Where does streamwater come from in low relief forested watersheds? A dual isotope approach

J Klaus[1,2], JJ McDonnell[2,3], CR Jackson[4], E Du[5], and NA Griffiths[6]

[1]{Centre de Recherche Public – Gabriel Lippmann, Department of Environment and Agro-biotechnologies, Belvaux, Luxembourg}

[2]{Global Institute for Water Security, University of Saskatchewan, Saskatoon, SK, Canada}

[3]{University of Aberdeen, School of Geosciences, Aberdeen, United Kingdom}

[4]{Warnell School of Forestry and Natural Resources, University of Georgia, Athens, GA, USA}

[5]{Climate Science Department, Lawrence Berkeley National Laboratory, Berkeley, CA, USA}

[6]{Climate Change Science Institute and Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA}

Correspondence to: J. Klaus (klaus@lippmann.lu)

Abstract

The time- and geographic sources of streamwater in low relief watersheds are poorly understood. This is partly due to the difficult combination of low runoff coefficients and often damped streamwater isotopic signals precluding traditional hydrograph separation and convolution integral approaches. Here we present a dual isotope approach involving ^{18}O and ^{2}H of water in a low angle forested watershed to determine streamwater source components and then build a conceptual model of streamflow generation. We focus on three headwater lowland sub-catchments draining the Savannah River Site in South Carolina, USA. Our results for a 3-year sampling period show that the slopes of the meteoric water lines/evaporation water lines (MWL/EWL) of the catchment water sources can be used to extract information on runoff source in ways not considered before. Our dual isotope approach was able to identify unique hillslope, riparian and deep groundwater, and

streamflow compositions. The streams showed strong evaporative enrichment compared to the local meteoric water line ($\delta^2H = 7.15*\delta^{18}O +9.28‰$) with slopes of 2.52, 2.84, and 2.86. Based on the unique and unambiguous slopes of the EWLs of the different water cycle components and the isotopic time series of the individual components, we were able to show how the riparian zone controls baseflow in this system and how the riparian zone "resets" the stable isotope composition of the observed streams in our low angle, forested watersheds. Although this approach is limited in terms of quantifying mixing percentages between different end-members, our dual isotope approach enable extraction of hydrologically useful information in a region with little change in individual isotope time series.

1   Introduction

The spatial and temporal sources of runoff in low angle, forested headwater watersheds are poorly understood. Most of what we know of runoff generation in forested terrain comes from steep humid sites where elevation potential dominates and runoff responses are high (for review see Bachmair and Weiler, 2011). Much recent work has focused on the threshold sequencing of spatial sources in upland forested watersheds (Sidle et al., 2000; Seibert and McDonnell, 2002), hillslope-riparian connectivity (McGlynn and McDonnell, 2003), and the importance of spatial patterns of hillslope-riparian-stream connectivity (Jencso et al., 2009; Jencso and McGlynn, 2011). Such connectivity may be strongly non-linear (Buttle et al., 2004; Zehe et al., 2007; Penna et al., 2011). Consequently, streamflow chemistry in upland forested watersheds is often determined by volume ratios of water sourcing in the hillslopes compared to riparian zone water (McGlynn and McDonnell, 2003) with many watersheds showing only brief expressions of adjacent hillslope water chemistry during large rainfall and snowmelt events (Burns et al., 2001).

Unlike the distinct watershed components found in steeper headwater counterparts (hillslope, hollow, riparian), low angled terrain smears the boundary between the riparian zone and hillslope and presents little in the way of obvious geomorphic units that might be considered for model construction. Early work in low angled terrain showed how matric potential (rather than elevational potential) dominates total potential and resulting subsurface runoff flowpaths (Anderson and Kneale, 1982). More recent work in lowland forests has shown that runoff may be generated from only small proportions of the watershed (Devito et al., 2005a). Lowland areas often exhibit a complex groundwater – surface water interaction. Water fluxes between slopes and wetlands are generally small (Devito et al., 2005a; Branfireun and Roulet,

1   1998), and hillslope-stream connectivity is rare (Redding and Devito, 2010; Ali et al., 2011).

2   These features in lowland forested watersheds appear to be controlled by the complex, and

3   poorly understood, interplay of climate, soils, and geology (Devito et al., 1996; Devito et al.,

4   2005b, Slattery et al., 2006, Sun et al., 2002). Furthermore, topography is not a clear driver of

5   runoff generation (Buttle et al., 2004; Devito et al., 2005b) since vertical subsurface flow

6   often dominates over lateral subsurface flow (Todd et al., 2006). Saturation excess overland

7   flow often dominants runoff response in these areas (Eshleman et al., 1994; Slattery et al.,

8   2006; La Torre Torres et al., 2011), but the linkages between hillslopes, riparian zones and the

9   stream are difficult to observe, conceptualize, and quantify.

10   Ordinarily, streamwater stable isotope tracing and isotope hydrograph separation would help

11   with questions of source components of streamflow (Klaus and McDonnell, 2013). However,

12   areas with low runoff coefficients, small event water contributions, or long transit times have

13   stream isotopic signals that are difficult to decipher due to the damping of the atmospheric

14   input signal. Despite this, La Torre Torres et al. (2011) have noted the pressing need for

15   isotope studies to "identify the sources of storm flow and base flow to better understand flow

16   generation mechanisms" in watersheds in low relief areas (in their case, the Atlantic Coastal

17   Plain of the USA).

18   So what can be done in low relief areas to quantify runoff sources when streamwater isotope

19   signals are muted and the flow itself in headwater streams is often very ephemeral? Here, we

20   present new work that addresses this fundamental question using a dual isotope approach

21   involving ^{18}O and ^{2}H. While numerous studies have used water lines based on dual isotopes in

22   various water cycle applications (Gonfiantini, 1986; Gibson et al., 2008; Yi et al., 2010;

23   Gibson et al., 2010; Zhang et al., 2013) we are unaware of any to date that have used this

24   approach to determine streamwater source components and hence, use them to build a

25   conceptual model of streamwater generation. We concentrate our efforts here on the lowland

26   forested watersheds draining the Savannah River Site (SRS) in the Coastal Plain of South

27   Carolina, USA and show the relationships of ^{2}H and ^{18}O for various water cycle components

28   in three headwater catchments over a three year observational period. We show proof of

29   concept of this approach to quantify the source(s) of streamflow, particularly during baseflow

30   conditions. We present evidence that the slopes of the meteoric water lines/evaporation water

31   lines (MWL/EWL) of the catchment water sources may be used to extract information on

32   runoff sources in ways not considered before. We then show how these distinct slopes may be

1   an aid to separate and quantify where stream water comes from in our low angle, forested

2   watersheds and develop a conceptual understanding of where water comes from in these

3   catchments. Lastly, we use a combination of $\delta^{18}O$ and $\delta^{15}N$ of nitrate to compare to our dual

4   isotope interpretation of water contributions to streamflow.

