THE PETRIFIED RIVER AND THE BIOGEOCHEMICAL PROCESSES THAT GENERATE THIS UNUSUAL OCCURRENCE IN THE KARST OF THE PĂDUREA CRAIULUI MOUNTAINS

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Abstract. The petrifying springs with tufa formation are a very rare habitat in Romania, protected under EC Habitats Directive (92/43/EEC), Annex 1: *H7220 Petrifying springs with tufa formation*. The Petrified River with the two petrifying springs represent a unique occurrence for the Pădurea Craiului Mountains, which recently gained the protected natural area status of county interest. In order to understand the processes underlie the Petrified River we collected two sample sets (summer and autumn) from nine water sources from the southern part of the Pădurea Craiului Mountains. We investigated the geology of the local area, as well as the physicochemical and biological characteristics of the waters that form the Petrified River, versus the adjacent freshwaters, and a petrifying waterfall. Geologically, the investigated water sites differ fundamentally: The Petrified River with its springs and their tributaries are developed in the sedimentary rocks, such as Middle Triassic limestones and marls; while in the upper part of the Sohodol Valley dominated the igneous lithology, and the Vadu Crişului Fall represented a cave emergence developed in Upper Jurassic and Lower Cretaceous limestones. As a result of the distinct geological structure, the water sources showed different chemical composition. We found that the two petrifying springs derived from two different underground streams had distinct chemical features and different proportion of microbial contamination, the water fall had a chemical composition similar to the petrifying waters, while the freshwaters from volcanic rocks showed small quantities of dissolved carbonates, and different concentration of trace elements and nutrients. The biota, represented by viable microbes and meiofauna communities, showed a seasonal response and contributed to the creation of the particular environment that facilitated the tufa formation, especially in summer. Our observation confirmed that the mechanism of carbonates precipitation was different in the Petrified river from Vadu Crişului Fall, despite their similar carbonates content: in the Petrified river the deposition was formed along the riverbed due to the lower flow that quickly had risen to the ambient temperature, while in the case of the Vadu Crişului Fall the deposition is done only at the cascade, due to the agitation of the water falling in condition of a high flow with a high thermic inertia.

Key words: petrifying springs, Petrified River, tufa, Pădurea Craiului Mountains, water chemistry, microbial content, meiofauna.

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1. INTRODUCTION

The Petrified River represents an unusual karstic occurrence from the Pădurea Craiului Mountains. It is developed in the Gropii Valley, tributary to the upper basin of the Căbeştilor-Sohodol Valley (right side), which is one of the important hydrographic networks in the southern part of the Pădurea Craiului Mountains (ONAC, 2002). The Petrified River originated from two limestone precipitating springs, which contributed together to the petrification of the Gropii Valley.

The limestone precipitating springs are those ambient-temperature springs that achieved sufficient oversaturation of $CaCO_3$, mainly through physical CO_2 degassing and photosynthetic activity, thus depositing limestone. In Europe, these springs are a protected spring category, in contrast with other countries worldwide (CANTONATI *et al*., 2016). Thus, under the name *Petrifying springs with tufa formation (Cratoneurion)* the limestone precipitating springs represent a habitat which is subject to the conservation legislation in the frame of the Natura 2000 Coordinated Network of Protected Areas (EU-Code 7220, Annex I, Council Directive 92/43/EEC, 1992). This habitat is described as hardwater springs with active formation of travertine or tufa that are found in such diverse environments as forest or open countryside, and are generally small and dominated by bryophytes (EUR 28, 2013). In Romania, the habitat 7220 is limited as occurrence in sixteen Natura2000 sites, but was not reported in ROSCI0062 Defileul Crişului Repede – the Pădurea Craiului Mountains, or in the Pădurea Craiului Mountains. Regarding the surface, this habitat represents circa 3.16% of all Natura2000 sites, ranging between 0.00005% and 1% (ONETE *et al*., 2014).

The term tufa is used to indicate any freshwater carbonate, developed under ambient temperature conditions (the meteogene type) and included abundant fossil moulds and casts of plants and trees (PEDLEY, 2009). Tufa is distinguished from the travertine that developed in non-saline hydrothermal conditions (the thermogene type), where the water is too hot for enabling growth of macrophytes (plants and trees), although bacteria and cyanobacterial colonization is possible and widespread (PEDLEY, 1990; FORD AND PEDLEY, 1996; PEDLEY, 2009). Both terms, tufa and travertine were used indiscriminately as alternative names for the same material, or even applied to cave deposits or speleothems, sometimes described as hypogean travertine (PENTECOST, 1981, 2005). In caves, the calcareous depositions are common and form a large category of speleothems (e.g. stalactites, stalagmites, flowstones). But speleothems are composed predominantly of concentric bands of well-crystalized calcite, whereas tufa refers to the subaerial deposits produced by carbonate precipitation from ambient temperature waters, in the presence of prokaryotes, micro- and macrophytes (PEDLEY, 2000, 2009). Typical speleothems never presented plant remains, and the micritic and peloidal bands are generally thin or absent. The CO_2 origin is also distinct in the three types. In meteogene tufa, the CO_2 derived from soils and epigean atmosphere, whereas in thermogene travertine, it derived from the contact of hot fluids involved in hydrolysis and

oxidation of reduced carbon, decarbonation of limestone, or directly from the upper mantle (PEDLEY, 2009). Instead, speleothems are formed by precipitation of calcium carbonate from supersaturated cave waters, by degassing of CO_2 from drip water, which enters the cave through fractures. Degassing occurs because the water was previously equilibrated with CO_2 at elevated partial pressure in the soil percolation zone and degasses upon emergence into the lower CO_2 pressure of the cave ventilated gallery (LAURITZEN AND LUNDBURG, 1999).

Based on geometry, profile details, typical bed phyto-associations, and characteristic facies, FORD AND PEDLEY (1996) classified outcrop-based tufa in five depositional models: perched springline, cascade, fluvial, lacustrine and paludal. But individual faces can occur in more than one model, because each of the models is part of a facies continuum. According to this classification, the Petrified River, together with the two petrifying springs belong to the perched springline model of deposition, which typically develops in hilly countries (PEDLEY, 2009). Same as the other examples of this model, like those from Spain and Sicily for example (PEDLEY *et al*., 2003), the Petrified River developed on steep valley sides and is composed of two elements: a proximal deposit that corresponds to the point sources, and a distal deposit. The bedrock of the Petrified River is covered by a thick deposit of calcareous tufa, forming many barriers, curved dams and basins, different in forms and sizes, in which the water is collected and slowly drains out to meet other water courses, also tributary to the Sohodol Valley. Small waterfalls, often over 1 meter high, contribute to the beauty of this karstic landscape, as well. The distal deposits are composed of tufa intraclasts that were transported and deposited on the lower valley slopes. The presence of tufa is also common in waterfalls, where the calcium saturated groundwater emerges to the surface, and the Carbon dioxide is released by the water agitation. The Vadu Crişului Fall, located also in the Pădurea Craiului Mountains, belongs to the cascade model of PEDLEY (1990). The underground river that exits the cave follows a vertical fall of 9 meters, which flows directly into the Crişul Repede River.

Neither as spectacular as similar deposits of calcareous tufa from other karstic areas such as Plitvice Lakes, Croatia (MARKOWSKA, 2004), nor as numerous as the petrifying springs from the Slive Bloom, Ireland (HEERY, 2007), the Petrified River is though unusual in Romania. It has a large part (about 300 meters long) of its riverbed covered in a thick layer of tufa deposits. Due to the unusual character of this river and to the need of conservation, the Petrified River (Valea Gropii) from Sohodolul Căbeştilor, a karstic landscape that includes the freshwater course together with the two springs that formed it, recently became a protected natural area of county interest (Decision 253/2021).

