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GEOLOGICAL AND HYDROGEOLOGICAL FEATURES OF CERNA VALLEY (ARŞASCA-IUTA AREA, SW ROMANIA)

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Abstract: Cerna Valley is a distinct tectonic sector of the Southern Carpathians, where the Late Cretaceous collision generated a large nappe stacking and a frontal accretionary prism dominated by mélange formations of olistostrome or tectonosome type, with a deformed, black argillaceous matrix, which contains many limestone blocks. Locally, we found fragments of *piggy-back* sedimentary basins; the deposits were previously described as the Arjana molasse formation. Gravitational collapse and slip due to the fluids pressure are the most important processes of the Late Cretaceous tectonic phase. Late extensional tectonics of transpressional-transtenssional type (the strike-slip tectonics) and the uplift of the crustal blocks on normal faults have created an asymmetrical half-graben structure with many secondary Riedel faults and characteristic secondary folds (flower structures). The very complex structures and morphology have created an intricate system of channels, less karstified, in which the groundwater flow is slow (6.66-20.8 m/h). The flower structures can be involved in the groundwater flow; these features favor the high flow rates of the Pişetori Springs. The water chemical composition is calcium-bicarbonate, Ca^{2+} and HCO_3^- being the predominant ions.

Key words: carbonate facies types, mélange, flower structures, karstic springs, groundwater flow, hydrochemistry, Southern Carpathians

1. INTRODUCTION

Within the Southern Carpathians, Cerna Valley occupies a special place (Fig. 1), because of the strong link between the lithology and the complex tectonics, which led to a particular morphology of the landforms.

Figure 1. Location of the study area within Romania.

Cerna Valley is a *graben-type valley*, with straight linear flow along the major tectonic fault of the graben, and bordered by a 300-800 m high fault escarpment on the eastern slope, which dips down in many steps towards the valley.

The tributary streams encountered on the right slope are numerous, and most of them are perennial. A different setting is present on the left (eastern) slope where the streams display a temporary character, except for the Arşasca Valley, which crosses the granite bodies. The most prominent landforms which can be noticed east of Cerna Valley are the karst plateau located southward from the Vârful lui Stan (Povară, 2012), and the two-three rows of limestone bars extending parallel to the river (Török-Oance, 2012).

2. HISTORY OF GEOLOGICAL AND HYDROGEOLOGICAL RESEARCH

The earliest accounts on the stratigraphy and he tectonics of the region date back to the last years of the 19th century, when there was also mentioned the graben-like structure of the valley. Historically important are the geological studies of Schafarzik (1891), Murgoci (1905, 1910), Popescu-Voiteşti (1921, 1929), Streckeisen (1934), Codarcea (1940), Năstăseanu (1967, 1980), the detailed studies of Preda et al., (1974), Iancu (1976), Stănoiu (1982), Berza & Drăgănescu (1988), Balintoni (1999), but also the geographical and hydrogeological studies of Martonne (1907), Povară (2012), Simion et al., (1984), Povară & Lascu, (1978), and Panaiotu (1993).

Cerna River, striking N-S, separates two well-defined morphological and geological units: the Cerna and the Godeanu Mountains - to the west, and the Mehedinţi Mountains - to the east. Correspondingly, Cerna Valley is developed along an extensional and strike-slip line, which splits the Danubian realm into the Upper Danubian - on the western slope of the river, and the Lower Danubian - on the eastern one.

The Danubian realm corresponds to the basal tectonic units of the Southern Carpathians nappe system, being often designated in the literature as *the Danubian window*, described as *autochthonous* by Murgoci (1905, 1910), and later assigned to a *basement nappe duplex system* – Kräutner & Krstič (2006), Berza & Drăgănescu, (1988), Iancu (1976). The Upper and the Lower Danubian nappes consist of a metamorphic basement intruded by granites, covered by various Alpine sedimentary formations or by basin fills. Our new approach to the regional tectonics considers the role of the transpressional tectonics in the genesis of the secondary *flower structures*. These features are similar to those described from many oilfields and deep drillings, and as results of a laboratory experiment (Fossen, 2010).

3. MATERIALS AND METHODS

In order to highlight the flower structures, a detailed (1:10,000) geological and tectonic mapping was performed, the results being correlated on a regional scale (1:25,000). The groundwater flow paths were established by dye-tracing tests with fluorescein and rhodamine. Tracer concentrations in spring water were measured during a time period of two weeks, using a Perkin-Elmer spectrofluorometer model LS 45. The lowest measurable concentration in the spring water was 0.02 μg/L for fluorescein (uranine) and 0.25 μg/L for rhodamine. The stochastic analysis (Mangin, 1975) was used for the hydrological study of the two most important karst springs.

All the water samples have been collected on 25 and 27 July 2005. The bottles used for the storage of the collected samples were of the Nalgene High-Density Polyethylene (HDPE) type. When the samples were collected, the water temperature and pH were measured with a Crison PH 25 portable instrument (Wilde et al., 2006). The water total alkalinity was determined by means of Gran electrometric titration, with a 0.05 M HCl solution (Rounds, 2006), within a time interval of less than 24 hours after sampling. The complete chemical analysis of all collected water samples (major cations and anions, as well as trace components) was conducted in the laboratory of the "Emil Racoviţă" Institute of Speleology of the Romanian Academy.

The Na, K, Mg and Ca concentrations were determined by means of standard flame-atomic absorption spectrometry methods. The analyses were carried out with a Perkin-Elmer atomic absorption spectrometer model AAnalyst 700, equipped with deuterium arc background correction system. The calibration lines were traced using solutions prepared on the basis of CertiPUR® (Merck) standard solutions. Aluminium and barium concentrations were measured by the means of a GF-AAS methods described in Marin et al., (2010) and, respectively, in Tudorache et al., (2010). The Mn and Fe concentrations were analyzed by standard GF-AAS methods. The methods accuracy and precision have been tested by using the 1643e NIST Standard Reference Material.

