.018	3.6	2.8	1.5	852
Median	37.0	8.0	2.70	8.40	9.20	0.79	7.6	3.90	0.09	0.00	0.06	0.27	0.36	0.006	0.016	3.0	3.0	1.4	370
C.V.	0.3	0.4	0.48	0.22	0.20	0.33	0.7	0.26	0.64	1.93	0.72	0.31	0.32	0.464	0.484	0.4	0.3	0.4	1
Min.	22.0	5.2	1.72	5.80	7.20	0.57	5.5	2.80	0.02	0.00	0.00	0.20	0.20	0.004	0.004	3.0	1.1	0.6	70
Max.	62.0	17.5	6.70	10.70	14.00	1.44	26.0	6.10	0.20	0.07	0.14	0.43	0.59	0.014	0.042	8.5	3.4	3.0	4700
Soil (Cluster II)																			
n	10	10	10	6	10	10	10	10	10	10	35	24	35	35	35	35	7	29	35
Mean	25.9	6.8	2.13	10.95	7.80	0.60	6.4	5.19	0.17	0.01	0.49	0.31	0.83	0.009	0.027	3.8	1.8	3.5	1027
Median	25.5	6.8	2.15	10.90	7.80	0.60	6.3	4.85	0.18	0.01	0.49	0.29	0.81	0.007	0.022	3.0	1.8	3.0	280
C.V.	0.2	0.1	0.14	0.07	0.06	0.20	0.2	0.22	0.29	0.37	0.45	0.35	0.29	0.604	0.686	0.8	0.6	0.7	2
Min.	19.2	5.2	1.50	9.90	7.10	0.46	4.8	3.60	0.07	0.00	0.15	0.16	0.41	0.004	0.010	1.4	0.6	1.1	40
Max.	34.0	8.1	2.50	12.00	8.80	0.81	8.7	6.90	0.25	0.02	0.94	0.62	1.22	0.032	0.110	19.0	3.0	14.0	13000
Surficial (Cluster III)																			
n	4	4	4	1	4	4	4	4	4	4	23	11	23	23	23	22	3	16	23
Mean	21.1	7.0	2.03	13.40	7.53	0.64	7.6	6.73	0.12	0.01	1.32	0.36	1.68	0.008	0.028	7.9	2.2	5.6	454
Median	21.0	6.9	2.05	13.40	7.65	0.63	7.2	6.75	0.13	0.01	1.28	0.34	1.60	0.006	0.018	4.0	3.0	4.4	200
C.V.	0.2	0.1	0.05	0.00	0.06	0.08	0.2	0.04	0.34	0.43	0.22	0.32	0.24	0.829	0.872	1.3	0.6	0.6	1
Min.	15.4	6.1	1.91	13.40	6.90	0.59	6.6	6.40	0.06	0.01	0.97	0.24	1.20	0.004	0.008	3.0	0.7	2.3	20
Max.	27.0	8.0	2.10	13.40	7.90	0.70	9.2	7.00	0.15	0.02	2.00	0.63	2.70	0.030	0.100	42.0	3.0	13.7	2200

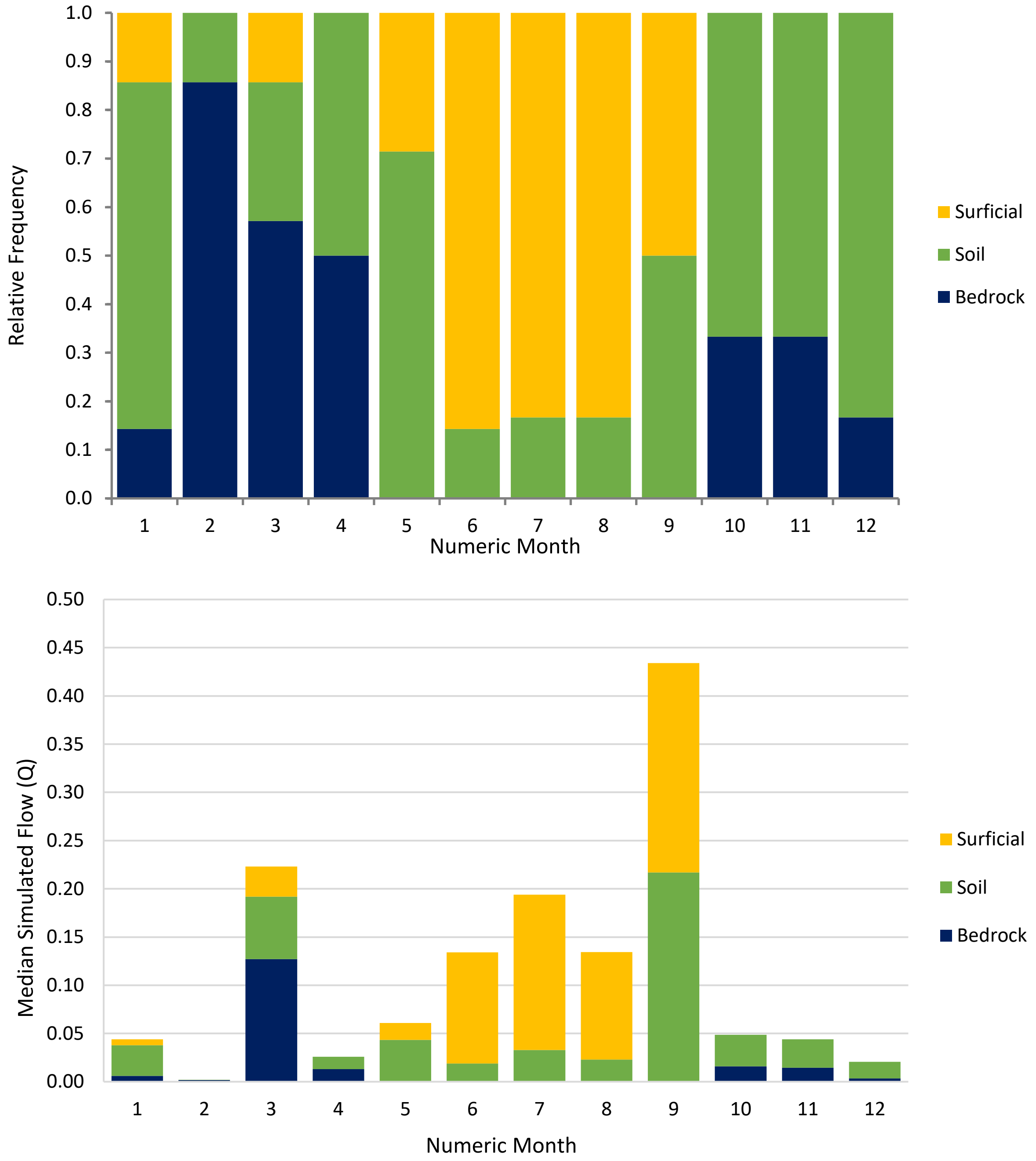

Figure 5: a) Relative frequency and b) proportion of compartmental source water (Cluster) for a 3-compartment separation by month for the Old Balfour Rd monitoring site, Waimea Valley, Southland (Environment Southland data).

Moving beyond monthly patterns in water source, stream flow samples dominated by a single compartment, i.e., ≥0.90, are apparent in the data record. As such, these samples can be used to provide constraints over the end-member compositions and associated water quality of each relevant compartment (Table 9).

Table 9: Table of Endmember Hydrological and Water Quality Signatures at Old Balfour Rd. Endmembers statistics are derived for samples with a cluster membership of ≥0.9 and differ from summary statistics by 'winner' cluster.

	Q (simulated)	Soil Moisture (%)	Soil Temp at 10 cm	48 Hr Rainfall	NNN	TKN	TN	DRP	TP	TSS	VSS	Turbidity	E.Coli
Bedrock (Cluster I)													
n	10	5	5	5	10	5	10	9	9	7	4	9	10
Mean	0.003	42.6	13.1	0.2	0.0	0.3	0.4	0.008	0.018	4.2	2.6	1.4	1189
Median	0.001	40.9	14.5	0.0	0.0	0.2	0.3	0.009	0.014	3.0	3.0	1.4	670
C.V.	2.483	0.1	0.2	1.4	0.6	0.3	0.4	0.484	0.575	0.5	0.4	0.2	1
Min.	0.000	39.6	9.7	0.0	0.0	0.2	0.2	0.004	0.008	3.0	1.1	0.9	70
Max.	0.026	46.3	15.4	0.5	0.1	0.4	0.6	0.013	0.042	8.5	3.4	2.0	4700
Soil (Cluster II)													
n	18	12	12	12	17	12	17	17	17	17	3	15	17
Mean	0.079	45.4	13.0	2.6	0.5	0.3	0.8	0.009	0.029	3.8	2.2	3.4	1329
Median	0.049	44.8	14.1	0.8	0.5	0.3	0.8	0.007	0.025	3.0	3.0	3.0	310
C.V.	1.424	0.1	0.2	2.0	0.2	0.4	0.2	0.481	0.466	0.6	0.6	0.5	2
Min.	0.001	42.3	6.6	0.0	0.3	0.2	0.6	0.004	0.010	1.5	0.7	1.7	40
Max.	0.469	49.9	16.7	19.0	0.6	0.6	1.1	0.0	0.1	12.0	3.0	8.2	13000
Surficial (Cluster III)													
n	12	4	4	4	12	4	12	12	12	11	2	8	12
Mean	0.46	49.6	7.1	5.3	1.4	0.4	1.7	0.008	0.030	7.7	3.0	5.3	395
Median	0.28	50.0	6.3	0.3	1.4	0.4	1.7	0.006	0.019	4.0	3.0	4.3	200
C.V.	1.16	0.0	0.3	1.9	0.1	0.4	0.1	0.871	0.786	1.3	0.0	0.5	1
Min.	0.08	47.4	5.5	0.0	1.1	0.3	1.4	0.004	0.008	3.0	3.0	2.9	130
Max.	2.00	50.9	10.1	20.5	1.6	0.6	2.2	0.028	0.092	35.0	3.0	11.7	1400

Only those samples that are significantly correlated with flow, tier-I-III tracers, are considered likely to be broadly representative of the compartmental composition. Tracers that fall below the 0.7 thresholds and yet are still statistically significant with flow can be used to infer hydrological flow path (O'Brien and Hendershot, 1993). Those measures that are not statistically significant with flow are less likely to retain the signature of the compartment supplying stream or the specific hydrological flow path and as such are not suited for inferring water source or hydrological flow path. Although further work is required to verify, non-significant measures may provide insight as to the seasonality of land use practices such as Farm Dairy Effluent (FDE) irrigation or stocking of Bedrock/Hill Country areas over the growing season (see Summary). Given the suitability of the standard water quality measures NNN and TN, there is little value in gathering repeat measures of other potential tier-I tracers (i.e., Si and F) at this site.

5.2.3 Murphy Road

The capture zone associated with the Murphy Rd site encompasses an area of 4,918 Ha and is characterised by an assemblage of 52% Bedrock/Hill Country and 48% Lowland type physiographic units. The Lowland component of the capture zone is dominated by the Gleyed (34.5%) physiographic unit type with the Oxidising and Old Mataura physiographic unit types making up a total of 13.5% of the capture zone (Table 1, Figure 1). Relative to the Old Balfour site, mean, median and max flow values across the sample record are 1.6, 1.7 and 1.5 times larger. Here two distinct geographical sources (i.e. different recharge domains) supply stream flow presenting an inherently more mixed and as such complex water source setting. Between the Old Balfour Rd and Murphy Rd capture zones, there is a large increase, c. 2,251 Ha in the proportion of Lowland physiographic units, including 1,600 Ha of 'Gleyed' type physiographic unit and 661 Ha of Oxidising/Old Mataura physiographic units (Table 1).

On the basis of the Old Balfour separation, flow measures and physiographic assemblages we hypothesise that 1 key compartment from Bedrock/Hill Country and 3 key lowland compartments will dominate streamflow (i.e., 4 main compartments). From Bedrock/Hill Country we expect the surficial compartment to play the greatest role in water composition at Murphy Rd during the wettest and coldest times of the year. We propose that lateral soil zone drainage associated with the abundance of poorly drained soils and the Gleyed physiographic type unit will make an important volumetric contribution to stream across the Lowland portion of the capture zone. For the same physiographic reasons, the volumetric contribution from the lowland aquifer compartment to flow is expected to be relatively minor due to the predominance of imperfectly to poorly drained soils. Instead, we anticipate base flow to be sustained by soil zone drainage. Therefore, according to our hypotheses and for the purpose of interrogating the data 3, 4 and 5-compartment separations were run using tier-I tracers TN and NNN.

Contrary to our hypotheses, a 5-compartment separation appears to make the most sense from a hydrochemical and hydrological standpoint. Therefore, the results and interpretation for Murphy Road are based on the 5-compartment separation (Table 10, Figure 6).

Table 10: Summary statistics by dominant ('winner') cluster for a 5-compartment separation at Murphy Road.

