Responses to referee comment R1 on:

A method for predicting hydrogen and oxygen isotope distributions across a region's river network using reach-scale environmental attributes

By Bruce D. Dudley, Jing Yang, Ude Shankar and Scott Graham

Referee comment (RC):

Generally, the authors have addressed my comments well. The overall narrative of the paper has improved. The authors also demonstrated how the final regression kriging is better than ordinary kriging because of environmental variables. If the authors can address the following comments, this work could be publishable.

My main remaining comment is how monthly isotope data from 58 sites for 3 years can be justified in producing representable maps for 600,000 reaches and over 400,000 kilometres of rivers. When the authors have only 58 sites for 600,000 reaches, we will always have a question of how much we can trust the maps generated from this study. Nevertheless, the authors added t values and P values in Table 2 to provide us with some statistics to illustrate the usefulness of five selected environmental variables and give us some confidence in their maps.

To further see how these five environmental variables for these 58 locations can be represented for 6000,000 reaches, the authors should provide scatter plots between hydrogen & oxygen isotopes and five environmental variables, so that we can see these empirical relationships qualitatively. I would expect that some scatterplots would have poor linear relationships or highly clustered data points (e.g. isotopes vs SiteElev). However, I would like to see these plots presented frankly.

Response (R):

We appreciate the reviewer's general concern that 58 sites cannot represent an entire river network. However, this is the essence of our water balance-based regression kriging approach. As we note in the manuscript, a simple kriging of sampled values may give poor predictions. However, by accounting for spatial variation in precipitation isotopes and flowpaths using the water balance model, then (in the regression correction step) including well known drivers of other processes contributing to variation in river water isotopes (such as isotopic fractionation), we can extrapolate our results more widely. We have added further references supporting this approach.

We note that we have produced scatter plots between hydrogen & oxygen isotopes at the 58 sites used in our study and environmental variables for a previous paper: Figure 6 of Yang et al. (2020) - below.

