6th FORUM CARPATICUM - Linking the Environmental, Political and Societal Aspects for Carpathian Sustainability (Brno, 21-25 June 2021)

Stable isotope variability in precipitation and underground drip water along an orographic transect (South Carpathians, Romania)

Visegrad Fund

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Introduction

The stable isotope ratios in precipitation water ($\delta^{18}O$ and $\delta^{2}H$) are ideal tracers in the hydrological cycle, providing information about air mass history, moisture sources, or underground flow. The stable isotope composition of precipitation is site-specific and reflects the geographic characteristics of each location in relation with its source of moisture (Dansgaard, 1964). The isotopic ratios are subject to fractionation (depletion) due to a complex of regional and local conditions, commonly named effects, such as: latitude, continentality, seasonality, precipitation amount, altitude, etc. (Rozanski et al., 1993).

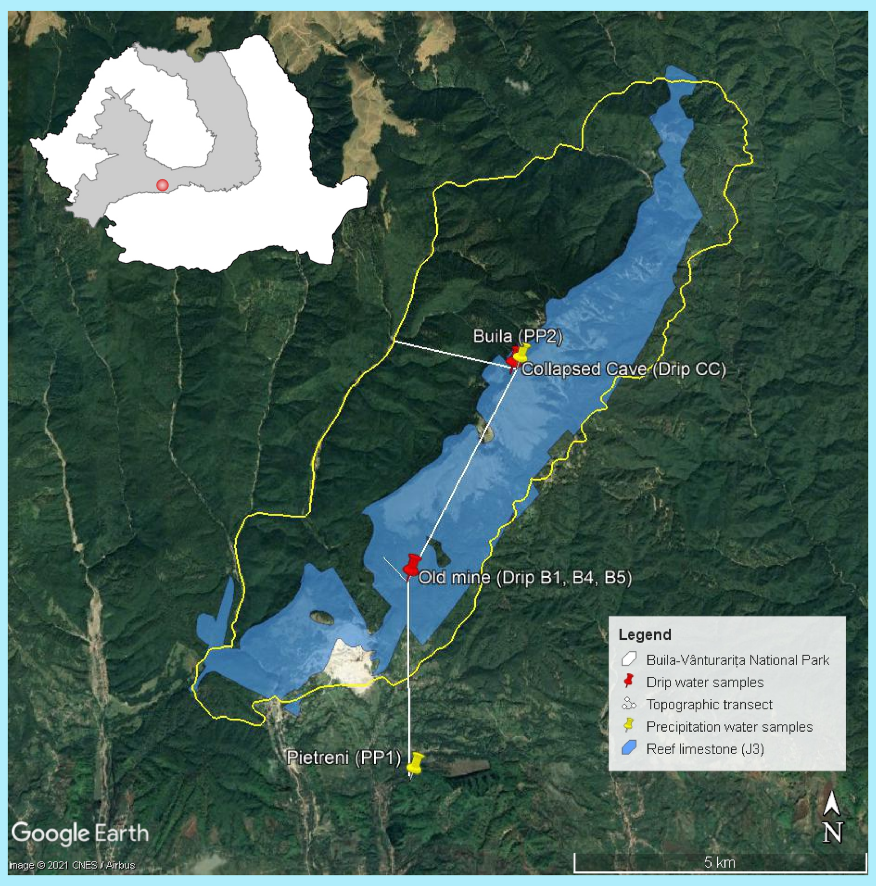
Isotopic fractionation occurred during water infiltration into the bedrock due to a complex of processes leads to more negative values of $\delta^{18}O$ and $\delta^{2}H$, a phenomenon which can be best observed in stable underground environments like caves or artificial tunnels.

We present here the isotopic composition of precipitation and cave drip water along the south-facing side of the Buila–Vânturarița Massif (central South Carpathians), in order to identify the isotopic response of local waters to site-specific environmental conditions.

Geographic setting

The monitoring activities were carried out in the **Buila-Vânturarița National Park** (South Carpathians).

Local geology consists in a metamorphic basement and sedimentary cover of the Getic Unit, mainly reef limestones of Upper Jurassic age. Elevations reach up to 1875 m in the Vânturarița Peak. The limestone ridge is oriented NE-SW and is frequently subjected to mountain storms due to its sharp rise against the dominant western (North Atlantic) airmass circulation.



