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# Major and minor elements contribution to discriminate between karst drainage watersheds and to outline underground hydrological connections. An example from Sohodol Valley (Vâlcan Mountains, Romania)

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**Abstract**

Water samples for chemical analyses have been collected from impenetrable karst springs and from water flows intercepted by caves within the area of Sohodol valley. The analyzed inorganic constituents were noticed to belong to two distinct categories. One category included solutes of variable concentrations, likely related to local allochtonous inputs (Al, NO3) and to local occurrences of decaying organic matter (PO4, NO3), such solutes being hence irrelevant in terms of regional patterns of rock weathering. The other category of solutes (Ca, Mg, Na, K, Sr, Ba, Rb, Fe, HCO3 and SiO2) proved to have concentrations that did not differ between two interconnected water flows (e.g., impenetrable karst springs that discharged from a common water body; a cave stream connected to an impenetrable karst spring). Accordingly, the concentrations of this second group of constituents represented reliable chemical fingerprints of a particular karst watershed. And implicitly, water flows having contrasting concentrations of such solutes were conjectured to belong to distinct karst watersheds, which likely differed in terms of chemical composition of the karstifiable rocks, and/or of the impervious rocks which provided allochtonous recharge to the concerned karst drainage systems.
**Keywords:** *groundwater chemistry, karst spring, karst watershed, natural tracer, Sohodol valley*

## Introduction

In a karst region, distinct occurrences of flowing underground water may significantly differ from each other in terms of their content of dissolved inorganic constituents. Such differences are mainly lithologically-controlled, because: (i) karst aquifers can extend over domains which include various types of soluble rocks (limestone, dolomite, evaporites); (ii) allochtonous recharge may originate in non-karstifiable rocks having lithologies that can also differ from one supply area to another. Several works (e.g., Díaz-Puga et al., 2016; Han & Liu, 2004; Karimi et al., 2005; Katsanou et al., 2017; Petelet et al., 1998) have illustrated how karst groundwater compositions mirrored the weathered rock formations various lithologies.

However, no previous studies seem to have considered chemical indicators in order to diagnose whether distinct sampling sites in a karst area were actually hydrologically linked - or not - to each other. We consequently attempted to investigate if the dissolved inorganic constituent contents of certain karst water flows displayed similarities consistent with actual hydrological connections existing between the concerned sampling sites.

Our study has focused on a rather small region, where there were concentrated (Iurkiewicz & Mangin, 1994) a large number of impenetrable karst springs (both perennial and temporary), as well as caves intercepting underground streams.

We have considered simultaneously sampled occurrences of underground water flows and tested if most of their dissolved inorganic constituents (minor elements included) displayed similar concentrations. When the degree of similarity was accordingly assessed for the overall inorganic solute contents, two distinct types of settings appeared to be relevant: (a) one impenetrable spring being compared to another; (b) an impenetrable spring being compared to a possibly connected cave water occurrence. For each of those two settings, the contrasting behavior that a few solutes displayed with respect to the remaining majority was suggestive of local physico-chemical processes operating in the underground.

It was eventually possible to discriminate in this way between (at least) two large-scale watersheds, each of them discharging by outlets that displayed distinctive chemical signatures.

## Physiographic, geologic and hydrogeological setting

Sohodol is one of the main streams flowing on the southern slopes of Vâlcan mountains (the South Carpathians range). Within the mountains domain (1600-300 m altitude), the stream catchment extends over almost 120 km$^2$. About two thirds of this surface, mainly at the headwaters of Sohodol trunk stream and of its tributaries (Fig. 1a), are occupied by metamorphic and granitic terrains of Precambrian and Paleozoic age (Stan et al., 1979). A Mesozoic cover, consisting mainly of Dogger-Aptian carbonate rocks, underlain by a thin siliciclastic formation of Early Jurassic age, occupies most of the remaining one third of the catchment. The several hundred meters thick carbonate series is partly overlain by Middle-Late Cretaceous clastics. Still the Dogger-Aptian limestones and dolomites are encountered not only below that Late Cretaceous cover, but also thrust above it, forming the so-called Cerna Nappe (Stănoiu et al., 1997). In some places, uplifted bodies of granitic and metamorphic formations also interrupt the lateral continuity of the carbonate rocks blanket.

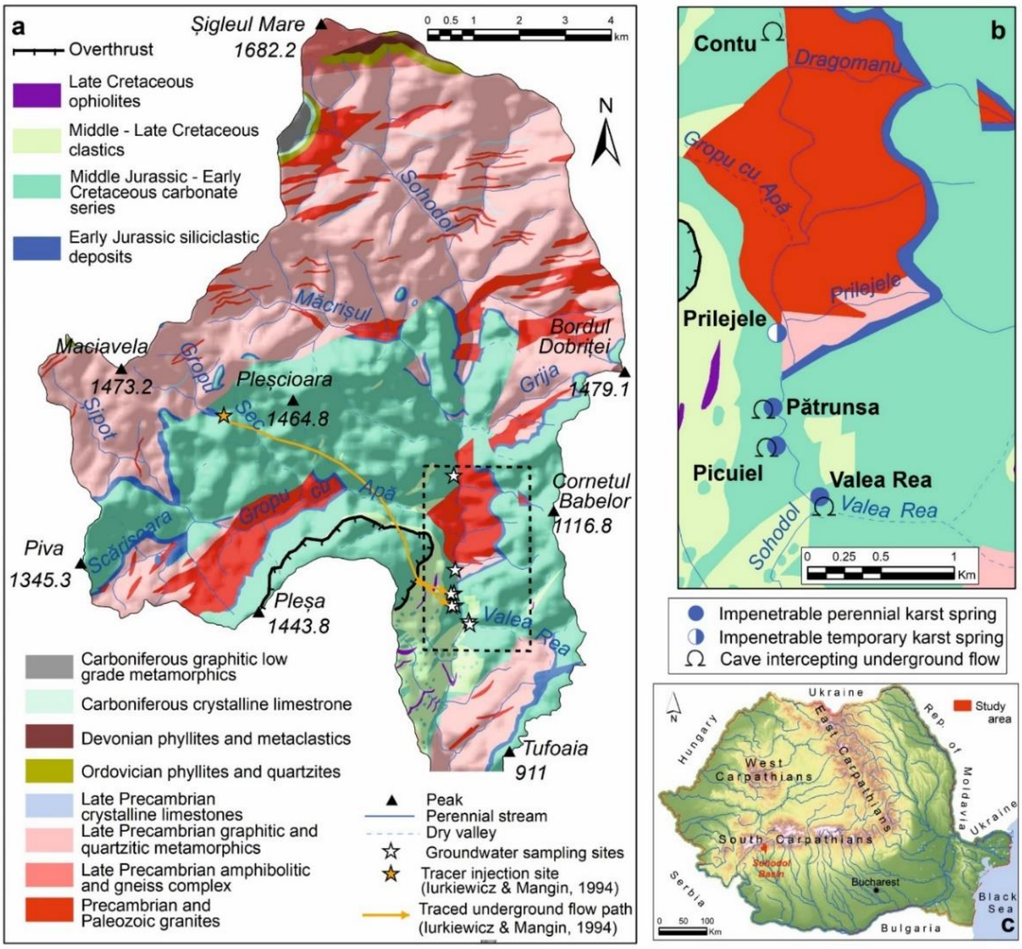


**Figure 1. Location of the investigated area: a. Whole catchment of Sohodol valley within the mountains domain (geological background compiled, in a simplified form, from Pop, 1973, and Stan et al., 1979); b. Detail (area bordered by dashed line in panel a) illustrating the type and location of the groundwater sampling sites; c. Position of Sohodol catchment within Romania**

Our study has addressed a carbonate rocks domain which extended within the median section of Sohodol catchment (Fig. 1 a, b). A distinctive feature of the considered limestone area is given by the presence of three abundant perennial karst springs. They are distributed along the Sohodol stream course, just 200-500 m away from each other. Two of the springs, Pătrunsa and Picuiel, are located on the right side of the valley, while the third one, Valea Rea, is located on the left side (Table 1, Fig. 1b). All three outflows were conjectured by Iurkiewicz & Mangin (1994) to be discharges of a single karst drainage system. A fourth, temporary spring, Prilejele, is positioned further upstream (600 m ca.) on the right side of Sohodol, and it was inferred by the indicated authors to act as an overflow of the karst network which supplied the three above-mentioned perennial springs.

