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REGIONAL ANALYSIS OF THE HEAVY METAL CONTENT OF SOILS ON THE NE-PEDIMENTS OF THE MÁTRA MTS.[1]

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Introduction

Although metals including heavy metals are natural compounds of our environment, the atmosphere, pedosphere and hydrosphere, according to some predictions they seem to be major polluting agents in the decades to come. Owing to the effects of different physical, biological and chemical parametres (like reaction, temperature or land use changes, heavy metals can be remobilized and re-accumulated at certain spots exceeding health limits (Reiche 1992, Fillus, Richter 1991). Human activity (agricultural fertilizers, manure, communal waste, metal foundries, air pollution from chemical factories, lead emission of motor traffic etc. all contribute to heavy metal accumulation. The above reasons recommend their detailed investigation and the definition of their role in landscape development.

In this study the areal distribution of metal ions and its regularities manifested are being surveyed in the heterogenious soil of a physical geographical unit (a catchment area) having various economic land use classes (forest, agriculture, mining). In the first stage of the survey to reveal landscape links the relations of these important, environmental-reflexive elements were studied with other measurable soil or morphological parametres. The measured values were then compared both with the European average and the health limits.

Geographical outlining of the test area

A hydrogeographically unified, but geologically, morphologically versatile surface with various land use types was chosen for detailed survey of landscape factors. The area is situated in the NE of the Mátra Mts in the Mátra Foothill and Parád--Recsk Basin microregions (Figure 1). The central settlement of the approximately 6 km long and 3-5 km wide catchment is Bodony. The boundary of the test area is represented by the dividing line marking the Kataréti Brook's and Áldozó Brook's catchment (Figure 2).

The area is elevated to 200-880 m above sea level. It is a low hilly region or infrabasin hills, sloping mainly to N-NE, The average watercourse density of its erosionally and derasionally dissected surface is 4.2-4.7.

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[1] The survey was performered in F4016 OTKA project