5   ## 2   Study site and Methods

6   ### 2.1   Study area

7   The study was conducted in three adjacent forest headwater watersheds that are tributaries to

8   Upper Fourmile Branch, at the Savannah River Site, a National Environmental Research Park.

9   The three watersheds have areas of 0.45 km^2 (R watershed), 1.69 km^2 (B watershed), and 1.17

10   km^2 (C watershed). The watersheds are located within the Aiken plateau of the Upper Atlantic

11   Coastal Plain in South Carolina, USA (Fig. 1). Average annual precipitation is 1225 mm

12   distributed evenly throughout the year (Fig. 2). The climate is characterized by long, hot

13   summers with an average daily maximum temperature of 32.3 °C and relatively mild winters

14   with an average temperature of 8.6 °C (Rebel, 2004). Measured average annual pan

15   evaporation over 30 years was 1448 mm (Blacksville, SC, ~25 km distance from SRS) (Kilgo

16   and Blake, 2005) and calculated average annual potential Evapotranspiration is 1443 mm,

17   based on the Priestley-Taylor equation (Rebel 2004). Actual evapotranspiration is

18   approximately 90% of the potential (Riha and Rebel, 2004; Samuelson et al. 2006). Potential

19   transpiration is about 95% in the summer and 82% in the winter of potential

20   evapotranspiration (Rebel, 2004). On six experimental plots throughfall was reduced by 10.1

21   to 16.4% compared to open precipitation (Hitchcock and Blake, 2003). Annual runoff

22   coefficients are as low as 0.01 (Du et al., In Review). The R watershed ranges from 70-106

23   MASL (meters above sea level), the B watershed from 80-108 MASL, and the C watershed

24   from 70-103 MASL. The upslope areas are characterized by gently rolling hills with an

25   average slope of ~2-3%, stream valleys (representing the riparian zone) consisted of long, flat,

26   forested wetlands as well as Carolina Bay wetlands that are characteristic of the Upper

27   Atlantic Coastal Plain. The hillslopes and ridges are covered by longleaf pine

28   (*Pinuspalustris*), loblolly pine (*P. taeda*), and slash pine (*P. elliottii*), while mixed hardwoods,

29   mainly sweet gum (*Liquidambar styraciflua*), dominate the riparian areas. The soils are well-

30   drained, loamy, siliceous, thermic Grossarenic Paleudults (Rasmussen and Mote, 2007), with

31   an argillic Bt horizon. Hydric soils are occupying the riparian zone and depressions such as

32   wetlands and Carolina bays. Surface soils contain 80-90% sand; the clay content increases to

1   35% or more in the Bt horizon (Kilgo and Blake, 2005). In-situ hydraulic conductivity (Ksat)

2   measurements with a compact constant head permeameter indicate medians around 10 cm/hr

3   in the topsoil and 0.5 cm/hr in the argillic horizon with anomalies of clearly higher Ksat (Du

4   et al., In Review) allowing vertical recharge. Mapping of the depth to the argilic horizon at a

5   40 x 40 m plot (2 x 1 m grid) in the R watershed revealed an average depth of 0.76 m (ranging

6   from 0.19 m to 1.62 m). At three excavated trenches (30-121 m) the depth to clay showed

7   median values of 0.5-0.8 m and ranged from 0.15 m to 2.0 m, and the thickness of the argillic

8   layer varied from 1.3 to 3.0 m, with a mean thickness of 2.1 m (Du et al., In Review). The

9   underlying geology consists of Late Cretaceous quartz sand, pebbly sand, kaolinitic clay,

10   Paleocene clayey and silty quartz sand, glauconitic sand, and silt from bottom to top (Wyatt

11   and Harris, 2004).

2.2 Sampling and Isotope Analysis

13   Sampling on the site is an ongoing process. In the paper we chose to limit the data in this

14   paper until mid May 2012 (records started in mid 2010 in watersheds B and C, and 2007 for

15   watershed R), as harvest of 40% of the forests in watersheds B and C was performed in

16   Spring 2012 and completed by May 2012.

17   At the outlet of each watershed, an H-flume and automatic sampler (ISCO 6712, Teledyne

18   ISCO, Lincoln, NE) were installed to collect streamwater samples and record water level for

19   calculation of streamflow. Sampling of streamwater was done by the automated sampler and

20   grab samples on a weekly basis. The R stream was sampled from April 2007, the B and C

21   streams from March 2010 until the streams felt dry during May 2011. Adjacent to the each

22   stream gauge (Figure 1), two shallow piezometers were installed in the riparian zone to

23   sample riparian groundwater from the hydric soil at monthly intervals. Event-based (six

24   events in between February 2011 and May 2012) lateral subsurface flow was sampled at a

25   120 m trenched hillslope (0.057 km^2) in the R watershed either as composite samples for

26   events, or with several discrete samples per event. Precipitation was sampled at approximately

27   weekly intervals, collecting the bulk sample (Feb 2007 until May 2012). Evaporation

28   influenced samples were removed from the data set (deuterium excess<0 and precipitation

29   amount <3mm). Throughfall was sampled weekly to bi-weekly at three locations within each

30   catchment (starting November 2010), where a ~200 cm^2 funnel collected the water.

31   Groundwater was sampled from 14 wells, all located in the same strata, between two and

32   twelve times per well over an 8 month period from September 2011 to May 2012. The water

1   samples were analyzed for stable isotopes of water, the ratio of $^{2}H/^{1}H$ and $^{18}O/^{16}O$ of liquid

2   water samples was measured with a Los Gatos Research (LGR) liquid water isotope analyzer

3   (LWIA) that utilizes off-axis integrated cavity output spectroscopy (Baer et al., 2002), and

4   converted to $\delta^{2}H$ and $\delta^{18}O$ using the VSMOW.

5   For stable isotopes of nitrate, water samples were collected in the field from stream water,

6   riparian groundwater, throughfall, and lateral flow from the trenches. Water samples were

7   immediately filtered (GF/F, Whatman Inc.) into acid-washed, HDPE bottles, and frozen until

8   analysis. Nitrate concentrations were measured using the cadmium reduction method (APHA

9   2005) on a SEAL Analytical AA3 autoanalyzer. Stable isotopes of nitrate were measured

10   using the denitrifier method with *Pseudomonas aureofaciensand* P. *chlororaphis* bacteria

11   (Sigman et al. 2001; Casciotti et al. 2002) at the UC Davis Stable Isotope Facility. The ratios

12   of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ were measured on a Thermo Finnigan Gas Bench and PreCon trace

13   gas concentration system with a ThermoScientific Delta V Plus isotope-ratio mass

14   spectrometer, and a minimum of 1 μM NO_3 was required for analysis. $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$

15   were determined against standards USGS 32, USGS 34, and USGS 35, and reported relative

16   to N_2 in air for $\delta^{15}N_{NO3}$, and relative to the Vienna Standard Mean Ocean Water (VSMOW)

17   for $\delta^{18}O_{NO3}$.

18   **3   Results**

19   **3.1   Hydrological and isotopic dynamics**

20   Precipitation totaled 1373 mm in 2009, 964 mm in 2010, and 989 mm in 2011 (Fig. 3a). The

21   below average annual precipitation amount in 2010 and 2011 led to dry streams in spring

22   2011 until the end of the observation period. Generally, streamflow in all three streams was

23   intermittent with zero-flow periods. Streamflow was usually generated when the wetland zone

24   in the valley bottom was saturated. Some of the precipitation (Fig. 3a) events generated short-

25   lived hydrograph peaks in the three watersheds and the hillslope trench (Fig. 3 b-e). Overall,

26   storm runoff ratios were extremely low ($<2.3\%$) and streams, even when flowing, were very

27   muted in the response to heavy rainfall (Fig. 3b-d). While some deeper groundwater wells

28   showed groundwater depths of ~10 m, the well in the riparian zone of the C watershed

29   approached the soil surface (<1 m) during wet periods.

30   The isotopic ratios in precipitation varied between -17.3‰ and +3.9‰ for ^{18}O, and -122.7‰

31   and +37.4‰ for ^{2}H, respectively (Fig. 3a and 4a). The $\delta^{18}O$ and $\delta^{2}H$ values for stream water

were much less variable, and averaged around -4‰ and –23‰, respectively for all three streams. The streamwater values varied between -5.5‰ and -2.3‰ (^{18}O) and -26.6‰ and -18.0‰ (^{2}H) for the R stream, -4.9‰ and -1.7‰ (^{18}O) and -26.7‰ and -14.7‰ (^{2}H) for the B stream, and -4.6‰ and -2.7‰ (^{18}O) and -24.4‰ and -17.2‰ (^{2}H) for the C stream (Fig. 3b-d, ^{2}H not shown). We attempted to fit an input-output transfer function between observed precipitation and runoff isotope ratios (McGuire and McDonnell, 2006), to determine catchment transit times. Only very poor fits were possible, suggesting that the transit time is much longer than the data series length and likely beyond the scope of naturally-occurring stable isotopes, consistent with water balance calculation of stream transit time (Du et al., In Review).

