

## Reply to Referee #4

In the following please find the corrections and comments to the referee's response. For clarity, the comments of the referee were copied in black and our comments are in blue.

The manuscript is presenting an impressive set of stable isotope and deuterium excess data collected over a two year period from a low slope and low elevation catchment in Germany. Focus of the work is on precipitation input, river water, soil water and groundwater interactions and processes. The manuscript is well written and structured. I recommend a publication of the manuscript in HESS after revisions. My comments below are in addition to all the points that were raised by the prior reviewers and I aim for additional improvements of the paper.

We thank referee #4 for the valuable comments. We substantially changed the manuscript according to the reviewer's suggestions. Details are listed hereafter in response to the corresponding comment.

### General comments

Since snowmelt was found to play a fundamental role (Page 1810, Line 10), it would be helpful for the readers to get more details on sampling methods in the monitoring section (e.g., page 1817, line 12). Did you take several / replicate snow samples at the same site? Did you sample integral snow cores over the entire snow depth? Or were snow lysimeters installed? Any information on snow depths, snow density and water contents would be helpful.

We acknowledged the fact that we did not consider details on snow sampling in the Materials and Methods part: *"In winter 2012 to 2013, snow core samples over the entire snow depth of <0.15 m were collected in tightly sealed jars at same sites as open rainfall was sampled. We sampled shortly after snow was fallen because sublimation, recrystallization, partial melting, rainfall on snow, and redistribution by wind can alter the primary isotopic composition of the snowfall (Clark and Fritz, 1997b). Samples were melted overnight following Kendall and Caldwell (1998), and analysed for their isotopic composition."*

Moreover, the following sentence was included in the Discussion: *"However, one should be aware that differences in the snow sampling method (new snow, snow pit layers, meltwater) can affect the isotopic composition (Penna et al., 2014; Taylor et al., 2001)."*

You do not give additional accuracies for soil water that was cryogenically extracted. I am impressed about your results concerning the soil studies and find it would be worth to better focus these. Your error bars in Figure 9 are sometimes larger than +/- 10 ‰ for d2H. Did you test your extraction method? Comments or a short reference would be helpful.

The cryogenic extraction method was thoroughly tested by Orłowski et al. (2013). The error bars represent the natural isotopic variation of the replicates taken during each sampling campaign (summer = 7, winter = 7, spring = 2) under different vegetation cover and thus, do not only represent the uncertainty of the extraction method itself. We therefore added this information to the figure caption of Figure 9 (now Fig. 6), too.

We additionally referred to this reference in the following sentence: *“Soil water was extracted cryogenically with 180 min extraction duration, a vacuum threshold of 0.3 Pa, and an extraction temperature of 90°C following Orłowski et al. (2013).”*

For LGR measurements you give accuracies of 0.6 and 0.2 ‰ for d2H and d18O respectively, but you do not further comment on drift and memory corrections. Do you use such for your isotope measurements? Laser instruments are known to be sensitive to organic content in waters (especially soil water). Are you able to check / correct for this? Or was this not problematic in your case?

We included the following information in the revised manuscript: *“Within each isotope analysis three calibrated stable water isotope standards of different water isotope ratios were included (LGR working standard number 1, 3, and 5; Los Gatos Research Inc., CA, US). After every fifth sample the LGR working standards are measured. For each sample, six sequential 900 µL aliquot of a water sample are injected into the analyser. Then, the first three measurements are discarded. The remaining are averaged and corrected for per mil scale linearity following the IAEA laser spreadsheet template (Newman et al., 2009). Following this IAEA standard procedure allows for drift and memory corrections.”*

We agree with the referee that leaf water extracts typically contain a high fraction of organic contaminations (West et al., 2010), which might lead to spectral interferences when using isotope ratio infrared absorption spectroscopy (Leen et al., 2012), causing erroneous isotope values (Schultz et al., 2011). Therefore, isotopic data of plant water extracts are usually checked for spectral interferences using the Spectral Contamination Identifier (LWIA-SCI) post-processing software (Los Gatos Research Inc.). However, for soil water extracts no evidence for such interferences have been observed so far (Schultz et al., 2011; Zhao et al., 2011). Thus, there exists no need to check/correct such data.

This paragraph is likewise included in the revised manuscript.

Is the isotope data you present weighed by precipitation amounts or do you present individual values for collected events?

We present data of individual precipitation events in the manuscript.

Figure 4 and 5: You state outlier values in March 2012 and 2013 that are most likely due to snowmelt. How do you explain outlier values for Schwingbach site 64 in 9/2012 and for V-site 13 in 5/2012?