In Romania, the petrifying spring with tufa formation habitats were studied only under the aspect of vegetation associations, spatial distribution, pressures, threats, and the need of conservation (OPREA *et al*., 2007; STANCU, 2013; ARSENE *et al*., 2021). This work tackles the geology of the local area as well as the physicochemical, microbiological characteristics and meiofauna of the water sources that form the Petrified River, in order to designate the local conditions and the

processes that contributed to the deposition of tufa on the riverbed. In this regard, we analysed the petrifying springs and all water courses who have joined the main river course, by comparing data with the characteristics of the nearest rivers, and of the Vadu Crişului Fall. The purpose of our work was to understand the biogeochemical processes that generate this unusual occurrence in the Pădurea Craiului Mountains and why this karstic phenomenon is so rare in Romania.

2. METHODS

2.1. GEOLOGICAL FRAMEWORK

In order to establish the geological framework of the sample sites, we developed field observation for details of the geological structure, followed by stereoscope analyses of the sampled rocks.

2.2. SITE DESCRIPTIONS AND SAMPLE POINTS

The Petrified River also known by local people as the Gropii Valley is tributary to the Chinciu Valley (right side), which is also tributary to the Sohodol Valley (right side), in the southern part of the Pădurea Craiului Mountains (Western Romanian Carpathians) (Figure 1 a, b). The water sampling included nine freshwater sites (2 springs, 6 water courses and 1 fall), as follows (Figure 1c):

1. The Petrifying spring (PS), located in the course of the valley, at the beginning of the petrified sector. It was sampled at the site of emergence from underground;
2. The White spring (WS) named here ‘white’ due to the colour of the carbonate precipitate deposits. It is located in the left versant of the Gropii Valley, few meters away from the main water course, and also from PS. WS was also sampled at the site of emergence from underground.
3. The Petrified river (PR) sampled from the semi-stagnant water of the tufa basins;
4. The Upstream river (UR) tributary to the Petrified river (right side);
5. The Downstream river (DR) tributary to the Petrified river (left side);
6. The Chinciu Valley (CVC) sampled downstream from the confluence with the Petrified River, the Upstream river and the Downstream river.
7. Upstream from the Sohodol Valley (USV), 4 km away from the confluence with the Chinciu Valley, in front of a high limestone pick, locally known as *Cucuruz* due to its tall and narrow shape, well delimited in the surrounding landscape (*Cucuruz* is the Romanian traditional regional term for ear corn).
8. Downstream from the Sohodol Valley (DSV), sampled after the confluence with the Chinciu Valley;
9. The Vadu Crişului Fall (VCF), sampled where the river exits the cave, about 50 meters upstream from the fall.

Two sets of samples were collected, in August 2021, after a dry period, and in October 2021 after a raining period, respectively. The purpose was to observe how the water volume influences the water physicochemical and microbiological profile.

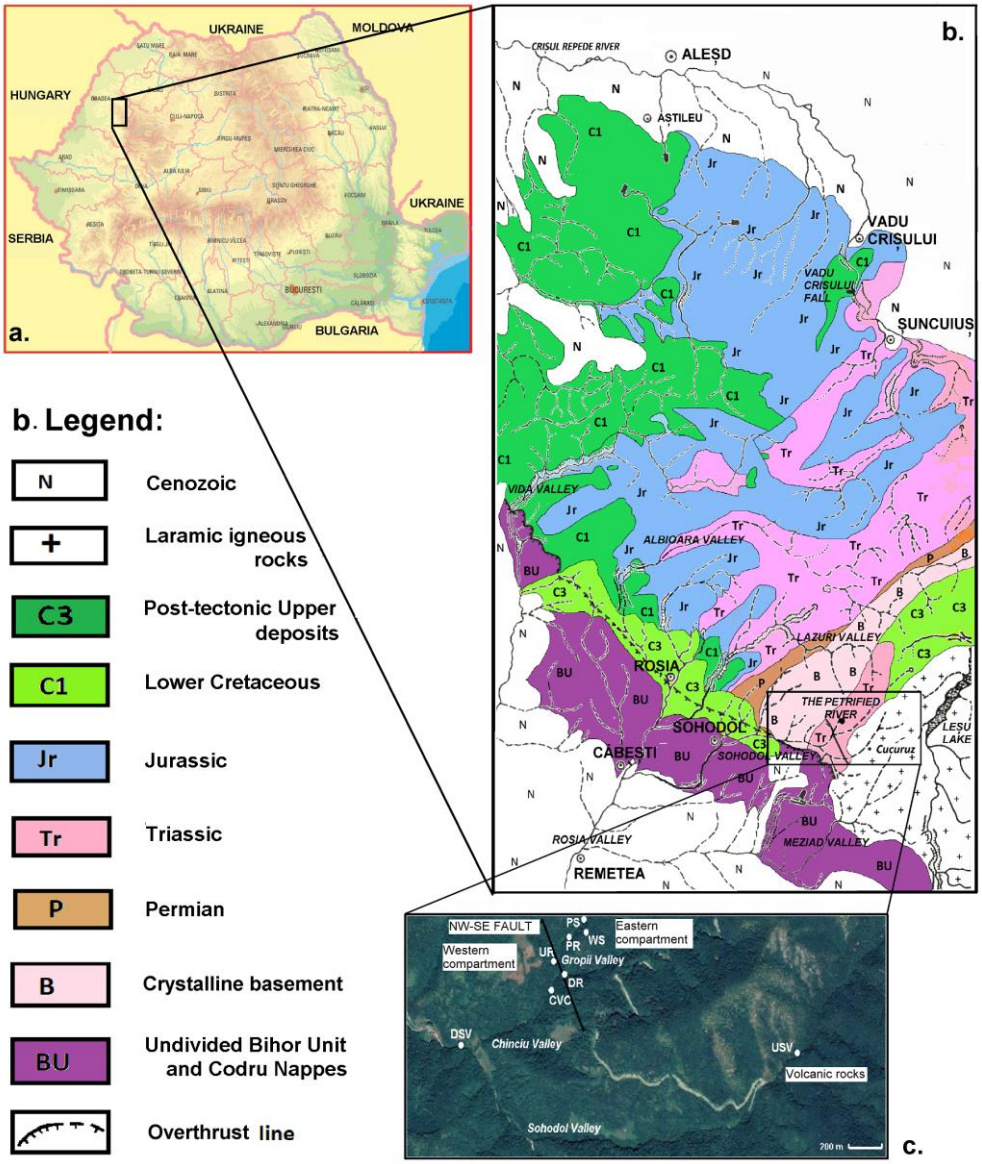

Fig 1. The Petrified River: **a.** Map showing Romania,
b. Geological map of the central part of Pădurea Craiului, **c.** Location of surveyed sites.

2.3. WATER ANALYSES

2.3.1. Physicochemical parameters

Water temperature (t^oC), pH, resistivity (R), conductivity (C), total dissolved solids (TDS), oxidation-reduction potential (ORP), and salinity (S) were measured directly on site, using a Multiparameter from Hanna Instruments (HI 9828 series). For additional details regarding the accuracy of the methods see Borda *et al.* (2019).

