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Hydrogeochemical and Isotopic Characterisation of the Učja Aquifer, NW Slovenia

Hidrogeokemična in izotopska karakterizacija vodonosnika Učje, SZ Slovenija

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Abstract

The groundwater characteristics of the Učja aquifer were investigated using geochemical and isotopic data. The water discharge and physico-chemical properties of the groundwater and the Učja River reflect the climate that is characteristic of the area. The mixed snow/rainfall regime is characteristic for the Učja Valley, with the highest discharges appearing during the spring snowmelt and autumn precipitation, and the lowest discharges in the winter and especially summer months. The temperature of the groundwater and the Učja River is lower in winter and higher in summer. The specific electrical conductivity values indicate a very permeable carbonate aquifer. Higher conductivity values were observed in spring and autumn at all sampling sites, which is related to snowy and rainy periods. The groundwater from the Učja aquifer indicates a uniform type of water (Ca-Mg-HCO_3), with Ca^{2+}, Mg^{2+} and HCO_3^- the most abundant ions. Differences in Ca^{2+} and Mg^{2+} concentrations and in the Mg^{2+}/Ca^{2+} molar ratio between sampling sites were observed. Those springs with lower Mg^{2+} and lower Mg^{2+}/Ca^{2+} molar ratios indicate limestone recharge areas, and those springs with higher Mg^{2+} and molar ratios indicate interaction with the dolomite hinterland. The pH values confirm alkaline waters characteristic of carbonate aquifers. The hydrogen (δ^2H) and oxygen (δ^{18}O) isotope values suggest the main source of water is from precipitation from a complex mixing of maritime and continental air masses. An altitude isotopic effect is observed with minor δ^{18}O and δ^2H depletion at higher altitude sampling sites compared to those springs at lower altitudes. The altitude isotopic effect is most prominent in spring. The $\delta^{13}C_{DIC}$ values indicate the dissolution of carbonates and the degradation of organic matter.

Izvleček

Značilnosti podzemne vode vodonosnika doline Učje so bile raziskane z uporabo geokemijskih in izotopskih podatkov. Pretoki in fizikalno-kemijski parametri reke Učje in podzemne vode na izvirih odražajo podnebne značilnosti območja. Za dolino Učje je značilen mešani snežno-dežni režim z največjimi pretoki v času spomladanskega taljenja snega in jesenskih padavin ter najnižjimi pretoki pozimi in predvsem poleti. Temperatura podzemne vode in reke Učje je pozimi nižja in poleti višja. Rezultati specifične elektroprevodnosti kažejo na zelo prepusten karbonatni vodonosnik. Na vseh vzorčnih mestih so bile izmerjene višje vrednosti spomladi in jeseni, kar povezujem s snežnimi in deževnimi obdobji. Podzemna voda vodonosnika doline Učje je enotnega tipa (Ca-Mg-HCO_3) z najvišjimi koncentracijami Ca^{2+}, Mg^{2+} in HCO_3^- ionov. Med vzorčnimi mesti so bile ugotovljene razlike v koncentracijah Ca^{2+} in Mg^{2+} ter molskim razmerjem Mg^{2+}/Ca^{2+}. Izviri z nižjimi vrednostmi Mg^{2+} in nižjim molskim razmerjem izkazujejo apnenčevo napajalno območje, izviri z višjimi vrednostmi Mg^{2+} in višjim molskim razmerjem pa interakcijo z dolomitom. Vrednosti pH potrjujejo alkalnost voda, značilnih za karbonatne vodonosnike. Vrednosti izotopov vodika (δ^2H) in kisika (δ^{18}O) kažejo, da so glavni vir vode v vodonosniku padavine, ki nastanejo ob kompleksnem mešanju morskih in celinskih zračnih mas. Višinski izotopski efekt je opazen v nižjih vrednostih δ^{18}O in δ^2H na vzorčnih mestih višjih nadmorskih višin v primerjavi z izviri na nižjih nadmorskih višinah. Višinski izotopski učinek je najizrazitejši spomladi. Vrednosti $\delta^{13}C_{DIC}$ odražajo raztapljanje karbonatov in razgradnjo organske snovi.

Introduction

Geochemical studies of surface and groundwater play an important part in understanding the mechanisms determining water chemistry (Gibbs, 1970). Karst and fractured aquifers pose a specific challenge due to their heterogeneity and the special geochemical processes at work in aquifers (Ford & Williams, 2007; Moral et al., 2008; Newman, 2005; White, 1988). Understanding the water flow in aquifers and the connections between the atmosphere and deeper aquifers is essential (Allshorn et al., 2007; Keim at al., 2012; Maurice et al., 2021). The characteristics of spring water are the result of the mixing of groundwaters, interaction with the host rocks in the aquifer, and fresh surface water from precipitation with specific climate-related characteristics (Khadka & Rijal, 2020; White, 2010). Karst springs often respond very quickly and intensively to rainy events, while their response to snowmelt varies in space and time (Weber et al., 2016) and also depends on other climatic factors. Both sources of water contribute considerably to aquifer recharge and are useful in understanding the impact of the composition of precipitation on groundwater (spring water).

Hydrogeochemical and isotopic data provide us with information about groundwater sources and residence times, aquifer properties, water-rock interaction along the flow path, and the mixing of different types of water (Cartwright et al., 2012). The temporal and spatial variability of major ions in karstic waters is important in an understanding of chemical and physical processes influenced by geological conditions, climate, and anthropogenic activities (Gibbs, 1970; Meybeck, 1987). The isotopic compositions of hydrogen and oxygen of water and carbon in the dissolved inorganic carbon, in combination with meteorological, hydrological, hydrogeological, and physicochemical data all help us to characterise and trace waters through the hydrological cycle (Dansgaard, 1964; Kendall & Doctor, 2003; Kanduč et al., 2012; Torkar et al., 2016; Calligaris et al., 2018; Shamsi et al., 2019; Serianz et al., 2021 and others). Stable isotopes of hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) are used to determine the source of the water and residence time, the flow of water through the water body, or to quantify exchanges of water, solutes, and particulates between hydrological compartments to indicate the potential water inputs to the system and characterize the influence of different processes during infiltration, and to determine the mixing of waters of different origins within the system (Aggarwal at al., 2005; Clark & Fritz, 1997; Glynn & Plummer, 2005; Rodgers et al., 2005). Carbon isotopes help us to assess the origin of dissolved inorganic carbon (DIC), the main component in waters draining carbonate systems. The isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) is used to understand the biogeochemical reactions controlling alkalinity and to trace the origin of the bicarbonate ion, which is the dominant anion in the shallow groundwater (Bullen & Kendall, 1998).

Almost half of the Slovenian territory is characterized by karst (Gams, 1974, 2004; Gostinčar & Stepišnik, 2023). These systems are often vast reservoirs of high quality water and thus important sources of drinking water (Ravbar & Kovačič, 2006). Studies of karst aquifers are complex but pose important research challenges within the frame of determining and protecting potential sources of drinking water.

In the past, various hydrogeological research has been carried out in the area of the Kanin (Komac, 2001; Turk et al., 2014; Zini et al., 2014; Russo, 2015) and Kobariški stol aquifers (Brenčič et al., 2001), while the Učja Valley has not yet been studied in detail. The Učja aquifer represents a cross-border karstic aquifer, which may contain large amounts of quality groundwater (Brenčič et al., 2001; Rejc, 2014), and could in the future represent an important source of drinking water or a commercial source as well, as it could be used as a significant water resource for cross-boundary supply. As a result, a comprehensive survey of the potential of the Učja aquifer was carried out.

Various geological studies have been made of the wider investigated area in the past, which provide basic data for detailed lithological and structural maps of the territory. The first geological studies were made already in the 1970s and 1980s to produce basic geological maps (Kuščer, 1974; Buser, 1986, 1987). Later, due to the very complex tectonic structure of the area, numerous regional and local studies of the Učja Valley and its surroundings were elaborated (Čar & Pišljar, 1991, 1993; Vrabec, 2012). The lithology of the Mt. Kobariški Stol area, which represents the southern slopes of the Učja Valley, was described by Šmuc (2012) and is currently investigated in greater detail (Rožič et al., 2022; Vantur, 2023). From the hydrogeological point of view, the springs of the wider area were listed and described (Brenčič et al., 2001; Janež, 2002), whereas within the framework of national monitoring only hydrological measurements of surface water on the Učja River are carried out. A basic hydrogeological analysis of the Učja was also described (Rejc, 2014).

The aim of this paper is to characterise the groundwater of the Učja aquifer. Physico-chemical parameters (T, EC, pH), hydrogeochemical composition (cations and anions) and isotopic tracers (δ^2H, δ^{18}O, $\delta^{13}C_{DIC}$, ^{3}H) were used to characterize the (1) water–rock interaction in the aquifer, (2) the origin of the groundwater using isotopic tracers, and (3) the origin of carbon in the dissolved inorganic carbon to evaluate the biogeochemical processes at work in the groundwater. The presented results, in combination with other segments of the aquifer (geological conditions, climate land use characteristics, geochemical modeling etc.), will provide a useful basis for the further planning of the use and protection of the Učja water resource. The importance of the results extends beyond Slovenia's borders, in terms of cross-border sharing of knowledge, coordination, and the potential cross-border planning and management of common water resources.

Study area

Sampling location

The Učja Valley is located in NW Slovenia between the towns of Bovec and Kobarid. The valley extends in the W-E direction, and is bounded on the south and north by mountain ridges: the Kobariški stol ridge (with the highest peak Stol or Veliki Muzec, 1673 m) in the south and the ridge with the Skutnik peak (1721 m), which is part of the Kanin ridge in the north. The western border is defined by the state border with the Republic of Italy, and to the east by the Soča River valley near the village of Žaga (Fig. 1). The W-E orientation of the Učja Valley is unique from a tectonic point of view, as it almost perpendicularly cuts the entire fault zone of the Idrija fault (Fig. 2), one of the most prominent fault zones in western Slovenia (Čar & Pišljar, 1991; Vrabec, 2012).

