

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 4

We are pleased that the reviewer believes that we have presented and demonstrated “an effective approach for analysing a watershed system using a large water-quality database to characterise and interpret surface water and groundwater quality interactions”. The reviewer makes five specific comments to which we reply below.

1. The reviewer makes four comments with respect to the hydrochemical database:

- a. It would be helpful to include the range of depths of the groundwater samples.

We agree. In a revised manuscript, the last paragraph of Section 3.1 would state: “The resulting output was thus a 50 parameter x 305 site data array. 239 of these 305 sites were groundwater bores ranging from 2.0 to 113.0 m depth (25th, 50th and 75th percentiles of 7.8, 16.0 and 35.8 m respectively).”

- b. Were the sites examined for the magnitude of seasonal trends? Did the chemistry of surface water change seasonally or with flow?

We did not perform tests to assess seasonal patterns in hydrochemistry. Hence our conclusion states “...local scale studies...demonstrate that monitoring sites can show temporal variability in water quality and shift between cluster groupings. It is essential for future research to determine the impact that this temporal shift in cluster assignment is likely to have on the interpretation of surface water and groundwater interaction.”

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.

- c. Fe and Mn concentrations can be high in anoxic groundwater. Could exclusion of Fe and Mn from the calculation of charge balance error (CBE) have led to high CBE values and exclusion of such groundwaters from the subsequent statistical analysis?

This is a good point. We calculated CBE values for each site using the median concentrations of the cations Na, K, Ca, Mg and the anions HCO₃, Cl and SO₄. Other analytes (e.g. Mn, NH₄, NO₃, Fe) were excluded from the CBE calculations because they had not been analysed at a significant

number of sites. We went back to the data and calculated CBE both with and without the inclusion of Fe, Mn, NO₃ and NH₄ for sites at which these other parameters had been analysed. This comparison showed that the concentrations of Fe, Mn, NO₃ and NH₄ are low and so their inclusion in the calculations affected CBE values by less than 0.5%. Hence the CBE values based on major ion concentrations are considered meaningful for this study. We would convey this information more clearly in a revised manuscript.

- d. How many of the final 305 sites were surface water and how many were groundwater?

See our response to 1a. above.

2. The reviewer makes two comments with respect to Section 4.2, which deals with hydrochemical differences between the clusters identified by HCA.
 - a. The reviewer recommends subdividing this section into four subsections: results of the cluster analysis; the effect of the number of clusters on the analysis; the results of PCA; and comparison to other indicators of water source and age.

While we are all in favour of making manuscripts as readable as possible, the whole section is only six paragraphs long, and so we believe that subsections are not really needed.

- b. The reviewer requests clarification in the text about how excess air measurements are made and what high concentrations of excess air might mean.

This is a good comment. High concentrations of excess air might indicate rainfall recharge or, if the groundwater is anoxic, some degree of denitrification, or a combination of the two. For the sites in the Wairarapa Valley, Morgenstern (2005) concluded that rainfall recharge is the likely cause of high values of excess air. However, we acknowledge that excess air has been measured at relatively few sites. There are several sites assigned to Cluster B that have anoxic groundwater but have not been analysed for excess air. It is possible that denitrification is occurring at some such sites.

In a revised manuscript we would change the last paragraph of Section 4.2 to state: “Morgenstern (2005) used measured concentrations of dissolved nitrogen and argon to calculate excess air concentrations for groundwaters in the Wairarapa Valley. Morgenstern (2005) interpreted values of excess air greater than 2 mL at STP per kg to indicate groundwater recharge primarily from rainfall, values close to zero to indicate recharge primarily from river seepage, and values significantly less than zero to indicate degassing taking place in reduced groundwater. High values of excess air can also result from denitrification in anoxic groundwater (Hinkle et al., 2010).” We would also change the last sentence in this paragraph to read:

“Negative values or highly positive values of excess air suggest that cluster B contains some highly reduced groundwaters, i.e. which may be influenced by degassing and denitrification, respectively.”

3. Our original manuscript states that there is little or no evidence of groundwater-surface water interaction in the lower Wairarapa Valley. The reviewer generally concurs but points out that the anomalously shallow B5-type groundwaters in the lower valley might indicate influence by agricultural activity, which would imply some degree of groundwater-surface water interaction.

We agree. We did not rule out this possibility in our original manuscript, in which the last paragraph of Section 4.3 stated: “Saltwater intrusion can likely be attributed to high Na, Cl, SO₄ and subsequent conductivity at sites located by Lake Onoke, while localised volcanic deposits and/or *leaching from fertilizer inputs* may have caused elevated SO₄ at the remaining two B5 groundwater sites further inland” (italics added).

We accept that our original manuscript didn't explain clearly enough the possibility of groundwater-surface water interaction in the lower valley. In a revised manuscript we would change text in the last paragraph of Section 4.2 to state: “Saltwater intrusion is the likely cause of high Na, Cl, SO₄ and subsequent conductivity at sites located by Lake Onoke. Other relatively shallow B5 groundwaters further inland may be influenced by some degree of groundwater-surface water interaction. For example, leaching from fertilizer inputs may have caused elevated SO₄ exhibited in these groundwaters. The hydrochemistry of these groundwaters might also be affected by interaction with localised volcanic deposits (McLaren and Cameron, 1996; Stanton, 1972).”

4. In the second paragraph of the conclusion in our original manuscript we stated that B1-type groundwaters and surface waters are found in the vicinity of the Whangaehu and Taueru Rivers. We concluded that this indicates that the groundwaters receive recharge from B1-type rivers. The reviewer points out that it could also be the other way around, i.e. that rivers receive baseflow from B1-type groundwaters.

We agree with the reviewer's thought process, but this is a simple misunderstanding caused by omission of an important detail in our original manuscript: many of the rivers in question are shown to be losing water to groundwater based on concurrent gauging surveys. We would clarify this in our revised manuscript by stating: “B1-type groundwaters were located in close proximity to *losing reaches* of these river systems on the eastern side of the valley and showed in an increase in concentrations of Mn, Fe and NH₄ concentrations, suggesting the onset of slightly anoxic conditions. It is possible that recharge is provided to these groundwaters from overlying B1-type surface waters.” (Italics added for emphasis only.)

5. The reviewer identifies six minor typographical errors.

These minor typographical errors would be corrected in our revised manuscript.