The chemical profile of the water was determined in laboratory using the Photometer Multiparameter from Hanna Instruments (HI 83300). Based on photocolorimetric methods we measured: Manganese (Mn), Zinc (Zn), Iron (Fe), Copper (Cu), Chromium (Cr), Calcium and Magnesium Hardness, Calcium (Ca^{2+}), Nitrates (NO_3^-), Nitrites (NO_2^-), Ammonium (NH_4^+), and Phosphates (PO_4^{3-}).

2.3.2. Water microbial content

We identified and quantified the viable colony forming units (CFU) from 1 mL of water, using the following media cultivation plates (R-Biopharm production): Compact Dry TC for the total aerobic mesophilic counts (TAC), Compact Dry EC for *Escherichia coli* (Ec) and total coliforms (TC), and Compact Dry YM for yeast (Y) and moulds (M). After 48 hours of incubation at 36°C, readings of TAC, Ec, and TC growth were scored. For Y and M, the incubation time was 5 days at 25°C.

2.3.3. Meiofauna and the aquatic invertebrates

Ten litres of sampling water were collected from each site, then filtered by a 50 μm sieve, and preserved in 70% ethanol. The major groups of meiofauna (protists and invertebrates < 500 μm size) and the aquatic invertebrates (≥500 μm size) were counted and sorted in laboratory, under the stereoscope (OPTIKA Microscopes Italy, SZR model).

3. RESULTS

3.1. GEOLOGICAL FEATURES

Following field observations regarding the geology of the Gropii Valley, we identified a fault line, NW-SE oriented, located in the proximity of the Petrified River. This fault separates an elevated compartment with metamorphic rocks, sandstones, and Lower Triassic marls at the surface (non-karstificable rocks) in the west, by another compartment positioned on a lower level and covered with Middle

Triassic limestones in the east. Both compartments belong to the Bihor Unit (Figure 1b). Due to their thickness and large area occupied, these limestones create conditions for the development of underground galleries that collect the rainwater and guide it underground, via complicated ways, inaccessible to human. In the vicinity of the fault that separates the two compartments, the water exits the underground through two neighbouring springs: the Petrifying spring, and the White spring (Figure 1c). These two petrifying springs, despite the fact that they had low flows of less than 1L/s (at the sampling time), they developed (right below their resurgences) lenticular, lobate and fan-shaped deposits, coloured green-greyish for the former spring, and yellowish-white for the latter. Together, the PS and the WS form the mainstream of the Petrified River. A succession of channels enforced by levees which prevent water leakage developed on the upper surface of the deposits. Sinuous tufa walls, arcuate dams transversally developed by the water flow, barrage basins of different sizes, and a succession of 1–2 m high cascades had extended few hundred meters from the inception points (Figure 2 a, b).

a. **b.**

Fig 2. The Petrifying River: **a.** arcuate dams and barrage basins;
b. succession of cascades (Photos: D. Borda).

3.2. PHYSICOCHEMICAL FEATURE OF THE PETRIFYING WATERS AND THE ADJACENT FRESHWATERS

The physicochemical parameters measured on site, trace elements, water hardness and nutrients measured in all sampled points are centralized in Table 1. According to our findings the petrifying springs (PS and WS), the Petrified River (PR), and the Vadu Crişului Fall (VCF) were considered as petrifying waters, while the tributary rivers (UR, DR), the Chinciu Valley and the Sohodol Valley were conventional freshwaters.

Table 1

The physicochemical features of the petrifying waters (PS*, WS*, PR*, and VCF*) compared with the adjacent freshwaters (UR, DR, CVC, USV, and DSV)

	PS*	**WS***	**PR***	**UR**	**DR**	**CVC**	**USV**	**DSV**	**VCF***
	Physical parameters measured on site								
Temperature (^{O}C)	10.01	10.52	9.26	8.87	9.4	9.72	7.92	8.69	10.41
pH	7.87	7.67	7.86	8.13	7.98	8.02	7.45	7.85	7.42
Resistivity (kω·cm)	2.4	2.4	2.7	3.4	3.7	3.3	15.4	4.6	2.6
Conductivity (μs/cm)	304	303	259	201	192	217	44	142	279
TDS (ppm)	210	209	185	145	136	153	32	108	193
Salinity (Δ Seawater)	0.2	0.2	0.18	0.14	0.13	0.15	0.03	0.1	0.19
ORP	120	136	96.4	93.4	85.1	69	125	58.2	15.3
	Hardness								
Ca Hardness (mg/L $CaCO_3$)	131	111	116	108	110	119	26	95	195
Mg Hardness (mg/L $CaCO_3$)	67	60	65	43	26	41	2	11	7
Calcium (mg/L Ca^{2+})	21	5	81	91	37	12	0	2	97
	Trace elements								
Manganese (mg/L Mn)	0.4	0.4	0.4	0.4	0.5	0.3	0.4	0.5	1
Zinc (mg/L Zn)	0.13	0.11	0.29	0.09	0.23	0.35	0.05	0.12	0.03
Copper (mg/L Cu)	0.03	0	0.04	0.04	0.01	0.01	0	0.02	0.01
Iron (mg/L)	0.073	0.011	0	0.019	0.002	0.024	0	0	0
Chromium (mg/L Cr^{6+})	0	0.021	0	0	0.031	0	0.003	0	0.031
	Nutrients								
Nitrite (mg/L NO^{-}_{2})	0	0	0	0	0	0	0	0	0
Nitrate (mg/L)	0	0	0	0	0	0	0	0	0
Ammonium (mg/L NH_4)	0.01	0.05	0.04	0.05	0.08	0.09	0.08	0.05	0.09
Phosphate (mg/L PO_4^{3-})	0.4	0.1	0	0.3	0	1.2	0.5	0.7	0

Figures 3–6 show differences in the physicochemical profile measured on site (Figure 3), trace elements (Figure 4), water hardness (Figure 5) and nutrients loading (Figure 6) between summer and autumn seasons for the most relevant petrifying waters (PS*, WS*, and PR*) and conventional freshwaters (UR, DR, and USV). The summer sampling was done in a dry period, marked by lower levels of the water in springs and rivers. Moreover, the majority of the barrage basins of the Petrified River were completely dry. In contrast the autumn sampling was done after a rainy period, when the water levels were high and the basins were mostly full of water.

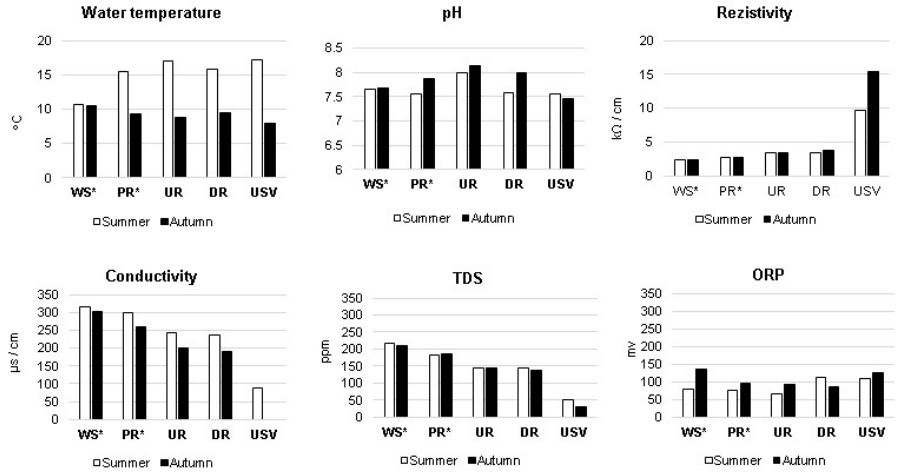

Fig 3. Physicochemical parameters of petrifying waters (marked with *) versus conventional freshwaters (without *) in Pădurea Craiului Mountains.

