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Research papers

Identifying the hydrological behavior of a complex karst system using stable isotopes

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ABSTRACT

Karst systems can be generally characterised by their high hydrological heterogeneities related mainly to highly variable permeabilities, which can significantly change over small spatial scales. This makes tracing and quantification of water flow pathways an extremely demanding task. In this study we present an analysis of hydrological characteristics of a complex karst system, the Ljubljanica river catchment in central Slovenia. Spatially distributed data on stable isotope composition ($\delta^{18}O$, $\delta^{2}H$) of precipitation as inputs, and of several karst springs/sinks as outputs, were obtained. These data were used to identify spatial and seasonal patterns and hydrological behaviour of the karst system in contrasting hydrological conditions. The intensive mixing of continental and Mediterranean air masses over the Ljubljanica river catchment makes the precipitation source identification difficult. However, the results of the precipitation isotopic composition analysis indicate a spatial pattern that could be recognised also in the $\delta^{18}O$ and $\delta^{2}H$ values of the karst springs and sinks. Along the prevailing karst conduits, the spatial differences in the $\delta^{18}O$ and $\delta^{2}H$ values decreased. The mean transit time (MTT) estimates using $\delta^{18}O$ or $\delta^{2}H$ as tracers were similar, with those for the main karst conduits and tributaries ranging between 0.34 and 0.74 years. Such a relatively short MTT could be expected for karst catchments without extensive deep groundwater storage. The fraction of young water (F_{yw}) for the whole catchment was 0.28, meaning that more than one-quarter of the total discharge was younger than approximately 2.3 months (assuming that the catchment transit time is described by exponential distribution). Small differences in the MTT over different parts of the karst catchment area might indicate intensive mixing and homogenisation of water along the underground conduits. However, the catchment's homogenisation strongly depends on the preceding hydrological conditions; the differences in the isotope composition can be identified during low-flow conditions, which might indicate the dominant influence of the local recharge of the karst springs.

1. Introduction

In many parts of the world, karst aquifers are important freshwater resources and their management requires improved quantitative understanding of the hydrologic functioning of karst catchments in order to develop water resources protection, determine the potential impact of contaminants, and plan management strategies. This is becoming increasingly important in light of future climate change related alterations of precipitation patterns, which will affect the transport of water and solutes through karst hydrogeological systems and consequently strongly influence water availability for different uses, as water scarcity is an increasingly pressing issue in many karst areas (Hartmann et al., 2014; Chen et al., 2018).

Generally, the hydrological behaviour of a karst system can be characterised by temporally and spatially highly variable processes of recharge (diffuse and concentrated), storage (in epikarst, vadose, and phreatic zones), and flow type (diffuse and along preferential conduits) (White, 2002; Perrin et al., 2003; Ford and Williams, 2007). Karst catchments as hydrological systems express a high degree of complexity and heterogeneity in the karst aquifer structure, which can be roughly characterised by the processes of concentrated and diffuse infiltration, predominant conduit flow, and rapid flow that can reach long distances in the underground conduit systems (Ravbar et al., 2012). Basic hydrological characteristics of karst systems are conceptually relatively

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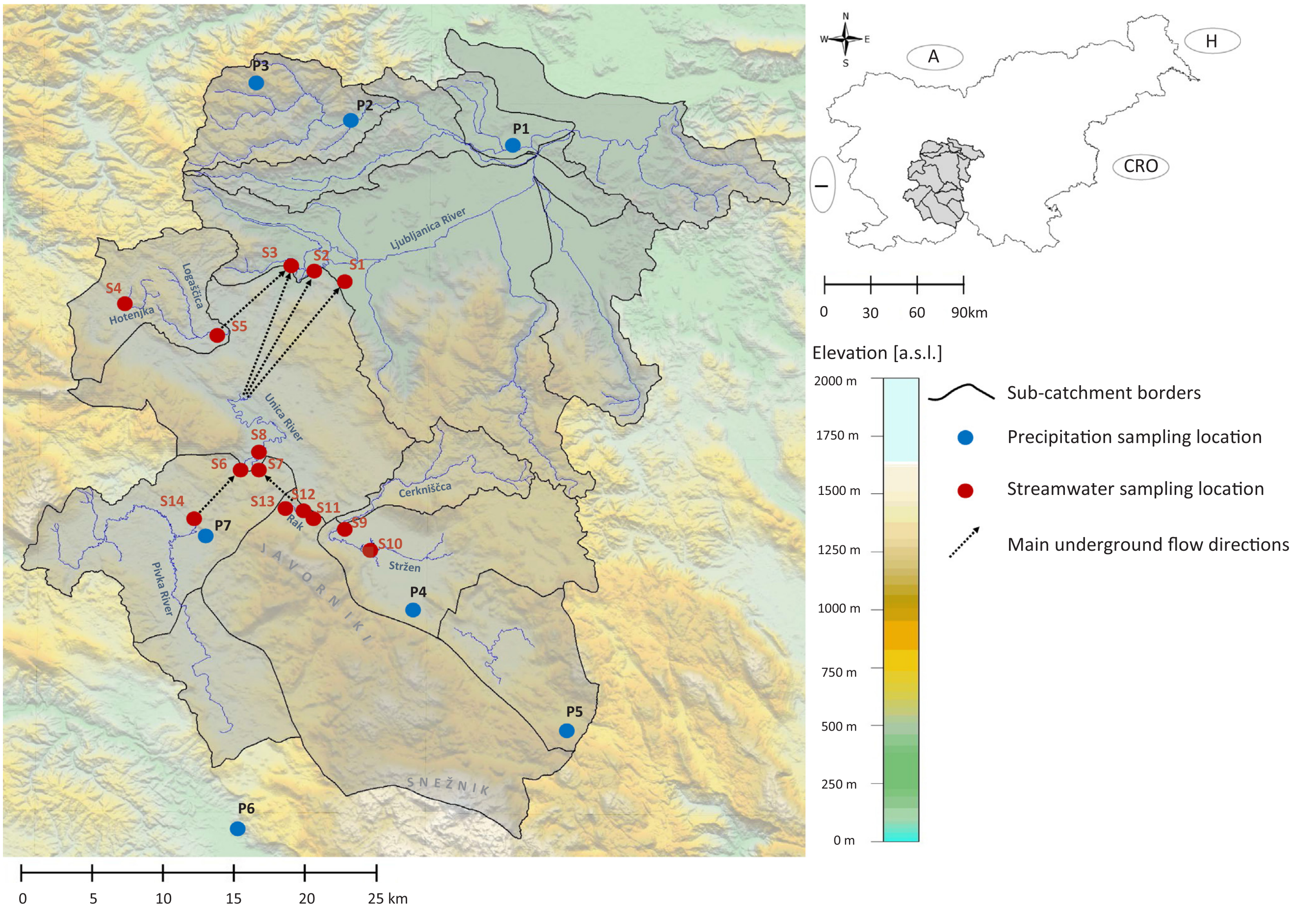

Fig. 1. The Ljubljanica river catchment. Blue dots indicate precipitation sampling locations, red dots indicate streamwater sampling locations. Dashed arrows illustrate main underground flow directions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

well known; however, the role of particular hydrological processes and their dominance during different hydrological conditions are often difficult to quantify. High karstic hydrogeological heterogeneity poses an additional challenge, as it restricts spatial extrapolation of many small-scale processes to larger (catchment) scales.

