



## Comment on hess-2021-246

Anonymous Referee #2

---

Referee comment on "Saline groundwater evolution in Luanhe River Delta, China since Holocene: hydrochemical, isotopic and sedimentary evidence" by Xianzhang Dang et al., Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2021-246-RC2>, 2021

---

### General Comments

This is potentially an interesting and valuable dataset; however, the paper as written does not do it justice. Most of the sections of the paper are too long and lack focus. The Introduction and Study Area sections are generally clearly written but it is not always clear how the information here relates to the groundwater chemistry (which is the main topic). They should be shorter and better focussed on the specifics of the work carried out.

Unfortunately, the Results and Discussion sections which are critical to the study are very hard to follow. Material is repeated, the writing is difficult to understand in places, and it is not clear what is important. The interpretation of the data (in particular the 14C) is superficial and uncritical. These sections really need rewriting.

The Conclusions and Abstract also need to convey something of the general importance of this study and how it relates to work occurring elsewhere. Case studies are publishable in international journals such as HESS. However, unless they have relevance to researchers working elsewhere, they may be better in a regional journal.

### Specific Comments

#### Abstract

The abstract is not clearly written and not that informative. For example, "The results of hydro-geochemical modeling (PHREEQC) suggest that the salty sources of salinization are seawater and concentrated saline water (formed after evaporation of seawater)" is not clear.

There is also a lot of repetition: Page 2 lines 10-20 give the same information three times and some of the same information also appears on Page 3 lines 1 to 6.

Try to put a bit more detail into the abstract (report the important results and highlight the important general points) rather than just the repeated brief summaries. Abstracts are important as they are what the reader uses to see if the paper might be worth reading, so they need to convey enough detail and a sense of importance.

## Introduction

The introduction covers a lot of topics, but it is not clear how the paper will address these topics. It has a general literature review feel to it rather than setting up the study. The final sentence seems to be indicating how prior research on sediment cores helps, which is not what the paper is about. Try to focus on aspects that relate more directly to the study and add an objectives section at the end so the reader has an idea of what you are trying to achieve.

## Study area

This is comprehensive, but like much of the paper it is long. What details are important here and focus on those. Some of the geological history is a bit superfluous.

## Results

The sections on major ion geochemistry (4.1) and stable isotopes (4.2) present the data but could be more succinct. There is a tendency to repeat information (especially in the major ion section).

More importantly, there are some data that you interpret in Section 5 that would have been better presented here, for example you introduce Fig. 6 in section 5. If you are going to split the discussion from the results, make sure that you are not describing data in the discussion section.

## Radiocarbon (Section 4.3)

This section deals with the data in a superficial way. Conventional radiocarbon ages assume simple one-dimensional, non-dispersive flow (piston flow) such that all the groundwater collected at the well was recharged at the same time. This is obviously an oversimplification as groundwater flows along paths of varying lengths and undergoes hydrodynamic dispersion and diffusion. Thus, groundwater has a range of residence times and, while a mean residence time may be defined, this does not equate to a specific age (Maloszewski and Zuber, 1982; Cook and Bohlke, 2000; Suckow, 2014).

The use of a uniform input value for  $^{14}\text{C}$  of 100 pMC rather than accounting for the long-term variation in atmospheric  $\delta^{14}\text{C}$  also yields "ages" in radiocarbon years (not ages BP as is in Table 2).

The combination of a variable atmospheric  $\text{A}^{14}\text{C}$  and more realistic flow models makes a non-trivial difference to calculated residence times of up to several thousand years in some cases (i.e. it is not just a matter of terminology: e.g., Cartwright et al., 2020).

Additionally, many regional aquifers show macroscopic mixing between younger and older groundwater such that there are large volumes of groundwater that contain tritium but which also have "old"  $^{14}\text{C}$  (Jasechko, 2016; Jasechko et al., 2016). While you may not have the data to assess some of these issues, you should at least acknowledge them and recognise the limitations.

The correction for addition of  $^{14}\text{C}$ -free carbon from the aquifer matrix is not always correct. A simple way to check on the reasonableness of this calculation is to estimate what the initial  $\text{A}^{14}\text{C}$  of the Modern waters are. Those waters were recharged over the last few decades (post nuclear tests) so there has been negligible decay of  $^{14}\text{C}$  and the initial  $\text{A}^{14}\text{C} = \text{measured } ^{14}\text{C} / q$ . The estimated initial  $\text{A}^{14}\text{C}$  values for the data in table 2 are:

G01 = 125 pMC, G06 = 169 pMC, G07 = 104 pMC, G08 = 150 pMC, G09 = 139 pMC

The  $^{14}\text{C}$  activities in the atmosphere were as high as this following the nuclear tests but soil zone  $\text{CO}_2$  (from where groundwater derives its DIC) are generally below 120 pMC (Jenkinson et al., 1992; Tipping et al., 2010) and I am not aware of modern groundwater with  $^{14}\text{C}$  activities any higher than that. Anomalously high estimates of initial  $\text{A}^{14}\text{C}$  (above 120 pMC) indicate that the correction cannot be correct. That is not necessarily surprising as the  $^{13}\text{C}$  of the end-members are not always well known and can be locally variable, and there are other unaccounted for processes (such as methanogenesis, open-system calcite dissolution, recharge from river systems) that may be locally important. However, this needs to be recognised rather than just presenting the results uncritically.

