Reply to Referee #1

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.

This study presents stable water isotopic data for a catchment in Germany. While there is much variability in the precipitation isotopes, there was little in the groundwater and stream water. The manuscript is well written and easy to read, however, lacks rigor and has limited quantifications backing up the main conclusions. This makes it difficult to see novelty and assess what the actually contribution of the work is toward advancing understanding of rainfall-runoff processes in a general sense (i.e., beyond the empirical sense of this specific location). The challenge to the authors, which will require significant revision and additional analysis, is to take their data and develop a procedure/approach overcoming the lack of variability. While I can appreciate that the lack of variability "restricted the use of classical isotope hydrology techniques" (P1810L25), it leads to two clear questions: (1) Why not develop a new method to leverage the data you have or (2) Why not measure other tracers (geochemicals or electrical conductivity come to mind) that better map the flow domain? The authors opt towards choice (1) which I can agree with since it is difficult to add analysis and sampling after the fact. This makes the central question of this research how to turn lemons into lemonade? Personally, I think this is a pretty important central question given the ubiquity with which stable water isotopic data is currently being collected. However, the approach developed is extremely qualitative so it leaves the reader wondering what we have learned here and how to learn the same thing at a different location. The authors do a good job highlighting the need for such knowledge (see around P1812L2-6) but the study leaves something to be desired on how to achieve such knowledge.

Of course, I do not have any great suggestions on what that method/approach could be since that is the core of the research. What I am looking for here is a methodology that can allow for comparisons of this site to others. For example, perhaps the connections to land cover could be leveraged to develop a basic mixing model allowing for characterization of impacts of spatial vegetation pattern heterogeneity on hydrological response in these types of landscapes? Then you could do some cross validation estimates (bootstrap or leave-on-out type) on the error and uncertainties incurred? Development of a modeling extension (in whatever form) is recommended here to help provide a clear hypothesis testing/quantification framework. This would help demonstrate exactly how "conducting a stable water isotope study in Schwingbach catchment helped to identify relationships between precipitation, stream, soil, and groundwater in a developed catchment" (P1832L13). That would constitute a significant contribution and move this study beyond its heavy empirical tilt (which is needed).

We gratefully acknowledge the comments of the reviewer, which helped us to improve the manuscript. In general, we performed additional statistical analyses and set up a new hydrological model for the Vollnkirchener Bach subcatchment to explain mixing processes.

1) As a new data analysis tool, we used a network map (Kolaczyk, 2014) in combination with a principal component analysis to demonstrate the isotopic relationships between surface and groundwater sampling points.

2) We further utilized the isotope data to calculate the mean transit times (MTT) for the Vollnkirchner Bach (sites 13, 18 and 94) and the Schwingbach (sites 11, 19 and 64) using FlowPC. We bias corrected the input data (precipitation) to improve model results and statistically compared these results with the initial non-corrected model results. Different models (dispersion model, exponential model, exponential-piston-flow model, linear model, and linear-piston-flow model) were compared for their results (sigma as goodness of fit) as well as statistical comparisons for site differences were run (bootstrapping for cross-validation). However, the calculated output data did not fit the observed values in terms of the quality criterion sigma and model efficiency, even after bias-correcting the input data. This was mainly due to the small seasonal variations in stream water isotopic signatures. Therefore, we conclude that the application of MTT estimation methods based on stable water isotopes failed in the Schwingbach catchment and developed a new data-driven groundwater model to simulate observed stable water isotope data.
3) To further overcome the criticized qualitative data analyses approach and to verify and validate the hydrological processes, the Catchment Modelling Framework (CMF) by Kraft et al. (2011) was used to setup a hydrological model for the Vollnkirchner Bach subcatchment. Thereby, we were able to estimate spatially distributed groundwater ages. The flexible setup of CMF and the variety of available flow-accounting equations allows customizing the setup making this modeling framework especially suitable to be used in our isotope tracer study (Windhorst et al., 2014). The additional data analyses now allow a better comparison of our study area to other sites.

We refrained from using other tracers, since intense measurement and sampling campaigns have already been conducted in previous studies (Lauer et al., 2013, Orlowski et al., 2014).

Good that the hypotheses are clearly stated. However, there are some ambiguous words in there that reinforce the qualitative nature of the study and it is questionable how testable these really are. For example in hypothesis (1), what do you really mean by strong? Does it mean high in amplitude or quick changes (steep slopes in time)? It would be good to put this in the context of something measureable or quantifiable. For hypothesis (2), there is an inherent assumption of instantaneous mixing throughout the groundwater. Early work from Sarah Dunn [Dunn SM, McDonnell JJ, Vache KB. 2007. Factors influencing the residence time of catchment waters: A virtual experiment approach. Water Resources Research 43: W06408] and more recent work by others (e.g., Markus Hrachowitz [Hrachowitz M, Savenije H, Bogaard TA, Tetzlaff D, Soulsby C. 2013. What can flux tracking teach us about water age distribution patterns and their temporal dynamics? Hydrology and Earth System Sciences 17: 533–564]; Ype van der Velde [Van der Velde Y, Torfs PJJF, van der Zee SEATM, Uijlenhoet R. 2012. Quantifying catchment-scale mixing and its effects on time-varying travel time distributions. Water Resources Research 48: W06536]) have really questioned such complete mixing. So, this might actually be a rather poorly constructed hypothesis. Lastly, hypothesis (3) would require measuring physical distributions of flow pathways in the subsurface at a scale not really achieved here, would it not? Why not focus in on a clear and testable hypothesis to better streamline the presentation of a central key finding? I think this will be achieved when considering the recommendations of the previous paragraph.

We have revised the Introduction completely. The section now reads as follows: *“The application of stable water isotopes as natural tracers in combination with hydrodynamic methods has been proven* *to be a valuable tool for studying the origin, formation, and interrelationship between surface water and groundwater (Blasch and Bryson, 2007; Goni, 2006), partitioning evaporation and transpiration (Phillips and Gregg, 2003; Rothfuss et al., 2010, 2012; Wang and Yakir, 2000), and further mixing processes between various water sources (Aggarwal et al., 2007; Clark and Fritz, 1997c; Kendall and Coplen, 2001; Wu et al., 2012). Particularly in catchment hydrology, stable water isotopes play a major role since they can be utilised for hydrograph separations (Buttle, 2006; Hoeg et al., 2000; Ladouche et al., 2001; Munyaneza et al., 2012), to calculate the mean transit time (McGuire et al., 2002, 2005; Rodgers et al., 2005b), to investigate water flow paths (Barthold et al., 2011; Goller et al., 2005; Rodgers et al., 2005a), or to improve hydrological model simulations (Birkel et al., 2010; Koivusalo et al., 1999; Liebminger et al., 2007; Rodgers et al., 2005b). However, spatio-temporal sources of stream water in low angle, developed catchments are still poorly understood. This is partly caused by damped stream water isotopic signatures excluding traditional hydrograph separations (Klaus et al., 2015). Unlike the distinct watershed components found in steeper headwater counterparts, lowland areas often exhibit a complex groundwater–surface water interaction (Klaus et al., 2015). This interaction between groundwater and surface water remains poorly understood in many catchments throughout the world but process understanding is fundamental to effectively manage the quantity and quality of water resources (Ivkovic, 2009). Sklash and Farvolden (1979) showed very early, that groundwater plays an important role as a generating factor for storm and snowmelt runoff processes. In many catchments, streamflow responds promptly to rainfall inputs but variations in passive tracers such as water isotopes are often strongly damped (Kirchner, 2003). This indicates that storm runoff in these catchments is dominated mostly by "old water" (Buttle, 1994; Neal and Rosier, 1990; Sklash, 1990). However, not all "old water" is the same (Kirchner, 2003). This catchment behaviour was described by Kirchner (2003) as the old water paradox. Thus, there is evidence of complex age dynamics within catchments and that much of the runoff is stored in the catchment for much longer than event water (Rinaldo et al., 2015). Still, some of the physical processes controlling the release of "old water" from catchments are poorly understood, roughly modelled, and the observed data do not suggest a common catchment behaviour (Botter et al., 2010).*

Moreover, due to human-induced alterations of river systems (e.g. channelisation of streambeds or draining) (O'Driscoll et al., 2010), water fluxes in developed (managed) landscapes can be especially diverse. Almost all European river systems were already substantially modified by humans before river ecology research developed (Klapper, 1990; Allan, 2004). Through changes in land use, land cover and irrigation, agriculture has substantially modified the hydrological cycle in terms of both water quality and quantity (Gordon et al., 2010) as well as altered the functioning of aquatic ecosystem processes (Pierce et al., 2012; Rockström et al., 2014). This complex character of developed, agricultural dominated catchments is often disregarded and established research approaches often failed to fully capture agro-ecosystem functioning at multiple scales (Orlowski et al., 2014). Since agricultural land use (arable land, permanent crops, and grassland) is the most dominant land use in Europe (UNEP, 2002), there exists a pressing need to understand biogeochemical fluxes (e.g. nitrogen compounds or pesticides) coupled with water fluxes in these managed landscapes (Orlowski et al., 2014) and to figure out a way to embed this landscape heterogeneity or the consequence of the heterogeneity into models (McDonnell et al., 2007).

One way to better understand the relationship between precipitation, stream, soil, and groundwater, is a detailed knowledge about the isotopic composition of the various water sources (surface, subsurface, and groundwater) and their variation in space and time. In principal, isotopic signatures of precipitation are altered by temperature, amount (or rainout), continental, altitudinal, and seasonal effects. They are mainly influenced by prevailing atmospheric conditions during rainfall and snowfall causing a depletion of isotopes (Araguás-Araguás et al., 2000; Blasch and Bryson, 2007; Clark and Fritz, 1997c; Gat, 1996; Rohde, 1998). The input signal becomes more pronounced in snow-dominated systems where snowfall and snowmelt are depleted in heavy stable water isotopes relative to rainfall (Maule et al., 1994; O'Driscoll et al., 2005). Stream water isotopic signatures can reflect precipitation isotopic composition and moreover, depend on discharge variations affected by seasonally variable contributions of different water sources such as bidirectional water exchange with the groundwater body during baseflow, or high event-water contributions during stormflow (Genereux and Hooper, 1998; Koeniger et al., 2009). Following the way of precipitation over the unsaturated zone to the groundwater, the process of infiltration in itself is known to be a non-fractionating process (Gonfiantini et al., 1998), except for mixing between different water pools (e.g. moving and standing water) (Gat, 1996). However, precipitation falling on vegetated areas is intercepted by plants and re-evaporated thus isotopically fractionated. The remaining throughfall infiltrates slower and can be affected by evaporation resulting in an enrichment of heavy isotopes, particularly in the upper soil layers (Gonfiantini et al., 1998; Kendall and Caldwell, 1998). In the soil, specific isotopic profiles develop, characterized by an evaporative layer near the surface especially under arid and semi-arid climate. This decreases exponentially with depth (Zimmermann et al., 1968), representing a balance between the upward convective flux and the downward diffusion of the evaporative signature (Barnes and Allison, 1988). In humid and semi-humid areas, this exponential decrease is generally interrupted by the precipitation isotopic signal. Hence, the combination of the evaporation effect and the precipitation isotopic signature determine the isotope profile in the soil (Song et al., 2011). Once soil water reaches the saturated zone, this isotope information is finally transferred to the groundwater (Song et al., 2011). Soil water can therefore be seen as a link between precipitation and groundwater, and the dynamics of isotopic composition in soil water are indicative of the processes of precipitation infiltration, evaporation of soil water, and recharge to groundwater (Blasch and Bryson, 2007; Song et al., 2011).

To compare different water sources on the catchment-scale, a local meteoric water (LMWL) line is developed and evaporation water lines (EWLs) are used. They represent the linear relationship between δ^2H *and* $\delta^{18}O$ *of meteoric waters (Ingraham, 1998) in contrast to the global meteoric water line (GMWL), which describes the world-wide average stable isotopic composition in precipitation (Craig, 1961a). Thus, the comparison of stable isotope data for stream, soil, or groundwater samples relative to the global or local meteoric water lines can provide general understandings on water cycle processes at specific research sites (Song et al., 2011).*

Identifying the origin of water vapour sources and moisture recycling (Gat et al., 2001; Lai and Ehleringer, 2011), the deuterium-excess (d-excess), defined by Dansgaard (1964) as $d = \delta^2H - 8 \times \delta^{18}O$ *can be used, since the d-excess mainly depends on the mean relative humidity of the air masses formed above the ocean surface (Zhang et al., 2013). In addition, the d-excess reflects the prevailing conditions during evolution, interaction, or mixing of air masses en route to the precipitation site (Froehlich et al., 2002).*

To capture spatial landscape heterogeneity, but to keep data acquisition simple, stable water isotope data were coupled with hydrodynamic data from a previous study by Orlowski et al. (2014) in the developed Schwingbach catchment (Germany) to unravel water flow paths and interactions between different water cycle components. Results obtained through this earlier study imply that the Schwingbach catchment is highly responsive indicated by fast runoff responses to precipitation inputs (Orlowski et al., 2014). Moreover, groundwater reacted almost as quickly as streamflow to precipitation events with raising head levels. Thus, the catchment showed "old water" paradox like behaviour (Kirchner, 2003). We further showed that streamflow was predominantly generated in the catchment headwater area and that gaining and losing stream reaches occurred in parallel along the studied stream affected by the underlying geology.

Thus, stable water isotopes in combination with hydrodynamic data of a two-year monitoring period (July 2011 to July 2013) were utilised to explore spatio-temporal isotopic variations, unravel linkages between the different water cycle components, investigate the transformations from precipitation to soil and groundwater, and analyse the effect of small-scale landscape characteristics (i.e. soil physical properties, topographic wetness index (TWI), distance to stream, and vegetation cover) on soil water isotopic composition. Further, stable water isotope data was utilized to estimate groundwater ages and flow directions in the Vollnkirchener Bach subcatchment via an hydrological model setup based on the findings of Orlowski et al. (2014)."

Lastly, the results and discussion should be separated. Having them combined contributes to the qualitative feel of the presentation. It makes the results read more like a story than a presentation of substantial findings.

We have separated the results and discussion section.

Further, the findings seem to echo much of what is already seen in the literature. This potentially points to a lack of novelty. With this, I think the study has a bit farther to come before it can be considered ready for publication in HESS. As it reads now, it is more suitable for a regional journal or a journal with a more empirical focus (which I think the authors can move beyond).

We have revised and improved the whole manuscript and e.g. included a hydrological model to estimate groundwater ages and flow directions in the Vollnkirchener Bach subcatchment. Our model provides the opportunity to make use of stable water isotope information along with climate, land use, and soil type data, in combination with a digital elevation map to estimate residence times >5 years. Such long residence times could previously only be determined via other tracers such as Tritium (e.g. Michel (1992)). If stable water isotope information is used alone, it is known to cause a truncation of stream residence time distributions (Stewart et al., 2010).

Thus, we are convinced that the manuscript is now ready for publication in HESS.

Minor/Editorial Comments

The title does not seem grammatically correct. Should be something like: "Exploring water cycle dynamics by sampling a multitude of stable water isotope pools: : :" or "Exploring water cycle dynamics through sampling multiple stable water isotope pools: : :"

The title now reads as follows: "*Exploring water cycle dynamics by sampling multiple stable water isotope pools in a small developed landscape of Germany"*

The last paragraph of the introduction is awkward. Since this is the paragraph that sets the tone for the presentation, it is fairly important. What was the "former" study? Are you referencing previous work that already used these data? Please improve this (see also general comments).

When referring to the "former" study we are talking about the findings of a previous study by Orlowski et al. (2014) conducted in the same catchment. The findings from the previous study were useful and, in fact, necessary to successfully complete the current research. As such, the present analysis complements the one published in the previous paper (Orlowski et al., 2014), but has a distinct different focus. However, the previous study does not make use of isotope data presented in this manuscript.

We have generally revised the Introduction section (see reply above).

Reply to Referee #2

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.

This paper presents an extensive data set from an agricultural catchment in central Germany, where various parts of the water cycle, streams, groundwater, precipitation and soil water are sampled for about 2 years. This data set is used to investigate runoff generation and connectivity between the water cycle components and builds up on a hydrometric paper published in 2014. The paper states that the groundwater system controls streamflow, and no strong influence of precipitation on groundwater and streamflow was observable. The paper is very well written, very informative in background, and the field effort and the data set are great. Nevertheless, there are also several shortcomings in the paper that need attention. I think the analysis needs some more rigor and attempts to a better quantification should be made.

We thank Referee #2 for the comments which were very useful to improve the paper and prepare an improved version of the manuscript. We answer below to each comment in a point-to-point reply.

At first, the paper often claims statistical differences etc., without presenting p-values etc. These p-values need to be reported, this would be absolutely necessary for the reader to be convinced. I understand that lacks of variability in stable isotopes restrict the use of the classical tools, but I do not fully agree about the lack of variability in this work. In my opinion, there is a variability of δ2H in Figure 4. Just plotting a moving average in the stream flow stable isotopes should present some variability. In the lowest panel you clearly see the heaviest stable isotopes values around 7/1 or 8/1, while the values in later winter early Spring are lightest (not sure how important snow in the area would be). Reporting this, e.g. temperature would be good, I don't think this area (with this elevation) has a long term snow cover over the winter. But that said, the variation seem to be 5-6‰ (the figures are not that easily visible). This variation is a factor ten above measurement precision, and comparable (or even higher) than the differences in McGuire et al. (2005, WRR) (their figure 4). They used 1‰ (and clearly less for 18O) for mean transit time estimations in the HJA.

We made substantive changes to the previous version of the manuscript. In general, we improved the quality of the manuscript by including additional statistical analyses and a hydrological model for the Vollnkirchener Bach subcatchment to bring together hydrometric observations and isotopic based process understanding. We further estimated mean transit times (MTT) for the Vollnkirchner Bach (sites 13, 18 and 94) and the Schwingbach (sites 11, 19 and 64) using FlowPC (Version 3.1, Małoszewski and Zuber (1996)). Different models (dispersion model, exponential model, exponential-piston-flow model, linear model, and linear-piston-flow model) were compared for their results (sigma as goodness of fit) as well as statistical comparisons for site differences were run (bootstrapping for cross-validation). However, the calculated output data did not fit the observed values in terms of the quality criterion sigma and model efficiency. This was mainly due to the small seasonal variations in stream water isotopic signatures. We also bias-corrected the precipitation input data with two different approaches: the mean precipitation value was subtracted from every single precipitation value and then divided by the standard deviation of precipitation isotopic signatures. Afterwards, this value was subtracted from the weekly precipitation values (bias1). For the second approach, the difference of the mean stream water isotopic value and the mean precipitation value was calculated and also subtracted from the weekly precipitation values (bias2).

However, even these bias corrections of the input data did not improve the model outputs (see Table 1), further down).

We plotted the moving average through the streamflow as well as through the groundwater isotope data as recommended by the reviewer (now Fig.7 and 8).

Through the application of a new data analysis tool, topology inference network mapping (Kolaczyk, 2014) in combination with a principal component analysis (Jolliffe, 2002), we further showed the δ^{18}O isotope relationships between surface and groundwater sampling points based on significant correlations ($p<0.05$).

Further, the previous paper (Orlowski et al., 2014, Water) presents one events that showed reaction of stable isotopes on incoming precipitation. I am not aware of the number of sampled events, but I think the authors should clearly put more effort on presenting individual events, perform Isotope hydrograph separation on them, and present when and when we do not have some precipitation influence on the response and why. This would be a very good link with the hypothesis 1 (where you should clarify the meaning of “strong temporal” (page 1814), because every reader will have a different perception of such a subjective term), and the importance of the switch between different sources in a catchment and the link to catchment stage are important.

Unfortunately, the event data is rather limited and especially not based on sequential sampling. Thus, we could not present further data showing the influence of event/pre-event water on the isotopic streamflow dynamics.

Here I would suggest the TRANSIT approach (Weiler et al., 2003, WRR), since it could yield comparable results to the presented response times in Orlowski et al (2014). Further you can present what the difference between the two streams is, if they are individually sampled.

We estimated MTT for the two studied streams (Schwingbach and Vollnkirchener Bach). However, we did not obtain any meaningful results. Alternatively, we set up a hydrological model for the Vollnkirchener Bach subcatchment using CMF (Catchment Modelling Framework) by Kraft et al. (2011). CMF is a modular framework for hydrological modelling based on the finite volume approach by Qu and Duffy (2007). We used CMF to simulate water fluxes and advective transport of stable water isotopes (^{18}O and ^{2}H) to study the origin (Windhorst et al., 2014) and age of water. The generated model is a highly simplified representation of the Vollnkirchener Bach subcatchment’s groundwater body. For estimating the age of groundwater and its flow direction in the subcatchment, a virtual tracer with a given concentration and a fixed decay rate was used in CMF. This approach allowed overcoming the lack of temporal variation in surface and groundwater isotopic signatures. Our model further provides the opportunity to make use of stable water isotope information along with climate, land use, and soil type data, in combination with a digital elevation map to estimate residence times >5 years. We think that this CMF-based method is superior in obtaining catchment functioning insights as compared to classical MTT estimations that empirically try to match observed stable water isotopes.

Beyond, the limitations of the methods/or result presentation I think the merger of results and discussion was not that efficient for the paper. This takes out some clarity, and leaves the reader with some wondering what's new. And I don't think this actually accounts for the information wealth the paper delivers. Thus I would like to see a separation of results and discussion in the revised version, and a discussion that also outlines what we learnt new compared to the current understanding in runoff generation in developed/agricultural catchments.

As recommended by the reviewer, we separated the results and discussion section and restructured the manuscript.

The discussion and the cited references need some stronger focus on the research question of the paper, e.g. I do not think that a general discussion of how the precipitation compares to other precipitation stable isotope studies is necessary. Same holds for discussing stable isotopes in soil water. All valid and interesting points, but please present in the results only data in detail that is necessary for the research question, and shorten the presentation of precipitation data. This will help the paper to get more focussed and will eventually help a clear discussion of the generated understanding.

Following the recommendations of the reviewer, we shortened the section on precipitation isotopes. However, we do not agree that the soil water isotope section should thoroughly be reduced, since most of the process understanding could be gained through soil water isotope data. In addition, this would also conflict with suggestions of other reviewers.

In the introduction you outline general effects of fractionation, precipitation behavior of stable isotopes in detail, while this is not the focus of the work. Please present towards the end of the introduction (Page 1811 and 1812 are really nice) why this work was performed, and how these hypotheses are based on the current research need. I had the feeling this was not convincingly presented, this will also help to present the novelty in the discussion. In summary**,** add event based result section, were you can present response (also hydrometric) for several events, e.g. using TRANSEP (if sequential precipitation stable isotope data is available for events), and explain differences between the events. Second, separate results and discussion, and focus in the discussion points that are clearly related to the research questions, and how that compares to other work.

Since we did not sample precipitation sequentially, we did not add an additional results section on that topic. However, different rainfall-runoff event types could be detected using the lag-to-peak-time approach in a previous study by Orlowski et al. (2014) and a hydrograph separation was presented likewise in that earlier study in the same catchment.

General comments: The manuscript seems to have some problems with "ff".

P1810L2: I think the abstract would need an introduction sentence that sets the research field and reasoning.

We edited the abstract. It now reads as follows: *"A dual stable water isotope (δ^2H and δ^{18}O) study was conducted in the developed (managed) landscape of the Schwingbach catchment (Germany). The two-year weekly to biweekly measurements of precipitation, stream, and groundwater isotopes revealed that surface and groundwater are decoupled from the annual precipitation cycle but showed* *bidirectional interactions between each other. Apparently, snowmelt played a fundamental role for groundwater recharge explaining the observed differences to precipitation δ-values.*

A spatially distributed snapshot sampling of soil water isotopes in two soil depths at 52 sampling points across different land uses (arable land, forest, and grassland) revealed that top soil isotopic signatures were similar to the precipitation input signal. Preferential water flow paths occurred under forested soils explaining the isotopic similarities between top and subsoil isotopic signatures. Due to human-impacted agricultural land use (tilling and compression) of arable and grassland soils, water delivery to the deeper soil layers was reduced, resulting in significant different isotopic signatures. However, the land use influence smoothed out with depth and soil water approached groundwater δ-values. Seasonally tracing stable water isotopes through soil profiles showed that the influence of new percolating soil water decreased with depth as no remarkable seasonality in soil isotopic signatures was obvious at depth >0.9 m and constant values were observed through space and time.

Since classic isotope evaluation methods such as mean transit time calculation failed, we established a hydrological model to estimate groundwater ages and flow directions within the Vollnkirchener Bach subcatchment. Our model revealed that complex age dynamics exist within the subcatchments and that much of the runoff must has been stored in the catchment for much longer than event water.

Tracing stable water isotopes through the water cycle in combination with a hydrological model was valuable for determining interactions between different water cycle components and unravelling age dynamics within the study area. This knowledge can further improve catchment specific process understanding of developed, human-impacted landscapes."

P1811L13 "Garvelmann et al., 2012", I do think this is a wrong citation, there is not transit time work involved there. Please re-check, otherwise this would be confusing.

We deleted this reference here.

Same line: "transit", sometimes you are using "transit" sometimes "residence" time in the manuscript, please unify where it makes sense.