Biogeochemical cycles, contaminant transport, and chemical weathering are regulated by the speed at which precipitation travels through landscapes until it reaches streams. Regional and temporal variations of isotopic fractionation because of latitudinal, continental, altitude, and seasonal effects (Kendall and Doctor, 2004; Urresti-Estala et al., 2015) can help to define flow patterns. Streamflow is a mixture of young and old precipitation, but proportions of these young and old components are usually rather unknown. In view of the unique hydrological characteristics, the study of karst aquifers requires specialized investigation methods (Goldscheider and Drew, 2007). A wide array of groundwater physico-chemical parameters was used to obtain information on the hydrological behaviour of karst catchments; however, hydrochemical data rarely deliver straightforward and unambiguous interpretations on karst catchment functioning during non-stationary (contrasting) hydrological conditions. In this respect, naturally occurring environmental isotopes (e.g. ^{18}O, ^{2}H) provide additional information about specific underground flow paths and transit times of water within karst catchments. Such information is crucial in our endeavour to characterize different components of the transit time distribution (McDonnell et al., 2010). Several studies have applied environmental isotopes of water to estimate mixing between source components in karst aquifers, provided some insight into karst aquifer recharge characteristics under different flow conditions, and tried to estimate the mean transit time (MTT) in karst catchments (e.g. Maloszewski et al., 2002; Perrin et al., 2003; Doctor et al., 2006; Hu et al., 2015). Water isotopes are excellent conservative tracers as they are naturally "injected" in a diffuse way over the whole catchment during rainfall events (McGuire and McDonnell, 2008). They are considered perfect tracers for hydrological applications as these elements belong to the water molecules themselves and are not chemically reactive within the environment at ambient temperatures (Gat, 1996). Stable isotopes (^{18}O, ^{2}H) vary in the rain signal both on a seasonal scale and during a recharge event and keep a stable ratio in the karst aquifer (Maloszewski et al., 2002). In a karst catchment, artificial tracers are usually injected into sinkholes and they supply information mainly on preferential flow paths along subsurface conduits.

On the other hand, spatial heterogeneity in stable isotope inputs (e.g. precipitation) and outputs (hydrogeological characteristics across the catchments) has been, along with time heterogeneity (changing hydrological conditions), widely recognised as a fundamental problem in stable isotope applications in the catchment hydrology literature. Further, selection and interpretation of mixing models in view of catchment characteristics involving a limited number of tracers is often ambiguous (Kirchner, 2016a). Despite of their limitations, stable isotopes can be used to improve our understanding of complex, heterogeneous hydrological systems, such as karst catchments (Hartmann et al., 2014).

In this study, stable isotopes ($\delta^{18}O$, $\delta^{2}H$) have been monitored to improve our understanding of the hydrological functioning of a complex karst system of the Ljubljanica river in Slovenia. We investigated spatial heterogeneity of stable isotopes in precipitation inputs and the dynamics of recharge from different parts of the catchment. The goals of this study were to:

1) Obtain insight into spatial and temporal variability of precipitation stable isotope inputs over the studied Ljubljanica river catchment, with a climate characterised as a transitional area.
2) Improve understanding of karst aquifer behaviour during diverse hydrological conditions using stable isotope measurements.
3) Assess the mean transit times (MTTs) of water and the fraction of young water (F_{yw}) in different parts of the karst catchment and evaluate how stable-isotope analysis agrees with the results of other studies where different artificial tracers were used.

2. Study area

The investigated Ljubljanica river catchment, located in south and central Slovenia, can be characterised as a complex, hydrologically highly heterogeneous karst catchment (Fig. 1). The catchment covers an area of approx. 1880 km^2, the altitude ranges between 300 m a.s.l. and 1800 m a.s.l. The Ljubljanica river is a typical karst river with its karst hinterland consisting of significantly fissured, porous carbonate rock (mainly limestone and dolomite). Only the northern lowland part of the catchment consists of non-carbonate rocks. Because of the complex hydrogeological structure of the area, surface river flows are generally short; rivers and streams sink underground several times along the main flow paths. Consequently, the Ljubljanica river is known as a river of different names.

In the upper part of the Ljubljanica karst catchment, the Unica and Malenščica springs form the Unica river. Its catchment can be divided into three hydrologically connected parts, i.e. the Javorniki, Pivka, and Cerknica parts of the catchment. The central area (Javorniki part) is the karst massif of Javorniki and Snežnik, which borders the eastern side of the valley of the Pivka river and its tributaries (Pivka part), and the western side of a string of karst poljes (the biggest of these is Cerknica polje) that are distributed gradually in the southeast–northwest direction (Cerknica part). The Pivka Valley is covered by very poorly permeable Eocene flysch draining the surface network of the Pivka river which sinks into the world famous Postojna Cave, then follows the so-called Pivka Cave stream of the Planina Cave and emerges again as the Unica spring. The Pivka Cave stream is joined underground by the Rak Cave stream, which collects groundwater mainly from the areas of karst poljes in the Cerknica part of the catchment (Petrič, 2010). The majority of the catchment belongs to the Javorniki karst plateau, composed of well-karstified Jurassic and Cretaceous limestones with karst-fissure porosity. The carbonate rocks are more than 1000 m thick and the depth of the unsaturated zone can reach up to several hundred meters (Ravbar et al., 2012). In the Javorniki part, the underground flow is dominant, while surface streams are also present in the other two parts. They are recharged mainly by karst waters, and after appearing as surface flows, they sink underground again.

Downstream of the Unica and Malenščica springs, the Unica river flows over the Planina polje, sinks again and re-emerges as the Ljubljanica river at several springs (the two main ones are the Retovje and Močilnik springs) and the Ljubljanica river karstic tributaries (such as the Bistra spring). These springs extend along the non-carbonate lowland and carbonate rock higher terrain contact at the south-western border of the Ljubljana Marshes. The hydrogeology and underground connections of this particular karst system have been the subject of several studies in the past (e.g., Gams, 1970; Gospodarič and Habič, 1976; Pezdič in Urbanc 1987; Gabrovšek and Turk, 2010; Blatnik et al., 2017). To the west, there are the Hotenjka and Logaščica sinking streams, which also recharge the springs of the Ljubljanica river.

Recent hydrogeological and hydrological studies focused on the hydraulic connections and hydrodynamic behaviour of the aquifer system using natural and artificial tracers (e.g., Kogovšek, 2001; Kogovsek, 2004; Gabrovšek et al., 2010; Kogovšek and Petrič, 2010; Ravbar et al., 2012; Petrič et al., 2018). However, the study area has not yet been investigated in detail by stable isotope measurements. The use of various artificial tracers revealed the relations between various contribution areas to the springs of the Planina polje. In general, the Malenščica spring is recharged mainly from the Cerknica direction and the Javorniki karst aquifer, and there is no direct connection with the ponor of the Pivka river sinking in the Postojna cave. During high streamflows, when discharges of the Malenščica spring are above approx. 6 m^3/s, inflows from the Cerknica part dominate. This is related to high water levels in the intermittent Cerknica Lake. On average, the water stays in Cerknica lake for 260 days/year and high-water levels are present 17 days/year (Kranjc, 1985). Then the outflow from the Malenščica spring is constrained and the Rak Cave stream in the Planina Cave acts as an overflow. The Rak Cave stream is recharged from both the Cerknica and Javorniki parts, and the Pivka Cave stream from the Javorniki and the Pivka parts (Ravbar et al., 2012). Long-term mean daily discharge from the whole studied karst catchment is 24 m^3/s, the discharge can drop to approx. 1 m^3/s during prolonged dry periods.

In view of its climate, the Ljubljanica river catchment is a transitional area between sub-Mediterranean and temperate continental climates (oceanic climate subtype Cfb according to the Köppen-Geiger climate classification system). The prevailing direction of wet air masses is SW to NE, which is also reflected in spatially declining rainfall sums in this direction. However, highly variable wet air mass directions and rainfall formation processes can be observed in different seasons (Krklec et al., 2018) or even during particular rainfall events. Highest rainfall sums can be observed along the orographic barriers of the Snežnik karst plateau (rainfall sums exceeding 3000 mm/year) and along the Javorniki karst plateau (rainfall totals exceeding 2000 mm/year). The long-term mean annual rainfall in the north-eastern part of the Ljubljanica river catchment is approx. 1400 mm/year and the mean air temperature is between 8 and 10 °C. The mean monthly reference evapotranspiration (calculated for the period 1971–2000 using the Penman–Monteith equation) at meteorological station Postojna (rainfall sampling point P7, Fig. 1) is 15 mm for the winter months (December to February) and 112 mm for the summer months (June to August). The long-term mean annual reference evapotranspiration is 720 mm.