Mature to old-growth beech forest covers the bedrock above the old mine, whereas the ridge top is the habitat of *alpine and subalpine calcareous shrubs and grassland*. Vegetation structure could influence its control over water infiltration regime into the underground.

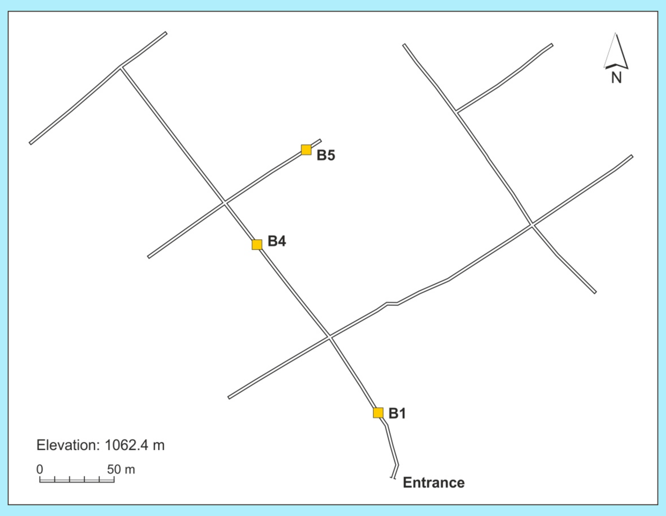


Figure 1. Location map of sampling sites in the South Carpathians (left) and inside the old mine

Materials and methods

We collected the water samples between April 2017 and October 2020, from three main stations:

- Pietreni (570 m) - precipitation water (PP1)
- Old mine (1062 m) - drip water from three underground sub-stations (B1, B4, B5)
- Buila Mount (1820 m) - precipitation (PP2) and cave drip water (Collapsed Cave)

Precipitation water was collected in plastic bottles of 5 l during November 2016 - January 2018. Drip water samples were collected in 2-ml bottles between April 2017-October 2020 and stored at 4°C until stable isotope analysis. The $^{2}H/^{1}H$ and $^{18}O/^{16}O$ isotopic ratios were determined at the Stable Isotopes Laboratory of Northumbria University, by using a LGR IWA-45EP isotope water analyzer.

The results of isotopic fractionations were reported as deviations versus the Vienna Standard Mean Ocean Water (VSMOW), and expressed in delta (δ) notation:

