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RESEARCH ON THE HEAVY METAL POLLUTION OF SOME CAVE WATERS OF THE KARSTS OF AGGTELEK FROM 2000 UNTIL NOW

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Összefoglalás – Napjainkban a környezetszennyezések vizsgálata során egyre gyakrabban előtérbe kerül a nehézfém terhelések táji értékelése. Annak ellenére, hogy a nehézfémek környezetünk természetes alkotóelemei közé sorolhatóak, potenciálisan toxikus anyagoknak tekintjük azokat. Afémek biológiailag nem bonthatók le, az élő szervezetbe kerülve ott felhalmozódhatnak. 2000 decemberétől az Aggteleki-karszt területén 7 alkalommal volt lehetőségünk mintavételezésre. A terület fémszennyezettségét nem csak vízminták (forrásvizek, barlangi csepegővizek), hanem több helyről gyűjtött barlangi agyag alapján is vizsgáljuk. A kutatás része annak a vizsgálatnak, amely a karsztterületek talajainak és azok növényzetének nehézfémszennyezettség vizsgálatát is célozza. Amennyiben kimutatható a talaj – növényzet – és vízrendszer terhelésének kapcsolata, az a tájkezelés számára a jövőbeni környezetvédelmi problémák egy szegmensének feladatait is megjelölheti.

Summary – Nowadays, the research of environmental pollution come to the front the importance of heavy metals in the landscape classification. However the heavy metals are the natural component of the environment, we have to look them toxic materials. Our goal is to determinate the degree of the impact of heavy metals on the karsts, which are sensitive for the environmental changes. Since 2000, we collected cavewater samples from five different locations of caves and springs and we have also clay samples from the Baradla cave, that was analysed too. Until now the results shows, the content of metallic contents in the cave waters are higher than the expected. The analysis of heavy metal-contamination cave waters is a part of the investigation of heavy metal pollution in karst soils and vegetation. In case, we can to detect the interaction among soil, vegetation and hydrology, that would show to a new way in the managemant of future environmental problems.

Key words: metal pollution, karst water, Aggtelek National Park

INTRODUCTION

Nowadays the evaluation of heavy metal pollution on the landscape level is gaining importance. Although heavy metals are natural components of the environment, we have to consider them potentially toxic materials.

Heavy metal concentration has increased in the air, soil and waters, especially in the cities and industrial areas. According to predictions based on research monitoring changes in the metal concentrations in the soil and plants, heavy metals will probably become important environmental stress factors over the next decades (*Pais*, 1992). One reason for this is that the metals are not biodegradable therefore they get cumulated in living organisms. This makes it absolutely necessary to investigate these toxic metals in the karsts as well.

Karsts are one of the most sensitive areas from the environmental and conservation point of view (*Jakucs*, 1971). The karst is a complex system formed by the interaction of the geological construction, the water, the soil and the vegetation (*Keveiné Bárány,* 1998). The effects of these factors on each other are very diverse; if any of these factors change, the whole system will be modified in a way that is hard to predict. Karsts react very fast to anthropogenic impact because their hydrological system is open and has a 3-dimensional surface.

The motor of the evolution and change of karst areas is water that also plays an important role in providing the drinking water supply. 25% of the world's population gets the drinking water from karst waters, therefore the effects of pollution cannot be neglected in future research (*Keveiné Bárány et al.*, 1999).

In our investigations we try to trace the heavy metal pollution of the Aggtelek Karsts by the analysis of samples collected in the catchment areas of the Baradla-, Béke-, Kossuth- and Vass Imre caves. We have had the possibility to collect samples 7 times since December 2000. Besides investigating the metal pollution on the basis of water samples (spring-waters, caves dropping waters) we also used clay from the caves, collected in different places. Our aim is to answer the following questions:

- Is there significant pollution in the examined waters?
- Is there any similarity between the water qualities of the different sampling points?
- How does the metal concentration change in the studied karstic hydrological systems, is there any self-cleaning or does the strain increase in the karsts?
- Is it possible to conclude the place and the properties of the pollution sources from the results?