The area has a typical mountain morphology with steep slopes in the north and south, with the gorge of Učja River between them (Fig. 1). The northern and southern slopes descend towards the valley at an average gradient of 25–45°, with vertical slopes of some mountains, ridges, and gorges. The northern slopes in some parts above the river rise vertically up to 300 m, but then decrease slightly (on average 40°). Due to the prominent ruggedness and especially steep slopes of the terrain, some parts are completely impassable and work in such areas is very difficult. Towards the west of the researched area, where the Učja River flows into the Soča River, the slope of the

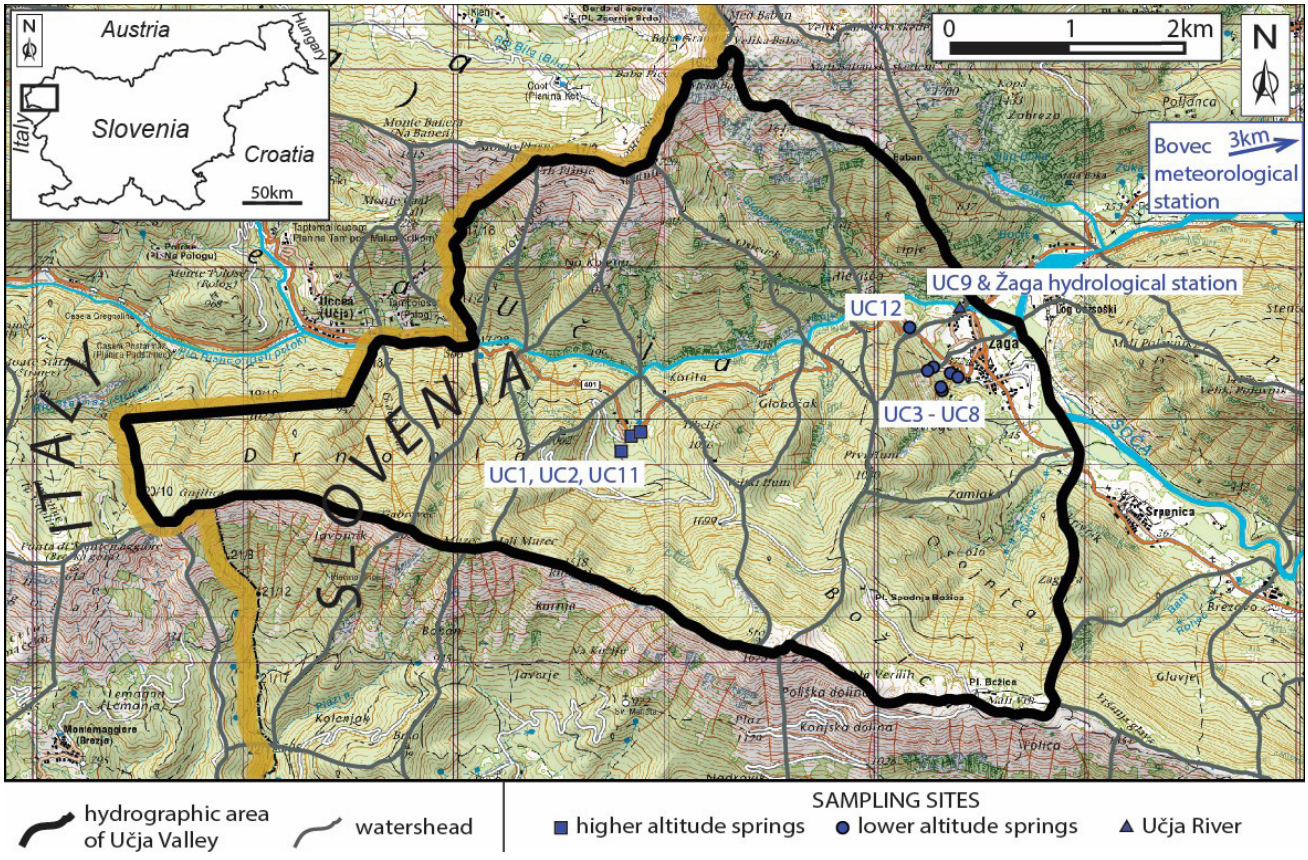

Fig. 1. Geographic location of the Učja Valley with marked sampled springs in the study area (source map Geopedia; 13.36402° W, 13.52413° E, 46.33777° N, 46.26382° S). The hydrographic area of the Slovenian part of the Učja Valley is presented (ARSO, 2019b).

terrain decreases considerably (15–20°) and finally levels out on the alluvial plain of the Soča River. The Učja river originates under the western slopes of the Kanin ridge in Italy and flows into Slovenia through a narrow gorge. After 18 km, the Učja River flows into the Soča River as the right and second largest tributary near the village of Žaga. The Učja gorge is registered in the Nature Conservation Atlas (ZRSVN, 2023) as Natural Value (ID 775).

The Hydrogeological characteristics of the Učja Valley are directly dependent on the geological characteristics of the wider area (Fig. 2). Most of the main springs are located at the foot of the mountain slopes near the transition to the alluvial plain of the Soča Valley and appear along the Idrija fault (Fig. 1 and 2). A few springs were defined along the Učja riverbed (Čar & Pišljar, 1991), and individual springs higher up on the slopes, most likely linked to lithological changes or strong tectonic structures. Part of the groundwater (springs) is captured for drinking water in the public water supply network, while some springs are used for private drinking water supply. These springs also have water permits. Water protection zones are not defined for any of the springs (ARSO, 2019a).

Water for geochemical and isotopic analyses was sampled at 13 locations in the Učja Valley (Fig. 1 and 2). The spring water (groundwater) was sampled at twelve sampling sites (UC1-UC8, UC10-UC13) as well as one additional water sample from the Učja River (surface water, UC9). In this work, the results of 11 sampling sites are presented (Table 1), while two sites (UC10, UC13) are not considered in the evaluation due to a lack of data. Seven sampling sites were positioned at the foot of the mountain slopes (UC3-UC8, UC12; on figures marked with circles), near the transition to the alluvial plain of the Soča Valley. These springs are located west of the Idrija fault zone and one of them (UC12) in the fault zone. These sampling sites are located at altitudes of 389–480 m asl. Three sampling sites (UC1, UC2, UC11; on figures marked with squares) are located on the slopes of the Kobariški stol ridge near the former border crossing station with the Republic of Italy. These sampling sites are located at altitudes of 758–700 m asl. Sampling site UC9 (Učja stream water; on figures marked with a triangle) was located approximately 50 m upstream of the road bridge at the Žaga hydrological station.

Table 1. Details of sampling locations in the Učja Valley (*not considered in this research), sampling periods of in-situ field measurements (physico-chemical parameters) and periods of laboratory analyses (geochemical and isotopic analyses – $\delta^{18}O$, $\delta^{2}H$, total alkalinity, $\delta^{13}C_{DIC}$ ^{3}H).

Label	LAT [°]	LONG [°]	Altitude [m]	Water type	Sampling period (in-situ field measurements)	Sampling period (laboratory measurements)		
						Geochemical analyses	$\delta^{18}O$, $\delta^{2}H$, total alkalinity, $\delta^{13}C_{DIC}$	Tritium (^{3}H)
UC1	46,29615	13,43663	758	Spring	December 2017, January 2018, March 2018, April 2018, 2x June 2018, July 2018, August 2018, October 2018, November 2018, December 2018, March 2019	December 2017, April 2018	December 2017, April 2018, July 2018, October 2018	December 2017
UC2	46,29750	13,43778	707	Spring	December 2017, January 2018, March 2018, April 2018, 2x June 2018, November 2018, December 2018, March 2019	Same as UC1	December 2017, April 2018	Same as UC1
UC3	46,30250	13,47594	437	Spring	Same as UC1	Same as UC1	Same as UC1	Same as UC1
UC4	46,30222	13,47611	449	Spring	Same as UC1	Same as UC1	Same as UC1	Same as UC1
UC5	46,30398	13,47432	480	Spring	Same as UC1	Same as UC1	Same as UC1	Same as UC1
UC6	46,30431	13,47498	451	Spring	Same as UC1	Same as UC1	Same as UC1	Same as UC1
UC7	46,30347	13,47806	389	Spring	Same as UC1	Same as UC1	Same as UC1	Same as UC1
UC8	46,30377	13,47710	411	Spring	Same as UC1	Same as UC1	Same as UC1	Same as UC1
UC9	46,30972	13,47805	342	River	Same as UC1	Same as UC1	Same as UC1	Same as UC1
UC10*	46,30996	13,47887	367	Spring	December 2017, January 2018, March 2018, April 2018, June 2018	–	–	–
UC11	46,29795	13,43901	700	Spring	January 2018, March 2018, April 2018, 2x June 2018, November 2018, December 2018, March 2019	April 2018	December 2017, April 2018	–
UC12	46,30787	13,47196	447	Spring	December 2017, January 2018, March 2018, April 2018, 2x June 2018, October 2018, November 2018, December 2018, March 2019	April 2018	April 2018, October 2018	–
UC13*	46,29218	13,44839	985	Spring	June 2018	–	–	–

Geological setting

The area of the Učja Valley structurally belongs to the Southern Alps and is characterized by Miocene south-directed thrusting (Fig. 2). The major part of the Učja Valley consists of a succession of the Tolmin Nappe, i.e. the lowest of the Southalpine nappes, whereas the highest peaks of the Kanin ridge (northern slopes of Učja Valley) are composed of the structurally higher Krn (Julian) Nappe. Thrust units are further displaced by neotectonic strike-slip faults (Placer, 1999, 2008). The most prominent is the NW-SE oriented Idrija fault zone that generally runs east of the Učja Valley, i.e. along the Soča Valley between the town of Tolmin and the village of Žaga, through the Kanin ridge and enters the Rezija (Resia) Valley near Mt. Skutnik. A few minor faults parallel to the Idrija fault zone run across the Učja Valley. On the southern slopes of the Učja Valley important E-W trending vertical faults divide two slightly diverse stratigraphic successions (Buser, 1987).

