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HEAVY METAL CONCENTRATIONS IN THE SOILS AND VEGETATION OF THE BÉKE-CAVE WATERSHED (AGGTELEK-KARST, HUNGARY)

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Abstract

Our research took place on karstic area in Aggtelek National Park in Hungary. The heavy metal content of soils with three different texture and in the plants of the natural vegetation (oak- , hornbeam-, corn leaves, greenery) were studied. Ratio of total (acid soluble) metal contents and bioavailable metal contents of the soils were calculated. Based on these results we determined the mobility of the metals in different soils. Used the metal contents of the soils and the vegetation we set up a sequence of the mobility of the metals between the soil and the most frequent plant species.

Keywords: Aggtelek Karst, soils, vegetation, heavy metal contamination

1. Introduction

This research has been complemented in recent years with studies on the heavy metal load in the soil-plant system. Contaminants in the soil including metals get into the system with the water infiltrating through the soil. In our test area, Aggtelek National Park anthropogenic impact has lately diminished, but traces of former pollution are still present, and contaminants can also enter from the atmosphere through dry and wet deposition from both domestic and transboundary sources. This was observed in the early 2000's (Szőke – Keveiné Bárány, 2003).

On karsts, as in other areas, the vegetation determines the organic matter content and the pH conditions of the underlying soil, which greatly affects the immobilization of metals. The vegetation of nature conservation areas is not harvested each year, so the majority of metals taken up by the plants build up in the soil over the years. If the metals are mobilized, they are returned to the soil, and through the infiltrating water, they contaminate the drinking water supplies of the karstic watersheds. The heavy metals could be present in soils in several forms. There are bound forms, not available for the plants. If the soil's nutrient retention capacity is analyzed, it is not enough to examine the "total" (acid-soluble) metal content of the soils, but we need to determine the amount plants are potentially able to uptake (= "bioavailable" metal content).

The present study examines the heavy metal uptake of plant samples (Sessile oak – Quercus petraea, cornel – Cornus sp., Hornbeam – Carpinus betulus, and the herbaceous layer as a mix) collected from the catchment area of the Béke Cave (Aggtelek-karst) concentrating on the amount of metal that different plants are able to extract from the soil. At the same time we also examined whether the "plant-extractable" metal element content extracted using EDTA solution actually meets the quantities taken up by the different plant species.

2. Showing of the studied area

The study was carried out in the catchment area of the Béke Cave (Aggtelek-karst), in an area of approx. 10 km^2 (Fig. 1.). The surface development of the northern and southern part of the catchment was different. The northern part is formed mainly on well karstifiable Lower Triassic limestone bedrock with real rendzina soils, typical of true karsts. The southern part is a covered karst, where forest soils prevail, formed on Miocene and Pannonian sediments. The rendzina soils covering the surface are red clayey, brown and black rendzinas (Zámbó, 1971). In many places the limestone is covered by a relict red clay layer of variable depth (e.g. in the Red Lake area), which fills the bottom of the dolines, but also appears on the slopes, lower ridges, and rarely even on higher surfaces (Zámbó, 1970). On this layer red clayey and brown rendzina soils were developed with horizontal gradual transition. On the loose Tertiary sediments brown forest soils (brown forest soils with clay illuviation and Ramann brown soils, Luvisols) can be found. In addition, slope sediment soils, and small barren rocky surfaces also occur here