3.2   Isotopic water lines of water cycle components

The δ^2H- δ^{18}O relation for precipitation, streamwater, groundwater, and subsurface stormflow is shown in Figure 4. These data show that the slopes of each of these lines are systematically offset from local precipitation (Fig. 4a). The local meteoric water line (LMWL) and the global meteoric water line (GMWL) are compared in Figure 5. We found that the LMWL for precipitation was:

δ^2H = 7.15*δ^{18}O +9.28‰

where the R^2= 0.93, p<<0.01 (t-test), and the total number of discrete rainfall samples was 145.

Throughfall was slightly enriched compared to open precipitation. The slope of the throughfall water lines varied between 6.00 and 7.03, and intercepts between 5.51 and 8.96 for different locations. The evaporation water lines (EWL) of the three streams (Fig. 4b) showed very strong evaporative enrichment of heavy isotopes, based on measured slope and intercept as shown below:

R: δ^2H = 2.52*δ^{18}O -11.88‰, R^2= 0.40, p<<0.01, n=134.

B: δ^2H = 2.86*δ^{18}O -9.66‰, R^2= 0.78, p<<0.01, n=38.

C: δ^2H = 2.84*δ^{18}O -9.95‰, R^2= 0.55, p<<0.01, n=76.

The EWLs of the riparian groundwater (Fig. 4c) were very similar to the EWLs of the streams and showed the same strong enrichment:

1 R riparian: $\delta^2H = 2.09*\delta^{18}O -14.89‰$, $R^2= 0.67$, p<<0.01, n=38.

2 C riparian: $\delta^2H = 2.52*\delta^{18}O -12.21‰$, $R^2= 0.62$, p<<0.01, n=35.

3 We are not presenting the regression relations between ^{18}O and ^2H for the samples of the two

4 piezometers in the riparian zone of the B stream, since the regression was not significant

5 (p>0.05). Water collected as lateral subsurface stormflow from the hillslope trench (shown in

6 Fig. 1) in watershed R combined soil water and event precipitation. The EWLs of these

7 mobile, shallow subsurface waters (Fig. 4d) fell between the slope of precipitation and

8 streamwater:

9 SSF: $\delta^2H = 4.58*\delta^{18}O – 2.11‰$, $R^2= 0.75$, p<<0.01, n=22.

10 Groundwater from the 14 wells also showed distinct evaporative enrichment:

11 GW: $\delta^2H = 3.53*\delta^{18}O – 8.27‰$, $R^2= 0.45$, p<<0.01, n=117.

12 We did not further differentiate the EWLs of different groundwater wells due to the low

13 number of samples for each well. The $\delta^{18}O$ (and δ^2H, not shown) values of the riparian zone

14 water were closely linked to the values observed in the corresponding streams (Fig. 6).

15 Especially in the R watershed, $\delta^{18}O$ from both piezometers were very similar to the observed

16 values in the stream over the observation period (Fig. 6a). The same pattern was observed in

17 the B watershed (Fig. 6b), while the $\delta^{18}O$ values of riparian groundwater in the C watershed

18 were often lighter than the corresponding stream water (Fig. 6c). During March 2011 some

19 differences between the piezometers and the stream values were observable. Stream discharge

20 was very low at this point so that some direct precipitation onto the channel itself may explain

21 this effect. In March, we observed one precipitation sample with a very heavy $\delta^{18}O$ value of

22 3.9‰.

23 Further, it is important that the various compartments have significantly different EWLs. This

24 would eventually allow to unambiguously differentiate them. We used a two sample t-test to

25 evaluate this. The results are summarized in Table 1 and indicate that most components are

26 indeed significantly different from each other.

27 **3.3 Isotopes of nitrate in water cycle components**

28 The dual isotope plot of $\delta^{18}O_{NO3}$ vs. $\delta^{15}N_{NO3}$ (Fig. 7) showed distinct differences in the

29 signatures of nitrate in the different water cycle components in the R watershed. The

30 signatures of the stream water overlap with those of the riparian zone. In contrast, nitrate

isotope signatures of subsurface stormflow from the trench can reach high values that approach the signatures in throughfall, suggesting a fast transformation of throughfall into subsurface stormflow.

4 Discussion

The three watersheds showed very low annual runoff ratios during the three year record, combined with long spells of zero flow. This is similar to Sun et al. (2002) who showed highly ephemeral stream discharge patterns for their Coastal Plain site. Like Amatya et al. (1996) and Slattery et al. (2006) we found that soil properties, especially buried argillic horizons with low permeability (i.e. the throttle for lateral flow), strongly influenced runoff generation in these low relief Coastal Plain regions. In related work at our site, Du et al. (In Review) observed that the trenched hillslope (draining 13% of the R watershed) can generate higher discharge peaks than measured at the catchment outlet. For another catchment in the Atlantic Coastal Plain La Torre Torres et al. (2011) showed the importance of evapotranspiration on runoff generation, due to its effect on water table position and its subsequent control on runoff. They also found a strong seasonality in runoff ratios based on the seasonality in evapotranspiration and rain amount during wet periods, consistent with the catchment behavior in our study.

Our site, like that reported by Devito et al. (2005a), showed that dry catchment conditions frequently led to disconnectivity of the uplands with the valley bottom and stream. This resulted in low runoff coefficients and the dominance of evaporation in the water balance. In addition, direct precipitation on the stream channel can alter the isotope signal, when flow is close to zero some. This was observed during March 2011, when very heavy precipitation ($\delta^{18}O=3.9‰$) led to a deviation between stream isotope signals and riparian isotopic signals adjacent to the streams throughout the area. Figure 8 conceptually summarizes the runoff generation and isotopic signature at the study site. Key element is the rare or non-existing connectivity in the hillslope-riparian-stream continuum and the enrichment in heavy water isotopes in the riparian zone/wetlands that supplies baseflow. Further, the deeper groundwater system can interact with the groundwater of the riparian zone during wet conditions and is likely a major contributor to the riparian groundwater.

4.1 What do the slopes of different source components mean and are they realistic?

Evaporation between rain events had a significant effect on the isotopic composition of streamflow. Isotopic fractionation via evaporation leads to a stronger kinetic effect for ^{18}O compared to ^{2}H, resulting in evaporative enrichment of the water along an evaporation water line with a lower slope relative to the original water (Gonfiantini, 1986). While the variability in stream ^{18}O and ^{2}H is low over time, the isotope data exhibited a strong enrichment in heavy isotopes compared to precipitation and throughfall. Our samples of groundwater, subsurface stormflow, and streamflow all exhibited significant ($p \leq 0.05$) isotopic enrichment compared to the local precipitation. The observed slopes are lower than expected for South Carolina based on the work of Gibson et al. (2008), who modeled a slope of 4-5 for open water bodies and 3-4 for soil water for the region. The strong evaporative enrichment of groundwater suggests groundwater recharge influenced by enriched soil water. Streams and riparian groundwater were even more enriched in heavy isotopes suggesting further isotopic enrichment of the riparian groundwater as it remerged in the low relief and slow moving stream floodplain. Our measured isotopic enrichment and the low annual runoff coefficients suggest that evapotranspiration strongly influences the runoff dynamics in the R, B, and C watersheds, consistent with the behavior of other lower relief watersheds in the Atlantic Coastal Plain of the USA (La Torre Torres et al., 2011) and elsewhere (Devito et al., 2005a).

To our knowledge such shallow slopes for streamwater have not been reported in the literature. We think that measurement errors are unlikely since the slopes of the LMWL of our precipitation sample fit the expectations. The statistical significance of the relationship of ^{2}H and ^{18}O was significant ($p \leq 0.05$) for all three streams, indicating that these EWLs are describing the streamflow. Furthermore, the removal of several relatively high isotopic values from the stream EWL (Fig. 4) does not significantly change the slope, suggesting the relationship is robust across the measured ^{18}O and ^{2}H values. Surface water sampled from two Carolina Bay wetlands also showed strong evaporative enrichment, suggesting that the observed stream EWLs are not simply a mixing line between an evaporative groundwater and a rain fed wetland that suddenly becomes connected to the stream outlet. Lower slopes than predicted by Gibson et al. (2008) could also derive from mixing processes of water vapor between terrestrial and oceanic air masses leading to evaporation lines with lower slopes.

