Carpathian Journal of Earth and Environmental Sciences, February 2012, Vol. 7, No. 1, p. 193 - 204

POTENTIALLY TOXIC METALS CONCENTRATIONS IN SOILS AND CAVE SEDIMENTS FROM KARST AREAS OF MEHEDINȚI AND GORJ COUNTIES (ROMANIA)

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Abstract: Karst geosystems, such as Zăton-Bulba (Ponoarele), are among the most vulnerable to contamination with potentially toxic metals (PTM) that affect soils, epikarst network and springs. PTM are related both to the natural background and to the anthropogenic input. Assessing the PTM levels in soils and cave sediments, we studied the Ponoarele area and extended our research to the Lupşa Valley and the southwestern part of the Vâlcan Mountains. Grain size, rock magnetic properties and organic matter content (LOI) were determined on cave sediments only, while AAS and XRF analyses were performed both on cave sediments (mainly arenites, with high organic content) and soils (districambosoil and erodosoil). The rock magnetic analyses revealed a pedogenesis-related provenance for certain cave sediment samples. We identified 9 PTM (by AAS) and, respectively, 15 elements (by XRF), but the measured levels are often moderate or even low (for Hg), excepting several higher values recorded for Cd, Pb, Zn, V, S, Ni, Rb and Zr. Along with Cu, all these elements are mainly related to the Cyprus-type copper-pyrite ores from the Ponoarele area (to the natural background); the human impact is chiefly a result of mining activities. The data showed different bioaccumulation/biosorption degrees, higher for Cu and Zn, lower for Mn and Hg. Despite the considerable anthropogenic pressure on the Ponoarele area, there are no proofs of a significant road- or residentially-induced PTM contamination.

Keywords: Karst ecosystems, cave sediments, soils, PTM, grain size, rock magnetic properties, LOI, AAS, XRF, Mehedinți Plateau Geopark.

1. INTRODUCTION

The socio-economic development has put a considerable pressure on the environment, one of the most frequent forms of natural elements degradation being the land contamination with potentially toxic metals (PTM), ubiquitous in atmospheric, marine and terrestrial settings.

Karst geosystems are vulnerable to an extensive contamination, due to the dynamics of the processes, which allows a fast downstream transfer of the contaminant (Giurginca et al., 2010). In karst environments, PTM can be found at three different levels: soils, the matrix-fracture-conduit system, and springs (Fig. 1). PTM-rich minerals may form different types of deposits: dripstones, flowstones, rimstones, coatings, fillings or rinds. Moreover, PTM may be identified in the water of springs and cave streams or associated with suspended and bed sediments (Vesper, 2005).

The presence of PTM can be related both to the natural background (lithology, hydrogeology) and to the anthropogenic input (diffuse - emissions from fuel combustion or local - point-source discharges from households and manufacturing facilities - Vesper, 2005).

There are well-documented cases of high PTM levels within urban areas of Romania (Lăcătuşu et al., 2004; Giurginca et al., 2008; Lăcătuşu et al., 2008; Brănescu et al., 2008; Damian et al., 2008a; Damian et al., 2008b), but the studies on the PTM contamination of Romanian karst areas are only in an initial stage. Although, it should be mentioned the paper of Giurginca et al., 2010, focused on the PTM concentration in leaf-litter and two groups of invertebrate species (Oniscidea and Diplopoda) from karst areas of the Mehedinți Plateau Geopark.

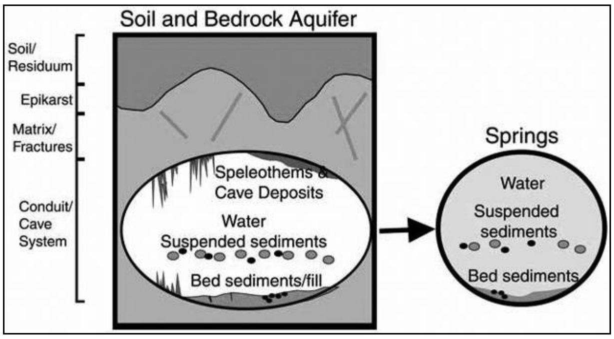

Figure 1. PTM storage in karst settings (after Vesper, 2005).

We developed our research by analyzing samples of soils and cave sediments collected from the same points, located within an extensive karst system (Zăton-Bulba) and on the Lupşa Valley, but also further eastward, in the southwestern part of the Vâlcan Mountains.

2. GEOLOGICAL AND GEOMORPHOLOGICAL SETTING

The Mehedinți Plateau comprises three structural components: Danubian Autochthonous, grouping the most external elements, folded and fractured during the Cretaceous tectogenetic stages, the Getic Nappe (outcropping as outliers) and the Severin Unit, interpreted as para-autochtonous, overlying the Danubian Autochthonous and overthrusted by the Getic Nappe.

On the Mehedinți Plateau, the limestones, occupying only 25 km^2 (Vlaicu et al., 2010), outcrop on a very elongated, but narrow area (less than one kilometer wide), crossed by the general underground drainage. Hence, well-developed karst systems were formed, e.g. Zăton-Bulba and Topolnița. The region worth a special mention for the "limestone bar karst type", for the extensive karren fields, for the particular landforms (limestone hills), known as "cornete", and for the very important and scenic subterranean realm. The diversity, the scientific importance of karst landforms and the necessity to preserve unaltered their natural character, determined in 2004 the foundation of the Mehedinți Plateau Geopark (106,000 ha), which encompasses remarkable exokarst and endokarst features (more than 200 caves, cumulating over 45 km development - Vlaicu et al., 2010).

The Zăton-Bulba karst test area (see Giurginca et al., 2010, Fig. 1) is located on the northern boundary of the Mehedinți Plateau, in the region of the Ponoarele locality (Mehedinți County), marked by certain well-known karst features - a natural bridge, karren fields (e.g. on the Peşterii Hill), sinkholes, springs and caves (e.g. the Zăton Cave, the Podul Natural Cave and the Bulba Cave).

The area has the aspect of a tectono-erosional window (striking NE-SW, bounded by the Brebina Valley, in the north, and by the Zăton Lake alignment, in the south, 250-450 m a.s.l.), in which the Danubian Autochthonous outcrops, forming the Baia de Aramă-Ponoarele limestone bar, developed on the Carpathian structures direction (NNE-SSW).

The pre-Hercynian crystalline basement consists of mesometamorphic crystalline schists (the Lainici-Păiuş Group: gneisses, amphibolites, micaschists, quartzites etc., intruded by the Tismana granites).

The sedimentary cover includes: non-karst detrital deposits (Lower Jurassic), in a very fossiliferous, coal-containing Gresten-type facies; massive reef limestones (Upper Jurassic-Lower Cretaceous), initially in a Stramberk-type facies (Kimmeridgian-Tithonian), followed by similar carbonate rocks, grey or white, massive or bedded bioclastic limestones, in an Urgonian-type facies (Barremian-Aptian), in which the Zăton-Bulba karst system is been developed; marly limestones, marls, sandstones - the Nadanova Formation (Vraconian-Cenomanian) with *Parahibolites turtiae*, *Rotalipora appenninica*, *Globotruncana stephani* etc.; wildflysch (Turonian-Senonian) with *Globotruncana lapparenti*, *G. stuarti* etc. (Mutihac et al., 2004).

The pre-Alpine mesometamorphic crystalline schists pertaining to the Getic Nappe (Sebeş-Lotru Group: micaceous paragneisses, various gneisses, micaschists, amphibolites, manganiferous schists, quartzites etc., interspersed with pegmatite and serpentinite lenses) outcrop in two synclinoriums, on the corridor margins, forming parallel ridges (600-700 m a.s.l.).

