

REGIONAL-SCALE IDENTIFICATION OF SURFACE WATER AND GROUNDWATER INTERACTION USING HYDROCHEMISTRY AND MULTIVARIATE STATISTICAL METHODS, WAIRARAPA VALLEY, NEW ZEALAND.

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Response to comments from Reviewer 3

We are pleased that the reviewer considers our manuscript to be interesting and well written. The reviewer makes six specific comments, to which we reply below.

1. The reviewer states that we are justified to exclude outliers in HCA for the purpose of our study, but notes that the outlier sites still contain important information that can assist with understanding the groundwater resources in the study area.

We agree completely. In a revised manuscript we would change the text in the first paragraph of Section 4.1 to read as follows: “Although further analysis of these outliers is not warranted in this paper, it should be noted that the outlier sites can still provide important information for understanding the water resources of the study area.”

2. The reviewer notes that we used eight parameters in HCA but five additional parameters were added for PCA (the reviewer mistakenly indicates that only four additional variables had been considered in PCA). The reviewer comments that in most applications of this type the same variables are included in HCA and PCA because PCA is often applied to help explain the results of HCA.

In our study, PCA was applied as an independent technique, not strictly to understand the results of HCA. It is for the same reason that Figure 5 shows box-whisker plots for some variables that were not included in HCA. We believe that the inclusion of the additional variables in PCA and the box-whisker plots helps to understand the hydrochemical variation in the study area in a slightly broader sense than can be achieved with HCA alone. For example, the effect of redox condition is revealed more strongly through PCA than HCA.

Following this argument one might then ask why the variables Fe, Mn, NO₃, NH₄ and PO₄ were not included in HCA (since they provided useful information when included in PCA and the box-whisker plots). It is because HCA automatically excludes any sample that does not have a result for every input variable. As stated in Section 3.2 of our manuscript, “...many additional parameters (e.g. nutrients, pH) were missing from individual samples and monitoring sites. If these additional parameters were included in the clustering processes they would have substantially reduced the number of sites analysed.”

3. The reviewer states that an increase in TDS does not always indicate an increase in groundwater age. The reviewer further suggests that inverse modelling might

be helpful to try to understand the relationships between TDS and groundwater age.

We agree. In the manuscript we point out that groundwaters assigned to clusters A1 and B1 are both inferred to be young but the latter water type has higher TDS: “This increased concentration of solutes in B1-type rivers likely derives from the easily eroded Pliocene marine sedimentary lithology of the eastern hills, relative to the chemically more resistant Mesozoic Torlesse greywacke that forms the western ranges.” In other words, a groundwater assigned to cluster A1 might have the same TDS as a groundwater assigned to cluster B1, but the latter would probably be younger because it would be sourced from a catchment with more chemically reactive rocks.

In considering the potential application of inverse modelling, we think it is useful to assess the strengths and weaknesses of data-driven vs. process-driven approaches for interpretation of water chemistry. The data-driven approaches include the statistical and artificial intelligence techniques. Such techniques seek to identify commonalities and patterns in the data as a primary objective, and from this infer the processes that cause them. Conversely, process-based techniques, such as forward or inverse hydrochemical modelling, first attempt to simulate mechanistic processes that are believed to control groundwater quality, such as geochemical reactions between water and rock, and secondly to compare modelled results to observations. The main advantage of the data-driven approaches for groundwater investigations is that they do not rely on knowledge of the spatial variation of properties such as mineralogy, porosity, reactive surface area, etc. that are required as input for process-driven approaches. The main advantage of the process-driven techniques is that they provide information on controlling factors that may be hard to infer or elucidate using the data-driven techniques.

We agree that inverse modelling has potential benefit in a study like ours. The main reason that we have not undertaken inverse modelling in our study is that the required input data on site mineralogy, porosity, etc. are not available for the majority of sites in the Wairarapa Valley. We are therefore left with the data-driven approaches. Of these, we have shown the effectiveness of HCA and PCA, which operate without *a priori* assumptions about aquifer lithology, confinement, style and rate of water-rock interaction, or any other factors that might control the categorization.

4. The reviewer asks how we determined the redox state of the water samples.

E_H was not measured directly. Instead, the redox condition of the groundwater is determined based on the measured concentrations of the redox-sensitive substances Fe, Mn, NO_3 , NH_4 and SO_4 . In a revised manuscript we would clarify this in the second paragraph of Section 4.2 as follows: “The seven clusters identified by HCA were largely differentiated by their TDS concentrations (determined by summation of major ion concentrations), redox potential (inferred from measured concentrations of Fe, Mn, NO_3 , NH_4 and SO_4) and major ion ratios”.

5. The reviewer states: “Inclusion of filtered and unfiltered samples in the dataset is problematic without further justification. Unfiltered samples will often produce higher solute values due to dissolution of particulates when acidified. Since the TDS was generally calculated, this could be a problem since charge balance does not address this issue.”

We agree that erroneous results may be obtained if TDS is calculated from concentrations measured in unfiltered acidified samples. However, we do not believe this is a concern in our study on account of the QA/QC procedures we applied. Charge balance error (CBE) was calculated for each site. CBE values for unfiltered acidified samples would be significantly positive if the cation concentrations were affected by dissolution of particulates. This is why all sites with CBE values outside the range from -7% to +7% were excluded from subsequent statistical analysis. Thus, the calculated TDS values that we present are reasonable because they are based only on analytical results that have passed the CBE test.

6. The reviewer comments that sites that are affected by groundwater-surface water interaction are likely to have seasonal patterns in water chemistry, and hence our conclusion that most sites do not display temporal trends appears to be a contradiction.

We performed the seasonal Mann-Kendall trend test, which only identifies long-term changes in water chemistry and does not assess seasonality. The test is referred to as “seasonal” because it is performed by comparing samples collected in each season only with samples collected in the same season but in subsequent years. For example, samples collected in January 2001, January 2002, January 2003, etc. would be compared, and samples collected in June 2001, June 2002, June 2003, etc. would be compared. The seasonal Mann-Kendall trend test would not compare samples collected in Januarys vs. samples collected in Junes. This means that the trend test might indicate no significant year-to-year change in water quality even if a seasonal pattern exists. Because we did not actually test for seasonality, there is no contradiction in our results: locations where groundwater-surface water interaction is occurring can still show no temporal trend.

We do however agree with the reviewer’s thought process: looking for seasonal or even shorter-duration variations in water chemistry could be a powerful means of identifying locations where groundwater-surface water interaction is occurring. Indeed, for exactly this reason, we have undertaken an investigation of hydrochemical variations in the Wairarapa Valley using sampling with high temporal frequency. The manuscript resulting from this study will be submitted to HESS very soon.