A porewater-based stable isotope approach for the investigation of subsurface hydrological processes

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Abstract. Predicting and understanding subsurface flowpaths is still a crucial issue in hydrological research. We present an experimental approach to reveal present and past subsurface flowpaths of water in the unsaturated and saturated zone. Two hillslopes in a humid mountainous catchment have been investigated. The $\text{H}_2\text{O} (\text{liquid}) - \text{H}_2\text{O} (\text{vapor})$ equilibration laser spectroscopy method was used to obtain high resolution $\delta^{2}H$ vertical depth profiles of pore water at various points along two fall lines of a pasture hillslope in the southern Black Forest, Germany. The Porewater-based Stable Isotope Profile (PSIP) approach was developed to use the integrated information of several vertical depth profiles of deuterium along transects at the hillslope.

Different shapes of depth profiles were observed in relation to hillslope position. The statistical variability (interquartile range and standard deviation) of each profile was used to characterize different types of depth profiles. The profiles upslope or with a weak affinity for saturation as indicated by a low topographic wetness index preserve the isotopic input signal by precipitation with a distinct seasonal variability. These observations indicate mainly vertical movement of soil water in the upper part of the hillslope before sampling. The profiles downslope or at locations with a strong affinity for saturation do not show a similar seasonal isotopic signal. The input signal is erased in the foothills and a large proportion of pore water samples are close to the isotopic values of $\delta^{2}H$ in streamwater during base flow conditions indicating the importance of the groundwater component in the catchment. Near the stream indications for efficient mixing of water from lateral subsurface flow paths with vertical percolation are found.

1 Introduction

The stable isotope ratios of deuterium ($^{2}H$) to hydrogen ($^{1}H$) and of oxygen-18 ($^{18}O$) to oxygen-16 ($^{16}O$) of water have been used as natural tracers in many studies in order to explore hydrological processes at the hillslope and catchment scale (e.g. McDonnell, 1990; Kendall and McDonnell, 1998; Uhlenbrook et al., 2002; Vitvar et al., 2005; Tetzlaff et al., 2009). As the stable isotope ratios of precipitation are strongly correlated with air temperature, a distinct seasonal pattern of rainfall more enriched in heavy isotopes during summer and more depleted in winter is found in humid climates (Dansgaard, 1964). In the absence of kinetic fractionation this variability determines the atmospheric boundary condition for hydrological stable isotope studies at the plot scale. The propagation and attenuation of the seasonal isotope signal with increasing soil depth allows for an investigation of vertical water movement in the unsaturated zone at the plot scale (Zimmermann et al., 1967; Maloszewski et al., 1983; Stewart and McDonnell, 1991; Gehrels et al., 1998). Vertical stable isotope pore water profiles in the unsaturated zone have also been used to investigate recharge mechanisms and recharge rates in the vadose zone (e.g. McConville et al., 2001; Saxena, 1984).

The water isotopes in soil water fractionate only slightly in humid climates. An enrichment of heavy isotopes in the subsurface may occur in the uppermost part of the soil column due to evaporation. Evaporation from plant interception or from ponding water in filled surface depressions entails kinetic fractionation effects, however transpiration is a non-fractionating process from a hydrological perspective.
(Zimmermann et al., 1967; Allison et al., 1984). Mixing, water uptake by plants and hydrodynamic dispersion alter the meteoric input signal in the unsaturated zone of humid environments (Barnes and Turner, 1998). As a result of these processes an increased attenuation of the isotopic precipitation signal with increasing soil depth can be observed regularly. Time series of the stable isotope signature of pore water derived with suction lysimeter at different soil depths show this damping behavior (Maloszewski et al., 1983, 2002; Stewart and McDonnell, 1991; DeWalle et al., 1997; Asano et al., 2002; Wenninger, 2007).

McDonnell et al. (1991) showed that the age of subsurface water along a hillslope characterized by an almost impermeable bedrock base and shallow soil increases considerably in downslope direction. This lateral aging of soil water is caused by a constant lateral movement of soil water in the soil matrix between storms. In a small Japanese catchment with weathered bedrock material, Asano et al. (2002) identified only vertical aging of percolating water while no evidence of an increase of residence time was found downslope. Uchida et al. (2006) integrated these findings and concluded that bedrock permeability and soil depth have an effect on the direction of increases of residence time in the unsaturated zone.