We unified the terminology throughout the manuscript.

P1811L17: You have quite some substantial elevation difference in the catchment, more than 100m, and call the catchment low-mountanious, I don't think this is comparable to real low angle catchments.

There does not exist an international standard definition of a mountain (Goudie and Goudie, 2013) and thus, a low-mountainous terrain. The definition of mountain regions is largely arbitrary because multiple criteria can be used to define such areas, e.g. relative relief, threshold altitude (1000 m) etc. (Perry and Taylor, 2009). Following Perry and Taylor (2009) a hilly terrain, which we equate with a low-mountainous terrain, has an altitudinal difference of 50-100 m (over 5 km distance). In the Schwingbach catchment, 28% of the area exhibits slopes with a gradient >10%. Over a 5 km longitudinal section an altitudinal difference of 92 m could be observed, however, highly depend on the transect. In general, elevation in the Schwingbach catchment ranges between 233–415 m a.s.l..

We conclude that the catchment belongs to the low-mountainous region according to these classifications.

Further, you need to better support this claim of poorly understood, I am not sure about that. What exactly? Further, I think here and in the following lines you need to better describe what was done and understood in developed catchments (also make the difference developed in sense of urbanisation or agriculture or both) and what is still a question of research. Please cite the necessary references to lay out the claim.

P1811L22-24: You need to support this claim better with (more) references, and clearly state why it is limited. The why helps to focus the paper, the "that" is not so important.

We have edited this section as follows: *"Moreover, due to human-induced alterations of river systems (e.g. channelisation of streambeds or draining) (O'Driscoll et al., 2010), water fluxes in developed (managed) landscapes can be especially diverse. Almost all European river systems were already substantially modified by humans before river ecology research developed (Klapper, 1990; Allan, 2004). Through changes in land use, land cover and irrigation, agriculture has substantially modified the hydrological cycle in terms of both water quality and quantity (Gordon et al., 2010) as well as altered the functioning of aquatic ecosystem processes (Pierce et al., 2012; Rockström et al., 2014). This complex character of developed, agricultural dominated catchments is often disregarded and established research approaches often failed to fully capture agro-ecosystem functioning at multiple scales (Orlowski et al., 2014). Since agricultural land use (arable land, permanent crops, and grassland) is the most dominant land use in Europe (UNEP, 2002), there exists a pressing need to understand biogeochemical fluxes (e.g. nitrogen compounds or pesticides) coupled with water fluxes in these managed landscapes (Orlowski et al., 2014) and to figure out a way to embed this landscape heterogeneity or the consequence of the heterogeneity into models (McDonnell et al., 2007).*

One way to better understand the relationship between precipitation, stream, soil, and groundwater, is a detailed knowledge about the isotopic composition of the various water sources (surface, subsurface, and groundwater) and their variation in space and time."

P1812L1 "few hydrological and especially stable water isotope". Are you really sure about this? In the following you cite some work from agricultural catchments (e.g. Cey et al., 1998) about tracer work. You can also find some citations of agricultural catchments and stable isotope work in Klaus and McDonnell (2013, JoH, their table 2). There are also quite some more studies in agricultural catchments. I do see limitations here.

We deleted this section from the manuscript and changed the paragraph as mentioned above.

P1812L7ff: This is very detailed information about stable isotopes in precipitation, while this seems not to be the focus of the paper. I think this can be substantially shortened, and a stronger focus on runoff generation should be introduced (if this is the main focus). From these lines on, please try to focuss on research gaps to better support the hypotheses.

We shortened this paragraph but still kept important information to understand the results and discussion section on *"Variations of precipitation isotopes and d-excess"*.

P1812L24: “residence time” unify terminology.

We unified the terminology throughout the manuscript.

P1812L28: “Kendall and McDonnell, 1998” The book consists of individual chapters from various authors, please cite the author of the relevant chapter, and have the Editor of the book in the reference list. Please improve throughout the manuscript.

We corrected it throughout the manuscript.

P1813L25: “water lines” in general a catchment should have one LMWL, since it describes the precipitation, it reads confusing here. Since water sources other than precipitation cannot have a LMWL.

We changed the sentence as follows: *“To compare different water sources on the catchment-scale, a local meteoric water (LMWL) line is developed and evaporation water lines (EWLs) are used.”*

P1814L24 “strong temporal” Please avoid subjective descriptions. You also could relate this hypothesis to new/old water paradox work from Kirchner and other authors.

We moved away from stating hypotheses and changed the paragraphs as follows: *“…This interaction between groundwater and surface water remains poorly understood in many catchments throughout the world but process understanding is fundamental to effectively manage the quantity and quality of water resources (Ivkovic, 2009). Sklash and Farvolden (1979) showed very early, that groundwater plays an important role as a generating factor for storm and snowmelt runoff processes. In many catchments, streamflow responds promptly to rainfall inputs but variations in passive tracers such as water isotopes are often strongly damped (Kirchner, 2003). This indicates that storm runoff in these catchments is dominated mostly by “old water” (Buttle, 1994; Neal and Rosier, 1990; Sklash, 1990). However, not all “old water” is the same (Kirchner, 2003). This catchment behaviour was described by Kirchner (2003) as the old water paradox. Thus, there is evidence of complex age dynamics within catchments and that much of the runoff is stored in the catchment for much longer than event water (Rinaldo et al., 2015). Still, some of the physical processes controlling the release of “old water” from catchments are poorly understood, roughly modelled, and the observed data do not suggest a common catchment behaviour (Botter et al., 2010).”*

“…To capture spatial landscape heterogeneity, but to keep data acquisition simple, stable water isotope data were coupled with hydrodynamic data from a previous study by Orlowski et al. (2014) in the developed Schwingbach catchment (Germany) to unravel water flow paths and interactions between different water cycle components. Results obtained through this earlier study imply that the Schwingbach catchment is highly responsive indicated by fast runoff responses to precipitation inputs (Orlowski et al., 2014). Moreover, groundwater reacted almost as quickly as streamflow to precipitation events with raising head levels. Thus, the catchment showed “old water” paradox like behaviour (Kirchner, 2003). We further showed that streamflow was predominantly generated in the catchment headwater area and that gaining and losing stream reaches occurred in parallel along the studied stream affected by the underlying geology.

Thus, stable water isotopes in combination with hydrodynamic data of a two-year monitoring period (July 2011 to July 2013) were utilised to explore spatio-temporal isotopic variations, unravel linkages between the different water cycle components, investigate the transformations from precipitation to soil and groundwater, and analyse the effect of small-scale landscape characteristics (i.e. soil physical properties, topographic wetness index (TWI), distance to stream, and vegetation cover) on soil water isotopic composition. Further, stable water isotope data was utilized to estimate groundwater ages and flow directions in the Vollnkirchener Bach subcatchment via an hydrological model setup based on the findings of Orlowski et al. (2014)."

P1815L3ff: Please make this more clear.

We thoroughly edited the Introduction (see above) and included the following: *"To compare different water sources on the catchment-scale, a local meteoric water (LMWL) line is developed and evaporation water lines (EWLs) are used. They represent the linear relationship between δ^2H and δ^{18}O of meteoric waters (Ingraham, 1998) in contrast to the global meteoric water line (GMWL), which describes the world-wide average stable isotopic composition in precipitation (Craig, 1961a). Thus, the comparison of stable isotope data for stream, soil, or groundwater samples relative to the global or local meteoric water lines can provide general understandings on water cycle processes at specific research sites (Song et al., 2011)."*

P1815L10ff: You should make clearer when you write about the one stream and about the other. Present the individual catchment boundaries in fig1. In the text it needs be more clear what information is linked to what (sub-) catchment.

We edited the respective paragraphs in the manuscript to make the description of the two streams clearer. Moreover, we modified Figure 1 and included the Vollnkirchener Bach subcatchment boundaries as well as the names of the streams in Figure 1c. In addition, Figure 1 now encompasses a map showing the location of the study area in Germany (Fig. 1a) and a map of the soil sampling points along the Vollnkirchener Bach (Fig. 1d).

P1816L6ff.: Do you have long term data for the area, would be better than presenting precip sum for only one year. Catchment outlet referes to the Schwingbach Catchment?

For comparisons, we included the following section in the manuscript: *"The climate in the study area is classified as temperate with a mean annual temperature of 8.2°C. An annual precipitation sum of 633 mm (for the hydrological year 1 November 2012 to 31 October 2013) was measured at the catchment's climate station (site 13, Fig. 1b). The year 2012 to 2013 was an average hydrometeorological year. For comparison, the climate station Giessen/Wettenberg (25 km N of the catchment) operated by the German Meteorological Service (DWD, 2014) records a mean annual temperature of 9.6 °C and a mean annual precipitation sum of 666 ± 103 mm for the period 1980 to 2010."*

P1816L19 "Significant" should only be used in relation to statistical tests. Please avoid otherwise.

The sentence now reads as follows: *"Substantial snowmelt peaks were observed during December 2012 and February 2013."*

P1816L9ff. “>114 L s-1”. Why “>” and not the exact value? I think the unit might be better in depth (mm)/area to have comparability if this is a lot or not.

We included the following information in the sentence: *“Discharge peaks from December to April (measured by the use of RBC-flumes with maximum peak flow of 114 L s^{-1}, Eijkelkamp Agrisearch Equipment, Giesbeek, NL) and low flows occur from July until November.”*

Moreover, we changed the discharge unit to mm d^{-1}.

P1818L9-12: I think such information should be in the introduction, not in the method section.

We edited the Introduction and decided to move the sentence to the Results section: *“Distances to the stream are linked to water flow path lengths and were therefore supposed to be a controlling factor. However, no impact of different distances to the stream on soil water isotopic signatures could be observed.”*

P1820, Chapter 3.1. Here a decision regarding the focus is necessary; the whole section of precipitation is very detailed, while not really linked to the hypotheses/research question. In general this could be shortened. Further I think the introduction of the LMWL (3.5) should be together with chapter 3.1.

We decided not to shorten the section on “Variations of precipitation isotopes and d-excess” but to strengthen it and to include results of Figure 10 on the LMWL and EWLs (now Fig. 3) in this section.

P1824L19ff: As outlined earlier, there are variations, with heavier values in summer/fall and lighter values in spring. It is not even close to a straight line.

As described above the MTT calculations with FlowPC did not provide meaningful results, not even after bias-correcting the precipitation input data (Table 2). The failure of the MTT estimations is mainly attributed to the little variation in stream water isotopic signatures, which have to be weekly averages for the calculations with FlowPC. Thus, potential variations in stream water isotopes are averaged out.

P1825L8: Here again, standard deviation is already 3 times higher than analytical precision.

See argumentation above.

P1825L21: Did you try some mixing calculations?

We included the following sentence in the Discussion section: *“Just by comparing mean precipitation ($\delta^{18}O = -6.2\pm3.1$), stream (e.g. $\delta^{18}O = -8.4\pm0.4$ for the Vollnkirchener Bach), and groundwater isotopic signatures ($\delta^{18}O = -8.2\pm0.4$ for the meadow) (Tab. 1), it is obvious that simple mixing calculations do not work either.”*

P1826L4/5 “Statistically similar”, please provide p-value (t-test?)

We applied a new data analysis tool, network mapping (Kolaczyk, 2014) in combination with a principal component analysis (Jolliffe, 2002) to determine the δ^{18}O isotope relationships between surface and groundwater sampling points based on significant correlations ($p<0.05$). These new results are included in the the Section on "Isotopes in groundwater".

P1826L14: Please also report p-value here and throughout the manuscript.

See reply above.

P1826L23-27: These lines are not needed. This should be clear from intro and method, here you should just report the results.

We deleted this sentence from the manuscript.

P1827L12-13: ". . .(Fig. 8).", this is difficult to see, please test statistically incl. p-value. Same for lines 16 and 20.

We generally included p-values in the revised manuscript where necessary.

P1827L22-24: What did you expect to see? So how should rainfall influence the groundwater signal? Maybe the volume of preferential flow is low compared to the volume of GW and no (strong) effect can be seen.

The following paragraph was already given in the manuscript as explanation: *"Subsoil isotopic values were statistically equal to stream and groundwater isotopic values (Fig. 4) implying that the catchment was under baseflow conditions during the sampling campaign and that capillary rise of groundwater occurred. Nevertheless, the rainfall isotopic signal was not directly transferred through the soil to the groundwater body, even so prompt groundwater head level raises as a result of rainfall-runoff events occurred. This likewise supports the assumption of double paradox-like catchment behaviour."*

P1827-1828L28-2: It would be important to work out the site differences and related the differences in measurement to this.

We edited this paragraph as follows: *"Garvelmann et al. (2012) obtained high resolution δ^2H vertical depth profiles of pore water at various points along two fall lines of a pasture hillslope in the southern Black Forest (Germany) by applying the H_2O(liquid)–H_2O(vapor) equilibration laser spectroscopy method. The authors showed that groundwater was flowing through the soil in the riparian zone (downslope profiles) and dominated streamflow during baseflow conditions. Their comparison indicated that the percentage of pore water soil samples with a very similar stream water δ^2H signature is increasing towards the stream channel (Garvelmann et al., 2012). In contrast, we found no relationship between the distance to stream and soil isotopic values in the Vollnkirchener Bach subcatchment over various heights above sea level (235–294 m a.s.l.)."*

P1830L10ff. Lots of details, but it needs to be clearer what the message is. I think with separating results/discussion this will automatically become clear, if the discussion is related to the hypotheses and general progress in the field.

We separated the Results and Discussion and changed the order of the sections in the revised manuscript.

P1831L5: If the focus is on the LMWL please add this to the precipitation isotope section. If you want to compare the water lines of individual water cycle components make that clear, and the analysis statistically more sound.

We moved the paragraph on the LMWL and EWLs to the Section on “Variations of precipitation isotopes and d-excess” and shortened it.

P1831L21: How do you exclude moisture recycling?

We edited the respective paragraphs to make it clearer: *“Considering d-excess values, it is well-known that precipitation events originating from oceanic moisture show d-excess values close to +10‰ (Craig, 1961a; Dansgaard, 1964; Wu et al., 2012) and one of the main sources for precipitation in Germany is moisture from the Atlantic Ocean (Stumpp et al., 2014)…Continental precipitation events originating from oceanic moisture can approach d-excess values of +10‰ (Wu et al., 2012) (Fig. 2, solid line). Air mass trajectories at intercontinental, southern and eastern regions are suggested to be more stable with less variable moisture sources in these regions compared to sites near the coast (Stumpp et al., 2014). Therefore, rainout histories on the continent itself are more stable (Stumpp et al., 2014).”*

P1832L5-6: From the elevation range they seem not to be comparable.

See argumentation above on low-mountainous regions.

P1832L17: Here event based hydrograph separation would be nice, they should present how much % groundwater contributions are during events.

See argumentation above.

P1832L20: “a larger contribution. . .” You did not present calculations.

We edited the sentence as follows: *“Even so streamflow and groundwater head levels promptly responded to precipitation inputs, there was no obvious change in their isotopic composition due to rain events (old water paradox behaviour).”*

Figure 1: Please present sub-catchments. Fonts are too small to decipher.

Changed as recommended.

Figure 2: What is the relation to hypotheses/research questions? I think this figure could be removed.

Deleted Figure 2 from the mansucript.

Figure 4: Too small. For trying, plot a moving average, I guess you start seen some seasonal patterns.

Changed as recommended.

Figure 5: Larger fonts needed.

Changed as recommended.

Figure 8: font size

Changed as recommended.

Figure 10: please report equations of water lines, here.

We included the respective equations in Figure 10 (now Fig. 3).

Reply to Referee #3

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.

General comments:

The authors present an interesting case study and an extensive dataset about the water cycle dynamics in the developed Schwingbach catchment based on stable isotope data from the water components precipitation, soil water groundwater, and stream water. The presented sampling approach and the methods used are valid so far and described in detail. The observed signatures of the individual components and their interactions are described in detail. The reactions of groundwater and stream water to precipitation events have been already described in an earlier study and this process knowledge is now supported with the stable isotope sampling carried out in the Schwingbach catchment. It seems that groundwater dynamics are dominating the hydrological system of the Schwingbach catchment. The submitted study presents no new methods or the identification of unknown processes. However, substantial stable isotope datasets in developed landscapes are rare and improved process knowledge is important for hydrological modeling and for a better understanding of biogeochemical processes as mentioned in the introduction section of the presented manuscript. It would be an asset for the study to include additional findings about the groundwater dynamics and the process of recharge in the study landscape. The spatially distributed stable isotope soil profiles together with the groundwater signatures would be a perfect dataset. The study is in the scope of the journal and I recommend the presented case study for publication in HESS after revising the submitted manuscript based on the suggestions of the review process.

We thank referee #3 for the valuable comments and technical corrections which helped us to improve the manuscript. All the suggested changes have been included. Find the answers to each comment below.

In general, we improved the quality of the manuscript by including additional statistical analyses (network mapping in combination with a principal component analysis) and a hydrological model for the Vollnkirchener Bach subcatchment. This hydrological model was setup with CMF (Catchment Modelling Framework by Kraft et al. (2011)) and builds on the conceptual model of groundwater-surface water interactions presented by Orlowski et al. (2014). We further estimated mean transit times (MTT) for the Vollnkirchner Bach (sites 13, 18 and 94) and the Schwingbach (sites 11, 19 and 64) using FlowPC (Version 3.1, Małoszewski and Zuber (1996)).

Specific comments:

The introduction section is well written and the relevant processes and fundamentals of stable isotope hydrology for this study are addresses. However, I suggest modifying the structure at one point. There are some research needs (Page 1811, Line 21 – Page 1812, Line 6) mixed with more fundamental background information. Please add a few words about the relevant processes of groundwater-surface water interactions and add some benchmark studies (e.g. Sklash and Farvolden, 1979) in the groundwater part of the introduction section.

We included some benchmark papers on groundwater-surface water interactions in this paragraph of the introduction, which now reads as follows: *"…Unlike the distinct watershed components found in steeper headwater counterparts, lowland areas often exhibit a complex groundwater–surface water interaction (Klaus et al., 2015). This interaction between groundwater and surface water remains poorly understood in many catchments throughout the world but process understanding is fundamental to effectively manage the quantity and quality of water resources (Ivkovic, 2009). Sklash and Farvolden (1979) showed very early, that groundwater plays an important role as a generating factor for storm and snowmelt runoff processes. In many catchments, streamflow responds promptly to rainfall inputs but variations in passive tracers such as water isotopes are often strongly damped (Kirchner, 2003). This indicates that storm runoff in these catchments is dominated mostly by "old water" (Buttle, 1994; Neal and Rosier, 1990; Sklash, 1990). However, not all "old water" is the same (Kirchner, 2003). This catchment behaviour was described by Kirchner (2003) as the old water paradox. Thus, there is evidence of complex age dynamics within catchments and that much of the runoff is stored in the catchment for much longer than event water (Rinaldo et al., 2015). Still, some of the physical processes controlling the release of "old water" from catchments are poorly understood, roughly modelled, and the observed data do not suggest a common catchment behaviour (Botter et al., 2010)."*

The reference Garvelmann et al. (2014) is not appropriate on page 1811, Line 13, since no MRT calculations have been conducted in this study.

We deleted this reference here.

The expression "stable isotope components" might be more appropriate at some passages than using "stable isotope pools" (e.g. Page 1814, Line 21).

We changed the expression to "stable isotope components".

Please provide the catchments size and the altitudes at the beginning of the study area section.

We shifted the following paragraph to the beginning of this section: *"The whole Schwingbach catchment encompasses an area of 9.6 km^2, with an altitude range from 233–415 m a.s.l. The Vollnkirchener Bach tributary is about 4.7 km in length and drains a 3.7 km^2 subcatchment area (Fig. 1c), which ranges in elevation from 235–351 m a.s.l."*

Furthemore, I suggest to provide the discharge (additionally) in millimeters to allow a better comparison between the two catchments.

We changed the discharge unit to mm d^{-1}.

How was snow sampled (Page 1817, Line 12)? This is an important information. Solid samples were used in a number of past studies. This is valid for characterising the stable isotope signature of precipitation input. However, Taylor et al. (2001, 2002) have shown that there is a significant difference between the stable isotope signature of solid samples and meltwater samples and they suggest to use meltwater samples in hydrological studies. I suggest to at least shortly discuss this issue in the paper.

We included the following paragraph under the section "Monitoring network and water isotope sampling": *"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. Open rainfall was collected in self-constructed samplers."*

Including equation 1 (Page 1819, Line 15) is not crucially necessary.

According to the reviewer, we deleted the respective equation.

Can you explain in more detail, why the isotopic signature of stream flow seems be influenced by snowmelt only at site 64?

Unfortunately, our sampling only captured the snowmelt influence at site 64 as well as at groundwater sampling points 27 and 32.

That groundwater is mainly recharged during the winter season well known. During this period the transpiration by vegetation is significantly reduced and water available for recharge. Please include this point in your discussion on groundwater recharge on page 1825.

As recommended by the reviewer we included the following paragraph: *"Generally, less than 5 to 25% of precipitation infiltrates to the groundwater table in temperate climates; the rest is lost to runoff, evaporation from soils and transpiration by vegetation (Clark and Fritz, 1997a). During spring runoff when soils are saturated, temperatures are low, and vegetation is inactive, recharge rates are generally highest. In contrast, recharge is very low during summer when most precipitation is transpired back to the atmosphere (Clark and Fritz, 1997a)."*

Why are the groundwater stable isotope signatures so different? Please explain the statistical differences in more detail. It seems to be related to the different land use forms as you mentioned in the paper. Please provide additional information about this issue. There is probably more potential to explain this issue in combination with the soil profiles.

We performed new statistical analysis and replaced Figure 6 by the results of our new topology interference network map (Kolaczyk, 2014) which is combined with a principal component analysis (Jolliffe, 2002) (now Fig. 9). The network map depicts relationships between surface and groundwater sampling points based on significant correlations ($p<0.05$).

You explain the values observed at piezometer 32 with the influence of snowmelt. Again, why seems the snowmelt signal only influence the values at this location? Please provide more information about this particular site compared to the other piezometer sites.

We included the following information in the discussion section of the groundwater isotopic signatures: *"As shown by Orlowski et al. (2014) piezometer 32 is highly responsive to rainfall-runoff events and groundwater head elevations showed significant correlations with mean daily discharge at this site. Further, effluent conditions and lowest* K_{sat} *values (7–14* $mm\cdot h^{-1}$*) were measured in this stream section (piezometers 32–35) (Orlowski et al., 2014)."*

We further included δ^2H values and groundwater head levels of site 27 in Figure 5 (now Fig. 8). Groundwater isotopic signatures at this site likewise showed snowmelt influenced δ-values in the winter period of 2012 to 2013. Site 32 and 27 were exemplarily selected to show the translocation of snow isotopic signatures to the groundwater in the study area. Additionally, moving averages were plotted through the groundwater and stream water isotope time series (now Fig. 7 and 8).

It would be nice to show the soil moisture values of the soil profiles in section 3.4. Please clearly mention in your discussion of the stable isotope profiles that the study of Garvelmann et al. (2012) was carried out on a hillslope. Therefore the results of the two studies are not directly comparable due to the differing topography of the study areas.

Soil water contents of the spatially distributed soil sampling can be found in Table 2. Soil moisture data for the seasonal soil sampling was included in Figure 9 (now Fig. 6).

We included the following sentence in the section “Spatial variability”: *“Soil samples were taken at four consecutive rainless days (1 to 4 November 2011) at altitudes of 235–294 m a.s.l..”*

Moreover, we edited the following sentences: *“Garvelmann et al. (2012) obtained high resolution δ^2H vertical depth profiles of pore water at various points along two fall lines of a pasture hillslope in the southern Black Forest (Germany) by applying the H_2O(liquid)–H_2O(vapor) equilibration laser spectroscopy method. The authors showed that groundwater was flowing through the soil in the riparian zone (downslope profiles) and dominated streamflow during baseflow conditions. Their comparison indicated that the percentage of pore water soil samples with a very similar stream water δ^2H signature is increasing towards the stream channel (Garvelmann et al., 2012). In contrast, we found no relationship between the distance to stream and soil isotopic values in the Vollnkirchener Bach subcatchment over various heights above sea level (235–294 m a.s.l.).”*

I suggest including the information about precipitation and the local meteoric water line in section 3.5 into the description of the precipitation values (section 3.1).

It would also be nice to show the deuterium-18-O plots at the beginning of the results section for an overview of all samples used in the study.

We moved the description about the LMWL and EWLs to the Results section on “Variations of precipitation isotopes and d-excess” as well as the respective Figure.

Technical comments

Page 1812, Line 7-9: Please revise the structure of this sentence.

We rephrased the sentence as follows: *“One way to better understand the relationship between precipitation, stream, soil, and groundwater, is a detailed knowledge about the isotopic composition of the various water sources (surface, subsurface, and groundwater) and their variation in space and time.”*

Page 1816, Line 19: was instead of were

Precipitation data is plural. Thus, “were” is correct in this context.

Page 1820, Line 15: “: …rainfall was collected at 15 open field site locations..”

We edited the sentence as recommended by the reviewer.

Page 1820 Line 17-19: Please revise this sentence for more clarity. Which information refers to which citation?

