General comments to the Editor and Reviewer

We thank the Editor Matijn Westhoff and both Reviewer for their time to provide critical feedback to our manuscript. We believe that their specific suggestions, which we widely implemented into the revised manuscript, improved the clarity of our study.

To make the assessment of our revision as easy as possible for the Editor, we list below first the main six changes done for the revised manuscript. We also added the responses to the two reviewers below and the minor changes to the responses already published in the HESS discussion forum are highlighted via track changes. Examples from text that was changed in the revised manuscript are in quotation marks and the font is in *italic*. The reviewer's comments are given in Times New Roman font.

The revised manuscript with changes highlighted via track changes is at the end of this document.

We hope that this will allow the editor to assess the revision without another round of peer-review, since the requested changes were minor and all remarks of the reviewers were accounted for.

The main changes done were:

1.) Rephrasing parts of the abstract and introduction to highlight the novelty (see examples below)

We rephrased some parts of the abstract:

"Some studies found based on stable isotope (^{2}H and ^{18}O) data that water infiltrating into soils can bypass older pore water. Though, the mechanisms leading to a separation between water routed to the streams and water held tightly in smaller pores are yet unclear. Here, we address the current limitations of the understanding in subsurface mixing and its consequences for the application of stable isotopes in ecohydrological studies. We present an extensive data set,…"

We changed in the introduction:

"It has been hypothesized by Brooks et al. (2010) that rainwater refilling the dry soil at the end of a dry season would lead to a distinct signal between mobile and tightly bound water. Though, the mechanisms leading to a separation between water routed to the streams and water held tightly in smaller pores are unclear and currently under debate (Sprenger et al., 2016b; Berry et al., 2017; Dubbert et al., 2019)"

And we added the limited sampling numbers in older studies:

"So far, the experimental set up of studies addressing the disconnection between water flow across different pore spaces had limited sampling frequencies and sample numbers (maximum twice per year in Brooks et al., 2010; Goldsmith et al., 2012, and five per year in Hervé-Fernández et al., 2016), which impeded progress in understanding of the mechanisms explaining the disjunct subsurface water pools."

2.) Adding a figure showing the locations of the hydrometric measurements and stable isotope sampling. (Reviewer #1)

3.) Adding info on the suction lysimeter. (Reviewer #1)

4.) Adding discussion on water volumes stored in the tightly bound water pool (Reviewer #2)

5.) Rephrasing sections where we used expressions like “no mixing” or “disconnected” and changed it to “little mixing” and “disjunct”, as we cannot exclude that there is no exchange at all taking place.

6.) To better explanation of Figure 7 (former Figure 6):

“Figure 7 summarizes our field observations and their potential implications. Due to the nature of two disjunct pore spaces, a seasonally varying isotopic composition in the rainfall will not be preserved across the soil profile (as in Sprenger et al. (2016a) and Figure S1), but the fast and slow flow domains contain of waters of different isotopic compositions with higher seasonal variation in the mobile water (Figure 7b) than in the tightly bound water (Figure 7c). The different water retention characteristics (as derived in section 2.4) for the fast and slow flow domain (e.g., Gerke and van Genuchten, 1993) are directly linked to the soil pore diameters (Schjonning, 1992). The different flow pattern and the lack of exchange between the mobile and tightly bound water result in the distinct isotopic compositions across the pore space at the same soil depth (red and blue shaded in Figure 7e).”

Responses to the reviewer comments. Differences to the already published responses in the HESS discussion forum are highlighted via track changes.

Reviewer #1

The manuscript titled “Mechanisms of consistently disconnected soil water pools over (pore) space and time” describes a study that uses the stable isotopes of hydrogen and oxygen in soil water, precipitation, local streams, and groundwater to identify apparently separate soil water pools and assess specific processes that result in bypass flow in soils. This study adds to the increasing amount of evidence that confirms the occurrence of the partitioning of soil water between tightly bound immobile water and mobile water that moves downward to discharge in streams and recharge groundwater, as suggested by the two water worlds hypothesis. In addition, this study puts effort into assessing the mechanisms that result in this partitioning.

Overall, this paper is very well written. It addresses a very relevant scientific question that has implications for determining the proper way to interpret stable isotope data in ecohydrology and for better understanding the local water balance in different areas. The scientific methods and assumptions are valid and sound, and the conclusions, which are supported by the results, add significantly to our understanding of ecohydrology.

Response: We are glad to hear that the reviewer believes that our work contributes to a better understanding of ecohydrological processes.

The only significant modification to the paper that I would suggest is the addition of a figure that shows:

1) The global, regional, and local location of the study area

2) Soil and water sample locations

Response: In the revised manuscript, we ~~will~~ added a figure that shows the location of the Can Vila research catchment in Spain, the study site, where the soil water sampling, piezometer sampling and rainfall sampling were done within the catchment, and the outlet, where stream water isotopes and discharge were measured.

