GEOLOGICAL AND ECOLOGICAL ASSESSMENT OF THE EXPOSURE DEGREE OF THE ZĂTON-BULBA KARST SYSTEM (MEHEDINȚI PLATEAU) TO ANTHROPOGENIC HAZARDS: INTRINSIC VULNERABILITY AND BIODIVERSITY STUDY

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Abstract. The Mehedinți Plateau represents an area highly marked by the intensity of the karst processes and by the diversity of the exokarst and endokarst features. The analyzed area includes two parallel limestone bars, developed on the Carpathian structures direction (NNE-SSW). The geological and geomorphological research, guided by a working protocol similar to that of the EPIK method, highlighted the role played by the lithology, structure, tectonics, epikarst and protective cover, related to the infiltration conditions, flow parameters and impact area of a potential contamination event; also, we carried on microtectonic studies on the Bulba Valley, Peşterii Hill, Podul Natural Cave and Bulba Cave. In addition to the results obtained following the EPIK method protocol, we bring forward data concerning the water quality, performing hydrogeochemical analyses on water samples collected from the main sources in the region. Our research has been focused on TDS, on cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}) and on anions (HCO_3^{-}, Cl^{-}). We conclude by modelling the cumulative abundance and the species richness of the harvestmen (Opiliones) in the studied area, under different degrees of human impact on habitats.

Key words: intrinsic vulnerability, EPIK, karst groundwater, Opiliones, Mehedinți Plateau.

1. INTRODUCTION

1.1. GEOGRAPHIC POSITION OF THE TEST AREA AND ANTHROPOGENIC IMPACT

The Mehedinți Plateau (Fig. 1), on which limestones outcrop on a small area only (25 km^2), represents one of the most significant Romanian karst areas, due to the intensity of karst processes and to the diversity of the exokarst and endokarst features. Singled out by a “limestone bar karst”, this plateau encompasses over 200 caves (cumulative development exceeds 45 km).

Other characteristic is the presence of a special relief type – “cornet” (calcareous hill), result of the limestone bands fragmentation, followed by their clear separation by the interagency of karst piracy depressions, relief covered by wide karren fields.

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Fig. 1 – The geographic position of the test area.

The Ponoarele locality limits are overlapping both karst systems. Most settlements are scattered, being situated on plateaus or water divides. The economic activities are rudimentary, as the industrial enterprises are less developed and the arable land covers only small areas; the main occupations of the population consist in animal husbandry and fruit tree growing. However, two of the most inhabited villages are placed on the limestones of the Zăton-Bulba karst system, the dwellings having no sewage or waste disposal facilities. Traditionally, the manure is regionally used as fertilizer for gardens and pastures. The main road of the area, disposed along the limestone bar, is another pollution factor.

Our research has been focused on the Zăton-Bulba karst system features and vulnerability factors. In order to establish reference elements, the study area has been extended; hydrogeochemical analyses of the Morilor Valley springs and ecological investigations of the Lupşa Valley (located 15 km northward, with low anthropogenic influence) have also been performed.

Human activities usually determine changes of natural habitats that may negatively affect harvestmen (Opiliones) species. They can be sensitive to changes in habitat structure and to different human impacts, such as: the use of fertilizers and pesticides (PEKAR, 1997), the presence of other pollution factors (RABITSCH,

1995) and certain forest management practices (JENNINGS *et al.*, 1984). Previous studies on habitat use have shown that the harvestmen species from the Ponoarele area prefer moist areas of abundant vegetation (PLĂIAȘU & BĂNCILĂ, 2008).

1.2. GEOLOGICAL AND GEOMORPHOLOGICAL SETTING

The analyzed area includes two parallel limestone bars, developed on the Carpathian structures direction (NNE-SSW) and differentiated, on the basis of lithostructure and altitude, by the granitic basement and by the Miocene graben.

The eastern karst area, higher and authigenic, forms the Gârdăneasa-Băluța aquifer system, while the western karst area, with binary functioning and located in a corridor, forms the Zăton-Bulba aquifer system.

The systems are connected, as the water outflowing from the main outlets of the first one (springs from the Morilor Valley) is caught by a karst depression in the second one.

The relief units from the northern part of the Mehedinți Plateau are described by a double fracturing, generating morpho-petrographic and morpho-structural discontinuities, dividing the relief in blocks with different geological and morphological features.

From a geological point of view, they belong to the Southern Carpathians ensemble, formed by the closure of a marine basin (Kimmeridgian-Tithonian), followed in the Upper Cretaceous by the subduction and the overthrusting of the lithosphere and the continental margins sediments, including the carbonate ones (the Danubian Autochthonous and the Getic Nappe). The geological structure of the test area comprises lithostructurally unitary longitudinal bands, striking NNE-SSW, separated by major Carpathian faults and crossed by strike-slip or transversal faults, on a W-E orientation, generated during the Neogene uplifts.

The Ponoarele karst area is aligned within a tectono-erosional window, having the aspect of a NE-SW corridor (250–450 m a.s.l.), in which the Mesozoic sedimentary outcrops, along with the metamorphic basement of the Southern Carpathians autochthonous (the Danubian Domain). On both sides of this corridor, two synclinoriums are set, being composed by Paleozoic crystalline schists (Getic Nappe), forming higher parallel ridges (600–700 m a.s.l.). The Mesozoic karst rocks were deposited in two distinct sedimentary areas of the Danubian Domain, explaining the presence of two parallel limestone bars (the western and the eastern karst areas).

The Upper Jurassic-Lower Cretaceous limestones overlay non-karst detrital Liassic successions and are covered by marls, marly limestones and wildflysch deposits (Cenomanian-Middle Turonian and Upper Turonian-Senonian). The Pliocene-Quaternary evolution of the region led to an altimetric gradient between the two limestone bars, while the karst processes generated the catchment of the entire hydrographical network in the underground and the forming of certain drainage systems.

The western karst area (Baia de Aramă-Ponoarele) is developed on the Badenian-Aptian limestones (grey or white, massive or bedded Urgonian bioclastic limestones).

It is comprised between the Brebina Valley (in the north) and the Zăton Lake alignment (in the south), inheriting the corridor aspect and the hydrographical network convergence in the limestone bar. Upstream, two closed depressions, Zăton and Ponoarele (flooded at high flow rates) are developed on both sides of the limestones: the entire surface hydrographical network is caught inside by the interagency of the caves Zăton (105 m development) and Bulba (5 km long, developed on three levels). Levels of this drainage have also been found in the Podul Natural Cave (734 m development), with large passageways, joining the Zăton Depression with the Ponoarele Depression.

Outside, on top of the Peşterii Hill, there is one of the most interesting karren fields from Romania. In this area, two karst systems with distinct functioning and impluvia are formed.