The entire area is dominated by a thick succession of Upper Triassic carbonates (Fig. 2). In the Kobariški stol ridge the succession starts with the Norian Hauptdolomit (Main Dolomite) formation passing upward into the Norian-Rhaetian Dachstein Limestone formation, which is covered further by Lower Jurassic platform limestone (Buser, 1986, 1987). Above the stratigraphic gap, the Middle Jurassic limestone breccia and thin-bedded hemipelagic limestone follows and is in turn replaced by Upper Jurassic ammonitico rosso-type limestone of the Prehodavci formation, and finally the end Jurassic-earliest Cretaceous pelagic Biancone Limestone formation. These three units are condensed, only reaching several tens-of-meters in thickness (Šmuc, 2012; Rožič et al., 2022; Vantur, 2023). Above, an end-Cretaceous Upper flyschoid formation is deposited, composed of alternating shale/marl and graded sandstone. At the base of the formation, laterally discontinuous limestone breccia beds are deposited. Similar beds occur also as interbeds within flysch-type deposits (Vantur, 2023).

North of the E-W trending fault, i.e. in the central part of the Učja Valley, only the Norian-Rhaetian is developed as the Hauptdolomit formation. With the erosional contact, it is overlain with Upper Cretaceous deep-marine Volče Limestone formation (resedimented and pelagic limestone) and upwards by an Upper flyschoid formation highly similar to the one described above. The Krn Nappe, which is thrust over the soft bed of the Upper flyschoid formation, is composed almost exclusively of the Norian-Rhaetian Dachstein Limestone formation with only local occurrences of dolomite (Buser, 1986, 1987).

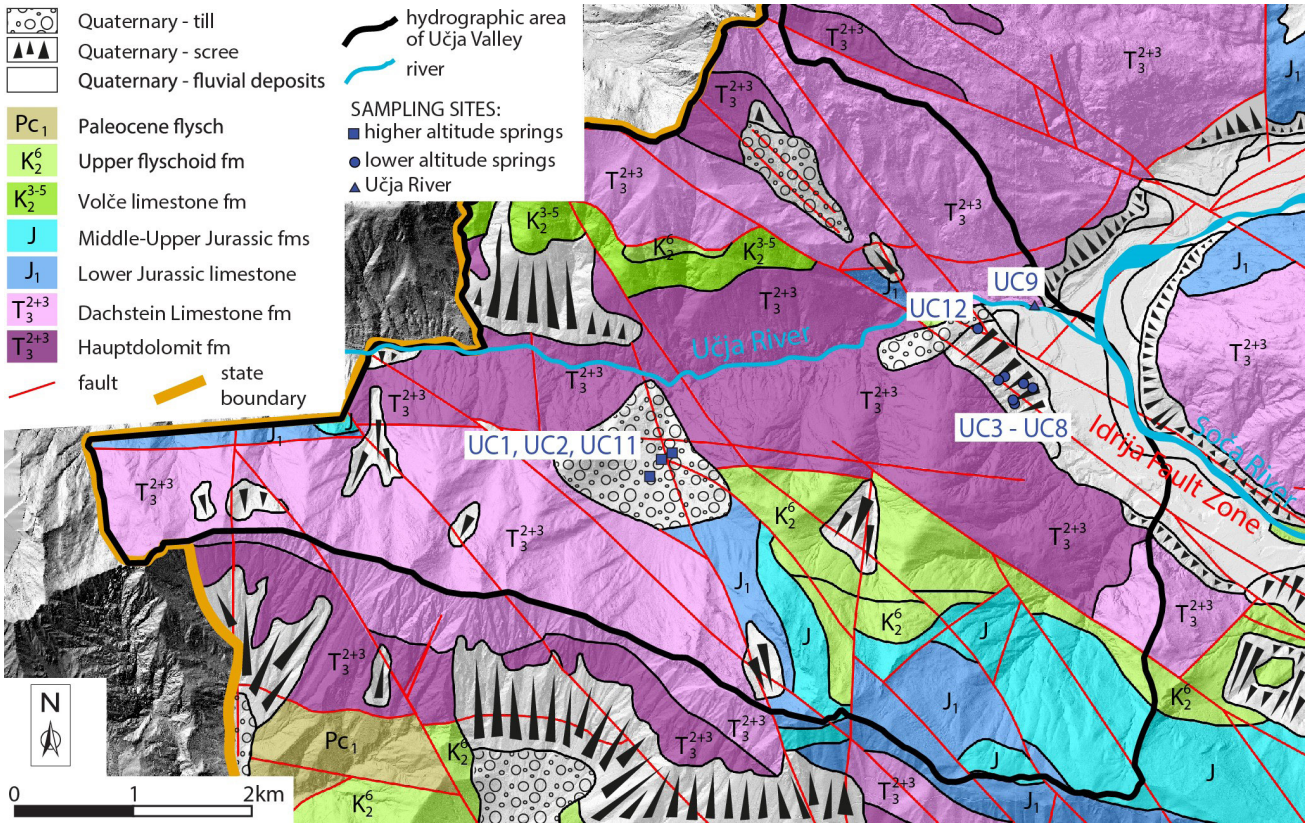

Fig. 2. Geological map of the Učja Valley with sampled springs marked (modified after Buser, 1987; source map in background from ARSO, 2019a; 13.36482° W, 13.50750° E, 46.33294° N, 46.27038° S). The hydrographic area of the Slovenian part of the Učja Valley is presented (ARSO, 2019b).

Materials and methods

In-situ measurements and water sampling were carried out from December 2017 to March 2019. Information about sampling and laboratory analyses for individual sampling sites is presented in Table 1. The missing measurements in the table are the result of the absence of spring water (springs were dry) at the time of sampling.

The measurements of *physico-chemical parameters* (temperature, pH, specific electrical conductivity) were measured on a monthly basis or at least every two months (Table 1) using a WTW Multi 3430 Multiparameter probe (WTW GmbH, Weilheim, Germany). Additionally, the *discharge* of springs was observed and, where possible, measured in the field using a bucket (Fig. 5). The Učja River discharge and the precipitation of the area is measured in the frame of the Slovenian national monitoring system. Data from the gauging hydrological station Žaga – Učja (46.30978° N, 13.47774° E, 342 m a.s.l.) was used to analyse the discharge of the Učja River (ARSO, 2019c). Discharge measurements at the gauging station are monitored every 10 minutes. Data from the Bovec meteorological gauging station (46.33171° N, 13.55382° E, 441 m a.s.l.) was used to analyse the precipitation fluctuations in the area (ARSO, 2023). The amount of precipitation at the gauging station is measured every half hour.

Two rounds of hydrogeochemical analysis and four rounds of isotopic analysis were performed on a seasonal basis (Table 1). Water samples for *hydrogeochemical analysis* were collected in 50 mL in high-density polyethylene HDPE bottles. For cations, the water was further filtered through a 0.45 μm nylon filter and pre-treated with HNO_3^- on site. Analyses were performed in the ActLabs accredited laboratory (Activation Laboratories Ltd., Ancaster, ON, Canada). Cations (major, minor, and trace) were analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), with some of the major cations (e.g. Ca^{2+}, Mg^{2+}) also analysed using Overrange Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) due to some excessively high concentrations for ICP-MS, and major anions (Br^-, Cl^-, F^-, NO_2^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}) were determined using Ion Chromatography (IC). Internal laboratory reference materials and independent quality control with duplicates (one for each measurement campaign) were measured. Detection limits for each element or compound for individual methods are reported on the ActLabs homepage (ActLabs, 2023).

Water samples for *oxygen ($\delta^{18}O$) and hydrogen isotope (δ^2H) analysis* (Table 1) were collected in 50 mL HDPE bottles. The isotopic composition of oxygen and hydrogen was determined at the Jožef Stefan Institute using the H_2 – H_2O (Coplen et al., 1991) and CO_2 – H_2O (Avak & Brand, 1995; Epstein & Mayeda, 1953) equilibration technique on a dual inlet isotope ratio mass spectrometer (Finnigan MAT DELTA plus) with a CO_2 – H_2O and H_2 – H_2O HDOeq 48 automatic equilibrator and a water bath at 18°C (Kanduč et al., 2018a, 2018b, 2018c, 2018d). CO_2 (Messer 4.7) and H_2 (IAEA) gasses were used as working standards for water equilibration. Two laboratory reference materials (LRM), such as W-3896 and W-3871, calibrated to the international VSMOW-SLAP scale, were used to normalize the data. LRM W-45 and commercial reference materials USGS 45, USGS 46, and USGS 47 were used for the independent quality control of measurements as also described in Žvab Rožič et al. (2021). The average repeatability of the samples was 0.02 ‰ for $\delta^{18}O$ and 0.3 ‰ for δ^2H, with results expressed as a δ-value per mil (‰).

