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COMPARITIVE EXPERIMENTS OF KARSTIC SOILS ON THE CATCHMENT BASIN OF BÉKE CAVE IN AGGTELEK EXAMINING PARTICULARLY THE RELATIONSHIP BETWEEN THE PHYSICAL QUALITY AND THE METAL CONTENTS OF THE SOILS

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Summary: The paper presents the formation and comparison of the acid and EDTA soluble metal content of the soils collected from the catchment of Béke Cave in Aggtelek. The results show the behaviour of the examined metals in open karstic, and covered karstic areas in soils with different physical qualities.

Key words: metal content, clay, loam

1. INTRODUCTION

Karstic landscapes are sensitive, because the storage water which comes up to the surface provides drinking water. The conservation of this natural resource for the future explains the holistic examination of the influential parameters of the water quality. The soil compound and its physical and chemical features in the karstic area influence mostly the content of the infiltrating water and the processes which occur during the solution in the karstic water system.

The examined area is a catchment of Béke Cave in Aggtelek National Park (Fig. 1), which is divided in two different parts. The northern part is covert open karst covered with rendzina soil on limestone. The southern part is covered by a non-karstic sediment (Miocene/Pliocene sand, clay and pebble), foothill colluvium and forest soils. The two different bedrocks are characterised with different soils.

The aim of the present study is to explore the two soil types, their characteristics, and based on the knowledge gained the interpretation of the distinctness of the karstic processes. The study reveals the physical quality of the karstic soils, and presents their behaviour in terms of the behaviour of certain metals.

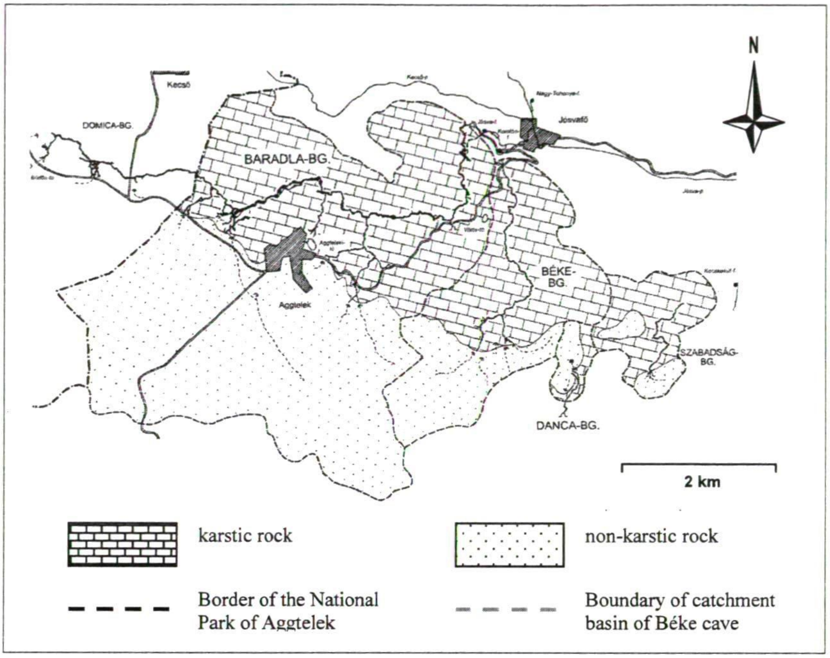

Fig. 1 The geological map of Aggtelek Mountains (Baross 1998)

