

SOME ENVIRONMENTAL PROPERTIES OF FOREST SOILS OF THE MALÉ KARPATY MTS.

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Geochemical research of forest soils of the Malé Karpaty Mts. was aimed to study relationships between humus substances and toxic elements. We found out that in the studied profile Sv. Jur - Stupava 1) content of Hg, Pb, As and Zn correlates with content of humic and fulvic acids; 2) majority of toxic elements is concentrated in the uppermost horizons; 3) humus compounds are concentrated especially in the eastern part of the mountains; 4) forest soils of the Malé Karpaty Mts. are still able to receive heavy metals in order $Zn \gg Cu = Cd \gg Hg$; this means that these elements are bonded in specific way to the soil components.

1. Introduction

Soil represents complicated biotic - abiotic, heterogeneous system. Many of its properties act independently or as a whole in innumerable interactions. Special importance from environmental viewpoint bear clay minerals and other inorganic components, similarly as humus compounds, simply called humus. While environmental properties of inorganic soil components are generally well known, properties of humus and its single parts are understood rather poorly.

Humus itself is a complicated system composed mainly of organic compounds in different stages of decomposition of plant and animal remnants. Inorganic substances, occurring along with the organic ones, are connected with them by bonds of different strength and type. These bonds may originate in many various ways.

Commonly the humus compounds are comprehended as humic, fulvic and hyalomelanine acids, their complexes or bonds with certain elements - humates and fulvates (organomineral complexes). Hraško (1983) defines these compounds as specific humus compounds.

In order to complete characteristics of humus compounds, so called not specific compounds have to be added. They play important and yet not fully understood role in formation of different bonds. Let's mention at least several simple acids, and/or their compounds: asparagine, citric, lactic, acetic, salicylic, tartaric acids etc., and more complicated compounds as aminoacids, proteins, saccharides, polysaccharides, lignines, lipides, waxes etc.

Soil humus acts as a complicated, very active part of soil. The best known is humus activity as source of nutrients and physiologically active compounds important for plants. Lately, great attention is devoted to toxic components which concentrate in soils in course of many complicated migration processes. Part of them comes from bedrock, part from atmosphere, including dust fall, part from natural and artificial fertilizers and from different sprays.

Preliminary research in the network of grant project "Environmental geochemistry of Protected landscape area Malé Karpaty Mts." (No. 1/90-92) showed higher concentrations of some toxic elements in forest soils horizons which seemed to be connected with organic, humus compounds. We decided to investigate these relationships, mainly because no attention was paid to them up to now.

2. Experimental part

2.1. Experimental procedures

The soil samples were collected at 11 places in profile across the Malé Karpaty Mts. between villages Sv. Jur and Stupava (Fig. 1). Samples 1 through 6 were taken from soils on granites, samples 8 - 11 on carbonatic rocks and sample 7 from soils on the rock boundary. Moreover, samples of stream sediments and peat were taken from some places of the investigated profile.

Soil samples were collected from subhorizon A₀ (depth 3 - 5 cm), horizon A (10 - 15 cm) and horizon B (30 - 50 cm). In case of stream sediments, fine-grained mud material was collected.

Sampled material was dried and sieved, in case of samples from horizon A on sieve with mesh size 2 mm (Králová et al., 1991), from other horizons fraction under 0.125 mm was used (Forgáč, Streško, 1993).

The pH values of the stream sediments and peat were determined electrometrically directly in field with portable pH-meter CPH 51, the other samples in laboratory in suspension 1:2.5 (Králová et al., 1991) with pH-meter MS 11.

Content of chemical elements was determined in laboratories of Geological Institute of Comenius University, Bratislava, by spectrometer TMA (Hg) and atomic absorption spectroscopy (K, Na, Ca, Mg) and in laboratories GEMATRIX, Praha (AAS and XRF - As, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Zn).

Cation exchange capacity was determined by displacement by 1 M ammonium acetate (Králová et al., 1991).

Isolation and analysis of single fractions of organic compounds was performed following slightly modified basic procedures recommended in monography Králová et al. (1991).

So called free fulvic acids (FK) were extracted by solution of 0.2 M sulphuric acid by 1 hour shaking, 16 hour standing, repeated 1 hour shaking. Solution of sodium sulphate was added and FK were separated in centrifuge. The bonded FK were separated afterwards by 0.1 M NaOH solution following the same procedure. Solution containing originally bonded FK and HK was obtained by centrifugation and water rinsing. Oxidizable carbon (C_{ox}), corresponding to the sum of

HK+FK, was determined in aliquot fraction of eluate. The other fractions were used to separate FK by acidification of the solution to pH 2, 4 hour standing, 1 hour heating in water bath, cooling and centrifugation. C_{ox} content, corresponding to bonded FK, was determined in sheer solution. So called residual oxidizable carbon was determined after separation of free and bonded FK and HK.

Content of FK and HK is considered to be proportional to content of oxidizable carbon C_{ox} including residual C_{ox} , carbon was determined by wet analysis - oxidation of 0.2 $K_2Cr_2O_7$ with sulphuric acid. Corresponding amount of oxidized $K_2Cr_2O_7$ was determined indirectly iodometrically.

Reproducibility of isolation procedures and analytical determinations was controlled in series of ten runs with sample No. 2 from horizon A_0 .

2.2. Results

2.2.1. Sample moisture and the pH values

Natural moisture of the samples, especially from the A_0 horizon, was very high, ranging in interval 17 - 48 %. The stream sediments and peat had moisture 43 - 79 %.

The pH values were mostly very low. Fig. 2 shows measurements of samples from the A_0 horizon; the pH values from lower horizons did not differ considerably, e.g. the values of sample 7, in direction A_0 to A to B (respectively): 6.75 - 6.93 - 7.95; sample 3: 4.53 - 4.53 - 4.87; sample 2: 5.01 - 4.66 - 4.74; sample 8: 4.26 - 4.22 - 4.55; sample 11: 5.53 - 5.47 - 5.45. Surficial acidity clearly penetrates downward.

