# TRACES OF EFFECTS OF ACID RAIN (SEDIMENTATION) IN THE RE-DISSOLUTION OF CAVE DRIPSTONES

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## Resum

Des del 1980 vaig començar a observar que certs espeleotemes (especialment estalagmites) de coves càrstiques d'Hungria presentaven fenòmens de redissolució, els quals no havien estat visibles en aquestes coves 5-10 anys abans. Aquestes deformacions inqüestionablement es deuen als efectes corrosius de les aigües càrstiques que alimenten els esmentats espeleotemes. Amb la intenció de clarificar les causes d'aquest efecte, els meus companys i jo mateix començàrem les investigacions no tan sols a Hungria sinó també en coves de Txecoslovàquia, Rumània, Bulgària, Iugoslàvia i Austria. Fou possible establir que l'extensió del fenomen és universal a Europa Central, encara que en diversos graus depenent de les particulars condicions naturals de cada cova.

*Signes de la síndrome de degradació recent dels espeleotemes:* cràters irregulars de voreres agudes i dentades; calderes amb els costats soscavats; solcs de drenatge poc fondos, amb voreres tallants; redissolució superficial de l'espeleotema en la zona d'esquits produïts per degotaments des d'una certa altura; sovint, el subsegüent reblaniment del material dels espeleotemes, que presenten, així, un aspecte cremós.

Les investigacions que he realitzat fins ara indiquen que una gran gruixa de la coberta edàfica bioactiva i permeable que reposa sobre la roca carstificable, així com la major profunditat de les arrels de la macrovegetació (arbres de fulla caduca) desenvolupada sobre l'esmentat sòl, són responsables d'una gran incidència i extensió d'aquest nou tipus de redissolució d'estalagmites i espeleotemes en general. En base a les dades disponibles, pareix probable que els boscos de pins tinguin un paper una mica diferent en aquest aspecte, en comparació amb el paper desenvolupat pels boscos d'arbres de fulla caduca, per exemple, roures, faigs, etc.

Es pot comprovar un cert grau de proporcionalitat inversa entre la freqüència de la síndrome de degradació dels espeleotemes i la profunditat de la cova en qüestió respecte de la superfície. A una cova situada a menys profunditat amb relació a la superfície, li correspon una presència més probable d'aquest nou tipus de degradació d'espeleotemes.

Subsegüentment, vaig realitzar una sèrie d'anàlisis per establir de quina manera la síndrome de degradació observada es correlaciona amb el pH del sòl càrstic i amb els paràmetres microbiològics i de composició del sòl. Foren documentades les tendències en els canvis químics de les aigües càrstiques que penetren en les coves.

Es pot constatar que, en comparació amb les dades d'anàlisis d'aigües realitzats el 1929, els quals foren emprats com a base de referència, hi ha hagut un increment del 400-600 % en el contingut de sulfats de les aigües càrstiques que gotegen en idèntics punts de les coves; foren observats també petits increments en els continguts de nitrats i clorurs. En aqueixes coves i, en particular, en les zones on la redissolució dels espeleotemes era especialment intensa, el contingut de sulfats de les aigües càrstiques era més alt que la mitja.

Les meves investigacions suggereixen, per tant, que *aquesta degradació dels espeleotemes pot ser induïda pel recent i fort increment de la concentració de sulfats en les aigües càrstiques, o indirectament per qualsevol dels factors responsables de l'esmentat increment en el contingut de sulfats.*

## Summary

From 1980 on, I began to discover that certain dripstones (mainly stalagmites) in karstic cave systems in Hungary were exhibiting re-dissolution phenomena which had not been visible in the caves 5-10 years previously. These deformations unquestionably arise from the corrosional effects of karst-waters permeating onto the dripstones. With a view to clarifying the causes of this effect, my colleagues and I commenced researches in situ not only in Hungary, but also in caves in Czechoslovakia, Rumania, Bulgaria, Yugoslavia and Austria. We established that the spreading of the phenomenon is universal throughout Central Europe, though to different extent in caves with different natural features.

*Signs of the recent dripstone degradation syndrome:* sharp, jagged-edged, irregular-shaped craters; «calderas» with undermined sides; sharp-edged, basin-like drainage trenches; areal dripstone

surface re-dissolution in the splash-spray zone of the water drops falling from the heights; in certain cases almost total dripstone dissolution; often, the subsequent softening of the material of the dripstones, which become cream-like.

My investigations to date indicate that, the thicker the bioactive and permeable soil layer covering the karst rock, and the deeper the roots of the macrovegetation (deciduous trees) growing in this soil, the more frequent or the more extensive the new type of dripstone re-dissolution. On the basis of the available data, it seems probable that pine woods play a somewhat different role in this correlation system from the role of deciduous woods, e.g. oak, beech, hornbeam, etc.

A certain degree of inverse proportionality can be documented between the frequency of occurrence of the dripstone degradation syndrome and the depth of the cave zone in question beneath the surface. The smaller the depth of a cave system beneath the surface, the more likely the occurrence of this new type of dripstone degradation in it.

I subsequently made a wide-ranging analysis of how the observed degradation syndrome is correlated with the pH of the karst soil and with the microbiological and soil-composition parameters. The trends in the chemical changes of the karst-waters entering the caves were documented.

