





## HYDROCHEMICAL CHARACTERIZATION AND INTEGRATED WATER QUALITY ASSESSMENT OF TRANSBOUNDARY KARST SPRINGS IN THE ALBANIAN ALPS (ALBANIA–MONTENEGRO)

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### ABSTRACT

This study investigates the hydrochemical characteristics and water quality of transboundary karst springs located in the Albanian Alps along the Albania–Montenegro border. Eleven representative springs were sampled and analyzed for 26 physical, chemical, and trace-element parameters during two sampling campaigns conducted in November 2024 (high-flow conditions) and June 2025 (dry season period). The investigated springs are associated with carbonate formations of Triassic, Jurassic, and Cretaceous age, forming highly karstified aquifers characterized by high permeability and rapid groundwater circulation. The hydrochemical composition of the springs was evaluated using major ion analysis, hydrochemical diagrams, and two widely applied water quality indices: the Water Quality Index (WQI) and the Heavy Metal Pollution Index (HPI). Spring discharges range from less than 1 l/s to several tens of liters per second, reflecting the heterogeneity of the karst aquifer systems. Results indicate that most springs are dominated by calcium-bicarbonate hydrochemical facies typical of carbonate aquifers. The calculated WQI values classify the majority of the springs as having excellent to good water quality for drinking purposes, while HPI values indicate minimal heavy metal contamination. The high-water quality observed in the study area is primarily related to the dominance of carbonate aquifers, limited anthropogenic pressure, and the progressive depopulation of rural mountainous areas. However, increasing tourism activity highlights the need for sustainable groundwater management, particularly in a transboundary context. The findings provide valuable baseline data and contribute to improved understanding, monitoring, and joint management of transboundary groundwater resources in the Albanian Alps within the broader Dinaric karst region.

**Keywords:** Karst hydrogeology; Transboundary aquifer; Groundwater quality; WQI; HPI; Cemi/Cijevna basin; Monitoring network.

### 1. INTRODUCTION

The protection and sustainable management of groundwater resources in karst environments represent a major challenge, particularly in transboundary regions where water systems extend across national borders (Ford & Williams, 2007; White & White, 1989). Albanian Alps, part of the Dinaric karst, one of the most extensive karst systems in Europe, are characterized by highly permeable carbonate formations, complex underground drainage networks and strong interactions between surface and groundwater (DIKTAS Project, 2015; Stevanović et al., 2016).

In this context, the Cem (Cijevna) River basin constitutes a typical transboundary karst system shared between Albania and Montenegro. The basin is dominated by Mesozoic carbonate formations,

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mainly limestones and dolomites, which form highly karstified aquifers with rapid groundwater circulation and high infiltration capacity (Domenico & Schwartz, 1998; Ford & Williams, 2007). These characteristics make the system particularly vulnerable to environmental pressures, but also highly important as a freshwater resource (Chaudhari et al., 2024).

Despite the recognized hydrogeological importance of the basin, previous studies have mainly focused on hydrology, basin management and environmental assessment, while detailed hydrochemical investigations of karst springs remain limited. In particular, there is a lack of comprehensive studies that combine physico-chemical analysis, heavy metal assessment and quantitative evaluation of water quality using integrated indices.

At the same time, the study area has undergone significant socio-economic changes during the last decades. Rural depopulation has led to a substantial decrease in traditional agricultural activities and livestock pressure, which may have contributed to the preservation of groundwater quality. Conversely, the rapid growth of tourism in the Albanian Alps introduces new potential pressures on fragile karst water systems, highlighting the need for systematic monitoring and assessment.

This study aims to evaluate the hydrochemical characteristics and water quality of karst springs located in the transboundary Cem/Cijevna basin along the Albania-Montenegro border. A total of 11 representative springs were analyzed for 26 physical, chemical and trace element parameters. Water quality was assessed using the Water Quality Index (WQI) and the Heavy Metal Pollution Index (HPI), while hydrochemical processes were interpreted through major ion analysis and hydrogeological context (Shanmugasundharam et al., 2023).

The results of this study provide new insights into the functioning of transboundary karst aquifers and contribute to the scientific basis for sustainable groundwater management in the Dinaric region.

## 2. STUDY AREA

The study area is located in the northern part of Albania, within the Albanian Alps (Prokletije Mountains), and forms part of the transboundary Cemi/Cijevna River basin shared between Albania and Montenegro. The investigated sector corresponds to the upstream mountainous portion of the basin, where a series of karst springs emerge and represent key groundwater discharge points.

The basin is characterized by rugged mountainous terrain with strong altitudinal contrasts and deeply incised valleys. The hydrographic network is dominated by the Cemi/Cijevna River and its tributaries, which originate in the Albanian territory and flow towards Montenegro, where they join the Morača River system. The geomorphology of the area is closely controlled by tectonic structures and intensive karst processes that have shaped the landscape. From a geological perspective, the study area is dominated by Mesozoic carbonate formations, mainly limestones and dolomites of Triassic, Jurassic and Cretaceous age. These formations are strongly fractured and exhibit a high degree of karstification. As a result, the aquifer system is characterized by very high permeability, allowing rapid infiltration and groundwater circulation through fissures, conduits and karst channels.

Karstification is particularly well developed along river valleys and structural zones, where dissolution processes have created an interconnected network of underground flow paths. In these conditions, infiltration rates are very high and a significant proportion of precipitation contributes directly to groundwater recharge. Surface runoff is therefore limited, while subsurface flow dominates the hydrological regime.

All investigated springs are associated with carbonate aquifers and emerge either directly from exposed limestone formations or from zones with a very thin eluvial cover. Most springs are characterized by direct discharge from karstified limestone, indicating minimal natural protection from surface contamination. Only a limited number of springs show a partial cover of unconsolidated deposits, which may locally influence infiltration processes. The springs are mainly located along valley bottoms, structural contacts and zones where the piezometric surface intersects the topography (**Fig. 1**). Their discharge varies significantly, ranging from very small local springs used by rural communities to larger karst springs with higher and higher discharge. This variability reflects the heterogeneity of the karst aquifer system and the complexity of groundwater flow paths.