The pH values of the stream sediments were considerably higher (6.15 - 7.25). The only exception was stream sediment taken in surroundings of sample 5, with pH 4.60. The peat samples had also higher pH values (5.74 - 6.12).

The pH values of surficial waters (creeks), measured directly in field, were 5.65 - 7.50.

2.2.2. Content of oxidizable carbon, humic and fulvic acids

Content of total C_{ox} and sum of C_{ox} corresponding to HK and FK, as well as content of C_{ox} corresponding to so called free and bonded FK and bonded HK, is indicated in Fig. 3 and 4. Content of residual C_{ox} can be calculated by subtraction of C_{ox} and C_{ox} corresponding to HK+FK (Fig. 3).

Stream sediments and soil samples do not differ markedly in content of C_{ox} , two peat samples taken from different places is very similar: C_{ox} 16.8 - 17.2 %; residual C_{ox} 13.0 - 13.1 %; C_{ox} FK 2.2 - 3.0 %; C_{ox} HK 1.6 - 1.1 %.

Repeated analysis of sample 2 from the A_0 horizon (Table 1) document good reproducibility of measurements of single C_{ox} forms with regard to supposed heterogeneity of the samples.

Tab. 1. Results of the repeated analysis of single C_{ox} forms of the sample 2 from the A_0 horizon

No. of anal.	% C_{ox} free FK	% C_{ox} bond. FK	% C_{ox} bond. HK	residual C_{ox} - %	ΣC_{ox} %
1	0,80	1,53	1,44	2,28	6,05
2	0,71	1,65	1,13	2,18	5,67
3	0,59	1,66	1,13	2,26	5,65
4	0,63	1,52	1,26	2,35	5,76
5	0,68	1,68	1,06	2,09	5,51
6	0,71	1,68	1,06	2,27	5,73
7	0,73	1,74	1,14	2,21	5,83
8	0,61	1,64	1,08	2,26	5,59
9	0,70	1,67	1,22	2,20	5,79
10	0,69	1,68	1,14	2,32	5,83
X	0,69	1,65	1,17	2,24	5,74
δ	$\pm 0,06$	$\pm 0,07$	$\pm 0,13$	$\pm 0,07$	$\pm 0,15$

2.2.3. Determination of cation exchange capacity

Cation exchange capacity was investigated only at samples from horizon A_0 and some sediment specimens. We determined amounts of releasable Na, K, Ca, Mg. Fig. 5 represents amount of released cations where the largest portion belongs to potassium, less to sodium. Calcium and magnesium were released in negligible amounts. Almost all the sediment samples, including peat, had higher values of releasable cations. Again, potassium dominates over sodium (about 1.5 - 2 times).

2.2.4. Content of some toxic elements

Fig. 6 represents content of mercury in samples in all the horizons, next figures present similar data for arsenic (Fig. 7), copper (Fig. 8), lead (Fig. 9) and zinc (Fig. 10) in horizons A and B. Content of the other toxic elements - Cd, Co, Mn, Mo, Ni, Sb is low.

2.2.5. Experimental sorption - exchange capacities of forest soils of the Malé Karpaty Mts.

Ability of the forest soils of A_0 horizon to bind certain toxic elements was experimentally investigated following the principles published by the authors. Results are summarized in Fig. 11 (for Hg), 12 (for Cd), 13 (for Cu) and 14 (for Zn). Amount of elements bound is marked as sorption - exchange capacity because it is impossible to distinguish unambiguously between sorption and exchange.

3. Discussion

The data set about individual groups of bonds of oxidizable carbon needs to be completed by several facts. So called free FK can be represented not only by the fulvic acids themselves, but also by other simple acids or aminoacids, as it is mentioned in introduction. The free FK were extracted in acid environment with pH 2 and therefore they need not include only free acids but also their bonds (e.g. acetates, tartarates) which decompose in acid solutions. Content of C_{ox} extracted by water was in interval of analytical error.

Residual C_{ox} corresponds to those carbon bond forms which do not pass into acid (0.2 M H_2SO_4) or basic (0.1 M NaOH) extract. Their specification is complicated. We may be dealing with cellulose, lignin and other substances coming from fragments of roots, leaves or other plant parts. Lipides, waxes and other substances may be found too. No detailed specification of these compounds was performed, mainly because we do not suppose their active role in environmental processes.

Total content of oxidizable compounds (C_{ox} , Fig. 3) exhibits three marked tendencies: 1) content of oxidizable compounds is considerably higher in the A_0 horizon and it decreases downward; 2) higher contents were found in the eastern part of the Malé Karpaty Mts.; 3) samples of soils on carbonate bedrock (localities 8 - 11) possess minimal concentration of oxidizable compounds. It is interesting that these tendencies concern all the horizons and all the basic types of C_{ox} bonds with only several samples from localities 2, 3, and 5 being exceptional.

Spatial distribution of active forms of carbon compounds - free and bonded FK and bonded HK (Fig. 4) - exhibits also several relationships. HK clearly concentrate in the uppermost horizon A_0 , while FK dominate in lower horizons, either in soluble or chiefly in bonded form. Bonded FK dominate over the free ones in all the horizons; this is especially marked in the A horizon.

Higher content of FK than HK in horizons A and B is probably caused by higher migration ability of FK (production of soluble bonds).

More attention should be paid also to the samples from places with carbonatic bedrock where content of both FK forms does not match with samples from above granites (samples 1 - 7). Content of free fulvic and corresponding acids reaches approximately identical concentration as content of bonded FK. It is obvious that FK and HK bonds in soils on carbonates differ from those on granites.

Expectably, values of cation exchange capacities (Fig. 5) anticorrelate with content of organic compounds. According to our earlier published results (Babčan, et al., 1990), HK and FK do not form with sodium and potassium any stable bonds of insoluble compounds.

Illite in the finest fraction causes high exchange capacity in the sample from locality 2 as well as in the sediment samples. Presence of illite was confirmed by X-ray diffraction analysis.

