

TRACE ELEMENT DISTRIBUTION AMONG THE COMPONENTS OF SOILS IN ŽITNÝ OSTROV REGION, SOUTHWESTERN SLOVAKIA

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Abstract: Fifteen soil profiles were selected from agricultural areas in Žitný ostrov, and sixty one samples were analysed for their total contents of several trace elements, viz. Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Ga, Hg, Ni, Pb, Sn, Sr, V, Zn, and Zr. In addition, other soil characteristics have also been determined, viz. particle size, organic carbon, carbonate, cation exchange capacity, and pH. The relations of trace elements with these characteristics were studied using statistical multivariate analysis. Generally, most of the trace elements show strong association with the clays and particularly the organic matter. Consequently, they exhibits strong positive correlation with the cation exchange capacity. They also show strong inter-element relationships which reflect their common occurrence in the clays and organic matter. Sr alone occurs in the carbonate fraction, and Zr in the sand fraction. Vertical distribution of all studied parameters within the soil profiles also proves these conclusions.

Key words: trace elements, total contents, soil properties.

Introduction

Žitný ostrov is situated close to Bratislava in the south-western part of Slovakia enclosed between the Danube and Little Danube rivers (Fig. 1). Economically, it is very important because it represents a very big water and food resource for the country. It represents a very notable geochemical landscape system due to its geological, hydrogeological, and hydrogeochemical conditions.

Geologically, it is formed by Quaternary gravels which occur in different amounts, but locally reach 300 m thickness, and are covered by Pleistocene and Holocene sediments of different textures.

The groundwater of Žitný ostrov is supplied from the Danube River, and flows through the permeable strata toward the southeast almost parallel to the Danube River. The water of the Danube is calcium bicarbonatic, weakly alkaline, and slightly mineralized. Due to the interaction in the soil-rock-water system the chemistry of groundwater gradually changes (Ca^{2+} , Mg^{2+} - Ca^{2+} , Mg^{2+} - Na^+ , HCO_3^-) with increasing mineralization. Groundwater is also characterized by its fluctuation in correspondence to the fluctuation in the Danube River. Generally, it fluctuates during the year between 4-7 m in the upper part of the area, 2-4 m in the middle part, and 0-2 m in the lower part (Porubský et al. 1971; Kalnová 1976). The zonal character in groundwater chemistry is reflected in soil chemistry, and the different hydromorphic influence leads to the evolution of different soil units and hence the soil cover of the area is relatively variegated (Fulajtár & Čurlík 1991). In the upper part of the region with a deep groundwater table, automorphic soils prevail (represented by Calcaro-haplic Chernozem and Haplic Phaeozem). In the middle part Phaeozems with the signs of former (relict) or recent hydromorphic influence are present. In the

lower part more hydromorphic Fluvi-mollic Gley soils have developed together with the highly alkaline and salt-affected soils on places with highly mineralized groundwater.

The area is climatically hot and dry with an average annual temperature of 9 °C, precipitation of 570 mm, and potential evaporation of 832 mm. Hence, evapotranspiration (potential evaporation) exceeds precipitation creating a permanently evaporative climatic regime. Consequently, mineral salts (mainly carbonates) accumulate in the soil cover from the groundwater.

Total trace element contents provide a useful but only preliminary indication of the risk of toxicity as plant uptake depends on the availability of the metals concerned, soil type, and plant species. The present study tries to assess the influence of different soil properties such as particle size fractions, organic C content, carbonate content, in addition to other properties like pH and cation exchange capacity (CEC) on the distribution of trace elements in the soil profile, based on their total contents.

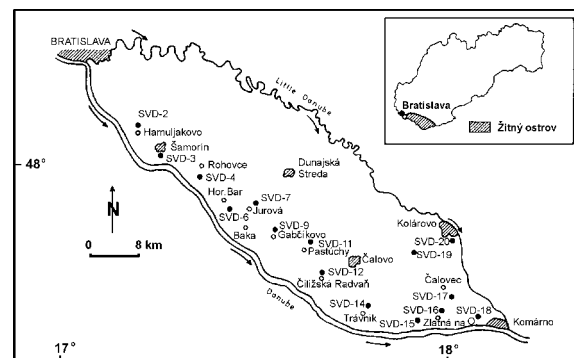


Fig. 1. Žitný ostrov and the locations of the soil profiles investigated.

