GEOLOGICAL AND HYDROGEOCHEMICAL RESEARCH, TOOLS FOR KARST MANAGEMENT IN THE NORTH OF THE CARAŞ GORGES (BANAT MOUNTAINS, ROMANIA)

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Abstract. The karst geosystems functioning frequently implies very quick mass and energy transfers, which make them highly sensitive to any natural or anthropogenic disturbance. Therefore, the groundwater resources, threatened by agricultural and industrial pollution, should be carefully exploited, taking into account the intrinsic vulnerability of the region. This paper aims to present the results of the geological, geomorphological and hydrogeochemical studies carried out in the Banat Mountains (Romania), in order to widely assess and map the vulnerability of the most exposed karst aquifers. Following the principles of the EPIK method and using GIS, we were able to delineate upon degree 4 vulnerability classes (low, moderate, high, very high). Moreover, each unit has been assigned to a specific protection framework, comprising suitable management solutions, designed for environmental managers.

Key words: intrinsic vulnerability, EPIK, GIS, karst groundwater management, Banat Mountains.

1. INTRODUCTION

1.1. GEOGRAPHIC SETTING

Located in the southwestern part of Romania, the Banat Mountains, present specific karst landforms, spread on a wide area (807 km^2 – Bleahu *et al.,* 1976), marked by the particular structure (lithological diversity, intense folding and faulting) and by the unique features of climate (denoting Atlantic and Mediterranean influences), hydrology, flora and fauna.

Over the years, the development of the region increased the anthropogenic risks incidence on the natural resources, by deforestation, quarrying, road building and tourism. Pollution can irremediably affect the aquifers, exploited for economic and household purposes; therefore, some natural protected areas have been designated.

In order to evaluate the exposure degree and to adopt the most adequate measures to avoid contamination events, we have selected a study perimeter situated on the Aninei Mountains territory. It comprises partially the Semenic-Caraş Gorges National Park and some adjacent zones (Fig. 1).

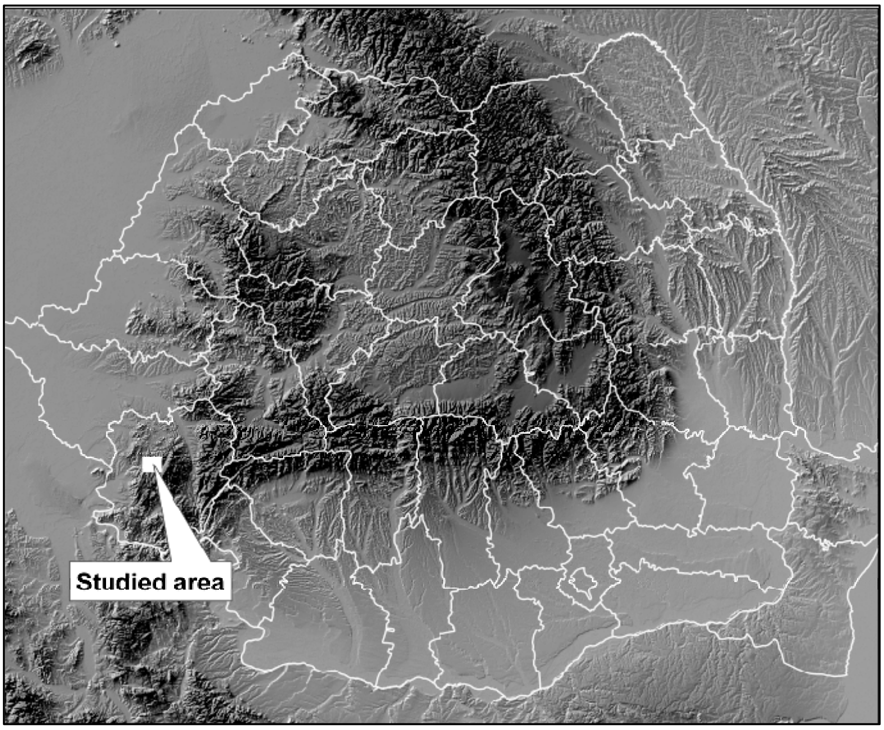

Fig. 1 – The studied area.