We deleted reference “Gat et al. (2011)” and rephrased the sentence.

Page 1821, Line 28: Schürch, Schurch or Schuerch? Check also in refernces list.

We could not find anything wrong with this reference (Schürch et al., 2003). It was consistently cited throughout the manuscript.

Page 1822, Line 8: Deuterium-excess of what? (Please remove section title or reviose)

We combined all findings on precipitation isotopes (i.e. d-excess and LMWL) under the same section *“Variations of precipitation isotopes and d-excess”.*

Page 1824, Line 24: mean transit time

We revised the whole section 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 1829, Line 24-25: Please revise this sentence for more clarity.

We edited the sentence as follows:

“Isotope compositions of soil water varied seasonally: More depleted soil water was found in the winter and spring (Fig. 9); contrary, soil water was enriched in summer due to evaporation during warmer and drier periods (Darling, 2004).”

Figure 1: Is it possible to include the locations of the stable isotope soil profiles?

We included the locations of the snapshot as well as of the seasonal soil samplings in Figure 1.

Figure 3: There is no dashed line at d=10 (or the quality of the figure was to bad: : :)

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 GNIP station Koblenz for the same period as the measured data of the Schwingbach catchment (2011 to 2013).

Figure 4+5: Please provide the discharge in mm/day. It would be nice to include the average stable isotope values with a fine solid line for a better comparison.

The discharge unit was changed as recommended. We plotted a moving average through the streamflow as well as through the groundwater isotope time series for Figure 4 (now Fig. 7 and 8). Average stable isotope values were already provided in Table1.

I kindly invite the authors to recheck the citations and the references list very carefully in the manuscript. For example Klaus et al. is from 2015 (please revise throughout the manuscript).

We checked and edited the reference list where necessary.

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 Orlowski 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 Orlowski 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 δ^2H) 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 δ^2H. 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 δ^2H) 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^{-1} 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 δ-values (−43.9±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 µL 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/22sd 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.

Relevant changes

- Included additional statistical analyses, e.g. new data analysis tool: network map (Kolaczyk, 2014) in combination with a principal component analysis to demonstrate the isotopic relationships between surface and groundwater sampling points
- Calculated the mean transit times (MTT) for the Vollnkirchner Bach (sites 13, 18 and 94) and the Schwingbach (sites 11, 19 and 64) using FlowPC
- Catchment Modelling Framework (CMF) by Kraft et al. (2011) was used to setup a hydrological model for the Vollnkirchner Bach subcatchment to estimate groundwater ages and flow directions
- Restructured the whole manuscript: Revised the Introduction completely and separated the Results and Discussion section

All changes we made to the manuscript can be found in the “Manuscript version showing changes” below.

Manuscript version showing changes

Exploring water cycle dynamics ~~through~~by sampling ~~multitude~~multiple stable water isotope pools in a small developed landscape of Germany

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Abstract

~~Conducting a~~A dual stable water isotope (δ^2H and δ^{18}O) study was conducted in the developed (managed) landscape of the Schwingbach catchment (Germany~~) helped to unravel connectivity and disconnectivity between the different water cycle components.~~). The two-year weekly to biweekly measurements of precipitation, stream, and groundwater isotopes revealed that surface and groundwater are decoupled from the annual precipitation cycle but showed bidirectional interactions between each other. ~~Seasonal variations based on temperature effects were observed in the precipitation signal but neither reflected in stream nor in groundwater isotopic signatures.~~ Apparently, snowmelt played a fundamental role for groundwater recharge explaining the observed differences to precipitation δ-values.

A spatially distributed snapshot sampling of soil water isotopes in two soil depths at 52 sampling points across different land uses (arable land, forest, and grassland) revealed that top soil isotopic signatures were similar to the precipitation input signal. Preferential water flow paths occurred under forested soils explaining the isotopic similarities between top and subsoil isotopic signatures. Due to human-impacted agricultural land use (tilling and

compression) of arable and grassland soils, water delivery to the deeper soil layers was reduced, resulting in significant different isotopic signatures. However, the land use influence smoothed out with depth and soil water approached groundwater δ-values. Seasonally tracing stable water isotopes through soil profiles showed that the influence of new percolating soil water decreased with depth as no remarkable seasonality in soil isotopic signatures was obvious at depth >0.9 m and constant values were observed through space and time.

~~Little variation in individual~~Since classic isotope ~~time series of stream and groundwater restricted the use of classical isotope hydrology techniques e.g.~~ evaluation methods such as mean transit time ~~estimation or hydrograph separation. Still, tracing~~calculation failed, we established a hydrological model to estimate groundwater ages and flow directions within the Vollnkirchener Bach subcatchment. Our model revealed that complex age dynamics exist within the subcatchment and that much of the runoff must has been stored in the catchment for much longer than event water.

Tracing stable water isotopes through the water cycle in combination with a hydrological model was valuable for determining interactions between different water cycle components and ~~gaining catchment~~ unravelling age dynamics within the study area. This knowledge can further improve catchment specific process understanding ~~in a~~of developed, human-impacted ~~landscape~~landscapes.

~~1 Introduction~~

~~The application of stable water isotopes as natural tracers in combination with hydrodynamic methods has been proven to be a valuable tool for studying the origin, formation, and interrelationship between surface water and groundwater (Blasch and Bryson, 2007; Goni, 2006), partitioning evaporation and transpiration (Phillips and Gregg, 2003; Rothfuss et al., 2010, 2012; Wang and Yakir, 2000), and further mixing processes between various water sources (Aggarwal et al., 2007; Clark and Fritz, 1997; Kendall and Coplen, 2001; Wu et al., 2012). Particularly in catchment hydrology, stable water isotopes play a major role since they can be utilised for hydrograph separations (Buttle, 2006; Hoeg et al., 2000; Ladouche et al., 2001; Munyaneza et al., 2012), to calculate the mean transit time (Garvelmann et al., 2012; McGuire et al., 2002, 2005; Rodgers et al., 2005b), to investigate water flow paths (Barthold et al., 2011; Goller et al., 2005; Rodgers et al., 2005a), or to improve hydrological model simulations (Birkel et al., 2010; Koivusalo et al., 1999; Liebminger et al., 2007; Rodgers et~~

~~al., 2005b). However, spatio-temporal sources of stream water in low angle, developed catchments are still poorly understood. This is partly caused by damped stream water isotopic signatures excluding traditional hydrograph separations (Klaus et al., 2014). Unlike the distinct watershed components found in steeper headwater counterparts, lowland areas often exhibit a complex groundwater–surface water interaction (Klaus et al., 2014). Moreover, the complex character of developed, agricultural dominated catchments is often disregarded and established research approaches often failed to fully capture agro-ecosystem functioning at multiple scales (Orlowski et al., 2014). This is mainly because almost all European river systems were already substantially modified by humans before river ecology research developed (Klapper, 1990; Allan, 2004). While agricultural land use (arable land, permanent crops, and grassland) is the most dominant land use in Europe (UNEP, 2002), few hydrological and especially stable water isotope studies have been conducted in these human-impacted landscapes and catchments. The challenges of future research are therefore to gain knowledge about the water pathways and interplay of the water cycle components in developed landscapes to improve our understanding of biogeochemical fluxes such as nitrogen compounds or pesticides in these managed landscapes (Orlowski et al., 2014).~~

1 ~~To explore~~Introduction

The application of stable water isotopes as natural tracers in combination with hydrodynamic methods has been proven to be a valuable tool for studying the origin, formation, and interrelationship between surface water and groundwater (Blasch and Bryson, 2007; Goni, 2006), partitioning evaporation and transpiration (Phillips and Gregg, 2003; Rothfuss et al., 2010, 2012; Wang and Yakir, 2000), and further mixing processes between various water sources (Aggarwal et al., 2007; Clark and Fritz, 1997c; Kendall and Coplen, 2001; Wu et al., 2012). Particularly in catchment hydrology, stable water isotopes play a major role since they can be utilised for hydrograph separations (Buttle, 2006; Hoeg et al., 2000; Ladouche et al., 2001; Munyaneza et al., 2012), to calculate the mean transit time (McGuire et al., 2002, 2005; Rodgers et al., 2005b), to investigate water flow paths (Barthold et al., 2011; Goller et al., 2005; Rodgers et al., 2005a), or to improve hydrological model simulations (Birkel et al., 2010; Koivusalo et al., 1999; Liebminger et al., 2007; Rodgers et al., 2005b). However, spatio-temporal sources of stream water in low angle, developed catchments are still poorly understood. This is partly caused by damped stream water isotopic signatures excluding traditional hydrograph separations (Klaus et al., 2015). Unlike the distinct watershed components found in steeper headwater counterparts, lowland areas often exhibit a complex groundwater–surface water interaction (Klaus et al., 2015). This interaction between groundwater and surface water remains poorly understood in many catchments throughout the world but process understanding is fundamental to effectively manage the quantity and quality of water resources (Ivkovic, 2009). Sklash and Farvolden (1979) showed very early, that groundwater plays an important role as a generating factor for storm and snowmelt runoff processes. In many catchments, streamflow responds promptly to rainfall inputs but variations in passive tracers such as water isotopes are often strongly damped (Kirchner, 2003). This indicates that storm runoff in these catchments is dominated mostly by “old water” (Buttle, 1994; Neal and Rosier, 1990; Sklash, 1990). However, not all “old water” is the same (Kirchner, 2003). This catchment behaviour was described by Kirchner (2003) as the old water paradox. Thus, there is evidence of complex age dynamics within catchments and that much of the runoff is stored in the catchment for much longer than event water (Rinaldo et al., 2015). Still, some of the physical processes controlling the release of “old water” from catchments are poorly understood, roughly modelled, and the observed data do not suggest a common catchment behaviour (Botter et al., 2010).

Moreover, due to human-induced alterations of river systems (e.g. channelisation of streambeds or draining) (O’Driscoll et al., 2010), water fluxes in developed (managed) landscapes can be especially diverse. Almost all European river systems were already substantially modified by humans before river ecology research developed (Klapper, 1990; Allan, 2004). Through changes in land use, land cover and irrigation, agriculture has substantially modified the hydrological cycle in terms of both water quality and quantity (Gordon et al., 2010) as well as altered the functioning of aquatic ecosystem processes (Pierce et al., 2012; Rockström et al., 2014). This complex character of developed, agricultural dominated catchments is often disregarded and established research approaches often failed to fully capture agro-ecosystem functioning at multiple scales (Orlowski et al., 2014). Since agricultural land use (arable land, permanent crops, and grassland) is the most dominant land use in Europe (UNEP, 2002), there exists a pressing need to understand biogeochemical fluxes (e.g. nitrogen compounds or pesticides) coupled with water fluxes in these managed landscapes (Orlowski et al., 2014) and to figure out a way to embed this landscape heterogeneity or the consequence of the heterogeneity into models (McDonnell et al., 2007).

One way to better understand the relationship between precipitation, stream, soil, and groundwater, is detailed knowledge ~~of~~about the isotopic composition of the ~~various~~different water sources (surface, subsurface, and groundwater) and their variation in space and time~~ is required~~. In principal, isotopic signatures of precipitation are altered by temperature, amount (or rainout), continental, altitudinal, and seasonal effects. They are mainly influenced by prevailing atmospheric conditions during rainfall and snowfall causing a depletion of isotopes ~~(Araguas-Araguas et al., 2000; Blasch and Bryson, 2007; Clark and Fritz, 1997; Gat, 1996; Kendall and McDonnell, 1998).~~(Araguás-Araguás et al., 2000; Blasch and Bryson, 2007; Clark and Fritz, 1997c; Gat, 1996; Rohde, 1998). The input signal becomes more pronounced in snow-dominated systems where snowfall and snowmelt are depleted in heavy stable water isotopes relative to rainfall ~~(Maule et al., 1994; O'Driscoll et al., 2005).~~(Maule et al., 1994; O'Driscoll et al., 2005). Stream water isotopic signatures can reflect precipitation isotopic composition and moreover, depend on discharge variations affected by seasonally variable contributions of different water sources such as bidirectional water exchange with the groundwater body during baseflow, or high event-water contributions during stormflow ~~(Kendall and McDonnell, 1998; Koeniger et al., 2009). To distinguish between the direct contribution of precipitation input and groundwater to storm runoff, isotope hydrograph separation can be applied (Buttle, 1994, 2006; Cey et al., 1998). Furthermore, if the isotopic composition of the input signal is known, understanding of recharge areas (altitude), times of recharge (season) as well as residence times and influencing processes (e.g. evaporation and mixing) can be gained (Koeniger et al., 2009).~~

(Genereux and Hooper, 1998; Koeniger et al., 2009). Following the way of precipitation over the unsaturated zone to the groundwater, the process of infiltration in itself is known to be a non-fractionating process ~~(Kendall and McDonnell, 1998)~~(Gonfiantini et al., 1998), except for mixing between different water pools (e.g. moving and standing water) ~~(Gat, 1996).~~(Gat, 1996). However, precipitation falling on vegetated areas is intercepted by plants and re-evaporated thus isotopically fractionated. The remaining throughfall~~ – less in volume in comparison to the total rain input –~~ infiltrates slower and can be affected by evaporation resulting in an enrichment of heavy isotopes, particularly in the upper soil layers ~~(Kendall and McDonnell, 1998). The amount of water lost by evaporation, transpiration, and interception and thereby the magnitude of isotopic change mainly depends on climate and vegetation cover (Kendall and McDonnell, 1998).~~(Gonfiantini et al., 1998; Kendall and Caldwell, 1998). In the soil, specific isotopic profiles develop, characterized by an evaporative layer near the surface especially under arid and semi-arid climate. This decreases exponentially with depth ~~(Zimmermann et al., 1968)~~(Zimmermann et al., 1968), representing a balance between the upward convective flux and the downward diffusion of the evaporative signature ~~(Barnes and Allison, 1988)~~(Barnes and Allison, 1988). ~~This early observation (Zimmermann et al., 1968) has been broadly used to determine the infiltration profile and rate of evaporation in arid and semi-arid regions (Brunner et al., 2008). However, in~~In humid and semi-humid areas, this exponential decrease is generally interrupted by the precipitation isotopic signal. Hence, the combination of the evaporation effect and the precipitation isotopic signature determine the isotope profile in the soil (Song et al., 2011). Once soil water reaches the saturated zone, this isotope information is finally transferred to the groundwater (Song et al., 2011). Soil water can therefore be seen as a link between precipitation and groundwater, and the dynamics of isotopic composition in soil water are indicative of the processes of precipitation infiltration, evaporation of soil water, and recharge to groundwater ~~(Blasch and Bryson, 2007; Song et al., 2011)~~(Blasch and Bryson, 2007; Song et al., 2011).~~ They can further be understood as a long term average of rain events (Clark and Fritz, 1997).~~

To compare different water sources on the catchment-scale, a local meteoric water (LMWL) line is developed and evaporation water lines (~~LMWL~~EWLs) are used. They represent the linear relationship between δ^{2}H and δ^{18}O of meteoric waters ~~(Kendall and McDonnell, 1998)~~(Cooper, 1998) in contrast to the global meteoric water line (GMWL), which describes the world-wide average stable isotopic composition in precipitation ~~(Craig, 1961a).~~(Craig, 1961a). Thus, the comparison of stable isotope data for stream, soil, or groundwater samples relative to the global or local meteoric water lines can provide general understandings on water cycle processes at specific research sites (Song et al., 2011).

Identifying the origin of water vapour sources and moisture recycling ~~(Gat et al., 2001; Lai and Ehleringer, 2011)~~(Gat et al., 2001; Lai and Ehleringer, 2011), the deuterium-excess (d-excess), defined by ~~Dansgaard (1964)~~Dansgaard (1964) as $d = \delta^{2}H - 8 \times \delta^{18}O$ can be used, since the d-excess mainly depends on the mean relative humidity of the air masses formed above the ocean surface ~~(Zhang et al., 2013)~~(Zhang et al., 2013). In addition, the d-excess reflects the prevailing conditions during evolution, interaction, or mixing of air masses en route to the precipitation site (Froehlich et al., 2002).~~ Consequently, the d-excess has been used as a powerful tool to reconstruct temporal changes in moisture supply for a given location (Feng et al., 2009).~~

~~In order to improve our understanding of developed landscapes, we performed a multi-method hydrodynamic-based study in the observation area of the Schwingbach catchment (Germany) first. Results obtained through this former study imply that the catchment is highly responsive indicated by fast runoff responses to precipitation inputs (Orlowski et al., 2014). Moreover, groundwater reacted almost as quickly as stream water to precipitation events with raising head levels. We further showed that streamflow was generated in the catchment headwater area and that gaining and losing stream reaches occurred in parallel along the studied stream affected by the underlying geology. To back up the results obtained by Orlowski et al. (2014) on the level of hydrological processes, we investigated stable water isotope pools and fluxes in the same catchment. Stable water isotopes in combination with hydrodynamic data of a two-year monitoring period (July 2011–July 2013) were utilised to test the following hypotheses:~~

~~(1) Highly responsive rainfall-runoff behaviour results in strong temporal variation of stream water isotopic signatures.~~

~~(2) The rainfall isotopic signature is quickly transferred to the groundwater, since fast groundwater head level rises are attributed to rainfall events.~~

~~(3) Due to different flow paths of groundwater along the stream, distinguished groundwater isotopic signatures can be found.~~

~~Exploring the spatio-temporal isotopic variations in precipitation, stream, soil, and groundwater will further help to establish a local meteoric water line and investigate the transformations from precipitation to soil and groundwater. Moreover, the effect of small-scale landscape characteristics such as topographic wetness index (TWI), distance to stream, and vegetation cover on soil water isotopic composition – as interface between precipitation and groundwater – will be examined for testing hypothesis (2).~~

To capture spatial landscape heterogeneity, but to keep data acquisition simple, stable water isotope data were coupled with hydrodynamic data from a previous study by Orlowski et al. (2014) in the developed Schwingbach catchment (Germany) to unravel water flow paths and interactions between different water cycle components. Results obtained through this earlier study imply that the Schwingbach catchment is highly responsive, indicated by fast runoff responses to precipitation inputs (Orlowski et al., 2014). Moreover, groundwater reacted almost as quickly as streamflow to precipitation events with raising head levels. Thus, the catchment exhibited “old water” paradox like behaviour (Kirchner, 2003). We further showed that streamflow was predominantly generated in the catchment headwater area and that gaining and losing stream reaches occurred in parallel along the studied stream affected by the underlying geology.

Thus, stable water isotopes in combination with hydrodynamic data of a two-year monitoring period (July 2011 to July 2013) were utilised to explore spatio-temporal isotopic variations, unravel linkages between the different water cycle components, investigate the transformations from precipitation to soil and groundwater, and analyse the effect of small-scale landscape characteristics (i.e. soil physical properties, topographic wetness index (TWI), distance to stream, and vegetation cover) on soil water isotopic composition. Further, stable water isotope data was utilized to estimate groundwater ages and flow directions in the Vollnkirchener Bach subcatchment via an hydrological model setup based on the findings of Orlowski et al. (2014).

2 Materials and methods

2.1 Study area

The research was carried out in the Schwingbach catchment (50°30'4.23"N, 8°33'2.82"E) (Germany) (Fig. 1a). The Schwingbach and its main tributary the Vollnkirchener Bach are low-mountainous creeks (Fig. ~~1~~1c) with an altered physical structure of the stream system (channelled stream reaches, pipes, drainage systems, fishponds). The whole Schwingbach catchment encompasses an area of 9.6 km^2, with an altitude range from 233–415 m a.s.l. The Vollnkirchener Bach tributary is about 4.7 km in length and drains a 3.7 km^2 subcatchment area (Fig. 1c), which ranges in elevation from 235–351 m a.s.l. Almost 46% of the overall Schwingbach catchment is forested, which slightly exceeds agricultural land use (35%) (Fig. ~~1a~~ 1c). Grassland (10%) is mainly distributed along streams and smaller meadow orchards are located around the villages. ~~The catchment encompasses an area of 9.6 km^2, with an altitude range from 233–415 m a.s.l. The Vollnkirchener Bach tributary is about 4.7 km in length and drains a 3.7 km^2 subcatchment area, which ranges in elevation from 235–351 m a.s.l (Fig. 1a).~~

~~The Schwingbach catchment is underlain by argillaceous shale in the northern parts, serving as aquicludes (Mazor, 2003). Graywacke zones with lydit in the central, as well as limestone, quartzite, and sandstone regions in the headwater area provide aquifers with large storage capacities (Marinos et al., 1997; Mazor, 2003) (Fig. 1d). Loess covers Paleozoic bedrock at north- and east bounded hillsides (Fig. 1c). Streambeds consists of sand and debris covered by~~

~~loam and some larger rocks (Lauer et al., 2013). Many downstream sections of both creeks are framed by armor stones (Orlowski et al., 2014). Figure 1c shows that the dominant soil types in the study area are Stagnosols (41%) and mostly forested Cambisols (38%). Stagnic Luvisols with thick loess layers are under agricultural use. The same is true for Regosol, Luvisols, and Anthrosols, which encompass an area of 7%. Gleysols are found predominantly under grassland sites along the creeks.~~

~~[Figure 1 near here]~~

~~The climate is classified as temperate with a mean annual temperature of 8.2 °C. An annual precipitation sum of 633 mm (for the hydrological year 1 November 2012–31 October 2013) was measured at the climate station at the catchment outlet (site 13, Fig. 1b). Discharge peaks from December to April (>114 L s~~$^{-1}$~~) and low flows occur from July until November. Significant snowmelt peaks were observed during December 2012 and February 2013. Furthermore, May 2013 was an exceptional wet month. Likewise, characterised by discharge >114 L s~~$^{-1}$~~. A more detailed description of runoff characteristics, especially for the Vollnkirchener Bach is given in Orlowski et al. (2014).~~

~~2.2 Monitoring network and water isotope sampling~~

~~The monitoring network consists of an automated weather station at the catchment outlet (Campbell Scientific Inc., AQ5, UK; equipped with a CR1000 data logger collecting air temperature at 2 m height, wind speed and direction, relative humidity, and solar radiation), three tipping buckets, and 15 precipitation collectors, six stream water sampling points, and 22 piezometers (Fig. 1 a–b). Precipitation data were corrected according to Xia (2006).~~

The Schwingbach main catchment is underlain by argillaceous shale in the northern parts, serving as aquicludes (Mazor, 2003). Graywacke zones with lydit in the central, as well as limestone, quartzite, and sandstone regions in the headwater area provide aquifers with large storage capacities (Choi, 1997; Mazor, 2003) (Fig. 1f). Loess covers Paleozoic bedrock at north- and east bounded hillsides (Fig. 1f). Streambeds consists of sand and debris covered by loam and some larger rocks (Lauer et al., 2013). Many downstream sections of both creeks are framed by armor stones (Orlowski et al., 2014). Figure 1e shows that the dominant soil types in the overall study area are Stagnosols (41%) and mostly forested Cambisols (38%). Stagnic Luvisols with thick loess layers are under agricultural use. The same is true for Regosol, Luvisols, and Anthrosols, which encompass an area of 7%. Gleysols are found predominantly under grassland sites along the creeks.

[Figure 1 near here]

The climate in the study area is classified as temperate with a mean annual temperature of 8.2°C. An annual precipitation sum of 633 mm (for the hydrological year 1 November 2012 to 31 October 2013) was measured at the catchment's climate station (site 13, Fig. 1b). The year 2012 to 2013 was an average hydrometeorological year. For comparison, the climate station Giessen/Wettenberg (25 km N of the catchment) operated by the German Meteorological Service (DWD, 2014) records a mean annual temperature of 9.6 °C and a mean annual precipitation sum of 666 ± 103 mm for the period 1980 to 2010. Discharge peaks from December to April (measured by the use of RBC-flumes with maximum peak flow of 114 L s^{-1}, Eijkelkamp Agrisearch Equipment, Giesbeek, NL) and low flows occur from July until November. Substantial snowmelt peaks were observed during December 2012 and February 2013. Furthermore, May 2013 was an exceptional wet month characterised by discharge of 2–3 mm d^{-1}. A more detailed description of runoff characteristics, especially for the Vollnkirchener Bach is given in a previous study by Orlowski et al. (2014).

2.2 Monitoring network and water isotope sampling

The monitoring network consists of an automated climate station (site 13, Fig. 1 b–c) (Campbell Scientific Inc., AQ5, UK; equipped with a CR1000 data logger collecting air temperature at 2 m height, wind speed and direction, relative humidity, and solar radiation), three tipping buckets, 15 precipitation collectors, six stream water sampling points, and 22 piezometers (Fig. 1 b–c). Precipitation data were corrected according to Xia (2006).