For the analysis of *total alkalinity (TA) and isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$)* (Table 1), water was filtered through a 0.45 μm pore-sized membrane filter. Samples were stored in 30 mL HDPE bottles for TA and 12 in mL Labco glass vials with septum, without headspace, for $\delta^{13}C_{DIC}$ analyses. Before TA analyses in the laboratory, pH was measured using a pH meter (Mettler Toledo AG 8603, Schwerzenbach, Switzerland). Total alkalinity (TA) was measured within 24 hr after sampling using the Gran titration method (Gieskes, 1974; Kanduč, 2006) to determine the results with an accuracy of ±1%. Approximately 8 g of the water sample was weighed into a plastic container and placed on a magnetic stirrer. A calibrated pH electrode (7.00 and 4.00 ± 0.02) was placed in the sample and the initial pH was recorded. Titration was performed using a CAT titrator (Ingenierbüro CAT, M. Zipperer GmbH Ballrechten-Dottingen, Germany). Reagencon HCl 0.05 N (0.05 M) was used for the titration (Kanduč et al., 2018a, 2018b, 2018c, 2018d). The method is described in detail by Zuliani et al. (2020).

The isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined according to the Spötl procedure (Spötl, 2005; Kanduč, 2006). Ampoules of saturated phosphoric acid (100-20 μL) were flushed with pure helium, 6 ml of the water sample was added, and headspace CO_2 was measured. The $\delta^{13}C_{DIC}$ values were determined using a continuous flow Europa Scientific 20-20 isotope mass spectrometer with the ANCA - TG preparation module (Sercon Limited, Crewe, UK). A standard solution of Na_2CO_3 (Carlo Erba reagents,

Val de Ruil, France) and a Scientific Fischer sample with known $\delta^{13}C_{DIC}$ values of -10.8 ‰ ± 0.2 ‰ and -4.8 ‰ ± 0.1 ‰ were used to calibrate the measurements. Messer reference gas with known $\delta^{13}C_{CO2}$ -35.5 ‰ ± 0.2 ‰ was also used. The reference material (Carlo Erba solution) was used to convert the analytical results to the Vienna Pee Dee Belemnite (VPDB) scale. The average sample repeatability was 0.2 ‰. Two replicates of each sample were measured. Results are expressed as a δ-value per mil (‰) (Kanduč et al., 2018a, 2018b, 2018c, 2018d).

For *tritium* (^{3}H) the water was sampled once in 1 L HDPE bottles. The tritium (^{3}H) was measured in Hydrosys Labor Ltd. in Budapest using a liquid scintillation counting (LSC) TriCarb 3170 TR/SL (PerkinElmer, Waltham, MA, USA). Before analysis, the sample was treated and prepared using electrolytic enrichment. Analysis error was ±0.3 TU, with a detection limit of 3 TU.

Results and discussion

Climate conditions and discharge regime

The wider Učja Valley is located in a transition area between Alpine and Sub-mediterranean climate zones. Winters are long and snowy, with December and January the coldest months (Fig. 3).

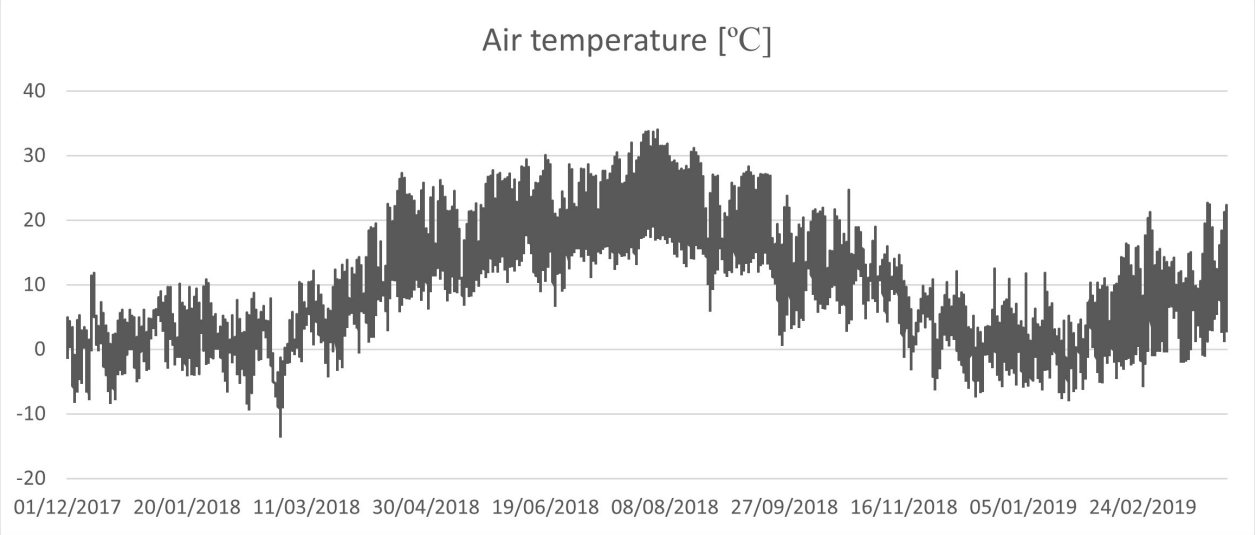

Fig. 3. Air temperature measured at the Bovec meteorological gauging station (ARSO, 2023).

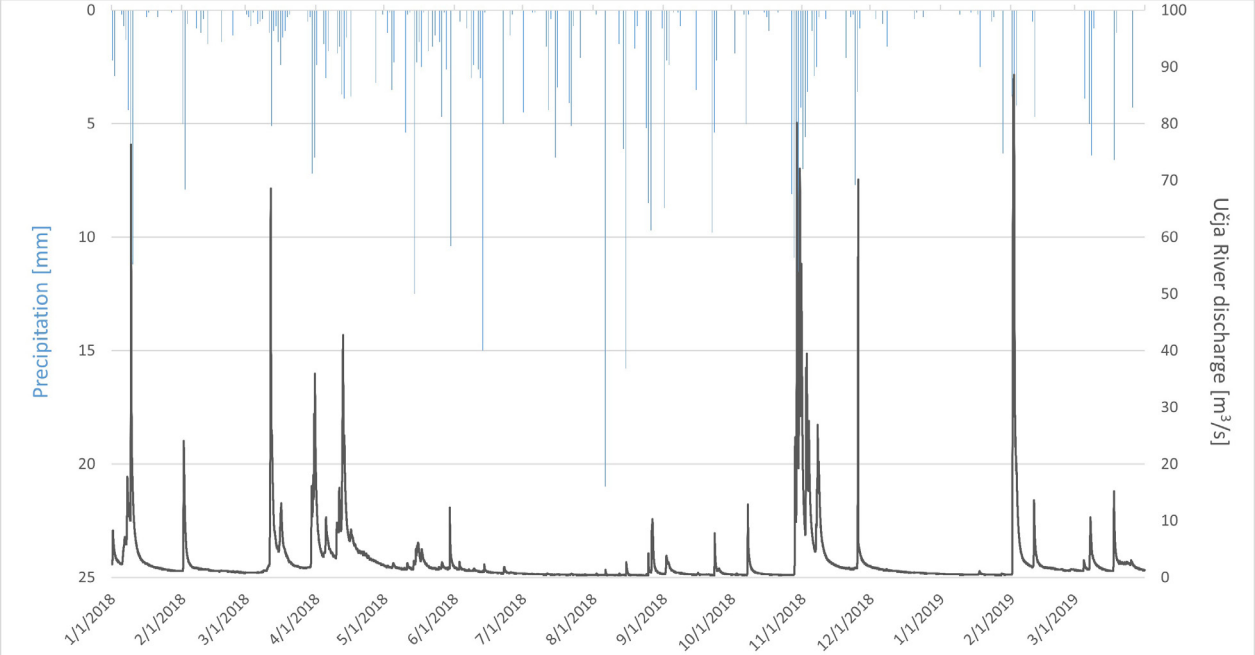

Fig. 4. Precipitation (blue) measured at the Bovec meteorological gauging station (ARSO, 2023) and discharge (dark grey) of the Učja River at the Žaga – Učja hydrological gauging station (ARSO, 2019c) for 2018.

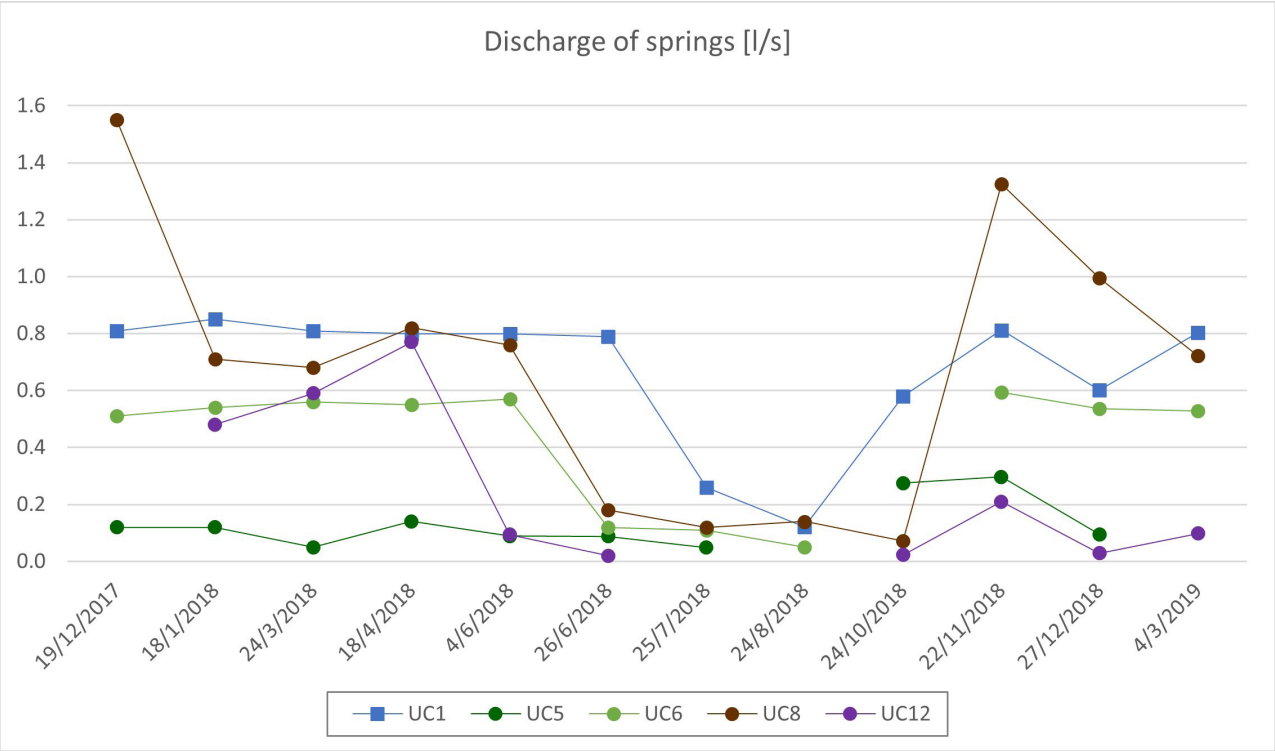

Fig. 5. Discharge of springs where taking of measurements was possible. Missing measurements are the result of the absence of spring water (springs were dry) at the time of sampling.