1 Further work to explore the exceptionally low slopes is needed as this is an interesting
2 phenomena in and of itself.

4.2 The dual isotope approach for conceptualizing flow sources in low angled terrain

5 The use of stable isotopes of water has been a valuable tool for determining the geographic
6 sources and temporal components of hydrographs (Klaus and McDonnell, 2013). When
7 isotopes are combined with chemical tracers, they may also be useful for determining the
8 importance of different landscape elements in the generation of flow at the catchment scale
9 (Burns et al., 2001; McGlynn and McDonnell, 2003; Ocampo et al, 2006). Key prerequisites
10 for all of these approaches are distinct end members and an isotope time series that deflects
11 through time from pre-event conditions (Sklash and Farvolden, 1979). Our streamwater
12 isotopic time series showed (with few exceptions) few deflections through time and,
13 consequently, provided little insight into time- and source-components and hillslope-riparian-
14 streamflow connectivity. Furthermore, our isotope time series did not yield a meaningful
15 transit time estimate, suggesting that transit times are longer than the range used for stable
16 isotopes, likely >5 years.

17 In the low relief watersheds at the SRS, where the classical methods of isotope hydrology are
18 limited by the lack of temporal dynamics of the stable isotope time series, our dual isotope
19 approach was useful for determining the connectivity/disconnectivity between different water
20 cycle components. The use of the individual water lines adds value to our understanding of
21 runoff generation in this low angled terrain and is consistent with hydrometric observations
22 (Du et al., In Review) and nitrate stable isotopes. The use of the water line approach clarifies
23 the close link between the groundwater, the riparian water, and the stream and shows that the
24 riparian zone controls the isotopic composition of streamflow.

25 This method is useful to constrain the linkages in low angled terrain but also allows additional
26 insight in data scarce catchments that can give a fundamental understanding where water
27 comes from. While the water line approach is able to constrain a general conceptual model
28 (Fig. 8) of where water comes from, the approach exhibits clear limitations. Mixing of two
29 water types with clearly different isotopic enrichments can lead to mixing lines in the
30 resulting water that can infer with a meaningful interpretation of the resulting water lines. The
31 relative position of a sample along this mixing line indicates contribution of multiple water

sources with a different degree of evaporative enrichment. This will prohibit a quantitative mixing calculation based on the characteristics of the water lines for a distinct sample of stream water. Nevertheless, the presented approach during baseflow conditions can clearly constrain where water comes from at different antecedent conditions in a watershed, confirmed by nitrate isotope data.

5 Conclusions

We examined the source of runoff in a set of lowland forested watersheds in South Carolina, USA. Streamflow was very ephemeral and the time series of stable isotopic composition of streamwater showed minimal temporal dynamics compared to rainfall. Notwithstanding, our dual isotope approach based on the water lines was able to isolate and separate hillslope, riparian and deep groundwater, and streamflow compositions. The streams in each of our watersheds showed strong evaporative enrichment compared to the local meteoric water line ($\delta^2H = 7.15*\delta^{18}O +9.28‰$) with slopes of 2.52, 2.84, and 2.86. Based on the unique and unambiguous slopes of the EWLs of the different water cycle components and the isotopic time series of the individual components we were able to show how the riparian zone controls baseflow in this system and how the riparian zone is "resetting" the stable isotope composition of the observed streams in our low angle, forested watersheds. Deeper groundwater likely supplies the riparian groundwater system. These findings were supported by the overlap of nitrate stable isotope signatures ($^{18}O_{NO3}$ and $^{15}N_{NO3}$) between riparian groundwater and stream water in the R watershed. Our approach allowed for a general description of long term sources to streamflow, especially baseflow even though in-situ mixing calculations were not possible.

References

Ali, G.A., L'Heureux, C., Roy, A.G., Turmel, M.C., and Courchesne, F. : Linking spatial patterns of perched groundwater storage and stormflow generation processes in a headwater forested catchment, Hydrol. Process., 25 (25), 3843-3857, doi: 10.1002/hyp.8238, 2011.

Amatya, D.M., Skaggs, R.W., and Gregory, J.D.: Effects of controlled drainage on the hydrology of drained pine plantations in the North Carolina coastal plain, J. Hydrol., 181 (1-4), 211-232, doi: 10.1016/0022-1694(95)02905-2, 1996.

Anderson, M.G. and Kneale, P.E.: The influence of low-angled topography on hillslope soil-water convergence and stream discharge, J. Hydrol., 57 (1-2), 65-80, doi: 10.1016/0022-1694(82)90103-2, 1982.

Bachmair, S. and Weiler, M.: New dimensions of Hillslope Hydrology, in: Levia, D.F., Carlyle-Moses, D., and Tanaka, T. (Editors), Forest Hydrology and Biogeochemistry. Springer Netherlands, Amsterdam, 455-481, 2011.

Baer, D.S., Paul, J.B., Gupta, M., and O'Keefe, A.: Sensitive absorption measurements in the near-infrared region using off-axis integrated cavity output spectroscopy, International Symposium on Optical Science and Technology, International Society for Optics and Photonics, 167-176, 2002.

Branfireun, B.A. and Roulet, N.T.: The baseflow and storm flow hydrology of a precambrian shield headwater peatland, Hydrol. Process., 12 (1), 57-72, 1998.

Burns, D.A., McDonnell, J.J., Hooper, R.P., Peters, N.E., Freer, J.E., Kendall, C., and Beven,K.: Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA), Hydrol. Process., 15 (10), 1903-1924, doi: 10.1002/hyp.246, 2001.

Buttle, J.M., Dillon, P.J., and Eerkes, G.R.: Hydrologic coupling of slopes, riparian zones and streams: an example from the Canadian Shield, J. Hydrol., 287 (1), 161-177, doi: 10.1016/j.jhydrol.2003.09.022, 2004.

Casciotti, K.L., Sigman, D.M., Hastings, M.G., Böhlke, J.K., and Hilkert, A.: Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method, Anal. Chem., 74 (19), 4905-4912, doi: 10.1021/ac020113w, 2002.

Devito, K.J., Hill, A.R., and Roulet, N.: Groundwater-surface water interactions in headwater forested wetlands of the Canadian Shield, J. Hydrol., 181 (1), 127-147, doi: 10.1016/0022-1694(95)02912-5, 1996.

Devito, K.J., Creed, I.F., and Fraser, C.J.D.: Controls on runoff from a partially harvested aspen-forested headwater catchment, Boreal Plain, Canada, Hydrol. Process., 19 (1), 3-25, doi: 10.1002/hyp.5776, 2005a.

Devito, K.J., Creed, I.F., Gan, T., Mendoza, C., Petrone, R., Silins, U., and Smerdon, B.: A framework for broad-scale classification of hydrologic response units on the Boreal Plain: is topography the last thing to consider? Hydrol. Process., 19 (8), 1705-1714, doi: 10.1002/hyp.5881, 2005b.

Du, E., Jackson, C.R., McDonnell, J.J., Klaus, J., Griffiths, N.A., Williamson, M.F., Greco, J.L., Bitew, M.: More fill, less spill: interflow behavior over a low-angle argillic layer, In Review.

Eshleman, K.N., Pollard, J.S., and O'Brien, A.K.: Interactions between groundwater and surface water in a virginia coastal plain watershed. 1. Hydrological flowpaths, Hydrol. Process., 8 (5), 389-410, doi: 10.1002/hyp.3360080504, 1994.

Gibson, J.J., Birks, S.J., and Edwards, T.W.D.: Global prediction of δA and $\delta2H$-$\delta18O$ evaporation slopes for lakes and soil water accounting for seasonality, Global Biogeochem. Cy., 22 (2), GB2031, doi: 10.1029/2007GB002997, 2008.

Gibson, J.J., Fekete, B.M., and Bowen, G.J.: Stable Isotopes in Large Scale Hydrological Applications, in: Isoscapes, Springer, 389-405, 2010.