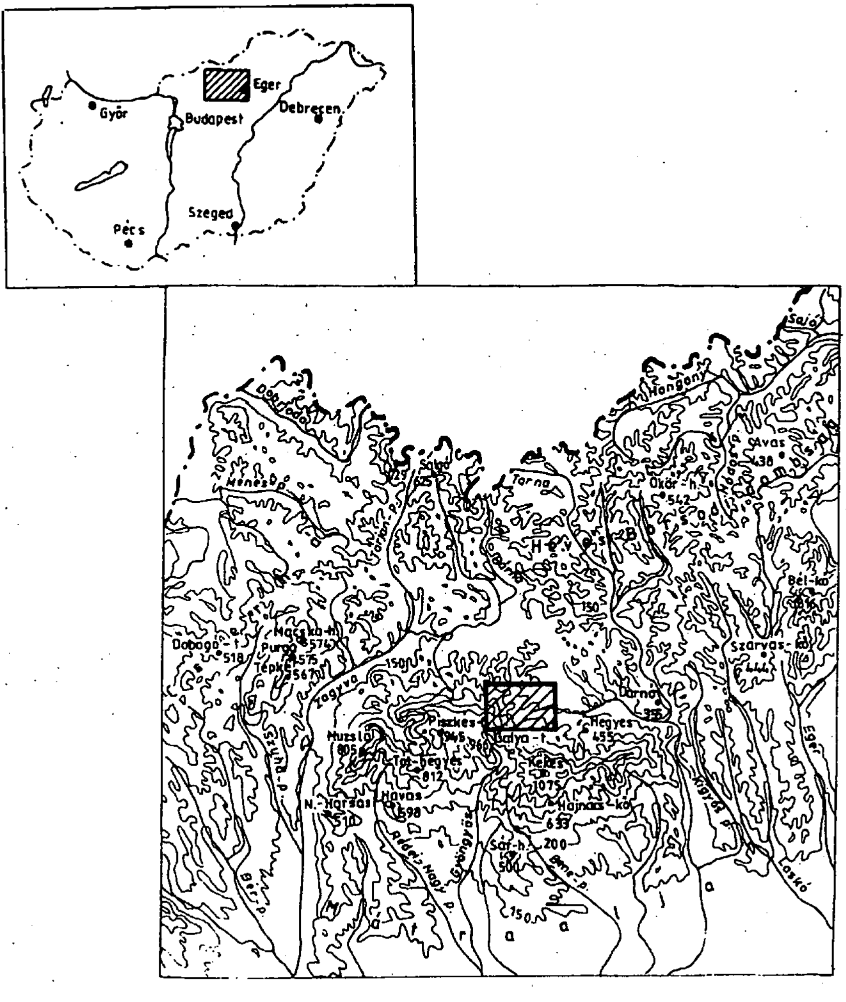

Figure 1 *Location of the test area*

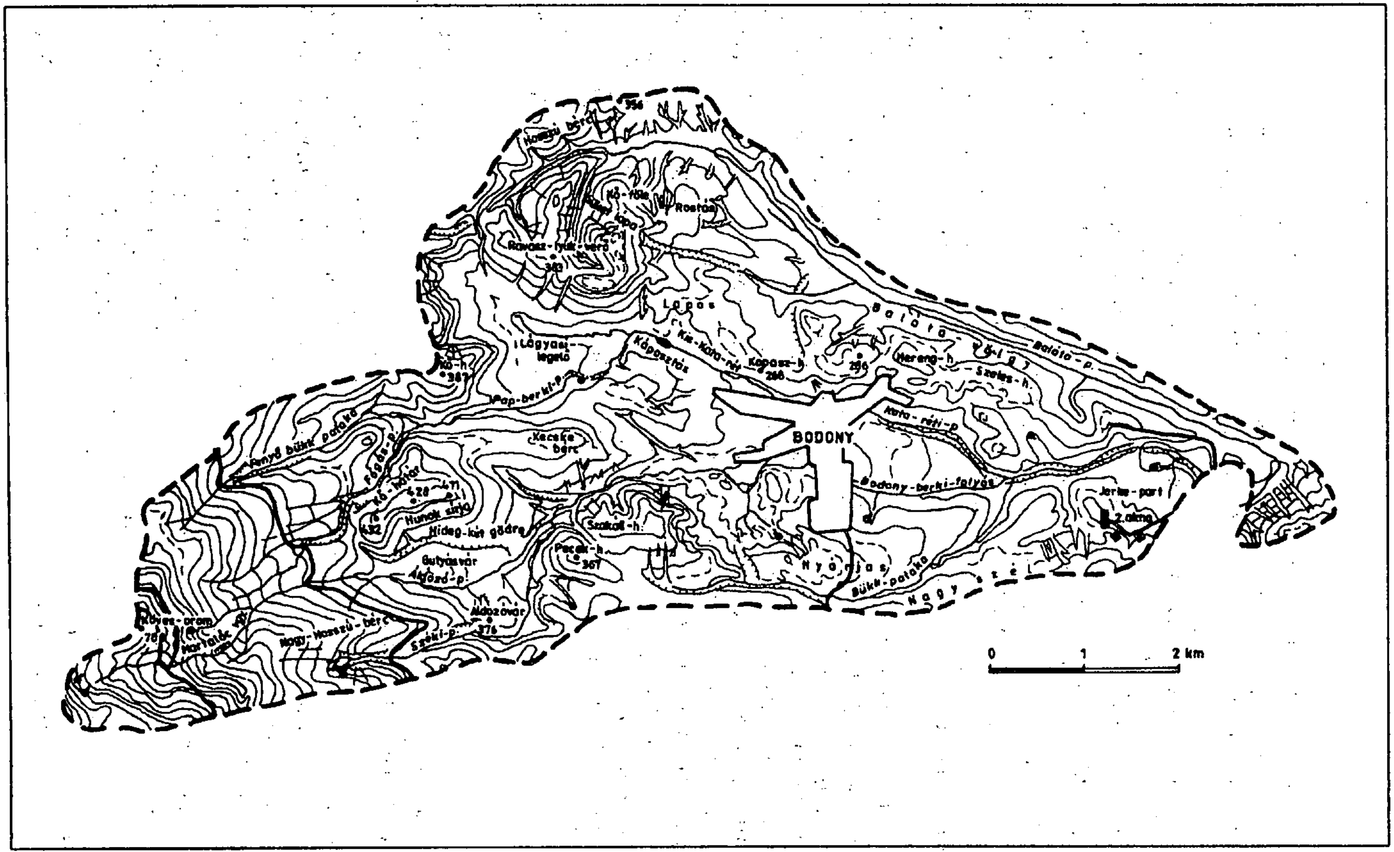

Figure 2 *Topographic map of the test area*

Geologically it has a double character. The geological structure of the region is manifested on the surface in Upper Eocene andesite and dacite and their tuffites. The parts in the basin are covered with Middle Oligocene clay, clay marl and schlieren (Figure 3).

Its climate is temperately cool and humid. The annual mean temperature is 8.3-8.5. °C and the number of sunshine hours is about 1900. The annual average precipitation is 650-750 mm. Its climate and endowments favour sylcanoculture, but also agriculture if less temperature dependent species are concerned.

Its soil is clayey brown forest soil (95 %) developed partly on andesite and andesite tuffite detritus, partly on Tertiary sediments. Its mechanical composition is loam and clayey loam. Soils have neutral or weak acid reaction and the W-SW, forested slopes have definite acid reaction. In the brooks' valleys there are young, raw alluvial soils with clayey composition and acid reaction.

From land use point, the catchment has again a double character: its W-SW part is forested (Turkey oak and oak, sessile oak and hornbeam), its E part is cultivated (croplands mainly).

Sampling and methods of analysis

More than 150 soil samples were taken from some 20 km^2 large area in the summer of 1992. Soil profiles were sampled by 25 cm down to 150-200 cm in the area covered with Tertiary sediments. In the rougher W-SW areas, samples were taken down to the parent rock that is only 30-40 cm at places. Considering the heterogenity of the area, samples were taken relatively densely and evenly. There was no sampling within the settlement limits, in private orchards and in the non-trespassing area of the Recsk Copper Mines on and around Lahóca Hill. Sampling sites are about 200-400 m from one another. The heavy metal content, reaction and hydrolytic acidity tests were performed on samples from 30-40 cm depth. The vertical heavy metal tests of soil profiles (Frühauf 1992) are suitable to detect the metal content of lithogenic origin and that of deposited from human-technical impact, if the samples are from this depth. There were 128 samples analyzed. (Figure 4)

Chemical reaction (H_2O) was measured by an electric pH meter, while hydrolytic acidity (Y_1 value) was defined by volumetric analysis with phenoltalein indicator in calcium acetate solution. Metal content of the soil was detected for 9 elements (Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn). Selection of elements is defined by several factors. Having considered the dominant rock type of the area (andesite), metals from that had to be measured (Cd, Cu, Ni, Zn). Iron, mangane, aluminium oxides of the soil do influence the occurrance and affinity of the heavy metals. Pb and Cd were measured due to possible human impact. The values of microelement content were obtained through JY-24 type spectroscopic analysis of 1 g soil sample after the hydration approach with recirculating drip refrigerator.

Samples having deviated from the average were taken out of further analysis after the distribution analysis of the parametres (Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn, pH, hydrolytic acidity). Their control measurement was to be performed seperately.