For the total dissolved silica (Pakalns & Flynn, 1967), sulphate (Aminot, 1974), chloride (Florence & Ferrar, 1971), ammonium (Mackereth et al., 1978), and nitrate (APHA, 1985) the concentration assessments were conducted in laboratory, by the means of a molecular absorption spectrometer in the visible and ultraviolet spectra, of the Perkin-Elmer Lambda 25 model. All the solutions have been prepared with ultra-pure water (TKA Ultra Pure System GenPure, electric resistance 18.2MΩ×cm).

The total dissolved solids (TDS) content was calculated as the sum of the total dissolved ion concentrations and by additionally making the adjustment of bicarbonate to carbonate ions (Hem, 1985). The speciation calculations were performed by means of the PHREEQC code, version 2.18.3.5570 (August, 2011) (Parkhurst & Appelo, 1999), with the Lawrence Livermore National Laboratory database.

4. RESULTS AND DISCUSSION

4.1. Geology

The Danubian realm of the Southern Carpathians consists of two major structural units (Săndulescu, 1984), both developed within the Cerna Valley catchment area (Figs. 2 and 3).

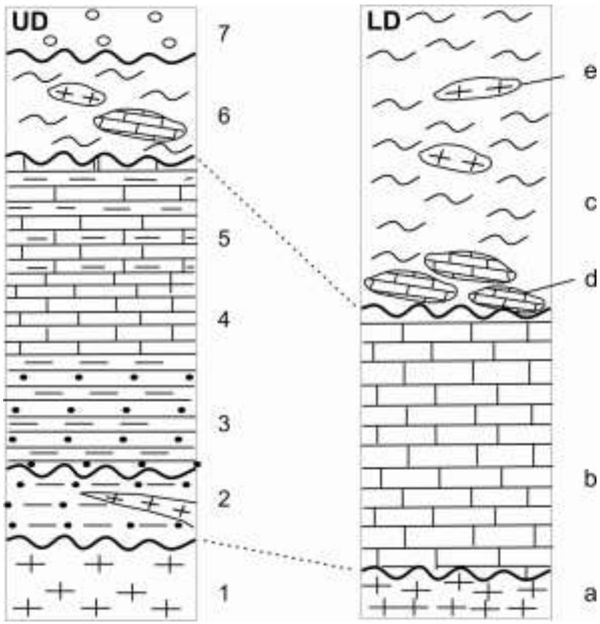


Figure 2. Lithostratigraphic logs through the Danubian Units outcropping in Cerna Valley: **UD** (Upper Danubian):
1. granites; 2. volcano-sedimentary rocks (Permian); 3. sandstones and shales (Lower Jurassic); 4. micritic limestone (Middle Jurassic to Lower Cretaceous); 5. Iuta Beds preflysch formation (Ab-Cn); 6. mélange formation (various olistolithes in Upper Cretaceous argillite matrix); 7. Arjana Fm. (conglomerates and contourites). **LD** (Lower Danubian): a. granites; b. Urgonian limestone facies; c. mélange formation (limestone blocks in Upper Cretaceous argillite matrix; d. blocks of tectonosome type; e. various blocks of ophiolitic olistostrome type.

The Upper Danubian units, developed on the western slope of Cerna Valley, are intruded by Precambrian granites and covered by an Upper Paleozoic (Permian) volcano-sedimentary complex, and by a Presacina/Arjana-type Mesozoic sedimentary cover, forming 2-3 small scale nappe structures, previously comprehensively addressed as the Băile Herculane Nappe (Balintoni, 1999), which also includes the Cerna Syncline (Năstăseanu, 1980).

Lower Danubian units. Across Cerna Valley, to the east, one can note a different geological aspect. The bedrock, consisting of the Precambrian granites that outcrop in Arşasca Valley and which pertain to the Drăgşani crystalline series, is covered by 200-300 m thick limestone sequences of Urgonian facies (Lower Cretaceous age). *The Urgonian limestones* consist of allochemical limestones (*sensu* Folk's Laboratory Classification). The entire sequence is largely bedded (in 1-2 m thick beds, crossed by dendritic cracks of hydraulic pressure origin, filled up with calcite) (Fig. 3). In contrast to the Presacina/Arjana stratigraphic sequence present on the western slope of the valley, on the eastern slope there are lacking the Liassic clastic suites, as well as the pre-flysch rhythmic sequence: black micritic limestones-marlstones, designated as the Iuta Beds (Nadanova Beds), of Cenomanian-Turonian age. On the eastern slope of Cerna, the Urgonian limestones are covered only by the *mélange formation* of Senonian age (previously designated as the wildflysch formation).

Mélange formation. A lithologic unit comprising large blocks embedded in a slaty argillaceous matrix was first described from the Alpine-Mediterranean belts, and for a while it has been designated both as wildflysch, and as *"mélange"*. Mélange is a highly fragmented formation, devoid of any stratigraphic sequences. It includes a matrix of fine grained material, black shales, with a typical tectonic fabric of small and medium scale. In the matrix there are embedded autochthonous and exotic blocks, with lenticular or rounded forms, some of them related to an unknown source area. Many blocks are bounded by small scale fault planes with shear traction and slickenlines. There are abundant calcite veins. This brittle fracturing is favoured by the high fluid pressure. The clay dessication process transformed the matrix in a slate which preserved nodules of clastic and volcano-clastic debris (grain size class: 1-3 cm). Below and above the contact with the nearby formation there are clear unconformities. Among the exotic blocks, one can notice diabases, serpentinites, black shales, retromorphic gneisses related to the Getic Nappe etc. But there are also some rhythmic clastic sequences (sandstones, conglomerates, contourites) embedded in the slaty matrix. These features, well illustrated within the Arjana flysch-molasse formation, on the western slope of the valley may be indicative of fragmented *piggy-back* basins, transported away from the subduction plane by the strike-slip motion or by the gravitational collapse.

