

**ACIDIFICATION AND OTHER KARST SOIL  
PROCESSES IN HUNGARY**

**ZAKISLJEVANJE IN DRUGI PROCESI V  
KRAŠKI PRSTI NA MADŽARSKEM**

**I. BÁRÁNY-KEVEI & L. MUCSI**

**Izvleček**

UDK 631.415:551.44(439)

**I. Bárány-Kevei & L. Mucsi: Zakisljevanje in drugi procesi v kraški prsti na Madžarskem**

Vzrok zakisljevanja rjave gozdne prsti je v temnosivem skrilavcu, proces pa pospešuje tudi kisli dež. Ker je plast skrilavca vedno tanjša, se večja delež kalcija v prsti, s tem pa tudi puferska kapaciteta. Ta je dovolj dobra na kamnitih prsteh in črnih rendzinah, toda vedno več anionov absorbirajo površine koloidov.

Ključne besede: krasoslovje, pedologija, kraška prst, zakisljevanje, mikroklima, procesi v prsti, korozija

**Abstract**

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**I. Bárány-Kevei & L. Mucsi: Acidification and other karst soil processes in Hungary**

The cause of the acidification in brown forest soil is the dark grey shale, and this process is made stronger by the acid rain. Thickness of the shale decreased and calcium content and the buffer capacity increased. The buffer capacity of rocky soil and of the black rendzina is good enough, but more and more anions are absorbed on the colloid surfaces.

Key words: karstology, pedology, karst soil, acidification, microclimate, soil process, corrosion

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## INTRODUCTION

On hidden opened karst areas (the karstic rock covered by soil, Bárány-Kevei - Jakucs 1984.) the effects of microclimate and plant cover success through the soil. The thickness of the soil layer, its permeability, as well as the physical and chemical properties take a significant part in the subsoil corrosion.

## DISCUSSION

The content of the water soluble anions and cations has important effect on the chemical properties of the soil, therefore their investigation is indispensable from the point of view of subsoil corrosion.

Fig. 1-2 shows the content of water soluble anions and cations in the soil of dolines and karst surfaces in Bükk Mountains and we present some data of soil type of Dinaric Karst. We can find low anion and cation content in the soil of dolines in Bükk, especially if we compare them with the data of Dinaric Karst.

The soil as a horizon of the activity of biogene factors also takes an important part in the process of karst corrosion. Apart from the fact that the roots of macroflora emit carbon dioxide during the root respiration, millions of microorganisms appear in the soil, producing carbon dioxide during the decay of organic materials. At the same time, they modify the chemical properties of the soil and have an influence on the aggressivity of the soluble water. The microbiotic activity is very effective in 0.5-1 m depth, which results in significant carbon dioxide emission. In the deeper soil layers, the activity of microorganisms decreases, then becomes strong again on the soil-rock boundary. The density of the bacterium population is in close connection with the soil moisture and pH value.

These exogenic ecologic factors can modify the process of weathering in a favourable or unfavourable direction. In this level, there may be some possibilities for intervention to decrease the unfavourable (for example the environmental pollution) effects.

The properties of infiltrating soluble water cannot be modified if it reaches the deeper rock layers the reactions are unreversible, such as