Content of toxic elements and their bonding to soil components has to be evaluated from several viewpoints. The only analysed element in samples from the A_0 horizon was mercury (Fig. 6). It correlates very well with content of humic and fulvic acids (Fig. 4). Mercury shows good correlation with sum of HK and FK also in the B horizon, but in horizon A, concretely in the sample 9, correlation of

mercury differs from bond to organic compounds. Noteworthy is higher mercury content in the stream sediments and peat which had also higher C_{ox} content, but in these cases especially content of residual C_{ox} . The lead content (Fig. 9) matches practically in the entire A horizon very well with content of HK and FK (Fig. 3), similarly as in the B horizon with exceptional samples 3, 4. Zinc shows similar behaviour; exceptions are the samples 2 and 4 (Fig. 10).

Copper concentrates in both horizons in the marginal parts of the mountains (localities 1, 3 and 10, possibly 11) and in the central part of profile, without any conspicuous bond to organic compounds (proximity of vineyards?).

Arsenic practically does not correlate with content of bound HK and FK either in horizon A or B. Except for two samples (2,7), marked decrease of arsenic content downward was confirmed.

Content of most analysed elements decreases downward in all the horizons. This finding is valid also for cadmium, molybdenum and antimony. Zinc with approximately identical content in both horizons represents an exception. Reversed tendency is characteristic for cobalt and nickel.

The discussed trend of decrease of most elements toward lower horizons points at introduction of these elements into soil from atmosphere. The decisive proof for this assumption has to be found in the ways these elements reach the entire area of the Malé Karpaty Mts.

Sorption - exchange capacity of selected elements on forest soil from the Malé Karpaty Mts. concern only horizon A_0 (Fig. 4). In order to illustrate the relationship, the figure is supplemented by results of experimental studies of mercury (Hg^{2+}) bonds with humic and fulvic acids in dependence on pH of the environment. It is interesting that the bond of Hg^{2+} to the forest soils is not consistent with the experimental results. Insoluble complexes of mercury should be formed in solutions with pH over 4.0 (Fig. 2). Sorption - exchange capacity with regard to Cu, Cd and Zn is considerably higher while the mole values are various ($Zn \gg Cu = Cd \gg Hg$) which points at specific bond forms of single elements to soil components.

Sorption - exchange capacity was investigated also in the sediment samples. In contrary with soil samples, sorption - exchange capacity of copper, cadmium and zinc is twice as large, and that of mercury even 4 times higher.

Cadmium (Fig. 12) and copper (Fig. 13) exhibit similar dependence of sorption - exchange capacity as mercury. Complicated relationships in system $Cd^{2+}(Cu^{2+})$ - HK - FK - H_2O - pH investigated in our previous experiments are depicted in the presented graphs.

Zinc (Fig. 14) usually correlates with content of HK and FK, except for sample 7. In this case higher sorption of zinc is probably caused by high pH value of the sample - 6.75.

Presented results are not consistent with behaviour of mercury in sorption - exchange experiments where mercury tends to form insoluble bonds with HK and FK (Babčan, Ševc, 1994). pH values of the natural soil samples vary within pH interval where mercury forms insoluble bonds with HK as well as FK. Consequently, mercury in samples with sufficient amount of humus compounds should be totally bonded. Different behaviour of mercury in natural systems indicates presence of compounds which are able to form soluble systems with this element.

4. Conclusions

The environmental and geochemical study of forest soils of the Malé Karpaty Mts. in profile between villages Sv. Jur and Stupava in relationship to soil components provides us with these important facts:

1. Content of the most important toxic elements - Hg, Pb, As, Zn - does correlate with content of humic and fulvic acids.
2. Majority of toxic elements (Hg, Pb, As, Cd, Mo, Sb) are concentrated especially in the upper horizons (A_0 , A); cobalt and nickel show reversed tendency, content of zinc is identical in all the studied horizons (A_0 , A, B).
3. Copper has the highest concentration in marginal parts of the mountains where its probable source are sprays in vineyards.
4. Higher content of toxic elements was found also in fine mud stream sediments, but their content correlates with not specific humus compounds like simple aliphatic acids and their salts, aminoacids, saccharides, lignines, lipides, waxes etc.
5. The most important exchangeable cations are not bonded to humus compounds, but to clay substances.
6. Spatial distribution of humus compounds shows three marked tendencies:
 - a) the highest content of humus compounds is in the eastern part of the profile across the mountains;
 - b) their content decreases downward;
 - c) soils on carbonate bedrock have considerably lower content of humus compounds than soils on granites.
7. Experiments confirmed that forest soils of the Malé Karpaty Mts. are still able to receive certain amounts of toxic elements in order $Zn \gg Cu = Cd \gg Hg$. This witnesses about specific form of binding of some elements to soil components.

HUMUSOVÉ LÁTKY MALOKARPATSKÝCH LESNÝCH POD A ICH ENVIRONMENTÁLNE VLASTNOSTI.

Súhrn:

Geochemický výskum malokarpatských pôd bol zameraný na štúdium vzťahov humusových látok a toxických prvkov. V skúmanom profile Sv. Jur - Stupava bolo zistené: 1) že obsahy Hg, Pb, As, Zn korelujú s obsahmi humínových a fulvokyselín; 2) že väčšina toxických prvkov má najväčšie zastúpenie v najvyšších horizontoch; 3) že rozmiestnenie humusových látok sa koncentruje najmä vo východnej časti pohoria; 4) že karpatské lesné pôdy sú schopné prijať ďalšie podiely ťažkých kovov v poradí $Zn \gg Cu = Cd \gg Hg$, z čoho vyplýva, že tieto prvky sa špecifickým spôsobom viažu na pôdne zložky.

