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Relating stable isotope and geochemical data to conclude on water residence times in four small alpine headwater catchments with differing vegetation cover

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Abstract

The mean water residence time (MRT) in a catchment gives information about storage, flow pathways, sources of water and thus also about retention and release of solutes in a catchment. To our knowledge there are no catchment studies on the influence of vegetation cover change on base flow mean water residence times. The main changes in vegetation cover in the Swiss Alps are massive shrub encroachment and forest expansion into formerly open habitats. Four small and relatively steep catchments in the Swiss Alps (Ursern valley) were investigated to relate different vegetation cover to water residence times and geochemical behaviour of runoff.

Time series of water stable isotopes were used to calculate mean water residence times. The high temporal variation of the stable isotope signals in precipitation was strongly dampened in stream base flow samples. Mean water residence times of the four catchments were 64–98 weeks. The strong dampening of our input signal might point to deeper flow paths and mixing of waters of different ages at the catchments outlets. Parent geological materials are mainly gneisses and schists but they can contain dolomite, carbonate or gypsum rich zones. The major part of the quickly infiltrating precipitation likely percolates through these deeper zones. Relatively high stream water pH, Ca and SO_4^{2-} concentrations in micro catchment outlets support this conclusion.

We conclude that in mountainous headwater catchments with relatively thin soil layers the geological and topographical situation and snow dynamics influence storage, mixing and release of meteoric waters and its geochemistry in a stronger way than vegetation cover or catchment size do.

1 Introduction

The time of water circulating in a catchment (mean water residence time, also known as "mean water transit time" or "water age") gives information about storage, flow pathways, sources of water and thus also about retention and release of solutes in a catchment (McDonnell et al., 2010; McGuire et al., 2005). The mean water residence time can for example be calculated via stable isotopes of the water molecule (McGuire and McDonnell, 2006). In regions with seasonally varying air temperatures the stable isotope signature in precipitation also varies seasonally (Dansgaard, 1964). This variability can also be observed in stream flow samples but often is delayed and/or dampened depending on the mean water residence time (McGuire and McDonnell, 2006).

The role of landscape structure and topography as controlling factors on mean water residence times are still debated (McGlynn et al., 2003; McGuire et al., 2005; Rodgers et al., 2005; Soulsby and Tetzlaff, 2008). McGuire et al. (2005) found catchment slope and indices representing the flow path distance and flow path gradient to the stream network to be correlated with mean water residence time. Storage capacity of the catchment (unsaturated zone and groundwater) is also considered to control mean water residence time (Capell et al., 2012; Dunn et al., 2007; Fenicia et al., 2010). According to Uchida and Asano (2010) only few studies investigated the role of bedrock groundwater on mean water residence times in wet mountainous catchment areas. Soulsby and Tetzlaff (2008) found that mean water residence time correlates negatively with the percentage of responsive soils and (counter-intuitively) positively with mean catchment slope. They argued that they found more free-draining soils at steeper slopes which facilitates mixing of waters and leads to longer mean residence time estimates. McGuire et al. (2005) on the other hand found flow path gradient to the stream network to be correlated negatively to mean water residence time. Catchment area does not seem to influence mean water residence time (McGuire et al., 2005; Tetzlaff et al., 2011). Asano et al. (2002) hypothesized that vegetation cover could shorten soil- and groundwater residence times through the reduction of stored soil water which is triggered by root water uptake. To our knowledge there are no catchment studies on the influence of vegetation cover on base flow mean water residence times and only few studies on the influence of land use on the reaction of the catchments during storm events (Buytaert et al., 2004; Monteith et al., 2006; Wenjie et al., 2011). Wenjie

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et al. (2011) investigated the impact of land use on runoff generation processes. They concluded that runoff generation processes can be altered by soil compaction. Monteith et al. (2006) studied hydrographs and groundwater residence times in a harvested and an undisturbed hardwood forest. They found that mean groundwater residence time was not influenced by land use at least not during a snow melt period. According to Clark and Fritz (1997) differences in land use can alter the isotopic (^{18}O or ^{2}H) balance of weighted precipitation inputs and the output. For example, evaporative losses can lead to an isotopically depleted soil water beneath permanent grass cover compared to arable plots (Darling and Bath, 1988). They denoted that in their study this effect was balanced presumably by a modified flow pattern. Consequently the isotopic depletion was not detected in the recharge water measured in a lysimeter. In other lysimeter studies with different crop growth, Stumpp et al. (2009b) and Stumpp et al. (2012) showed that soil hydraulic properties were changed by vegetation cover changes which led to different flow velocities. The main changes in vegetation cover in the Swiss Alps are massive shrub encroachment and forest expansion into formerly open habitats (Tasser et al., 2005; Wettstein, 1999). We therefore hypothesized that shrub encroachment could alter water flow patterns in the unsaturated zone and possibly could influence water residence times e.g. through higher infiltration rates compared to grassland sites. In four alpine micro catchments we modelled the mean water residence time for base flow conditions. We used stable isotopes values of the water molecule. Our sampling approach enabled us to estimate the influence of vegetation cover as well as the scale dependency of mean water residence time under the same geological and climatological conditions. Furthermore, our study includes additional geochemical data e.g. pH, major alkali and earth alkali metals and anions, since water residence time influences nutrient cycling and transport (Johnson et al., 1981; McGuire and McDonnell, 2006). Our geochemical characterisation also allows us to estimate the contribution of groundwater to base flow runoff and its mean residence time.

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2 Material and methods

2.1 Study site

The Ursern valley has a U-shaped profile and is characterized by a rugged terrain. Elevation ranges from 1400 to 3200 m a.s.l. The southern mountain ridge is build by the gneiss massif of the Gotthard system whereas the northern mountains are part of the granite massif and the pre-existing basement of the Aar system (Labhart, 1977). The two massifs are separated by intermediate vertically dipping layers along a geological fault line which corresponds to the valley axis. These layers consist of Permocarbonic and Mesozoic sediments and they comprise sandstones, rauhwackes, dolomites, dark clay-marls and limestones. Throughout the formation of the Alps the material was metamorphosed to schist (Kägi, 1973; Angehrn, 1996). Due to erosion of these soft layers a depression developed (Kägi, 1973). The soluble limestones and also gypsum rich rocks underlie the outcropping rocks or are incorporated as lenses in the granites and gneisses (Ambuehl, 1929; Buxtorf, 1912; Labhart, 1977; Winterhalter, 1930). The most abundant outcropping bedrock material is a white mica-rich gneiss. This was confirmed by the detection of phyllosilicates (muscovite/illite) in the soil by X-ray diffraction (Schaub et al., 2009).

Podsols, Podzocambisols and Cambisols are the dominant soil types in the valley (Meusburger and Alewell, 2008). At higher altitudes and on steep valley slopes, Leptosols are common. At the valley bottom and lower slopes, predominantly clayey gleyic Cambisols, Histosols, Fluvisols and Gleysols developed.

The valley is characterised by a high mountain climate with a mean air temperature of 3.1 °C (1901–1961). Mean annual rainfall at the climate station in Andermatt (1442 m a.s.l.) of MeteoSwiss is about 1400 mm. The valley is snow covered for 5 to 6 month (from November to April) with the maximum snow height in March (Angehrn, 1996). Runoff is usually dominated by snowmelt in May and June.

Vegetation shows strong anthropogenic influences due to pasturing for centuries (Kägi, 1973). An invasion of shrubs mainly by *Alnus viridis*, *Calluna vulgaris*, *Salix* *appendiculata*, *Sorbus aucuparia*, and *Rhododendron ferrugineum* was identified, particularly on the north-facing slopes (Kägi, 1973; Küttel, 1990; Wettstein, 1999). The south-facing slopes are dominated by dwarf-shrub communities of *Rhododendron ferrugineum* and *Juniperus sibirica* (Kägi, 1973; Küttel, 1990) and diverse herbs and grass species. Wettstein (1999) estimated that approximately one third of shrubs (mainly consisting of *Alnus viridis* and *Sorbus aucuparia*) invaded since 1959. For a more detailed information about the Ursern valley the reader is referred to Meusburger and Alewell (2008).