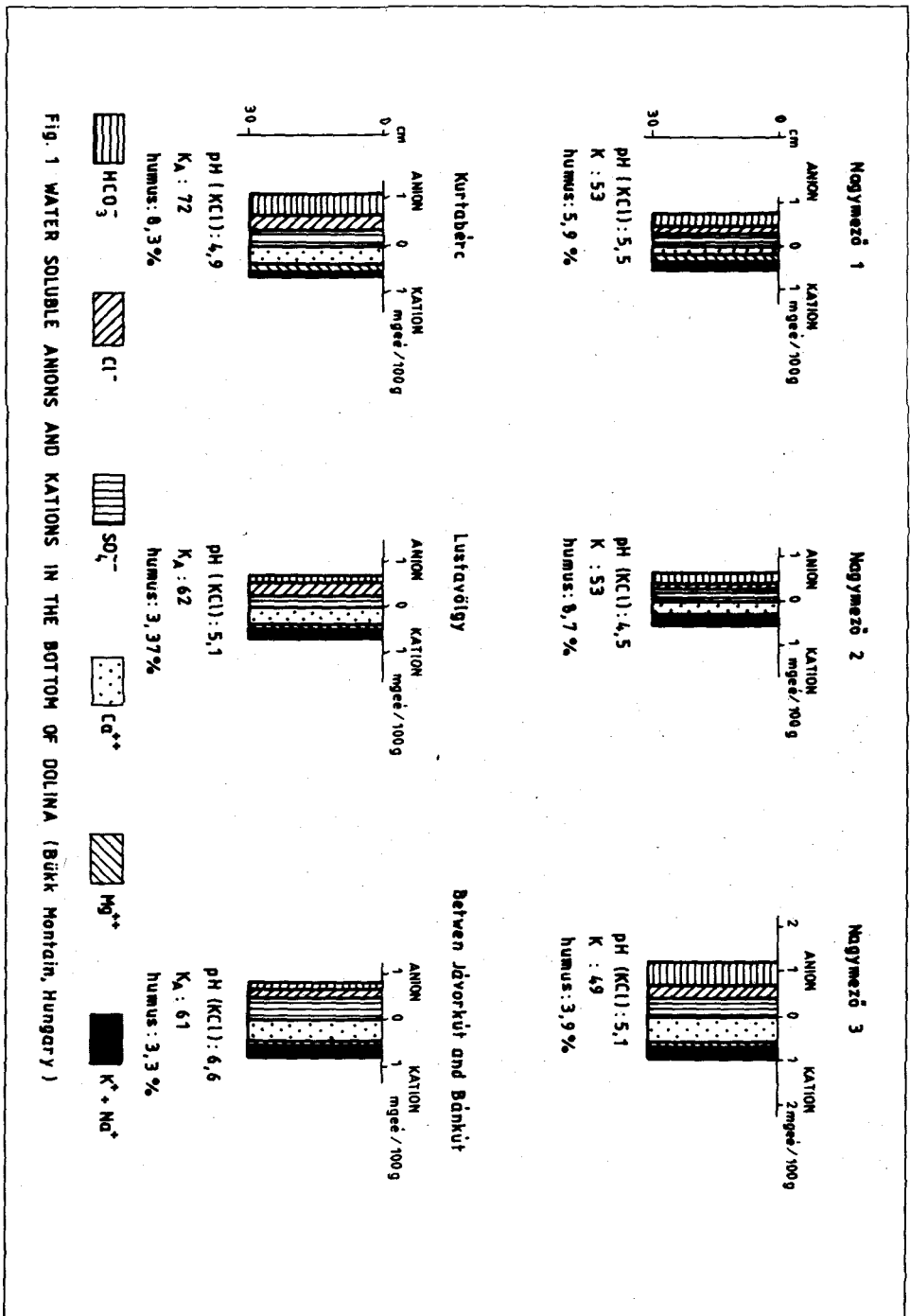
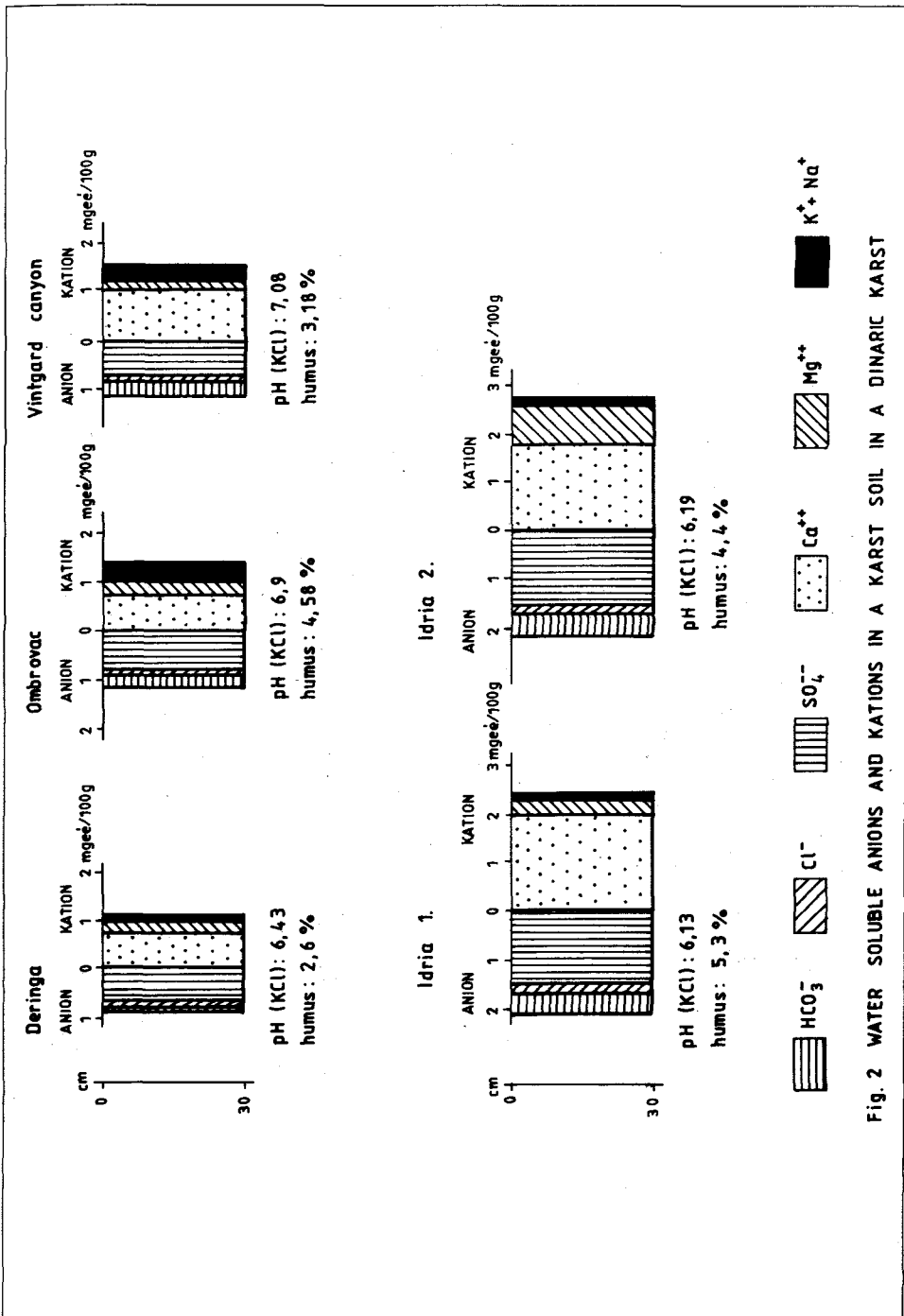