Stewart and McDonnell (1991) identified a mean residence time of more than 100 days for soil water near streams and 14 days for soil water upslope. Soil water at shallow depth in unsaturated soil responded to recent rainfall input, whereas deeper soil water and water near the stream showed much less variation compared to local precipitation and was considerably delayed and attenuated by ongoing mixing and progressive displacement of subsurface water. This behavior has also been shown by Horton and Hawkins (1965) and Zimmermann et al. (1966) with tritiated (3H) water.

There are numerous techniques for extracting pore water from soil for stable isotope analysis (e.g., suction lysimeter, centrifugation of soil samples, distillation techniques). These methods are technically complex and time-consuming. Comparisons of pore water extraction techniques reveal large variations in the obtained data and the results appeared not very accurate (Ingraham and Shadel, 1992; Walker et al., 1994). Nevertheless these techniques have often been used to extract pore water from soil in certain temporal intervals to gain subsurface information in hillslope studies. Therefore there is a need for experimental techniques that can be rapidly and efficiently applied at the hillslope scale and that provide useful information about subsurface processes and hydrological hillslope behavior. In this study we further develop the H2O(liquid) – H2O(vapor) equilibration and laser spectroscopy method presented by Wassenaar et al. (2008) to obtain stable isotope data of pore water of vertical depth profiles along two transects at a study hillslope. This Porewater-based Stable Isotope Profile (PSIP) approach will be used to explore the potential of this approach for the investigation of subsurface hydrological processes at the hillslope scale.

We hypothesize that there are locations along the hillslope where the isotopic precipitation input signal is preserved in the unsaturated zone and locations that show an attenuation of the meteoric isotope input signal due to mixing and hydrodynamic dispersion.

2 Materials and methods

2.1 Study site

The study area is a 0.9 km², humid catchment in the southern Black Forest, Germany (48°14’55” N, 7°53’27” E). Mean annual precipitation amounts to approximately 1070 mm for the study area (Trenkle, 1988), the mean annual temperature is about 9 °C and the mean annual actual evapotranspiration is around 600 mm (WaBoa, 2007). The study was conducted on a north-west facing hillslope covered with pasture and at an elevation of 290 m a.s.l. at the stream and 360 m a.s.l. at the water divide. There are only a few trees at the watershed divide and a solitary tree on the hillslope (Fig. 1). The length of the hillslope is about 300 m and the mean slope is 13°. The soil at the hillslope site is a cambisol with a sandy texture. The soil in the riparian zone is an alluvial soil with a sandy-loamy texture. Typical cambisols in the study area have a coarse stone material content from 10% to 40%. The transition to the compact bedrock consists of a well-evolved weathering zone. The bedrock is a paragneiss with a fine-grained configuration (Groschopf and Schreiner, 1980). The hydrogeology of the bedrock is determined by a system of connected fissures. The volumetric porosity of the gneiss bedrock is between 0.1% and 2.1% and the hydraulic conductivity range from 10 −10 m s −1 to 10 −5 m s −1 (Stober, 1995). Baseflow components originate from the fractured bedrock and the deeper parts of the weathering zone (Uhlenbrook, 1999). There is no evidence for periglacial drift covers in the study area.