3. Methods

3.1. Sampling and analysis

Precipitation samples for stable isotope analysis (δ^{18}O, δ^{2}H) were collected monthly from May 2016 to May 2018 at 7 meteorological stations operated by the Slovenian Environmental Agency (ARSO), shown in Fig. 1. Precipitation data were obtained by Onset RG2-M tipping bucket rain gauges and OTT Pluvio^2 L weighting rain gauges. The rainfall samples for the stable isotope values analysis were collected daily at stations P1, P5, P6, and P7 and transferred to a larger bottle that was stored in a dark, cold place and replaced every month. The rainfall samples at stations P2, P3, and P4 were collected in plastic containers installed in approx. 0.5 m deep trenches, covered by brick plate and grass turf to minimize temperature variations and prevent evaporation. The plastic containers were emptied each month. The position of precipitation collectors assured relatively good spatial coverage of heterogeneity in precipitation input amounts.

Water samples at karst river sinks (ponors) and springs were collected at 14 stations covering all main Ljubljanica river flowpaths and its main tributaries (Fig. 1). Stream water samples were initially collected in August 2016 and January 2017. During the 1-year period, i.e. from June 2017 to May 2018, the stream water samples were collected on a monthly basis. Water samples at stations S9 (Stržen stream) and S10 (Cerkniščica stream) were collected only occasionally during middle-flow conditions due to the intermittent character of both streams during dry periods and the formation of the intermittent

Table 1
Precipitation sampling locations with basic descriptive statistics.

Location	Name	Elevation [m a.s.l.]	Precipitation Sum (2016) [mm]	Precipitation Sum (2017) [mm]	Weighted mean δ^{18}O [‰]	Weighted mean δ^{2}H [‰]
P1	Ljubljana	291	1317	1531	−8.6	−56
P2	Dvor	344	1366	1669	−8.3	−55
P3	Črni Vrh	811	1607	1854	−8.5	−56
P4	Laze	586	1692	1957	−8.3	−55
P5	Babno Polje	754	1599	1530	−8.7	−57
P6	Ilirska Bistrica	455	1492	1536	−7.1	−45
P7	Postojna	533	1548	1836	−8.0	−52

Table 2
Karst spring and ponor location data summary (*– data are weighted using discharge data from the nearest water station; ** – data collected only occasionally; NA – data not available).

Location	Name	Type	Mean/Max./Min. discharge [m^3/s]	Weighted mean δ^{18}O [‰]	Weighted mean δ^{2}H [‰]
S1	Bistra	karst spring	7.5/20.5/0.9	−8.7	−56
S2	Retovje	karst spring	NA	−8.6*	−56*
S3	Močilnik	karst spring	NA	−8.5*	−55*
S4	Hotenjka	sinking stream	0.2/15.4/0	−8.7*	−57*
S5	Logaščica	sinking stream	0.5/17.2/0	−8.6	−56
S6	Unica	karst spring	15.6/88.9/0	−8.3	−54
S7	Malenščica	karst spring	6.6/11.2/1.1	−8.8	−57
S8	Unica Hasberg	river	22.2/90.2/0.9	−8.7	−56
S9	Stržen	sinking stream	NA	−9.0**	−59**
S10	Cerkniščica	sinking stream	1.1/37.3/0	−9.1**	−61**
S11	Rak$_1$	karst spring	4.2/35.5/0	−8.5	−55
S12	Rak Kotliči	karst spring	NA	−8.5*	−56*
S13	Rak$_2$	sinking stream	NA	−8.5*	−55*
S14	Pivka	sinking stream	4.3/43.3/0	−7.7	−49

Cerknica Lake during wet hydrological conditions, when the lake water body joins and overflows both sampling points. At streamwater sampling locations we measured water temperature (T), pH, and electrical conductivity (EC) using Hydrolab MS5 and the Hach Pocket Pro + Multi 2 tester. At most sampling locations, the discharge is monitored as part of the hydrological monitoring operated by ARSO. The precipitation sampling locations and the streamwater sampling locations with some descriptive parameters are summarized in Tables 1 and 2, respectively. Because precipitation and streamflow rates varied considerably during the observed period, the tracer samples were weighted by its associate volume (monthly precipitation amount and mean monthly discharge). At streamwater sampling locations where the discharge data are not available, the mean monthly discharge data from the nearest sampling station with known discharges were used as an approximation for assigning weights.

The isotopic composition of oxygen and hydrogen was measured after equilibration with CO_2 (2 h) and H_2 (6 h) at 18 °C, respectively, in the DHOEQ48 equilibration unit. The measurement was done using the Finnigan MAT Delta plus isotope ratio mass spectrometer. Results are reported as the conventional delta (δ) notation (δ^{18}O and δ^{2}H), i.e. the relative deviation of the heavy-to-light isotope ratio of the sample from that of the standard (VSMOW) expressed in per mil (‰). In-house reference materials calibrated vs. VSMOW2 and SLAP2 international reference standards were used to calibrate the measurements. The accuracy was checked using the USGS45 and USGS47 certified reference materials as controls randomly distributed in each batch. The measurement uncertainty (determined as long-term deviation of control materials from their respective certified δ values) was 0.05‰ for δ^{18}O and 0.7‰ for δ^{2}H.

3.2. Calculation and data analysis

The monitoring of the precipitation isotope characteristics at 7 locations assured good spatial coverage over the studied catchment. The spatial variability of monthly precipitation sums and the monthly precipitation isotopic composition over the sub-catchment areas of selected karst springs and sinks was considered by using Thiessen polygons. The assessment of karst sub-catchment areas extension was based on previous natural and artificial tracer (dye) tests done mainly by the Karst Research Institute. In some parts of the Ljubljanica river catchment, where additional data from tracers' tests were not available, the karst sub-catchment areas were assessed using surface topography analysis.

Given the basic data set available in terms of temporal (monthly) resolution, the sine wave method was used, which compares the amplitude of seasonal variations in δ^{18}O and δ^{2}H in precipitation and streamwater and uses the degree of damping to estimate the transit time. The seasonal sine wave model for description of δ^{18}O time series was defined as (Rodgers et al., 2005):

$$\delta^{18}O = \delta^{18}O_{mean} + A_{PorS} \bullet [\cos(c \bullet t - \theta)] \quad (1)$$

where δ^{18}O and $\delta^{18}O_{mean}$ are the modelled and the mean annual measured δ^{18}O values, respectively, $A_{P\ or\ S}$ are the calculated (fitted) annual amplitudes of precipitation and of streamwater, respectively, c is the radial frequency of annual fluctuations (0.017247 rad/day), t is the time in days after the start of the sampling period, and θ is the phase lag. The same method was used for the δ^{2}H values. For fitting the sinusoidal cycle of precipitation and streamwater δ^{18}O and δ^{2}H, the iteratively reweighted least squares (IRLS) regression was used in order to limit the influence of outliers. The shape of the travel-time distribution (TTD) and its corresponding mean travel time (MTT) reflect storage and mixing processes in the catchment (Kirchner et al., 2001; Hrachowitz et al., 2010a, Kirchner, 2016b). Estimates of TTD and MTT have been in the literature correlated with a wide range of catchment characteristics (e.g. McGuire et al., 2005; Soulsby and Tetzlaff, 2008; Tetzlaff et al., 2009; Hrachowitz et al., 2010b; Asano and Uchida, 2012). Since a prevalence of flow paths with short transit times can be generally expected for karst aquifers (e.g. along preferential conduits, epikarst fissures), the exponential distribution of the TTD was assumed. The MTT for the exponential model is estimated by the following equation:

$$MTT = c^{-1}[(A_S/A_P)^{-2} - 1]^{0.5} \quad (2)$$

where A_P is the amplitude of precipitation, A_S is the amplitude of the streamwater outputs, and c is the radial frequency of annual fluctuations as defined in Eq. (1).

Past studies using different artificial tracers revealed that the relations between various contribution areas of the observed springs are strongly dependent on temporal hydrologic conditions (Petrič, 2010; Ravbar et al., 2012). Therefore, to make a general differentiation in the hydrological conditions at the study area, we considered monthly periods when the discharges at the sampling points were lower than the long-term mean discharge values under low-flow conditions, whereas discharges higher than the mean values were denoted as high-flow conditions.