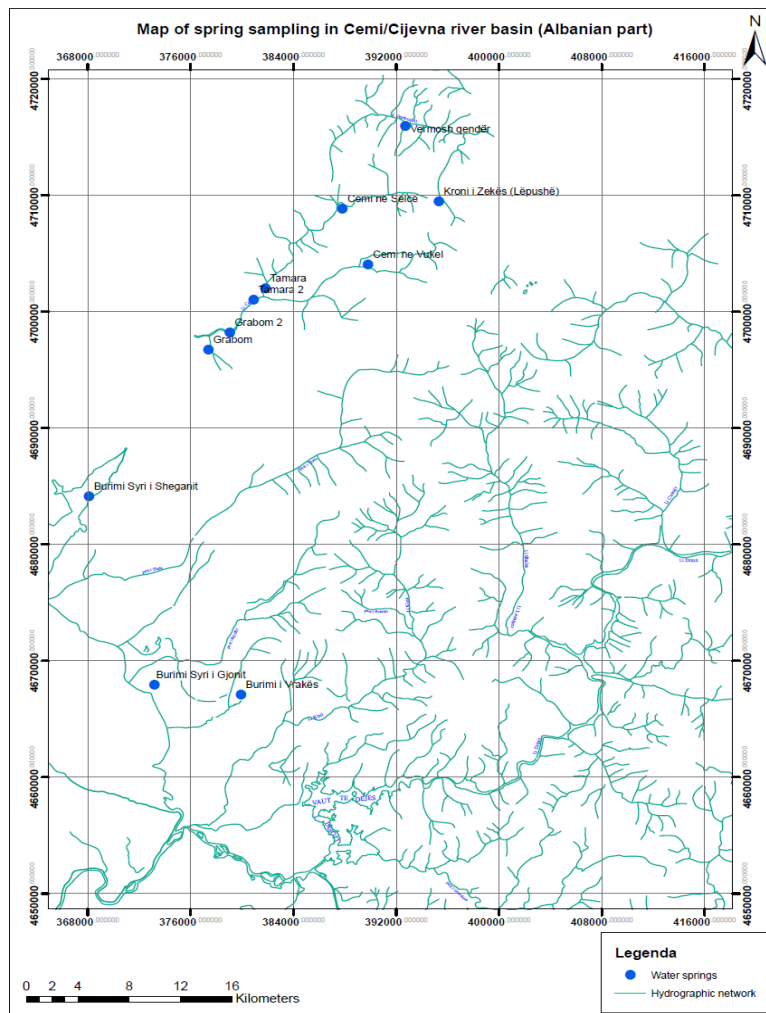


Fig. 1. The map of spring sampling - Cemi/Cijevna river basin catchment.

An important characteristic of the study area is the relatively low level of anthropogenic pressure. During the last 10-15 years, many rural settlements in the Albanian Alps have been partially or completely abandoned, leading to a decrease in agricultural activities and livestock pressure. This has likely contributed to the preservation of groundwater quality. However, in recent years the region has experienced a noticeable increase in tourism, which may introduce new environmental pressures, particularly in sensitive karst environments.

The hydrogeological system of the Cem/Cijevna basin is therefore controlled by the interaction of highly karstified carbonate formations, tectonic structures and climatic conditions. This results in a dynamic groundwater system characterized by rapid recharge, short residence times and strong connectivity between surface and groundwater, which has important implications for both water quality and resource management in this transboundary basin. The hydrogeological behavior of the study area is strongly controlled by karstified carbonate formations, which allow rapid infiltration and complex subsurface flow paths. In such environments, groundwater divides rarely coincide with surface watershed boundaries. In the Cemi/Cijevna basin, the spatial distribution of springs suggests a hydrogeological system extending beyond the topographic catchment. This interpretation is consistent with regional tectonic structures controlling groundwater flow.

Field observations indicate the possibility of localized river water losses, particularly along the Tamarë-Grabom segment. However, this hypothesis remains unconfirmed due to the lack of tracer tests and continuous monitoring data. Given the transboundary nature of the system, such interpretations must be approached with caution.

The proposed monitoring network represents a critical step toward reducing hydrogeological uncertainty. It includes monitoring wells, hydrological stations, and isotopic measurements, enabling a better understanding of groundwater flow dynamics and potential hydraulic connections between Albania and Montenegro. In addition, recent socio-economic changes, including rural depopulation and increasing tourism, may influence future water use and quality, highlighting the need for sustainable management strategies. The spatial distribution of sampling points covers the extended basin, including springs with varying discharge rates and elevations. The geological setting is dominated by kastic limestone and dolomite, which strongly influence groundwater chemistry through dissolution processes.

### 3. DATA AND METHODS

#### 3.1. Sampling design and timeframe

Groundwater samples were collected during two distinct field campaigns: (i) November 2024, representing high-flow conditions in springs hydraulically connected to high-altitude recharge zones of the Albanian Alps, and (ii) June 2025, representing dry-season conditions. Three springs (Syri i Sheganit, Syri i Gjonit, and Vraka spring) were sampled during the November 2024 campaign, while the remaining springs were sampled in June 2025. These two campaigns capture contrasting hydrological conditions (low-flow vs. dry season), providing a representative snapshot of the hydrochemical variability of the investigated karst systems. Although continuous seasonal monitoring was not conducted, the selected periods allow for a preliminary assessment of hydrochemical stability and variability.

Sampling locations were selected to represent the main transboundary karst systems along the Albania–Montenegro border, taking into account geological structure, discharge variability, and accessibility, while also ensuring that samples reflect natural hydrochemical conditions.

All samples were collected directly at spring outlets, avoiding areas potentially affected by surface contamination such as livestock shelters, tourist paths, or surface runoff accumulation zones. The sampling network includes both high-discharge karst springs and smaller local springs that are directly used by rural communities and livestock. Although some springs exhibit relatively low discharge, they were intentionally included due to their socio-economic importance as local drinking water sources.

#### 3.2. Standard analytical procedures

All samples were analyzed at the ALPHA Studio laboratory following standard analytical procedures. Quality assurance and quality control (QA/QC) measures included calibration using certified reference standards, duplicate analyses, and ionic balance error verification to ensure analytical reliability.

All concentrations were initially expressed in mg/l and subsequently converted into meq/l and meq%. These conversions are presented in the respective **Tables 1-3** and are essential for hydrochemical interpretation. Hydrochemical analysis included:

Major ions:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$

Heavy metals: Fe, Mn, Pb, As, Cr (VI), Co.

This approach ensures that the obtained data reflect the intrinsic hydrochemical characteristics of the karst aquifer system rather than localized external impacts.

Table 1.

## Physical and general parameters.

Category	Parameter	Unit
Physical parameters	pH	–
	Electrical conductivity (EC)	µS/cm
	Total dissolved solids (TDS)	mg/l
	Dissolved oxygen (DO)	mg/l
	Organic matter	mg/l
Major cations	Calcium (Ca <sup>2+</sup> )	mg/l
	Magnesium (Mg <sup>2+</sup> )	mg/l
	Sodium (Na <sup>+</sup> )	mg/l
	Potassium (K <sup>+</sup> )	mg/l
Major anions	Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	mg/l
	Sulfate (SO <sub>4</sub> <sup>2-</sup> )	mg/l
	Chloride (Cl <sup>-</sup> )	mg/l
	Nitrate (NO <sub>3</sub> <sup>-</sup> )	mg/l
	Nitrite (NO <sub>2</sub> <sup>-</sup> )	mg/l
	Ammonium (NH <sub>4</sub> <sup>+</sup> )	mg/l
	Phosphate (PO <sub>4</sub> <sup>3-</sup> )	mg/l
	Fluoride (F <sup>-</sup> )	mg/l
Hydrochemical parameters	Total hardness	mg/l as CaCO <sub>3</sub>
	Total mineralization	mg/l
Trace elements (heavy metals)	Iron (Fe)	µg/l
	Manganese (Mn)	µg/l
	Lead (Pb)	µg/l

Table 2.