It turned out that, compared to the water analysis data from 1929, which were used as reference basis, there had been an increase of 400-600 % in the sulphate content of the karst-water dripping in at the same points of the caves; smaller increases were also observed in the nitrate and chloride contents. In those caves and on those dripstones where the dripstone re-dissolution was particularly extensive, the sulphate content of the karst-water was higher than average.

My researches therefore suggested the result that the recent dripstone degradation may be induced *either by the recent strong increase in the sulphate concentration of the karst-waters, or indirectly by one or other of the factors responsible for the increase in the sulphate content.*

In karst caves one can encounter extensive signs of dripstone degradation processes induced by some form of corrosion, i.e. the re-dissolution of the material of the dripstone. There may naturally be numerous causes of corrosional dripstone degradation, and the system of the mechanism of action, involving the correlations between the inducing factors and the resulting degradation symptoms, are fairly well known. A number of types of corrosional dripstone degradation are known which have *age-independent* genetics, i.e. which may occur in *all phases* of the development of a cave system; the system of conditions for their formation were present in the distant past of the cave (or in certain periods in the distant past) in the same way as in the present day. Unfortunately, however, the results of my researches indicate that there are also certain corrosional processes which are causing the degradation of cave dripstones *only in the present;* prior to the period covering the past 10-20 years, these processes have not been manifested anywhere or at any time in cave formations.

The first group, i.e. the group of corrosion variants manifested *independently of the age,* include corrosion by *unsaturated cave waters, mixing corrosion, humidity condensation dripstone corrosion,* the *corrosion of cave soils and karst-water clay, guano corrosion* and the corrosion of dripstones of cave entrances. These are the *traditional* or *permanent* types of corrosional dripstone degradation.

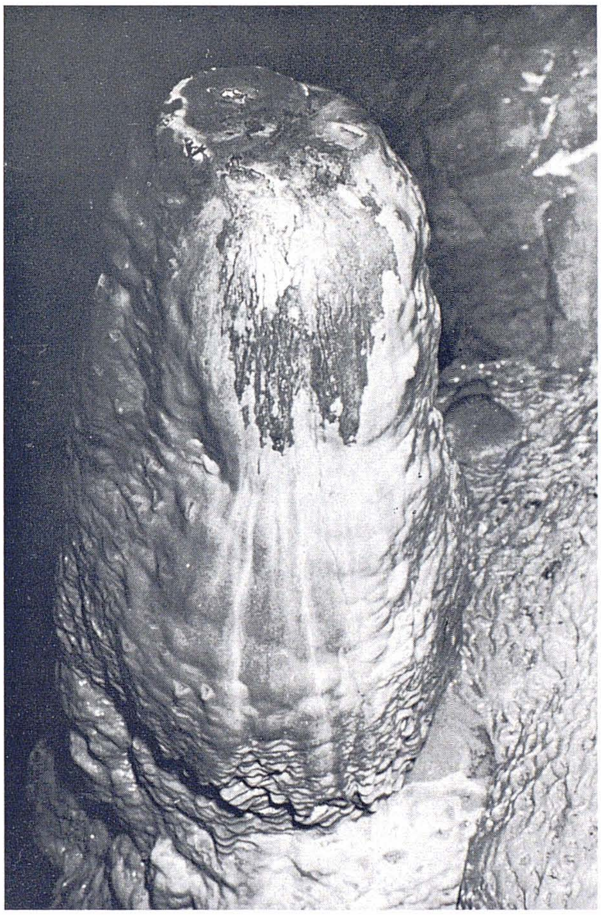

Photo 1. A stalagmite that has been degrading seriously for several years in the chamber «Magyarok-bejövetele» in the Baradla Cave in Hungary. The recent corrosion by the continuously dripping karst-water has etched away the outermost (youngest) dripstone layers.

These may be clearly distinguished from a characteristic group of symptoms of dripstone degradation which were earlier *never* observed anywhere in caves. The latter have appeared in the second half of the twentieth century, and I have therefore named this phenomenon the *recent dripstone degradation syndrome.*

From 1980 on, I began to discover that certain dripstones (mainly stalagmites) in karstic cave systems in Hungary were exhibiting re-dissolution phenomena which had not been visible in the caves 5-10 years previously. These deformations unquestionably arise from the corrosional effects of karst-waters permeating onto the dripstones. With a view to clarifying the causes of this effect, my colleagues and I commenced researches in situ not only in Hungary, but also in caves in Czechoslovakia, Rumania, Bulgaria, Yugoslavia and Austria. We established that the spreading of the phenomenon is universal throughout Central Europe, though to different extents in caves with different natural features.

## Signs of the recent dripstone degradation syndrome

Sharp, jagged-edged, irregular-shaped craters; «calderas» with undermined sides; sharp-edged, basin-like drainage trenches; areal dripstone surface re-dissolution in the splash-spray zone of the water drops falling from the heights; in certain cases almost total dripstone dissolution; often, the subsequent softening of the material of the dripstones, which become cream-like (See Photos 1-3).

