

Hydrol. Earth Syst. Sci. Discuss., author comment AC1
<https://doi.org/10.5194/hess-2021-424-AC1>, 2022
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Reply on RC1

Bruce D. Dudley et al.

Author comment 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 et al., Hydrol. Earth Syst. Sci. Discuss.,
<https://doi.org/10.5194/hess-2021-424-AC1>, 2022

In this manuscript, the authors produce isoscapes for the river networks of New Zealand, based on reach-scale environmental attributes. Their data and new maps for the surface runoff isotopes could be useful contributions in the region, although there are some issues related to the contributions, data, methods and results.

Main issues

(a) The authors have to articulate their contributions clearly. They should not include irrelevant claims which take away people's attention on their real contributions of the work.

Response: We have interpreted this comment as a summary of the bullet points given below under the reviewer's section (a), and address these individually.

The main contributions of this work can be (1) new isotope validation dataset (File S1; e.g. Additional monthly data for New Zealand in 2017-2020), and (2) the isotope maps of surface runoff based on precipitation isotope maps and other reach-scale environmental attributes.

R: We agree that our stream measurements dataset, and modelled reach scale values (i.e. those available at <https://shiny.niwa.co.nz/nzrivermaps/> as shown below) may be useful contributions regionally.

However, we note that the method used to derive modelled reach scale values improves

upon a method originally applied to the continental USA (Bowen et al. 2011). Our improved method is transferrable to other parts of the world and may thus be of value for an international audience. To better clarify to readers of the novelty of this method and the improvement it offers relative to other methods of mapping river water isotope values, we will improve description of the regression kriging method, its uses elsewhere, and the novelty in its application to river water isoscapes (as suggested by reviewer 2).

Our readers would want some more specific information related to the specific contributions of this paper on the data legacy and isoscapes in New Zealand.

Instead of just giving a summary of general processes related to rainout or temperature effects of isotopes, which has been routinely discussed in other similar previous works, the authors could provide a review of the history of environmental isotope studies over New Zealand, so that they can introduce all the crucial datasets or sampling campaigns in the country.

R: We think a brief review of the history of environmental isotope studies in New Zealand is a good idea. We will add text to the introduction to supplement the description of the literature validation dataset in the methods (section 2.4). In response also to comments below from both reviewers, will add a table to show the sources, size and duration of datasets and how these data are used in developing, calibrating and validating the models.

It will be good that the author can include the georeferenced maps (e.g. the GeoTIFF files) in their supplementary materials.

Response: We will include the GeoTIFF files for precipitation and river isoscapes in our supplementary materials.

One of the main contributions of this paper is that the authors generated surface water maps from a precipitation map. Therefore, please show the river network and catchments in Figure 1 to give people some ideas of how different isotope sampling locations can be related to their data sources or references.

Response: Figure 1 already shows the river network (panel F) and the locations of validation sites (panel G). It is an issue that at national scale, in panel F the smaller reaches and catchments blend together so that only larger rivers are visible. For this reason, panels A-F show only the Canterbury region of New Zealand. We cannot show

every catchment in high detail, but a 'zoomed-in' example comparing model results for individual reaches to values from monitoring sites is presented in Figure 7.

For the reader with further interest in the river network and catchments we will add more detail as follows:

- Add reference Smith and McBride (1990) to panel G in Figure 1; this reference describes the design of New Zealand's national river water quality network, and the catchments from which monthly isotope samples were taken.
- Add text at the start of section 3 to give the reader better access to information about monitoring sites and their catchments, including design of the monitoring network (Smith and McBride 1990), and descriptions of physical (catchment), flow and chemical conditions at monitoring sites (Davies-Colley et al. 2011; Julian et al. 2017; Yang et al. 2020).

Although the author used water balanced methods, I did not really see any results related to surface flow mixing or patterns. Moreover, the authors have to recognise their main contribution of the work is not about isotopes in animals or plants. Only the implication of this work can be related to isotopes in animals or plants. However, the current abstract makes people think that the main topic of this work is about isotopes stored in animal and plant issues.