Two stream water sampling points (sites 13 and 18) in the Vollnkirchener Bach are installed with trapezium shaped RBC-flumes for gauging discharge (Eijkelkamp Agrisearch Equipment, Giesbeek, NL~~),~~) and a V-weir is located at sampling point 64. RBC-flumes and V-weir are equipped with Mini-Divers® (Eigenbrodt Inc. & Co. KG, Königsmoor, DE) for automatically recording water levels and deriving continuous discharge data through the given stage-discharge relationships ~~(Eijkelkamp, 2013).~~(Eijkelkamp, 2014). Discharge at the remaining stream sampling points was manually measured applying the salt dilution method (WTW-cond340i, WTW, Weilheim, DE), which can be precise to ±5% ~~(Day, 1976; Moore, 2004)~~(Day, 1976; Moore, 2004). The 22 piezometers (Fig. 1b) situated between the conjunction of the Schwingbach with the Vollnkirchener Bach and the upper RBC-flume of the Vollnkirchener Bach (site 18) are made from perforated PVC tubes sealed with a bentonite clay at the upper part of the tube to prevent contamination by surface water. For monitoring shallow groundwater levels, either combined water level/temperature loggers (Odyssey Data Flow System, Christchurch, NZ) or Mini-Diver® water level loggers (Eigenbrodt Inc. & Co. KG, Königsmoor, DE) are installed. Accuracy of Mini-Diver® is ±5 mm and for Odyssey data logger ±1 mm. For calibration purposes, groundwater levels are additionally measured manually via an electric contact gauge.

Stable water isotope samples of rainfall, stream-, and groundwater were taken over a two-year observation period (July 2011~~–~~ to July 2013) approximately on weekly intervals, except for the winter period. ~~Snow~~In winter 2012 to 2013, snow core samples over the entire snow depth of <0.15 m were ~~taken~~collected in ~~winter 2012–2013. Each precipitation~~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. Open rainfall was collected in self-constructed samplers. Each collector was made from a 1 L glass bottle prepared with a circular funnel of 0.10 m in diameter. Funnels were covered with a mosquito net to keep out leaves, insects, or windblown debris. Bottles were placed in PVC tubes to avoid heating, screwed to wooden pales, and installed 1 m above ground. To avoid sample evaporation, a table tennis ball was placed into each funnel and two layers of small plastic balls were inserted into the glass bottles (Windhorst et al., 2013).

Stream water samples were taken as grab samples at six locations – three sampling points at each stream (Vollnkirchener Bach sites: 13, 18, and 94; Schwingbach sites: 11, 19, and 64) (Fig. ~~1a–b~~1b–c). To account for possible spatial variation in groundwater, grab samples were collected from 17 piezometers (Fig. 1b). Since spatial variations between the piezometers under meadow was small, the amount of sampled piezometers was reduced to three sampling points under meadow (sites 1, 6, and 21), five under the arable field (sites 25–29), and four beside the Vollnkirchener Bach (sites 24, 31, 32, and 35). Additionally, a drainage pipe (site 15) located ~226 m downstream of site 18 was sampled. According to IAEA standard procedures, all samples were filled and stored in 2 mL brown glass vials~~ covered by silicone septa~~, sealed with a solid lid, and wrapped up with Parafilm® (Mook, 2001).

2.3 Isotopic soil sampling

2.3.1 Spatial variability

In order to analyse the effect of small-scale characteristics such as distance to stream, TWI, and land use on soil isotopic signatures as connecting compartment between precipitation and groundwater, we sampled a snapshot of 52 points evenly distributed over a 200 m grid around the Vollnkirchener Bach~~. Soil samples were taken at four consecutive rainless days (1–4 November 2011). The TWI was chosen as it combines topography and slope, which were assumed to have an impact on soil water isotopic signatures (Garvelmann et al., 2012).~~ (Fig. 1d). Soil samples were taken at four consecutive rainless days (1 to 4 November 2011) at altitudes of 235–294 m a.s.l.. ~~Distances to the stream are linked to water flow path lengths and were therefore supposed to be a controlling factor. Vegetation has already been proven to have an impact on soil water isotopes (Brodersen et al., 2000; Gat, 1996; Li et al., 2007), and hence was expected to be a controlling factor as well.~~

Sampling sites were selected via a stratified, GIS-based sampling plan (ArcGIS, Arc Map 10.2.1, Esri, California, USA), including three classes of topographic wetness indices (TWIs: 4.4–6.5; 6.5–7.7; 7.7–18.4), two different distances to stream (0–121 m, 121–250 m), and three land use units (arable land, forest, and grassland), with each class containing the same number of sampling points. Samples were collected at depths of 0.2 m and 0.5 m. Gravimetric water content was measured according to DIN-ISO 11465 by drying soils for 24 h at 110 °C. Soil pH was analysed following DIN-ISO 10390 on 1:1 soil-water-mixture with a handheld pH-meter (WTW cond340i, WTW Inc., DE). Bulk density was determined according to DIN-ISO 11272, and soil texture by finger testing (~~Brajendra et al., 2007; ~~Whitefield, 2004).

2.3.2 Seasonal isotope soil profiling and isotope analysis

In order to trace the seasonal development of stable water isotopes from rainfall to groundwater, seven soil profiles were taken in the dry summer season (28 August 2011), seven in the wet winter period (28 March 2013), and two profiles in the transitional season spring (~~14~~24 April 2013) under different vegetation cover (arable land and grassland) (Fig. 1d). Soil was sampled utilising a hand-auger (Eijkelkamp Agrisearch Equipment BV, Giesbeek, DE). Samples were taken from the soil surface to 2 m depth. Samples were collected in greater detail near the soil surface since this area is known to have the greatest isotopic variability ~~(Barnes and Allison, 1988; Hsieh et al., 1998; Zimmermann et al., 1968)~~(Barnes and Allison, 1988; Hsieh et al., 1998; Zimmermann et al., 1968).

Soil samples were stored in amber glass tubes, sealed with Parafilm®, and kept frozen until water extraction ~~(Orlowski et al., 2013). Soil water was extracted cryogenically with 180 min extraction duration, a vacuum threshold of 0.3 Pa, and an extraction temperature of 90°C. Isotopic signatures of~~ ~~δ^{18}O and δ^{2}H were analysed following the IAEA standard procedure (Newman et al., 2009) via off-axis integrated cavity output spectroscopy (OA-ICOS) (DLT-100, Los Gatos Research Inc., Mountain View, CA, USA). Isotopic ratios are reported in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW)~~ (Orlowski et al., 2013). 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 Orlowski et al. (2013). Isotopic signatures of δ^{18}O and δ^{2}H were analysed via off-axis integrated cavity output spectroscopy (OA-ICOS) (DLT-100, Los Gatos Research Inc., Mountain View, CA, USA). 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. Isotopic ratios are reported in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) (Craig, 1961b)~~:~~. Accuracy of analyses was 0.6‰ for δ^{2}H and 0.2‰ for δ^{18}O (LGR, 2013). 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 or correct such data.

~~$\delta^2H \ or \ \delta^{18}O = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000$ (1)~~

~~Here, R_{sample} and $R_{standard}$ are $^2H/^1H$ or $^{18}O/^{16}O$ ratios of the sample and standard, respectively. Accuracy of analyses was 0.6‰ for δ^2H and 0.2‰ for $\delta^{18}O$ (LGR, 2013).~~

2.4 Mean transit time estimation

To understand the connectivity between the different water cycle components in the Schwingbach catchment, the mean transit times (MTT) for the Vollnkirchner Bach (sites 13, 18, and 94) and the Schwingbach (sites 11, 19, and 64) were calculated using FlowPC (Małoszewski and Zuber, 1996). Different models (dispersion model with different dispersion parameters D_p = 0.05, 0.4, and 0.8, exponential model, exponential-piston-flow model, linear model, and linear-piston-flow model) were compared for their results (sigma as goodness of fit and model efficiencies (ME)). A model efficiency ME = 1 indicates an ideal fit of the model to the concentrations observed, while ME = 0 indicates that the model fits the data no better than a horizontal line through the mean concentration observed (Maloszewski and Zuber, 2002). The same is true for sigma.

For calculations with FlowPC, weekly averages of precipitation and stream water isotopic signatures were calculated. We also bias-corrected the precipitation input data with two different approaches: the mean precipitation value was subtracted from every single precipitation value and then divided by the standard deviation of precipitation isotopic signatures. Afterwards, this value was subtracted from the weekly precipitation values (bias1). For the second approach, the difference of the mean stream water isotopic value and the mean precipitation value was calculated and also subtracted from the weekly precipitation values (bias2).

2.5 Hydrological model setup

To estimate the age dynamics of the groundwater body in the Vollnkirchener Bach subcatchment, a hydrological model was established on the basis of the conceptual model presented by Orlowski et al. (2014). For this purpose the *Catchment Modelling Framework* (CMF) by Kraft et al. (2011) was used. CMF is a modular framework for hydrological modelling based on the concept of finite volume method by Qu and Duffy (2007). CMF is applicable for simulating one- to three-dimensional water fluxes but also advective transport of stable water isotopes (^{18}O and ^{2}H). Thus, it is especially suitable for our tracer study and can be used to study the origin (Windhorst et al., 2014) and age of water.

The generated model is a highly simplified representation of the Vollnkirchener Bach subcatchment's groundwater body. The subcatchment is divided into 353 polygonal shaped cells ranging from 101.7–38940.1 m², manually adjusted on the basis of land use, soil types, and contour lines following Qu and Duffy (2007) and Windhorst et al. (2014). Each cell contains two layers, one comprises a water storage. The upper layer, representing the groundwater body, is generated based on soil depth measurements and reaches down to 20 m below the surface. Due to the fact that groundwater depth was not measured, the layer-thickness is a rough estimation. The second layer (20–40 m below the surface) represents the bedrock. The main fresh water input is the groundwater recharge, which is a constant value over time for each cell. It is calculated as the difference between rainfall, evapotranspiration, and the change in stored water. Precipitation and evapotranspiration values are calculated using a fully distributed 3D model established through CMF with a one year simulation period of the same subcatchment. The change in stored water is set to zero since a steady state is simulated (see below) and therefore the water content in the system is stable.

Besides the groundwater recharge, a combined sewer overflow (site 38) is considered as an additional water input based on findings of Orlowski et al. (2014). Moreover, there are two water outlets in the two lowest cells for efficient draining. Both cells are located in the very north of the subcatchment. The compartments within the system are linked by a series of flow-accounting equations: Richards equation for percolation, Darcy equation for lateral subsurface flow, Neumann boundary condition for input of fresh water (groundwater recharge, pipe source), and constant Dirichlet boundary conditions representing the system outlets.

For estimating the groundwater age, a virtual tracer is used. It is modelled as a radioactive decay tracer with a fixed concentration at the input to the system. From the modelled concentration of the tracer in each cell, the mean age of the water for this cell is derived.

Model assumptions: The saturated hydraulic conductivity of the groundwater body is set to 0.1007 m d^{-1}, as measured in the study area. For the bedrock compartment there is no data available. However, expecting a high rate of joints, preliminary testing revealed that a saturated hydraulic conductivity of 0.25 m d^{-1} seemed to be a realistic estimation (based on field measurements).

~~2.4~~2.6 Statistical analyses

For statistical analyses, we used IBM SPSS Statistics (Version 22, SPSS Inc., Chicago, IL, US~~).~~) and R (version Rx64 3.2.2). The R package igraph was utilized for plotting (Csardi and Nepusz, 2006). Studying temporal and spatial variations in meteoric and groundwater, isotope data were tested for normal distribution. Subsequently, t-tests or Multivariate Analyses of Variances (MANOVAs) were applied and Tukey-HSD tests were run to determine which groups were significantly different ($p \leq 0.05$). Event mean values of isotopes in precipitation, stream, and groundwater were calculated when no spatial variation was observed.

~~For comparisons, precipitation isotope data from the closest GNIP (Global Network of Isotopes in Precipitation) station Koblenz (DE; 73.8 km SW of the study area, 97 m a.s.l) was used (IAEA, 2014). For monthly mean calculations, e.g. monthly d-excess values of the GNIP station Koblenz and its comparison to the Schwingbach event mean d-excess; the utilised data set comprises 24 values starting from July 2003–July 2005. For the calculation of the LMWL of Koblenz, the complete available GNIP data set was used (monthly means from 1 March 1981–1 December 2005; N = 294 values).~~

We used a topology inference network map (Kolaczyk, 2014) in combination with a principal component analysis (Jolliffe, 2002) to show δ^{18}O isotope relationships between surface and groundwater sampling points. To explore the sensitivity of missing data, we used both the complete isotope time series and randomly selected 80% of the whole data sets. Overall, the cluster relationships of the surface and groundwater sampling points are largely similar for both whole and subsets of isotope data sets, despite some differences of the exact cluster centroid locations. We therefore decided to use randomly selected 80% of the isotope time series to illustrate our results. In the network map, each node of the network represents an isotope sampling point. The locations of the nodes are based on the first two components (PC1 and PC2). The correlations between isotope time series are represented by the edges connecting nodes. The thickness of edges characterizes the strength of the correlations. The p-values of correlations are approximated by using the F-distributions and mid-ranks are used for the ties (Hollander et al., 2013). Only statistically significant connections ($p<0.05$) are shown in the network diagram. Basic background information related to graph theory can be found in Wallis (2007).

For comparisons, precipitation isotope data from the closest GNIP (Global Network of Isotopes in Precipitation) station Koblenz (DE; 73.8 km SW of the study area, 97 m a.s.l) was used (IAEA, 2014; Stumpp et al., 2014). 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.

3 Results ~~and discussion~~

Descriptive statistics of isotopic composition in precipitation, stream-, and groundwater are shown along with d-excess values in Table 1 and are described in detail in the following:

[Table 1 near here]

3.1 ~~Isotopes~~Variations of precipitation isotopes and d-excess

The δ^2H values of all precipitation isotope samples (N = 592) taken throughout the observation period (July 2011 ~~– July 2013) ranged from −167.6 to −8.3‰. To examine the spatial isotopic variation in precipitation, open rainfall was collected at 15 locations throughout the Schwingbach main catchment (Fig. 1a–b) for a 7-month period. Mook et al. (1974) observed for north-western Europe that the δ^{18}O values of precipitation collected over periods of 8 and 24 h from three locations within 6 km^2 at the same altitude were consistent within 0.3‰ (Gat et al., 2001). Likewise~~ to July 2013) ranged from −167.6 to −8.3‰. To examine the spatial isotopic variation, rainfall was collected at 15 open field site locations throughout the Schwingbach main catchment (Fig. 1b–c) for a 7-month period. However, no spatial variation could be observed in the Schwingbach catchment. Thus, rainfall was collected at the catchment outlet (site 13) from 23 October 2014 onward and event mean δ-values were calculated for the previous isotope data.

Analysing effects that influence the isotopic composition of precipitation, neither an amount effect nor an altitude effect was found – not surprisingly, as the greatest altitudinal difference between sampling points was only 101 m. Nevertheless, a slight temperature effect

(R^2 = 0.~~54~~5 for δ^{2}H and R^2 = 0.~~61~~6 for δ^{18}O, respectively) was observed showing enriched isotopic signatures at higher temperatures~~ (Fig. 2).~~.

~~[Figure 2 near here]~~

~~The linear relationship between air temperature (T in °C) and δ^{18}O values in precipitation at the Schwingbach catchment δ^{18}O = 0.44T−12.05‰ compares reasonably well with a correlation reported by Yurtsever (1975) based on north Atlantic and European stations from the GNIP network δ^{18}O = (0.521±0.014)T−(14.96±0.21)‰. Rozanski et al. (1982) calculated δ^{2}H = (2.4±0.3)T−(80.5±4.2)‰ (R^2 = 0.89) at the GNIP station Stuttgart, which is located 196 km South of the Schwingbach study area. This relationship is likewise similar to the correlation found for the Schwingbach catchment (Fig. 2). However, 53% of the events were sampled at daily mean temperatures >10°C, resulting in a slight overrepresentation of values measured at warmer temperatures. Nevertheless, such a correspondence between the degree of isotope depletion and the temperature reflects the influence of the temperature effect in the catchment, which mainly appears in continental, middle high latitudes (Jouzel et al., 1997; Wu et al., 2012). Furthermore, the correlation between δ^{2}H in monthly precipitations and local surface air temperature becomes increasingly stronger towards the centre of the continent (Rozanski et al., 1982).~~

Strong temporal variations in precipitation isotopic signatures, as well as pronounced seasonal isotopic effects were measured with greatest isotopic differences occurring between summer and winter. Samples taken in the fall and spring were isotopically similar, however, differed from winter isotopic signature, which were somewhat lighter (Fig. ~~3~~2). Furthermore, in the winter of 2012–13 snow could be sampled, which decreased the mean winter isotopic values for this period in comparison to the previous winter period (2011–12). No statistically significant ($p>0.05$) inter-annual variation was detected between the summer periods of 2011 and 2012 (Fig. ~~3~~2), which could have reflected varying local climate conditions (Koeniger et al., 2009).

[Figure 2 near here]

Examining the influence of moisture recycling on the isotopic compositions of precipitation, the deuterium-excess (d-excess) was calculated for each individual rain event at the Schwingbach catchment. For the two-year observation period, d-excess values (N = 108) ranged from –7.8‰ to +19.4‰ and averaged +7.1‰ (Fig. 2). In general, 37% of all events were sampled in summer periods (21 June to 21/22 September) and showed lower d-excess values in comparison to the 19% winter precipitation events (21/22 December to 19/20 March) (Fig. 2). D-excess greater than +10‰ was determined for 22% of all events. As a reference the d-excess of the GMWL d = 10 is depicted in Figure 2 (solid line). Lowest values corresponded to summer precipitation events with evaporation of the raindrops below the cloud base at mean daily air temperatures between 12–18°C. Most of the higher values (>+10‰) appeared in cold seasons (fall/winter) and winter snow samples of the Schwingbach catchment with very depleted δ-values showed highest d-excess values (Fig. 2).

In comparison with the GNIP station Koblenz (years 2011–2013), the mean annual d-excess at the Schwingbach catchment was on average 3.9‰ higher (7.1‰ for 2011–12 and 2012–13, respectively), showing a greater impact of oceanic moisture sources than the further south-west located station Koblenz. The unweighted mean annual d-excess at the GNIP station Koblenz was 2.9‰ for July 2011 to June 2012 and 3.6‰ for July 2012 to June 2013, whereas the long-term mean was 4.4‰ (1978–2009) (Stumpp et al., 2014). Nevertheless, highest d-excesses at the GNIP station matched highest values in the Schwingbach catchment, both occurring in the cold seasons (October to December 2011 and November to December 2012). Since no amount effect on the δ^2H and δ^{18}O values was observed in the Schwingbach, also no linear regression of event d-excess with precipitation amount was detected.

The linear relationship of δ^2H and δ^{18}O content in local precipitation, results in a local meteoric water line (LMWL) (Fig. 3), which can be utilised to link the relative contribution of seasonal precipitation to ground and surface water sources (Wassenaar et al., 2011). The global meteoric water line (GMWL) established by Craig (1961a), and more recently refined by Rozanski et al. (1993) is $\delta^2\text{H} = 8.13 \times \delta^{18}\text{O}+10.8$ ‰, provides a valuable benchmark against which regional or local waters can be compared (Song et al., 2011). The slope of the LMWL of the Schwingbach catchment is well in agreement with the one from the closest GNIP station in Koblenz ($\delta^2\text{H} = 7.66 \times \delta^{18}\text{O} + 2.0$ ‰; $R^2 = 0.97$; 1978–2009 (Stumpp et al., 2014)), but is slightly lower in comparison to the revised GMWL, showing stronger local evaporation conditions. Since evaporation causes a differential increase in δ^2H and δ^{18}O values of the remaining water, the slope for the linear relationship between δ^{2}H and δ^{18}O is lower in comparison to the GMWL (Rozanski et al., 2001; Wu et al., 2012). The lower intercept (d-excess), dependent on the humidity and temperature conditions in the evaporation region (Mook, 2001), nevertheless shows that moisture recycling did obviously not play a major role in the study area.

[Figure 3 near here]

Considering isotope samples of the different water cycle components in comparison with the LMWL revealed that mean isotope values of snow samples were for δ^{2}H approximately 84‰ lighter that mean precipitation isotopic signatures (Fig. 3). Stream water isotope samples of both creeks (Schwingbach and Vollnkirchener Bach) fell on the LMWL, showing slight evaporative enrichment for few samples (Fig. 3). Moreover, isotopic values for stream water were almost identical to those found in groundwater (Table 1, Fig. 3).

3.2 Isotopes of soil water

3.2.1 Spatial variability

Determining the impact of landscape characteristics on soil water isotopic signatures, we found no relationship between the parameters distance to stream, TWI, soil water content, soil texture, pH, and bulk density with the soil isotopic signatures in two depths (0.2 and 0.5 m), except for land use. This was potentially attributed to the small variation in soil textures (mainly clayey silts and loamy sandy silts), bulk densities, and pH values for both soil depths (Table 2). Water contents showed the greatest standard deviation within the two soil depths (Table 2), however, exhibited no effect on soil water isotopes. Moreover, no tendency of higher TWI values with decreasing distance to stream was obvious. Distances to the stream are linked to water flow path lengths and were therefore supposed to be a controlling factor. However, no impact of different distances to the stream on soil water isotopic signatures could be observed.

[Table 2 near here]

The mean δ-values in the top 0.2 m of the soil profile is higher than further below, reflecting a stronger impact of precipitation in the topsoil (Table 2, Fig. 4). The δ-values of top soil and precipitation did not vary significantly statistically ($p>0.05$), which is not the case for precipitation and subsoil (Fig. 4). Subsoil isotopic values were statistically equal to stream and groundwater isotopic values (Fig. 4).

[Figure 4 near here]

Generally, all soil water isotopic values fell on the local meteoric water line, indicating no evaporative enrichment of soil water (Fig. 5). Comparing soil isotopic signatures between different land covers showed generally higher and statistically significantly different δ-values ($p \leq 0.05$) at 0.2 m soil depth under arable land as compared to forests and grasslands. However, all top soil isotopic values reflected precipitation isotopic signals (Fig. 5, top). For the lower 0.5 m of the soil column, isotopic signatures under all land use units showed statistically similar values; nevertheless, differing significantly from precipitation ($p \leq 0.05$) (Fig. 5, bottom).

[Figure 5 near here]

Comparing soil water δ^2H values between top and subsoil under different land use units showed significant differences ($p \leq 0.05$) under arable and grassland but not under forested sites (Fig. 5, capital letters).

3.2.2 Seasonal isotope soil profiling

Isotope compositions of soil water varied seasonally: More depleted soil water was found in the winter and spring (Fig. 6); contrary, soil water was enriched in summer due to evaporation during warmer and drier periods (Darling, 2004). For summer soil profiles in the Vollnkirchener subcatchment, no evidence for evaporation was obvious below 0.4 m soil depth. However, snowmelt isotopic signatures could be traced down to a soil depth of 0.9 m during spring rather than winter, pointing to a depth-translocation of meltwater in the soil, more remarkable for the deeper profile under arable land (Fig. 6, upper left panel). Furthermore, shallow soil water (<0.4 m) showed larger standard deviations with values closer to mean seasonal precipitation inputs (Fig. 6, upper panels). Winter profiles exhibited somewhat greater standard deviations in comparison to summer isotopic soil profiles. The observed seasonal amplitude smoothed out with depth as soil water isotope signals approached groundwater average. Generally, deeper soil water isotope values were relatively constant through time and space.

[Figure 6 near here]

3.3 Isotopes of stream water

Analysing spatial differences in isotopic compositions between Schwingbach (sites 11, 19, and 64) and Vollnkirchener Bach (sites 13, 18, and 94) stream water resulted in no statistically significant differences for all sampling points (Fig. 7). In general, δ^{18}O values varied for the Vollnkirchener Bach by −8.4±0.4‰ and for the Schwingbach by −8.4±0.6‰ over the two-year observation period (Table 1).

[Figure 7 near here]

Stream water isotopic signatures in the Schwingbach catchment were by approximately −15‰ in δ^{2}H more depleted than precipitation signatures (Table 1). However, surface water isotopic compositions were similar to groundwaters (Table 1).

Examining temporal isotopic variations, damped seasonality (less variation) of the isotope concentration in stream water in comparison to precipitation was measured with main seasonal differences occurring between summer and winter periods (Fig. 7). Most outlying depleted stream water isotopic signatures (e.g. in March 2012 and 2013) could be explained by snowmelt (Fig. 7). However, the outlier at the Schwingbach stream water sampling site 64 (−66.7‰ for δ^{2}H) is by 8.5‰ more depleted than the two-year average of Schwingbach stream water (Table 1). Rainfall falling on 24 September 2012 was −31.9‰ for δ^2H. 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 δ^2H) 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^{-1} and a 2.9 mm 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 δ-values (−43.9±23.4).

Calculated MTT for the Schwingbach ranged between 52 and 67 weeks and for the Vollnkirchener Bach between 47 and 66 weeks, whereby linear and exponential models provided the best fits for all sampling points. However, the calculated output data did not fit the observed values in terms of the quality criterion sigma and model efficiency (Timbe et al., 2014). Model efficiencies for the Schwingbach sampling points were −0.1–0.0 and for the Vollnkirchener Bach 0.0–0.4. Sigma values for all sampling points were 0.1 for the best fit models, respectively. Even a bias correction of the input data (precipitation) did not improve the model outputs (sigma = 0.1). Therefore, we conclude that the application of MTT estimation methods based on stable water isotopes failed in the Schwingbach catchment and developed a new data-driven groundwater model to simulate observed stable water isotope data.