It must repeatedly be emphasized that the recent dripstone degradation syndrome I have investigated and described involves damage to dripstones that has occurred for at most few years (possibily around a decade). This damage is observed virtually exclusively at those points in the dripstone caves that are subject to the most continuous dripping; similar changes are never to be seen in or on the long ago formed layers or surfaces of the same formations. This correlation can be checked particularly easily in those caves which have long been known and visited, and in which, in the period of visits by torchlight (right up to the beginning of the twentieth century), a layer of soot of various thicknesses was deposited from the torch smoke onto the dripstone and the rock surfaces. To outline the essence: *the dripstone degradation syndrome I was studying is not present anywhere under the soot layer.* This means that in the course of development of these caves *a clear distinction may be made between a «pre-soot», symptom-free developmental period lasting for many thousands of years and very brief, «post-soot» active degradation period lasting at most a few decades* (but in my view probably rather only a few years), which has left active recorrosional (re-dissolution) traces on the surfaces of many cave dripstones, and which has even led in one or two cases to the total destruction of the dripstone formation (see Photo 4).

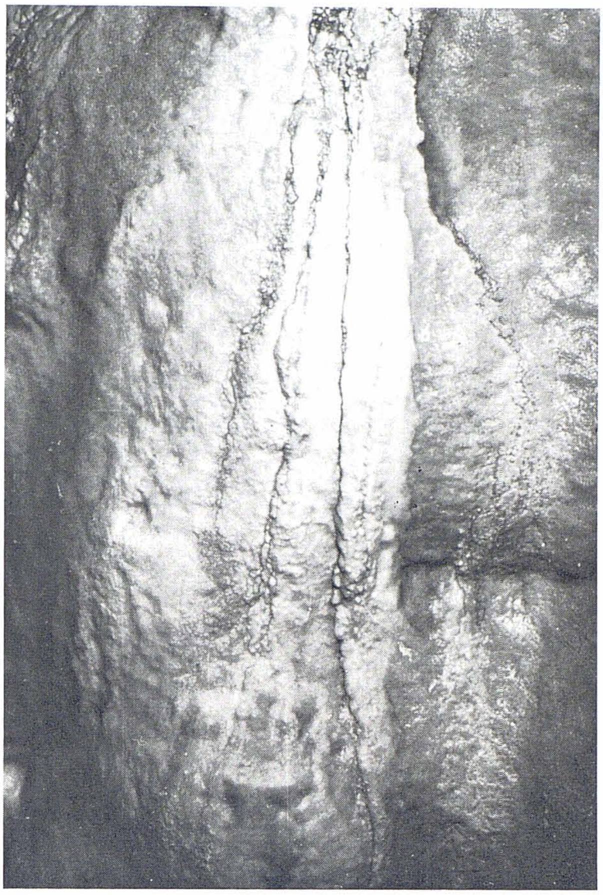

Photo 2. The altered character and effects of the water dripping onto the dripstones are indicated by the sharp-edged corrosion pits at several sites on the sides of the stalagmites. The photo was taken in the «Meseország» section of the Aggtelek Cave in Hungary.

## Research into the causes of the degradation syndrome

This recent dripstone re-dissolution is generally displayed by the youngest dripstone formations, which are still active as regards water-dripping, and which in the vast majority of the cases are light in colour (frequently white). The phenomenon is to be observed only in certain zones of the caves. The degradation usually exhibits group occurrence, but stalagmites not showing signs of re-dissolution may be encountered in the immediate vicinity of degrading dripstones. Research into the causes of the symptoms is still continuing, but