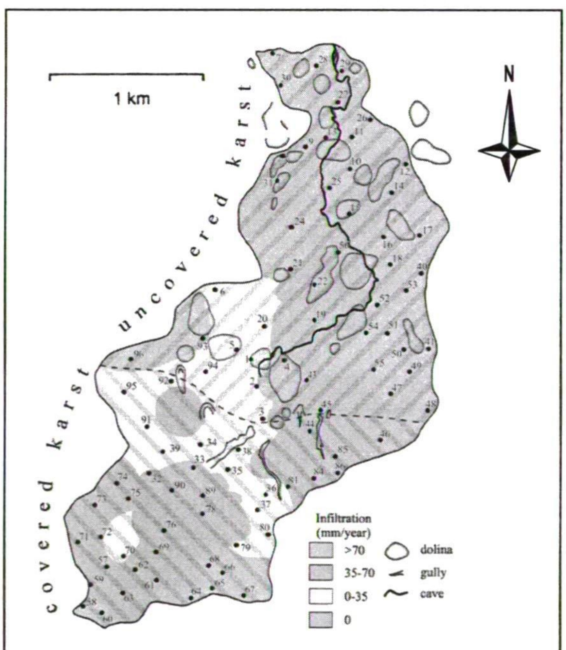

Fig. 2 The infiltration situation and the sampling points of Béke Cave (Zámbó 1986)

2. METHODS

2.1. The position of the study area and its features

The northern part of the catchment basin is uncovered karst, which forms part of the Aggteleki-hegység landscape unit (Aggtelek Mts.). In most areas the bedrock is Middle and Upper Triassic karstic limestone, dolomite, Lower Triassic limestone with Pleistocene pebble intrusions. The typical young break directions of the landscape unit are N-S and NE-SW, which also indicates the direction of the caves. The relief with a broken creased construction is typical of its topographic features, which partly consist of hills, but mostly low mountains of medium height. The geographic structure of the area is rich in transit caves with dry valleys and karstic valleys as well as karstic forms. Red clay is found on the limestone in a lot of places, which influences soil formation. The clayish brown forest soils are formed with the combination of clay-loam on the Pannonian loose sediments and on the Triassic slate (Dövényi 2010).

The southern part of the examined area is covered karst which reaches into the landscape unit called Putnok hills, the surface of which is mostly covered with Pliocene clayish sandy sediments and Pleistocene loam. Triassic limestone formations and Devonian-Carboniferous metamorfits can be found here. Oligocene gritstone and marl intrusions are present in the western and south-western part at the rock basin. The typical features of its relief are: south and south-eastern flow hills are fragmented by valleys. Some 20-20% of the surface of the landscape unit is occupied by tops, ridges and river floodplains with mostly loose sediments; about 5% is terrace surface and 55% is foothill slope. The surface of the area of the basin in the landscape unit is mostly covered by clay and sand along with Pliocene andesite tuff and loess-like sediments in smaller patches. Most of the soils (82%) are of a clay-loam texture, mostly clayish brown forest soil. Apart from this rendzina soils can be found on the limestones. Chernozems are present in a small area as well as Ramann brown soil and meadow illuvial soil (Dövényi 2010).

2.2. Sampling and methods

We collected soil samples (Fig. 2) from 98 sampling points during the summer of 2003. The soil samples came from two depths: one from the surface (0-10 cm) and the other from 20-30 cm. We determined the pH, organic matter-content, the acid- and EDTA soluble heavy metal content and the particle size distribution of the soils.

The acid soluble heavy metal-content was determined after digestion with an acid mixture (HNO_3-H_2O_2-$HClO_4$) (Rowell 1994).

The EDTA soluble metal content was determined after shaking with 0.02 M EDTA solution (pH=4.65 ± 0.05) and filtering it (Lakanen and Erviö 1971). The manganese, iron, magnesium, calcium, potassium and aluminium content of the vegetation and the soils were determined with ICP-AES techniques, and the copper and zinc with FAAS techniques. The measurements took place at the University of Veszprém.

2.3. Discussion

The texture of the examined soil samples can be classified as clay, clay-loam, and loam. Since the grain size influences the binding of the metals I evaluated the physical classification of identical soils and the metal contents and after that I averaged them. Table 1 shows the metal content of the different soils in different depths.