The area presents the general NNE-SSW strike and an altitude variable between 955 m a.s.l. (Culmea Certej) and 200 m a.s.l. The main geomorphological peculiarity resides in the low mountains aspect, with the interchange of long and parallel ridges, separated by karst valleys or plateaus.

At the Anina station (650 m a.s.l.) a yearly average rainfall value of 1005.5 mm has been recorded, while at the Oravița station (220 m a.s.l.) the rainfall amount has reached the value of 849.7 mm/year (IURKIEWICZ *et al.*, 2005).

The area includes many natural resources which require protection: a wild beech forest, rare biota, a sinkhole valley and major karst systems, established by important water inputs and discharged by springs with high flow rates. There are 37 cavities discovered until now, very densely distributed (caves, such as Țolosu, Subcetate, Liliecilor etc. and potholes). Certain underground networks are sheltering endemic fauna species or archaeological and palaeontological sites (PNSCC, 2009).

1.2. GEOLOGICAL SETTING

The investigated area belongs to the Reşița-Moldova Nouă zone (Fig. 2), a wide synclinorium from the inner part of the Getic Nappe.

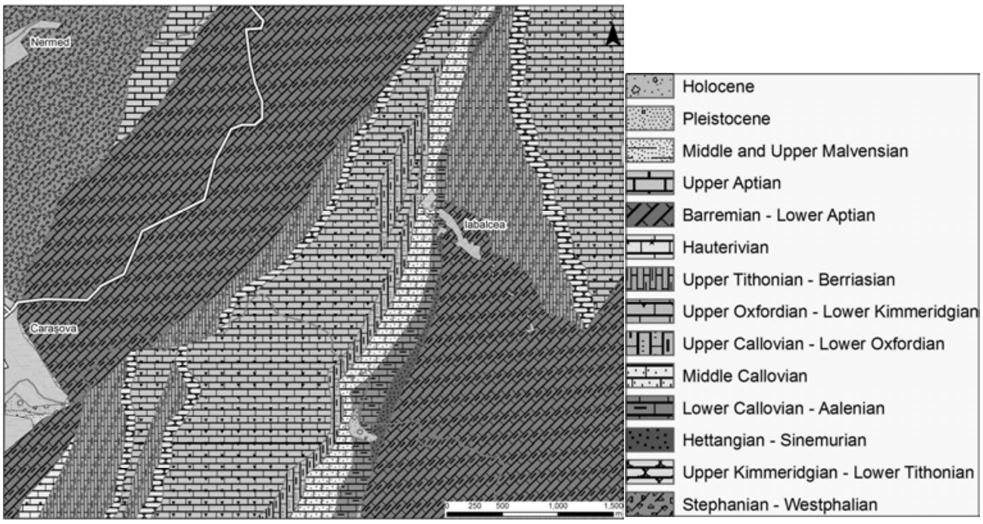

Fig. 2 – Geological map of the studied area (after NĂSTĂSEANU *et al.*, 1985).

The crystalline basement consists of Lower Proterozoic mesometamorphic rocks pertaining to Sebeş-Lotru Lithogroup (micaceous paragneisses, ocular gneisses, spotted gneisses, micaschists, amphibolites and manganiferous schists – Mutihac *et al.,* 2004).

The sedimentary cover mainly comprises Mesozoic formations (Fig. 3); only a small accumulation of Neozoic deposits appears in the southwest. During the Jurassic and the Lower Cretaceous, the zone acted as a relatively narrow subsiding linear trough, enframed by two main thresholds (Bucur, 1997).

The Steierdorf Formation (Hettangian-Pliensbachian) – conglomerates, sandstones with coal layers and bituminous shales, deposited in the Gresten facies – is overlayed by *the Zânei Hill Marls Formation* (Toarcian-Lower Callovian), which integrates marly limestones, sandstone-like marls, microrudites and arenites with carbonate matrix.

The succession continues with *the Gumpina Limestones Formation* (Middle Callovian), illustrated by a series of sandstone-like, siliceous limestones, locally pointed by concretions (ellipsoidal silica nodules) and followed by *the Tămaşa Marly Limestones Formation* (Upper Callovian-Lower Oxfordian), mainly embounding sandstone-like, marly limestones.