	Flow (simulated)	Soil moisture (%)	Soil temp at 10 cm (deg. C)	48 hr rain. (mm)	Water Temperature	pH	Conductivity (us/cm)	DO
Carbonate Aquifer (Cluster I)								
n	10	5	5	5	10	10	5	9
Mean	0.05	42.6	13.2	0.6	11.8	7.4	188.2	9.08
Median	0.009	40.7	12.8	0.0	11.8	7.6	198.0	10.30
C.V.	2.2	0.10	0.1	1.8	0.2	0.0	0.4	0.32
Min.	<0.001	39.6	11.6	0.0	6.1	6.8	95.0	5.12
Max.	0.34	49.7	15.2	2.5	16.3	7.8	256.0	12.50
Alluvial Aquifer (Cluster II)								
n	23	17	17	17	23	23	19	20
Mean	0.14	46.4	11.5	1.6	11.0	7.5	158.7	11.00
Median	0.11	46.5	11.7	0.5	11.2	7.5	154.0	11.85
C.V.	1.2	0.07	0.3	1.4	0.4	0.0	0.1	0.30
Min.	<0.001	40.9	6.4	0.0	5.4	6.8	124.0	3.07
Max.	0.72	50.9	16.7	8.0	17.8	8.0	222.0	15.50
Soil I (Cluster III)								
n	19	10	10	10	17	19	10	16
Mean	0.27	44.1	13.7	3.2	12.1	7.3	138.6	10.57
Median	0.05	44.0	14.9	0.5	12.7	7.4	135.5	9.89
C.V.	2.5	0.0	0.2	1.8	0.2	0.0	0.2	0.17
Min.	0.006	41.1	9.3	0.0	7.7	6.7	87.0	8.62
Max.	2.9	47.6	16.0	19.0	15.4	7.7	213.0	15.30
Soil II (Cluster IV)								
n	19	11	11	11	19	18	11	17
Mean	0.46	49.6	6.7	4.1	6.7	7.3	165.1	12.42
Median	0.15	50.4	6.5	0.5	5.5	7.3	166.0	12.10
C.V.	1.5	0.04	0.3	1.7	0.5	0.0	0.1	0.18
Min.	0.008	45.5	3.9	0.0	3.2	6.7	141.0	8.68
Max.	2.9	50.9	10.9	20.5	15.6	7.7	181.0	19.40
Surficial (Cluster V)								
n	8	1	1	1	8	8	1	8
Mean	0.36	50.8	4.0	0.00	4.0	7.2	176.0	13.78
Median	0.26	50.8	4.0	0.00	3.3	7.1	176.0	13.80
C.V.	1.06	0.00	0.0	****	0.5	0.1	0.0	0.04
Min.	0.10	50.8	4.0	0.00	1.6	6.8	176.0	12.90
Max.	1.25	50.8	4.0	0.00	7.5	7.7	176.0	14.60

Table 10 continued: Summary statistics by dominant ('winner') cluster for a 3-compartment separation at Old Balfour Rd.

	Talk	Ca	Mg	Si	Na	K	Cl	SO_4	Fe	Mn	NNN	TKN	TN	DRP	TP	TSS	VSS	Turb.	E.Coli
Carbonate Aquifer (Cluster I)																			
n	4	4	4	2	4	4	4	4	4	4	10	5	10	10	10	7	4	10	10
Mean	67.3	13.7	8.45	14.30	16.23	0.97	19.7	5.83	0.17	0.01	0.95	0.35	1.31	0.019	0.032	3.3	2.0	3.0	659
Median	76.5	15.1	9.55	14.30	18.05	0.92	22.5	6.05	0.18	0.01	0.31	0.29	0.55	0.015	0.030	3.0	2.1	2.5	275
C.V.	0.5	0.4	0.58	0.34	0.37	0.35	0.4	0.23	0.60	0.89	1.48	0.48	1.12	0.503	0.450	0.4	0.6	0.6	2
Min.	23.0	6.6	2.10	10.90	7.80	0.61	8.6	4.00	0.04	0.00	0.01	0.22	0.30	0.009	0.012	1.2	0.7	1.1	10
Max.	93.0	18.0	12.60	17.70	21.00	1.42	25.0	7.20	0.29	0.03	4.00	0.63	4.40	0.039	0.056	6.1	3.0	7.2	4600
Alluvial Aquifer (Cluster II)																			
n	10	10	10	6	10	10	10	10	10	10	23	18	23	23	23	22	8	21	23
Mean	38.7	12.6	4.98	10.82	11.34	1.06	13.7	12.89	0.18	0.01	1.67	0.50	2.17	0.016	0.032	3.3	2.3	3.4	284
Median	37.0	12.5	5.00	10.80	10.95	0.96	13.2	12.25	0.12	0.01	1.37	0.48	1.72	0.012	0.028	3.0	3.0	2.8	200
C.V.	0.3	0.1	0.16	0.25	0.15	0.24	0.2	0.26	0.79	0.21	0.81	0.25	0.66	0.622	0.479	0.4	0.5	0.7	1
Min.	22.0	10.7	4.00	7.60	9.50	0.77	9.1	8.90	0.04	0.01	0.02	0.32	0.33	0.004	0.010	1.2	0.6	1.8	40
Max.	58.0	15.4	6.30	14.30	14.00	1.53	17.6	18.20	0.44	0.02	4.20	0.88	4.70	0.040	0.060	8.0	3.0	13.0	1200
Soil I (Cluster III)																			
n	5	5	5	3	5	5	5	5	5	5	19	9	18	18	18	17	3	13	18
Mean	29.2	9.6	3.38	10.07	9.38	1.16	11.0	9.94	0.15	0.01	1.33	0.54	2.03	0.028	0.060	6.6	1.4	3.7	1869
Median	26.0	10.9	3.50	10.40	9.50	1.12	12.1	10.40	0.11	0.01	1.21	0.47	1.66	0.025	0.048	3.0	0.7	3.2	595
C.V.	0.2	0.2	0.25	0.24	0.10	0.23	0.2	0.33	0.55	1.13	1.00	0.31	0.76	0.558	0.618	1.4	0.9	0.5	1
Min.	23.0	6.3	2.20	7.50	8.00	0.79	7.6	5.70	0.09	0.00	0.01	0.35	0.25	0.011	0.018	1.1	0.6	1.3	60
Max.	40.0	11.2	4.20	12.30	10.20	1.49	12.3	13.90	0.28	0.04	5.64	0.83	7.00	0.064	0.140	40.0	3.0	8.4	10000
Soil II (Cluster IV)																			
n	4	4	4	1	4	4	4	4	4	4	18	11	18	18	18	18	2	17	19
Mean	29.5	14.0	4.60	9.50	9.98	1.17	12.9	17.48	0.09	0.02	3.03	0.62	3.60	0.011	0.038	11.4	3.0	11.9	640
Median	30.5	13.7	4.50	9.50	10.10	1.22	12.8	18.40	0.09	0.02	3.14	0.51	3.55	0.009	0.019	3.0	3.0	4.7	180
C.V.	0.2	0.1	0.09	0.00	0.06	0.25	0.2	0.23	0.09	0.12	0.48	0.43	0.43	0.846	0.894	2.3	0.0	1.9	2
Min.	19.9	11.8	4.20	9.50	9.20	0.77	10.2	12.10	0.08	0.01	0.06	0.30	0.56	0.004	0.008	3.0	3.0	1.8	40
Max.	37.0	16.7	5.20	9.50	10.50	1.46	15.9	21.00	0.10	0.02	5.70	1.03	6.10	0.045	0.121	114.0	3.0	95.0	6000
Surficial (Cluster V)																			
n	0	0	0	0	0	0	0	0	0	0	8	1	8	8	8	8	0	2	8
Mean	****	****	****	****	****	****	****	****	****	****	4.11	0.45	4.73	0.006	0.029	5.0	****	3.1	672
Median	****	****	****	****	****	****	****	****	****	****	3.81	0.45	4.45	0.005	0.015	3.0	****	3.1	64
C.V.	****	****	****	****	****	****	****	****	****	****	0.26	0.00	0.22	0.396	1.182	1.1	****	0.5	3
Min.	****	****	****	****	****	****	****	****	****	****	3.10	0.45	3.70	0.004	0.008	3.0	****	1.9	20
Max.	****	****	****	****	****	****	****	****	****	****	6.30	0.45	6.90	0.010	0.110	19.0	****	4.2	5000

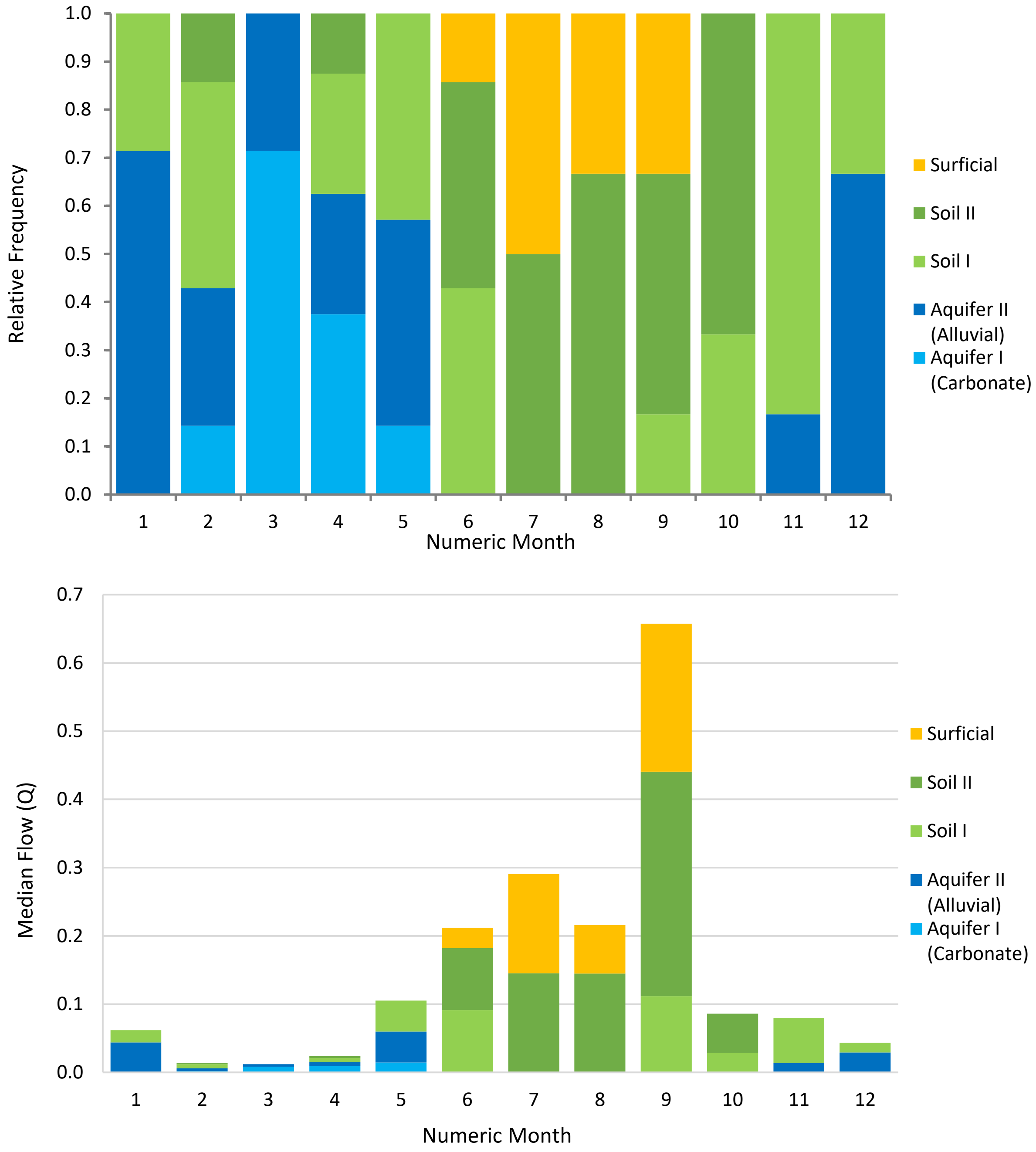

Figure 6: a) Relative frequency and b) proportion of compartmental source water (Cluster) for a 5-compartment separation by month for the Murphy Rd monitoring site, Waimea Valley, Southland (Environment Southland data. Soil moisture and flow are lowest when the carbonate Aquifer source is present and highest when the Surficial source is present.

Specifically, cluster I is associated with the lowest flows and soil moisture and the warmest soil and water temperatures. These waters are highly evolved with median conductivity, Total Alkalinity, Na and Cl concentrations that are at least twice that of other compartments (clusters) with saturation indices suggestive of a carbonate aquifer source. Redox signatures (i.e., DO, NNN, Fe^{II}) are also indicative of strongly reducing (i.e., Fe^{III}-buffering) conditions all of which are consistent with a highly evolved groundwater source derived exclusively from Local Land Surface Recharge (LLSR). The carbonate aquifer compartment (cluster I) signal is only evident during February – May and with the exception of March is seldom the dominant water source (Figure 6). Despite a dominantly deep groundwater source carbonate aquifer signal is associated with the highest mean and median *E. coli* counts, which is inconsistent with an aquifer source suggesting an alternative origin.

Cluster II suggests a secondary aquifer compartment associated with a shallow alluvial system that overlays the carbonate aquifer compartment. Hydrochemically these waters are less evolved and compositionally similar to shallow, unconfined, groundwaters sampled from the alluvial system associated with the Gleyed type physiographic unit (Environment Southland data). Specifically, the alluvial aquifer waters are weakly reducing (i.e., mixed(oxic-anoxic)) with low (<1.5 mg/L) NNN concentrations and share similar median Cl, NNN and TN concentrations to cluster II waters. The lowland alluvial aquifer compartment is an important source of water to stream over the autumn and early summer. However, on the basis of the data record, this water source is not volumetrically or hydrochemically important during the wettest times of the year (months 6 – 10). The latter is thought to reflect dilution by the volumetrically much larger contribution from shallow soil and surficial runoff compartments during 'cold-wet' periods of the year (Table 10 and Figure 6). Despite a dominant groundwater source, the alluvial aquifer signal is associated with the second highest mean and median *E. coli* counts, whereas local groundwater samples do not show elevated *E. coli*.