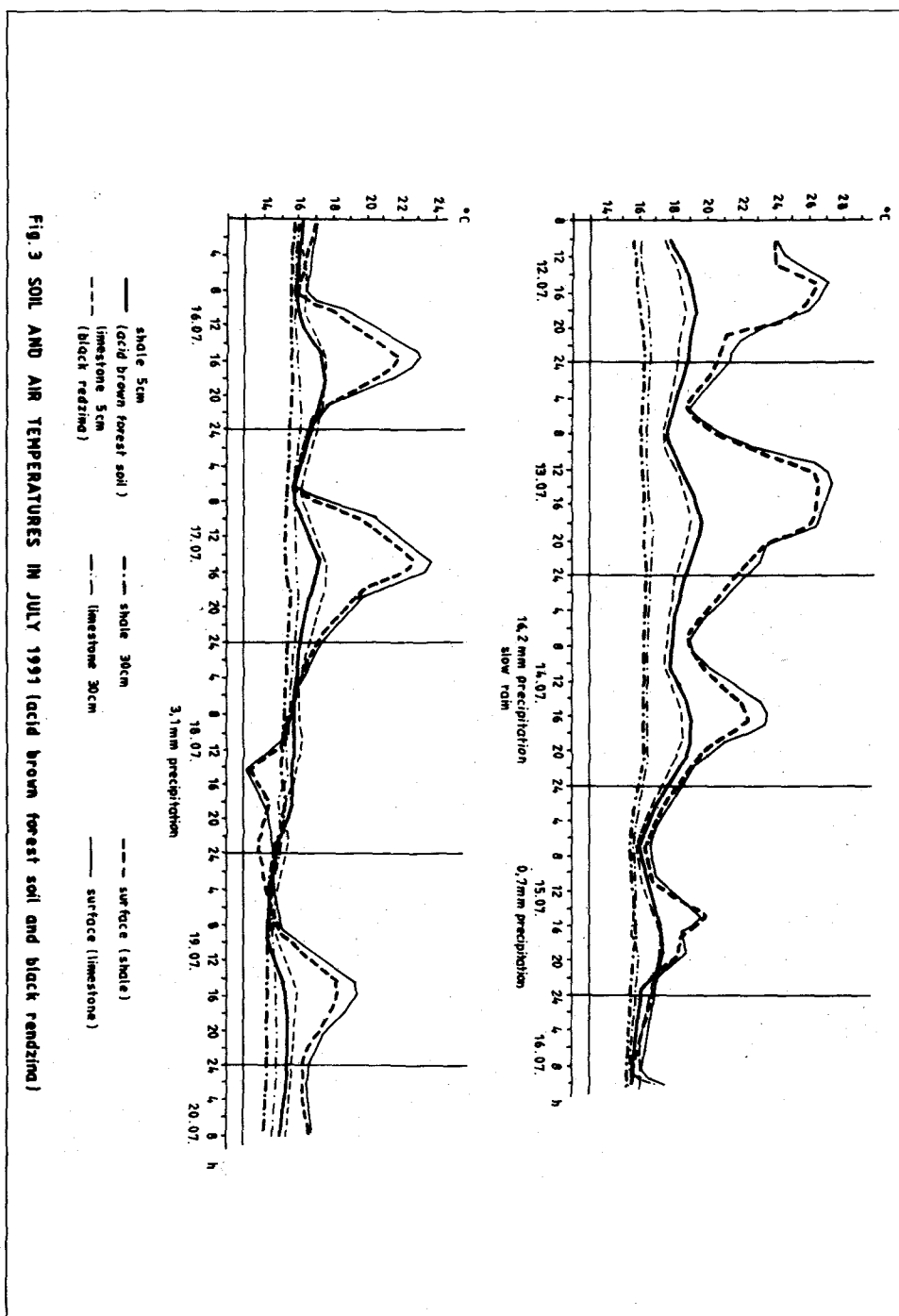