Stănoiu (1982) described in the Mehedinţi area a formation similar to the *olistostrome*. Our investigation on the eastern slope of Cerna Valley pointed to a much more complex setting. Above the Pişetori Springs, medium-sized and large blocks of Urgonian limestones displaying small paleokarst voids and channels, show a brittle fracturing contact and they are cemented with small-sized, heterogeneous limestone fragments.

The above-mentioned lithologic sequences are identical with the *tectonosomes* described by Pini (1999, 2012) from the *Scaglia Formation* (Appenines Mountains, Italy). According to this author, the term *olistostrome* must be applied only when the olistolithic blocks are of different age and provenance, from microscopic to macroscopic scale (Fig. 4).

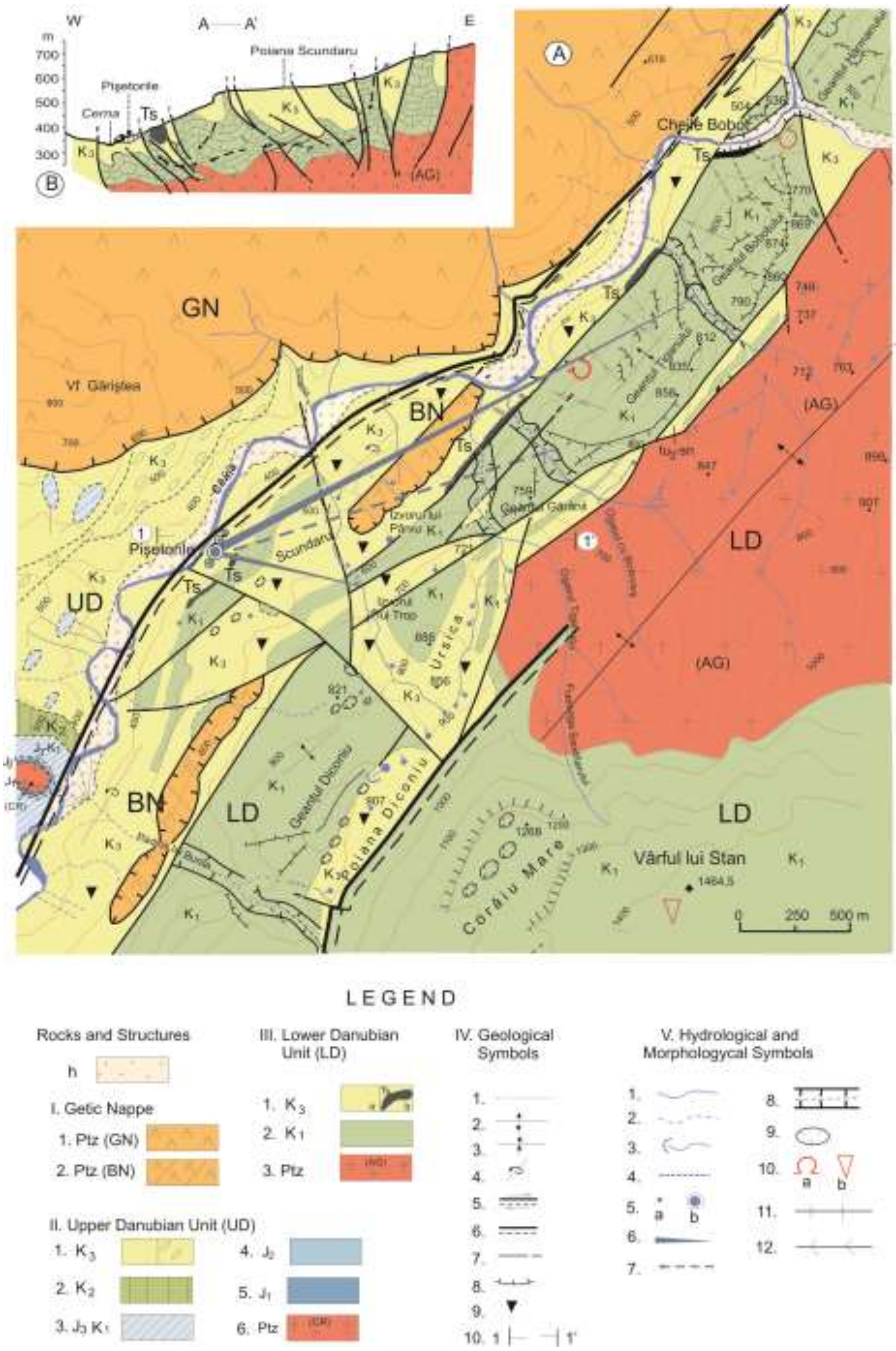


Figure 3. **A**. Geological and hydrological map of a sector of Cerna Valley (Pişetori Springs-Arşasca). 1. Holocene alluvia. **I.** *Getic Nappe*: 1. Godeanu Nappe (GN, mesometamorphic micaceous rocks); 2. *Borăscu Nappe* (BN, retromorphic Alpine gneisses and micaceous rocks); **II**. *Upper Danubian Unit* (UD): 1. Mélange formation of Presacina/Arjana type, a. black shales (deformed matrix), b. conglomerates and contourites within fragmented *piggy-back*,basins; 2. Iuta/Nadanova beds (pre-flysch formation); 3. lithographic limestones and limestones with nodules; 4. limestones,and sandstones; 5. Lower Jurassic sandstones; 6. red granites of Cracu Roşu type (CR). **III**. *Lower Danubian Unit* (LD): 1a. black shales (deformed matrix) with limestone olistoliths; 1b. tectonosome over Urgonian limestones; 2. massive Urgonian limestone; 3. Arşasca granites (AG) intruded in the Drăgşani crystalline series; **IV**. *Geological symbols*: 1. general geological boundaries; 2. normal anticline; 3. normal syncline; 4. secondary reversed anticline; 5. strike-slip master fault with the area of ductile deformation and shear direction; 6. uplifted hanging wall with the area of brittle deformation; 7. Riedel-type faults; 8. nappe limit; 9. olistolithic blocks; 10. hydrogeological cross-section line; **V**. Hydrological and morphological symbols: 1. perennial surface stream; 2. temporary surface stream; 3. sinking stream; 4. temporary stream; 5. non-karst spring (a); karst spring (b); 6. groundwater flow path established by dye-tracing tests; 7. hypothetical groundwater flow direction; 8. gorge; 9. sinkhole; 10. cave (a); pothole (b); 11. limestone ridge; 12. steep valley. **B.** Hydrogeological cross-section.

The tectonosomes (Pini, 1999; 2012) are defined as blocks embedded in the rock matrix (Fig. 5), deriving from the initially *in-situ* lithologic unit (Fig. 6).

Figure 4. Olistostrome block with injected material related to the hydraulic pressure, located downslope of Geanţul Ţiganului (left).

Figure 5 Tectonosome block - Urgonian limestones cemented with small-sized, heterogeneous limestone fragments, located to the east of Pişetori Springs (right).

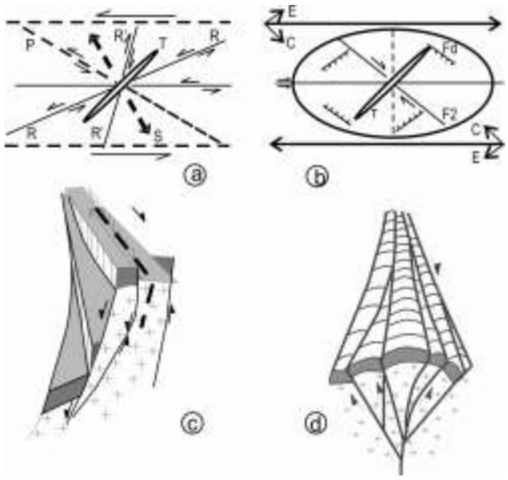
4.2. Tectonic aspects