2.2 Fieldwork

The field work was conducted at the end of August 2009. The weather conditions during the field campaign were warm and sunny with daytime temperatures around 25 °C. The total precipitation for August was about 50 mm which is below the long-term mean, whereas July was above the long-term mean. Within two field days 15 soil profiles with a depth between 90 cm and 250 cm and a horizontal spacing of approximately 40 m were extracted with a gas-powered soil core drill along two hillslope catenas, labeled as transect T1 and transect T2 (Fig. 1). Since the hillslope has no clear planar topography, transect T1 was sampled on a convex part of the hillslope and transect T2 in a concave situation. In order to achieve data consistency, the sampling of each transect was conducted within one day. Since we had no experience regarding the time it takes to sample one transect, we started the first transect (T1) with soil core depths of one meter. We
recognized that sampling of deeper soil profiles is feasible within one day and therefore drilled deeper soil cores at transect T2. The soil cores were divided in the field into subsamples of 8 cm length, packed into plastic Ziploc bags and stored in a cool box in order to determine the stable isotopic composition of the pore water, the gravimetric soil moisture and the soil texture in the lab. Streamwater and groundwater was sampled for stable isotope analysis on the second field day (20 August 2009). The streamwater was sampled at the foot of the study hillslope, whereas the groundwater was sampled in a well about 200 m distance from the hillslope.

2.3 Stable isotope analysis

The stable isotope signature of the pore water was determined by the $\text{H}_2\text{O}_{(\text{liquid})} - \text{H}_2\text{O}_{(\text{vapor})}$ equilibration and laser spectroscopy method. This technique provides the possibility to obtain $\delta$-values of the pore water by measuring the stable isotopic composition of the headspace water vapor in a bag with the sampled soil material (Wassenaar et al., 2008). After breaking the soil samples into smaller aggregates the Ziploc backs were filled with completely dehumidified air and heat sealed in another plastic back to reduce diffusion as much as possible. For calibration two samples with completely dried soil material from the experimental hillslope were moistened with different water isotope standards of known isotopic composition and treated the same way as described above. After 15 h in a temperature controlled and air-conditioned room an isotopic equilibrium between the headspace water vapor and the liquid pore water of the soil material in the plastic bags was assumed. The stable isotope analysis of the headspace water vapor of the soil samples and the calibration standards was conducted with a Picarro Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) analyzer. The measurement accuracy for this analysis was 0.16‰ for $\delta^{18}\text{O}$ and 0.6‰ for $\delta^{2\text{H}}$, respectively. Since the WS-CRDS analyzer measures $\delta$-values relative to an interior standard we used the calibration standard to calculated $\delta$-values of the headspace water vapor relative to the Vienna Standard Mean Ocean Water (VSMOW). Under the assumption of isotopic equilibrium the phase change in the water liquid – water vapor system can be calculated with the fractionation factor $\alpha$. Since $\alpha$ is temperature dependent we used the equilibration coefficients according to Majoube (1971) for the measured equilibration temperature (25°C) of the 15 h equilibration period. The $\delta^{2\text{H}}$ values of the headspace vapor were subsequently converted via the fractionation factor $\alpha$ into $\delta^{2\text{H}}$ values of the pore water of the soil samples. The results are reported in $\delta$ notation relative to VSMOW. Because for laser isotope spectrometry the relative measurement accuracy is better for deuterium than for $^{18}\text{O}$ and deuterium is less sensitive to kinetic fractionation effects (e.g. evaporation) we used the deuterium values to study the vertical depth profiles of the pore water.

2.4 Additional data analysis

In order to describe the variability of the collected pore water deuterium values we show the data per site as boxplots. The inter quartile range (IQR) of the data describes the variability between the 25th and the 75th percentiles. The standard deviations (SD) of the deuterium profile data were calculated as additional statistical indices describing the variability of each vertical depth profile. As a result of dispersion the variability of isotope values along a depth profile is in inverse proportion to the residence time of water.

To describe the topographic location of each profile along the transects a LiDAR derived DEM with a resolution of 1 m was resampled to a spatial resolution of 5 m. The higher resolution appears too susceptible to micro-topographic influences and a slightly lower resolution yields more realistic results for hydrological landscape analysis (Jencso et al., 2012).
Fig. 2. Gravimetric soil moisture and soil texture with matrix permeability after Scherrer (2006) of soil samples from every vertical depth profile for both study hillslope transects.

2009). The topographic wetness index (TWI) was calculated for every profile position along the study hillslope according to the approach described by Beven and Kirkby (1979) with the multiple triangular flow direction algorithm (Seibert and McGlynn, 2007).

