



# Hydrogeological characterization of karst springs of the white (*Proteus anguinus anguinus*) and black olm (*Proteus anguinus parkelj*) habitat in Bela krajina (SE Slovenia)

## Hidrogeološka karakterizacija kraških izvirov na območju habitata belega (*Proteus anguinus anguinus*) in črnega močerila (*Proteus anguinus parkelj*) v Beli krajini (JV Slovenija)

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*Ključne besede:* hidrogeologija, močeril, ekologija, nitrat, monitoring

### Abstract

The springs west of Črnomelj, in SE Slovenia, are the habitat of the black (*Proteus anguinus parkelj*) and the white olm (*Proteus anguinus anguinus*). Some of these springs are also the only known habitat in the world of endemic species of black olm. A steady decline in olm populations has been observed in this area over the past decades. Owing to the rapid runoff and groundwater flow high-resolution monitoring is essential in providing better insight into the hydrogeological characterization of the catchment area of springs. Specific factors and critical parameters of water behind said olm degradation have not yet been defined. Because the olm's environment is largely aquatic, one potential critical parameter could be the higher water temperatures (>12 °C) or higher nitrate concentration (>9.2 mg/l). The six-month observation of the springs (July – December 2021) point to water temperature as a potential critical parameter since the water temperature of the springs exceeded 12 °C in months July and August. Nitrate concentrations could also be a second critical parameter in the degradation of the olm's habitat. Maximum nitrate concentrations above 9.2 mg/l throughout much of the observation period (except for Dobljčica spring). Due to less agricultural activity in December in the spring catchment area and a higher dilution rate due to reduced evapotranspiration and increased effective precipitation during this time of the year, the nitrate concentrations are decreased. The results of the measured parameters of groundwater could show the hydrogeological connection between the Otovski and Pački breg springs and between Šotor, Jamnice and Dobljčica. The Obršec spring has an independent catchment area. A detailed estimation of the springs catchment area is possible due to a detailed geologic map. It is necessary to determine the origin of the nitrate (nitrate isotope analysis), to quantify the threshold values of the critical parameters, to define precisely all the causes of the olm deterioration, and to make proposals for appropriate measures to limit or even stop the decline of the olm population.

### Izvleček

Izviri zahodno od Črnomlja, v JV Sloveniji so habitat črnega (*Proteus anguinus parkelj*) in belega močerila (*Proteus anguinus anguinus*). Nekateri od teh izvirov so tudi edini znan habitat te endemične vrste črnega močerila. V zadnjih desetletjih je opazen upad populacije močerilov. Za boljši vpogled in ocenitev hidrogeoloških značilnosti prispevnega območja izvirov, je zaradi hitrega odtoka in toka podzemne vode pomembno pogosto spremljanje stanja. Potencialni vplivni dejavniki in parametri podzemne vode, ki bi lahko vplivali na slabšanje stanja ohranjenosti močerila še niso opredeljeni. Ker močeril večino časa živi v vodi, bi lahko potencialni kritični dejavnik bila višja temperatura vode (>12 °C) ali višja vsebnost nitrata v vodi (>9.2 mg/l). Izsledki šestmesečnega spremljanja kažejo, da bi potencialni kritični parameter za slabšanje stanja ohranjenosti močerila bila temperatura vode nad 12 °C v mesecih julij in avgust v opazovanem obdobju. Vsebnost nitrata bi prav tako lahko bil kritični parameter oz. razlog za upad števila močerilov in slabšanje stanja tega habitata. Najvišje vsebnosti nitrata so mejno vrednost za močerila presegale skoraj čez celotno opazovalno obdobje (z izjemo izvira Dobljčice), razen v mesecu decembru. Vzrok za to je zelo verjetno zmanjšana kmetijska dejavnost oz. višja stopnja razredčenja v tem delu leta zaradi zmanjšane evapotranspiracije in višjih količin efektivnih padavin. Rezultati izmerjenih parametrov podzemne vode kažejo, na verjetno hidrogeološko povezavo med izviri Otovski in Pački breg ter med izviri Šotor, Jamnice in Dobljčica. Izvir Obršec ima samostojno prispevno območje. V prihodnje bo podrobnejša opredelitev prispevnega območja izvirov mogoča z detajlnim geološkim kartiranjem. Potrebno je ugotoviti izvor nitrata (izotopske analize nitrata), kvantificirati mejne vrednosti kritičnih parametrov, določiti vse možne vzroke za slabšanje stanja ohranjenosti populacije močerila in opredeliti predloge ukrepov za preprečevanje oz. ustavitev upada populacije močerilov.

## Introduction

Some springs and caves in the Bela krajina region (SE Slovenia), in the area west of Črnomelj, are especially important and should be kept in good hydrogeological and geochemical condition (or work towards improvement), since they are the habitat of the black (*Proteus anguinus parkelj*) and white olm (*Proteus anguinus anguinus*). The black olm is an endangered endemic subspecies known only from a few springs over less than 3 km<sup>2</sup> in the W part of Bela krajina. Based on Annex 6 (Red List of Amphibians) of the Habitats Directive (Council Directive 92/43/EEC), the white and black olm are classified as rare and vulnerable species. The classification of the white and black olm as rare and vulnerable species was made based on a long-term scientific research of the distribution and decline in the olm population in the Bela krajina area. The problem of deterioration of the olm's habitat has also been noted by locals, among them the students of the Črnomelj secondary school, who work to raise awareness among the wider local community and draw attention to the problem. Cave pollution and the consequent polluted groundwater affects these groundwater-dependant ecosystems (Mezga et al., 2016). In the long term, this could cause the decline of one of the most important symbols of subterranean biodiversity, the white olm, as well as the black olm in Bela krajina (Sket, 1997; Aljančič et al., 2014; Ribeiro & Tičar, 2017).

Olm lives in aquatic environments, in still and oxygen-rich waters with stable temperatures of 8 to 11 °C. Occasionally, enters the phreatic and epiphreatic zones at high water levels (Aljančič et al., 2014; Mezga et al., 2015). Based on the conditions under which olm lives, water temperature above 12 °C could also be a potentially critical parameter for its degradation.

Potential factors and related critical parameters affecting the preservation status of the olm's habitat have not yet been properly defined. Past research (NLZOH, 2017) has determined the nitrate threshold value for olms, which consists of the predicted no-effect concentration (PNEC), the natural background concentration, and the expected variation of the natural background concentration. The main toxic effect of nitrate on aquatic animals appears to be the conversion of oxygen-carrying pigments (hemoglobin, hemocyanin) into forms incapable of transporting oxygen (methemoglobin, methemocyanin) (Jensen, 1996; Scott & Crunkilton, 2000).

If the assessed critical parameters are found to have a significant influence, the next step is to find the causes behind certain excessive critical pa-

rameter in groundwater and to limit or lower them using appropriate measures.

The aims of this study are (I) to assess the basic hydrogeological characteristics (water level, water temperature and electrical conductivity) of the observed springs as a response to water levels and water temperatures to precipitation (II) to determine whether water temperatures and nitrate concentrations are in a range suitable for the olm, (III) to determine whether long-term national monitoring would provide a realistic assessment of the quality of spring water, and (IV) to determine whether there is a possible geological or hydrogeological connection between the studied springs.

## The study area

### Geographical settings

The study area lies in SE Slovenia, in Bela krajina, west of the town of Črnomelj (Fig. 1), with a focus on six springs that are the habitat of white and black olm. The black olms were detected in the springs of Obršec, Šotor, Jamnice (also known as Jelševnik spring) and Dobljučica, while only the white olm is known from Otovski breg and Pački breg springs (Gorički, 2017). In the catchment area of these six springs are village settlements, which have regulated water supplies but no sewage system. On the slopes west of the springs (Dobljučka gora, Stražni vrh, Rodine) there are homes with vineyards and permanently inhabited houses spread over a wider area of the catchment area of the studied springs. The potential sources of anthropogenic impacts in this part of the karst area mainly consist of illegal landfills, the use of septic tanks in households, and the use of manure. Furthermore, in the immediate vicinity of the Obršec spring an illegal settlement with uncontrolled sewage disposal.

