

Interactive comment on “Groundwater mean transit times, mixing and recharge in faulted-hydraulic drop alluvium aquifers using chlorofluorocarbons (CFCs) and tritium isotope (^3H)” by Bin Ma et al.

Anonymous Referee #2

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As indicated by the title, this manuscript presents the results of a groundwater dating and mixing study conducted using two different atmospheric tracers (CFCs and tritium). The two aims of the study were to (i) relate “ages” to local and general hydrogeological conditions and (ii) explore the possibility to use mineralisation as proxy for environmental tracers. I agree with referee #1 concerning the style, which is a huge disservice to the manuscript by its approximate use of technical terms and the general turn of phrase. I disagree however with the novelty (I do not see any) and the “substantial conclusions” (very unsubstantial and too dependent on mean transit time

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calculations that at present look extremely weak). As far as comment 4 of referee #1 is concerned, I think it is simply a matter of opinion and taste to use “transit time” instead of “residence time” (I prefer transit time because my work is related to solute transport problems, and “transit time” conveys this very idea of transport). One can argue over that, but it is really a hair splitting exercise.

Overall, the authors seem to have read sufficiently thoroughly the existing literature on the subject as well as the most recent developments (such as Kirchner’s analysis of the effect of heterogeneity on mean transit time estimation using amplitude damping) and understood the different problems and pitfalls relevant for their study. However, the phrasing is sometimes very awkward and tends to obfuscate what the authors mean (see specific comments below). But above all, I am missing a strong reason for this study to be published at all. As case study, it does not go beyond the classical scheme of sampling a few boreholes, analyse the groundwater samples for one or more tracers, calculate some kind of “age” and correlate it to depth or water chemistry. Doing so however, the authors try to apply different methods (lumped-parameter modelling, binary mixing) without presenting a clear roadmap. Model choice in particular is strangely presented: first, “apparent age” is presented as “based on the hypothesis of piston-flow”. Then that very piston-flow model is used although mixing is supposed to be “most likely” either within the aquifer or at the sampling point. This is completely contradictory and there is no reason not to apply another model to the CFC data (and for that matter, to the ^{14}C data as well. See Custodio et al., 2018). I know it is customary to interpret CFC data assuming piston-flow, but it is nonetheless a priori wrong. Model choice must be substantiated from knowledge of the hydrogeological situation and the sampling scheme (Maloszewski and Zuber, 1982; Leray et al., 2016). Later on in the manuscript however different models are used in the binary mixing plots, and model choice is discussed briefly. Why use the “apparent age” concept at all, then ? This is confusing and reads like the two authors have written separately different parts of the manuscript and then pasted the two parts together. I also have my doubts concerning the calculations of the mean transit times as they are presented. The method

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with which the tritium input has been reconstructed is not documented properly (which stations were used, and how long were the available time series ?) and the estimated modern value (31 TU) seems extremely high compared to Western Europe for instance (about 6 TU). Is that because of the Chinese nuclear tests of the 60s and 70s that are being referred to in the introduction, or the result of some kind of regional effect ? Furthermore, the authors do address the non-uniqueness problems that are bound to arise when calibrating an exponential piston-flow or a dispersion model (2 free parameters each) using a single tritium measurement in aquifers that still retain some of the “bomb tritium” (see Stewart et al., 2010 for details), but in a terribly confusing way and without first explaining the rationale and the approach taken. I suppose figure 8 was meant to show the range of parameters that match the measured tracer concentrations. That’s commendable, but badly explained. In the final step relating mineralisation to transit time, the authors finally select the EPM calibrated with the CFC12 measurements, but this is once again presented in a unclear fashion.

The discussion is too long, relies too much on untested and untestable hypotheses, and presents so many singular and unfocused results that it is difficult for the reader to grasp a clear picture of their meaning and significance. The paragraph on “apparent age” should be scraped altogether and the different estimates of “age” (i.e. mean transit time of the respective model) and mixing ratios organised in a clear and synthetic manner.

All in all, the manuscript must be seriously reorganised and streamlined. The calculation of mean transit times of the different tracers must be redone, removing entirely the “apparent age” nonsense and explaining clearly the different steps taken by the authors to (I) select a model (II) explore model parameter range and (III) compare the different results obtained from tritium, the CFCs and carbon 14. Interpretation of the obtained “ages” in terms of hydrogeology and its correlation to hydrochemistry must then be presented in a clear and synthetic fashion. Only when this is done might the manuscript rise above an unoriginal and confusing rehash of previous studies, and

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could be considered for publication.