It is really important to know these processes because the results can only be seen after a certain time, when it is already impossible to interfere. Still, the reclamation of the bigger karst springs is still in process, they are being joined to the water-supply systems. Some of these satisfy local needs (Babot-well, spring Kis-Tohonya) but the newly claimed springs also help to solve the water supply problems of remote settlements (spring Pasnyag and Papkerti).

During the last decades some similar researches were taken, on an international level, but the karst springs of the Aggtelek region in Hungary have never been examined from this point of view yet. Since spring water is an important basis of the drinking water supply it is extremely important to research today's moderate pollution to be able to take protection measures in the future.

The examination is expensive and requires a lot of data. The elemental composition of the dropping waters can change very fast, even day by day; therefore if we talk about the general trends we cannot base our research with total confidence on random samples and momentary measuring results. We dedicate our data to attract attention to the problem and to serve as a basis for the next researches. For further research we will need further measurements from a longer period, and to start monitoring.

SAMPLING POINTS AND METHODS

The metal content of the water samples was defined by the use of an atomabsorption spectrophotometer in the laboratory of the Department of Physical Geography (University of Szeged).

Due to the geological, tectonical ad morphological diversity of the Aggtelek-Rudabánya karst area, there are 90 smaller ad bigger karst springs that bring the karst waters of the different chalk and dolomite areas to the surface. The rising places of the karst springs are determined by the geological structural lines. Among these, we selected 5 springs situated relatively close to each other. At least one cave belongs to each spring and one of the selection criteria was the accessibility of the caves' interior. We examined the following caves:

- Baradla-cave – Jósva-springs:
  - Rövid-cave spring
  - Hosszú-cave spring
- Béke-cave – Komlós spring
- Kossuth-cave – Nagy-Tohonya spring
- Vass Imre cave – Kis-Tohonya spring
- Rákóczi I. cave
- Földvári cave

We collected water samples in the Baradla cave from at least 3 different places. One of these is Acher in the Orchestra Hall, which is situated in the built up part of the Aggtelek side of the Baradla cave. In rainy weather we collected from the Styx, also at the Orchestra Hall. The Retek branch is at the middle of the cave; its water usually comes from the Zombor-Lyuk sinkhole. The active dropping water of Csipkés-well is situated at the Vörös-lake entrance on the Jósvafő side.

Sometimes, in rainy periods we also took some dropping water samples, usually around the Orchestra Hall. We also collected the clay samples around the Orchestra Hall and from the Kúszó branch of the Retek branch.

DISCUSSION AND RESULTS

Chalks do not generally have a high level of heavy metals concentration. According to *Merian* (1984) chalks contain the following average heavy metal concentrations: Cu: 4, Co: 2, Cd: 0.165, Ni: 15, Pb: 5, Zn: 23, Mn: 700 ppm.

Kabata-Pendias and Pendias (1984) present the data regarding the metals in intervals: Cu: 2-10, Co: 0.1-30, Cd: 0.035, Ni: 7-20, Pb: 3-10 ppm. *Brümer* (1991) created a mobility order based on pH: Cd: pH<6-6.5, Mn, Ni, Zn, Co pH<5.5, Al, Cu pH<4.5, Pb becomes more mobile at pH < 4. From this it is clear, that lower pH usually increases the heavy metals' mobility, and so their getting into the soil suspense.

We have determined the following metals' concentration in the water samples: lead, cadmium, zinc, cobalt, copper, iron, manganese, nickel and chrome.

The results of the 7 rounds of water samples from Aggtelek were quite in harmony with our previous examinations *(Keveiné Bárány et al.,* 1999).

All the samples are polluted with lead; the concentrations are higher than the threshold limit for drinking water. Between 2000 and 2002 we found cadmium pollution in the water, but this pollution has disappeared from the karsts by now.