### Geological settings

Bela krajina can be geotectonically divided into its NE part, which belongs to the transition area between the Internal and External Dinarides, and the remaining part, which belongs to the External Dinarides (Placer, 2008), where our study area is located. The lithostratigraphic succession of the study area is largely characterized by shallow marine limestones and dolomites of Jurassic and Cretaceous age (Fig. 2) (Bukovac et al., 1984a, 1984b; Vlahović et al., 2005). The studied area is characterised by outcrops of Jurassic and Cretaceous carbonates. The Upper Jurassic bedded limestones and bedded to massive dolomites are tectonically fractured and exhibit strong secondary porosity.

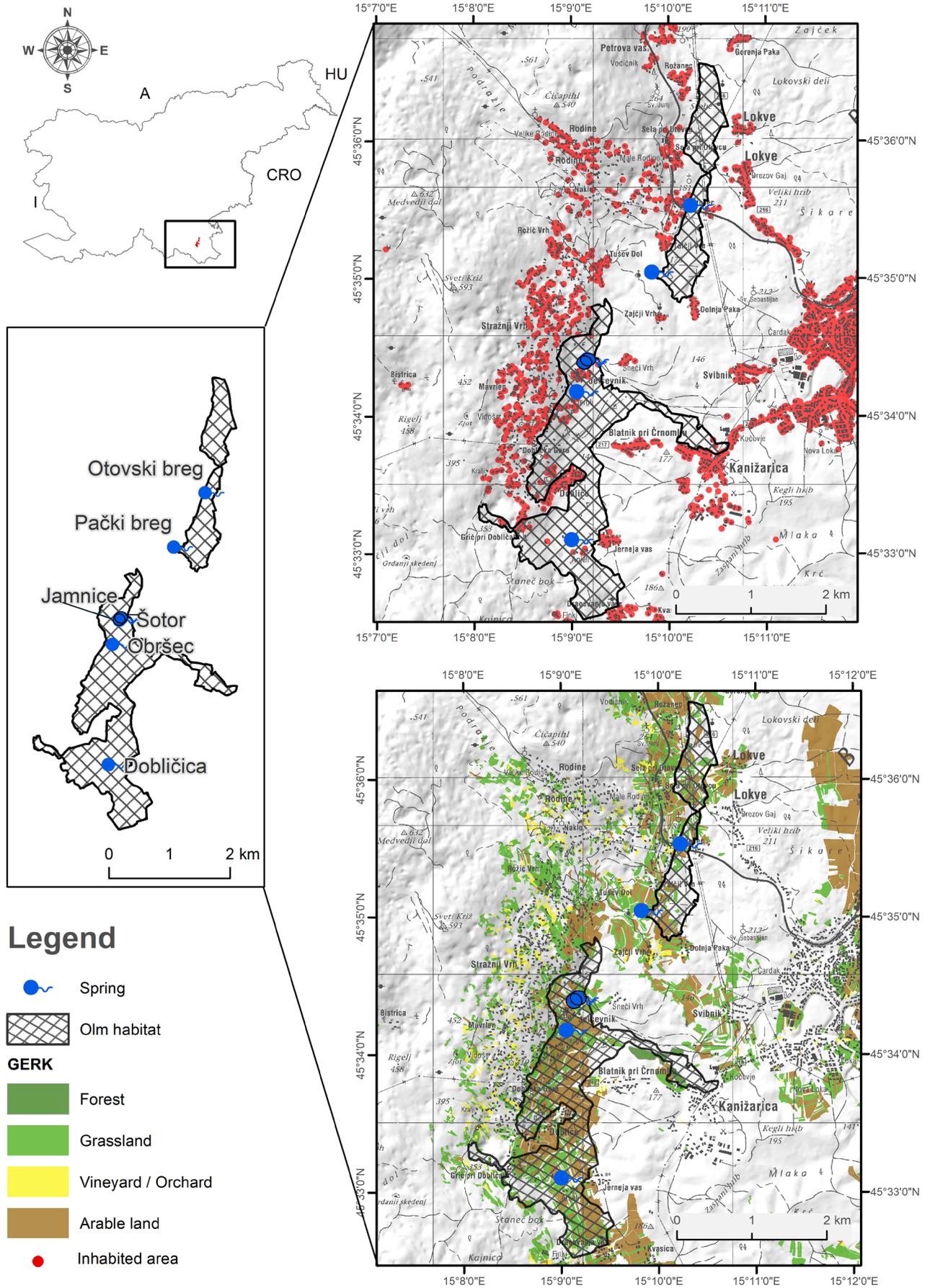


Fig. 1. Geographical location with observation springs, inhabited area (GURS, 2016) and land use (GERK, 2023) in the study area.

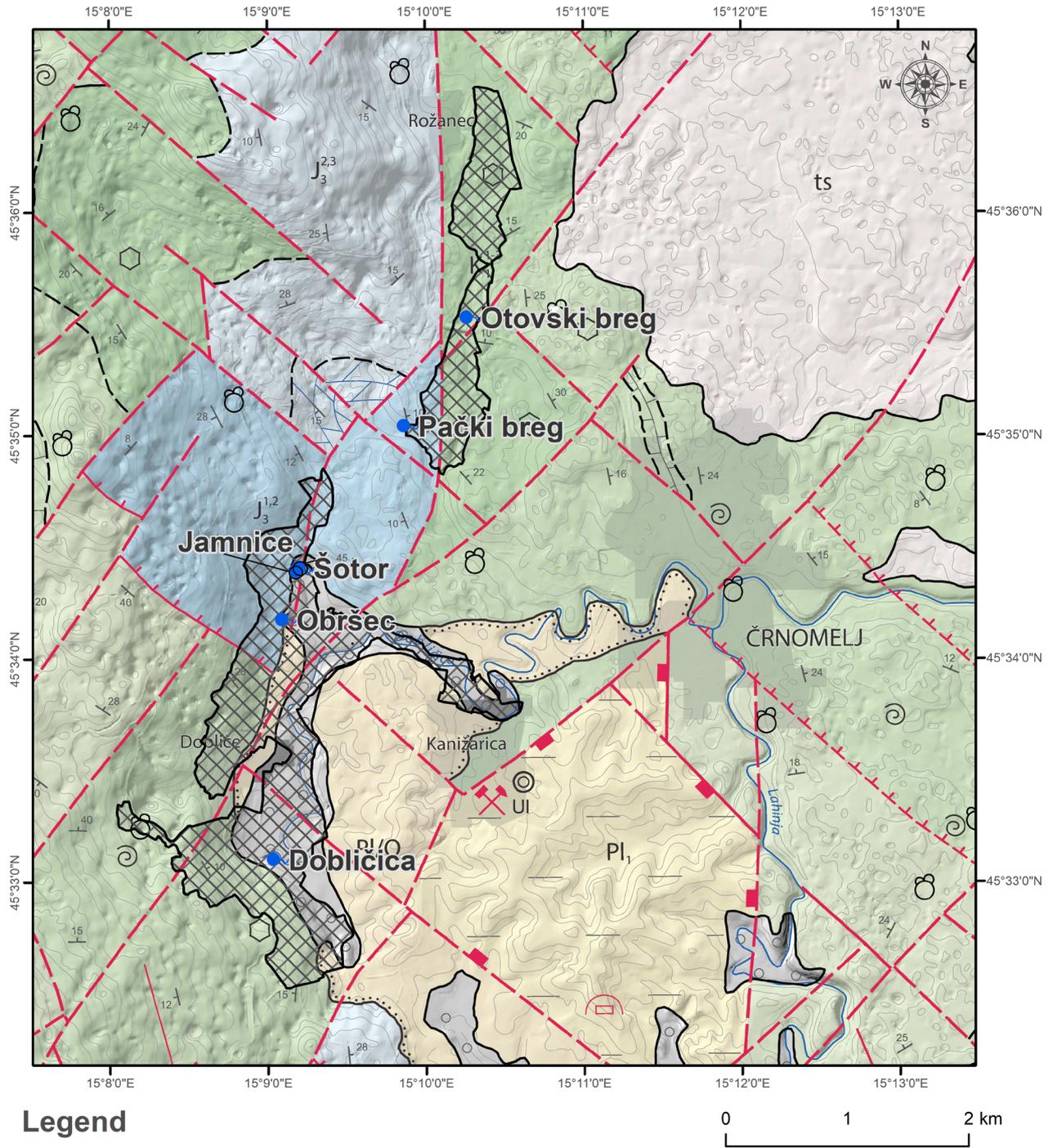


Fig. 2. The geological settings of the study area (modified after Bukovac et al., 1984a, 1984b).