An artificial tracer test (Iurkiewicz & Mangin, 1994) has substantiated the interconnection between Pătrunsa and Picuiel springs, indicating that both of them were partly supplied by Gropu Sec swallet (Fig. 1a). Still, no tracer evidence was so far provided about the involvement of Valea Rea perennial spring and of Prilejele temporary spring in the same underground drainage system.

**Table 1. The sampling sites within the investigated karst area of Sohodol valley**

| Side of Sohodol | Type | Name | Latitude N | Longitude E | Elevation (m a.s.l.) | Estimated flow rate* (L/s) |
|---|---|---|---|---|---|---|
| right | impenetrable perennial spring | Picuiel | 45°10'37.97" | 23° 7'59.02" | 425 | 100-200 |
| | | Pătrunsa | 45°10'44.40" | 23° 7'56.43" | 430 | 100-500 |
| | impenetrable temporary spring | Prilejele | 45°11'3.66" | 23° 7'59.04" | 445 | 0-400 |
| | cave intercepting an underground flow | Picuiel** (2114/15 - Peştera de la Picuiel)*** | 45°10'38.02" | 23° 7'58.44" | 437 | n.e. |
| | | Pătrunsa** (2114/4 - Peştera de la Pătrunsa)*** | 45°10'44.67" | 23° 7'56.05" | 460 | n.e. |
| | | Contu** (2114/14 - Peştera de la Contu)*** | 45°12' 6.69" | 23° 7'54.81" | 510 | 0-50 |
| left | impenetrable perennial spring | Valea Rea | 45°10'24.04" | 23° 8'9.83" | 410 | 80 |
| | cave intercepting an underground flow | Valea Rea** (2114/5 - Peştera de la Gura Văii Rele)*** | 45°10'23.14" | 23° 8'10.80" | 415 | n.e. |

** - according to Iurkiewicz and Mangin (1994)*
*** - the indicated coordinates correspond to the cave entrance*
**** - official code and name, according to the national caves inventory (Goran, 1982)*
*n.e. - not estimated*

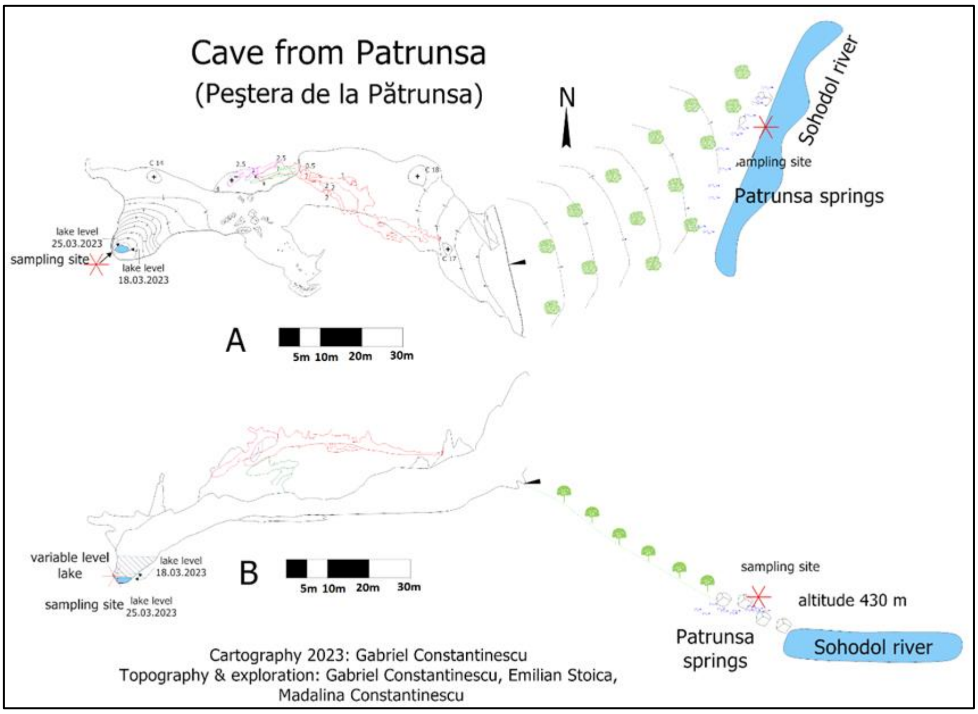

**Figure 2. Pătrunsa cave map. A. Horizontal plane view. B. Cross-section as othogonal projection on a W-E direction**

Both Pătrunsa and Picuiel impenetrable perennial springs have in their proximity a cave that possibly intercepts the corresponding water discharges. The cave located close to Pătrunsa spring (Belecciu, 1987; Constantinescu, 1975) is 0.4 km long (Fig. 2), while the cave located close to Picuiel spring (Sencu, 1972) was currently explored on about 0.6 km length (Belecciu et al., 1983; Besesek, 2023). Each cave is designated by the name of the nearby impenetrable spring (Table 1, Figs. 2, 3). The corresponding cave maps, devised in 2023 for the present research purpose, include only the cave areas extending next to the sampling sites (namely a lake, pool or sump inside the cavity, as well as the springs outside). Cross-sections were represented as orthogonal projections, in order to indicate the relative position of the outside spring with respect to the water sampling site inside the cave.