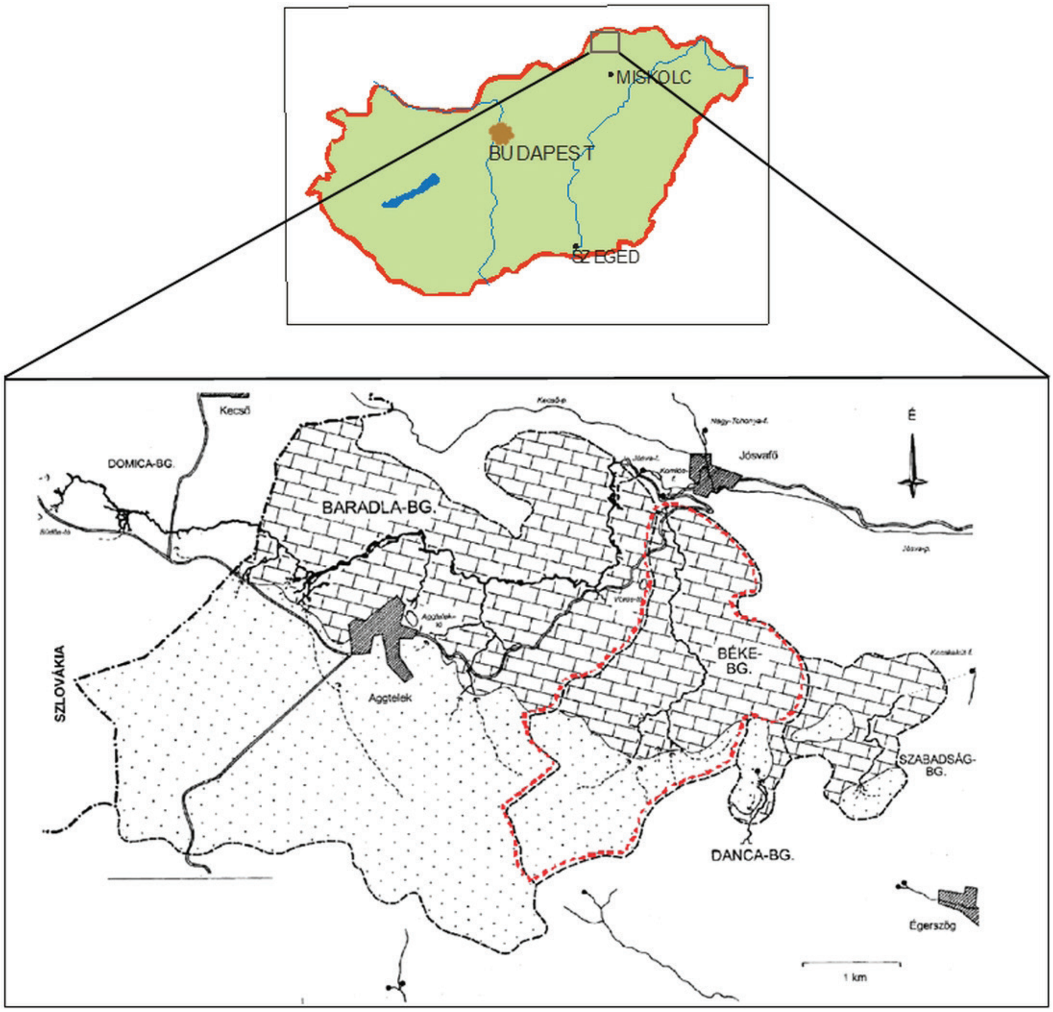

Fig. 1. Aggtelek-Égerszög area's caves with stream and their catchment basin (dotted area = non karstic rocks; rectangle area = karstic rocks). The catchment of Béke cave is indicated with red line (Jakucs, 1985, Balázs, 1961)

(Marosi – Somogyi, 1990; Stefanovits, 1996, 1999; Zámbó, 1998).

The potential vegetation are Turkey and downy oak-dominated forests (Quercetum petraae-pubescentis) and in the eastern part of the watershed sessile oak-hornbeam (Quercetum petraae – Carpinetum betulis) stands. The south-facing rocky slopes support rocky grasslands, ash-lime forests and slope steppes, with sub-montane alder groves along the surface streams and in some places planted coniferous stands. Crop production only occurs in areas adjacent to the settlements and on the border of the karstic and non-karstic areas (Marosi – Somogyi, 1990), mostly in the form of small arable lands.