5. References

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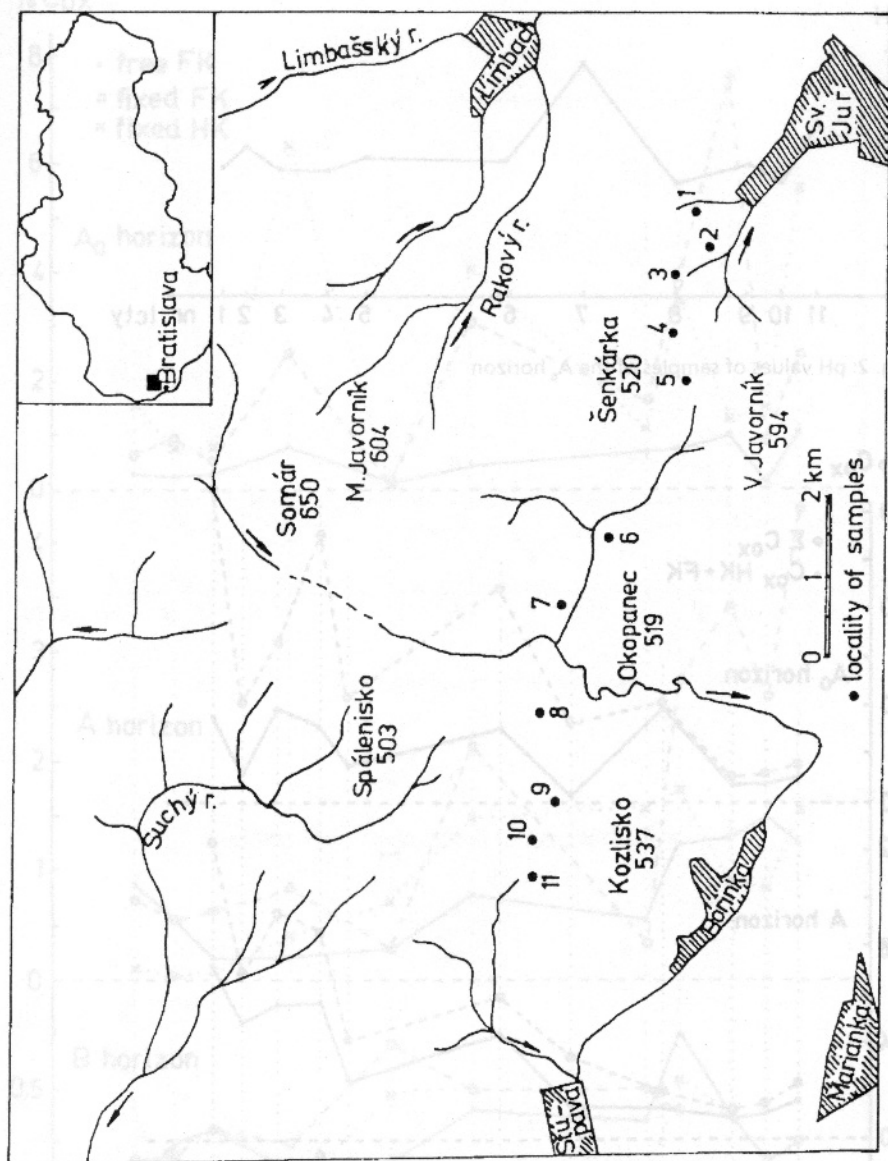


Fig. 1: Localisation of places of the samples collected in profile across the Malé Karpaty Mts. (FORGÁČ, STREŠKO, 1993, modif.)