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000\ (‰)$$

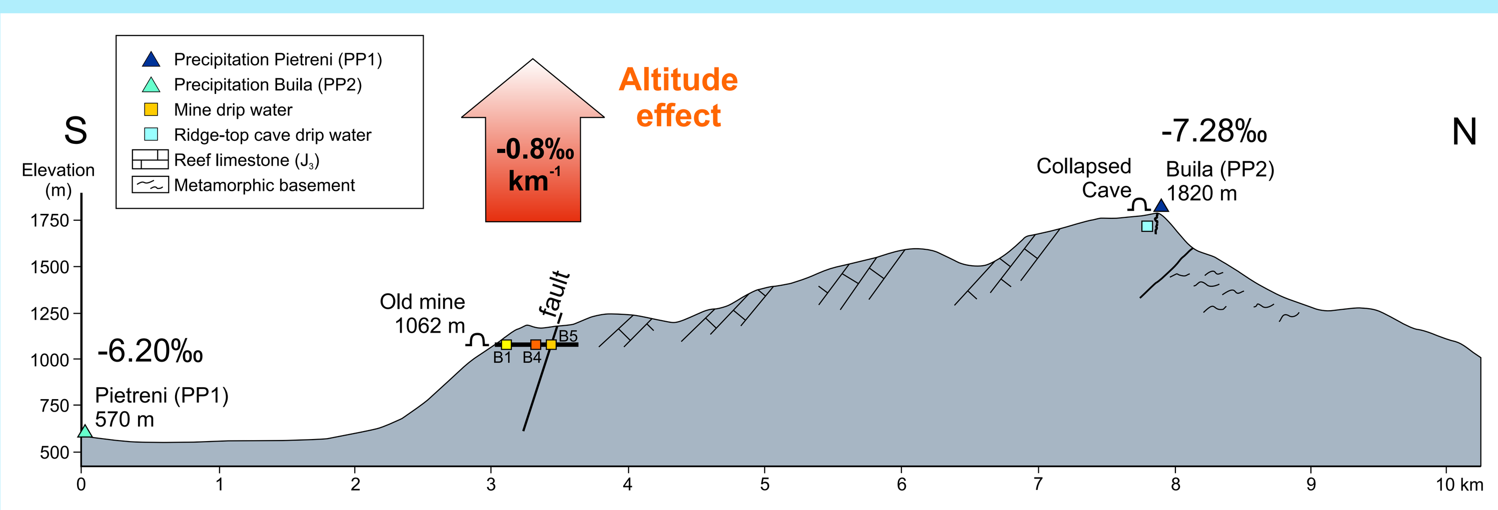


Figure 2. Distribution of sampling sites along the orographic transect, with the average $\delta^{18}O$ values reflecting seasonality and altitude effects in precipitation (data from April-August 2017)

Results and discussion

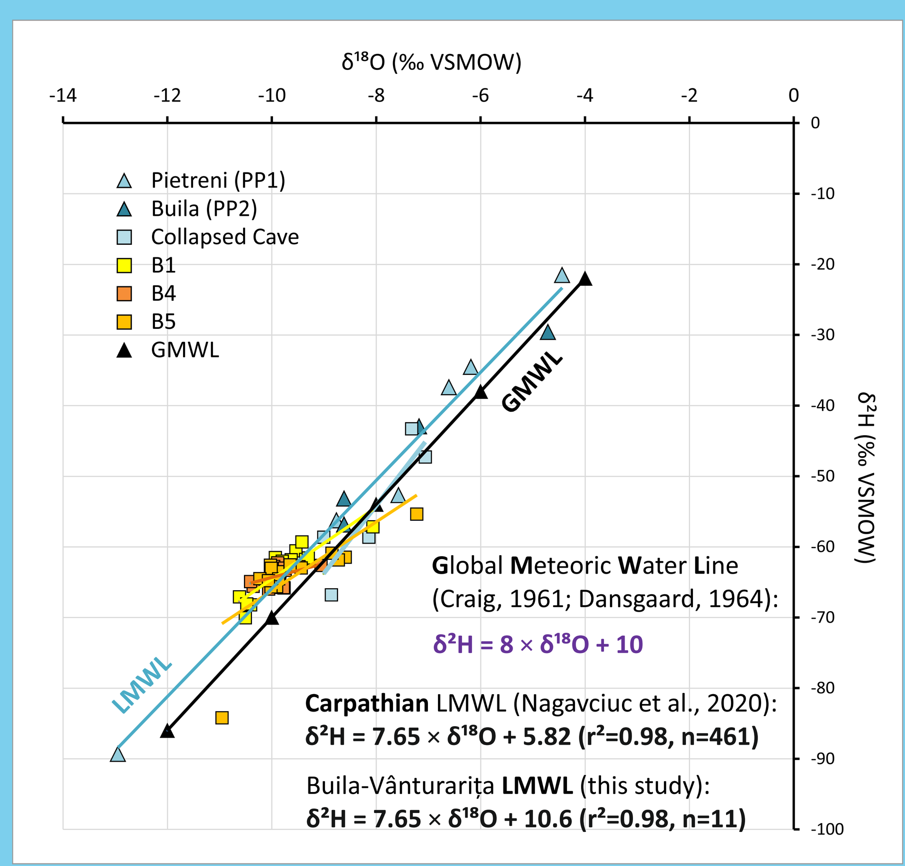
The local meteoric water line (LMWL), aggregated from all precipitation isotopic values for April - August 2017, plots to the left of the global meteoric water line, showing that vapor and condensation was produced under low humidity and high evaporation typical to warm season. Both slope and intercept are similar to GMWL (Craig, 1961) and other Carpathian LMWLs (e.g., Drăgușin et al., 2017; Nagavciuc et al., 2020).

The $\delta^{18}O$ and $\delta^{2}H$ winter average values (–13‰; –90‰) are considerably lighter than summer values (–5.5‰; –30‰). A discrete altitude effect is given by a difference in $\delta^{18}O$ values ranging between 0.3‰ in summer to 1‰ in spring, resulting in a lapse rate of –0.8‰ km^{-1}.

