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Reply on RC1

Dylan J. Irvine et al.

Author comment on "Depth to water table correction for initial carbon-14 activities in groundwater mean residence time estimation" by Dylan J. Irvine et al., Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2021-276-AC1>, 2021

Review by Marina Gillon

Thank you for your comments. We respond beneath each comment below in italics.

General comments

The authors propose a simple method to determine the initial carbon-14 activity of groundwater for ^{14}C -dating of groundwater, using an empirical relationship between the depth and $A^{14}\text{C}$ of CO_2 in the unsaturated zone. This approach is very interesting as the role of the unsaturated zone can be taken into account even when data of the unsaturated zone are not available.

Response: Thank you. We expect that the simple equations provided here will be useful to account for the unsaturated zone, even when data are not available.

I have four main remarks and questions: *(numbers, i.e. (1), below added by manuscript authors)*(1) The relationship between depth and $A^{14}\text{C}$ of CO_2 in the unsaturated zone have been determined from data measured after nuclear tests. Is it reasonable to use this approach for water recharged before nuclear tests?

Response: The approach is intended to test the sensitivity of the ^{14}C input in cases where the unsaturated zone is deep and/or there is no data on unsaturated zone ^{14}C . It should be reasonable to use this approach for water recharged before nuclear tests. This conclusion is based on modelling by Thorstenson et al. (1983), who simulated diffusive ^{14}C transport in the unsaturated zone for a 30 year period from 1951 to 1981, with an atmospheric ^{14}C boundary which varied from 100 pmC ('pre-bomb'), rising to ~ 180 pmC in 1964 before declining to 130 pmC in 1981. Results showed a relatively vertical ^{14}C profile in the unsaturated zone, with only a 'slight bulge' reflecting the changing atmospheric ^{14}C . In reality, as the reviewed data shows, unsaturated zone processes are likely to impact unsaturated zone ^{14}C independent of the atmospheric boundary, so the findings of this modelling are difficult to test. Hence the approach could be tested for water recharged before nuclear tests, but care should be taken in interpreting results.

To address this point, we will add the following text in the revised manuscript:

The data presented in Fig. 2 were collected after nuclear tests. Modelling by Thorstenson et al (1983) showed that a variable atmospheric ^{14}C boundary is unlikely to significantly impact ^{14}C profiles in unsaturated zone soil gas. Therefore, Eqns. 2-4 could be used to determine $^{14}\text{C}_i$ for the analyses of water recharged before nuclear tests, however, care should be taken in interpreting results.

(2) The evolution of $A^{14}\text{C}$ of CO_2 in the unsaturated zone is in part linked to gas-water-rock interactions (and organic matter for some sites). These interactions modify both $A^{14}\text{C}$ and $\delta^{13}\text{C}$ of CO_2 . Several correction models in carbonated aquifers use the $\delta^{13}\text{C}$ of soil CO_2 . Isn't there a risk of over-correction of the effect of water-carbonate interactions if the $A^{14}\text{C}_i$ is already modified in the unsaturated zone and not the $\delta^{13}\text{C}$? Use the $\delta^{13}\text{C}$ of CO_2 for the groundwater level depth (as for $A^{14}\text{C}$) would probably avoid this problem, which means that a relation between depth and $\delta^{13}\text{C}$ of CO_2 would also be necessary.

Response: The approach that we discuss here is independent of the subsequent corrections for addition of ^{14}C -free C from the aquifers that is typically due to closed-system calcite dissolution. In many cases, the use of ^{13}C to calculate the extent of dilution with ^{14}C -free carbon is problematic (due to: the calcite ^{13}C being poorly constrained; uncertainties in the ^{13}C of recharge; and other processes such as open-system calcite dissolution, methanogenesis, and/or input of geogenic CO_2). In some cases, those processes lead to over-corrected ^{14}C residence times. We will make this clearer in the text.

We also note that many measured $d^{13}\text{C}$ profiles show an almost vertical profile with depth (e.g. Walvoord et al., 2005; doi:10.1029/2004WR003599, Fig. 4; Wood et al. 2017, doi:10.1002/2015WR018424, Fig. 5) and we will also discuss this in the text.

(3) The depth of groundwater level used in the calculations is important due to the depth of water level in the borehole where water is collected is not necessarily the same as groundwater level in recharge area (especially for confined aquifers) and varies in time. Authors talk rapidly of this problem, in the last part of paper. Perhaps, authors should talk about it earlier in the text, and justify their choice of groundwater level for their sites (at the sampling borehole and not in recharge area). They should also discuss about uncertainties associated to the choice of groundwater level (recharge area or sampling location; time variation), does these uncertainties be problematic or negligible?

Response: We agree that this is an important point that was also raised by the anonymous referee. We will address this comment by extending the discussion on this point earlier in the manuscript, and in the discussion. The two sections of text would read as:

Text to add to Section 2.2 - Saturated zone data collection:

It is likely that the DTW in the recharge zone is more relevant. One approach could have been to determine DTW from spatially mapped water levels (e.g. Wood et al., 2017). Nonetheless, the simple approach to estimate DTW from the sampled wells allows for a demonstration of the methods outlined here.

Text to add to Section 4 - Discussion:

The example applications presented here used the DTW at the sampling well was used to estimate the $^{14}\text{C}_i$ values. These DTW values are likely greater than the DTW at the recharge zone, at the time of recharge, leading to minor over-corrections of $^{14}\text{C}_i$ values from Eqns. 2-4. For example, for Well ID 7022-128 (Sample ID = 16, $\text{Clgw} = 13.35 \text{ pmC}$, $\text{DTW} = 27.47 \text{ m}$, see Table S3) the MRT using Eq. 2 was 13,180 y. If the DTW was assumed to be 5 m shallower (22.47 m), the MRT increased to 13,880 y (700 y, or ~5%).

