

Interactive comment on “Application of tritium in precipitation and river water in Japan: A case study of groundwater transit times and storage in Hokkaido watersheds” by M. A. Gusyev et al.

Anonymous Referee #1

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This study presents a new dataset of river water samples that have been analyzed for their oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$, ^3H) isotope compositions and their dissolved major ion and nutrient concentrations. The work builds on a strong background of tritium-based explorations developed by several of the coauthors of the manuscript. It is my opinion that some rewording and additional discussion could help this paper, which is already quite strong, to better relate its findings to other partially-overlapping fields, two of which include groundwater storage-depth characterizations, and stable-isotope-based transit time evaluations.

1. Stable O and H isotope versus tritium based approaches: One key and sometimes overlooked issue with the stream water transit time status quo is the roughly order-

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of-magnitude difference between stable isotope based transit times (reported transit times of a few months up to about five years) and tritium based transit times (reported transit times generally ranging from years to decades; McGuire and McDonnell, 2006). A helpful review of this inter-tracer difference was written by Stewart et al. (2010). Although a time series of stable isotopes was not developed in this study, I think a short discussion about how the storage volumes calculated here compare to stable isotope based storage volumes (e.g., Leopoldo et al. 1992) could benefit the manuscript. Doing so may help to relate the manuscript findings to work completed by research groups publishing rather different mean transit times based on ^{18}O and ^2H , plausibly linked to assumptions about age distributions. At a minimum, I think some discussion about the numerous stable isotope based studies of mean transit time with citations to these works could help to better connect these different takes on stream water age.

2. Ambiguity of tritium ages and importance of time-series sampling: I think some statements about the uniqueness of ages and their determination based on a single sample should be softened. Vulnerabilities of stable isotope based mean transit times to aggregation error has been recently discussed by Kirchner et al. (2016a, b). I think that it remains a possibility that tritium based calculations are also susceptible to aggregation error, yielding calculated mean ages that differ substantially from true mean ages. I agree with the authors' statement that a time series of stream tritium could lead to new insights about mean transit times and flow conditions, as it has in their past works (e.g., Morgenstern et al., 2015). However, I think that without these time series data (and perhaps even with these data) there remains at least some room for ambiguous ages, as one could always postulate different mixtures of waters—however unlikely—that yield near-identical tritium concentrations in the mixed sample, but have different true average ages.

3. Framing findings in terms of baseflow (e.g., article title): The authors may, after possible additions or changes resulting from the following point 5 of this review, consider revising the title wording, replacing “groundwater” with “baseflow.”

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4. Units normalized to catchment area: The groundwater storage volumes reported in the text and in Table 1 could be more straightforwardly compared among the study catchments and with other studies if normalized by catchment area (e.g., point 5 below).

5. Comparing and connecting the calculated groundwater storage with other works: For catchment 1, the reported volume (82.3 million cubic metres of water) and catchment area (104 square kilometres) point to a groundwater storage volume totaling ~ 0.8 m. The reported groundwater storage for catchment 1 (0.8m) is more than 100 times smaller than recent estimates of groundwater storage at a global scale (180m; Gleeson et al., 2016), perhaps due to this manuscript's focus on the groundwater that moves into streams as baseflow as the authors do point out. The calculated storage volume is reported to be large on line 18 (pp. 12), but "large" is relative. Juxtaposed against the estimated 180m of groundwater in the upper 2km of the crust, the calculated storage appears rather small. However, on the other hand, the reported catchment 1 storage is more than 10 times larger than terrestrial waters that are stored for less than a few months before entering streams (~ 55 mm or less; Jasechko et al., 2016). I think that the manuscript's findings may better connect to a broader audience of water scientists that focus on both groundwater and surface water ages if two elements could be added: 5a) a clear and, if possible, quantitative definition of what the storage calculated in the manuscript refers to; and, 5b) further discussion of groundwater/surface water connectivity, groundwater flow velocity with depth and how the storage volumes calculated in this work relate to other published groundwater age and storage estimates

6. Assumptions and limits of the cited and applied transit time model: The lumped parameter model used in this study (Jurgens et al., 2012) can provide a helpful foundation for interpreting tracer measurements. I do suspect that the researchers that developed this model would agree that using the ratio of 70% exponential and 30% piston flow includes assumptions that remain to be validated, and that the model will not characterize flow in all hydrologic settings. For example, other works using different assumptions

