

ARE RECENT KARST PROCESSES INFLUENCED BY SOIL HUMIC SUBSTANCES?

Monika Schwarzová – Jiří Faimon

Institute of Geological Sciences, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic;
13255@sci.muni.cz, faimon@sci.muni.cz

Abstract: Soil samples from the Macocha Plateau (north part of the Moravian Karst, Czech Republic) were leached by distilled water and KCl solution. The pH-values of leachates indicate that soil pH is generally low near ground surface (in A-horizon). The acidity decreases with the depth in soil profile and is completely neutralized in the deeper part of soil profile. Humic substances evidently support limestone weathering in the upper epikarst. Mass spectrometry analyses proved that approximately 50 % of humic substances in karst soil leachates are identical with those in cave dripwaters. The role of humic substances in dissolution/growth speleothems is still poorly understood.

Key words: dissolution, growth, humic substances, karst, leachate, limestone, pH-values, soil

INTRODUCTION

Humic substances (**HSs**) represent a significant part of soil organic matter. They are composed of carbon, oxygen, hydrogen, nitrogen and sulfur and are organized in carbon chains or 4-, 5- or 6-member carbon rings (Visser, 1983). Based on the solubility at different pH-values, **HSs** are subdivided into three major fractions: humins, humic acids and fulvic acids. Humins are macromolecular species insoluble in solutions at any pH-value and resistant to decomposition. Humic acids are the species of lower molecular weight, which are soluble in alkaline solutions. Fulvic acids, molecular weight of which is lower than that of humic acids, are soluble at all pH-values (in acidic, neutral and alkaline solutions). Fulvic acids contain carboxyls (-COOH) and hydroxyls (-OH), which make them chemically reactive (Pettit, 2004). There exists a hypothesis that dissolved **HSs** (humic and fulvic acids especially) could influence recent karst processes as limestone dissolution and speleothem growth/dissolution. Such possibility was tested in the Moravian Karst (Czech Republic).

METHODS

Soils were sampled on Macocha Plateau (north part of the Moravian Karst, Czech Republic) at four sites with a different type of vegetation (young/old coniferous and deciduous forest). Twenty complete vertical soil profiles were removed by steel bar and consecutively divided into individual samples (each about 10 cm in length, i. e., about 25 g of weight). In laboratory, the samples were dried at room temperature and leached (the soil/solution ratio was 1:5) by distilled water and KCl solution (25 %). pHs of all leachates was measured (pH-meter WTW pH 330i with combined electrode) twice within 24 hours.

Dripwater was sampled at the Hus speleothem in the Masaryk Dome chamber (Punkevní Caves). Both the soil leachates and dripping water were analyzed by mass spectrometry (MALDI TOF, Department of Analytical Chemistry, MU, Brno).

RESULTS AND DISCUSSION

Mass analysis confirmed a presence of similar **HSs** both (1) in soil leachates and (2) in cave dripwater (about 50 % agreement). Based on the results, it was concluded that dissolved **HSs** are released from soils, penetrate limestones and reach caves. In cave environment, **HSs** could influence carbonate equilibrium and dynamics of speleothem growth/dissolution. In fact, the detail mechanisms and extent of such influence are still poorly understood. Except the latter effects, **HSs** can possibly be incorporated between submicroscopic crystal subunits at calcite precipitation (Ramseyer et al., 1997).

The actual distribution of pH-values across soil profile was deduced from the leachate pH: Near surface (A-horizon), pH-values are generally low in both soils under coniferous forest (pH = 3.72 /KCl solutions/ and pH = 4.67 /distilled water/) and under deciduous forest (pH = 3.71 /KCl solutions/ and pH = 5.05 /distilled water/). Under deciduous vegetation, the low pH-values stagnate to the depth of approximately 25 cm and then steeply increase to the values of 7.02 (KCl solution) and 8.25 (distilled water) at the depth of 55 – 65 cm. In the soils under coniferous vegetation, on the other hand, pH-values gradually increase to pH = 5.61 (KCl solution) and pH = 6.81 (distilled water) at the depth of 75 – 85 cm. Therefore, the acidity which is neutralized in deeper part of soil profile can not be responsible for speleothem corrosion in cave. In fact, somewhat lower

pH-values and deeper soil profiles under coniferous forest indicate that soil solutions in this environment are more aggressive and increase limestone weathering rate on karst surface.

SUMMARY

Dissolved humic substances (humic and fulvic acids) penetrate limestones and migrate from soil into caves.

Due to humic substances, soil leachates show considerable acidity. This acidity decreases with the depth and is completely neutralized in the deeper part of soil profile. Therefore, soil acidity cannot contribute to speleothem corrosion in cave. Nevertheless, it evidently contributes to a limestone weathering in the upper epikarst.

This weathering is more intensive under coniferous forest as indicated by (1) more acid leachates of the deeper parts of soil profiles under coniferous forest and (2) deeper soil profiles under coniferous forest in comparison with those under deciduous forest.

The role of dissolved humic substances itself at speleothem growth/dissolution is still poorly understood.

This work was funded by the grant 205/03/1128 of the Grant Agency of Czech Republic.

REFERENCES

PETTIT, R. E. 2004. Organic matter, humus, humate, humic acid, fulvic acid and humin: their importance in soil fertility and plant health. <http://www.humatech.com/humate.info>

RAMSEYER, K. – MIANO, T. M. – D'ORAZIO, V. – WILDBERGER, A. – WAGNER, T. – GEISTER, J. 1997. Nature and organic matter in carbonates from speleothems, marine cements and coral skeletons. *Org. Geochem.* 26, No. 5/6, 361–378.

VISSER, S. A. 1983. Humic substances in the environment. *Environ. Sci. Technol.* 17, 1393.