Cluster III is associated with wetter soil conditions and cooler temperatures with a median flow value of 0.11 m^3/s more than twice that of cluster II (alluvial aquifer). Hydrochemically, these waters show less evidence of reduction, with median DO, Mn^{II}, TN and NNN concentrations that are slightly elevated relative to cluster II (alluvial aquifer). These waters are also associated with lower dissolved Fe^{II} and DRP concentrations along with elevated K and SO_4 indicating lesser opportunity for regulation by redox and ion-exchange processes. These soil waters contribute to flow across the majority of the year although are notably absent during the coolest and wettest periods of the year (June – September) when stream flow is at a maximum (Figure 6). The latter suggests significant volumetric dilution by additional water sources that dominate during the cooler and wetter months of the year.

Cluster IV is only present during the wettest and coolest times of the year and is associated with a median flow value of 0.15 m^3/s over the data record. Soil moisture is elevated and soil temperatures are low (median 6.5°C). Hydrochemical signatures are consistent with a relatively shallow and poorly evolved water source characterised by the second highest median TN, NNN and SO_4, highest ammoniacal N and yet the lowest DRP, TP and *E. coli* concentrations and pH. Significantly, SO_4, NNN is very low in groundwater derived flows as previously identified for groundwaters across this area (Rissmann et al., 2016; Hughes et al., 2016). These signatures in conjunction with hydrological measures are most consistent with a dominant lowland soil zone water source associated with lateral soil zone drainage of imperfectly to poorly drained lowland soils under cool wet conditions. A dominantly Lowland soil water source is consistent with a median flow for Cluster IV that is 2.7 times that of the 'cool-wet' Bedrock/Hill Country Soil compartment identified at Old Balfour Rd. Furthermore, Na and Cl concentrations are twice that of the Bedrock/Hill Country Soil compartment again indicating a significant lowland source.

We propose that the difference between cluster IV (soil II) and cluster III (soil I) is a factor of soil moisture and temperature conditions. Specifically, Cluster IV dominates under 'cool-wet' soil conditions whereas cluster III (soil I) waters are associated with the residual discharge of stored soil waters under drier conditions. This interpretation is consistent with both hydrological measures but also hydrochemical indicators of water maturity, with more evolved waters associated with Cluster III (soil I) waters.

Cluster V waters are only present during the coldest and wettest months of the year (June – September) and are correlated with peak soil moisture and stream flow. Peak flow measures and attendant soil moisture and temperature measures are similar for both Old Balfour and Murphy Rd sites. Temperatures for some peak runoff values are as low as 1.6°C with conductivity values identical to those for surficial runoff from the Bedrock/Hill Country headwaters. Notably, median DRP, TP, *E. coli*, Turbidity and TSS concentrations are lowest in these peak flows, probably reflecting the lower intensity of land use associated with the Bedrock/Hill Country setting and relatively rapid source depletion. We also note that median flows at Old Balfour and Murphy Rd for each respective surficial compartment are similar, although conductivity, Na and Cl measures all indicate that whilst surficial runoff from Bedrock/Hill Country appears to dominate volumetrically, the contribution of a volumetrically smaller yet more concentrated lowland water source, i.e., soil water (cluster IV), does influence the concentration of highly water-soluble ions including NNN, Cl and Na. NNN peaks under surficial runoff conditions reflecting greater flushing of the lowland soil zone.

On a monthly basis not one of the 5-compartmental water sources supplying stream flow at Murphy Rd occur on their own. However, across the calendar year, there is a clear temporal pattern in the volumetric significance of the hypothesised compartmental water sources supplying stream. This general pattern is associated with variation in the magnitude of the contribution of water from each compartment to stream. Despite this overlap, it is possible to isolate hypothesised ‘end-member’ samples associated with each compartment using the TRaCS method (Table 11). However, it is important to note that the tracers used to separate the hydrograph are theoretically discriminating the water source and that water quality measures associated with the dominance of flow from one particular compartment may also be influenced by land use activities. For example, *E. coli*, Particulate P and some sediment measures peak under low flows associated with the alluvial and carbonate aquifer compartments at Murphy Rd and yet these water quality measures are not elevated in samples from local aquifer systems suggesting an alternative source possibly associated with FDE irrigation over top of poorly drained soils (Environment Southland Data).

Table 11: Table of Endmember Hydrological and Water Quality Signatures at Murphy Rd. Endmembers statistics are derived for samples with a cluster membership of ≥0.9 and differ from summary statistics by ‘winner’ cluster.

	Q (simulated)	Soil Moisture (%)	Soil Temp at 10 cm	48 Hr Rainfall	NNN	TKN	TN	DRP	TP	TSS	VSS	Turbidity	E.Coli
Carbonate Aquifer (Cluster I)													
n	3	3	3	3	3	3	3	3	3	3	3	3	3
Mean	0.020	41.2	14.2	0.2	0.2	0.3	0.5	0.023	0.036	3.4	1.6	2.7	243
Median	0.005	40.7	14.5	0.0	0.1	0.3	0.4	0.016	0.028	3.0	1.1	2.3	280
C.V.	1.4	0.0	0.1	1.7	1.3	0.2	0.5	0.604	0.434	0.7	0.8	0.3	0
Min.	0.003	39.6	12.8	0.0	0.0	0.2	0.3	0.014	0.026	1.2	0.7	2.2	170
Max.	0.052	43.5	15.2	0.5	0.5	0.4	0.8	0.039	0.054	6.1	3.0	3.7	280
Alluvial Aquifer (Cluster II)													
n	6	5	5	5	6	4	5	5	5	5	1	4	5
Mean	0.048	44.4	14.8	0.7	0.9	0.6	1.6	0.025	0.044	3.8	0.6	2.8	504
Median	0.041	44.0	15.2	0.5	1.1	0.5	1.7	0.028	0.044	3.0	0.6	3.2	520
C.V.	0.6	0.0	0.1	1.5	0.7	0.3	0.4	0.405	0.375	0.6	0.0	0.4	1
Min.	0.022	43.3	12.1	0.0	0.2	0.4	0.7	0.013	0.021	1.1	0.6	1.3	90
Max.	0.096	46.1	15.8	2.5	1.7	0.8	2.5	0.0	0.1	7.0	0.6	3.6	1100
Soil I (Cluster III)													
n	4	0	0	0	4	0	4	4	4	4	0	1	4
Mean	0.47	****	****	****	4.1	****	4.8	0.006	0.038	7.0	****	1.9	1280
Median	0.27	****	****	****	3.5	****	4.4	0.005	0.017	3.0	****	1.9	49
C.V.	1.14	****	****	****	0.4	****	0.3	0.483	1.270	1.1	****	0.0	2
Min.	0.10	****	****	****	3.1	****	3.7	0.004	0.008	3.0	****	1.9	20
Max.	1.25	****	****	****	6.3	****	6.9	0.010	0.110	19.0	****	1.9	5000
Soil II (Cluster IV)													
n	6	3	3	3	6	3	6	6	6	6	1	6	6
Mean	0.75	50.3	5.8	7.2	3.1	0.6	3.7	0.008	0.034	5.8	3.0	6.8	320
Median	0.26	50.2	5.9	1.0	3.1	0.5	3.6	0.007	0.018	3.5	3.0	4.3	135
C.V.	1.5	0.0	0.1	1.6	0.4	0.6	0.4	0.418	0.949	1.0	0.0	0.9	1
Min.	0.06	49.9	5.0	0.0	0.9	0.3	1.3	0.006	0.017	3.0	3.0	1.8	70
Max.	2.9	50.7	6.6	20.5	5.1	1.0	5.8	0.015	0.097	18.0	3.0	18.3	1000
Surficial													
n	12	8	8	8	12	8	12	12	12	11	2	10	12
Mean	0.112	44.9	13.4	1.1	1.2	0.5	1.7	0.018	0.037	3.0	1.8	3.6	403
Median	0.108	44.4	13.7	1.0	0.9	0.5	1.5	0.014	0.039	3.0	1.8	2.4	315
C.V.	1.2	0.1	0.2	0.9	1.0	0.3	0.8	0.705	0.484	0.3	0.9	0.9	1
Min.	<0.001	40.9	10.1	0.0	0.0	0.3	0.3	0.004	0.010	1.2	0.6	1.8	130
Max.	0.47	49.8	16.7	2.5	3.8	0.9	4.7	0.0	0.1	5.0	3.0	13.0	1200

5.2.4 Pahiwi – Balfour Road

The capture zone associated with the Pahiwi site encompasses an area of 15,520 Ha with an assemblage of 26% Bedrock/Hill Country and 73% Lowland type physiographic units. The Lowland component of the capture zone is comprised of 53% Gleyed and 21% Oxidising and Old Mataura type physiographic units. Relative to the Murphy Rd site, mean, median and max flow values across the sample record are 3.9, 4.9 and 3.0 times larger. Here the relative contribution from Bedrock/Hill Country makes up <1/3rd of the capture zone area. Due to the presence of 2 distinct geographical sources (i.e. different recharge domains) and varied physiographic units, the source of water supplying stream is inherently complex (Table 12).

On the basis of Old Balfour and Murphy Rd separations, flow measures and physiographic assemblages we propose a relatively minor contribution from Bedrock/Hill Country associated with peak runoff (surficial compartment) and 4 key lowland compartments. Due to the larger proportion of well-drained soils and oxidising aquifers, we propose a larger volumetric contribution from two separate aquifers to streamflow at the Pahiwi site. The remaining compartments will be associated with 'dry' and 'wet' lowland soil compartments and similar surficial compartments. Accordingly, for purposes of interrogating the data 3, 4, 5 and 6-compartment separations were run using tier-II (turbidity) and tier-III (pH) tracers (Table 12). The addition of SO_4 would likely improve the quality of the separation at this site.

On the basis of hydrological and hydrochemical data, the 5-compartment separation identified two groundwater components, one soil and two surficial signatures. The 6-compartment solution further subdivides the high flow compartment (cluster V) into two (Table 14, Figure 7)). Proceeding with a 6-compartment separation, soil moisture increases across clusters I – VI, from 0.14 -1.8 m^3/s and 41.0 – 50.5%, respectively. The 3-compartment separation combines both aquifers, both soil and both surficial compartments identified by the 6-compartment separation into one single compartment each. The 4-compartment solution subdivides the soil compartment from the 3-compartment separation into two.

Proceeding with the 6-compartment separation, cluster I is associated with the lowest flows and soil moisture and the warmest soil and water temperatures. These waters are highly evolved with saturation indices suggestive of a carbonate aquifer source, the lowest median SO_4 (8.3 mg/L), K (0.7 mg/L), and highest conductivity, Ca, Mg, Si, Total Alkalinity, Na and Cl concentrations of all clusters consistent with a highly evolved groundwater source derived exclusively from LLSR. In terms of redox, the aquifer is strongly oxidising with the second highest median DO, NNN and TN concentrations of the 6 compartments (Table 12). The carbonate aquifer compartment (cluster 1) signal is only evident during Dec – April and with the exception of March is seldom the dominant water source (Figure 7). On the basis of the data record, cluster I (carbonate aquifer) source is not volumetrically or hydrochemically important during the wettest times of the year (months 5 – 11) reflecting dilution by the volumetrically more significant shallow soil and surficial runoff compartments during wetter periods of the year (Table 12 and Figure 7).

Cluster II suggests a secondary aquifer compartment associated with a shallow alluvial aquifer system that overlies the carbonate aquifer compartment (cluster I). Cluster II waters are associated with the second lowest median flow, soil moisture and joint highest water temperature. Unfortunately, major ion data is missing for these waters although water quality and hydrological measures support a slightly less evolved groundwater source that is second only to cluster I (carbonate aquifer) in terms of median conductivity and clarity and second lowest turbidity and E. coli. The lowland alluvial aquifer compartment is an important source of water to stream over the autumn and early summer yet is not volumetrically or hydrochemically important during the wettest times of the year (months 5 – 8). The latter is thought to reflect dilution by the volumetrically much larger contribution from shallow Soil and Surficial runoff compartments during cold wet periods of the year (Table 12 and Figure 7). In this setting, Mg appears a better indicator of a groundwater flowpath but does not meet the suitability criteria to be used for flow separation.

Cluster III waters are associated with higher median flow and soil moisture and lower soil temperatures than cluster I (carbonate aquifer) and II (alluvial Aquifer) waters. Hydrochemically, these waters contain SO_4 concentrations that are c. 2 times those of aquifer dominated clusters which in conjunction with higher K, DOC and lower pH are all consistent with a greater soil zone source. Local groundwaters are depleted in SO_4, DOC and K and have significantly higher pH values (Rissmann et al., 2016; Hughes eta l., 2016). Sulphate is regulated by anion exchange, DOC via physical exclusion and K by ion-exchange (Rissmann et al., 2016). In terms of temporal distribution these waters appear to be important over the shoulders of the season, early summer and autumn suggesting residual soil drainage or 'first-flush' derived soil waters.

Cluster IV is associated with the 4th highest median flow and soil moisture and the second lowest soil temperature conditions of all clusters. Hydrochemical signatures are consistent with a relatively shallow and poorly evolved water source characterised by the second highest median K, Mn^{II}, Fe^{II}, TKN and Turbidity values and the lowest TN and NNN concentrations of all clusters. Sulphate is also elevated indicating a shallow source as groundwaters are depleted in SO_4. Lateral soil zone drainage of the large area of imperfectly to poorly drained lowland soils that make up 52% of the capture zone of the Pahiwi-Balfour Rd site is considered the main compartmental source of this water. In addition to hydrochemical signatures, a dominantly lowland soil water source is supported by median flow values that are ~8.4 times the median value for Bedrock/Hill Country sourced soil water at the Murphy Rd site. The relative frequency of cluster IV soil waters peak in April and October but are less dominant over the winter due to higher volumetric contributions from other sources (i.e., clusters V and VI).