3 Results

The results of the soil texture analysis and the gravimetric soil moisture are presented in Fig. 2. The soils at the upper parts of the study hillslope have a high sand content. The tendency for finer particle sizes is increasing in downslope direction. The highest soil moisture values were observed at the hillslope foot and also hydromorphic features could be found at these near stream profiles. The observed soil moisture patterns of the upper hillslope soil profiles are very similar. The soil properties along the hillslope are very homogenous revealing a high content of sand and therefore a good matrix permeability.

The relation between $\delta^{18}$O and $\delta^{2}$H of pore water, groundwater and streamwater is presented in Fig. 3. The $\delta^{18}$O of the pore water samples range from $-12.0\%e$ to about $0\%e$ and from $-85\%e$ to about $-10.0\%e$ for $\delta^{2}$H, respectively. Streamwater and groundwater samples plot close to the global meteoric water line (GMWL) and within a very narrow range isotopically close to each other. A linear regression of pore water samples from T1 and T2 has a slope of 6.6 and deviates from the global meteoric water line with slope 8 and intercept 10. This is an indication of a weak isotopic enrichment of some pore water samples. Since soil evaporation is dependent on atmospheric boundary conditions and soil characteristics (Gonfiantini et al., 1998) the observed enrichment of heavy isotopes may have occurred by evaporation of soil water in the uppermost soil layers. Most care was taken to avoid kinetic fractionation during sampling and transport, still a weak secondary enrichment cannot be strictly excluded.

Figure 4 shows the vertical depth profiles for deuterium of the pore water along the studied hillslope transects. On the x-axis the $\delta^{2}$H values in per mill relative to VSMOW and on the y-axis the soil depth in cm of the deuterium profiles is given. The vertical dashed line highlights the $\delta^{2}$H value of the sampled streamwater ($-58.15\%e$). Figure 5 shows the seasonal $\delta^{2}$H dynamics in precipitation. We can clearly see a seasonal variation with enriched $\delta^{2}$H values in summer and depleted $\delta^{2}$H values during the winter months.
All vertical depth profiles at transect T1 show a similar characteristic. The $\delta^2$H values are getting continuously lighter with increasing soil depth. The soil depth with the lightest deuterium value can be interpreted as the precipitation falling during the winter with the lightest deuterium values. In most profiles the winter minimum is observed at a depth of 45 to 65 cm. Below this peak there is a trend towards heavier $\delta^2$H values again. Thus, the vertical depth deuterium profiles along transect T1 show a typical seasonal pattern: soil water stemming from summer rainfall near the surface and an increasing proportion of soil water from winter precipitation with increasing soil depth.

In contrast to hillslope transect T1, the deuterium profiles at T2 show a partly different behavior. The deuterium profiles T2-1, T2-2, T2-3 and T2-4 also still exhibit the seasonal variation described before. The values are getting more depleted with depth and the peak of the winter precipitation is found between 62 cm and 87 cm from the soil surface. Below the winter-peak values are getting isotopically enriched again. Deuterium profile T2-5 shows a continuous decline of
deuterium values with increasing soil depth down to 50 cm without any indication of a clear peak. Deuterium profile T2-6 is characterized by similar δ²H values throughout the whole sampling depth. Profile T2-7 is the deepest profile and it has a relatively small variation in δ²H values close to streamwater composition with some erratic outliers. The deuterium profile closest to the stream (T2-8) is characterized by decreasing deuterium values down to a soil depth of 80 cm. All samples below that depth plot very close or even on the dashed line representing the streamwater deuterium signature.

Boxplots and standard deviations of data from each vertical depth deuterium profile were calculated in order to quantify deuterium variability at each profile position along the experimental hillslope (Fig. 6a, b). The 2nd to 4th downslope profile of transect T2 indicate a clear deviation from the other profiles with a lower standard deviation and also have a different range and median highlighted by the boxplots. In order to allow a direct comparison of the soil profile data from transect T1 with the deeper soil profiles along T2 we additionally plotted the boxplots and standard deviations for the upper 1 m of the T2 profiles.

