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Data Article

Dataset on hydrogeochemical characteristics of spring and surface waters in the complex karst catchment area of Southern Dalmatia (Croatia) and Western Herzegovina (Bosnia and Herzegovina)

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ABSTRACT

Large and complex karst catchments, like the one in Southern Dalmatia (Croatia) and Western Herzegovina (Bosnia and Herzegovina), are fragile environments requiring careful protection and sustainable water resources management. Understanding the processes that influence karst aquifer water chemistry is essential for the effective protection of water quality and quantity, ensuring sustainable resource availability and minimizing vulnerability to contamination.

A hydrogeochemical dataset comprising over 30 groundwater (springs) and surface water samples, was collected in this cross-border catchment area from September 2013 to September 2020, accounting for seasonal variations. Parameters such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-} and SO_4^{2+} were analysed using atomic absorption, spectrophotometry and ion chromatography at the Croatian Geological Survey's Hydrochemical Laboratory. Alkalinity was measured through volumetric titration and in-situ pH, electrical conductivity

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(EC), and temperature (T) were measured using a multi-parameter probe.

Additionally, stable sulphur isotope 34 ($\delta^{34}S$) analysis was conducted on ten samples collected during two hydrological extremes (April and October 2019) using an IRMS analyser at the Jožef Stefan Institute in Slovenia.

These data provides a baseline assessment of the hydrogeochemistry of the area, facilitating research on isotope hydrology, particularly $\delta^{34}S$ studies. It could also be used in implementing measures to protect and safeguard groundwater, assess its vulnerability to contamination, and improve existing catchment recharge zones.

Specifications Table

Subject	Hydrogeology
Specific subject area	Surface water and groundwater (springs) hydrogeochemistry
Data format	Raw, Analysed
Type of data	Tables, Figures
Data collection	Data were obtained by analysing surface water and spring water samples collected at sampling points in the Southern Dalmatia and Western Herzegovina cross-border karst catchment. The geographical coordinates of the sampling locations were determined using the Global Positioning System (Garmin Montana 680t). Physico-chemical parameters (EC, T, pH, O_2), ion concentrations and stable sulphur isotope 34 ($\delta^{34}S$) concentrations were observed. EC, T, pH and O_2 were measured at all sampling sites with WTW probes. Atomic absorption, ion chromatography and spectrophotometry were used to identify the major ions, including Na^+, Ca^{2+}, Mg^{2+}, Cl^-, K^+, SO_4^{2+} and NO_3^-, at the Croatian Geological Survey laboratory. Titration method was used to identify HCO_3^- ions *in situ*. $\delta^{34}S$ were analysed at the Josef Stefan institute in Slovenia using the Isoprime 100 with a Pyro Cube elemental analyser.
Data source location	Institution: Croatian Geological Survey City / Town / Region: Southern Dalmatia and Western Herzegovina Country: Croatia and Bosnia and Herzegovina Latitude and longitude (GPS coordinates) for collected samples/data: Doljanka 43.719063, 17.592107; Donja voda 43.484515, 17.369967; Blidinje lake 43.607357, 17.503754; Lištica – Borak 43.395448, 17.595487, Opačac 43.450825, 17.176077; Grudsko vrelo 43.389613, 17.368004, Vrelo Tihaljine 43.336623, 17.323943; Klokun BiH 43.28158, 17.429162; Vrioštica – Vitina 43.237789, 17.48579; Krenica 43.218729, 17.387174; Banja 43.220211, 17.368822; Nuga 43.179017, 17.351056; Butina 43.177204, 17.407659; Stinjevac 43.174555, 17.418144; Lukavac 43.169273, 17.431179; Staševica 43.139093, 17.429619; Klokun 43.070887, 17.434767; Mandina mlinica 43.084582, 17.360972; Mandina mlinica spring 43.08503, 17.361313; Čeveljuša 43.053893, 17.463832; Strimen 43.062713, 17.526167; Modro oko 43.057512, 17.510708; Prud 43.095055, 17.619605; Tunnel – T2 43.082717, 17.43357; Crniševo lake 43.0732, 17.408038; Oćuša lake 43.079492, 17.421557; Oćuša spring 43.085336, 17.425892; Mindel 43.079595, 17.406408; Tunnel – T3 43.069437, 17.423752; Neretva River 43.054814, 17.648975
Data accessibility	Repository name: Mendeley Data Data identification number: 10.17632/rhbfrfvrmm.3 Direct URL to data: https://data.mendeley.com/datasets/rhbfrfvrmm/3
Related research article	M. Filipović, J. Terzić, J. Lukač Reberski, I. Vlahović: Utilizing a multi-tracer method to investigate sulphate contamination: Novel insights on hydrogeochemical characteristics of groundwater in intricate karst systems. Groundwater for Sustainable Development. 10.1016/j.gsd.2024.101350