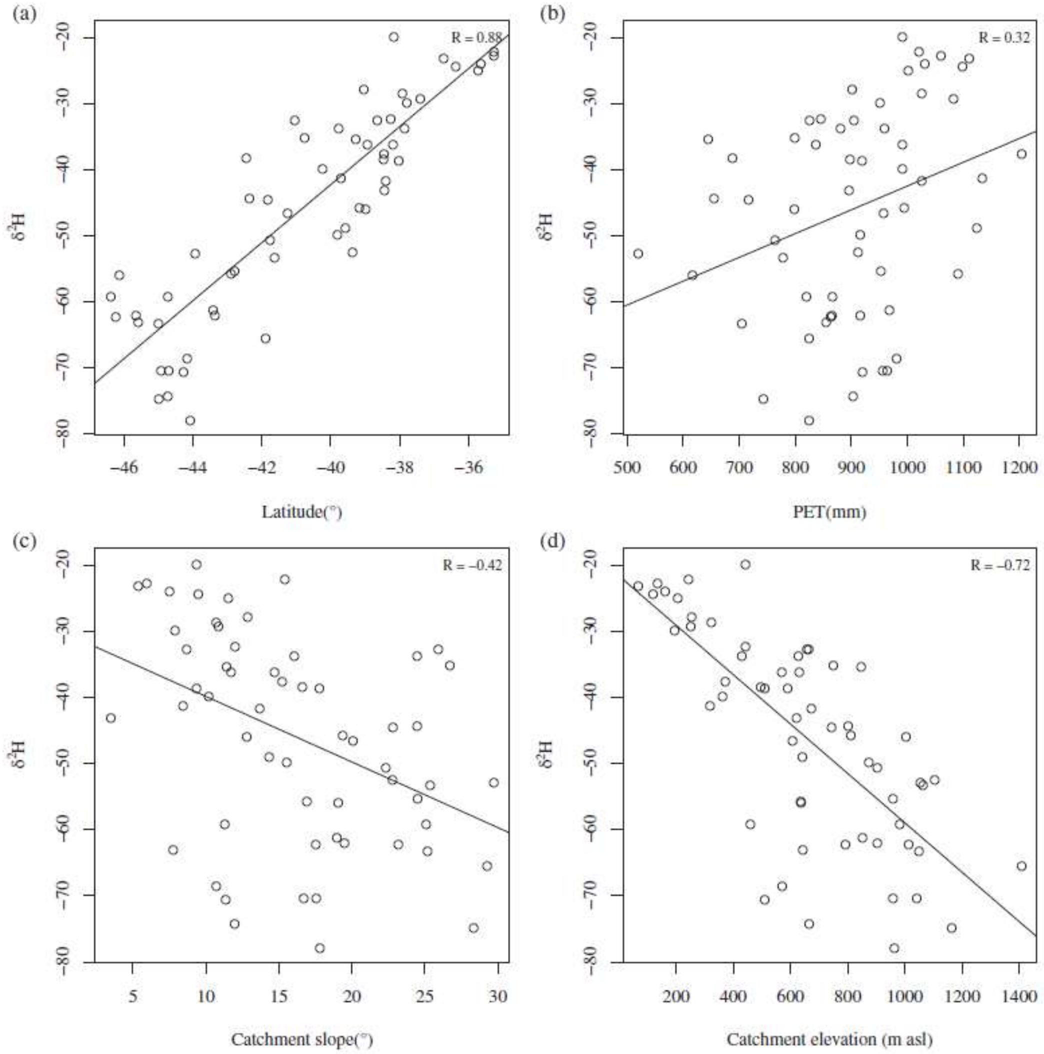


FIGURE 6 Relationships between catchment environmental factors and δ^2H of river water at all NZRWQN sites

Indeed, these relationships helped to inform our approach in this manuscript, as we have described on L 167-171. However, we think there would be little benefit in reproducing something like these in the current manuscript either to support the accuracy of our maps, or aid interpretation of our results for the following reasons:

Regarding the accuracy of our maps:

1. Figure 5 in our current manuscript gives fit statistics for linear regressions between δ^2H predictions from our model and hundreds of independent data points from among the 600,000 reaches of the NZ river network. These independent δ^2H measurements are not from the 58 sites sampled (for 36 months) for model correction. We used these independent δ^2H measurements in Figure 5 of the current manuscript to quantify the performance of the model. δ^{18}O fits are reported in the manuscript text.

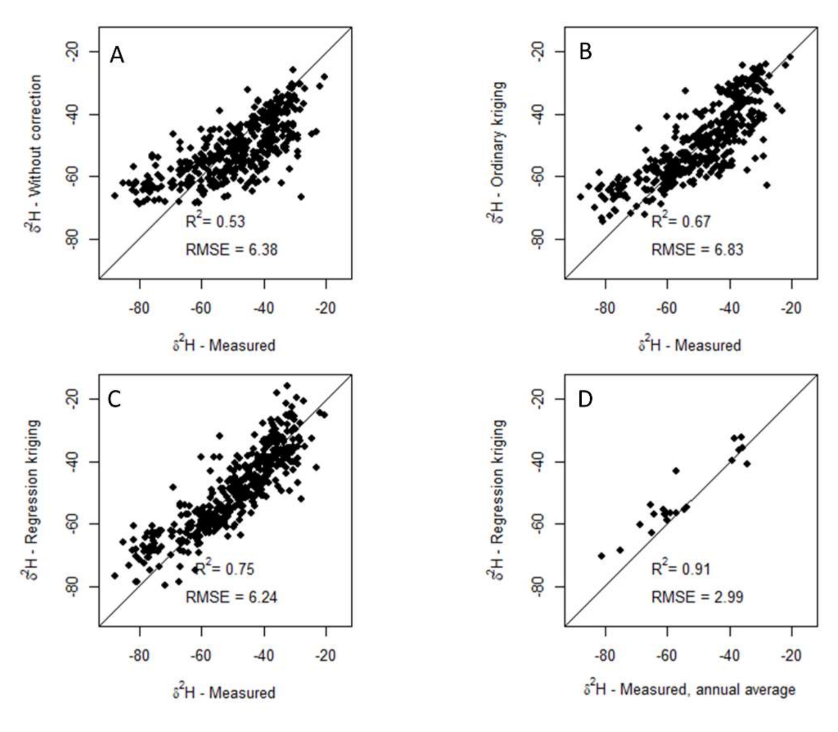


Figure 5.

2. Panels C and D of Figure 5 show that the residual-corrected model used to make final maps gives:

a. An improvement over the uncorrected model (Panel A) and:

b. A good fit to literature data (R^2 = 0.91 and RMSE = 2.99‰ for δ^2H when compared to independent long-term monitoring data (Figure 5D)). For comparison, the final model of Bowen et al. (2011) had a RMSE for δ^2H of 9.2‰ when compared to long-term monitoring data - equivalent to our Figure 5D.