Four micro catchments located on north-east and north-west facing slopes in the Ursern valley (Table 1 and Fig. 1) were chosen with regard to their differing percentage of shrub cover. The steep micro catchments are smaller than 1 km^2 and shrub vegetation covers a range from 13.8 to 82.2 %. From field observations we can assume that mean discharge during the snow covered period is at the lower end of the discharge range given in Table 1. In all micro catchments smalls springs could be indentified as the starting point of the streams permanently discharging water (also observed in winter months) (Fig. 1).

2.2 Sampling and analysis

2.2.1 Stable water isotopes

We bi-weekly sampled precipitation and stream base flow. Precipitation was sampled near the catchment outlets with a 200 cm^2 totalisator and a buried and covered 5 l bottle to protect the water from evaporation. Precipitation amount was determined and a subsample was transferred in a 250 ml poly ethylene (PE) bottle. Stream water was sampled by hand also with 250 ml PE bottles which were filled completely. Snow was sampled during the winter period as bulk samples with a plastic tube of 2 m length and a diameter of 3.5 cm. Samples were transferred into 2 l PE bottles. Snow water equivalent was calculated from the known snow volume, snow depth and water volume. Monthly samples were taken near the micro catchments outlets. In march 2010, 2011 and 2012 when snow height reached its maximum we sampled snow spatially distributed over several kilometres along the valley slopes from 1500 to 2600 m a.s.l. A few snow samples on shadowed spots were also taken at the end of april 2011 when substantial snow melt in most parts of the catchments already happened.

Stable isotopes were measured with a Thermo Finnigan DELTAplus XP continuous flow mass spectrometer (CF-IRMS, DELTAplus XP, Thermo, Bremen, Germany) and a liquid water isotope analyzer (Los Gatos Research, Inc. (LGR), Mountain View, USA). Results are reported as $\delta^{18}O$ or $\delta^{2}H$ in ‰ vs. the V-SMOW standard.

2.2.2 Additional geochemical parameters

In addition to the use of stable isotopes as a time orientated tracer we also measured various geochemical parameters which served as geogenic tracers. Alkali and earth alkali metals (Ca, Mg, K, Na) and silicon (Si) were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Spectro Genesis, Spectro Analytical Instruments, Germany). These elements can be found in aqueous solutions due to weathering of minerals and can be an indicator of the type of rocks which are weathered (Stumm and Morgan, 1996). Major anions (nitrate and sulfate) where measured by ion chromatography (761 Compact IC, Metrohm, Switzerland). Sulfate in stream water can be an indicator for weathering of gypsum bearing rocks (Stumm and Morgan, 1996). PH was measured continuously during the vegetation period with a CS525 ISFET pH Probe (Campbell Scientific, UK) and on a monthly basis during winter with a portable pH 340i probe (WTW, Weilheim, Germany).

All stream water samples for geochemical parameter determination were taken by hand in the field, filtered with 0.45 µm filters (Rotilabo-filter, PVDF, Roth, Switzerland), cooled during transport to the laboratory, and kept frozen at −20 °C until analysis.

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2.3 Mean water residence time modelling

With bi-weekly stable isotope data of precipitation (corrected for the altitude effect and linearly interpolated for monthly winter samples) and stream base flow ($\delta^{18}O$ of H_2O) we modelled mean water residence times. We used the modelling procedure suggested, e.g. by Maloszewski and Zuber (1982, 2002) and their provided software FlowPC. From a known isotope input signal (precipitation samples) and our measured output signal in the four streams (base flow samples) mean residence times can be modelled by solving a convolution integral which relates input and output stable isotope signals with mean water residence time:

$$\delta^{18}O_{out}(t) = \int_0^\infty \delta^{18}O_{in}(t-\tau)g(\tau)\mathrm{d}\tau \quad (1)$$

where $\delta^{18}O_{out}$ is the output signal, $\delta^{18}O_{in}$ is the input function, $g(\tau)$ the system response function and τ is the mean residence time.

Despite some assumptions which are not always met in nature (e.g. steady state of flow) these lumped parameter models offer the advantage that they only require few parameters and are useful in catchments where information on hydraulic properties of underlying material is scarce (Maloszewski and Zuber, 1982, 2002). The modeller has to chose a system response function $g(\tau)$ which describes the residence time distribution in the aquifer and hence implicitly include hydraulic properties of the aquifer. Furthermore the provided software does not require extensive hydrological or meteorological data. Especially discharge data was not available for the winter periods in our micro catchments because streams and installed weirs were completely snow covered and/or frozen during this period.

In a first step we tested all the different system response functions $g(\tau)$ (also called flow models) in the software: exponential model (EM), exponential-piston-flow model (EPFM), dispersion model (DM), piston flow model (PFM) and the linear model (LM).

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More detailed information about the flow models can be found in Maloszewski and Zuber (1982).

The stable isotope input function for the mean residence time modelling has to be weighted with the precipitation amount and recharge factor α (also called infiltration coefficient in the cited literature) (Maloszewski and Zuber, 1982, 2002; Grabczak et al., 1984):

$$\delta^{18}\mathrm{O}_{\mathrm{in}}(t_i) = \frac{N \cdot \alpha_i \cdot P_i}{\sum_{i=1}^{N} \alpha_i \cdot P_i} \cdot (\delta^{18}\mathrm{O}_i - \delta G) + \delta G \qquad (2)$$

N is the number of single sampling events, P_i and δ^{18}O are precipitation rates and its isotope values and δG is the mean value of δ^{18}O of the local groundwater originating from recent precipitation. Recharge factors are often difficult to estimate or even unknown (Grabczak et al., 1984; Maloszewski and Zuber, 2002). They can for example be estimated as a ratio of summer recharge to winter recharge from stable isotope data (Grabczak et al., 1984) (Eq. 3) or calculated from the water balance (Stumpp et al., 2009a) (Eq. 4).

$$\alpha = \frac{(\overline{\delta P_{\mathrm{W}}} - \delta G) \sum_i (P_i)_{\mathrm{W}}}{(\delta G - \overline{\delta P_{\mathrm{S}}}) \sum_i (P_i)_{\mathrm{S}}} \qquad (3)$$

$$\alpha_i = \frac{P_i - \mathrm{ET}_{\mathrm{a},i}}{P_i} \qquad (4)$$

$\overline{\delta P_{\mathrm{W}}}$ and $\overline{\delta P_{\mathrm{S}}}$ are the long-term weighted mean values of δ^{18}O for the winter and summer precipitation (P), respectively and $\mathrm{ET}_{\mathrm{a},i}$ is the actual evapotranspiration.

Since in our case the volume weighted mean stable isotope signal in precipitation for the whole observation period equals the mean of base flow stream samples we conclude that summer and winter precipitation equally contribute to the stable isotope signal in stream base flow. Therefore the recharge factor calculated according to

Grabczak et al. (1984) as a ratio of summer recharge to winter recharge is equal to 1. This would not represent the real situation since snow accumulates from november to march and recharge during winter would only occur when short warm periods induce snow melting. The isotope signal from this winter precipitation will substantially recharge and contribute to the base flow signal only during the spring snow melt. We therefore made a simplification and estimated the recharge factors for the snow accumulation period to be 0.01. This low value is justified because only small amounts of melt water were measured in several snow lysimeter studies during accumulation period (Gurtz et al., 2003; Whitaker and Sugiyama, 2005; Winkler et al., 2005).