Experimental procedure

Chemical analyses of total trace element contents

Fifteen soil profiles have been selected from the area of Žitný ostrov (Fig. 1) and sixty one representative samples have been chemically analysed for their total contents of eighteen trace elements, viz. Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Ga, Hg, Ni, Pb, Sn, Sr, V, Zn, and Zr. Analyses have been carried out in the laboratories of the Geological Institute, Faculty of Natural Sciences, Bratislava. Different analytical procedures have been applied for these analyses, and basic parameters of precision, accuracy and detection limits were determined for all used analytical methods (Medved' et al. 1992). Trace elements Ag, B, Ba, B, Co, Cr, Cu, Ga, Ni, Pb, Sn, Sr, V, and Zr have been analysed by optical emission spectroscopy (OES). Spectra were obtained by the excitation of solid samples mixed with graphite powder and spectrochemical admixture of Li_2CO_3 in ratio of 3 : 6 : 1. They were recorded on a grid spectrometer PGS 2 using a DC arc with an intensity of 6 A during 90 seconds.

The atomic absorption spectrometry (AAS) has been applied for the analysis of As, Cd, Hg, and Zn, using PERKIN-ELMER (USA) 380 spectrometer. Both As and Hg were analysed using separate techniques. The absorption signals of As were obtained by hydride techniques after dissolution of the sample. Hg was determined from solid samples after thermal evaporation in oxygen flow and its concentration in an amalgamator. Cd and Zn were determined from solution by atomization in an acetylene-air flame.

For the aim of these analyses a soil subsample (approximately 5 g) of the <0.056 mm (fine earth) air-dried fraction of the soil was ground to a fine powder and homogenized in an agate mortar. The samples were then dried at 28–30 °C before ignition at 650 °C for two hours. The total dissolution of soil samples was performed by a mixture of HNO_3 , HClO_4 , and HF acids.

Other analyses

Forty seven samples have been chosen for several analyses that determine some of the soil characteristics in order to enable comparison of their total trace element contents with the different soil properties. All these analyses have been done in the laboratories of the Soil Fertility Research Institute, Bratislava.

The following particle size fractions were determined according to the method described by Hraško (1962): medium and coarse sand (2–0.25 mm), fine sand (0.25–0.05 mm), coarse silt (0.05–0.01mm), fine silt (0.01–0.001mm), clayey parts (<0.01 mm), and clay (<0.001 mm).

The electrometrical pH determination of H^+ -activity was done by mixing one part of soil with two and half parts of distilled water, and the pH of the obtained soil–water suspension is measured according to the method described by Hraško (1962).

The method used for the determination of carbonate content is described by Hraško (1962). It depends on the destruction of the carbonate by 10 % HCl and gas volumetric deter-

mination with Janko's calciometer. The organic carbon content has been determined according to the method of extraction by chromium sulphuric acid, described by Nikitin (1972, in Sotáková 1988).

The total cation exchange capacity has been determined according to the method described by Sotáková (1988).

Materials

The location of the soil profiles under investigation and their general characteristics are listed in Table 1. These soils are generally variegated and belong to different soil types, Calcaric Fluvisol, Calcaro-haplic Chernozem, Fluvi-Haplic-calcaric Phaeozem, Fluvi-gleyic-calcaric Phaeozem, and Fluvi-mollic-calcaric Gleysol. All the soil profiles studied are calcareous, with carbonates (both pedogenic and inherited) dispersed in the whole profile. They are slightly alkaline with a pH range of 8–9. Their texture is very diverse but the loamy (muddy) dominates. Their parent materials are light to heavy calcareous alluvial sediments. The field areas from which these soils were taken are currently agriculturally intensively and diversely used for different crops, but mainly for wheat, corn, sugar-beet, barley, sunflower, and soya-bean. A lot of fertilizers and pesticides are applied in this area, and added to its soils through the agricultural production which could represent a further source of trace elements in these soils.