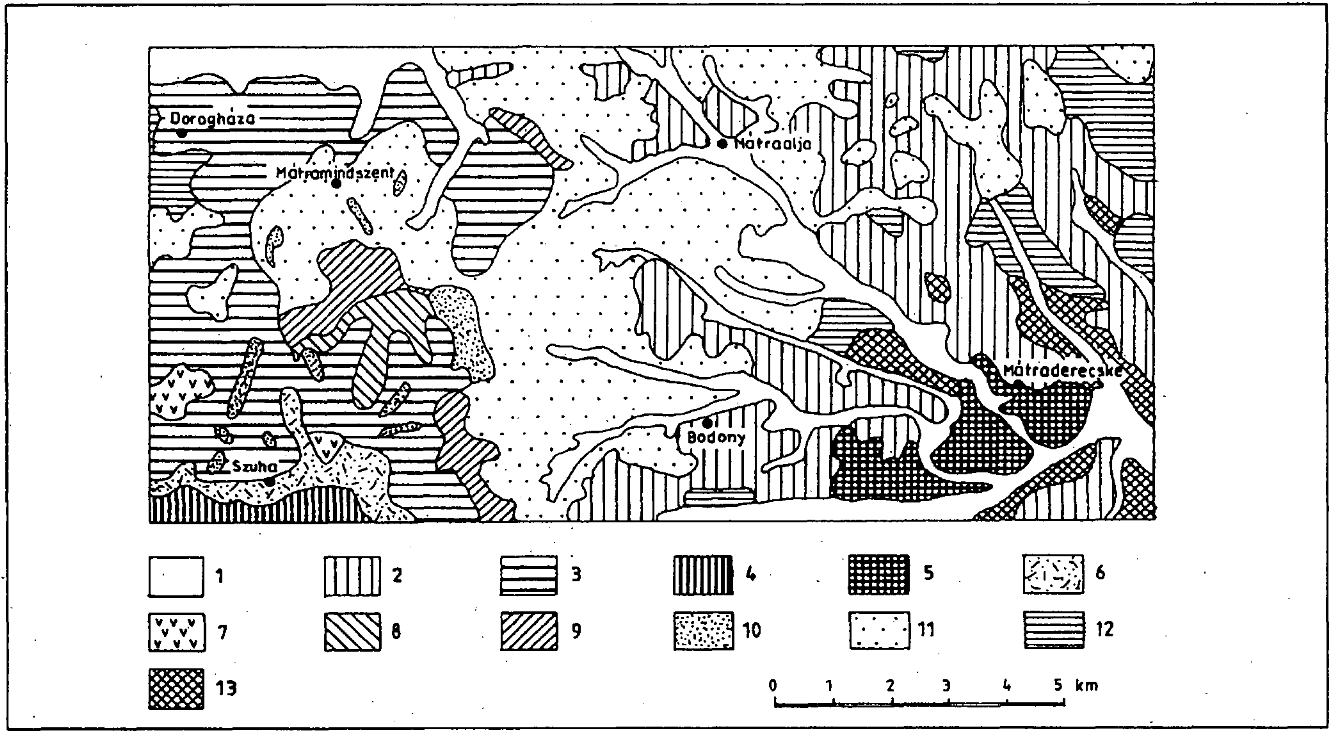

Figure 3 *Geological map of the test area*
1=Holocene in general 2=Pleistocene in general 3=slope clay 4=various andesite beds 5=pyroxene andesite 6=middle rhyolite tuff 7=andesite, lava flow. laccolith 8=direct cover of beds with brown coal layers 9=lower rhyolite tuff 10=sand, gravel, variegated clay 11=sand, sandstone 12=grey sandy clay 13=foraminiferal clay marl