Gonfiantini, R.: Environmental isotopes in lake studies, Handbook of environmental isotope geochemistry, 2 113-168, 1986.

Hitchcock, D., and Blake, J.I.: Effectiveness Monitoring Report MWMF Tritium Phytoremediation Interim Measures, Technical Report, USDA Forest Service, Savannah River, New Ellenton, SC, 2003.

Jencso, K. G., McGlynn, B. L., Gooseff, M. N., Wondzell, S. M., Bencala, K. E. and Marshall, L. A.: Hydrologic connectivity between landscapes and streams: Transferring reach- and plot-scale understanding to the catchment scale, Water Resour. Res., 45(4), W04428, 2009.

Jencso, K.G. and McGlynn, B.L.: Hierarchical controls on runoff generation: Topographically driven hydrologic connectivity, geology, and vegetation, Water Resour. Res., 47 (11), doi: 10.1029/2011WR010666, 2011.

Kilgo, J.C. and Blake, J.I.: Ecology and management of a forested landscape: Fifty years on the Savannah River, Island Press, Washington, DC, 2005.

Klaus, J. and McDonnell, J.J.: Hydrograph separation using stable isotopes: Review and evaluation, J. Hydrol., 505 (0): 47-64, doi: 10.1016/j.jhydrol.2013.09.006, 2013.

La Torre Torres, I.B., Amatya, D.M., Sun, G., and Callahan, T.J.: Seasonal rainfall-runoff relationships in a lowland forested watershed in the southeastern USA, Hydrol. Process., 25 (13), 2032-2045, doi: 10.1002/hyp.7955, 2011.

McGlynn, B.L. and McDonnell, J.J.: Quantifying the relative contributions of riparian and hillslope zones to catchment runoff, Water Resour. Res., 39 (11), 1310, doi: 10.1029/2003WR002091, 2003.

McGuire, K.J. and McDonnell, J.J.: A review and evaluation of catchment transit time modelling, J. Hydrol., 330 (3-4), 543-563, doi: 10.1016/j.jhydrol.2006.04.020, 2006.

Ocampo, C.J., Sivapalan, M., and Oldham, C.: Hydrological connectivity of upland-riparian zones in agricultural catchments: Implications for runoff generation and nitrate transport, J. Hydrol., 331 (3), 643-658, doi: 10.1016/j.jhydrol.2006.06.010, 2006.

Penna, D., Tromp-van Meerveld, H.J., Gobbi, A., Borga, M., and la Fontana, G.: The influence of soil moisture on threshold runoff generation processes in an alpine headwater catchment, Hydrol. Earth Syst. Sci., 15 (3), 689-702, doi: 10.5194/hess-15-689-2011, 2011.

Rasmussen, T.C. and Mote, T.L.: Monitoring surface and subsurface water storage using confined aquifer water levels at the Savannah River Site, USA, Vadose Zone J., 6 (2), 327-335, doi: 10.2136/vzj2006.0049, 2007.

Rebel, K. T.: Using trees to remediate tritium contaminated groundwater: a modeling and tracer study, Ph.D thesis, Cornell University, 173 pp., 2004.

Redding, T. and Devito, K.: Mechanisms and pathways of lateral flow on aspen-forested, Luvisolic soils, Western Boreal Plains, Alberta, Canada, Hydrol. Process., 24 (21), 2995-3010, doi: 10.1002/hyp.7710, 2010.

1   Riha, S. and Rebel, K.: Savannah River Site Mixed Waste Management Facility Southwest

2   Plume Tritium Phytoremediation Evaluating Irrigation Management Strategies Over 25

3   Years, Technical Report, USDA Forest Service, Savannah River, New Ellenton, SC, 2004.

4   Samuelson, L., Stokes, T., and Farris, M.: Measuring Transpiration to Regulate Winter

5   Irrigation Rates, Final Report 06-27-R USDA Forest Service, Savannah River, New Ellenton,

6   SC, 2006.

7   Seibert, J. and McDonnell, J.J.: On the dialog between experimentalist and modeler in

8   catchment hydrology: Use of soft data for multicriteria model calibration, Water Resour. Res.,

9   38 (11), 1241, doi:10.1029/2001WR000978, 2002.

10   Sidle, R. C., Tsuboyama, Y., Noguchi, S., Hosoda, I., Fujieda, M., and Shimizu, T.:

11   Stormflow generation in steep forested headwaters: a linked hydrogeomorphic paradigm,

12   Hydrol. Process., 14(3), 369-385, 2000.

13   Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M., and Böhlke, J.K.: A

14   bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, Anal.

15   Chem., 73 (17), 4145-4153, doi: 10.1021/ac010088e, 2001.

16   Sklash, M.G. and Farvolden, R.N.: The role of groundwater in storm runoff, J. Hydrol., 43

17   (1), 45-65, 10.1016/0022-1694(79)90164-1, 1979.

18   Slattery, M.C., Gares, P.A., and Phillips, J.D.: Multiple modes of storm runoff generation in a

19   North Carolina coastal plain watershed, Hydrol. Process., 20 (14), 2953-2969, doi:

20   10.1002/hyp.6144, 2006.

21   Sun, G., McNulty, S.G., Amatya, D.M., Skaggs, R.W., Swift Jr, L.W., Shepard, J.P., and

22   Riekerk, H.: A comparison of the watershed hydrology of coastal forested wetlands and the

23   mountainous uplands in the Southern US, J. Hydrol., 263 (1), 92-104, doi: 10.1016/S0022-

24   1694(02)00064-1, 2002.

25   Todd, A.K., Buttle, J.M., and Taylor, C.H.: Hydrologic dynamics and linkages in a wetland-

26   dominated basin, J. Hydrol., 319 (1), 15-35, doi: 10.1016/j.jhydrol.2005.05.001, 2006.

27   Wyatt, D.E. and Harris, M.K.: Overview of the history and geology of the Savannah River

28   Site, Environmental Geosciences, 11 (4), 181-190, doi: 10.1306/eg.06220404022, 2004.

1 Yi, Y., Gibson, J.J., Hélie, J.F., and Dick, T.A.: Synoptic and time-series stable isotope
2 surveys of the Mackenzie River from Great Slave Lake to the Arctic Ocean, 2003 to 2006, J.
3 Hydrol., 383 (3-4), 223-232, doi: 10.1016/j.jhydrol.2009.12.038 2010.

4 Zehe, E., Elsenbeer, H., Lindenmaier, F., Schulz, K., and Blöschl, G.: Patterns of
5 predictability in hydrological threshold systems, Water Resour. Res., 43 (7), doi:
6 10.1029/2006WR005589, 2007.