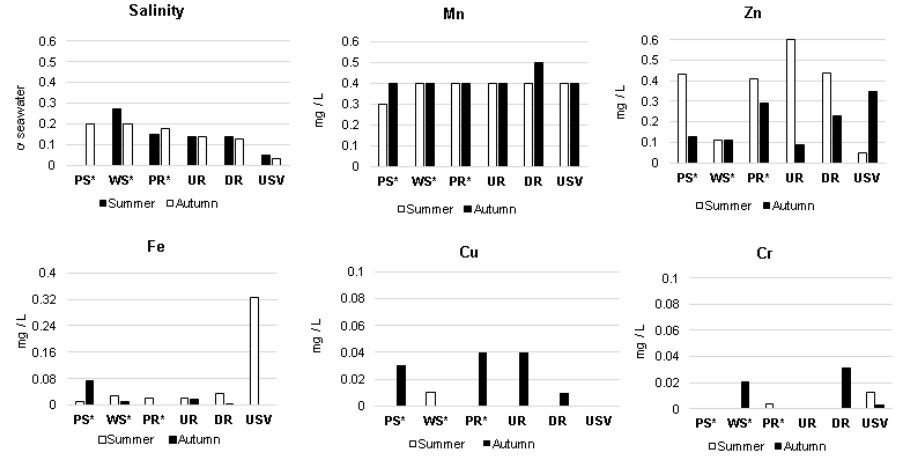

Fig 4. Trace elements from petrifying waters (marked with *) versus conventional freshwaters (without *) in Pădurea Craiului Mountains.

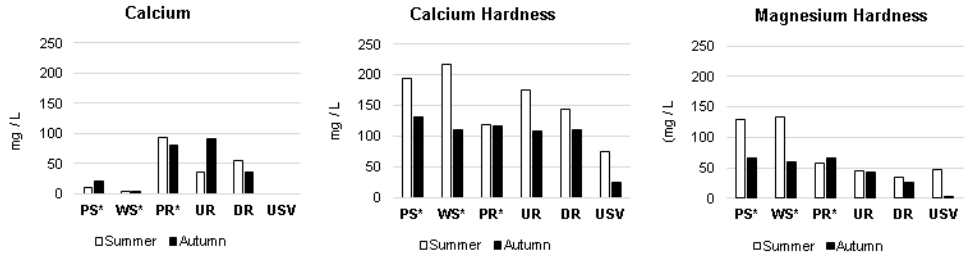

Fig 5. Water hardness and calcium ionic concentration in petrifying waters (marked with *) versus conventional freshwaters (without *) in Pădurea Craiului Mountains.

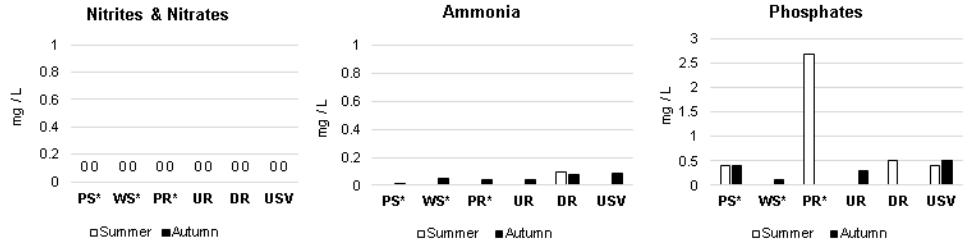

Fig 6. Nutrients from petrifying waters (marked with *) versus conventional freshwaters (without *) in Pădurea Craiului Mountains.

3.3. BIOTIC FEATURES OF THE PETRIFYING WATERS AND THE ADJACENT FRESHWATERS

3.3.1. The microbial content

Table 2 shows the concentration of the three groups of viable microbe categories, total aerobic count, total coliforms, *Escherichia coli*, and yeast & moulds, per 1 mL sample from the petrifying waters (PS*, WS*, PR*, and VCF*) and conventional freshwaters (UR, DR, CVC, USV, and DSV). Figure 7 shows the content of the three groups of microbes found in summer, compared to autumn for the Petrified River and its tributary rivers, UR and DR.

Table 2

The microbial content of the petrifying waters (PS*, WS*, PR*, and VCF*) compared with the adjacent freshwaters (UR, DR, CVC, USV, and DSV)

	PS*	WS*	PR*	UR	DR	CVC	USV	DSV	VCF*
	Microbial content								
Total Aerobic Count (UFC/ml)	116	22	93	145	112	65	16	104	38
Total Coliforms (UFC/ml)	11	15	52	18	25	18	12	24	n/a
***E. coli* (UFC/ml)**	0	0	27	0	3	2	0	0	
Yeast & Molds (UFC/ml)	28	0	29	0	0	6	1	2	0
	Meiofauna								
Larval Insects	2	0	1	0	2	0	0	0	0
Water Mites	0	0	0	2	0	0	0	0	0
Flatworms (Turbellaria)	0	0	0	0	0	0	2	0	0
Amphipods	0	0	1	11	0	0	0	0	0
Ostracods	0	0	0	1	0	0	0	0	0
Copepods, Harpacticoids	0	0	0	0	1	0	0	0	0

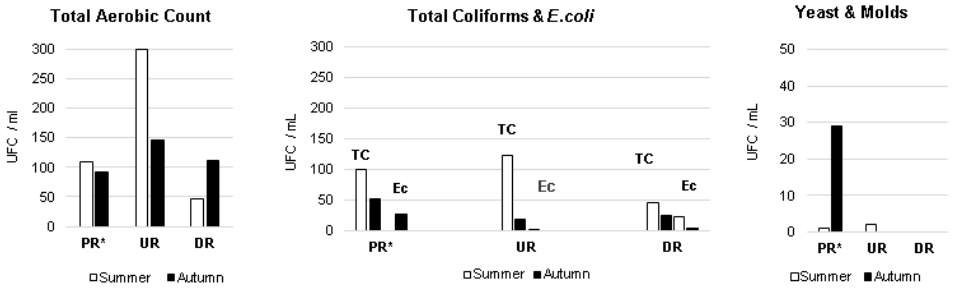

Fig 7. Microbial content of petrifying waters (marked with *) versus conventional freshwaters (without *) in Pădurea Craiului Mountains.

3.3.2. Meiofauna and the aquatic invertebrates

Meiofauna and the aquatic invertebrates found in 10 L of filtered water were centralised, in terms of number of individuals, and major groups of organisms (Table 2). Figure 8 shows the frequency and the diversity in petrifying waters and conventional freshwaters, and also shows comparatively the abundances and the group diversity of the petrifying waters and conventional freshwaters in the two seasons, with dry and rainy periods.