Table 1 The relationship of texture and metal content on the karstic soils

Acid soluble metal content (mg/kg)	Depth F=near surface A=lower layer	clay	clay-loam	loam
Cu	F	20.19	20.00	14.57
	A	21.18	20.68	13.05
Ni	F	25.16	29.98	15.17
	A	33.01	26.65	14.93
Zn	F	109.66	93.39	109.99
	A	98.15	101.20	87.77
Co	F	9.48	11.64	8.41
	A	12.31	11.46	8.73
Cr	F	40.89	46.66	27.16
	A	53.69	67.18	16.10
Cd (μ/kg)	F	293.36	184.10	153.16
	A	161.11	156.32	85.42
Mn	F	924.31	950.65	1171.14
	A	692.81	867.45	878.87
Fe	F	26394.70	24741.37	17174.90
	A	30143.93	25779.82	17278.52
Al	F	36885.01	39210.33	22143.06
	A	45306.31	37815.40	22834.27

The results show that in the case of copper, zinc and cadmium the values are lower on the deeper level, which indicates that these metals are accumulated near the surface layer, less mobile in the other. Of course, the pH value plays a considerable role in the establishment of this tendency. At the same time it may signal the vegetation uptake in the root zone of the plants (on the deeper levels) or leaking into the system may cause this tendency.

We examined the changes of the acid soluble metal content with depth in soils with different texture.

Higher concentration of copper can measured in clay and clay-loam soils in both depths. The copper content is nearly similar in the two soil fractions. The concentration is the lowest in loam soils in both depths. The copper concentration of loam soils decreases with depth, while in the case of the clay-loam it does not change significantly. Small-scale rise can be observed only on clay soils.

The nickel content of the soils is the highest in the near-the-surface samples in clay-loam. The highest concentration is from the deeper level samples in the clay soils. In both depths the nickel concentration is the lowest in the loamy soils. In the loam and in clay-loam soils it decreases on a small-scale with depth, while in the case of clay growth can be experienced in the nickel concentration.

The zinc content in the surface clay and loamy soils is almost identical; on the other hand it is the lowest in clay-loam soils. Opposite to this the highest concentration is measurable in the lower level in clay-loam soils; the zinc concentration is lowest in the case of loam soils. With depth the decrease of concentration (of zinc level) is experienced in clay and loam soils, and in the case of clay-loam soils an increase is experienced.

The cobalt concentration in the upper level in clay-loam soils is the highest one, while the deep samples of clayish soils show the highest value. In two depths the lowest concentration is measured in the loam soils. With depth increase can be observed in the case of clay soils, while no considerable difference can be observed in the other two soil types.

At the time of the examination the chromium content of the soils in both depths is the highest in clay-loam and the lowest concentration is found in loam soils. With depth there is a concentration decrease in loam soil and increase can be observed in clay and clay-loam soils.

The cadmium content of the soils in both depths is highest in the clay samples, the lowest in the loam soils. With depth a decrease can be experienced in all three soil texture types.