## Springs and analyses expressed in meq/l.

Sample	Ca meqL	Mg meqL	Na+K meqL	HCO <sub>3</sub> meqL	SO <sub>4</sub> meqL	Cl meqL
1. Grabom	1.99	0.98	0.15	2.86	0.07	0.2
2. Grabom 2	2.39	0.69	0.12	2.45	0.00	0.08
3. Tamara	2.79	0.39	0.14	2.54	0.00	0.06
4. Tamara 2	2.54	0.88	0.12	2.45	0.01	0.15
5. Vermosh Q.	2.29	1.67	0.20	2.70	0.13	0.11
6. Kroni i Zekës	1.59	0.79	0.11	2.45	0.05	0.09
7. Cemi Selcë	1.99	0.49	0.10	1.96	0.00	0.11
8. Cemi Vukël	2.09	0.29	0.09	1.96	0.00	0.08
9. Vrakë	1.99	0.19	0.10	1.76	0.02	0.13
10. Syri i Sheganit	1.99	0.59	0.11	2.13	0.00	0.15
11. Syri i Gjonit	1.79	0.593	0.09	1.83	0.02	0.13

Table 3.

## Physico-chemical characteristics.

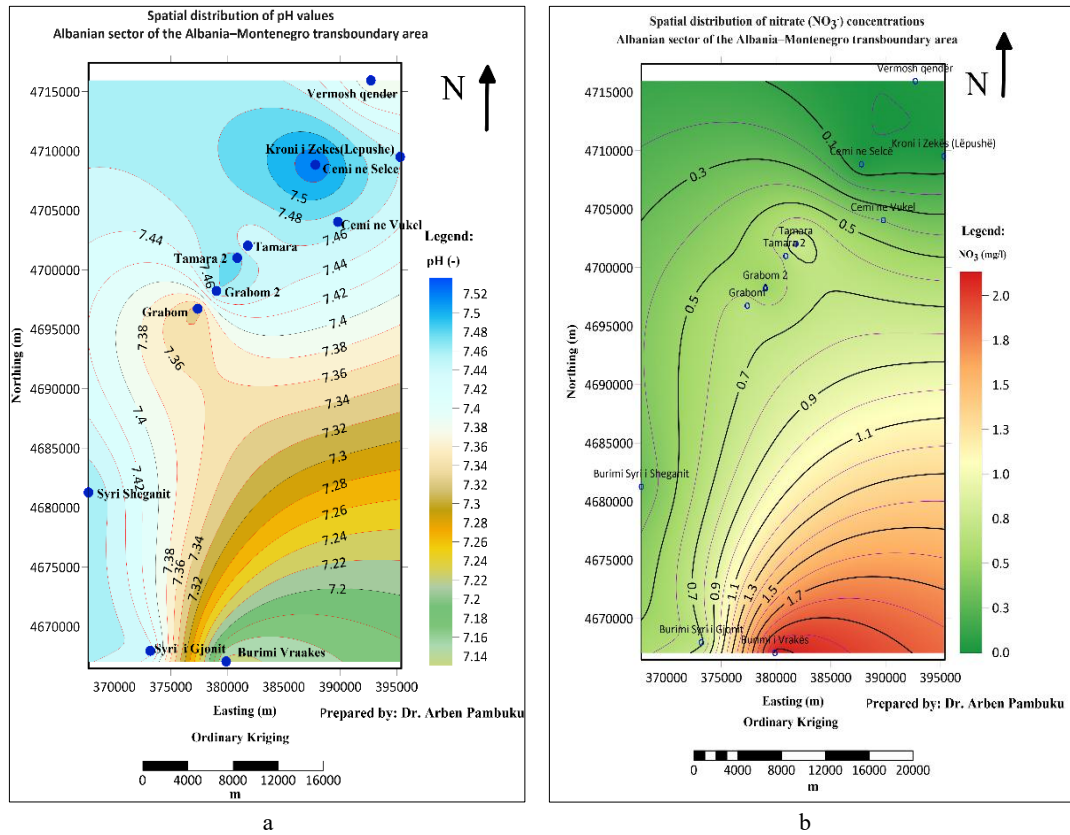
Sample	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	HCO <sub>3</sub> mg/l	SO <sub>4</sub> mg/l	Cl mg/l
1. Grabom	40	12.0	3.51	0.15	175	3.62	7.09
2. Grabom 2	48	8.40	2.66	0.27	150	0.38	2.84
3. Tamara	56	4.80	3.13	0.26	155	0.31	2.13
4. Tamara 2	51	10.80	2.87	0.18	150	0.50	5.67
5. Vermosh Q.	46	20.40	4.06	0.93	165	6.31	3.97
6. Kroni i Zekës	32	9.60	2.49	0.18	150	2.50	3.54
7. Cemi Selcë	40	6.00	2.47	0.05	120	0.44	4.25
8. Cemi Vukël	42	3.60	2.14	0.04	120	0.37	2.84
9. Vrakë	40	2.40	2.15	0.38	108	1.30	4.96
10. Syri i Sheganit	40	7.20	2.34	0.52	130	0.20	5.67
11. Syri i Gjonit	36	7.20	1.95	0.42	112	1.20	4.96

## 4. RESULTS

### 4.1. The physico-chemical characteristics

The physico-chemical characteristics of the investigated springs show a consistent hydrochemical behavior typical of groundwater circulating within carbonate karst systems.

The measured pH values range between 7.3 and 7.5, indicating neutral to slightly alkaline conditions. This reflects a well-buffered hydrochemical system controlled by carbonate equilibria, particularly the interaction between dissolved carbon dioxide and carbonate minerals. Such conditions are characteristic of groundwater circulating in limestone and dolomite formations (**Fig. 2a**).



**Fig. 2.** Spatial distribution of:

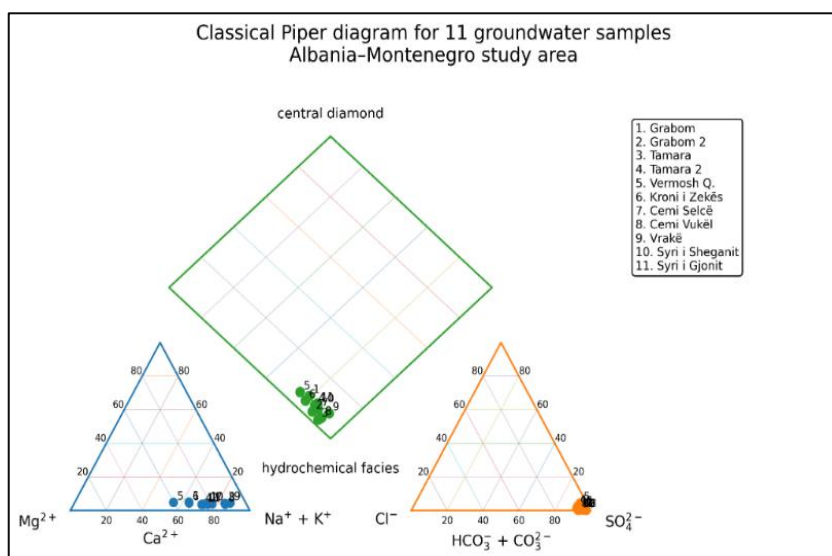
- groundwater pH values in the Albanian Alps (Albania–Montenegro transboundary area), interpolated using the Ordinary Kriging method based on point measurements from groundwater sources (WGS 1984 / UTM Zone 34N), indicating predominantly neutral to slightly alkaline conditions controlled by lithological and hydrogeological settings;
- nitrate ( $\text{NO}_3^-$ ) concentrations in groundwater across the same area and projection, derived from measured values using the same interpolation approach, showing generally low levels and suggesting limited anthropogenic impact and good groundwater quality.