Dripwater shows more depleted isotopic values and mirror the site-specific infiltration mechanisms. Short infiltration paths reflect higher ranges (1.5–2‰ in $\delta^{18}O$ and 13–23‰ in $\delta^{2}H$), closer to the seasonal isotopic values of precipitation. The isotopic differences between B1 and B4 sites were interpreted as an effect of bedrock thickness (40 m vs 110 m, respectively). Outlier values could be explained by the rapid infiltration of ^{2}H- and ^{18}O-enriched water along open fractures, under dryer climatic conditions. The most homogenous values were identified at B4, where bedrock is 100 m in thickness and lacks significant fractures.

The isotopic values in dripwater collected from the ridge–top cave (1820 m a.s.l.) fall around –8‰ in $\delta^{18}O$ and –55‰ in $\delta^{2}H$, very close to precipitation values. We interpret these results by the lower bedrock thickness above the sampling site (~20 m) and the lower capacity of grassland than that of forest in retaining water.

The ^{18}O enrichment seen in precipitation water is higher than the average value of ~–8 ‰ over the Romanian territory versus the VSMOW (0‰), mainly because they reflect the warm season conditions. Typically, summer precipitation show isotopically enriched values, whereas winter precipitations are depleted.



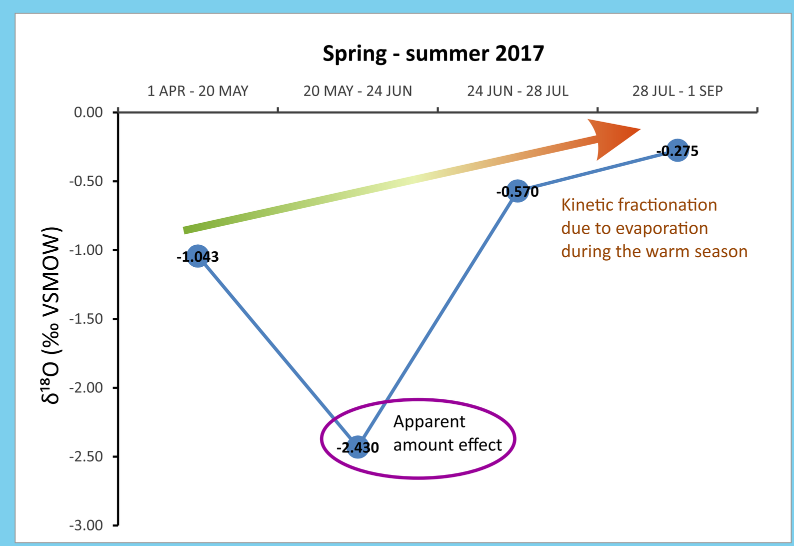


Figure 3. Local altitude, seasonality, and amount effects in precipitation recorded in the isotopic differences between PP1 and PP2.

Figure 4. Plots of local $\delta^{2}H$ vs $\delta^{18}O$ values in precipitation and cave drip water against the GMWL.