With regards to interpreting drivers of residuals:

1. Table 2 already gives t values and P values for regressions between isotope residuals and environmental variables.

2. From panel A of Figure 5 we can see that most of the variance in δ^2H values of river water was explained by the combination of a precipitation isoscape and a simple water balance model. This point was noted by reviewer 2 in their first review and highlights how important the precipitation model is for river water model accuracy.

3. Currently, we think much of the residual correction using the 5 environmental variables in Table 2, and isotope data from our 58 monitoring sites is correcting for errors in the precipitation model. We explain this from L. 419 onwards. We do not think it is worthwhile to present plots of these regressions in the manuscript because while they would be very interesting with an accurate precip. model they are less interesting hydrologically if the precipitation model is inaccurate.

Changes made:

- Added labels A, B, C, D to Figure 5. These were omitted in error and might have made Figure 5 hard for the reviewer to interpret.

- Text added to L. 357 '*…and see Yang et al. (2020)*.'
- Text added to L. 135: '*Measurements from this network have been used to develop and calibrate a range of hydrological and water quality models (e.g. Alexander et al. (2002), (Elliott et al. 2005))*.'

Minor comments

(M1) In Line 23, please state clearly what "additional hydrological processes" are.

R: Yes, good idea.

Change made: Sentence changed to '*Hence, additional hydrological process information such as evaporation effects can be incorporated into river isoscapes using regression kriging of residuals*.'

(M2) Please explain why the important ranks of environmental factors in Table 2 for oxygen and hydrogen isotopes differ, using some explanations based on New Zealand's physical environments.

R: We can certainly speculate, but our analysis does not allow us to say for certain.

Change made: Text added to L. 264: '*A possible cause for the higher ranking of upstream lake and wetland area in the* $\delta^{18}O$ *regression is the greater sensitivity of the* ^{18}O *component of water to kinetic fractionation effects than the* ^{2}H *component (Craig 1961; Gat 1996)*.'

(M3) The authors want their isoscapes to be used for hydrological studies (Line 25). It would be useful if the authors could have regression kriging of four environmental variables (i.e. SiteElev, usCatElev, usAveSlope and ust.WArea) for Figures 4, 6 and 7. In hydrological studies, precipitation variations are commonly used. Regression kriging models based on four environmental variables without using precipitation as a dependent variable will be more useful for hydrological studies based the water budget.

R: Our understanding is that the reviewer is asking for us to remove the top predictor from our residuals regression (usAnRainVar, Table 2) and reanalyse without it.

We'd prefer to keep the current regression structure (i.e. 5 environmental variables) for the following reasons:

1. Removing the top predictor from our residuals regression will make our maps less accurate.

2. We think that the <u>main</u> benefits of our work rely on accurate maps of river water isotope values that will allow hydrologists (and others) to identify useful isotope gradients; for example, differences between local precipitation/recharge, groundwater and river water.

Change made: No change made.

(M4) It is great that the authors provide their information on https://shiny.niwa.co.nz/nzrivermaps/. The problem is that https://shiny.niwa.co.nz/nzrivermaps/ is very bulky and it is not easy to use.

At the moment, I could not produce a plot like Figure 7 that includes gauging sites, from https://shiny.niwa.co.nz/nzrivermaps/

The authors should provide a note of how to use https://shiny.niwa.co.nz/nzrivermaps/ to generate Figure 7. If the authors use R to generate their maps, they can provide their code and data.

R: We have now provided careful instructions on how to visualise and download our model data using nzrivermaps. These are in supplementary file S3. In the same file we have also provided instructions on how to compare these nzrivermaps data to measured data from NRWQN sites, and environmental classes across the river network (see below).

Many different applications can simply be used to make maps using the data we have provided. We used a mix of ARCGIS and R and we don’t think providing our R mapping code would help the reader much. We have recommended the use of ARCGIS in supplementary file S3.