While in 2000 we found lead to have the highest concentrations in the Hosszú cave of the Jósva spring and in 2004 again in the Hosszú cave and in the Babilon's mount 10.153 mg/lt. In the Nogy-Tohonya spring lead content was higher (in 2000 0.042 m/l, in 2004 0.118 mg/l) than in the siphon lake at the end of the Kossuth cave (2000 0.025 mg/l, in 2004 0.094 mg/l). In the past 5 years the concentration of lead increased in the water samples so we can suppose that lead concentration in the caves is being replenished and so getting higher. The lead and cadmium content of the karsts waters in December 2002 increased significantly compared to the concentrations measured in August 2002 and all are higher than the drinking water threshold limit. The highest level of lead pollution was found in the Retek branch (over 0.39 mg/l), the lowest in the Kis-Tohonya and the Nagy-Tohonya springs.

There's an opposite tendency in the Béke cave during the years 2000-2001. The lead concentration of the water in the cave was higher (0.029 mg/l) than at the Komlós spring where the concentration was exactly at the threshold limit (0.01 mg/l). The reason for this can be the pool dammed up by the sinter. From this pool the occasional pollution gets to the surface slower (this can be proved by a further analysis of the lake's mud). Another reason for this might be that the water got mixed with water from other springs and got attenuated (this will be the object of further investigations). Still, by December 2004 we found just half of the earlier concentrations at the Béke cave (0.0525 mg/l, after measuring samples taken from 2 different places) and the spring's lead concentrations were higher.

The same tendency appears in the case of cadmium concentrations in 2003 and 2004. The zinc, cobalt, copper and nickel concentrations did not exceed the threshold limit for drinking water in 2000 and 2004. In the samples from 2000 the quantity of chrome exceeded the limit only at the Béke cave (0.062 mg/l). However, high chrome concentrations could also be observed in the Komlós spring. In the other springs chrome hardly ever appeared, so it is only typical at the Béke cave catchment area. In 2001 chrome did not appear in any of the springs save Béke cave, however, the concentrations there were also lower than in the previous year and did not exceed the drinking water threshold limit.

In the samples of 2002 the chrome concentrations of all the catchment areas were already high, several times the threshold limit. The highest concentrations were found in the Baradla cave, in August (in the Retek branch, we found a concentration of 1.722 mg/l. In the Csipkés-well, which is active dropping water so chrome could not get concentrated behind a sinter, we measured 1.652 mg/l and the threshold limit is 0.05 mg/l!) The highest concentrations appeared in the Alsó-Hosszú cave of the Baradla cave and in the Rövid cave. The Baradla cave catchment area was obviously affected by serious pollution, followed by that of the Vass Imre and Béke caves. In the Kossuth cave catchment area chrome did not appear in August, only in October. So we suppose that the pollution arrived at the area from the north-west because the highest concentrations were found there.

By October 2002 the chrome concentrations in the Baradla cave were lower than in August; highest were those in the Rövid cave of the Jósva springs. By December the chrome concentrations were reduced; they were still higher than the drinking water threshold limit but much lower than in October. Thus, we supposed that the pollution was gradually leaving the cave. Each of the measured concentration levels exceeded the drinking water threshold limit (*Figs. 1-3*). We measured similar values in the dross samples brought from the Baradla cave.

In December 2004 we only found detectable chrome quantities in the Baradla cave at the Acheron (0.025 mg/l), at the Nagy-Tohonya spring (0.008 mg/l) and at the Komlós spring (0.0064 mg/l) but these were under the threshold limit *(Fig. 4)*. Therefore we can conclude that there was a self-cleaning process in the caves after a major chrome pollution in 2002.