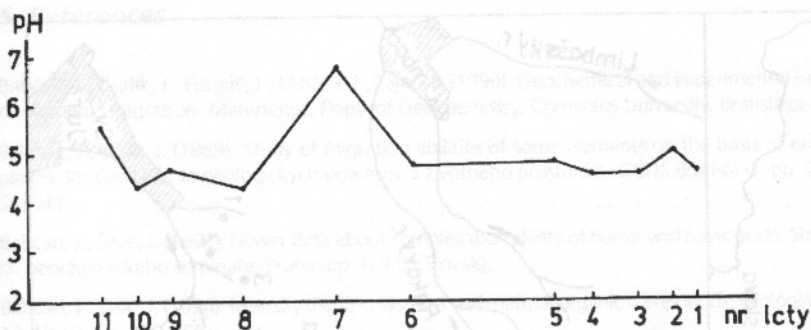


Fig. 2: pH values of samples of the A₀ horizon

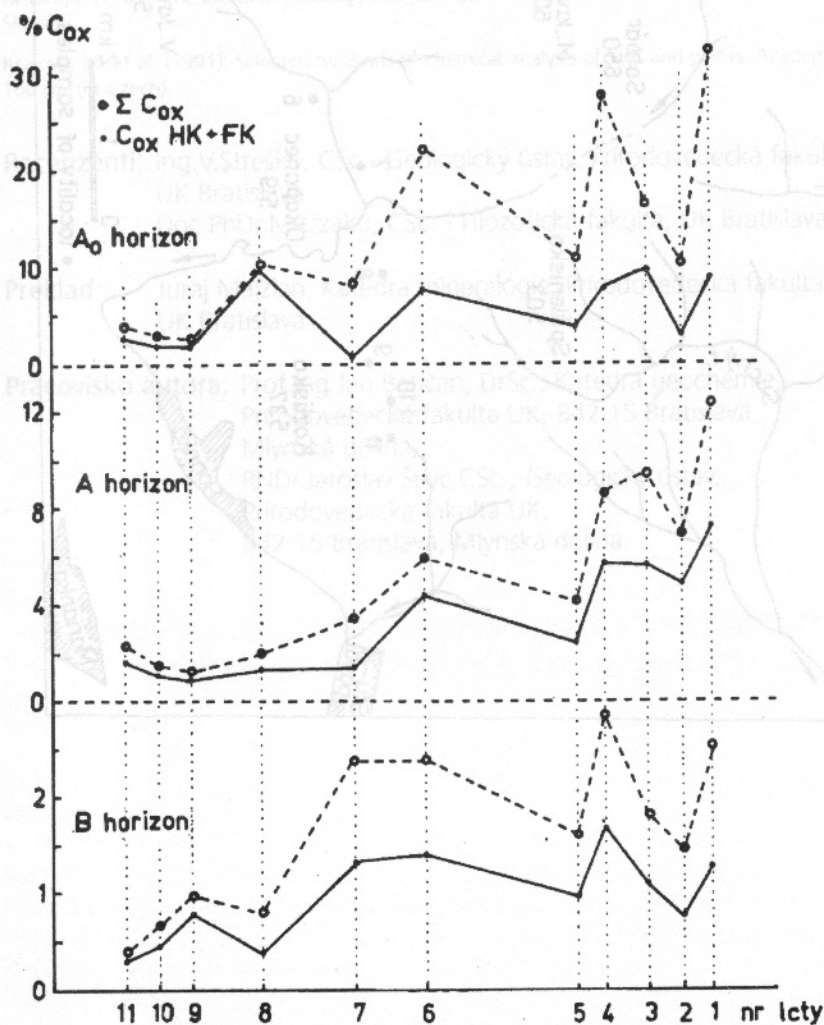


Fig. 3: Content of total C_{ox} and sum of C_{ox} corresponding to the humic and fulvic acids

% C_{ox}

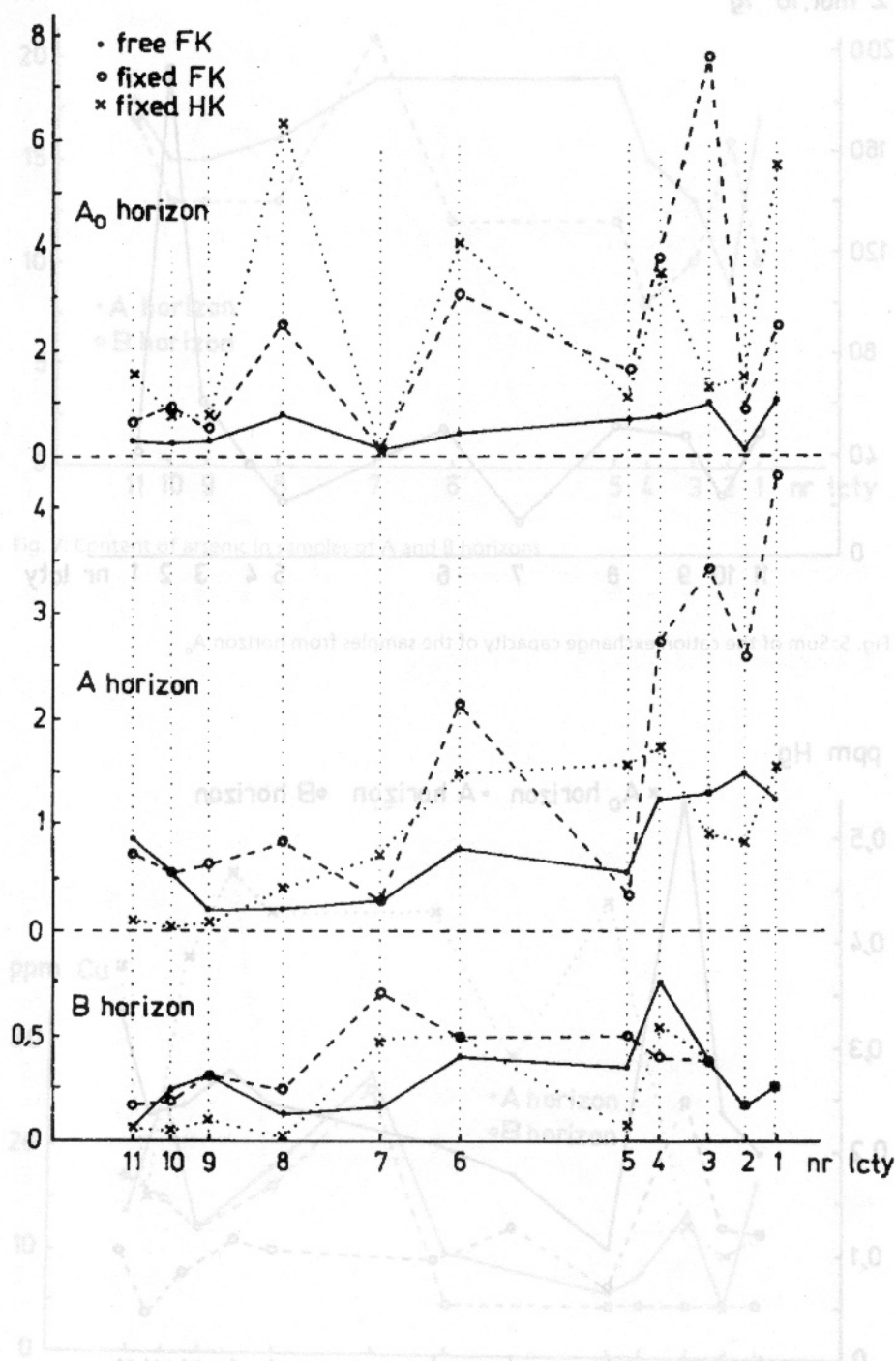


Fig. 4: Content of free and bonded fulvic acids and bonded humic acids according to the C_{ox} content