Snow melt was introduced into the model via the weighing procedure by recharge factors (set to 1) and precipitation amounts which accumulated during the winter season. From field observation and data from MeteoSwiss (2012) we know that snow melt occurs from the end of march until the beginning of may. Accumulated snow during winter was therefore released during snow melt within six weeks in our model. At the lower part of our micro catchments snow had molten at the beginning of april whereas snow in the upper regions lasted a few weeks longer.

The recharge factor during the summer period was calculated similar to Stumpp et al. (2009a) by correcting measured precipitation for evapotranspiration and direct flow (which was calculated from the hydrographs by the Institute of Geography, Section Hydrology of the University of Bern).

2.4 Vegetation cover and topographic analysis

Vegetation cover and catchment topography were assessed by van den Bergh et al. (2011) and by Fercher (2012) by a combination of satellite images and field observation. Vegetated and bare lands were classified using maximum likelihood classification and a number of training samples on a composite spot image from the summer of 2004/2005. A map of vegetated and non-vegetated land was thus created. The remaining vegetation cover classes were manually drawn from Swissimage orthophotos (van den Bergh et al., 2011). Further topographic analysis was performed with

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a digital elevation model with a cell size of 2 × 2 m below 2000 m a.s.l. and 25 × 25 m above 2000 m a.s.l. We used the geographic information system (GIS) software ArcGIS (ESRI) version 10 and its included hydrology tools.

To relate mean water residence time to topographic features of the micro catchments we determined ranges and means of the following parameters: slope, elevation, flow length, topographic wetness index, stream length and drainage density. Flow length was calculated as the downslope distance from each cell to the catchment outlet along the flow path. Topographic wetness index was computed as

$$\mathrm{TWI} = \ln \frac{a}{\tan \beta} \tag{5}$$

where a is the upslope area per unit contour length and $\tan\beta$ is the local slope (Beven and Kirkby, 1979). For stream length we determined two values. We defined length of base flow stream as the length of the perennial streams. Length of event flow streams additionally includes ephemeral streams which are presumably activated during rainfall events. Drainage densities were computed for both length parameters by dividing stream length by micro catchment area.

3 Results and discussion

3.1 Stable water isotopes in precipitation and runoff

In summer 2010 we measured stable isotopes in precipitation along an altitudinal gradient. Decrease in δ^{18}O was 0.15 ‰ per 100 m elevation increase. This is only slightly lower than measured for locations on the Swiss Plateau and in the Western Alps by Siegenthaler and Oeschger (1980) but in general in good agreement with other values from the Austrian Alps (Ambach et al., 1968). We could not detect a clear trend in δ^{18}O with elevation during winter. Ambach et al. (1968) also measured an altitude effect during summer but not for snow samples in the Austrian Alps. They concluded that successive evaporation from the falling precipitation from clouds at the same altitude caused this altitude effect in summer. This successive evaporation is low for solid precipitation. Moreover the elevation effect can be reversed on lee slopes (Friedman and Smith, 1970; Moran et al., 2007). This was also observed in some of our samples (data not shown).

Stream water and especially precipitation samples cover a wide range of δ^{18}O and δ^{2}H values (Fig. 2). The local meteoric water line (LMWL) nearly matches the global meteoric water line (GMWL) (Craig, 1961). The GMWL gives the relation between δ^{2}H and δ^{18}O in meteoric waters (including, e.g. precipitation, water from streams or lakes, and groundwaters) on a global scale which have not undergone excessive evaporation. Our stream water samples are between the minimum and maximum values of our measured precipitation samples (Fig. 2). Therefore stream water most likely represent a mixture of local precipitation from different dates. Since stream water samples plot around the LMWL we can presume that evaporation or other processes which would move the stream samples away from the LWML are negligible (Clark and Fritz, 1997).

As expected, the stable isotope signal (δ^{18}O) of precipitation strongly varied between seasons and ranged from −2.5 ‰ during summer storms to −25 ‰ (V-SMOW) for fresh snow samples (Fig. 3). The δ^{18}O values of the four micro catchments followed a rather parallel pattern even though they are distributed along the valley within a distance of about 8 km (Fig. 1). The δ^{18}O values of precipitation samples slightly decrease from the Chämleten to the Laubgädem micro catchment. This east-west trend could be attributed to an air temperature trend with decreasing temperature from east to west along the valley (note that the difference of mean δ^{18}O values of precipitation is statistically not significant). The east-west trend is more pronounced and consistent throughout the year in the base flow samples (Fig. 3). The difference of mean base flow samples between the Chämleten and Laubgädem micro catchments is about 1 ‰ ($p < 0.01$). This could point to a stronger influence of isotopically lighter winter precipitation from higher altitudes in the Laubgädem micro catchment.

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The parallel pattern in the precipitation samples was only interrupted at the beginning of the winter in 2010 when first freshly fallen snow was sampled. Generally high variations can be detected in solid precipitation samples of single precipitation events since formation of solid precipitation is a non-equilibrium process (Koeniger et al., 2008).

The strong seasonal variability of δ^{18}O values in precipitation could hardly be detected in our bi-weekly base flow samples due to a strong dampening of isotope input signals. The isotope signal of precipitation was however reflected in the stream water during snowmelt. The strong attenuation of the input signal implies that only small fractions of the precipitation waters leave the basin via runoff immediately (Herrmann and Stichler, 1980). However, it is important to note that this does not directly imply that no major floods will occur. Investigations of Alaoui et al. (2012) clearly show that flood events are very likely in the investigated catchments and that these events are influenced by vegetation cover to a certain extent.

Variability of δ^{18}O of stream water was most pronounced in the Chämleten micro catchment with δ^{18}O values of −15 ‰ in winter and up to −11.5 ‰ in summer. δ^{18}O of stream water varied very little in the other micro catchments. Especially the Laubgädem micro catchment exhibits an extremely dampened isotope signal with the exception of the 29 April 2010, when discharge was highly increased due to high snow melt inputs. These very sharp snow melt peaks were not detected in spring 2011 and 2012. Snow melt in 2010 occurred later than in 2011 but in a shorter time period. Therefore the isotope signal of the snow was transferred to the stream and produced a sharp peak in 2010. In 2011 there was only half of the snow amount (snow depth was around 50 cm at the onset of snow melt) and snow melt took place earlier. We therefore might have missed the sharp peak in 2011. From a more detailed sampling during the snow melt in the Wallenboden and Bonegg micro catchments in 2012 (data not shown) we know that these very sharp peaks appear within a few days only, which are easily missed by the 14 day sampling interval. On the 28 April 2012 the stream in the Bonegg micro catchment for example had a δ^{18}O value of about −16 ‰ which was not captured with the 14 day sampling approach.

In contrast to the snow melt period, all $\delta^{18}O$ values of stream water were extremely stable during the winter period (Fig. 3). $\delta^{18}O$ values of stream water is reflecting the approximate weighted mean $\delta^{18}O$ of previous winter and summer precipitation. Hence, the isotope signal of snow is only transferred to the streams during snow melt. It then can mix with "older" waters in the systems or at the systems' outlets. During the winter 2010/2011 there was an increase in $\delta^{18}O$ of base flow samples especially in the micro catchments Bonegg and Laubgädem. This was not the case in the next winter of 2011/2012. This could be explained by the higher precipitation amounts in summer 2010 which then discharged during the winter 2010/2011. In summer 2011 there were 160 mm less precipitation than in 2010 which corresponds to an decrease of about 25 % of summer precipitation.

