

Interactive comment on “Application of pore water stable isotope method to characterise a wetland system” by Katarina David et al.

Anonymous Referee #2

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General comments:

The manuscript "Application of pore water stable isotope method to characterize a wetland system" by Katarina David et al. aims at characterizing an intact, vegetated wetland system located in the Australian highland and potentially endangered by anthropogenic activity, namely mining. For this purpose, the authors used hydrogeological and isotopic data and combined the latter with a model originally developed for arid zones. While the employed model yielded high evaporation rates based on water stable isotopes, no quantitative statements were made on transpiration or groundwater flow. Based on their findings, the authors developed a conceptual model that emphasizes the importance of lateral groundwater inflow for the persistence of such wetland systems.

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While I personally support the motivation of this study and also the propagation of isotope methods I regret to say that I have several issues regarding this manuscript:

Title: The title does not fully reflect the work described here. Not only isotope data have been collected and used and the manuscript's main conclusion is based on other data.

Main outcome: The most important, yet qualitative finding of this study is groundwater flow through the wetland system. The presence of high groundwater levels despite high evaporation rate estimates led to the indirect conclusion that lateral groundwater inflow must be effective. This could already be expected, given just the combination of slope (5%), groundwater levels (high) and permeability of bedrock (sandstone → high). The vulnerability of such systems following e.g. mining activity is based on potential changes of groundwater flow. The main effort of this study, however, was the estimation of evaporation rates which will most likely not be altered by e.g. mining activity. Furthermore, the application of the direct vapor equilibration method was never methodically restricted to non-wetlands and therefore does not constitute a challenge itself that needs to be emphasized.

Model selection: The selected model was developed and applied in desert regions with only vertical water flow, no vegetation, and no lateral groundwater contribution to the zone under investigation. I therefore doubt that invariance of isotopologue diffusivities is an exhaustive criterion for model selection. Furthermore, the assumption of steady-state conditions in a region with pronounced wet and dry season seems to be very far-fetched. The authors should either provide more details why the selected model is still applicable in a vegetated wetland environment with vertical and lateral water flow components or they should use a different approach that better considers subsurface water flow velocities and directions under both dry and wet conditions.

Data collection: The description of the calibration and validation routine of water stable isotope data is quite confusing. Why did the authors not use the linear regression be-

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tween known values of liquid standards and raw readings of the respective headspace vapors to calibrate the unknown sample values? What did they correct the readings for? Or did they mean “calibrate” when they wrote “correct”? Why did they (have to) calculate individual fractionation factors? This would not have been necessary if all standards and samples had been stored sufficiently long and analyzed subsequently in a temperature-controlled environment following the principle of identical treatment. Also, reported uncertainties as measures of data quality are meaningless if they are not based on the authors’ applied standard operation procedures.

Specific comments and Technical corrections:

P2 L7-8: “aiming at” instead of “enabling”. The ability to quantify components of the water balance depends on environmental conditions, not on the method of data collection.

P2 L8-10: insert “potentially” before “enables”. Otherwise this statement is too strong. The technique itself only enables collection of isotope data. Understanding of processes is a different thing.

P2 L11 & elsewhere: the numbers following the delta symbol have to be in superscript

P2 L12: is the porewater compression technique the most widely applied and accepted benchmark?

P2 L19-21: the finding of sand underlying the swamp can’t really be credited to this study as it had been described before in studies cited by the authors.

P3 L9: multi, not muliti; sedimentary, not sedimentatry

P3 L11 and throughout MS: the references cited in the MS do not match the ones listed in the references section. I was therefore often unable to find the referenced statements in the cited literature

P3 L12, 16 & 19: why do the authors distinguish between Australian and international

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literature? Is one more relevant or trustworthy than the other?

P3 L17: insert “other” before “environmental tracers”

P3 L18: please specify the processes you are referring to

P3 L26: all THPSS terms should start with capital letters. Or none.

P3 L31 & elsewhere: citation style: put years in braces

P4 L3: “swamp behavior” is too sloppy, please specify

P4 L18: given that especially rainfall and surface water can vary on very short timescales with unknown time lags relative to soil water which in turn is subject to dispersion, how can these be considered distinct endmember points?

P5 L5: a verb is missing after “and”

P6 L2-4: if this does not affect the site under investigation, then why mention?

P6 L7: “fed by groundwater discharge” is a contradiction. I suggest to use the expression “fed by lateral groundwater inflow”

P6 L16-19: please provide numbers rather than “below average” or “above average”

P7 L5: can you please provide here already the number of samples as well as the achieved spatial depth resolution of sampling?

P7 L7: why had sampling holes to be restored or why is this important to be mentioned?

P7 L7: excess of what? Why was not all soil material sampled?

P7 L13: please specify what you mean by “nature”

P7 L13: “were described” instead of weredescribed”

P7 L16: why were samples vacuum packed? How and how long were they stored prior to analysis?

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P8 L1: insert “data” before “for precipitation“

P8 L9: 17-24 hours is too short for reaching complete isotopic equilibrium between soil water and headspace vapor. It should be several days, up to one week for clayey samples (Wassenaar et al, 2008). Or do the authors have indication that complete isotopic equilibrium between all relevant fractions of soil water was reached? If so please describe

P8 L10: I suppose this concentration range yields minimum data noise on a LGR instrument? Such a large range of vapor concentrations, however, probably indicates non-isothermal storage prior to and during analysis. Can the authors please comment on pre-analysis storage conditions with respect to the principle of identical treatment of samples and standards?