The slopes of Cerna Valley display various tectonic styles. On the western slope, the subhorizontal tectonic structures (small or large scale nappes), i.e. the Cerna reversed syncline (Năstăseanu, 1980) and the Băile Herculane Nappe (Balintoni, 1999), are the most important features. On the eastern slope of the valley, with high and steep landforms, large graben structures developed during the Oligocene/Miocene. A huge scarp of 300 to 800 m, extending from Vârful lui Stan Peak towards Domogled - Băile Herculane, marks the eastern hanging wall of the graben.

In contrast, the footwall is developed along the valley, and it marks the tectonic contact between the Upper and the Lower Danubian units, the so-called *master fault* (the Cerna-Jiu Fault), with dextral strike-slip motion, forming graben like structures. The graben structure is asymmetrical, with the western edge marked by the "master fault". In the geological literature, this structure has been named a *half-graben*. The asymmetry is important in defining the tectonic mechanism: shear movement in the west and strong uplift in the east of the graben.

Our research undertaken between the "master fault" and the eastern fault of the graben, led to the description of a new tectonic style, similar to the classic *thin-skinned tectonics*, involving different behaviours of the granitic basement, Urgonian limestones and black shales related to the mélange formation. These rocks are faulted and secondary folded in the *flower tectonic style* (Fig. 6), with negative flower structures on the slope towards the Cerna River, and positive features on the high plateau of the Mehedinţi Mountains, with subhorizontal bedding. The secondary folds and faults are of Riedel type, and they cut the major structures.

Figure 6. Arrangement of secondary folds and faults in an ideal right-lateral strike-slip fault, in transpressional tectonics (after Fossen, 2010). Strike-slip faults consist of a series of subparallel shear faults of two types, *pinnate* and *en echelon*. The subparallel faults are shear or shear plus tensile fractures. The secondary folds (rock bridges) are structural highs or uplifted blocks. Finally, the positive flower structures are created by the uplifted blocks, while the negative flower structures are related to the sunken blocks. (a) Fractures related to the strike-slip faulting: R, R', P - shear fractures; T, S - tensional and extensional fractures; (b) ideal model of shear fractures parallel to the main fault zone: C, E - constrictional and extensional direction; Fd - secondary folds; F2 - secondary shear; T - tensional fractures; (c) negative flower structures on the granitic basement and Mesozoic sedimentary cover on the eastern slope of Cerna Valley; (d) positive flower structure on the high plateau of Vârful lui Stan.



4.3. Hydrogeological issues

Although the Urgonian limestones outcrop on a relatively large area, on the Cerna River left slope, south of Bobot Gorge, in the corresponding region there are encountered just a few karst springs, most of them with small flow rates. Only the Pişetori springs group is more significant. The springs are spread on a ca. 200 m wide area, above the Cerna River streambed, at 396 m a.s.l. (40 m relative altitude). The springs are covered by deluvial-colluvial deposits, partly cemented by a travertine formation, thicker than 4 m. The 7 karst outlets out of which only two discharge permanently, occur along a fault line delineating the Urgonian limestones from the wildflysch (springs no. 2 and 5 shown in Fig. 7).