3.4 Isotopes of groundwater

Since groundwater head levels responded almost as quickly as streamflow to rainfall events, rainfall isotopic signatures were assumed to be rapidly transferred to the groundwater. This was likewise underlined by the fact that Orlowski et al. (2014) observed bidirectional water interactions between the groundwater body and the stream. Studying groundwater isotopic signatures at the downstream section of the Vollnkirchener Bach, almost constant isotopic values (Fig. 8, Table 1) throughout the study period were observed (δ^2H: −57.6±1.6‰ for piezometers under meadow). Most depleted groundwater isotopic values (<−80‰ for δ^2H) were measured for piezometer 32 during snowmelt events in March and April 2013 as well as for piezometer 27 from December 2012 to February 2013. As shown by Orlowski et al. (2014) piezometer 32 is highly responsive to rainfall-runoff events and groundwater head elevations showed significant correlations with mean daily discharge at this site. Further, effluent conditions and lowest K_{sat} values (7–14 mm h^{-1}) were measured in this stream section (piezometers 32–35) (Orlowski et al., 2014).

In the Schwingbach catchment, groundwater under meadow differed from mean precipitation values by about –14‰ for δ^2H showing no evidence of a rapid transfer of rainfall isotopic signatures to the groundwater.

[Figure 8 near here]

Due to different water flow paths of groundwater along the studied stream, distinguished groundwater isotopic signatures were assumed to be found. In fact, we could identify spatial statistical differences between grassland and arable land groundwater isotopic signatures (Fig. 9). Groundwater isotopic signatures under arable land (sites: 25–29, Fig. 1b) showed more enriched values (Fig. 8) and showed significant correlations ($p<0.05$) among each other (Fig. 9). Arable land groundwater plotted furthest away from surface water sampling points in our network map, showing no significant correlations to either the Schwingbach or the Vollnkirchener Bach. This hydrological disconnectivity was already observed in the study of Orlowski et al. (2014). In general, $\delta^{18}O$ time series of piezometers along the stream and under the meadow showed close relations to surface water sampling points (Fig. 9). We further found high correlations ($R^2>0.6$) of $\delta^{18}O$ time series of piezometers located under the meadow (sites: 3, 6, and 21) among each other. Additionally, $\delta^{18}O$ values of piezometer 3 correlated significantly ($p<0.05$) with surface water sampling points 18 and 94 ($R^2=0.6$ and 0.8, respectively) and piezometer 32 with sampling points 13 and 64 ($R^2=0.8$ and 0.6, respectively).

[Figure 9 near here]

We further observed close relations ($p<0.05$) among $\delta^{18}O$ values of Vollnkirchener Bach sampling sites 13, 18, and 94 as well as of Schwingbach sites 11, 19, and 64 along with correlations between each other.

3.4.1 Modelled groundwater age

Since MTT calculations failed, we modelled the groundwater age in the Vollnkirchener Bach subcatchment using CMF, involving observed hydrometric as well as stable water isotope data (Fig. 10).

[Figure 10 near here]

The maximum age of water is highly variable throughout the subcatchment, which results in a very heterogeneous spatial age distribution. The groundwater in most of the outer cells is very young (0–10 years), whereas the inner cells, which incorporate the Vollnkirchner Bach, contain older water (>30 years). The oldest water (≥55 years) can be found in the Northern part of the catchment (Fig. 10, detail view), where the Vollnkirchner Bach drains into the Schwingbach. The main outlets of the subcatchment (dark red coloured cell and green cell) even reach an age of 100 and 55 years, respectively. This can be explained by the fact that these are the lowest cells within the subcatchment. Thus, water flows from the higher to the lower cells and water from the whole subcatchment accumulates at these cells. The overall flow path to these cells is the longest and as a consequence the groundwater age of these cells is the highest.

In general, six cells contain groundwater that is older than 50 years (1.7% of cells), and two cells reveal ages >70 years (0.6%). In contrast, 47 cells (13.3%) contain water with an age of less than one year and 52.4% with an age <15 years. Thus, most of the cells contain young to moderately old water (<15 years), while few cells comprise old water (>50 years). The average groundwater age in the Vollnkirchener Bach subcatchment is 16 years. Relating the groundwater age to the distance to the stream, we found a linear correlation ($R^2 = 0.3$) with a distinct trend: The water tends to be younger with greater distance to the stream.

The modelled main flow direction is towards the Vollnkirchener Bach (Fig. 10). The amount of flowing water depicted by the length of the arrows is generally higher near the stream, whereas in most of the outer cells the amount of water is very low (Fig. 10).

4 Discussion

4.1 Variations of precipitation isotopes and d-excess

Analysing effects that influence the precipitation isotopic composition, no spatial variation in precipitation isotopes was observed throughout the Schwingbach catchment. Mook et al. (1974) also observed for north-western Europe that precipitation collected over periods of 8 and 24 h from three different locations within 6 km^2 at the same altitude were consistent within 0.3‰ for $\delta^{18}O$. Further, no amount or altitude effect for isotopes in precipitation was found. However, the observed linear relationship ($\delta^{18}O = 0.44T-12.05‰$) between air temperature and precipitation $\delta^{18}O$ values compares reasonably well with a correlation reported by Yurtsever (1975) based on north Atlantic and European stations from the GNIP network $\delta^{18}O = (0.521 \pm 0.014)T-(14.96 \pm 0.21)‰$. ~~Inter-seasonal differences were mainly~~Rozanski et al. (1982) calculated $\delta^2H = (2.4 \pm 0.3)T-(80.5 \pm 4.2)‰$ ($R^2 = 0.89$) at the GNIP station Stuttgart, which is located 196 km South of the Schwingbach study area. This relationship is similar to the correlation found for the Schwingbach catchment. Stumpp et al. (2014) analysed long-term precipitation data from meteorological stations across Germany and found that 23 out of 24 tested stations showed a positive long-term temperature trend over time, whereas the precipitation amount was not a key factor for explaining isotope distributions or average values in German precipitation. The temperature–isotope relationship was likewise strongly influenced by seasonality (Stumpp et al., 2014). For the Schwingbach catchment, 53% of the events were sampled at mean daily temperatures >10°C, resulting in a slight overrepresentation of values measured at warmer temperatures. Nevertheless, the observed correspondence between the degree of isotope depletion and the temperature reflects the influence of the temperature effect in the Schwingbach catchment, which mainly appears in continental, middle–high latitudes (Jouzel et al., 1997; Wu et al., 2012). Furthermore, the correlation between δ^2H in monthly precipitations and local surface air temperature becomes increasingly stronger towards the centre of the continent (Rozanski et al., 1982).

Thus, the observed inter-seasonal differences in precipitation δ-values in the Schwingbach catchment could mainly be attributed to seasonal differences in air temperature and water vapour and their effect on evaporation ~~(Schürch et al., 2003) and the presence of snow in the winter of 2012–13 (Fig. 3~~(Schürch et al., 2003) and the presence of snow in the winter of 2012–13 (Fig. 2). This observation is well in agreement with ~~Gat et al. (2001)~~Gat et al. (2001) who stated that for temperate climates the $\delta^{18}O$ values generally do not vary by more than 1‰

inter-annually, and a large part of the spread is caused by variations in the average annual temperature. Moreover, the interior of the continent is obviously far more stable with regard to isotopic inputs than areas under greater influence of ~~the~~ Atlantic weather patterns. Perhaps in view of this stability, only few isotope data are available for this region, apart from the general GNIP-maps ~~(Bowen and Wilkinson, 2002; Darling, 2004; IAEA, 2014), for which this work contributes some~~(Bowen and Wilkinson, 2002; Darling, 2004; IAEA, 2014) and recent work (Stumpp et al., 2014), for which this work contributes valuable information.

Considering d-excess values, it is well-known that precipitation events originating from oceanic moisture show d-excess values close to +10‰ (Craig, 1961a; Dansgaard, 1964; Wu et al., 2012) and one of the main sources for precipitation in Germany is moisture from the Atlantic Ocean (Stumpp et al., 2014). Lowest values corresponded to summer precipitation events with evaporation of the raindrops below the cloud base at mean daily air temperatures between 12–18°C. Same observations were made by

~~[Figure 3 near here]~~

~~**Deuterium excess**~~Rozanski et al. (1982) for European GNIP stations. Accordingly, even more negative summer d-excess values were measured at air temperatures around 26–27°C for a study site in Greece (Argiriou and Lykoudis, 2006). Most of the higher values measured in the Schwingbach catchment (>+10‰) appeared in cold seasons (fall/winter) (Fig. 2), similar to d-excess values observed by Wu et al. (2012) for a continental, semi-arid study area in Inner Mongolia (China). Winter snow samples of the Schwingbach catchment with very depleted δ-values showed highest d-excess values, which was again well in agreement with results of Rozanski et al. (1982) for European GNIP stations. Continental precipitation events originating from oceanic moisture can approach d-excess values of +10‰ (Wu et al., 2012) (Fig. 2, solid line). Air mass trajectories at intercontinental, southern and eastern regions are suggested to be more stable with less variable moisture sources in these regions compared to sites near the coast (Stumpp et al., 2014). Therefore, rainout histories on the continent itself are more stable (Stumpp et al., 2014). The observed differences in d-excess values between the Schwingbach catchment and the GNIP station Koblenz can be attributed to differences in elevation range and the different regional climatic settings at both sites (Koblenz is located in the relatively warmer Rhine river valley). Further, no amount effect on d-excess could be determined for the Schwingbach catchment, which generally occurs most likely in the tropics

(Bony et al., 2008) or for intense convective rain events (Gat et al., 2001) at monsoon-dominated sites (Risi et al., 2008).

~~3.1.1~~

~~Examining the influence of moisture recycling on the isotopic compositions of precipitation, the deuterium-excess (d-excess) was calculated for each individual rain event at the Schwingbach catchment. For the two-year observation period, d-excess values (N = 108) ranged from −7.8‰ to +19.4‰ and averaged +7.1‰ (Fig. 3). In general, 37% of all events were sampled in summer periods (21 June–21/22 September) and showed lower d-excess values in comparison to the 19% winter precipitation events (21/22 December–19/20 March) (Fig. 3). D-excesses greater than +10‰ were determined for 22% of all events. It is well-known that d-excess values for precipitation events originating from oceanic moisture are close to +10‰ (Craig, 1961a; Dansgaard, 1964; Wu et al., 2012). As a reference the d-excess of the GMWL d = 10 is depicted in Figure 3 (dashed line).~~

~~Lowest values corresponded to summer precipitation events with evaporation of the raindrops below the cloud base at mean daily air temperatures between 12–18°C. Same observations were made by Rozanski et al. (1982) for European GNIP stations. Accordingly, even more negative summer d-excess values were measured at air temperatures around 26–27°C for a study site in Greece (Argiriou and Lykoudis, 2006).~~

~~Most of the higher values (>+10‰) appeared in cold seasons (fall/winter) (Fig. 3) similar to d-excess values observed by Wu et al. (2012) for a continental, semi-arid study area in Inner Mongolia (China). Winter snow samples of the Schwingbach catchment with very depleted δ-values showed highest d-excess values, which was again well in agreement with results of Rozanski et al. (1982) for European GNIP stations.~~

~~In comparison with the GNIP station Koblenz, the mean annual d-excess at the Schwingbach catchment was almost 5‰ higher (7.1‰ for 2011–12 and 2012–13, respectively), showing a greater impact of oceanic moisture sources than station Koblenz. Continental precipitation events originating from oceanic moisture can approach d-excess values of +10‰ (Wu et al., 2012) (Fig. 3, dashed line). Mean annual d-excess at the GNIP station Koblenz was 3.1‰ for 2003–2004 and 2.4‰ for 2004–2005. Nevertheless, highest d-excesses at the GNIP station matched highest values in the Schwingbach catchment, both occurring in the cold season. Differences in d-excess values between the Schwingbach catchment and the GNIP station~~

~~Koblenz can be attributed to the fact that different observation periods were considered and likewise different climatic settings.~~

~~An amount effect on the d-excess has most likely been detected in the tropics (Bony et al., 2008) or for intense convective rain events (Gat et al., 2001) at monsoon-dominated sites (Risi et al., 2008). Since no amount effect on the δ^{2}H and δ^{18}O values was observed in the Schwingbach, also no linear regression of event d-excess with precipitation amount was detected.~~

~~3.2~~4.2 Isotopes of ~~stream~~soil water

~~In order to prove hypothesis (1) stream water isotope data were examined for their spatio-temporal variation. Analysing spatial differences in isotopic compositions between Schwingbach (sites 11, 19, and 64) and Vollnkirchener Bach (sites 13, 18, and 94) stream water resulted in no statistically significant differences for all sampling points (Fig. 4). Examining temporal isotopic variations, damped seasonality (less variation) of the isotope concentration in stream water in comparison to precipitation was measured with main seasonal differences occurring between summer and winter periods (Fig. 4). There was no evidence of rainfall affected stream water isotopic signatures throughout the two-year study period (Fig. 4) leading to the rejection of hypothesis (1). However, outlying depleted stream water isotopic signatures (e.g. in March 2012 and 2013) especially at site 64 can be explained by snowmelt (Fig. 4). In general, δ^{18}O values varied for the Vollnkirchener Bach by −8.4±0.4‰ and for the Schwingbach by −8.4±0.6‰ over the two-year observation period (Table 1). Schürch et al. (2003) likewise observed damped river water isotopic signatures as compared with precipitation isotopic signatures for sampling points of the "Swiss National Network for the Observation of Isotopes in the Water Cycle". For larger rivers like the Elbe at Torgau in eastern Germany seasonal isotopic composition varied with an amplitude of 1.5‰ in δ^{18}O (Darling, 2004).~~

~~[Figure 4 near here]~~

~~Stream water isotopic signatures in the Schwingbach catchment were by approximately −15‰ in δ^{2}H more depleted than precipitation signatures (Table 1). However, surface water~~

~~isotopic compositions were similar to groundwaters (Table 1), assuming that groundwater predominantly feeds baseflow. Even during peak flow occurring in January 2012, December–April or May 2013, rainfall input does not play a major role for stream water isotopic composition although fast rainfall-runoff behaviours were observed by Orlowski et al. (2014).~~

~~In conclusion, stream water isotopic time series of the Vollnkirchener Bach and Schwingbach showed (with few exceptions) little deflections through time and, consequently, provided little insight into time and source-components connectivity. Klaus et al. (2014) likewise had difficulties to apply traditional methods of isotope hydrology (mean transit time 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). However, little information is available for developed low-angle catchments so far. Furthermore, our and their isotope time series did not yield a meaningful transit time estimation (results not shown), suggesting that transit times are longer than the range used for stable water isotopes, likely >5 years (Klaus et al., 2014).~~

~~3.31.1 Isotopes of groundwater~~

~~Since groundwater head levels responded almost as quickly as streamflow to rainfall events, rainfall isotopic signatures were assumed to be rapidly transferred to the groundwater. This hypothesis (2) was likewise underlined by the fact that Orlowski et al. (2014) observed bidirectional water interactions between the groundwater body and the stream. Studying groundwater isotopic signatures at the downstream section of the Vollnkirchener Bach, almost constant isotopic values (Fig. 5, Table 1) throughout the study period were observed (δ^2H: −57.58±1.6‰ for piezometers under meadow). Most depleted groundwater isotopic values (<−80‰ for δ^2H) were measured for piezometer 32 during snowmelt events in March and April 2013. Meltwater is known to be depleted in stable isotopes as compared to the annual mean of precipitation or groundwater (Kendall and McDonnell, 1998). In the Schwingbach catchment, groundwater under meadow differed from mean precipitation values by about −14‰ for δ^2H showing no evidence of a rapid transfer of rainfall isotopic signatures to the groundwater. As groundwater isotopic values are less variable through time, they rather seemed to be a mixture of former lighter precipitation events and snowmelt. We therefore assume that groundwater is mainly recharged throughout the winter. Likewise, O'Driscoll et al. (2005) showed that summer precipitation does not significantly contribute to recharge in the Spring Creek watershed of central Pennsylvania (USA) since δ^{18}O values in summer~~

~~precipitation were enriched compared to mean annual groundwater composition. The hypothesis (2) of a quick transfer of recent rainfall isotopic signatures to the groundwater could therefore be falsified.~~

~~[Figure 5 near here]~~

~~Due to different water flow paths of groundwater along the studied stream distinguished groundwater isotopic signatures were hypothesised (3) to be found. In fact, we could identify spatial statistical differences between grassland and arable land groundwater isotopic signatures. Groundwater isotopic signatures under arable land (sites: 25–29, Fig. 1b) showed more enriched values (Fig. 6). Isotopic signatures within piezometers under arable land varied among themselves, indicating hydrological disconnectivity between each other and the Vollnkirchener Bach as already stated by Orlowski et al. (2014). In contrast, the δ^2H and δ^{18}O values of the piezometers located beside the Vollnkirchener Bach (sites: 24, 31, 32, and 35) were statistically similar to the mean groundwater isotopic composition measured under meadow (sites: 3, 6, and 21). Moreover, groundwater isotopes under meadow were in close relation to stream water isotopes (Table 1). Orlowski et al. (2014) showed that influent and effluent conditions occurred simultaneously at different stream sections of the Vollnkirchener Bach affecting stream and groundwater isotopic compositions, likewise. Since groundwater head levels in the Vollnkirchener Bach subcatchment closely followed stream runoff-dynamics and responded to stormflow events with rising head levels (Fig. 5), we conclude that bidirectional water exchange between the groundwater body and the Vollnkirchener Bach occurred. However, both water compartments differed significantly from rainfall isotopic signatures (Table 1).~~

~~Nevertheless, δ-values of piezometer 32 showed statistically highest variation around the mean (Fig. 6), which is attributable to the influence of snowmelt that could only be detected for this piezometer (Fig. 5). As groundwater at the observed piezometers in the Vollnkirchener subcatchment is shallow (Orlowski et al., 2014), the snowmelt signal is allowed to move rapidly through the soil. Pulses of snowmelt water causing a depletion in spring and early summer was likewise observed by other studies (Darling, 2004; Kendall and McDonnell, 1998; Kortelainen and Karhu, 2004).~~

~~[Figure 6 near here]~~

~~3.4 Isotopes of soil water~~

~~3.4.1~~4.2.1 Spatial variability

~~Since soil water represents the interface~~Determining potential relationships between ~~precipitation and groundwater, we did a snapshot soil sampling on four consecutive rainless days (1–4 November 2011) with additional information on~~small-scale characteristics such as distance to stream, TWI, and land use~~, soil water content, soil texture, pH, and bulk density in the Vollnkirchener Bach subcatchment contributing to test hypothesis (2).~~

~~Determining the impact of landscape characteristics~~ on soil ~~water~~ isotopic signatures, ~~we found no relationship between the above-mentioned soil parameters with the soil isotopic signatures in two depths (0.2 and 0.5 m), except for land use. This was potentially attributed to the small variation in soil textures (mainly clayey silts and loamy sandy silts), bulk densities, and pH values for both soil depths (Table 2). Water contents showed the greatest standard deviation within the two soil depths (Table 2), however exhibited no effect on soil water isotopes. Moreover,~~ no tendency of higher TWI values with decreasing distance to stream was obvious. Garvelmann et al. (2012) ~~found for~~ investigated two hillslopes in a humid 0.9 km^2 ~~humid~~ catchment in the southern Black Forest (Germany) and found that soil profiles upslope or with a weak affinity for saturation (low TWIs) preserved the precipitation isotopic signal.

~~[Table 2 near here]~~

~~Generally, all soil water isotopic values fall on the local meteoric water line, indicating no evaporative enrichment of soil water (Fig. 8).~~ In our study, the~~The mean δ-values in the top 0.2 m of the soil profile is higher than further below, reflecting a stronger impact of precipitation in the topsoil (Table 2, Fig. 7). The~~ δ-values of top soil and precipitation did not vary significantly statistically (Fig. ~~7~~4), which is not the case for precipitation and subsoil. A mixing and homogenization of new and old soil water with depth could not clearly be seen in 0.5 m soil depth, which would have resulted in a lower standard deviation (Song et al., 2011), but standard deviations of isotopic signatures in top and subsoil were similar (Table 2). Subsoil isotopic values were statistically equal to stream and groundwater isotopic values (Fig. ~~7~~4) implying that the catchment was under baseflow conditions during the sampling campaign and that capillary rise of groundwater occurred. Nevertheless, the rainfall isotopic signal was not directly transferred through the soil to the groundwater body, ~~resulting in~~even so prompt groundwater head level raises as a result of rainfall-runoff events occurred. This supports the ~~rejection of hypothesis (2). Similar observations were made by~~ assumption of double paradox-like catchment behaviour.

Garvelmann et al. (2012)~~.~~ obtained high resolution δ^2H vertical depth profiles of pore water at various points along two fall lines of a pasture hillslope in the southern Black Forest (Germany) by applying the H_2O(liquid)–H_2O(vapor) equilibration laser spectroscopy method. The authors showed that groundwater was flowing through the soil in the riparian zone (downslope profiles) and dominated streamflow during baseflow conditions. Their comparison indicated that the percentage of pore water soil samples with a very similar stream water δ^2H signature is increasing towards the stream channel (Garvelmann et al., 2012). In contrast, we found no relationship between the distance to stream and soil isotopic values in the Vollnkirchener Bach subcatchment~~.~~ over various heights above sea level (235–294 m a.s.l.).

~~[Figure 7 near here]~~

~~Comparing soil isotopic signatures between different land covers showed generally higher and statistically significantly different δ values at 0.2 m soil depth under arable land as compared to forests and grasslands. However, all top soil isotopic values reflected precipitation isotopic signals (Fig. 8, top). For the lower 0.5 m of the soil column, isotopic signatures under all land use units showed statistically similar values; nevertheless, differing significantly from precipitation (Fig. 8, bottom).~~

~~[Figure 8 near here]~~

Comparing soil water δ^{2}H values between top and subsoil under different land use units showed significant differences ($p \leq 0.05$) under arable and grassland but not under forested sites (Fig. ~~8, capital letters).~~5). This could be explained through the occurrence of vertical preferential flow paths and interconnected ~~macro pore~~macropore flow ~~(in~~such as continuous root channels or earthworm burrows~~)~~ ~~(Buttle and McDonald, 2002)~~(Buttle and McDonald, 2002) characteristic for forested soils ~~(Alaoui et al., 2011)~~(Alaoui et al., 2011). ~~Alaoui et al. (2011)~~Alaoui et al. (2011) showed that macropore flow with high interaction with the surrounding soil matrix occurred in forest soils, while macropore flow with low to mixed interaction with the surrounding soil matrix dominates in grassland soils. The authors attributed the low efficiency of grassland soil macropores in transporting all water vertically downward to the fine and dense few topsoil layers caused by the land use that limit water flux into the underlying macropores. In general, the upper part of most agricultural human-impacted soils is restructured annually due to seasonal tilling, whereas the structure of forest soils, may remain unchanged for years and be uninterrupted throughout the entire soil profile (in particular ~~the~~ macropores and biopores) ~~(Alaoui et al., 2011).~~(Alaoui et al., 2011). Considering the bulk density in the Schwingbach catchment increasing values from forest (1.10 g cm^{-3}) over grassland (1.25 g cm^{-3}) to arable land soils (1.41 g cm^{-3}) were measured in the top soil. As reported in a study by ~~Price et al., (2010)~~Price et al. (2010) for North Carolina (USA), soils underlying forest trees generally feature low bulk density in a comparison with soils impacted by human land use. The reduced hydrological connectivity between top and subsoil under arable and grassland observed in the Vollnkirchener Bach subcatchment therefore led to different isotopic signatures (Fig. ~~8~~5).

Although, vegetation cover has been proven to have an impact on soil water isotopes ~~(Brodersen et al., 2000; Gat, 1996; Li et al., 2007), only few data are available for Central Europe (Darling, 2004). Burger and Seiler (1992) found that soil water isotopic enrichment under spruce forest in Upper Bavaria was double that beneath neighbouring arable land. However, in their study soil water isotopic signatures were not comparable to groundwater isotope values (Burger and Seiler, 1992). Brodersen et al. (2000) reported the effect of vegetation structure on δ^{18}O values of rainwater and soil water in the unsaturated zone in southern Germany. In their study, throughfall isotopic signatures of different tree species (spruce and beech) seemed to have a negligible effect on soil water isotopes, since soil water~~

~~in the upper layers followed the seasonal trend in the precipitation input and had a very constant signature in greater depth. In contrast, Gehrels et al. (1998) detected slightly heavier isotopic signatures under forested sites at a field site in the Netherlands in comparison to non-forested sites (grassland and heathland), both showing isotopic signatures comparable to precipitation signals. For the Schwingbach catchment~~(Brodersen et al., 2000; Gat, 1996; Li et al., 2007), only few data are available for Central Europe (Darling, 2004). Burger and Seiler (1992) found that soil water isotopic enrichment under spruce forest in Upper Bavaria was double that beneath neighbouring arable land. However, soil water isotopic signatures were not comparable to groundwater isotope values (Burger and Seiler, 1992). Brodersen et al. (2000) reported the effect of vegetation structure on δ^{18}O values of rainwater and soil water in the unsaturated zone in southern Germany. In their study, throughfall isotopic signatures of different tree species (spruce and beech) seemed to have a negligible effect on soil water isotopes, since soil water in the upper layers followed the seasonal trend in the precipitation input and had a very constant signature in greater depth. In contrast, Gehrels et al. (1998) detected slightly heavier isotopic signatures under forested sites at a field site in the Netherlands in comparison to non-forested sites (grassland and heathland), both showing isotopic signatures comparable to precipitation signals. For the Schwingbach catchment, we conclude that the observed land use effect in the upper soil column is mainly attributed to different preservation and transmission of the precipitation input signal. It is most likely not attributed to distinguished throughfall isotopic signatures since top soil water isotopic signals followed the precipitation input signal under all land use units. The precipitation influence smoothed out with depth since soil water isotopes approached groundwater signatures at 0.5 m soil depth.

