NUTRIENT MANAGEMENT AND HEAVY METAL LOADING OF SOILS IN KARST AREAS

PhD Thesis

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1. Preliminaries, objectives

In the last decades the research in karst areas turned to the research of environmental effects on the karst as well as of the karst as an ecological system. Soils play very important role in the karst ecological system through their filtering, buffering and transforming capacity. The water seeping through the soil affects the intensity of karst corrosion as well as the soil having the appropriate characteristics steadily or at least temporarily could neutralise those adverse environmental effects that could quickly proceed in the sensitive 3D structure of karsts.

In the international and in the Hungarian literature we can find a lot of papers dealing with the examination of karst soils. However, the majority of the examinations deals with the role played by the soil in the evolution and the development of karst landform. Only few researchers deal with the examination of the connection between karst soils and land use and minimal of them provide concrete data on the nutrient content of karst soils.

Within the processes taking place in the karst system, **nutrient management and nutrient provision of soils** is one of the important indicators of the changes in the soil composition caused by the environment. Substances stemming from anthropogenic activities, from deposition and even soil erosion damage the soil horizon close to the surface and rich in nutrients. We can find a lot of literature about nutrient management of soils, but only a very few of them deal with the nutrient management of *karst* areas in spite of the fact that further development of these soils is important from the point of view of the utilisation (sylvicultural, agricultural as well as pasture-type) of the areas. The presence of nutrients of order of different magnitudes affects the other soil components (e.g. trace element content) and the characteristics thereof.

One of the adverse environmental effects on soils - nowadays is more and more paid attention to - is the **contamination** of soils **by heavy metals**. Like in general in the case of damaging pollutants, it is also true that soil has to have more and more effective filtering and buffering capacity as the load grows in order to neutralise the adverse effects. The amount of publications issued on heavy metals is increasing but very few of the articles are on researches taking place on clean or hardly polluted areas. It is more and more necessary to have enough information on these areas since the degree of pollution can only be determined by knowing the background concentrations. In karst areas, and mainly in open karsts (due to the sensitivity of the system) the heavy metal examinations are important.

The dissertation evaluates *the nutrient and heavy metal content of soils of three Hungarian karst areas* (8-8 km^2 area between Aggtelek and Jósvafő of Aggtelek Karst and of Bükk Plateau as well as karst area south Orfű in the Western Mecsek). The aim of research was the state assessment, the qualification of present state for giving information to the practical experts for formation of the future treatment and landscape utilisation. At the same time I also examined how the *vegetation and the slope position affect* the development of the examined soil parameters. According to the objectives I took the following examinations:

- soil samples from areas with various ecological features in the chosen areas were collected, species lists of the vegetation in the sample areas were enrolled,
- the collected soil samples were analysed in laboratory (in terms of pH(H_2O), pH(KCl), calcium carbonate content, organic matter content, Ca^{2+}, Mg^{2+}, K^+, Na^+ content available for plants, total and plant available Zn, Cd, Pb, Co and Cr content),
- comparative evaluation regarding the differences between pH, calcium carbonate, organic matter, plant available nutrient and heavy metal content of soils of different areas was performed,
- the connection between the nutrient content of soils and the vegetation was examined,
- correlation between available calcium, magnesium and potassium content of soils was checked up and the effect of pH and organic matter content on the nutrient and heavy metal content of soils was performed,
- the received heavy metal contents by chloronitrous acid disintegration (total heavy metal content) and by the Lakanen-Erviö method (heavy metal content available for plants) were compared, and the mobility order of the examined heavy metals was determined on the basis of the results,
- differences of the single soil parameters by quarters in the dolinas were examined,
- effect of the relief to the organic matter, nutrient and heavy metal contents of soils was examined.