The deposits of the Severin Unit also outcrop in the region, being represented by the Ophiolitic Formation (basalts and ultramafic serpentinized rocks), along with the Severin Flysch - shales, marly limestones, sandstones, conglomerates (Tithonian-Aptian). The Ophiolitic Formation contains Cyprus-type copper-pyrite ores; the pyrite, chalcopyrite, pyrotine, blend and galena occur as lenses, disseminations and small dykes.

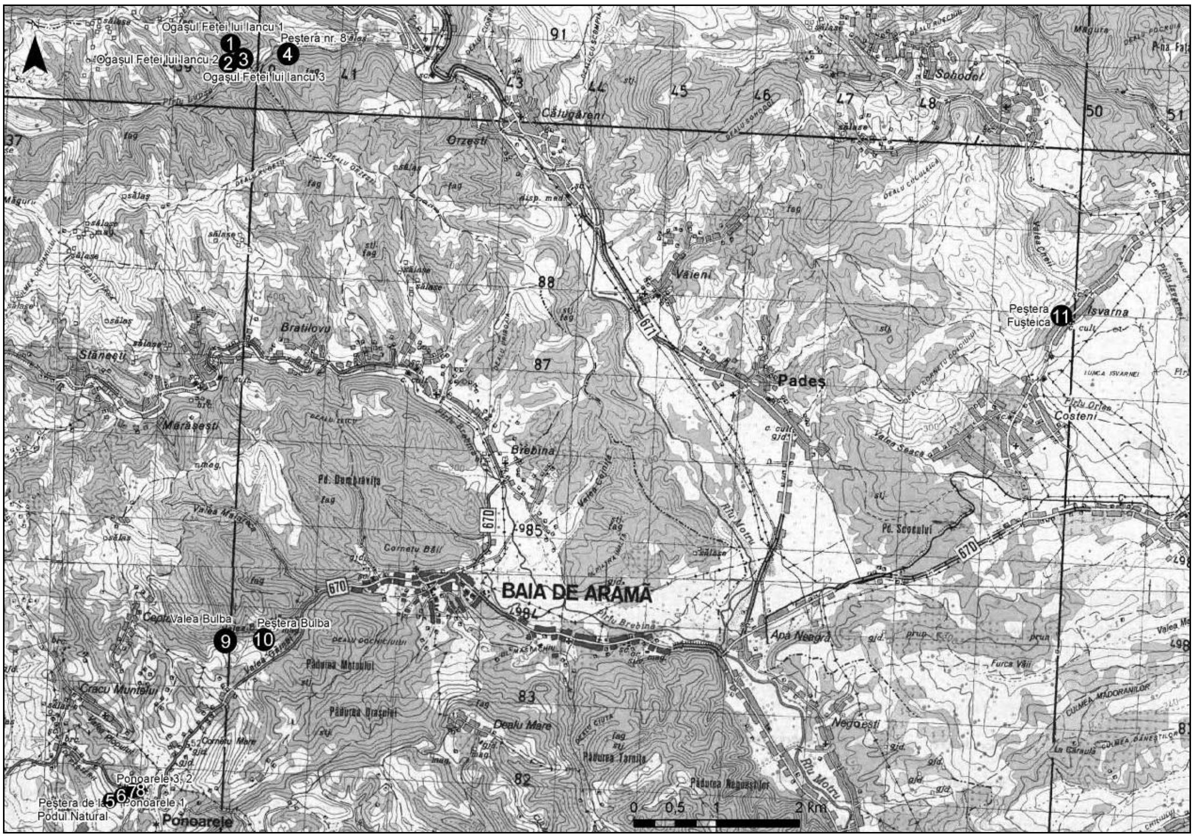

Figure 2. Sampling points location on the topographic map of Romania, sheets L-35-106-D and L-35-118-B (partially) -1-3: Ogaşul Feţei lui Iancu; 4: Cave No. 8 from the Lupşa Valley; 5: Podul Natural Cave; 6-8: Ponoarele; 9: Bulba Valley; 10: Bulba Cave; 11: Fuşteica Cave.

The Ponoarele-Baia de Aramă area (Fig. 2) is hydrogeologically connected with the Gârdăneasa-Băluţa area (Giurginca et al., 2010) and presents binary functioning and hydrographic network convergence in the limestone bar. Upstream, two closed depressions (Zăton and Bulba), can be flooded at high flow rates; the inlet of the karst system is the Zăton Sinkhole, while the outlet is the Bulba Cave; the entire surface hydrographic network is drained through the underground environment (Vlaicu et al., 2010).

The preferential fissure trends for the Peşterii Hill, nearby the Zăton-Bulba karst system inlet are N15°E, N15°W, N30°W (tension fissures), N80°W (pseudocleavage of the limestone outcrop), W-E (shear fissures, parallel to the Izverna - Ponoarele - Baia de Aramă strike-slip system), while for the Bulba Valley, close to the outlet of the system, these are N-S (parallel to the Motru Fault, with extensional regime), W-E (the same type as the above-mentioned) and N85°E (Vlaicu et al., 2010).

In the north of the Mehedinţi Mountains, in the Gorj County, along a creek - Ogaşul Feţei lui Iancu - left side tributary of the Lupşa Valley Basin (6 km long, striking E-W), the reference area is developed. The Danubian Autochthonous outcrops in the area (see Giurginca et al., 2010, Fig. 2), the stratigraphic succession starting either with a metamorphic basement consisting in quartzites, paragneisses and micaschists, or with Lower Jurassic detrital deposits, mostly covered by limestones (Middle Jurassic-Neocomian and Barremian-Aptian).

Upper Turonian-Senonian marl/clay shales (striking N25°E and dipping 25°E - Botoşăneanu et al., 1967), interbedded with sandstones, in the lower part of the sequence, followed by sandstones, interlayered with conglomerates, in the upper one, overlaying the carbonate deposits, are joined in the Wildflysch Formation, on which the Lupşa Valley Basin is developed. Mostly Barremian-Aptian limestones, but also Cenomanian-Middle Turonian marly limestones, marls and marl/clay shales outcrop as olistolithes within the Wildflysch Formation. On the limestone olistolithes, several karst landforms have been developed, such as the 16 caves located on the right slope of the Lupşa Valley, at 390-400 m a.s.l. (in the west) and at 364-373 m a.s.l. (in the east), 0-15 m relative elevation, and the only pothole identified on the left slope, at 430 m a.s.l., 44 m relative elevation (Botoşăneanu et al., 1967). The confluence between Ogaşul Feţei lui

Iancu and the Lupşa Valley is comprised within the outcropping area of the limestone olistolithes, but the tributary creek mainly crosses non-karst deposits, and only downstream the carbonate rocks.

The main regional tectonic features are the Motru Fault, along the N-S trend (the contact between the Tismana granites and the Barremian-Aptian limestones), and the Măgura Fault, striking NE-SW (the contact between the carbonate rocks and the Wildflysch Formation - Diaconu, 1990).

We extended our research to the Vâlcan Mountains, typical for the Mesozoic deposits of the outer part of the Danubian Autochthonous. The area consists of metamorphic and igneous rocks, pertaining to the pre-Alpine crystalline basement, along with a Mesozoic and Tertiary sedimentary cover.

The crystalline basement is represented by the Lainici-Păiuş Group, outcropping on the widest area and forming a thick, frequently bedded, relatively constant, mainly quartzite succession. To the upper part of the sequence, the quartzite rocks are interlayered with chlorite-sericite schists and metabasalts (Pop, 1973).

The Tismana granites, intruding the Lainici-Păiuş Group and forming either homogeneous massifs or septa within the metamorphic rocks, present a holocrystalline, porphyroid structure and a massive texture; the crystalline rocks, including the Tismana granites, are locally intruded by andesite dykes.