3. Methods

98 soil samples were collected from different locations from a depth of 20-30 cm. This particular soil depth was chosen because the majority of the examined plants take up nutrients from this section of the soil profile. The plant samples were collected from individuals at the sampling locations. Of the woody plants, the mature leaves of the most common trees: oak, cornel and hornbeam were collected while samples from the mixed herbaceous vegetation were collected with mowing. The soil samples were dried and pulverized, the particle size distribution, pH and organic matter content were determined, and the heavy metal content was measured using two different methodologies. The "total" metal content was determined using a mix of nitric acid-hydrochloric acid-perchloric acid, which takes into solution any type of compound except silicates. The granulometric composition of soil samples were determine according to elutriation method, with this end in view of Atterberg partice size categories.

The "plant-extractable" or "bioavailable" element concentration was determined using the Lakanen-Erviö method. The greenery samples were dried on room-temperature and they were milled. 10 ml cc. HNO_3 was added to 1 g of plant sample, and held in a Gerhardt Kjeldatherm-type digester for 2-3 hours at a temperature of 120 °C, until the mixture became gelatinous. After cooling the sample under a fume hood, 3 cm^3 cc. $HClO_4$ was added and the mixture further heated for one hour at 120 °C. After cooling, the result was washed into a 50 cm^3 measuring flask (HS-08-1783-1:1983). The Cu, Zn, Ni, Co, Fe, Mn and Pb concentrations of the produced solution were determined using the ICP-OES method at the University of Veszprém, Department of Earth and Environmental Sciences.

4. Bioavailable heavy metal concentrations as a function of soil texture

Soils with different texture absorb heavy metals in a different way therefore we examined the ratio of the bioavailable heavy metal concentrations to the total according to soil texture properties (Table 1a., b.). Soil texture varies in the study area; the southern part is covered karst whereas in the northern open karst the heavy metal load can be significantly influenced by soil texture in the case of mobilization.

We can state that the ratio of "available" to "total" heavy metal content is highest in the

Table 1a. The "total" and "bioavailable" heavy metal content of the soils (mg/kg) and their ratio (%)

	Cu			Ni			Zn		
	total	available	*ratio (%)*	total	available	*ratio (%)*	total	available	*ratio (%)*
clay	21.18	8.06	38.06	33.01	1.72	5.21	98.15	6.76	6.89
clayey loam	20.68	7.75	37.47	26.65	1.68	6.32	101.20	7.97	7.88
loam	13.05	8.93	*68.39*	14.93	1.62	*10.88*	87.77	11.58	*13.20*

Table 1b. The "total" and "bioavailable" heavy metal content of the soils (mg/kg) and their ratio (%)

	Co			Mn			Pb			Fe		
	total	avail-able	*ratio (%)*	total	avail-able	*ratio (%)*	total	avail-able	*ratio (%)*	total	avail-able	*ratio (%)*
clay	12.31	4.04	32.79	692.81	343.05	*49.52*	32.86	11.37	*34.61*	30143.93	125.83	0.42
clayey loam	11.46	3.80	*33.16*	867.45	349.87	40.33	34.64	10.82	31.23	25779.82	135.69	*0.53*
loam	8.73	1.97	22.63	878.87	186.30	21.20	15.84	5.16	32.57	17278.52	86.82	0.50

loamy soils for Cu, Ni and Zn.

Only a very small fraction of iron is present in the soil in a plant-available form, in all 3 texture types. For the other examined elements, this ratio is much higher. In the case of Mn and Pb the ratio is highest in clayey soils whereas for Co it is highest in the clayey loam soils. In clay and clayey loam soils 38-45% of copper is in an "available" form, in loamy textured soils its ratio is 70%. This high value is in accordance with data reported in the literature. According to Győri (1984) the total Cu content of the soils in Hungary is usually between 3.2-38 mg/kg while the bioavailable Cu content is between 4-20 mg/kg (Szabó et al., 1987).