Notably, the 6-compartment solution supports a larger component of lowland land surface recharge for the Pahiwi-Balfour Rd site. Here, median flows associated with both the carbonate and alluvial aquifer compartments are 16.8 and 5.4 x larger than the equivalent compartments occurring at the Murphy Rd site, indicating significant flow gain over the 7.6 km of stream reach. From a hydrochemical standpoint, the significant gain in Aquifer derived baseflow appears to be mainly associated with oxidising and NNN-rich groundwaters hosted by the stratified aquifer system that underlies the historical Balfour 'hot-spot' area. A proportionally larger groundwater contribution from the Balfour aquifer system relative to aquifers associated with the greater area of Gleyed type physiographic units is consistent with soil zone hydrological controls over recharge. Specifically, aquifer derived contributions to flow across areas of imperfectly to poorly drained soils are generally smaller than those from areas of well-drained soils (see Katsuyama et al., 2001, 2009). Ostensibly, the main difference between the Murphy Rd and Pahiwi-Balfour Rd sites is the soil environment, which appears to strongly influence aquifer through flow and the redox status of soil water recharge. Specifically, deep recharge is favoured in areas of well-drained soils across the Balfour area, driving considerable throughput of highly oxidised soil waters that discharge to stream. Upgradient within the Murphy Rd site, the predominance of the 'Gleyed' physiographic type unit favours lateral soil zone drainage resulting in lesser volumetric flushing of the underlying aquifer as well as lesser exchange with the atmosphere and meteoric oxygen, resulting in more reducing conditions.

Cluster V waters are associated with the highest median soil moisture, lowest soil temperatures and the second highest median flow values with a minor correlation with high-intensity rainfall events. These waters peak over the cool wet periods of the year and make up a significant proportion of the flow volume over these months. Cluster V waters are not represented in the data record from October to February. These waters have the highest DRP and show elevated K relative to Si, elevated Ca, DOC, SO_4, dissolved Fe, Mn and yet lower conductivity, Na and Cl relative to other clusters with hydrochemical data, all of which supports a surficial source. Importantly key measures of surficial runoff such as E. coli, TAM, TKN, TP, TSS and Turbidity are significantly lower that cluster VI (high-intensity rainfall cluster) suggesting a lower surface wash or runoff component under lower intensity rainfall.

Cluster VI waters are associated with the highest median flow but only the second highest soil moisture and by far the highest 48Hr rainfall intensity of all clusters. This cluster is prevalent from March – September and appears to correlate with higher intensity rainfall events. Hydrochemical data is lacking for this cluster, but water quality data supports a very immature and shallow contaminant source consistent with surficial runoff. Specifically, the highest median E. coli, NNN, TAM, TKN, TN, TP, TSS, Turbidity and the lowest pH of all clusters. Ostensibly, these waters reflect a larger infiltration excess component, dominated by surficial wash/runoff. If the McCale Rd and Old Balfour sites are considered representative of Bedrock/Hill Country inputs, the bulk of contaminants appear to originate from lowland areas. Here, measures of the stable isotopes of water would help constrain the volumetric contribution from Lowland and bedrock/Hill Country sources. Cluster VI waters are most frequent during later summer, through to September but are absent in the data record from October – February. A 7-compartment separation further subdivides cluster VI waters into ‘warm-dry and ‘cool-dry’ high-intensity runoff events.

Table 12: Summary statistics by dominant ('winner') cluster for a 6-compartment separation at Pahiwi - Balfour Road.

	Flow (simulated)	Soil moisture (%)	Soil temp at 10 cm (deg. C)	48 hr rain. (mm)	Water Temperature	pH	Conductivity (us/cm)	DO
Aquifer I (Cluster I)								
n	10	7	7	7	10	10	7	10
Mean	0.22	42.06	14.37	0.21	14.69	8.08	213.43	12.62
Median	0.14	40.92	14.60	0.00	15.30	8.00	216.00	12.70
C.V.	1.03	0.07	0.09	1.84	0.16	0.03	0.03	0.08
Min.	0.10	39.55	11.70	0.00	11.10	7.80	203.00	10.80
Max.	0.86	48.10	15.60	1.00	17.60	8.70	218.00	14.40
Aquifer II (Cluster II)								
n	14	7	7	6	14	14	7	13
Mean	0.31	43.74	14.47	1.42	15.25	8.45	209.00	12.46
Median	0.25	42.39	14.80	1.00	15.60	8.35	209.00	12.70
C.V.	0.47	0.06	0.17	1.27	0.20	0.04	0.08	0.19
Min.	0.13	40.95	11.17	0.00	9.00	8.10	188.00	7.24
Max.	0.54	47.74	17.63	4.50	18.90	9.40	233.00	16.70
Soil I (Cluster III)								
n	10	8	8	8	10	10	8	7
Mean	0.38	45.78	11.37	0.88	12.08	7.65	208.88	12.34
Median	0.32	45.10	10.47	0.00	11.45	7.60	213.00	12.60
C.V.	0.46	0.05	0.33	1.58	0.39	0.02	0.06	0.07
Min.	0.17	43.33	6.70	0.00	6.20	7.40	187.00	11.30
Max.	0.69	49.72	15.91	3.50	21.00	7.90	223.00	13.60
Soil II (Cluster IV)								
n	18	9	9	9	17	18	10	16
Mean	0.60	46.83	10.39	1.56	10.41	7.72	191.20	12.86
Median	0.49	46.40	9.85	0.50	10.20	7.70	192.00	12.70
C.V.	0.82	0.06	0.32	1.41	0.34	0.03	0.11	0.14
Min.	0.17	43.26	5.26	0.00	4.80	7.30	153.00	10.30
Max.	2.22	50.68	15.21	5.50	17.20	8.00	219.00	16.00
Surficial I (Cluster V)								
n	9	2	2	2	9	9	2	9
Mean	3.59	48.88	10.71	14.83	8.34	6.91	93.55	12.15
Median	1.78	48.88	10.71	14.83	7.70	7.10	93.55	12.40
C.V.	0.86	0.03	0.44	0.49	0.40	0.07	1.16	0.19
Min.	0.16	47.78	7.36	9.65	3.00	5.70	17.10	8.36
Max.	8.93	49.98	14.06	20.00	13.30	7.20	170.00	15.70
Surficial II (Cluster VI)								
n	17	11	11	11	17	17	11	17
Mean	1.48	49.78	7.86	3.09	7.72	7.38	192.82	12.16
Median	1.16	50.49	6.75	0.50	7.30	7.40	195.00	12.10
C.V.	0.65	0.03	0.44	1.73	0.44	0.02	0.06	0.15
Min.	0.52	46.21	3.66	0.00	3.30	7.20	171.00	9.10
Max.	3.43	50.93	14.75	18.00	15.30	7.60	210.00	15.60

Table 12 continued: Summary statistics by dominant ('winner') cluster for a 6-compartment separation at Pahiwi - Balfour Road.

	Talk	Ca	Mg	Si	Na	K	Cl	SO_4	Fe	Mn	NNN	TKN	TN	DRP	TP	TSS	VSS	Turb.	E.Coli
Aquifer I (Cluster I)																			
n	7	7	7	3	7	7	7	7	7	7	10	6	10	10	10	9	6	10	10
Mean	51.71	13.89	8.67	17.70	15.90	0.74	18.90	8.33	0.06	0.01	4.34	0.37	4.75	0.01	0.03	2.60	2.12	1.48	241
Median	53.00	13.70	8.50	17.00	15.90	0.60	19.00	7.30	0.06	0.01	4.50	0.32	4.85	0.01	0.03	3.00	2.65	1.43	175
C.V.	0.06	0.06	0.08	0.17	0.10	0.43	0.04	0.39	0.54	0.55	0.26	0.36	0.24	0.49	0.32	0.25	0.53	0.22	1
Min.	45.00	12.80	7.50	15.10	12.90	0.46	17.50	5.10	0.02	0.00	2.59	0.24	3.00	0.01	0.02	1.20	0.60	0.96	83
Max.	55.00	15.20	9.50	21.00	18.40	1.27	19.70	15.10	0.12	0.01	6.30	0.59	6.90	0.03	0.04	3.00	3.00	2.20	540
Aquifer II (Cluster II)																			
n	0	0	0	0	0	0	0	0	0	0	14	7	14	14	14	12	0	10	14
Mean	****	****	****	****	****	****	****	****	****	****	3.62	0.47	4.15	0.01	0.03	3.26	****	2.72	310
Median	****	****	****	****	****	****	****	****	****	****	3.72	0.48	4.30	0.02	0.03	3.00	****	2.55	235
C.V.	****	****	****	****	****	****	****	****	****	****	0.23	0.21	0.20	0.32	0.20	0.19	****	0.19	1
Min.	****	****	****	****	****	****	****	****	****	****	2.16	0.34	2.80	0.01	0.03	3.00	****	2.10	20
Max.	****	****	****	****	****	****	****	****	****	****	5.10	0.61	5.50	0.02	0.05	5.00	****	3.80	900
Soil I (Cluster III)																			
n	7	7	7	4	7	7	7	7	7	7	10	8	10	10	10	8	6	10	10
Mean	43.14	15.00	7.90	15.30	13.17	1.25	18.71	13.77	0.07	0.01	4.13	0.52	4.66	0.02	0.03	3.20	2.62	2.28	347
Median	44.00	15.40	8.30	14.90	13.20	1.40	18.20	12.50	0.06	0.01	4.10	0.49	4.65	0.02	0.03	3.00	3.00	2.35	235
C.V.	0.16	0.11	0.11	0.08	0.08	0.39	0.09	0.25	0.33	0.23	0.20	0.18	0.16	0.25	0.25	0.23	0.36	0.09	1
Min.	34.00	12.70	6.30	14.40	11.20	0.57	16.90	10.30	0.05	0.01	2.40	0.43	3.20	0.02	0.03	2.60	0.70	1.93	60
Max.	52.00	17.50	8.70	17.00	14.40	1.75	21.00	19.20	0.12	0.02	5.60	0.71	6.00	0.03	0.05	5.00	3.00	2.50	970
Soil II (Cluster IV)																			
n	3	3	3	2	3	3	3	3	3	3	18	9	17	17	17	17	1	13	17
Mean	39.33	11.70	5.87	16.25	12.13	0.96	14.33	9.53	0.11	0.01	3.47	0.50	4.03	0.02	0.04	4.29	1.00	3.57	395
Median	37.00	10.10	5.60	16.25	11.90	0.91	13.80	8.40	0.11	0.01	3.22	0.50	3.80	0.02	0.04	3.00	1.00	3.50	170
C.V.	0.15	0.25	0.24	0.06	0.07	0.20	0.09	0.34	0.42	0.01	0.26	0.18	0.22	0.47	0.41	0.64	0.00	0.20	1
Min.	35.00	9.90	4.60	15.60	11.40	0.80	13.40	7.00	0.06	0.01	2.30	0.36	2.80	0.00	0.01	3.00	1.00	2.60	40
Max.	46.00	15.10	7.40	16.90	13.10	1.18	15.80	13.20	0.15	0.01	5.48	0.65	6.10	0.03	0.07	14.00	1.00	4.70	1800
Surficial I (Cluster V)																			
n	0	0	0	0	0	0	0	0	0	0	9	2	9	9	9	8	0	5	9
Mean	****	****	****	****	****	****	****	****	****	****	4.76	0.93	5.57	0.03	0.09	17.18	****	16.91	5760
Median	****	****	****	****	****	****	****	****	****	****	3.98	0.93	5.20	0.02	0.10	9.65	****	4.60	3000
C.V.	****	****	****	****	****	****	****	****	****	****	0.32	1.26	0.28	0.74	0.64	0.92	****	1.15	2
Min.	****	****	****	****	****	****	****	****	****	****	3.03	0.10	3.50	0.01	0.03	3.00	****	1.34	24
Max.	****	****	****	****	****	****	****	****	****	****	6.90	1.76	8.00	0.06	0.19	43.00	****	44.00	35000
Surficial II (Cluster VI)																			
n	6	6	6	3	6	6	6	6	6	6	17	11	17	17	17	17	4	14	17
Mean	37.00	15.10	6.57	15.47	12.15	1.45	16.78	16.27	0.11	0.02	4.51	0.69	5.19	0.03	0.06	8.58	1.98	10.29	3870
Median	37.50	15.00	6.55	16.40	12.25	1.59	17.10	17.30	0.09	0.02	4.60	0.69	5.30	0.02	0.04	5.00	2.10	6.75	160
C.V.	0.19	0.08	0.13	0.11	0.10	0.20	0.12	0.20	0.65	0.29	0.18	0.40	0.15	1.16	1.18	1.61	0.61	1.41	3
Min.	27.00	13.70	5.40	13.50	10.40	1.06	13.20	10.70	0.04	0.01	2.80	0.43	3.90	0.01	0.03	1.70	0.70	2.90	10
Max.	48.00	16.70	7.90	16.50	13.90	1.72	19.00	19.30	0.24	0.02	5.70	1.44	6.30	0.15	0.34	61.00	3.00	60.00	44000