In all the samples of 2002 zinc concentrations exceeded the drinking water threshold limit; they reached the highest values at the Komlós spring but by the end of 2004 they got lower and stayed under the limit. Similarly as in the case of the chrome content we can conclude that the pollution was leaving the territory. We reached this conclusion on the basis of the metal concentrations of the samples from the Baradla cave; in the sample taken in August the metal content was higher at the side nearer to the sinkholes while in October higher concentrations were found at the springs. Meanwhile in August concentrations were higher than in October. We can compare the spreading of the pollution to the passing of a wave. High zinc content is not only characteristic of the Baradla cave catchment area since we also met high concentrations in the Komlós spring; therefore we suspect the concentrations also increased at the Béke cave catchment area.

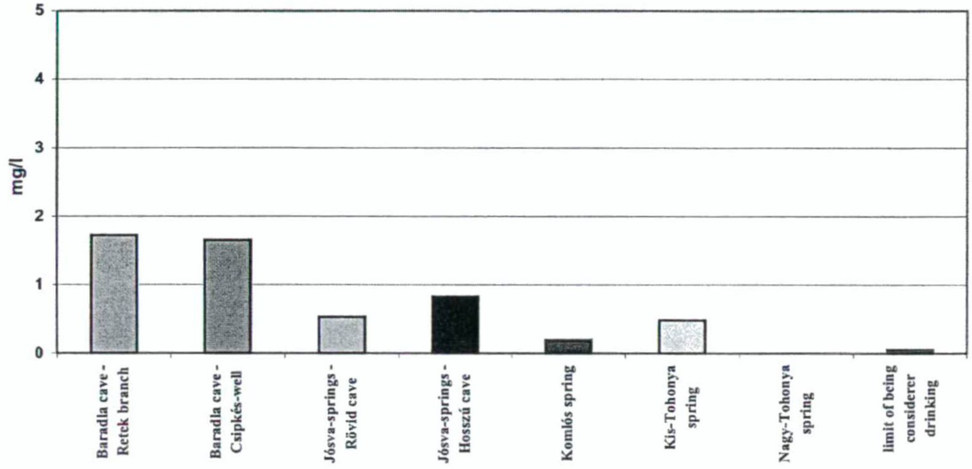

Fig. 1 Chromium content of the Aggtelek karst waters in August 2002

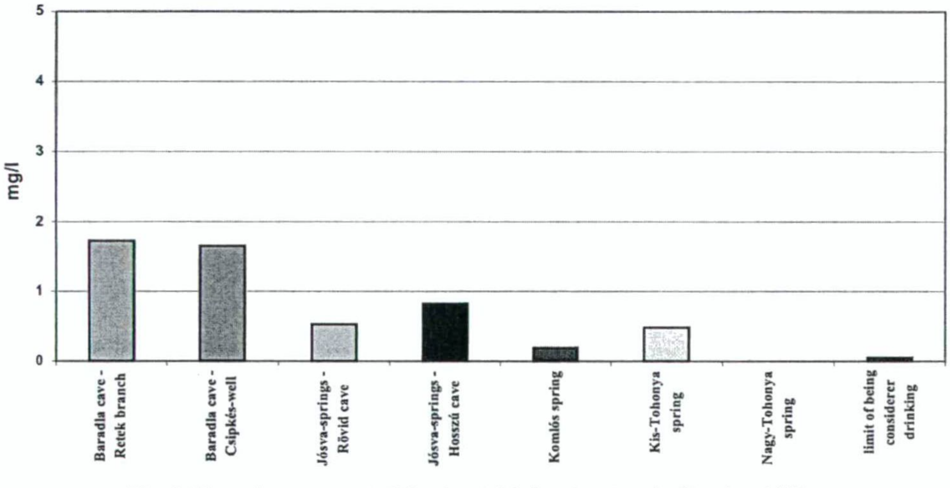

Fig. 2 Chromium content of the Aggtelek karst waters in October 2002

In the samples of August 2002 of the Baradla and Vass Imre cave's catchment areas we found nickel concentrations higher that the threshold limit. In the Retek branch the nickel content reached a value of 0.312 mg/l (the drinking water threshold limit is 0.2 mg/l) and in the Hosszú cave the concentration was 0.288 mg/l. Of the samples taken in October only the Hosszú cave sample (0.43 mg/l) exceeded the drinking water threshold limit. In August 2004 we only found higher nickel concentrations in the Komlós spring and in the Hosszú cave of the Jósva springs (0.321 mg/l and 0.253 mg/l) where the concentrations decreased to a value of 0.1 mg/l by December 2004.