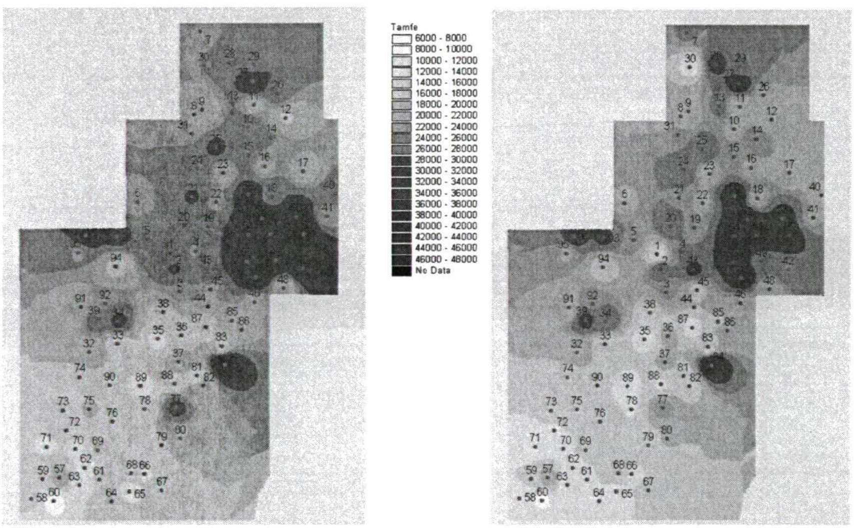

Fig. 3 Distribution of the acid soluble iron in lower and the surface layers in the study area (the presented surface is the result of an IDW interpolation, carried out for a better visualization of the results)

It can be verified that the manganese concentration shows the highest values in loam soil both in surface samples and deep samples. We measured the lowest concentrations in the clayish soils. With depth an obvious decrease can be observed in all three soils.

In the case of the iron content the highest concentration can be measured in clay soils in both depths and the lowest concentration in loam soils (Fig. 3). With depth the clay and clay-loam soils show considerable, while the loamy soils a small-scale increase.

The concentration of the aluminium examined in the upper layer of the soils shows the highest content in clay-loam soils and the lowest in loamy soils. In the sample originating from the deeper layers the highest concentration can be measured in clay soil while the lowest in the loamy soil. The aluminium concentration is growing in the clay soils with depth whereas it decreases in clay-loam, (at a bigger rate) and in the loamy soils (at a smaller rate).

The two maps in Fig. 3 illustrate clearly that the acid soluble metal content, in the hidden open karstic area covered with soil is higher, and this confirms the statement that the probability is higher for the mobilisation of metals here, and thus the risk of hazard is also higher.

We present the proportion of soluble metal contents of the acid soluble and EDTA soluble metal content regarding different metals, and different soil types (Table 2). The EDTA soluble metals are important, because these may get into the system or the plants soon and may cause damage. Where the EDTA soluble metal content represents a bigger proportion of metals soluble with acid, there is a bigger part available for plants, but they may leak into the mobile heavy metal system, which increases the potential danger of the pollution of the natural, karstic water directly (Zseni 2003).

Table 2 The proportion of EDTA soluble metal content.

Element (%)	Depth F=near the surface A=lower layer	clay	clay-loam	loam
Cu	F	46.0	38.2	64.4
	A	38.0	40.7	79.0
Ni	F	8.9	7.5	12.4
	A	5.4	7.9	10.4
Zn	F	12.3	15.2	16.8
	A	7.5	10.4	12.3
Co	F	30.7	31.9	20.9
	A	37.8	40.1	21.7
Cr	F	0.2	2.6	1.3
	A	1.3	3.0	1.5
Mn	F	45.7	51.8	31.0
	A	50.7	43.2	21.5
Fe	F	0.9	0.9	1.0
	A	0.5	0.6	0.5
Al	F	0.9	0.7	0.8
	A	0.6	0.6	0.8

Copper is the most mobile in the loam soils, in the lower level of these soils 79% of all the copper content is present in a form which is easily soluble. In the surface soil it is the most mobile in loamy soils, on the other hand it is the least mobile in clay-loam soils. In the lower level the highest value of copper is in the loam soils, the lowest value can be measured in clay soils. In the case of clay it decreases with depth, in the case of loam there is a small-scale increase while in clay-loam stagnating values can be observed.

In the mobile nickel content it can be experienced that in the upper level the lowest value is in clay-loam soil samples, the highest one is shown in the loamy samples. In the lower level the proportion is the lowest in clay-, the highest in loam samples. With depth a decrease in metal content can be experienced in all three types of soil texture.

Zinc is most mobile in the upper samples in clay-loam, in the lower level in the loamy soils. The lowest mobility is in the clay soils in both depths. With depth a decrease in the mobility of zinc can be measured in the case of all three soils.

In all three cases the cobalt content is the lowest in loamy soils, the highest values can be measured in clay-loam samples. With depth it grows in clay and loam soils, and decreases in clay-loam soils.