The Anina Valley Limestones Formation (Upper Oxfordian-Lower Kimmeridgian) is distiguished by its clear bedding, marked by silica intercalations.

Covering it, *the Brădet Limestones Formation* (Upper Kimmeridgian-Lower Tithonian) follows, outcropping in a nodular, lenticular or breccious facies, along with subordinate clays and marls.

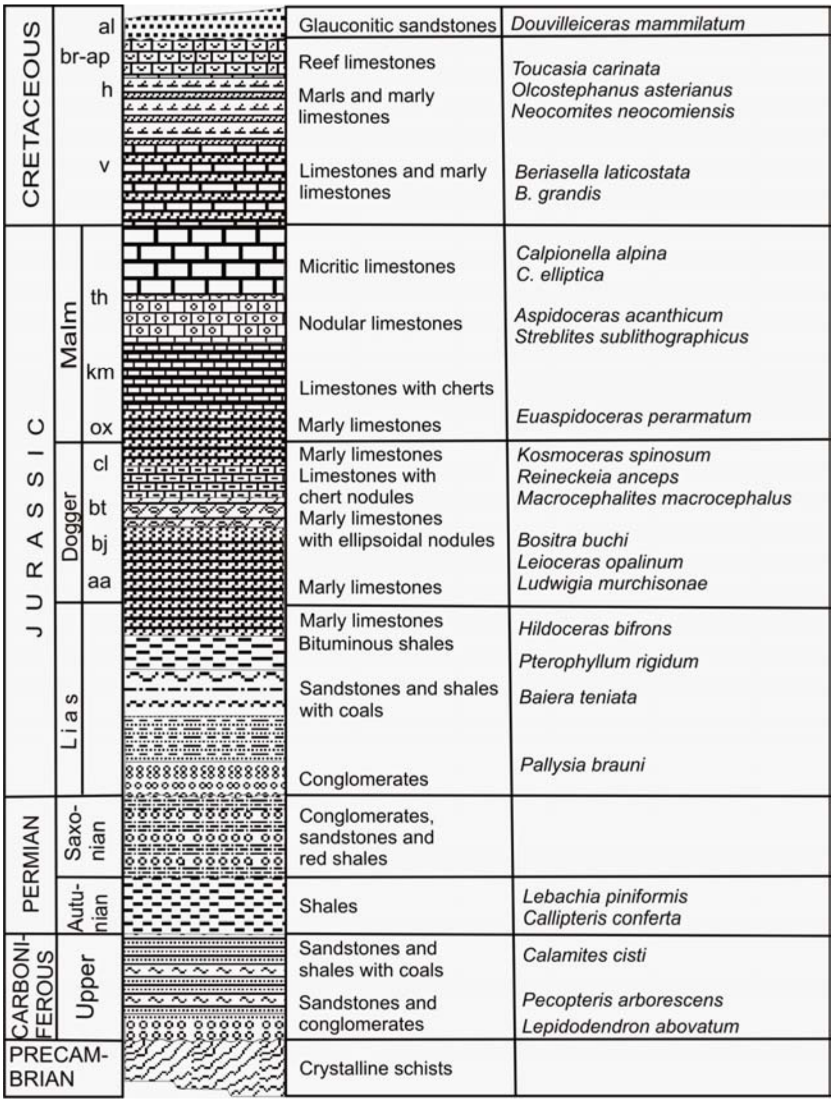

Fig. 3 – Stratigraphic log of the Reşiţa-Moldova Nouă zone (after MUTIHAC *et al.*, 2004).

The Miniş Valley Limestones Formation (Upper Barremian-Middle Aptian) has been partially eroded.

Post-Albian, the whole territory emerged from below sea level (RĂILEANU *et al.*, 1957; BUCUR, 1991). Continental sands, argillaceous sands and gravels were sedimented in the Pontian.

From the tectonic point of view, the perimeter has a faulted nappe folds structure (MUTIHAC *et al.*, 2004), result of the Hercynian and Alpine orogenies

(NĂSTĂSEANU, 1964). The Getic overthrust was set up in two distinct stages, Austrian (intra-Aptian) and Laramide (post-Lower Senonian – SĂNDULESCU, 1984). The region is active, dominated by deep crustal faulting, in the framework of a major strike-slip system (BUCUR, 1997).