Electrical conductivity values generally range from approximately 250 to 300  $\mu\text{S}/\text{cm}$ , while total dissolved solids (TDS) vary between about 120 and 200 mg/l. These relatively low values indicate limited mineralization and confirm that the investigated waters belong to fresh groundwater systems. The low mineralization is consistent with rapid groundwater circulation and limited residence time within the aquifer. Dissolved oxygen concentrations are relatively high, typically between 9 and 10 mg/l, suggesting active recharge conditions and rapid infiltration processes. This is a typical feature of karst systems, where water infiltrates quickly through fractures and conduits, maintaining high oxygen levels.

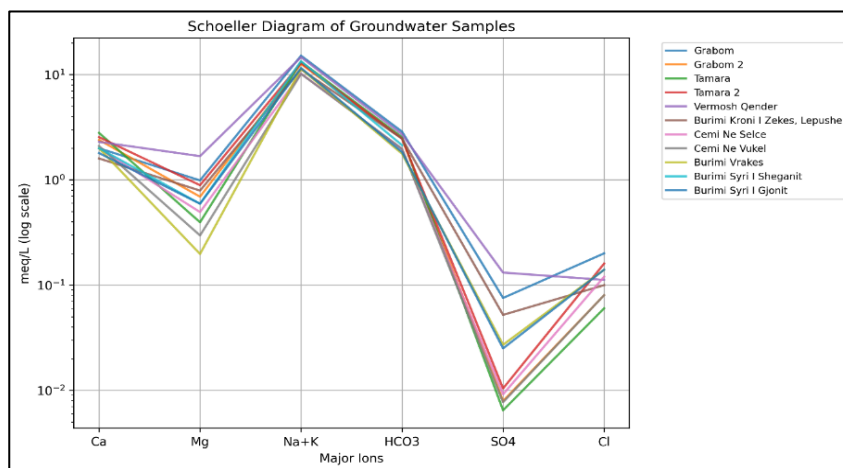
Nutrient concentrations ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ ) are generally very low across all sampling points (**Tab. 1-3**). This indicates the absence of significant anthropogenic contamination sources such as agriculture or wastewater infiltration, and reflects the relatively preserved environmental conditions of the study area. The concentration of  $\text{NO}_3^-$ -N (**Fig. 2b**), commonly derived from agricultural runoff and human activities, serves as a significant indicator of nutrient pollution, which can result in eutrophication (Dewata et al., 2025).

#### 4.2. The hydrochemical diagrams and interpretation

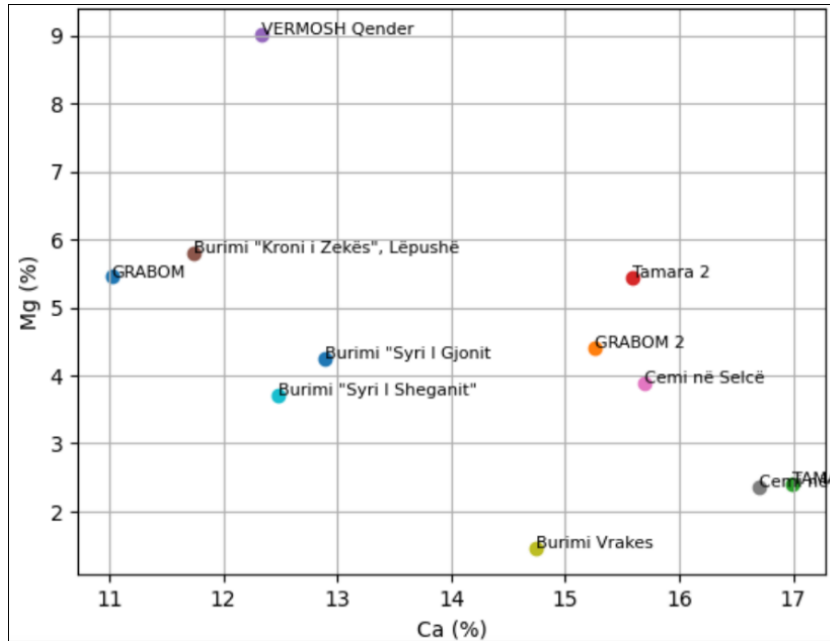
The hydrochemical characterization of groundwater was performed using three complementary diagrams: the Piper diagram (**Fig. 3**) as the primary classification tool, the Schoeller diagram (**Fig. 4**) for comparative analysis of major ions, and the Chadha diagram (**Fig. 5**) for validation of hydrochemical facies.



**Fig. 3.** Hydrochemical characterization based on the Piper diagram.



**Fig. 4.** Hydrochemical characterization based on the Schoeller Diagram.



**Fig. 5.** Chadha diagram – validation.

These diagrams are complementary and together provide a robust interpretation of hydrochemical processes. The hydrochemical signature observed in the Piper diagram is consistent with the geological context of the Albania-Montenegro border region, which is largely dominated by carbonate formations. Similar hydrochemical patterns have been reported in recent studies of karst aquifers, where carbonate dissolution dominates groundwater chemistry (Gu et al., 2021), (Zhang et al., 2023).

The prevalence of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  ions indicates intensive water–rock interaction, dissolution of calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) (Appelo & Postma, 2004; Drever, 1997). This hydrochemical signature is typical for groundwater circulating in carbonate aquifers and reflects equilibrium processes between  $\text{CO}_2$ , water and carbonate minerals (Hem, 1985; Plummer et al., 1978). This suggests that groundwater circulation occurs mainly through karstic and carbonate aquifers, with relatively short to moderate residence times. The Piper diagram (Fig. 3) is widely used as a standard tool for hydrochemical classification of groundwater (“A Graphic Procedure in the Geochemical Interpretation of Water-analyses,” 1944) and confirms that all samples fall within the Ca– $\text{HCO}_3$  facies.

To further interpret the hydrochemical characteristics of the groundwater system, Scholler and Chadha diagrams were employed to classify the water types and identify dominant geochemical processes. The hydrochemical characteristics of the investigated groundwater samples were evaluated using a combined Schoeller semi-logarithmic diagram, which allows a comparative visualization of major ion concentrations expressed in milliequivalents per liter (meq/l). The Schoeller diagram provides a comparative representation of major ion concentrations and is particularly useful for identifying similarities and differences between groundwater samples (Schoeller, 1965).