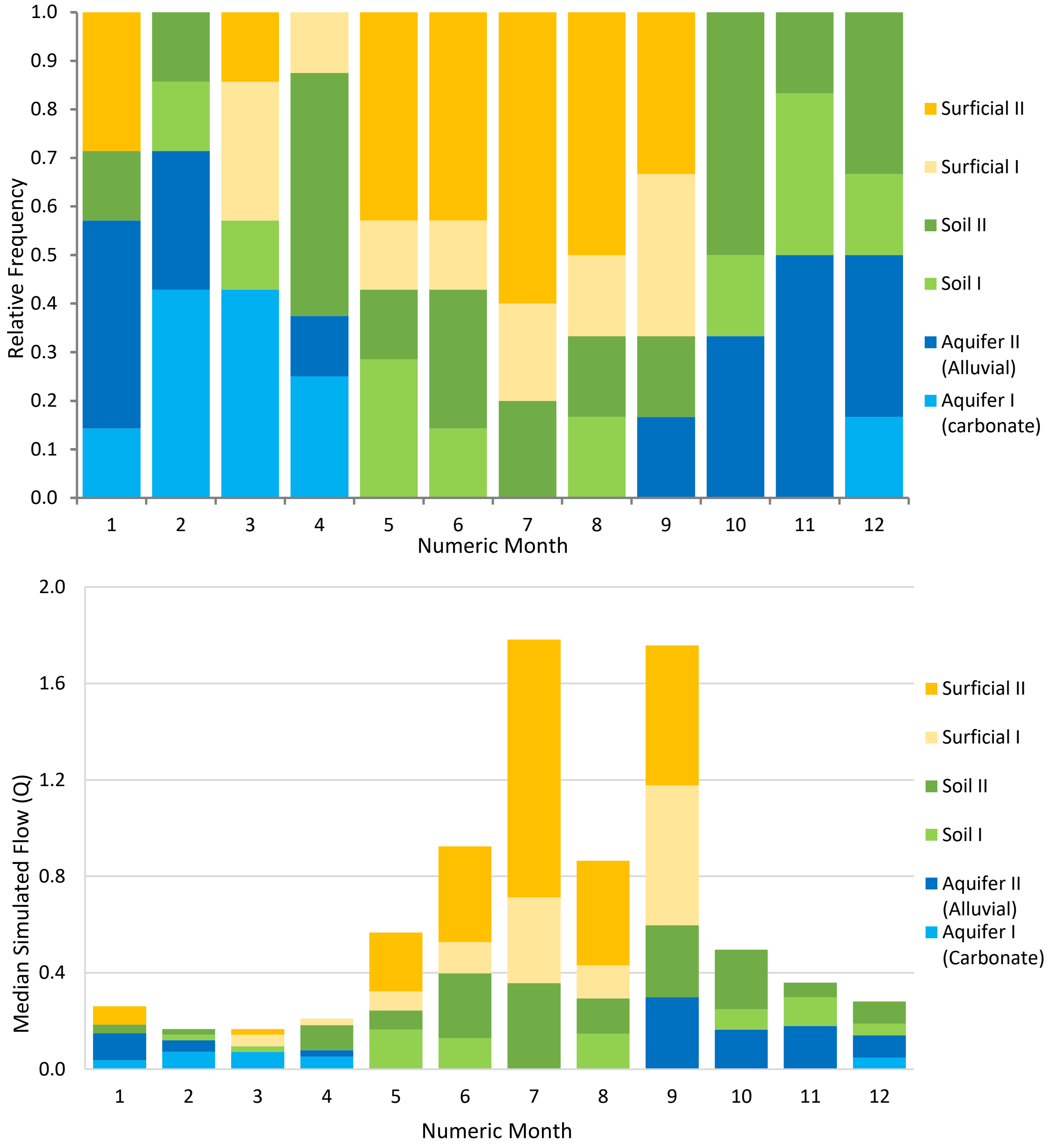

Figure 7: Relative frequency of water source for a 6-compartment (Cluster) separation by month for the Pahiwi-Balfour Rd monitoring site, Waimea Valley, Southland (Environment Southland data). Soil moisture and flow are lowest when the Carbonate Aquifer source dominates and highest when the Surficial source is present.

On a monthly basis not one of the 6-compartments supplying stream flow at Pahiwi-Balfour Rd occur on their own. However, across the calendar year, there is a clear temporal pattern in the volumetric significance of the hypothesised compartmental water sources supplying stream. Moving beyond monthly patterns in water source, stream flow samples dominated by a single compartment, i.e., ≥0.90, are apparent in the data record. As such, these samples can be used to provide constraints over the end-member compositions and associated water quality of each relevant compartment (Table 13).

Table 13: Table of Endmember Hydrological and Water Quality Signatures at Pahiwi - Balfour Rd. Endmembers statistics are derived for samples with a cluster membership of ≥0.85 and differ from summary statistics by 'winner' cluster.

	Q (simulated)	Soil Moisture (%)	Soil Temp at 10 cm	48 Hr Rainfall	NNN	TKN	TN	DRP	TP	TSS	VSS	Turbidity	E.Coli
Aquifer I (Cluster I)													
n	2	2	2	2	2	2	2	2	2	2	2	2	2
Mean	0.12	40.80	15.10	0.25	4.70	0.32	5.00	0.01	0.02	1.55	0.70	1.47	125
Median	0.12	40.80	15.10	0.25	4.70	0.32	5.00	0.01	0.02	1.55	0.70	1.47	125
C.V.	0.22	0.00	0.05	1.41	0.09	0.00	0.08	0.28	0.32	0.32	0.20	0.02	0
Min.	0.10	40.68	14.59	0.00	4.40	0.32	4.70	0.01	0.02	1.20	0.60	1.45	110
Max.	0.14	40.92	15.60	0.50	5.00	0.32	5.30	0.02	0.03	1.90	0.80	1.49	140
Aquifer II (Cluster II)													
n	2	2	2	2	2	2	2	2	2	2	1	2	2
Mean	0.45	46.21	13.34	1.25	4.05	0.57	4.60	0.02	0.04	2.80	0.70	2.30	530
Median	0.45	46.21	13.34	1.25	4.05	0.57	4.60	0.02	0.04	2.80	0.70	2.30	530
C.V.	0.43	0.07	0.27	1.41	0.02	0.04	0.03	0.39	0.41	0.10	0.00	0.06	0
Min.	0.32	43.97	10.78	0.00	4.00	0.55	4.50	0.02	0.03	2.60	0.70	2.20	460
Max.	0.59	48.45	15.91	2.50	4.10	0.58	4.70	0.03	0.05	3.00	0.70	2.40	600
Soil I (Cluster III)													
n	4	3	3	3	4	3	4	4	4	3	0	4	4
Mean	0.30	43.69	15.25	1.33	4.13	0.50	4.60	0.02	0.04	3.00	****	2.58	545
Median	0.26	42.39	16.70	2.00	4.20	0.51	4.75	0.02	0.04	3.00	****	2.55	530
C.V.	0.60	0.08	0.22	0.87	0.21	0.23	0.19	0.09	0.10	0.00	****	0.04	1
Min.	0.13	40.95	11.41	0.00	3.00	0.38	3.40	0.02	0.03	3.00	****	2.50	220
Max.	0.54	47.74	17.63	2.00	5.10	0.61	5.50	0.02	0.04	3.00	****	2.70	900
Soil II (Cluster IV)													
n	6	3	3	3	6	3	6	6	6	6	0	3	6
Mean	0.59	48.25	10.30	2.33	3.42	0.51	3.98	0.02	0.04	5.00	****	3.60	498
Median	0.58	50.36	9.60	2.00	3.55	0.49	4.05	0.02	0.04	3.00	****	3.50	275
C.V.	0.48	0.08	0.45	1.08	0.19	0.25	0.15	0.31	0.53	0.89	****	0.10	1
Min.	0.26	44.01	6.10	0.00	2.40	0.40	3.00	0.01	0.01	3.00	****	3.30	70
Max.	0.92	50.38	15.21	5.00	4.00	0.65	4.70	0.03	0.07	14.00	****	4.00	1800
Surficial I (Cluster V)													
n	3	1	1	1	3	1	3	3	3	3	0	3	3
Mean	2.11	50.49	6.28	1.00	4.64	0.79	5.43	0.02	0.06	8.00	****	8.13	6127
Median	2.40	50.49	6.28	1.00	5.14	0.79	5.70	0.02	0.06	9.00	****	10.50	310
C.V.	0.70	0.00	0.00	0.00	0.21	0.00	0.19	0.34	0.50	0.57	****	0.56	2
Min.	0.52	50.49	6.28	1.00	3.50	0.79	4.30	0.01	0.03	3.00	****	2.90	70
Max.	3.43	50.49	6.28	1.00	5.27	0.79	6.30	0.03	0.08	12.00	****	11.00	18000
Surficial II (Cluster VI)													
n	4	0	0	0	4	0	4	4	4	3	0	2	4
Mean	4.67	****	****	****	5.42	****	6.23	0.03	0.07	8.43	****	4.10	1840
Median	4.22	****	****	****	5.47	****	6.00	0.02	0.07	8.30	****	4.10	1800
C.V.	0.83	****	****	****	0.27	****	0.23	0.62	0.56	0.30	****	0.17	1
Min.	1.34	****	****	****	3.98	****	4.90	0.01	0.04	6.00	****	3.60	60
Max.	8.93	****	****	****	6.77	****	8.00	0.05	0.12	11.00	****	4.60	3700

5.2.5 Mandeville

The capture zone associated with the Mandeville site encompasses an area of 38,838 Ha with an assemblage of 33% Bedrock/Hill Country and 77% Lowland type physiographic units. The Lowland component of the capture zone is comprised of 43% Gleyed and 23% Oxidising and Old Mataura type physiographic units. The remaining 1 % is comprised of Peat Wetland and Riverine type physiographic units and minor blank space associated with small towns/villages. Relative to the Pahiwi Rd site, mean, median and max flow values across the sample record are 3.9, 4.9 and 3.0 times larger. Here the relative contribution from Bedrock/Hill Country makes up ~1/3rd of the capture zone area. Due to the presence of 2 distinct geographical sources (i.e. different recharge domains) and varied physiographic units, the source of water supplying stream is inherently complex (Table 14). On the basis of previous separations and the physiographic setting we once again propose a 5 to 6 compartment separation for the Mandeville site using tier-II (turbidity) and tier-III (pH and water temperature) tracers in order to maximise the data record (n = 122 samples) for analysis. Subsequently, a tier I separation was run using Na and SO_4 for 68 measures but is not discussed here.

Between the Pahiwi-Balfour Rd and Mandeville capture zones, there is a 6.8% increase, c. 2,655 Ha in the proportion area of Bedrock/Hill Country, a 9% decrease in the area of Gleyed (3,573 Ha) and a small increase of c. 2%, 817 Ha, of Oxidising/Old Mataura physiographic units. In terms of proximity to the monitoring site, the Oxidising/Old Mataura units occur significantly up gradient with only a few minor discontinuous units south of the Waimea Stream at Nine Mile Rd site. Accordingly, we theorise that the majority of groundwaters will be sourced from upgradient of the monitoring site with a lesser contribution from Gleyed and negligible contribution from Bedrock/Hill Country units to stream. Importantly, south of the Pahiwi-Balfour Rd site the proximity of the steep northern escarpment of the Southland Syncline, relative to the Waimea Stream, and the large number of small tributaries that drain to the Waimea are expected to play an important role over water composition, especially during periods of high-intensity rainfall.

On the basis of hydrological and hydrochemical data, the 5-compartment separation identified two groundwater components, one soil and two surficial signatures. The 6-compartment solution subdivides the soil compartment into two (Figure 8, Table 14). Proceeding with a 6-compartment separation, median flow and soil moisture increases across clusters I – VI, from 0.36 -12.53 m^3/s and 42.7 – 50.8%, respectively. Median soil temperature and baseflow estimates from a 3-pass recursive filter for the Mandeville site decreases across clusters I – VI, from 14.9 to 6.9°C and 90 to 20%, respectively. Median water temperature also decreases systematically from cluster I – VI.

Table 14: Summary statistics by dominant ('winner') cluster for a 6-compartment separation at Manderville.

	Q (Recorder)	Baseflow Proportion	Soil Moisture (%)	Soil Temp at 10 cm	48 Hr Rainfall	Water Temperature	pH	Conductivity (us/cm)	DO
Aquifer I (Cluster I)									
n	8	7	8	8	8	8	8	8	8
Mean	0.54	92.72	43.58	14.19	1.38	16.35	8.40	199.38	12.58
Median	0.39	95.87	43.21	14.95	0.00	17.65	8.20	197.50	12.65
C.V.	0.55	0.09	0.05	0.22	2.42	0.24	0.07	0.06	0.13
Min.	0.28	75.43	40.38	10.02	0.00	11.00	7.90	180.00	10.60
Max.	1.09	99.14	46.46	17.97	9.50	21.50	9.30	215.00	15.50
Aquifer II (Cluster II)									
n	12	12	12	12	12	12	12	12	12
Mean	0.76	82.77	44.25	12.42	2.63	13.62	8.13	196.25	12.20
Median	0.72	84.29	43.83	13.32	1.00	15.10	8.00	196.50	12.05
C.V.	0.60	0.20	0.08	0.26	1.43	0.30	0.05	0.10	0.09
Min.	0.23	50.51	39.76	5.34	0.00	7.30	7.60	150.00	10.70
Max.	1.78	99.64	51.06	15.60	11.50	18.80	8.90	232.00	14.00
Soil I (Cluster III)									
n	11	11	5	5	5	8	9	3	5
Mean	0.86	76.35	44.05	11.89	1.10	10.64	7.83	190.33	12.46
Median	0.78	79.91	43.25	12.27	0.00	9.60	7.80	195.00	12.60
C.V.	0.60	0.27	0.08	0.28	1.99	0.45	0.05	0.14	0.08
Min.	0.26	31.15	40.04	7.90	0.00	2.50	7.10	162.00	11.10
Max.	1.61	96.86	47.65	16.38	5.00	18.80	8.50	214.00	13.50
Soil II (Cluster IV)									
n	7	7	3	3	3	7	7	3	5
Mean	2.77	69.02	49.75	8.01	1.00	7.34	7.61	213.00	12.08
Median	1.60	78.72	50.74	7.12	0.00	6.10	7.70	212.00	12.30
C.V.	0.86	0.34	0.04	0.42	1.73	0.47	0.06	0.01	0.10
Min.	0.45	29.75	47.58	5.20	0.00	3.50	7.00	211.00	10.60
Max.	6.78	93.57	50.93	11.71	3.00	12.20	8.30	216.00	13.60
Surficial I (Cluster V)									
n	7	7	7	7	7	7	7	7	7
Mean	17.34	20.89	50.16	7.98	16.06	7.54	7.29	187.14	11.86
Median	9.91	14.19	50.42	6.47	15.50	6.00	7.30	187.00	11.40
C.V.	0.85	0.78	0.02	0.33	0.53	0.40	0.03	0.11	0.17
Min.	1.30	5.97	48.71	5.03	7.00	4.80	7.00	162.00	10.10
Max.	43.65	52.26	51.18	11.56	31.00	13.10	7.60	226.00	16.30
Surficial II (Cluster VI)									
n	10	10	8	8	8	10	10	8	10
Mean	5.21	36.95	49.46	9.33	6.38	9.54	7.50	184.50	12.20
Median	4.87	38.64	50.03	10.42	1.75	10.80	7.45	183.50	11.70
C.V.	0.45	0.42	0.04	0.42	1.35	0.43	0.03	0.04	0.22
Min.	2.48	11.30	45.05	3.57	0.00	3.30	7.20	173.00	9.76
Max.	8.64	63.23	51.23	13.90	20.50	14.50	8.00	194.00	18.70

Table 14 continued: Summary statistics by dominant ('winner') cluster for a 6-compartment separation at Manderville.