Results

The average of total trace element contents together with the other soil characteristics are listed in Table 2 and their comparison in the soil profile is graphically illustrated in Fig. 2. This figure shows the close relations among the trends of most trace elements (decreasing downwards) and the trends of clay and organic carbon, being concentrated in surface horizons and depleted in lower horizons, which is also expressed by the similar trend for CEC, while the sand fraction shows an opposite trend. Carbonates show an increase with depth in line with the Sr trend and pH.

Particle size

A strong association between particle size and trace element concentrations often exists because the large surface area per unit volume found in small particles accentuates adsorption. Among the particle size fractions studied the clay fraction (<0.001 mm), clayey part (<0.01mm), and fine silt (0.01–0.001 mm) have significant positive correlations with most of the trace elements investigated, namely B, Ba, Be, Co, Cr, Cu, Ga, Ni, Pb, Sn, V and Zn (Table 3 and Fig. 3). This indicates the affinity of these elements to be adsorbed on the surfaces of clay minerals. It is worth mentioning here that the quality of clay fraction in the studied soils is characterized by illite + chlorite, in addition to small admixtures of kaolinite and/or smectite (Mejeed & Čurlík 1992).

Only Zr shows a significant positive correlation with the fine sand fraction (0.25–0.05 mm) which indicates the occurrence of Zr as an independent phase in zircon. Both Sr and

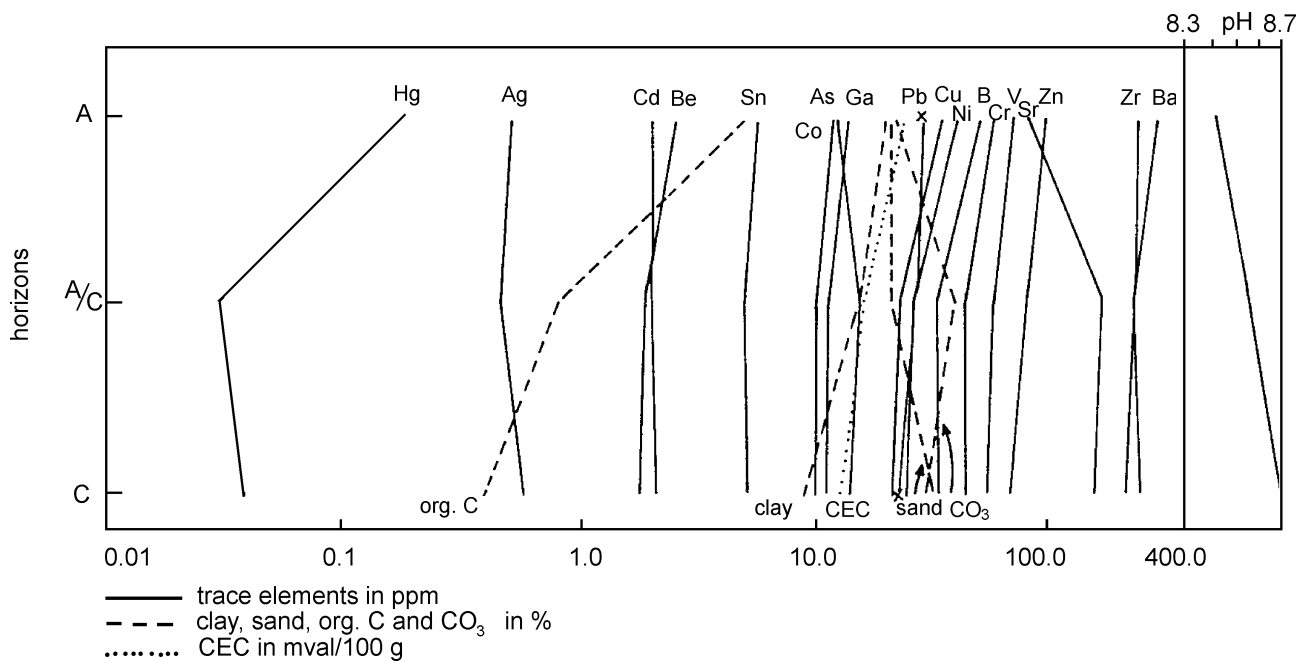


Fig. 2. Comparison of the average trace element contents and other soil characteristics in the different soil horizons.