Lower Cretaceous limestones (Bukovac et al., 1984a, 1984b) in some parts also contain lenses of dolomite and a breccia horizon. The entire Cretaceous succession exhibits strong and deep karstification, which is reflected in a large number of karst dolines, vertical shafts, and caves. To the east, the study area is bounded by the tectonic contact with the Kanižarica coal basement, which formed in the Pliocene and was filled with fine-grained lake sediments and organic matter (coal) (Šinigoj et al., 2012). The Jurassic, Cretaceous and Neogene rocks and their contacts in the lower parts of the shallow karst are covered by clays of the Plio-Quaternary age, a thick (2–6 m) cover of residual and resedimented terra rossa and Quaternary sediments of the Dobljčica and Jelševniščica floodplains. Structurally, the wider area of Bela krajina is characterized by NW–SE trending Dinaric longitudinal structures (folds and faults). The fault planes are mostly characterized as reverse faults with their dip towards the SW (Bukovac et al., 1984a, 1984b). The springs of the study area lie on the potential continuation of the reverse fault, defined on the basic geological map as the “Bosiljevo–Črnomelj” thrust (Bukovac et al., 1984a, 1984b; Habič et al., 1991b; Novak, 1996; Šinigoj et al., 2012). From the Dobljčica spring towards the Šotor, Obršec, and Jamnice springs, this zone is covered by the Quaternary flood plain of the Dobljčica River. N–S orientated fault zone outcrops only in some locations E of the village of Dobljče and W of village Otovec. Different structural trends can be observed NW of the village Dobljče (Šinigoj et al., 2012). There the fault system shows NW–SE orientation. The structural relations between these two fault systems are not clear, as the possible fault intersection is covered by Quaternary sediments. These fault zones could be an important factor for groundwater conduction (Čar, 2018). The springs studied are classified as karst springs. Dobljčica and Otovski breg flow from Lower Cretaceous limestone and could not be directly connected to any of the known fault systems, while Obršec, Šotor, Jamnice and Pački breg springs flow from the Upper Jurassic limestone and dolomite and are probably located in a tectonic zone running in the NNE–SSW direction (Bukovac et al., 1984b; Habič et al., 1991b; Šinigoj et al., 2012).

### Observation springs

Otovski breg is a spring in an unroofed cave from which the water flows to the surface through two syphons. Close by, another monitored spring is located (approximately 1 km SW from Otovski

breg) called Pački breg. The white olm is present in these two (Pački breg & Otovski breg) observed springs. Both springs are located in the northern part of the studied area near the villages of Otovec and Tušev dol (Fig. 1). In Pački breg there are three smaller springs that are a mere one meter apart and never run dry. The water flows to the surface in two horizontal syphon springs. In the third, the water springs vertically, which is obvious when observed at high water level.

The habitat of the black olm consists in the four observed springs located in the southern part of the studied area (Fig. 1) near the villages of Jelševnik and Dobljče. Šotor is a spring located on the Zupančič farm in Jelševnik, only 50 m away from the Jamnice spring. It is about 4.5 m wide, and the water comes to the surface in several syphons. The Šotor spring is covered with a tent to simulate a dark environment and a camera is installed to observe the olms. The Jamnice spring is a funnel-shaped spring some about 2 m wide from where water outflows to the lake at the Zupančič farm. The Obršec spring is located 500 m south of the village of Jelševnik with two larger syphons 5 m apart. The southernmost and observably largest is the Dobljčica spring. The spring Dobljčica is located 2.4 km SE from the village Jelševnik (springs Šotor and Jamnice) and is a spring with a depth of more than 100 m (Novak, 1996). The spring is protected by a groundwater protection zone and is part of the public drinking water supply system.

## Material and Methods

### Effective precipitation ( $P_{ef}$ ), evapotranspiration (ETR)

Data on hourly measurements of precipitation and daily potential evapotranspiration were obtained from the meteorological station Črnomelj-Dobljče (SEA 2022a, 2022b). The effective precipitation ( $P_{ef}$ ) is the amount of total precipitation without runoff and evapotranspiration. Based on hourly measurements of precipitation and daily evapotranspiration we calculated the highest amount of precipitation ( $P_{tot}$ ) in one day, in a one-hour event, and the monthly volume. We also calculated the daily evapotranspiration (ETR) and effective precipitation. Based on the daily total precipitation ( $P_{tot}$ ) and the daily potential evapotranspiration (ETR) in the meteorological station Črnomelj – Dobljče, we simplified and assessed the amount of daily effective precipitation (Eq. 1).

$$P_{ef} = P_{tot} - ETR [mm] \quad [Eq. 1]$$

Table 1. Characteristics of sensors for water level, temperature and electrical conductivity measurements (Eltratec GSR 130NTG).

Observation point	Monitoring period	Interval	Water level	Temperature	Electrical conductivity
Obršec	July – December 2021	1 h	0 – 9.99 m	0 – 50 °C ± 0.3 °C	10 – 2000 µS/cm ± 50 µS/cm (< 2 %)
Šotor	July – December 2021	1 h	0 – 9.99 m	0 – 50 °C ± 0.3 °C	10 – 2000 µS/cm ± 50 µS/cm (< 2 %)
Pački breg	August – December 2021	1 h	0 – 99.99 m	0 – 50 °C ± 0.4 °C	0.1 – 10 mS/cm ± 400 µS/cm

### Field measurements

Field measurements of water levels, temperature, and electrical conductivity were carried out using the water level measurement logger Eltratec GSR 130NTG with sensors for water level, temperature, and electrical conductivity (Table 1). The loggers were installed at the Obršec and Šotor springs from July to December 2021 and at the Pački breg spring from August to December 2021. The loggers recorded measurements at one-hour intervals. The water level, electrical conductivity and water temperature in Jamnice and Otovski breg were not monitored, we only measured nitrate content.

Data on water levels and temperature is recorded every five minutes at the Dobljučica spring and was provided by Komunala Črnomelj, a public utility company. Due to the wide measurement range and high measurement uncertainty of the electrical conductivity probe installed at Pački breg ( $\pm 400 \mu\text{S}/\text{cm}$ ), the data obtained during the study for this spring was omitted. In this case, we monitored only the relative fluctuations in electrical conductivity.

### Response of water level (WLR) on rainfall event

We defined the rain event as a maximum daily amount of precipitation ( $P_{\text{tot}}$ ) of more than 25 mm. This rainfall amount (25 mm/day) was determined based on a significant simultaneous rise in water level in the observed springs, which occurred as a peak just a few hours after the rain event began. All rain events began with a rainfall rate greater than 0.2 mm/hour. The time of the beginning of the rainfall event ( $t_{\text{start}}$ ) is the so-called beginning of the rainfall event. During this time, the water level does not change ( $WL_{\text{start}}$ ). After some time during the rain event ( $t_{\text{max}}$ ), the peak or maximum spring water level ( $WL_{\text{max}}$ ) is measured. Based on the rainfall events and the water level rise in response to the rainfall event, we calculated the response rates or water level rise rate (WLR), which is a very simplified tool to roughly evaluate the response of the karst spring to rainfall events (Eq. 2).

$$WLR = \frac{WL_{\text{max}} - WL_{\text{start}}}{t_{\text{max}} - t_{\text{start}}} \quad [\text{m}/\text{h}] \quad [\text{Eq. 2}]$$

### Water sampling

Sampling for nitrate concentrations was carried out at weekly intervals between July and December 2021 at the Obršec, Šotor, Jamnice, Otovski breg, Pački breg and Dobljučica springs (Fig. 1). Sampling was performed in collaboration with students from Črnomelj High school (Gymnasium Črnomelj), that were included into research as citizen science members. For sampling, we used 100 ml plastic bottles or two 50 ml plastic tubes for each sampling location and stored at 2–5 °C. Before collecting the water samples, the bottles were washed with water from the individual spring. Then the samples were taken to the Geological Survey of Slovenia laboratory to a dark and cool place.