2. Applied methods

2.1. Soil sampling, sample preparation, measurement

Soil samples were collected from areas with various ecological conditions. On the **Bükk Plateau** we sampled soils of beech forest, coniferous woodland mixed with beech, coniferous woodland, nursery garden and open meadows; **between Aggtelek and Jósvafő** we collected samples from soils of oak woodland, mixed beech forest, coniferous woodland, cereal stubble field and open meadows; **in the Western-Mecsek** we examined soils of oak woodland, mixed oak woodland, ravine woodland and pioneer grassland in clear-cut. Soils were sampled till the depth of 40 cm by 10 cm. Where we reached the parent material at a smaller depth as well as the very high rock content impeded the deeper sampling, we collected less samples. In the areas of both Aggtelek Karst and Bükk Plateau we also **examined dolinas**. Sampling took place at the slopes of the four quarters of the dolinas – at the middle of slope –, at the bottom of the dolina and at the edge of it as well. In the course of the research the **examination of the effect of the relief** occurred, too. So we sampled the soils of two slopes in the area at Aggtelek, three slopes in the Bükk Plateau and in the Mecsek Mountains at the bottom, the middle and the top of the slopes.

I dried the soil samples till air-dry condition at room temperature. Rock pieces and plant remains were removed by riddling through a screen of 2 mm mesh from the soils.

The determination of the **pH** occurred electrometrically, with a digital pH meter, in 1 to 2.5 soil-distilled water as well as in soil-1 mol/dm^3 KCl suspension. The **calcium carbonate content** was measured with Scheibler's calcimeter. The **organic matter content** of soils was determined with spectrophotometer after dichromate oxidation. I performed the examination of **potassium, calcium and magnesium available for plants** with ammonium acetate method. The exchangeable K^+ and Na^+ ions were determined with flame photometer, the Ca^{2+} and Mg^{2+} ions with atomic absorption spectrophotometer.

At the examination of the **heavy metal content** of soils I performed two types of disintegration. The two methods were justified by the fact that heavy metals are present in soils in various forms (in different strong linkages) and it was felt necessary to know both the total heavy metal content present in soil and the mobile one, available for plants. The **chloronitrous acid disintegration** serves the determination of total quantity of heavy metals present in soil. The **Lakanen-Erviö method** serves to disintegrate the heavy metal content available for plants, namely the easily mobilisable one. I measured heavy metals in both

disintegration methods with Perkin Elmer 3110 type atomic absorption spectrophotometer. The examined heavy metals were: Zn, Cd, Pb, Co and Cr.

In the course of the data procession I performed the calculations, the graphic presentations (figures) with the Microsoft Excel ®2000. I also used Excel for correlation analysis. For normality tests and a part of correlation analysis I used the SPSS® for Windows^{TM} 8.0.0 software.

In the course of the **examination of vegetation** the surveying of vegetation of the sampling areas occurred. Detailed species lists were prepared in the sampling areas at Aggtelek, Bükk as well as in the Mecsek. Having this species list I evaluated vegetation on the basis of ecological indices. Out of ecological indices I used nature conservation categories, figures of Zólyomi's heat budget, water budget and soil reaction.

3. Results

1. In terms of soil pH I found that *weakly acid and acid soils were prevailing* in the examined areas. The fundamental *difference* between the pH of soils of the single sampling areas can be explained by the *different soil types*: in the shallow tilth rendzina soils (mixing with rock pieces) pH are higher, ΔpH figures are lower than the deep red clay soils and brown forest soils with clay illuviation. pH grows by the depth in the soils. This growth is more expressed in soils not mixed with rock pieces, which indicates recalcification. ΔpH figures about 1 indicate that a certain part of soils (mainly brown forest soils) is prone to acidification. The presence of calcium carbonate could only be registered in soils mixed with rock pieces.

2. The **organic matter content of soils** is high, in some cases very high. The organic matter content of soil samples of Bükk Plateau is higher than that of Aggtelek Karst. It can be partially explained by the higher degree of soil erosion of the soils at Aggtelek. There are mainly rendzina soils in the Bükk Plateau that are characterised by very high organic matter content. Out of the soils of Aggtelek areas the red clay and forest soils with high clay content prevail. Due to the lower temperature and more precipitation in Bükk Plateau, the decomposition of organic matters is slow so soil contains more not disintegrated as well as semi-disintegrated organic residues. Because of this, the quality of organic matter is not the best, but the *high organic matter content* of the examined areas *promotes the fixation of heavy metals* so the soil is able to take temporarily out the heavy metals possibly occurring in a polluting amount from the food chain.