Normally distributed data were analysed using the *t*-test for testing the differences in the measured parameters at different locations. A significance level of 0.05 was selected.

4. Results

4.1. $\delta^{18}O$ and $\delta^{2}H$ values of precipitation

The precipitation $\delta^{18}O$ and $\delta^{2}H$ values in monthly samples indicate continental effects, a general decreasing trend of heavy isotope content in the SW–NE direction. This is the main direction of the wet air masses approaching the study area from the Mediterranean. The highest $\delta^{18}O$ and $\delta^{2}H$ values (weighted mean −7.1‰ and −45‰, respectively) were observed at rainfall station P6 (Ilirska Bistrica) located few kilometres outside the catchment area to the south. The lowest $\delta^{18}O$ and $\delta^{2}H$ values (weighted mean −8.7‰ and −57‰) were observed at station P5 (Babno Polje). The differences between weighted mean annual $\delta^{18}O$ and $\delta^{2}H$ values at stations positioned in the north-eastern part of the catchment (P1–P5) were rather small (differences in $\delta^{18}O$ values below 0.4‰ and in $\delta^{2}H$ values below 3‰). Interestingly, the calculated $\delta^{18}O$ gradient for the neighbouring stations P2 (Dvor) and P3 (Črni vrh) positioned at different elevations was only −0.2‰ (for the elevation difference of approx. 450 m), which is lower than the elevation gradient of −0.24‰ to −0.3‰ per 100 m reported for the N Adriatic area (Vreča et al., 2006), but still within the limits published by Windhorst et al. (2013). The differences between some neighbouring precipitation stations (e.g. P1, P2, and P3; P4 and P5) were not statistically significant with the selected significance level of 0.05 for both $\delta^{18}O$ and $\delta^{2}H$ values.

The records of $\delta^{18}O$ and $\delta^{2}H$ values of precipitation have a seasonal cycle that is in phase with monthly air temperatures. Distinctive seasonal variations were observed at all stations with lower $\delta^{18}O$ and $\delta^{2}H$ values in winter. The lowest values were measured during the cold and snowy February 2018 (−16.7‰ and −122‰, respectively, at station P5). The highest values were measured in the summer of 2017 (−2.8‰ and −12.5‰, respectively, at station P6). Fig. 2 shows the seasonal trend of the $\delta^{18}O$ and $\delta^{2}H$ values for the two most contrasting stations, P6 and P5. The $\delta^{18}O$ and $\delta^{2}H$ values could not be measured at any of the precipitation stations in December 2016 when there was no precipitation. Larger seasonal variations in $\delta^{18}O$ and $\delta^{2}H$ were observed at station P5 (12.7‰ and 101.3‰) compared to station P6 (7.4‰ and 56.4‰, respectively). The differences in the $\delta^{18}O$ and $\delta^{2}H$ seasonal amplitudes can be related to higher mean monthly air temperature variations at station P5 (25.1 °C) compared to the air temperature variation at station P6 (23.6 °C). Whereas the summer $\delta^{18}O$ and $\delta^{2}H$ values at both stations are relatively similar, the highest differences can be observed in the winter period when the average differences in the mean monthly air T between the two stations were higher (3.5 °C) compared to the difference in summer months (2.7 °C). The statistically significant Pearson correlation coefficient ($r^2 > 0.6$ and p-value < 0.001) was calculated between the mean monthly air T and monthly precipitation $\delta^{18}O$ and $\delta^{2}H$ values for all precipitation sampling locations. The Pearson correlation coefficient between monthly $\delta^{18}O$ and $\delta^{2}H$ values in precipitation and the monthly amount of precipitation was relatively low ($r^2 < 0.1$) and not statistically significant at the selected significance level of 0.05.

The seasonal variability of precipitation isotopic composition is evident when dividing all the monthly data (P1-P7) into seasons, i.e. spring: March-May, summer: June-August, autumn: September-November and winter: December-February (Fig. 3(left)). While the values of the spring and autumn months are in the middle of the scatter, the most and least negative values of the isotopic composition of precipitation can be seen for winter and summer months. However, the scatter in the seasonal data is relatively high.

The relation between $\delta^{18}O$ and $\delta^{2}H$ for all precipitation sampling stations is shown in Fig. 3 (right) together with the Global Meteoric Water Line (GMWL). The Local Meteorological Water Lines (LMWL) at the precipitation sampling points are close to the GMWL. The orthogonal regression equations between the isotopic values of individual monthly samples representing LMWLs are summarized in Table 3. The Pearson correlation coefficients (r) between $\delta^{2}H$ and $\delta^{18}O$ values are high for all stations ($r > 0.95$) and all LMWLs are close to the GMWL. There is no evident change in the LMWL slope but there is an increase in the LMWL intercept with station elevation, the only exception being station P6 where considerably higher $\delta^{18}O$ and $\delta^{2}H$ values were observed compared to other stations.

The monthly deuterium excess (d-excess) ranged between 17‰ (station P3) and 7‰ (station P7). Highest d-excess values were generally observed in autumn (October and November) and the lowest values in the late spring and summer (May to July). The highest mean annual d-excess value (13‰) was at station P3 (Črni vrh), the precipitation sampling location positioned at the highest elevation.

4.2. $\delta^{18}O$ and $\delta^{2}H$ values of karst springs and sinks

Following the spatial patterns of the precipitation $\delta^{18}O$ and $\delta^{2}H$ values, the highest streamwater $\delta^{18}O$ values (weighted mean values

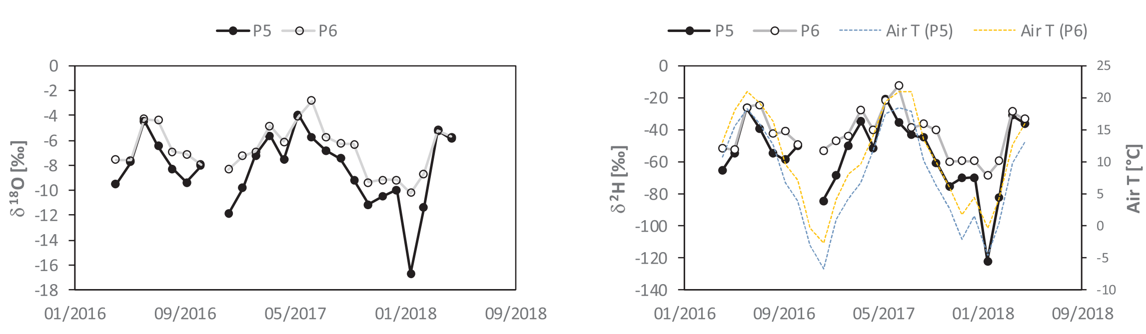

Fig. 2. Seasonal trend of the $\delta^{18}O$ (left), $\delta^{2}H$, and monthly air temperatures (right) for stations P5 and P6.

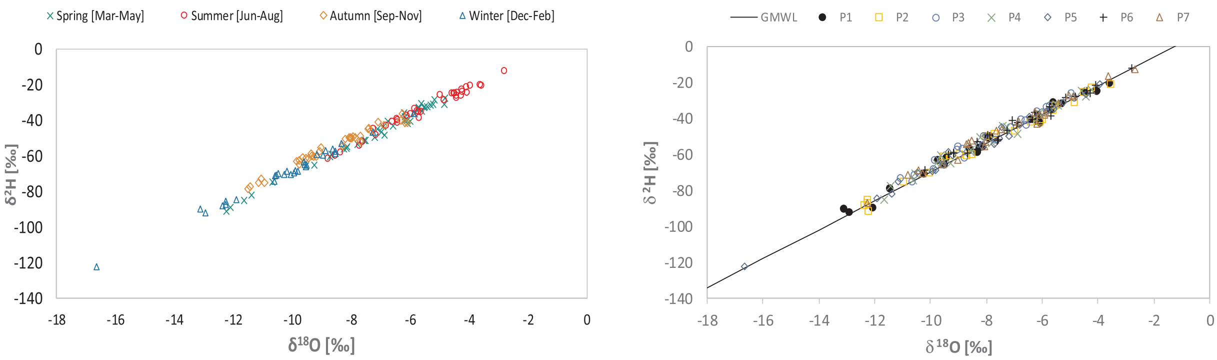

Fig. 3. (left) Seasonal variability of monthly precipitation isotopic composition. (right) The relation between monthly precipitation δ^2H and δ^{18}O values at stations P1 to P7 together with the GMWL.