The eastern karst area (Gârdăneasa-Băluța) has a plateau morphology, levelled at ±550 m a.s.l. and slightly tilted eastward, its western margin being marked by an altitudinal gradient towards the Baia de Aramă-Ponoarele area. On the surface of the limestones (bioclastic, micritic, peletal or pointed by siliceous nodules), a hydrographical network pre-existed (before the faulting and the flysch erosion), on which a W-E drainage was set up, underlined today by important valleys with sinkholes (Vârtopu, Împărțitoarea, Prislop). The water was afterwards caught in the underground, by the Zăton-Bulba karst system (the Morilor Valley springs).

2. MATERIALS AND METHODS

2.1. MICROTECTONIC STUDIES

Aiming to improve the geological knowledge of the area, we carried on microtectonic studies on the Peşterii Hill, the most developed diffuse infiltration area, showing the largest epikarst extent, and on the Bulba Valley, where the system outlet is located.

On the Peşterii Hill, we performed a series of measurements with a Freiberger geological compass, using the “dip and strike” method. Further on, appealing to cave mapping data, we were able to get the orientations of the Podul Natural Cave passageways.

The data (the strike frequencies) have been processed with the Rose 1.0 software and systematized on two rosette diagrams, one for each subject (the class size: 5°, the display mode: bidirectional, the graph type: equal area).

We have also researched the Bulba Valley limestone succession, investigating the fracturing of the outcrops, following the same methodology; in addition, we have used the mapping data acquired from the Bulba Cave passageways.

2.2. INTRINSIC VULNERABILITY ASSESSMENT

The assessment of intrinsic vulnerability has been based on the rating of the four parameters mentioned by the EPIK method (DOERFLIGER & ZWAHLEN, 1998): development of the epikarst (**E**), protective cover (**P**), infiltration conditions (**I**) and development of the karst network (**K**).

The categories of the E parameter have been defined based on the results of geomorphological studies and airborne images.

The subdivision of the protective cover has been possible due to the field observations. Only the depth of the cover has been considered in the evaluation of the P parameter. It has been defined by field observations, using the principle of morphological equivalence.

The evaluation of the infiltration conditions (I) has been made by the identification of concentrated infiltration zones (swallow holes) and diffuse infiltration zones.

For the assessment of the karst network (K) parameter, we took into account cave register data.

Throughout the area, all parameters have been mapped and a weighting coefficient has been assigned to each of them, according to their protection function. Different index values have been grouped in four classes, related to their vulnerability degree. In this way, a map has been drawn, representing the spatial distribution of the vulnerability.

2.3. HYDROGEOCHEMICAL ANALYSES

The water samples have been collected by using a Crison PH 25 portable instrument, in order to perform all the temperature and pH measurements.

The pH-meter has been calibrated using two pH standard solutions purchased from Crison: one having the pH 4.01 (code 94–60) and the other – pH 7.00 (code 94–61).

The hydrogencarbonate ion content has been assessed by titration with a 0.05 M HCl solution, by using a solution of bromocresol green and methyl red as indicator – SR-ISO-9963-1 (A 99), 2002.

All the concentration assessments for chloride (SR-ISO-9297, 2001), sulfate (ASTM, 1995), silica (PAKALNS & FLYNN, 1967), ammonium (MACKERETH *et al.*, 1978), nitrite (MACKERETH *et al.*, 1978) and nitrate (MACKERETH *et al.*, 1978) have been conducted in laboratory, by the means of a Perkin-Elmer Lambda 25 molecular absorption spectrometer, in the visible and ultraviolet spectra.

The aqueous model used during this study is contained in the PHREEQC 2.12.5 software. PHREEQC calculates both activities of aqueous species and departure from equilibrium (saturation index, SI) for many solid phase (minerals) and gases that might be in contact with the aqueous phase.

2.4. BIODIVERSITY STUDY

The study has been carried out in two areas: Ponoarele (the Zăton-Bulba karst system) and the Lupşa Valley. The sampling took place in 2007 and 2008, between April and May. Harvestmen species have been collected using two sampling methods: pitfall traps, consisting in groups of three traps in a triangle design, with 2 m distance between traps, and Winkler method, consisting in 1/m^2 samples of leaf litter and soil.

Rather than analyzing each method data separately, we modeled the cumulative abundance and the species richness. We built species accumulation curves, in order to assess the adequacy of our sampling methods and the effectiveness of sampling effort for each of the two studied regions.

Since the species accumulation curves did not reach an asymptote neither for the Lupşa Valley, nor for the Ponoarele region, we used richness estimators: **Chao 2** (the incidence-based estimator of species richness) and **ACE** (the abundance-based coverage estimator of species richness) to improve the species richness estimates over the observed richness value.

An one way ANOVA analysis has been used to determine if the observed species richness differed between the two regions. Since the sample size (number of captured individuals) was uneven between studied regions, the rarefaction curve has been used to correct the unbalanced sample sizes.

A principal component analysis (PCA) on a covariance matrix has been used to determine which harvestmen species and sites contributed most to variation among communities.

3. RESULTS AND DISCUSSIONS

3.1. MICROTECTONIC FRAMEWORK

Concerning the diagram obtained for the Peşterii Hill, we emphasize the relatively wide range of values spanned by the fissures strike. The tension fissures are outlined by the N15°E, N15°W and N30°W orientations, while the fissures with W-E orientation describe the trend of the Izverna-Ponoarele-Baia de Aramă strike-slip fault (actually, the analysis of the strain ellipsoid has shown that these are shear fissures); another orientation, N80°W, is also present, related to the pseudocleavage of the limestone outcrop. Comparing these orientations with the main trends of the Podul Natural Cave passageways: N-S, N10°E, N40°E and N45°W, we mention that in this case, without excluding the tectonic influence, a much important role in the karstogenesis has been played by other features and processes, controlled by the relationships with a deep base level.

Analyzing the diagram drawn for the Bulba Valley, we can affirm that the strike is spanning again a wide range of values, easily permitting the access and the circulation of water within the karst massif.

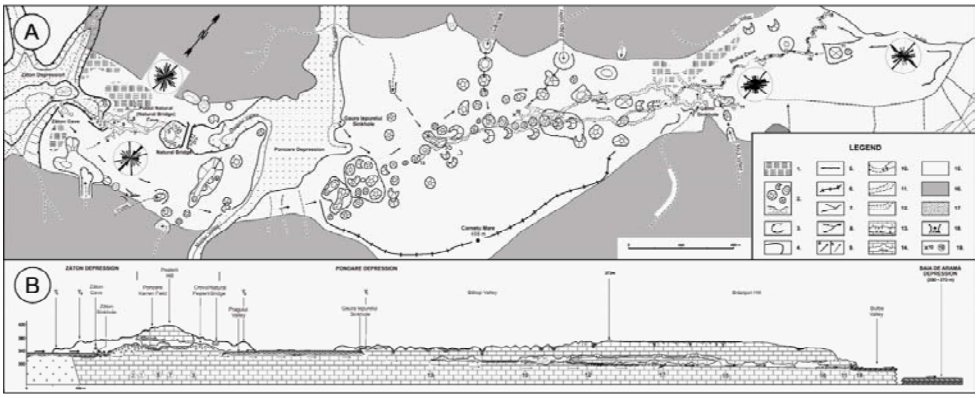

Fig. 2 – Zăton-Bulba karst system (Mehedinți Plateau): 1. karren field; 2. sinkhole; 3. blind valley; 4. karst depression; 5. vertical cliff; 6. limestone ridge; 7. river; 8. swallow hole; 9. underground drainage; 10. active passageway; 11. temporary active passageway; 12. dry passageway; 13. speleothems; 14. collapsed rocks; 15. limestone; 16. non-karst rocks, 17. alluvial layer; 18. settlement; 19. mapping point (after GORAN, 1978, modified).