The springs no. 1 and 2 were rigged with V-notch (triangular) weirs, levelling rods and water level gauges. A rain gauge has also been set up nearby, in order to simultaneously record the rainfall amount. In contrast with the results of the measurements carried out between 1979-1983, once a month, by ISPIF Bucharest (Q_{min} = 5.0 l/s; Q_{max} = 443 l/s; Q_{med} = 93.6 l/s), much lower values have been obtained during our monitoring operation (which was conducted between 09.04.2005-17.03.2006, over a time period which displayed rainfall amounts below the average). The average recorded flow rates were 37.4 l/s for the spring no. 2, and 9.5 l/s for the spring no. 1, the latter getting dry during the extreme drought periods. The evolution of the flow rates recorded at the springs no. 1 and 2 is shown in figure 8.

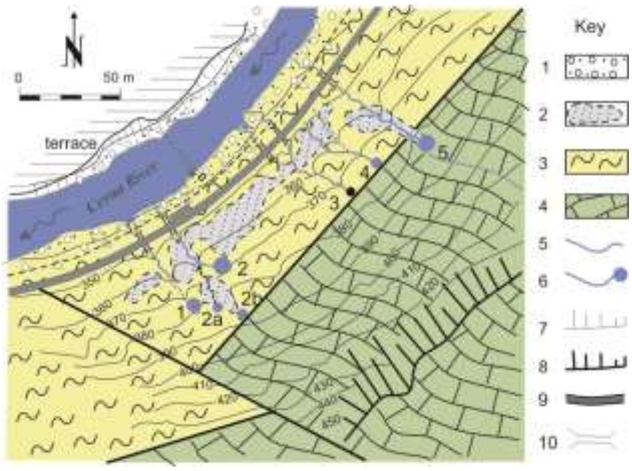


Figure 7. The discharge area of the Pişetori springs group (detail): 1. alluvial deposits; 2. travertine deposits; 3. mélange formation; 4. Urgonian limestone; 5. creek; 6. spring; 7. frontal terrace; 8. subvertical wall; 9. road; 10. bridge.

The flow rate analysis performed according to the methodology developed by Mangin (1975) led to the conclusion that for the springs no. 1 and 2, the most frequent flow rate values ranged in the class 30-35 l/s, which had been recorded for 64 days, (20.8% of the entire monitoring time span, Fig. 9 a).

The flow recession curve (Fig. 9 b) shows that the influence of the water input resulting from the snow-melting occurred during the 2005 spring season ceases 26 days after the end of the melting period; subsequently, the karst aquifer discharges only the base flow amount.

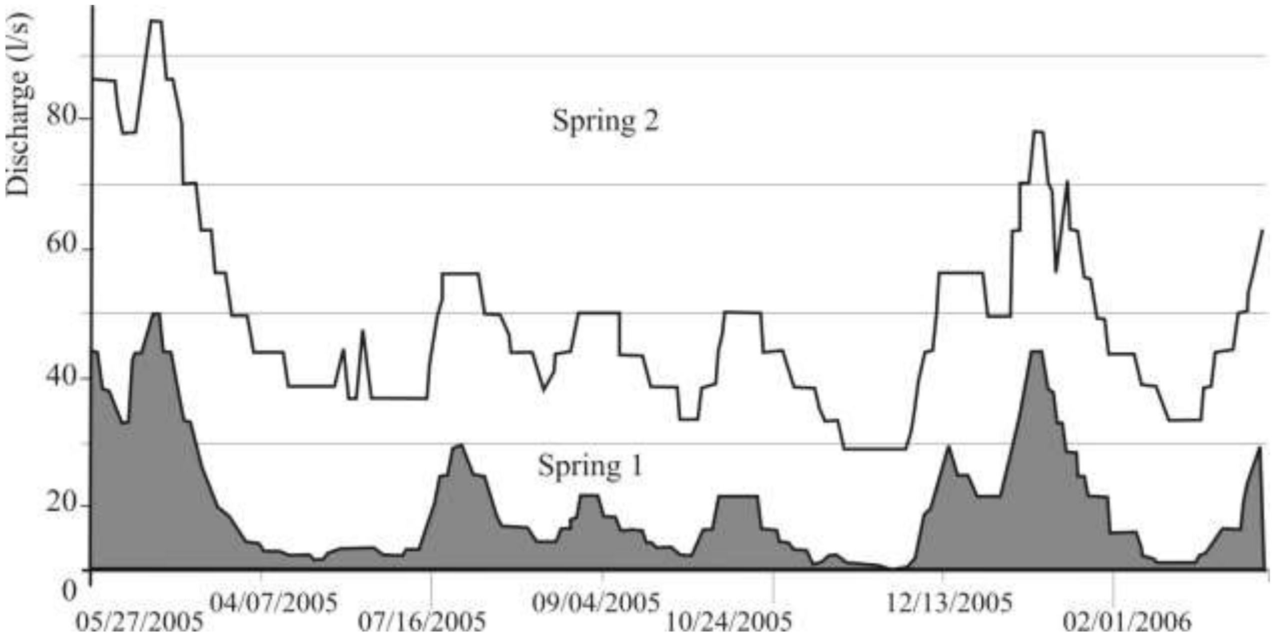


Figure 8. Flow rate record of the Pişetori springs no. 1 and 2 for the time interval 09.04.2005-17.03.2006.