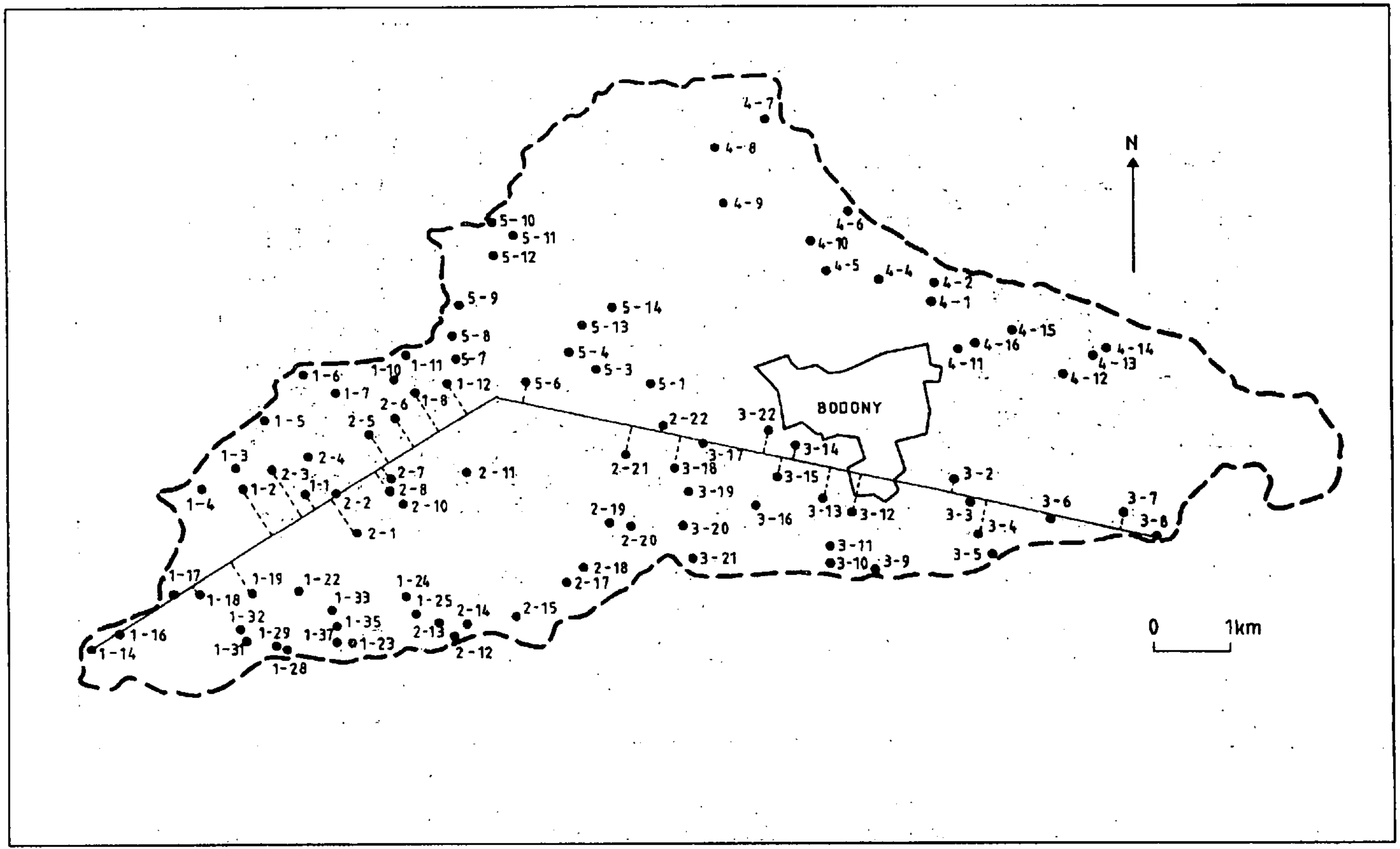

Figure 4 *Sampling sites in the test area*

Evaluation of results

In surveying the relations among landscape factors, the relations of the compounds of the geofactors also have to be examined in detail today. So far the metal content of soil has been investigated from the viewpoint of their biological role. The main natural and human sources of trace elements filtering into soil are known (Papp 1983). Also, the global biochemical circulation of the metals is known (Papp, Kümmel 1992). However, the spatial distribution of these elements have also to be examined. What are the relations to be found between them and between other areal factors liable to undergo changes?

The average values of the metal content of soils on the basis of the samples collected from the test area are the following in ppm: Al - 22246, Cd - 2.2, Co - 9.9, Cu - 14.2, Fe - 25441, Mn - 899, Ni - 26, Pb - 17, Zn - 61. These values are similar to the ones occurring in an area having no or very moderate human impact (Brümmer et al 1991; e.g. Cu: 2-40 ppm, Ni: 5-50 ppm, Pb: 2-60 ppm and Zn: 10-80 ppm). In case of cadmium, however, this average value is 0.1-0.6 ppm. In the test area it is several times higher (2.2 as in Figure 5), being very close to health limit (3 ppm in Brümmer et al 1991). The volume of cadmium in the polluted soils is determined first of all by the parent rock. From human impact two thirds of Cd can be emitted into the atmosphere through the metallurgy of precious metals (zinc and copper). From the air it is deposited dry onto the soil (Mészáros et al 1993). Waste burning and the producion of phosphate fertilizers are another source of Cd. The samples taken from the test area, however, do not allow human impact, because the correlation between Zn and Cd is strong (0.69 coefficient) that shows a significant relation on the 0.001 level. This strong, almost linear correlation can be seen easily in the Cd-Zn diagram too (Figure 6). The enrichment of Zn is known in the test area and it had been mined for years. This high value of Cd ought to be due to the parent rock therefore.