Fig. 1 WATER SOLUBLE ANIONS AND KATIONS IN THE BOTTOM OF DOLINA (BUKK MOUNTAIN, HUNGARY)





dripstone degradation in the European caves recognized by us. The effect of the polluting materials is similar to this process when they reach the karst water system, getting through the limestone layers and appearing in the karst springs.

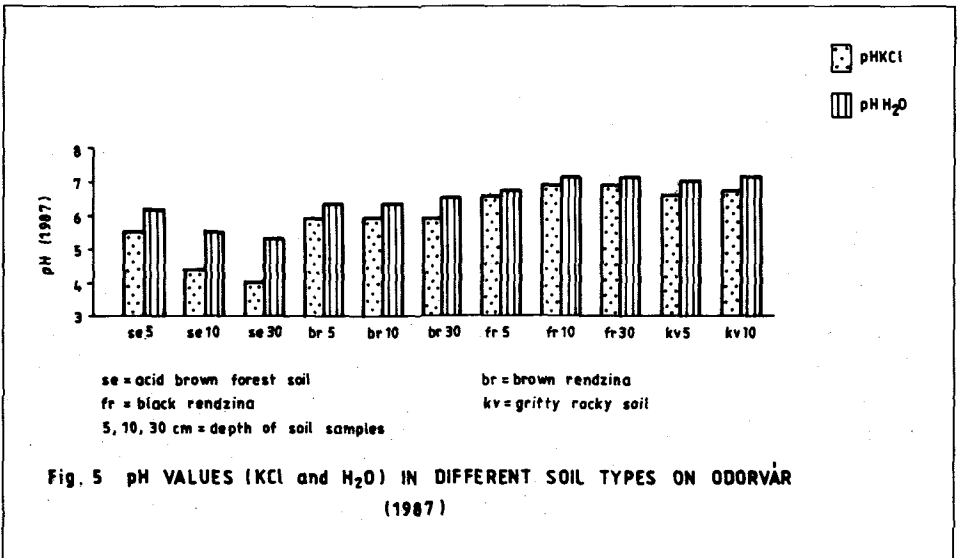
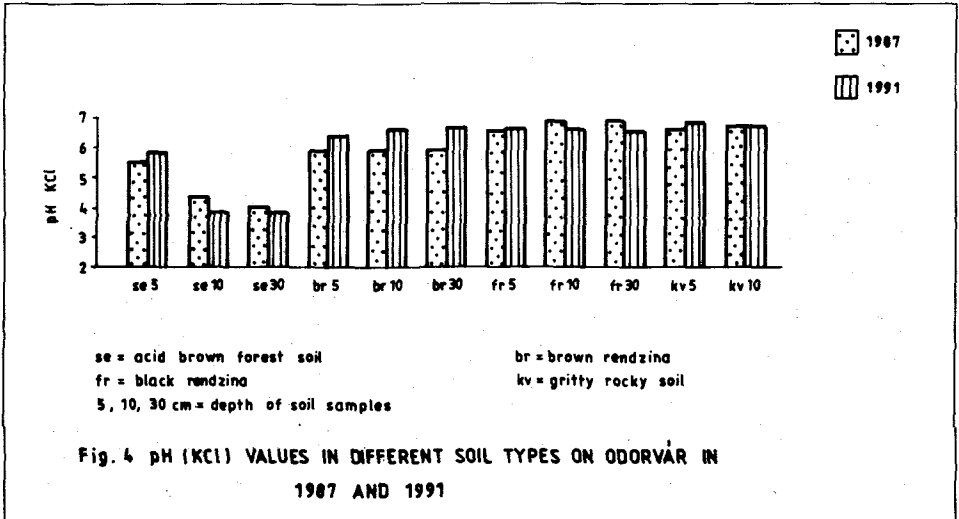
The climate is the one of the most important ecological factor of karst processes. Amongst the climatical factors, the rain and temperature have very strong influence on the intensity of karst processes. The microclimate could effect the microkarst processes such as development of solution forms. Differences in microclimate can be the causes of the formation of asymmetrical solution dolines (Bárány-Kevei, I.-Mezősi, G.1991).