### Nitrate measurements

Measurements of nitrate concentrations in water were carried out in the hydrogeological laboratory of the Geological Survey of Slovenia using a UV-VIS Spectro:lyser™ spectrometer. Based on the reflection of laser beams, the spectrum and nitrogen content of nitrate ( $\text{NO}_3\text{-N}$ ) are determined. Measurements were performed no later than 72 hours after sampling. The spectrometer is calibrated to the primary standards using known values. For a quality control check prior to sample measurement, the in-house standard (ultrapure water) was measured first, and the second in-house standard (tap water) was measured at the end of the measurement process. The same sample from one bottle was measured three times. All measured values are corrected with the correction equation obtained using primary standards with known values and checked with in-house standards.

## Results

### Effective precipitation ( $P_{\text{ef}}$ ) and evapotranspiration (ETR) and rain events

In the observation period July – December 2021, the highest monthly amount of precipitation ( $P_{\text{tot}}$ ) came in July (141.99 mm) and the lowest in September (79.17 mm). The highest evapotranspiration (ETR) coincided with higher air

Table 2. Precipitation, evapotranspiration and effective precipitation in Črnomelj – Dobliče meteorological station (July – December 2021) (SEA 2022a, 2022b).

Month/Year	Precipitation ( $P_{tot}$ ) N=9169			Evapotranspiration) (ETR) N=185		Effective precipitation ( $P_{ef} = P_{sum} - ETR_{sum}$ )	
	Max [mm/h]	Sum [mm/month]	Max [mm/day]	Sum [mm/month]		Sum [mm/month]	
7/21	50.9	141.99	6.8	137.2		4.79	
8/21	23.5	108.25	5.3	106.0		2.25	
9/21	34.4	79.17	3.5	73.7		5.47	
10/21	27.0	105.83	2.6	31.2		74.63	
11/21	23.6	131.77	1.4	14.4		117.37	
12/21	33.9	97.57	1.2	9.4		88.17	

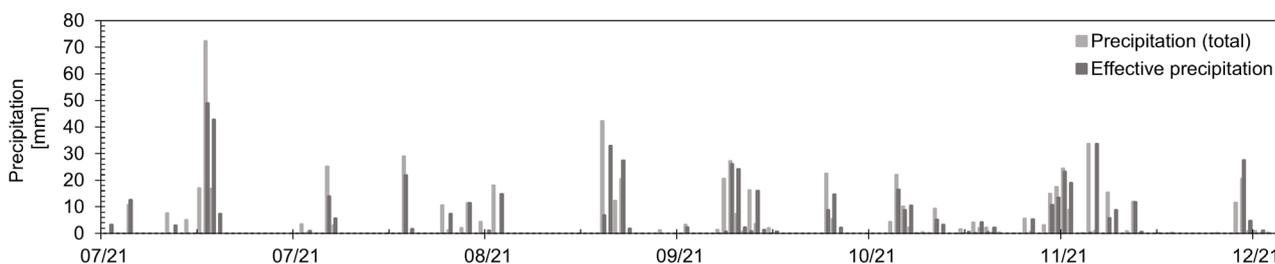


Fig. 3. Total daily precipitation and effective precipitation in Črnomelj-Dobliče meteorological station (July – December 2021) (SEA 2022a, 2022b).

temperatures and higher plant transpiration, in July (137.2 mm), with the lowest volumes in December (9.4 mm). The lowest monthly amount of effective precipitation ( $P_{ef}$ ) was in August (2.25 mm), and the highest in November (117.37 mm) (Table 2).

In the period July – December 2021 we defined five rain events: at July 16 (72.3 mm/day), August 17 (29 mm/day), September 17 (42.1 mm/day), October 6 (27.1 mm/day) and December 2 (33.6 mm/day).

### Water level, temperature, and electrical conductivity in the observed springs

In the period July – December 2021 we observed the hourly change in water level (WL), temperature (T), and electrical conductivity (EC) in three springs – Pački breg, Obršec, and Šotor. The measured values are presented in Figure 4, 5, 6, and 7. The highest and lowest water level values, temperatures, and electrical conductivity of these four springs are presented in Table 3.

Table 3. Highest and lowest water level, electrical conductivity water temperature in observed springs (July – December 2021).

Month/Year	Pački breg						Obršec						Šotor						Dobličica					
	WL [m]		EC [ $\mu$ S/cm]		T [ $^{\circ}$ C]		WL [m]		EC [ $\mu$ S/cm]		T [ $^{\circ}$ C]		WL [m]		EC [ $\mu$ S/cm]		T [ $^{\circ}$ C]		WL [m]		T [ $^{\circ}$ C]			
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min		
07/21	/	/	/	/	/	/	1.91	0.76	452	424	13.9	11.5	1.47	0.48	535	357	17.3	10.5	1.43	0.37	25.6	10.7		
08/21	0.53	0.33	930*	620*	11.8	11.5	1.44	0.56	451	420	14.7	11.5	0.71	0.40	442	403	11.3	10.5	0.42	0.37	14.1	11		
09/21	0.59	0.25	970*	920*	12.0	11.7	1.63	0.29	474	431	14.1	11.4	1.03	0.41	435	418	10.7	10.5	0.83	0.43	13	10.9		
10/21	0.76	0.27	990*	890*	11.9	11.4	1.63	0.3	507	430	12.8	11.2	1.9	0.54	549	418	11	10.4	1.82	0.39	12.4	9.7		
11/21	0.85	0.41	970*	900*	11.7	10.9	1.82	1.19	489	452	11.6	11.3	2.09	0.81	625	435	11.8	10.2	1.96	0.49	10.7	9.0		
12/21	0.86	0.42	960*	900*	11.5	10.9	1.8	1.36	461	450	11.5	11.4	2.08	0.91	695	442	11.9	10.1	1.91	0.49	10.7	8.3		