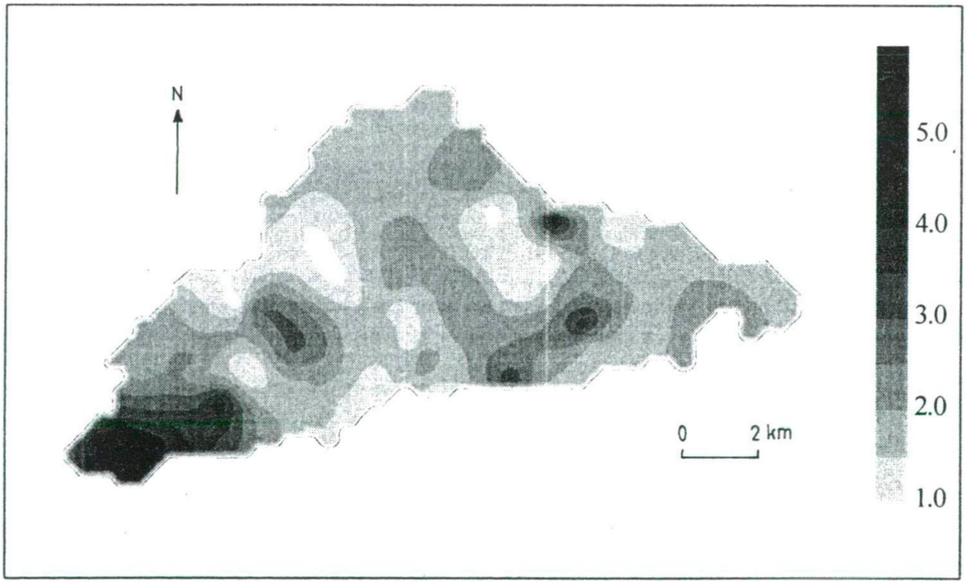

Figure 5 *Regional distribution of Cd content of soils (ppm)*

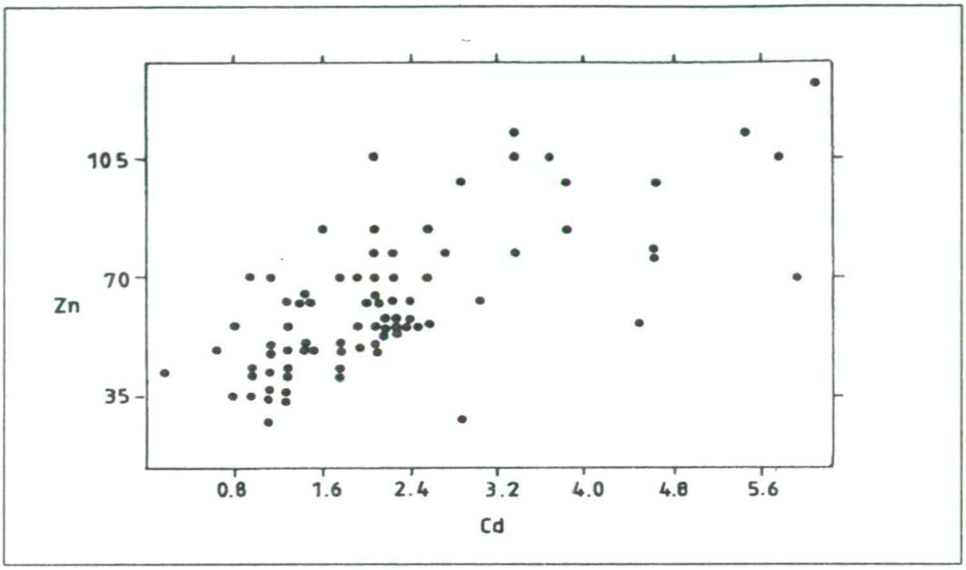

Figure 6 *Zn - Cd diagram (values in ppm)*

Cd compounds have a toxic effect on the haematotherma. They can easily reach man at the end of the food-chain and their threshold values for human health are very low, This enrichment of this element has to be the objective of further investigations.

The spatial distribution of metal contents are shown in Figures 5 and 7-9. Having compared them with the elevation contour line map of the area, their relation with elevation is easy to be seen. It is also proved by the strong correlation between the soil sampling sites' elevation above sea level and the metal concentration levels. (With the exception of copper, all metal concentrations show a significant correlation of 0.001 level with the elevation; see Figures 10-11). It can be explained by a third factor, the parent rock that cannot be described numerically. In the active valleys, the metal content was found to be lower than towards the water divide on the combs. It is especially well-marked in the SW of the test area, where relief energy is the largest (the dividing line is at Galyatető), on the Pecek Hill (367 m) and Kecske Hill (340 m). The soils of the above mentioned sites were formed on andesite or on its tuffs. Here, owing to the greater slope angle, the depth of soil is thinner than elsewhere in the basin (on the slopes of Galyatető it is only 30-40 cm). Moreover, the effect of the parent rock is rather great on lithomorphic soils.

The E part of the test area has more metal content and there are several other factors modifying the relations between parent rock, morphology and metal content. The Jerke part (250 m) outstanding of its surroundings and its parent rock (andesite) have influence on metal concentration. The number 2 shaft of the Recsk Copper Mines, its waste rock pile and a sewage sludge depository can also be found in the test area. They excersise influence on the soil of their immediate environment through the definition of this impact requiring a more detailed sampling.