The dominance of bicarbonate ions over sulfate and chloride confirms that groundwater chemistry is mainly controlled by carbonate dissolution processes rather than evaporation or anthropogenic inputs (Appelo & Postma, 2004; Gibbs, 1970).

In particular, the concentrations of  $\text{Na}^+ + \text{K}^+$  exhibit the highest values among the cations, followed by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . This distribution indicates a significant contribution from both carbonate rock dissolution and possible silicate weathering processes.

Among the anions, bicarbonate ( $\text{HCO}_3^-$ ) clearly dominates over sulfate ( $\text{SO}_4^{2-}$ ) and chloride ( $\text{Cl}^-$ ), confirming that the groundwater is primarily controlled by carbonate equilibrium reactions. The relatively low concentrations of sulfate suggest a negligible influence of evaporitic formations such as gypsum or anhydrite, while the moderate chloride levels indicate limited anthropogenic impact and minimal influence from saline intrusion or wastewater sources.

The overall hydrochemical facies of the groundwater can therefore be classified predominantly as Ca-Na- $\text{HCO}_3$  type, with a tendency towards Na- $\text{HCO}_3$  facies in some samples. This variability reflects differences in residence time, water-rock interaction intensity, and local geological heterogeneity within the study area.

Furthermore, the relatively narrow spread of the Schoeller curves (**Fig. 4**) suggests a certain degree of hydrochemical homogeneity among the samples, although subtle variations in magnesium and chloride concentrations indicate localized geochemical processes. These differences may be attributed to variations in lithology, permeability, and recharge conditions across the investigated zones.

The absence of significant sulfate and chloride enrichment, combined with the dominance of bicarbonate ions, indicates that the groundwater is largely of natural origin and has not been substantially affected by anthropogenic contamination. This is consistent with the hydrogeological setting of the area, which is characterized by carbonate formations and active recharge conditions.

Overall, the Schoeller diagram proves to be an effective tool for identifying the hydrochemical signature of the groundwater system and supports the interpretation of a predominantly carbonate-controlled aquifer with minor contributions from other geochemical processes.

The Chadha diagram (**Fig. 5**), derived from the differences between major cations and anions, provides a simplified yet powerful classification of hydrochemical facies.

All samples plot in the upper-right quadrant, which corresponds to waters dominated by:

alkali metals ( $\text{Na}^+ + \text{K}^+$ ) over alkaline earths ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ )

weak acids ( $\text{HCO}_3^-$ ) over strong acids ( $\text{Cl}^- + \text{SO}_4^{2-}$ )

This confirms that the groundwater belongs predominantly to the Na- $\text{HCO}_3$  type, reflecting advanced stages of geochemical evolution.

### **4.3. Relationship between discharge and water chemistry**

The analyzed springs exhibit a wide range of discharge values, reflecting the heterogeneity of the karst aquifer system. Larger springs tend to show more stable physico-chemical characteristics, while smaller springs display slightly higher variability. These characteristics confirm that the investigated springs represent high-quality karst groundwater systems with minimal anthropogenic impact, controlled primarily by natural geological processes.

A general trend can be observed in which springs with higher discharge tend to exhibit lower mineralization, as indicated by lower TDS and EC values. This behavior is typical for karst systems, where high-discharge springs are often associated with rapid groundwater circulation and shorter residence times. In contrast, smaller springs may be influenced by localized hydrogeological conditions, leading to slightly higher variability in chemical composition (**Tab. 4**).

The measured pH values range between 7.3 and 7.5, indicating neutral to slightly alkaline conditions. This reflects a well-buffered hydrochemical system controlled by carbonate equilibria, particularly the interaction between dissolved carbon dioxide and carbonate minerals. Such conditions are characteristic of groundwater circulating in limestone and dolomite formations.

Electrical conductivity values generally range from approximately 250 to 300  $\mu\text{S}/\text{cm}$ , while total dissolved solids (TDS) vary between about 120 and 200 mg/l. These relatively low values indicate limited mineralization and confirm that the investigated waters belong to fresh groundwater systems. The low mineralization is consistent with rapid groundwater circulation and limited residence time within the aquifer.

Dissolved oxygen concentrations are relatively high, typically between 9 and 10 mg/l, suggesting active recharge conditions and rapid infiltration processes. This is a typical feature of karst systems, where water infiltrates quickly through fractures and conduits, maintaining high oxygen levels.

Nutrient concentrations ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ ) are generally very low across all sampling points. This indicates the absence of significant anthropogenic contamination sources such as agriculture or wastewater infiltration, and reflects the relatively preserved environmental conditions of the study area.

**Table 4.**  
**Summary of physico-chemical parameters of the investigated springs and interpretation.**

Parameter	Min	Max	Average (approx.)	Interpretation
pH	7.3	7.5	~7.4	Neutral–slightly alkaline
EC ( $\mu\text{S}/\text{cm}$ )	250	300	~275	Low mineralization
TDS (mg/l)	120	200	~160	Fresh groundwater
DO (mg/l)	9.0	10.0	~9.5	Well oxygenated
$\text{NO}_3^-$ (mg/l)	very low	very low	–	No agricultural impact
$\text{PO}_4^{3-}$ (mg/l)	very low	very low	–	Minimal contamination

*Major ions and hydrochemical facies.* The chemical composition of the analyzed springs is dominated by calcium ( $\text{Ca}^{2+}$ ) among cations and bicarbonate ( $\text{HCO}_3^-$ ) among anions. Magnesium ( $\text{Mg}^{2+}$ ) is present in secondary concentrations, while sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) are found in relatively low amounts.

Among anions, bicarbonate clearly dominates, whereas sulfate ( $\text{SO}_4^{2-}$ ) and chloride ( $\text{Cl}^-$ ) occur in significantly lower concentrations. This ionic composition reflects the dissolution of carbonate rocks as the main geochemical process controlling groundwater chemistry (**Tab. 5**).

**Table 5.**  
**Generalized major ion composition, their importance and geology influence.**

Ion group	Dominant ions	Relative importance	Hydrogeochemical significance
Cations	$\text{Ca}^{2+}$	High	Carbonate dissolution
	$\text{Mg}^{2+}$	Moderate	Dolomite contribution
	$\text{Na}^+$ , $\text{K}^+$	Low	Minor influence
Anions	$\text{HCO}_3^-$	Very high	Carbonate equilibrium
	$\text{SO}_4^{2-}$	Low	Limited sulfate sources
	$\text{Cl}^-$	Low	Minimal external inputs

Based on the relative distribution of major ions, all investigated springs can be classified within the Ca– $\text{HCO}_3$  hydrochemical facies, which is typical of groundwater circulating in carbonate aquifers. This hydrochemical signature indicates that the dominant geochemical processes are related to carbonate weathering, particularly the dissolution of calcite and dolomite under the influence of carbon dioxide-rich water

*Heavy metals.* The concentrations of trace elements (Fe, Mn, Pb, Cr VI, Co and As) are generally very low in all analyzed samples. Most measured values are below or close to detection limits and remain well within international drinking water standards (**Tab. 6**). Low concentrations of trace elements are commonly associated with natural geogenic background levels in carbonate aquifers (Adimalla et al., 2022).

