



## **Research on heavy metal contamination in the Aggtelek karst area in Hungary**

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### **Introduction**

In our days' pollution hazard researches there's an increasing emphasis placed on the examination of heavy metal contamination in different landscapes. Despite heavy metals being part of the natural environment, in concentrations above certain threshold limits they are considered toxic materials. According to predictions from researches dealing with changes in the element content of soils and cultivated plants heavy metals may become a major stress factor in the next decades. (PAIS, 1992) The main reason for this is that metals cannot be biologically decomposed so they accumulate in living organisms. From an environmental point of view, karsts belong to the most sensitive areas. Due to its open hydrological system and 3-dimensional reaction surface a karstic area reacts very fast to anthropogenic activity.. We determined the heavy metal content in the catchment area of Aggtelek, in springs and dripping waters, also in the soil and plants.

### **Methods**

The soil and the greenery samples were collected during the summer of 2002. The soil samples derived from two depths: one from the surface (0-10 cm) and the other from 20-30 cm depth. The acid soluble heavy metal-content was measured by ICP-OES techniques after digestion with acid mixture ( $\text{HNO}_3\text{-H}_2\text{O}_2\text{-HClO}_4$ ). The heavy metal-content of the greenery was also determined by ICP-OES techniques after digestion with  $\text{HNO}_3$  (ROWELL, D.L. 1994).

The water samples were collected from the springs, caves and few sinkholes and dripping waters in the period between 2000 and 2002. We determined the concentration of different heavy metals with a Perkin-Elmer atomic adsorption spectrophotometer

(ASS).

## Results

The catchment area of the Béke-cave is situated in the southwestern part of the Aggtelek National Park. In the northern part of the area Triassic limestone comes up to the surface, so for this reason it is called an 'uncovered karst' ic area. In the southern part of the area this limestone is overlain by pannon sediments. The soils that developed on the different parent material show this duality well. In the northern part of the area mainly reddish clay residual soils can be found which are rich in clay minerals; there are also brown forest soils. On the other hand in the covered karstic area bright, yellowish-brown coloured soils can be found, which contain loam and sand (remains, like terra fusca).

The vegetation of the open karstic area is hornbeam-oak forest mixed with beech (*Carpinus Quercetum Fagetosum*) and with scattered undergrowth. In some places we can find warmphilous cornel-oak forest (*Corno Quercetum Pubescenti Petrea*). In the treeless places juniper (*Juniperus Communis*) and blackhorn build up impenetrable scrub. Most of the southern terrain is covered with slope steppe-grassland (*Salvio festucetum rupicole*).

The pH value and organic-matter content of the soils considerably contribute to the fixation and mobilisation of the metals. The pH value of the analysed soils is neutral and weakly acid. There is a clear difference between the values in the northern and the southern part of the area. The pH value of forest soils, which contain clay mineral, is about 6, and the remains of terra fusca are about  $\text{pH} \cong 5$ . There are also differences in the organic matter contents. The soils from the northern part (sample number lower than 30) of the area contain 11-12% of organic matter and soils from the southern part contain only 6-7% organic matter.

We determined the zinc, cobalt, cadmium, copper, nickel, chromium content of the soils. In the metal content the duality can also be found between the clay contented residual soils in the northern part and the loamy soils in the southern part. The concentrations of the cobalt and copper are close to the background level. The zinc and the nickel concentrations are generally above the background level and some samples approach the contamination threshold limit. In general we can say that in the southern part, probably because of the lower organic matter and clay mineral content, the metal concentration of the soils has lower value.

The heavy metal uptake of the plants is variable, depending on species. For this reason those species were chosen which could be found almost in the whole study area. On the basis of this information leaves of the following plant species were collected:

hornbeam (*Carpinus betulus*), oak (*Quercus petraea*), and cornel (*Cornus mas*).

To examine the relationship between the heavy metal content of the soil and the vegetation we counted the ratio of concentration of soil samples from 20-30 cm depth and the metal content of vegetation from the same place. The technical literature uses this ratio for the usage of the greenery (for example the sheep graze it and some metal can accumulate in the organism). The results of the hornbeam and oak show that the chromium content of the soils gets into uptakeable form if the pH value of the soil is about 5. The cobalt for the oak is not reachable, while cornel from the same place contains 2,2 ppm cobalt. Its reason can be the physiology of plant, but we need further experiments to prove that. In the case of oak and hornbeam it can be observed, that higher nickel content coincides with higher concentrations of copper and zinc.

The water samples were collected from springs of Jósza, Komlós, Nagy-Tohonya and Kis-Tohonya, also from the Rákóczi and Földvári caves and few sinkholes and dripping waters in the period between 2000 and 2002. All the water samples from 2000 and 2001 are contaminated with lead and cadmium and the concentrations exceed the threshold limit for drinking water in several cases. The highest lead concentration (0,095 mg/l) in these years can be found in the Jósza springs that come from the Baradla cave. In the Béke cave the dripping waters show the highest lead concentration (0,029 mg/l). In the spring coming from the cave the concentration was the same as the threshold limit (0,01 mg/l). The same trend can be seen in the cadmium values while the concentrations of zinc, cobalt, brass and nickel are below the limit set for drinking water in the specified years. Chromium concentration only exceeds the threshold limit in the Béke cave, in the other caves and springs this metal is barely present at all. However, in the samples from 2002 the chromium content was very high, several times the value of the threshold limit. Zinc concentration exceeds it too; its highest values were found in Komlós spring. In the catchment area of the Baradla and Vass Imre caves nickel concentration also exceeds the threshold limit.

## Conclusion

Based on the geological inhomogeneity of the catchment area of the Béke cave we can distinguish two different (in physical and chemical properties) soils. Because of the difference in the pH value and the organic matter content of the soils, the metal binding capacity is also various in the collected soils. This duality can also be found in the heavy metal content, and it means that the uptaking possibility of the vegetation is different.

As for the vegetation it can be proved that the metal uptake of *Carpinus betulus* is more than that of *Cornus mas* or *Quercus petraea*. It is *Carpinus betulus* that contains Ni, Co and Cu in the highest concentration. The element content of the vegetation from the

northern part of the area exceeds the element content of the covered-karst vegetation.

The reason for this is that the pH value, the organic matter-, and clay mineral-content are also lower in the southern part, and the soil is not able to bind (ab-, and adsorption) metals. If the metals remain in the soil solution, they are available for vegetation and percolating water to uptake. The high chromium concentration observed in the water analysis might relate to changes in the chromium content of the soil and vegetation. The higher Ni, Co and Cu content in *Carpinus betulus* can be explained by the mobilisation of these elements. This aspect is being studied further.

On the basis of the water analysis we stated that the area was polluted with lead and cadmium. In 2000 in certain places higher chromium concentrations were found, while in 2001 lead and manganese were added to that. In 2002 a pollution wave could be observed, values of chromium, nickel and zinc concentrations were very high in the analysed samples from the Aggtelek study area.

#### References

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