7 Zhang, Y., Shen, Y., Chen, Y., and Wang, Y.: Spatial characteristics of surface water and
8 groundwater using water stable isotope in the Tarim River Basin, northwestern China,
9 Ecohydrology,   6   (6),   1031-1039,   doi: 10.1002/eco.1416,   2013.
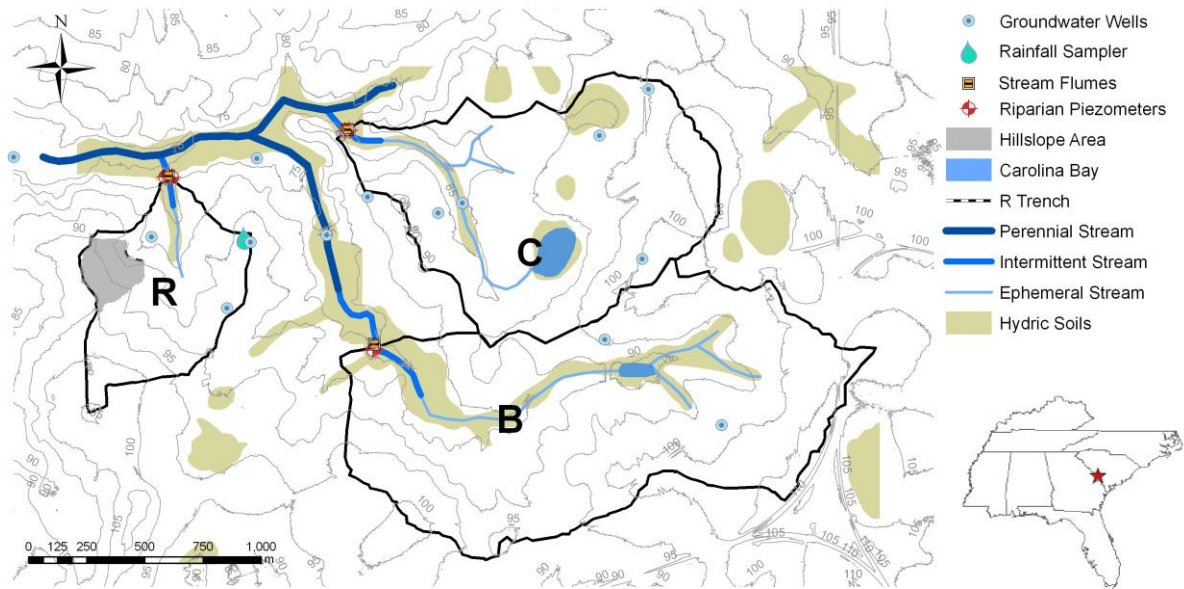
Figure 1. Study site with the three watersheds (R, B, C), the trenched hillslope, streams, instrumentation, the distribution of hydric soils, and the location within the United States.
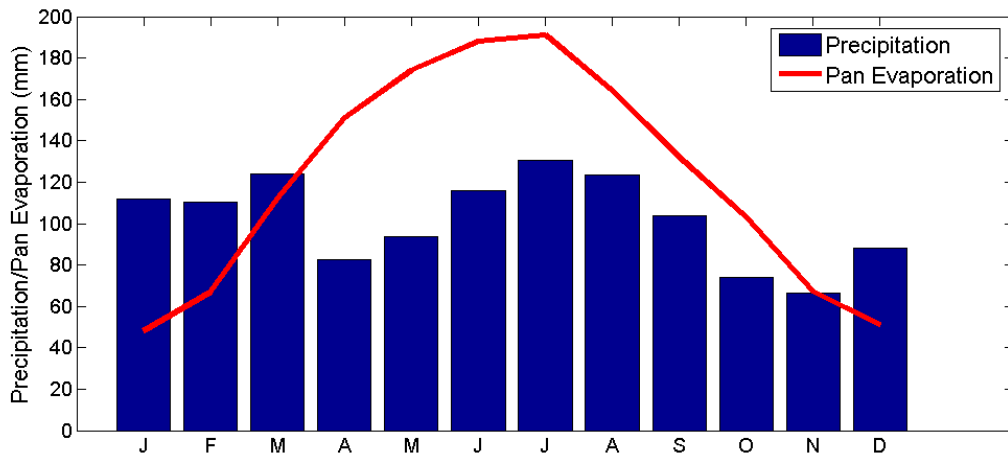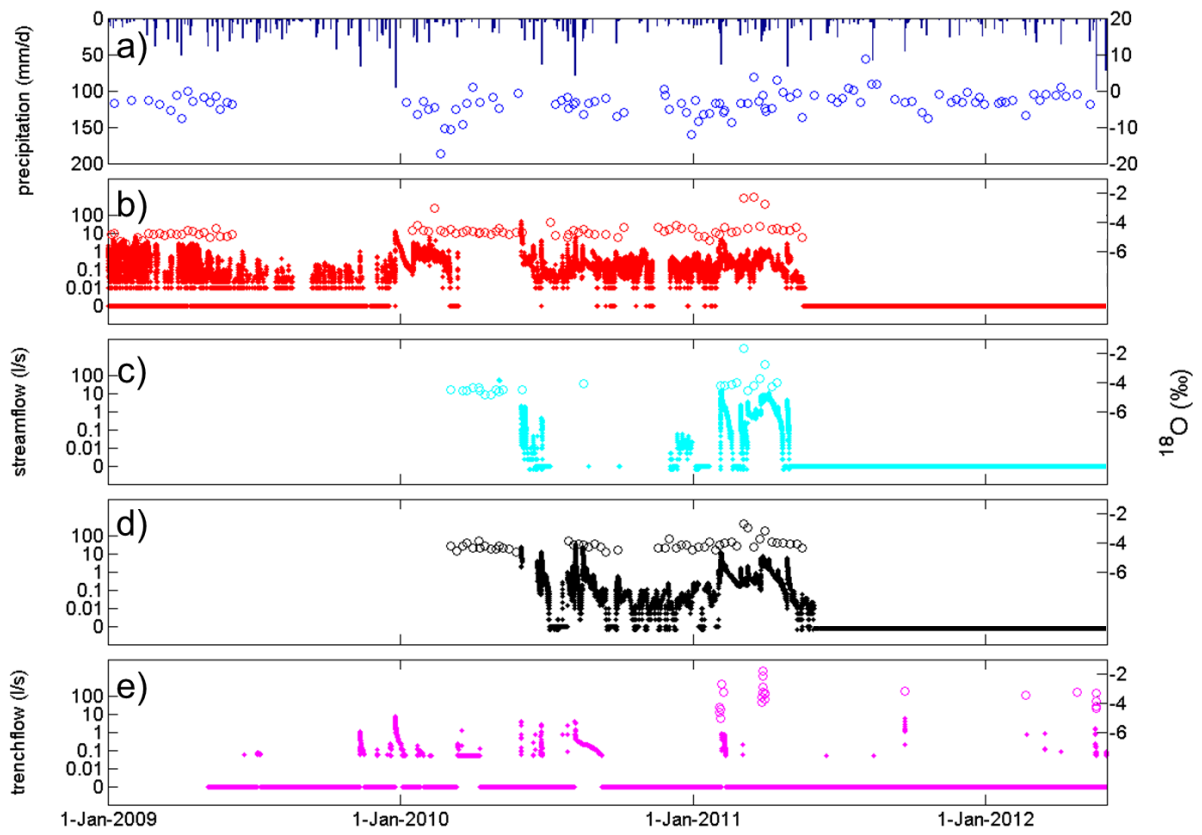
1

2   Figure 2: Average monthly precipitation and monthly pan evaporation for the study area (data

3   from Kilgo and Blake, 2005).

