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CONTRIBUTION TO KNOWLEDGE OF THE CONTENT OF HEAVY METALS (Pb, Cu, Zn and Cd) IN SPELEOLOGICAL OBJECTS IN THE RISNJAK NATIONAL PARK (CROATIA)

PRISPEVEK K POZNAVANJU VSEBNOSTI TEŽKIH KOVIN (Pb, Cu, Zn in Cd) V SPELEOLOŠKIH OBJEKTIH NARODNEGA PARKA RISNJAK, HRVAŠKA

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Abstract UDC: 504.05:546.3/.9(497.5)

Boris Vrbek & Nenad Buzjak: Contribution to knowledge of the content of heavy metals (Pb, Cu, Zn and Cd) in speleological objects in the Risnjak national park (Croatia)

Samples of silt were taken from six speleological objects in the Risnjak National Park in Gorski kotar area (NW Croatia). The samples were taken from almost inaccessible rock fissures and shafts in order to find the most natural sediment outside the reach of anthropogenic pollution. The samples were examined in the Laboratory of the Forest Research Institute, where standard pedological analyses were performed, and the content of several heavy metals (Pb, Cu, Zn and Cd) was determined. The results indicate relatively low values of the content of lead, copper and zinc, while the values of cadmium in the sediment were increased above the limit level of 2 $mgkg^{-1}$ in the majority of speleological objects. The content of other heavy metals (Pb, Cu and Zn) in $mgkg^{-1}$ was lower than previously determined in samples taken from other speleological objects on the Croatian territory. Also, the content of heavy metals was lower in relation to surface soil samples taken from the humus horizon and mineral part of the soil under the parent rock of limestone, when sampling the soils of the Risnjak National Park
Key words: heavy metals, cave sediments, speleological objects, Risnjak, Gorski kotar.

Izvleček UDC: 504.05:546.3/.9(497.5)

Boris Vrbek & Nenad Buzjak: Prispevek k poznavanju vsebnosti težkih kovin (Pb, Cu, Zn in Cd) v speleoloških objektih Narodnega parka Risnjak, Hrvaška

Vzorce mulja smo nabrali v šestih jamah v Narodnem parku Risnjak v Gorskem kotarju. Da bi kar najbolj omejili neposreden antropogeni vpliv, smo vzorčili v težko dostopnih razpokah in breznih. Vzorce smo pedološko analizirali in jim izmerili vsebnost težkih kovin. Rezultati so pokazali nizko vsebnost svinca, bakra in cinka, ki je nižja kot v večini hrvaških jam, medtem ko je vsebnost kadmija višja kot v drugih jamah. Vsebnost težkih kovin v jamah je nižja kot v humusnem horizontu.
Ključne besede: težke kovine, jamski sedimenti, jame, Risnjak, Gorski kotar.

INTRODUCTION

The atmosphere is an immense and important media for transportation of heavy metals great distances from various sources. Although soils may be a hundred or more kilometres from the source of pollution, they can be polluted due to constant sedimentation and accumulation of heavy metals (ALLOWAY 1995). They reach the soil by sedimentation from distant sources in the air as parts of aerosols varying in size from 5 nm to 20 μm, although the majority are between 0.1 to 10 μm in diameter and remain present in the air for 10 to 30 days (BOWEN 1979). A large share of present-day heavy metal sedimentation is of anthropogenic origin. Even prior to the massive industrial use of metals the large quantity of burning out fossil fuel contributed to the increase of heavy metals in the atmosphere, and thus in the soil.