~~3.4.2~~4.2.2 Seasonal isotope soil profiling

~~Examining the temporal effect of precipitation isotopic shifting in the soil, showed that isotope compositions of soil water varied seasonally (Fig. 9). Generally, more depleted soil water was found in the winter and spring (Fig. 9). Contrary, soil water was enriched in summer due to evaporation during warmer and drier periods (Darling, 2004)~~Soil water was enriched in summer due to evaporation during warmer and drier periods (Darling, 2004). The depth to which soil water isotopes are significantly affected by evaporation is rarely more than 1–2 m below ground, and often less under temperate climates ~~(Darling, 2004)~~(Darling, 2004). In contrast, winter profiles exhibited somewhat greater standard deviations in comparison to summer isotopic soil profiles~~. For summer soil profiles in the Vollnkirchener subcatchment, no evidence for evaporation was obvious below 0.4 m soil depth. However, snowmelt isotopic signatures could be traced down to a soil depth of 0.9 m during spring rather than winter, pointing to a depth-translocation of meltwater in the soil, more remarkable for the deeper profile under arable land (Fig. 9, left panel). Furthermore, shallow soil water (<0.4 m) showed larger standard deviations with values closer to mean seasonal precipitation inputs (Fig. 9). Winter profiles exhibited somewhat greater standard deviations in comparison to summer isotopic soil profiles~~, indicative for wetter soils (Fig. 6, lower panels) and shorter residence times ~~(Thomas et al., 2013).~~(Thomas et al., 2013). Generally, deeper soil water isotope values were relatively constant through time and space.~~ The observed seasonal amplitude smoothed out with depth as soil water isotope signals approached groundwater average. Generally, deeper soil water isotope values were relatively constant through time and space.~~ Similar findings were made by Foerstel et al. (1991) on a sandy soil at Juelich, western Germany and by ~~McConville et al. (2001)~~McConville et al. (2001) under predominately agriculturally used gley and till soils in Northern Ireland. ~~Thomas et al. (2013)~~Thomas et al. (2013) likewise observed that soil water isotope samples from shallow soils (≤30 cm) were comparable to precipitation isotopic composition, while samples from intermediate soils (40–100 cm) plot near the groundwater average for a forested catchment located in central Pennsylvania, USA. Furthermore, Tang and Feng (2001) showed for a sandy loam soil sampling site in New Hampshire (USA) that the influence of summer precipitation decreased with increasing depth, and soil at 0.5 m can only receive water from large storms. For summer soil profiles under arable land, precipitation input signals ~~likewise~~similarly decreased with depth (Fig. ~~9,~~6, upper left panel).

~~[Figure 9 near here]~~

Generally, the replacement of old soil water with new infiltrating water is dependent on the frequency and intensity of precipitation and the soil texture, structure, wetness, and water potential of the soil ~~(Li et al., 2007; Tang and Feng, 2001)~~(Li et al., 2007; Tang and Feng, 2001). It is usually more efficient in a wet year than in a dry year (Tang and Feng, 2001). As a result of soil water recharge near the surface, the amount of percolating water decreases with depth and consequently, deeper soil layers have less chance to obtain new water (Tang and

Feng, 2001). Summer and winter profiles show higher water contents in the upper 0.2 m than further down (Fig. 6, lower panels). Furthermore, in the growing season, the percolation depth is additionally limited by plants' transpiration (Tang and Feng, 2001). For the Schwingbach catchment we conclude that the influence of new percolating soil water decreased with depth as no remarkable seasonality in soil isotopic signatures was obvious at >0.9 m and constant values were observed through space and time.

~~3.5~~4.3 ~~Local Meteoric Water Line and isotopic comparison of~~ Linkages between water cycle components

In general, stream water isotopic time series of the Vollnkirchener Bach and Schwingbach showed (with few exceptions) little deflections through time and, consequently, provided little insight into time and source-components connectivity. Schürch et al. (2003) likewise observed damped river water isotopic signatures as compared with precipitation isotopic signatures for sampling points of the “Swiss National Network for the Observation of Isotopes in the Water Cycle”. For larger rivers like the Elbe at Torgau in eastern Germany seasonal isotopic composition varied with an amplitude of 1.5‰ in δ^{18}O (Darling, 2004).

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.

Due to isotopic similarities of stream and groundwater, we assume that groundwater predominantly feeds baseflow. Even during peak flow occurring in January 2012, December to April or May 2013, rainfall input did not play a major role for stream water isotopic composition although fast rainfall-runoff behaviours were observed by Orlowski et al. (2014). Same observations were made by Jin et al. (2010) for the Red Canyon Creek watershed (Wyoming, USA), indicating good hydraulic connection between surface water and shallow groundwater and by Klaus et al. (2015) for a low-mountainous forested watershed in South

Carolina (USA), comparable to the Schwingbach catchment. The damped groundwater isotopic signatures, which likewise showed little variation through time, rather seemed to be a mixture of former lighter precipitation events and snowmelt, since meltwater is known to be depleted in stable isotopes as compared to the annual mean of precipitation or groundwater (Rohde, 1998). 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). As groundwater at the observed piezometers in the Vollnkirchener subcatchment is shallow (Orlowski et al., 2014), the snowmelt signal is allowed to move rapidly through the soil. Pulses of snowmelt water causing a depletion in spring and early summer was also observed by other studies (Darling, 2004; Kortelainen and Karhu, 2004). We therefore assume that groundwater is mainly recharged throughout the winter. Generally, less than 5 to 25% of precipitation infiltrates to the groundwater table in temperate climates; the rest is lost to runoff, evaporation from soils, and transpiration by vegetation (Clark and Fritz, 1997a). During spring runoff when soils are saturated, temperatures are low, and vegetation is inactive, recharge rates are generally highest. In contrast, recharge is very low during summer when most precipitation is transpired back to the atmosphere (Clark and Fritz, 1997a). Similarly, O'Driscoll et al. (2005) showed that summer precipitation does not significantly contribute to recharge in the Spring Creek watershed of central Pennsylvania (USA) since $\delta^{18}O$ values in summer precipitation were enriched compared to mean annual groundwater composition.

Further, Orlowski et al. (2014) showed that influent and effluent conditions occurred simultaneously at different stream sections of the Vollnkirchener Bach affecting stream and groundwater isotopic compositions, equally. Since groundwater head levels in the Vollnkirchener Bach subcatchment closely followed stream runoff-dynamics and responded to stormflow events with rising head levels (Fig. 8), we conclude that bidirectional water exchange between the groundwater body and the Vollnkirchener Bach occurred. Our network map supported this assumption (Fig. 9) as surface water samplings points plotted close to groundwater sampling points (especially to the sampling points under the meadow and along the stream). However, both water compartments differed significantly from rainfall isotopic signatures (Table 1). These divergent isotopic signatures but the prompt reaction of the groundwater body to rainfall-runoff events indicate that 'old' groundwater can be released during very short times (Kirchner, 2003). Thus, our catchment showed double water paradox behaviour as described earlier by Kirchner (2003) as the fast releasing of very old water with little variation in tracer concentration. This paradox behaviour could likewise be a reason for the failure of the MTT estimation. Just by comparing mean precipitation ($\delta^{18}O = -6.2\pm3.1$), stream (e.g. $\delta^{18}O = -8.4\pm0.4$ for the Vollnkirchener Bach), and groundwater isotopic signatures ($\delta^{18}O = -8.2\pm0.4$ for the meadow) (Table 1), it is obvious that simple mixing calculations do not work either.

Nevertheless, to still estimate groundwater ages in the Vollnkirchener Bach subcatchment, we established a hydrological model. Our model results suggest that the main groundwater flow direction is towards the stream and the quantity of flowing water is highest near the stream (Fig. 10). This further supports the assumption that stream water is mainly fed by groundwater. Moreover, the simulation underlines the conclusion that the groundwater body and stream water are disconnected from the precipitation cycle, since only 13.3% of cells contained water with and age <1 year. The results of the model reveal a spatially highly heterogeneous age distribution of groundwater throughout the Vollnkirchener Bach subcatchment. The age varies from about two days to more than 100 years with oldest water near the stream. Thus, our model provides the opportunity to make use of stable water isotope information along with climate, land use, and soil type data, in combination with a digital elevation map to estimate residence times >5 years. Such long residence times could previously only be determined via other tracers such as tritium (e.g. Michel (1992)). If stable water isotope information is used alone, it is known to cause a truncation of stream residence time distributions (Stewart et al., 2010). Moreover, our model facilitates the estimation of spatially distributed groundwater ages, which opens up new opportunities to compare groundwater ages from over a range of scales within catchments.

The observation that gaining and losing stream reaches occur simultaneously along the Vollnkirchner Bach could similarly be supported by our model results. However, due to the model assumption of a constant groundwater recharge over the course of a year, no seasonality was simulated. Moreover, model results differ somewhat from the conceptual model of Orlowski et al. (2014). This is due to the fact that the hydrological model only estimates groundwater fluxes but not surface water fluxes. Moreover, no spatial differences in soil properties of the groundwater layer were considered. Nevertheless, as shown by the diverse ages of water in the stream cells and the assumption of spatially gaining conditions, the model confirms that the stream contains water with different transit times. Therefore, the stream water does not have a discrete age, but a distribution of ages due to variable flow paths throughout the subcatchment (Stewart et al., 2010). Heidbüchel et al. (2012) proposed the concept of the master transit time distribution that accounts for temporal variability of MTT. Our model provides a different approach that considers spatial aspects of transit times and gives a much deeper understanding of the groundwater-surface water connectivity across the landscape than a classical MTT calculation could provide.

However, our semi-conceptual model approach has also some limitations. During model setup a series of assumptions and simplifications were made to develop a realistic hydrologic model without a severe loss in performance. Therefore, several parameters such as the depth of the groundwater body are only rough estimations, while others like evapotranspiration are based on simulations. Moreover, the groundwater body is highly simplified since e.g. properties of the simulated aquifer are assumed to be constant over the subcatchment. However, the complexity of the model is higher than in a simple one dimensional model (with only one cell and one layer), which results in a better spatial resolution, but lower than in a fully distributed variable saturated 3D model. In future models a more diverse groundwater body based on small-scale measurements of aquifer parameters should be implemented. Especially data of saturated hydraulic conductivity with high spatial resolution, as well as the implementation of a temporal dynamic groundwater recharge could lead to an enhanced model performance. Nevertheless, our hydrological model enables a good assessment of the groundwater age for the Vollnkirchner Bach subcatchment and supports the assumption that surface and groundwater are disconnected from precipitation.

~~The linear relationship of δ^{2}H and δ^{18}O content in local precipitation, results in a local meteoric water line (LMWL) (Fig. 10), which can be utilised to link the relative contribution of seasonal precipitation to ground and surface water sources (Wassenaar et al., 2011). The global meteoric water line (GMWL) established by Craig (1961a), and more recently refined by Rozanski et al. (1993) is δ^{2}H = 8.13 × δ^{18}O+10.8 ‰. It provides a valuable benchmark against which regional or local waters can be compared (Song et al., 2011). The slope of the LMWL of the Schwingbach catchment is well in agreement with the one from the closest GNIP station in Koblenz (δ^{2}H = 7.67 × δ^{18}O + 2.48 ‰; R^{2} = 0.98), but is slightly lower in comparison to the revised GMWL, showing stronger local evaporation conditions. Since evaporation causes a differential increase in δ^{2}H and δ^{18}O values of the remaining water, the slope for the linear relationship between δ^{2}H and δ^{18}O is lower in comparison to the GMWL (Rozanski et al., 2001; Wu et al., 2012). The lower intercept (d-excess), dependent on the~~

~~humidity and temperature conditions in the evaporation region (Mook, 2001), nevertheless shows that moisture recycling did obviously not play a major role in the study area.~~

~~Considering isotope samples of the different water cycle components in comparison with the LMWL revealed that mean isotope values of snow samples were for δ^2H approximately 84‰ lighter that mean precipitation isotopic signatures (Fig. 10). Stream water isotope samples of both creeks (Schwingbach and Vollnkirchener Bach) fell on the LMWL, showing slight evaporative enrichment for few samples (Fig. 10). Moreover, isotopic values for stream water were almost identical to those found in groundwater (Table 1, Fig. 10).~~

~~[Figure 10 near here]~~

~~Same observations were made by Jin et al. (2010) for the Red Canyon Creek watershed (Wyoming, USA), indicating good hydraulic connection between surface water and shallow groundwater and by Klaus et al. (2014) for a low mountainous forested watershed in South Carolina (USA), comparable to the Schwingbach catchment. Furthermore, isotopic similarities between stream and groundwater pointed out that surface water was mainly replenished by the groundwater, except for extreme storm events (Orlowski et al., 2014). Same was observed by Zhang et al. (2013) for the Tarim River Basin in China. However, in the Vollnkirchener subcatchment arable land groundwater isotopes were slightly heavier and hydrologically decoupled from the Vollnkirchener Bach.~~

~~4~~5 Conclusions

Conducting a stable water isotope study in the Schwingbach catchment helped to identify relationships between precipitation, stream, soil, and groundwater in a developed (managed) catchment. The close isotopic link between groundwater and the streams revealed that groundwater controls streamflow. Moreover, it could be shown that groundwater was predominately recharged during winter but was decoupled from the annual precipitation cycle. Even so streamflow and groundwater head levels ~~rapidly~~promptly responded to precipitation ~~input~~inputs, there was no ~~evidence for a larger contribution of precipitation~~obvious change in their isotopic composition due to ~~both~~rain events (old water ~~cycle components.~~paradox behaviour). This was underlined by the fact that no remarkable seasonality in soil isotopic signatures as interface between precipitation and groundwater was obvious at >0.9 m and constant values were observed through space and time.

Nevertheless, the lack of temporal variation in stable isotope time series of stream and groundwater (with few exceptions) limited the application of classical methods of isotope hydrology~~ (mean transit time estimation, hydrograph separation) in the Schwingbach catchment. Still, our dual isotope approach was valuable for determining the connectivity and disconnectivity between different water cycle components. Together with results of a former hydrometric study in the same catchment (Orlowski et al., 2014), knowledge about water cycle component interactions will be utilised to develop catchment specific process-based hydrological models. Since groundwater seems to be the major driver of streamflow, a groundwater dating campaign is planned in the future~~, i.e. mean transit time estimations in the Schwingbach catchment. We therefore setup a hydrological model with CMF to estimate groundwater ages and flow directions in the Vollnkirchener Bach subcatchment. Our model result supported the finding that the water in the catchment is >5 years (on average 16 years) and that stream water is mainly fed by groundwater. Our modelling approach was valuable to overcome the limitations of MTT calculations with traditional methods and/or models. Thus, our dual isotope study in combination with a hydrological model approach was valuable for determining the connectivity and disconnectivity between different water cycle components.

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Table 1. Descriptive statistics of δ^{2}H~~ and~~, δ^{18}O~~ in~~, and d-excess values for precipitation, stream~~,~~, and groundwater over the two-year observation period including all sampling points.

Sample type	~~Min~~Mean±SD		~~Max~~Min		~~Mean~~Max			D-excess mean±SD				N
	δ^{2}H [‰]	δ^{18}O [‰]	δ^{2}H [‰]	δ^{18}O [‰]	δ^{2}H [‰]	δ^{18}O [‰]		~~δ^{2}H [‰]~~				~~δ^{18}O [‰]~~
Precipitation	−43.9±23.4	−6.2±3.1	−167.6	−22.4	−8.3	−1.2		~~−43~~5.9±5.7	~~−6.2~~	~~23.4~~	~~3.1~~	592
Vollnkirchener Bach	−58.0±2.8	−8.4±0.4	−66.3	−10.0	−26.9	−6.7		~~−58~~9.0±2.3	~~−8.4~~	~~2.8~~	~~0.4~~	332
Schwingbach	−58.2±4.3	−8.4±0.6	−139.7	−18.3	−47.2	−5.9		~~−58~~9.0±2.2	~~−8.4~~	~~4.3~~	~~0.6~~	463
Groundwater meadow	−57.6±1.6	−8.2±0.4	−64.9	−9.2	−50.8	−5.7		~~−57.6~~7.9±5.5	~~−8.2~~	~~1.6~~	~~0.4~~	375
Groundwater arable land	−56.2±3.7	−8.0±0.5	−91.6	−12.3	−49.5	−6.8	~~−56.2~~	~~−8~~1.7±5.0	~~3.7~~	~~0.5~~		338
Groundwater along stream	−59.9±6.8	−8.5±0.9	−94.5	−13.0	−49.5	−7.0	~~−59.9~~	~~−~~8.2±1.5	~~6.8~~	~~0.9~~		108

Gelöschte Zellen

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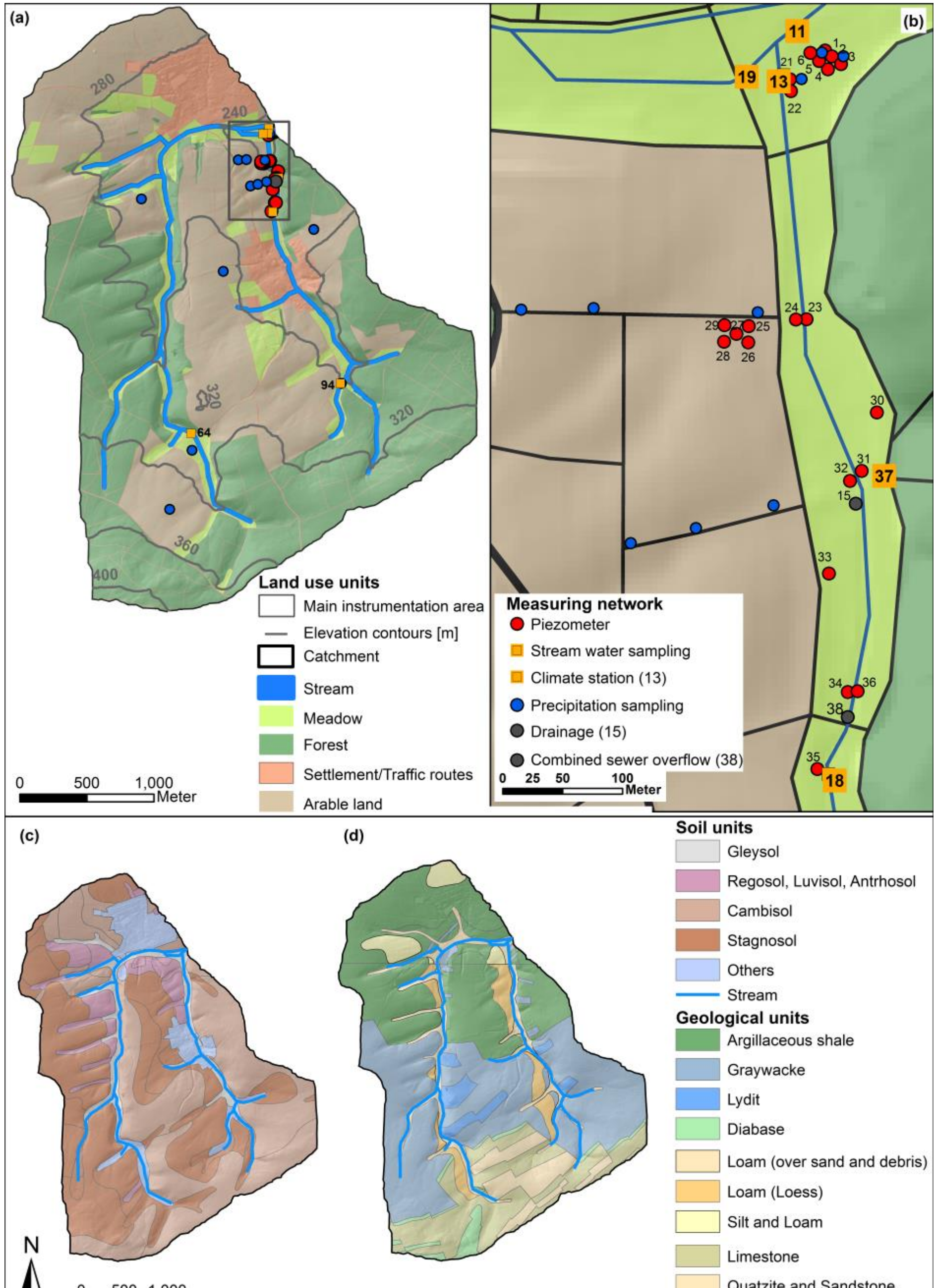
Table 2. Mean and standard deviation for isotopic signatures and soil physical properties ~~and isotopic signatures~~ in 0.2 m and 0.5 m soil depth (N = 52 per depth).

	δ^{2}H [‰]		δ^{18}O [‰]		water content [%~~-~~ w/w]		pH		bulk density [g cm^{-3}]	
	0.2 m	0.5 m	0.2 m	0.5 m	0.2 m	0.5 m	0.2 m	0.5 m	0.2 m	0.5 m
Mean±SD	−46.9±8.4	−58.5±8.3	−6.6±1.2	−8.2±1.2	16.8±7.2	16.1±8.3	5.0±1.0	5.3±1.0	1.3±0.2	1.3±0.2
~~±SD~~	~~8.4~~	~~8.3~~	~~1.2~~	~~1.2~~	~~7.2~~	~~8.3~~	~~1.0~~	~~1.0~~	~~0.2~~	~~0.2~~


(a)
280
240
320
320
360
400
94
64
Land use units
Main instrumentation area
Elevation contours [m]
Catchment
Stream
Meadow
Forest
Settlement/Traffic routes
Arable land
0 500 1,000
Meter
(b)
11
19
13
1 2 3 4 5 6
21
22
24 23
29 27 25
28 26
30
31
32
37
15
33
34 36
38
35
18
Measuring network
Piezometer
Stream water sampling
Climate station (13)
Precipitation sampling
Drainage (15)
Combined sewer overflow (38)
0 25 50 100
Meter
(c)
(d)
Soil units
Gleysol
Regosol, Luvisol, Antrhosol
Cambisol
Stagnosol
Others
Stream
Geological units
Argillaceous shale
Graywacke
Lydit
Diabase
Loam (over sand and debris)
Loam (Loess)
Silt and Loam
Limestone
Quatzite and Sandstone
N
0 500 1,000

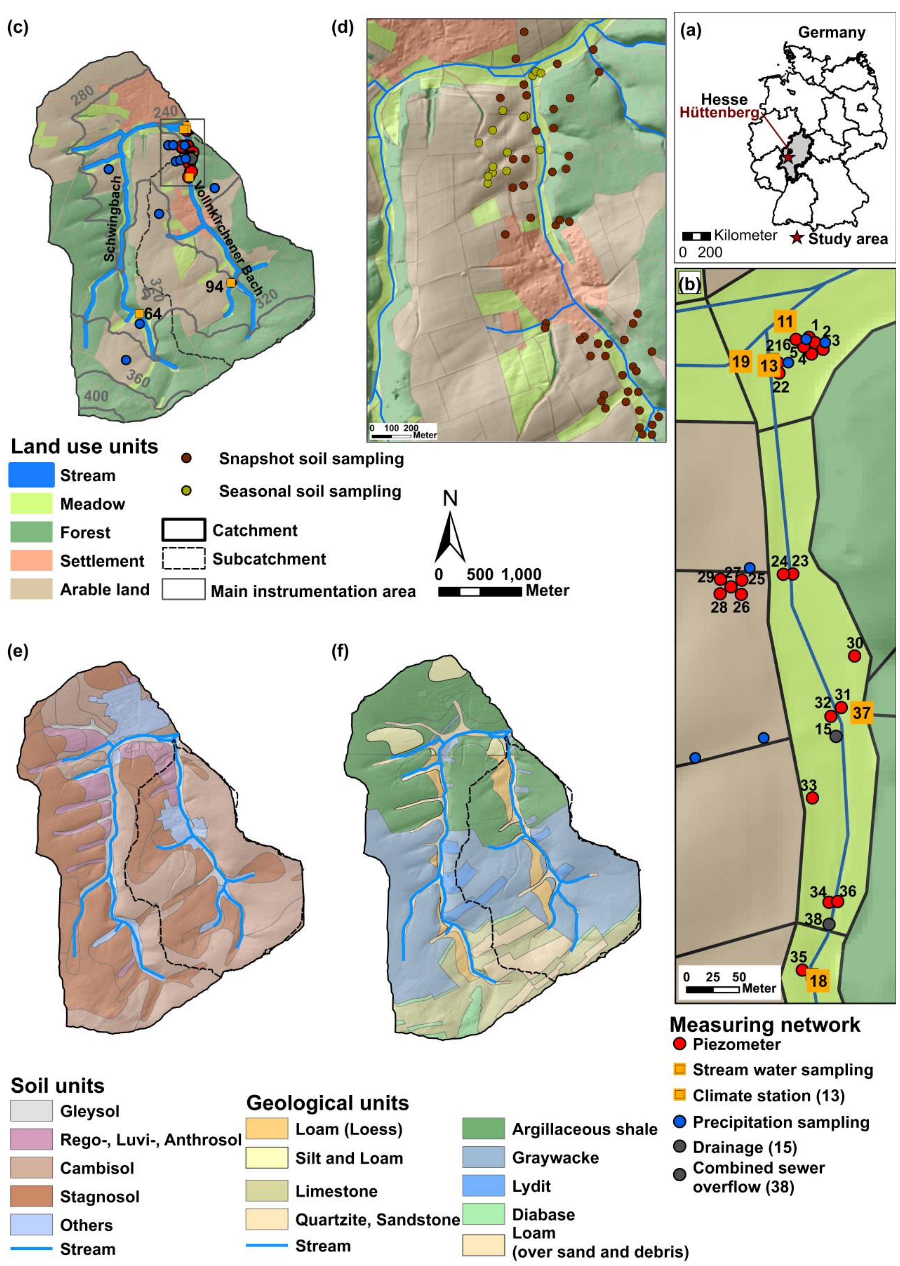
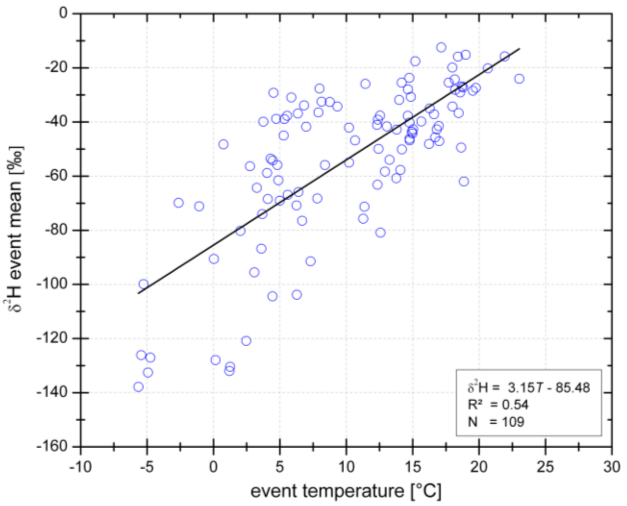


Figure 1. Maps ~~of~~show (a) the location of the Schwingbach catchment in Germany, (b) the main monitoring area, (c) the land use, elevation, and instrumentation, (~~b) main monitoring~~

~~area, (c) soils~~d) the locations of the snapshot as well as the seasonal soil samplings, (e) soil types, and (~~d~~f) geology of the Schwingbach catchment including the Vollnkirchener Bach subcatchment boudaries.