4

Figure 3. a) Daily precipitation amount and $\delta^{18}O$ of precipitation, b) streamflow and $\delta^{18}O$ in the R watershed, c) streamflow and $\delta^{18}O$ in the B watershed, d) streamflow and $\delta^{18}O$ in the C watershed, d) trenchflow and $\delta^{18}O$ in the hillslope trench of the R catchment
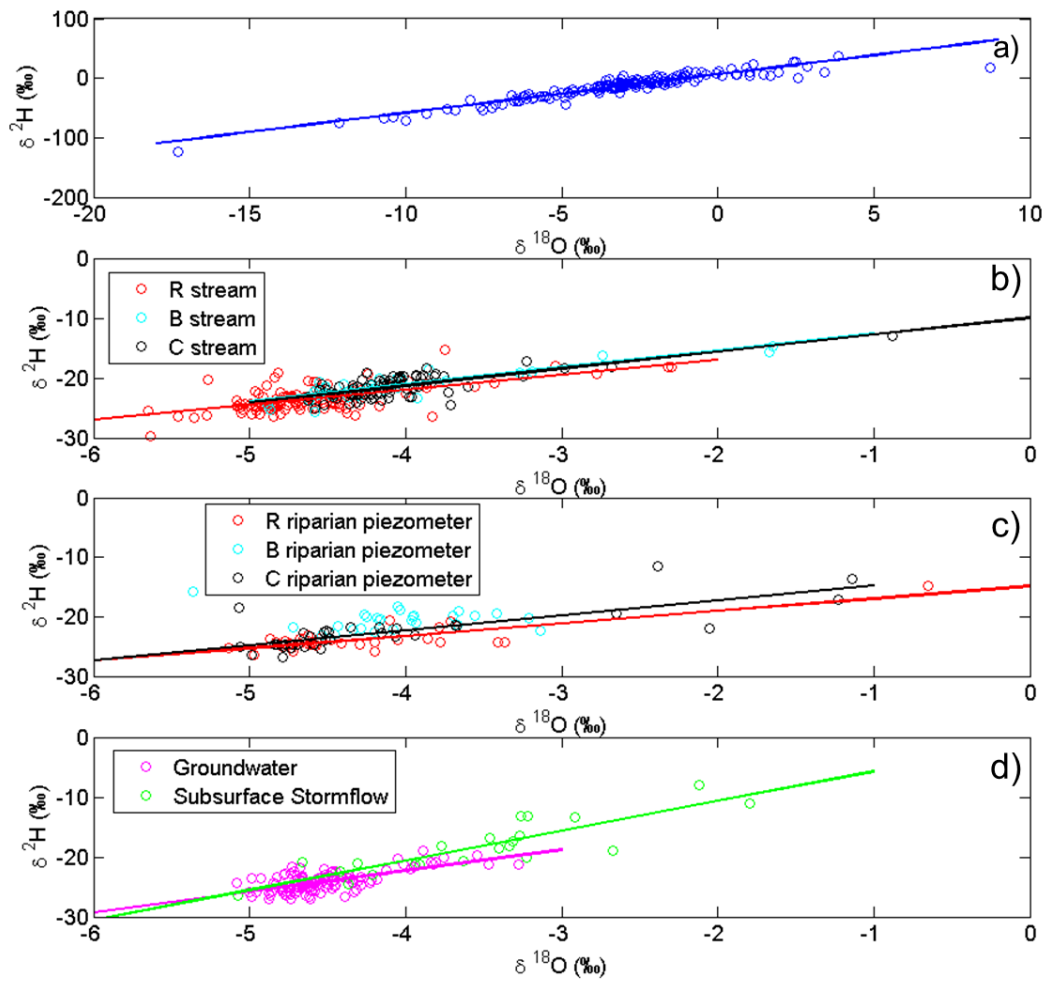
Figure 4. ^{2}H versus ^{18}O and the Meteoric and Evaporation Water Lines for a) precipitation, b) streamflow of the three streams, c) the groundwater in the riparian piezometers in each watershed, and d) subsurface stormflow in the R watershed and groundwater. Note the different x- and y-axes on the first vs. the lower 3 panels.
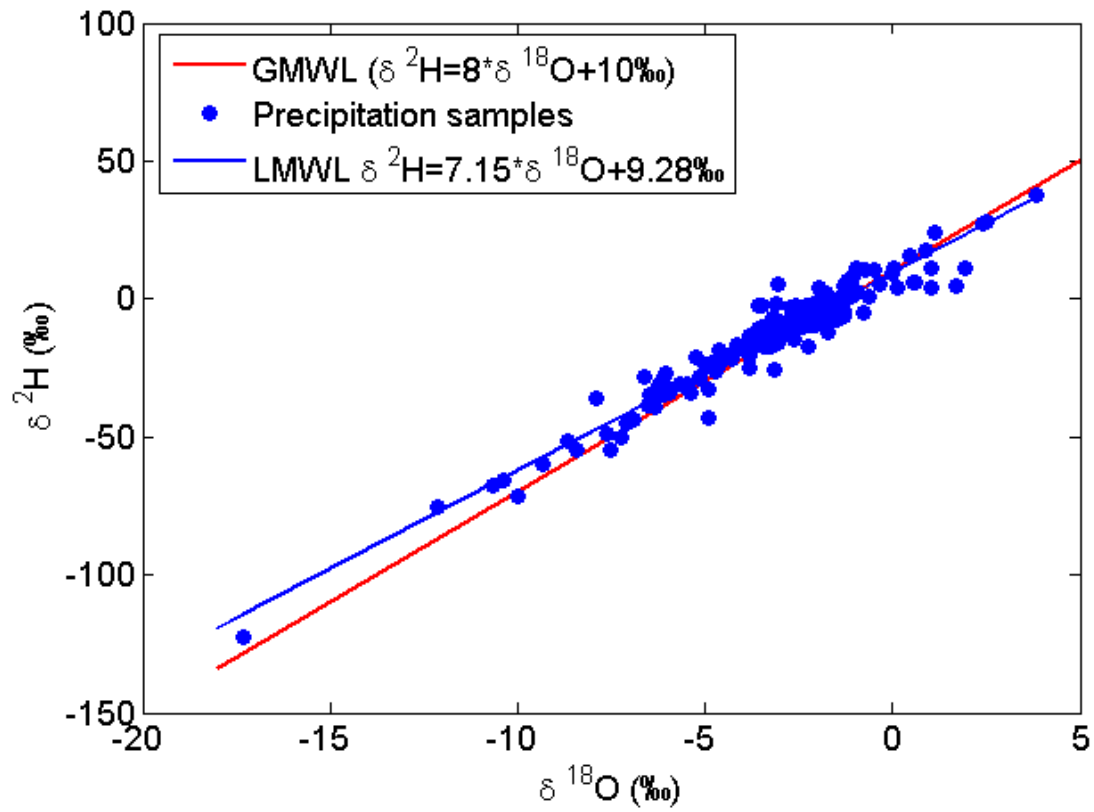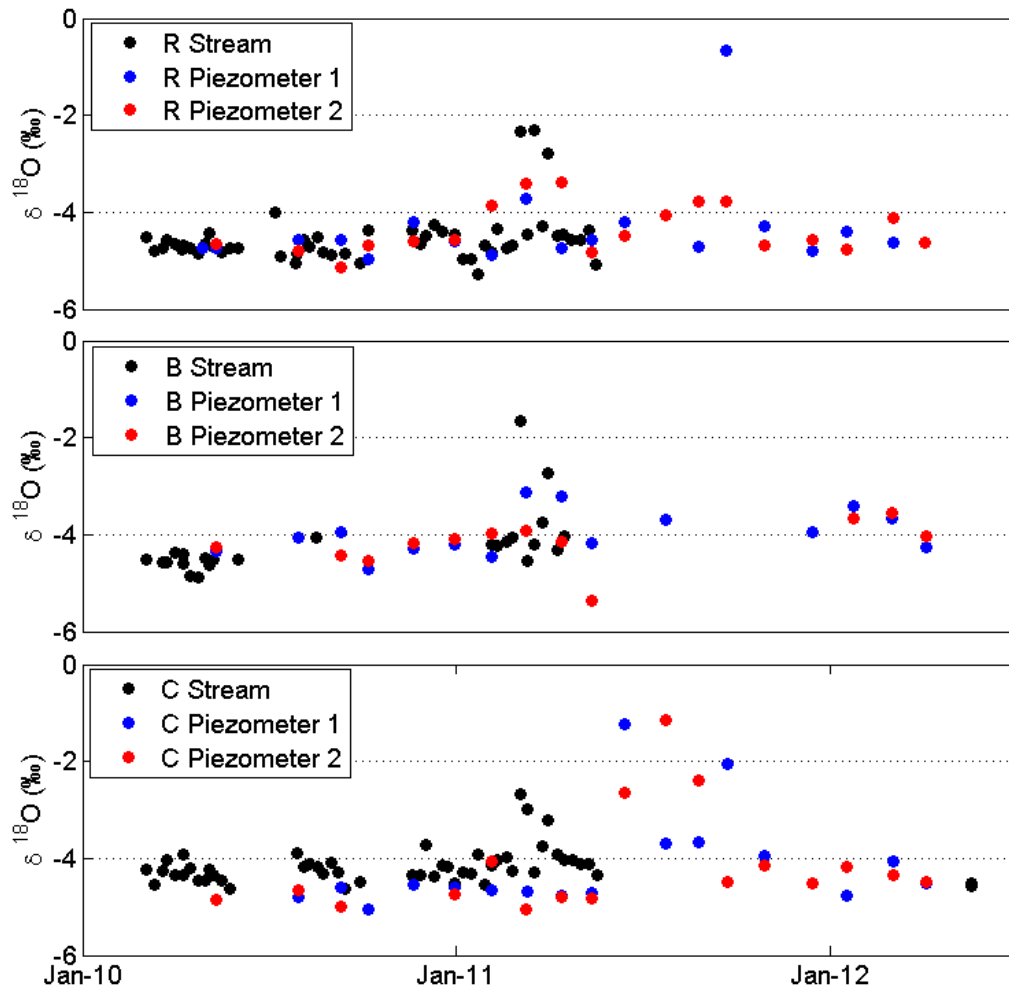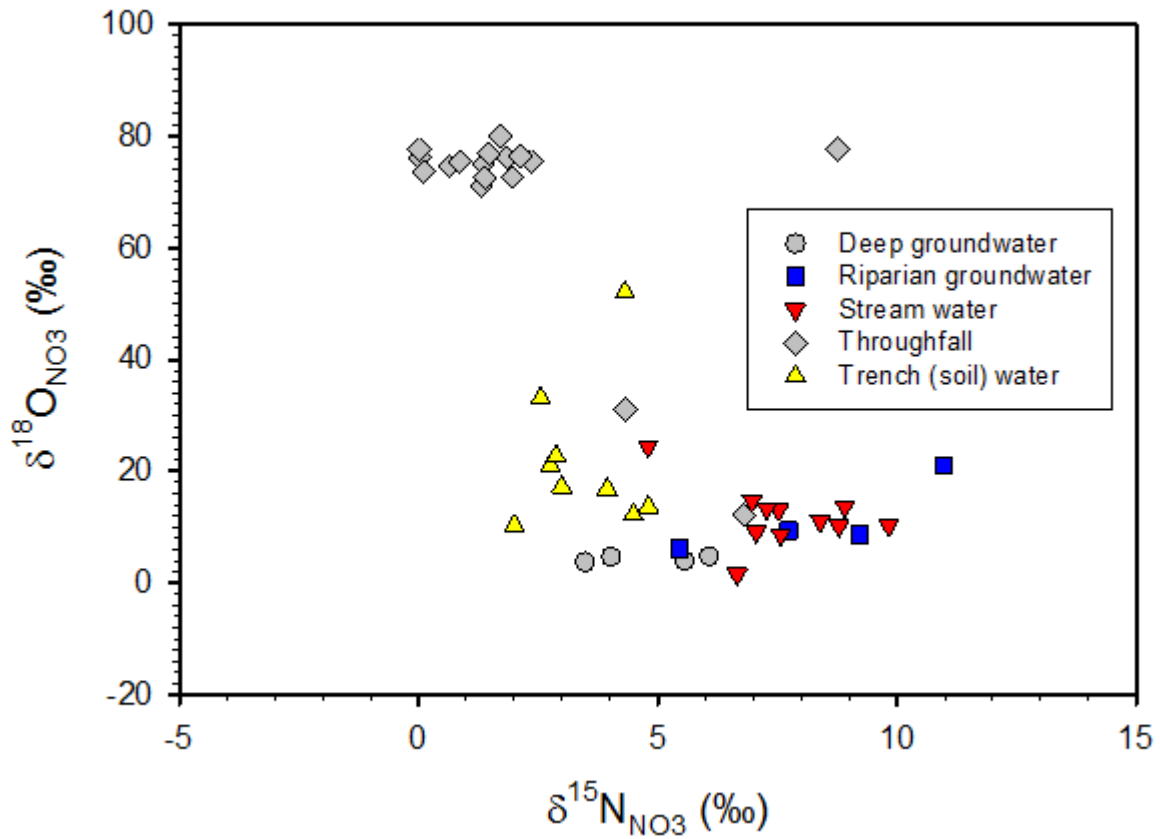
1