In the Padeş-Izvarna area (Gorj County), on the southwestern border of the Vâlcan Mountains, the crystalline basement is overlaid by Jurassic-Lower Cretaceous sedimentary deposits. The Lower Jurassic arkosic arenites are followed by 1-20 m thick carbonate rocks sequences, pertaining to Middle Jurassic and partially to Upper Jurassic, with many lateral and vertical facies changes. There are mainly biosparitic, pelsparitic and micritic, highly fossiliferous, limestones and dolomites. The Upper Jurassic is also represented by similar, very fossiliferous, white and grey limestones and dolomites, marked by cherts, overlaying a conglomerate level, with rolled granite, white and grey quartzite and blackish limestone clasts, in a greenish clay matrix, followed by 4 m thick purple clays and grey marly limestones. To the upper part, the lithology is gradually changing to mainly micritic, apparently bedded, ca. 50 m thick Neocomian limestones. The biosparitic, biopelsparitic, peletal and micritic, ca. 300 m thick, highly fossiliferous, massive reef Barremian-Aptian limestones, developed in an Urgonian-like facies, outcrop on a wide area (Pop, 1973).

3. CAVE SITES BRIEF DESCRIPTION

The caves were selected to be representative for different types of detrital facies - *sensu* Bosch & White, 2004: slackwater facies (Podul Natural Cave, Mehedinți Plateau), channel facies (Bulba Cave, Mehedinți Plateau), backswamp facies (Cave No. 8 from the Lupşa Valley, Mehedinți Mountains) and diamicton facies (Fuşteica Cave, Vâlcan Mountains).

The Podul Natural Cave (Fig. 3a) is included in the upstream sector of the Zăton-Bulba karst system and located on the Peşterii Hill, at 365 m a.s.l., 25 m relative elevation, close to the natural bridge, within Barremian-Aptian limestones (Vlaicu et al., 2010). The cave is a complex, multi-level, quasi-horizontal cavity, which has been developed on bedding planes (Bleahu et al., 1976) and it can be entered through any of the two entrances (Zăton and Podul Natural - Orghidan et al., 1984). The total development of the cave reaches 734 m, while its total depth is 101 m (Goran, 1982). At the uppermost level of the cave, the Inactive Passageway, sheltering several dripstones and flowstones, has been carved out. Below it, the 10-12 m wide and 5-8 m high, temporarily active, Main Passageway yields significant fine detrital deposits, which have been sampled (silts and clays, locally slightly sandy), along with limestone breakdown fragments and organic debris (Bleahu et al., 1976). After snow melting or heavy rainstorms, it entirely fills with water, one of the access ways for this being the central, funnel-like estavelle, witness of the water table level changes. The 6 m deep shaft gives access to the lower, active level of the cave (Orghidan et al., 1984).

The Bulba Cave (Fig. 3b) marks the downstream part of the Zăton-Bulba karst system and it is located on the right slope of the Bulba Valley, at 325 m a.s.l., 0 m relative elevation, within Barremian-Aptian limestones. The multi-level, quasi-horizontal cave comprises three levels of over 5 km total development and 40 m total depth (Goran, 1982). The inactive level consists of three important passageways, filled up with detrital deposits, dripstones, flowstones, rimstones and organic debris. The two passageways of the temporarily active level, which present a smaller number of speleothems, are crossed by the water at high flow rates only, when occasionally a small creek flows. The trend of the level is marked at the surface by the sinkholes alignment (Bleahu et al., 1976). On the active level, the underground stream flows, draining the water of several sinkholes from the area. The morphology of the passageway, initially wide and high, changes to a succession of 9 sumps, easily filled up with water; afterwards, for the final part of the level, it regains the initial aspect. In the alluvial, fine (clays, silts) to coarse (sands, gravels), guano-rich sediments, sampled for the present study, several terraces have been developed. On the cave walls, erosion levels and massive flowstones can be noted (Bleahu et al., 1976).

The Cave No. 8 (Fig. 3c) has been developed on the right slope of the Lupşa Valley, within the Barremian-Aptian limestones of the Dosul Lupşei Massif, at 398 m a.s.l., 8 m relative elevation. It is a small (20 m total development - Botoşăneanu et al., 1967), horizontal, inactive cave, developed on bedding planes (N20°E) and joints (N45°E). The cavity mainly yields detrital deposits, which were sampled - clays, silts and sands, mixed with limestone fragments and organic debris, along with dripstones and flowstones, on smaller areas (Botoşăneanu et al., 1967).

The Fuşteica Cave (Fig. 3d) is located in the southwesten part of the Vâlcan Mountains, within the Isvarna village (Orlea-Pocruia karst basin), in Barremian-Aptian limestones, at 200 m a.s.l. A total development of 1270 m has been registered for the cave, while its total depth is 10 m (Goran, 1982). It is a horizontal cave, active after heavy rainstorms or snow melting, consisting of a single passageway. This has been developed on relatively narrow, 2.5-7 m high joints, on the most significant part, and on bedding planes at the end, where the ceiling lowers to 0.3 m (Burghele-Bălăcescu & Avram, 1966). The cave bed and walls are covered with important, guano-rich detrital deposits, comprising the entire grain size range, from gravels and large boulders (at the entrance) to sands, silts and clays. The detrital deposits covering the cave walls and forming sedimentary bodies that flank the sides of the passageway, sampled by us, attest a phase of intense cave filling, followed by the partial washout of the sediments. Several dripstones, flowstones and rimstones should be also mentioned.

4. MATERIALS AND METHODS

The soil samples were collected by average sampling, near the 21 pitfall traps placed, in groups of three, for collecting the invertebrate species (Giurginca et al., 2010). The average sampling was based on a 5x5 m square network, the individual samples being collected from the corners and the intersection point of the diagonals, from the upper soil horizon (5-10 cm).

The 7 soil samples were collected from beech forest (three samples on the Ogaşul Feței lui Iancu Creek - A1S-A3S, and one sample on the Bulba Valley - A4S) and from the Ponoarele karren field (three samples - A5S-A7S). From the caves, the samples were also collected by average sampling, using the same method, in two distinct points of each cavity, from a depth of ca. 10 cm, but due to the cave sampling conditions, on a 5x5 cm square network. The samples were labeled: PPN1 and 2 (Podul Natural Cave), PB1 and 2 (Bulba Cave), PL8-1 and 2 (Cave No. 8 from the Lupşa Valley) and PF1 and 2 (Fuşteica Cave - see Fig. 3).

In order to determine their physical properties, the sediment samples were subjected to grain size and magnetic susceptibility measurements, their chemical composition being established by loss on ignition (LOI), atomic absorption spectrometry (AAS) and X-ray fluorescence spectroscopy (XRF). The latter methods were also used to determine the soils chemical composition.

Grain size measurements were performed by vibrating dry sieving ca. 100 g of the bulk sample, and weighing the sample quantity retained on each sieve of the set, down to the 500 µm fraction. A quantity of aproximately 5 g of the 500 µm fraction was treated for 14 days, in a plastic box, with ca. 0.4 ml of a dispersive inorganic reagent - a 1% solution of $Na(PO_3)_n$, n ≈ 25 - Graham's salt (Merck).

A quantity of ca. 2.5 g sample was later extracted from the plastic box, and treated again with ca. 0.2 ml of 2% solution of Graham's salt. The fractions finer than 500 µm were highlighted by analyzing each sample on a Horiba Partica LA-950V2 Laser Scattering Particle Size Distribution Analyzer. In order to process the results and to plot the graphs, the GRADISTAT v. 8 software (Blott, 2010) was used.

Rock magnetic properties - magnetic susceptibility and its frequency and field dependence - were measured on samples packed in 6 cm^3 plastic cubes, on a MFK1 Kappabridge (AGICO), at 3 frequencies: 976 Hz (χ_1), 3904 Hz (χ_2) and 15616 Hz (χ_3), and two values of the field: 200 A/m (for each frequency) and 700 A/m (for χ_1).