We remark that the large scale outcropping of the karst rocks, typified by tectono-structural features which intricate the drainage processes, is leading to an increased degree of exposure to hazards, both natural (collapses, floodings) and anthropogenic (contamination). The non-karst rocks are disposed in narrow bands or cover only small scattered areas, meaning that the aquifers are just locally protected.

2. MATERIALS AND METHODS

2.1. INTRINSIC VULNERABILITY ASSESSMENT

We have selected the EPIK method (DOERFLIGER & ZWAHLEN, 1998), aiming to estimate the intrinsic vulnerability of the karst hydrostructures within the study area. This multiparameter method has been previously tested in Romania and it has proved to be suitable for assessment (IURKIEWICZ *et al.*, 2005).

The research implied field activities (epikarst and protective cover mapping, infiltration conditions appraisal), along with the use of the orthoimages at 0.5 m resolution and the cave register data (necessary for the evaluation of the karst network development).

Additional spatial data have been obtained by digitizing topographic maps (1:10000 scale) and geological maps (1:50000 scale), georeferenced to Stereo 70 national projection grid.

After the GIS mapping, weighting and adding of all attributes, we were able to calculate the protection index (F) and to draw its map, on which sectors with different vulnerability degrees have been delineated.

The parameters, variously influencing the vulnerability dependent on the environment features (porosity, permeability, aquifer depth and recharge rate etc.) have been divided in 3 categories (1: the most vulnerable, 3: the less vulnerable), according to the EPIK method principles (DOERFLIGER & ZWAHLEN, 1998).

2.2. 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 fluoride content in the samples has been directly determined by using an ISE method.

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.

3. RESULTS

3.1. INTRINSIC VULNERABILITY ASSESSMENT

For **the E (epikarst) parameter** (Fig. 4) we should mention the next categories:

- E_1: terrains with dolines, karren fields or intensely fractured outcrops, covering almost 48% of the total area;
- E_2: intermediate zones disposed in the doline fields and dry valleys (50%);
- E_3: the rest of the catchments (2%).

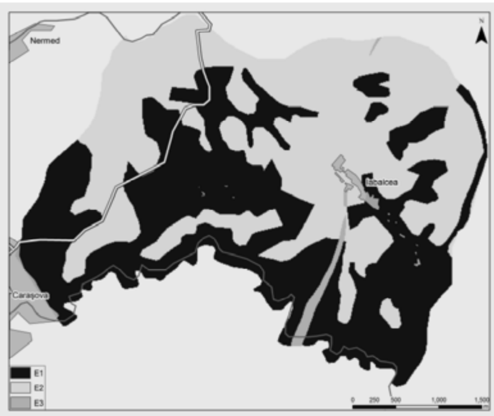

Fig. 4 – The E parameter map.

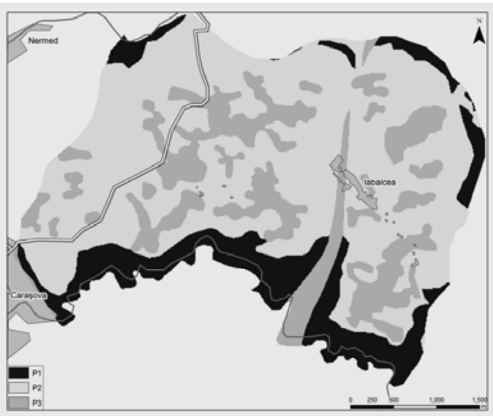

Fig. 5 – The P parameter map.

The P (protective cover) parameter (Fig. 5) categories are:

- P_1: areas covered by forests, marked by a good epikarst development and a soil thickness of less than 20 cm (15%);
- P_2: perimeters covered by meadows and pastures, with approximately 1 m thick soil, directly overlaying the limestone formations (50%);
- P_3: sectors in which the soil thickness exceeds 1 m over the limestone bedrock (35%).