We included the following sections in the manuscript: *“The outlier at the Schwingbach stream water sampling site 64 (-66.7‰ for  $\delta^2\text{H}$ ) is by 8.5‰ more depleted than the two-year average of Schwingbach stream water (Table 1). Rainfall falling on on 24 September 2012 was -31.9‰ for  $\delta^2\text{H}$ . This period in September was generally characterized by low flow and little rainfall (antecedent precipitation index: AP8 was 8mm). Thus, little contribution of new water was observed and stream water isotopic signatures were groundwater-dominated.*

*For site 13 the outlier in May 2012 (-44.2‰ for  $\delta^2\text{H}$ ) was by 13.8‰ more enriched than the average stream water isotopic composition of the Vollnkirchener Bach over the two-year observation period (Table 1). A runoff peak at site 13 of 0.152 mm d<sup>-1</sup> and a 2.9mm rainfall event were recorded on 23 May 2012. Moreover, AP8 was 23.2 mm. Thus, this outlier could be explained by precipitation*

*contributing to stream flow causing more enriched isotopic values in stream water, which approached average precipitation  $\delta$ -values ( $-43.9 \pm 23.4$ )."*

#### Specific comments

##### Study area:

Page 1815, line 11: It would be helpful to include latitude, longitude of the study site

We included the latitude and longitude in the first sentence of the study area description: *"The research was carried out in the Schwingbach catchment (50°30'4.23"N, 8°33'2.82"E) (Germany) (Fig. 1a)."*

Page 1817, line 28: (...all samples were filled and stored in 2 mL brown glass...(Mook, 2001).). Mook (2006) recommends 50 mL glass bottles tightly closed to prevent evaporation. Did you really store your "field samples" in 2 mL autosampler bottles closed with septa? Are replicate measurements possible - with such small amounts just out of one bottle?

For the isotope analyses, a 900  $\mu$ L aliquot of a water sample is required. Thus, replicate measurements could be conducted on the 2 mL sample and the collected amount is sufficient concerning this matter. We sampled and stored the water in 2mL amber glass vials sealed with a solid lid and wrapped up with Parafilm®. We made this clearer in the respective paragraph.

##### Results and discussions

Page 1824, line 23: "Furthermore, our and their isotope...". Please rephrase!

We edited the whole paragraph as follows: *"As described above, MTT calculations did not provide meaningful results. The failure of the MTT estimations is mainly attributed to the little variation in stream water isotopic signatures. Just as in the here presented results, Klaus et al. (2015) had difficulties to apply traditional methods of isotope hydrology (MTT estimation, hydrograph separation) to their dataset due to the lack of temporal isotopic variation in stream water of a forested low-mountainous catchment in South Carolina (USA). Furthermore, stable water isotopes can only be utilised for estimations of younger water (<5 years) (McGuire et al., 2005; Stewart et al., 2010), suggesting that transit times in the Schwingbach catchment are longer than the range used for stable water isotopes."*

Page 1825, line 8: I recommend d2H value with one digit after the comma (-57.6).

Correction made as recommended.

##### Figures and Tables:

Table 1. I would recommend placing the mean values and SD of mean values first, and further to include a column for d-excess values.

We edited Table 1 as recommended by the reviewer and included d-excess values for each water cycle component (precipitation, stream, and groundwater)

Figure 1: an overview map for the location in Germany / or Europe would eventually be helpful for non-European readers.

A new version of Figure 1 showing the location of the Schwingbach catchment in Germany as well as a map of the soil sampling sites is included in the revised version of the manuscript.

Figure 3: ( $d = 10$ ; dashed line) is not visible on my printout. Why do you give the 2003 to 2005  $d$ -excess values from Koblenz and not the long-term mean  $d$ -excess values? Was the meteorology during 2003 to 2005 comparable to your study period?

The dashed line ( $d=10$ ) is now a solid black line. We also improved the quality of the figure as well as included monthly  $d$ -excess values of the GNIP station Koblenz for the same period as the measured data of the Schwingbach catchment (2011-2013).

Technical corrections

Page 1813, line 2: "...and re-evaporated thus isotopically fractionated."

Correction made as recommended by referee #4.

Page 1820, line 3-6: This sentence is hard to understand.

We rephrased the sentence as follows: *"For monthly comparisons with Schwingbach  $d$ -excess values, we used a data set from the GNIP station Koblenz that includes 24 values starting from July 2011 to July 2013."*

I recommend to avoid short forms for date and time in the text: e.g., would recommend (July 2011 to July 2013) (Page 1820, line 14), or...(21st June to 21st/22nd September) (Page 1822, line 13 and 15) instead.

We edited this throughout the manuscript.

Page 1822, line 15:  $d$ -excess instead of Dexcesses: " $d$ -excess greater than +10 ‰ was...".

Correction made as recommended.

Figures and Tables:

Table 2. Legend should first mention: mean and SD for isotope signatures and soil physical properties. The alignment of numbers in the table should be restructured.

Correction made as recommended by referee #4.