In 2011 we also measured stable isotopes of the Reuss river (Fig. 3). Our sampling point was the outlet of a 132 km^2 subcatchment of the Ursern valley which drains north and south facing slopes (note that the whole Ursern catchment has an area of 191 km^2). Because the sampling point integrates a much larger catchment than our micro catchments, we can compare hydrological characteristics of different scales. The data series for the larger Reuss catchment only covers the summer period in 2011 and we consider this time span too short for quantitative modelling of mean water residence time. But from the similar pattern of the micro catchments and the Reuss subcatchment we can conclude that stream base flow probably has a mean water residence time in the same order of magnitude as the micro catchments (see below). We conclude that stored waters in the fractured bedrock equally contributes to base flow in our catchments of different sizes.

We also determined $\delta^{18}O$ values of subsurface/overland flow which we collected in a wetland soil site in the Chämleten micro catchment during or shortly after precipitation events (Fig. 3). They are more enriched than the respective stream water samples (taken at base flow conditions). This indicates the meteoric origin of the subsurface/overland flow and implies that these waters represents a mixture of pre-event groundwater and precipitation.

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3.2 Mean water residence time modelling

3.2.1 Mean water residence times

Modelled and measured $\delta^{18}O$ of H_2O of base flow samples are given in Fig. 4. For all four micro catchments the exponential model (without a piston flow component) gave the best fits for mean water residence time. Measured data were in general reproduced well for all catchments. Mean residence times range from 64–98 weeks. The slightly higher $\delta^{18}O$ values in summer precipitation samples from 2011 compared to 2010 (Fig. 3) are also reflected in the slightly higher base flow $\delta^{18}O$ values in all four micro catchments. This effect was more pronounced in the modelled than in the measured data. In autumn and winter 2011 the model overestimates the stream $\delta^{18}O$ for Wallenboden, Bonegg and Laubgädem. This can be either due to heavy rains in July which produce a steplike increase in modelled autumn/winter values. On the other hand the increase in the measured data is maybe small because the subsurface reservoir is refilled after the relatively dry periods in spring and summer 2011. Afterwards this water discharges to the streams. Therefore Chämleten must have a smaller storage reservoir since its reaction to precipitation input is more pronounced. Wallenboden has the same calculated mean water residence time despite the strongly dampened measured $\delta^{18}O$ output compared to Chämleten. The steeper increase of $\delta^{18}O$ values in summer 2010 in Chämleten was not clearly reproduced by the model. It underestimates the variability of $\delta^{18}O$, which is higher in Chämleten than, for example, in Wallenboden. We therefore think that mean water residence time for Chämleten should be lower than for Wallenboden even if they are both 70 weeks for the best model fits (results for sensitivity analysis see below).

Snow melt was in general represented well with a six weeks snow melt approach. Especially the fast decline of $\delta^{18}O$ at the onset of snow melt was reproduced quite well by weighting the $\delta^{18}O$ values of snow with the accumulated snow depths. Nevertheless very sharp stream water peaks during snow melt in march and april could not be modelled adequately in all cases. We measured for example a -15 ‰ $\delta^{18}O$ signal in

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the streams in 2010 in the Chämleten, Wallenboden and Bonegg micro catchments. These samples do not represent base flow samples by definition. But since snow melt takes places during several weeks and it constitutes a substantial part of the water cycle in our micro catchments we included them in the modelling procedure. The probably shorter snow melt period in 2010 can especially be seen in the Laubgädem micro catchment were we have a very sharp peak with a δ^{18}O value of about −17 ‰ which increases to −14 ‰ after 14 days only. This phenomenon can also not be reproduced by the model. After the six weeks of snow melt in the lower parts of the catchments the residual accumulated snow of the upper parts presumably slowly refills the reservoirs.

3.2.2 Fractionation of stable isotopes

Evaporation of soil water

Evaporation of soil water can alter isotopic signals (Zimmermann et al., 1967). Viville et al. (2006) and Stumpp et al. (2009a) stated that the stable isotope input function for modelling mean water residence times can be improved by taking evapotranspiration into account. According to Barnes and Turner (1998) the influence of evaporation on stable isotopes signals is rather small in humid areas since other processes are prevailing (e.g. mixing and dispersion). Water uptake by plants does not alter isotope signatures of soil water (Bariac et al., 1989; Dawson and Ehleringer, 1991; Ehleringer and Dawson, 1992; Zimmermann et al., 1967) but it could of course reduce amounts of precipitation water entering the deeper soil layers and the bedrock. In our micro catchments the volume weighted stable isotope signal of the precipitation input equals the mean stable isotope signal of the stream water output. We therefore conclude that evapotranspiration from the north facing slopes played a negligible role, because otherwise the seasonal difference between a dominant winter influence and less contribution of summer precipitation should be seen. Moreover the δ^{18}O vs. δ^{2}H plot does not indicate substantial evaporation since base flow, precipitation and snow samples plot near the global meteoric water line.

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Evaporation through interception

Evaporation of water by interception can also change isotope signals in precipitation. Generally throughfall enrichment is between 0.1 to 1.2 ‰ (Ingraham, 1998; Kabeya et al., 2007; Kubota and Tsuboyama, 2004; Saxena, 1986) but there are also studies in which throughfall was depleted compared to precipitation (Saxena, 1986). In our study we found some samples of throughfall in shrub sites to be enriched by about 1.5 ‰ but more samples to be depleted by about 0.6 ‰ compared to precipitation samples in grass land sites. Since there was no general pattern, the differences were small, and micro catchments include different vegetation cover types from vegetation (grass and shrubs) to bare rocks we neglected the possible influence of evaporation through interception.

Evaporation of snow during winter and melt period

Snow melt water input into the system could also be a critical input component in mean water residence time modelling. Evaporation during the winter and fractionation processes during melt can alter isotopic composition of the water infiltrating in the soil (Moser and Stichler, 1975). Evaporation during the winter can be excluded because no shift from the local meteoric water line was measured for the bulk snow samples. These were taken a few days before the onset of snow melt. Evaporation in march and april in our micro catchments is estimated to be very low (Baumgartner et al., 1983).

The bulk snow samples show slight enrichment of the heavier isotopes with time towards the end of the winter from about −17 to −15 ‰ . But the samples shortly after snow melt which were taken on some shadowed locations were snow still was available only showed a small enrichment compared to the samples before the onset of snow melt. Moreover they plot around the local meteoric water line even after snow melt in the lower parts of the micro catchments occurred (Fig. 2). These facts indicate that evaporation (under equilibrium) during melt occurred to a certain extend. But for a rough estimation we can assume that the isotope signal from our depth integrating

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bulk snow samples just before the onset of snow melt can be regarded as our input signal in our modelling interval of two weeks. This is justified because micro catchments cover a wide range of elevations and the stable isotope input signal for snow melt represents a mean value for the range we measured in our spatially distributed snow samples. Therefore we can also neglect the fact that in general the isotope signal of the first melt water differs from the melt water at the end of the snow melt period (Sueker et al., 2000; Taylor et al., 2001; Laudon, 2002).

3.2.3 Length of data record

McGuire and McDonnell (2006) argued that the length of the data record for the input function should exceed the length of the output record by a factor of 4. This would ensure that tracer mass recovery would be nearly 100 %. Our record is about 2 yr and mean water residence times are 1.2–1.9 yr. We therefore extended our input record backwards in time by correlating stable isotopes in precipitation with air temperature. With this prolongated time series we tested the modelling procedure for the Laubgädem micro catchment. We could not improve model results of mean water residence time calculation with the longer data record. Therefore we used our measured input record of 2 yr to reduce input uncertainties introduced by the residuals of the regression model.

3.2.4 System response function (flow model)

The best fits were obtained with the exponential distribution model (see Sect. 3.2.5). This model is mathematically equivalent with a well-mixed reservoir, but it is important to mention that mixing only occurs at the system outlet (Maloszewski and Zuber, 1982, 2002). There is no exchange of tracer along the flow lines in the aquifer. The dispersion model on the other hand allows mixing of tracer within the aquifer itself. With an apparent dispersion parameter (P_D = reciprocal of the Péclet number) of 0.5–0.8 we also got very good fits for our models. Wider and more asymmetrical distributions of residence times are characterised by higher values of P_D (Maloszewski and Zuber, 2002). Using the exponential model would imply that there exists water with very short and water with very long residence times which only mix at the outlet. With the chosen P_D values the dispersion and the exponential distributions are quite similar. Nevertheless, due to the hydrogeological situation we preferred the exponential model because a good mixing of all the waters within these steep aquifers is highly unlikely.