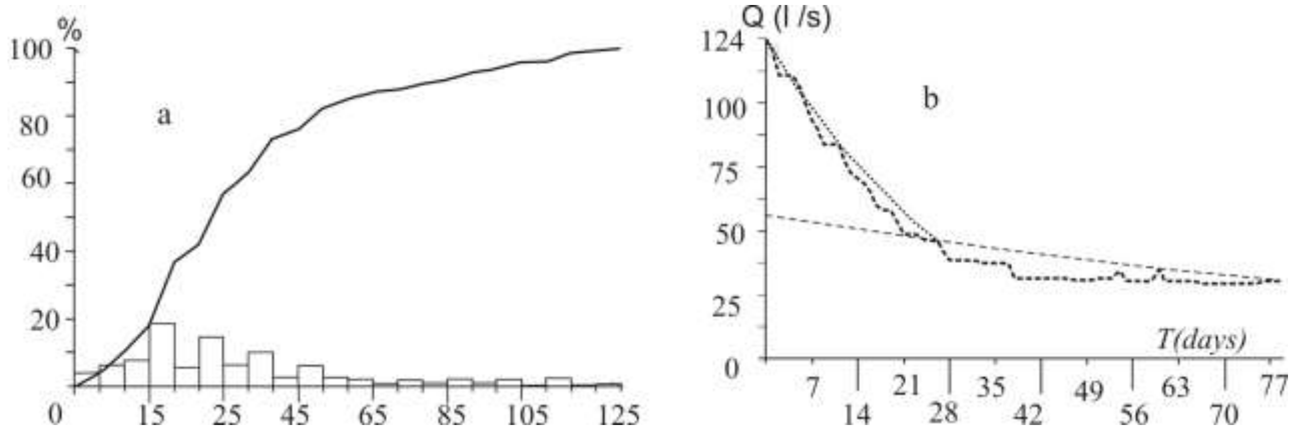


Figure 9. Cumulative percentages corresponding to the flow rates values recorded at the Pişetori springs no. 1 and 2 during the time interval 09.04.2005-17.03.2006 (a); flow recession curve of the Pişetori springs no. 1 and 2 for the time interval 09.04.2005-17.03.2006 (b).

The low value of the base flow coefficient (the recession coefficient), $\alpha = 0.00795$, points to a slow groundwater flow, through fissures and small karst voids, less affected by the widening process related to the karst dissolution. This value, considered along with the relatively high value of the karst system memory (ME = 22 days, Fig. 10), is indicative of an important karst water reservoir.

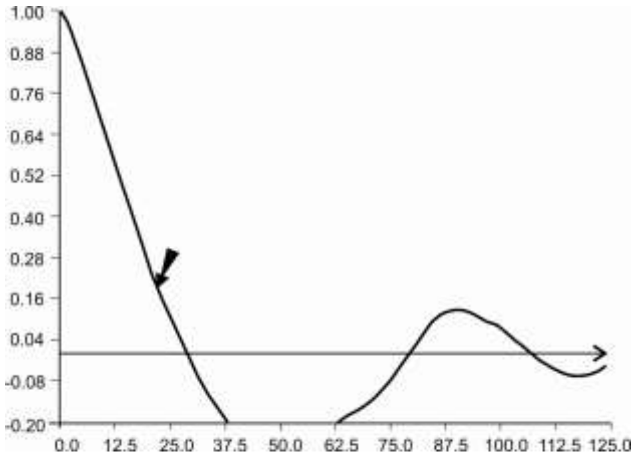


Figure 10. Simple correlogram of the flow rates of the Pişetori springs no. 1 and no. 2.

In order to delineate the springs recharge area, fluorescein (F) and rhodamine (R) tracers were injected into the creeks which cross the Barremian-Aptian limestones outcropping on the Cerna River left slope and, respectively, into Ogaşul Bobotului and Ogaşul Ţiganului. The tracers were detected in all springs, and the recorded travel times of the tracer corresponded to theoretical average velocities in the range 150-216 m/day, characteristic for a deep flow, along completely flooded conduits (Table 1).

The low velocity of the groundwater flow is related to the hydrogeological characteristics of the Cerna River left slope. The Urgonian limestones which outcrop on the high plateau of the Mehedinţi Mountains dip down in steps, from the east to the west, towards the Cerna River, along several fault lines parallel to the graben fault, with tens or hundreds meters high fault scarps. At depth, the water flows from one sector to another under the Cretaceous flysch, across or along the structure.

Table 1. Dye-tracing tests on the Cerna River left slope, between the Arşasca and Ţăsna valleys.

Surface stream	H (m)	Tracer	Spring	H (m)	L (km)	V (m/h)
Og. Bobotului	560	F	ri spring	350	2.60	6.66
Og. Ţiganului	560	F		350	1.25	11.25
Izvorul lui Trop	680	R		350	0.85	20.8

4.4. Hydrochemistry

Within the study area, eight water samples collected from surface streams (samples no. 1 and 2 from the Table 2) and from the most important springs, were analyzed. Two samples collected from well-known karst springs were also analyzed, for comparison (samples no. 9 and 10 from the Table 2).

The samples collected from the Pişetori karst springs were labeled in table 2 as sample no. 3 (no. 2 in Fig. 5) and sample no. 4 (no. 5 in Fig. 5). All the analyzed water samples have low mineralization, alkaline pH values and a chemical composition dominated by the hydrogen carbonate anion (HCO_3), and by the Ca^{2+} and Mg^{2+} alkaline earth cations (Table 2).

Table 2. Chemical composition of the analyzed water samples collected from the Arşasca-Iuta area.

No.	Source	T (°C)	pH	Conduc-tivity (mS/cm)	TDS[†] (mg/L)	TA[‡] (mg/L)	Si total (mg/L)	NH_4 (mg/L)
1	Ogaşul Ţiganului	10.1	8.10	0.023	132	129.6	5.0	0.058
2	Izvorul lui Trop	11.6	8.16	0.018	209	227.6	2.4	0.013
3	Pişetori, main spring	9.1	8.27	0.026	174	182.5	1.8	0.049
4	Izvorul Robu	8.9	7.95	0.036	184	193.7	2.4	0.039
5	Izvorul de sub Scundaru	10.3	7.42	0.112	281	292.1	2.5	0.045
6	Izvorul lui Pârvu	8.6	7.42	0.008	149	158.1	2.1	0.059
7	Ogaşul Scundaru	9.4	7.90	0.044	277	241.9	2.9	0.025
8	Izvorul Ţiganului	8.1	7.84	0.022	133	129.9	4.3	0.044
9	Izvorul de sub Piatra Cerbului	7.0	7.74	0.018	168	170.3	2.9	0.001
10	Izvorul Beletina Sud	6.7	7.44	0.018	127	124.8	2.8	0.037