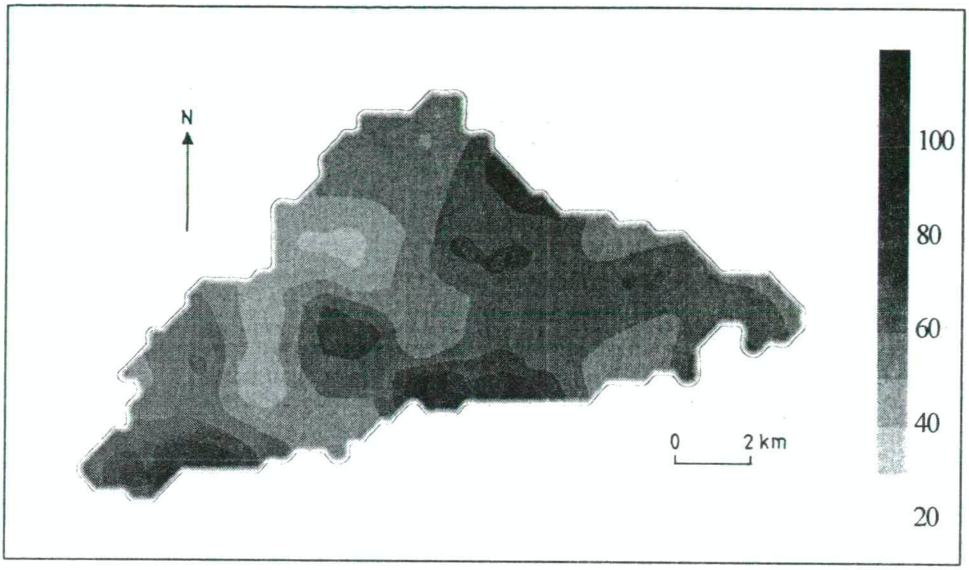

Figure 7 *Regional distribution of Zn content of soils (ppm)*

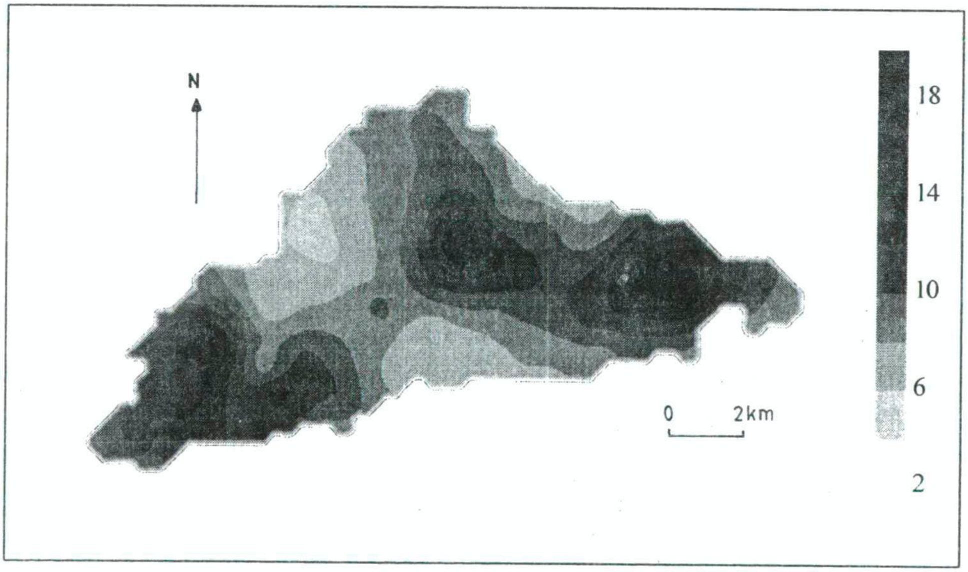

Figure 8 *Regional distribution of Co content of soils (ppm)*

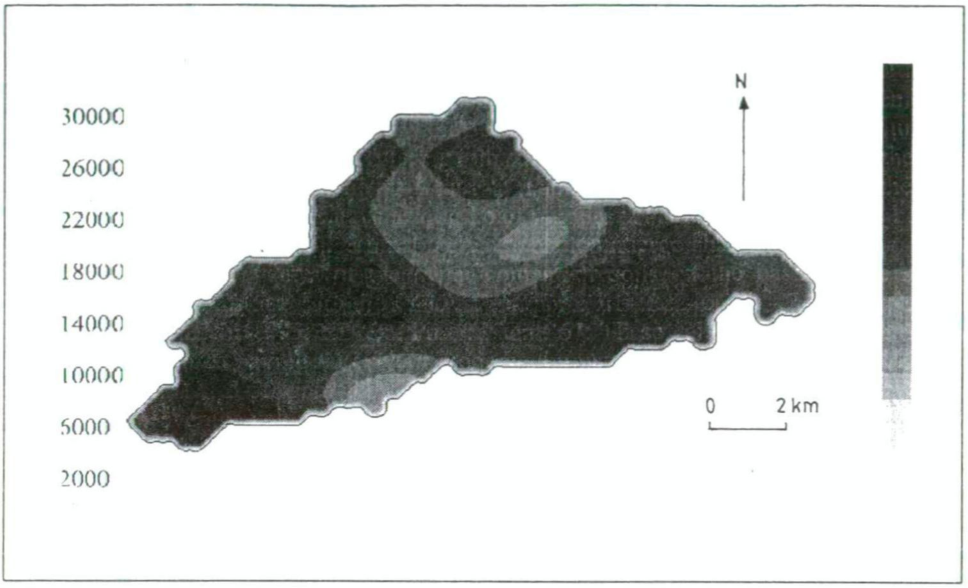

Figure 9 *Regional distribution of Al content of soils (ppm)*

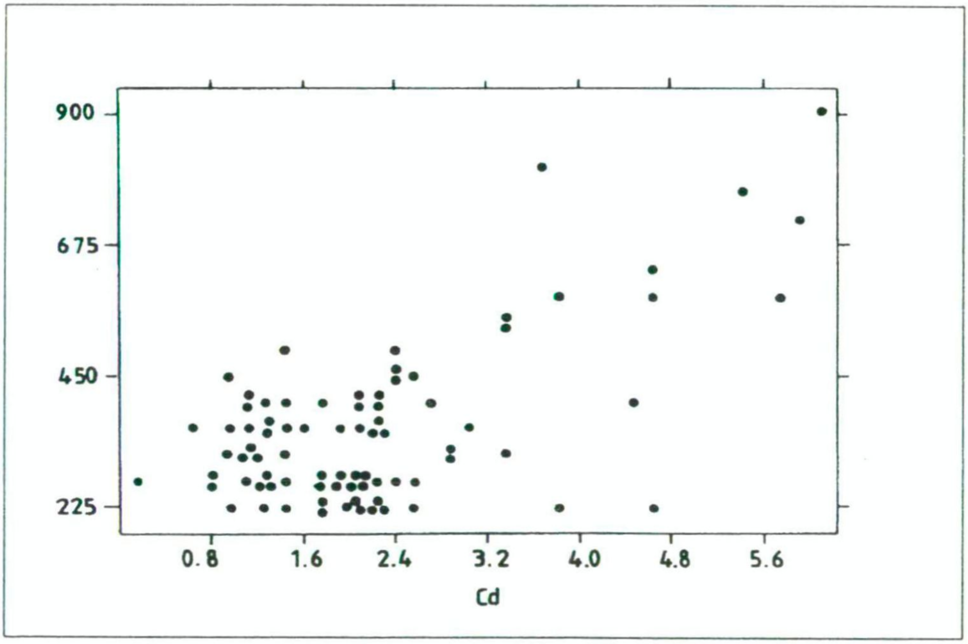

Figure 10 *Elevation (in m) - Cd (in ppm) diagram*

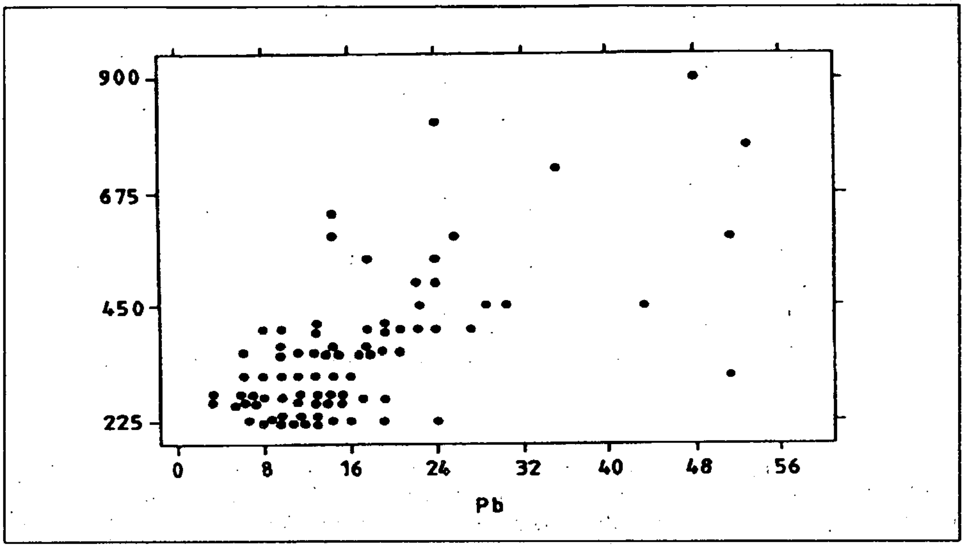

Figure 11 *Elevation - Pb diagram*

The soil reaction also contributes to the metal holding capacity, mobility and metal content of the soil (Vermes et al 1993). Table 1 shows the relation between soil reaction and metal linkage analysed in this research (Leser, Klink 1989). The values of the Table represent soils of low humus content and sandy loamy soils. In case of larger humus content or other mechanical composition these values will be slightly modified. In the test area there are loamy and clayey loamy soils. So now, these values ought not to be modified (Blume, Brümmer 1987 in Leser, Klink 1989). Values describing ion-linkages can be interpreted as below: 0 = none; 1 = very slight; 2 = slight; 3 = medium; 4 = strong; 5 = very strong.