Maximum and minimum temperature measured in the dolines show a considerable extreme values. The extreme values of temperature in karstic soil show considerable large differences on various slopes and various levels of soils (Bárány-Kevei, 1985., Mucsi L. 1992. Fig. 3).

In 0.5-1.0 m deep soil zone, the microbial activity results in a huge amount carbon dioxide production. On the soil-rock boundary, increased bacterial activity could be observed (Table 1). Our previous investigations carried out on the surface near dolines as well as the presented results suggest that the bacterial activity is the most important factor in the upper soil layer and on the soil-rock boundary. Further investigations should be focused in

depth (m)	aerob (10 <sup>6</sup> /g soil)	anaerob (10 <sup>6</sup> /g soil)
0.2	2.1	7.0
0.5	1.2	10.5
1.0	0.2	5.0
1.5	0.08	1.2
2.0	0.002	-
2.5	0.008	0.05
3.0	0.023	0.05
3.5	0.006	0.25
4.0	0.194	0.55
4.5	0.06	0.6
5.0	0.06	0.6
5.5	0.133	0.3
6.0	0.53	0.3
6.5	0.126	0.05
7.0	0.001	0.2
soil-rock boundary	0.256	0.3
crumled remnants	1.04	8.5
rock surface	3.86	2300.0

*Table 1. Numbers of aerobic and anaerobic bacteria in soil samples of doline:*



these zones (Bárány-Kevei, I. - Zábó, L. 1988) .

During the investigation of genetic soil-types on the area of Odorvár (Bükk Mountains) we recognized different processes connected with soil acidification. The most important factors in the acidification are

- pH of the precipitation
- buffer capacity of the soil
- chemical and physical properties of the base rock.



We have drawn patterns from 4 different soil-types in 1987 and in 1991 and have investigated their physical and chemical properties in connection with changes in acid properties.

### **Acidification in acid, non podzolic brown forest soil**

The acidification in brown forest soil is natural, non anthropogenic process. This soil type is formed on shale, phyllite, porphyrite and hydroandesite. It contains clay minerals formed before the beginning of soil formation. These minerals lose in their colloid properties significantly. The brownish-black illuvial layer is rich in humus, its structure is crumbled and grained. The pH value ranges from 3.5 to 4.5. We can always find aluminium and iron ions among the changeable cations. In the alluvial layer the acidification is a significant process as well (Stefanovits, P. 1981).

The acid property of brown forest soil is traceable quality of disintegrated remnants of dark grey shale, which is the base of the soil formation. The remnants of rocks which are poor in basic materials can be reduced in these components and this process produces favourable conditions for acidification (Máté, F. 1987).

We examined the changes in pH values in 1987 and in 1991. Figure 4 shows the pH values in three layers (5, 10 and 30 cm depth). The pH (H<sub>2</sub>O) values were 6.2, 5.5 and 5.3, while the pH (KCl) values were 5.5, 4.4 and 4.0. If the difference of distinctive pH value (e.g. pH (H<sub>2</sub>O)-pH (KCl)=1.3 in 30 cm) is greater than 1 in a special layer, it indicates to intensive acidification (Fig. 5).

The acidification in brown forest soil is basically formed by the chemical properties of dark grey shale, but this process may become harder due to the imission of acid materials of the atmosphere. Therefore we have investigated the sulphate and nitrate ion contents in distinctive soil-types. These materials are imitted onto the Earth's surface by dry and wet imission and they are washed down into the lower soil layers by precipitation. In connection with the buffer capacity of the soil we have found lower nitrate content in the lower layers, while the distribution of sulphate ions was more uniform in the whole soil profile. In 1987 the nitrate contents in different soil layers were 8.3, 2.3 and 1.5 ppm, while in 1991 the ion contents were 8 times greater than four years before (64.7, 11.5 and 4.8 ppm). The sulphate content also increased, but not so significantly. In 1987 the sulphate content was 10.8, 11 and 25.4 ppm, while in 1991 it was 18.6, 16.6 and 22.1 ppm (Fig.6).

The development of acid brown forest soil shows that the acid rainfall makes stronger the process of soil acidification. Due to the low buffer capacity, this tendency will continue.

### Process of acidification in soil types formed on limestone

Besides the geologic composition of the area of Odorvár, the acidification is being modified by climatic conditions. Basic materials are washed out from the upper soil layer by the seeping precipitation. The most soluble ions of alkaline metals and later their hydrocarbonates are carried away in the first stage.