Table 3
Local meteoric water lines and mean d-excess values for precipitation sampling locations. ± represents slope, intercept and d-excess SD.

Station	δ^2H/δ^{18}O correlation equation	d-excess
P1	δ^2H = (7.6 ± 0.1) δ^{18}O + (8.3 ± 1.6)	11.2 ± 2.5
P2	δ^2H = (7.7 ± 0.2) δ^{18}O + (8.4 ± 0.9)	10.1 ± 3.2
P3	δ^2H = (7.8 ± 0.4) δ^{18}O + (10.6 ± 2.2)	12.6 ± 2.3
P4	δ^2H = (7.7 ± 0.3) δ^{18}O + (8.6 ± 1.9)	11.3 ± 2.5
P5	δ^2H = (7.8 ± 0.2) δ^{18}O + (9.9 ± 1.4)	11.4 ± 2.1
P6	δ^2H = (7.4 ± 0.3) δ^{18}O + (7.7 ± 2.4)	11.6 ± 2.3
P7	δ^2H = (7.6 ± 0.3) δ^{18}O + (9.3 ± 1.7)	11.9 ± 2.5

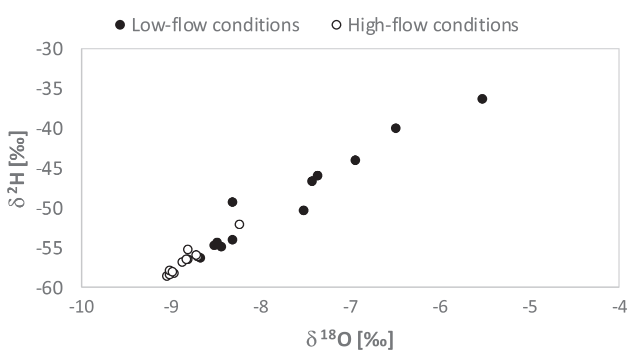

Fig. 4. Scatter plot of the δ^{18}O vs δ^2H values during low-flow (August 2017) and high-flow conditions (December 2017).

−7.7‰ and −49‰, respectively) were measured at sampling point S14 (sink to Postojna cave) and the lowest streamwater δ^{18}O and δ^2H values (weighted mean values −8.8‰ and −57‰, respectively) were measured at sampling point S7 (Malenščica spring). The discharge weighted δ^{18}O and δ^2H values (Table 2) at the sampling stations following the two prevailing karst conduit directions (the Pivka river branch of the catchment following sampling point direction S14 → S6 → S8; the Cerknica branch of the catchment following sampling point direction S9(S10) → S11 → S13 → S7 → S8) indicate the differences between the sampling points located in the headwater part of the catchment (e.g. differences in the δ^{18}O and δ^2H values between sampling points S9/S10 and S14). The differences in the streamwater δ^{18}O and δ^2H values at sampling stations S1-S3 downstream of the sampling point S8 (confluence of the two prevailing karst conduits) are very small (< 0.2‰ for δ^{18}O and < 2‰ for δ^2H values). Fig. 4 shows the scatter plot of δ^{18}O vs δ^2H values during sampling campaigns in August 2017 and December 2017. In August 2017, the lowest mean monthly discharges were measured during the entire sampling period. At the Unica-Hasberg water station (sampling point S8), positioned downstream of the confluence of the Unica river, and the Malenščica stream (sampling point S7, Fig. 1), whose catchment area covers approx. 750 km^2, the average daily discharge was only 3.3 m^3/s. During the December 2017 sampling campaign, the highest mean monthly discharge (77.2 m^3/s) in the sampling period was measured. During low-flow conditions, the difference between sampling points shown in Fig. 4 is much higher compared to the difference between the sampling points that were collected during high-flow conditions. The differences between some neighbouring sampling stations (e.g. S1, S2, and S3; S4 and S5; S11 and S12) were not statistically significant with the selected significance level of 0.05 for both δ^{18}O and δ^2H values, when considering the whole dataset in the statistical analysis. The pH (ranging between 7.5 and 8.5) and EC (ranging between 350 and 550 µS/cm) measurements did not show statistically significant differences between the analysed karst springs and sinks that would indicate a spatial pattern; we noticed a general decrease of the EC values with increasing discharge.

The Pearson correlation matrix calculated based on the δ^{18}O and δ^2H values for the low-flow conditions is shown in Table 4. High correlation for both δ^{18}O and δ^2H values is observed between some of the sampling points positioned along the prevailing karst conduit directions (e.g. sampling stations S8 and S1, S2; S6 and S3, p-value < 0.01). On the other hand, there is a low correlation between sampling point S14 (the most headwater station along the Pivka river karst conduit branch) and other downstream sampling points (e.g. S6, S7). There is a high correlation between sampling stations S1, S2, and S3, which might indicate the presence of a common local recharge of the karst springs during low-flow conditions when the catchment's contribution from headwater parts to the Ljubljanica river discharge becomes very small. On the other hand, the low correlation between sampling points S3, S4, and S5 for δ^{18}O values could indicate hydrological heterogeneities in the local recharge of the karst springs. The Hotenjka stream (sampling point S4) and the Logaščica stream (sampling point S5) are both intermittent karst sinking streams which collect water mainly from local surface and near-surface flows. Additionally, the differences between the sampling stations (S1 and S2; S4 and S5; S11 and S12) are not statistically significant with the selected significance level of 0.05 for both δ^{18}O and δ^2H values, when considering only the data collected during low-flow conditions.

High correlation was calculated for both δ^{18}O and δ^2H values, between the sampling point located at the Logaščica stream (S5) and sampling point S14 (The Pivka stream); these two sampling points are not hydrologically connected. The relatively important influence of surface drainage is a common characteristic of both sampling points, which is apparent from previous tracer experiments conducted in the catchment.

4.3. Seasonal δ^{18}O and δ^2H cycles and estimation of MTT

The seasonal cycle in δ^{18}O and δ^2H values in precipitation and streamwater were used to assess MTT. Fig. 5 shows the seasonal cycle at

Table 4
Correlation matrix for the $\delta^{18}O$ (left) and $\delta^{2}H$ (right) values. R values above 0.8 are highlighted.

$\delta^{18}O$:

	S2	S3	S4	S5	S6	S7	S8	S11	S12	S13	S14
S14											
S13											0.55
S12										0.77	0.69
S11									0.76	0.72	0.84
S8								0.51	0.44	0.58	0.54
S7							0.94	0.42	0.38	0.47	0.49
S6						0.76	0.81	0.74	0.66	0.89	0.65
S5					0.73	0.53	0.58	0.84	0.82	0.69	0.96
S4				0.42	-0.08	-0.08	-0.12	0.16	0.62	0.06	0.29
S3			-0.11	0.65	0.96	0.8	0.89	0.65	0.63	0.86	0.57
S2		0.94	-0.02	0.69	0.88	0.89	0.97	0.58	0.56	0.7	0.61
S1	0.99	0.92	-0.03	0.64	0.84	0.91	0.98	0.52	0.52	0.66	0.57

$\delta^{2}H$:

	S2	S3	S4	S5	S6	S7	S8	S11	S12	S13	S14
S14											
S13											0.65
S12										0.94	0.76
S11									0.86	0.75	0.83
S8								0.51	0.74	0.59	0.5
S7							0.99	0.51	0.76	0.62	0.55
S6						0.82	0.81	0.78	0.95	0.91	0.7
S5					0.73	0.6	0.54	0.77	0.82	0.74	0.96
S4				0.93	0.57	0.54	0.47	0.57	0.69	0.63	0.83
S3			0.58	0.66	0.95	0.9	0.89	0.66	0.92	0.85	0.58
S2		0.94	0.58	0.59	0.85	0.94	0.95	0.53	0.79	0.66	0.52
S1	0.99	0.95	0.58	0.58	0.86	0.95	0.95	0.5	0.8	0.71	0.49

sampling points S3 and S14, i.e. the most downstream and headwater sampling points, respectively, together with the seasonal cycle in precipitation over the selected sampling points' sub-catchments. The spatial distribution of seasonal variations in $\delta^{18}O$ and $\delta^{2}H$ values weighted by precipitation amounts was determined using the Thiessen polygons over the sampling points' sub-catchment areas. The MSE for the regression models of the $\delta^{18}O$ cycle in precipitation over the selected sub-catchment areas was between 0.4‰ (sampling point S7) and 0.7‰ (sampling point S1). For the $\delta^{2}H$ cycle in precipitation, the regression model MSE was between 2‰ (station S1) and 3‰ (station S14). The MSE for the regression models of the $\delta^{18}O$ cycle in streamwater ranged between 0.1‰ (station S5) and 0.2‰ (station S13); for the $\delta^{2}H$ cycle in streamwater, the MSE was between 1‰ (station S5) and 3‰ (station S4). There was approximately a 1-month lag between the seasonal cycle in precipitation and streamflow.