Chemical reaction of the soil can be described another way. Hydrolytic acidity can be defined from the samples collected to analyse their metal content. There was a strong positive correlation found between these values and that of metal concentrations. The relation is also manifested regionally. The reaction of the soil is changing parallel with the elevation contour lines, though it is not enough in itself to have an impact on the spatial distribution of the metals (apart from local deviations), if the above Table is considered, since the dominant reaction values are 5.5-6.5. The mobility increasing chemical reaction of soils occurs at 5.5 pH value, or at greater acidity than that (see Table 1, Brümmer et al 1991).

There is an E-W or NE-SW trend of change of morphological, geological and techno-pollutional values in the area. So the change of metal concentration values is also worth examining in a cross section of similar direction (Figure 4). The relations between heavy metal concentration and geomorphology, and between heavy metal concentration and geology are evident as far as Zn, Pb and Cd are concerned (Figure 12). In their examples, the three peaks of the concentration are connected to the above mentioned geomorphological units, while the sudden rise in the E part represents a transition towards the Lahóca Hill that could not be sampled.

metal	*pH ($CaCl_2$)*									
	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7
Cd	0	0-1	1	1-2	2	3	3-4	4	4-5	5
Mn	0	1	1-2	2	3	3-4	4	4-5	5	5
Ni	0	1	1-2	2	3	3-4	4	4-5	5	5
Co	0	1	1-2	2	3	3-4	4	4-5	5	5
Zn	0	1	1-2	2	3	3-4	4	4-5	5	5
Al	1	1-2	2	3	4	4-5	5	5	5	5
Cu	1	1-2	2	3	4	4-5	5	5	5	5
Pb	1	2	3	4	5	5	5	5	5	5
Fe^{3+}	1-2	2-3	3-4	5	5	5	5	5	5	5

Table 1

The last stage of the survey to reveal this connection was a cluster analysis performed to group the ten variables (AL, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn, hydrolytic acidity). Forming the clusters was done with the farthest neighbour method, observing the Euclidean standard. A simplified dendogram of the clusters is shown in Figure 13. The three major sample groups (A1, A2, B) are clearly seperated in space, mappable (Figure 14) and show a strong correlation with morphology. Table 2 displays the characteristic average values of the groups.

metal	A_1	A_2	A_3
Zn	61.6	45.1	82.6
Cd	2.0	1.17	3.9
Cu	13.8	15.4	13.8
Pb	15.7	13.2	24.1
Co	9.7	6.7	13.9
Ni	28.5	25.1	22.0
Fe	24509.3	14364.8	40588.9
Mn	706.5	1090.9	1132.6
Al	21184.4	14922.4	33327.8
hydrolytic acidity	12.8	12.6	25.1

Table 2

In the cluster map the representative groups answer the major morphological units of the test area. A part of the samples classified into group B is situated on the hillside sloping towards Galyatető, while the other part can be found around the waste rock pile belonging to shaft 2 of the Recsk Copper Mines. The majority of the samples of group A1 can be found in the basin, while that of group A2 in the low hilly region.