To quantify the organic matter content of the sediments, LOI analysis, based on mass difference, was carried on, the samples being dried at 105°C, for 3 h, in a Caloris oven, and afterwards treated at 550°C, for 6 h, in a Caloris furnace. For the AAS, the sample preparation followed the procedure suggested by Drobne & Hopkin (1995): 1. drying at 60°C for 12 h; 2. wet grinding; 3. heat treatment with *aqua regia* - HNO_3 65% (Merck) and HCl 37% (Merck); 4. dilution with HNO_3 1M; 5. filtering and filling up to 50 ml with bi-distilled water. The concentrations of Pb, Cd, Fe, Cu, Co, Cr, Mn and Zn were measured by an atomic absorption spectrometer AAS - Vario 6 (Analytik Jena). For Hg determination, a DMA 80 Hg analyzer (Milestone) was used. In order to plot the calibration curves and for the optimization of the working conditions, Merck standard solutions (1000 mg/l) were used.

Ground in an agate mortar, another part of each sample was subsequently loaded into small plastic cylinders and XRF-analyzed on a Horiba XGT-7000 X-ray Analytical Microscope.

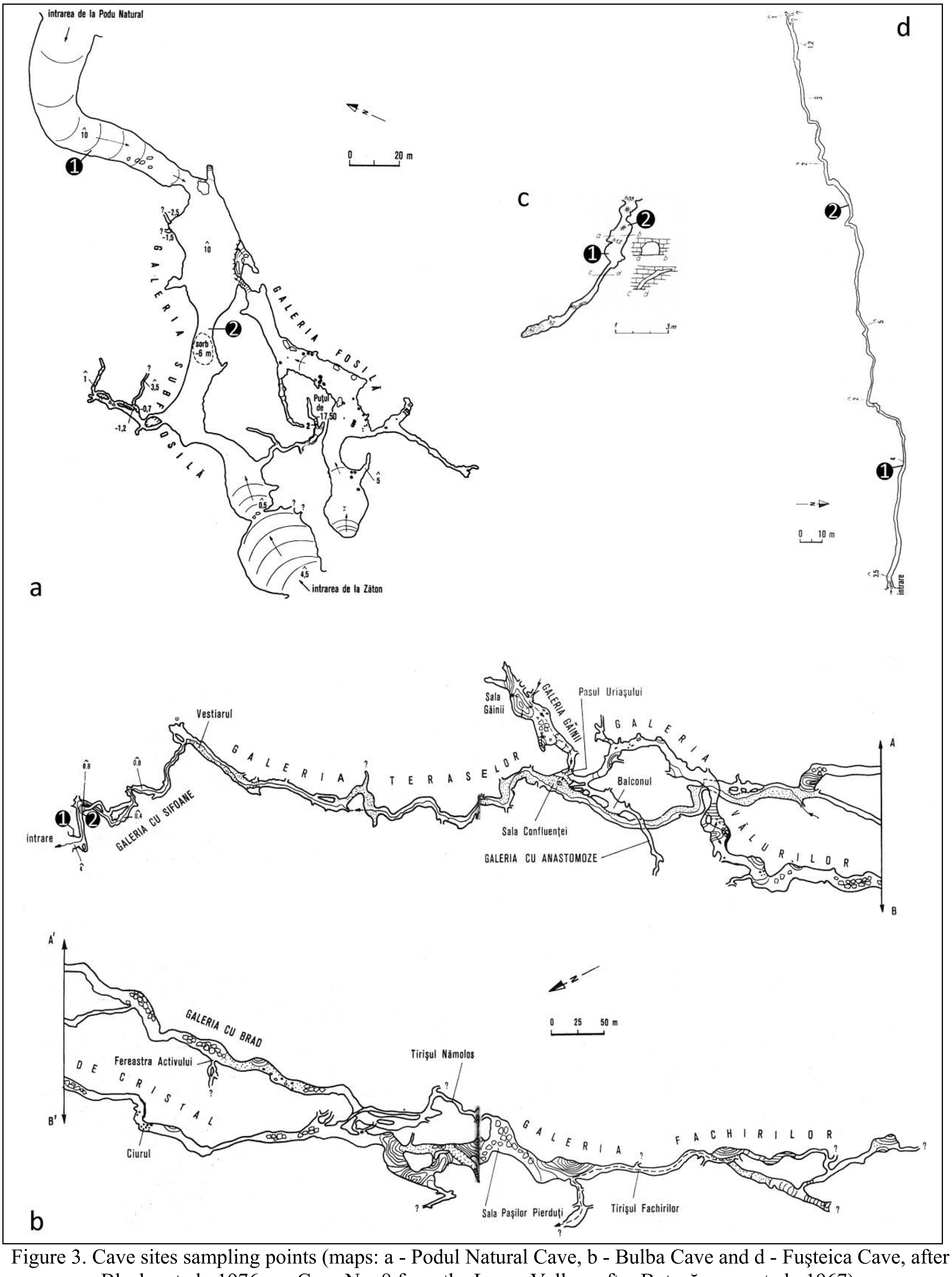

Figure 3. Cave sites sampling points (maps: a - Podul Natural Cave, b - Bulba Cave and d - Fuşteica Cave, after Bleahu et al., 1976; c - Cave No. 8 from the Lupşa Valley, after Botoşăneanu et al., 1967).

5. RESULTS AND DISCUSSIONS

The soil samples A1S-A4S are pertaining to the districambosoil type, covered by a 5-20 cm thick leaf-litter, while the samples labeled A5S-A7S should be included in the erodosoil type.

The cave sediment samples present certain variations of the sedimentological parameters (Fig. 4), explained by the different facies, as a consequence of the various depositional conditions.

The PPN1 sample is a very poorly sorted, coarse arenite (textural group: gravelly muddy sand) - very fine rudite: 24.3%, arenite: 59.7%, silt: 16%, with a trimodal, very fine skewed, platykurtic distribution (mode 1: 2500 μ; median - D_{50}: 916.2 μ). The sample was collected from a bend of the passageway, where the primary alluvial deposit has been frequently affected by the transport of the soil washed from the surface, and by the limestone breakdown.

The PPN2 sample is comprised within the very poorly sorted, very coarse silt type (sandy mud) - arenite: 32.7%, silt: 66.8%, lutite: 0.5%, with a bimodal, very coarse skewed, very platykurtic distribution (mode 1: 815 μ; D_{50}: 12.33 μ). The sample was collected from the proximity of the central estavelle; the dual function of the shaft has been also reflected in the sedimentological parameters of the deposit - on water inflow, more diamictic, coarser silts and arenites have been accumulated, while on water outflow, more uniform, finer silts and clays have been added to the cave detrital filling.

The PB1 sample consists of a very poorly sorted, fine arenite (gravelly muddy sand) - very fine rudite: 14.9%, arenite: 45.9%, silt: 39.2%, with a polymodal, symmetrical, very platykurtic distribution (mode 1: 2500 μ; D_{50}: 134.3 μ). The sample was collected from a point where multiple processes interfere, forming the deposit: alluvial deposition, transport of the soil washed from outside the cave, limestone breakdown, biological processes - bat guano accumulation.

The PB2 sample is a moderately sorted, coarse arenite (slightly gravelly sand) - very fine rudite: 3.5%, arenite: 95.2%, silt: 1.3%, with a unimodal, symmetrical, leptokurtic distribution (mode: 565 μ; D_{50}: 606 μ). The sample was collected from a point bar deposit.

The PL8-1 sample is comprised within the very poorly sorted, medium arenite type (gravelly muddy sand) - very fine rudite: 24.2%, arenite: 48%, silt: 27.8%, with a trimodal, very fine skewed, very platykurtic distribution (mode 1: 2500 μ; D_{50}: 934.3 μ). The sample was collected from a point where the alluvial sediments, accumulated in the past, are mixed with fine detrital material transported through the epikarst network, limestone and speleothems breakdown fragments and organic debris.