Iron (Fe) and manganese (Mn) are present in low concentrations, consistent with natural geogenic background levels in carbonate environments. Toxic elements such as lead (Pb), arsenic (As) and chromium (Cr VI) show very low concentrations, indicating the absence of significant contamination sources.

This distribution suggests that groundwater quality is not affected by industrial, agricultural or urban pollution, and that the hydrochemical composition is primarily controlled by natural geological processes.

**Table 6.**

Summary of heavy metal concentrations.

Metal	Observed level	Standard comparison	Interpretation
Fe	very low	below limits	Natural background
Mn	very low	below limits	Geogenic origin
Pb	very low	below limits	No contamination
As	very low	below limits	No contamination
Cr (VI)	very low	below limits	No contamination
Co	very low	below limits	Minimal presence

The analyzed springs exhibit a wide range of discharge values, reflecting the heterogeneity of the karst aquifer system. Larger springs tend to show more stable physico-chemical characteristics, while smaller springs display slightly higher variability.

A general trend can be observed in which springs with higher discharge tend to exhibit lower mineralization, as indicated by lower TDS and EC values. This behavior is typical for karst systems, where high-discharge springs are often associated with rapid groundwater circulation and shorter residence times. In contrast, smaller springs may be influenced by localized hydrogeological conditions, leading to slightly higher variability in chemical composition.

#### 4.4. Water quality indices

The Water Quality Index (WQI) is widely applied as an integrated tool for assessing the suitability of groundwater for drinking purposes, as it combines multiple physico-chemical parameters into a single representative value (Shanmugasundharam et al., 2023; Vasanthavigar et al., 2010). This approach facilitates a comprehensive evaluation of water quality and allows for easier comparison across different sampling locations. The classification of water quality in this study follows internationally recognized standards, particularly those established by the European Commission (2020), ensuring consistency and reliability in the interpretation of results. (European Commission, 2020).

##### 4.4.1. Overall Water Quality (WQI)

The WQI approach applied in this study is widely used in recent hydrogeochemical research for integrated groundwater quality assessment (Li et al., 2013; Shanmugasundharam et al., 2023).

The Water Quality Index (WQI) was applied to evaluate the overall suitability of the investigated spring waters for drinking purposes (Tab. 7-8). The index integrates multiple physico-chemical parameters into a single value, allowing a comprehensive assessment of water quality.

Based on the calculated WQI values, all investigated springs fall within the categories of excellent to good water quality, indicating that the water is generally suitable for human consumption without significant treatment. The low WQI values are mainly controlled by: low TDS concentrations, stable pH conditions, very low nutrient content and absence of significant contamination

The WQI was calculated using the weighted arithmetic index method:

$$WQI = \frac{\sum(W_i \times Q_i)}{\sum W_i} \quad (1)$$

where:

$W_i$  is the weight assigned to each parameter

$Q_i$  is the quality rating of each parameter

The quality rating  $Q_i$  was calculated as:

$$Q_i = \frac{(C_i - C_{ideal})}{(S_i - C_{ideal})} \times 100 \quad (2)$$

where:

$C_i$  is the measured concentration

$S_i$  is the standard permissible value

$C_{ideal}$  is the ideal value (usually 0, except for pH and DO)

The classification of water quality based on WQI values is as follows:

**Table 7.**  
**The classification of water quality based on WQI values**

WQI	Water quality
< 50	Excellent
50–100	Good
100–200	Poor
200–300	Very poor
> 300	Unsuitable for drinking

**Table 8.**  
**WQI classification of the investigated springs.**

Spring	WQI (approx.)	Class	Water quality
Grabom	25–35	< 50	Excellent
Grabom 2	30–40	< 50	Excellent
Tamara	35–45	< 50	Excellent
Tamara 2	40–50	50 (limit)	Excellent–Good
Vermosh center	30–40	< 50	Excellent
Kroni i Zekës	35–45	< 50	Excellent
Cemi – Selcë	40–55	50–100	Good
Cemi – Vukël	35–50	< 50	Excellent
Syri i Sheganit	25–35	< 50	Excellent
Burimi i Vrakës	30–45	< 50	Excellent
Syri i Gjonit	30–45	< 50	Excellent

The low WQI values are mainly controlled by: low TDS concentrations, stable pH conditions, very low nutrient content and absence of significant contamination. The predominance of excellent WQI values reflects minimal anthropogenic pressure, efficient natural filtration processes, rapid groundwater circulation typical of karst systems. The slightly higher values observed in some springs may be related to local hydrogeological variability and minor influence of surface conditions.

#### 4.4.2. Heavy Metal Pollution (HPI)

The Heavy Metal Pollution Index (HPI) was used to assess the overall impact of trace elements on water quality. The HPI was calculated using the expression:

$$HPI = \frac{\sum(W_i \times Q_i)}{\sum W_i} \quad (3)$$

where:

$W_i$  is the unit weight of each metal

$Q_i$  is the sub-index of each metal

$$Q_i = \frac{(M_i - I_i)}{(S_i - I_i)} \times 100 \quad (4)$$

where:

$M_i$  is the measured concentration

$S_i$  is the standard permissible value

$I_i$  is the ideal value (usually 0)

Interpreted HPI classification is shown at the **Table 9**.

**Table 9.**

**HPI values for the investigated springs.**

Spring	HPI (approx.)	Category	Interpretation
Grabom	10–20	< 50	Low contamination
Grabom 2	15–25	< 50	Low contamination
Tamara	20–30	< 50	Low contamination
Tamara 2	20–35	< 50	Low contamination
Vermosh center	10–25	< 50	Low contamination
Kroni i Zekës	15–30	< 50	Low contamination
Cemi – Selcë	25–40	< 50	Low contamination
Cemi – Vukël	20–35	< 50	Low contamination
Syri i Sheganit	10–20	< 50	Low contamination
Burimi i Vrakës	15–25	< 50	Low contamination
Syri i Gjonit	15–25	< 50	Low contamination

**Table 10.**  
The HPI classification.

HPI	Interpretation
< 50	Low contamination
50–100	Moderate contamination
> 100	High contamination

The Heavy Metal Pollution Index (HPI) (Tab. 9-10) was calculated to evaluate the potential impact of trace elements on water quality. The obtained HPI values are consistently low across all sampling points, remaining well below the critical threshold of 100 (Fig. 6a and 6b).

The very low concentrations of heavy metals indicate the absence of significant anthropogenic contamination and reflect natural geogenic background levels (Edmunds & Smedley, 2000; Papazotos, 2021) also: absence of heavy metal pollution, dominance of natural geochemical background levels and lack of industrial or urban contamination sources. This is particularly important given the vulnerability of karst systems, which are typically highly sensitive to contamination due to rapid infiltration and limited natural filtration. The hydrochemical composition of the investigated springs is predominantly characterized by calcium-bicarbonate facies. Spring discharge values vary significantly, reflecting the heterogeneity of the karst system and differences in recharge conditions.