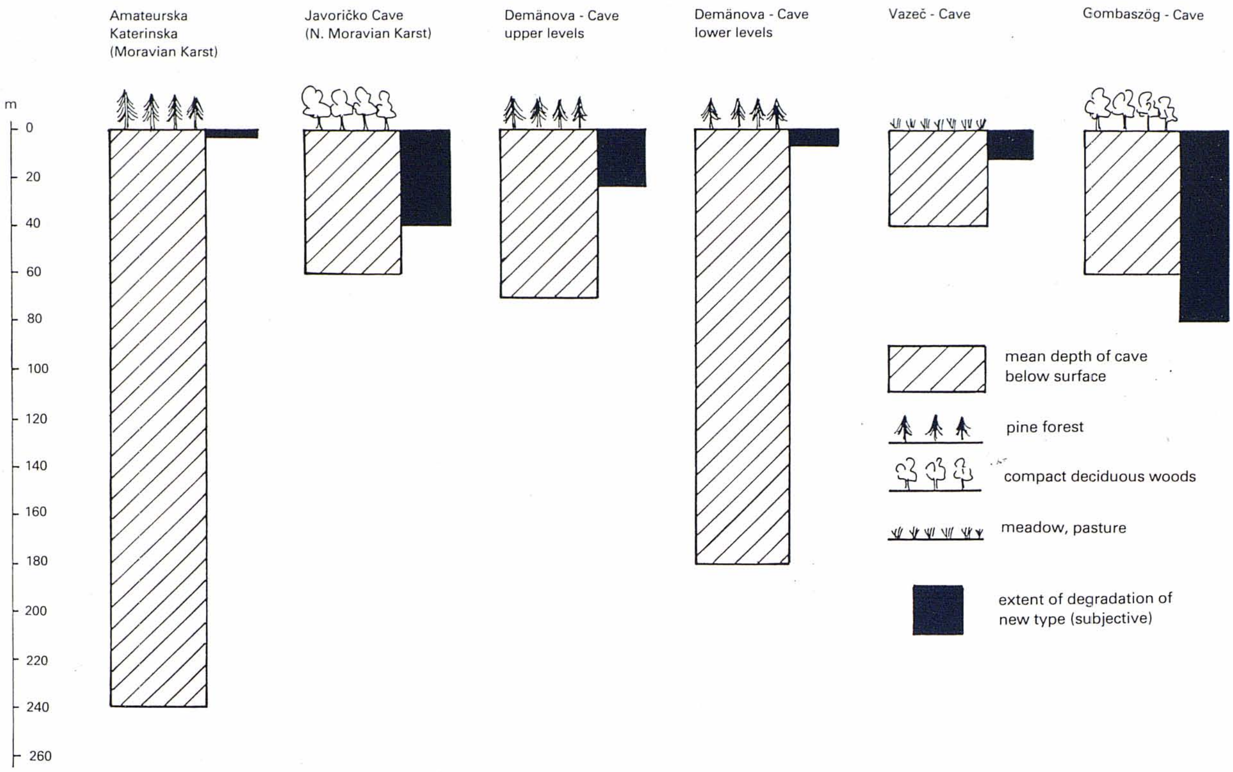


Figure 1. Assumed correlation system between depths of some czechoslovak cave systems below the surface, the type of surface vegetation, and the degree of present dripstone degradation (original).

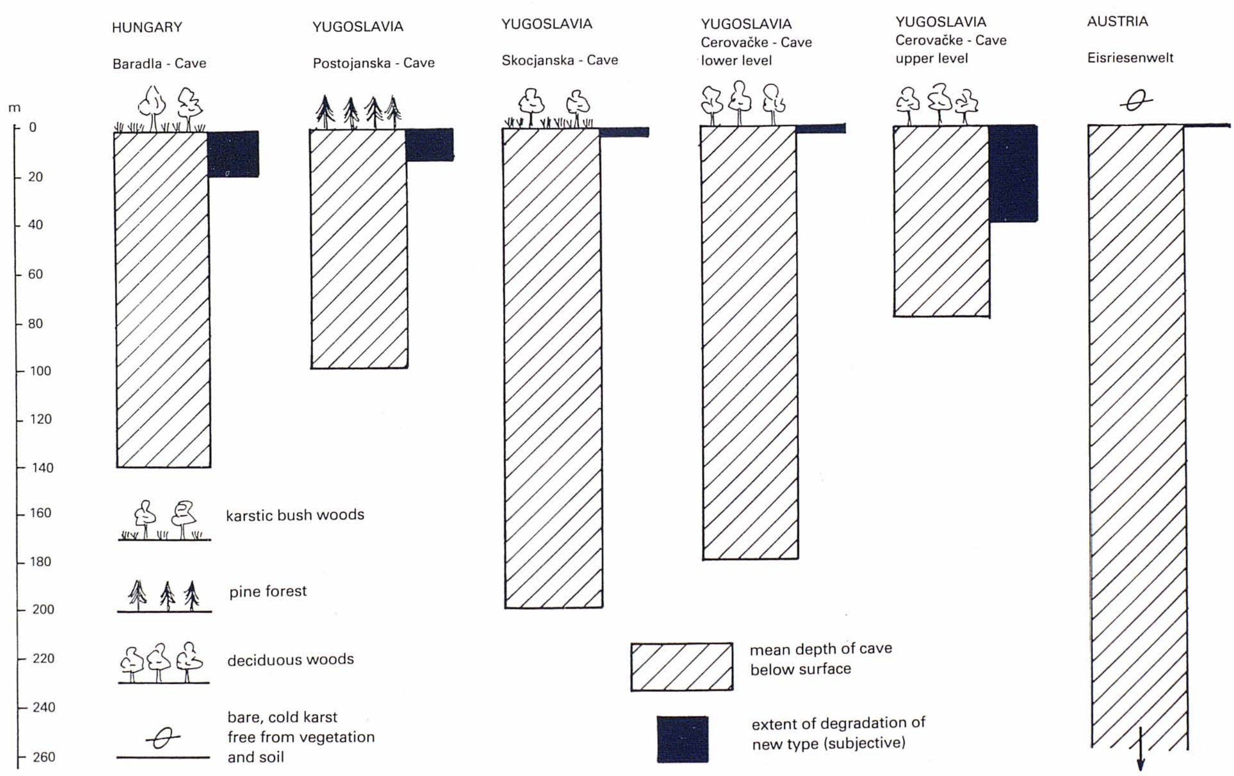


Figure 2. Assumed correlation system between depths of some hungarian and foreign cave systems below the surface, the type of surface vegetation and the degree of present dripstone degradation (original).