The PL8-2 sample also consists of a very poorly sorted, medium arenite (gravelly muddy sand) - very fine rudite: 27.2%, arenite: 45.7%, silt: 27%, lutite: 0.1%, with a bimodal, very fine skewed, very platykurtic distribution (mode 1: 2500 μ; D_{50}: 802.7 μ). Due to the small dimensions of the Cave No. 8 from the Lupşa Valley, the sampling conditions for PL8-1 and PL8-2 were alike, explaining the similarity between the sedimentological parameters of the two samples.

The PF1 sample is a moderately sorted, very coarse arenite (gravelly sand) - very fine rudite: 15.8%, arenite: 83.8%, silt: 0.4%, with a unimodal, symmetrical, platykurtic distribution (mode: 815 μ; D_{50}: 1013.6 μ). The sample was collected from a small niche on a wall of the Fuşteica Cave, where alluvial sediments transported in suspension have been accumulated.

The PF2 sample consists of a poorly sorted, fine arenite (slightly gravelly muddy sand) - very fine rudite: 3.1%, arenite: 85.7%, silt: 11.2%, with a bimodal, fine skewed, very leptokurtic distribution (mode 1: 281.4 μ; D_{50}: 275.8 μ). The sample was collected from a small point bar deposit.

The rock magnetic analyses of cave sediments (Fig. 5) revealed a variable magnetic susceptibility ($4.74\text{-}5.21 \cdot 10^{-7}$ m^3kg^{-1} on average). The maximum value is reached for PB1 sample ($1.24\text{-}1.38 \cdot 10^{-6}$ m^3kg^{-1} on average), which can be explained by the very diverse sediment constituting the deposit, transferred to the site by multiple agents (stream, seepage, gravitation, wind etc.). This diversity raises the chances of a higher content of magnetic minerals. There is an opposite case for PF1 sample, as the sediment is fluvially derived; it contains the smallest amount of magnetic minerals - its magnetic susceptibility was the lowest ($6.83\text{-}7.59 \cdot 10^{-8}$ m^3kg^{-1} on average). Notable oscillations of field and frequency dependence were also recorded. The highest values of kd12 and kd13, i.e. those recorded for the samples collected from the Cave No. 8 from the Lupşa Valley (PL8-1 - kd12: 8%; kd13: 11.8%; PL8-2 - kd12: 7.7%; kd13: 10.9%) or from the Podul Natural Cave (PPN1 - kd12: 7.8%; kd13: 11.6%) suggest the presence of fine magnetite produced by pedogenesis. Except for PF1 and 2 and PB2, we found very high organic matter contents - Fig. 6 (7.01% on average), explained by an at least partial sediment provenance from soil, but also by an intense biotic activity - in all 4 caves bats (Chiroptera) have been encountered.

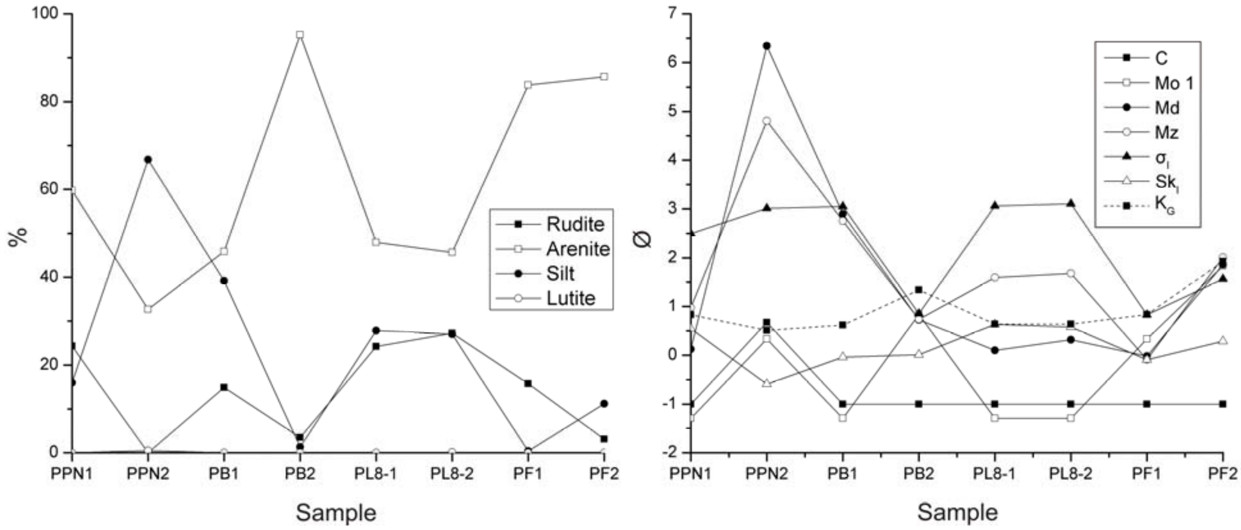

Figure 4. Grain size parameters of cave sediments (left - main grain size classes; right - statistical grain size parameters: coarsest first percentile, first mode, median, mean, standard deviation, skewness and kurtosis).

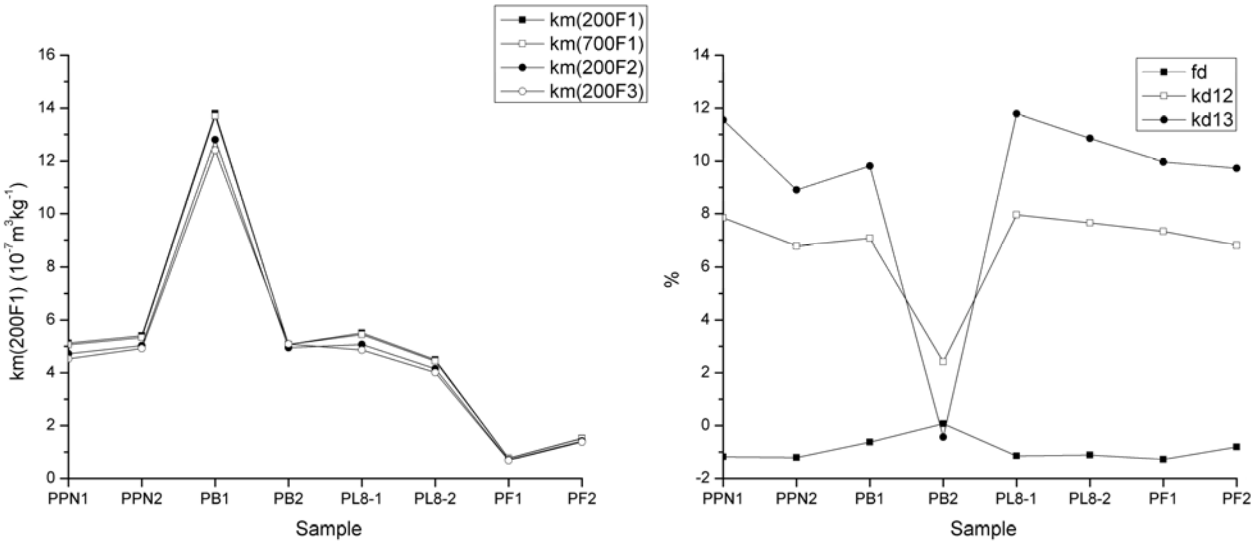

Figure 5. Rock magnetic properties of cave sediments.