No.	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	NO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Ba (µg/L)	Mn (µg/L)	Fe (µg/L)	Al (µg/L)
1	2.3	0.5	1.1	43.6	2.00	7.6	0.8	11.17	n.a.	5.77	8.36
2	1.2	0.4	1.0	77.3	1.98	9.5	0.6	13.75	10.0	139.40	49.65
3	0.9	0.2	1.3	64.4	2.24	10.7	0.9	33.95	5.0	1.89	2.39
4	1.0	0.5	1.1	67.7	2.75	9.3	1.3	10.38	0.0	2.53	1.84
5	2.6	1.1	1.7	102.9	9.73	10.2	4.0	13.80	n.a.	58.58	28.65
6	1.8	0.7	0.7	54.6	2.12	6.9	0.3	5.59	n.a.	7.67	5.53
7	2.7	1.2	7.7	87.7	2.03	48.5	1.6	56.88	n.a.	199.50	34.38
8	2.1	0.5	1.1	43.2	2.34	10.0	0.8	14.49	19.0	1.76	7.73
9	1.3	1.0	0.9	60.4	2.50	11.0	0.6	24.44	n.a.	10.85	4.96
10	1.1	0.3	0.7	45.6	2.80	8.4	0.6	18.78	40.0	7.41	2.16

[†]TDS: total dissolved solids values, calculated by summing the major ionic constituents and converting bicarbonate into equivalent carbonate. [‡]TA: total alkalinity, expressed as HCO_3.

Table 3. Saturation index values of the mineral species calculated for the analyzed groundwater samples.

Mineral	Formula	Izvorul lui Trop	Pişetori main spring	Izvorul Robu	Izvorul lui Pârvu	Izvorul Ţiganului
log P_{CO2}	CO_2	-2.903	-3.121	-2.770	-2.321	-2.829
Andradite	$Ca_3Fe_2(SiO_4)_3$	5.234	1.075	-0.167	-3.035	-1.017
Anhydrite	$CaSO_4$	-2.870	-2.896	-2.942	-3.129	-3.055
Anorthite	$CaAl_2(SiO_4)_2$	-2.785	-5.642	-5.607	-4.947	-3.977
Aragonite	$CaCO_3$	0.619	0.528	0.260	-0.432	-0.199
Barite	$BaSO_4$	-1.105	-0.588	-1.167	-1.525	-0.920
Boehmite	AlO_2H	1.947	0.632	0.832	1.783	1.595
Calcite	$CaCO_3$	0.766	0.675	0.406	-0.285	-0.052
Chalcedony	SiO_2	-0.043	-0.119	0.017	-0.021	0.302
Diaspore	$AlHO_2$	2.373	1.063	1.263	2.214	2.027
Dolomite	$CaMg(CO_3)_2$	0.989	0.967	0.317	-1.158	-0.408
Epidote	$Ca_2FeAl_2Si_3O_{12}OH$	5.985	1.145	0.812	0.642	2.113
Gibbsite	$Al(OH)_3$	1.846	0.550	0.752	1.704	1.520
Goethite	FeOOH	5.332	3.361	3.481	3.836	3.286
Gypsum	$CaSO_4:2H_2O$	-2.555	-2.556	-2.599	-2.783	-2.704
Hematite	Fe_2O_3	11.601	7.651	7.890	8.601	7.499
Illite	$K_6Mg_{25}Al_{1.8}Al_{0.5}Si_{3.5}O_{10}(OH)_2$	4.308	0.985	1.775	3.249	4.374
Kaolinite	$Al_2Si_2O_5(OH)_4$	4.770	2.005	2.678	4.505	4.778
Feldspar	$KAlSi_3O_8$	1.557	-0.124	0.550	0.939	2.012
Monohydrocalcite	$CaCO_3:H_2O$	-0.044	-0.128	-0.396	-1.086	-0.851
Montmorillonite-Ca	$Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	4.121	1.691	2.220	3.056	4.484
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	6.782	2.483	3.558	5.849	6.548

Table 3 (continued)

Nontronite-Ca	$Ca_{0.165}Fe_2Al_{0.33}Si_{3.67}H_2O_{12}$	14.921	10.301	11.004	11.704	11.852
Quartz	SiO_2	0.241	0.167	0.303	0.266	0.589
Sanidine (high)	$KAlSi_3O_8$	0.269	-1.429	-0.757	-0.371	0.700
Tridymite	SiO_2	0.047	-0.029	0.107	0.069	0.392
Witherite	$BaCO_3$	1.685	2.132	1.330	0.467	1.231

These features are related to the circumstance that water flows through carbonate rocks (mainly limestones). Moreover, the ammonium (NH_4) and nitrates (NO_3) concentrations are low, as the mountain areas are sporadically grazed. The nitrites (NO_2) were not identified in the tested water samples. The natural origin of the chloride (Cl) in the groundwater can be related to the rainfall input.

Chloride concentration values exceeding 1 mg/L are probably indicative of an anthropogenic pollution event. Such a case was recorded for Izvorul de sub Scundaru, where the nitrates concentration also exceeded the area average. Significant levels of potentially toxic metals (Cr, Co, Cd, Hg, Pb, etc.) were recorded in the soil and cave sediments samples collected from the Mehedinţi Mountains and Plateau (Giurginca et al., 2010; Munteanu et al., 2012). These metals were not identified in the water of the Pişetori karst springs.