Analyses of soil samples for the content of heavy metals (lead, copper, zinc and cadmium) in the region of the Risnjak National Park determined increased value of lead in the surface soil horizons (VRBEK et al 1991, VRBEK and GAŠPARAC 1992). According to different authors the natural content of heavy metals in soil amounts for lead to 10-35 $mgkg^{-1}$ of soil, zinc 70-90 $mgkg^{-1}$, copper 20-30 $mgkg^{-1}$ and cadmium up to 1.0 $mgkg^{-1}$ of soil (SMITH 1990, FRIEDEMAN 1989, FRIEDLAND et al 1984). Thus, it is important to have knowledge of the naturally acquired "geogenic-pedogenic" condition of heavy metals in soil (MARTINOVIĆ 1997). According to the literature data it is most frequently assumed that for copper it is (Cu) 5-20 $mgkg^{-1}$, zinc (Zn) 10-50 $mgkg^{-1}$, lead (Pb) up to 10 $mgkg^{-1}$ and cadmium (Cd) up to 0.5 $mgkg^{-1}$. However, the natural content of lead, as well as other heavy metals, is not the same for all rocks from which soil originates. According to the data of NRIGAU (1978) in the case of limestone and dolomites (which comprise 5% of sedimentation rocks in the World) lead values can amount up to 71 $mgkg^{-1}$. Literature data show different values for unpolluted soils. Thus, NRIGAU (1978) reported mean values of cca 17 $mgkg^{-1}$ for lead, URE et al (1982) reported 29 $mgkg^{-1}$, while DAVIES (1983) ascertained that the soil surface (0-15 cm) contained between 15 and 106 $mgkg^{-1}$ of lead. With regard to the Croatian Karst these values vary for the mineral part of soil and concentrations are lower than in the humus A horizon (VRBEK and PILAŠ, 2001) reported mean values of 30 $mgkg^{-1}$ Pb for humus horizon, and 13 $mgkg^{-1}$ Pb for the mineral part of the soil. Zinc also shows different values (depending on the nature of the parent rock), and according to KABATA-PENDIAS and PENDIAS (1992) they range from 10 to 300 $mgkg^{-1}$ with mean value of cca 50 $mgkg^{-1}$. According to literature data (ALLOWAY 1995) average values for copper and cadmium for soils on limestone are cca 40 $mgkg^{-1}$ Cu, and 0.53 $mgkg^{-1}$ Cd. In Croatia, cca 55 samples of sediments from different speleological sites (objects) have so far been analysed from 1985 to 2003 (VRBEK 1998a). Some samples from caves and pits (shafts) had increased content of heavy metals, particularly lead (VRBEK 1988, 1989). However, these samples were taken from contaminated area of speleological objects, such as the Đulin ponor cave below the town of Ogulin, or from a contaminated shaft, into which rubbish used to be dumped. The latest findings from the pit system on the Velebit Mountain (Vrbek 1998 b) and from some localities in caves which are very far from the entrance, indicate the possibility of finding sediments with significantly lower values of heavy metals.

The Risnjak National Park is situated in Gorski kotar in north-western Croatia (Fig.1). In an area of 64 km^2 the vegetation, characteristic of the Gorski kotar region and numerous karst phenomena, are protected. There are numerous dolines and speleological objects. In the north-eastern region of the park is the source and upper course of the Kupa river, the largest river in this part of Croatia.

Systematic speleological researches of this area have continued since 1994 (BUZJAK 1999). Since 2001 the most intensive investigations have been carried out by the Caving Club Samobor.

Most of the investigated area consists of Upper Jurassic calcareous layers (dominantly limestone, more rarely dolomites) where the greatest number of speleological objects, dominated by shafts, has been investigated. The deepest shafts reach 140-200 m in depth. They are mainly angled, morphologically formed in water-rich conditions.

WORK METHOD

Samples were collected in six speleological objects during the Speleological Expedition "Risnjak 2002" (Fig. 1). The samples were collected in rock fissures, outside the reach of pollution effect. In the Jama (=shaft) Elkabong a sample was taken at a depth of 33 m, in the Hircova jama 55 m, in the Spilja (=cave) pod Kaličakom 40 m, in the Banditska spilja 8 m, in the Svjetleća jama 15 m, and Jama Kardar 15 m. Approximately 1 kg sediment was packed in a plastic bag, carefully closed and marked. The average depth of sampling ranged from 1 to 15 cm (Fig. 2). Standard analyses were carried out in the Laboratory of the Forest Research Institute, Jastrebarsko, in the Department of Forest Ecology and Silviculture. The following were determined:

- Soil reaction on the application of a glass electrode in H_2O and M-KCl,
- Quantitative content of carbonate by Scheibler calcimeter,
- Content of humus by bicromate method according to Alten and Wrandovski,
- Total nitrogen according to Kjeldah,
- Content of physiologically active potassium and phosphorus by Al-method,
- Heavy metals were determined by the BRÜNE-ELLINGHAUS method (1981), by extraction with 2N HCl, with determination on AAS Perkin-Elmer 3000 S. This method is also used to separate soil total lead, 75% copper and 30% zinc.

RESULTS AND DISCUSSION

It was realistic to assume that a relatively pure sample of sediment, which pedophysiologically is similar to the soil of the pedosphere with a natural content of heavy metals, preserved from any anthropogenic effect, would most likely be found in the depth of the speleological object. Sediment samples with relatively low content of lead, copper and zinc, with values below or near the 'geogenic' state, were found in the speleological objects of the Risnjak National Park. This was not the case with regard to cadmium. The amounts of cadmium in some samples exceeded the limit values of 2 $mgkg^{-1}$.