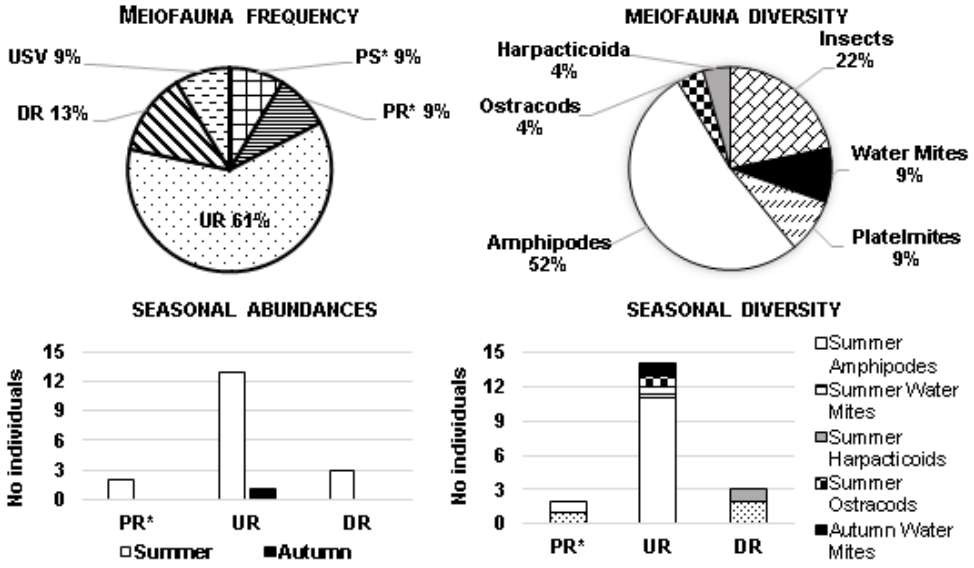

Fig 8. The frequency and diversity of meiofauna (top), and the seasonal abundances and diversity (bottom) in petrifying waters (marked with *) versus conventional freshwaters (without *).

4. DISCUSSIONS

4.1. THE GEOLOGICAL STRUCTURE OF THE SOUTHERN PART OF THE PĂDUREA CRAIULUI MOUNTAINS AND THE GEOLOGICAL SIGNATURE ON THE PETRIFYING WATERS

Between the northern, southern or south-western parts of the Pădurea Craiului Mountains, differences in the succession and the facies of Mesozoic sediments were observed. At the beginning of the 20th Century it was hypothesized that the southern parts overlap the northern part (PÁLFY, 1915, 1916; ROZLOZSNIK, 1920). The southern and south-western part of the Pădurea Craiului Mountains are dominated by sedimentary rocks that were deposited in deeper environments compared with those from the northern part (PATRULIUS, IN IANOVICI *et al*. 1976). The Roşia Depression, which extends over the Sohodol Valley until reaching the Sohodol village is located on the boundary that separates these two parts. This hypothesis was reconfirmed by KRÄUTNER (1939, 1941) and is accepted today by geologists (PATRULIUS, IN IANOVICI *et al*. 1976). Over time, more tectonic units in an overlap relation were separated (e.g. the Bihor Unit and the Codru Nappes-Vălani, Finiş, Arieşeni) (PATRULIUS, IN IANOVICI *et al.* 1976). Due to the tectonic complexity, there was no unanimity among geologists regarding the local units and structures, and there are still interesting unresolved issues (Balintoni, 1994).

According to the geological maps (BORDEA *et al*. 2006, 2018), the succession of the Mesozoic sedimentary rocks appears on the upper course of the Sohodol Valley that belongs to the Bihor Units, where the limestones cover large areas, being dominated especially by Triassic limestones (PATRULIUS, IN IANOVICI *et al*. 1976).

The situation is quite different on the upper course of the Sohodol Valley, where a very large area of volcanic rocks (igneous) is developing towards east, reaching the Vlădeasa peak. Their contact with the sedimentary rocks is visible in many outcrops, proving that this area is one of the rising magma, of the rooting and breaking-up of the metamorphic rocks and Triassic or Upper Cretaceous ('Senonian') sediments, by the igneous molten mass. In the eastern areas, the igneous rocks usually cover the Mesozoic layers (including the Upper Cretaceous ones) or can be found between sedimentary layers, generating subvolcanic rocks. In the place called *La Cucuruz* there is a Triassic limestone peak, of approximately 25 meters in height and 15 meters wide, slightly flattened, located parallel to the valley. It stands above of igneous rocks, porphyric riolites with flow structures, typical for the whole Vlădeasa area. Next, eastwards, at approximately 30 meters distance from it, another peak, more modest in height, reveals the same geology, but passes almost unnoticed in contrast to the giant beside him. It is probably the only proof that in this area, the ascension towards surface of the colder and viscous acidic magma of Vlădeasa that elevated a part of the Triassic limestone layers. Most of these limestones have been fragmented and covered by molten lava, a frequent situation in the Vlădeasa area. But in the case of the Sohodol Valley, the limestone was erected over the viscous molten mass, being cracked and fractured by lava movements. Consequently, the limestone peaks were quickly penetrated and dissolved by surface waters, who had actually secondly reshaped them.

The fault line that exists in the proximity of the Gropii Valey separates two compartments of Bihor Unit, non-karstificable rocks in the west, from the karstificable Middle Triassic limestones in the east. The two neighbouring springs (PS and WS) that form the Petrifying River show different water proprieties suggesting that they are draining different underground networks with uneven scale deposition rates. A very high-rate calcium carbonate deposition, especially for the White spring from the left-hand slope that represents the eastern part of the Petrified River is evidence that these springs come from deep underground, where a large amount of limestone on their subsurface flow was dissolved. It is known that the dissolution capacity increases with acidity, with decreasing temperature, and an increase in pressure due to the water column. Usually, the water acidity is due to the humic acid in the soil, carbonic acid in the atmosphere, or due to the volcanic activity etc. In the present case, excluding the volcanic activity, absent here for a very long time (for 65 million years, since the upper Cretaceous), we suspect the water circulation at great depths having around 10^{o}C. The rise of water to the surface causes an accelerated carbonates deposition, considering the loss of pressure, the temperature rises and the release of carbon dioxide. The springs with low flow, such as PS and

WS, due to the fan dispersion of the water in the basins, quickly take over the ambient temperature, such that they quickly reach from 10°C to over 15°C in summer. Consequently, they rapidly lose dissolved CO_2, accelerating the process of calcium precipitation, with or without biogenic intermediation. This leads to the development of curved barrage basins, in different sizes, sometimes exceeding 1m high, similar to those created inside the caves called *gours* (limestone dams), who generate a spectacular morphological landscape. The phenomenon is also known from other places, but the formation of tufa along the river is unusual in Romania. In other countries, such as Croatia (HORVATINČIĆ, 2000), Spain (ORTIZ *et al*. 2009), Germany (MEGERLE, 2021), Italy (BROGI, 2012), Turkey (TOKER, 2017) there are more spectacular examples. But not the same process happens in high debit flow, as in the case of the waterfall from the Vadu Crişului Cave, where the temperature practically does not change in the short distance from the cave exit, until the waterfall. Consequently, only the agitation of the falling water determines the loss of CO_2 and the precipitation of $CaCO_3$.

4.2. THE PHYSICOCHEMICAL FEATURE OF THE PETRIFYING WATERS, COMPARED WITH ADJACENT FRESHWATERS IN DRY AND RAINY PERIODS

4.2.1. Physicochemical parameters measured on site

The water temperature reflects the environmental temperature and the origin of the water sources. Thus, the measured values showed higher amplitude in summer, and lower in autumn. In contrast, the two springs and VCF showed almost constant temperatures in both seasons, reflecting their underground provenance. All sampled waters had a slightly alkaline pH, which is characteristic to calcareous areas. These values indicated that, in autumn, when the temperatures were lower and the process of limestone dissolution was more pronounced, the pH was slightly higher in the sampled waters, excepting the USV, where this relation was inversed because of the predominantly volcanic lithology.