The water MTTs of the karst springs and ponors are shown in Fig. 6.

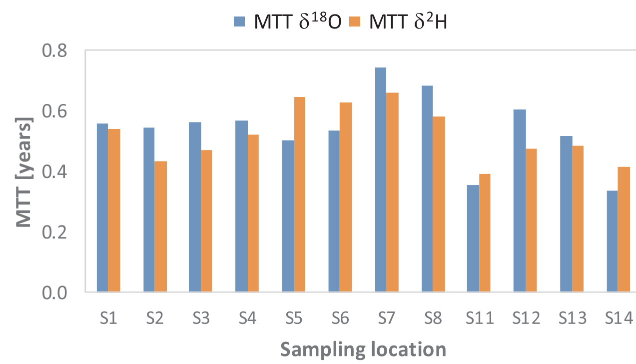

Fig. 6. MTTs of water at the karst springs and ponors.

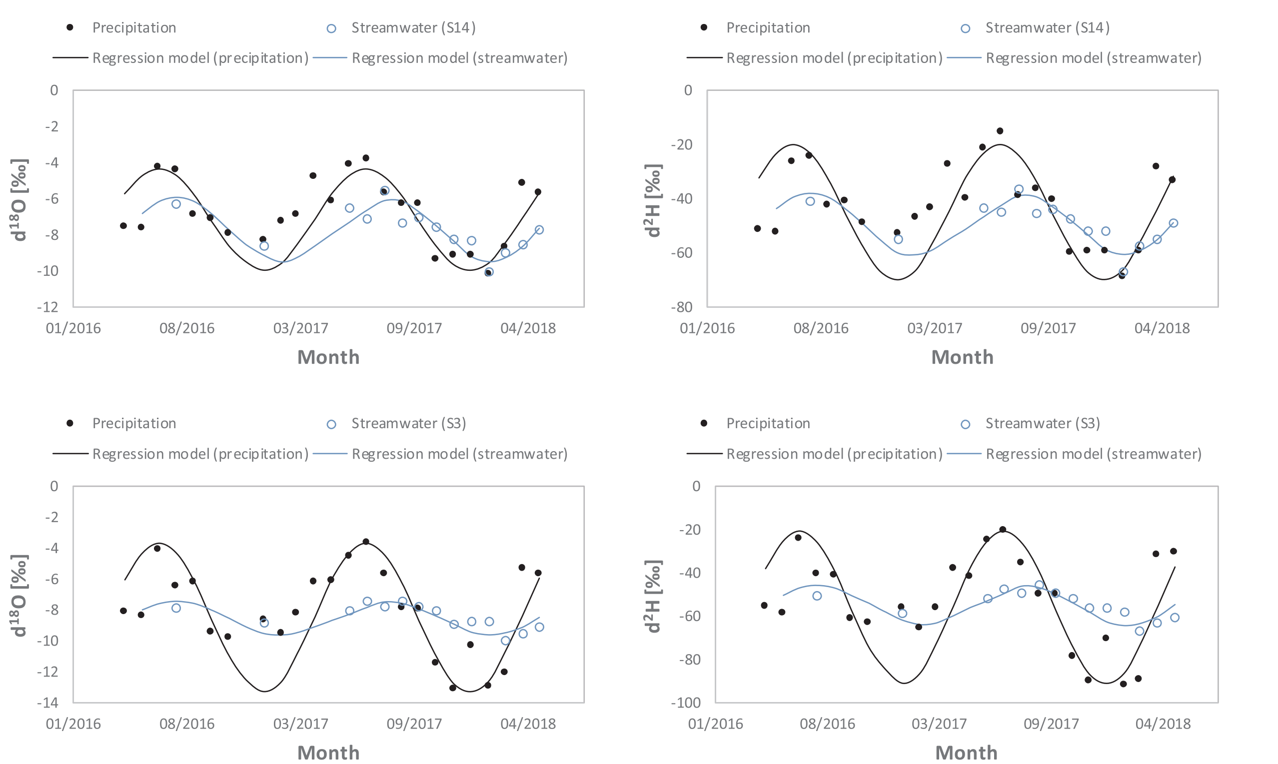

Fig. 5. Seasonal cycle in $\delta^{18}O$ and $\delta^{2}H$ values in precipitation over the sub-catchment areas and streamwater at sampling points S3 (bottom) and S14 (top).

The shortest MTTs were calculated for stations S14 (0.34 years using $\delta^{18}O$ and 0.41 years using $\delta^{2}H$) and S11 (0.36 years using $\delta^{18}O$ and 0.39 years using $\delta^{2}H$). Station S14 is the most headwater station located at the ponor into the Postojna Cave, whereas station S11 is located at the spring of the Rak stream. The water MTTs at other sampling locations are rather similar, ranging generally between 0.5 and 0.8 years. An increasing trend in the MTT of water could be noticed along the karst conduit system of the Pivka branch connecting the sampling points S14 → S6 (MTT of 0.54 years using $\delta^{18}O$ and 0.63 years using $\delta^{2}H$). Similar behavior could be observed for the Cerknica branch of the karst conduit system S13 (MTT of 0.51 years using $\delta^{18}O$ and 0.48 years using $\delta^{2}H$) → S7 (MTT of 0.74 years using $\delta^{18}O$ and 0.66 years using $\delta^{2}H$).

MTTs for the sampling points located at the Ljubljanica river karst tributaries are rather similar: S1 – Bistra stream (MTT of 0.56 years using $\delta^{18}O$ and 0.54 years using $\delta^{2}H$); S4 – Hotenjka stream (MTT of 0.57 years using $\delta^{18}O$ and 0.52 years using $\delta^{2}H$) and S5 – Logaščica stream (MTT of 0.50 years using $\delta^{18}O$ and 0.64 years using $\delta^{2}H$).

5. Discussion

5.1. $\delta^{18}O$ and $\delta^{2}H$ values of precipitation over the catchment and their relation to meteorological conditions

Precipitation is a major input component of water to the catchments. Understanding the formation and sources of precipitation in terms of its spatial and temporal variability is crucial for any catchment hydrology studies. The isotopic composition of precipitation is strongly controlled by the precipitation formation processes; therefore, the precipitation stable isotope composition can be very useful in explaining the precipitation sources. In view of weather conditions, the Ljubljanica river catchment is an area where intensive mixing of continental and Mediterranean air masses takes place. This makes precipitation source identification difficult. Recently, Krklec et al. (2018) showed a dense and highly scattered distribution of locations from where air masses passed over the study area and collect moisture; nearly half of the precipitation originated from continental sources (recycled moisture) and more than 40% originated from central and western Mediterranean. Consequently, the inter-month variability in precipitation isotope composition can be high and might even disrupt the identification of the seasonal cycle.