Changes made:

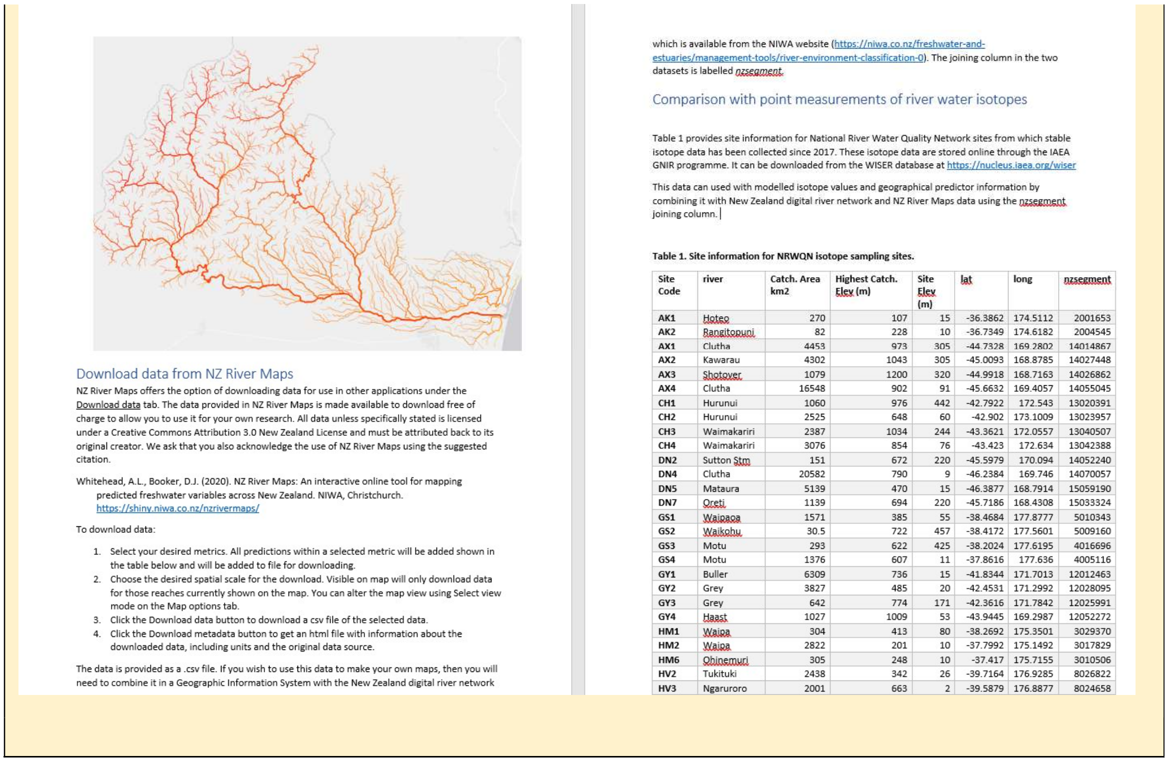
- Supplementary file S3 added
- Text added to ‘Code and data availability’ section ‘*Instructions for accessing and comparing datasets used in this work are provided in supplementary file S3.*’

(M5) From https://shiny.niwa.co.nz/nzrivermaps/, we know that there are different climate classes, geology classes, landcover classes, Strahler stream orders, valley landform classes and topographical classes. Please provide a table to show how the 58 NRWQN stations and 600,000 reaches are distributed in these classes to let our readers know how these 58 NRWQN stations represent 600,000 reaches.

R: This network of sites was designed to be representative of New Zealand River environments, to facilitate analyses of the type performed in this study. We have already directed the reader to the information the reviewer is requesting - on L. 130, which reads ‘*Modelled river water isotope values were compared to annual average values from 58 sites from the National river water quality network (NRWQN; selected to represent catchments nationally (Yang et al. 2020)). Design of the NRWQN is described by Smith and McBride (1990), while descriptions of physical (catchment), flow and chemical conditions at monitoring sites can be found in Davies-Colley et al. (2011), Julian et al. (2017), and Yang et al. (2020).*’

We also now note that other studies that use data from these sites to calibrate large-spatial-scale water chemistry models include Alexander et al. (2002) and (Elliott et al. 2005).

We have added a table of site information to Supplementary file S3, as shown in the screenshot below. This includes the river segment identifier that allows the reader to compare data from the 58 NRWQN sites with information from the entire River Environment Classification (REC) database including all of the classes the reviewer mentions, and many others.