Our results concerning the bioavailable Ni content in the area seem to be lower than in literature sources (Fig. 2.). According to Fekete (1988), Szabó (2000) the bioavailable Ni content in Hungary (based on the data of 6000 soils) is 4.43 mg/kg, however compared to the data of Bárány-Kevei et al. (2001) our measurements resulted in lower values. They latter source also mentions an available/acid-extractable Ni ratio of 5-7% in samples from Aggtelek karst while the present results show higher values, especially in loam textured soils.

The total Pb content of the soils is lower than the results reported by Zseni (2001), also from the Aggtelek area (36-96 ppm). Her results for the plant extractable Pb (5-14 mg/kg) are higher, than those of Fekete (1988) who reports a mean of 6.43 mg/kg based on 6000 soil samples from Hungary. Our measurements show a higher available Pb content (32-34 %). The ratio of available/

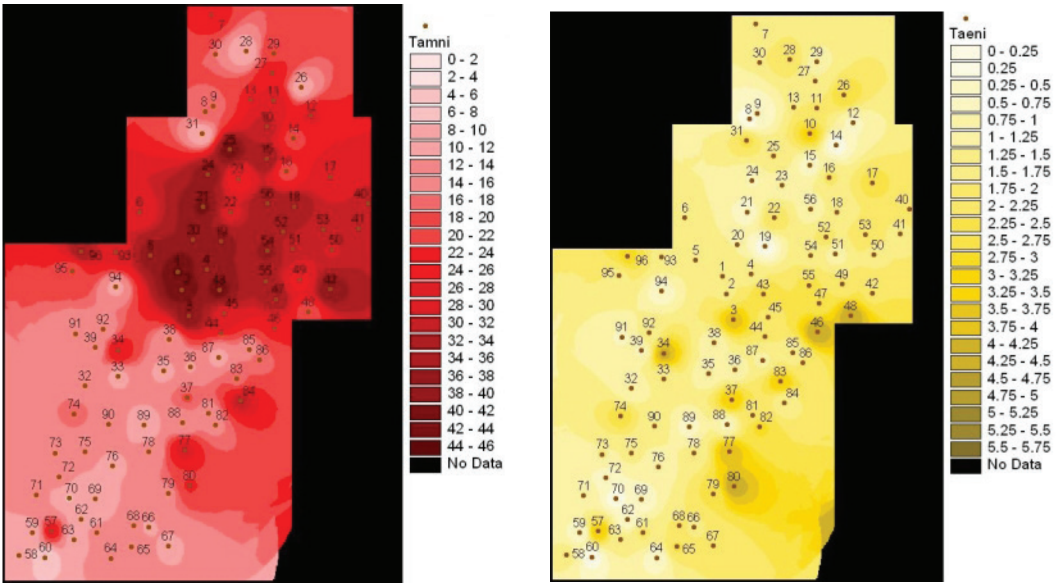

Fig. 2. The distribution of acid soluble (total) and EDTA extractable (bioavailable) Ni concentration on the studied area

total lead content is similar to the results (35%) presented in the study of Szabó (2000).

The acid-soluble Zn content is between 87 and 110 mg/kg, which corresponds to the results of Bárány-Kevei et al. (2001), who examined soil samples from Aggtelek. There are differences between the “available” Zn content, since according to the already mentioned study of Szabó (2000), the plant extractable Zn content is between 3-10 ppm whereas our measurements gave a result of 6.5 mg/kg (in the present study, we measured 6-12 mg/kg). The bioavailable/total Zn ratio (6-16%) that we found is consistent with the findings of Szabó (2000) (12%).

The total amount of Co (Fig. 3.) is also similar to results from earlier literature (Szabó, 2000; Bárány-Kevei et al. 2001) as well as the bioavailable amount (1.7 to 4 mg/kg according to our findings), and the bioavailable/total ratio (literature 21-33%, own measurements 21-32 %). The total Mn content is 780 ppm, the bioavailable amount is 190-420 ppm and the ratio of them varies between 21-49%.