Summers are moderately warm (around 20 °C) with rare air temperatures above 30 °C (Fig. 3). Higher amounts of precipitation fall in autumn and spring, and lower amounts in winter and summer (local showers) (Fig. 4). Precipitation in the region (measured at Bovec meteorological gauging station; ARSO, 2023) and at the Učja River discharge (measured at the Žaga – Učja hydrological gauging station; ARSO, 2019c) is plotted in Fig. 4. The most pronounced increase of Učja River discharge in spring (March-April) and autumn (November) is in accordance with the mixed snow/rainfall regime. Lower discharges are recorded in winter and especially during summer, and the highest discharges during the spring snowmelt and with autumn precipitation. A quick and intense response in the discharge of the river is also observed twice in winter. During the summer, the response of river discharge to precipitation is not so intense, which may be the result of short and local summer showers (the Bovec gauging station is located some 10s of km northwest in the Soča Valley) and more intense evapotranspiration. Similar trends are also seen in the measured springs, with two periods of higher water discharge in the spring and autumn, and low or even no discharge in the summer (Fig. 5).

Physico-Chemical Parameters of Učja aquifer

Measured physico-chemical parameters are presented in Figures 6 and 7. The entire range of results are presented in common database in Pangaea repository (Žvab Rožič et al., 2024). The groundwater temperature of the springs and water from Učja River (Fig. 6) generally follow the fluctuations in air temperature (Fig. 3), and therefore reflect the significant seasonal temperature conditions of the area. The highest water temperatures were measured in summer (max 18.7 °C at UC6 in July 2018) and the lowest in winter (min 3.6 °C at UC9 in December 2017 and 2018). More noticeable changes are recorded at the springs where the watershead area of the springs is smaller and significantly lower discharges were observed in the summer months. The quick response of groundwater temperature to fluctuations in air temperature is also the result of water heating in the shallow or surface pipelines and reservoirs from which the water was sampled. The springs at higher altitudes (UC1, UC2, UC11; Fig. 1, Table 1) show less markable temperature fluctuations. This may be the result of higher elevations and the shadier locations of spring areas in the valley and probably deeper local recharge areas. The temperature trend of these springs is also less than entirely clear, because the temperature was not measured at some sampling sites (UC2, UC11) due to a lack of water in the summer months.

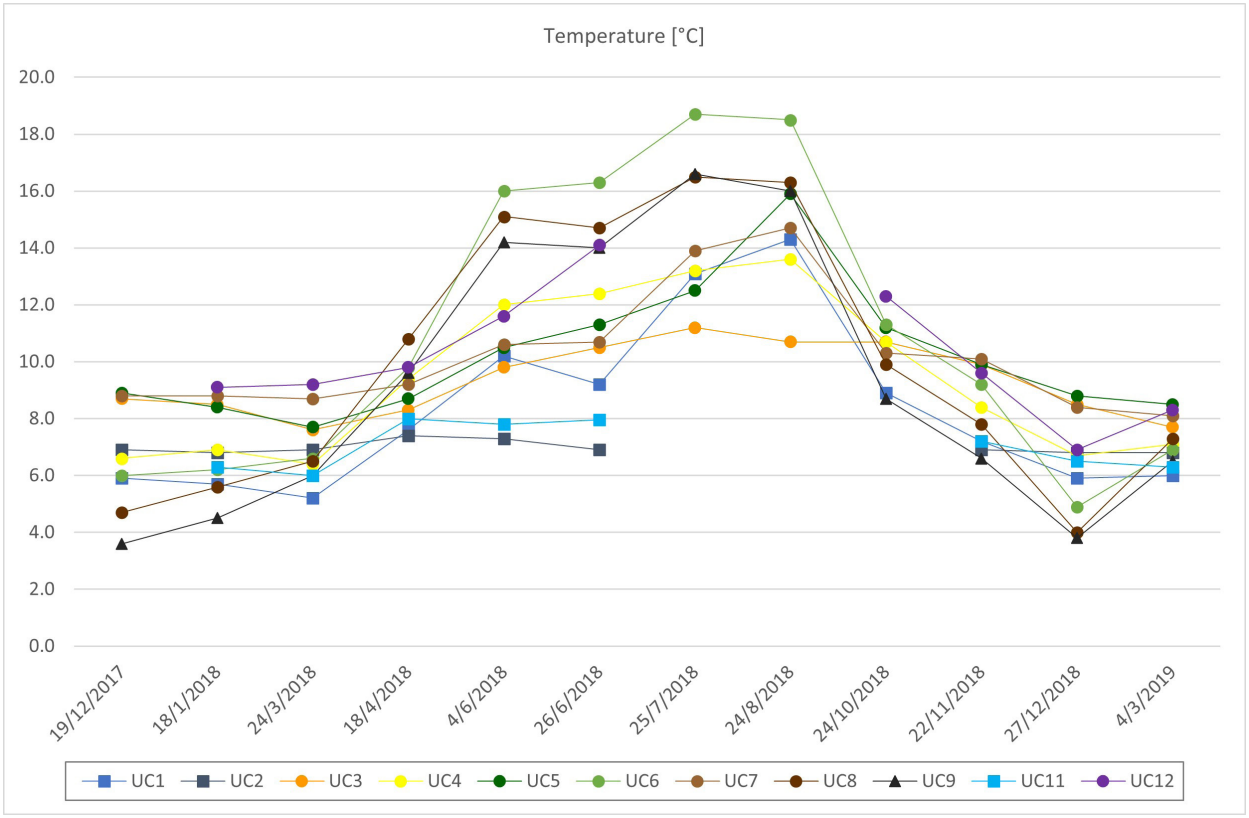

Fig. 6. Measured water temperatures (°C) at sampling sites in the Učja Valley.

The specific electrical conductivity (EC) of sampling water ranges from 186 to 438 µS/cm (average 266 µS/cm) (Fig. 7). The EC values indicate a highly permeable carbonate aquifer with a low resistence time as also described in Torkar & Brenčič (2015). The highest EC was observed at sampling site UC12 (max 438 µS/cm) and the lowest at sampling site UC2 (min 186 µS/cm). Lower EC values were generally measured in spring waters at higher altitudes (UC1, UC2, UC11 – marked with squares; Fig.1, Table 1) and in the water from the Učja River (UC9 – marked with

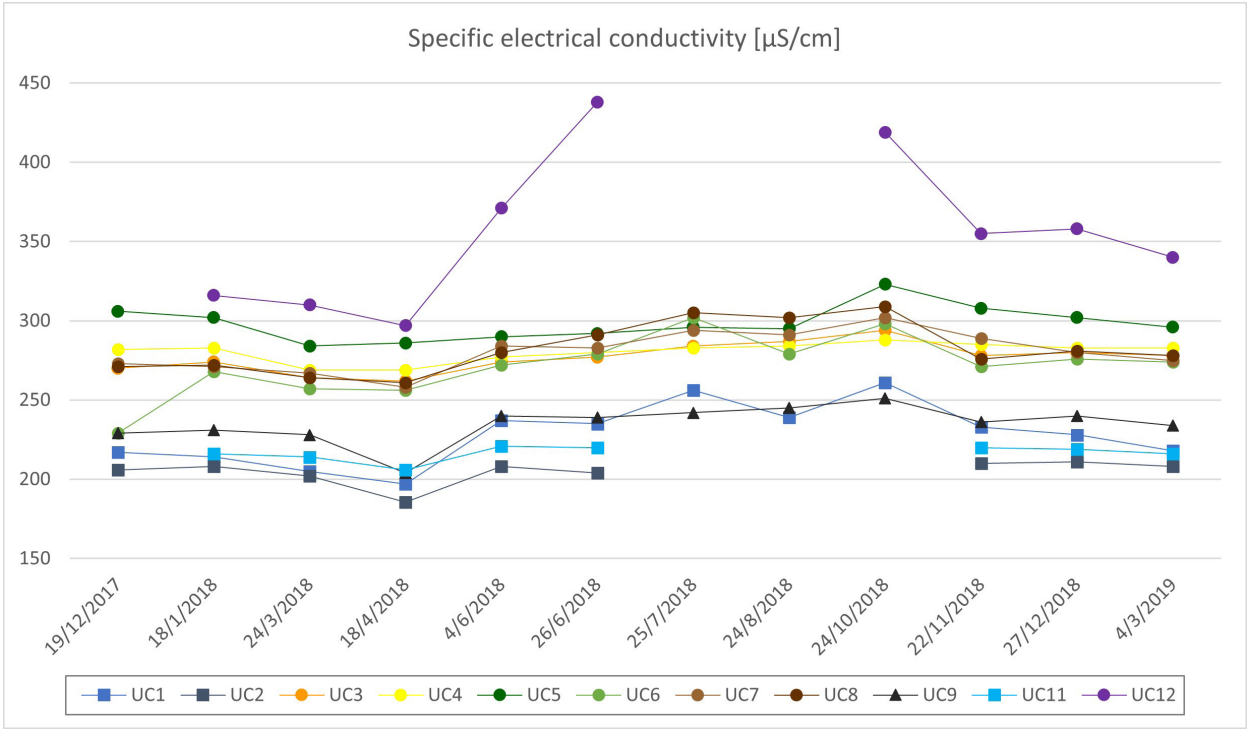

Fig. 7. Field measurements of specific electrical conductivity (µS/cm) at sampling sites in the Učja Valley.

a triangle). The EC inversely related to elevation was also described for fractured dolomite aquifers in central Slovenia (Verbovšek & Kanduč, 2016). Slight fluctuations in EC values at all sampling sites is observed throughout the year. Rather lower EC values were recorded in April-March and November-December, and related to snowmelt in spring and rainy periods in autumn (Fig. 4), and most likely also to lower evapotranspiration. A more prominent EC fluctuation is noticeable at the UC12 sampling site, with the lowest values in the spring and a marked decrease in November, which is associated with rainy periods (Fig. 4), and the highest in the summer before the spring dries up. The spring is also located within the tectonic zone of the Idirja fault (Čar & Pišljar, 1991, 1993; Vrabec, 2012), where inflow and mixing with deeper waters with higher EC could occur. However, more precise explanations and processes in the aquifer remain to be developed and investigated.