The diagram is slightly modified, due to the local tectonic conditions. The most important orientations of the fissures are: N-S, W-E and N85°E. Comparing these results with the main directions of the Bulba Cave passageways (N-S, W-E and N45°E), we have ascertained the concordance between the first two pairs.

For the last direction case, the importance of the tectonic conditioning decreases, some different features, like the bedding joints, playing a decisive role. We have also noted other orientations, illustrating a variable influence of the tectonic factor: N25°E, N55°E, N60°E and N40°W. The N-S direction is parallel to the Motru fault, with extensional regime, while the shear fissures, pertaining to the Izverna-Ponoarele-Baia de Aramă strike-slip system, are disposed along the W-E direction.

The studies have provided additional tools for the vulnerability assessment within the test area. Practically, we rendered evident the epikarst extension and the fragmentation density, important for the I parameter appraisal. The sector is covered by wide karren fields, like those located on the Peşterii Hill and above the Bulba Cave, typified by intense fracturing, on various directions, allowing a fast diffuse infiltration, on a large scale, making vulnerable the karst massif.

As it is obvious from the Fig. 2, the sinkhole alignments are marking the orientation of the main drainage and its tributaries; by the size of the covered area, the quick diffuse infiltration contributes to an increase of the exposure degree in the case of a contamination event. Three main swallow holes (Zăton, Gaura Iepurelui and Găinii) also supply in a concentrated way the karst system. The water flowing from the Găinii swallow hole and from other small inlets is driven by the pseudocleavage orientation. The essential drainage feature, influencing the karst functioning and the K parameter, consists in the convergent pattern of the underground flow, conditioned by the extensional regional faulting.

3.2. INTRINSIC VULNERABILITY ASSESSMENT

The E parameter (Fig. 3) has been subdivided in three categories:

- category 1 (E_1) indicates the most vulnerable areas and has been assigned to the sectors with swallow holes, sinkholes, karren fields, fractured zones;
- category 2 (E_2) refers to the intermediate zones of these features;
- category 3 (E_3) includes the rest of the catchments.

As P_1 (Fig. 4) represents mapped area with karren fields, with soil thickness under 20 cm, P_2 includes areas with soil thickness between 20 and 100 cm. The P_3 category illustrates a succession of soil and low permeability geological formations, with protective cover thickness of more than 1 m. Last category (P_4) shows a protective cover of more than 5 m, overlaying the large sinkholes and the morphological contact depressions (in the case of the Zăton Lake and the Ponoarele Depression).

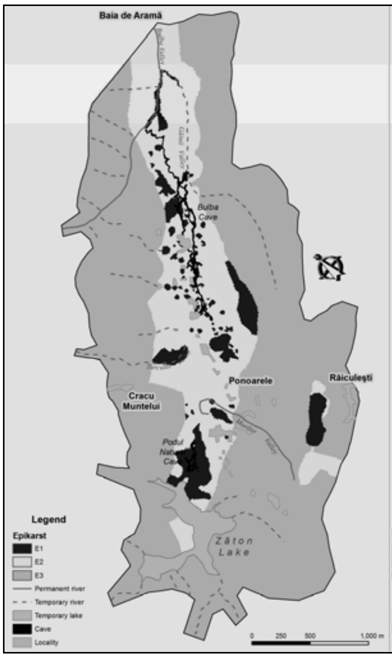

Fig. 3 – The E parameter map.

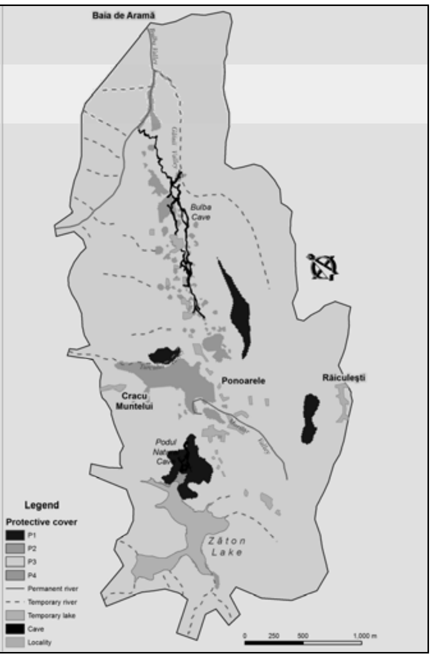

Fig. 4 – The P parameter map.

Category I_1 (Fig. 5) covers the same area as the E_1 epikarst parameter; I_2 and I_3 have been separated using the criteria of MUSY (2009), while I_4 represents the rest of the catchment area.

The K parameter (Fig. 6) has been divided in three categories, ranging from the most vulnerable to the least vulnerable. In this case, for a developed karst network with decimeter to meter wide conduits (caves) and potholes (swallow holes), we have assigned a K_1 category.

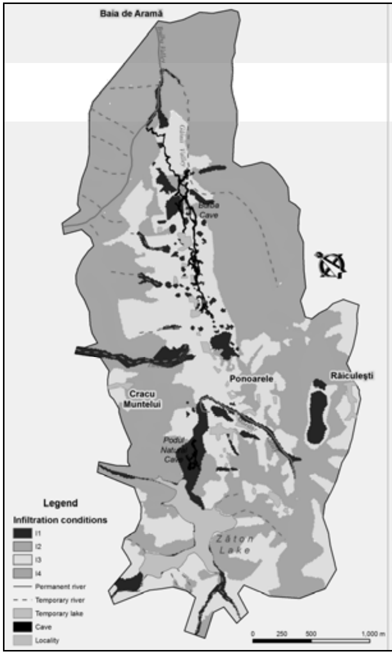

Fig. 5 – The I parameter map.

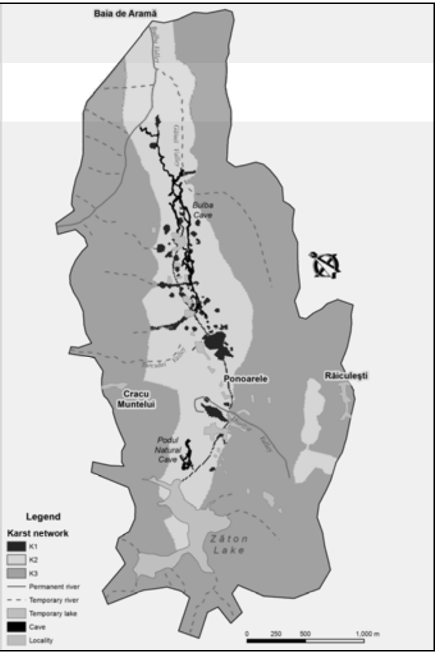

Fig. 6 – The K parameter map.