3.2.5 Sensitivity analysis

The sensitivity analysis revealed that model parameters can be identified unambiguously (Fig. 5). With regard to the quality of the fit we compared the calculated σ values for the different models and parameters (Maloszewski and Zuber, 1982, 2002):

$$\sigma = \frac{\sqrt{\sum_{i=1}^{n} (c_{mi} - c_i)^2}}{n} \tag{6}$$

c_{mi} = measured stable isotope value at time i;
c_i = calculated stable isotope value at time i;
n = number of measurements.

Small values of σ indicate small differences between measured and modelled stable isotope values and are therefore considered as "good fits". The piston flow and the linear model gave high values of σ and we therefore focused on the exponential model, the exponential-piston-flow model, and the dispersion model. The exponential flow model gave the best fits (the smallest values of σ, Fig. 5) and it also performed slightly better than the dispersion model (data not shown). A minimum could be detected clearly in each case (Fig. 5, small insert).

In a second step we tested the model for sensitivity to a reduced summer precipitation input for example due to an increase in evapotranspiration by shrub encroachment or climate change. We assumed the same stable isotopes input signals and reduced precipitation in each modelling interval from may to September from 1 to 20 mm in each model run. This translates to an overall reduction of 10 to 200 mm of summer precipitation, the latter being an extreme reduction. We then calculated the δ^{18}O of stream

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water for the Wallenboden micro catchment using mean residence times of 70 and 100 weeks and the exponential model.

With a mean residence time of 70 weeks the reduction of summer precipitation shifts the calculated output to more negative values and the modelled curve does not fit the measured output curve anymore if precipitation is reduced by 100 or 200 mm (Fig. 6). The influence of winter precipitation with lower δ^{18}O signals clearly increases. If the mean water residence time is increased to 100 weeks the whole set of curves is shifted to more positive values (Fig. 6, right panel). The curve with 200 mm reduction and a mean residence time of 100 weeks reproduces the measured values to a certain extend but the latter are overestimated in most cases.

This implies that a reduction of summer precipitation input to the hydrological system (e.g. by increased evapotranspiration) can lead to longer mean water residence times which results from the longer time span it takes to refill the subsurface reservoirs. But in our study the calculated output curves as shown in Fig. 4 reproduce the measured δ^{18}O signals more consistently. Additionally Alaoui et al. (2012) argued that the effect of vegetation cover change and evapotranspiration in the Ursern valley on the hydrological balance plays a minor role.

3.3 Geochemistry

Mean metal concentrations (Ca, Mg, Na, K, Table 2) are higher than can expected from similar geological and climatological settings with mainly granitic or gneiss materials (Drever and Zobrist, 1992; Keppler, 1996; Ofterdinger, 2001; Tardy, 1971; Uhlenbrook, 1999). Keppler (1996) and Ofterdinger (2001) studied both stable isotopes and geochemical parameters in the fractured granitic Aar and Gotthard massifs in the vicinity of the Ursern valley. They measured for example calcium concentrations of about 0.3–9 mg l^{-1} for surface waters, springs and groundwaters. Angehrn (1996) measured calcium concentration in groundwater wells in the Ursern valley bottom of up to about 40 mg l^{-1} which is also higher than we would expect in this geological and climatological setting.

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Mean sulfate concentrations range from 7.3 to 19.7 $mg\,l^{-1}$ (Table 2) which is also slightly higher than we would expect from a mere magmatic or metamorphic geological setting (1–8 $mg\,l^{-1}$) (Drever and Zobrist, 1992; Uhlenbrook, 1999). Sulfate rich minerals seem to be dissolved by the percolating water. Oxidation of sulfides can be another source of sulfate, but this process would drop pH significantly (Ralph, 1979).

Mean silicon concentrations (Table 2) are slightly lower than compared to other granitic or gneiss regions with comparable climate (Drever and Zobrist, 1992; Uhlenbrook, 1999). This also shows that dissolution of magmatic or metamorphic minerals alone can not account for the measured concentrations of solutes. Silicon could be a product of weathering of quartz veins which are very common in this zone of fractured rocks (Winterhalter, 1930). Additionally stable isotopes of base flow samples plot slightly above the LMWL (Fig. 2, insert) which could indicate hydration of silicates (Clark and Fritz, 1997) (more probably quartz than for example feldspar or mica which dissolve even more slowly than quartz).

We infer from our data that waters are circulating through deeper rock zones and dissolve evaporative minerals like gypsum, dolomite or calcite. The pH values of more than 7 support our conclusion of dissolution of evaporative minerals. Moreover, soil pH in our micro catchments is about 4–5. Therefore infiltrating precipitation must be strongly buffered in the deeper aquifer below the soils. Dissolution kinetics suggest that buffering happens mainly through evaporative than metamorphic and magmatic minerals alone (Merkel and Planer-Friedrich, 2008). Low pH of water leaching from the soil in turn could accelerate weathering of rocks.

3.4 Influences on mean water residence time

3.4.1 Effect of vegetation cover and topography

The two largest micro catchments Wallenboden and Bonegg with a shrub cover of 13.8 % and 38.5 % respectively and the smallest micro catchment Chämleten with the highest shrub cover of 82.2 % have a similar range of mean water residence times

(64–70 weeks) (Fig. 7). Moreover the micro catchments Laubgädem and Wallenboden with a similar fraction of shrub cover have mean water residence times of 98 and 70 weeks respectively. The correlation between mean water residence time and shrub cover is very weak ($r^2 = 0.19$, $p = 0.56$) and we therefore conclude that shrub cover does not influence base flow mean residence times in these steep alpine head water catchments.

Additionally, in contrast to the findings of McGlynn et al. (2003), McGuire et al. (2005), Rodgers et al. (2005), and Soulsby and Tetzlaff (2008) mean water residence time in our study does not seem to correlate with any of the calculated topographic indices (Fig. 7). Slight trends can be seen, but they are statistically not significant. McGuire et al. (2005) found correlations of mean water residence time with mean catchments slope and also the topographic wetness index (TWI). But since the range of mean water residence time in our study is small and the range of most of the calculated topographic indices is relatively high in our study we conclude that at our sites mean water residence time does not depend on any of the calculated topographic indices or vegetation cover. Moreover Figs. 5 and 7 highlight the cluster of mean water residence times of the micro catchments Chämleten, Wallenboden and Bonegg. They seem not to be affected by any topographic or vegetation cover feature. Tetzlaff et al. (2011) stated that a greater contribution of groundwater inputs weakens the influence of topographic controls. This supports our findings and highlights the importance of groundwater contribution even in these steep alpine headwater micro catchments.

According to several authors mean water residence time does not correlate with catchment size (McGlynn et al., 2003; McGuire et al., 2005; Rodgers et al., 2005; Soulsby and Tetzlaff, 2008; Tetzlaff et al., 2009). In our study the largest and the smallest micro catchments Wallenboden and Chämleten have the same mean water residence time of 70 weeks. If we compare these results with the time series of the Reuss river (Fig. 3) we can assume that there exists no correlation between catchment size and mean water residence time. However, the range of our catchment size is small compared to other studies at least for the micro catchments (Tetzlaff et al., 2009).