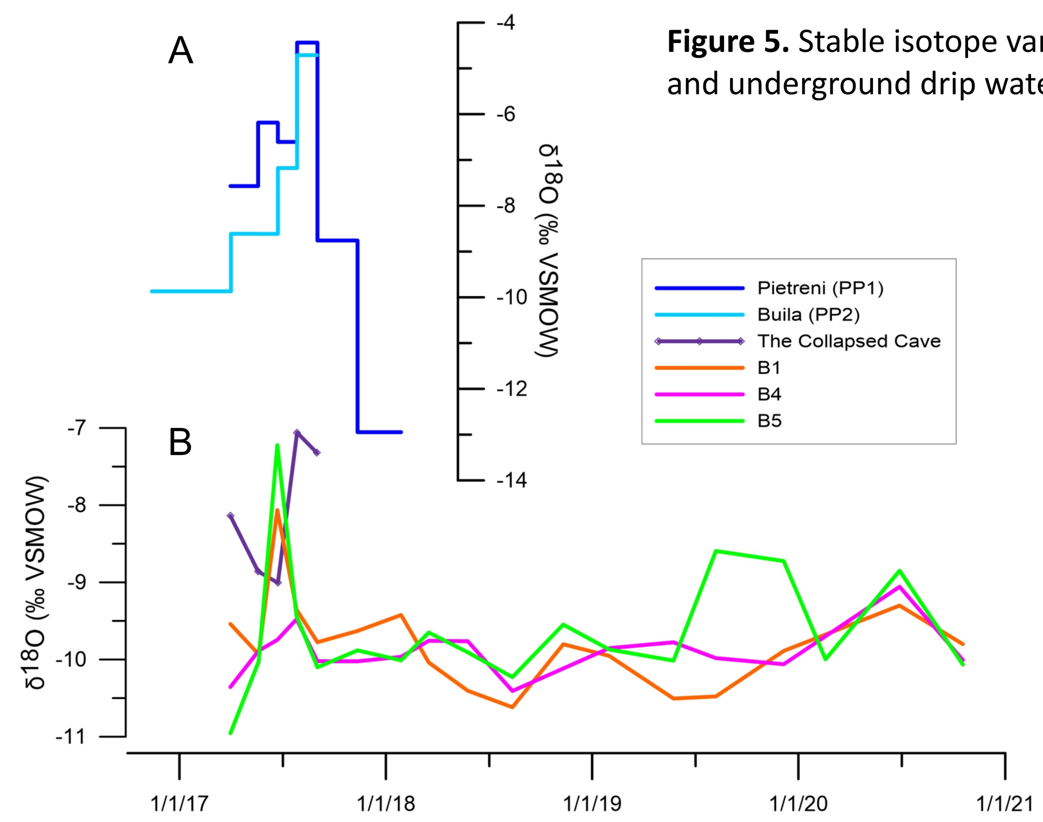


Figure 5. Stable isotope variability in precipitation (A) and underground drip water (B).

Average $\delta^{18}O$ values of cave drip water:

B1 = –9.794‰

B4 = –9.884‰

B5 = –9.596‰

Collapsed Cave = –8.08‰

The low isotopic differences between B1, B4, and B5 sampling sites (0.1–0.3‰) could be attributed to local joints and fractures, leading to ^{18}O depletions. If compared to the isotopic values of dripwater from the ridge-top cave, the difference is considerably higher (1.6–1.9‰).

This could indicate in part the role of forest as a potential regulatory factor of water recharge into the underground, compared to grassland vegetation.

Conclusions

- **Stable isotope variability of $\delta^{18}O$ and $\delta^{2}H$ in precipitation water collected during the spring-summer of 2017 along a 8-km transect in the South Carpathians mostly reflects the temperature-dependent seasonality and altitude effects, and an apparent amount effect during the rainy period.**
- **The isotopic composition of cave drip water outlines the role of bedrock properties (higher thickness, lower porosity) in controlling the residence time of water, which results in more homogenous values of $\delta^{18}O$ (<1‰ in range) and $\delta^{2}H$ (<3‰). Local fractures favor a more rapid infiltration and provide connections between multiple recharge sources.**
- **Isotopic differences between the mine and ridge-top cave drip waters could reflect the role of forests in controlling the water recharge mechanism, with benefits for the functioning and resilience of karst systems.**
- **The local meteoric water line (LMWL) is very similar to the meteoric water line aggregated from the Carpathian region, and close to the global one. This pattern indicates the North Atlantic as the most important moisture source, and the connections between NAO and climate variability over the South Carpathians.**

Acknowledgements

The authors acknowledge the Commission on Speleological Heritage and administration of Buila-Vânturarița National Park for authorizing fieldwork activities. We are grateful to M. Stoica for supporting fieldwork and water sampling. The Visegrad Foundation (supported by the International Visegrad Funds), is acknowledged for co-financing this conference.

References

- Craig, H., 1961. Isotopic Variations in Meteoric Waters. Science, 133, 1702–1703.
- Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus, 16(4), 436-468.
- Drăgușin, V., Balan, S., Blamart, D., Forray., F.L., Marin, C., Mirea, I., Nagavciuc, V., Orășeanu, I., Perșoiu, A., Tîrlă, L., Tudorache, A., Vlaicu, M., 2017. Transfer of environmental signals from the surface into the underground at Ascunsă Cave, Romania. Hydrol. Earth Syst. Sci. 21, 5357–5373.
- Nagavciuc, V., Bădăluță, C.-A., Ioniță, M., 2020. The influence of the Carpathian Mountains on the variability of stable isotopes in precipitation and the relationship with the large-scale atmospheric circulation. Geological Society, London, Spec. Publ., 507, https://doi.org/10.1144/SP507-2020-69.
- Rozanski, K., Araguás-Araguás, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: Swart, P.K. et al. (Eds), Climate change in continental isotopic records.