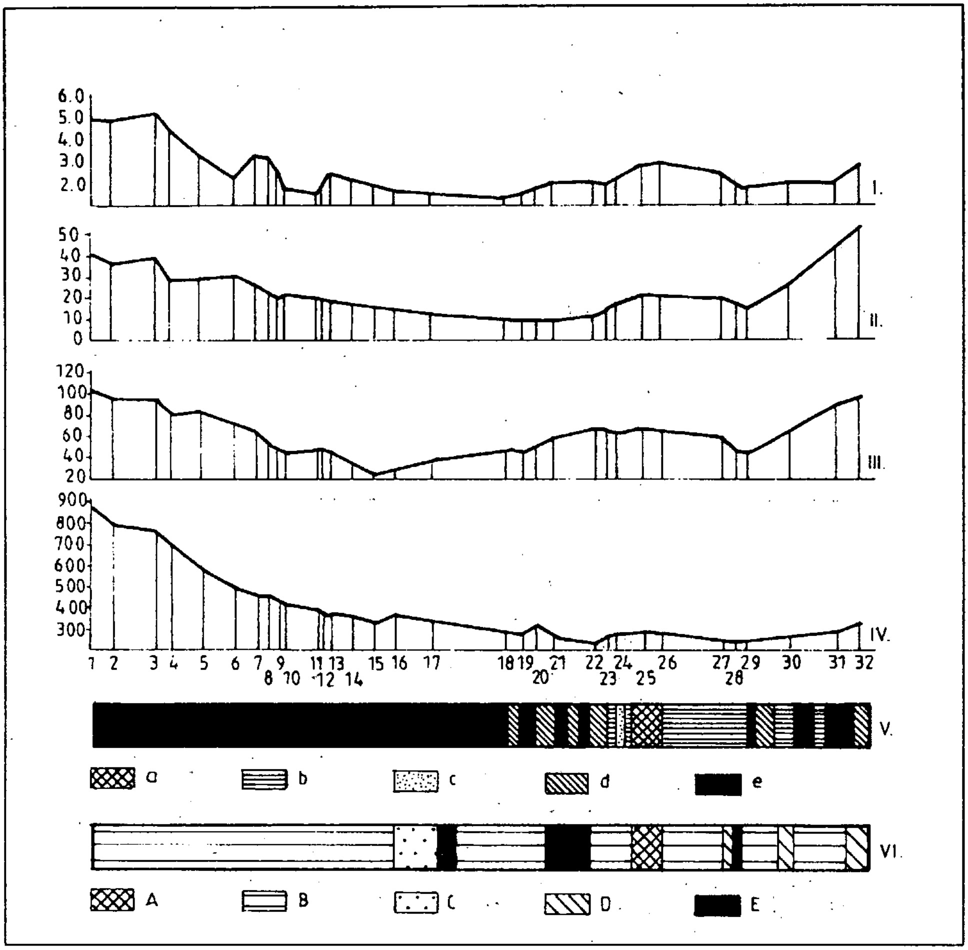

Figure 12 I.- *Cd distribution in the E-W cross section of the test area*
II. *Pb distribution in the E-W cross section of the test area,*
III. *Zn distribution in the E-W cross section of the test area*
IV.: E-W section of morphology of the area (y axis= elevation in m),
V: land use in the E-W crossection of the area,
VI: soil types in the E-W section of the area
a=settlement, b=meadow, c=orchard, vineyard, d=pasture, e=forest
A=settlement, B=brown forest soil, C=pseudo gley brown forest soil,
D=rusty brown forest soil, E=humic alluvial soil
sample sites on I-IV.figures:
1=1-14, 2=1-16, 3=1-17, 4=1-18, 5=1-19, 6=1-2, 7=2-3, 8=1-1, 9=2-1, 10=2-2
11=2-8, 12=2-7, 13=2-5, 14=2-6, 15=1-8, 16=1-12, 17=5-6, 18=2-21, 19=2-22,
20=3-18, 21=3-17, 22=3-22, 23=3-15, 24=3-14, 25=3-13, 26=3-12, 27=3-2,
28=3-3, 29=3-4, 30=3-6, 31=3-7, 32=3-8,

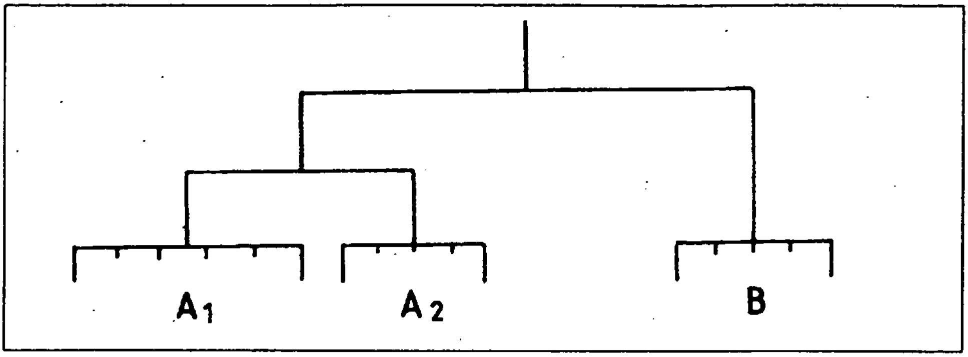

Figure 13 *Simplified diagram of the cluster analysis (on the basis of all variables with Euclidean standard)*

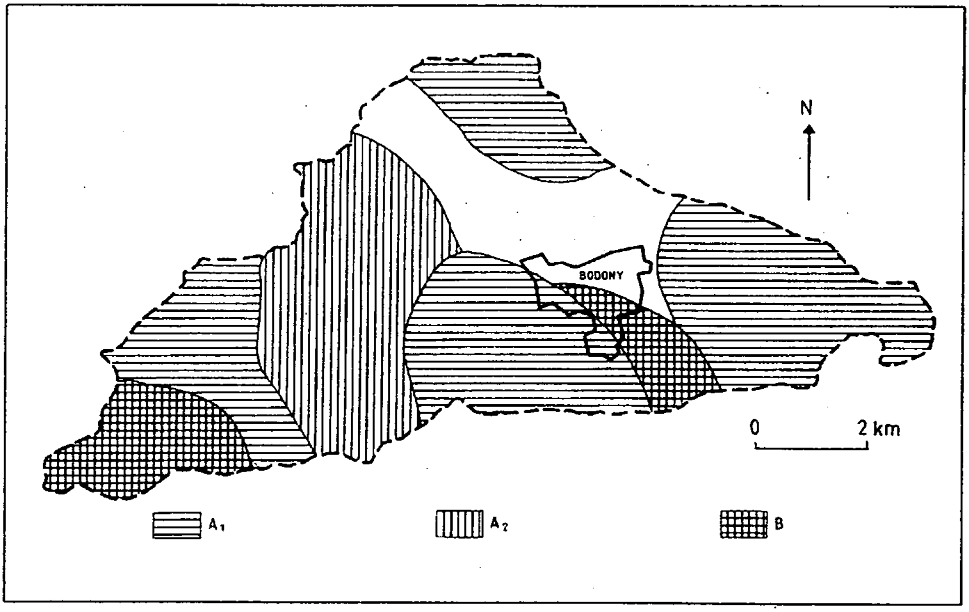

Figure 14 *Cluster map of the test area*

Summary

From among the relations of the landscape factors, the relationships between the metal content of soils and morphology and the chemical reaction of soils have been examined along with their spatial distribution. The results of the above examination reveal the defining role of geological condition (and partly that of the reaction, the humus and clay content of soils) in the regional variability of metal ions of soils. (It is especially true for the soils of neutral or slightly acid reaction.) Most metal content of soils can be regarded as lithogenic. The relation between the parent rock that cannot be described numerically, and the elevation above sea level is detectable in the test area. It results in the virtual connection between the metal content of soils and the sampling sites' elevation above sea level. A more detailed investigation of the vertical soil profiles from the polluted areas in order to detect the human-technical impact included in their metal content is under way. Similarly further examination is needed to establish the interrelation between the metal content of soils and other landscape factors.

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