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Our geochemical data of stream base flow samples (Table 2) and the topographic analysis (Fig. 7) suggest that especially the (hydro)geological situation plays a major role regarding mean base flow residence time. Laubgädem for example is a very small micro catchment with relatively high mean slope and a short mean flow path length (compared to Bonegg and Wallenboden) but has the longest mean water residence time of all the micro catchments. Probably water also enters the systems from upslope bedrock which would produce a discrepancy between surface and subsurface catchment areas. This in turn could mask possible influences of topographic indices on mean water residence times since these indices were calculated for the surface catchment areas.

3.4.2 Implications from hydrogeological aspects

Ofterdinger et al. (2004) studied stable isotopes of groundwater in a tunnel in the western Gotthard massif (granitic Rotondo massif) only a few km south-west of our sites. They concluded that water can percolate in these highly fractured granitic rocks which will lead to a strong dampening of the stable isotope input signal. Additionally the phenomenon of strong isotope signal dampening is especially known from karstic environments (Bakalowicz et al., 1974; Maloszewski et al., 1992, 2002; Perrin et al., 2003; Schwarz et al., 2009). This in turn means that the rocks in our test sites must be highly fractured and have a high porosity and storage capacity. Water circulating in these system will have relatively longer residence times compared to an unfractured system with low storage capacity. Of course the mean water residence time will then also depend on the form and extend of fractures and fissures and their connectivity and not only on their frequency. Therefore we used the calculated mean water residence times (Fig. 4) and the mean discharge (Table 1) to calculate the mobile catchment storage (Table 3). This gives more information on the hydrogeology of the system and insights into its storage capacity. Via the geographic information system we estimated the volume of rocks in the catchments. With Darcy's law, the mobile catchment storage and our calculated topographic parameters (e.g. flow length and hydraulic gradient) we estimated porosity

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and hydraulic conductivity of the rocks (Table 3) (Maloszewski and Zuber, 2002). We estimated porosities of 3.46×10^{-4} to 4.09×10^{-2} which are in the range of values given by Frick (1994) and Himmelsbach et al. (1998) for a geological complex in the Aar massif containing fault zones. They measured porosities between 7.4×10^{-3} and 1.3×10^{-3} respectively. Porosity in the intact Rotondo granite with moderate fracturation are lower and range from 2.4×10^{-5} to 2.9×10^{-4} (Ofterdinger, 2001). Our estimates for hydraulic conductivities (Table 3) are at the upper end together with fault zone and sedimentary rocks (Ofterdinger, 2001). Ofterdinger (2001) gave hydraulic conductivities for different rock types in the Rotondo area ranging from 5.3×10^{-9} to 4.0×10^{-7} m s^{-1}. This strongly supports the conclusion of fractured rocks in the micro catchments in which water can percolate into deeper zones. The delay and dampening of the stable isotope input signal can therefore be explained by a combination of water circulating in the fractures and faults of the rocks and in cavities which are produced by dissolution of readily soluble minerals. Moreover, we found that mobile catchment storage does not correlate with catchment area (Fig. 8). This indicates that surface and subsurface catchment area are not equal and water is delivered via subsurface flow paths to the micro catchments. Our findings therefore support the conclusions of Burns et al. (1998), Fenicia et al. (2010), Gabrielli et al. (2012), Martinec et al. (1974), Katsuyama et al. (2010) and Shaman et al. (2004) who underlined the importance of flow and volumes of the subsurface storage and its control on mean water residence.

4 Conclusions

We investigated four micro catchments with differing percentage of shrub cover to delineate its influence on mean water residence times. Stable isotope signals in stream water during base flow conditions for a period of two years point to mixing of waters of different ages and mean water residence times of at least 1 yr. Geochemical data (SO_4^{2-}, Ca, Mg, K, pH) from stream water suggest karst formation in the deeper rock layers. This in turn favors mixing of water and storage in the bedrock which leads to

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strong buffering of precipitation input in our small alpine head water catchments. Furthermore, our estimates of hydrogeological parameters indicate that subsurface storage and flow paths play an important role for mean water residence time. Our data suggest that shrub vegetation cover and topography do not influence base flow mean residence time and factors controlling mean water residence time do not seem to scale with catchment size. Snow melt input into the micro catchments and its release during spring was identified as an important influence on stable isotope signals and for mean water residence time modelling. We therefore conclude that in mountainous headwater catchments with relatively thin soil layers the hydrogeological situation and snow dynamics influence storage, mixing and release of meteoric waters and its geochemistry in a stronger way than vegetation cover does. The major part of precipitation enters the bedrock systems rather quickly which leads to a sustained discharge of this bedrock groundwater to base flow in our micro catchments. Consequently the mean water residence is not only an intrinsic property of the hydrogeological system itself but also depends on external climatological factors like snow dynamics.

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Table 1. Characteristics of micro catchments (vegetation data from van den Bergh et al. (2011) and Fercher (2012) (modified), discharge data from Lagger (2012) and Schmidt (2012)).

	Chämleten (CH)	Wallenboden (WB)	Bonegg (BO)	Laubgädem (LB)
projected area (km^2)	0.01981	0.56431	0.34302	0.02981
shrub cover (mainly *Alnus viridis* and *Sorbus aucuparia*) (%)	82.2	13.8	38.5	14.5
vegetation cover (%)	100.0	78.9	95.9	100.0
elevation range (m a.s.l.) mean elevation (m a.s.l.)	1669–1810 1740	1501–2354 2082	1551–2492 2026	1721–1915 1836
slope range (°) mean catchment slope (°)	4.0–55.7 24	0.6–60.5 20	0.5–73.1 28	0.3–49.3 20
exposition	NE	NNW	NW	NE
range of discharge ($l s^{-1}$) (vegetation period 2010 and 2011)	0.09–36.02	0.46–44.03	2.00–93.54	0.10–14.61
mean discharge ($l s^{-1}$) (vegetation period 2010 and 2011)	1.08	2.42	6.3	2.91

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Table 2. Geochemical parameters of stream base flow samples in $mg\,l^{-1}$. Mean (standard deviation).

	Chämleten	Wallenboden	Bonegg	Laubgädem
Ca ($n = 20$)	16.25 (1.76)	27.42 (3.56)	22.79 (3.67)	19.41 (1.74)
Mg ($n = 20$)	0.85 (0.11)	1.63 (0.11)	2.22 (0.31)	0.8 (0.09)
Na ($n = 20$)	0.89 (0.1)	1.02 (0.08)	1.27 (0.13)	0.73 (0.09)
K ($n = 20$)	1.11 (0.15)	2.12 (0.19)	2.59 (0.34)	1.71 (0.14)
Si ($n = 29$)	2.63 (0.84)	2.39 (0.69)	2.99 (1.00)	1.86 (0.58)
SO_4^{2-} ($n = 27$)	10.82 (1.53)	14.69 (1.43)	19.68 (3.21)	7.31 (0.71)
pH (summer)	7.35 (0.18)	7.65 (0.25)	7.55 (0.14)	7.35 (0.32)
pH (winter)	7.3 (0.26)	7.54 (0.26)	7.56 (0.25)	7.68 (0.13)

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Table 3. Hydrogeological parameters of the micro catchments.