The distribution of  $^{14}\text{C}$  activities with depth implies that the general interpretation here is correct; however, the details of the interpretation are oversimplified; at the very least some error propagation is needed.

## Discussion

This is not very well written and it loses focus. I generally agree with the results but the explanations tend to be overly long and very confused.

### Section 5.1

The relative residence times here are fine; however, this section needs to deemphasise the discussion of absolute ages (see above).

Some of the terminology is poor (“has a slightly higher stable isotope content than deeper groundwater, which is typical of the recharge source as the atmosphere has changed since the last deglaciation”) – I can guess what this means but it is verging on being unintelligible.

Some of the material here is repeated later – for example you discuss mixing at the bottom of page 20, but that is repeated in Section 5.3

### Section 5.2.

I am not sure what the Scholler plot adds. It is a common observation that saline groundwater has a similar geochemistry to ocean water (not because it is always necessarily derived from ocean water as mineral precipitation and ion exchange can modify its geochemistry during evaporation). You have reported the salinities and water types, which is enough.

Here again, the explanation of the results is not always clear (e.g., “the salinity of salinization groundwater mainly originates from seawater or, the CSW which is subject to evaporated seawater” and “Due to reach saturation, there were loss of ions follow mineral precipitation such as...” and “Calcite and gypsum will be dissolved along with surface water during lateral recharge, resulting in brackish groundwater samples plotted above the mixing line, highlighting surface water flushing processes in the study region”). Having to guess the meaning of these sentences detracts from the study.

It is not always clear what the important points are here, so while you are probably interpreting the processes correctly, why are they important? Somewhere in this section, you need to explain how this information relates to your overall objectives and why these pieces of information are important.

### Section 5.3.

The general model of mixing (Fig. 9) is also probably correct and it is clearer from the

objectives why you are doing this. However, again this section could be shorter; the general introduction on the first few lines is probably not needed and the explanations on Pg 25 are repetitious. As with the rest of the discussion section, there are no attempts to justify the results (the end-members for example are just assigned without comment).

## Section 6

This is far better written than most of the paper. It is still long and some of the narrative could be shorter. This material is not generally well linked to the geochemistry and it is not always clear how much it is a synthesis of previous studies rather than a discussion of this study.

## Conclusions

Most of these repeat details from the main part of the study. It would be better with a much briefer summary of these and some consideration of how what you have done here has improved understanding of processes in these environments more generally. Also, how do your results fit into the broader research going on elsewhere. Explaining that will give the paper more impact.

The last paragraph does not relate well to the study as there is no discussion of groundwater levels, monitoring, or policy. While those things may be important, it is not clear how your research informs them. Perhaps that could be the focus of this section?

Cartwright, I., Currell, M., Cendon, D., Meredith, K., 2020. A review of the use of radiocarbon to estimate groundwater residence times in semi-arid and arid areas. *J. Hydrol.*, 580, 124247. <https://doi.org/10.1016/j.jhydrol.2019.124247>

Cook, P.G., Bohlke, J.K., 2000. Determining timescales for groundwater flow and solute transport. In: Cook, P.G., Herczeg, A.L. (Eds.), *Environmental Tracers in Subsurface Hydrology*. Kluwer, Boston, pp. 1–30.

Jasechko, S., 2016. Partitioning young and old groundwater with geochemical tracers. *Chem. Geol.* 427, 35–42. <https://doi.org/10.1016/j.chemgeo.2016.02.012>.

Jasechko, S., Perrone, D., Befus, K.M., Bayani Cardenas, M., Ferguson, G., Gleeson, T., Luijendijk, E., McDonnell, Jeffrey J., Taylor, R.G., Wada, Y., Kirchner, J.W., 2017. Global aquifers dominated by fossil groundwaters but wells vulnerable to modern contamination. *Nat. Geosci.* 10, 425. <https://doi.org/10.1038/ngeo2943>.

Jenkinson, D.S., Harkness, D.D., Vance, E.D., Adams, D.E., Harrison, A.F., 1992. Calculating net primary production and annual input of organic matter to soil from the amount and radiocarbon content of soil organic matter. *Soil Biol. Biochem.* 24, 295–308.

Jurgens, B.C., Bohlke, J.K., Maloszewski, P., Zuber, A., 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers: 1. Models and their applicability. *J. Hydrol.* 57, 207–231. [https://doi.org/10.1016/0022-1694\(82\)90147-0](https://doi.org/10.1016/0022-1694(82)90147-0).

Suckow, A., 2014. The age of groundwater – definitions, models and why we do not need this term. *Appl. Geochem.* 50, 222–230. <https://doi.org/10.1016/j.apgeochem.2014.04.016>.

Tipping, E., Chamberlain, P.M., Bryant, C.L., Buckingham, S., 2010. Soil organic matter turnover in British deciduous woodlands, quantified with radiocarbon. *Geoderma* 155,