Figure 7a shows the mean gravimetric soil moisture of the vertical depth profiles along the two experimental transects. At transect T2 there is an increase of soil moisture in downslope direction. The soil moisture is highest near the stream and lowest in upslope positions close to the watershed divide. The observed soil moisture at the T1 profiles is very similar with values between 12 % and 17 % along the whole transect. A similar pattern can be observed when plotting the TWI along the experimental hillslope (Fig. 7b). At transect T2 there is a distinct increase of the TWI in downslope direction, whereas at transect T1 there is no continuous trend along the hillslope. The TWI is very similar along the whole transect.

A positive correlation with $R^2 = 0.55$ between mean gravimetric soil moisture and TWI supports the observed similarity among the two variables. Since, the Topographic Wetness Index (TWI) can be interpreted as a relative wetness index it can be used to indicate the landscape position wetness affinity. We did not observe saturated conditions along the two transects. However, there is still a tendency
Fig. 8. Relationship between TWI and the Inter Quartile Range IQR (a) and standard deviation SD (b) of the vertical depth deuterium profiles.

Fig. 9. Difference from streamwater $\delta^2$H as a function of soil depth and distance to the stream for all samples along both study hillslope transects ($n = 248$).

for wetter soils and in average a lower depth to groundwater in downslope direction (especially at the concave transect T2) indicated by the calculated TWI.

The observed deuterium variability along the hillslope as described by the IQR has a negative correlation ($R^2 = 0.47$) with the relative wetness index TWI (Fig. 8a). A similar result is obtained using SD as a variability indicator (Fig. 8b). In other words, the variability within the vertical depth profiles of deuterium is decreasing as a function of increasing wetness or relative saturation along the experimental hillslopes.

Figure 9 shows the difference between the vertical depth profile $\delta^2$H data and the sampled streamwater $\delta^2$H as a function of soil depth and distance to the stream in order to study the relevance of the pore water deuterium signature on the streamwater stable isotope signal observed during the sampling campaign in summer. A positive difference indicates an enrichment of pore water $\delta^2$H, a negative difference indicates depletion of pore water $\delta^2$H, compared to the sampled streamwater. The percentage of data points with a difference between $+10%e$ and $-10%e$ to streamwater $\delta^2$H was calculated (Table 1).

As a result of this classification we found a high percentage of similar isotope values (within $\pm 10%e$ from streamwater $\delta^2$H) as profiles got deeper and closer to the stream. The pore water deuterium signature of the soil samples at the foot of the experimental hillslope and in the riparian zone was very similar to the observed streamwater deuterium signature.

4 Discussion

In several studies time series of the stable isotope signature of pore water in different soil depths has been collected with suction lysimeters in order to use the variability of the stable isotope time series signal for the investigation of subsurface hillslope processes and behavior (McDonnell et al., 1991; Stewart and McDonnell, 1991; Asano et al., 2002). However, the suction lysimeter technique is very time consuming and a useful dataset needs a sampling period of at least one year. The presented approach allows collecting comparable stable isotope data within one or few field working days. The vertical depth profiles of the pore water deuterium signature presented in this study provide time series information because one can see precipitation water from different seasons. With this information it is possible to explore the history of subsurface flowpaths at the hillslope scale within the timeframe of the observed isotopic signal.

Altitude effects could be neglected in the study because of a limited elevation range of the hillslope. Therefore, one can expect a spatially uniform stable isotope precipitation signal along the whole hillslope. In a completely flat environment with homogeneous soil properties and only vertical water movement, all vertical depth profiles of deuterium should be relatively similar. This behavior was not observed on the study hillslope and implies that the observed variations of the vertical depth profiles are caused by lateral subsurface flow pathways of the experimental hillslope and by mixing with streamwater of indirect stream recharge. The presented data show that the upslope profiles and the profiles along the whole transect T1 with a convex morphology still reflect the