Because of the wide extent of forests in the region, we have rated **the I (infiltration conditions) parameter** (Fig. 6) by also using for I_2 and I_3 the criteria issued by MUSY (2009):

- I_1: permanent or temporary swallow holes, banks and beds of the supplying streams, infiltrating superficial flow (1%);
- I_2: areas with slopes steeper than 10% for arable lands, than 25% for meadows and pastures or than 35% in the case of forests (30%);
- I_3: perimeters with slopes lesser than 10% for arable lands, than 25% for meadows and pastures or than 35% in the case of forests (69%).

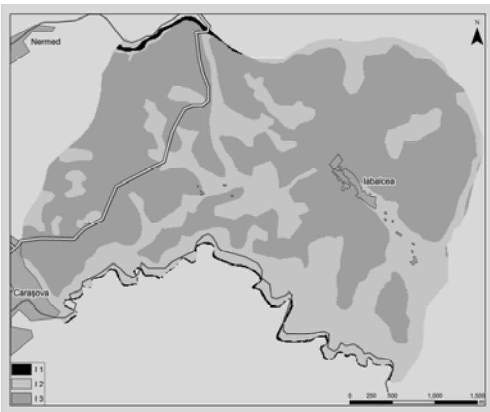

Fig. 6 – The I parameter map.

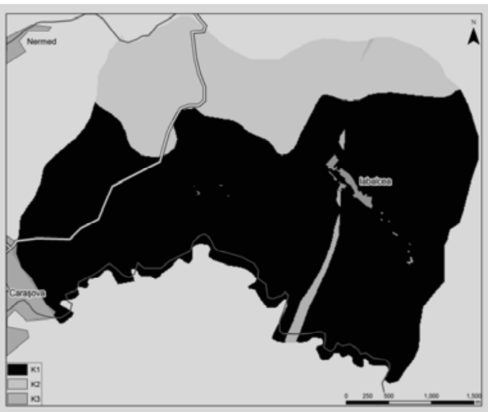

Fig. 7 – The K parameter map.

The K (karst network development) parameter (Fig. 7) has been assessed by taking into account speleometric and hydrogeochemical data, along with archive information, especially related to the number of springs.

The main categories of the K parameter are:

- K_1: well or moderate developed karst networks, with decimeter to meter wide, interconnected conduits (60%);

- K_2: poorly developed karst networks, with smaller diameters of the conduits, which can be locally clogged (38%);
- K_3: mixed or fissured aquifers (2%).

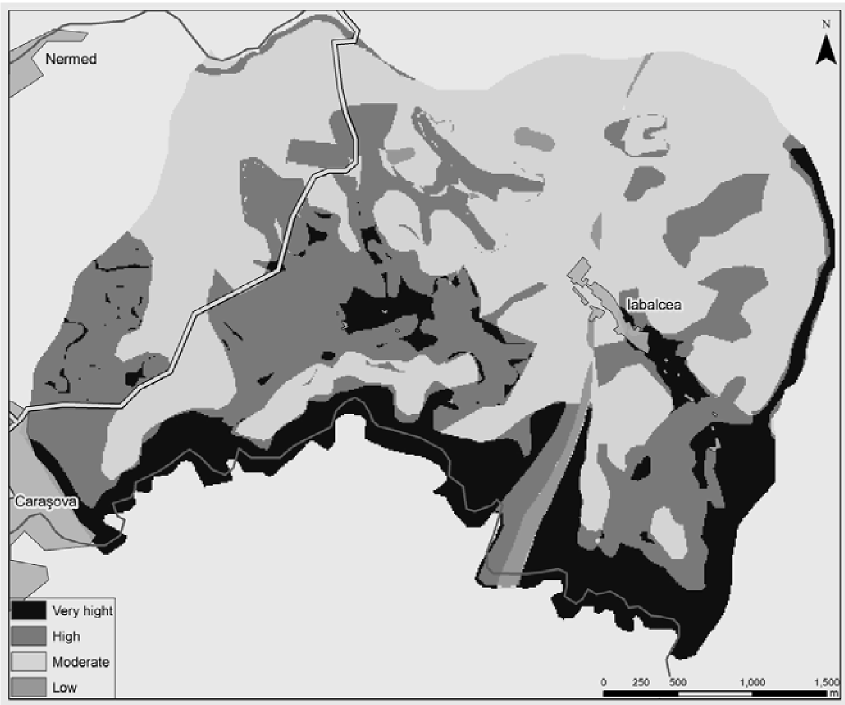

Fig. 8 – The vulnerability map.