 \*wide measuring range – deviations of  $\pm 400 \mu$ S/cm

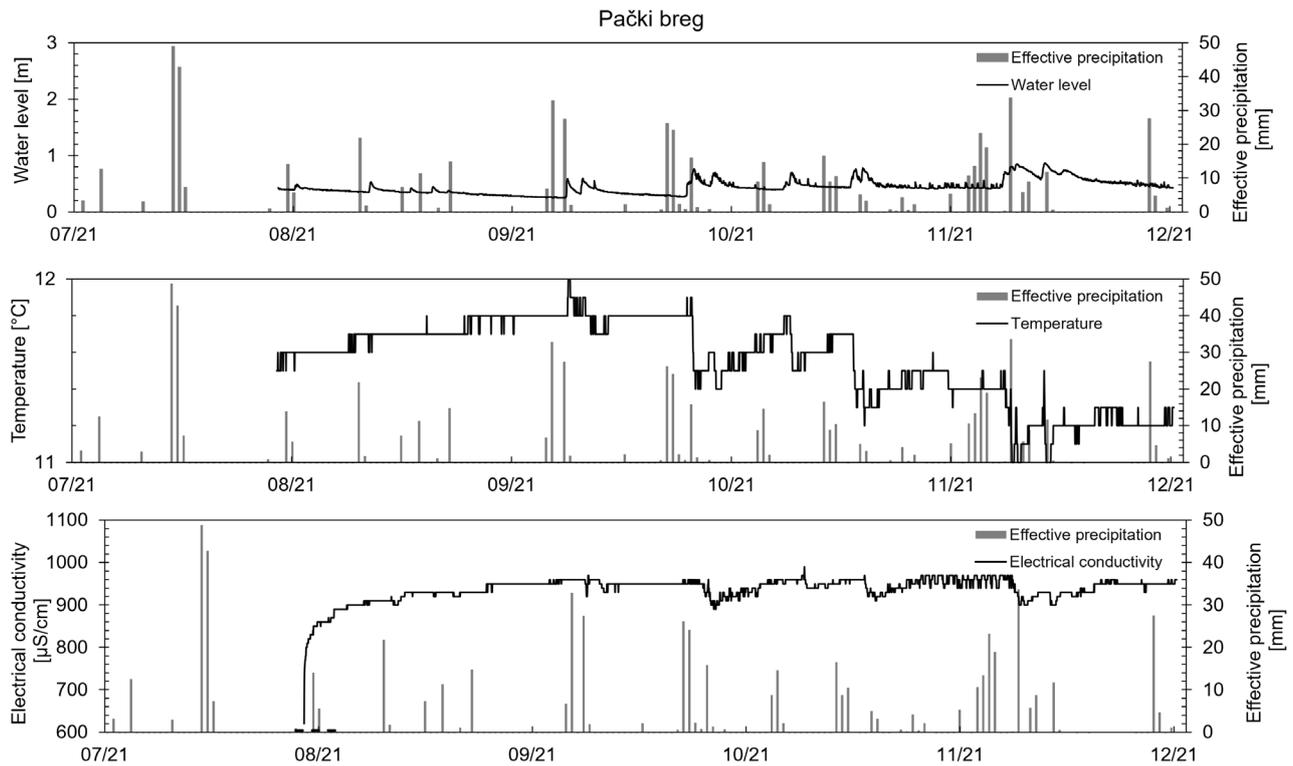


Fig. 4. Water level, temperature and electrical conductivity in Pački breg in comparison with effective precipitation.

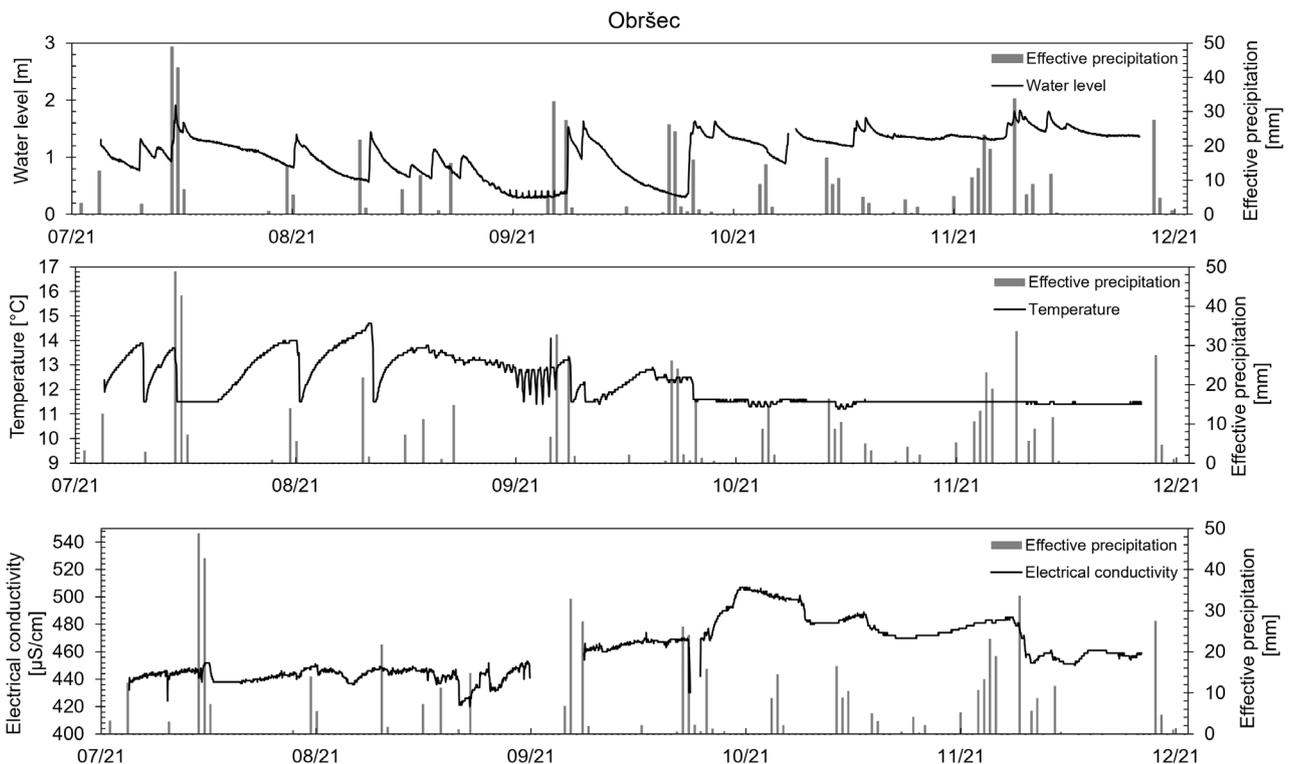


Fig. 5. Water level, temperature and electrical conductivity in Obršec in comparison with effective precipitation.

The highest water level in Pački breg spring (Fig. 4) was recorded in December (0.86 m) with the minimum evapotranspiration, and the lowest water level (0.25 m) in September, when the lowest total precipitation and highest water temperature

were recorded. The highest water level in Obršec (1.91 m) (Fig. 5) was measured in July, when evapotranspiration and effective precipitation also reached their maximum. The lowest water level in Obršec (0.29 m) was recorded in September,

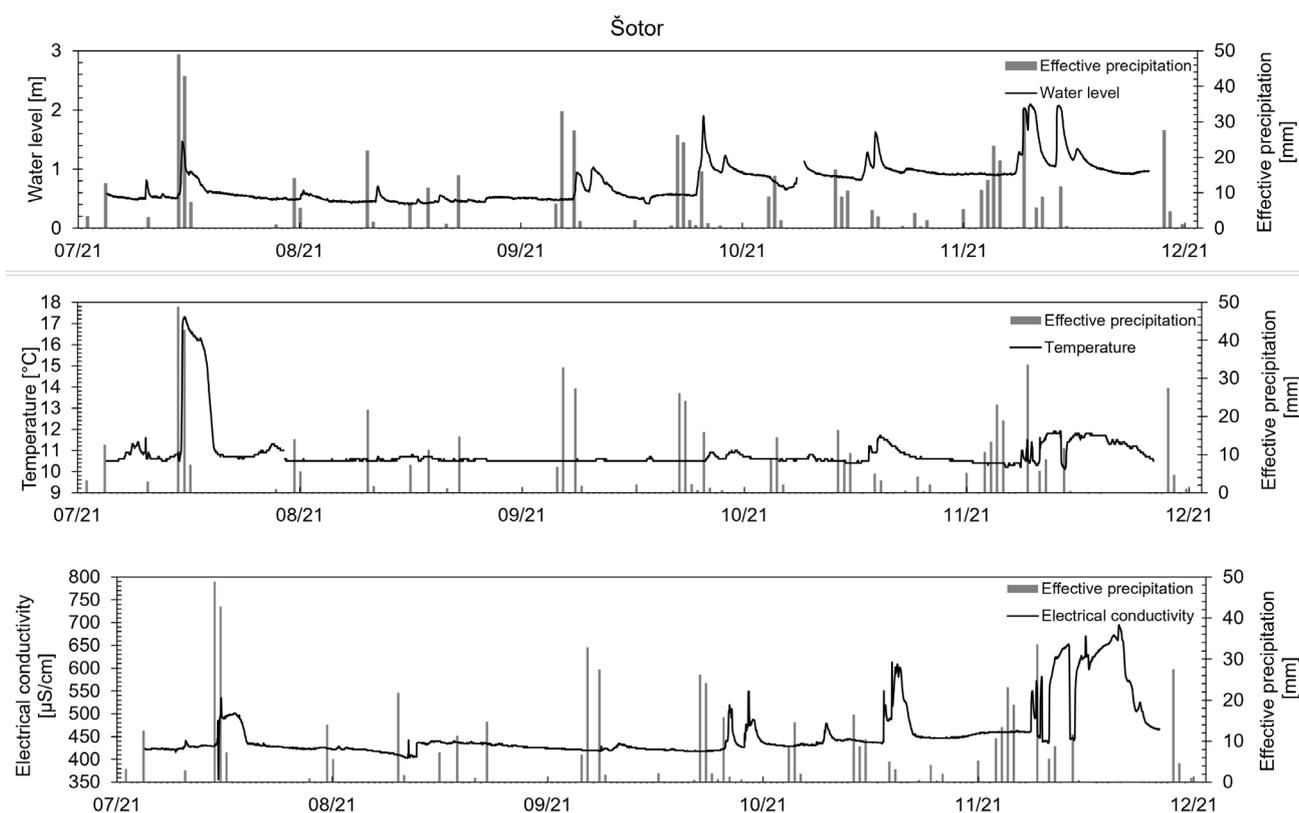


Fig. 6. Water level, temperature and electrical conductivity in Šotor in comparison with effective precipitation.