The resistivity and conductivity of the water were in inverse proportionality, reflecting the concentration of dissolved substances, which were also reflected by the TDS values. Our measurements showed a high content of dissolved substances in all sampled sources from the area of the Petrified River, with a maximum in WS, PS and VCF, thus proving their underground provenience. Slightly lower values were measured in tributaries waters (UR, DR) and after their confluence with the Chinciu and the Sohodol valleys (CVC, DSV). Instead, regarding USV (upstream of the Sohodol Valley), which was sampled in the proximity of *Cucuruz*, the conductivity and TDS decreased very much, while the resistivity increased more, which reflected the presence of small quantities of substances dissolved in this stream, being also typical of waters from volcanic rocks. ORP had high values in the petrifying waters (PS, WS, PR) and also in the left tributary (DR) and USV, reflecting a good capacity of water decontamination. The lowest ORP was

measured in VCF. In the case of the Vadu Crisului karstic system, we suggest as possible explanation the oxygen consumption during the decomposing processes of the organic matter with no possibility of replacing it due to the long underground water course below the hydrostatic level. In contrast, the petrifying springs probably have a shorter karstic system, closer to the hydrostatic level where the oxygen exchanges take place easier. ORP offer additional information of the water quality and degree of pollution, because it reflects the ability of waters to 'cleanse' themselves from contaminants. In clean good quality waters, ORP is known to have high values (between 300–500 mV), which imply high concentrations of dissolved oxygen and other elements that can function like oxygen, enabling an environment where bacteria can function more efficiently for decomposing dead tissue and contaminants (HORNE AND GOLDMAN, 1994). We also observed that the ORP decreased with increasing pH, fact that was also reported beforehand (COPELAND AND LYTLE, 2014). With one exception, in DR, the ORP showed increased values in autumn, compared to summer, because smaller temperatures generally contribute to maintaining the gases in solutions.

Salinity had higher values in the petrifying waters (PS, WS, PR, and VCF) and lower concentrations in the Sohodol river (USV and DSV) suggesting that this natural salinity is a result of dissolution of carbonates from bedrocks (Krishan, 2019). No striking seasonality of salinity was observed on the sampled waters.

4.2.2. Trace elements

The chemical composition of the sampled waters indicated relatively constant amounts of manganese in the analyzed waters, except of VCF that showed a double value. We consider that this is due to the different age of bedrocks: Middle Triassic in the petrifying springs area, compared with Upper Jurassic and Lower Cretaceous limestones in the Vadu Crişului area (COCIUBA, 2000; BRUCHENTAL *et al*., 2014). These concentrations were considered high, because the limit of this mineral in drinking water is 0.05 mg/mL (Law 458/2002, the consolidated form on 31 December 2017). The manganese compounds gave a brown color to the tufa deposits, which could explain the green-brownish tone of the petrified riverbed. The zinc concentration of PS, WS, and PR showed that during the limestone deposition, Zn did not precipitate together with $CaCO_3$. This observation is also supported by the higher concentration of Zn observed in the summer samples, compared to the autumn samples, which proved that Zn accumulated when the water level was low. The differences in zinc concentration in the water sources reflected the lithological differences between the flow paths. The lowest value was detected in VCF. Iron was found in very high concentration in USV in summer, and was explained by iron content of many minerals from the volcanic rocks through which the water flows. In all other sampled water sources, the concentration of iron was more reduced, compared with the limits for the drinking water, for which the national legislation, established a maximum of 0.2 mg/L. Copper showed very

small concentrations in the sampled waters in summer, and slightly higher in autumn. Chromium is another trace element that had been identified only in very low quantities in the petrified waters (WS, PR, and VCF), and in the surface freshwaters (DR and USV), without any differences between the two categories.

4.2.3. Water hardness

The water hardness is mainly due to the concentration of calcium and magnesium ions, and to a much lower extent, due to iron, manganese and zinc. What is interesting in the context of specific deposits of petrifying waters is the temporary carbonic hardness, as a result of calcium and magnesium bicarbonate. Thus, in both seasons, the petrifying waters (WS, PS, and VCF) showed higher values of calcium and magnesium hardness, because the water crossed the underground and dissolved large amounts of calcium and magnesium carbonate. The adjacent streams (UR and DR) also had high content of calcium and magnesium, because they flow on marls that contain these minerals. However, these waters are dissolving less of these salts, due to a lower pressure that equals the atmospheric pressure, to which the temperature factor is added, being generally higher in summer for the surface waters, compared to the underground waters. But the lowest hardness was observed upstream of the Sohodol Valley, because the water course is crossing the volcanic rocks with low soluble calcium and magnesium content. It should be noted that in summer, PR presents, in its basin, a lower hardness than the average of the two sources of origin (PS and WS). This is explained by the fact that on approximately 200 m of riverbed the PR has deposited by precipitation a part of the carbonate loaded.

4.2.4. Water nutrients

Nitrates and nitrites had not been detected in any of the water samples, neither in summer, nor in autumn. An ammonia pollution was detected in summer only in DR, and in autumn for all water sources, but with values less than 0.1mg/L. This may indicate a slightly contamination from organic origin, most likely originating from the domestic animals that occasionally graze or transit the water collection basins. Due to the chemical instability of ammonia, its values rarely exceed 0.1 mg/L in groundwater (BURKART AND STONER 2008). However, the analyzed waters can be considered free from anthropogenic pollution, as only values above 10 mg/L of nitrates are considered indicators for this type of pollution (MUELLER AND HELSEL, 1996; CLABBY *et al*., 2008). Instead, we identified large amounts of phosphates (2.7 mg/L) in PR in summer (Table 1 and Figure 5). Phosphorous originated from the organogenic limestones through which these waters flow, and which it dissolves. Together with nitrogen and carbon, phosphorus is one of the basic nutrients necessary for the development of aquatic organisms. CLABBY *et al.* (2008) believed that values above 0.03 mg/L of phosphorus can lead

to water eutrophication. In favorable climatic conditions, like summer season for example, the excess of these nutrients contributes to eutrophication of the stagnant or smoothly flowing waters, with overgrowth of algae and cyanobacteria. These conditions were found in the barrage basins of the Petrified River in summer, when we measured the highest phosphate concentration. It actually contributed to the favorable conditions for the development of algae and cyanobacteria. That also explained the green-brown color of PR bedrocks, which quickly replaced the 'white' of the calcium carbonate that emerged from WS.

4.3. THE BIOTIC FEATURE OF THE PETRIFYING WATERS, COMPARED TO ADJACENT FRESHWATERS IN DRY AND RAINY PERIODS

The viable microbes were found in high number that indicated the presence of the contamination sources, including faecal contamination in the water catchment area. The tributary rivers, together with PR were the most polluted water courses. The two springs (PR and WS) showed extremely different concentration values of microbes; that denoted once again the distinct underground paths with different contamination sources. The geochemical conditions and nutrients contributed to the creation of a favourable environment for the growth and multiplication of bacteria, especially in summer (Table 2 and Figure 7). This way, the heterotrophic bacteria biomediate the calcium carbonate precipitation and the tufa formation in the slow flow waters (PAYANDY-ROLLAND *et al*. 2019). In contrast, the number of viable fungi was very low in summer and more increased in autumn, and therefore consistent with the seasonality of fungi development (KUHNERT *et al.*, 2012). Yeast and moulds were found predominantly in the petrified waters with tufa formation, the highest content being registered by PS and PR (Table 2 and Figure 7). Significant microbiological contamination of water means that these springs and streams do not have drinking qualities, as the standards for water quality in Romania (Law 458/2002) require 0 CFU / 100 ml for *E. coli* and the absence of colonies incubated at 37^{o}C. In the absence of microbiological analyses there is a risk of the association of numerous gastrointestinal and even respiratory or skin diseases in the case of water consumption, in which the development of pathogenic bacteria and fungi is favoured (ASHBOLT, 2015).