Response:

Regarding the presentation of results related to surface flow mixing or patterns:

As noted in L. 16, We used a water balance-based method to generate the river isoscape. Patterns of surface flow and mixing are therefore represented by the isoscape outputs in figures 6 and 7, in the reach scale values available at <https://shiny.niwa.co.nz/nzrivermaps/> and will be available in the GeoTIFF files for river isoscapes we will add as supplementary material.

Regarding the comment about the main contribution of the work is not being about isotopes in animals or plants:

We will remove mention of animals and plants from the first sentence of the manuscript. This will read: 'Stable isotope ratio measurements (isotope values) of surface water reflect hydrological pathways, mixing processes, and atmospheric exchange within catchments.'

We will slightly alter the last sentence of the abstract to make it clear that we haven't measured any animals or plants. This will read: 'The resulting river water isoscapes have potential applications in ecological, hydrological and provenance studies for which understanding of spatial variation in surface water isotope values is required'

In Section 3, the authors should articulate their overall results by removing irrelevant and weak discussions.

(b) The authors have to clarify the details of the data and methods. In this study, the

used methods are a well-developed kriging approach. Although these used methods may not be a significant advancement for spatial analysis, they should be suitable for this manuscript's purpose. Even though it is somewhat expected, the authors showed their regression-based kriging was better than the ordinary kriging.

Response: We have interpreted these comments as a summary of the bullet points given below under this review section (b), and address these individually.

The authors recognise that that "distance-based" geospatial and statistical interpolation is less appropriate (Ln 15 and Ln 54), but their regression-based kriging methods is still "distance-based" geospatial and statistical interpolation at the end of day.

Response: We agree. We will address this by providing more background on the differences between ordinary kriging and regression kriging (as requested by reviewer 2) and using the term 'simple distance-based' to describe ordinary kriging in lines 15 and 54.

In Section 2, there are not many details about how to select five environmental variables in Table 1 from Table S1 (Ln164-Ln165). There are some logic issues here. The authors used the small number of available samples to justify the use of stepwise regression to reduce the number of independent variables.

Response: We will provide more detail and support our choice of method with a reference at this point. E.g. 'From the list of independent variables in Table S1, five were selected for the regression analysis based on BIC (Bayesian Information Criteria), following the "one in ten rule" (e.g. Harrell Jr (2015)), i.e. one predictive variable can be included for every ten sites in the dataset.'

We will add t values and P values to this table.

A table of the data for developing, calibrating and validating the models should be provided. Therefore, in the table, the authors should give the details of data sources (e.g. related publications), locations (e.g. south or north islands), sampling periods (2007-2009 in Ln 114) and number of samples (e.g. 51 sites Ln113).

Response: Really good idea. Thanks. Reviewer 2 also had trouble working out which datasets were used in which step, and what data these contained. We will add a table to make this clearer.

The authors should think clearly why they choose the data between 2017 and 2020 for the residual calculation (Ln 126).

Response: We will try to make this clearer using the addition of a table as described in the previous comment.

As described in a response to reviewer 2, the 2017 to 2020 river water monitoring data were monthly samples over three years (36 samples per site) from 58 sites spread across the major catchments of New Zealand. Site mean values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ from this dataset are appropriate for correcting the river isotope model; the model gives an estimate of 'average' river water isotope values for each reach in the river network.

Other data collated from the literature used in final checking of the model (figure 5, and supplementary material S1) is largely from 'one-off' samples from river reaches, which are less appropriate for correcting the model because river water isotope values vary seasonally, and under changing flow conditions (Yang et al. 2020). These data do however provide a good independent check of how the model performs compared to other model approaches.

The author mentioned a poorer longer-term fit in the other study (Ln 200). Let's think about it together here. For the annual values between 2007 and 2010, there could be only four data points for computing the correlation...

Response:

We will make sure this field precipitation dataset and its use in model checking are clearly described using the additional table suggested above.