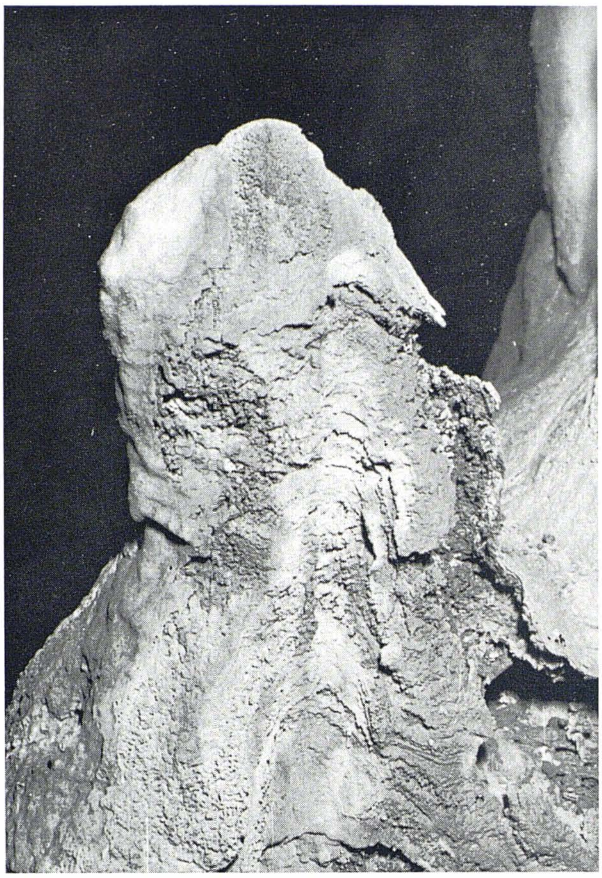

Photo 3. A stalagmite about 30 cm high in the Gombaszög Cave in Czechoslovakia. Within a few years, one side of the previously intact, smooth-surfaced stalagmite has been totally degraded by the phreatic water permeating through the wood-covered soil.

Photo 4. In recent years the dripping karst-waters have in some places become strongly aggressive towards lime. They no longer build up the stalagmites, but degrade them to their component layers. The dripstone has degraded to a loose structure, and the outer residues break away from the disintegrating figure. The photo also reveals how the rebounding karst-water spray is re-dissolving the dripstone layers of the rock walls too (Gombaszög Cave, Czechoslovakia).

it appears that sufficient data are already available for some assumptions to be made concerning the correlations. These are as follows:

1. In all cases, the re-dissolution of the dripstone is caused by the same water-dripping as that which earlier caused the build-up of the dripstone (primarily stalagmites are involved). The fact of degradation is therefore evidence that a change has occurred in the chemical or physicochemical properties of the water dripping onto the stalagmite.

2. My investigations to date indicate that, the thicker the bioactive and permeable soil layer covering the karst rock, and the deeper the roots of the macrovegetation (deciduous trees) growing in this soil, the more frequent or the more extensive the new type of dripstone re-dissolution. On the basis of the available data, it seems probable that pine woods play a somewhat different role in this correlation system from the role of deciduous woods, e.g. oak, beech, hornbeam, etc.

3. A certain degree of inverse proportionality can be documented between the frequency of occurrence of the dripstone degradation syndrome and the depth of the cave zone in question beneath the surface. The smaller the depth of a cave system beneath the surface, the more likely the occurrence of this new type of dripstone degradation in it.

The correlations referred to in points 2 and 3 are illustrated in Figs 1 and 2 on the example of some caves in Czechoslovakia, Hungary, Rumania and Austria.

I subsequently made a wide-ranging analysis of how the observed degradation syndrome is correlated with the pH of the karst soil and with the microbiological and soil-composition parameters. The trends in the chemical changes of the karst-waters entering the caves were documented.

It turned out that, compared to the water analysis data from 1929, which were used as reference basis, there had been an increase of 400-600 % in the sulphate content of the karst-water dripping in at the same points of the caves; smaller increases were also observed in the nitrate and chloride contents. In those caves and on those dripstones where the dripstone re-dissolution was particularly extensive, the sulphate content of the karst-water was higher than average.

My researches therefore suggested the result that the recent dripstone degradation may be induced *either by the recent strong increase in the sulphate concentration of the karst-waters, or indirectly by one or other of the factors responsible for the increase in the sulphate content.*

With the help of my colleague Ilona Bárány-Kevei, I was similarly able to document how the trends in the composition of the karst soils and in their microbiological conditions are correlated with the atmospheric acid sedimentation. On this basis it appears to be proved that the modifications in the chemical characteristics of the karst-water are connected with the trends in the physicochemical changes in the karst soil and with the present distortions in the ecological conditions of the soil micro-organisms. The recent dripstone degradation syndrome therefore provides *an overall indication of the effects of acid rain or sediments in the complex concatenation of correlations in the deeper karst levels* (see Tables 1-4 and Figs 3-5).