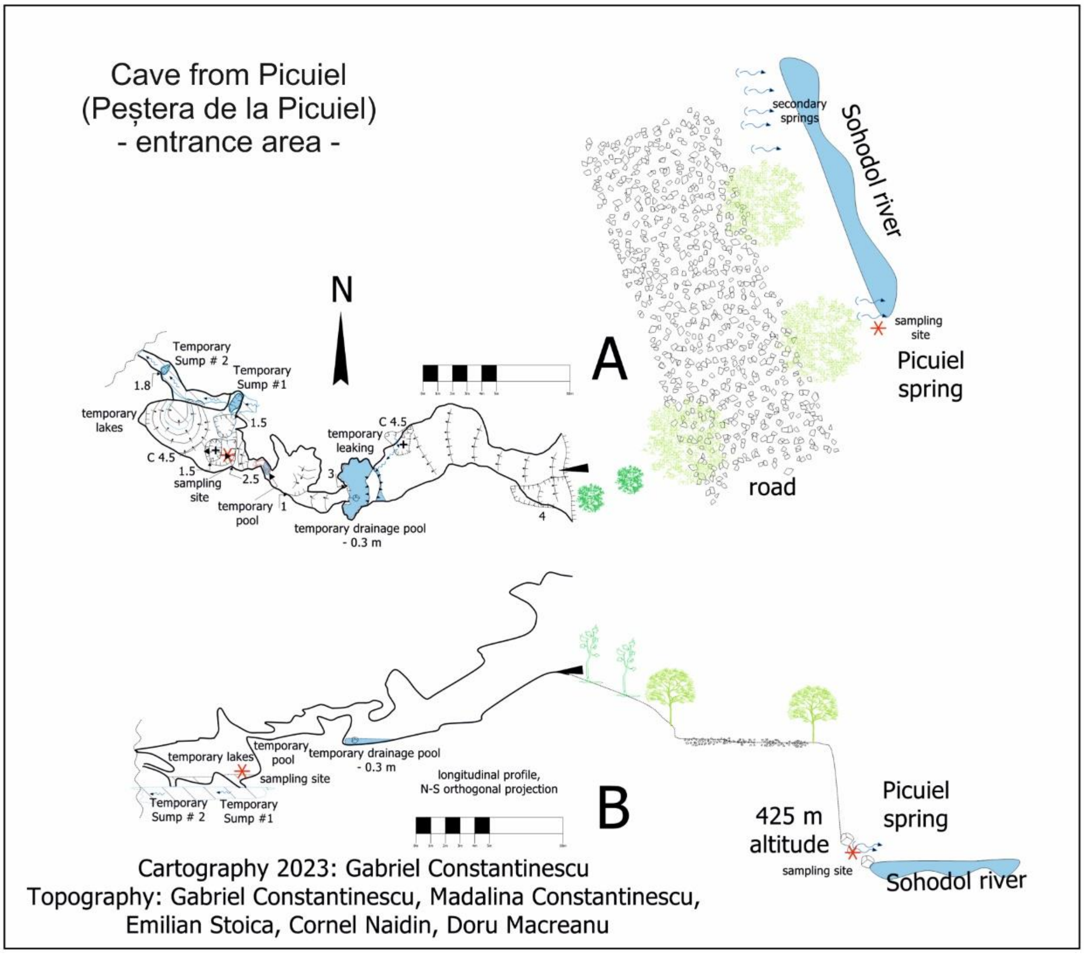


**Figure 3. Picuiel cave. Entrance area map. A. Horizontal plane view. B. Cross-section as othogonal projection on a W-E direction**

A series of other sites, besides the previously indicated ones, are possibly related to the underground drainages addressed in the study of Iurkiewicz & Mangin (1994), who however did not dedicate a detailed discussion to those sites. Our geochemical survey therefore included also such objectives of potential interest, namely (Table 1, Fig. 1b):

- Valea Rea cave. It is a 0.7 km long, permanently outflowing stream cave (Belecciu et al., 1983; Constantinescu, 1975; Rădulescu, 1992). Its entrance is located very close to the previously mentioned Valea Rea impenetrable spring and 5 m above it (Fig. 4). No inferences have been made so far about possible relationships between the stream intercepted in the cave and the nearby spring discharge. The preparation of the map in Fig. 4 followed the same principles as those previously indicated for the maps in Figs. 2 and 3.

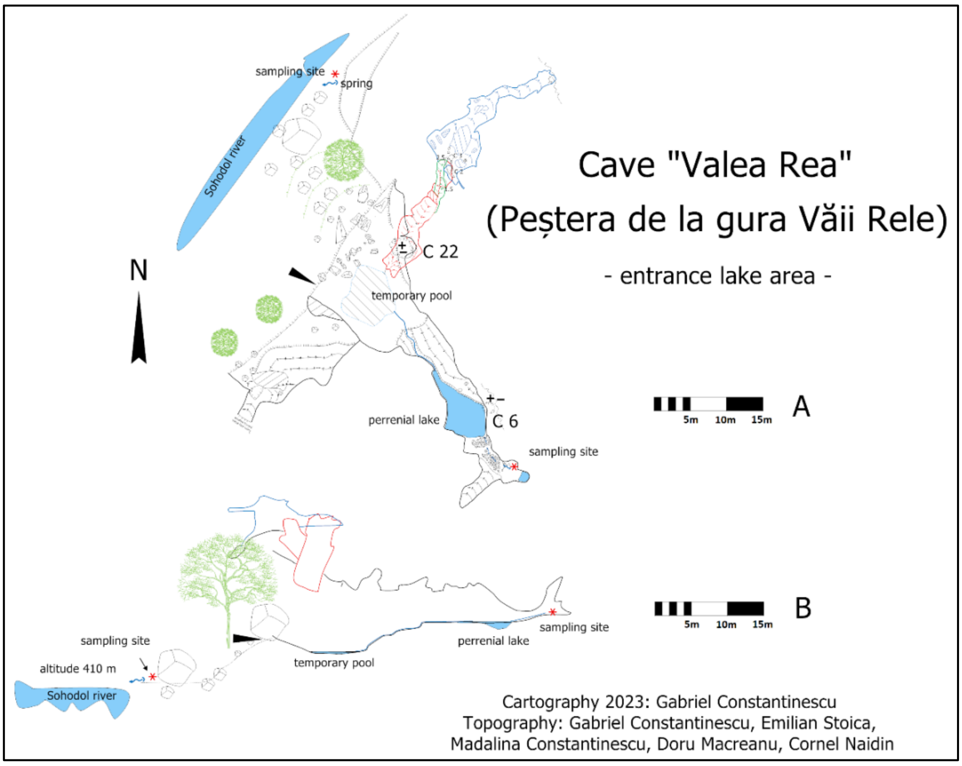


Figure 4. Valea Rea cave. Entrance lake area map. A. Horizontal plane view. B. Cross-section as othogonal projection on a NNW-SSE direction