Other studies of precipitation isotope composition over the wider south-western part of Slovenia demonstrated the predominant influence of Atlantic air masses in the area, although the influence of Mediterranean air masses could not be excluded; their contribution to precipitation in Ljubljana was estimated to be in the range 15–26% (Vreča et al., 2008). Additionally, the seasonal variations in the d-excess values indicate the influence of Mediterranean air masses, which are characteristic in the autumn and winter months when the Mediterranean cyclogenesis prevails over the study area. Namely, higher d-excess values are characteristic for precipitation in the Mediterranean area, reaching up to 25‰, whereas d-excess values around 10‰ are typical for Atlantic air masses (Gat and Carmi, 1970; Merlivat and Jouzel, 1979; Lykoudis and Argiriou, 2007; Vreča et al., 2007; Gat et al., 2011). According to the results of precipitation isotopic composition analysis in this study, most monthly d-excess values, most evidently in autumn, are above 10‰ and might indicate the influence of Mediterranean air masses over the region. The lowest values were observed in late spring and summer months (May to July); this could indicate the evaporation process at high temperatures and low relative humidity conditions and possibly also partial evaporation from the rain gauges. Good correlation between $\delta^{18}O$ and $\delta^{2}H$ values of precipitation and the mean monthly air T shows that the temperature appears to be a major parameter controlling the behaviour of the precipitation isotopic composition in the region, similarly as discussed by Vreča et al. (2006).

Spatial coverage of the precipitation sampling stations enabled us to obtain relatively good insight into the spatial distribution of $\delta^{18}O$ and $\delta^{2}H$ values. They considerably decrease from station P6 (mean weighted $\delta^{18}O$ and $\delta^{2}H$ values −7.1‰ and −45‰, respectively) towards station P7 (-8.0‰ and −52‰) and P5 (−8.7‰ and −57‰) when wet air masses travel along the main SW–NE direction over the high terrain of the Javorniki ridge and the Snežnik plateau (Fig. 1). A further decrease in the precipitation $\delta^{18}O$ and $\delta^{2}H$ values towards the sampling point located in the northern part of the catchment is much smaller (e.g. mean $\delta^{18}O$ values −8.6‰ and mean $\delta^{2}H$ values −56‰ at station P1).

5.2. MTT in light of the catchment characteristics

Water transit time is widely recognised as one of the fundamental catchment descriptors that reveal information about storage, flow pathways, and source of water (Kirchner et al., 2000; McDonnell et al., 2010). However, most of the calculated MTTs are exposed to problems related to a priori selection of the travel time distribution and the problem of aggregation in spatially heterogeneous systems, as recently discussed by Kirchner (2016a,b). Very little guidance exists for catchment hydrologists on the use and interpretation of the transit time modelling approaches for complex catchment systems (McDonnell et al., 2010). In complex karst catchments, where spatial hydrogeological heterogeneity defines the temporal hydrological responses of the catchment to rainfall inputs and further, the actual extent of the karst catchment areas, the travel time estimation problem becomes even more pronounced. Additional uncertainty in MTT estimates could be related to the influence of isotopic fractionation due to evapotranspiration. Comparison of local meteoric water lines' slopes for all precipitation stations (Table 1) with those of the karst springs and sinks (Table 2) shows no measurable effect of evaporation on the isotopic composition of the analysed water. This is in line with the findings of Krklec et al. (2018) who analysed the contribution of local moisture to the precipitation in the Postojna area (station P7) and estimated that in the overall recycling of water, the contribution of evaporation is minor compared to that of leaf transpiration, which contributes water vapor to the atmosphere, with an oxygen isotope composition equal to that of soil water (Farquhar et al., 2007). Furthermore, Riechelmann et al. (2017) reported that evaporation in the soil, epikarst, and cave generated no significant imprint on drip water isotopic signature at a temperate European setting. Similarly, Domínguez-Villar et al. (2018) compared the isotopic composition of precipitation and drip water in the Postojna cave in 2009 and 2010 and found that the mean annual $\delta^{18}O$ values of drip water at 9 sampling sites in the cave resembled those of annual weighted mean $\delta^{18}O$ values of precipitation. Therefore, in the studied catchment, the potential effect of evapotranspiration on the isotopic composition of infiltrated water and, consequently, on the MTT estimates, is in our view relatively limited and was not considered in the MTT calculations.

Kirchner (2016a) proposed an alternative catchment storage metrics, the young water fraction (F_{yw}) in streamflow as the proportion of the transit-time distribution younger than the threshold age of streamflow (T_{yw}). He demonstrated that seasonal tracer cycles, as the ones used in our study, predict the F_{yw} in runoff from a heterogeneous mixture of sub-catchments much more reliably compared to the widely used estimates of MTT, which are exposed to aggregation bias that arises from strong nonlinearity in the relationship between the tracer cycle amplitude and MTT. Additionally, the TTD used to assess the MTT is usually selected arbitrarily (as in our case by selecting the exponential distribution) as the "real" TTD for a particular heterogeneous catchment is unknown. As an alternative approach, Kirchner (2016a) showed that the amplitude ratio A_S/A_P nearly equals F_{yw}, not only in individual catchments but also in the combined runoff from heterogeneous landscapes, which is characteristic for karst catchments.

The discharge weighted F_{yw} for the streamwater sampling stations varies between 0.2 and 0.3, the estimated T_{yw} for the exponential

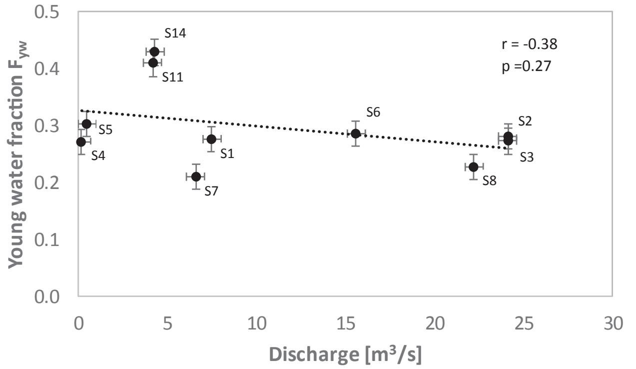

Fig. 7. Scatter plot of the F_{yw} vs. discharge for the selected sampling points. Error bars show ± 1 SE.

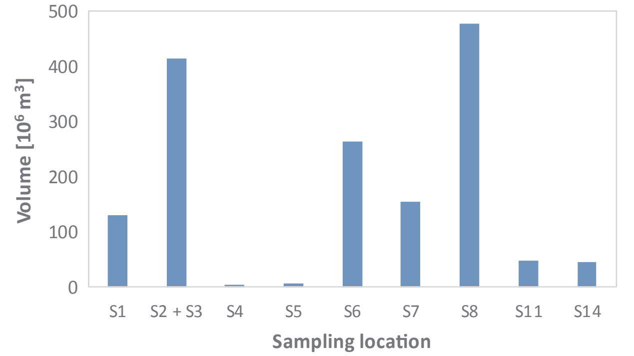

Fig. 8. The catchment storage estimates based on long-term mean daily discharge data and calculated MTTs.

distribution is 0.19 years. Only the results for the F_{yw} using δ^{18}O as a tracer are shown, since the T_{yw} values using the δ^{2}H as a tracer are very similar. Fig. 7 shows the scatter plot of F_{yw} vs. the mean long-term daily discharge at the selected sampling points. Decrease in the F_{yw} vs. the mean daily discharge can be observed; however, the relationship is not statistically significant with the selected significance level of 0.05. We might conclude that important proportions of the streamwater at the selected sampling points can be considered as young water. Small karst sub-catchment areas (e.g. headwater areas of sampling points S11 and S14) have higher F_{yw} reaching up to 0.4. This agrees with the intermittent nature of the streams in this part of the Ljubljanica karst catchment. Namely, the Pivka river (sampling point S14) discharge is controlled also by the surface and near-surface water currents from flysch areas. For the Rak stream (sampling point S11), the contribution of the Cerkniščica stream with its developed surface and subsurface drainage network in porous dolomite is substantial.