The K_2 category includes karst areas with poorly developed karst network. Finally, the K_3 category has been assigned to mixed and fissured non-karst aquifers.

The vulnerability map presented in Fig. 7 displays a complex pattern of vulnerable zones. The **F** index (protection factor) has been divided in four vulnerability classes, corresponding on the map to the areas of very high, high, moderate and low vulnerability.

The first category, with high vulnerability, has been assigned to the areas directly connected to swallow holes or to diffuse infiltration zones, resulting from the well developed epikarst (karren field) and thin soil layer. The rest of the karst area indicates a high or moderate vulnerability. On the other hand, the low vulnerable perimeters are mostly those parts of the catchments with lower ground slopes, lacking karst features.

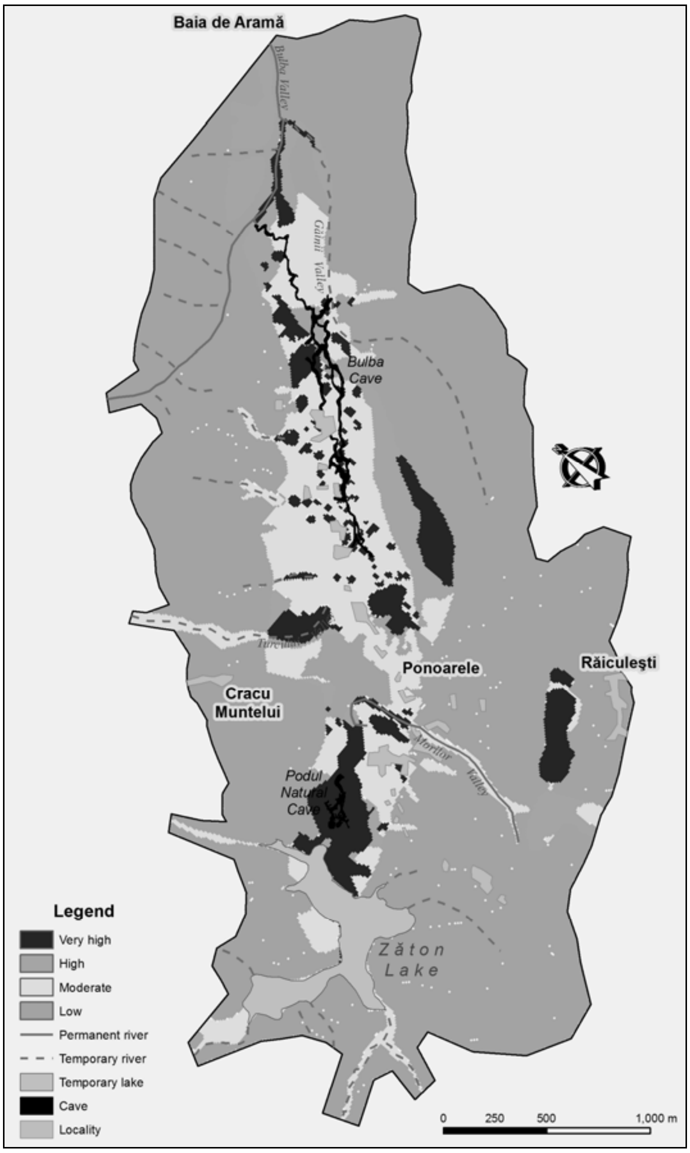

Fig. 7 – The vulnerability map.

3.3. HYDROGEOCHEMICAL DATA

In the natural water from the test area, dissolved solids (TDS) concentrations vary from 142 mgL^{-1} to 631 mgL^{-1} (Table 1). Within the area, the dominant cations are Ca^{2+} and Mg^{2+}, while the dominant anion is HCO_3^-. The TDS content of groundwater have a distribution accounting for the petrographic nature of the water flow substratum.

Calcium (Fig. 8) is a principal component of the major minerals in the investigated area and, therefore, a main dissolved constituent in groundwater, in most of the region. Concentrations of calcium ion (Ca^{2+}) in water vary from 21.1 mgL^{-1} to 127.6 mgL^{-1}. The concentration of Ca^{2+} is controlled throughout by the mineral saturation and/or by the cation exchange.

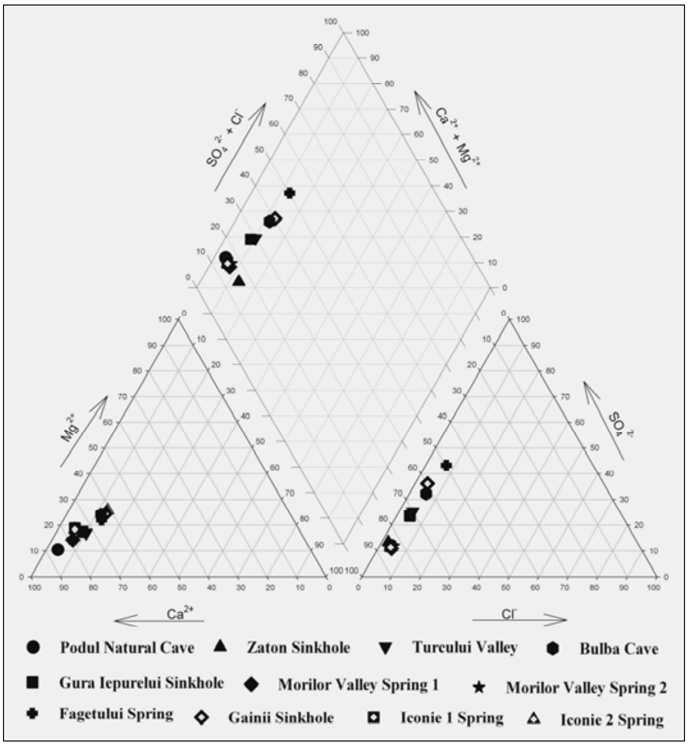

Fig. 8 – The Piper diagram of the sampled sources.

Magnesium is a major component of dolomite and a minor component of calcite. Mg^{2+} concentrations in water from the studied area range from 0.4 mgL^{-1} to 12.6 mgL^{-1}.

We have noticed that in the groundwater the spatial distribution of Ca+Mg concentrations is virtually identical to that of the TDS content. The space and time distribution of the main parameters describing the evolution of equilibria in a carbonate system, namely the CO_2 partial pressure (pCO_2), as well as the saturation index (SI) with respect to calcite and dolomite (Table 2), provide valuable information concerning the main flow directions established within the area.

The principal anion in most of the groundwater in the studied area is hydrogencarbonate (HCO_3^-), its concentrations range from 85.2 to 305.3 mgL^{-1}. Sources of HCO_3^- in natural water are: (1) dissolution of CO_2 gas in recharge water, principally within the soil layer, (2) dissolution of carbonate minerals and (3) biochemical oxidation of organic materials.