Laboratory analyses show a high content of $CaCO_3$ (Table 1). In sediments it amounts to 83.66% (Banditska spilja). All samples have alkaline reaction, while pH in M-KCl ranges from 7.5 to 8.0 (Table 1). The content of physiologically active phosphorus and potassium varies considerably, which is also the case for humus. In cases where organic pollution is possible phosphorus shows a multiple increase (sample from the Spilja pod Kaličakom: 101.2 mg/100g soil). Other sediment samples are poorly (under 10 mg/100g soil) to moderately (10-20 mg/100g soil) supplied with phosphorus and potassium. This is slightly more in the sediment from the Banditska spilja (1.92%) and Jama Kardar (3.66%). Samples from the Banditska spilja and Jama Kardar are rich to very rich with nitrogen (0.13-0.30%), while others are very low with nitrogen (under 0.06%). With regard to the mechanical composition the sediments belong to different textural classes: sandy clay, clay, loam and loamy sand.

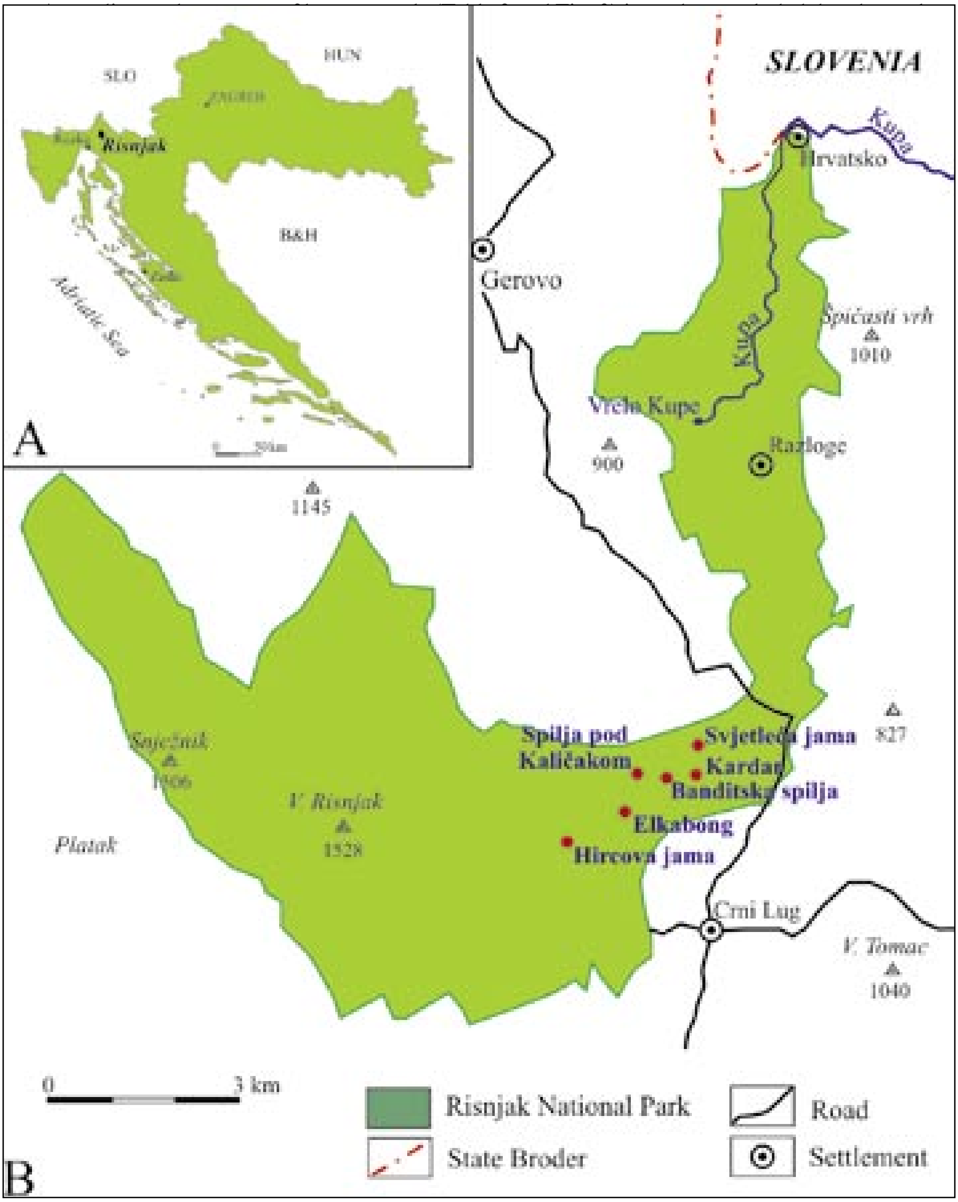

Fig. 1: Position of the Risnjak National Park and speleological objects from which samples were collected

Fig. 2: Sampling of sediments in speleological objects. (Photo: B. Vrbek)