| water - sampling site | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 11. | 12. | 13. | 14. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| date of examination | 10.02. 1960. | 21.08. 1960. | 05.03. 1982. | 20.11. 1957. | 05.03. 1982. | 22.11. 1957. | 19.08. 1960. | 06.03. 1982. | 22.09. 1979. | 22.09. 1979. | 26.11. 1929. | 23.07. 1969. | 08.07. 1981. | 07.03. 1982. |
| pH | 7.1 | 7.3 | 6.6 | 7.2 | 7.0 | 7.2 | 7.1 | 7.0 | 6.9 | 6.9 | 7.5 | 7.2 | 7.0 | 6.9 |
| $Ca^{++}$ mg/l | 103.0 | 124.0 | 86.0 | 92.0 | 83.0 | 101.0 | 122.0 | 99.0 | 92.2 | 98.6 | 54.2 | 106.0 | 111.0 | 83.8 |
| $Mg^{++}$ mg/l | 1.0 | 2.2 | 1.4 | 4.5 | 2.2 | 1.9 | 1.9 | 3.7 | 12.2 | 11.3 | 3.2 | 2.1 | 3.1 | 3.3 |
| $HCO_3^-$ mg/l | 298.0 | 370.0 | 281.0 | 322.0 | 267.0 | 288.0 | 380.0 | 235.0 | 238.0 | 226.0 | 174.0 | 303.0 | 310.0 | 266.0 |
| $SO_4^{--}$ mg/l | 14.0 | 9.2 | 47.0 | 8.5 | 33.4 | 12.2 | 17.0 | 27.7 | 307.0 | 250.0 | 16.1 | 8.9 | 24.1 | 29.9 |
| $Cl^-$ mg/l | 3.0 | 3.6 | 8.2 | 4.1 | 6.8 | 2.3 | 2.1 | 16.1 | 11.0 | 11.0 | 3.6 | 5.0 | 14.3 | 6.5 |
| $NO_3^-$ mg/l | 16.2 | 14.8 | 43.2 | 13.7 | 40.9 | 12.2 | 14.2 | 9.7 | 5.9 | 2.2 | 1.0 | 4.2 | 20.3 | 23.5 |

1, 2, 3 = Baradla - Cave, Lace Well (Jakucs)
6, 7, 8 = Béke - Cave, Amphora (Jakucs)
10 = Létrási - vizes - Cave, Point 7 (Lénárt)
12, 13 = Postojanska - Cave, Calvary (Jakucs)
4, 5 = Baradla - Cave, Chinese Pagoda (Jakucs)
9 = Létrási - vizes - Cave, Point 4. (Lénárt)
11 = Baradla - Cave, Dessewffy Well (Maucha)
14 = Domica - Cave, Hall of Indian Pagodas (Jakucs)

Table 1. Comparative chemical analyses of various cave dripwaters at different and identical times

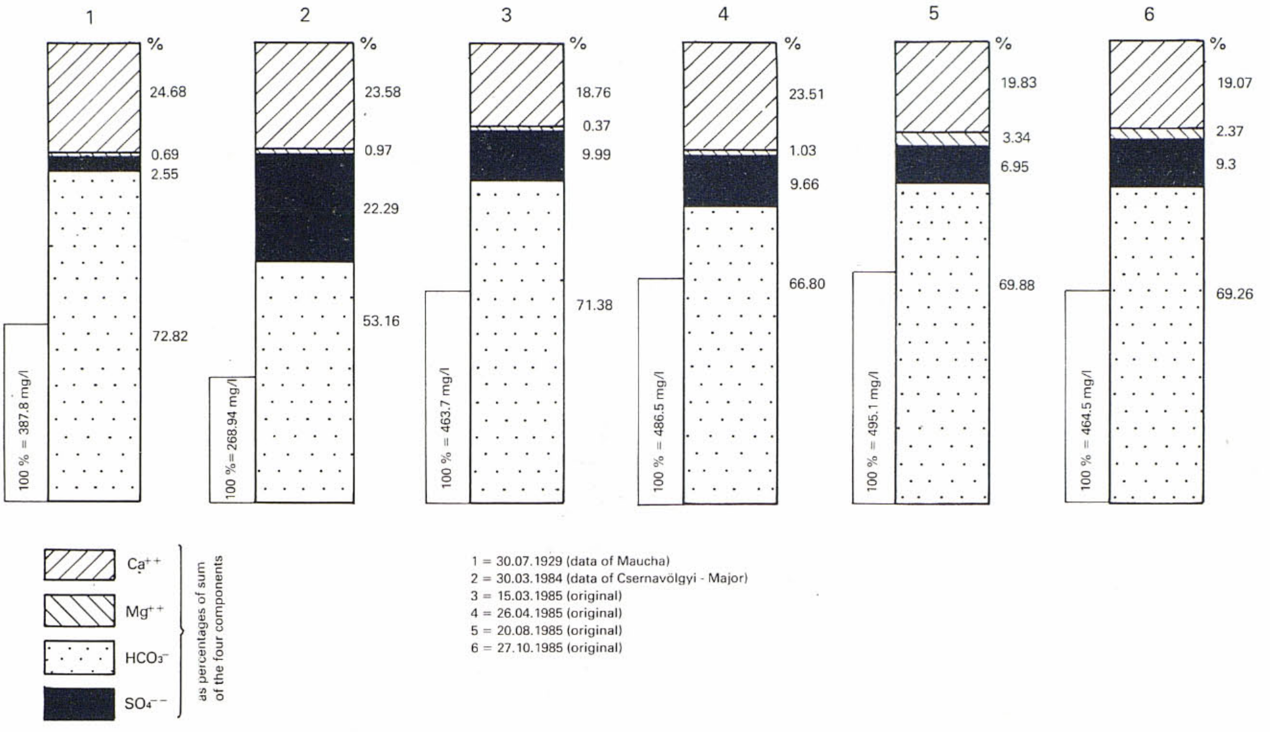


Figure 3. Water of «királykút» dripstone basin (Baradla - Cave at Aggtelek)