Based on the ratio of the amount of “available” heavy metals to the amount of the “total” heavy metal content, we defined the mobility order (using the means of the ratios in the lower soil layers):

In clay soils: Pb>Mn>=Cu>Co>>Zn>Ni>Fe

In clayey loam soils: Mn>Cu>Pb>Co>Zn>Ni>Fe

In loam soils: Cu>Pb>Mn>Co>Zn>Ni>Fe

The mobility order shows that iron (Fe) is present in the soils in the most bound form, followed by manganese, lead and copper. Cobalt, zinc and nickel are moderately mobilized (all 3 are in a similar situation in the mobility order).

5. Comparative analysis of the heavy metal content of soil and plant samples

At first we tried to define how the heavy metal content of the examined species answer compared to the total heavy metal content of the soil samples taken from the same location. To do this, we determined the value of the soil-plant transport coefficient. Then we calculated the ratio (%) of the heavy metal content of the plants and the “total” heavy metal content measured in the soil (Table 2.).

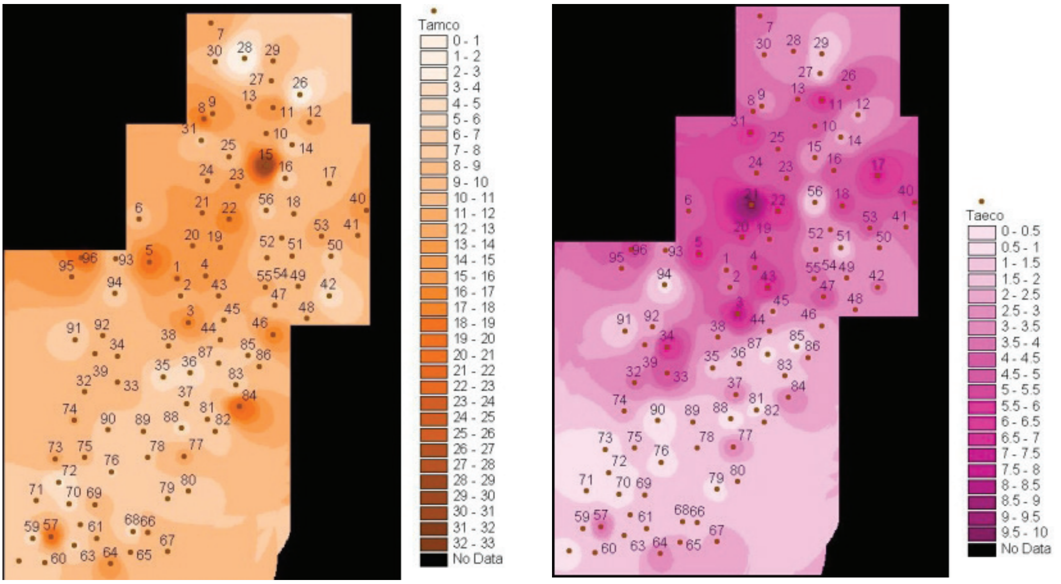

Fig. 3. The distribution of acid soluble (total) and EDTA extractable (bioavailable) Co concentration on the studied area

Table 2. The ratio of the heavy metal content of the plants and the “total” heavy metal content measured in the soil (%)