The dataset of field precipitation samples used for this correlation/model checking contained monthly values from 51 sites between 2007 and 2010. So, ca. 1400 data points for computing the monthly correlation, and 51 data points for the annual average correlation (not 4). We will add these samples size values to the manuscript text alongside the R^2 and RMSE values. We note that this correlation method and the field dataset are the same as used by Baisden et al. (2016). Using the same correlation method and field dataset allowed us to check our precipitation model replicated their published one well.

At the moment, the model in Equation 3 is only a first order model of environmental variables. Authors may explain why they did not try to explore higher order models for the environmental variables.

Response: We didn't apply nonlinear regression simply because it would increase the complexity for parameter estimates. This was inappropriate given limited number of sites (58) available for validation. We will make this clear in the manuscript.

In Section 3, the authors should try to discuss how their selected environmental variables can be related to ground water and vegetative surface (Ln49-Ln50). The author did recognise that their model system was biased (Ln 403) which is very likely related to their selected environmental variables in Table 1.

Response: We will revise this section for clarity.

Spatial patterns of residuals in our method, and predictors (e.g. those in Table 1) could be

used to increase understanding of hydrological processes. A simple example of this is that upstream wetland and lake area, which leads to higher evaporative fractionation and thus higher river water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, explained spatial patterns of residuals in our study, which used the (Bowen et al. 2011) water balance model that assumes no evaporative fractionation.

A similar approach may be taken for lowland reaches gaining a large portion of their flow from high-elevation-derived groundwater. These reaches may show up as more isotopically negative than would be expected based on recharge and surface routing of local, low-elevation rainfall.

HOWEVER – our manuscript shows that this type of approach, and similar approaches in isotope enabled hydrological models (e.g. Belachew et al. (2016)) are reliant on the accuracy of the precipitation isotope model. We believe that some of the variables in table 1 reflect correction of spatial inaccuracies of the precipitation model.

We will adjust the discussion accordingly.

In Equation 1, there is no storage consideration. In the implication section, the authors should discuss how storage can affect their overall map results in Section 3.

Response: Our method is fairly robust in this respect. Because both input data and data used to correct the model are averaged to give 'steady state' values, seasonal variation in contributions of surface and groundwater flows (which may have differing isotope values) to rivers is incorporated.

We will add brief discussion on this point.

(c) Some interpretation of results can be problematic and speculative. More discussion of the limitations of the study is needed.

We have interpreted this comment as a summary of the specific bullet points given below under this review section (c), and address these individually.

In L260-L285, the discussions and interpretations related to air masses, regional circulations and orographic effects are very speculating. These discussions are without much strong quantitative evidence in the manuscript.

We agree that the discussion of the effects of origin of air masses on precipitation isotope values currently looks speculative because we haven't referenced previous work well enough. We will add references to studies of isotopes in precipitation in New Zealand (e.g. McDonnell 1988) to back up this point.

We feel our discussion of regional orographic effects is well supported by the work of Purdie et al. (2010) and Kerr et al. (2015), which we have referenced in the manuscript. We have gone to further effort to back up our statements using Appendix Figure 1 and its accompanying text. However, we will add international references showing the same effects in other mountainous regions worldwide to support our statements.

For example, the results in L223-L235 are very hypothetical. They are also very repetitive

in the manuscript, because the authors repeat these speculations again in Section 3.4. Moreover, the current results are only marginally or speculatively related to cloud processes in Ln43.

Response: Firstly, we will directly reference Figure 2 in the statement on L. 225-226; i.e. 'of the eight sites where predicted $\delta^{18}\text{O}$ values exceed average measured $\delta^{18}\text{O}$ values by > 1‰ (**Figure 2**), seven are in alpine-fed rivers on the leeward east of New Zealand.

We agree that there is some unnecessary repetition between sections 3.2 and 3.4. We will work to reduce or remove this.

We will revise the discussion to improve the description of links between:

- The predictors of residuals in Table 1
- The spatial inaccuracy of the precipitation model (and its likely causes)
- Our ability to improve understanding of processes in hydrology using our approach.

Put simply, Table 1 currently contains predictors that correct for spatial inaccuracy of the precipitation model. If we can improve the precipitation model, our method will be more useful for understanding of processes in hydrology (such as evaporation and groundwater contributions to surface water) that change in isotope values of river water.