<table>
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<tr>
<th>Profile</th>
<th>Hillslope</th>
<th>Hillslope &lt; 100 m</th>
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<tbody>
<tr>
<td>Entire vertical depth profiles ($n = 248$)</td>
<td>56.05%</td>
<td>81.61%</td>
</tr>
<tr>
<td>Vertical depth profiles ($n = 119$)</td>
<td>82.61%</td>
<td>87.50%</td>
</tr>
<tr>
<td>Profiles &gt; 0.8 m ($n = 48$)</td>
<td>82.61%</td>
<td>87.50%</td>
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Table 1. Percentage of the vertical depth deuterium profile data along T1 and T2 between $+10%e$ and $-10%e$ difference to streamwater $\delta^2$H.
seasonal variability of the meteoric input signal of about one year with isotopically enriched summer rainfall in the upper soil profile and isotopically depleted winter precipitation in the lower profile. This can be clearly seen when comparing the upper 1 m of the T2 profiles with the T1 profiles having the same depth. This variability was not observed for the deuterium profiles in the lowest part of the hillslope close to the stream which were only sampled at transect T2. This also entailed a lower statistical variability of the deuterium vertical depth profiles. Both observations indicate that the variability of seasonal stable isotope input is modified by other processes.

We observed that the streamwater stable isotope value was comparable to the groundwater deuterium signature within the catchment. This would imply that the catchment was in baseflow conditions during the sampling campaign. Baseflow usually reflects a stable deuterium signature if the mean residence time is long enough to fully attenuate and disperse the seasonal and recharge-weighted input. In order to show that groundwater flows through the soil in the riparian zone and dominates streamflow during baseflow conditions, we compared the observed deuterium pore water values with the streamwater stable isotope signature, which are comparable to the sampled groundwater. This comparison indicated that the percentage of pore water soil samples with a very similar streamwater deuterium signature is increasing towards the stream channel. Figure 10 summarizes the findings of this study in a perceptual model. The deuterium pore water profiles at upslope positions reflect the variability of the meteoric input signal. At these positions the history of the soil water movement is dominated by vertical infiltration (dashed vertical arrows). Contrary to this the observed pore water deuterium profiles at positions along the hillslope foot and close to the stream with a high affinity for saturation (TWI) do not reflect this signal and it seems that the input signal is damped at these positions. This observation supports the idea of a subsurface mixing zone characterized by a long transit time history of the flowpaths (dashed horizontal arrows).

The data collected in this study could also be used to benchmark hydrological hillslope models like HYDRUS-2D (Simunek et al., 1996) and HillVi (Weiler and McDonnell, 2004) that are able to simulate the observed pore water stable isotope signatures. But also with models unable to simulate transport processes, the simulated groundwater level variations and flow pathways could be compared with the observed isotopic depth profiles. Furthermore the PSIP approach could be used to collect data from various hillslopes in order to verify hydrological catchment models. For this study groundwater level was not monitored at the hillslope site. In future, it would also be interesting to compare the stable isotope data of sampled profiles with groundwater level data at the base of a hillslope in order to improve the understanding of the dynamic of the saturated zone along the hillslope.
5 Conclusions

The Porewater-based Stable Isotope Profile (PSIP) approach presented in this study was applied to an experimental hillslope in order to cover the variability of possible stable isotope profiles from the watershed divide to the stream. 15 vertical soil profiles were extracted along two catenas at the experimental hillslope. The collected soil samples were used to analyze the pore water deuterium signature with an innovative measurement technique obtaining vertical depth deuterium profiles of the pore water to investigate subsurface hydrological processes. The results suggest a vertical movement of soil water at upslope positions indicated by a preservation of the seasonal precipitation trend in the subsurface. This characteristic signal is destroyed for the isotope profiles at the hillslope foot and close to the stream. The topographic wetness index provided a good indicator for the relative influence of direct vertical recharge and indirect lateral subsurface flow.

The presented approach is less time consuming than conventional techniques used in hillslope and catchment hydrology to observe subsurface processes. The approach is suited to investigate and characterize subsurface hydrological processes at the hillslope scale and could be used to verify the performance of hydrological hillslope models. We could show that the PSIP approach could be used to determine dominant flow pathways of the last several months in a hillslope and potentially also for a catchment by only collecting soil water samples of stable isotopes at a high vertical resolution.

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