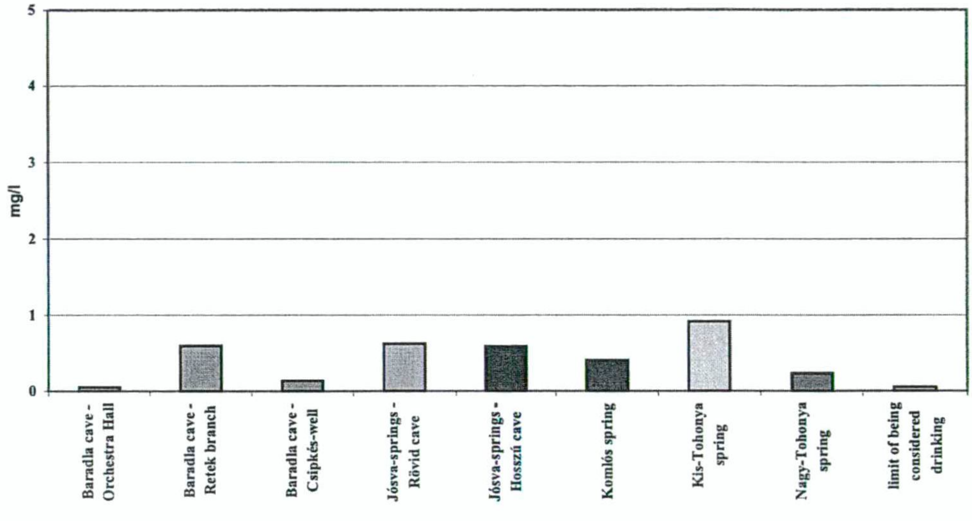

Fig.3 Chromium content of the Aggtelek karst waters in December 2002

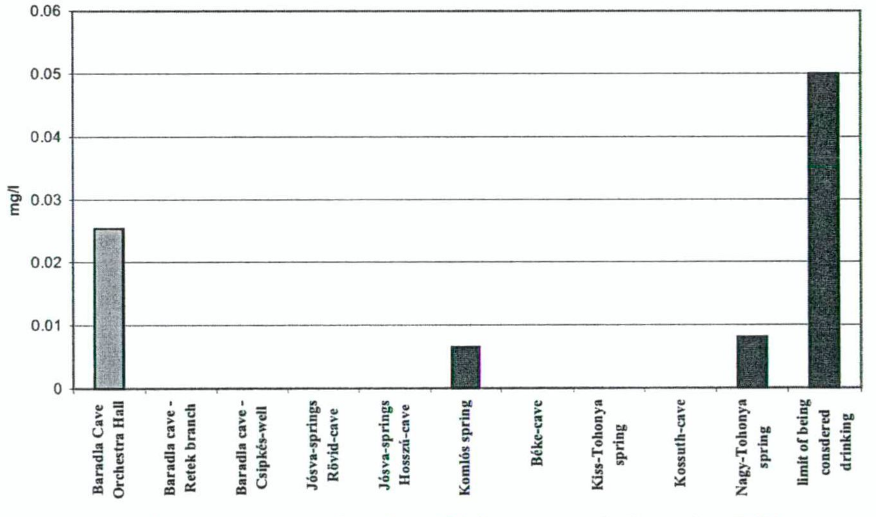

Fig.4 Chromium content of the Aggtelek karst waters in December 2004

In October and December 2002 the manganese content of the Retek branch of the Baradla cave (1.977 mg/l than 12.220 mg/l) significantly exceeded the threshold limit (0.5 mg/l). We did not find high concentrations elsewhere on any other occasion.