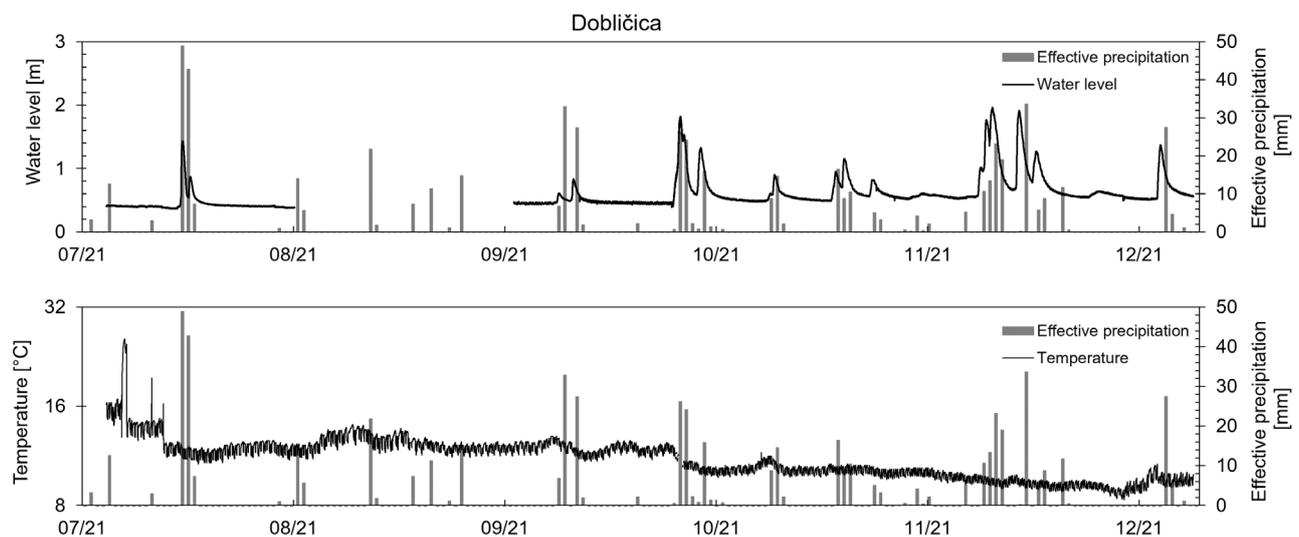


Fig. 7. Water level and temperature in Dobljičica in comparison with effective precipitation.

like in Pački breg, when the lowest total precipitation was measured. The highest water level in Šotor (Fig. 6) was recorded in November (2.09 m) as well as in Dobljičica spring (1.96 m) (Fig. 7), when maximum effective precipitation was also recorded. The lowest water level in Šotor (0.4 m) and Dobljičica (0.37 m) was observed in August, coinciding with the lowest effective precipitation.

The maximum water temperature of the Šotor (Fig. 6) and Dobljičica springs (Fig. 7) was recorded in July, and the minimum in December, along with the highest and lowest evapotranspiration rates. The highest water temperature in Pački breg (Fig. 4) was recorded in September (12.0 °C) in Šotor (Fig. 6) (17.3 °C) and Dobljičica (Fig. 7) (25.6 °C - logger likely dry; other

maximum 12.4 °C) in July, and in Obršec in August (14.7 °C). The maximum water temperature exceeded the limit of 12 °C in Šotor spring in July (17.3 °C), several times in Obršec between July and October (14.7–12.8 °C) and in Dobljučica also between July and October. Highest water temperatures were measured simultaneously with the highest evapotranspiration (Table 3).

The highest electrical conductivity in Pački breg was recorded in October (990  $\mu\text{S}/\text{cm}$ ). The lowest electrical conductivity in Pački breg (620  $\mu\text{S}/\text{cm}$ ) was in July, during the period of highest evapotranspiration. The highest electrical conductivity in Obršec (507  $\mu\text{S}/\text{cm}$ ) was, as in Pački breg, also recorded in October. In this spring the lowest electrical conductivity was detected in August (420  $\mu\text{S}/\text{cm}$ ), during the period of lowest effective precipitation. The highest electrical conductivity in Šotor was recorded in December (695  $\mu\text{S}/\text{cm}$ ), when minimum water temperatures and evapotranspiration were recorded. The lowest electrical conductivity in Šotor (357  $\mu\text{S}/\text{cm}$ ) was recorded in July, during the period of maximum evapotranspiration.

### Response of water level to rainfall events

Based on the rainfall events determined in the period July – December 2021 and water level rise in a spring after a short time at the beginning of the rain event we calculated the water level rise rate (WLR) (Table 4). In average, among other springs in Obršec water level rise is the fastest (0.1 m/h) and in Pački breg the slowest (0.04).

### Concentration of nitrates in springs

Nitrate concentrations measured weekly in collected water samples from the six monitored springs over a six-month period (July–December 2021) are shown in Figure 8. The basic statistical analysis and the highest and lowest maximum concentrations in the springs are shown in Table 5.

The highest concentration of nitrates in Pački breg (25.3 mg/l) and Otovski breg (29.2 mg/l) was recorded in September, when the lowest amount of total precipitation was recorded. The highest nitrate concentration in Pački breg (20.8 mg/l) was in October. In Šotor the highest concentration of nitrates was recorded in July (15.1 mg/l), as in Jamnice (29.2 mg/l), during the period of maximum evapotranspiration.

Since spring 2010, Jamnice (also named Jelševnik), Otovski breg, Pački breg, and Dobljučica are included in the national monitoring of the qualitative status of groundwater. At the beginning, the national monitoring included sampling twice

Table 4. Water level rise rate (WLR) in Pački breg, Obršec, Šotor and Dobljučica spring (July – December 2021) as a response to a rainfall event.

Month/ Year	Pački breg				Obršec				Šotor				Dobljučica							
	WT <sub>start</sub>	WT <sub>max</sub>	$\Delta t$ [h]	$\Delta WL$ [m]	WLR [m/h]	WT <sub>start</sub>	WT <sub>max</sub>	$\Delta t$ [h]	$\Delta WL$ [m]	WLR [m/h]	WT <sub>start</sub>	WT <sub>max</sub>	$\Delta t$ [h]	$\Delta WL$ [m]	WLR [m/h]	WT <sub>start</sub>	WT <sub>max</sub>	$\Delta t$ [h]	$\Delta WL$ [m]	WLR [m/h]
07/21	/	/	/	/	/	16/7, 18:00	17/7, 11:00	17	0.99	<b>0.06</b>	16/7, 17:00	17/7, 10:00	17	0.96	<b>0.06</b>	16/7, 18:15	17/7, 14:15	23	1.04	<b>0.05</b>
08/21	17/8, 04:00	17/8, 10:00	6	0.16	<b>0.03</b>	17/8, 02:00	17/8, 10:00	8	0.88	<b>0.11</b>	17/8, 00:00	17/8, 08:00	8	0.26	<b>0.03</b>	/	/	/	/	/
09/21	17/9, 15:00	17/9, 18:00	3	0.29	<b>0.10</b>	17/9, 14:00	17/9, 19:00	5	1.12	<b>0.22</b>	17/9, 07:00	17/9, 20:00	13	0.45	<b>0.03</b>	17/9, 15:00	17/9, 21:00	6	0.12	<b>0.02</b>
10/21	6/10, 20:00	8/10, 00:00	28	0.47	<b>0.02</b>	6/10, 19:00	7/10, 17:00	22	1.24	<b>0.06</b>	6/10, 18:00	7/10, 21:00	27	1.31	<b>0.05</b>	6/10, 21:00	8/10, 01:00	29	1.33	<b>0.05</b>
12/21	2/12, 14:00	3/12, 00:00	10	0.26	<b>0.03</b>	2/12, 12:00	2/12, 23:00	11	0.35	<b>0.03</b>	2/12, 14:00	2/12, 20:00	6	0.99	<b>0.17</b>	2/12, 14:00	3/12, 02:00	12	1.22	<b>0.10</b>
Average WLR			0.04					0.1					0.07					0.05		