Within the studied karst region, the carbonate system is the strongest natural buffer, tending to maintain the groundwater pH within the range 6.73 to 8.63. In this range, the predominant carbonate species is HCO_3^-.

The concentrations of the dissolved sodium (Na^+) and potassium (K^+) in the Ponoarele area water range in 0.4–14.2 mgL^{-1}, respectively 0.6–6.4 mgL^{-1}. Potassium concentrations in most water from the studied area are low, because K^+–bearing minerals in the local aquifers are present only in trace amounts.

Aluminosilicate minerals containing potassium (glauconite, potassium feldspar), probably present in trace quantities, can dissolve and add very small amounts of K^+ to groundwater.

Chloride concentrations vary from 0.5 to as much as 10.5 mgL^{-1}. In this karst area, the natural origin of the Cl^- anion may be prevalently associated with the rainfall water inflow. In those zones where Cl^- concentrations exceed 1 mgL^{-1}, groundwater contamination with domestic disposals is quite probable to occur. Natural salts of Cl^- (evaporite minerals) are not present in this region.

Ammonium in groundwater is frequently associated with animal-waste sources (manure applied as fertilizer) and with septic systems. Background levels for natural nitrate in groundwater are less than 3 mgL^{-1}. Higher concentrations might indicate that nitrate from sources like human and animal waste or fertilizers have entered the groundwater, but such levels have not been recorded by us.

The concentrations of certain elements (Cu, Zn, Ni, Cd, Pb, As, Se, Sb, F) were below detection limit.

3.4. BIODIVERSITY DATA

The sampling effort in the two areas resulted in 412 individuals belonging to 14 species. Nine species have been collected from both areas, whereas *Lophopilio palpinalis*, *Platybunus pallidus*, *Trogulus oltenicus* occurred only in the Lupşa Valley, while *Mitostoma chrysomelas* and *Platybunus pinetorum* only in Ponoarele.

The species accumulation curves (**Sobs**) have shown an increase in the number of species with the number of samples, but did not reach an asymptote neither for the Lupşa Valley, nor for the Ponoarele area (Fig. 9a and Fig. 9b).

Both the Chao 2 and the ACE estimators have shown higher values than the observed values of the species richness for the Lupşa Valley area (Fig. 9a and Fig. 9b).

The one-way ANOVA analysis (ANOVA factor – $F = 0.46$, significance level – $p> 0.05$) shows no significant differences in species richness between the two areas, when rarefaction curve has been used for an equal sampling effort (using identical number of individuals, $n = 120$) (Fig. 10).

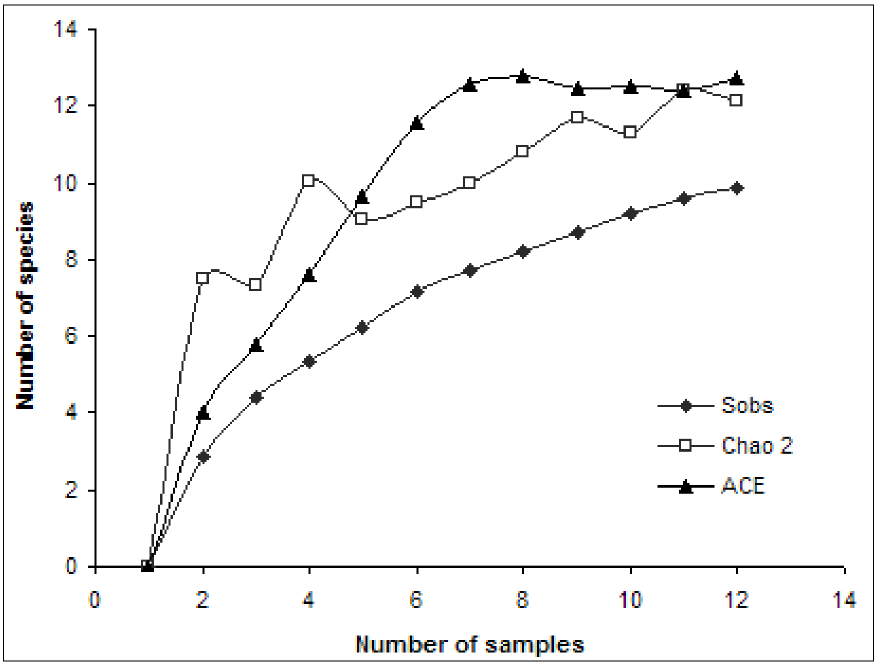

Fig. 9a – Observed species richness and estimated species richness of the harvestmen from the Lupşa Valley: Sobs – number of observed species, Chao 2 – incidence-based estimator of species richness and ACE – abundance-based coverage estimator.

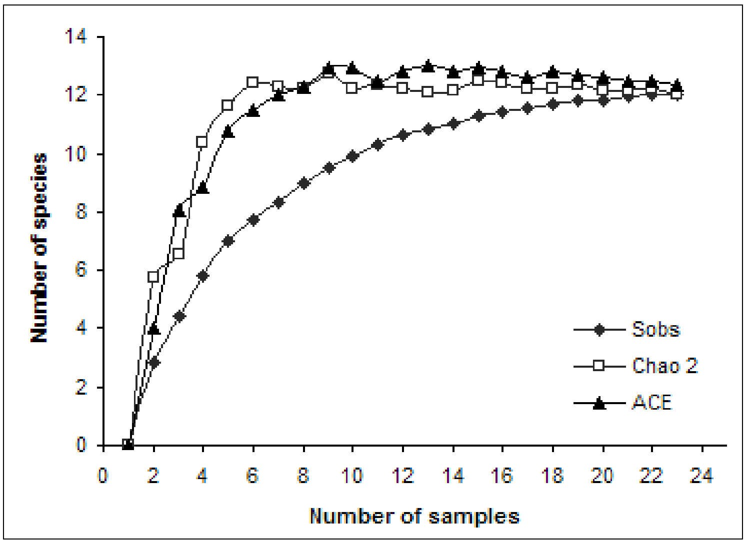

Fig. 9b – Observed species richness and estimated species richness of the harvestmen from Ponoarele: Sobs – number of observed species, Chao 2 – incidence-based estimator of species richness and ACE – abundance-based coverage estimator.