1. Value of the Data

- Measurements of ion concentrations are valuable for comprehending and managing the hydrogeochemical properties of both spring water and surface water in a complex karst catchment dealing with elevated Ca^{2+}, Na^{+}, Cl^{-}, HCO_3^{-} and SO_4^{2-} concentrations in different parts of the aquifer.
- Physico-chemical data offer valuable insights into the dynamics of both spring water and surface water as well as the inherent characteristics of the aquifer.
- Stable sulphur isotope 34 data ($\delta^{34}S$) as a natural tracer can offer insights into catchment recharge zones, groundwater mixing processes, and the origin of sulphates in water. Presented data, particularly $\delta^{34}S$, may be important for other researchers dealing with hydrogeochemistry of complex karst systems and isotope hydrology.
- The dataset can serve as an input for enhancing measures to protect and safeguard groundwater, identifying contaminant sources, and forming the basis for the improvement of sanitary zone delineation.
- Due to the extensive datasets, various statistical methods — such as factor analysis, principal component analysis, and multivariate analyses — can be utilized to better showcase the functioning of the catchment and its recharge areas.

2. Background

Elevated sulphate ion concentrations are present in the water of Southern Dalmatia and Western Herzegovina catchment area, as indicated by previous studies [1–7]. However, there is a notable absence of data on stable sulphur isotope ($\delta^{34}S$) analysis in this catchment, thus prompting this research. The purpose of this study was to determine the origin and age of sulphate ions in the water, employing natural tracer methods such as stable $\delta^{34}S$ isotope analysis of groundwater (springs) and surface water. Furthermore, physico-chemical parameters and hydrogeochemical ion data analyses enabled the assessment of drainage structures, transit times, and recharge processes within the complex karst flow system (*cf.* [8–12]). Moreover, data used for aquifer characterisation contributed to a more efficient interpretation of the $\delta^{34}S$ isotopes.

3. Data Description

The sampling locations chosen within the complex karst catchment area of Southern Dalmatia and Western Herzegovina are shown in Fig. 1, while their coordinates (in WGS84) are given in Table 1. Two additional sampling locations, Doljanka and Blidinje lake, are outside the catchment area boundaries.

The dataset consisting of 30 tables in the “ions worksheet” and two tables in the “sulphur worksheet” is available within the article. The first worksheet presents the monitoring of ion and physico-chemical parameters in groundwater (springs) and surface water. The monitoring period spanned from September 25, 2013, to September 30, 2020, with samples collected on an approximately monthly basis, except from December 10, 2014, to November 30, 2017, during which they were collected quarterly. The sampling campaigns occurred on the following dates: September 25, 2013 to March 8, 2016; November 29, 2017 to August 28, 2018; and September 25, 2018 to September 30, 2020. Sampling in Western Herzegovina was impossible from February 26, 2020, to August 25, 2020, due to the COVID-19 pandemic.

The second worksheet presents two additional sampling campaigns involving stable sulphur isotope analysis. In April 2019 eight groundwater (springs) and one surface water samples were collected, and in October 2019 an additional seawater sample was included in the analysis.