Given that Eqs. 2-4 are straightforward to implement, the impact of uncertainty on the DTW could be easily investigated.

(4) The geology of sites where the $A^{14}C$ of CO_2 have been measured is not indicated in the paper. It is important to indicate and discuss it because the gap between min and max relationship between depth and $A^{14}C$ of CO_2 in the unsaturated zone can be a consequence of differences in geologic properties of aquifers (porous aquifer, fractured aquifer, presence or not of carbonate minerals...).

Response: An additional column "Geological description of site" will be added to Table 1 to provide descriptions of geology from unsaturated zone ^{14}C sites.

Specific comments

L96-103 see general comment N°3

Response: As per comment (3) above, we will provide additional discussion to justify the reason why this decision was made and its potential implications.

L105-109 More details about the method or a reference where details are given, would be interesting.

Response: Additional explanation that the fitting approach will be added. The approach used determined two unknowns a and b in the equation $Cluz = a \exp(bz)$. The updated explanation will read as:

The unsaturated zone sample depth- $^{14}C_{uz}$ relationship was produced by fitting the $^{14}C_{uz}$ and sample depth data (Table S1) using the `curve_fit` function in the `scipy.optimize` library and the `nominal_values` function from the `uncertainties.unumpy` libraries in Python. The curve fitting approach was used to determine the coefficients a and b in the equation $Cluz = a \exp(bz)$. This approach also was used to find the best fit to the data, as well as to produce upper and lower bounds on the best fit relationship based on the standard deviation of the observed data.

L124-125 I don't understand the link between small size of sample and the fact to not take into account the sampling year. Year-to-year variability can exist regardless of the sample size.

Response: We agree that the sentence appears unclear. The goal of the paragraph was to highlight that accounting for the complex input function to groundwater (related to, but not the same as in the atmosphere) is challenging. An option could have been to produce multiple lines of best fit for time periods, for example (i.e. each line would be informed by less data).

We will rephrase the sentence to focus on the challenge of incorporating the complex input function. Text will read as:

Owing to the abovementioned complexities, the sample date was not taken into account in the fitting process.

L216-225 you should also compare the results of min or max relationship with the calculation using the $A^{14}C_i$ equal to 100pMC and discuss it.

Response: To ensure that figures were legible, the approach taken in the original submission was to (1) show corrected (mean, i.e. Eq. 2 to determine $^{14}C_i$) vs. uncorrected mean residence times (Figure 3), and then to show the min (Eq. 4), mean

(Eq. 2) and max (Eq. 2) results. Our preference is to retain the plots as presented.

L235-236 More information could be provided on the construction of the envelopes on the figure 5, especially what do you mean by « variety of flow geometry » ?

Response: The envelopes in Fig. 5 were constructed following Cartwright (2017; doi: 10.1016/j.jhydrol.2017.10.053) using a range of lumped parameter models that relate the ^{14}C and ^3H activities of groundwater with different mean residence times to the input function of these tracers. The input functions are those appropriate to southeast Australia and the exponential piston flow and dispersion models were used to create the envelopes. We will provide these details in the revised manuscript.

L239-242 (and fig 5): Is it possible to differentiate the samples lying to the right due to a mixing between young and old water and the samples lying to the right due to an $A^{14}\text{C}_i$ different from 100pMC?

Response: That would be the case if a uniform A_0 of 100 pMC were used. However, the curves on Fig. 5 were constructed using an input function based on the variation of ^{14}C in the atmosphere (McCormac et al, 2004m, doi: <https://doi.org/10.1017/S0033822200033014>). Samples lying to the RHS of the curves have probably undergone mixing. Samples to the LHS would be over-corrected (i.e. their $A^{14}\text{C}$ is too high: e.g. Cartwright et al., 2013, doi: 10.1016/j.apgeochem.2012.10.023). We will add the detail of the input functions to the revised text that should make this point clear.

L265-266 see general comments N°3

Response: The point of the sentence identified was to highlight that the excluded data from the Yucca site was generally very deep. The water levels in the wells used in our manuscript was generally very shallow (and the water levels in the recharge zone would be shallower still). We will clarify this point in the revised manuscript. Text will read as:

The exclusion of the (generally deep) Yucca Mountain data in the generation of the DTW-correction relationships had only a minor influence on the interpretations of MRTs in the Limestone Coast and Ovens/ Goulburn-Broken catchments (Figs. 3, 4), owing to the depths to the water table at the time of sampling. This observation would hold even in the case where DTW values from the recharge zone, rather than sampling wells were used.

Caption of figure 6 : You talk about A_0 whereas you use A_i in the text. Does A_0 correspond to qA_i ? Why do you not use A_i in the figure 6 in order to show only the role of the unsaturated zone ? Have the depths indicated on the second x-axis been calculated for $q = 1$? it should be specified.

Response: Yes, A_0 referred to $^{14}\text{C}_{iq}$ (i.e. qA_i using your notation). This will be corrected in the caption in the revised manuscript. The caption will also be updated to identify that $q = 1$ in these calculations. Caption will read as:

Figure 6: Maximum difference in calculated MRT (y) where $^{14}\text{C}_{iq}$ on the x-axis is used, relative to the case where it is assumed to be 100 pMC. Secondary x-axis shows indicative water depths that correspond to $^{14}\text{C}_{iq}$ values shown on the lower x-axis according to Eq. 2. Result assumes $q = 1$.

We thank Dr. Gillon again for her comments.