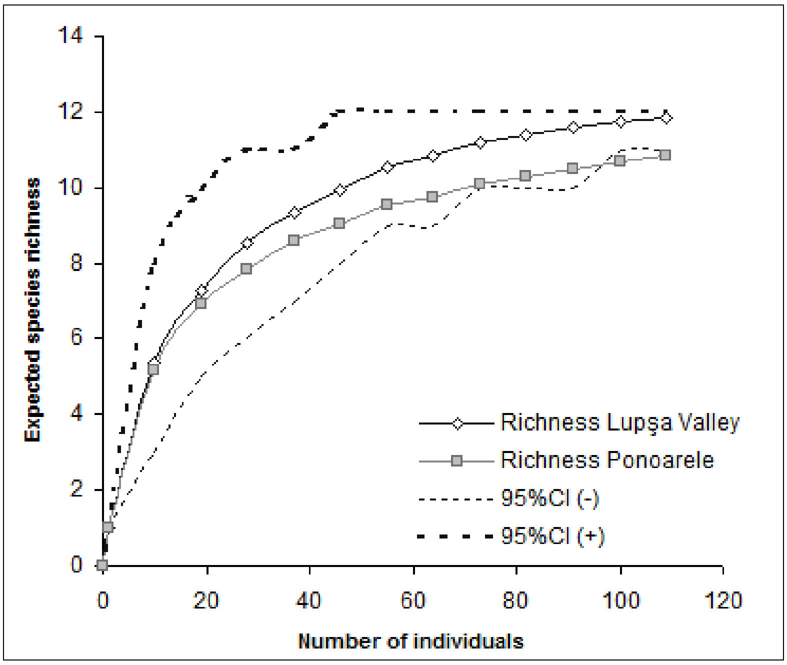

Fig. 10 – Rarefaction curves for the harvestmen of the Lupşa Valley and Ponoarele regions.

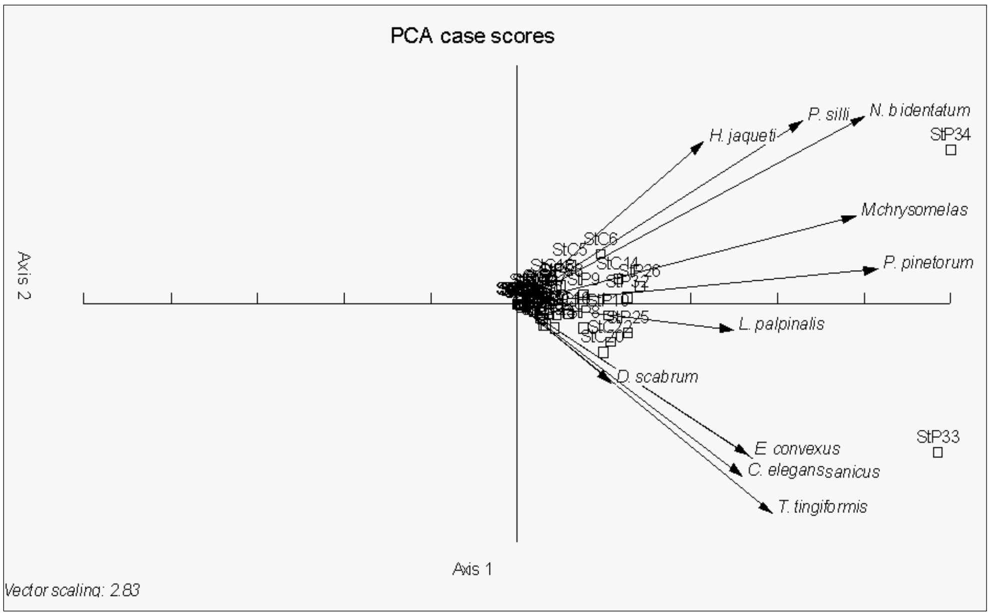

Fig. 11 – Principal component analysis (PCA) of the harvestmen community
from the Lupşa Valley and Ponoarele area.

The first three principal components explained together 54.46% of variance among communities. The first component (PC1) had higher positive weights related to species abundant in Ponoarele: *T. tricarinatus* and *T. tingiformis*.

PC2 explained 13.15% of the variance and gave higher negative weights to species like: *T. tingiformis*, *T. closanicus*, *C. elegans* and *E. convexus*, which were more abundant in Ponoarele than in the Lupşa Valley.

PC3 explained 9.8% of the variance and species more abundant also in Ponoarele than in the Lupşa Valley (*N. bidentatum sparsum*, *T. closanicus* and *L. palpinalis*) received the highest negative weights.

The eigenvectors are presented in Figure 11 and specify the direction in which the abundance of harvestmen species increases in studied sites. Sites 34 (StP34) and 33 (StP33) show the highest abundance values for 10 out of the 14 total species number.

4. CONCLUSIONS

The complexity of the karst landscapes and functioning, renders less effective the assessment of the karst vulnerability from a single point of view (geological, geomorphological or hydrogeological).

Therefore, we have diversified our approach, by adding hydrogeochemical and biological data.

The results of the biodiversity study have indicated no significant differences in species richness between the two studied areas at identical sampling effort. The species richness is also related to the habitat diversity and heterogeneity.

The creation or modification of the habitat structure has been postulated to be an important mechanism generating heterogeneity and thus high species richness (JONES *et al.*, 1997).

Although, one can properly estimate the effect of human impact only by fully sampling of the two areas and, accounting for differences in habitat characteristics, the results obtained in this study support the hypothesis that low human impact can increase the species richness. In addition to human impact, others factors, like habitat size, degree of isolation and vegetation, may be involved in the species richness and in the species assemblages of the harvestmen community.

We conclude that the threat of the anthropogenic impact on the karst ecosystems may be better assessed by combining the understanding of the processes acting within the karst terrains vulnerable framework with hydrogeochemical data and information concerning the cumulative abundance and the species richness of certain selected taxa.

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REFERENCES

ASTM: *Standard test method for sulfate ion in water*. ASTM-D516-07, 1995.

DOERFLIGER, N. & ZWAHLEN, F.: *Practical Guide: Groundwater Vulnerability Mapping in Karstic Regions (EPIK).* Swiss Agency for the Environment, Forests and Landscape (SAEFL), Bern, 56 p., 1998.

GORAN, C.: Le karst du Plateau de Mehedinți. I. Partie nord. *Travaux de l'Institut de Spéologie "Émile Racovitza"*, **XVII**, 165–184, 1978.

JENNINGS, D.T., HOUSEWEART, M.W. & COKENDOLPHER, J.C.: Phalangids (Arachnida: Opiliones) associated with strip clear-cut and dense spruce-fir forests of Maine. *Environmental Entomology*, **13**, 5, 1306–1311, 1984.

JONES, C.G., LAWTON, J.H. & SHACHAK, M.: Positive and negative effects of organisms as physical ecosystem engineers. *Ecology*, **78**, 1946–1957, 1997.

MACKERETH, F.J.H., HERON, J. & TALLING, J.F.: *Water analysis: Some revised methods for limnologists*. Freshwater Biological Association, Ambleside, 1978.

MUSY, A.: Cours Hydrologie Générale. Web site: *http://hydram.epfl.ch/e-drologie*. Cited on 08 June 2009.

PAKALNS, P. & FLYNN, W.W.: Spectrophotometric determination of traces of silicon by an extraction method. *Analytica Chimica Acta*, **38**, 3, 403–414, 1967.

PEKAR, S.: Effect of liquid fertilizer (UAN) combined with deltamethrin on beneficial arthropods in spring barley. *Ochrana Rostlin*, **33**, 257–264, 1997.