Meiofauna was most abundant in the tributary rivers (UR and DR) followed by PS, DR, and USV, the last three being equal in meiofauna abundance. Regarding the diversity, the communities were dominated by amphipods, followed by insects, which are considered temporary meiofauna (PALMER *et al*., 2007), when those adults are winged and can disseminate. We also observed a marked seasonality in abundance of meiofauna, in summer the animals being found in larger number and higher diversity. By contrast, in autumn, we have not found meiofauna in the majority of samples. In four water sources, including the petrifying waters (WS, VCF) and two freshwaters (CVC and DSV), no aquatic organisms were found. As a possible explanation, we assume that 10 L were not

enough to have a whole picture of meiofauna dynamics, under the conditions of the hard substratum. So, we would say that no significant differences were observed between the petrifying and conventional waters. It is known that the abiotic factors play an important role in abundance and distribution of meiofauna (PALMER, 1990; SEMPRUCCI, 2019). Our results indicated possible relations of meiofauna with water temperature, pH and ORP, and showed similar patterns with Zn, Ca hardness, and TAC (Figures 3, 4, 5, and 7). The different origin of the two petrifying springs was also reflected in the presence of meiofauna.

4.4. THE HUMAN IMPACT ON THE PETRIFYING SPRINGS

Due to the tectonic and lithological complexity of the southern part of the Pădurea Craiului Mountains, considering also the forests and the very steep slopes, the population density was and still is lower than in other areas. Consequently, at the surface, the degree of anthropogenic pollution is very low. Because we did not detect nitrates or nitrites neither in the petrified waters, nor in the surface waters, and measuring only low concentrations of ammonia ($\leq$ 0.1mg/L), we can consider that there were no active local sources of chemical pollution (nitrogen-based chemical fertilizers) that could contaminate the petrifying springs. Unfortunately, PS and UR seem to contribute to a high microbial content in this natural area, this being due to the faecal contamination of the groundwater who actually crosses a long distance in underground (at the Northern part in the case of PS), but also being due to contamination of the surface freshwater in the catchment area from the Western pastures (considering UR). The faecal contamination most likely originated from cow, sheep, or goats grazing, but also from inadequate storage of manure in the catchment area. The population growth and the need for resources, the practice of non-ecological tourism, and last but not least, the deforestation put a lot of pressure and destroy such areas day by day.

5. CONCLUSIONS

The geology of the Petrified River with its springs and tributaries differ fundamentally from the geology of the upper part of the Sohodol Valley. In the first area, the sedimentary rocks prevail, together with the Middle Triassic limestones and marls. In contrast, in the upper part of the Sohodol Valley, the igneous lithology predominates, inducing a special chemical composition of the water. The presence of isolated limestone bodies, such as *Cucuruz*, does not change the igneous character of the waters that cross this area. The water composition also indicated that the two springs that form the Petrified River originated from two different underground streams, with distinct water chemistry and different microbial contamination. Although limestones have different ages, the water of the Vadu Crişului Fall had chemical composition similar to the petrifying waters. But, while

the carbonates precipitation of the Vadu Crişului Fall is due to the agitation of the waterfall, in the petrifying waters instead, the deposition takes place due to the lower flows that quickly takes over the ambient temperature and loses CO_2, and thus deposits the carbonates.

The biota was well represented by mesophilic bacteria and, to a lesser extent, by yeasts, moulds and meiofauna. All biota showed a seasonal response in relationship with temperature, pH, ORP, Ca hardness, and Zn. The high content of the aerobic bacteria sustained the biogenic role of microorganisms in carbonates precipitation and tufa formation.

In conclusion, the geochemical signature, the flow characteristics of the waters and the high microbial content contributed to the creation of this particular environment that facilitated the tufa development, and the formation of the Petrified River. For these reasons, the conservation of the Petrified River should integrate the protection of the catchment area of the hydrographic basins, and also the underground waters with their tributaries, because they are all part of this unique karst phenomenon from the Pădurea Craiului Mountains.

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REFERENCES

ARSENE, G.G., IMBREA, I.M., PRUNAR, F.V, NEACȘU, A.G., BĂDESCU, B., PRUNAR, S., NICOLIN, A.L., *Current condition and conservation of the Habitat 7220* (Petrifying Springs with Tufa Formation) within Nera Gorges –Beușnița National Park and Site of Community Importance*, Research Journal of Agricultural Science, **53 (2)**: 16–27, 2021.

ASHBOLT, N.J., *Microbial contamination of drinking water and human health from community water systems*, Current Environ. Health Rpt, **2**: 95–106, 2015.

BALINTONI, I., *Structure of the Apuseni mountains.* Romanian Journal of Tectonics and Regional Geology, **75**: 51–58, 1994.

BORDA, D., EPURE, L., MELEG, I.N., COCIUBA, I. *Preliminary results on the quality of drinking water sources in the Runcuri PLATEAU.* Travaux de L'Institut de Spéologie "Emil Racovitza", **LVIII**: 19–46, 2019.

BORDEA, S., BORDEA, J., MANTEA, G., MARINESCU, F., ȘTEFĂNESCU, M., IONESCU, G., POPESCU, A., *Harta geologică a României scara 1:50.000, foaia Meziad*. Editura Institutului Geologic al României, București, 2018. ISBN 978-606-94601-2-2.

BORDEA, S., BORDEA, J., ȘTEFAN, A., MANTEA, G., DIMITRESCU, R., DIMITRESCU, M., *Harta geologică a României scara 1:50.000, foaia Stâna de Vale*. Editura Institutului Geologic al României, București, 2006.

BROGI, A., CAPEZZUOI, E., BURACCHI, E., BRANCA, M., *Tectonic control on travertine and calcareous tufa deposition in a low-temperature geothermal system Sarteano, Central Italy*. Journal of the Geological Society of London **169:** 461–476, 2012.

BRUCHENTAL, C., BUCUR, I., COCIUBA, I., HEBRIȘTEANU A., *Sea-level changes and sedimentary response across the Barremian-Early Aptian in Pădurea Craiului Mountains, Romania*. Acta Palaeontologica Romaniae, **9 (2):** 33–46, 2014

BURKART, M.R., STONER, J.D., *Nitrogen in groundwater associated with agricultural systems*. Hatfield, J.L., Follet, R.F., (eds.), Nitrogen in the Environment, Academic Press, 177–202, 2008.

CANTONATI, M., SEGADELLI, S., OGATA, K., TRAN, H., SANDERS, D., GERECKE, R., ROTT, E., FILIPPINI, M., GARGINI A., CELICO, FET AL., *A global review on ambient Limestone-Precipitating Springs (LPS): Hydrogeological setting, ecology, and conservation*, Sci Total Environ, **568**: 624–637, 2016.

CLABBY, K.J., BRADLEY, C., CRAIG, M., DALY, D., LUCEY, J., MCGARRIGLE, M., O'BOYLE, S., TIERNEY, D., BOWMAN, J., Water quality in Ireland. EPA, Wexford, 2008.

COCIUBA, I., *Upper Jurassic and Lower Cretaceous deposit in the south-western part of Pădurea Craiului. Formal lithotratigraphic units*. Studia Universitatis Babeş-Bolyai, Geologia, **XLV (2)**: 33–61. Cluj-Napoca, 2000.

COPELAND, A., LYTLE D. A. *Measuring the Oxidation–Reduction Potential of Important Oxidants in Drinking Water*. Journal American Water Works Association, **106 (1)**: E10–20, 2014.