	oak (*Quercus petraea*)						hornbeam (*Carpinus betulus*)					
	metal	clay	metal	clayey loam	metal	loam	metal	clay	metal	clayey loam	metal	loam
1.	Fe	0.002	Fe	0.002	Fe	0.004	Fe	0.004	Fe	0.004	Fe	0.007
2.	Pb	0.054	Ni	0.071	Pb	0.052	Pb	0.053	Pb	0.065	Co	0.062
3.	Ni	0.099	Co	0.091	Co	0.068	Ni	0.057	Ni	0.196	Pb	0.086
4.	Co	0.280	Pb	0.129	Ni	0.225	Co	0.090	Co	0.212	Ni	0.355
5.	Cu	0.372	Zn	0.227	Zn	0.312	Zn	0.293	Zn	0.268	Zn	0.500
6.	Zn	0.378	Cu	0.328	Cu	0.554	Cu	0.483	Cu	0.335	Cu	0.760
7.	Mn	1.734	Mn	2.026	Mn	3.011	Mn	1.446	Mn	1.950	Mn	3.802
	cornel (*Cornus sp.*)						herbaceous layer, mixed					
	metal	clay	metal	clayey loam	metal	loam	metal	clay	metal	clayey loam	metal	loam
1.	Fe	0.003	Fe	0.004	Fe	0.005	Fe	0.006	Fe	0.005	Fe	0.009
2.	Pb	0.029	Co	0.028	Co	0.029	Ni	0.050	Ni	0.057	Co	0.212
3.	Ni	0.040	Pb	0.031	Pb	0.049	Co	0.190	Mn	0.155	Ni	0.247
4.	Co	0.040	Mn	0.051	Mn	0.144	Mn	0.237	Co	0.311	Mn	0.300
5.	Mn	0.052	Ni	0.078	Ni	0.440	Zn	0.289	Zn	0.363	Zn	0.540
6.	Zn	0.208	Zn	0.211	Cu	0.442	Cu	0.401	Cu	0.660	Cu	0.761
7.	Cu	0.272	Cu	0.241	Zn	0.470	Pb	26.651	Pb	21.234	Pb	59.985

The serial numbers of Table 2. mark the order calculated on the basis of the maximum values. The highest value of each metal in a particular plant according to soil type is indicated in italics. The table shows that the heavy metal content of the plants compared to the total heavy metal content of the soils is usually the highest in the case of loam textured soils. This suggests that loamy texture provide favorable conditions for the plants to uptake metal. Of the arboreal species the tendencies are quite clear for the hornbeam and cornel, whereas in the case of oak the value is in some cases highest in the other soil types. The Table 3. compares data from the literature with our own measurements.

Based on the soil-plant transport coefficient, we defined the mobility order of the examined heavy metals in the plants on the different soil types:

Clay soils:

Oak: Fe<Pb<Ni<Co<Zn=Cu<Mn
Hornbeam: Fe<Pb=Ni<Co<Zn<Cu<Mn
Cornel: Fe<Pb<Co=Ni<Mn<Zn<Cu
Mixed herbaceous: Fe<Ni<Co<Mn=Zn<Cu<Pb

Clayey loam soils:

Oak: Fe<Ni<Co=Pb<Zn<Cu<Mn
Hornbeam: Fe<Pb<Ni<Co<Zn<Cu<Mn
Cornel: Fe<Co<Pb<Mn<Ni<Zn=Cu
Mixedherbaceous: Fe<Ni<Mn<Co<Zn<Cu<Pb

Loam soils:

Oak: Fe<Pb=Co<Ni<Zn<Cu<Mn
Hornbeam: Fe<Pb<Ni<Co<Zn<Cu<Mn
Cornel: Fe<Co<Pb<Mn<Ni=Cu<Zn
Mixed herbaceous: Fe<Co<Ni<Mn<Zn<Cu<Pb

According to the soil-plant transport coefficients it is clear that iron is the least extractable element in the examined soils. The iron content of the plants does not exceed

1% in any case. The lead, cobalt, and nickel values of 13, 31 and 44% respectively can be considered moderate. These are followed by zinc and copper with 54% and 76% content in the plants. The most mobile metal on the basis of the soil-plant system of transport coefficients is manganese. Plants are able to uptake and accumulate more of this metal than the soils' total content. The mobility order based on our results is different from those published in the literature (Kloeke et al., 1994; Szabó, 2000; Szabó, 2008). Especially manganese shifts towards the end of the line in our study (towards better availability) especially in the case of the trees; the mobility order of cornel is similar to those in the literature. For herbaceous plants lead was found to be one of the most mobile elements (at the end of the mobility order) for all soil types.