PLĂIAŞU, R. & BĂNCILĂ, R.I.: Habitate utilizate de opilionide (Arachnida: Opilionidae) în sistemul carstic Zăton-Bulba. Sesiunea de Comunicări a Institutului de Speologie "Emil Racoviță", Bucureşti, 17, 2008.

RABITSCH, W.B.: Metal accumulation in arthropods near a lead/zinc smelter in Arnoldstein, Austria. III. Arachnida, *Environmental Pollution*, **90**, 249–257, 1995.

SR-ISO-9297: *Water quality – Chloride content determination. Titration with silver nitrate using chromate as an indicator (Mohr Method)*. Romanian Standard. Collections of Standards ASRO, 2001.

SR-ISO-9963-1 (A 99): *Water quality – Determination of alkalinity. Part 1: Determination of total and permanent alkalinity*. Romanian Standard. Collections of Standards ASRO, 2002.

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Table 1

Chemical composition of the sampled groundwater sources from the Zăton-Bulba karst system (Mehedinți Plateau).

No.	Sample	Date	t	pH	Hardness	Alcalinity	Conductivity	TDS	Na	K	Mg	Ca	Ba	Mn	Fe	Al	Cr	HCO_3	Si	NH_4	NO_2	NO_3	SO_4	Cl	Error
			°C		°dH	mVal/L	mS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	μg/L	mg/L	mg/L	μg/L	μg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	(%)
1	Zăton Sinkhole	17.03.2007	25	6.94	n.a.	n.a.	n.a.	142	5.8	1.0	4.6	21.1	30.60	0.25	2.14	n.a.	n.a.	85.2	9.7	0.120	n.a.	3.2	4.1	6.8	0.04
		23.04.2007	25	7.22	n.a.	n.a.	n.a.	159	6.2	1.1	5.0	23.6	n.a.	n.a.	n.a.	n.a.	n.a.	98.6	9.7	0.030	n.a.	2.1	10.6	1.8	0.79
		12.05.2007	25	7.24	n.a.	n.a.	n.a.	183	6.2	1.3	5.3	28.5	n.a.	n.a.	n.a.	n.a.	n.a.	123.2	9.3	0	n.a.	2.9	3.8	2.0	0.87
		11.04.2008	12.5	7.95	4.5	1.630	0.21	166	6.2	1.3	5.3	23.1	5.41	0.29	4.13	15.80	0	99.5	9.1	0.011	0.070	1.9	17.1	2.2	0.69
2	Podul Natural Cave (seepage)	18.02.2007	25	7.98	n.a.	n.a.	n.a.	253	0.4	0.0	0.4	59.5	15.32	0.05	0.02	9.75	0.46	174.9	1.9	n.a.	n.a.	1.2	4.0	0.5	0.58
3	Turcului Valley	17.03.2007	25	7.35	n.a.	n.a.	n.a.	369	5.3	3.3	4.3	79.4	71.83	0.02	1.24	n.a.	n.a.	231.3	3.9	0.100	n.a.	4.4	35.1	2.1	0.16
4	Gaura Iepurelui Sinkhole	23.04.2007	25	7.75	n.a.	n.a.	n.a.	383	4.9	0.8	4.4	85.2	n.a.	n.a.	n.a.	n.a.	n.a.	250.8	3.7	0	n.a.	4.0	27.1	1.8	0.59
		12.05.2007	25	7.83	n.a.	n.a.	n.a.	341	4.9	1.1	4.2	72.9	n.a.	n.a.	n.a.	n.a.	n.a.	225.7	3.5	0	n.a.	3.5	23.4	1.6	0.74
		11.04.2008	11.8	8.63	14.7	4.367	0.56	434	6.3	1.4	5.7	96.1	36.71	0.03	0.50	7.70	0	266.4	3.7	0.003	0.002	3.7	48.0	2.6	0.86
5	Morilor Valley Spring 1 (upstream)	17.03.2007	25	7.20	n.a.	n.a.	n.a.	389	3.2	0.9	2.8	88.3	81.43	0.01	0.01	n.a.	n.a.	280.7	4.1	0.110	n.a.	5.9	1.0	2.4	0.25
		23.04.2007	25	6.78	n.a.	n.a.	n.a.	384	3.2	0.6	3.0	87.3	n.a.	n.a.	n.a.	n.a.	n.a.	278.4	3.9	0	n.a.	4.6	1.2	1.9	0.45
		12.05.2007	25	7.10	n.a.	n.a.	n.a.	398	3.3	0.7	3.0	89.7	n.a.	n.a.	n.a.	n.a.	n.a.	289.5	3.6	0	n.a.	4.4	2.5	1.7	0.31
		11.04.2008	10.8	7.52	12.5	4.313	0.47	378	3.7	1.8	2.9	84.9	37.40	0	0	0	0	263.2	3.6	0	0.001	5.8	9.1	2.9	0.03
6	Morilor Valley Spring 2 (downstream)	23.04.2007	25	6.91	n.a.	n.a.	n.a.	385	3.3	0.7	2.9	87.7	n.a.	n.a.	n.a.	n.a.	n.a.	276.0	3.9	0	n.a.	6.1	2.3	2.4	0.50
		12.05.2007	25	6.73	n.a.	n.a.	n.a.	364	3.2	0.8	3.1	82.5	n.a.	n.a.	n.a.	n.a.	n.a.	261.4	3.6	0	n.a.	4.9	2.8	2.1	0.54
		11.04.2008	10.7	7.56	13.7	4.617	0.51	407	3.4	1.4	3.1	92.7	44.84	0	0	0	0.23	281.7	3.5	0.002	0	5.6	12.6	2.9	0.18
7	Făgetului Spring	11.04.2008	8.4	7.46	20.7	5.003	0.82	631	14.2	6.4	12.6	127.6	0	0.05	0.08	27.80	0	305.3	10.7	0.002	0	12.8	130.6	10.5	0.19
8	Găinii Sinkhole	12.05.2007	25	7.82	n.a.	n.a.	n.a.	334	8.1	1.1	7.0	65.8	n.a.	n.a.	n.a.	n.a.	n.a.	195.8	9.1	0.150	n.a.	1.1	44.5	1.2	0.69
		11.04.2008	12.3	8.12	11.0	2.990	0.44	342	9.0	2.0	8.7	64.6	11.71	0.07	0.73	10.20	0	182.4	7.7	0.006	0.002	0.6	65.5	1.6	0.06
9	Bulba Cave	17.03.2007	25	7.16	n.a.	n.a.	n.a.	246	5.8	1.1	5.9	47.6	49.22	0.17	1.51	n.a.	n.a.	131.6	7.9	0.130	n.a.	4.3	37.9	3.3	0.79
		23.04.2007	25	7.43	n.a.	n.a.	n.a.	280	5.7	1.1	6.2	55.6	n.a.	n.a.	n.a.	n.a.	n.a.	159.9	7.5	0	n.a.	3.9	37.3	2.9	0.26
		12.05.2007	25	7.44	n.a.	n.a.	n.a.	317	5.9	1.2	6.6	63.3	n.a.	n.a.	n.a.	n.a.	n.a.	189.1	6.8	0	n.a.	3.4	38.0	2.5	0.36
		11.04.2008	9.6	7.77	7.3	2.181	0.30	237	5.8	1.2	5.6	43.0	13.35	0.30	3.79	35.20	0	133.1	7.2	0.011	0.017	3.9	34.7	2.6	0.01
10	Iconie 1 Spring (upstream)	11.04.2008	9.6	7.63	10.9	3.842	0.40	324	1.5	0.7	4.6	70.7	10.97	0.04	0	0	0.19	234.4	3.7	0.002	0.002	3.4	4.7	0.6	0.27
11	Iconie 2 Spring (downstream)	12.05.2007	25	7.29	n.a.	n.a.	n.a.	299	1.6	0.6	4.0	65.0	n.a.	n.a.	n.a.	n.a.	n.a.	216.7	4.0	0.020	n.a.	3.9	2.1	1.3	0.47
		11.04.2008	9.6	7.56	10.9	3.676	0.40	314	1.6	0.7	4.4	71.0	8.47	0.05	0.04	0	0.27	224.3	3.6	0.004	0.002	2.8	5.3	0.7	1.81