The data processing, simplified by the GIS software tools, allowed us to get a synoptic image of the protection index (F) distribution in the area of interest. Hence, on the final map (Fig. 8), areas with very high – F: 9–19 (15%), high – F: 20–25 (15%), moderate – F >25 (65%) and low vulnerability degree – F >25, in the presence of P_4 and I_3 categories (5%), have been delineated.

3.2. HYDROGEOCHEMICAL DATA

In the case of the Țolosu Cave (Table 1) higher concentrations of sodium (4–5%) in comparison with the background level (<1%) from other sources, have been recorded. Here, to the Na^+ higher concentration and to the significant amount of Mg^{2+} (6.5%), corresponds a high level of SO_4^{2-} (19.6%). We can ascertain a varied limestone petrology, reflected in the groundwater composition (Fig. 9).

Table 1

Chemical composition of the sampled groundwater sources from the north of the Caraş Gorges (Banat Mountains, Romania)

Sample	Nucilor Spring	Pod Spring	Subcetate II Cave	Subcetate II Spring	Ţolosu Cave
Date	25.08.2006	25.08.2006	25.08.2006	25.08.2006	16.02.2007
t (°C)	25	25	25	25	25
pH	7.31	7.48	7.65	7.36	6.96
Alkalinity (mVal/L)	4.831	3.878	4.026	4.772	n.a.
TDS (mg/L)	583	491	472	473	695
Na (mg/L)	2.7	3.7	2.0	1.9	16.8
K (mg/L)	0.6	1.0	0.6	0.6	0.7
Mg (mg/L)	3.0	3.8	2.5	2.5	13.9
Ca (mg/L)	135.8	105.1	109.5	110.8	138.6
Ba (μg/L)	6.7	20.18	22.44	21.38	29.94
Mn (mg/L)	0	0.02	0.02	0.04	0.03
Fe (mg/L)	0.07	0.14	0.07	0.12	0.07
Cu (μg/L)	0.07	0.15	0.06	0	0
Zn (μg/L)	0.45	0.82	0.60	0.24	32
Al (μg/L)	29.37	34.16	19.23	13.67	19.74
Ni (μg/L)	0.22	0	0.01	0.25	n.a.
Cr (μg/L)	0.29	0.25	0.39	0.65	0.49
HCO_3 (mg/L)	380.9	311.0	312.1	316.5	302.6
Si (mg/L)	3.23	4.46	3.11	3.31	22.24
NH_4 (mg/L)	0.040	0.012	0.010	0.022	n.a.
NO_3 (mg/L)	2.8	1.8	1.4	1.5	2.8
SO_4 (mg/L)	18.9	20.7	19.0	19.7	165.6
F (mg/L)	0.06	0.05	0.05	0.06	n.a.
Cl (mg/L)	5.1	4.8	2.8	2.6	11.6
Error (%)	2.39	0.47	1.41	1.21	0.26
Log P_{CO2}	–1.84	–2.13	–2.25	–1.93	–1.57
$SI_{Magnesite}$	–1.44	–1.27	–1.23	–1.49	–1.26
$SI_{Dolomite}$	–0.96	–0.85	–0.56	–1.08	–1.26
$SI_{Calcite}$	0.44	0.39	0.63	0.38	–0.03
$SI_{Anhydrite}$	–2.30	–2.33	–2.36	–2.34	–1.42
SI_{Gypsum}	–2.08	–2.11	–2.14	–2.12	–1.20
$SI_{Aragonite}$	0.30	0.25	0.49	0.23	–0.17
$SI_{Sepiolite}$	–6.55	–5.21	–5.37	–6.45	–4.21
$SI_{Chalcedony}$	–0.38	–0.24	–0.40	–0.37	0.45
$SI_{Cristobalite}$	–0.35	–0.21	–0.37	–0.34	0.48
$SI_{Silica\ gel}$	–0.92	–0.78	–0.94	–0.91	–0.08
$SI_{Thenardite}$	–11.77	–11.42	–11.99	–12.02	–9.27
$SI_{Mirabilite}$	–10.83	–10.49	–11.06	–11.09	–8.33
$SI_{Epsomite}$	–5.96	–5.78	–6.00	–5.99	–4.43