The pH of sampled water varied from 7.60 to 8.96, with an average value of 8.12, and reflects the common characteristics of a carbonate aquifer, with no differences between sampling sites. The pH values are comparable with groundwater samples from fractured dolomite aquifers in central Slovenia (Verbovšek & Kanduč, 2016).

Hydrogeochemistry of the Učja aquifer

The geochemical results for the Učja Valley aquifer are part of a common database in Pangaea repository (Žvab Rožič et al., 2024). The major composition of groundwater from the Učja aquifer does not change between the two sampling campaigns (December 2017 and April 2018) and is dominated by HCO_3^-, Ca^{2+}, and Mg^{2+} ions (Fig. 8), which is characteristic for carbonate types of waters. All samples belong to the Ca-Mg-HCO_3 facies with low K^+, Na^+, Cl^-, NO_3^- and SO_4^{2+} content (Jäckli, 1970). Comparable results are also described for karstic

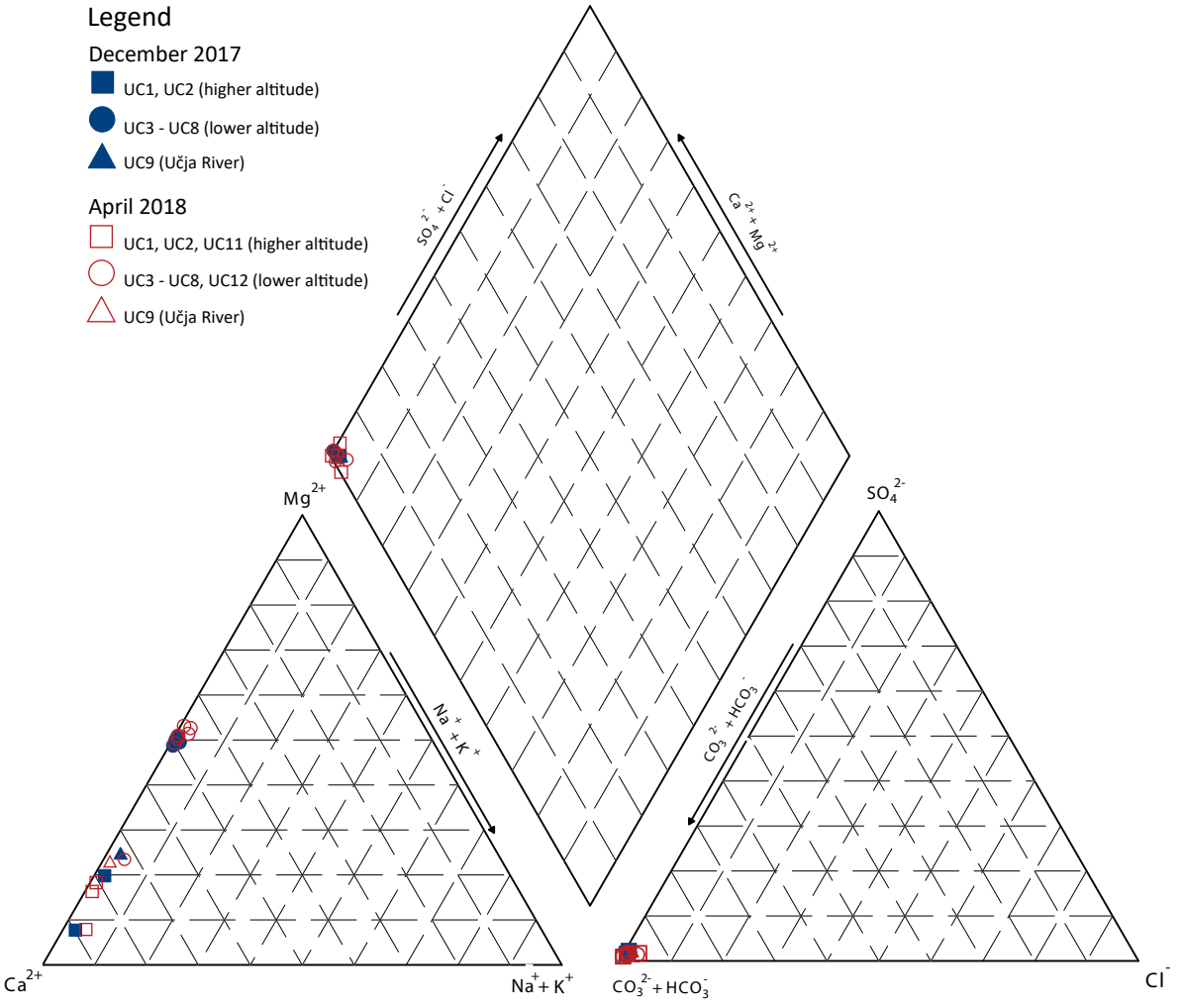

Fig. 8. Piper plot diagram of the Učja Valley water samples.

and fractured aquifers in Central Slovenia (Verbovšek & Kanduč, 2016) and for the Triglavska Bistrica River in Northern Slovenia (Serianz et al., 2021). Total alkalinity ranged from 1.95 mM (UC1) to 3.40 mM (UC5), and concentrations of Ca^{2+} and Mg^{2+} from 27.0 mg/L (UC6) to 47.9 mg/L (UC12) and from 1.96 mg/L (UC1) to 20.9 mg/L (UC5), respectively. The Mg^{2+}/Ca^{2+} molar ratio, which indicates the relative contribution of dolomite and calcite to the intensity of carbonate weathering in the groundwater, differs significantly between sampling sites: group I (UC1, UC2 and UC11) exhibits ratios ranging from 0.08 to 0.25 and group II (UC3-UC8) ratios ranging from 1.00 to 1.15. Sampling sites UC9 (Učja River) and UC12 show a Mg^{2+}/Ca^{2+} molar ratio of 0.32. The same grouping is also visible on the Piper plot diagram (Fig. 8). The Mg^{2+}/Ca^{2+} molar ratios are slightly higher than those found in descriptions of fractured dolomite aquifers in central Slovenia (Verbovšek & Kanduč, 2016). The results can be explained by the geological conditions of the area (Fig. 2). The springs from group II indicate that dolomite (the main rock in the catchment area) weathering is the source of the major solutes within the aquifer, while for group I the Ca^{2+} contribution from limestone layers (limestone breccia or thick platform limestone succession, as both are located south of the E-W trending fault) prevail (Fig. 2).

Isotopic characteristics of the Učja aquifer

The isotopic results for the Učja Valley aquifer are presented entirely in database in Pangaea repository (Žvab Rožič et al., 2024). The $\delta^{18}O$ and $\delta^{2}H$ values for the groundwater from the Učja Valley vary from −8.7 ‰ to −7.4 ‰ (average −8.0 ‰) and from −54.9 ‰ to −45.1 ‰ (average −49.5 ‰), respectively. The surface water of the Učja River has $\delta^{18}O$ values from −8.7 ‰ to −8.1 ‰ (average −8.4 ‰) and $\delta^{2}H$ values from −55.3 ‰ to −50.4 ‰ (average −52.6 ‰). $\delta^{18}O$ and $\delta^{2}H$ values vary seasonally at all sampling sites (Fig. 9). In general, the lowest values were measured during the spring sampling campaign (average -8.2 ‰ for $\delta^{18}O$ and -51.8 ‰ for $\delta^{2}H$) and the highest during the winter sampling campaign (average -7.8 ‰ for $\delta^{18}O$ and -48.0 ‰ for $\delta^{2}H$). Differences in the $\delta^{18}O$ values are noticeable between sampling sites (Fig. 9). Higher $\delta^{18}O$ values were recorded in springs UC1 and UC2 (from 0.6 to 0.7 ‰) and the Učja River (0.6 ‰), while in the remaining springs (UC3-UC8, UC12) the amplitudes are lower (from 0.3 to 0.5 ‰). This may indicate rather longer residence times for the springs at lower altitudes (UC3-UC8, UC12) due to the dolomite rocks in the watershed (Torkar et al., 2016).