FORD, T.D., PEDLEY, H.M., *A review of tufa and travertine deposits of the World*. Earth Sci. Revs. **41**:117–175, 1996.

HEERY, S., *A survey of tufa-forming (petrifying) springs in the Slieve Bloom, Ireland*. A Report for Offaly & Laois County Councils, Ireland, 55p, 2007.

HORNE, A.J., AND GOLDMAN, C.R. Limnology, 2nd edition. McGraw-Hill, Inc. 576 pp, 1994.

HORVATINČIĆ, N., ČALIĆ, R., GEYH, M.A., *Interglacial Growth of Tufa in Croatia*. Quaternary Research**, 53 (**2**):** 185–195, 2000.

IANOVICI, V., BORCOȘ, M., BLEAHU, M., *Geologia Munților Apuseni*, Ed. Academiei RSR, Bucuresti, 1976.

KRÄUTNER, T., *Die geologischen Verhältnisse des östlichen Teiles des Pădurea Craiului*. Bulletin de la Société Roumaine de Géologie, **IV**: 73–90, 1939.

KRÄUTNER, T., *Études géologiques dans la Pădurea Craiului*. Comptes Rendus de l'Institut Géologique, **XXV** (1936–1937): 145–156, 1941.

KRISHAN, G., *Groundwater salinity*. Current World Environment **14(2):** 186–188, 2019.

KUHNERT, R., OBERKOFLER, I., PEINTNER, U. *Fungal growth and biomass development is boosted by plants in snow-covered soil*. Microb Ecol **64**: 79–90, 2012.

LAURITZEN, S.E., LUNDBERG, J., *Speleothems and climate: a special issue of the Holocene*. The Holocene **9(6)**: 643–647, 1999.

MARKOWSKA, J., *The origins of the Plitvice Lakes (Croatia).* Miscellanea Geographica **11(1)**: 93–99, 2004.

MEGERLE, H.E., *Calcerous Tufa as Invaluable Geotopes Endangered by (Over-) Tourism: A Case Study in the UNESCO Global Geopark Swabian Alb, Germany.* Geosciences, **11**, 198–219, 2021.

MUELLER, D.K., HELSEL, D.R., *Nutrients in the Nation's Waters-Too Much of a Good Thing?* U.S. Geological Survey Circular, 1136, 1996.

ONAC, B.P, *Geografic and geologic settings*. In Racoviță, G., Moldovan, O., Onac, B.P., (Eds), The karst of Pădurea Craiului Mountains, Presa Universitară Clujana, Cluj-Napoca, 7–16, 2002.

ONETE M., ION, R., BODESCU, F.P., *Description and threats to Natura 2000 habitat 7220* Petrifying springs with tufa formations (Cratoneurion). A review*. Marisia, Stud. Mat. St. Nat., **XXXIII-XXXIV**: 71–79, 2014.

OPREA, A., ȘTEFAN, N., SÂRBU, I., LĂCĂTUȘU, C, *A natural habitat (7220*) threatened in Romania.* Analele ştiinţifice ale Universităţii "Al. I. Cuza" Iaşi, Biologie vegetală, **53**: 130–133, 2007.

ORTIZ, J.E., TORRES, T., DELGADO, A., REYES, E., DIAZ-BAUTISTA, A. *A review of the Tagus River tufa deposits central Spain; age and palaeoenvironmental record*. Quaternary Science Reviews **2**: 947–963, 2009.

PAYANDY-ROLLAND, D., ROCHE, A., VENNIN, E., VISSCHER, P., AMIOTTE-SUCHET, P., THOMAS, C., BUNDELEVA, I., *Carbonate Precipitation in Mixed Cyanobacterial Biofilms Forming Freshwater Microbial Tufa*. Minerals, **9**: 409, 2019.

PEDLEY, H.M., *Classification and environmental models of cool freshwater tufas*. Sed. Geol., **68**: 143–154, 1990.

PEDLEY, H.M., *Ambient temperature freshwater microbial tufas*. In Riding R., Awramik S.M. (Eds) Microbial Sediments, pp. 179–186. Springer, Berlin, 2000.

PEDLEY, M., GONZALEZ-MARTIN, J.A., ORDO´N˜ EZ DELGADO, S., GARCIA DEL CURA, M.A., *Sedimentology of Quaternary perched springline and paludal tufas: criteria for recognition, with examples from Guadalajara Province, Spain*. Sedimentology, **50**: 23–44, 2003.

PEDLEY, M., *Tufas and travertines of the Mediterranean region: a testing ground for freshwater carbonate concepts and developments.* Sedimentology, **56**: 221–246, 2009.

PÁLFY, M., *Geoloy of the Nagybánya Mining Region*. M. Kir Földt Int övi Jel 1914-föl: pp.385–398 (in Hungarian), 1915.

PÁLFY, M., *The Montane-Geoloy of Nagybánya, Karpatak, Felsöbány and Kisbánya*. M. Kir Földt Int övi Jel 1915-föl: pp.392–413 (in German and Hungarian), 1916.

PALMER, M.A., STRAVER, D.L., RUNDLE, S.D., *Meiofauna* in Hauer, F.R. and Lamberti, G.A., Eds., Ecology (Methods in Stream), 2nd Edition, Academic Press, 415–433, 2007.

PALMER, MARGARET A., *Temporal and Spatial Dynamics of Meiofauna within the Hyporheic Zone of Goose Creek, Virginia*. Journal of the North American Benthological Society, **9(1)**: 17–25, 1990.

PENTECOST, A., *The tufa deposits of the Malham District*. Field Stud., **5**: 365–387, 1981.

PENTECOST, A., Travertine. Springer, Berlin, 445 pp, 2005.

ROZLOZSNIK, P., *Vorläufiger Bericht über die Art des Auftretens der Bauxite in nördlichen Bihar (Királyerdö*). K. Ungarischen geol. Reichsanst. Jahresber. 1916, pp. 506–510, Budapest, 1920.

SEMPRUCCI, F., FACCA, C., FERRIGNO, F., BALSAMO, M., SFRISO, A., SANDULLI, R., *Biotic and abiotic factors affecting seasonal and spatial distribution of meiofauna and macrophytobenthos in transitional coastal waters*, Estuarine, Coastal and Shelf Science, **219**: 328–340, 2019.

STANCU, D.I., *The main alpine and subalpine habitats in Râiosu & Buda Mountains, Făgăraş Massif*. Muzeul Olteniei Craiova. Stud. Com. St. Nat., **29(2)**: 118–126, 2013.

TOKER, E., *Quaternary fluvial tufas of Sarıkavak area, southwestern Turkey: Facies and depositional systems*, Quaternary International, **437**: 37–50, 2017.

**Council Directive 92/43/EEC, 1992. The consolidated text, 2013. https://EUR-Lex - 01992L0043-20130701 - EN - EUR-Lex (europa.eu)

***Decision no. 253 of 26.10.2021 regarding the declaration of protected natural areas in order to establish the protected natural areas regime by county interest for: 1 Valea Dâlbii-Peştera Uşorilor-Cheile Strâmturii, 2. Râul Pietrificat de pe Sohodolul Căbeştilor (Valea Gropii), 3. Cucuruzul-Valea Cascadei-Valea Iederii de pe Sohodolul Căbeştilor, County Council Bihor, 2021.

****EUR28, Interpretation Manual of European Union Habitats, 2013. http://ec.europa.eu/environment/nature/legislation/habitatsdirective/docs/Int_Manual_EU28.pdf

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