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Reply on RC2

Michael Kilgour Stewart et al.

Author comment on "Comment on "A comparison of catchment travel times and storage deduced from deuterium and tritium tracers using StorAge Selection functions" by Rodriguez et al. (2021)" by Michael Kilgour Stewart et al., Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2021-146-AC3>, 2021

Reply to Reviewer #2 (R2)

R2: General Comments

The authors of the comment (referred to below as Stewart, 2021) provide a detailed discussion of the value of tritium analyses to constrain the travel time of streamflow, in response to a previously published paper in HESS (referred to below as Rodriguez, 2021). The comment (Stewart, 2021) specifically discusses the apparent "truncation" of travel time distributions (TTDs) derived from stable isotopes when compared to TTDs derived from tritium. This "truncation" is discussed by Rodriguez, 2021, as one of the incentives for the original study, to include both stable isotopes (i.e. ^2H) and tritium, within the age-ranked storage selection framework (SAS). By doing that, the original paper (Rodriguez, 2021) is a very valuable contribution to the scientific literature.

Authors: We agree.

R2: Specific Comments

It appears that the comment (Stewart, 2021) hinges on the interpretation of one sentence in the abstract of Rodriguez, 2021, quoted in Stewart, 2021 on line 23:

"We conclude that stable isotopes do not seem to systematically underestimate travel times or storage compared to tritium." (Rodriguez, 2021)

More specifically, in the conclusion section of Rodriguez, 2021, the authors "conclude that the perception that stable isotopes systematically truncate the tails of TTDs may not be valid." (Rodriguez, 2021)

They continue and recommend to "compare streamflow TTD and storage from the two tracers in larger catchments where older water is expected in order to give tritium more time to decay and to better leverage its ability to point out the presence of very old water." (Rodriguez, 2021)

Considering the sentences in the conclusion section, I interpret the abstract line to be a

site-specific conclusion, rather than a broad conclusion that the truncation hypothesis is "generally invalidated" (as stated by Stewart, 2021, on line 34).

The comment (Stewart, 2021) expands the interpretation of the limited conclusion by Rodriguez and states that it "does not mean that such old water does not exist in other catchments and therefore that the truncation hypothesis should be rejected for all catchments." I do not think Rodriguez intended to convey such a broad conclusion.

Recommendation

In my view, the commentary does not specifically respond to the conclusions of the Rodriguez paper, but rather to a broader interpretation that the original authors may not have intended to convey. As such, I have recommended to reject the publication of this comment as a response to the Rodriguez paper.

Authors: We feel that the issue raised in our comment (possible underestimation of the significance of old water contributions to streamflow based on stable isotope measurements only) is worthy of discussion here, in light of the statements by Rodriguez et al (2021) that "We conclude that stable isotopes do not seem to systematically underestimate travel times or storage compared to tritium" from the abstract and "we conclude that the perception that stable isotopes systematically truncate the tails of TTDs may not be valid" from the Conclusion. As pointed out by Reviewer#1 (R1), Rodriguez et al (2021) at least give the impression that they reject the truncation hypothesis for all catchments. In addition, our comment provides information on where and where not to expect the truncation issue

R2: In case the comment proceeds to publication, I have provided additional comments and suggestions below.

Specific Comments (continued)

L70 (Figure 1) It would be insightful to include the model curves for samples collected in 2010 or 2000 or 1990. For those decades, tritium may have been even less conclusive as an age tracer in streams in the Northern hemisphere. At the same time, high-frequency stable isotope studies became accessible, and was applied in northern hemisphere high-precipitation, low-ET catchments. The collective understanding of watershed response times may have been influenced by the availability of data during these decades.

Authors: We have added curves for 2000 to the graphs showing the situation with regard to tritium then.

R2: L77: Why $f=0.7$? This seems arbitrary.

Authors: $f = 0.7$ has been found to be an effective value in studies using tritium (e.g. Morgenstern and Daughney, 2012). Calculations were also made using $f = 0.5$ and results were found to be similar to those obtained using $f = 0.7$ (these were not shown in the Comment).