2

3

4

5

6

7

8

9

10

11

12

Figure 5. The Global Meteoric Water Line (GMWL) compared to the Local Meteoric Water Line (LMWL) of the study site.

1

2   Figure 6. Temporal dynamics of 18O in riparian groundwater and the stream outlet for the R,

3   B, and C watersheds.

1

2 Figure 7. Biplot of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ of nitrate (‰) in water samples collected from the

3 intermittent stream (white square), riparian groundwater (black circle), throughfall (light grey

4 triangle), deep groundwater (dark grey triangle), and trench flow water (grey diamond) in the

5 R watershed.
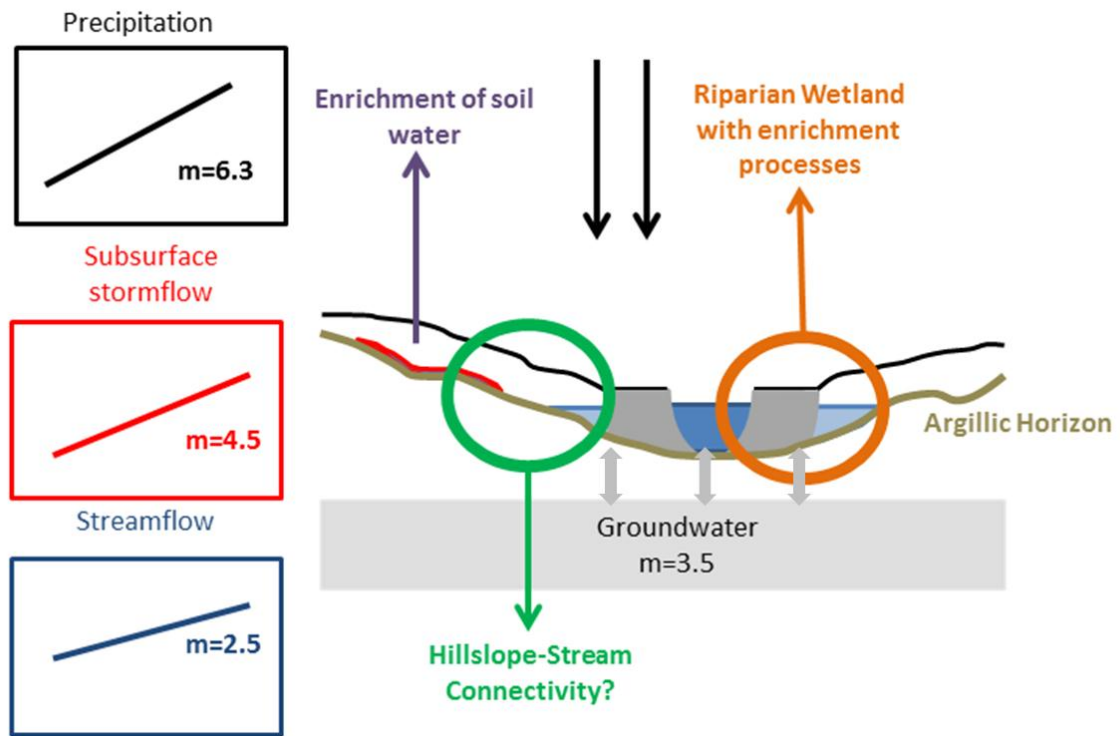
Figure 8. Conceptual model of baseflow runoff generation and enrichment in heavy isotopes from rainfall to streamflow. Key element is the disconnectivity between the hillslopes and the riparian-stream systems, which is likley sustained by precipiation and deeper groundwater.

1 **Tables**

2 Table 1: p-values to evaluate the differences between the LMWL/EWLs of the different water

3 compartments used to constrain the conceptual model.

	B stream	C stream	Riparian zone C-watershed	Groundwater	R stream	Precipitation	Riparian zone R-watershed	SSF
B stream	NA	0.58	<0.01	<0.01	<0.01	<0.01	<0.01	<0.0
C stream	0.58	NA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.0
Riparian zone C-watershed	<0.01	<0.01	NA	<0.01	0.99	<0.01	<0.01	<0.0
Groundwater	<0.01	<0.01	<0.01	NA	<0.01	<0.01	<0.01	<0.0
R stream	<0.01	<0.01	0.99	<0.01	NA	<0.01	<0.01	<0.0
Precipitation	<0.01	<0.01	<0.01	<0.01	<0.01	NA	<0.01	<0.0
Riparian zone R-watershed	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	NA	<0.0
SSF	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	NA

4