The authors should revise their discussion, similar to Ln 285-L302 where the authors discussed their result based on the fitted model variable results (e.g. usAnRainVar).

Response: As above, we will revise the discussion to improve the description of links between:

- The predictors of residuals in Table 1
- The spatial inaccuracy of the precipitation model (and its likely causes)
- Our ability to improve understanding of processes in hydrology using our approach.

For orographic effects, the authors may need to consider more about "aspect" and "wind" variables in their models, so that they can justify their discussion based on Kerr et al. (2015).

Response: Good point. In fact, the 'usAnRainVar' variable in Table 1 is strongly correlated with aspect. We will make this clearer as described above.

As I have mentioned in my first comments, the results of this work are unlikely to be useful for studying movement of aquatic organisms (L430). The current maps are only for hydrogen and oxygen. There were no other isotope results such as nitrogen. In general, the discussion of animal and plant tissues (Ln10) is far-fetching in this manuscript. The results of this paper are not really giving much insights into them.

Response: The reviewer is right that the current maps have potential use in hydrological studies. With the reviewer's comments and the readership of HESS in mind, we will make modifications to the abstract, introduction and discussion to lessen the focus on ecological implications of this work and increase focus on hydrological uses and implications.

We do not feel that the absence of nitrogen data from our paper negates the usefulness of our work to (for example) ecological research. While having MORE tracers is almost always better in mixing models (Fry 2006), hydrogen and oxygen stable isotopes are useful nonetheless for aquatic ecology (Soto et al. 2013).

We do not agree that the results of this work are unlikely to be useful for the ecological purposes we have outlined in our manuscript. The geographical distributions of hydrogen and oxygen isotopes in precipitation and surface water form underpin a rich and growing body of research into animal migrations, as well as other cross-disciplinary uses. Quoting from Bowen et al. (2009) 'Isoscapes have great power as a cross-disciplinary research tool, as exemplified by the translation of hydrology-focused GNIP [Global Network of Isotopes in Precipitation] data into tools for animal migration research.'. Examples of ecological (migration) research based on GNIP hydrogen and oxygen isotope data are included in a review by Hobson and Wassenaar (2018). The Global Network for Isotopes in Rivers (GNIR) has similar aims. Quoting from Halder et al. (2015) 'The aim of the GNIR programme is to collect and disseminate time-series and synoptic collections of riverine isotope data from the world's rivers and to inform a range of scientific disciplines including hydrology, meteorology and climatology, oceanography, limnology, and aquatic ecology.' However, the reviewer's comments make it plain that we have not conveyed this potential for cross-disciplinary use of our work adequately. To address this, we will add brief but specific examples to the manuscript on this topic to section 4.

The system bias of this study (L403) is unlikely to help others improve understanding of isotope patterns. Therefore, the authors should try to reframe their writing by reducing their discussion based on speculations, and suggest more how we can improve our understanding patterns of precipitation isotope values by using hydrological process-based models to investigate how flow and evaporation processes affect isotope patterns.

R: We will extend the focus of this paragraph outside of the scope of the current study, towards more general discussion of using river isotope models to understand hydrological processes.

We will restructure this paragraph as follows:

- Some isotope-enabled hydrological models (e.g. Belachew et al. (2016)) use precipitation isotope models as input data to give improved estimates of fluxes between components of the hydrological cycle.
- The accuracy of these flux estimates relies partly on accuracy in input data from precipitation isotope models
- Data from precipitation isotope models will always be imperfect, but improvements in the accuracy of precipitation isotope models can improve our understanding of flow pathways and evaporation processes at landscape scales.

Currently, I did not see much mixing and surface flow results which is suggested in Ln16. I also did not see the dam results mentioned in Ln13 and Ln68.

Response:

We will add t values and p values to Table 1 to better support the discussion around upstream lake and wetland area effects on $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of river water. We will refer the reader to these results in section 3.3.

Open water behind dams is included in the variable usLWArea. We will add a specific reference to dams to section 3.6.