Table 3. The transport coefficients of heavy metals in the soil-plant system based on literature data and own results

	Soil-plant transport coefficient		
	Kloeke et al.*	Szabó (2000)	this study
Cu	0.1-10	0.1-1.9	0.24-0.76
Ni	0.1-1.0	0.1-0.3	0.04-0.44
Zn	1-10	0.5-1.7	0.21-0.54
Co	0.01-0.1	<0.01-0.1	0.03-0.31
Mn	-	0.01-0.2	0.05-3.80
Pb	0.01-0.1	<0.01-0.1	0.03-0.13
Fe	-	0.001-0.03	0.002-0.009

(*Chojnacka et al. 2005)

6. Conclusion

In the present study we showed that in karst areas the ratio of plant-extractable ("available") to acid-soluble ("total") heavy metal content differs according to soil texture. In the loam soils (situated in the southern part of the study area, on the covered karst) copper, nickel and zinc show the highest available/total ratio, in the clay soils (mainly occurring in the open karst area) manganese and lead, whereas in clayey loam soils iron and cobalt can be found in the most available form. The examination of the metal content of some plant species showed that in the case of hornbeam, cornel and the mixed herbaceous layer most of the examined heavy metals can be found in the highest concentrations on the loam soils, except for cobalt. In the case of hornbeam the mobility order based on the soil-plant transport coefficient is the same for each of the three soil types. For the arboreal species (oak, hornbeam) the soil-plant transport coefficient of manganese is behind in the mobility order while those of cornel and the mixed herbaceous layer are in the middle. The herbaceous layer takes up lead in high proportions on all three soil texture types. This indicates that lead exposure on the karst must be prevented by all means, due to the risk presented by high mobility in these areas.

7. References

Bárány, I. (1985): Ökologische Untersuchung der Karstdolinen unter besonderer Berücksichtigung des Mikroklimas. Acta Geographica Univ. Szegediensis. Tom. 25: pp. 109-130.

Bárány-Kevei, I. (1998): The geo-ecology of the Hungarian karsts. Cave and Karst Science 25: pp. 113-117.

Bárány-Kevei, I. – Mezősi, G. (1999): The relationships between soil chemistry and the heavy-metal content of vegetation on karsts. In: Bárány-Kevei, I. – Gunn, J. (eds.). Essays in the Ecology and Conservation of Karst. Acta Geographica Szegediensis 36. Special Issue pp. 47-53.

Fekete, A. (1988): Nem esszenciális (toxikus) elemek a hazai talajokban. In: Mikroelemek az agrárkörnyezetben MAE Környezetvédelmi Szakosztály Ankétja. Gödöllő. Szerk. Fekete J. pp 93-112. In: Debreceni, B ., Czech, R: A műtrágyázás hatása a talajok könnyen oldható mikroelem-tartalmára. Agrokémia és Talajtan Tom. 40 (1-2): pp. 140-152.

Gillieson, D. – Smith, D. I. (1989): Resource Managenent in Limestone Landscapes: International Perspectives. Scpecial Publication 2, Department of Geography and Oceonography, University College, Australian Defence Force Academy, Canberra 260 p.

Győri, D. (1984): A talaj termékenysége. Mezőgazdasági Kiadó. Budapest In: Szabó S. A. – Regusiné Mőcsényi Á. – Győri, D. – Szentmihályi 1993. Mikroelemek a mezőgazdaságban I. Mezőgazdasági Kiadó. Budapest. 235p.

Bárány-Kevei, I., Goldie, H., Hoyk, E., Zseni, A. (2001): Heavy metal content of some Hungarian and English karst soils. Acta Climatologica Szegediensis Tom 34-35: pp. 81-92.

Jakucs, L. (1971). A karsztok morfogenetikája. Földrajzi Monográfiák 8. Akadémiai kiadó, Budapest. 310 p.