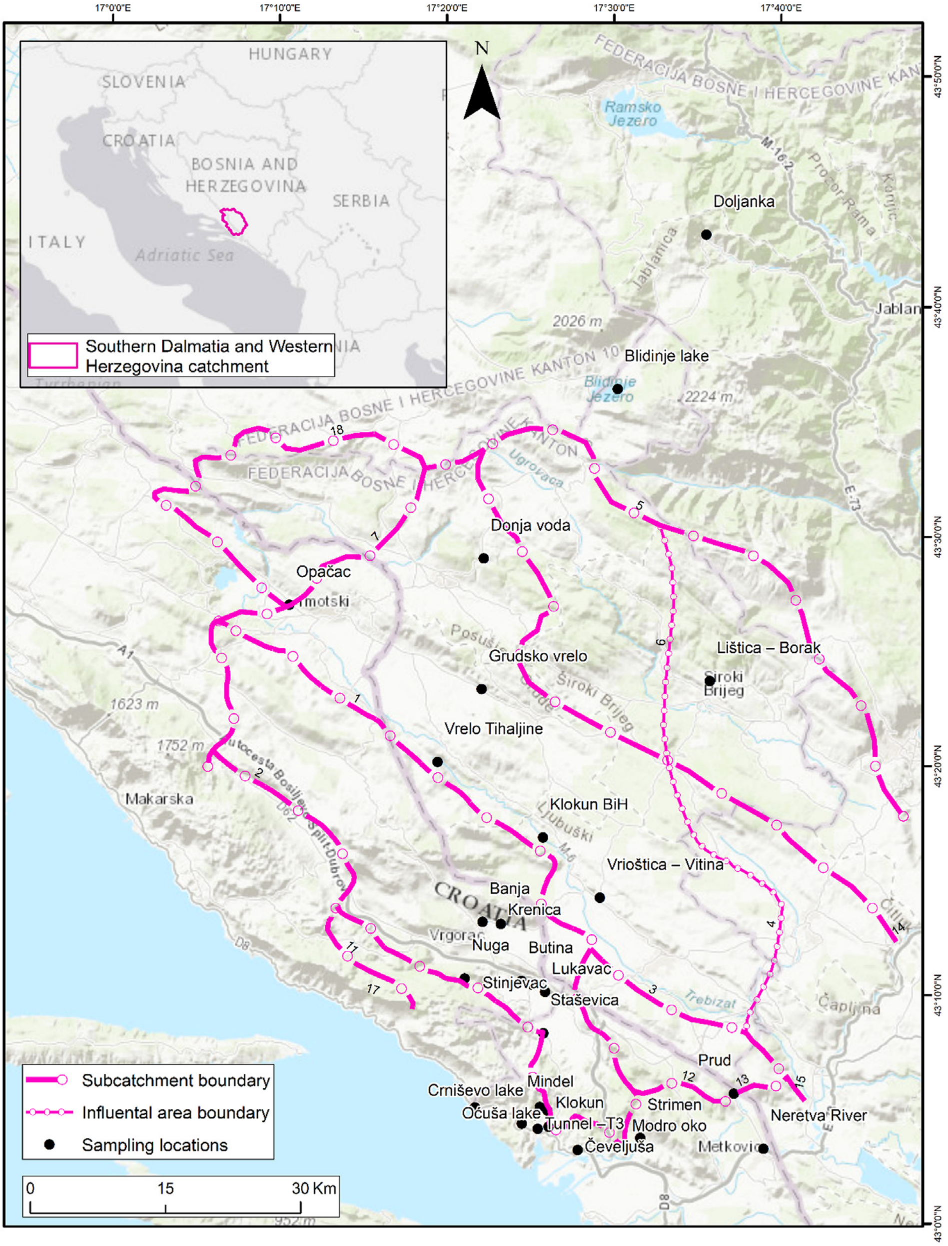

Fig. 1. Sampling locations and boundaries of the complex karst catchment area of Southern Dalmatia and Western Herzegovina.

Table 1
Locations names, sampling campaigns periods, and the corresponding latitude and longitude for the collected samples of the complex karst catchment area of Southern Dalmatia and Western Herzegovina.