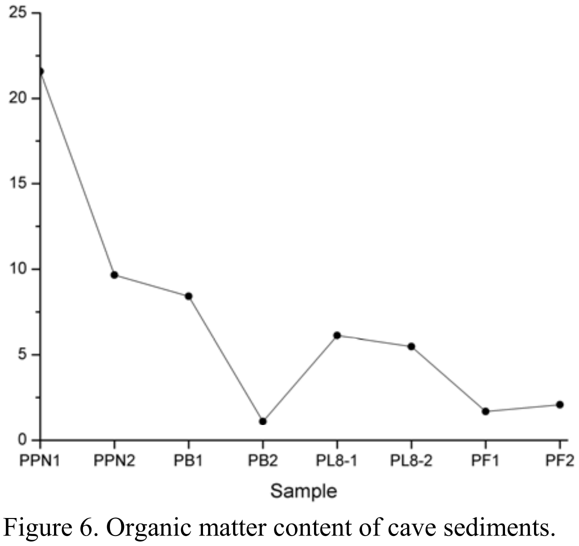

Figure 6. Organic matter content of cave sediments.

The maximum values were recorded for the Podul Natural Cave (PPN1: 21.58%; PPN2: 9.66%), the Cave No. 8 from the Lupşa Valley (PL8-1: 6.12%; PL8-2: 5.48%) and the PB1 sample from the Bulba Cave (8.41%), the results being consistent with the rock magnetic data.

The following 9 elements were determined by AAS, in both soils and cave sediments: Co, Mn, Zn, Cu, Hg, Fe, Cr, Pb and Cd (Fig. 7). Excluding iron (maximum concentration: 22.25 mg/g in soils and 28.42 mg/g in cave sediments), the other metals were found by AAS in low or very low levels. Only cobalt is more abundant in soils - 11.70-18.89 µg/g, versus 0.56-2.80 µg/g in cave sediments, while the content of lead is higher in cave sediments 26.44-55.80 µg/g, versus 4.59-16.47 µg/g in soils. There is a similarity between other PTM levels in soils (a) and cave sediments (b) - manganese (a: 0.54-1.20 mg/g; b: 0.38-1.28 mg/g), zinc (a: 0.03-0.12 mg/g; b: 0.003-0.374 mg/g), copper (a: 18.33-63.21 μg/g; b: 2.89-60.60 μg/g), mercury (a: 0-0.0013 μg/g; b: 0.0001-0.0002 μg/g), chromium (a: 54.07-96.85 μg/g; b: 22.23-121.42 μg/g) and cadmium (a: 0-2.48 μg/g; b: 0.54-6.90 μg/g). In comparison with the estimates of the trace-element composition of the upper continental crust, the levels are higher for Cd, for all samples, except for A4S, in which it was not identified - reference concentration: 0.075 μg/g (Shaw et al., 1967, 1976), 0.079 μg/g (Gao et al., 1998) or 0.102 μg/g (Wedepohl, 1995) - and lower for Hg, for all samples - reference concentration: 0.096 μg/g (Shaw et al., 1967, 1976), 0.0123 μg/g (Gao et al., 1998) or 0.056 μg/g (Wedepohl, 1995). Only in cave sediments lead levels exceed the reference concentration: 17 μg/g (Shaw et al., 1967, 1976 and Wedepohl, 1995) or 18 μg/g (Gao et al., 1998). Zinc levels are highly variable (reference concentrations: 52 μg/g - Shaw et al., 1967, 1976 and Wedepohl, 1995 or 70 μg/g - Gao et al., 1998), either higher - between 90 μg/g (A5S) - 120 μg/g (A7S) and 120 μg/g (PB2) - 374.2 μg/g (PPN1), or lower - 30 μg/g (A4S) and between 3 μg/g (PF2) - 3.4 μg/g (PF1).

By XRF (Fig. 8), we found 15 elements in soils and cave sediments: Mg, Al, Si, P, S, K, Ca, Ti, V, Mn, Fe, Ni, Zn, Rb and Zr. The highest concentrations were naturally recorded for Si (631.7 mg/g in A1S sample), Al (171.9 mg/g in A6S sample) and Fe (214.2 mg/g in A7S sample). In cave sediments, the same elements were found in the following maximum concentrations: Si: 745.3 mg/g (PF2 sample); Al: 158.1 mg/g (PL8-1 sample); Fe: 186.6 mg/g (PPN2 sample). Magnesium (a: 22.4-37.9 mg/g; b: 27.5-46.6 mg/g), potassium (a: 42.3-69.6 mg/g; b: 11.8-117.3 mg/g), calcium (a: 15.3-132.9 mg/g; b: 14.3-394.3 mg/g), phosphorus (a: 1.7-7.2 mg/g; b: 2-38.5 mg/g) and titanium (a: 14.2-25.8 mg/g; b: 2.8-23.8 mg/g) reach moderate levels, while the other elements are present as traces.

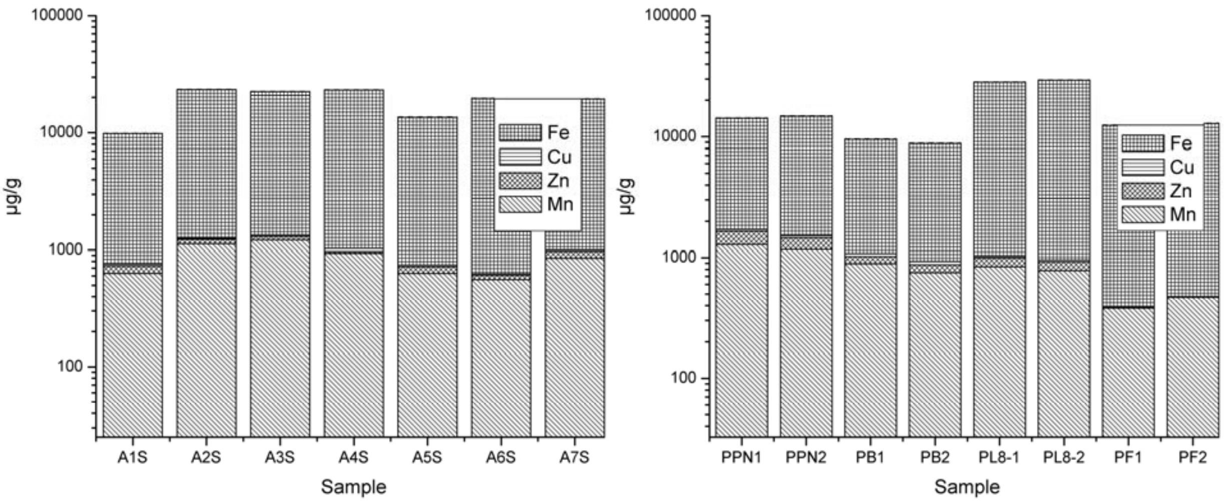

Figure 7. AAS-assessed PTM levels in soils (left) and cave sediments (right)

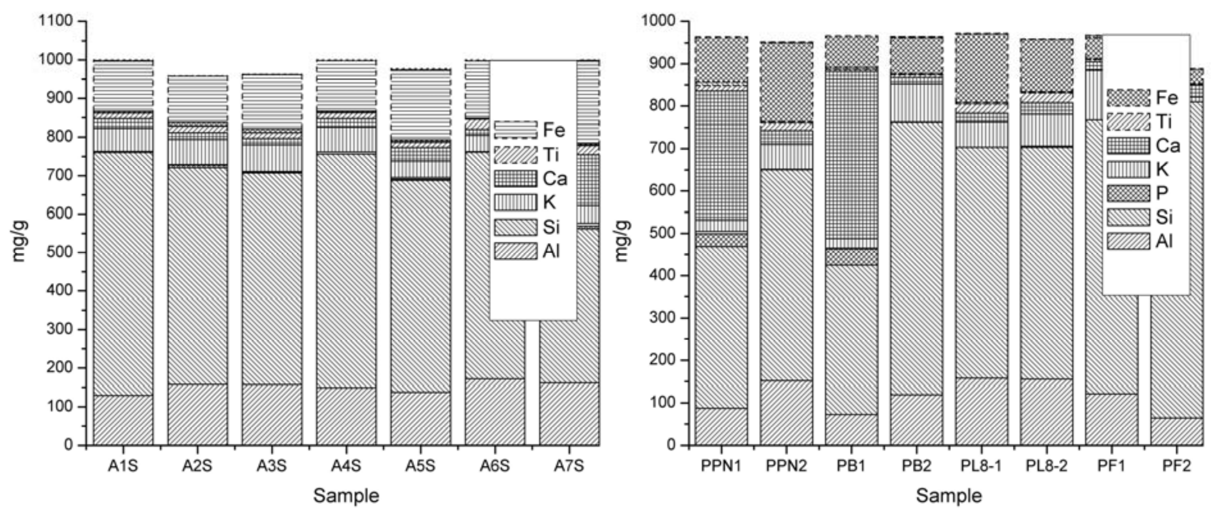

Figure 8. XRF-assessed PTM levels in soils (left) and cave sediments (right)