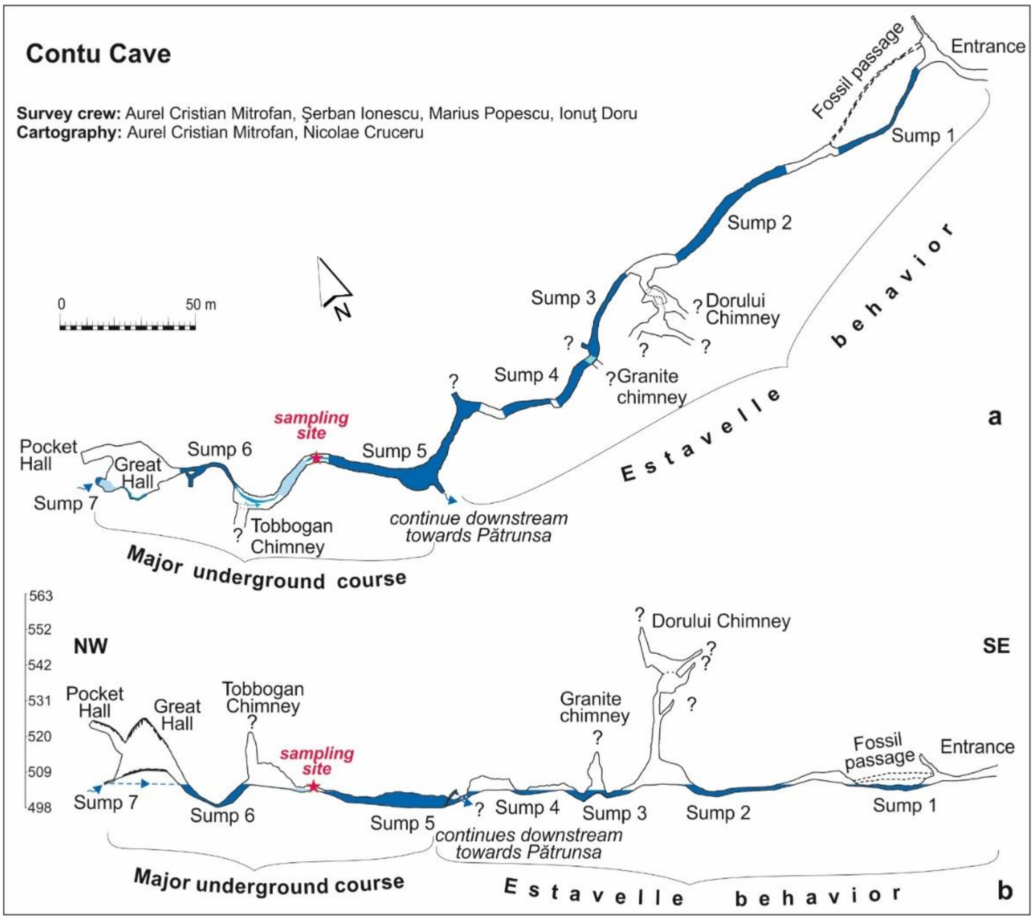


**Figure 5. Contu cave map. a. Horizontal plane view. b. Cross-section as othogonal projection on a NNW-SSE direction**

- Contu cave. Its entrance is located (Sencu, 1972) on the right side of Sohodol, about 2 km upstream Prilejele temporary spring. Most of the cave passages are permanently flooded, having been only recently explored (since 2021) by diving (Besesek, 2023). The entrance passage displays a typical estavelle behavior: during draught periods, the passage receives partial water losses from Sohodol surface stream and conveys them for about 300 m, to the junction with a major underground course (Fig. 5); but during floods, the same entrance passage acts as an overflow, conveying to the cave opening the main underground course excess flow, which cannot drain through the most downstream section of the cave. The presently surveyed cave length totals almost 0.7 km, and the major underground course exploration, both downstream and upstream the junction with the entrance passage, is currently under way.

## Materials and methods

In the framework of the present study water samples have been collected from all the above-indicated sites and the samples chemical composition was analyzed in terms of major and minor constituents. Based on the analyses results, we attempted to outline chemical signatures possibly associated with previously proven – or just supposed - hydrological connections. In addition, we aimed to identify chemical constituents that could exhibit significant concentration differences between the impenetrable perennial springs and the related water occurrences intercepted in the nearby caves. Such differences might point to physico-chemical processes locally operating in the spelean environment.

## Samples collection and analysis

The water samples for chemical analyses have been collected on two distinct instances (Table 2):

- during a period of relatively low discharge (29 October 2022), when the main stream of Contu cave, as well as the major impenetrable perennial springs Pătrunsa and Picuiel were sampled;

- about one month later (26 November 2022), when ensuing to a rainfall event, discharges had significantly increased comparatively to the previous instance; this latter sampling operation has covered each of the major impenetrable perennial springs Pătrunsa, Picuiel and Valea Rea, together with their nearby caves, as well as Prilejele impenetrable temporary spring.

The concentrations of the major and minor chemical constituents were determined in the Hydrogeochemistry Laboratory of the "Emil Racoviţă" Institute of Speleology in Bucharest, in accordance with the procedures described by Mitrofan et al. (2019). The analytical uncertainty estimation was performed in compliance with the ISO 11352:2012 standard. The analyses results are indicated in Table 2.

**Table 2. Chemical analysis results for ground water samples collected in the Sohodol valley karst area**

| Side of Sohodol | sampling site | sampling date | pH | conductivity | Na | K | Ca | Mg | $HCO_3$ | $NO_3$ | $SiO_2$ | $PO_4$ | Sr | Ba | Rb | Fe | Al |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | µS/cm | mg/L | | | | | | | µg/L | | | | | |
| Right | Pătrunsa impenetrable perennial spring | 29 Oct 2022 | 5.99 | 209.5 | 1.504 | 0.630 | 41.61 | 2.63 | 123.6 | 1.71 | 8.01 | 20.7 | 35.9 | bql | 0.626 | 77 | 10.1 |
| | Picuiel impenetrable perennial spring | | 6.20 | 209.9 | 1.516 | 0.644 | 40.16 | 2.66 | 120.1 | 1.74 | 8.13 | bql | 35.6 | bql | 0.657 | 78 | 7.5 |
| | Contu cave | | 6.08 | 202.3 | 1.532 | 0.703 | 39.52 | 2.72 | 111.4 | 0.78 | 7.97 | bql | 37.9 | bql | 0.710 | 71 | bdl |
| | Pătrunsa impenetrable perennial spring | 26 Nov 2022 | 6.02 | 206.4 | 1.015 | 0.490 | 45.66 | 3.27 | 152.7 | 1.46 | 6.37 | 16.1 | 30.4 | bql | 0.539 | 124 | 60.4 |
| | Pătrunsa cave | | 5.85 | 204.3 | 1.040 | 0.512 | 45.29 | 3.25 | 141.1 | 1.61 | 6.37 | 19.9 | 30.1 | bql | 0.542 | 111 | 34.8 |
| | Picuiel impenetrable perennial spring | | 5.91 | 207.9 | 1.025 | 0.488 | 44.91 | 3.22 | 138.2 | 1.60 | 6.35 | 16.2 | 29.9 | bql | 0.523 | 125 | 50.7 |
| | Picuiel cave | | 6.05 | 214.3 | 1.041 | 0.495 | 45.13 | 3.21 | 145.6 | 2.11 | 6.18 | 21.9 | 30.7 | bql | 0.506 | 127 | 47.5 |
| | Prilejele impenetrable temporary spring | | 6.57 | 200.0 | 0.987 | 0.473 | 44.89 | 3.20 | 142.2 | 1.67 | 6.11 | bql | 28.9 | bql | 0.523 | 128 | 62.3 |
| Left | Valea Rea impenetrable perennial spring | | 6.17 | 324.7 | 0.755 | 0.455 | 74.42 | 1.98 | 216.8 | 2.63 | 5.44 | 18.8 | 46.5 | 7.76 | bql | 156 | bql |
| | Valea Rea cave | | 6.29 | 255.4 | 0.936 | 0.470 | 58.31 | 1.87 | 166.9 | 2.03 | 6.07 | 16.8 | 40.3 | 9.68 | bql | 121 | 13.5 |

*bql – below quantification limit*

*bdl – below detection limit*

## Data processing

We expected that if two sampling sites displayed similar concentrations for most of the analyzed solutes, a hydrologic link most probably existed between those sites. Therefore, our first step was to compare the overall chemical composition between pairs of samples concomitantly collected from sites presumed to be hydrologically linked to each other. To this purpose, the concentrations of all analyzed constituents (minor elements included) were simultaneously plotted for such pairs of sampling points. In the corresponding diagrams there were not included concentration values which, for a given solute, fell below the quantification limit.

Next, the absolute difference between the concentrations that each specific constituent displayed in the two considered sites was normalized with the average of the two concerned concentrations. Then this normalized difference was compared (on the same diagram) with the normalized analytical uncertainty that corresponded to the concerned constituent. If the normalized difference did not exceed the normalized analytical uncertainty, there was assumed that the concerned solute concentrations were similar at the two sites; otherwise, the concentrations were considered to differ from one site to the other.