~~*The figure will look similar to the preliminary Figure 1.*~~

Other minor suggested edits include:

1) Abstract – The second sentence is awkward and should be revised. The third sentence appears to describe an observation from the study before the study objectives and other details are defined. This sentence (and one or two additional sentences) should describe observations of other researchers to define the problem that this study addresses.

Response: We ~~will~~ rephrased the second sentence and we actually intended to refer to earlier studies in the third sentence. We ~~will~~ revised this part of the abstract to be clear about that. The revised ~~part will~~ reads as follows:

"However, how much subsurface mixing of water occurs, how much of the water is available for plants or otherwise percolating to streams and the groundwater is not yet understood. Some studies found based on stable isotope (^{2}H and ^{18}O) data that water infiltrating into soils can bypass older pore water. Though, the mechanisms leading to a separation between water routed to the streams and water held tightly in smaller pores are yet unclear. Here, we address the current limitations of the understanding in subsurface mixing and its consequences for the application of stable isotopes in ecohydrological studies."

2) Page 1, line 28 – Change the word "since" to "for."

Response: ~~Will be c~~Changed as suggested.

3) Page 1, line 30 – Change the word "unraveled" to "of interest" or something similar.

Response: ~~Will be c~~Changed as suggested.

4) Page 3, line 2 – Add a citation for a reference that describes suction lysimeters or include more details about them.

Response: We ~~will~~ added and adjusted the following sentences to better describe~~provide a reference for~~ the suction lysimeters.: *"The lysimeters consisted of 15 cm long porous cups (RSK ADAS Ltd., UK) with 2 inserted tubes that allow to create the vacuum in the lysimeter and to sample soil water by injecting air into the lysimeter. We applied a suction of -700 hPa and sampled the water extracted within a few hours."*

5) Page 3, line 3 – Include a citation of the cryogenic extraction procedure.

Response: We ~~will~~ added a reference to (Martín-Gómez et al., 2015), where more details on the extraction can be found from the laboratory that conducted the extraction and isotope analysis.

6) Page 12, line 17 – change wording to "...mechanisms by which…"

Response: ~~Will be c~~Changed as suggested.

Other comments: The figures are quite complex, and it takes time to fully understand them, but they do show a lot of valid information. The authors state that tightly bound water is composed of relatively old water. I am wondering if they could suggest an actual age or range of ages for this tightly bound water (months, years, decades??).

Response: On Page 9, line 5 – 10, we briefly discuss the difficulty to assess how much the mobile and tightly bound water are in exchange with regard to their isotopic composition and we argue that numerical models would be a way to test different hypotheses of inter-pore mixing. We are currently not aware of an isotope enabled soil hydraulic model that could account for both a dual-permeabilty representation and a variable lower boundary condition, that accounts for temporarily pressure heads that reach the soil surface (as observed in the piezometer). However, we know that we are limited in our interpretation of stable isotope data to a few years due to the annual cycle of the rainfall isotope signal. Thus, if the tightly bound water would be older than two years, there would be no way in detecting that with the current data set. We ~~are planning to~~ added on page 9 the following to the discussion to pick up the idea of Reviewer #1 and a potential solution to this question:

"Thus, based on our field data, we can currently not assess the actual age (months or years?) of the tightly bound water, but experimental approaches with deuterated (enriched in 2H) water could help assessing how much of exchange between the mobile and tightly bound water can occur (Evaristo et al., 2019)."

References:

Evaristo, J., Kim, M., Haren, J., Pangle, L. A., Harman, C. J., Troch, P. A., and McDonnell, J. J.: Characterizing the fluxes and age distribution of soil water, plant water, and deep percolation in a model tropical ecosystem, Water Resour. Res., doi:10.1029/2018WR023265, 2019.

Martín-Gómez, P., Barbeta, A., Voltas, J., Peñuelas, J., Dennis, K., Palacio, S., Dawson, T. E., and Ferrio, J. P.: Isotope-ratio infrared spectroscopy: a reliable tool for the investigation of plant-water sources?, New Phytologist, 207, 914–927, doi:10.1111/nph.13376, 2015.

Reviewer #2

Content: The paper examines isotopic differences in water pools across depth and time to quantify the extent of mixing. They find that tightly bound water, defined as water not sampled via suction lysimeters, differed consistently from more tightly bound water.

Contextually, the paper is a comparison of two soil water extraction methodologies, it begs the question of whether the extraction technique equals the label applied here (and by many others!), i.e. if 'mobile' water and 'immobile' water (lysimeter and cryogenically sampled water, respectively) are truly so.

Response: Following Brooks et al. (2010) we refer to the differently sampled waters as "mobile" and "tightly bound" waters (Page 1 Line 15) and did not use the term "immobile" water in the paper. Indeed,

we assume that the water extraction methods (suction lysimeters and cryogenic vacuum extraction) correspond to two actual different degrees of soil water mobility.