3. *Rendzina soils* (mixed with rock pieces) *have higher* ***available calcium content*** *than red clay soils and brown forest soils with clay illuviation*, which unambiguously indicates recalcification. If we consider only the vegetation types, it is ascertainable that *the available calcium content of the soil under the forest vegetation is higher than that of meadow soils*. This is in connection with the fact, that under forests more salt can be accumulated because of the occlusion of root system. In terms of the average figures *the available calcium content of soil samples of Bükk Plateau is the highest* then comes Aggtelek and finally the Mecsek. *The Ca-supply of the soils in the examined soils is good. The percentages of the calcium from the exchangeable basic cation are different in the 3 examined areas*. Its figure is the highest in the soils of Bükk Plateau; it is averagely 96.6%. It is averagely 87.1% in the soil samples of Aggtelek and the lowest in the ones of Mecsek, 79.1%. The average exchangeable basic cation % of calcium is mainly characterized by the parent rock, and not by soil or vegetation types.

4. The **available magnesium quantity** is the highest in the rendzina soils of Mecsek then comes Aggtelek, then Bükk Plateau and brown forest soils with clay illuviation of Mecsek. *Mg-supply in the soils of Aggtelek Karst is good and medium,* in the soils of *Bükk Plateau is weak in the lower soil layers but medium and good in the upper layers.* Mg-supply in rendzina soils of *Mecsek* are *good,* in brown forest soils with clay illuviation are *medium and low.* Meadows are characterised by lower available magnesium content both in the case of soil samples from Aggtelek and Bükk than forest soils. (It is caused by the occlusion of root system.) The difference in the available magnesium content of the soils of the 3 areas reflected by the percentage of magnesium from the exchangeable basic cation. The exchangeable basic cation value of magnesium is average 2% in the samples of Bükk Plateau, 10% in Aggtelek and 17% in Mecsek. The exchangeable basic cation percentage of magnesium is significantly lower in meadow soils than in forest soils.

5. The **available potassium quantity** averagely is the highest in the soil samples of Aggtelek. There are more reasons of lower potassium content of soils on Bükk Plateau: the stronger leaching of soils on the Plateau, the difference in soil types. And thirdly, the fallen leaves of oak contains more potassium as the leaves of beech and this can manifest in the difference of K-supply of the soils as well. *K-supply in the soils of Aggtelek Karst is good and very good.* K-supply in the rendzina soils of *Bükk Plateau is mainly good and very good, while in the brown forest soils are weak or medium*. K-supply of rendzina soils in *Mecsek*

are very *good, while* of brown forest soils with clay illuviation are *medium and weak.* In terms of the available potassium content the differences between and among the vegetation types are smaller compared to the other two ions. The quantity of potassium decreases by the depth. The percentage of the potassium from the exchangeable basic cation is 2.7% in the soil samples of Mecsek, 2.2% of Aggtelek and 1% of Bükk. The exchangeable basic cation percentage of potassium is higher in meadow soils than in forest soils.

6. On the basis of the correlation analysis between **Ca, Mg and K-ions** the correlation is close in the Ca^{2+}-K^{+} relation in the case of soil samples of oak forest in Aggtelek and there is significant correlation between Ca^{2+} and Mg^{2+} in the case of meadow soils. In this latter case, however, the correlation coefficients are negative so samples with smaller calcium content have higher magnesium content. In the case of soil samples of Bükk Plateau in the Ca^{2+}-K^{+} relation correlation is significant to the three main vegetation types. So in soils, where the calcium content is higher, the potassium content is higher as well. This must be in connection with the higher pH caused by Ca, because leaching of K is less from neutral soils than from acid soils. The significant correlation coefficient between Ca and K proves that rendzina soils have higher available Ca and K content that brown forest soils with clay illuviation, red clay soils and soils in the bottom of dolinas. The significant correlation between K and Mg means that in rendzina soils not only the potassium but the magnesium content is higher. In the soil samples of Mecsek quantitative correlation can be detected in the case of all the three ion pairs.