## Results and interpretation

The previously described data analysis was conducted for two distinct settings, which will be next addressed in detail: (a) one impenetrable spring being compared to another; (b) an impenetrable spring being compared to a possibly connected cave water occurrence. Contrasting behaviors that a few constituents displayed, in each case, with respect to the majority of the remaining components will also be discussed, together with possible causes of such discrepancies.

### Examples of one impenetrable spring compared to another

We expected the most eloquent results to be provided by the perennial springs Pătrunsa and Picuiel, which according to the artificial tracer test published by Iurkiewicz and Mangin (1994), discharged from a common karst drainage body, partly supplied by Gropu Sec swallet (Fig. 1a).

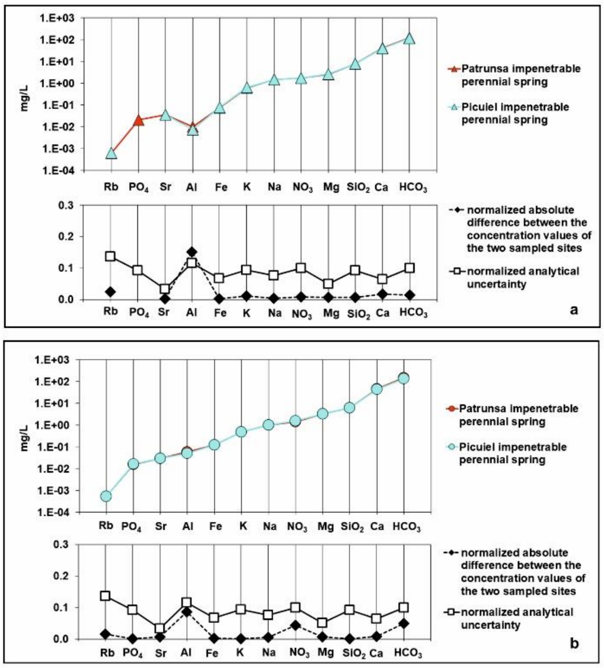


**Figure 6. Comparison between the chemical compositions of Pătrunsa and Picuiel impenetrable perennial springs. a. Sampling on 29 October 2022. b. Sampling on 26 November 2022**

The diagram which comparatively illustrates the chemistry of the Pătrunsa and Picuiel samples collected in October 2022 (Fig. 6a) shows that, as anticipated, almost all analyzed constituents had quite similar concentrations. This circumstance was eloquently mirrored by the fact that for most solutes, the concentration difference between the sampled sites was smaller than the analytical uncertainty corresponding to the concerned constituent. There was nonetheless recorded a slight Al enrichment displayed by Pătrunsa spring: since this element is considered (Cholet et al., 2019; Vesper & White, 2003) an indicator of the amount of allochtonous clay and silts conveyed by infiltration waters, such sediments must have been less abundant in Picuiel outflow. In addition, the $PO_4$ concentration in Pătrunsa exceeded (in contrast to the Picuiel concentration) the quantification limit: this could indicate a more significant contribution from animal bone remains leaching in Pătrunsa than in Picuiel.

Next we checked if the samples collected from Picuiel and Pătrunsa springs in November 2022 were chemically similar to each other, too, thus mimicking the situation recorded in October 2022. Fig. 6b indicates that this was indeed the case, with, moreover, no constituent concentration difference exceeding, on that sampling date, the corresponding analytical uncertainty.

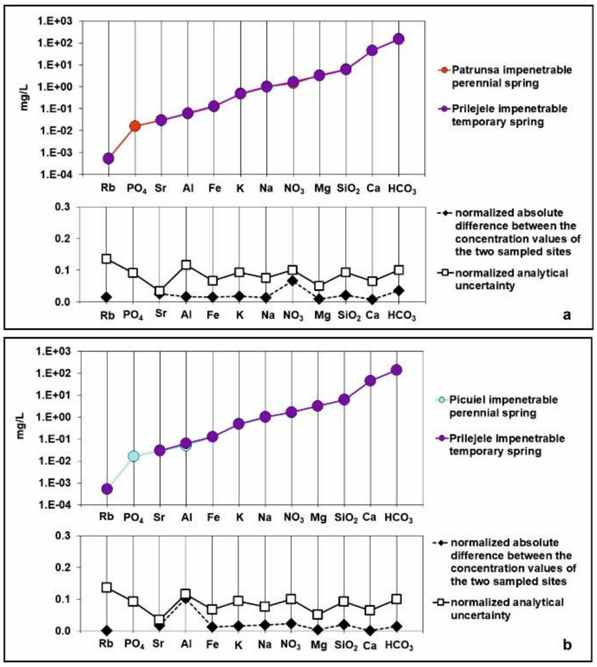


**Figure 7. Comparison between the chemical compositions of: a. Pătrunsa impenetrable perennial spring and Prilejele impenetrable temporary spring. b. Picuiel impenetrable perennial spring and Prilejele impenetrable temporary spring. Sampling on 26 November 2022**

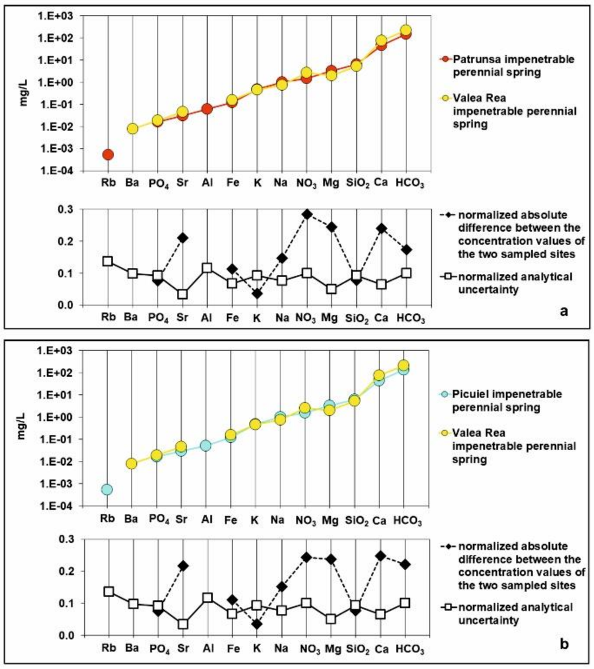


**Figure 8. Comparison between the chemical compositions of: a. Valea Rea and Pătrunsa impenetrable perennial springs. b. Valea Rea and Picuiel impenetrable perennial springs. Sampling on 26 November 2022**

An additional, temporary outflow of the aquifer discharging by Picuiel and Pătrunsa springs was assumed (Iurkiewicz & Mangin, 1994) to be the impenetrable temporary spring Prilejele. The latter had been sampled only in November 2022, so its water was compared with the simultaneously collected Pătrunsa and Picuiel spring waters (Figs. 7a and 7b, respectively). The overall chemical similarity with each of those two perennial springs is very good; thus, the inference that Prilejele is acting as a temporary overflow for the underground drainage directed to Pătrunsa and Picuiel springs was confirmed. It is nonetheless worth mentioning that the $PO_4$ concentration in the Prilejele overflow spring was lower than the quantification limit: this circumstance could indicate that no penetrable cave conduits are associated to this outlet, in contrast to the Pătrunsa and Picuiel outflows; in the two latter cases, bone remains in the nearby - and likely connected - caves (Picuiel and Pătrunsa respectively) could explain the quantifiable $PO_4$ concentrations recorded in the impenetrable springs.