	Talk	Ca	Mg	Si	Na	K	Cl	SO_4	Fe	Mn	NNN	TKN	TN	DRP	TP	TSS	VSS	Turb.	E.Coli
Aquifer I (Cluster I)																			
n	6	6	6	5	6	6	6	6	6	6	8	8	8	8	8	4	1	8	8
Mean	54.33	13.75	6.80	11.58	17.18	0.91	20.68	6.18	0.13	0.01	2.50	0.54	3.06	0.01	0.03	1.50	1.50	1.42	191
Median	54.50	14.05	7.00	10.00	17.25	0.78	21.00	5.00	0.12	0.01	2.60	0.56	3.05	0.01	0.03	1.50	1.50	1.35	165
C.V.	0.05	0.12	0.10	0.40	0.05	0.40	0.07	0.48	0.36	0.65	0.35	0.19	0.29	0.73	0.38	0.00	0.00	0.11	1
Min.	50.00	11.90	5.60	8.30	15.80	0.50	18.90	3.10	0.09	0.00	1.02	0.37	1.66	0.01	0.02	1.50	1.50	1.26	50
Max.	58.00	16.10	7.40	19.70	18.20	1.44	22.00	10.90	0.21	0.02	3.60	0.66	4.30	0.03	0.06	1.50	1.50	1.66	440
Aquifer II (Cluster II)																			
n	8	8	8	6	8	8	8	8	8	8	12	12	12	12	12	7	3	12	12
Mean	48.25	13.28	6.35	9.52	15.98	1.12	19.80	7.46	0.13	0.02	2.86	0.60	3.46	0.01	0.03	1.86	1.10	2.32	261
Median	52.00	12.90	6.50	9.90	16.20	1.01	20.50	4.80	0.13	0.01	2.90	0.58	3.50	0.01	0.03	1.50	1.50	2.30	305
C.V.	0.18	0.16	0.13	0.38	0.11	0.32	0.15	0.61	0.30	0.74	0.37	0.29	0.31	0.61	0.38	0.43	0.63	0.10	1
Min.	35.00	10.50	5.00	3.90	13.70	0.71	13.60	4.20	0.07	0.01	1.40	0.37	1.97	0.00	0.02	1.00	0.30	1.99	40
Max.	58.00	17.50	7.40	14.00	18.20	1.85	23.00	16.40	0.18	0.04	4.40	1.07	5.50	0.03	0.06	3.00	1.50	2.80	490
Soil I (Cluster III)																			
n	3	3	3	3	3	3	3	3	3	3	9	2	8	7	8	4	1	6	8
Mean	43.67	13.60	5.67	15.07	14.50	1.31	17.23	10.60	0.16	0.01	2.51	0.42	3.13	0.03	0.06	2.68	0.80	4.27	294
Median	44.00	14.30	5.10	15.10	14.00	1.25	16.90	11.80	0.14	0.01	2.20	0.42	3.10	0.02	0.05	2.20	0.80	4.20	265
C.V.	0.06	0.16	0.19	0.06	0.09	0.14	0.15	0.38	0.22	0.63	0.59	0.19	0.53	0.81	0.62	0.58	0.00	0.14	1
Min.	41.00	11.20	5.00	14.20	13.50	1.17	14.80	6.10	0.14	0.01	0.16	0.36	0.66	0.01	0.02	1.50	0.80	3.60	40
Max.	46.00	15.30	6.90	15.90	16.00	1.52	20.00	13.90	0.20	0.02	5.00	0.47	6.00	0.07	0.13	4.80	0.80	5.20	700
Soil II (Cluster IV)																			
n	2	2	2	2	2	2	2	2	2	2	7	3	7	7	7	5	1	5	7
Mean	48.00	16.10	6.65	8.30	14.75	1.14	19.70	13.70	0.17	0.02	4.40	0.56	4.83	0.02	0.03	3.88	0.80	5.18	219
Median	48.00	16.10	6.65	8.30	14.75	1.14	19.70	13.70	0.17	0.02	4.10	0.56	4.50	0.02	0.03	3.40	0.80	4.70	150
C.V.	0.24	0.14	0.12	1.31	0.15	0.68	0.01	0.57	0.13	0.57	0.40	0.24	0.32	0.58	0.31	0.48	0.00	0.36	1
Min.	40.00	14.50	6.10	0.59	13.20	0.59	19.50	8.20	0.15	0.01	2.50	0.43	3.20	0.00	0.02	1.50	0.80	3.80	100
Max.	56.00	17.70	7.20	16.00	16.30	1.69	19.90	19.20	0.18	0.03	6.90	0.70	7.30	0.03	0.05	6.00	0.80	8.30	530
Surficial I (Cluster V)																			
n	6	6	6	5	6	6	6	6	6	6	7	7	7	7	7	2	0	7	7
Mean	33.50	15.27	5.22	9.90	11.75	2.43	17.95	14.58	0.25	0.05	3.77	1.74	5.49	0.06	0.18	39.00	****	43.57	19186
Median	35.00	14.85	5.05	10.00	11.70	2.20	16.65	13.15	0.21	0.04	3.20	1.79	4.70	0.05	0.19	39.00	****	43.00	11000
C.V.	0.17	0.14	0.19	0.29	0.13	0.28	0.33	0.22	0.67	0.74	0.28	0.26	0.28	0.83	0.47	0.15	****	0.22	1
Min.	24.00	13.20	4.10	6.00	9.70	1.90	12.60	11.30	0.07	0.02	2.70	1.20	3.70	0.00	0.07	35.00	****	27.00	200
Max.	41.00	18.80	6.90	14.00	14.30	3.80	29.00	18.60	0.50	0.10	5.40	2.40	7.90	0.15	0.27	43.00	****	55.00	82000
Surficial II (Cluster VI)																			
n	5	5	5	4	5	5	5	5	5	5	10	8	10	10	10	6	1	10	9
Mean	40.60	15.18	5.72	11.05	13.04	1.31	16.22	12.68	0.14	0.01	3.04	0.82	3.88	0.03	0.07	7.40	1.50	10.33	2036
Median	39.00	15.50	5.70	11.15	13.10	1.32	15.70	13.80	0.13	0.01	3.10	0.75	3.80	0.03	0.05	6.50	1.50	9.30	1000
C.V.	0.24	0.08	0.05	0.18	0.08	0.12	0.10	0.33	0.26	0.27	0.29	0.34	0.23	0.62	0.48	0.38	0.00	0.23	1
Min.	27.00	13.50	5.30	8.70	12.00	1.11	14.40	7.90	0.09	0.01	1.64	0.52	2.30	0.01	0.04	5.00	1.50	7.40	20
Max.	52.00	16.30	6.10	13.20	14.70	1.49	18.50	17.90	0.19	0.02	4.18	1.32	5.20	0.06	0.13	12.00	1.50	14.10	7000

Cluster I is associated with the lowest flows and soil moisture and the warmest soil and surface water temperatures. Cluster II is associated with similar soil moisture and temperature conditions to cluster I but the median flow is 1.7x higher and surface water temperatures are lower. Baseflow contributions provided from a 3-pass recursive filter approach for Mandeville is highest for cluster 1 (90%) and slightly lower for cluster II (82%). Cluster I waters are only marginally more evolved with slightly higher median conductivity, Na, Cl and Mg and Total Alkalinity relative to cluster II waters. Notably, although Na and Cl peak in cluster I and II groundwaters, median Ca and Si, both of which are significantly correlated with flow, are of lower concentration in both groundwaters than they are in other clusters. Removal of Si and Ca from groundwater by ion exchange reactions have been noted by other workers (O'Brien and Hendershot, 1993). In this setting Mg appears a better indicator of a groundwater flow path but does not meet the suitability criteria to be used for flow separation.

Significantly, median SO_4 is low in both cluster I (5.0 mg/L) and cluster II (4.8 mg/L) waters as is consistent with a dominant groundwater source with the highest clarity, lowest turbidity and the lowest *E. coli*, DOC and TKN concentrations. Relative to Pahiwi-Balfour Rd, median dissolved Fe and Mn is ~2x higher and NNN 1 -2 mg/L lower for the carbonate and alluvial aquifer dominated clusters, suggesting a Gleyed aquifer component is important at Mandeville. Cluster I waters appear to be slightly more oxidising than cluster II waters and overall are the two most oxidising compartments supplying stream flow at Mandeville.

Overall, the difference in hydrochemical composition between these two clusters is small relative to that observed at the Old Balfour, Murphy and Pahiwi-Balfour Rd sites where the carbonate aquifer signature of cluster I waters is strongly contrasting with the shallow alluvial aquifer signature of cluster II waters. All the same, cluster I waters appear to retain a minor carbonate signature, higher Total Alkalinity, lower SO_4 and higher pH and conductivity, from upgradient aquifers, albeit significantly diluted by an alluvial signature, by the time the stream reaches Mandeville. Much of the groundwater inflow is anticipated to occur between the Pahiwi-Balfour and Longridge Stream confluence although there may be some small gain between the Longridge and the Nine Mile Road site in association with Oxidising/Old Mataura aquifers.

In terms of temporal distribution, the deeper and slightly more evolved cluster I groundwaters are absent during the cool wet months of the year (June – September) and peak during the warmer drier months when flow is at its lowest. Shallow, cluster II groundwaters are present almost all year round, with the exception of September when flow values peak in association with what is inferred to be drainage from soil and surficial runoff compartments.

Cluster III waters are associated with a slightly higher median and mean soil moisture and median flow and yet significantly lower baseflow proportion (69%) and soil and water temperatures relative to cluster II (aquifer II) (Table 14). The relative frequency of cluster III waters peaks in the warmer months, January – May, when flow is lower (Figure 8). Hydrochemically, cluster III waters are less evolved than cluster I and II groundwaters, with lower median pH and Total Alkalinity and higher median dissolved Mn, SO_4, K, DOC and TP suggestive of a weakly reducing soil zone source, not an oxidising aquifer.

Relative to cluster III soil waters, cluster IV waters are associated with cooler soil and water temperatures, higher median flow, soil moisture and a lower baseflow proportion. Cluster IV soil waters show less evolved signatures with higher NNN, Ca, TAM and DOC concentrations relative to cluster III soil waters. Overall, both soil zone signatures are consistent with weakly reducing, 'Gleyed' type, physiographic signals and the lowest NNN concentrations of all clusters. However, relative to cluster IV waters, cluster III soil waters are hydrochemically more evolved suggesting a longer residence time within the soil zone and the evolution of weakly reducing conditions, as characterised by higher median concentrations of dissolved Mn, Fe, DRP, Total Alkalinity, Si and yet lower NNN and K. In terms of relative frequency, cluster III soil waters peak in the warmer months of the year (i.e., Jan – April), whereas cluster IV soil waters peak in the cooler wetter months of the year (i.e., June – August).

Cluster V is associated with the highest median flow, by far the highest 24 and 48 Hr rainfall intensity and the lowest baseflow proportion of all clusters. Hydrochemical and water quality signatures for cluster V waters support a surficial runoff origin with the highest median F, TP, TKN, TN, DRP, TP, K, SO_4, TSS, Turbidity and E. coli of all clusters. At the same time, Na and Cl concentrations are at their lowest along with pH. These signals all indicate significant flushing of the surficial compartment following a period of relatively stable climatic conditions, generating large quantities of contaminants. Importantly, Na and Cl concentrations for cluster V waters are twice those for the surficial runoff cluster (III) for the Bedrock/Hill Country dominated Old Balfour Rd site, suggesting a significant lowland contribution. Given the association with high-intensity rainfall events, infiltration excess overland flow may play a more significant role in the generation of cluster V waters. A 7-compartment separation further subdivides cluster V waters into 'cool' and 'warm' high intensity rainfall event clusters.