The results of $\delta^{18}O$ and $\delta^{2}H$ measurements of Učja groundwater and the Učja River are presented in Figure 10. For comparison, the results of selected previous studies from Northern and Central Slovenia (Kanduč et al., 2012; Zega et al., 2015; Verbovšek & Kanduč, 2016; Torkar et al., 2016; Serianz et al., 2021) are presented together with selected water lines: global meteoric water line (GMWL; $\delta^{2}H = 8 \times \delta^{18}O + 1$ ‰; Craig, 1961), local meteoric water line for Kredarica ($LMWL_K$; $\delta^{2}H = 8.42\ (\pm 0.19) \times \delta^{18}O + 18.98\ (\pm 2.09)$; SLONIP, 2023), local meteoric water line for Zgornja Radovna ($LMWL_{ZR}$; $\delta^{2}H = 7.98\ (\pm 0.13) \times \delta^{18}O + 11.13\ (\pm 1.21)$; SLONIP, 2023), and local meteoric water line for Portorož ($LMWL_P$; $\delta^{2}H = 8.09\ (\pm 0.2) \times \delta^{18}O + 9.99\ (\pm 1.34)$; SLONIP, 2023). For Local meteoric lines the precipitated weighted reduced major axis regression (PWRMA LMWL) was used (Vreča et al., 2022; SLONIP, 2023). The isotopic composition of the groundwater from the Učja aquifer and the Učja River is similar to the isotopic composition of the Žveplenica sulfur karst spring (Zega et al., 2015), which is influenced by similar climate conditions. If we compare the results with the springs from Northern Slovenia (Kanduč et al., 2012), from karst and fractured aquifers in Central Slovenia (Verbovšek & Kanduč, 2016), Radovna Valley (Torkar et al., 2016), and Triglavska Bistrica (Serianz et al., 2021) (Fig. 10) the groundwater from the Učja Valley is enriched with heavier isotopes (i.e. ^{2}H and ^{18}O). This is attributed to the proximity of the Mediterranean climate, and the continental isotopic effect is reflected in precipitation (Kern et al., 2020; Vreča & Malenšek, 2016). The results from the Učja Valley show that all water samples are above the GMWL, $LMWL_{ZR}$ and $LMWL_P$, plotted between local meteoric water lines for Zgornja Radovna $LMWL_{ZR}$ and especially for Kredarica $LMWL_K$. As already described in some previous studies (Vreča et al., 2006; Torkat et al., 2016), the results from the Učja Valley suggest a complex mixing of maritime and continental air masses.

The $\delta^{18}O$ and $\delta^{2}H$ values in the groundwater of the Učja Valley reveal isotopic depletion (altitude isotopic effect) in the sampling locations (UC1, UC2, UC11) at higher altitudes (app. 720 m asl) compared to the locations (UC3-UC8, UC12) at lower altitudes (app. 440 m asl). In view of the difference between the UC1 (758 m asl) and UC7 (389 m asl) sampling sites, the average altitude effect for the Učja Valley is 0.11 ‰ per 100 m for $\delta^{18}O$ (the same as for the Radovna Valley; Torkar et al., 2016) and 0.45 ‰ per 100 m for $\delta^{2}H$. The altitude isotopic effect varies between seasons.

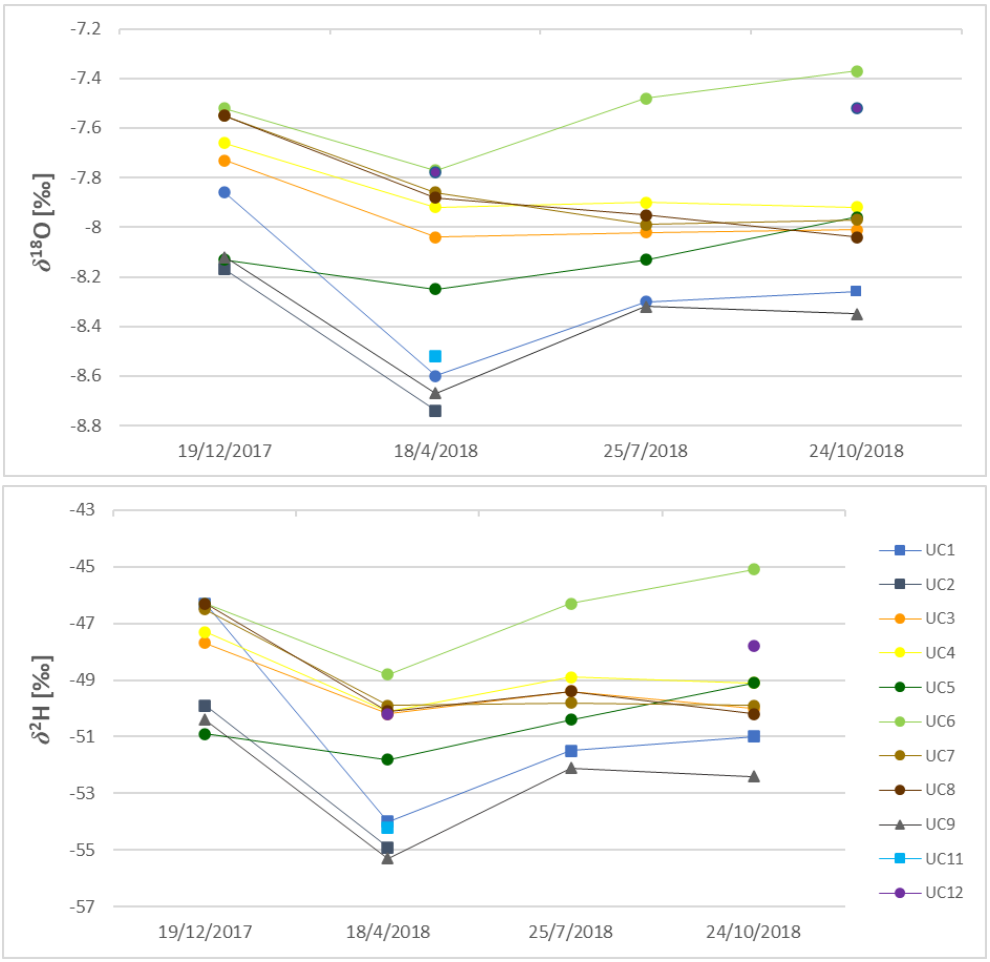

Fig. 9. Time series of isotopic compositions of $\delta^{18}O$ and $\delta^{2}H$ in groundwater of the Učja aquifer and the Učja River.

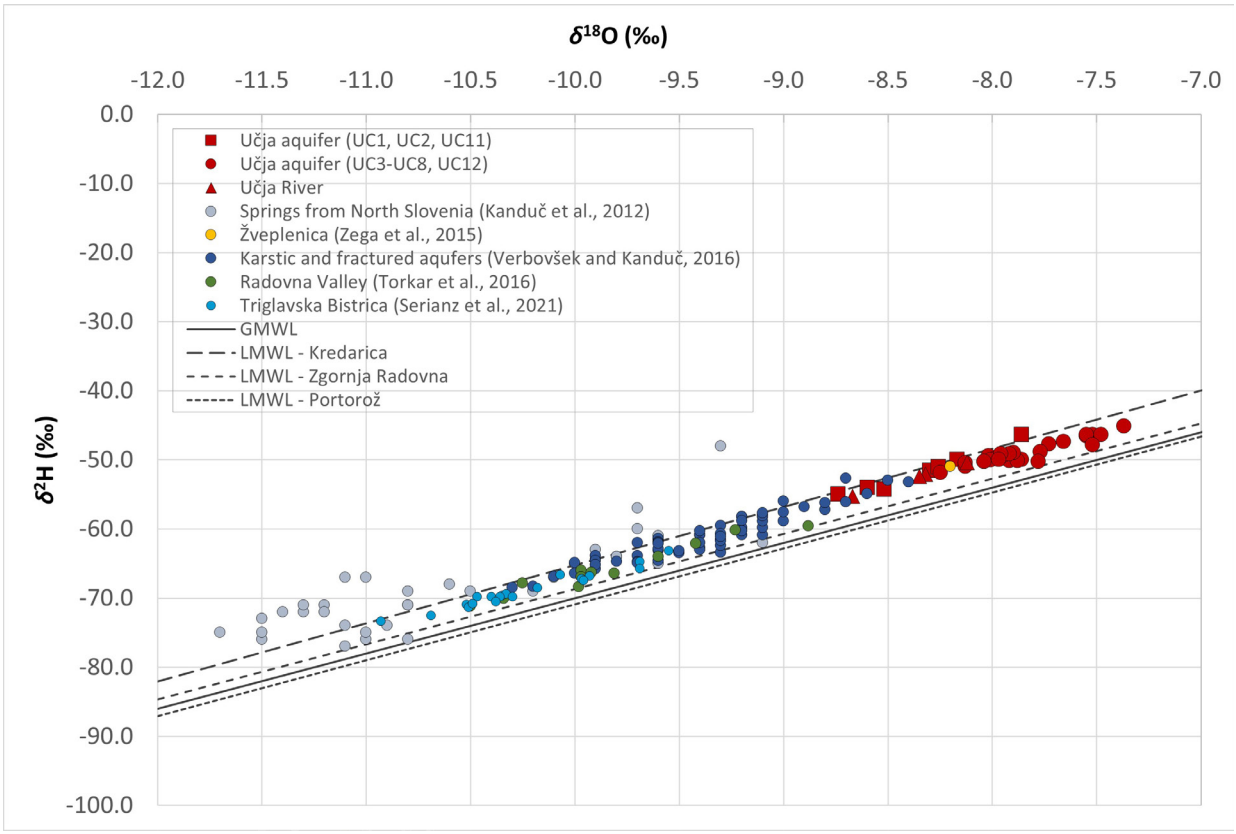

Fig. 10. Plot of $\delta^{18}O$ versus $\delta^{2}H$ values for groundwater of the Učja aquifer (groundwater) and the Učja River, the results from selected previous studies from Northern and Central Slovenia (Kanduč et al., 2012; Zega et al., 2015; Verbovšek & Kanduč, 2016; Torkar et al., 2016; Serianz et al., 2021), together with the global meteoric water line (GMWL) and the local meteoric water lines from Kredarica ($LMWL_K$), Zgornja Radovna ($LMWL_{ZR}$) and Portorož ($LMWL_P$) (Vreča et al., 2022; SLONIP, 2023).