	Chämleten	Wallenboden	Bonegg	Laubgädem
mean water residence time (weeks)	70	70	64	98
mobile catchment storage H_2O (m^3)	4.57×10^4	1.03×10^5	2.44×10^5	1.73×10^5
volume of rocks (m^3)	1.66×10^6	2.96×10^8	3.10×10^8	4.21×10^6
porosity (–)	2.75×10^{-2}	3.46×10^{-4}	7.87×10^{-4}	4.09×10^{-2}
hydraulic conductivity ($m\,s^{-1}$)	2.84×10^{-7}	4.33×10^{-8}	5.39×10^{-8}	5.33×10^{-7}

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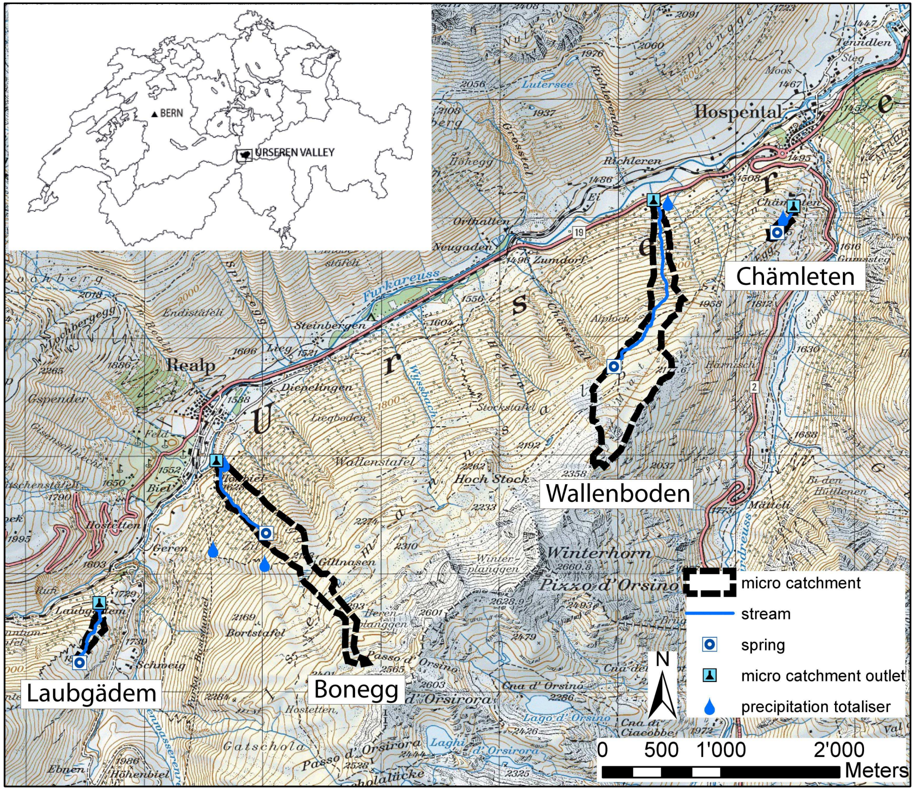

Fig. 1. Location of the micro catchments in the Ursern valley (micro catchment limits from van den Bergh et al. (2011) and Fercher (2012), modified), geodata reproduced by permission of swisstopo (BA12066).

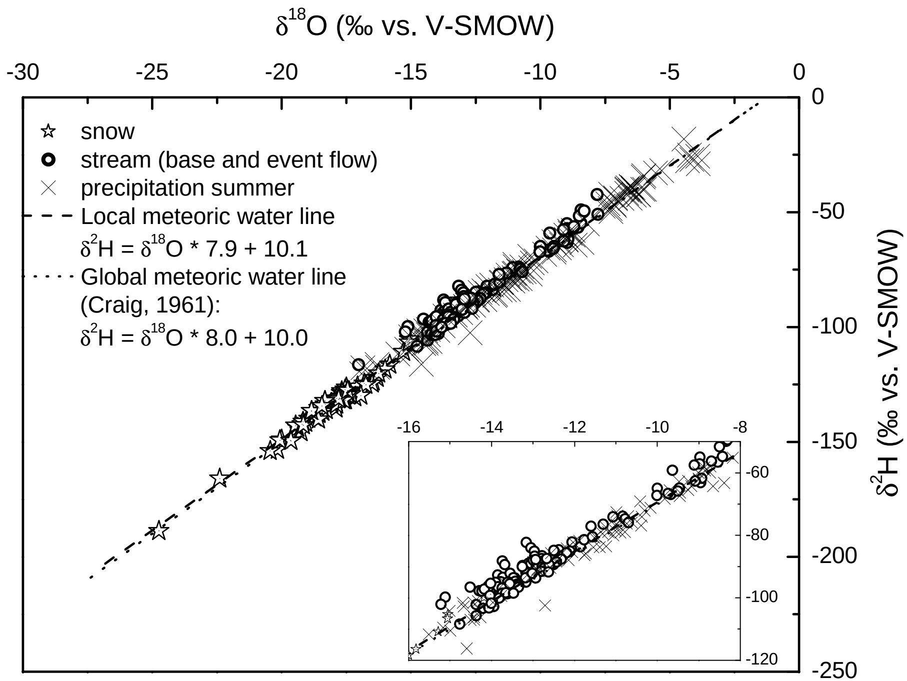

Fig. 2. δ^{18}O vs. δ^{2}H in precipitation and stream water (base flow and storm flow samples).

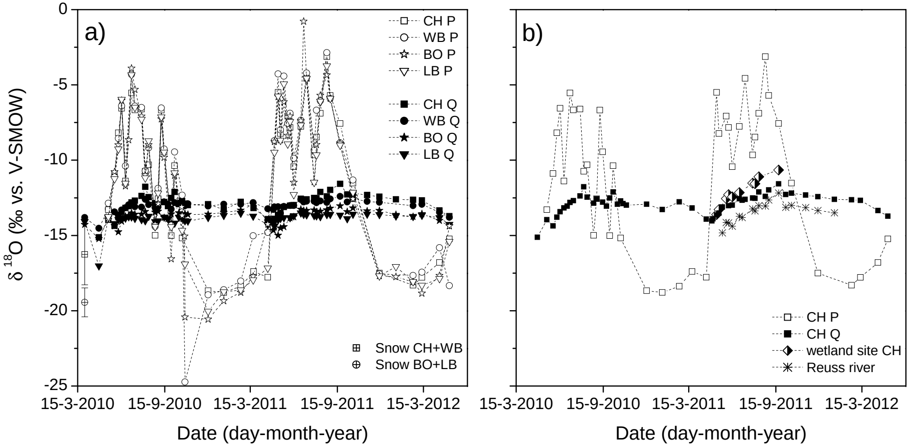

Fig. 3. (a) Stable isotopes (δ^{18}O of H_2O) in precipitation (*P*, open symbols) and stream water base flow (*Q*, filled symbols) in the four micro catchments. **(b)** Stable isotopes (δ^{18}O of H_2O) in precipitation (*P*), stream water base flow (*Q*) and subsurface/overland flow in a Chämleten wetland site and the Reuss river.

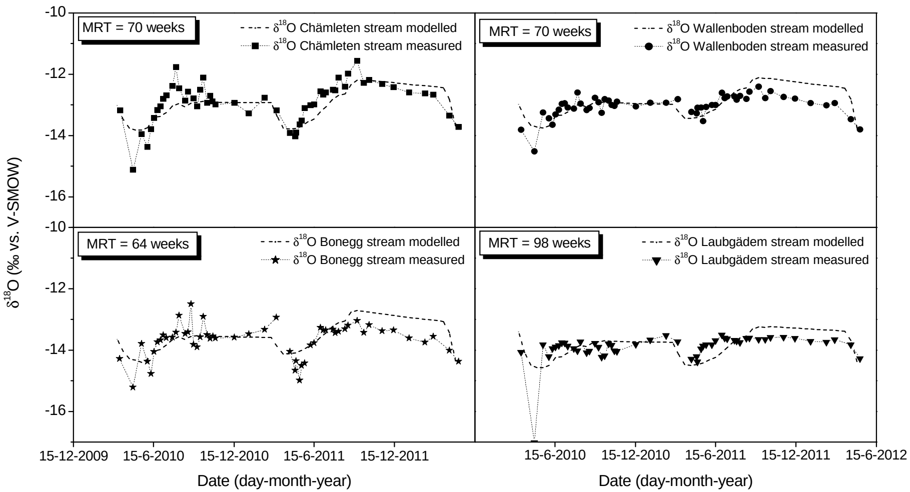

Fig. 4. Measured and modelled stable isotopes ($\delta^{18}O$ of H_2O) in stream water base flow in the four micro catchments.