Cluster VI (Surficial II) waters are characterised by the second highest median flow and baseflow proportion of all clusters and the lowest soil and stream water temperatures. Median 48Hr rainfall intensity is the second highest of all clusters but 4 times lower than cluster V waters. Hydrochemically, these waters are characterised by the highest median DOC, Ca, Fe^{II}, NNN and the second highest F, TP, TKN, TN, DRP, TP, K, SO_4, TSS, Turbidity and E. coli of all clusters. The difference between cluster V and cluster VI waters appears to relate to rainfall intensity with a more surficial signature and higher rates of surficial flushing associated with cluster V waters. Overall, these signals all suggest a shallow source most consistent with limited regulation of land use contaminants by processes such as matrix filtration, redox, ion-exchange and chemisorption, due to high hydraulic loading rates and imperfectly to poorly drained lowland (i.e. 'Gleyed' type) soils. The relative frequency of cluster VI waters, peaks in September and are largely absent over the summer months. By comparison, cluster V waters, driven by high-intensity rainfall events, are represented in all but 2 months of the year (i.e., February and December) for this data record.

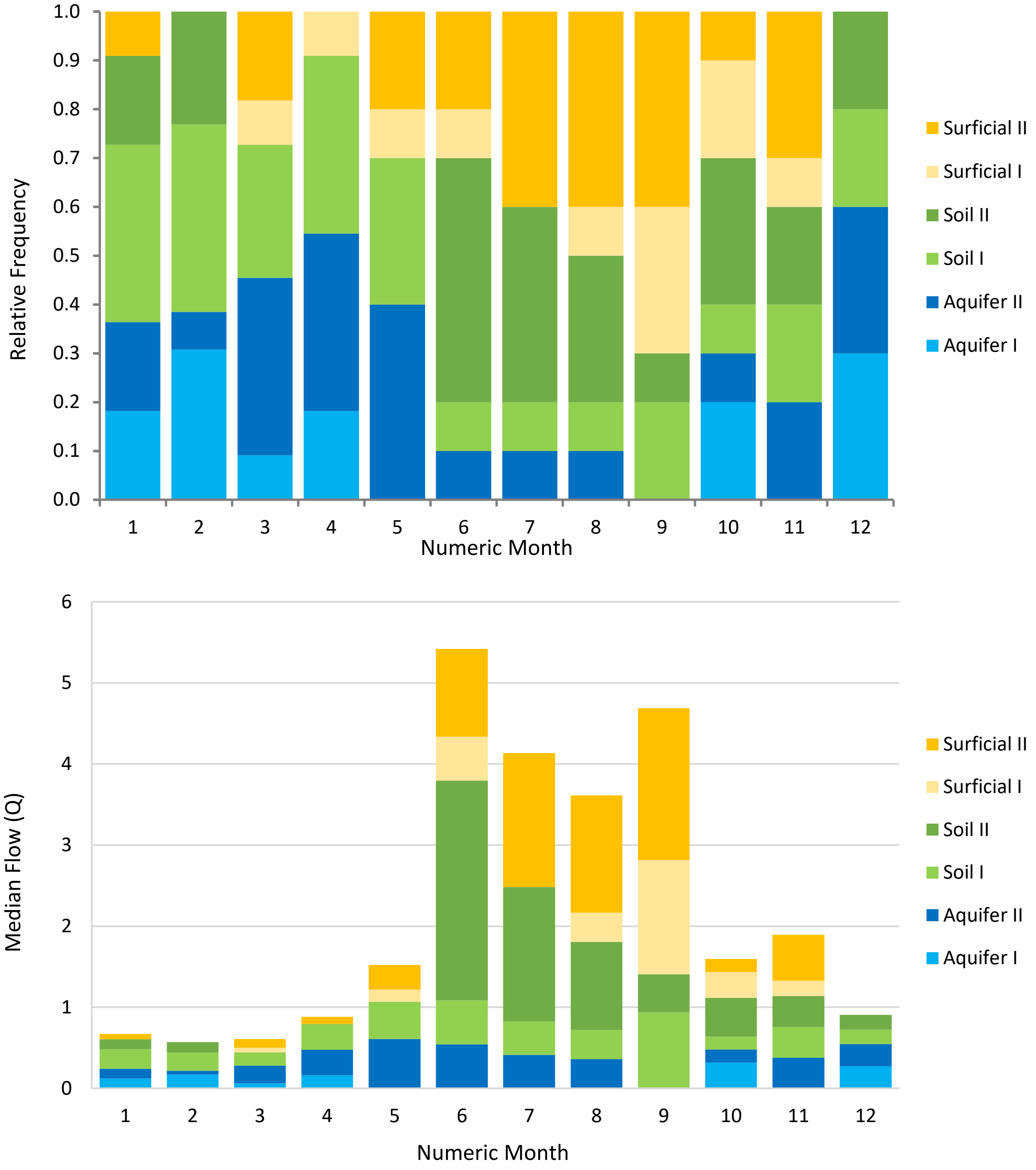

Figure 8: a) Relative frequency and b) proportion of flow of water source for a 6-compartment (Cluster) separation by month for the Mandeville Rd monitoring site, Waimea Valley, Southland (Environment Southland data). Soil moisture and flow are lowest when Aquifer 1 source dominates and highest when the Surficial-I ('high-intensity rainfall') compartment dominates.

Table 15: Table of Endmember Hydrological and Water Quality Signatures at Manderville. Endmembers statistics are derived for samples with a cluster membership of ≥0.85 and differ from summary statistics by 'winner' cluster.

	Q (Recorder)	Baseflow Proportion	Soil Moisture (%)	Soil Temp at 10 cm	48 Hr Rainfall	NNN	TKN	TN	DRP	TP	TSS	VSS	Turbidity	E.Coli
Aquifer I (Cluster I)														
n	6	5	6	6	6	6	6	6	6	6	2	0	6	6
Mean	0.40	90.24	42.66	15.56	1.83	2.36	0.59	2.96	0.02	0.04	1.50	****	1.34	230
Median	0.36	92.39	42.69	15.59	0.00	2.35	0.60	2.90	0.01	0.04	1.50	****	1.33	195
C.V.	0.38	0.10	0.04	0.14	2.07	0.42	0.11	0.34	0.66	0.35	0.00	****	0.06	1
Min.	0.28	75.43	40.38	12.08	0.00	1.02	0.50	1.66	0.01	0.02	1.50	****	1.26	120
Max.	0.70	97.10	44.88	17.97	9.50	3.60	0.66	4.30	0.03	0.06	1.50	****	1.48	440
Aquifer II (Cluster II)														
n	9	9	9	9	9	9	9	9	9	9	5	2	9	9
Mean	0.76	89.41	44.13	11.98	3.11	2.75	0.56	3.31	0.01	0.03	1.40	0.90	2.24	236
Median	0.51	92.26	42.44	12.03	1.50	2.60	0.57	3.20	0.01	0.03	1.50	0.90	2.30	240
C.V.	0.70	0.13	0.09	0.28	1.34	0.34	0.18	0.27	0.68	0.34	0.16	0.94	0.06	1
Min.	0.23	67.67	39.76	5.34	0.00	1.40	0.37	1.97	0.00	0.02	1.00	0.30	1.99	40
Max.	1.78	99.64	51.06	15.37	11.50	4.10	0.69	4.60	0.03	0.05	1.50	1.50	2.40	490
Soil I (Cluster III)														
n	2	2	1	1	1	2	1	2	2	2	1	0	2	2
Mean	0.86	85.33	47.65	7.90	0.00	2.76	0.36	3.30	0.01	0.04	4.80	****	3.90	370
Median	0.86	85.33	47.65	7.90	0.00	2.76	0.36	3.30	0.01	0.04	4.80	****	3.90	370
C.V.	0.13	0.19	0.00	0.00	****	0.59	0.00	0.43	0.65	0.45	0.00	****	0.07	1
Min.	0.78	73.80	47.65	7.90	0.00	1.61	0.36	2.30	0.01	0.03	4.80	****	3.70	40
Max.	0.94	96.86	47.65	7.90	0.00	3.90	0.36	4.30	0.01	0.05	4.80	****	4.10	700
Soil II (Cluster IV)														
n	1	1	0	0	0	1	0	1	1	1	1	0	0	1
Mean	6.78	46.95	****	****	****	6.60	****	7.30	0.02	0.05	5.50	****	****	210
Median	6.78	46.95	****	****	****	6.60	****	7.30	0.02	0.05	5.50	****	****	210
C.V.	0.00	0.00	****	****	****	0.00	****	0.00	0.00	0.00	0.00	****	****	0
Min.	6.78	46.95	****	****	****	6.60	****	7.30	0.02	0.05	5.50	****	****	210
Max.	6.78	46.95	****	****	****	6.60	****	7.30	0.02	0.05	5.50	****	****	210
Surficial I (Cluster V)														
n	4	4	4	4	4	4	4	4	4	4	2	1	4	3
Mean	5.43	34.84	49.34	9.54	10.25	2.75	0.89	3.65	0.04	0.08	9.00	1.50	10.95	3830
Median	5.31	35.57	50.62	9.42	10.00	2.45	0.86	3.40	0.04	0.08	9.00	1.50	10.35	4300
C.V.	0.60	0.30	0.06	0.48	1.07	0.31	0.38	0.20	0.55	0.51	0.47	0.00	0.21	1
Min.	2.48	21.46	45.05	5.41	0.50	2.10	0.52	3.10	0.01	0.04	6.00	1.50	9.00	190
Max.	8.64	46.74	51.06	13.90	20.50	4.00	1.32	4.70	0.06	0.13	12.00	1.50	14.10	7000
Surficial II (Cluster VI)														
n	5	5	5	5	5	5	5	5	5	5	1	0	5	5
Mean	20.97	23.76	50.40	7.73	17.25	3.74	1.77	5.48	0.07	0.19	35.00	****	43.60	24040
Median	23.89	24.44	50.87	6.35	15.75	3.20	1.93	4.70	0.05	0.23	35.00	****	43.00	13000
C.V.	0.78	0.80	0.02	0.36	0.58	0.32	0.30	0.32	0.79	0.47	0.00	****	0.27	1
Min.	1.30	5.97	48.77	5.03	7.00	2.70	1.20	3.70	0.00	0.07	35.00	****	27.00	200
Max.	43.65	52.26	51.18	11.56	31.00	5.40	2.40	7.90	0.15	0.27	35.00	****	55.00	82000

6 Summary

6.1 Key findings

Application of the TRaCS approach to the Waimea Stream, Southland identified considerable variation in the suitability of tracers between sites. This observation is consistent with other studies where tracer suitability varied in response to changes in landscape attributes. It was notable that the suitability of tracers appeared to vary with redox status and the degree of weathering of the geological units hosting the soil and shallow aquifer system, although this was not explored in detail in the above work.

In terms of hydrograph separation, using physiographic assemblages to hypothesise the number of compartments and subsequently varying the hypothesised number of compartments appeared to be a useful basis for refining and testing hypotheses. Overall the attendant hydrochemical signals appear to vary in a logical manner according to local climatic and hydrological data. However, it was apparent that the refinement of physiographic units could be aided by the TRaCS method. Specifically, TRaCS provided insight as to the existence of a stratified aquifer system beneath the Waimea Valley that is an important source of streamflow during the drier months of the year. Although knowledge of the existence of carbonate rocks underlying the alluvial aquifer is not new, this approach has confirmed the significance of this water source for the Murphy Rd and Pahiwi-Balfour Rd sites and to a lesser degree Mandeville. This knowledge had not been incorporated into regional physiographic mapping as Q-Map does not identify the underlying carbonate aquifer and groundwater samples are too sparsely populated to infer continuity. As such TRaCS could be used to aid in refining the vertical stratigraphic representation of the shallow aquifer systems supplying stream. Due to the strong contrast in hydrochemical signatures between aquifers and the dominance of carbonate outflows during the warmest months of the year the quality and attendant hydrochemical conditions, including elevated pH, may have implications for ecosystem function and the toxicity of ammoniacal nitrogen.

A similar analysis of the hydrochemical signatures of streams identified stratified aquifers within the Waimutuku (alluvial over carbonate) and Waituna streams (alluvial over lignite). The existence of stratified aquifers has significant implications for assessing groundwater contaminant lags with evidence that the shallow alluvial aquifer system decants relatively rapidly over the hydrological year. Rapid decanting of shallow aquifers to stream has been observed as a key control over nutrient export to streams and is especially relevant to regions, such as Southland, underlain by shallow and poorly permeable bedrock and where first- or second-order catchments drained by small streams (so-called headwater catchments) represent a large fraction of the total land area (Molenat et al., 2008).

In terms of separation, 3 compartments best explain the contributions from Bedrock/Hill Country dominated catchments. Although the addition of a 4-compartment separation further aids in discriminating between cool-wet and warm-dry surficial runoff events. Notably, E. coli peaks under dry soil and low flow conditions in Bedrock/Hill Country dominated catchments perhaps reflecting greater stock access and/or lesser dilution. Overall, the surficial runoff compartment was associated with the largest volume of water and the highest NNN and sediment signatures. However, relative to lowland sites the concentration of contaminants was low.

For sites draining two or more geographical domains (Bedrock/Hill Country and Lowland) and where the lowland setting is characterised by two or more lowland physiographic units, a 6-compartment separation was most suited. A 7-compartment separation provided additional temporal resolve over the timing of rainfall driven (high-intensity) runoff events. For monitoring sites with a significant area of Lowland physiographic units the largest volumetric and contaminant mass flux was associated with high-intensity rainfall events. These events are apparent at all lowland sites, with contaminant exports far larger than equivalent runoff events under near-saturated/saturated soil conditions but lower rainfall intensity. Water quality and hydrochemical signatures suggest high-intensity rainfall driven events are associated with a larger component of sheet-wash or overland flow with lesser soil water involvement. Given surficial runoff events export by far the greatest contaminant load, for all species, it suggested that peak runoff control structures could play an important role in reducing contaminant losses to the Waimea Stream. The important role of storm events in driving large magnitude losses of land use derived contaminants has long been recognised as a key driver of ecosystem decline.