0
-20
-40
-60
-80
-100
-120
-140
-160
δ^2H event mean [‰]
-10
-5
0
5
10
15
20
25
30
event temperature [°C]
δ^2H = 3.15T - 85.48
R² = 0.54
N = 109

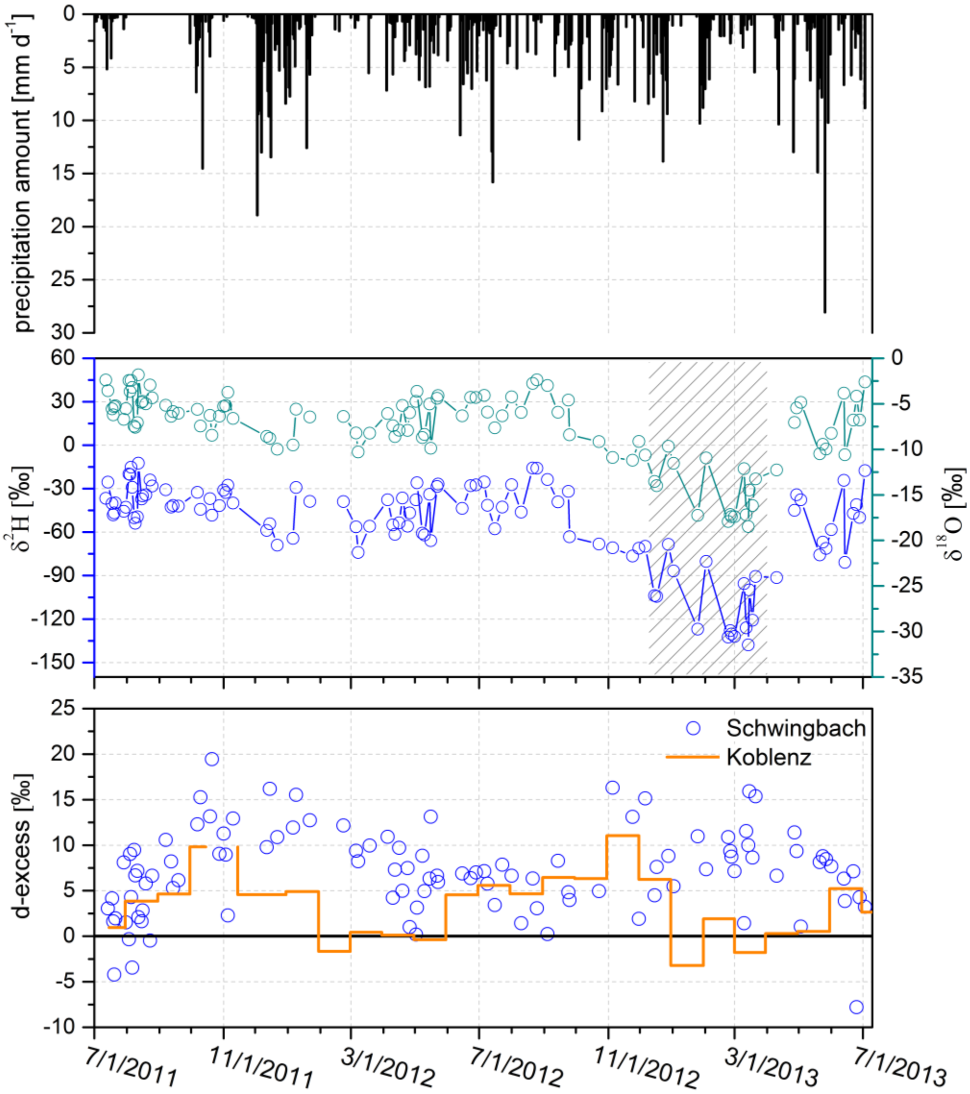
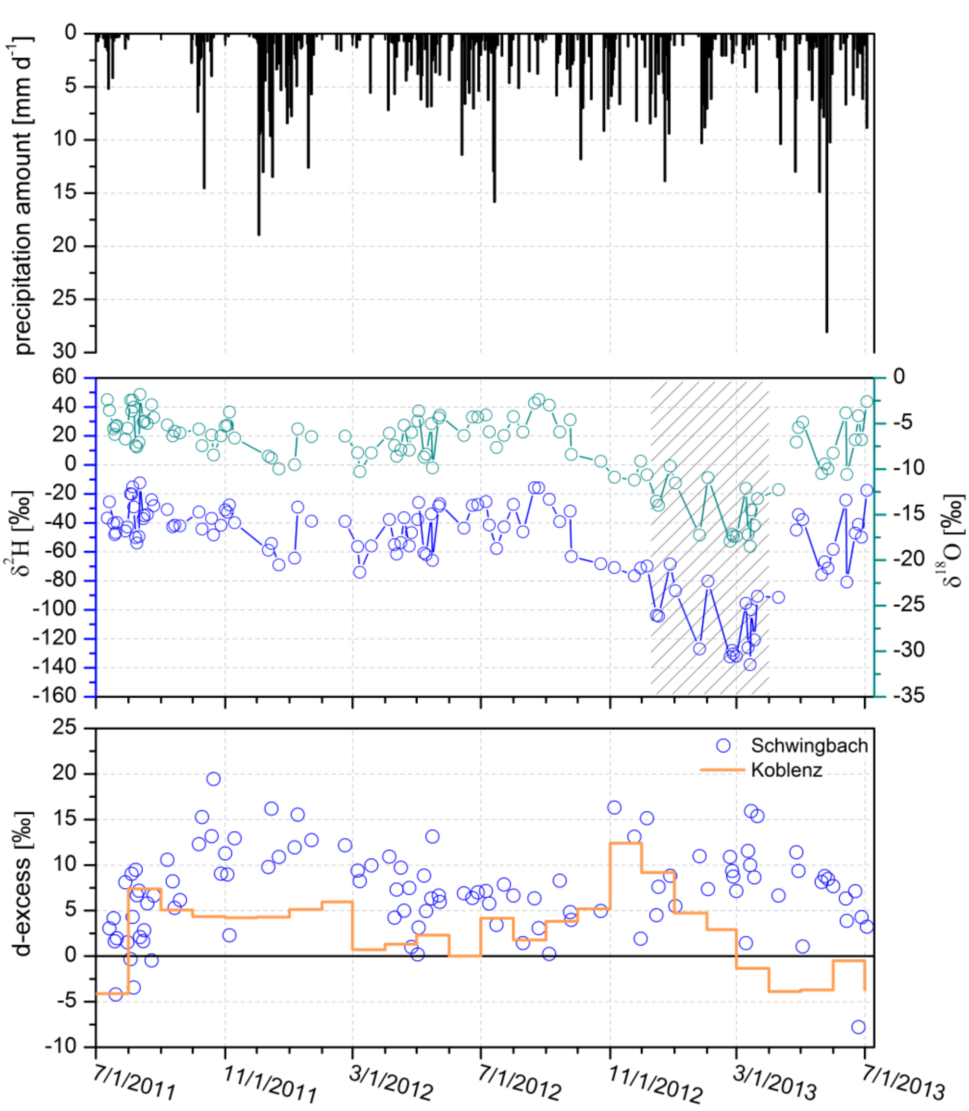


Figure 2. ~~Relationship between event mean δ^2H values in precipitation and air temperature.~~



~~Figure 3.~~ Temporal variation of precipitation amount, isotopic signatures (δ^2H and δ^{18}O) including snow samples (grey striped box), and d-excess values for the study area compared to monthly d-excess values (July ~~2003–~~2011 to July ~~2005~~2013) of GNIP station Koblenz with reference d-excess of GMWL (d = 10; ~~dashed~~solid black line).

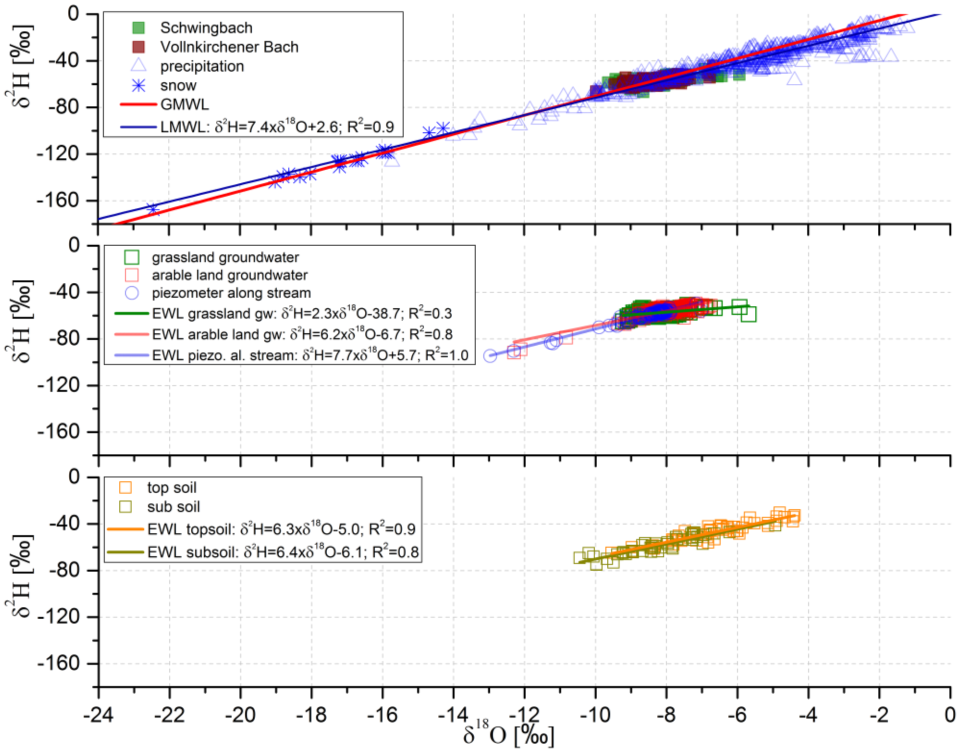


Figure 3. Local Meteoric Water Line for the Schwingbach catchment (LMWL) in comparison to GMWL, including comparisons between precipitation, stream water, groundwater, and soil water isotopic signatures and the respective EWLs.

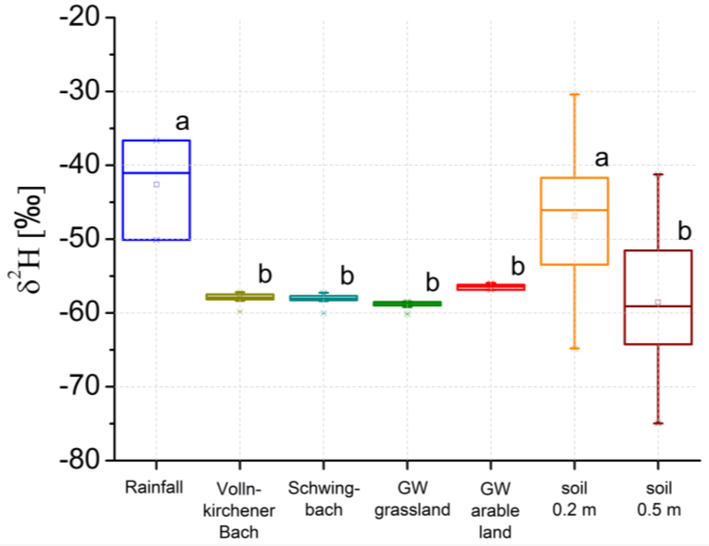


Figure 4. Boxplots of δ^2H values comparing precipitation, stream, groundwater, and soil isotopic composition in 0.2 m and 0.5 m depth (N = 52 per depth). Different letters indicate significant differences ($p < 0.05$).

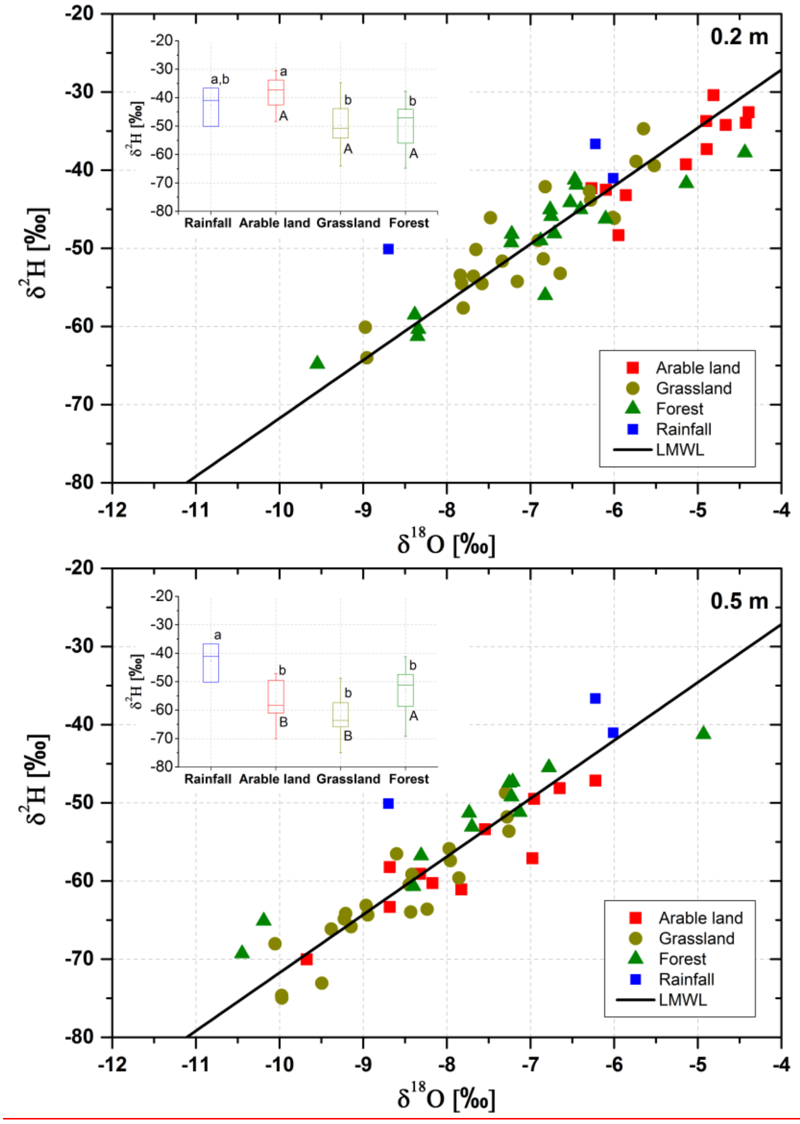


Figure 5. Dual isotope plot of soil water isotopic signatures in 0.2 m and 0.5 m depth compared by land use including precipitation isotope data from 19, 21, and 28 October 2011. Insets: Boxplots comparing δ^2H isotopic signatures between different land use units and precipitation (small letters) in top and subsoil (capital letters). Different letters indicate significant differences ($p \leq 0.05$).

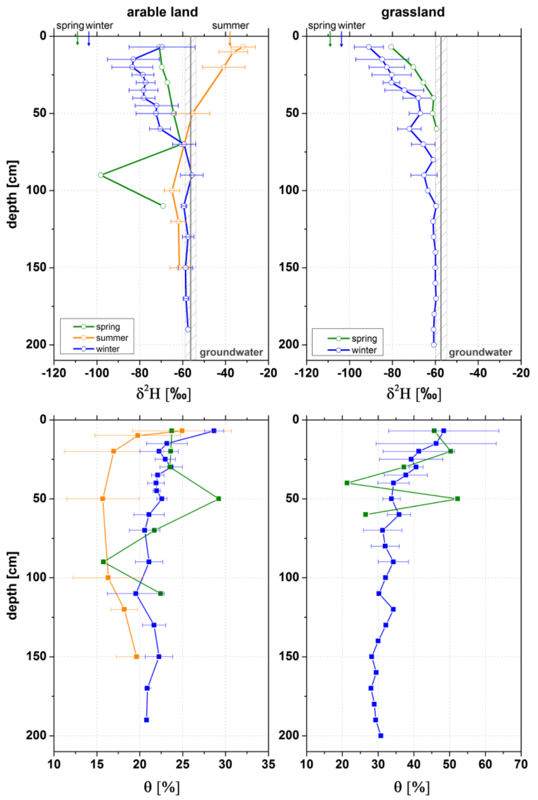
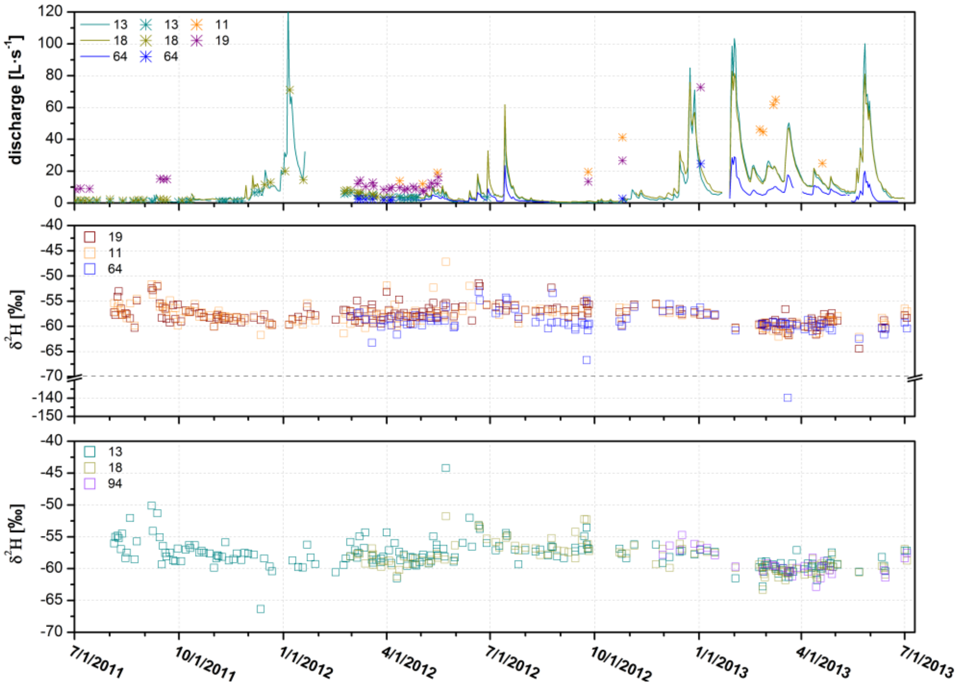


Figure 6. Seasonal δ^{2}H profiles of soil water (upper panels) and water content (lower panels) for winter (28 March 2013), summer (28 August 2011), and spring (24 April 2013). Error bars represent the natural isotopic variation of the replicates taken during each sampling campaign. For reference, mean groundwater (grey shaded) and mean seasonal precipitation δ^{2}H values are shown (coloured arrows at the top).


discharge [L·s-1]
120
100
80
60
40
20
0
13
18
64
13
18
64
11
19
δ2H [‰]
-40
-45
-50
-55
-60
-65
-70
-140
-150
19
11
64
δ2H [‰]
-40
-45
-50
-55
-60
-65
-70
13
18
94
7/1/2011
10/1/2011
1/1/2012
4/1/2012
7/1/2012
10/1/2012
1/1/2013
4/1/2013
7/1/2013

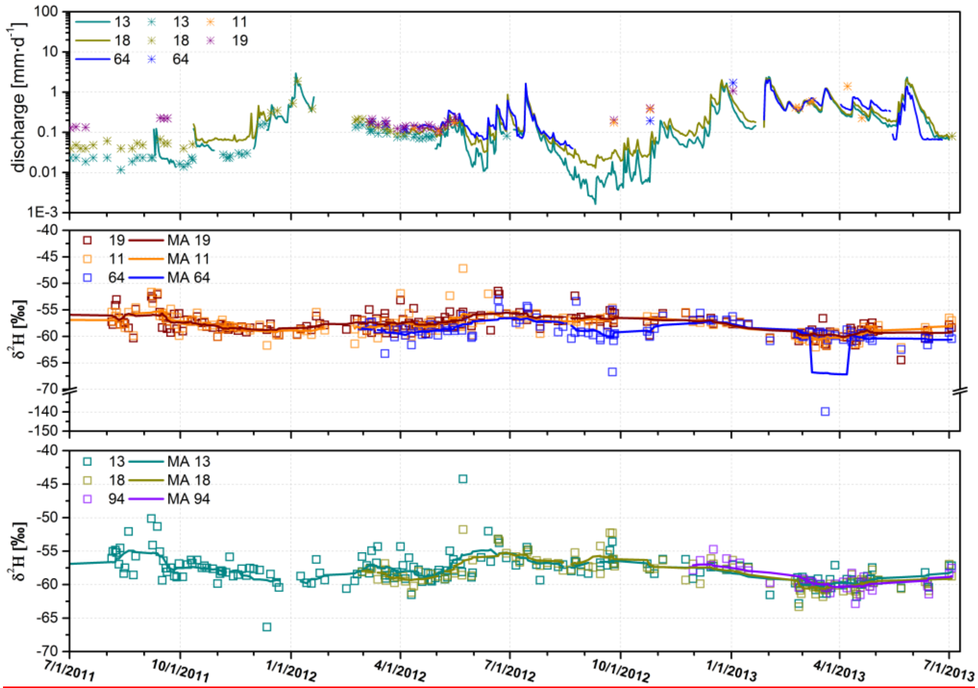
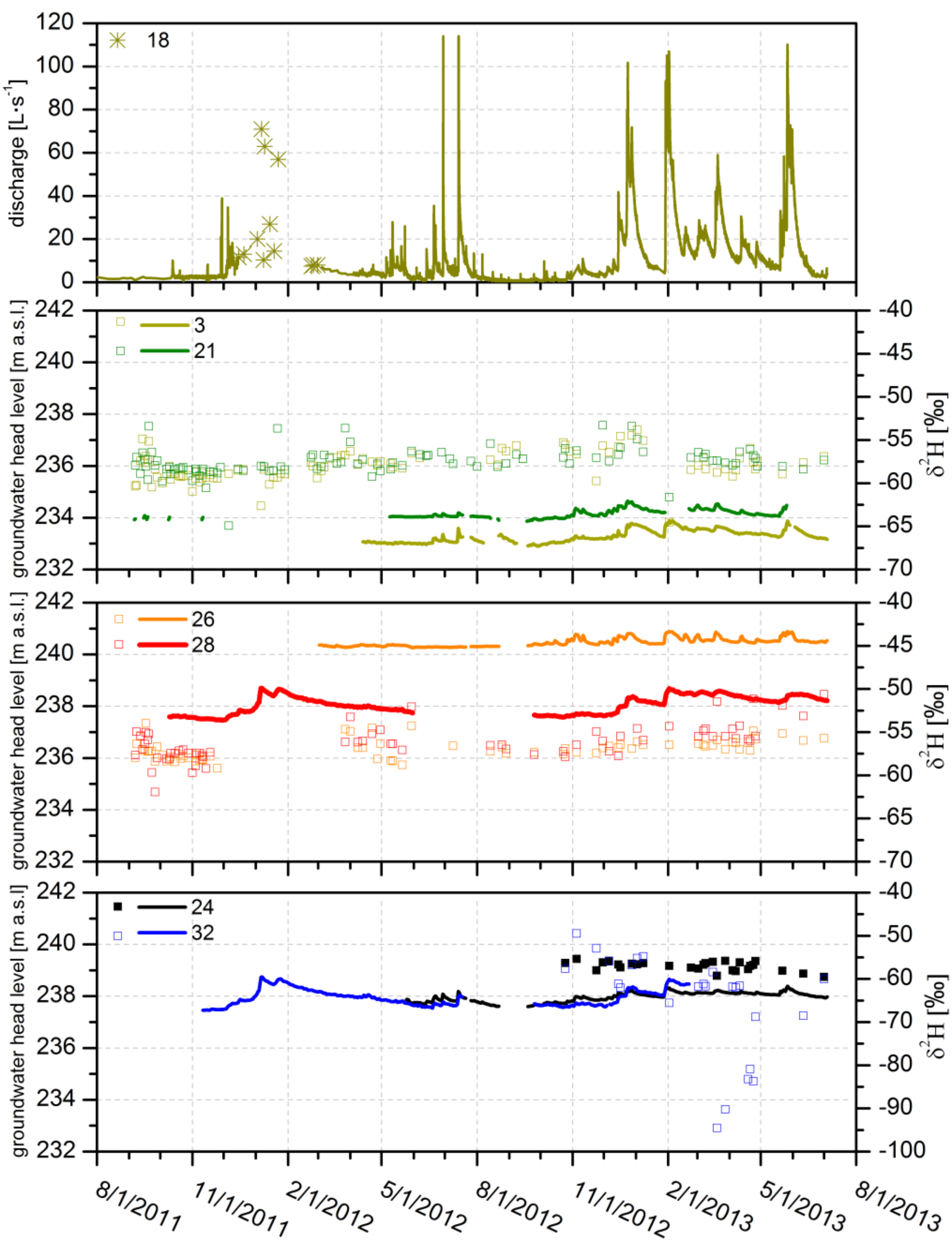