We can conclude that the concentrations in soils and cave sediments are also relatively similar, except for Al and Fe, which present higher concentrations in soils, and for Si, P, K and Ca, which are more abundant in cave sediments. Rubidium and zirconium, previously found in the leaf-litter from the same areas (Giurginca et al., 2010), were identified in the soils and cave sediment samples, sustaining the theory of a natural provenance of the elements, which can be uptaken by vegetation. Different than the reference concentrations from the upper continental crust are the higher levels of vanadium (reference concentration: 53 µg/g - Shaw et al., 1967, 1976 and Wedepohl, 1995, 98 µg/g - Gao et al., 1998) - between 200 µg/g (A4S) - 1300 µg/g (A5S) and between 200 µg/g (PL8-2) - 1400 µg/g (PF2). Higher levels were also recorded for sulphur (reference concentration: 600 µg/g - Shaw et al., 1967, 1976, 309 µg/g - Gao et al., 1998 or 953 µg/g - Wedepohl, 1995) - between 1500 µg/g (A2S and A6S) - 7000 µg/g (A7S) and between 900 µg/g (PL8-2) and 5800 µg/g (PPN1). The nickel and zinc contents exceed the estimates for the upper continental crust - Ni (reference concentration: 19 µg/g - Shaw et al., 1967, 1976 and Wedepohl, 1995, 38 µg/g - Gao et al., 1998) - 400 µg/g (A3S) and between 300 µg/g (PL8-2) - 500 µg/g (PB2 and PL8-1); Zn - between 300 µg/g (A2S) - 800 µg/g (A7S) and between 500 µg/g (PB1) and 1800 µg/g (PPN1). The rubidium and zirconium levels are also higher - Rb (reference concentration: 110 µg/g - Shaw et al., 1967, 1976 and Wedepohl, 1995, 82 µg/g - Gao et al., 1998) - between 500 µg/g (A3S and A4S) - 1100 µg/g (A1S) and between 300 µg/g (PF1) - 700 µg/g (PPN2, PB2 and PF2); Zr (reference concentrations: 237 µg/g - Shaw et al., 1967, 1976 and Wedepohl, 1995 or 188 µg/g - Gao et al., 1998) - between 600 µg/g - 3000 µg/g (A5S) and between 600 µg/g (PL8-2) - 4800 µg/g (PF1).

Regarding the differences between various PTM levels it should be mentioned that the storage of PTM within karst settings depends on physical processes, as well on the specific metal chemistry and on the chemical behavior of the surrounding environment (Vesper, 2005). Mineral-bound metals can be identified in soils, in bedrock, as secondary cave deposits, and as detrital material throughout karst systems; the transfer of PTM occurs either via chemical processes - dissolution, sorption, or desorption or via physical processes - deposition and entrainment (Fig. 9 - Vesper, 2005).

In our case, the presence of Mn and Fe, the high levels of the latter, and the low content of Cu and Hg reveal an oxidizing environment. Iron and manganese oxides and solids scavenge trace metals from solution and they often control the overall redox chemistry of the solution or sediment. Certain PTM, like Ni, Mn and Zn, can be thus related to iron oxides, while manganese oxides commonly contain Co or Pb. Trace metals may also be associated with soluble or insoluble organic compounds and inorganic coatings on particulates. The latter metal transport is enhanced during storms, when high groundwater velocities allow the metals to be entrained and suspended (Vesper, 2005).

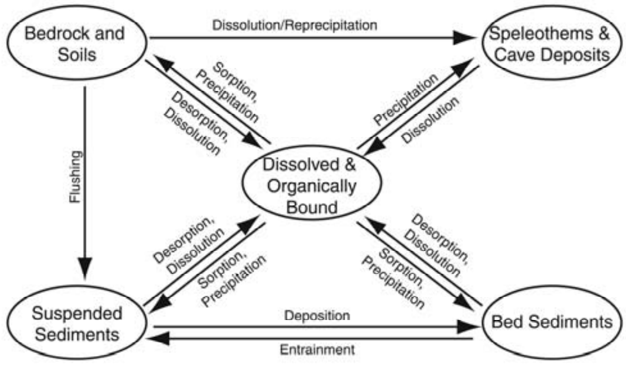

Figure 9. PTM transfer ways in karst settings (after Vesper, 2005).

A previous study (Giurginca et al., 2010) underlined the presence of copper in leaf-litter and invertebrates from Ponoarele and the Lupşa Valley, as the sole PTM representing a real threat to karst ecosystems. Now, only AAS provides reliable data on the Cu levels in soils and cave sediments - the maximum values are approximately eleven-fold higher than those recorded for leaf-litter (5.65 µg/g on Ogaşul Feţei lui Iancu), but five-fold lower than those measured on invertebrates (340 µg/g on *Pachyiulus hungaricus* from the Bulba Valley, Ponoarele). We could not make a comparison with the XRF data obtained by Giurginca et al., 2010, because of the different analytical method used for the present study. Copper and other PTM (Co, Ni, V, Fe, Zn, Cr, Pb, Cd, Rb, Zr, Hg etc.) can be mainly related to two Cyprus-type copper-pyrite ores - Cauna-Ponoarele and Gorunului Peak-Ocnelor Hill, which were intensely mined. Even the slag dumps from the Bulba Valley (Ponoarele), containing over 3000 µg/g Cu, can be sources of copper (Giurginca et al., 2010).

Cobalt shows roughly similar values in leaf-litter, invertebrates and cave sediments, but clearly, up to nearly seven-fold higher levels in soils, indicating the edaphic cover as a source of Co. The manganese concentrations are only slightly higher in soils and cave sediments than in the analyzed biotic components, the element being prone to bioaccumulation. Zinc levels in soils are lower than in cave sediments and invertebrates, attesting the high mobility of the PTM, which migrates from the soil; presenting the lowest Zn concentrations, the vegetal cover does not retain it much, but the PTM finds an appropriate sink in the invertebrates tissues. Mercury levels are similarly very low for the analyzed samples, excepting those recorded for the invertebrate species, e.g. *Armadillidium vulgare* from Ponoarele. As one can expect, iron concentrations in soils and cave sediments are higher than the PTM level in leaf-litter and invertebrates; as for the iron, the latter accumulate a higher quantity of PTM. In the leaf-litter and invertebrates we found only a small content of chromium, as deriving from the higher concentration of the PTM in the studied abiotic components of the karst ecosystems. The data revealed that lead was partially mobilized from soil to cave sediments and vegetation; yet, the invertebrates bioaccumulate an insignificant quantity of Pb. The behavior of cadmium is similar to that of lead, but the differences between the various ecosystem components are much smaller.

6. CONCLUSIONS

We extended our study - initially undertaken on leaf-litter and two groups of invertebrates - Oniscidea and Diplopoda (Giurginca et al., 2010) - to soils (districambosoil and erodosoil) and cave sediments. The latter are mainly arenites, with high organic matter content; the rock magnetic analyses revealed an at least partial pedogenesis-related provenance for certain cave sediment samples.