Table 2

Log pCO_2 and stability indexes (SI) of the sampled groundwater sources from the Zăton-Bulba karst system (Mehedinți Plateau).

No.	Sample	Date	Log pCO_2	Stability indexes												
				Magnesite	**Dolomite**	**Calcite**	**Anhydrite**	**Gypsum**	**Aragonite**	**Sepiolite**	**Chalcedony**	**Cristobalite**	**Silica gel**	**Thenardite**	**Mirabilite**	**Epsomite**
1	Zăton Sinkhole	17.03.2007	-2.01	-2.07	-3.22	-1.18	-3.54	-3.32	-1.32	-6.05	0.08	0.12	-0.44	-11.58	-10.65	-6.21
		23.04.2007	-2.22	-1.69	-2.45	-0.79	-3.07	-2.85	-0.93	-4.85	0.08	0.12	-0.44	-11.11	-10.17	-5.75
		12.05.2007	-2.15	-1.55	-2.12	-0.59	-3.45	-3.23	-0.74	-4.78	0.07	0.10	-0.46	-11.56	-10.62	-6.18
		11.04.2008	-2.79	-1.52	-0.33	-0.51	-3.02	-2.72	-0.66	-7.74	0.19	-0.10	-0.91	-10.74	-9.34	-5.69
2	Podul Natural Cave (seepage)	18.02.2007	-2.81	-1.93	-1.39	0.51	-3.17	-2.95	0.36	-6.27	-0.61	-0.57	-1.14	-13.92	-12.99	-7.39
3	Turcului Valley	17.03.2007	-2.00	-1.35	-1.18	0.14	-2.21	-1.99	0	-5.79	-0.30	-0.26	-0.83	-10.86	-9.93	-5.48
4	Gaura Iepurelui Sinkhole	23.04.2007	-2.37	-0.90	-0.26	0.61	-2.27	-2.05	0.46	-4.26	-0.33	-0.30	-0.87	-11.02	-10.08	-5.56
		12.05.2007	-2.50	-0.88	-0.26	0.58	-2.38	-2.16	0.44	-4.02	-0.35	-0.32	-0.89	-11.07	-10.13	-5.62
		11.04.2008	-2.79	-0.75	1.81	0.85	-2.13	-1.82	0.71	-7.01	-0.19	-0.48	-1.30	-10.41	-8.97	-5.38
5	Morilor Valley Spring 1 (upstream)	17.03.2007	-1.77	-1.59	-1.44	0.12	-3.73	-3.51	-0.01	-6.70	-0.29	-0.25	-0.82	-12.86	-11.92	-7.23
		23.04.2007	-1.35	-1.97	-2.23	-0.28	-3.61	-3.39	-0.42	-8.36	-0.30	-0.27	-0.84	-12.74	-11.81	-7.07
		12.05.2007	-1.65	-1.64	-1.55	0.06	-3.28	-3.06	-0.08	-7.18	-0.34	-0.30	-0.87	-12.39	-11.46	-6.75
		11.04.2008	-2.86	-1.00	1.57	0.85	-2.88	-2.56	0.71	-7.82	-0.17	-0.47	-1.29	-11.56	-10.09	-6.35
6	Morilor Valley Spring 2 (downstream)	23.04.2007	-1.48	-1.86	-1.98	-0.15	-3.32	-3.10	-0.30	-7.83	-0.30	-0.26	-0.83	-12.43	-11.50	-6.80
		12.05.2007	-1.32	-2.03	-2.38	-0.38	-3.24	-3.02	-0.52	-8.63	-0.34	-0.30	-0.87	-12.37	-11.43	-6.67
		11.04.2008	-2.82	-0.96	1.66	0.90	-2.72	-2.40	0.76	-7.87	-0.18	-0.48	-1.30	-11.51	-10.02	-6.20
7	Făgetului Spring	11.04.2008	-2.79	-0.49	2.19	0.94	-1.70	-1.35	0.79	-3.21	0.36	0.05	-0.78	-9.33	-7.74	-4.68
8	Găinii Sinkhole	12.05.2007	-2.55	-0.73	-0.23	0.46	-2.15	-1.93	0.32	-2.39	0.05	0.09	-0.47	-10.35	-9.41	-5.12
		11.04.2008	-2.94	-0.71	1.53	0.54	-2.13	-1.82	0.39	-4.33	0.12	-0.18	-0.98	-9.93	-8.52	-5.02
9	Bulba Cave	17.03.2007	-2.05	-1.61	-2.06	-0.47	-2.33	-2.11	-0.62	-5.30	0	0.03	-0.53	-10.70	-9.77	-5.24
		23.04.2007	-2.24	-1.24	-1.27	-0.05	-2.26	-2.04	-0.20	-4.26	-0.02	0.01	-0.55	-10.71	-9.78	-5.22
		12.05.2007	-2.18	-1.14	-1.04	0.07	-2.22	-2.00	-0.07	-4.32	-0.06	-0.03	-0.60	-10.69	-9.76	-5.20
		11.04.2008	-2.81	-1.36	0.29	-0.07	-2.54	-2.20	-0.22	-7.64	0.16	-0.14	-0.97	-10.54	-9.00	-5.42
10	Iconie 1 Spring (upstream)	11.04.2008	-2.95	-0.83	1.65	0.76	-3.24	-2.90	0.61	-6.72	-0.14	-0.44	-1.26	-12.62	-11.08	-6.41
11	Iconie 2 Spring (downstream)	12.05.2007	-1.96	-1.43	-1.39	0.01	-3.45	-3.23	-0.13	-6.01	-0.30	-0.26	-0.83	-13.08	-12.15	-6.66
		11.04.2008	-2.96	-0.88	1.58	0.74	-3.18	-2.84	0.59	-6.91	-0.15	-0.45	-1.27	-12.51	-10.97	-6.38