Valea Rea impenetrable perennial spring, which is located on the left side of Sohodol valley, has been assumed as well by Iurkiewicz & Mangin (1994) to discharge from the same aquifer as the springs Pătrunsa and Picuiel, that however are positioned on the valley right side (Fig. 1b). But the chemical comparison with those two outlets (Figs. 8a and 8b respectively) does not seem to support the conjectured hydrological connection: there are only a few chemical constituents (K, $SiO_2$, $PO_4$) for which the concentrations difference between each pair of considered sampling sites is smaller than the analytical uncertainty; whereas the concentrations of all other constituents are, in Valea Rea spring, significantly different from the concentrations recorded in either Picuiel, or Pătrunsa springs. In particular, two elements deserve to be mentioned:

- Rb, which was detected in quantifiable concentrations in Picuiel, Pătrunsa and Prilejele springs (Table 2, Fig. 6, and 7), but below quantification limit in Valea Rea spring (Table 2, Fig. 8);
- Ba, which, in contrast, occurred in concentrations lower than the quantification limit in Picuiel, Pătrunsa and Prilejele springs, but was quantifiable in Valea Rea spring (Table 2, Fig. 8).

This distinction in terms of Rb and Ba concentrations between karst drainage systems located on the right side of Sohodol valley, and flow systems on the valley left side, was confirmed also by the chemical analysis of the underground streams in the caves Contu and Valea Rea

(Table 2). Hence Rb and Ba seem to behave, in the considered karst area of Sohodol catchment, as natural tracers, able to discriminate between distinct karst catchments. Overall, these results strongly suggest that the karst drainage system discharging by Valea Rea impenetrable spring is completely different from the one which discharges by Picuiel and Pătrunsa impenetrable springs.

## Examples of an impenetrable spring compared to a possibly connected cave water occurrence

The most likely connections of this type were anticipated to exist between each of the caves Pătrunsa, Picuiel and Valea Rea, and the corresponding impenetrable perennial springs that discharged below their entrances.

The only water occurrence in Pătrunsa cave is within a shaft that pierces the cave floor, including the accumulated sediments (Fig. 2). The shaft is possibly supplied from its clay-coated bottom, as well as by a trickle coming from one of the walls. Overall, the shaft behavior reminds that of a “piezometer” which intercepts the underlying flow that discharges via the nearby Pătrunsa impenetrable spring. The chemical composition of the quasi-static water column in that shaft is largely similar to the spring water (Fig. 9a), except for Al. As already mentioned, this element is associated to allochtonous clay and silts flushed from the infiltration zone (Cholet et al., 2019; Vesper & White, 2003); such sediments are expected to be more abundant in the flowing spring water than in the quasi-stagnant piezometer pool - an instance that could explain the Al depletion of the water in the cave. A slight enrichment in $PO_4$ with respect to the spring discharge is possibly due to the contribution of seepage water leaching animal bones buried in the sediments that build up the shaft walls.

For the underground course intercepted in Picuiel cave (Fig. 3), most solutes displayed concentration values that were similar to those of the nearby Picuiel spring water (Fig. 9b), being accordingly suggested that the two flows were indeed interconnected. Still the cave stream was slightly enriched in $PO_4$ (probably ensuing to leaching of animal bones preserved in the spelean environment) and in $NO_3$ (derived most likely from organic matter present in cave passages).

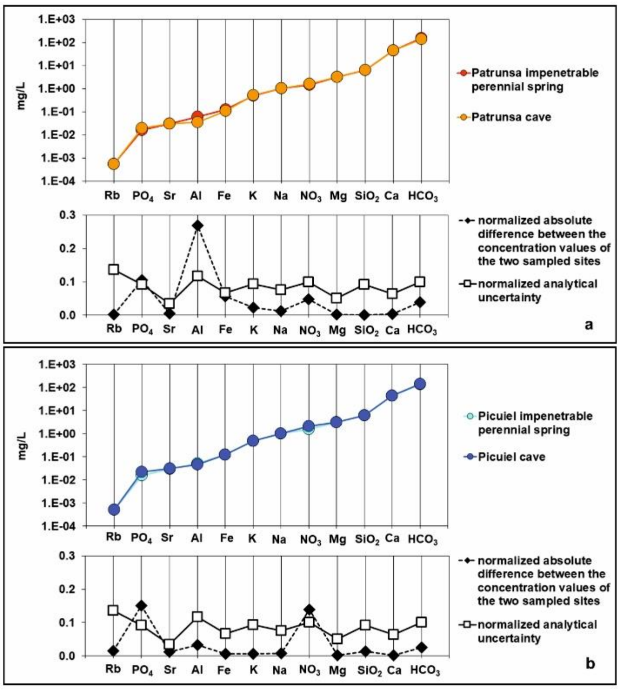


**Figure 9. Comparison between the chemical compositions of water: a. in Pătrunsa impenetrable perennial spring and in the nearby Pătrunsa cave. b. in Picuiel impenetrable perennial spring and in the nearby Picuiel cave. Sampling on 26 November 2022**

We next compared Pătrunsa and Picuiel springs samples with samples concomitantly collected from the more distant Contu cave: this cavity is located relatively close to the Sohodol streambed, on the right side of the valley, some 3 km upstream Picuiel and Pătrunsa perennial springs (Fig. 1b). At the sampling date (29 October 2022), the entrance passage of Contu cave behaved as a swallet: it conveyed a small fraction of Sohodol stream toward the major underground course that was intercepted about 300 m inside the cave. The water sample has been collected from that major underground course, upstream its junction with the entrance passage (Fig. 5).

It can be noticed that the concentration values which the major stream course in Contu cave displayed for most solutes were quite similar to those of Pătrunsa and Picuiel springs (Figs. 10a and 10b, respectively). Accordingly, it was suggested that the stream intercepted in the cave supplied those two outlets, and that the water experienced virtually no chemical changes along the flow path which extended between the sampling point in the cave and the outflow sites.

It is nevertheless worth mentioning that as compared to the Contu cave stream, both major impenetrable perennial springs were significantly enriched in Al and $NO_3$. These two constituents are considered fingerprints of allochtonous recharge (Caetano Bicalho et al., 2012; Celle-Jeanton et al., 2003; Cholet et al., 2019; Lastennet

& Mudry, 1997; Mudarra et al., 2014): therefore, their excess concentrations in the Pătrunsa and Picuiel springs suggest that the latter include, as compared to the main stream course of Contu cave, a significant additional fraction of relatively recently infiltrated water. On the other hand, $PO_4$ concentrations in Contu cave were below quantification limit, in contrast to the corresponding concentrations simultaneously recorded in Pătrunsa spring. There can be consequently conjectured that unlike the Pătrunsa outflow area, virtually no animal bone remains were leached by the main stream in Contu cave.