The entire Ponoarele area is affected by the Baia de Aramă - Drobeta-Turnu Severin road and by the households of two settlements, whose inhabitants directly discharge wastes into the Zăton-Bulba karst system, especially through the points described by Vlaicu et al., 2010, as highly vulnerable. Despite the considerable anthropogenic pressure, there are no proofs of a significant road- or residentially-induced PTM contamination. It is a difficult task to discriminate between the PTM related to the natural background and the PTM input of a contamination event. In any case, we would have expected higher PTM levels; probably, natural attenuation processes occur, mitigating the contamination effects.

Although the analyses allowed us to identify 9 PTM (AAS) and, respectively, 15 elements (XRF), the measured levels are often moderate or even low (e.g. those of mercury), excepting several higher values recorded for cadmium, lead, zinc, vanadium, sulphur, nickel, rubidium and zirconium. Along with copper, all these elements can be mainly related to the Cyprus-type copper-pyrite ores from the Ponoarele area, and, implicitly, to the natural background; the human impact occurs as a result of mining activities. The data highlighted different bioaccumulation/biosorption degrees, higher for Cu and Zn, lower for Mn and Hg.

ACKNOWLEDGEMENTS

The authors are grateful to Ms. Maria Luiza Stanomir, from the University Politehnica of Bucharest, for the AAS analyses. The study was financially supported by the Romanian Academy - Programme 1 (2011-2014) *"Structure, evolution and heritage value of karst environment components"*.

REFERENCES

Bleahu, M., Decu, V., Negrea, Ş., Pleşa, C., Povară, I. & Viehmann, I., 1976. *Caves of Romania*. Ed. Ştiinţifică şi Enciclopedică, Bucharest, 415 pp. (in Romanian).

Blott, S.J., 2010. *GRADISTAT Version 8.0 - A Grain Size Distribution and Statistics Package for the Analysis of Unconsolidated Sediments by Sieving or Laser Granulometer*.

Bosch, R.F. & White, W.B., 2004. *Lithofacies and transport of clastic sediments in karstic aquifers*. In: Studies of Cave Sediments: Physical and Chemical Records of Paleoclimate (I.D. Sasowsky & J.E. Mylroie, eds.), Kluwer Academic/Plenum Publishers, New York, 1-22.

Botoşăneanu, L., Negrea, A., Negrea, Ş., Decu, A., Decu, V. & Bleahu, M., 1967. *Researches on the Caves from Banat and Oltenia (Romania, 1959-1962)*. Centre National de la Recherche Scientifique (CNRS), Paris, 397 pp. (in French).

Brănescu, V.S., Popescu, A. & Marinescu, D., 2008. *Determining the Concentration of Some Heavy Metals in Olt River. The Impact of the Heavy Metals from the Waste Waters from Râmnicu Vâlcea Chemical Plant over Natural Emissary River Olt*. Revista de Chimie, 59(9), 986-1061.

Burghele-Bălăcescu, A. & Avram, Ş., 1966. *Studied caves from Oltenia, between Motrului and Tismanei valleys*. Lucrările Institutului de Speologie "Emil Racoviţă", V, 21-41 (in Romanian).

Damian, F., Damian, G., Lăcătuşu, R., Macovei, G., Iepure, G., Năprădean, I., Chira, R., Kollar, L., Raţă, L. & Zaharia, D.C., 2008a. *Soils from the Baia Mare Zone and the Heavy Metals Pollution.* Carpathian Journal of Earth and Environmental Sciences, 3(1), 85-98.

Damian, F., Damian, G., Lăcătuşu, R., Iepure, G., 2008b. *Heavy Metals Concentration of the Soils around Zlatna and Copşa Mică Smelters Romania*. Carpathian Journal of Earth and Environmental Sciences, 3(2), 65-82.

Diaconu, G., 1990. *Cloşani Cave. Mineralogical and genetic study of carbonates and clays*. Miscellanea Speologica Romanica, 2, 135 pp.

Drobne, D. & Hopkin, S.P., 1995. *The toxicity of Zinc to Terrestrial Isopods in a "Standard" Laboratory*

Test. Ecotoxicology and Environmental Safety, 31, 1-6.
Gao, S., Luo, T.C., Zhang, B.R., Zhang, H.F., Han, Y.W., Hu, Y.K. & Zhao, Z.D., 1998. *Chemical composition of the continental crust as revealed by studies in east China*. Geochimica et Cosmochimica Acta, 62, 1959-1975.
Giurginca, A., Murariu, A. & Giurginca, M., 2008. *Potentially Toxic Metals in the Oniscidea and Diplopoda from Bucharest.* In: Advances in Arachnology and Developmental Biology. Papers dedicated to Prof. Dr. Božidar Ćurčić (S.E. Makarov & R.N. Dimitrijević, eds.), Inst. Zool., Belgrade; BAS, Sofia; Fac. Life Sci., Vienna; SASA, Belgrade & UNESCO MAB Serbia. Vienna-Belgrade-Sofia, Monographs, 12, 201-207.
Giurginca, A., Munteanu, C.M., Stanomir, M.L., Niculescu, G. & Giurginca, M., 2010. *Assessment of potentially toxic metals concentration in karst areas of the Mehedinți Plateau Geopark (Romania)*. Carpathian Journal of Earth and Environmental Sciences, 5(1), 103-110.
Goran, C., 1982. *Romanian Caves Register*. Ed. Sport-Turism, Bucharest, 496 pp. (in Romanian).
Lăcătuşu, R., Kovacsovics, B., Lungu, M., Breabăn, I., Râşnoveanu, I., Rizea, N. & Lazăr, R., 2004. *Heavy metals in Bucharest parks soils*. Ştiința Solului, 1-2, 185-198 (in Romanian).
Lăcătuşu, R., Lăcătuşu, A.R., Lungu, M., Breabăn, I.G., 2008. *Macro- and Microelements Abundance in some Urban Soils from Romania*. Carpathian Journal of Earth and Environmental Sciences, 3(1), 75-83.
Mutihac, V., Stratulat, M.I. & Fechet, R.M., 2004. *Geology of Romania*. Ed. Didactică şi Pedagogică, Bucharest, 250 pp. (in Romanian).
Orghidan, T., Negrea, Ș., Racoviță, G. & Lascu, C., 1984. *Caves of Romania*. Ed. Sport-Turism, Bucharest, 454 pp. (in Romanian).
Pop, G., 1973. *Mesozoic Deposits from Vâlcan Mountains*. Ed. Academiei, Bucharest, 155 pp. (in Romanian).
Shaw, D.M., Reilly, G.A., Muysson, J.R., Pattenden, G.E. & Campbell, F.E., 1967. *An estimate of the chemical composition of the Canadian Precambrian shield*. Canadian Journal of Earth Sciences, 4, 829-853.
Shaw, D.M., Dostal, J. & Keays, R.R., 1976. *Additional estimates of continental surface Precambrian shield composition in Canada*. Geochimica et Cosmochimica Acta, 40, 73-83.
Vesper, D.J., 2005. *Contamination of cave waters by heavy metals*. In: The Encyclopedia of Caves (D. Culver & W. White, eds.), Academic Press, Amsterdam, 127-131.
Vlaicu, M., Munteanu, C.M., Goran, C., Marin, C., Giurginca, A., Plăiaşu, R., Băncilă, R.I. & Tudorache, A., 2010. *Geological and ecological assessment of the exposure degree of the Zăton-Bulba karst system (Mehedinți Plateau) to anthropogenic hazards: intrinsic vulnerability and biodiversity study*. Travaux de l'Institut de Speologie "Emile Racovitza", XLIX, 149-164.
Wedepohl, H., 1995. *The composition of the continental crust*. Geochimica et Cosmochimica Acta 59, 1217-1239.

Received at: 19. 06. 2011
Revised at: 03. 11. 2011
Accepted for publication at: 24. 11. 2011
Published online at: 05. 12. 2011