| mg/l | 30.07.1929. (Maucha) REFERENCE | 30.03.1984. (Csernavölgyi-Major) | 15.03.1985. (Jakucs-Franczia) | 21.03.1985. (Jakab-Major) | 26.04.1985. (Jakucs-Franczia) | 20.08.1985. (Jakucs-Franczia) | 27.10.1985. Jakucs-Franczia) |
|---|---|---|---|---|---|---|---|
| $Ca^{++}$ | 93.4 | 63.4 | 87.0 | 64.3 | 114.4 | 98.2 | 88.6 |
| $Mg^{++}$ | 2.7 | 2.6 | 1.7 | 12.7 | 0.5 | 3.3 | 2.4 |
| $HCO_3^-$ | 282.4 | 143.0 | 331.0 | 267.3 | 325.0 | 246.0 | 321.7 |
| $SO_4^{--}$ | 9.9 | 59.9 | 44.0 | 46.9 | 47.0 | 34.4 | 43.2 |
| $NO_3^-$ | 12.3 | −? | 20.2 | −? | 11.4 | 17.9 | 8.2 |
| $Cl^-$ | 2.7 | 25.4 | 7.1 | 1.8 | 14.4 | 21.0 | 5.8 |

Table 2. Analytical data on ions expressing the trends to change in the water composition of the "Királykút" dripstone basin in the Baradla cave

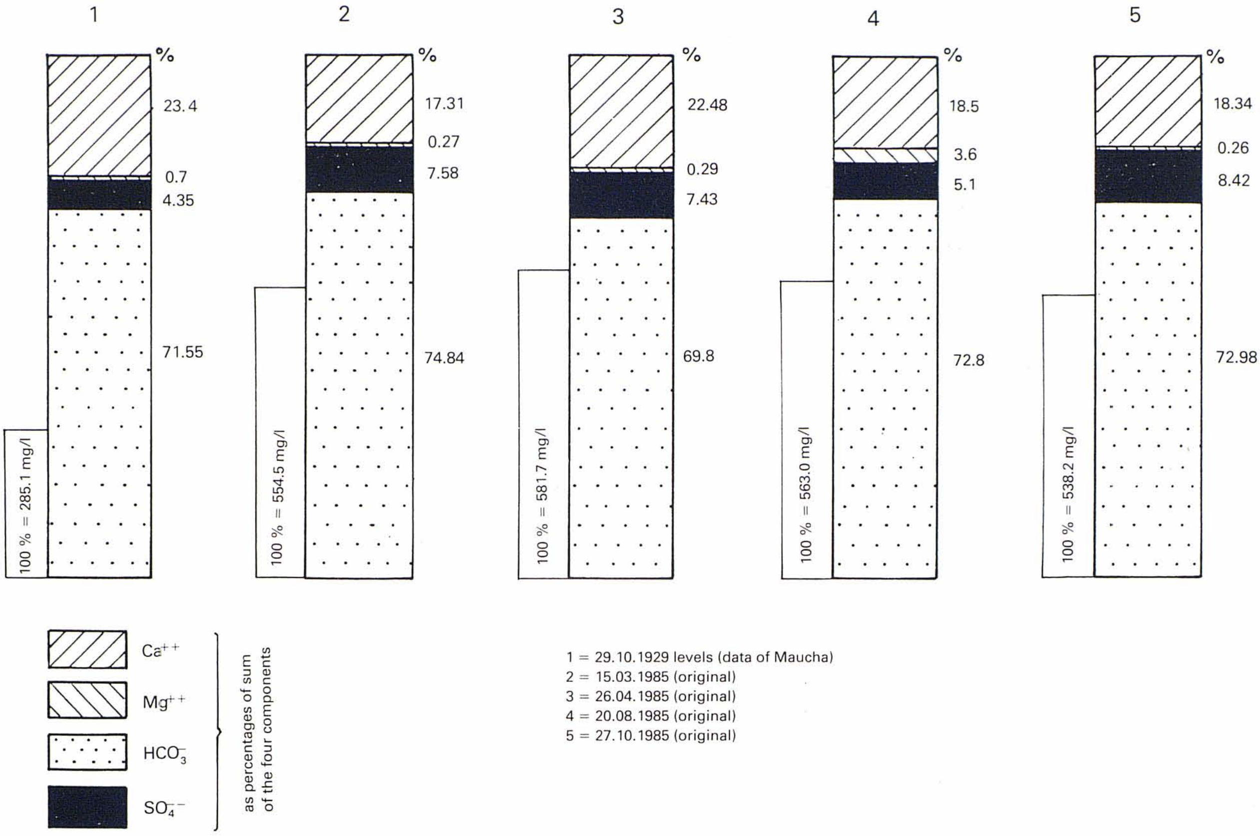


Figure 4. Water of «kéregetö - koldus» stalagmite (Baradla - Cave at Aggtelek)