Figure 7. Mean daily discharge at the Vollnkirchener Bach (13, 18) and Schwingbach (site 11, 19, and 64) with automatically recorded data (solid lines) and manual discharge measurements (asterisks), temporal variation of δ^{2}H of stream water in the Schwingbach (site 11, 19, and 64) and Vollnkirchener Bach (site 13, 18, and 94~~).~~) including moving averages (MA) for streamflow isotopes.


discharge [L·s^{-1}]
120
100
80
60
40
20
0
18
groundwater head level [m a.s.l.]
242
240
238
236
234
232
3
21
26
28
24
32
δ^{2}H [‰]
-40
-45
-50
-55
-60
-65
-70
-80
-90
-100
8/1/2011
11/1/2011
2/1/2012
5/1/2012
8/1/2012
11/1/2012
2/1/2013
5/1/2013
8/1/2013

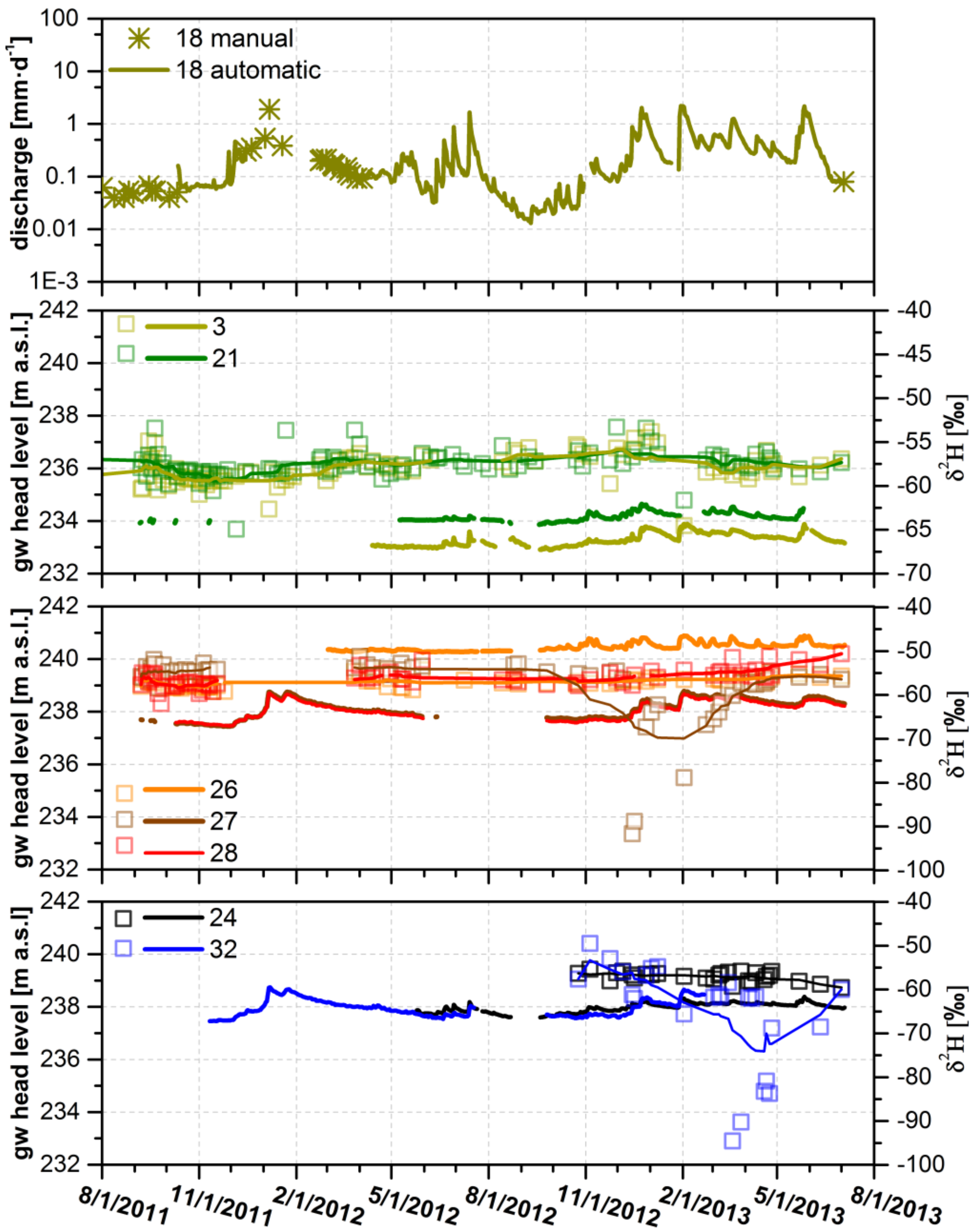
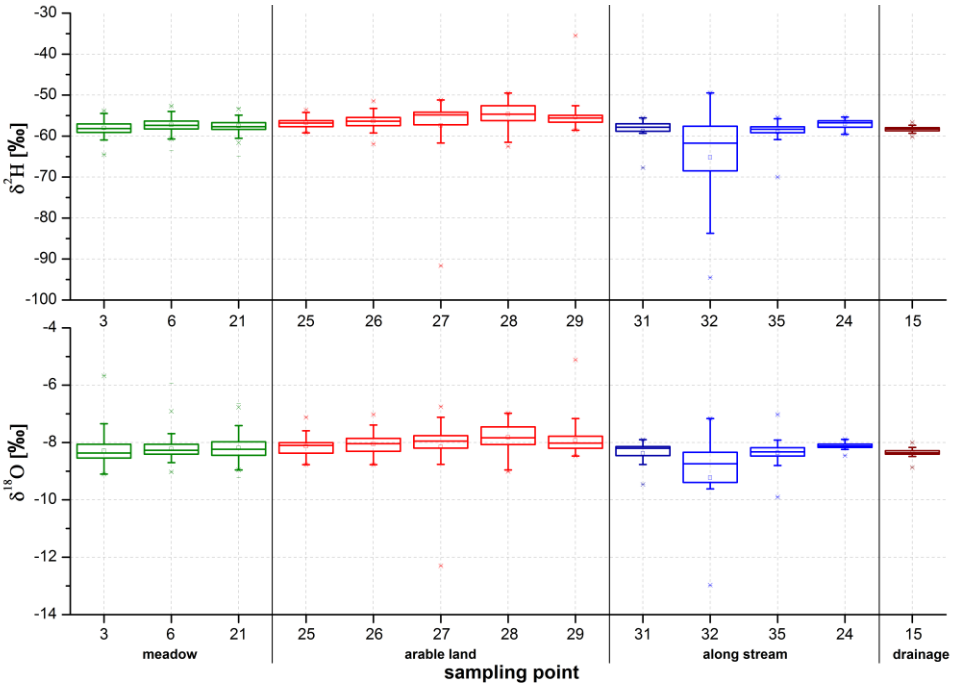


Figure 8. Temporal variation of discharge at the Vollnkirchener Bach with automatically recorded data (solid line) and manual discharge measurements (asterisks) (site 18),

groundwater head levels, and δ^{2}H values (coloured dots) for selected piezometers under meadow (site 3 and 21), arable land (site 26, 27, and 28), and beside the Vollnkirchener Bach (site 24 and 32~~).~~) including moving averages for groundwater isotopes.


-30
-40
-50
-60
-70
-80
-90
-100
δ^2H [‰]
-4
-6
-8
-10
-12
-14
$\delta^{18}O$ [‰]
3
6
21
25
26
27
28
29
31
32
35
24
15
meadow
arable land
along stream
drainage
sampling point

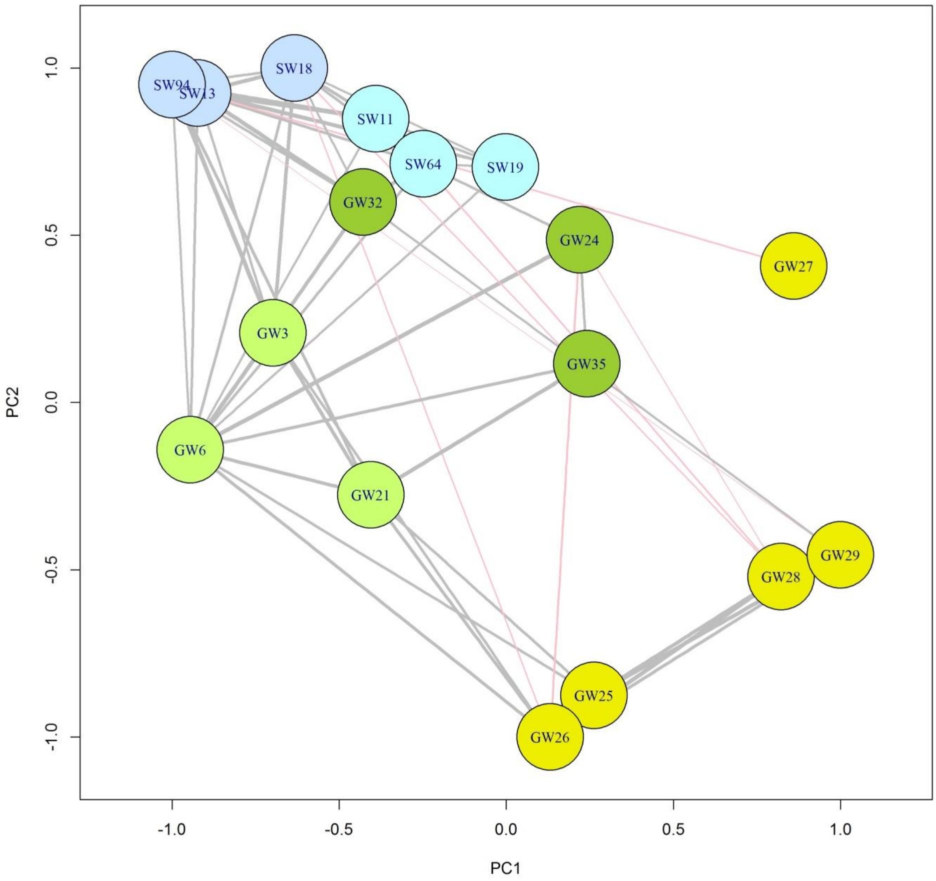
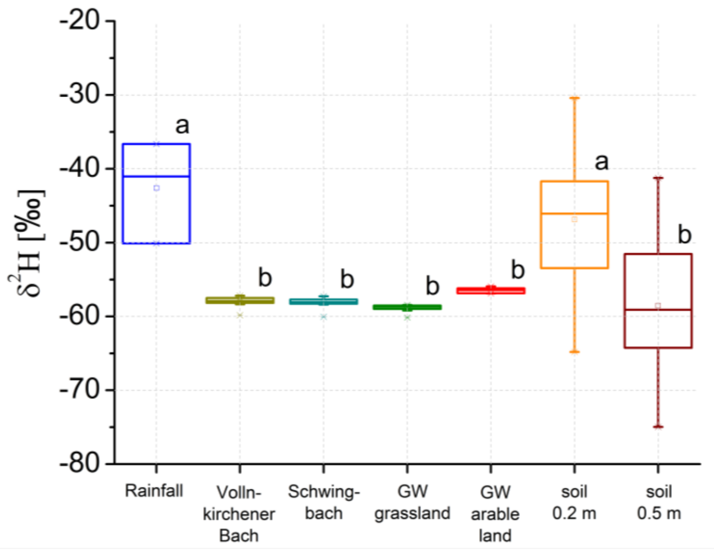


Figure 9~~. Boxplots of isotopic variation (δ^2H and δ^{18}O) in groundwater under meadow (site 3, 6, and 21), arable land (site 26–29), and along the stream (site 31, 32, 35, and 24) as well as for a drainage (site 15).~~



. Network map of δ^{18}O relationships between surface water (SW) and groundwater (GW) sampling points. Yellow circles represent groundwater sampling points on the arable field, light green circles are piezometers located on the grassland close to the conjunction of the Schwingbach with the Vollnkirchener Bach, and dark green circles represent piezometers along the Vollnkirchener Bach. Light blue circles stand for Schwingbach and darker blue circles for Vollnkirchener Bach surface water sampling points. See Figure 1 for an overview of all sampling points. Only statistically significant connections between δ^{18}O time series ($p<0.05$) are shown in the network diagram.

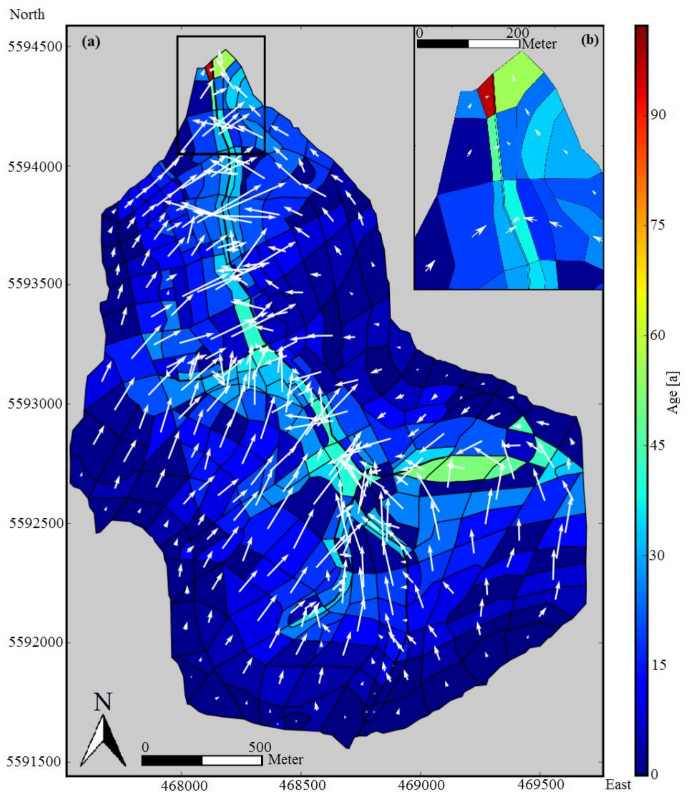


Figure 10~~.~~. Maps of modelled groundwater ages (colour scheme) and flow directions (white arrows) of (a) the Vollnkirchner Bach subcatchment and (b) detail view of the northern part of the subcatchment. The intensity of flow is depicted by the length of the white arrows.

~~Boxplots of δ^2H values comparing precipitation, stream, groundwater, and soil isotopic composition in 0.2 m and 0.5 m depth (N = 52 per depth). Different letters indicate significant differences ($p \leq 0.05$).~~

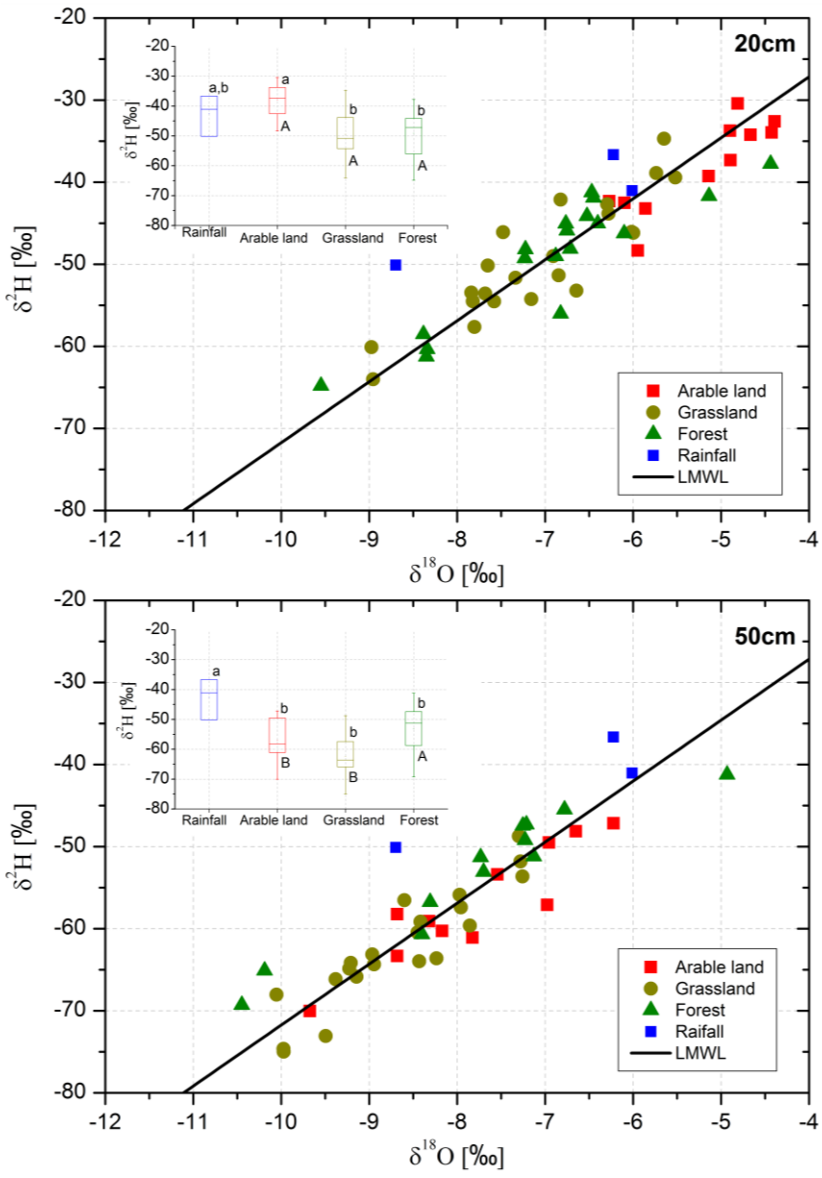
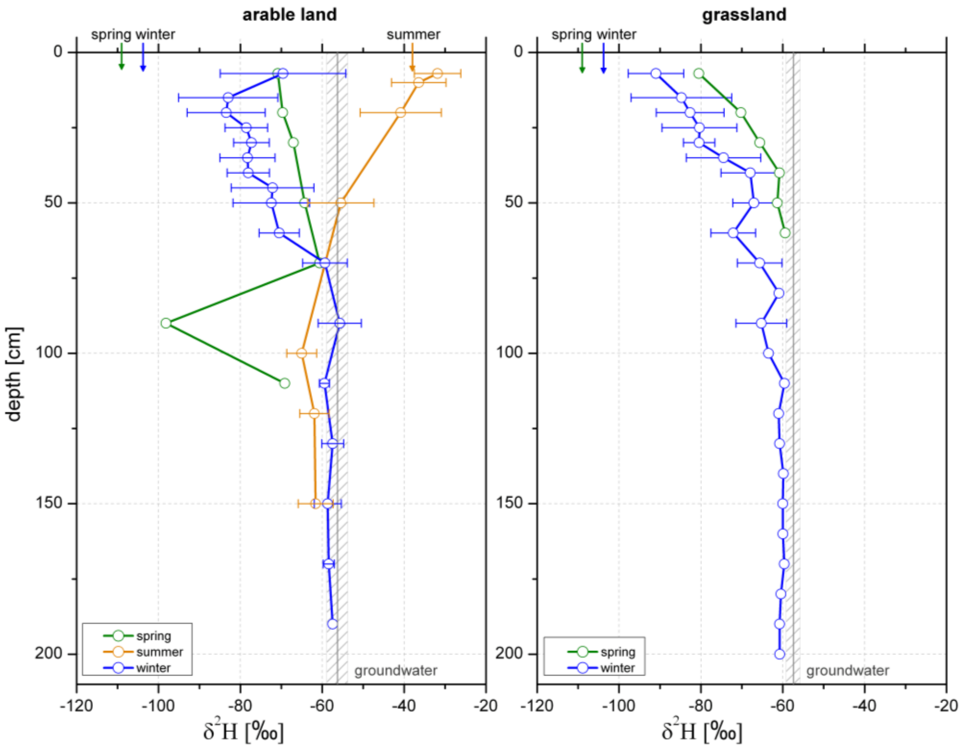
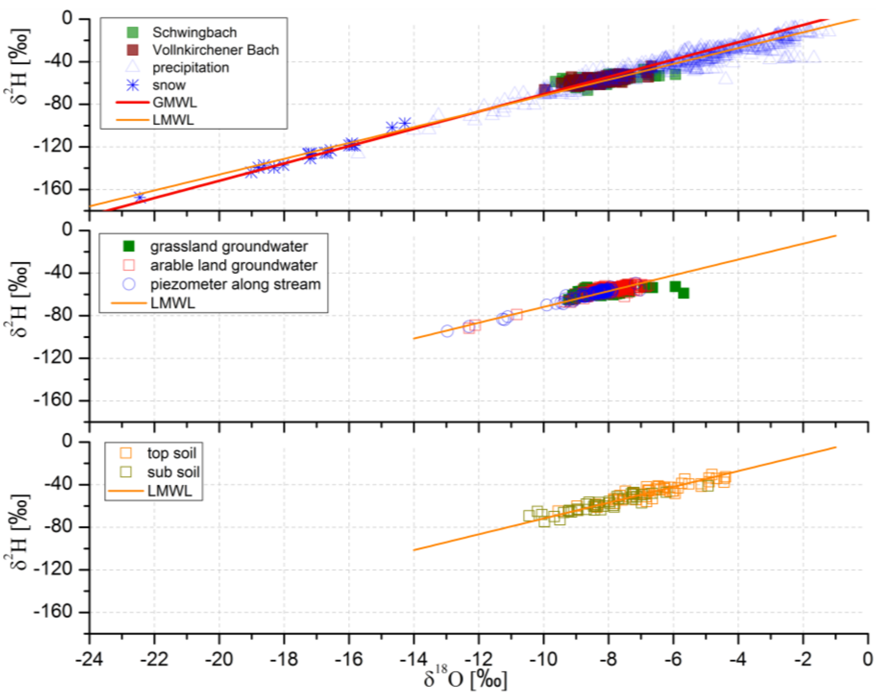


Figure 8.~~ Dual isotope plot of soil water isotopic signatures in 0.2 m and 0.5 m depth compared by land use including precipitation isotope data from 19, 21, and 28 October 2011. Insets: Boxplots comparing δ²H isotopic signatures between different land use units and precipitation (small letters) in top and subsoil (capital letters). Different letters indicate significant differences (p ≤ 0.05).~~



~~Figure 9. Seasonal δ^{2}H profiles of soil water for winter, summer, and spring based on soil samplings conducted on 28 August 2011 (summer), 28 March 2013 (winter), and 14 April 2013 (spring). For reference, mean groundwater (grey shaded) and mean seasonal precipitation δ^{2}H values are shown (coloured arrows at the top).~~



~~Figure 10. Local Meteoric Water Line for the Schwingbach catchment (LMWL) in comparison to GMWL, including comparisons between precipitation, stream water, groundwater, and soil water isotopic signatures.~~