Download data from NZ River Maps

NZ River Maps offers the option of downloading data for use in other applications under the Download data tab. The data provided in NZ River Maps is made available to download free of charge to allow you to use it for your own research. All data unless specifically stated is licensed under a Creative Commons Attribution 3.0 New Zealand License and must be attributed back to its original creator. We ask that you also acknowledge the use of NZ River Maps using the suggested citation.

Whitehead, A.L., Booker, D.J. (2020). NZ River Maps: An interactive online tool for mapping predicted freshwater variables across New Zealand. NIWA, Christchurch. https://shiny.niwa.co.nz/nzrivermaps/

To download data:

1. Select your desired metrics. All predictions within a selected metric will be added shown in the table below and will be added to file for downloading.
2. Choose the desired spatial scale for the download. Visible on map will only download data for those reaches currently shown on the map. You can alter the map view using Select view mode on the Map options tab.
3. Click the Download data button to download a csv file of the selected data.
4. Click the Download metadata button to get an html file with information about the downloaded data, including units and the original data source.

The data is provided as a .csv file. If you wish to use this data to make your own maps, then you will need to combine it in a Geographic Information System with the New Zealand digital river network which is available from the NIWA website (https://niwa.co.nz/freshwater-and-estuaries/management-tools/river-environment-classification-0). The joining column in the two datasets is labelled *nzsegment.*

Comparison with point measurements of river water isotopes

Table 1 provides site information for National River Water Quality Network sites from which stable isotope data has been collected since 2017. These isotope data are stored online through the IAEA GNIR programme. It can be downloaded from the WISER database at https://nucleus.iaea.org/wiser

This data can used with modelled isotope values and geographical predictor information by combining it with New Zealand digital river network and NZ River Maps data using the nzsegment joining column.

Table 1. Site information for NRWQN isotope sampling sites.

Site Code	river	Catch. Area km2	Highest Catch. Elev (m)	Site Elev (m)	lat	long	nzsegment
AK1	Hoteo	270	107	15	-36.3862	174.5112	2001653
AK2	Rangitopuni	82	228	10	-36.7349	174.6182	2004545
AX1	Clutha	4453	973	305	-44.7328	169.2802	14014867
AX2	Kawarau	4302	1043	305	-45.0093	168.8785	14027448
AX3	Shotover	1079	1200	320	-44.9918	168.7163	14026862
AX4	Clutha	16548	902	91	-45.6632	169.4057	14055045
CH1	Hurunui	1060	976	442	-42.7922	172.543	13020391
CH2	Hurunui	2525	648	60	-42.902	173.1009	13023957
CH3	Waimakariri	2387	1034	244	-43.3621	172.0557	13040507
CH4	Waimakariri	3076	854	76	-43.423	172.634	13042388
DN2	Sutton Stm	151	672	220	-45.5979	170.094	14052240
DN4	Clutha	20582	790	9	-46.2384	169.746	14070057
DN5	Mataura	5139	470	15	-46.3877	168.7914	15059190
DN7	Oreti	1139	694	220	-45.7186	168.4308	15033324
GS1	Waipaoa	1571	385	55	-38.4684	177.8777	5010343
GS2	Waikohu	30.5	722	457	-38.4172	177.5601	5009160
GS3	Motu	293	622	425	-38.2024	177.6195	4016696
GS4	Motu	1376	607	11	-37.8616	177.636	4005116
GY1	Buller	6309	736	15	-41.8344	171.7013	12012463
GY2	Grey	3827	485	20	-42.4531	171.2992	12028095
GY3	Grey	642	774	171	-42.3616	171.7842	12025991
GY4	Haast	1027	1009	53	-43.9445	169.2987	12052272
HM1	Waipa	304	413	80	-38.2692	175.3501	3029370
HM2	Waipa	2822	201	10	-37.7992	175.1492	3017829
HM6	Ohinemuri	305	248	10	-37.417	175.7155	3010506
HV2	Tukituki	2438	342	26	-39.7164	176.9285	8026822
HV3	Ngaruroro	2001	663	2	-39.5879	176.8877	8024658

Change made: Table 1 and instructions on downloading data, and comparing modelled and measured data across environmental categories added to Supplementary file S3.

References:

Alexander, R.B., A.H. Elliott, U. Shankar, and G.B. McBride. 2002. Estimating the sources and transport of nutrients in the Waikato River Basin, New Zealand. *Water Resources Research* 38: 4-1-4-23.

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