The F_{yw} for the whole catchment was 0.28, meaning that more than one-quarter of the total discharge was younger than approximately 2.3 months (assuming that the catchment transit times are described using the exponential distribution). Our F_{yw} results are within the range of young water fractions reported for rivers in mountainous regions in North America and central Europe by Jasechko et al. (2016). In view of the travel times, the young water could be related to the streamwater that follows well-developed karst conduits and the diffuse discharge through fissured and fractured vadose zone of the karst catchments. Rapid and considerably variable flow velocities through conduit systems reaching from a few m/h to several 100 m/h are indicative of karst aquifers (Ford and Williams, 2007; Kresic, 2007). In the studied catchment, the transport velocities observed by injecting artificial fluorescent tracers in periods of low discharges (Ravbar et al., 2012) were among the lowest reported for the karst aquifers, ranging between 5 and 22 m/h through well-developed karst conduits and 3–4 m/h through the vadose zone with the dominant influence of a diffuse recharge. However, there were considerable differences in the travel velocities and also travel directions during different hydrological conditions.

For the selected sampling points along the main karst conduits, the calculated MTTs are rather similar. The mean MTT is 0.54 years using δ^{18}O values and 0.52 years using δ^{2}H values and can be characterised as relatively short. Brkić et al. (2018) calculated MTTs ranging between 0.3 and 0.6 years for a well-developed karst aquifer system in western Croatia, which belongs to the same Dinaric area as the Ljubljanica river catchment. Such short MTT values could be expected for karst catchments without extensive deep groundwater storage as is the case with the large karst part of the Ljubljanica river catchment. The most headwater sampling points (S11 and S14) have shorter MTTs. The contribution of the Pivka River upstream of the sink to the Postojna Cave is small during low-flow conditions; the headwater part of the catchment along the Pivka branch of the karst conduit system could become (temporarily) disconnected from the downstream part of the catchment (e.g. sampling point S6), which is also indicated by the low correlation between sampling points S14 and S6 during low-flow conditions (Table 4). Similarly, the hydrological disconnection can be indicated through the low correlation between the headwater sampling point S11 and other sampling points (e.g. sampling points S6 and S7) for both δ^{18}O and δ^{2}H values. Namely, the streamwater at sampling point S11 is mainly fed from the intermittent Cerknica Lake area during middle- to high-flow conditions. Large proportions of the observed water flux that appears to have very short MTTs poses a potential risk to the water quality of the karst springs in the case of surface contamination.

By considering the long-term average daily discharge at the selected sampling points where discharge was measured and the MTT was calculated, theoretically, the total water storage in the karst aquifers can be estimated, as shown in Fig. 8. The storage of the two upstream branches (sampling point S14 – Pivka branch and sampling point S11 – Cerknica branch) is approx. $50 \times 10^{6}\,m^{3}$ whereas the total storage downstream to the confluence of the main three hydrological parts (sampling point S8) is $470 \times 10^{6}\,m^{3}$. The total storage from the studied part of the karst catchment is approx. $550 \times 10^{6}\,m^{3}$ (sampling points S1, S2, S3). However, as the karst massif is also drained by several small springs, the total volume of water is somewhat larger than the volume calculated in this study.

The rather small differences in the MTTs over the catchment area might suggest intensive mixing and homogenisation of the water along the prevailing underground flowpaths. The mixing and homogenisation processes might be indicated also by generally statistically insignificant differences in pH and EC values between the sampled karst springs and sinks positioned along the prevailing karst conduits. On the other hand, the contribution of local recharge during low-flow conditions is indicated by the high scatter in stable isotope values during low-flow conditions (Fig. 4). The study of solute transport processes in the studied catchment by Kogovšek and Petrič (2014) indicates an important role of the epikarst layer as the most important storage layer in the study area. However, the role of the karst vadose zone storage is significantly influenced by the preceding hydrological conditions. The local recharge could be amplified by intensive precipitation infiltration through the epikarst zone in the central part of the catchment where the surface stream network is scarce. During prolonged dry periods, some relatively large parts of the catchment could become hydrologically isolated, which is indicated by the scatter during the low flows in Fig. 4.

In general, longer input and output data records produce more reliable estimates of the transit time distribution (McGuire and McDonnell, 2006). In our case, the calculated MTTs and storage volumes are based on two years of precipitation and one year of karst springs/sinks monitoring, which raises the question of the MTT estimates' reliability. As discussed by Hassan (2003), the key to the successful validation process is the use of a diverse set of tests that should be designed to evaluate a diverse set of aspects related to the modelled processes. The differences in the calculated MTT values between neighbouring karst springs (S6, S7, and S14) generally agree well with the results of artificial tracers' applications presented by Ravbar et al. (2012). The longest delay in the artificial tracer detection was observed at station S7 which has, according to our results, the longest MTT. As artificial tracers are generally injected into preferential flow paths, the flow properties of the conduit system related to short transit times and high flow velocities can be investigated. However, these tracers omit the fissured-porous matrix of the aquifer, which plays an important role with respect to water storage in karst (Lauber and Goldscheider, 2014).

In view of the MTT calculation reliability, significant variations in the δ^{18}O and δ^{2}H values observed in precipitation samples over W Slovenia can lead to considerable deviations from the sinusoidal seasonal pattern, as reported by Krklec et al. (2018). Since the δ^{18}O and δ^{2}H variability in precipitation is much higher than that in karst springs/sinks samples, we performed a sensitivity analysis where we analysed the influence of a changed precipitation seasonal amplitude on the calculated MTTs. E.g., a ± 25% change in seasonal precipitation amplitude caused a change of ± 0.10 to ± 0.20 years (± 0.16 years on average) in the MTTs based on the δ^{18}O values and a change of ± 0.12 to ± 0.17 years (± 0.14 years on average) in the MTTs calculated from the δ^{2}H values. Undoubtedly, longer data series should be used to obtain more reliable results in view of contrasting hydrological conditions (longer wet and dry periods), which strongly influence the movement of water in the karst catchment.

6. Conclusion

Karst systems differ from other hydrological systems in terms of both their hydrogeological evolution and their hydrological behaviour. They can be characterised by their high hydrological heterogeneities related to highly variable porosities, which can significantly change over small spatial scales. Difficulties in collecting sufficient information about karst system properties in view of spatial heterogeneity and limited information on the discharge changes, especially during contrasting hydrological conditions, make the parametrisation and application of different hydrological analytical approaches highly uncertain. Therefore, specific exploration techniques such as the use of artificial or natural tracers are needed to improve our understanding of the complex karst systems.

In this study we used spatially well distributed data on the rainfall δ^{18}O and δ^{2}H inputs and streamflow outputs to study the hydrological behaviour of the Ljubljanica river karst catchment. Despite the changing influence of Atlantic and Mediterranean wet air masses over the studied catchment on the precipitation isotope composition, the monthly precipitation isotope composition was relatively homogenous in the northern part of the catchment. A transitional area over the high terrain of the Javorniki ridge and the Snežnik plateau in the central and south-eastern part of the catchment could be noticed where the δ^{18}O and δ^{2}H values in precipitation considerably decreased. The calculated MTTs for the sampling points located along the main conduits and some major tributaries show relatively high hydrological homogenisation of the catchment in terms of the water travel times. The catchment's homogenisation strongly depends on the preceding hydrological conditions; differences in the isotope composition can be noticed during low-flow conditions, which might indicate the dominance of the local recharge of the karst springs. Additionally, the fraction of the streamflow younger than the threshold age of 2.3 months is relatively high whereas the estimated MTTs are relatively short. The observed hydrological behaviour supports the previous studies where the dominance of the diffuse recharge through the vadose zone and the importance of the precipitation recharge by infiltration through the epikarst were assumed. The obtained information offers a valuable integrated assessment of the differences in the runoff processes in the catchment and is extremely important for the planning of karst water resource strategies. The short MTT indicates a high exposure of the water sources in the area to potential contamination. This could become even more problematic in the case of soil or epikarst removal (e.g. by quarrying) as this would further reduce the important storage element of the studied karst system.

CRediT authorship contribution statement

Simon Rusjan: Funding acquisition, Conceptualization, Writing - original draft, Writing - review & editing, Visualization. **Klaudija Sapač:** Project administration, Visualization. **Metka Petrič:** Funding acquisition, Conceptualization, Writing - original draft. **Sonja Lojen:** Funding acquisition, Conceptualization, Methodology, Validation, Writing - original draft. **Nejc Bezak:** Project administration.

Declaration of Competing Interest

None.

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