Table 1: General characteristics of the soils studied.

Profile	Location	FAO soil classification	Parent material	Texture	pH	Ground water table	Plant
SVD-2	Hamuliakovo	Jc	A	1	8.4	5-6	corn
SVD-3	Šamorín	Jc	B	1s	8.7	3-4	wheat
SVD-4	Rohovce	Chc	B	1	8.8	2-3	barley
SVD-6	Horný Bar	Hgcf	C	1	8.5	1-2	sunflower
SVD-7	Jurová	Hgcf	C	1c	8.4	1-2	sugar-beet
SVD-9	Gabčíkovo	Gmcf	A	1c	8.4	1-2	sugar-beet
SVD-11	Padaň	Hgcf	A	1	8.4	1-2	corn
SVD-12	Čilizská Radvaň	Hgcf	A	c	8.4	0-1	wheat
SVD-14	Trávník	Hhcf	C	1c	8.8	0-1	wheat
SVD-15	Zlatná na Ostrove	Hgcf	C	1	9.0	2-3	wheat
SVD-16	Zlatná na Ostrove	Hhcf	C	c	9.0	1-2	soya-bean
SVD-17	Čalovec	Hgcf	C	1c	8.7	2-3	wheat
SVD-18	Komárno	Hhcf	D	1c	8.9	1-2	wheat
SVD-19	Zemianska Olča	Hgcf	A	c	8.6	1-2	corn
SVD-20	Kolárovo	Jc	A	1c	8.5	0-1	sugar-beet

FAO soil classification:

Jc: Calcaric Fluvisol
 Chc: Calcaro-haplic Chernozem
 Hhcf: Fluvi-haplic-calcaric Phaeozem
 Hgcf: Fluvi-gleyic-calcaric Phaeozem
 Gmcf: Fluvi-mollic-calcaric Gleysol.

B: light calcareous alluvial sediments

C: loess
 D: calcareous alluvial gravel-sand.

Texture:
 1s: loamy sandy
 1: loamy
 1c: loamy clayey
 c: clayey.

Parent materials:

A: mildly heavy calcareous alluvial sediments

Table 2: Average contents of trace elements (ppm), different particle size fractions, organic carbon and CO₃, cation exchange capacity and pH.

Ag	As	B	Ba	Be	Cd	Co	Cr	Cu	
0.52	13.02	41.68	258.3	2.16	2.06	10.72	50.36	28.44	
Ga	Hg	Ni	Pb	Sn	Sr	V	Zn	Zr	
12.11	0.10	34.06	26.86	5.51	125.24	63.21	84.65	236.77	
particle size fractions %						org. C %	CO ₃ %	CEC mval/100g	pH
2-0.25	0.25 -0.05	0.05 -0.01	0.01 -0.001	<0.01	<0.001				
1.18	26.07	31.13	28.10	42.61	14.50	0.93	28.51	17.70	8.56

carbonate contents show positive correlations of (0.50) and (0.54) respectively with the coarse sand fraction (2-0.25 mm) which is attributed to the development of pedogenic carbonate nodules in these soils usually of sand size.

Organic carbon

Humus (herein studied as organic carbon) content and particularly its quality belongs to the most important factors that determine the content, availability, and distribution of trace elements in the whole soil profile. In the present study retention of trace elements strongly correlates with the organic carbon and this is obvious from the significant positive correlations of the organic carbon with each of B, Ba, Be, Co, Cr, Cu, Ga, Ni, Pb, Sn, V, and Zn suggesting their association with the organic matter (Table 3 and Fig. 3). Hg is one of the elements which did not show any significant correlation

Table 3: Significant correlation coefficients of trace elements with other soil characteristics (level of significance 0.05, sample size 47).