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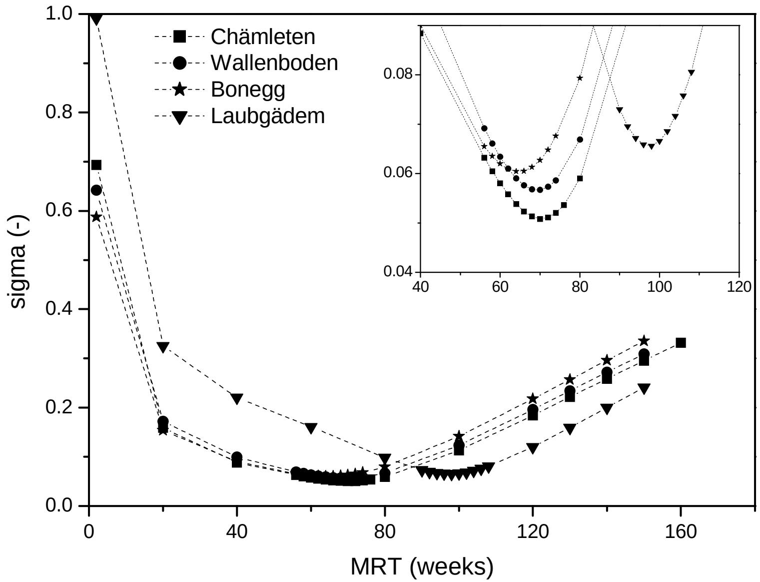

Fig. 5. Sensitivity analysis for the micro catchments and calculation of mean water residence time. The small insert shows sigma values on a smaller scale.

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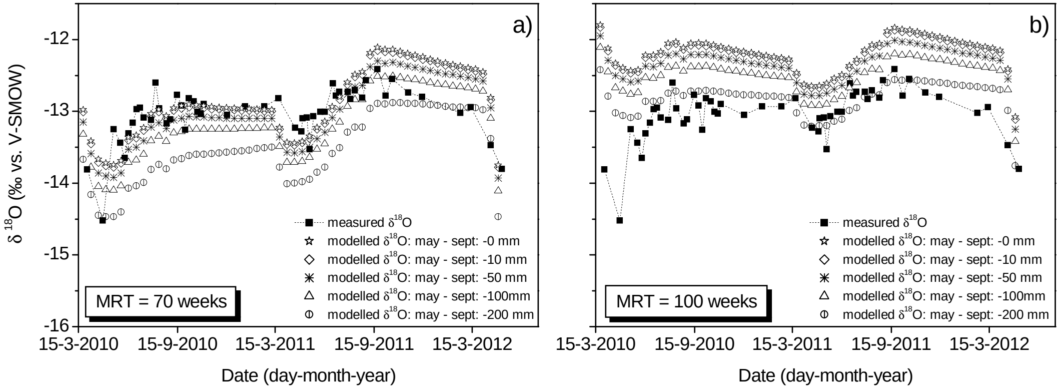

Fig. 6. Modelled and measured stream water stable isotope signals ($\delta^{18}O$) for reduced summer precipitation in the Wallenboden micro catchment. **(a)** mean water residence time = 70 weeks. **(b)** mean water residence time = 100 weeks. "−0 mm" refers to the modelled values of Fig. 4.

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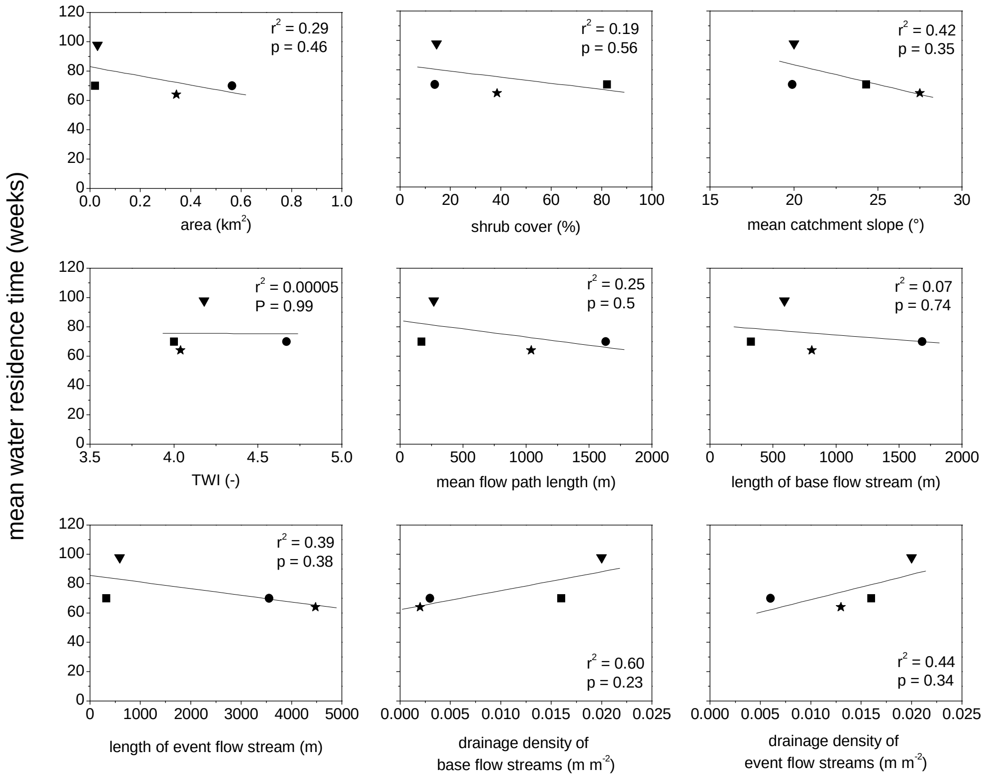

Fig. 7. Correlation of mean water residence time with topographic indices and shrub cover (■ = Chämleten, • = Wallenboden, ★ = Bonegg, ▼ = Laubgädem, micro catchment area and shrub cover data from Fercher (2012) and van den Bergh et al. (2011), modified).

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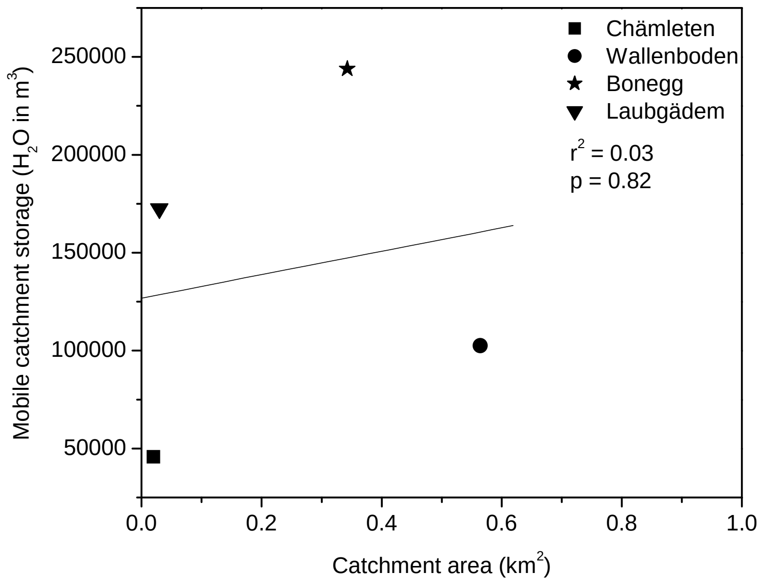

Fig. 8. Correlation of catchment area and mobile water stored in the catchments.