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about flow (50% exponential flow) have yielded rather impressive matches between modelled and measured spring water tritium (Morgenstern et al., 2015). I recommend a few changes that may help to convey throughout the manuscript that the mean transit times calculated here require assumptions that have not been fully validated. Some spots in the current text where a reminder to readers that the results should be interpreted as estimations include: 6a) pp 1 Line 18 – replace word "determine" with "estimate"; 6b) pp 1 Line 31 – replace words "determine the correct" with "estimate"; 6c) pp 11 Line 18 – add text similar to "if assumptions about age distributions are made" following "Japanese catchments"; 6d) pp 13 Line 24 – add text similar to ", assuming that the 70% exponential and 30% piston flow model applied here describes catchment flow conditions" following "Japanese catchments"; 6e) replace "found unique MTT" with "model a unique MTT"

7. Recent rains and snow: More than one sample was collected from a single river for several study watersheds (1, 8, 9, 10, 11; Table 2 in the manuscript). It appears that most of the paired samples have similar $\delta^{18}\text{O}$ values (within 0.3 per mille) and similar tritium concentrations (within 0.5 TU) when the two samples collected from one river are compared (sites 1, 8, 9, 10). At site 11 both the measured $\delta^{18}\text{O}$ value (difference of ~ 1.5 per mille) and the measured tritium activity (0.7 TU) differ between the June and October samples. It is possible that the observed seasonal difference in $\delta^{18}\text{O}$ and 3H at this site is related recent precipitation influxes to the river, since precipitation $\delta^{18}\text{O}$ and 3H vary intra-annually as the manuscript highlights in Figure 5. That the seasonality of river chemistry reflects a damped and phase-shifted precipitation stable isotope cycle has been highlighted by other works (e.g., McGuire and McDonnell, 2006), and a plausible explanation for the published data is that a fraction of the water in the river derives from precipitation that enters the stream quite quickly. Based on the flow model applied to this study, is it possible to include an estimate or to perhaps discuss the possible presence of water in the stream that is much younger than the reported mean transit times? Otherwise, perhaps the addition of a short discussion about intra-annual variability in river isotope compositions that points to the data for stream #11 could be

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a useful addition.

8. Calculations of the “average water depth” (e.g., pp. 13 on Line 24) might be better reported as a saturated thickness of water, rather than making an assumption about the porosity of the subsurface. Otherwise, the assumed porosity of 0.1 should be further discussed.

9. Hydrologic model: It is my opinion that this paper could be more cohesive and perceived stronger without the text describing a hydrologic model on page 12 starting at Line 20. If the authors choose to retain this subsection and results, some further description of the model may be useful. For example: why does exactly 20% of precipitation (rain?) and 80% of snow recharge the aquifer? Does the snow recharge the aquifer immediately, or is an energy balance used to model the timing of melt? Does all rain and snow recharge the aquifer or does some runoff? I do appreciate the use of a hydrologic model and its coupling to the analysis of tracer data, but feel that the strongest components of the current manuscript are found in other sections.

10. Minor suggestions:

i) Some of the acronyms used in the study could be somewhat distracting. The authors can consider removing the following acronyms, but this suggestion is, indeed, one of a personal preference for few acronyms: MCM, GNIP (at minimum the “GNIP” in parentheses can be removed from the abstract), MAFs, EMM, CDF, EPM, E70%PM.;

ii) Add a citation to earlier works that have used stream water tracers to calculate groundwater storage volume using a similar equation (e.g., Leopoldo et al., 1992);

iii) Superscript Line 3 on pp. 6;

iv) change “amsl” to the more common form “masl,” or add units of metres following numeric values in the text;

v) Line 29, pp. 8 “as” to “at”;

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vi) pp. 10 consider rewording “groundwater watershed”;

vii) Line 27, pp. 8 possible rewording from “groundwater transit times” to “baseflow transit times”;

viii) Line 17, pp. 11 remove “a”;

ix) Line 23 pp. 11 add “or differences in dissolution rates” following “younger MTTs.”;

x) Line 28 pp. 11 “volume” to “volumes”;

xi) Line 6, pp. 12 “ and” after “(#4).”;

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