The thermodynamic modelling of the natural water composition, performed with the PHREEQC code (Parkhurst, Appelo, 1999), allows the assessment of the water saturation state with respect to mineral species or gases, by calculating the saturation index, IS_{min} (Table 3). The corresponding results suggest that the most important geochemical reactions are the aluminosilicates and carbonates precipitation, and the SiO_2 and sulphates dissolution. The extensive travertine deposits present in the Pişetori springs area are related to the shifting of the carbonate equilibrium towards the precipitation of the corresponding mineral species (calcite, aragonite, dolomite, witherite).

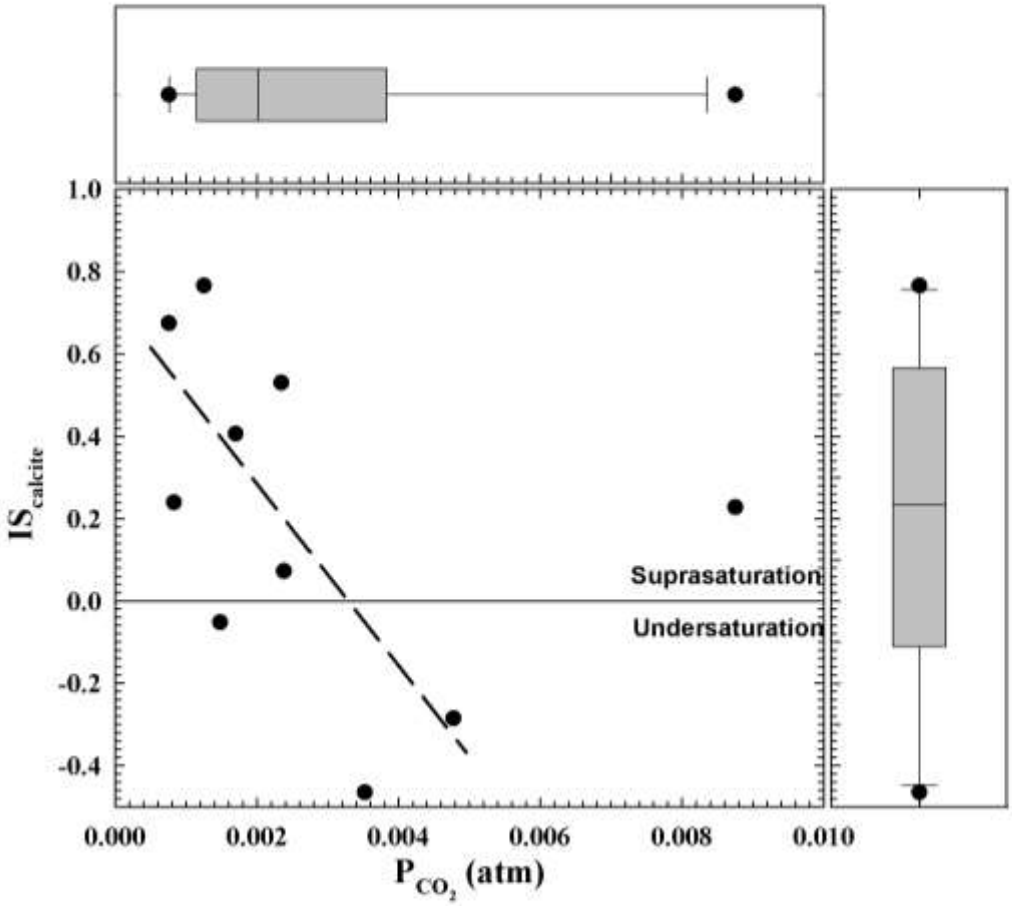


Figure 11. Correlation between the CO_2 partial pressure and the water saturation index with respect to calcite for the groundwater sampled within the Arşasca-Iuta area.

The process is also accompanied by the iron and aluminium coprecipitation; the main iron compounds are hematite, goethite and the mixed silicates (epidote, nontronite-Ca), while the most important aluminium compounds are boehmite, gibbsite, illite, kaolinite and muscovite. The diagram in Figure 9 shows that there is a relationship between the low CO_2 partial pressures (P_{CO2}) and the groundwater suprasaturation with respect to calcite, and, in general, with respect to the carbonate mineral species.

5. CONCLUSIONS

Cerna Valley is a distinct tectonic sector of the Southern Carpathians, where the Late Cretaceous collision generated a large nappe stacking and a frontal accretionary prism dominated by mélange formations of olistostrome or tectonosome type, with a deformed, black argillaceous matrix, which contains many limestone blocks. Also, within the same area, we found fragments of *piggy-back* sedimentary basins, previously described as the Arjana molasse formation by Năstăseanu (1980). Gravitational collapse and slip due to the fluids pressure are the most important processes of the Late Cretaceous tectonic phase.

Late extensional tectonics of transpressional-transtenssional type (the strike-slip tectonics) and the uplift of the crustal blocks on normal faults, have created an asymmetrical half-graben structure with many secondary Riedel faults and characteristic secondary folds (flower structures), similar to those described and experimentally obtained by Fossen (2010).

The very complex structures and morphology have created an intricate system of channels, investigated by dye-tracing tests with fluorescein. The flower structures can be involved in the groundwater flow; these features favour the high flow rates of the Pişetori Springs. The low groundwater flow velocities (6.66-20.8 m/h) are consistent with the geological structure and lithology of the area.

The water temperature during 2005 varied between 8.9-9.8 ^{o}C, while its chemical composition is Calcium-bicarbonate, as it is shown by the overwhelming levels of the Ca^{2+} and HCO_3^- ion concentrations.

The levels of both the potentially toxic metals and the pollution indicator anions in the springs water do not exceed the accepted potability threshold. The thermodynamic modelling of the water stability shows the deposition of carbonate minerals, accompanied by the coprecipitation of iron and aluminium oxides and hydroxides.

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