Sampling location	Description	$\delta^{34}S$	Latitude N	Longitude E	Elevation
Doljanka	Surface water	+	43.719063	17.592107	950
Donja voda	Spring	+	43.484515	17.369967	888
Blidinje lake	Surface water	–	43.607357	17.503754	1183
Lištica – Borak	Spring	+	43.395448	17.595487	271
Opačac	Spring	–	43.450825	17.176077	273
Grudsko vrelo	Spring	+	43.389613	17.368004	365
Vrelo Tihaljine	Spring	–	43.336623	17.323943	138
Klokun BiH	Spring	+	43.28158	17.429162	110
Vrioštica – Vitina	Spring	+	43.237789	17.48579	84
Krenica	Intermittent spring	–	43.218729	17.387174	62
Banja	Intermittent spring	–	43.220211	17.368822	26
Nuga	Estavelle	–	43.179017	17.351056	30
Butina	Spring	+	43.177204	17.407659	30
Stinjevac	Spring	–	43.174555	17.418144	34
Lukavac	Spring	–	43.169273	17.431179	28
Staševica	Spring	–	43.139093	17.429619	26
Klokun	Spring	–	43.070887	17.434767	2
Mandina mlinica	Spring	–	43.084582	17.360972	5
Mandina mlinica spring	Spring	+	43.08503	17.361313	10
Čeveljuša	Spring	–	43.053893	17.463832	1
Strimen	Spring	–	43.062713	17.526167	2
Modro oko	Spring	–	43.057512	17.510708	10
Prud	Spring	+	43.095055	17.619605	4
Tunnel – T2	Surface water	–	43.082717	17.43357	3
Crniševo lake	Surface water	–	43.0732	17.408038	65
Oćuša lake	Surface water	–	43.079492	17.421557	0
Oćuša spring	Spring	–	43.085336	17.425892	0
Mindel	Spring	–	43.079595	17.406408	1
Tunnel – T3	Surface water	–	43.069437	17.423752	1
Neretva River	Surface water	–	43.054814	17.648975	3

4. Experimental Design, Materials and Methods

4.1. Sample collection

To capture all hydrological conditions, monthly monitoring was conducted over a six-year period at 30 locations. Water samples for anion and cation analysis were collected directly from karst springs and surface water, except at the two lake locations where samples were collected at specific depths (Oćuša lake at 8 and 17 m, Crniševo Lake at 3, 11, 17, and 23 m). Sampling at the lakes was done using an Eijkelkamp Teflon sampler with 35 mm diameter and 0.69 l volume. Sampling equipment and bottles were rinsed with sample water before collecting the actual samples, which were then stored in 50 mL PE bottles. To remove particulate matter, cation samples were filtered using 0.45 µm CA filters and acidified with nitric acid (65 %) (method after [12]). No chemicals were added to samples for determination of anions. Samples were transported in a field refrigerator, stored in the dark at +8 °C, and analysed within one week. A Global Positioning System (GPS, GARMIN MONTANA 680t) was used to record the latitude and longitude of sampling locations, and a field report with photographs was prepared during each field trip.

Alkalinity was determined for all samples through volumetric titration with 1.6 N H_2SO_4 to reach a pH of 4.5, utilizing an HACH titrator. Furthermore, the same person conducted the sampling, adhering to protocols for sample collection and transport to avoid data inaccuracies.

Physico-chemical parameters were determined *in situ*. Temperature (T), electrical conductivity (EC), dissolved oxygen (O_2) and pH were measured using a WTW Multi probe and a multiparameter depth probe SEBA KLL-Q2-D8 with 200 m range in Oćuša and Crniševo lakes.

Samples for $\delta^{34}S$ were filtered using 0.45 µm CA filters and stored in 500 mL to 3 l PE bottles, depending on the SO_4^{2-} concentration. Samples were also stored in a field refrigerator.

4.2. Analytical methods

The major cations and anions were analyzed using standard procedures [13]. Concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, NO_3^- and Cl^- ions were determined at the Hydrochemical Laboratory of the Croatian Geological Survey. Due to the significantly long duration of measurements and sampling, the methodology employed in laboratory analyses underwent modifications with the procurement of newer and more advanced instruments. Therefore, three data sets are distinguished, as presented in Table 2.

Table 2
Sampling methods.

Date	Method – cations	Method – anions
25.9.2013.–8.3.2016.	Atomic absorption	Ion chromatography
29.11.2017.–28.8.2018.	Atomic absorption	Spectrophotometry
25.9.2018.–30.9.2020.	Ion chromatography	Ion chromatography

In the first and second campaign cations were determined using atomic absorption spectrophotometer (AAS; model Analyst 700, PerkinElmer Inc., Shelton, USA). AAS is an analytical technique for determining elements, compounds, and mixtures in water, soil, and sediment samples [14,15]. The method is based on the fact that compounds undergo dissociation through thermal means and the analysed atom is converted into a non-ionised and unexcited state (it has to be atomised). The water sample is introduced into an atomizer, usually a flame that converts compounds to their elemental form (converted into a plasma). Monochromatic light of a specific wavelength corresponding to the resonance line of an individual element is passed through the plasma, and atoms absorb the resonant wavelength, which is then detected.