	2	0.25	0.05	0.01	<0.01	<0.001	org. C	CO ₃	CEC	pH
	-0.25	-0.05	-0.01	-0.001						
Ag								-0.94		
As							-0.31			
B					0.32	0.54	0.63	-0.45	0.64	-0.36
Ba		-0.45		0.42	0.57	0.69	0.68	-0.36	0.75	-0.47
Be		-0.33		0.30	0.54	0.58	0.60	-0.38	0.65	-0.57
Cd										
Co		-0.50		0.53	0.61	0.59	0.57	-0.29	0.66	-0.52
Cr		-0.38		0.38	0.48	0.52	0.56	-0.42	0.63	-0.48
Cu				0.29	0.34	0.34	0.44		0.41	-0.29
Ga		-0.50		0.50	0.64	0.70	0.62	-0.36	0.70	-0.51
Hg										
Ni					0.31	0.32	0.42		0.41	-0.35
Pb		-0.28		0.28	0.34	0.36	0.36		0.33	-0.40
Sn		-0.50		0.55	0.59	0.50			0.39	-0.39
Sr	0.50						-0.47	0.60	-0.44	0.52
V		-0.49		0.47	0.59	0.63	0.65	-0.43	0.70	-0.51
Zn					0.29	0.39	0.51		0.53	
Zr		0.37		-0.34	-0.36	-0.30			-0.28	

and Fig. 3). This may indicate that Hg is more or less associated with the organic matter.

Carbonate

Carbonates (calcite and dolomite) in the soils studied are both of inherited and pedogenic origin (Mejeed, 1993). Pedogenic carbonates are precipitated in the soil profiles from the carbonatic groundwaters under the evaporitic climatic conditions prevailing in the area. Sr is the only trace element that is significantly positively correlated with this fraction indicating that carbonates govern the distribution of Sr in the soil profiles in this area (Table 3 and Fig. 3).

Cation exchange capacity (CEC)

This feature has the most marked influence and includes all other soil characteristics, humus, particle size, and pH. There is a significant positive correlation between CEC and all the elements which are well correlated with both the clay and organic fractions (Table 3), which affirms their adsorption on the surfaces of these fractions. The only significant negative correlation was observed with Sr and Zr which are not bound either to the clay or to the organic matter, or in other words, they are not controlled by sorption processes.

pH

It changes the chemical composition of the different soil horizons and the availability and mobility of trace elements. In this study, it has very significantly negative correlations to all elements which are positively correlated with the clay and organic matter (Table 3). The only significant positive correlation was observed with the carbonate and consequently with Sr. The negative correlations seem to be indirect. The positive correlation with the carbonate indicates that the pH in the soils studied (slightly alkaline) is attributed to hydrolysis of carbonates (Foth 1984), which indicates that the soil pH increases as the carbonate content increases, and this leads to dilution of the other major constituents including clays and organic matter to which most of the trace elements are attached and reflects in its turn the marked negative correlation between pH and trace elements.

Element correlations

Significant correlation coefficients among elements are illustrated in Fig. 4. The nature of these correlations is associated with the mineral phases to which the trace elements are bound. The elements Ag, As, Cd, Zr, occur alone and never show any common significant correlation with any of the other elements. Sr only has significant negative correlations with other elements because it occurs in the carbonate fraction which is a major constituent and any increase or decrease in its amount influences the amount of other major constituents such as clays and organic matter which govern the distribution of most trace elements in the samples under study. However, the majority of elements are significantly positively correlated and this reflects their common occurrence in both the organic and clay fractions.