The cumulative stream TTDs from Fig. 7c of Rodriguez et al. (2021) were compared with cumulative EPM curves for various values of f . The EPM curve with $f=0.7$ was found to give an approximate representation of the Weierbach curve. In addition, the flow-weighted cumulative stream age distributions from Fig. 7b of Visser et al (2019) are approximately consistent with the EPM($f=1$) curve (otherwise known as the exponential model) as noted in their paper. Hence, $f=0.7$ appears to be a reasonable choice.

The value of f is very important in describing the mixing between young and old water

that smooths out seasonal variations within a few years. In theory, maximum smoothing is given by $f = 1$ and minimum smoothing (i.e. none) by $f = 0$; the latter case would be very rare in streams.

R2: L94: "significant seasonal variation"

This is very relevant if precipitation and evapotranspiration are out of phase. Obviously, evapotranspiration is expected to remove more water in summer (when tritium concentrations in precipitation are higher) than in winter (when tritium concentrations in precipitation are lower). The degree of seasonality in evapotranspiration and tritium in precipitation, as well as the amount of mixing in the root zone, contribute to a possible bias of lower tritium concentrations in the stream, which would be interpreted as older ages.

An example (related to the cold-season-bias) is given by:

Jasechko, S.; Wassenaar, L. I.; Mayer, B., Isotopic evidence for widespread cold-season-biased groundwater recharge and young streamflow across central Canada. *Hydrological Processes* 2017, 31, (12), 2196-2209.

Authors: This is an important point that has been addressed in papers using tritium, by accounting for evapotranspiration losses (e.g. Stewart et al., 2007; Morgenstern et al., 2010). In Australia and New Zealand, tritium concentrations in precipitation tend to be higher in winter and early spring (Tadros et al., 2014).

The SAS method also accounts for this.

R2: L160: In addition, even if older TTs derived from tritium were selectively collected during base flow conditions, that would still be evidence that the stable isotope data collected year-round fail to capture the old component in baseflow.

Authors: Agreed. Most of the Australian studies captured MTTs at a range of flow conditions and the Cartwright & Morgenstern (2018) and Hofmann et al. (2018) ones specifically estimated MTTs during flow peaks. The flow peaks were found to contain water that was a few years old.

R2: L163: This first point also reflects (in my opinion) a sampling bias with respect to stable isotopes and tritium to derive residence times, specifically related to the choice of the isotope applied, sampled, analyzed, interpreted, and published. Isotopic tracer studies often build on prior hydrological investigations and limited research funds are directed towards the isotopic analyses that are expected to be most valuable. Stable isotopes have been applied more often in smaller catchments with faster response times and shorter (expected) residence times, whereas tritium has more often been applied in larger river basins with longer residence times. Recent studies combining both tracers have shown that a residence time interpretation of stable isotopes may be hiding the longer tail of the distribution that can be observed by tritium.

R2: However, Rodriguez shows that this is not the case in the Weierbach catchment.

Authors: Agreed

R2: L183: "no issue... of interest." is not clear to me.

Authors: We will revise this statement which is poorly phrased. It is meant to say that if estimates of TTDs could be made from each one of a series of tritium measurements they would allow the time variability of the stream TTD to be determined. Whereas stable isotopes require groups of measurements to determine TTDs, tritium in principle only

requires one provided radioactive decay can be used for dating and the form of the TTD can be estimated. In application, of course, the seasonal variation also needs to be considered.

R2: L186: The short term variability of tritium is still poorly understood and so far have mostly been a nuisance for applying tritium as a short-term age tracer, although recent advances using the origin of precipitation are promising:

van Rooyen, J. D.; Palcsu, L.; Visser, A.; Vennemann, T. W.; Miller, J. A., Spatial and temporal variability of tritium in precipitation within South Africa and it's bearing on hydrological studies. *Journal of Environmental Radioactivity* 2021, 226, 106354.

Visser, A.; Thaw, M.; Esser, B., Analysis of air mass trajectories to explain observed variability of tritium in precipitation at the Southern Sierra Critical Zone Observatory, California, USA. *Journal of Environmental Radioactivity* 2018, 181, 42-51.

Authors: Agreed, this would facilitate the use of tritium as a short-term age tracer, but would be less useful for use of tritium as a longer-age tracer for which it is potentially most useful.