In the first campaign anions were analysed using ion chromatography LabAlliance apparatus, while in the third campaign both cations and anions were analysed with ion chromatography Thermo Scientific Dionex ICS-6000 HPIC System. Ion chromatography is an analytical technique used for determining a mixture of anions and cations, often employed for assessing the chemical composition and quality control of water [12]. Its main advantage lies in its high speed, sensitivity, and precision of analysis, requiring only a very small quantity of water sample (approximately 6 mL). The technique itself is based on separating components by elution on synthetic ion exchange columns, followed by the detection of the analysed ions using a suitable detector, commonly a conductivity meter.

During the second campaign anions were analysed with spectrophotometry method using the HACH DR 9000 apparatus, which utilizes visible radiation separated into components to create a spectrum of different wavelengths. Qualitative spectrophotometry is based on the dependence of absorbance on wavelength, and by measuring the absorbance value at a specific wavelength; on the basis of that it is possible to identify the absorbing substance.

In this paper, raw data is presented, whereas in the analysis conducted in paper [16], only data demonstrating the reliability of the results—determined by the ionic balance of groundwater and surface water samples within an acceptable error range of 5–10 %—was shown.

Stable sulphur isotope concentrations ($\delta^{34}S$) in water samples were determined using IRMS Isoprime 100 with a Pyro Cube elemental analyser at the Jožef Stefan Institute in Ljubljana, Slovenia. The samples underwent a series of steps: they were filtered through a glass filter (GFF), acidified to achieve a pH <2, and then treated with an appropriate amount of 10 % $BaCl_2$ solution to precipitate all dissolved sulphates as $BaSO_4$ [17]. The precipitated $BaSO_4$ was then rinsed with water, filtrated through a 0.45 µm diameter membrane filter and dried in an oven at 50 °C. Prior to measurement, a method for the conversion of SO_4 to SO_2 included addition of 1 mg of tungsten oxide (WO_3) to the samples to determine the $^{34}S/^{32}S$ ratio [18]. Calibration against the VCDT standard was achieved using certified reference materials, namely NBS-127 ($\delta^{34}S = +20.3$ ‰ VCDT) and IAEASO6 ($\delta^{34}S = -34.1$ ‰ VCDT), while certified material NBS 123 was used for result accuracy control. The precision of the measurements was maintained within ± 0.3 ‰.

Results were reported using δ notation ($\delta^{34}S$ with respect to VCDT), representing the ratios difference in per mil between the heavier and lighter isotopes in the sample ($^{34}S/^{32}S$ sample) and the heavier and lighter isotopes in the standard ($^{34}S/^{32}S$ standard) [19].

Sulphur has several stable isotopes, with the most abundant being ^{32}S (95 %) and ^{34}S (4 %). The relationship between these two isotopes can be expressed by the formula:

$$\delta^{34}S = \left[\left(\left({}^{34}S/{}^{32}S\right)_{\text{sample}}/\left({}^{34}S/{}^{34}S\right)_{\text{VCDT standard}}\right) - 1\right] \times 1000[‰]$$

where $\delta^{34}S$ is the difference between the ratios of the heavier (^{34}S) and lighter (^{32}S) sulphur isotopes in the sample and the standard, expressed in per mil (‰). The standard is defined according to the Vienna Cañon Diablo Troilite (VCDT), representing the composition of a meteorite found in Arizona. The $\delta^{34}S$ value of the meteorite varies very slightly and is around 0 ‰.

Limitations

Sampling was not possible from February 26th 2020, to August 25th 2020, due to the COVID-19 pandemic restrictions.

Ethics Statement

The authors have read and follow the ethical requirements for publication in Data in Brief. The current dataset does not involve studies with animals and humans.

CRediT Author Statement

Marina Filipović: Conceptualisation, Methodology, Data curation, Writing – original draft, Visualization, Investigation. **Josip Terzić:** Supervision, Writing – review & editing. **Jasmina Lukač Reberski:** Investigation, Writing – review & editing. **Igor Vlahović:** Writing – review & editing.

Data Availability

Hydrogeology data_Southern Dalmatia and Western Herzegovina (Original data) (Mendeley Data).

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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