References: Custodio, E., Jodar, J., Herrera, C., Custodio-Ayala, J., Medina, A., Changes in groundwater reserves and radiocarbon and chloride content due to a wet period intercalated in an arid climate sequence in a large unconfined aquifer, *Journal of Hydrology* 556, 2018, 427-437

Leray, S., Engdahl, N.B., Massoudieh, A., Bresciani, E., McCallum, J., Residence time distributions for hydrologic systems: Mechanistic foundations and steady-state analytical solutions, *Journal of Hydrology* 543, 2016, 67-87

Maloszewski, P., Zuber, A., Determining the turnover time of groundwater systems with the aid of environmental tracers: 1. Models and their applicability, *Journal of Hydrology* 57, 1982, 207-231

Stewart, M.K., Morgenstern, U., McDonnell, J.J., Truncation of stream residence time: how the use of stable isotopes has skewed our concept of streamwater age and origin, *Hydrological Processes* 24, 2010, 1646-1659

Specific comments: Please ask the help of a proof reader to help improve readability

L11: Why is it crucial ? Please explain or leave that out.

L15: “indicating the rainfall recharge...” You mean that the young water component is higher than in samples with lower tritium activity.

L.29: The title of this section is not very telling, and this is not really what the study is about, is it?

L33: “may be renewable”. What do you mean ? Something about short turnover time ?

L37-39: Rewrite the entire sentence.

L38: “and may be inferred”. You mean “must be inferred”.

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- L39: “at” steady-state, not “in” steady-state.
- L40: “Three types of transit time”. You mean three time windows ?
- L46: It’s not variability, rather time span.
- L48: “in a similar function with” should read “in a similar way to”
- L51: replace “over” with “than”.
- L54: You mean that increasing transit time through the aquifer leads to increasing mineralisation.
- L55: Please explain why tritium is “the only true age tracer”, namely because it is part of the water molecule.
- L56 (entire paragraph): Why mention the southern hemisphere at all, since the study takes place in the northern hemisphere ? This is useless information.
- L66: “may be used to estimate MTTs” should read “must be used to estimate MTTs”. And explain why (non-unicity problems. . .).
- L69: You are confusing residence time and degradation half-life. The residence time of the CFCs in the atmosphere is no different from that of tritium or any other tracer. The difference lies in their half-lives (degradation for CFCs, decay for tritium), which are very long for the CFCs.
- L78-82: Please rephrase the entire sentence.
- L89: “Mixing [. . .] is particularly true...”. You don’t know that, it’s a probable hypothesis !
- L93-95: “The MTTs that impacted...”. This sentence makes no sense. Rewrite.
- L106: “with totally length” should read “with total length”.
- L107: “was intermittent activity” should read “was intermittently active”.

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- L110: So the different aquifers are all fractured rock aquifers.
- L114: “is macroscopically similar”. What do you mean with “macroscopically” ?
- L120: “is as large” should read “is as deep”.
- L124: How many samples were taken altogether ? And are there any information concerning screening depth and size (fully penetrating wells or not) ? This is important information to guide model choice.
- L126: What was the rationale for separating the samples into three groups ? For instance, why is G13 MG while G26 is DG ? DG seems like the downgradient boundary. Did you use the piper diagrams to separate the samples ?
- L152: “were followed” is used multiple times, but should read “after” or “following”.
- L173: “refers” is not the proper verb. Use “depends” for instance.
- L179: What are low latitude countries ?
- L189: The entire procedure is correctly explained, and also the fact that “apparent age” implies piston-flow transit time distribution, but why use apparent age in the first place ? Piston-flow is one model among many, as the authors explain later in the manuscript. Furthermore, the entire concept of “age” is problematic and should be replaced by mean transit time or mean residence time (for an in-depth discussion, see Suckow, The age of groundwater-Definitions, models and why we do not need this term, Applied Geochemistry 50, 2014, 222-230).
- L194: What do you mean by “closed system” ? Physically bounded ?
- L208: “were given below as transit time distribution function” should read “were selected and are given below”.
- L219: You should also explain here how you planned to choose between these competing models.

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L235: Why present an equation you will not be using for lack of appropriate data ?

L240: This is true for the piston-flow model only ! See Custodio et al. for details.

L250: So the entire paragraph boils down to using literature values for the initial ^{14}C activity. Make it shorter and to the point.

L264: Check the discussion paper by Benettin et al. in review in HESS for the latest developments on the “evaporation slope”.