$$\Delta t = t_{\text{max}} - t_{\text{start}} \text{ [h]}$$

$$\Delta WL = WL_{\text{max}} - WL_{\text{start}} \text{ [m]}$$

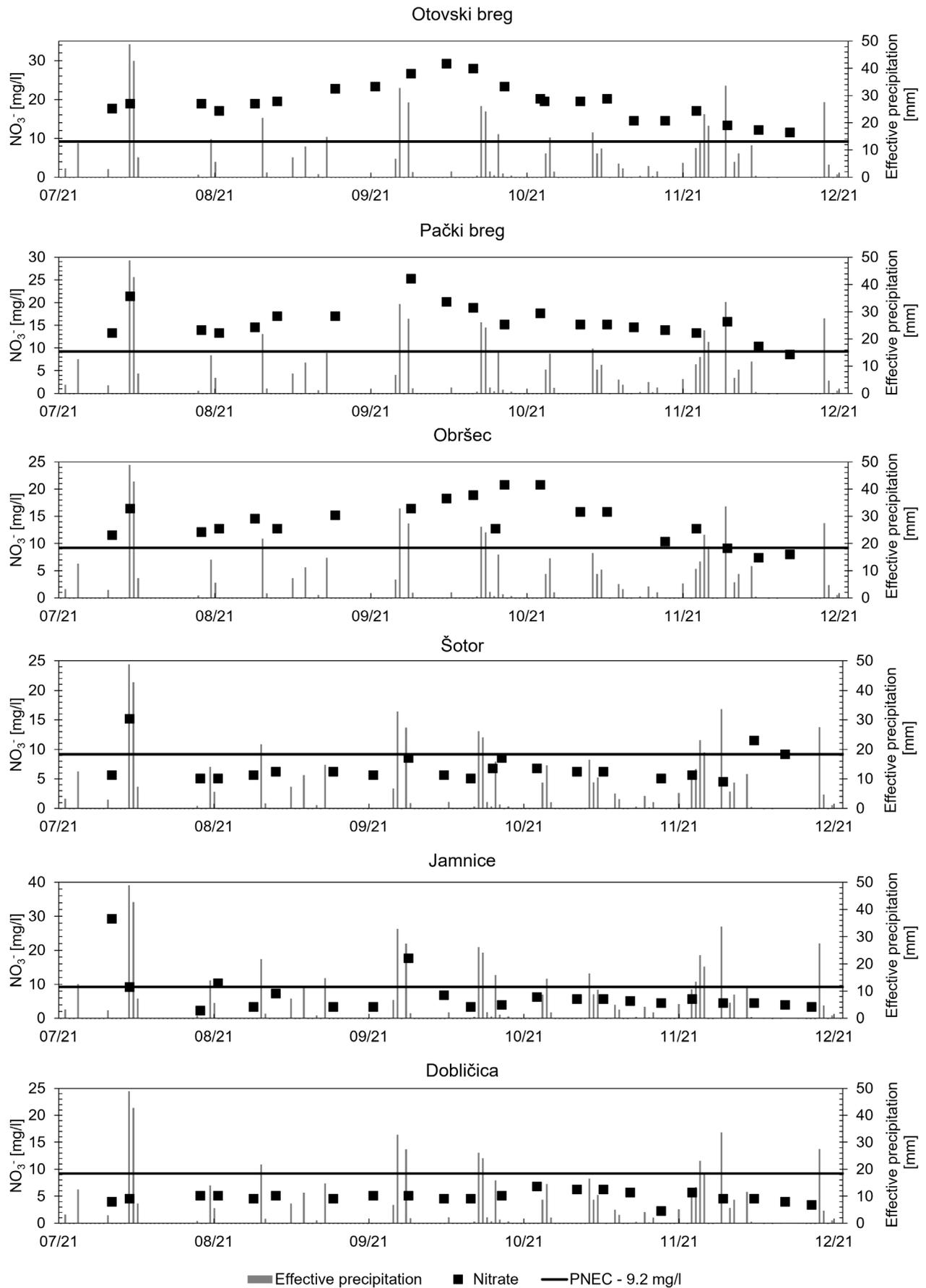


Fig. 8. Nitrate concentration in all observed springs with PNEC for olm.

Table 5. Highest and lowest monthly nitrate concentration in Pački breg, Otovski breg, Obršec, Šotor, Jamnice and Dobljučica in the period of July – December 2021.

Month/Year	Pački breg N=21		Otovski breg N=22		Obršec N=22		Šotor N=21		Jamnice N=22		Dobljučica N=22	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
07/21	21.4	13.3	18.9	17.6	16.4	11.5	15.1	5.6	29.2	9.1	4.5	3.9
08/21	17	14.5	19.5	18.9	14.5	12.1	6.2	5.6	7.3	3.3	5.1	4.5
09/21	25.3	17	29.2	22.7	18.2	15.1	8.5	5.6	17.6	3.3	5.1	4.5
10/21	18.9	15.1	27.9	19.5	20.8	15.8	8.5	5.1	6.2	3.3	6.8	4.5
11/21	15.8	13.3	27.9	13.3	15.8	9.1	6.8	4.5	5.6	4.5	6.2	2.2
12/21	10.3	8.5	12.1	11.5	9.1	7.4	11.5	9.1	4.5	3.3	4.5	3.3

Table 6. Basic statistical analysis and comparison of nitrate concentration of short-term observations (July – December 2021) and nitrate concentrations of national monitoring (2010–2018). Higher nitrate concentrations are marked in bold.

NO <sub>3</sub> <sup>-</sup> (mg/l)	median		mean		max	
	Jul–Dec 2021	(SEA 2022c) (2010–2018)	Jul–Dec 2021	(SEA 2022c) (2010–2018)	Jul–Dec 2021	(SEA 2022c) (2010–2018)
Jamnice	<b>4.76</b>	3.20 (Jelševnik)	<b>6.76</b>	3.27 (Jelševnik)	<b>29.22</b>	4.25 (Jelševnik)
Otovski breg	<b>19.18</b>	16.50	<b>19.36</b>	16.55	<b>29.22</b>	19.90
Pački breg	15.14	<b>15.20</b>	<b>15.71</b>	14.75	<b>25.27</b>	17.70
Dobljučica	<b>4.76</b>	3.19	<b>4.79</b>	3.31	<b>6.78</b>	5.55

in a year. In the last few years sampling was performed just one time in a year. We compared, where possible, long-term national monitoring nitrate concentrations (2010–2018) in these springs, with the results of our weekly observations and performed a basic statistical analysis of the data (Table 6). We calculated the median, mean, and maximum value of nitrate concentrations for all data obtained for the long-term (2010–2018) and the short-term (July – December 2021). The higher values of nitrate concentration are represented in bold.

## Discussion

Evapotranspiration, the sum of bare soil evaporation, plant transpiration, and evaporation from precipitation intercepted by the canopy (Pollard & Thompson, 1995) and rainfall determine the spatial and temporal distribution of groundwater recharge (Jukić & Jukić, 2015). Land cover, like vegetation, changes the evapotranspiration and consequently has an influence on groundwater recharge (Kovačič et al., 2020). Due to vegetation cover, evapotranspiration in that area has a higher impact on groundwater recharge.