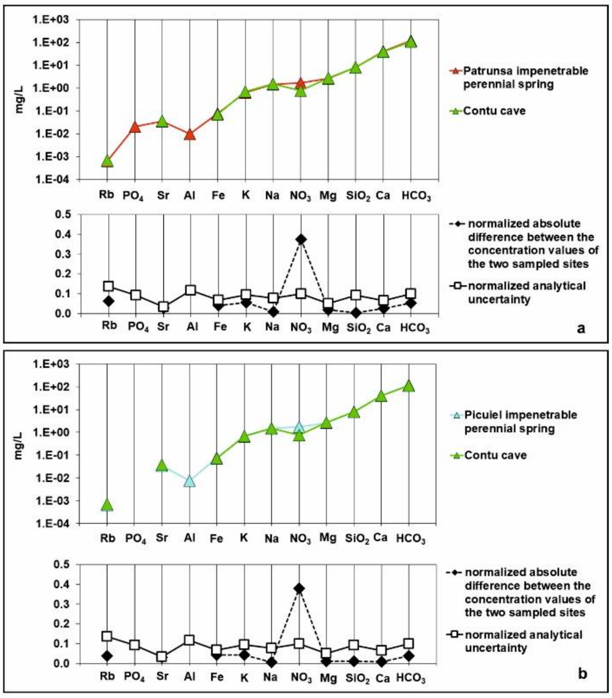


**Figure 10. Comparison between the chemical compositions of: a. Pătrunsa impenetrable perennial spring and the main stream in Contu cave. b. Picuiel impenetrable perennial spring and the main stream in Contu cave. Sampling on 29 October 2022**

A considerably different image was obtained (Fig. 11) when the stream flowing through Valea Rea cave (Fig. 4) was compared, in terms of chemical composition, with the Valea Rea impenetrable perennial spring that discharged below. There can be noticed that both flowing water occurrences displayed the common signature specific to the karst watershed of the Sohodol left side (Rb below quantification limit, and Ba above that limit – Table 2) in terms of the natural tracers Rb and Ba. But in spite of that, less than half of the quantified constituents (namely $PO_4$, K, Mg, $SiO_2$) had similar concentrations in the two sampling sites. The other solutes' concentrations differed between the cave stream and the impenetrable spring; yet except for Al, the differences only slightly exceeded the analytical uncertainty. It was accordingly suggested that although a rather similar chemical pattern was associated both to the Valea Rea impenetrable spring, and to the Valea Rea cave stream, still no direct hydrological connection existed between those two water flows.

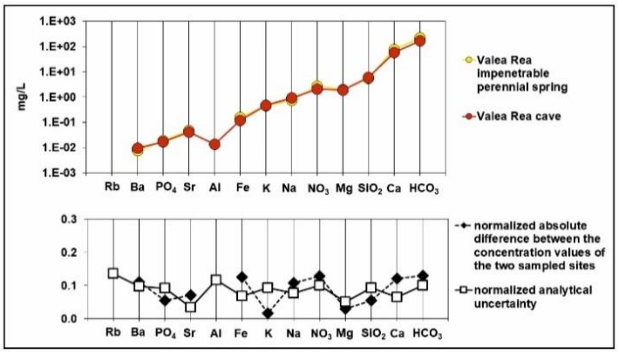


**Figure 11. Comparison between the chemical compositions of Valea Rea impenetrable perennial spring and of the stream in the nearby Valea Rea cave. Sampling on 26 November 2022**

## Discussion and conclusions

Intuitively, hydrological connections had been assumed to exist between various karst water occurrences (major impenetrable springs, caves intercepting underground flows) situated along Sohodol valley. Yet so far, only one such link has been confirmed by an artificial tracer test (Iurkiewicz & Mangin, 1994), being accordingly indicated that a common drainage body discharged by both Pătrunsa, and Picuiel impenetrable perennial springs. We expected that in such a case, the hydrologically connected water discharges must have quasi-identical chemical compositions. And indeed, the present study has shown that for most analyzed solutes (Ca, Mg, Na, K, Sr, Rb, Fe, $HCO_3$, $SiO_2$), the normalized concentration difference between samples simultaneously collected from the two indicated outflows was smaller than the normalized analytical uncertainty.

The same pattern has been recorded when samples collected from Pătrunsa and Picuiel springs were compared to a sample concomitantly collected from the impenetrable Prilejele temporary spring: it was thus confirmed the assumption (Iurkiewicz & Mangin, 1994) that Prilejele acted as a temporary overflow for the karst drainage system that discharged by Pătrunsa and Picuiel outlets.

Moreover, the underground flows intercepted in the caves that adjoined each of the impenetrable springs Pătrunsa and Picuiel had the same concentrations of Ca, Mg, Na, K, Sr, Rb, Fe, $HCO_3$, $SiO_2$ as the corresponding spring waters. And even the major stream intercepted in the more distant (~ 3 km away) Contu cave displayed for the indicated solutes similar concentrations, being thus suggested an underground hydrological connection with Pătrunsa and Picuiel springs.

Al, $PO_4$ and $NO_3$ are the only chemical constituents for which the normalized difference between the concentrations recorded at the above-indicated sampling sites occasionally exceeded the normalized analytical uncertainty. Since Al prevalently derives from flushed particles of clay and silt, the Al concentration contrast between two sampling sites enables to qualitatively differentiate the amounts of allochtonous infiltration that reaches each site. $PO_4$ is related to animal bones leaching, hence correspondingly recorded concentration differences can be linked to the abundance of such remains in caves connected to the sampled water occurrences. As for $NO_3$ concentration dissimilarities, they likely mirror the contrasting amounts of decaying organic matter leached by the concerned water flows.

It hence results that Al, $PO_4$ and $NO_3$ contents are not relevant in terms of chemical signatures due to regional rock weathering. In this respect, it is worth mentioning that in contrast to the behavior displayed by all above-mentioned sampling sites (each of them located on the right side of Sohodol valley), the Ca, Mg, Na, Sr, Ba, Rb, Fe and $HCO_3$ concentrations of Valea Rea perennial spring (situated on the valley left side), differed from the corresponding concentrations simultaneously recorded either at Pătrunsa, or at Picuiel springs: it is thus indicated that rock weathering processes which operate within the Valea Rea spring watershed are imposing a chemical signature that is clearly distinct from the signature displayed by the karst system which discharges by Pătrunsa and Picuiel springs. This instance implicitly suggests that - contrary to the assumption of Iurkiewicz & Mangin (1994) - the karst system discharging by Valea Rea spring is not hydrologically connected the one associated to the springs Pătrunsa and Picuiel. On the other hand, differences in terms of Ca, Na, Sr, Ba, Fe and $HCO_3$ contents are also recorded between Valea Rea spring itself, and the stream intercepted in Valea Rea cave, that is located in close proximity, on the same side of the Sohodol valley.

According to the geological information which is currently available for the considered karst region (Pop, 1973; Stan et al., 1979), the same Dogger-Aptian carbonate formation and underlying Early Jurassic siliciclastic rocks are encountered on both sides of Sohodol valley (Fig. 1a). And as well, no significant differences are reported to exist between the left and the right sides of the valley in what concerns the metamorphic and granitic basement formations which underlie the Mesozoic sediments. Yet the present groundwater chemistry results suggest that some formerly unidentified contrasts must exist between the right and left sides of Sohodol valley, in terms of chemical composition of the karstifiable rocks, and/or of the impervious rocks which provide allochtonous recharge to the concerned drainage systems. Ba and Rb appear to be outstandingly relevant for the distinction existing between karst watersheds on the right and left sides of Sohodol valley: Ba concentrations are below quantification limit in groundwater samples collected from the right side, but above quantification limit in samples collected from the left side, while Rb behavior is exactly opposite.

The chemistry differences recorded between the impenetrable Valea Rea spring and the stream in the nearby Valea Rea cave suggest that even on the same side (left) of Sohodol valley, two distinct karst drainage systems have developed relatively close to each other, each of them displaying distinct chemical fingerprints.