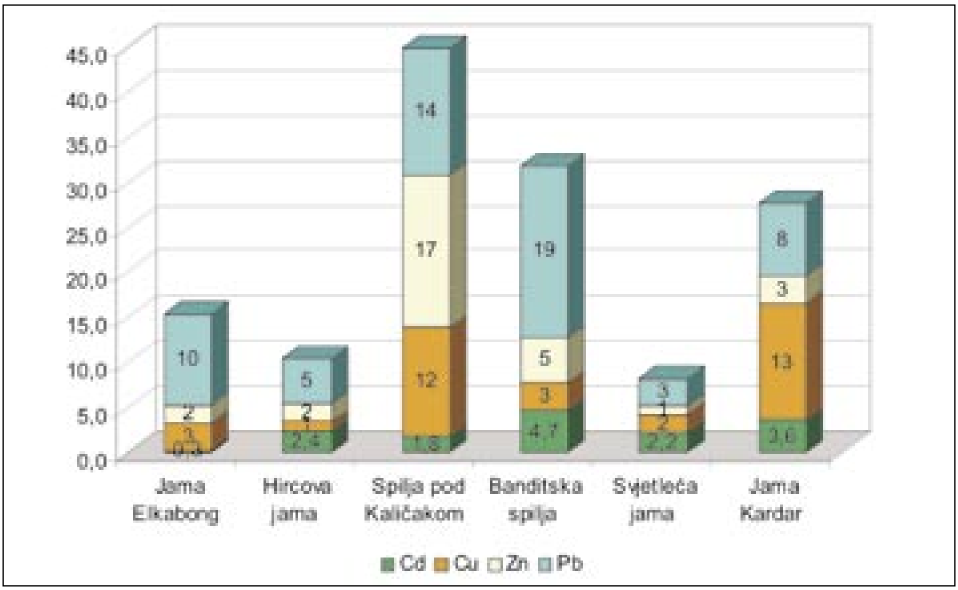

Fig. 3: Content of heavy metals ($mgkg^{-1}$) in the sediments of speleological objects in the Risnjak National Park.

and zinc, but are contaminated with cadmium. The content of cadmium is above the limit value of 2 $mgkg^{-1}$ on four localities: Hircova jama, Banditska spilja, Svjetleća jama and Jama Kardar.

The value of cadmium in the Spilja pod Kaličakom is close to the limit value, while the Jama Elkabong is practically uncontaminated by cadmium and other heavy metals. For the purpose of comparison the content of heavy metals is shown in Fig. 3. These experimental investigations have so far only been performed on 6 speleological objects. Sampling of sediments in other speleological objects is needed in order to determine the distribution and variability of heavy metals in the sediments of the karst underground in the Risnjak National Park.

CONCLUSIONS

According to the content of heavy metals in the samples collected from six speleological objects in the Risnjak National Park in Gorski kotar (NW Croatia), it can be concluded that the sediments in the speleological objects have until now remained outside the reach of contamination by lead, copper and zinc, but not cadmium. Samples collected in 4 speleological objects contained cadmium above the limit value of 2 $mgkg^{-1}$.

Locality	Sample	pH H_2O	pH M-KCl	$CaCO_3$ %	P_2O_5 mg/100g	K_2O mg/100g	N %	humus %	C %	C/N
Jama Elkabong	1	8,1	7,7	6,83	6,3	13,1	0,04	0,43	0,25	6,25
Hircova jama	2	8,2	8,0	47,38	2,8	6,4	0,02	0,13	0,08	4,00
Spilja pod Kaličakom	3	7,9	7,5	5,98	101,2	17,4	0,03	0,36	0,21	7,00
Banditska spilja	4	8,0	8,0	83,66	7,9	3,3	0,13	1,92	1,12	8,62
Svjetleća jam	5	8,1	7,7	41,40	2,2	14,3	0,03	0,68	0,40	13,33
Jama Kardar	6	8,0	7,7	3,41	11,6	15,8	0,30	3,66	2,13	7,10

Table 1: Chemical analyses of sediments in speleological objects.

Locality	Sample	Pb	Cu	Zn	Cd
		$mgkg^{-1}$			
Jama Elkabong	1	10	3	2	0,3
Hircova jama	2	5	1	2	2,4
Spilja pod Kaličakom	3	14	12	17	1,8
Banditska spilja	4	19	3	5	4,7
Svjetleća jam	5	3	2	1	2,2
Jama Kardar	6	8	13	3	3,6

Table 2: Heavy metal content of sediments in speleological objects.

Unexpected increase of cadmium in sediments should be investigated in more detail. During sampling maximum caution is required in order to avoid errors when taking 'natural' and pure sediment samples.

The content of lead, copper and zinc was lower than the expected values, and it can be concluded that natural values prevail in the sediments for the aforementioned heavy metals, or even slightly lower values than given in literature data.

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