L274: The entire paragraph is too short and should explain clearly the approach adopted to calculate “ages” from the tracer data (model and model parameter choices !). I strongly advise against using binary mixing diagrams, and encourage the authors to use a multi-tracer modelling approach trying to find a single optimum or optimal parameter regions for the different tracers.

L277: The paragraph on “apparent age” makes no sense for the reasons given above. I disagree with the proposition that “they [apparent ages] provide a good first approximation for groundwater age”. There is no reason to prefer the piston-flow model which is implied by the “apparent age” concept over other models. This argument has been for years a lazy way to skip responsibility in choosing one model based on knowledge of the hydrogeological situation and sampling.

L297: “which confirms”. A performative statement confirms nothing. You are supposing this is the case !

L317: Shortly explain the method used to estimate the tritium input (linear regression ? And how long were the time series used ?). The reference to Han et al. is not very useful as the authors of that paper themselves refer to an IAEA publication without further explanations.

L318: A background of 31 TU is very high compared to Western Europe (about 6 TU). How come ?

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L413: What do you mean by “serious” ?

L414: “tend toward more discrete with their increase”. I do not understand this part of the sentence.

L448: The paragraph on hydrochemistry is not bad, but underdeveloped and badly organised. State again what you’re looking for first. A good correlation between hydrochemistry and “ages” calculated using some of the TTD models might be a way to constrain or guide model choice, but the authors do not really state that explicitly, although that would be interesting and relatively new.

L491: The entire chapter 4.5.1 makes no sense. You must first decide which model is the most appropriate, and then calculate metrics such as mean transit time, young water fraction, etc. . . You cannot both calculate water fractions using a binary mixing strategy (assuming piston-flow) AND later use an EPM. The same remark applies to chapter 4.5.2.

L498: “no post-1988.5”. Please round this off. . .

L509: Why do you treat “apparent age” as some kind of different measure of transit time than MTTs “estimated from the EPM” ? This is doing the analysis the wrong way around. First find a way to select a model, then discuss the obtained “ages” instead of hypothesizing on tons and tons of different “ages” that are meaningless because they were obtained disregarding the actual situation. This leads nowhere.

L541: Before engaging in complicated mixing scenarios, you should first try to find one model and one parameterisation that fits both the CFCs, tritium and carbon 14. Only if that search does not succeed should additional mixing be introduced. Please note that the binary mixture approach proposed by Plummer et al. is only one way of doing so, and a particularly weak one at that because it assumes per default a piston-flow distribution of transit time of each component (other models can be integrated, but it becomes quickly very cumbersome). Another way to include the mixing of different

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reservoirs is to combine models (say two exponential models, each representing one distinct source) following Piotr Maloszewski and coworkers or Mike Stewart and Uwe Morgenstern. Binary plots such as those of figure 11 suffer from the limitation that you have to recalculate the mixing line for each parameterisation of each model, and they cannot really replace a multi-tracer lumped-parameter modelling approach, where the objective function reduces simultaneously the prediction error of all tracers.

L562: Solutions are obtained, explanations are devised.

L572: What are mixing rates ? You mean mixing ratios ?

L575: "The thrust faults were found to play a paramount role on groundwater flow path". These are not conclusions, but hypotheses very weakly suggested by the analysis of the environmental tracers, which is itself very shaky. I hardly call that evidence. Please refrain from drawing conclusions if the data necessary to test hypotheses is not available (as is the case here).

L585: "due to the highly complex groundwater system...". This is no explanation at all ! Indeed, devising a conceptual model that could explain why CFC derived "ages" correlate well with mineralisation while tritium derived "ages" do not could be a useful task (but you should first redo the calculation of the "ages" as suggested above). On the one hand, the correlation between CFC12 and hydrochemistry might be an artifact, given that the area sampled is so large and hydrogeologically diverse. On the other hand, there might be some kind of systematic shift between tritium and CFC ages if differences are due to the unsaturated zone. Maybe a diffusion model using the unsaturated zone thickness might be useful. Still much work to do. . .

Figure 7, 8 and 9: The figures are incredibly cluttered and very difficult to read, especially figure 9 (not to mention the legend).

Figure 10: Why are there so few points on each graph, since you sampled at 29 locations according to table 1 ?

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Figure 11: As I wrote above, binary mixing diagrams rapidly tend to show their limits. After two or three mixing lines for different models are drawn, reading becomes nigh impossible. Importantly, error bars are missing for the CFCs and for tritium. I suspect that with error bars, selecting a model visually will become impossible (the lack of sensitivity is another limitation of binary mixing diagrams,).

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2018-143>, 2018.

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