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Comment on hess-2021-276

Marina GILLON (Referee)

Referee 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-RC1, 2021

Review of paper: Depth to water table correction for initial carbon-14 activities in groundwater mean residence time estimation by Irvine et al.

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} 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. I have four main remarks and questions:

- The relationship between depth and A¹⁴C of CO₂ 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?
- The evolution of $A^{14}C$ 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 $A^{14}C$ and $\delta^{13}C$ of CO_2 . Several correction models in carbonated aquifers use the $\delta^{13}C$ of soil CO_2 . Isn't there a risk of over-correction of the effect of water-carbonate interactions if the $A^{14}C_i$ is already modified in the unsaturated zone and no the $\delta^{13}C$? Use the $\delta^{13}C$ of CO_2 for the groundwater level depth (as for $A^{14}C$) would probably avoid this problem, which means that a relation between depth and $\delta^{13}C$ of CO_2 would also necessary.
- 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 necessary the same of 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 no 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?

■ The geology of sites where the A¹⁴C of CO₂ 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 A¹⁴C of CO₂ 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...).

Specific comments

L96-103 see general comment N°3

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

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.

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.

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 » ?

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 $A^{14}C_i$ different from 100pMC?

L265-266 see general comments N°3

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.