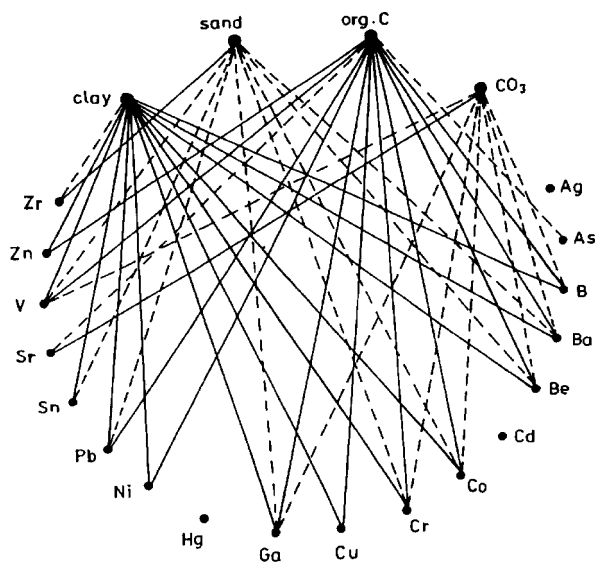


Fig. 3. Significant relationships of trace elements to some soil characteristics. Continuous lines represent the positive correlations, and dashed lines represent the negative correlations.

with any of the soil properties investigated. However, it has a relatively close correlation (0.26) with the organic carbon on one hand, and it also shows significant positive correlations with the elements Cu, Ni, and Zn which are particularly strongly bound to the organic matter in this study (Table 3

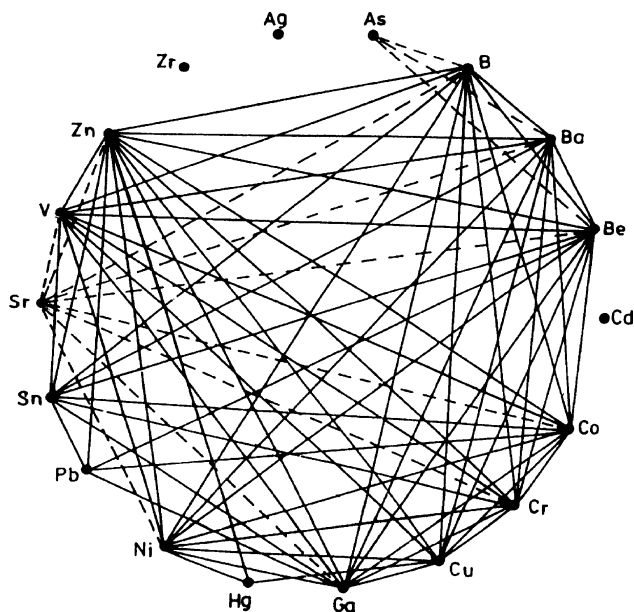


Fig. 4. Significant inter-element relationships. Continuous lines represent positive correlations, and dashed lines represent negative correlations.

Discussion

From the obtained results it is obvious that both clays and organic matter are the main contributors to most of the trace elements in consistency with the literature. Esser et al. (1991a, b) reported that most trace elements in soils in the Indiana Dunes show elevated bulk concentrations in the surface horizons and they attributed this accumulation to pollution sources, vegetation density, organic matter and clay contents. Le Riche (1973) attributed the high concentration of Cu in the surface horizons to organic matter. Berrow et al. (1978) stressed the affinity of V to be adsorbed on the clay. Murad & Fischer (1978) reported an enrichment of Pb in surface soil layers and they attributed this to the affinity of Pb for organic matter and, possibly to extraneous addition as a result of environmental pollution. Jones et al. (1986) recorded a strong association between Ag and organic matter and that Ag showed a marked surface enrichment in all cases. Lund & Fobian (1991) attributed the retention of As, Cu and Cr in the A horizon to high amounts of organic matter. Beneš & Pabianová (1983, 1984, 1987) and Trnčík & Beneš (1991) have also reported the significant correlations between trace element contents and the soil characteristics concerned in this study and ascertained the big influence exerted by all soil properties on the content and form of trace elements.