7. By examining the effects of the pH of soils and organic matter content thereof to the quantity of cations I established that there is a significant correlation between the pH and the quantity of calcium and potassium in the case of the soils of *Aggtelek area*: the higher the pH of soil the higher the Ca and K content of it. In the case of magnesium there is a significant negative correlation with pH regarding meadow soils. There is no significant correlation between organic matter content and quantity of Mg and K. There is significant correlation only between organic matter content and quantity of calcium in the case of meadow soils of Aggtelek area. In the area of *Bükk Plateau* (there are mainly rendzina soils) the available calcium quantity basically shows connection with pH. The correlation is significant between organic matter content and calcium content only in the soils of beech forests. However, in the case of magnesium and potassium organic matter content shows significant correlation, so not pH but the quantity of organic matter affects the quantities of these two

ions. So the organic matter content is a much stronger influencing factor in the soils of Bükk than of Aggtelek. In the case of soil samples of *Mecsek* the pH and organic matter content of soil thereof very strongly affects the quantities of all the three ions, the correlation is significant in each cases. In the shallow rendzina soils of Vörös-hegy pH, and the content of organic matter, plant available calcium, magnesium and potassium is higher than in the deep brown forest soils with clay illuviation of Szuadó- and Körtevélyesi-valley.

8. I examined the **heavy metal content** of the soils in the three areas. *The heavy metal content of the soils of Mecsek is the lowest*, in terms of all examined heavy metals. The heavy metal loading of soils of *Aggtelek Karst* is not remarkable in terms of Zn, Pb and Co: heavy metal contents do not exceed contamination limit values. In the case of *Cd and Cr there are excesses of limit values* (these are not considerable); but these soils belong to protected areas so the phenomenon has to be indicated. The heavy metal loading of the soils of *Bükk Plateau* is not serious in terms of Zn, Pb, Co and Cr contents: they do not exceed contamination limit values only in the case of lead, at two sampling points. However, *Cd content is above limit values* in the majority of the samples. As regards the soils of Aggtelek and of Bükk there were remarkable exceeds in the case of Cd, Co and Cr: the quantity of Cd is higher in the soil of samples of Bükk, the quantity of Co and Cr is higher in in the soil of samples of Aggtelek, compared to the other area.

Cadmium is the most dangerous out of the heavy metals being present above limit value since it is the most mobile out of the examined ones: it becomes mobile under pH 6-6.5. The Cd-pollution is high in Hungarian soils. It is mainly caused by the emission of industrial areas in East-Germany, Polland and Czech. It needs further investigation to clear up the role of antropogenic and geogen affects in the origin of Cd. The appropriate fixation of Cd can mainly be a problem in the upper soil layers with lower pH (pH<6.5). However, by knowing the available cadmium contents that *even the high pH* (around neutral) *and the very high organic matter content are not able to fix the metal appropriately*: this problem mainly arise in the soil samples of Bükk Plateau. It is important because even a neutral soil with very high organic matter content is not able to keep heavy metals fixed beyond certain limitations in the soils. The Cd content is lower in brown forest soils than in rendzina soils.

Only the soils of Aggtelek contain **chromium** above the contamination limit value. Since Cr becomes more mobile at pH<4.5 so an environment with appropriate buffering capacity is available for the soils in terms of pH. Cr

content available for plants is extremely low, and it can become mobile only if soil has a high degree of acidification.

It is ascertainable in the course of the evaluation of heavy metal content of soils bearing the main vegetation types of *Aggtelek area* that total Cd and Pb in terms of average value are present at similar concentration both in the soils of oak forests and meadows. The quantity of total Co and total Cr as well as the available Co is a bit higher in the soils of meadows as it is in the oak forests'. In turn the average total Zn content as well as the available Zn, Cd, Pb and Cr contents are higher in the soils of oak forests. On the basis of the researches performed in the *Bükk Plateau* the average total heavy metal contents of soils of beech forests exceed the total heavy metal content of the soils of pine forests and meadows in terms of all the examined heavy metals. In the case of the available heavy metals the highest figures characterise the soils of beech forests, too, except for Cr (that shows no significant difference in terms of vegetation types).

The characteristic surface concentration of Cd, Pb and Zn is in concord with the fact that the distribution of these metals is mainly determined by their strong fixation to organic matters so they can be found in larger quantity in the upper soil layer richer in organic matters.

On the basis of the percentage of the available heavy metal quantity out of the total heavy metal quantity (A/T%) I determined the **mobility order of heavy metals**:

In the case of soil samples of Aggtelek Karst: Cd >> Co > Pb >> Zn >> Cr.
In the case of soil samples of Bükk Plateau: Cd >> Pb >> Co > Zn >> Cr.
In the case of soil samples of Mecsek: Cd >> Pb > Co >> Zn > Cr.