P8 L13: what kind of plastic tube? Was it diffusion-tight material? Else, the authors might have sampled a mixture of sample headspace and an unknown fraction of ambient vapor.

P8 L15: 20 minutes appear way too short. See also comment to P8 L9

P8 L15 & elsewhere: the expression “ $\delta^{18}\text{O}/\delta^2\text{H}$ ” is conceptually wrong and misleading given that this could be interpreted mathematically as a ratio of two isotope ratios

P8 L18: what was the volume of the standards? Did you prepare replicates or were the standards’ headspaces analyzed repeatedly?

P8 L20-21: does this refer to liquid analyses or the direct vapor equilibration method?

P8 L21-22: how do these timespans compare to sampling time of the individual sample headspaces? If this is the precision reported by the manufacturer I would prefer to read about the precision the authors achieved when following their standard operation procedure (also in P9 L2)

P8 L26: LGR’s technology is called e.g. OA-ICOS, but not IRMS

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P8 L30: please provide a reference for the LOI method

P9 L5: this contradicts MS title which prominently mentions isotope data

P10 L4: what is “sub-angular” quartz?

P10 L5: please describe how grain size distributions were determined. If this information was taken from other publications it should appear in section 2 rather than the result section.

P10 L9: “dark” is not a color

P10 L10: can the authors please comment on the “organic smell”. Volatile organic compounds likely have a strong effect on laser-based isotope analysis that needs to be considered for such samples.

P11 L5: “can be explained” seems to be not only descriptive and should appear in the discussion rather than the result section

P12 L1: please insert some specification after “of”

P12 L3 & 8: the intercepts in the linear equations should have a the “unit” ‰

P12 L9: it appears to me that the slope is slightly higher but the intercept is similar

P13 L9: “likely to be”: see comment on P11 L5

P14 L3 & throughout MS + supplement: stable isotope data should be consistently reported with two decimal places for $\delta^{18}\text{O}$ data and one for $\delta^2\text{H}$ data

P14 L5 “it seems unlikely”: see comment on P11 L5

P14 L10: this seems to be a misinterpretation potentially affecting overall results. This regression line is not to be mixed up with evaporation lines (See Benettin et al, 2018, for details). Further, it should not be interpreted in the results section

P14 L14: Since the authors present a LMWL, I would suggest to report lc-excess

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values (Landwehr & Coplen, 2006) rather than D-excess values

P14 L15-20: this paragraph appears twice

P14 L23: “we would expect”: see comment on P11 L5

P14 L25: “seems to suggest”: see comment on P11 L5

P14 L29: “may be”: see comment on P11 L5

P15 L8: “assumed to be”: see comment on P11 L5

P16 L1 & 7: insert “values” or equivalent before “of pore”

P16 L8-9: “due to”: see comment on P11 L5

P16 L11: is the number in braces a $\Delta\delta$ -value?

P16 L11: “is a reflection”: see comment on P11 L5

P16 L13: isn't this just a water balance rather than a water and mass balance?

P16 L19: “very” = “vary”?

P16 L26-27: the description how data were collected should be provided in the method section

P17 L8 & 9: “is related to”: see comment on P11 L5

P18 L12: “groundwater recharge” is misleading as it describes the replenishment of groundwater. I suggest to use “lateral groundwater inflow” instead.

P18 L11-18: the information on e.g. slope, vegetation, age dating should be provided in the section describing the study site (section 2)

P18 L22: why not report salinity data? Do they support the surprisingly high evaporation estimates?

P18 L26: insert “values” or equivalent before “of pore”

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P18 L27: discharge: see comment on P6 L7

P18 L30: I would expect that upward flow supporting high evaporation rates would result in an increase of EC in surface water.

P20 L15-16: evaporation always occurs at the liquid-vapor interface (the “surface”). How can evaporation (“to at least 60cm”) occur below the water table (28-38cm)?

P20 L19: “measured”? This number was rather calculated than measured

P20 L25: this figure should be presented and described in the results section

P21 L5: “percolating” instead of “recharging”

P21 L6: “clearly defined endmembers”: see comment on P4 L18

P22 L1: difference in what?

P22 L9: “of precipitation” after “signature”

P22 L27-28: this conclusion has been drawn before (e.g. Wassenaar et al, 2008) and can't be credited to the present study

P22 L29-32: this statement is not conclusive and rather belongs to the introduction

Supplement: how come that foil weights differ by more than factor 4? Did the authors not use standardized sample bags (e.g. Ziploc) with comparable weights? If not this would be a violation of the principle of identical treatment.

References:

Benettin, P., T.H.M. Volkmann, J. Von Freyberg, J. Frentress, D. Penna, T. E. Dawson, and J.W. Kirchner (2018): Effects of climatic seasonality on the isotopic composition of evaporating soil waters. *Hydrol. Earth Syst. Sci.*, 22, 2881–2890

Landwehr, J.M. and T.B. Coplen (2006): Line-conditioned excess: a new method for characterizing stable hydrogen and oxygen isotope ratios in hydrologic systems. In:

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Isotopes in Environmental Studies, Aquatic Forum 2004: International Atomic Energy Agency, Vienna, Austria, IAEA-CSP-26, p. 132-135

Wassenaar, L. I., Hendry, M. J., Chostner, V. L., and Lis, G. P. (2008): High resolution pore water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurements by $\text{H}_2\text{O}(\text{liquid})\text{--H}_2\text{O}(\text{vapor})$ equilibration laser spectroscopy. *Environ. Sci. Technol.*, 42, 9262–9267

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