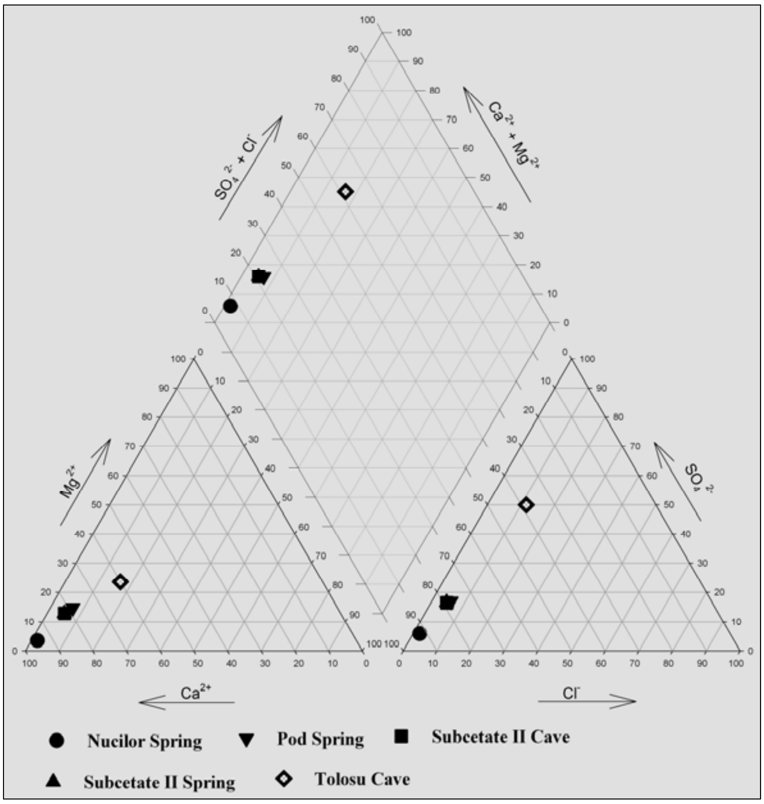

Fig. 9 – The Piper diagram of the sampled sources.

The presence of other pollution indicator elements in the water samples (Ba, Cu, Zn, Cr) is generally insignificant and may be attributed to the natural input due to the substratum dissolution. Moreover, no measurable traces of Cd, Pb, As, Se or Sb have been detected. On the other hand, only small amounts of NH_4^+ and NO_3^- (which point to a certain development of the anthropogenic activity) have been found. It should be taken into account that all analyzed sources correspond to a significant karst underground flow; the fact is argued by the high TDS level, linked with the high CO_2 partial pressures (p_{CO2}) and with usually positive values of the saturation index ($SI_{Calcite}$). We are concluding that for the analyzed cases, at least for the nitrate species, a natural attenuation process might occur.

4. DISCUSSIONS

In order to adopt the adequate management policies for all areas with specified vulnerability degree, a protection zoning, by assigning each of them to a particular protection framework, may be useful. As DOERFLIGER & ZWAHLEN (1998) have shown, there is an equivalency between the F index and the protection zones, labelled with S_{1-3} symbols.

Within the S_1 zones (corresponding to the most exposed areas, F_1), we recommend the highest precaution to any potentially damaging activity: deforestation, overgrazing of meadows and pastures, quarrying, infrastructure building works, overexploitation of the aquifers, uncontrolled and intensive tourism. Such activities should be totally excluded from these areas, to preserve unaltered the biological and geological diversity.

In the S_2 zones (equivalent to F_2), marked by the high vulnerability degree, any agricultural or industrial working should be excluded; only non-disturbing activities, like scientific research or small scale ecological tourism, strictly controlled, may be allowed.

Corresponding to F_3, the S_3 areas should play the role of buffer zones, in which one can be involved in traditional activities, without exceeding a pre-established time and intensity limit.