Anthropogenic impact in this part of the karst area consists of some illegal landfill, the use of septic tanks in households and pouring manure on agricultural land. Decomposition under anaerobic conditions produces leachate saturated with or-

ganic matter, which is characterized by a relatively high temperature, different from the temperature of the surrounding surface (Breg Valjavec & Zega, 2017). Additionally, in complex karst aquifers, significant temperature changes under a variety of hydrological conditions are a consequence of the inflow of water from different parts of the recharge area (Petrič & Kogovšek, 2010). So water temperature can be considered as a natural tracer of groundwater flow (Saar, 2010).

The electrical conductivity of water could also be used as a groundwater tracing tool. Electrical conductivity is determined by the dilution by precipitation during rain events and can also be reflected in higher concentrations of pollutants. The peaks in the electrical conductivity of monitored springs are likely controlled by the washing of pollutants from unsaturated zone during rain event (Kogovšek, 2011; Chang et al., 2021). Intensive transfer of contaminants occurred when the more permeable fissures were flushed out, while some of the pollutants were retained in the less permeable part of the thick vadose zone (Kogovšek, 2011).

The rough estimation of water level response (WLR) in Šotor and Dobljučica springs shows us the fast response in water level rise during a rain event in December, when the minimum evapotranspiration was recorded, which was considered as an indicator of the high impact of evapotranspiration on the Šotor and Dobljučica spring recharge

dynamics. The highest (November) and lowest (July) effective monthly precipitation and water levels in Šotor and Dobljičica spring were recorded in the same month. This basic assessment again demonstrates the important role of land cover in the Šotor and Dobljičica recharge area. The highest (July) and lowest (September) amounts of total precipitation and the highest and lowest water levels in the Obršec spring further indicate less impact from evapotranspiration and more direct infiltration, as well as the existence of a small independent catchment area of the Obršec spring, as previously proposed by Habič (1991a) and Novak (1996).

The nitrate ion ( $\text{NO}_3^-$ ), and consequently, nitrate toxicity for aquatic animals, is due to nitrate ions (Camargo & Alonso, 2006). Based on these facts nitrate could be one of the potential critical parameters affecting the proposed threshold concentration (PNEC), estimated at  $9.2 \text{ mg/l NO}_3^-$  (NLZOH, 2017). The nitrate ion occurs naturally in the nitrogen cycle and during nitrification but is also present in fertilizers in various forms. The most common anthropogenic sources of nitrate in groundwater are livestock and other agricultural production, wastewater, old landfills and illegal dumps, and fertilization with artificial fertilizers or digestate (NLZOH, 2017). The nitrate concentration above PNEC could be a major problem in Otovski breg, Pački breg, and Obršec, as concentrations throughout most of the entire monitoring period (July – November) was exceeded, and occasionally also in Šotor and Jamnice (July 2021). There are no problems with high nitrate concentrations in Dobljičica, as its catchment area is protected by the decree on water protection, wherein certain environmental interventions are not allowed (e.g. agriculture). The highest concentration of nitrates was recorded in October in Dobljičica, which did not exceed a concentration level of  $7 \text{ mg/l}$  ( $6.8 \text{ mg/l}$ ). Based on the geological and hydrogeological characteristics of Dobljičica, low nitrate concentrations could be the result of the higher dilution rate seeing as it has the largest catchment area of all studied springs (Habič et al., 1991; Šinigoj et al., 2012). The main factor behind the high nitrate concentrations in the July – November period in Otovski breg and Pački breg could be agriculture, as in the case of Obršec, which includes an unregulated communal system (Habič et al., 1991a) in the catchment area. In most of the springs, the lowest maximum nitrate concentrations were recorded in December, which could be the result of little or no agricultural activity at that time of the year. A potential measure that could

serve to ease nitrate concentrations would be to protect the springs with a decree limiting activities that contribute to high nitrate concentrations in the catchment area of such springs. One of the proposed measures should be the regulation of wastewater drainage or the arrangement of a public sewage system. Also working with farmers on developing new fertilization techniques could contribute to a solution.

We also compared the median, mean, and maximum nitrate concentrations of long-term national monitoring of the qualitative status of groundwater with low frequency of water sampling and short-term high-resolution sampling and measurements of nitrate concentrations. The comparison shows higher nitrate concentrations in the case of high-resolution sampling. In three of the compared springs – Jelševnik, Obršec and Otovski breg – nitrate concentrations are higher in the case of high-resolution sampling, whereas the median nitrate concentration in Pački breg is the exception. Owing to their high solubility and mobility, nitrates respond far more quickly and strongly to changes in hydrologic conditions and land use (Hem, 19985). So, in karst aquifers, low-resolution monitoring of nitrates is unlikely to adequately characterize the system, especially during rainfall events (Pu et al., 2011).

To assess the possible hydrogeological connection between the studied springs, preliminary results of detailed geological mapping at a scale of 1:5000 were used (Mušič et al., 2023). These data show some inconsistencies with previous geological maps of the area (Bukovac et al., 1984a, 1984b; Šinigoj et al., 2012) in terms of stratigraphy and structural relationships between fault zones. Therefore, only field verified (Mušič et al., 2023) fault zones were included in our interpretation. Thus, the majority of the connections currently evaluated are based primarily on the hydrogeologic data collected. The basic hydrogeological characteristics of the Otovski breg are similar with that of Pački breg, as variations in nitrate concentrations in these two springs are similar over the entire observation period. The connection between Otovski breg and Pački breg has already been confirmed by previous tracer tests (Habič, 1991b). Although in Otovski breg and Jamnice only nitrate concentrations were monitored, a hydrogeological connection is also likely between the springs of Jamnice and Šotor. Nitrate concentrations fluctuate similarly in both springs and are low compared to the rest of the monitored springs. Comparisons of water levels, WLR, as well as nitrate concentrations in Šotor and Dobljičica springs also show

similar spring dynamics. The Obršec spring has its own smaller catchment area and reacts quickly to precipitation, which drains in the NNE–SSW oriented fault zone (Bukovac et al., 1984a, 1984b; Šinigoj et al., 2012; Mušič et al., 2023).

### Conclusion

The results of this study support the established knowledge of the dynamics that characterize the karst springs in Bela Krajina, habitat of the black and white olm, and help to reveal the main problems that affect its conservation status. In order to try and solve the problem of the decline of the olm, it was first necessary to assess the basic hydrogeological characteristics of the six observed springs west of Črnomelj in Bela krajina – the habitat of the black and white olm – and to determine whether there were any possible geological or hydrogeological connections between the observed springs.

Due to their different hydrogeological characteristics, the springs react to weather phenomena differently, but some, like Pački and Otovski breg, have very similar dynamics, as do the Šotor and Dobljica springs. In the next step we evaluated the potential critical factors and water-related parameters (nitrate concentration and temperature). The next step would require finding and specifically defining the causes or critical water parameters using quantified threshold values and to take appropriate measures to slow or even halt entirely the decline of the olm. Nitrate concentrations throughout most of the entire monitoring period exceed the maximum threshold in Otovski breg, Pački breg and Obršec, and occasionally also in Šotor and Jamnice. During July – August (2021), the water temperature of the springs exceeded 12 °C in all four of the monitored springs.

The comparison of high and low-resolution sampling indicates the importance of the high-resolution monitoring in karst areas, where the runoff and groundwater flow are much faster compared to the flow in the intergranular aquifer.

Further research is needed to constrain the hydrogeological parameters over longer periods and to supplement our data using additional springs in the area. Said detailed hydrogeological data should also be further supplemented with a new detailed geological map of the area. It is necessary to define the origin of nitrate (nitrate isotope analysis), quantify threshold values of the critical parameters, specifically define all the causes of olm deterioration, and make proposals for the appropriate measures to limit or even stop the olm population decrease.

### Authors contributions

The authors' contribution is as follows: Katja Koren and Rok Brajkovič contributed to the conceptualization, analysis of data, writing, and review of the article. Authors Manca Bajuk, Špela Vraničar, and Vesna Fabjan, who participated in the present research as a Citizen Science Team, contributed through field observations, measurements, sampling, and participated in the discussion of the measurements. All authors read and agreed to the published version of the manuscript.

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