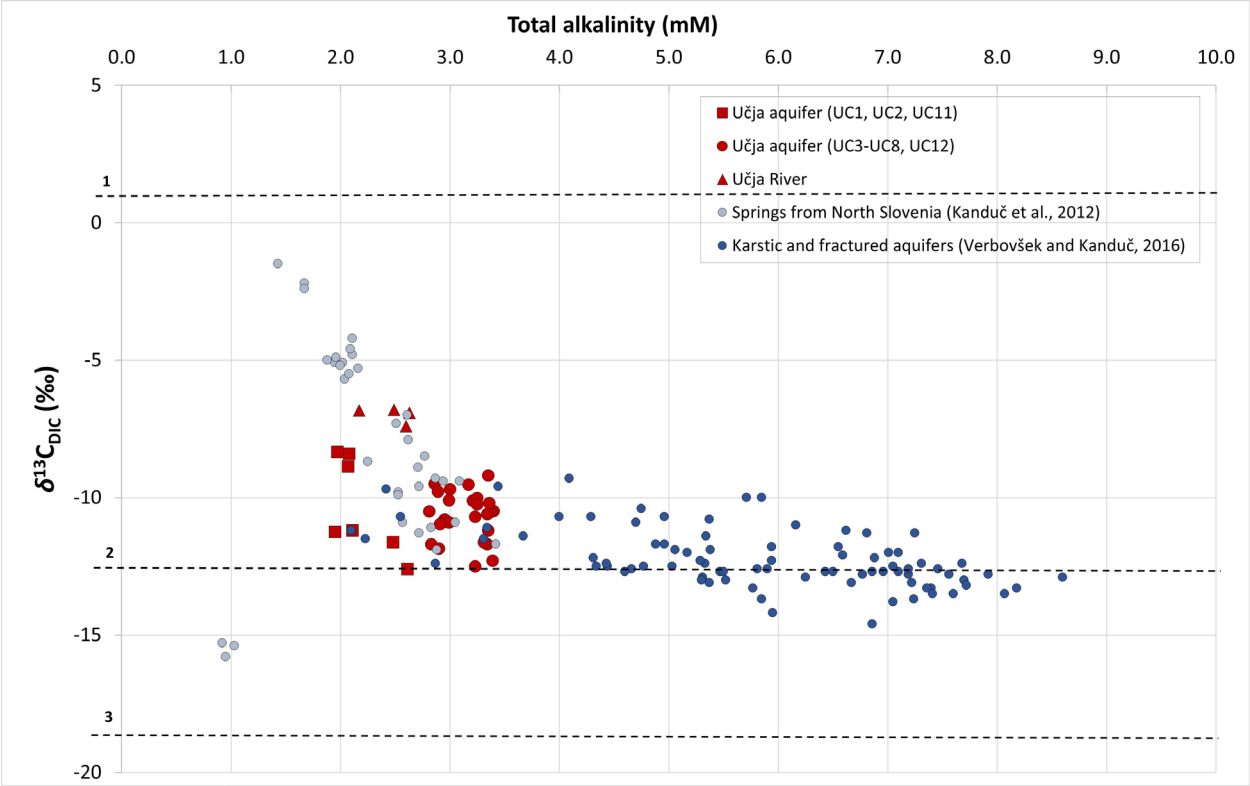

Fig. 11. Total alkalinity versus isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) of groundwater from the Učja aquifer and the Učja River, together with groundwater from northern Slovenia (Kanduč et al., 2012) and karstic and fractured aquifers from Central Slovenia (Verbovšek & Kanduč, 2016). See the explanation of dotted lines 1, 2, and 3 in Verbovšek & Kanduč (2016).

The least prominent altitude effect was found in winter (0.08 ‰ per 100 m for $\delta^{18}O$ and 0.05 ‰ per 100 m for $\delta^{2}H$), and the highest in spring (0.2 ‰ per 100 m for $\delta^{18}O$ and 1.11 ‰ per 100 m for $\delta^{2}H$). Seasonal differences in altitude effect were also described in precipitation across the Adriatic–Pannonian region (Kern et al., 2020).

The $\delta^{13}C_{DIC}$ values for the groundwater of the Učja Valley vary from –12.6 ‰ to –8.3 ‰ (average –10.7 ‰) and alkalinity from 2.0 mM and 3.4 mM (average 2.9 mM). The surface water of the Učja River has higher $\delta^{13}C_{DIC}$ values, from –7.4 ‰ to –6.8 ‰ (average –7.0 ‰), while the alkalinity is slightly lower than in groundwater, from 2.2 mM and 2.6 mM (average 2.5 mM). Seasonal variations of $\delta^{13}C_{DIC}$ are generally observed with slightly higher values in the summer and noticeably lower values in the winter. Similar trends were described for the Radovna Valley (Torkar et al., 2016). The geochemical processes influencing the $\delta^{13}C_{DIC}$ values in groundwater are presented in Figure 11 and described in Kanduč et al. (2012, 2016). Geochemical processes were calculated as follows: line1 (with a value of +1.2 ‰) – dissolution of carbonates according to the average $\delta^{13}C_{CaCO3}$ value – predicted value (Kanduč et al., 2012) resulting in 1 ‰ enrichment in ^{12}C in DIC (Romanek et al., 1992), line 2 (with a value of –12.5 ‰) – nonequilibrium carbonate dissolution by carbonic acid produced from soil zone CO_2 (Kanduč et al., 2012; Verbovšek & Kanduč, 2016), and line 3 (with a value of –18.2 ‰) open system equilibration of DIC with soil CO_2 originating from the degradation of organic matter with $\delta^{13}C_{soil}$ –27.2 ‰ (Kanduč et al., 2012; Verbovšek & Kanduč, 2016) (Fig. 8). There are a number of possible sources of carbon. All $\delta^{13}C_{DIC}$ values (Fig. 11) indicate that the groundwater from the Učja Valley is a resulting mixture of the dissolution of carbonates and the degradation of organic matter. The results are comparable with groundwater samples from springs of Northern Slovenia (Kanduč et al., 2012), individual karstic and fractured dolomite aquifers in Central Slovenia (Verbovšek & Kanduč, 2016), the Triassic aquifers of the Velenje Basin (Kanduč et al., 2016) and $\delta^{13}C_{DIC}$ measurements from the Radovna Valley (Torkar et al., 2016).

Tritium (^{3}H) concentrations in the groundwater from the Učja aquifer ranged from 3.0 to 4.5 TU (average 3.5 TU), which is close to the detection limit of the method. More measurements would be needed to understand the age of the water in more detail, and should be further investigated in the future.

Conclusions

The groundwater from the Učja aquifer, a cross-border karst aquifer in NW Slovenia, was characterised using geochemical and isotopic data. Analysis was carried out on water samples from 10 springs (groundwater) and on (surface) water from the Učja River. The measurements were performed over the period December 2017 to March 2019.

The water discharge and physico-chemical parameters of the Učja groundwater and the Učja River reflect the climate that is characteristic of the area. The mixed snow/rainfall regime is characteristic for the Učja Valley. Lower discharges of the Učja River are recorded in winter and especially during summer, with the highest discharges seen during the spring snowmelt (March-April) and in autumnal precipitation (November). Similar trends are also seen in groundwater from the area (spring water measurements), with two periods of higher water discharge in the spring and autumn, and low or no discharge (dry springs) in the summer. The temperatures of both the groundwater and the Učja River are lower in winter (min 3.6 °C) and higher in summer (max 18.7 °C). The EC values indicate a highly permeable carbonate aquifer with a low residence time. The fluctuation of specific electrical conductivity at all sampling sites throughout the year refelects depletions during the dry season and higher values in spring (March-April) and autumn (November-December) and are related to periods of snow and rain. Slight differences in physico-chemical parameters were observed between sampling sites of higher and lower elevations.

All water samples indicate the same Ca-Mg-HCO_3 facies, with the most abundant ions Ca^{2+}, Mg^{2+}, and HCO_3^-, and low concentrations of K^+, Na^+, Cl^-, NO_3^-, and SO_4^{2+}. Differences in concentrations of Ca^{2+} and Mg^{2+} and of the Mg^{2+}/Ca^{2+} molar ratio between the two groups of springs are observed. The limestone defines the recharge area for the first group of springs (UC1, UC2, UC11), while the dolomite prevails in the second group of springs (UC3-UC8, UC12). The Mg^{2+}/Ca^{2+} molar ratios for UC9 (Učja River) and UC12 (within the Idrija Fault zone) are rather higher than for first group of springs. The pH values (average 8.12) also indicate the rather alkaline waters characteristic of carbonate aquifers.

The hydrogen (δ^2H) and oxygen ($\delta^{18}O$) isotope values suggest the complex mixing of maritime and continental air masses. The isotopic composition of Učja groundwater reflects its proximity to the Mediterranean climate and to some degree the influence of continental precipitation as well. Minor depletions in the altitude isotopic effect are noted (0.11 ‰ per 100 m for $\delta^{18}O$ and 0.45 ‰ per 100 m for δ^2H) at sampling locations from springs at higher altitudes (UC1, UC2, UC11) compared to those springs at lower altitudes (UC3-UC8, UC12). The altitude isotopic effect varies between seasons and is most prominent in spring. The $\delta^{13}C_{DIC}$ values indicate the dissolution of carbonates and the degradation of organic matter.

The results contribute to a considerably better understanding of the aquifer recharge area, the origin of the water, and groundwater dynamics, and provide us with an important basis for a comprehensive interpretation of a potential natural water resource in the future.

Acknowledgments

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