$\Sigma \text{ mol.} \cdot 10^{-4} / \text{g}$

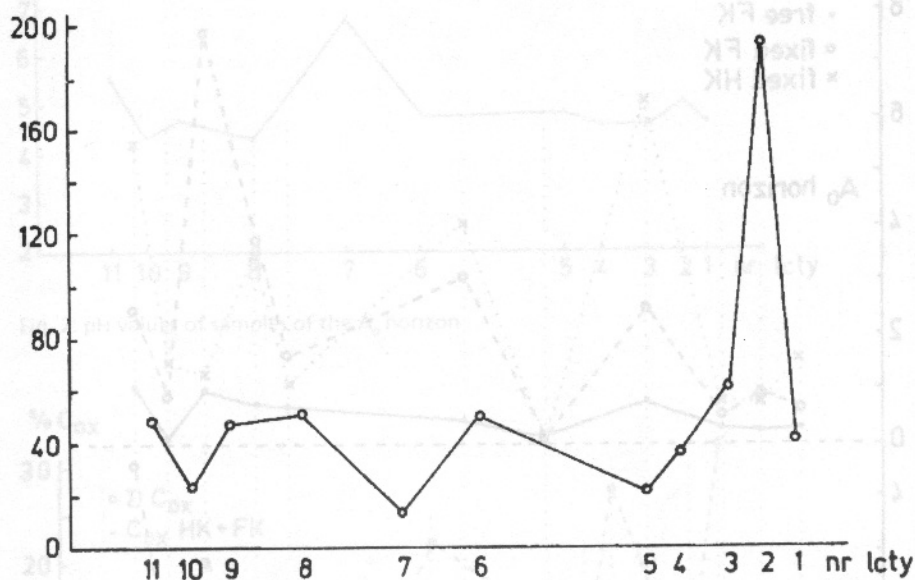


Fig. 5: Sum of the cation exchange capacity of the samples from horizon A₀

ppm Hg

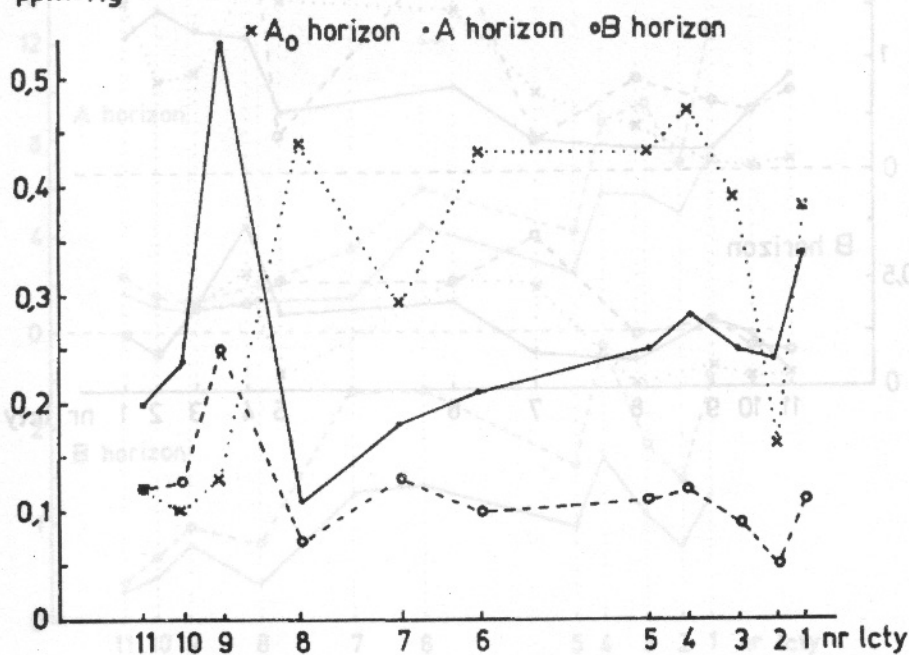


Fig. 6: Content of mercury in samples of A₀, A and B horizons

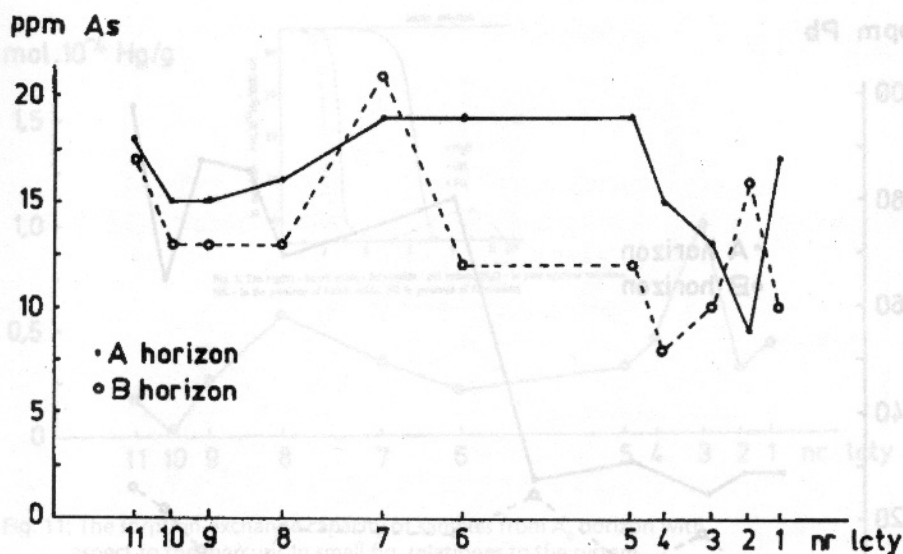


Fig. 7: Content of arsenic in samples of A and B horizons

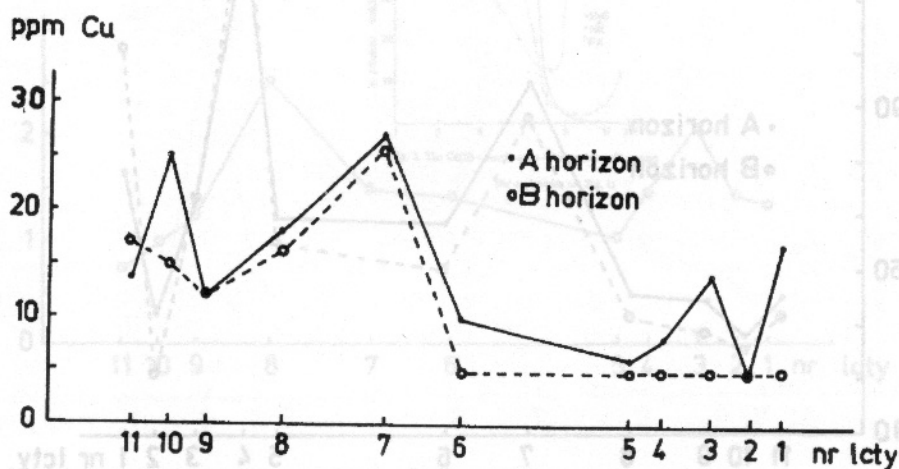


Fig. 8: Content of copper in samples of A and B horizons