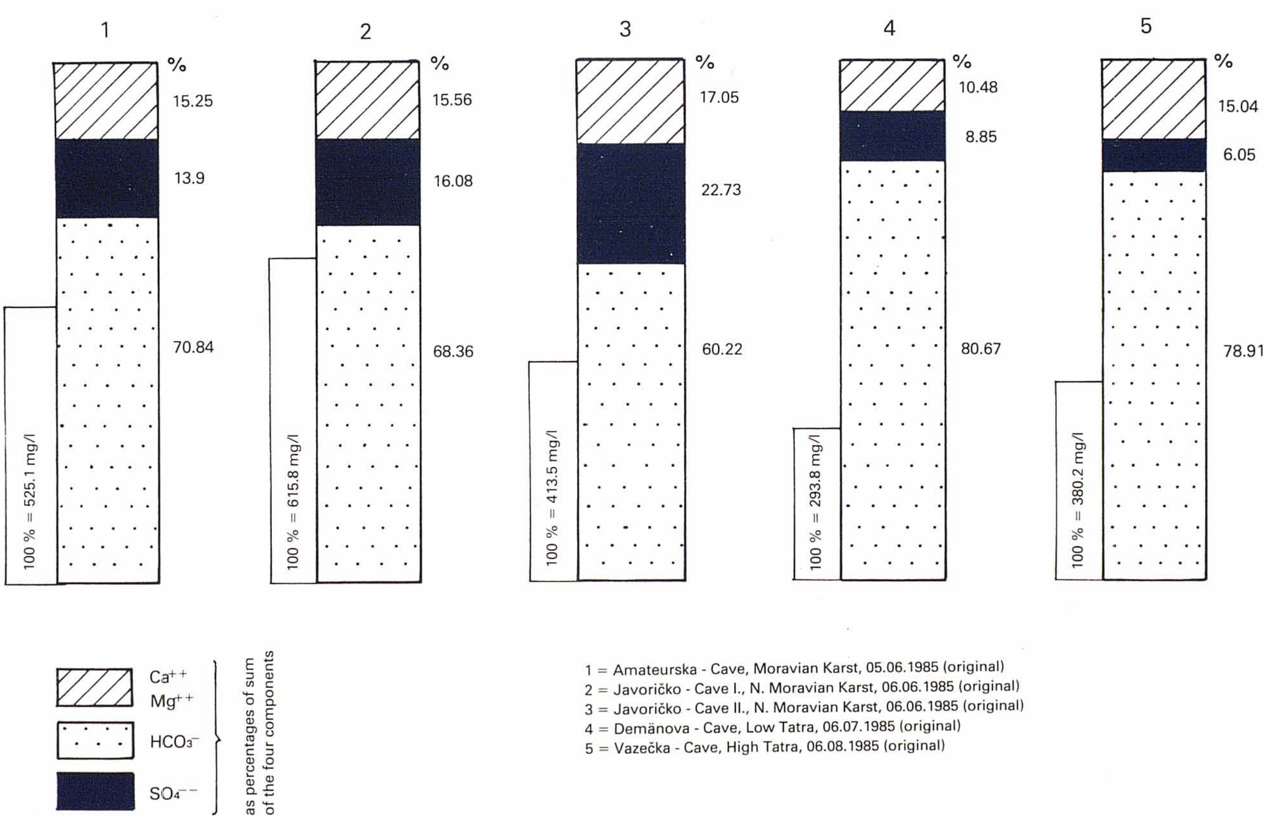


Figure 5. Waters of degrading stalagmites (Czechoslovak caves)

| mg/l | 29.10.1929. (Maucha) REFERENCE | 15.03.1985. (Jakucs-Franczia) | 26.04.1985. (Jakucs-Franczia) | 20.08.1985. (Jakucs-Franczia) | 27.10.1985. (Jakucs) |
|---|---|---|---|---|---|
| $Ca^{++}$ | 66.7 | 96.0 | 130.8 | 104.2 | 98.7 |
| $Mg^{++}$ | 2.0 | 1.5 | 1.7 | 20.2 (?) | 1.4 |
| $HCO_3^-$ | 204.0 | 415.0 | 406.0 | 410.0 | 392.8 |
| $SO_4^{--}$ | 12.4 | 42.0 | 43.2 | 28.6 | 45.3 |
| $NO_3^-$ | 8.5 | 14.2 | 1.8 | 17.5 | 8.2 |
| $Cl^-$ | 1.5 | 7.8 | 6.8 | 9.3 | 4.5 |

Table 3. *Analytical data on ions expressing the trends to change in the water composition of the "Kéregetö-koldus" stalagmite in the Baradla cave*

| mg/l | AMATEURSKA-CAVE 05.06.1985. | JAVORIČKO-CAVE I. 06.06.1985. | JAVORIČKO-CAVE II. 06.06.1985. | DEMÄNOVA-CAVE 07.06.1985. | VAZEČKA-CAVE 08.06.1985 |
|---|---|---|---|---|---|
| $Ca^{++} + Mg^{++}$ | 80.1 | 95.8 | 70.5 | 30.8 | 57.2 |
| $HCO_3^-$ | 372.0 | 421.0 | 249.0 | 237.0 | 300.0 |
| $SO_4^{--}$ | 73.0 | 99.0 | 94.0 | 26.0 | 23.0 |
| $NO_3^-$ | 1.77 | 11.0 | 15.0 | 6.03 | 1.8 |
| $Cl^-$ | 10.65 | 8.88 | 8.88 | 3.55 | 5.33 |

Table 4. *Analytical data on karst waters collected from dripstone formations attacked by recent corrosion in some czechoslovak caves*