In conclusion, we can say that according to our examinations of the samples of 2000, 2001 and December 2002 there was a cadmium pollution in the area, along with a constant lead pollution, while in 2000 a lead pollution occurred and in 2001 higher iron and manganese concentrations appeared. In 2002 a pollution wave swept over the area which means the chrome, nickel and zinc concentrations were especially high. This wave disappeared by 2004 due to a self-cleaning process in the karst.

The metal concentrations of the dross samples have exceeded the threshold limit only once but they were visibly lower in the orchestra hall then at the Kúszó branch junction of the Retek branch. The chrome concentration of the soil is 10 times higher than the threshold limit; this confirms also our conclusion that there has been chrome pollution at the territory.

POSSIBLE ORIGINS OF POLLUTION

Generally pollution can get to the karst interior in three ways *(Csernavölgyi,* 1978) The fastest way is through the sinkholes. Through an open sinkhole the water can get inside the rocks without any barrier. In case a non-karstic catchment area also belongs to the hydrologic system, the pollution originating from there also enters the karst without any barrier. In the case of temporal sinkholes, which are usually more or less filled up, there is a certain degree of filtering.

Infiltration at the rock border usually occurs next to a local erosion basis, especially if the surface landuse has high pollution potential (like intensive agriculture, garbage storage, etc.).

The third way is the infiltration from the surface. This is a slow but constant phenomenon that usually occurs in agricultural areas (due to the use of fertilisers, herbicides and other chemicals) and in settlements (sewage, polluted precipitation). The significance of the three ways and their proportion can be influenced by the surface weather conditions, especially by precipitation (*Parrag,* 1997).

Infiltrating water from precipitation plays the most important role in replenishing the karst water supply. According to the examinations of the VITUKI Research Centre the precipitation here is a bit acidic (pH=4-6) and rather polluted that is caused by the nitrate and ammonium concentrations being higher than the Hungarian average. Since the prevailing wind in the area is north-west, the pollution probably comes from Slovakia, from the industrial area west of Rozsnyó.

Heavy metals can settle from the atmosphere by dry or wet deposition, and in wet agent, with adequate pH conditions they become mobile and can enter the karst water system. On the Slovakian side of the karst, in Pelsőc, there was a galvanizing factory for decades. This factory was closed down in the early 90's. That brings up several questions: what kind of metals was the factory using as catalyst for producing galvanized metals? Could these catalysts get into the atmosphere and to the entrance of the Domica cave, only 6 kms from the spot? If they did, what effects did they have over the last years?

The other potential pollution source is Rozsnyó and the industrial area surrounding the city.

Pollution can get to the territory not only by deposition from the atmosphere but also by infiltration from the surface. In August 2002, between the Hungarian-Slovakian border and the Slovakian settlement of Hosszúszó (Dlha Ves), in the Domica-Baradla cave system's catchment area there were 3-4 heaps of building debris and communal garbage left by the road which could also be a potential pollution source.

Some of the water from the Kecső stream that issues by the Slovakian settlement of Kecső (Kecovo) gets to the Jósva spring so the communal waste in the stream channel is also to be considered an important pollution source (*Sásdi,* 1998).

Another problem can be the agricultural activity, cattle farming and gardening in the large catchment areas of the sinkholes both in Slovakia and around the Hungarian settlement of Aggtelek. Contaminants get to the karst water directly through the sinkholes or with the thermal waters moving through pannon loamy gravels (*Sásdi,* 1998). This is also true to the waste yard that was active a few years ago about 1 km south of the settlement. This source endangers mainly the waters of the Jósva spring.

CONCLUSION

These are just preliminary results and provide information about the actual stage. It is absolutely necessary to continue the investigation since the heavy metal pollution of the karst waters providing drinking water for the population can cause serious health problems.

The examination is part of the research that aims to analyse the heavy metal pollution of the soil and plants of the karst areas. If the pollution of the soil, plants and the water prove to be interrelated, it outlines a future environmental protection duty for the landscape management.

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