In spite of the fact that the elements Ag, As, and Cd exhibit no correlation to the remaining elements which may indicate an independent occurrence, they do not show any association with any of the soil characteristics and so their occurrence remains questionable. This may happen probably due to their low values especially for Ag and Cd which may consequently yield unreal correlations. Esser et al. (1991a) reported the presence of a significant correlation between As and the content of primary iron oxides in the very fine sand fraction and that As possibly occur in mineral inclusions such as zircon, monazite, and sulfides within the Fe oxides. Secondary Fe and Al-hydroxides play an important

role in the scavenging of trace elements that have been released by weathering (Jenne 1968; Koons et al. 1980). Arsenic of the present study shows its relatively strongest correlation (0.20) with the fine sand fraction. The prevalence of iron mottling in most of the soil profiles studied, as it is revealed from the morphological description, may indicate that iron (and manganese) oxides could significantly contribute to the distribution of trace elements in the soils studied.

However, the common occurrence of Ag, As, and Cd in phosphate fertilizers can also throw the light on the possible association of these metals with P. Jing & Logan (1992) concluded that the somewhat better correlation of the Cd/P contents of the sludges with sudax Cd uptake vs. that with sludge Cd content supports the suggestions that sludge P may reduce the solubility of sludge Cd by coprecipitating Cd as various phosphates, in correspondence with similar suggestions made by Logan & Feltz (1984).

Cluster analysis has also been used to determine the correlations and groups which may be found among the different trace elements. A dendrogram based on the euclidean distance, single linkage, nearest neighbour method (Fig. 5) represents the results of grouping trace elements according to their content. There is a primary separation which agrees with our previous discussion about the different phases to which trace elements are bound with the exclusion of Pb. Eight groups have been identified, among them two are substantial which owned their existence to both the clay and organic matter, but the first includes Cu, Hg, Ni, and Zn which are more inclined toward the organic matter. The second group include the remaining elements shared by both the clays and organic matter. The remaining groups represent elements that are assumed to occur as independent phases like Zr and Sr, or do not have clear relation with the other elements in the case of Ag, As, and Cd. However, even for Pb it shows the supposed association with the two substantial groups, but at higher distance level.

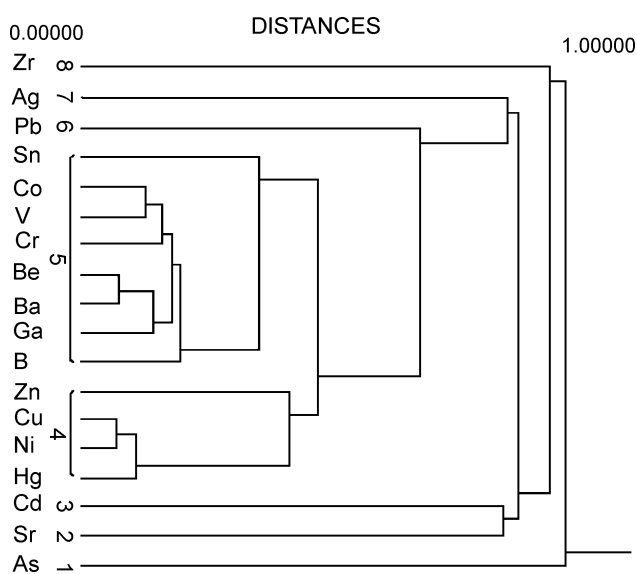


Fig. 5. Dendrogram showing the groups revealed by the trace elements under study.

Conclusions

From the viewpoint of landscape geochemistry it could be concluded that the majority of trace elements are concentrated in the upper part of soil profiles at the biogeochemical barriers (humus horizon), which reflects the weak leaching tendency in the soil profiles under the prevailing evapotranspirative conditions.

Generally, they show tendency to be associated with clay fraction and organic matter which suggests that their behaviour is mainly governed by sorption processes. From the environmental viewpoint, it means that most of the followed trace elements could be available to plants from the sorption complex.

Sr represents the only element concentrated at the carbonatic evaporative geochemical barriers. This indicates its addition from the groundwater to the soil profile.

All obtained results indicate that the geogenic factor (parent material) controls the distribution of trace elements in the studied soils, but groundwater also play a significant role by coprecipitating trace elements at the geochemical barriers, which confirms the geochemical influence of groundwater on soil cover in the Žitný ostrov region. A limited role could also be played by the anthropogenic factor, particularly the agricultural activities, as we pointed in a previous work (Mejeed & Čurlík 1993).

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