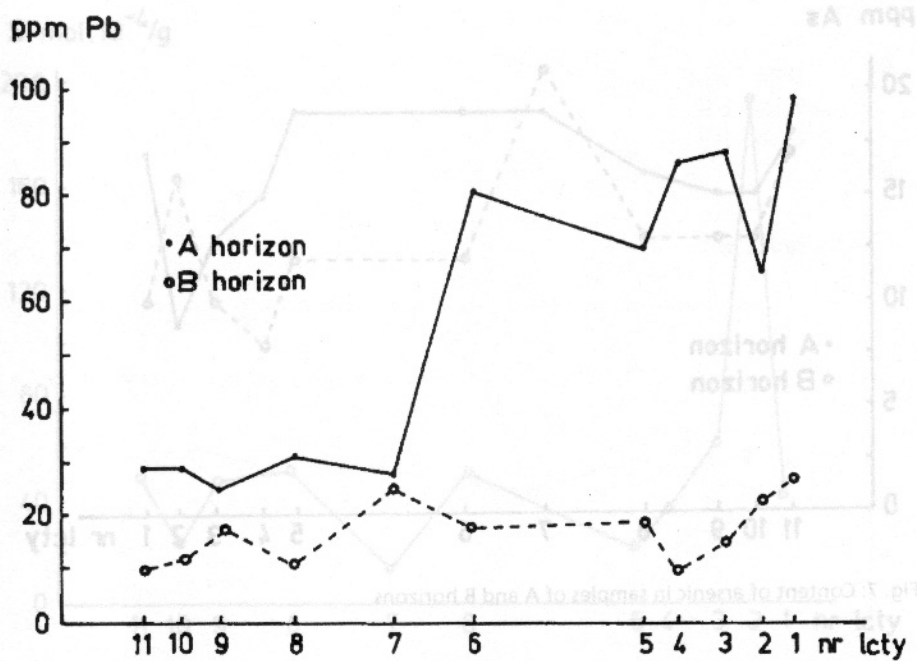


Fig. 9: Content of lead in samples of A a B horizons

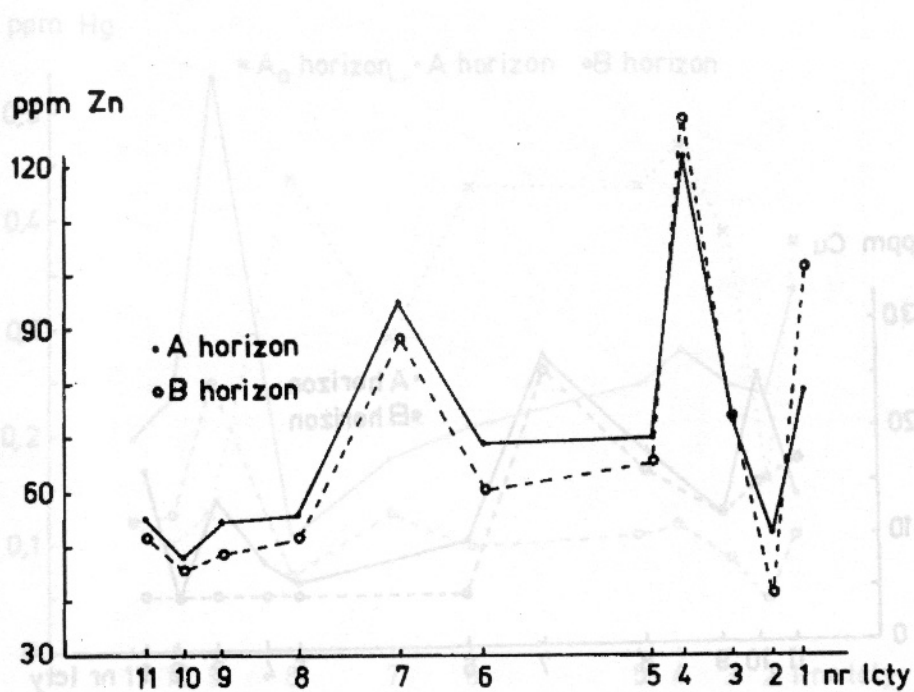


Fig. 10: Content of zinc in samples of A a B horizons

mol. 10^{-4} Hg/g

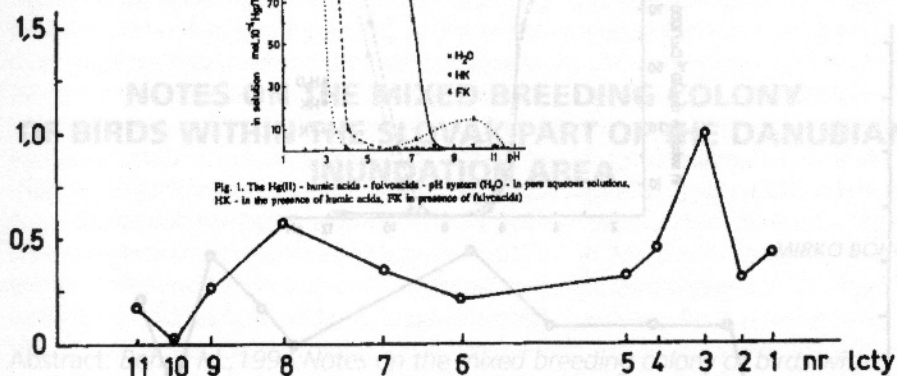


Fig. 11: The sorption-exchange capacity of samples from A_0 horizon with aspect to the mercury. In small fig. relations to the system Hg^{2+} -HK-FK- H_2O -pH (BABČAN, ŠEVČ, 1994)