During the changing of cations (calcium, magnesium cations and ions of metals found in soil) are the deputy of hydrogen ions of acids. Minerals are dissolved in precipitation and groundwater, which contain carbon dioxide. Positive ions of metals are carried away together with anions and negative bicarbonate ions by seeping water down to the lower soil layers. If later the sulphuric acid gets into the soil then magnesium and calcium ions are carried away by sulphate ions. While the sulphate solution transport the cations, hydrogen ions remain in the soil and these are the cause of the acidity of the soil (Mohnen, V. 1988).

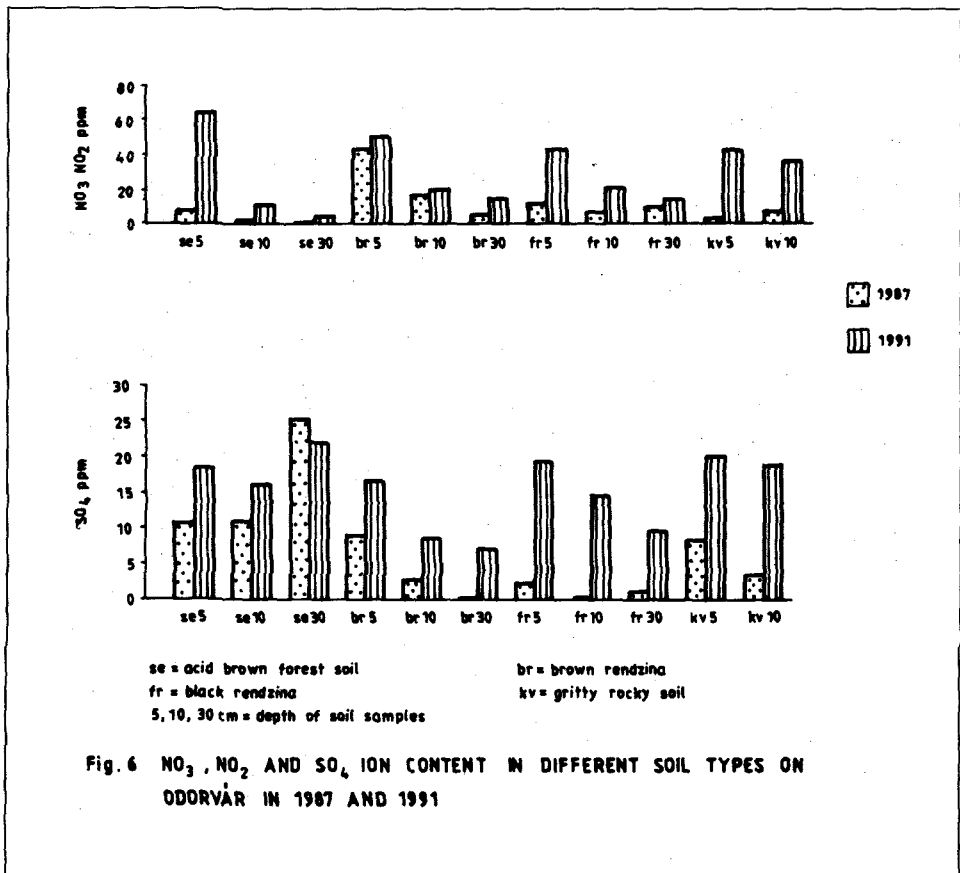


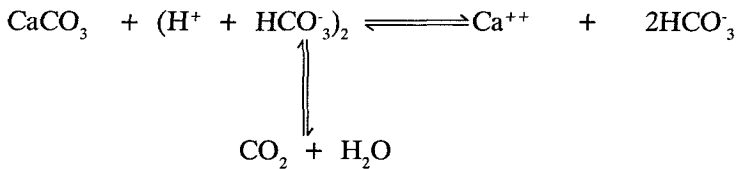
Fig. 6  $\text{NO}_3$ ,  $\text{NO}_2$  AND  $\text{SO}_4$  ION CONTENT IN DIFFERENT SOIL TYPES ON ODORVÁR IN 1987 AND 1991

The seeping water contains organic acids formed during the microbiological decomposition of plant residues, which are taking very important role in the acidification (biogenic factor). Acid organic materials arisen from the formation of humus combine with calcium ions into salt and calcium humate, if there is sufficient calcium carbonate in the soil. The chemical reaction of the soil solution does not change by acid and basic influences than that of the distilled water, because of the buffer capacity of the soil.