R2: L197: "Instead .. favoured." The design of such long term studies would also benefit from deliberately collecting tritium samples during high and low flow conditions throughout the study period to capture the time-variance of TTDs in response to hydrological conditions.

Authors: Agreed, the stream TTD response over all flow conditions is needed.

R2: L198: "Eventually, ... single tritium measurements." In my opinion, no single tritium measurement will be able to capture the TTD of streamflow. This statement should be removed or reworded. One tritium measurement may be able to constrain the mean travel time parameter of a TTD which shape needs to be assumed a priori.

Authors: We agree that no single tritium measurement could capture the TTD of streamflow. The last sentence is what we meant. Multiple tritium measurements are needed to capture the TTD of streamflow in different conditions.

R2: Technical Comments

L19: Please also include the Van der Velde paper presenting the SAS/STOP function concept:

Van der Velde, Y.; Torfs, P. J. J. F.; Van der Zee, S. E. A. T. M.; Uijlenhoet, R., Quantifying catchment-scale mixing and its effect on time-varying travel time distributions. *Water Resources Research* 2012, 48, (6), W06536.

Authors: Ok

R2: L45: As the travel times are a consequence of the physical and climatic characteristics of the watershed, b) should/could precede a).

Authors: We will think about this

R2: L50: I find it more useful to express catchment fluxes per unit area (in terms of m or mm, rather than volumetrically)

Authors: Ok

R2: L100: "using": That study didn't really "use" the variation of tritium in precipitation, but rather carefully incorporated it into the SAS modeling to avoid an old-tritium-age bias due to the strong seasonality of both ET and precipitation variation.

Authors: We will rephrase our statement.

R2: L140: A thorough analysis of the (in)ability of seasonal tracer cycles to quantify mean transit times is provided by Kirchner (2016, HESS).

Kirchner, J. W., Aggregation in environmental systems–Part 1: Seasonal tracer cycles quantify young water fractions, but not mean transit times, in spatially heterogeneous catchments. *Hydrology and Earth System Sciences* 2016, 20, (1), 279-297.

Authors: Yes

R2: L170: It would be helpful to provide a rebuttal to each argument listed here. (As is done for 1.)

Authors: We will consider this suggestion

L186: "In addition, to" Remove comma.

Citation: <https://doi.org/10.5194/hess-2021-146-RC2>

IAEA/WMO (current Year). Global Network of Isotopes in Precipitation. The GNIP Database. Accessible at: <https://nucleus.iaea.org/wiser>

Cartwright, I., Irvine, D., Burton, C., & Morgenstern, U. (2018). Assessing the controls and uncertainties on mean transit times in contrasting headwater catchments. *Journal of Hydrology*, 557, 16-29. doi:10.1016/j.jhydrol.2017.12.007)

Morgenstern U, Daughney CJ. 2012. Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification – The National Groundwater Monitoring Programme of New Zealand. *Journal of Hydrology*. 456–457:79–93. doi:10.1016/j.jhydrol.2012.06.010

Morgenstern, U., Stewart M. K., Stenger, R. 2010: Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit time with streamflow. *Hydrology and Earth System Sciences* 14, 2289-2301.

Stewart, M.K., Mehlhorn, J., Elliott, S. 2007: Hydrometric and natural tracer (^{18}O , silica, ^3H and SF_6) evidence for a dominant groundwater contribution to Pukemanga Stream, New Zealand. *Hydrological Processes* 21(24), 3340-3356. DOI:10.1002/hyp.6557.

Stewart, M. K., Morgenstern, U., Gusyev, M. A., and Maloszewski, P.: Aggregation effects on tritium-based mean transit times and young water fractions in spatially heterogeneous catchments and groundwater systems, *Hydrol. Earth Syst. Sci.*, 21, 4615–4627, <https://doi.org/10.5194/hess-21-4615-2017>, 2017.

Tadros, C. V., Hughes, C. E., Crawford, J., Hollins, S. E., & Chisari, R. (2014). Tritium in Australian precipitation: A 50 year record. *Journal of Hydrology*, 513, 262-273.