Jakucs, L., Keveiné Bárány, I., Mezősi, G. (1983):A karsztkorrózió korszerű értelmezése Földrajzi Közlemények 31: pp. 307-218.

Kaszala, R. – Bárány-Kevei, I. – Polyák, K. (2004): Further dates of heavy metal content on the soil and vegetation of Aggtelek Karst (Hungary), Acta Carsologica, 33 (2): pp. 169 - 180.

Kevei Bárány, I. – Zámbó, L. (1986): Study of the relationship between bacteria activity in karstic soils and corrosion. Annales Universitatis Scientiarum Budapestinensis de Rolando Eötvös Nominatae. Tomus 20-21: pp. 325-333.

Keveiné Bárány, I. – Zseni, A. – Kaszala, R. (2000): A talaj és növényzet nehézfém-tartalmának vizsgálata karsztos mintaterületen. Karsztfejlődés 7., BDF Természetföldrajzi Tanszék, Szombathely. pp. 297-315.

Kloeke, A. – Sauerbeck, D. R. – Vetter, H. (1994): In Changing Metal Cycles and Human Health. Ed. Nriagu, J. Springer-Veriag. Berlin 113 p.

Marosi, S. – Somogyi, S. (1990): Magyarország kistájainak katasztere I-II. MTA Földtudományi Kutató Intézet, Budapest. 985 p.

Stefanovits, P. – Filep Gy. – Füleky, Gy. (1999): Talajtan. Mezőgazda Kiadó p. 31.

Stefanovits, P. (1996): Talajtan Mezőgazda Kiadó pp. 131-132.

Szabó, Gy. (2000): Talajok és növények nehézfémtartalmának földrajzi vizsgálata egy bükkaljai mintaterületen, Studia Geographica, Institutum Geographiae, Universitas Debreceniensis, pp. 144-165.

Szabó, Sz. – Posta, J. – Gosztonyi, Gy. – Mészáros, I. – Prokisch, J. (2008): Heavy metal content of flood sediments and plants near the River Tisza. AGD Landscape & Environment 2 (2): pp. 120-131.

Szőke, E. – Keveiné Bárány, I. (2003): Karsztvíz vizsgálatok az aggteleki karszton, különös tekintettel a nehézfém szennyezésre. Karsztfejlődés 8. Szombathely, pp. 173-185.

Urushibara-Yoshino, K. (1991): The regionality of solution rate of limestone tablets in karst areas of Japan. Institute for Applied Geography, Komazawa Oniversity, Regional Views 4: pp. 107-117.

Urushibara-Yoshino, K. (1993): Human impact on karst soils Japanese and other examples. – Catena, Supplement (25) Clemingen, pp. 219-233.

Urushibara-Yoshino, K. – Kashima, N. – Enomoto, H. – Kuramoto, T. – Kina, H. – Nakahodo,T. – Higa, M. (1999): Inter-annual variation of limestone solution rates in Japan. In :Bárány-Kevei I. – Gunn J. (Eds.) Essays in the ecology and conservation of karst. Special Issue of Acta Geographica Szegediensis, Acta Geographica 36: pp. 201-211.

Zámbó, L. (1970): A vörösagyagok és a felszíni karsztosodás kapcsolata az Aggteleki-karszt délnyugati részén. Földrajzi Közlemények 18. kötet 281-293.

Zámbó, L. (1998): Felszínalaktani jellemzés In: Baross G. (Ed): Az Aggteleki Nemzeti Park Mezőgazda Kiadó. Budapest. pp 95-118.

Zseni, A. (2001) Nehézfém vizsgálatok az Aggteleki karszt, a Bükk-fennsík és a Nyugat-Mecsek karsztjának mintaterületén In: Farkas, Gy. – Zábrádi, Zs. (szerk.): Földrajzos Doktoranduszok VII. Országos Konferenciája. ELTE TTK Földrajzi Tanszékcsoport. Budapest. Paper 10: 9 p.