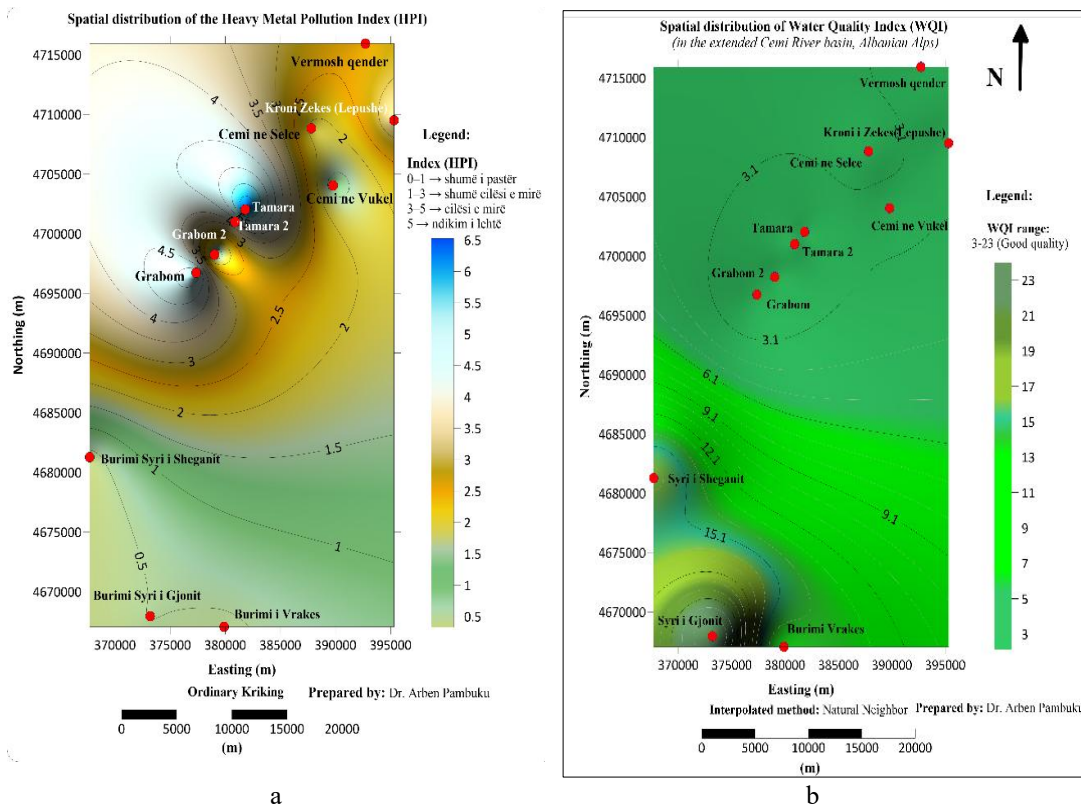
The analyzed physico-chemical parameters indicate generally stable hydrochemical conditions across the sampled springs, with no significant anomalies observed in major ion composition or trace elements. The relatively low mineralization values (TDS generally below 200 mg/l) indicate short groundwater residence times and rapid circulation within the karst system. This is consistent with the highly fractured and karstified nature of the Mesozoic carbonate formations, which allow fast infiltration and limited water-rock interaction time. The observed hydrochemical composition reflects typical karst geochemical processes, including carbonate weathering and minor contributions from silicate dissolution (Drever, 1997; Stumm, 1967).

The relatively low mineralization indicates short residence times and rapid groundwater circulation, which are characteristic features of karst aquifers (Freeze & Cherry, 1979; Zhang et al., 2023). The dominance of bicarbonate ions, combined with low sulfate and chloride concentrations, suggests that the hydrochemical evolution of groundwater is primarily controlled by natural geochemical processes rather than external inputs such as evaporation, anthropogenic contamination or interaction with evaporitic formations. Furthermore, the relatively uniform hydrochemical composition across all sampling points indicates a high degree of hydrogeological connectivity within the karst aquifer system. This suggests that groundwater flow paths are well developed and interconnected, allowing mixing and homogenization of water chemistry.

The Piper diagram (Fig. 3) shows that all samples fall within: Ca-HCO<sub>3</sub>, Ca-Mg-HCO<sub>3</sub> facies.

The Schoeller diagram (Fig. 4) confirms: consistent ion distribution and dominance of Ca and HCO<sub>3</sub>. The Chadha diagram (Fig. 5) provides further validation of the same classification.

Heavy metal concentrations (Table 7) are very low and within drinking water standards, indicating no significant anthropogenic impact.



**Fig. 6.** Spatial distribution of:

- the Heavy Metal Pollution Index (HPI) in groundwater of the study area, derived using the Ordinary Kriging interpolation method. The index integrates the concentrations of Fe, Mn, Cr(VI), Pb, and Co to assess the overall impact of heavy metals on water quality. Lower values (0–1) indicate excellent quality, moderate values (1–3) reflect good to acceptable conditions, while higher values (>3) suggest increasing levels of contamination. The spatial pattern reveals localized zones of elevated HPI influenced by geological and hydrogeochemical factors, with generally low to moderate contamination across the study area.
- the Water Quality Index (WQI) in the Cem River basin, Albanian Alps. The index was computed based on selected physicochemical parameters and standard guideline values. Spatial interpolation was carried out using Natural Neighbor, highlighting variations in groundwater quality, from good (green) to poor (red) conditions

## 5. DISCUSSION

This study provides the first integrated assessment of groundwater quality and quantity in the Albanian Alps, establishing a baseline for future hydrogeological investigations in this Albanian transboundary karst region. The findings contribute to a broader understanding of groundwater systems shared between Albania and Montenegro, where scientific data have historically been limited.

The dominance of Ca-HCO<sub>3</sub> hydrochemical facies reflects the strong influence of carbonate lithology (limestone and dolomite) and confirms that groundwater chemistry is primarily controlled by carbonate dissolution processes. This is characteristic of highly karstified aquifers with rapid groundwater circulation and limited water-rock interaction time.

Similar hydrochemical patterns have been widely reported in karst systems of the Dinaric Alps and other Mediterranean regions, where carbonate aquifers dominate and groundwater chemistry is largely governed by natural geogenic processes. This consistency supports the reliability of the obtained results and confirms that the investigated springs behave as typical karst groundwater systems.

The generally low concentrations of heavy metals and stable physicochemical parameters indicate minimal anthropogenic impact in the study area. This can be attributed to low population density, absence of industrial activities, and relatively preserved natural conditions. However, increasing tourism activity may represent a potential future risk, particularly through diffuse pollution and inadequate wastewater management.

From a transboundary perspective, the investigated karst aquifers represent interconnected groundwater systems that extend across national boundaries. Due to the high permeability and conduit-dominated flow in karst environments, groundwater flow paths are not constrained by political borders. This highlights the necessity for coordinated monitoring strategies and joint management approaches between Albania and Montenegro.