mol. 10^{-4} /g Cd

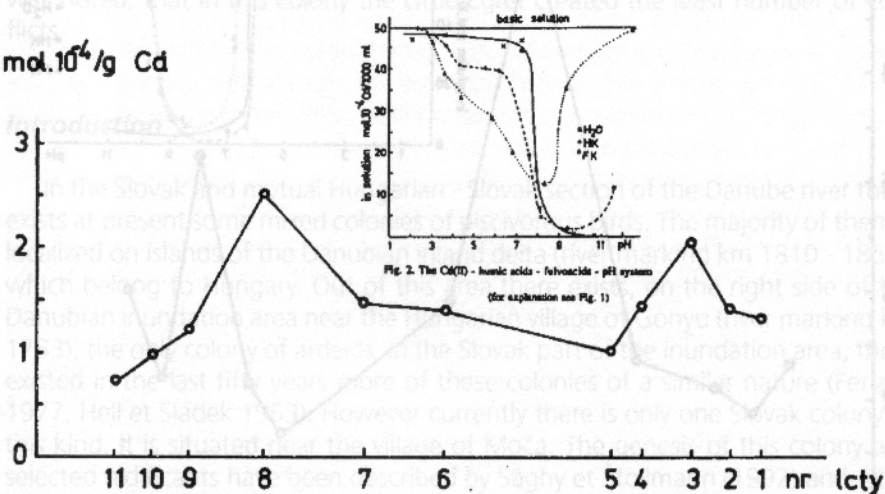


Fig. 12: The sorption-exchange capacity of samples from A_0 horizon with aspect to the cadmium. In small fig. relations to the system Cd^{2+} -HK-FK- H_2O -pH (BABČAN, ŠEVČ, 1991)

mol. 10^{-4} Cu/g

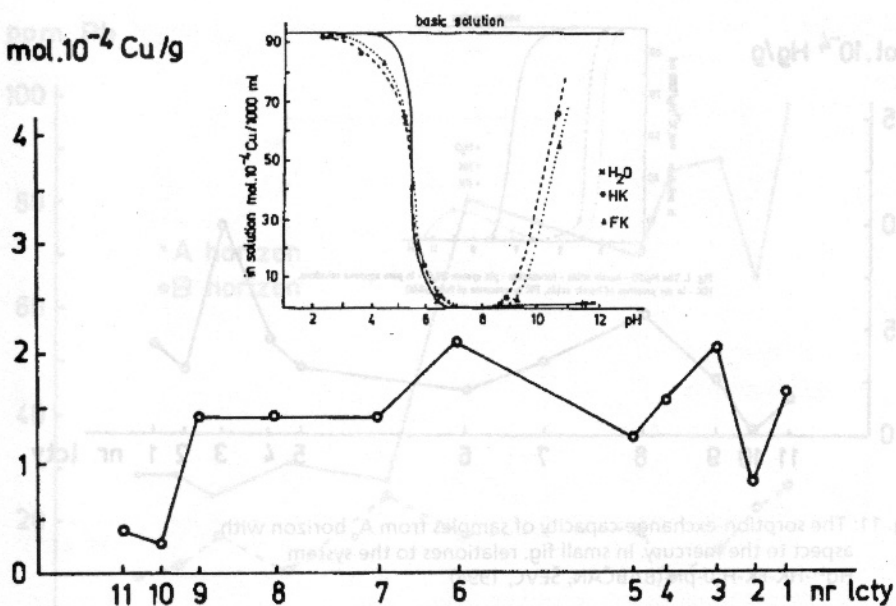


Fig. 13: The sorption-exchange capacity of samples from A₀ horizon with aspect to the copper. In small fig. relations to the system Cu²⁺-HK-FK-H₂O-pH (BABČAN, ŠEVC, 1991)

mol. 10^{-4} Zn/g

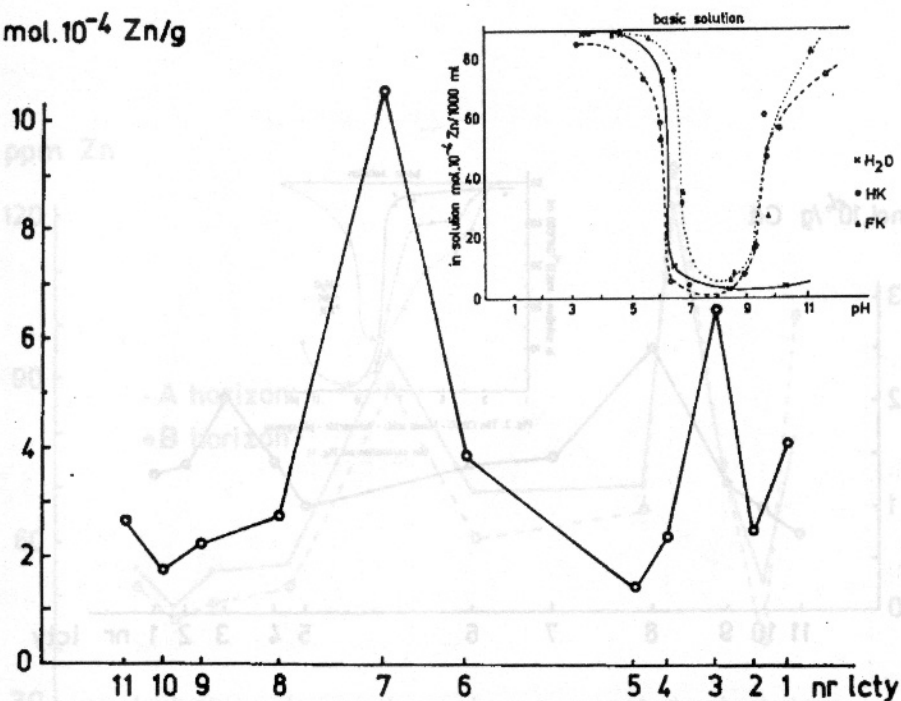


Fig. 14: The sorption-exchange capacity of samples from A₀ horizon with aspect to the zinc. In small fig. relations to the system Zn²⁺-HK-FK-H₂O-pH (BABČAN, ŠEVC, 1991)