The authors transform the isotopic signatures using a mass-balance approach but this is ultimately based on differences between extraction techniques. Others have reported similar observations of the differences between soil water, and attributed it to the same process where small pores retain water. This derives similar conclusions from a larger dataset and expands on dynamics in time. However, it does seem to re-hash, in greater detail, the observations and conclusions drawn by Brooks 2010 and leaves the reader questioning the novelty of the results (indeed, many papers have noted consistent differences between cryogenically-extracted water and soil lysimeters).

Response: We are surprised to read that the novelty is questioned. To our knowledge there are no studies that provide in a similar way an explanation on the differences in the stable isotopic composition of waters in the unsaturated zone. We refer to several studies that show these differences in mobile and bulk waters, but we did not find in any of these studies an explanation laying out the processes that lead to the observations. Brooks et al. (2010) suggested the filling of smaller pores during low soil moisture conditions but they could not underline the hypothesis with sufficient data (3 soil sampling campaigns and NO rainfall data prior to soil sampling). As pointed out by Reviewer #2, our study presents results "in greater detail". We truly believe that this "greater detail" allows us to go further in our observations and conclusions and therefore we think that our contribution do not deserve to be qualified as a "re-hash". We have seen numerous studies referring to "ecohydrological separation" and often limiting the analysis to comparisons of soil water and xylem water in dual isotope plots and then concluding that there is either an ecohydrological separation if they do not plot on top of each other, or there is (partially) no ecohydrological separation if they plot on top of each other. Therefore, we think that the fact that our study "expands on dynamics in time" (as acknowledged by Reviewer #2) is a truly new view on the issue.

Overall, the paper is a nice contribution to our understanding of partitioning of water in the subsurface. They refer to this as ecohydrologic separation but it seems more a function of meteorology and geology, with potential impacts on cycling of water and uptake by plants.

Response: We really only use the term "ecohydrological separation" once in our manuscript (Page 9 Line 30) when we discuss our findings in the context of the study by Brooks et al. (2010). We are glad that Reviewer #2 could follow our discussion that the observed separation stems from the interplay of the hydro-meteorological seasonality and the soil characteristics. This was one of our main messages and deriving this conclusion was only possible due to the long-term rainfall isotope and soil moisture observations.

Moreover, e.g. p9, line 5 (and elsewhere referred to) How many mm of water does this 'tightly bound', 'immobile' portion represent? What portion of the annual water budget at this field site is 'locked' away as suggested? Ultimately, how important is this water that doesn't mix? The various conclusions and potential impacts highlighted in the discussion section very much depend on an implicit assumption that this 'portion' is somehow significant.

Response: As indicated above, following Brooks et al. (2010) we are not using the term “immobile” water, but we highlight that this tightly bound water seems to play a minor role in the groundwater recharge and stream water contributions, as it does not mix well with the mobile water and has a lower hydraulic conductivity compared to the mobile water (compare thin blue and red lines in Figure S2).

According to the water retention curve (as shown with thick lines in Figure S2) the volumetric soil moisture of the more tightly bound water (h < -700 hPa) is 0.29 cm^3/cm^3. If we consider the studied upper 1 meter we would have about 290 mm stored in the soil matrix, which cannot be sampled with suction lysimeters. However, this water is not “locked away”, as it would be partly available for evaporation and transpiration (permanent wilting point is often assumed to be about -15.000 hPa) and percolates according to subsurface pressure differences. 290 mm are about 1/3 of the annual rainfall. Why this water is relevant is discussed on Page 11 Line 31 and following. However, the actual volume does not seem to be most important here, but the strong “non-uniform” character of subsurface flow that can be recognized with our data set is the most relevant point.

We ~~will~~ added to the revised manuscript the 290 mm of water in tightly bound water. ~~However, we will also~~We further rephrased the manuscript in a way to clarify that we cannot claim that the observed water pools do not mix at all, but mixing is very limited given the very distinct stable isotopic compositions between mobile and bulk soil waters.

Example of where we changed: *“The maximum water volume stored in the tightly bound water pool is about 290 mm if we consider the studied upper 100 cm (max ϑTW = 29 %, Figure S2). This represents about 1/3 of the annual average rainfall, but it cannot be considered as being in an inactive storage, since it would be partly available for evaporation and transpiration (permanent wilting point is often assumed to be about -15.000 hPa) and percolates according to subsurface pressure differences (likely at lower conductivities as shown in Figure S2).”*

Grammar: There were a fair number of mistakes in grammar and punctuation. Please revise professionally for verb tense agreement and use of imperfect tense, i.e. ‘we got it or we took it’ are informal and temporally less explicit than the perfect tenses.

Response: We ~~will~~ carefully revised the grammar in our manuscript. So far, we used a lot “We sampled…” or “We took…” as active voice is a more natural style. We will discuss with the Editor if that should be changed.