In terms of instream eutrophication during the summer months, nitrate is an important control where the soil zone and underlying aquifer are oxidising. Comparison of the Murphy Rd and Pahiwi-Balfour Rd sites suggest little difference in the underlying geology, with both sites characterised by a stratified aquifer system (alluvium over carbonate) and yet are overlain by soils of contrasting hydrological properties. Imperfectly to poorly drained soils across the lowland portion of the Murphy Rd capture zone direct recharge laterally via subsurface artificial drainage with lesser vertical drainage to the underlying aquifer and lower rates of flushing or throughflow. These same soils buffer the aquifer from exchange with the atmosphere and produce weakly reducing recharge waters. The combination of lower recharge rates, reducing soil drainage and lesser atmospheric coupling results in a more reduced aquifer system that contributes a smaller volume of water to stream. In contrast, well-drained soils adjacent to the Pahiwi-Balfour Rd site appear to favour a greater volumetric contribution to stream flow due to little lateral or surficial drainage. Higher recharge rates, oxidised soil water drainage and greater coupling to the atmosphere limit redox evolution beyond O_2-reducing conditions. Accordingly, it appears that despite similar aquifer properties at both sites, soil hydrology greatly influences the magnitude of the volumetric contribution from aquifers to stream as well as the redox status of shallow aquifer systems. Where runoff driven sediment deposition overlaps with inflows of oxidising groundwater high in NNN the risk of in-stream eutrophication, including excessive macrophyte and periphyton growth, is elevated.

Moving beyond monthly patterns in water source, stream flow samples dominated (i.e., ≥0.85) by a given compartment can be used to infer ‘end-member’ concentrations for each compartment. However, only those samples that are significantly correlated with flow, i.e., tier-I-III tracers, are considered representative of the compartmental composition. Those measures that are not statistically significant with flow are unlikely to retain the signature of the compartment supplying stream but may provide ancillary evidence as to land use sources that are driven by seasonal behaviours such as FDE effluent irrigation or stocking of Bedrock/Hill Country. For example, regional groundwaters seldom have elevated E. coli or Particulate Phosphorus (PP) and yet elevation of these species in surface waters under low or even drought flows indicate a legacy or active land use contribution. Further resolution of hydrological pathway may be provided by tracers that are statistically significant with flow but fail to meet tier I – III thresholds. These tracers are commonly correlated with across a particular compartmental streamflow range. For example, although TP may not be correlated with flow derived from aquifer or soil compartments it may show correlation with flows dominated by the surficial compartment and as such is a useful tracer of the hydrological flow path.

Finally, the inclusion of $\delta^{18}O$-H_2O and δ^2H-H_2O with monthly surface water quality measurements would further aid in differentiating between the volumetric water source, solute and particulate flux. Specifically, although Bedrock/Hill Country waters may be volumetrically important they do not appear to be a significant source of nutrients or sediment if the McCale Tributary and the Old Balfour sites are considered representative.

6.2 Assumptions and Limitations

In the above report, we applied a novel method for identifying the suitability of tracers and for separating hydrographs into compartmental sources using surface water monitoring data for long-term monitoring sites. The method first assesses the suitability of available tracers for hydrograph separation followed by separation into a hypothesised number of compartments according to the physiographic setting. The hypothesis is then tested and refined by varying the number of potential compartments supplying the stream and interrogating each hypothesised model against climatic, hydrological and hydrochemical signals to determine the optimal number of compartments.

This method is based upon several assumptions, specifically:

- The most suitable tracers can be identified according to their relationship with flow
- A tracer that is conservative with flow and highly correlated is a good volumetric tracer
- Low temporal resolution sampling over a longer time period (i.e. >5 years) can be used to provide a reasonable sub-sample of the 'actual variation' population variance
- Hypothesis testing and model evaluation is heuristic and based upon integrating climatic, hydrological and hydrochemical data to come to the 'best solution'
- The thresholds used to rank tracer suitability are reasonable
- Interpretations are limited to the sampling record.

Due to these assumptions, there are a number of potential limitations/requirements to the application:

- Each site must have a flow record or a reasonable proxy for flow variation
- Not all sites, especially those that only measure standard surface water quality measures, will have tracers suited to hydrograph separation
- The user must have a reasonable understanding of the hydrological and biogeochemical controls over hydrochemical and water quality signals, this introduces a degree of subjectivity or expert knowledge
- Interpretation of hydrograph separation is greatly aided by local, within the catchment, climatic measures of rainfall intensity, soil moisture and soil temperature. Groundwater level data, for the shallow aquifer system, is also of value as observed for the Waituna Lagoon Catchment (Rissmann and Beyer, 2018)
- Although physiographic mapping is not essential it is a valuable tool for forming relevant hypothesise as to the number of compartments supplying stream.
- Input from local staff familiar with stream, soil and aquifer composition and is important.

6.3 Future works

There are a number of key components that would benefit from a more thorough analysis, including:

- Assessment of the appropriateness of tier-I to III thresholds for assessing tracer suitability via incorporating all regional surface water sites and the development of an appropriate quantitative method to more rigorously assign thresholds.
- Quantification of differences, if any, in the apportionment of clusters (compartments) when different tracers are used to separate the hydrograph. Is there any meaningful loss of resolution when using tier-III vs. tier I tracers and/or an admixture of tracers are used?
- Analysis of any relationships between capture zone physiographic assemblage, using all four regional driver layers, and the likely tracer(s) that will be most suited to hydrograph separation. For example, we consider it likely that there will be predictable patterns in the likely suitability of tracers according to the physiographic setting.
- Addition of the stable isotopes of water to monthly sampling runs, for those catchments with multiple geographic water sources (two or more recharge domains). This would provide

additional insight as to the volumetric versus solute and particulate mass flux at a given site. For example, the volumetric mass flux of water may be dominated by a high-altitude source, e.g. an alpine headwater, whereas the solute and particulate mass flux might be dominated by the smaller volumetric contribution from the lowland portion of the capture zone. Recognising the difference between volumetric and contaminant mass flux is critical to effective management of water quality.

- If this method is seen as suitably rigorous then it could conceivably be used to quantify the contaminant loads from each compartment supplying stream as well as forming the basis for identifying stream-specific thresholds in catchment wetness (e.g. soil moisture or 24/48 Hr rainfall intensity) that correspond to particular in stream water quality outcomes (Rissmann and Beyer, 2018).
- Knowledge of the relationship between measures of catchment wetness and instream water quality can be used to provide a catchment or capture zone specific guide to the timing of a range of practical applications such as:
    - When to and when not to apply fertiliser
    - When to irrigate Farm Dairy Effluent (FDE) irrigation and when not to
    - What mitigations are likely to deliver the best 'bang for buck.'

7 Acknowledgements

This work is based upon data supplied by Environment Southland and utilises the physiographic mapping undertaken by the council in 2015 - 2016. We thank Tim Ellis and Karen Wilson for discussion around the approach and for the input of local knowledge/expertise that helped improve the interpretation of hydrograph separations. The bulk of this method was developed and refined within the Waituna Catchment as part of a contract between Land and Water Science Ltd and the Living Water Partnership (DOC-Fonterra). This work was funded through an Envirolink grant (1807-ESRC285).

8 References

Bazemore, D. E., Eshleman, K. N., and Hollenbeck, K. J. (1994). The role of soil water in stormflow generation in a forested headwater catchment: synthesis of natural tracer and hydrometric evidence. Journal of Hydrology, 162(1–2), 47–75. https://doi.org/10.1016/0022-1694(94)90004-3

Bishara, A. J., & Hittner, J. B. (2012). Testing the significance of a correlation with nonnormal data: Comparison of Pearson, Spearman, transformation, and resampling approaches. Psychological Methods, 17(3), 399–417. https://doi.org/10.1037/a0028087

Buttle, J. M. (1994). Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. Progress in Physical Geography, 18(1), 16–41. https://doi.org/10.1177/030913339401800102

Christophersen, N., Neal, C., Hooper, R. P., Vogt, R. D., & Andersen, S. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members—a step towards second-generation acidification models. Journal of Hydrology. https://doi.org/10.1016/0022-1694(90)90130-P

Elsenbeer, H., Lack, A., & Cassel, K. (1995). Chemical fingerprints of hydrological compartments and flow paths at La Cuenca, Western Amazonia. Water Resources Research, 31(12), 3051–3058. https://doi.org/10.1029/95WR02537

Elsenbeer, H., Lack, A., & Cassel, K. (1996). The stormflow chemistry at La Cuenca, Western Amazonia. Interciencia, 21(3), 133–139.

Güler, C., & Thyne, G. D. (2004). Delineation of hydrochemical facies distribution in a regional groundwater system by means of fuzzy c -means clustering. Water Resources Research, 40(12). https://doi.org/10.1029/2004WR003299

Hooper, R. P., & Shoemaker, C. A. (1986). A Comparison of Chemical and Isotopic Hydrograph Separation. Water Resources Research, 22(10), 1444–1454. https://doi.org/10.1029/WR022i010p01444

Hooper, R. P., Christophersen, N., & Peters, N. E. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members - An application to the Panola Mountain catchment, Georgia, U.S.A. Journal of Hydrology, 116(1–4), 321–343. https://doi.org/10.1016/0022-1694(90)90131-G

Hooper, R. P. (2003). Diagnostic tools for mixing models of stream water chemistry. Water Resources Research, 39(3). https://doi.org/10.1029/2002WR001528

Inamdar, S. (2011). The Use of Geochemical Mixing Models to Derive Runoff Sources and Hydrologic Flow Paths (pp. 163–183). Springer Netherlands. https://doi.org/10.1007/978-94-007-1363-5_8

James, A. L., & Roulet, N. T. (2006). Investigating the applicability of end-member mixing analysis (EMMA) across scale: A study of eight small, nested catchments in a temperate forested watershed. Water Resources Research, 42(8). https://doi.org/10.1029/2005WR004419

Katsuyama, M., Ohte, N., & Kobashi, S. (2001). A three-component end-member analysis of streamwater hydrochemistry in a small Japanese forested headwater catchment. Hydrological Processes, 15(2), 249–260. https://doi.org/10.1002/hyp.155

Katsuyama, M., Kabeya, N., & Ohte, N. (2009). Elucidation of the relationship between geographic and time sources of stream water using a tracer approach in a headwater catchment. Water Resources Research, 45(6). https://doi.org/10.1029/2008WR007458

Ministry for the Environment. (2014). National Policy Statement for Freshwater Management. ME Report 1155.

Molenat, J., Gascuel-Odoux, C., Ruiz, L., and Gruau, G. (2008). Role of water table dynamics on stream nitrate export and concentration in agricultural headwater catchment (France). Journal of Hydrology, 348(3–4), 363–378.

O'Brien, C., and Hendershot, W. H. (1993). Separating streamflow into groundwater, solum and upwelling flow and its implications for hydrochemical modelling. Journal of Hydrology, 146(C), 1–12. https://doi.org/10.1016/0022-1694(93)90266-C

Ogunkoya, O. O., & Jenkins, A. (1993). Analysis of storm hydrograph and flow pathways using a three-component hydrograph separation model. Journal of Hydrology, 142(1–4), 71–88. https://doi.org/10.1016/0022-1694(93)90005-T

Pearson, L., Rissmann, C., and Lindsay, J. (2018). Waituna Catchment: Physiographic Risk Assessment. Land and Water Science Report 2018/02. Prepared for Living Water. 46p.

Pinder, G. F., and Jones, J. F. (1969). Determination of the ground-water component of peak discharge from the chemistry of total runoff. Water Resources Research, 5(2), 438–445. https://doi.org/10.1029/WR005i002p00438

Ramsey, C. A., and Hewitt, A. D. (2005). A methodology for assessing sample representativeness. Environmental Forensics, 6(1), 71–75. https://doi.org/10.1080/15275920590913877

Rice, K. C., & Hornberger, G. M. (1998). Comparison of hydrochemical tracers to estimate source contributions to peak flow in a small, forested, headwater catchment. Water Resources Research, 34(7), 1755–1766. https://doi.org/10.1029/98WR00917

Rissmann, C. and Beyer, M. (2018). Waituna Catchment: Temporal Variation. Land and Water Science Report 2018/09. Prepared for Living Water, 11p.

Rissmann, C., Rodway, E., Beyer, M., Hodgetts, J., Pearson, L., Killick, M., Marapara, T.R., Akbaripasand, A., Hodson, R., Dare, J., Millar, R., Ellis, T., Lawton, M., Ward, N., Hughes, B., Wilson, K., McMecking, J., Horton, T., May, D., and Kees, L. (2016). Physiographics of Southland Part 1: Delineation of key drivers of regional hydrochemistry and water quality. Environment Southland Technical Report No. 2016/3. Invercargill, New Zealand.

Rissmann, C., Pearson, L., Lindsay, J. Marapara, M., and Badenhop, A. (2018). Waituna Catchment: Technical Information and Physiographic Application. Land and Water Science Report 2018/01. Prepared for Living Water, 134p.

Rissmann, C., Beyer, M., Pearson, L., … (in prep). A novel approach to hydrograph separation for long-term surface water quality monitoring sites.

Sklash, M. G., Farvolden, R. N., and Farvolden, R. N. (1979). The role of groundwater in storm runoff. Developments in Water Science, 12(C), 45–65. https://doi.org/10.1016/S0167-5648(09)70009-7