In the case of chromium there is a very small mobile part, the least in clay soils, the most in clay-loam soils. The mobile chromium content grows in clay soils with the increase of depth, decrease can be observed in the other two soil types.

Manganese is the most mobile in the surface layer in clay-loam soils, in the lower level in the clay soils. It is the least mobile in both depths in loam soils. The mobility increases with depth in clay, it decreases in loam and in clay-loam soils.

The iron shows a value of 1% in the surface samples of all three types of texture. It is the most mobile in the deeper level of clay-loam soils, but it is only 0.5%, and the mobile metal content is equal in clay and loam soils (Fig. 4). With depth a decrease can be observed in the case of all three soils.

Aluminium has the highest mobility in clay among the surface samples; the lowest value is in clay-loam soil. In a deep level sample the proportion of the mobile aluminium content is somewhat higher in loam soil than in clay and clay-loam soils. With depth a decrease can be experienced in case of all three soils.

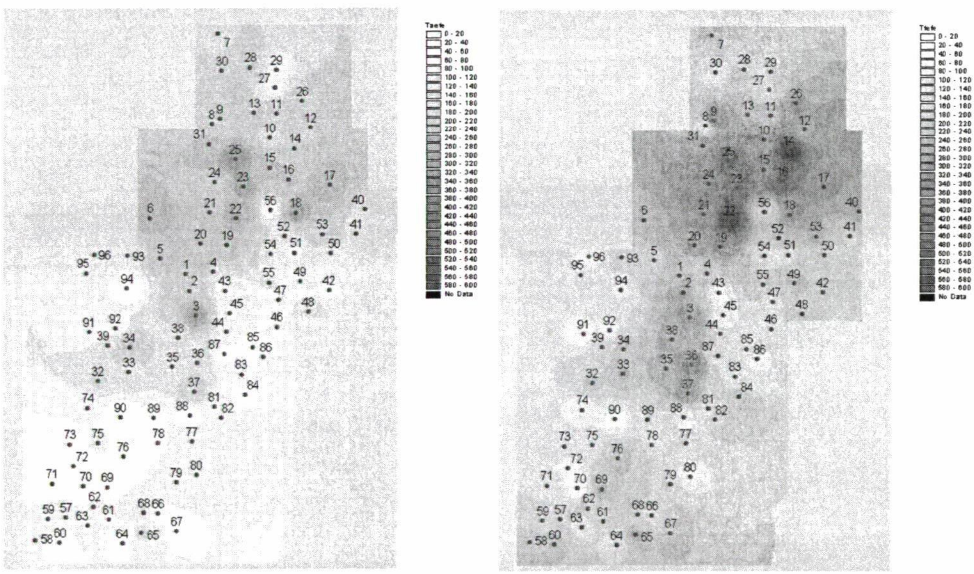

Fig. 4 The maps illustrate the distribution of EDTA soluble iron content in two depths (lower and near surface layers) in the study area.

3. CONCLUSIONS

On karstic soils the filtrations of water (which depend mostly on the soil texture) regulate the motion of metals. To sum up it can be stated that clay lets less water infiltrate, thus metals moving together with water must accumulate in clay. In soils with bigger pore volume the metals move more easily with the water. In karstic areas the motion of the metals is influenced greatly by the infiltrating water and metals can get into the karstic water system, thus plants can uptake them and later they can return it back into the system. This is the reason why it is very important to know the soil dynamics well as opposed to non-karstic areas.

Generally we can state that clay soils bind most of the metals and their concentration increases with depth. In the case of clay-loam and loam soils a lower concentration of metals can be found both in the near-surface layers and in lower levels. This special feature is in connection with the regional distribution of the different-textured soils in the catchment.

In the case of the mobile metal content we can say that copper, nickel and zinc have the highest mobility in the loam soils, while chromium is the most mobile in clay-loam soil. Soil texture has marginal influence on the mobility of iron and aluminium in the soil.

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