For clarity, we will replace abbreviated variable names (e.g. 'usLWArea') in the results and discussion text with full variable names (e.g. 'Upstream lake and wetland area').

Line 16 states 'We used a water balance-based method, which represents patterns of surface flow and mixing'. Thus, mixing results are incorporated into the water balance results shown in (for example) Figure 2, 6 and 7, and in the online maps shown below.

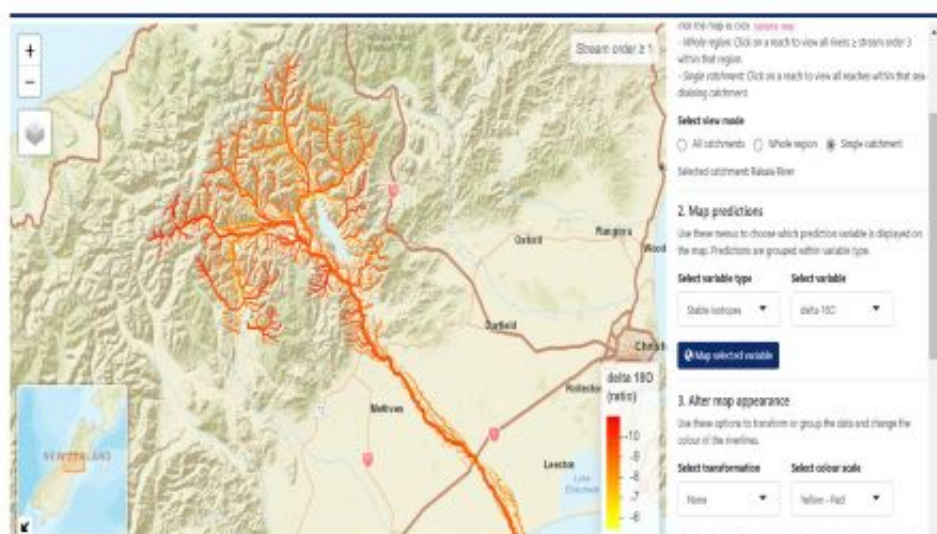
Until the authors could have results similar to Figure 7 for all the main catchments in New Zealand, the discussion in Ln355 - Ln379 could not be justified. For example, there are no similar results of Figure 7 for the South Island in the manuscript.

Response:

We will add t values and p values to Table 1 to better support this discussion section.

Discussion of relationships between environmental variables and river water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in Ln355 - Ln379 is backed up by multivariable regression results. Importance ranks for this regression for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ residuals are already given in table 1, based on t statistics. This regression used $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data from across New Zealand, not just the catchment in figure 7. Our discussion on Ln355 - Ln379 is limited to statistically significant predictors shown in table 1, of which upstream lake and wetland area is one.

We could produce plots similar to Figure 7 for all the main catchments in New Zealand, but it is not practical to show them all in the manuscript. Figure 7 gives an example. We have provided access to data shown in Figure 7 at <https://shiny.niwa.co.nz/nzrivermaps/>. A South Island example is shown below:



Monitoring data (i.e. equivalent to the points in Figure 7, but across major catchments

nationally) are available via the IAEA WISER portal.

Perhaps, the authors can have more discussion on how results in Figure 7 are related to the "dendritic" patterns (Ln62).

Response: Certainly. We will add some detail on this to the section in L. 364-378.

More insightful thoughts on variations between precipitation and surface water will be useful to demonstrate the values of this work. It would be great to have more quantification and discussion on how the precipitation and new runoff maps could be different in terms of their patterns.

Response: Really good point. We will add more discussion to section 4, focussing on implications of differences in isotopes in precipitation and those shown in our runoff maps. In terms of quantification, to some degree this is already visible in the isotopic differences between rivers fed by high elevation recharge and those fed by local lowland recharge (see above). We will add some text to this effect.

Overall, the data of this work could be useful regionally.

Thank you. As above, to better clarify to readers the international transferability of our work, we will improve description of the regression kriging method, its uses elsewhere, and the novelty in its application to mapping river water isotope values (as also suggested by reviewer 2).

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