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## Code availability

The Pătrunsa, Picuiel and Valea Rea caves were surveyed by using the DistoX2 device and the freely available TopoDroid software (https://sites.google.com/site/speleoapps/home/topodroid) running on Android mobile devices. Post-survey data was processed using CSurvey software freely available at https://www.csurvey.it/site/index.php/en/download.

## Author contribution

Conceptualization, H.M., N.C., M.V., G.C., C.N., A.C.M.; methodology, N.C., H.M., C.M., M.V., G.C., C.N., A.T., A.C.M., M.P., L.N., M.C., E.S.; formal analysis, N.C., H.M., C.M., G.C., A.T., A.C.M., L.N., M.V.; investigation, N.C., H.M., G.C., A.C.M., M.V.; writing – original draft preparation, H.M., N.C., M.V., G.C., A.C.M., L.N.; writing – review and editing H.M., N.C., M.V. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

The authors declare no conflict of interest.

## References

Belecciu, C., Beloiu, V., & Grad, O. (1983). Explorations in the Sohodol stream catchment (Vâlcan Mountains) (in Romanian). *Buletinul Clubului de Speologie " Emil Racoviţă" Bucureşti*, 8, 190-196

Belecciu, C. (1987). The caves in the Pătrunsa - Prajele area (Vâlcan Mountains) (in Romanian). *Buletin speo-*

*logic, Comisia Centrală de Speologie Sportivă*, 11, 211-215

Besesek, M. (2023): From one sump to another (in Romanian). Aragonit, *Buletinul Speologilor Arădeni*, 2.1,41-55

Caetano Bicalho, C., Batiot-Guilhe, C., Seidel, J.L., Van Exter, S., & Jourde, H. (2012). Geochemical evidence of water source characterization and hydrodynamic responses in a karst aquifer. *Journal of Hydrology*, 450-451, 206-218, https://doi.org/10.1016/j.jhydrol.2012.04.059

Celle-Jeanton, H., Emblanch, C., Mudry, J., & Charmoille, A. (2003). Contribution of time tracers ($Mg^{2+}$, TOC, $\delta^{13}C_{TDIC}$, $NO_{3-}$) to understand the role of the unsaturated zone: a case study - karst aquifers in the Doubs Valley, eastern France. *Geophysical Research Letters*, 30(6), 1322, https://doi.org/10.1029/2002GL016781

Cholet, C., Steinmann, M., Charlier, J.-B., & Denimal, S. (2019). Characterizing fluxes of trace metals related to dissolved and suspended matter during a storm event: application to a karst aquifer using trace metals and rare earth elements as provenance indicators. *Hydrogeology Journal*, 27(1), 305-319, https://doi.org/10.1007/s10040-018-1859-2

Constantinescu, T. (1975). Considérations sur les grottes situées entre les rivières Şuşiţa Verde et Sohodol (Monts Vâlcan - Carpates Méridionales). *Travaux de l'Institut de Spéologie "Emile Racovitza"*, 14, 169-188

Díaz-Puga, M.A., Vallejos, A., Sola, F., Daniele, L., Molina, L., & Pulido-Bosch, A. (2016). Groundwater flow and residence time in a karst aquifer using ion and isotope characterization. *International Journal of Environmental Science and Technology*, 13(11), 2579–2596, https://doi.org/10.1007/s13762-016-1094-0

Goran, C. (1982). Systematic catalogue of the caves in Romania (in Romanian). Consiliul Naţional pentru Educaţie Fizică şi Sport, Bucureşti

Han, G. & Liu, C.-Q. (2004). Water geochemistry controlled by carbonate dissolution: a study of the river waters draining karst-dominated terrain, Guizhou Province, China. *Chemical Geology*, 204, 1-21, https://doi.org/10.1016/j.chemgeo.2003.09.009

Iurkiewicz, A., & Mangin, A. (1994). Utilisation de l'analyse systémique dans l'étude des aquifères karstiques des Monts Vâlcan. *Theoretical and Applied Karstology,* 7, 9-96

Karimi, H., Raeisi, E., & Bakalowicz, M. (2005). Characterising the main karst aquifers of the Alvand basin, northwest of Zagros, Iran, by a hydrogeochemical approach. *Hydrogeology Journal*, 13(5), 787-799, https://doi.org/10.1007/s10040-004-0350-4

Katsanou, K., Lambrakis, N., D'Alessandro, W., & Siavalas, G. (2017). Chemical parameters as natural tracers in hydrogeology: a case study of Louros karst system, Greece. *Hydrogeology Journal*, 25(2), 487-499, https://doi.org/10.1007/s10040-016-1492-x

Lastennet, R. & Mudry, J. (1997). Role of karstification and rainfall in the behavior of a heterogeneous karst system. *Environmental Geology*, 32(2), 114-123, https://doi.org/10.1007/s002540050200

Mitrofan, H., Marin, C., Povară, I., Ioniţă, D.E., Tudorache, A., & Vişan, M. (2019): Better constraining silica-enthalpy mixing models in a setting of two separate (karst and non-karst) dilution regimes, *Hydrogeology Journal*, 27(1), 291-304, https://doi.org/10.1007/s10040-018-1846-7

Mudarra, M., Andreo, B., Barberá, J.-A., & Mudry, J. (2014). Hydrochemical dynamics of TOC and NO3-contents as natural tracers of infiltration in karst aquifers. *Environmental Earth Sciences*, 71(2), 507-523, https://doi.org/10.1007/s12665-013-2593-7

Petelet, E., Luck, J.-M., Ben Othman, D., Negrel, P., & Aquilina L. (1998). Geochemistry and water dynamics of a medium-sized watershed: the Hérault, southern France 1. Organisation of the different water reservoirs as constrained by Sr isotopes, major, and trace elements. *Chemical Geology*, 150(1-2), 63-83, https://doi.org/10.1016/S0009-2541(98)00053-9

Pop, G. (1973). The Mesozoic deposits of Vâlcan Montains (in Romanian). Editura Academiei, Bucureşti.

Rădulescu, A. (1992). The hose handling people (in Romanian). *Cercetări Speologice, Clubul Naţional de Turism pentru Tineret*, 1, 24-26

Sencu, V. (1972). Runcului Gorge. Geomorphological observations (in Romanian). *Studii şi Cercetări de Geologie, Geofizică, Geografie, seria Geografie*, 19(1), 81-94

Stan, N., Stănoiu, I., Năstăseanu, S., Moisescu, V., Seghedi, A., & Pop, G. (1979). Geological map of Romania scale 1:50 000, Câmpu lui Neag sheet. Institutul de Geologie şi Geofizică, Bucureşti

Stănoiu, I., Neagu, T., Dragastan, O., Melinte, M., Rădan, S. & Baltreş, A. (1997) – La stratigraphie des formations d'âge Jurassique supérieur-Crétacé inférieur de l'unité de la Cerna dans la région du Plateau Mehedinţi-Monts Vâlcan et Parâng (Carpathes Méridionales). *Studii şi Cercetări de Geologie*, 42, 63-80

Vesper, D.J., & White, W.B. (2003). Metal transport to karst springs during storm flow: an example from Fort Campbell, Kentucky/Tennessee, USA. *Journal of Hydrology*, 276(1-4), 20-36, https://doi.org/10.1016/S0022-1694(03)00023-4