In the rest of the catchment areas, non-disturbing activities may be permanently unfolded, potentially damaging workings being still kept under a specific code of regulations, in accordance with the type of threats, with the impacts magnitude and with the extension of the areas they can affect by pollution, by clogging of some karst conduits and flooding other etc. Because these areas are frequently very large, it is more convenient to manage the entire catchment, rather than just karst sectors.

We advise the environmental managers to comply with a basic rules set.

Hence, they should:

- build and permanently improve databases with archive information about the catchments;
- protect the catchments from deforestation, soil erosion, rock removal and water resources overexploitation;
- monitor the edaphic cover features (aeration, aggregate stability, organic matter content), which are essential for the aquifers protection, by influencing the natural attenuation processes;
- survey the quality and quantity of water inputs to karst systems;
- try to conceive the drainage peculiarities and the relationships between the karst and non-karst terrains or between the surface and the underground features (the complexity of the processes running in the three-dimensional framework of the karst systems);
- identify natural and anthropogenic hazards, assessing the potential impact on the threatened subject;
- remove or mitigate threats and try to restore the damaged features;

- provide educational activities, highlighting the importance of karst groundwater protection (NZDC, 1999).

Finally, we provide a chart (Fig. 10) showing the main steps and measures needed for the karst landscapes analysis and management (courtesy by Goran, unpublished sketch), particularly useful for the elaboration of groundwater protection norms.

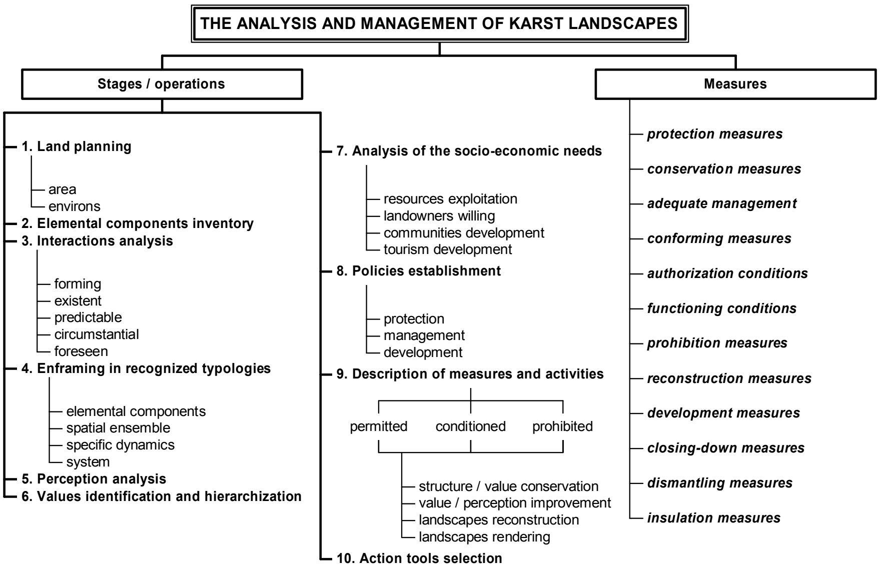

Fig. 10 – General karst landscapes management chart (after GORAN, unpublished sketch).

5. CONCLUSIONS

Dominated by thick limestone sequences, which undergone intense karst processes, the area comprises important natural resources. Our research highlighted that the southern part of the perimeter, especially nearby Caraş Gorges, has a high or even very high vulnerability degree. Therefore, a permanent and thorough monitoring of the respective area and an adequate set of management solutions are imperatively needed.

Regarding the protection zoning, we envisage that the presence of very high or high vulnerability areas in the proximity of the perimeter boundaries requires the designation of an external buffer zone (equivalent to a S_3 one) in the east and in the south.

The existence of many small or medium size sectors, marked by a very high vulnerability degree (S_1), within wide highly vulnerable areas (S_2), imposes the strict administration, as a whole, of a sinuous perimeter, extended between the western and the eastern boundaries of the investigated zone.

The greater extent of the moderate vulnerability areas, playing the role of internal buffer zones (S_3), allowed non-disturbing activities to be carried on, following the rules established by the environmental managers.

Some areas with low vulnerability degree, located in the north, or approximately on a N-S alignment, permanently allow the unfolding of the traditional and ecotouristic activities, without disturbing the natural equilibrium.

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