A limitation of the present study is the absence of continuous temporal monitoring, which restricts a comprehensive assessment of seasonal variability. However, the inclusion of two contrasting hydrological periods (high-flow and dry season) provides a useful initial insight into hydrochemical conditions. To address this limitation, a comprehensive and modern monitoring system has been proposed for the extended Cemi/Cijevna River basin, including multi-season sampling and tracer-based investigations aimed at improving the understanding of groundwater flow dynamics and transboundary connectivity.

The use of multiple graphical methods is justified by their complementary roles: the Piper diagram is primarily used for hydrochemical classification, the Schoeller diagram allows detailed comparison of ionic concentrations, and the Chadha diagram serves as a validation tool. The strong agreement between these diagrams significantly increases the reliability and robustness of the hydrochemical interpretation. Although small deviations are observed in some samples, these likely reflect minor local processes such as ion exchange or silicate weathering. However, these processes do not significantly alter the overall hydrochemical facies, which remains consistently dominated by carbonate dissolution mechanisms. The relatively low total dissolved solids (TDS < 200 mg/l), combined with high dissolved oxygen concentrations, indicate short groundwater residence times and rapid circulation within a highly karstified system. These characteristics reflect an active recharge regime and strong hydraulic connectivity, typical of karst aquifers.

Water quality assessment based on the Water Quality Index (WQI) demonstrates that most samples fall within the excellent to good categories. This confirms that groundwater is suitable for drinking purposes with minimal treatment. In parallel, the Heavy Metal Pollution Index (HPI) values indicate very low levels of heavy metal contamination, confirming the absence of significant anthropogenic pollution sources.

The spatial distribution of hydrochemical parameters (**Fig. 2**) supports the interpretation of a hydraulically connected system with relatively homogeneous hydrochemical behavior. This spatial coherence suggests that groundwater flow paths are well integrated within the karst system. Similar findings have been reported in recent studies, which indicate that groundwater quality in karst environments is primarily controlled by lithology, residence time, and recharge conditions (Adimalla et al., 2022; Li et al., 2013).

The transboundary monitoring network presented in **Fig. 7** (Cem/Cijevna River basin) further highlights the importance of integrated hydrogeological assessment. The map includes existing and proposed monitoring stations in both Albania and Montenegro, such as groundwater wells, hydrological stations, sampling points, and isotopic pluviometers. This network is designed to support the evaluation of surface water-groundwater interactions and to improve understanding of the karst aquifer system within the DIKTAS II framework (DIKTAS Project, 2015).

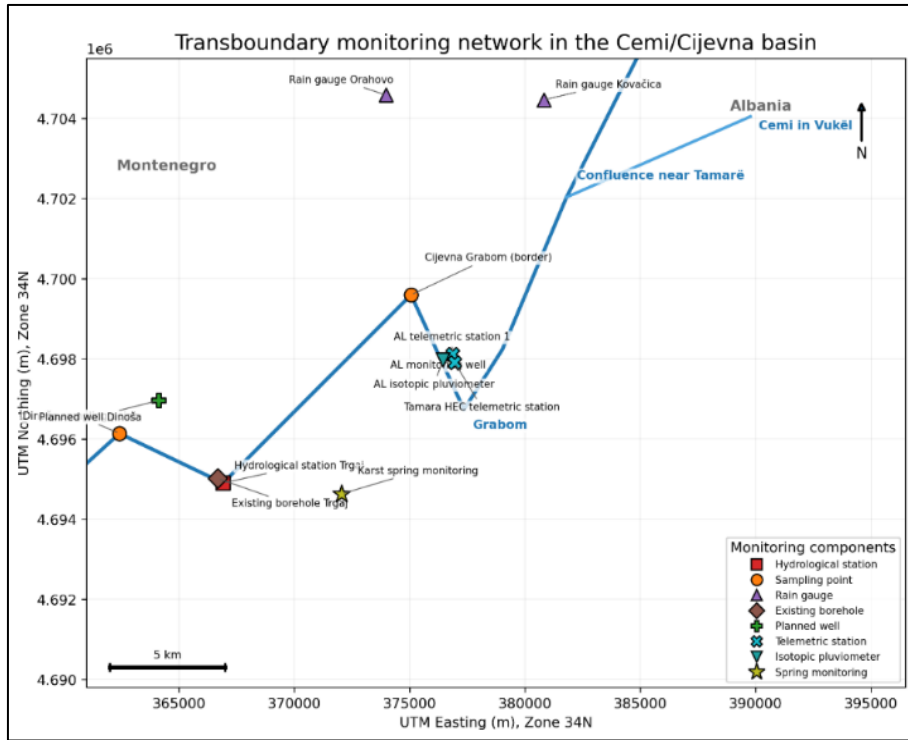


Fig. 7. Transboundary monitoring network in the Cemi/Cijevna River basins.

Despite the currently high groundwater quality, karst systems are inherently vulnerable. Rapid infiltration processes, thin soil cover, and limited natural filtration capacity make them particularly sensitive to contamination. Therefore, continuous monitoring is essential. An effective monitoring network should include all major springs, strategic locations along river systems, and seasonal sampling campaigns to capture temporal variability.

The observed limited anthropogenic impact is closely related to reduced agricultural activity and rural depopulation. However, increasing tourism development represents an emerging environmental pressure that may pose risks to groundwater quality in the future.

Overall, the results demonstrate that groundwater in the Cem/Cijevna basin is dominated by Ca-HCO<sub>3</sub> facies, controlled by carbonate dissolution processes, characterized by low mineralization, and exhibits excellent water quality with minimal pollution influence. The strong agreement between analytical data, hydrochemical diagrams, and quality indices confirms the robustness of the results and highlights the importance of this aquifer as a high-quality water resource that requires careful protection and sustainable management.

## 6. CONCLUSIONS

The present study provides a comprehensive hydrochemical characterization and water quality assessment of transboundary karst springs in the Albanian Alps. The results demonstrate that groundwater is predominantly characterized by Ca-HCO<sub>3</sub> facies, controlled by carbonate dissolution processes within highly karstified aquifers.

The applied water quality indices (WQI and HPI) indicate that groundwater quality is generally excellent to good and suitable for drinking purposes, with minimal evidence of heavy metal contamination. These findings reflect limited anthropogenic pressure and relatively preserved natural conditions in the study area.

The hydrochemical consistency observed across the investigated springs suggests strong hydraulic connectivity and well-developed karst flow systems. However, the intrinsic vulnerability of karst aquifers, combined with increasing tourism activity, highlights the need for careful management and protection of groundwater resources.

From a transboundary perspective, the results emphasize the importance of coordinated monitoring and joint management strategies between Albania and Montenegro. The proposed monitoring framework for the Cemi/Cijevna basin provides a basis for future research and supports the sustainable management of shared groundwater resources.

Overall, this study contributes valuable baseline data for a relatively understudied karst region and supports the development of integrated approaches for transboundary groundwater assessment and protection.

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