9. According to the **correlation analysis** in the case of soils in *Mecsek* area total **heavy metal contents** showed significant positive correlation **with pH of soils** except Co. The available Cr provides negative correlation: in the examined soils with lower pH the available Cr content is higher than in neutral soils. There is no significant correlation between pH and heavy metals in the case of *Aggtelek* soils. In the soils of *Bükk Plateau* the correlation between pH and total quantity of Cd and Cr is significant. The results not indicate that generally soils with higher pH have higher heavy metal content: it is proved only in the rendzina soils and some brown forest soils examined by me.

A close positive correlation can be detected **between organic matter content and heavy metal content** but in the case of soils of Aggtelek only available Cd, while in the case of soils of Bükk the available and total content of Zn and Pb and the available Cd and Co show correlation with organic matter

content. In the soils of Mecsek area the available and total Zn and Pb and the available Co-content has significant correlation with organic matter content.

On the basis of correlation coefficient the organic matter content has stronger effect on the quantity of available heavy metal content than on total heavy metal content. By examining together the data of all the three sampling areas it is ascertainable that mainly *the relevant total heavy metal content is responsible for the available quantities of Cd and Pb* (correlation coefficient is the highest in this case), *for the available* quantities of *Cr the responsible factor is pH*, while *for the available* quantity of *Co the responsible factor is* mainly *the organic matter content*. In the case of available Zn is difficult to decide whether the quantity of organic matter (Bükk Plateau) or the quantity of total Zn-concentration is the main responsible factor.

Correlation analyses performed between the concentrations of the single heavy metal-pairs showed that significant correlation exists between the amount of Zn-Cd, Zn-Pb and Cd-Pb in all the three areas.

10. In the course of the **dolina examinations** the *characteristic distribution of the single soil parameters by quarters is the most prominent result*. The sharpest differences can be found in the dolina of Bükk Plateau: in the soil of southern and western slopes pH, calcium carbonate and organic matter content as well as the quantity of cations and heavy metals are higher than in the two other slopes of the dolina as well as in the bottom of it. In the case of the dolina in Aggtelek Karst these differences are present but not in the case of all examined quantities (mainly not in terms of heavy metals) and not so strongly like in the dolina of Bükk Plateau. In the course of the examinations of heavy metal we found *Cd and Cr in the dolina in Aggtelek Karst to exceed the contamination limit value*, while *Cd in the dolina in Bükk* (like in the case of the soils of areas). *My investigations support the result of earlier researches: soil characteristics are different in different quarters of dolina, in connection with the special microclimate and vegetation conditions which affect soil development.*

11. Slope examinations showed slope redeposition only in the slope of Szuadó-valley (limestone covered with loess). All the examined parameters (content of organic matter, heavy metals, calcium, magnesium, potassium) are higher in the bottom of slopes than in the top of slopes. But along the other slopes the quantities of several parameters decrease. Among the examined slopes the Körtevélyesi- and Szuadó-valley is covered by loess (above limestone). There is only limestone on the slopes of Bükk Plateau. The limestone slopes in Aggtelek area are usually covered by red clay. The results justify, that *in soils with*

limestone parent rock the processes of slope redeposition differ from that, which occurs in soils with non-karst parent rocks. The rate of surface erosion is limited on slope with limestone parent rock: water can penetrate in the limestone fissures while transporting a lot of material to the depth. The other specific difference is, that soils on the top of slope generally thinner and mixed with limestone rocks, so they are mainly neutral or weakly acid. While soils on the bottom of slope are usually deeper, clayer and there are no or less limestone fragments in them so usually have lower pH. The vertical transport processes can differ according to pH. So *in karst area is not enough to consider only the slope redeposition processes: we must examine the vertical leaching effects in the deeper soils on the bottom of slopes as well.*

So soils are of very high importance in the development of karsts, in the changes of karst ecosystems. *Soil is quasi an indicator sphere of changes therefore the manifold examination of it (nutrient and heavy metal researches) is important both in the judgement of the current state and in terms of the future utilisation.*

List of publications appeared on this topic:

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