Different soil-types were formed on limestone on the area of Odorvár. The gritty, rocky soil is the erosional residue of black rendzina. The fragments of limestone and the calcium ion content of seeping water are the cause of the high buffer capacity of this soil-type. The surplus hydrogen ions are absorbed in the soil containing calcium and magnesium carbonates and chemical reaction of the soil layer is regulated by the



buffer system in accordance with the following chemical reaction (Filep, Gy. 1988.).



Therefore, the pH value of the soil solution does not decrease, while there are sufficient calcium and magnesium carbonates in the solid phase of the system. Calcium and magnesium ions can be washed out by seeping water if they are in solution.

Gritty, rocky soil does not cover the limestone surface continuously on the eastern, southeastern and southern slopes of Odorvár. The precipitation reaching the covered and uncovered surfaces can be a considerably acid solution.

The pH of the precipitation, because of the absorbed free carbon dioxide content of the air, is about 5.6, but the pH value can be 4.5 or lower if it dissolves air pollution emitted by industry (Mészáros, E.-Horváth, L. 1980.). Dissolution of limestone by runoff is started in spite of the high water velocity of the sinking water (rillen karren). If the sinking water is not saturated then it is able to absorb further calcium ions in the fractures of the limestone or in the soil. The process is made stronger by humus acids created by the decomposition of organic materials. The humus content of black rendzina

ranges from 5.5% to 10% (Fig. 7).

The most important factor in the soil acidification is the acid rain. We have found enormous differences between the sulphate and nitrate contents in soil sample gathered in 1987 and 1991. The sulphate contents was 8.4 and 3.5 ppm in 1987. We could pick up samples from two layers because this soil-type is strongly eroded by external forces. The sum of nitrate and nitrite ion content was 2.9 and 6.6 ppm. In 1991 the sulphate content was 20.4 and 19.2 ppm in the samples, while the sum of nitrate and nitrite ions was 42.5 and 5.5 ppm. The distribution of these anions shows that this very thin soil layer can absorb the acid factors of precipitation by its hard buffer capacity. The increasing sulphate and nitrate content proves that more and more anions are being absorbed on the colloid surfaces. If the sulphate and nitrate content of the precipitation does not decrease then the buffer capacity of the soil will become impoverished. If it ensues then the seeping water will not be saturated and it can dissolve the dripstones formed in the caves. On the area

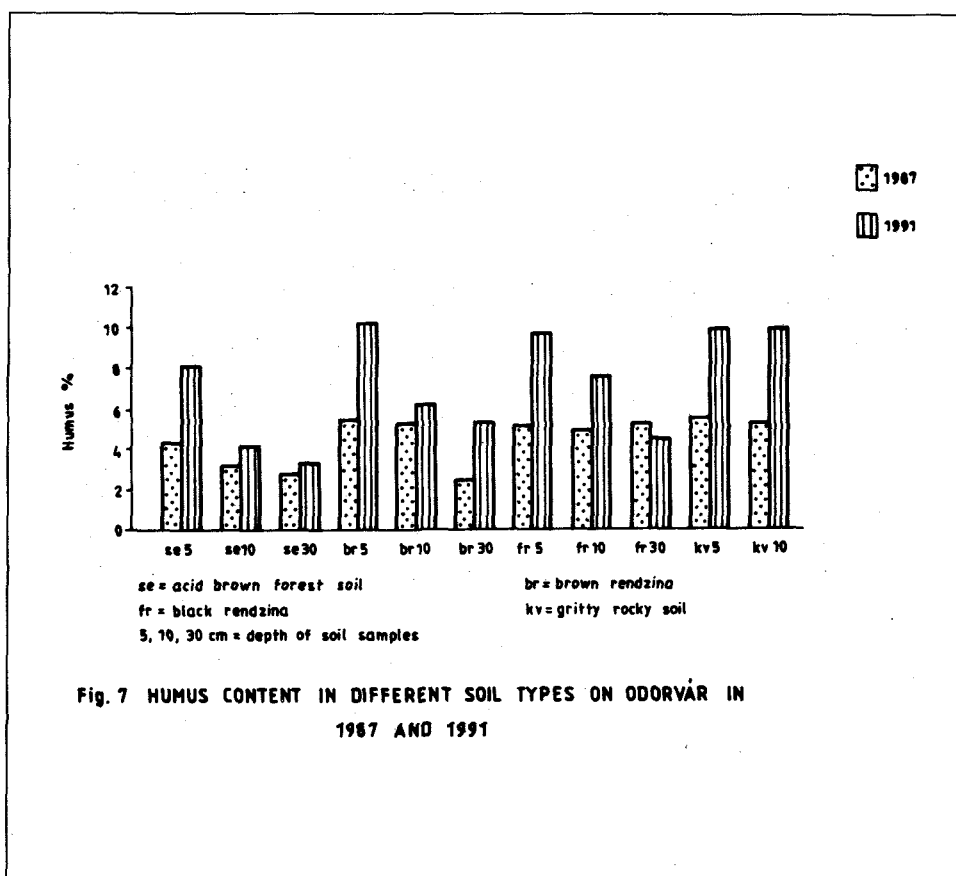


Fig. 7 HUMUS CONTENT IN DIFFERENT SOIL TYPES ON ODORVÁR IN 1987 AND 1991

of Odorvár, we can find very thin limestone layer over the Giant-chamber of Hajnóczy-cave. The degradation of dripstone phenomena can be traced back to other two reasons besides the effects of aggressive seeping water:

- a, there is lower relative humidity (80-85 % than in other chambers, therefore the dripstone layers are broken off from the stalagmites (physical process),
- b, the other reason for degradation is the guano of bats living in the cave. The dropping water is sinking through the guano, which can be 10 cm thick, and the seeping water becomes aggressive again.

## RESULTS

1. The cause of the acidification in brown forest soil is the chemical property of dark grey shale, and this process is made stronger by the acid rain.
2. The dark grey shale is eroded by the external forces, its thickness is decreased and calcium content and the buffer capacity of the soil are increased.
3. The buffer capacity of gritty, rocky soil and that of the black rendzina is good enough, but more and more anions are absorbed on the colloid surfaces.
4. Acidification in soil-types formed on limestone is made stronger by acid rains.

## REFERENCES

- BÁRÁNY, I. 1980. Some data about the physical and chemical properties of the soil of karst dolines. *Acta Geogr. Szegediensis* pp. 37-49.
- BÁRÁNY, I. 1985. Ökologische Untersuchung der Karstdolinen unter besonderer Berücksichtigung des Mikroklimas. *Acta Geogr. Szegediensis* Tom. XXV. pp. 109-130.
- BÁRÁNY-KEVEI, I - MEZŐSI, G. 1991. Further morphometrical data from some important Hungarian karst area. *Proceedings of the Int. Conf. on Environmental Changes in Karst Areas. Italy, 15-27 sept. 1991.* pp. 137-142.
- BÁRÁNY-KEVEI, I. - ZÁMBÓ, L. 1988. Study of the relationship between bacteria activity in karstic soils and corrosion. *Ann. Univ. Scient. Budapestensis de R. Eötvös Nom. Sectio Geographica. Tom. XX-XXI.* pp. 325-334. *Geographica. Tom. XX-XXI.* pp. 325-334.
- BOHN, H. L. - McNEAL, B. L. - O'CONNOR, G.A. 1985. *Talajkémia. Mezőgazdasági Kiadó - Gondolat Kiadó Bp.* 270 p.
- FILEP GY. 1988. *Talajkémia - Akadémiai Kiadó Bp.* 293 p.
- MÁTÉ F. 1987. *Talajsavanyodás - környezetsavanyodás. Term. Vil. 5.sz.* p. 146-148.
- MÉSZÁROS E. - HORVÁTH L. 1980. A levegő regionális háttér-szennyezettsége

- Magyarországon - Időjárás 84. p. 135-142.
- MOHNEN, V.A. 1988. A savas eső - Tudomány, p. 10-18.
- MUCSI L. 1989. Karsztalajvizsgálatok Odorvár környékén Szakdolgozat - Szeged p. 1-76.
- MUCSI L. 1989. Connection between different soil-types and seeping water system in the cave-Hajnóczy, Budapest X. International Speleological Congress II. Proceeding. p. 226-228.
- STEFANOVITS P. 1981. Talajtan - Mezőgazdasági Kiadó Bp. p.380.

## **ZAKISLJEVANJE IN DRUGI PROCESI V KRAŠKI PRSTI NA MADŽARSKEM**

### **Povzetek**

Na pokritem odprtem krasu (na kraški kamnini, pokriti s prstjo) (Bárány-Kevei & Jakucs 1984) segajo vplivi mikroklima in rastlinskega pokrova skozi prst. Debelina prsti, njena prepustnost, kot tudi njene kemijske in fizikalne značilnosti so pomembni dejavniki subkutane korozije.

Vzrok zakisljevanja rjave gozdne prsti je temnosivi skrilavec, proces pa podpira tudi kisli dež.

Temnosive skrilavce erodirajo eksogene sile, zato so vedno tanjši, obenem pa se povečuje v prsti vsebnost kalcija in se večja puferska kapaciteta. Ta je v kamniti prsti in v črni rendzini dovolj dobra, toda vedno več anionov absorbirajo površine koloidov. Zakisljevanje tipov prsti na apnencih pa pospešuje tudi kisli dež.