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## GEOCHEMISTRY OF ZAGYVA'S FLOODPLAIN DEPOSITS NEAR APC (NORTHERN HUNGARY) – THE PRELIMINARY RESULTS\*

**Key words:** floodplain deposits, multicultural site, arsenic, chromium, copper, nickel, lead, zinc

### Introduction

The natural element cycle in environment is often disturbed by human activity. The first geochemical changes had occurred with the appearance of settled people in Neolithic Age who started farming cultures. However, this primitive cultivation and animals raising had local character, so an introduction of heavy metals to soils, water and air was limited to concrete areas. What is most important, changes which occurred in Neolithic Age was convertible. Irreversible and sometimes global disturbances was started by Industrial Revolution in 18<sup>th</sup> century. Therefore the part of elements have been running in natural cycle (for example Zn, As, Pb) or its migration accelerated (22). It is worth remembering that part of these elements represent of harmful element group called by *P e r e l m a n* (14) as excessive elements (depending on the geochemical landscape). An increased content of these substances is often dangerous for biosphere because its toxicity.

In this paper analyzed a degree of contamination five heavy metals: chromium, copper, nickel, lead and zinc, and also one semi-metal, arsenic.

High accumulation of arsenic, mainly in surface layers of soil and deposits, indicates the anthropogenic origin. Metalloid As<sup>0</sup> and organic form of arsenic are harmless, in contrast to inorganic form of arsenic, especially As<sup>3+</sup>. In soils with the high content of clayey fraction and organic soils noted the biggest contaminations of arsenic. Anthropogenic arsenic comes from metallurgy, chemical, cosmetic, pharmaceutical industry and tannery (7).

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Chromium occurs the most in  $\text{Cr}^{3+}$  form which is necessary for human health, and inaccessible for plants.  $\text{Cr}^{6+}$  and its compounds show a strong toxicity; that form is the most available for flora, unfortunately. The most important of anthropogenic sources of chromium contamination are tanneries and electroplating plants (10; 12).

The biggest role in copper fixation in soils fulfill the organic matter, clayey fraction and iron and manganese hydroxides. It is one of most important element for plants growth, animals and human health, but significantly exceedances of this heavy metals caused lot of disturbances. Apart from the industry emission, significant sources of copper are mineral and organic fertilization, using crop protection chemicals and municipal wastes (7).

The predominant form of nickel occurrence is binding to the organic matter and clay minerals, but mobile chelats and easily soluble form are also common. The important role of nickel concentration plays the mother-rock, pedogenesis and also anthropogenic influence. Except some functions nickel is useless for plant (11), and its increased content is harmful. Nickel has a wide application in industry, mainly in metallurgy, galvanization and in anticorrosive coatings production (7).

Lead is small active heavy metals in soils, therefore its content is connected especially with composition of parent rock. Unless cases of plant hiperaccumulators of lead are known, then so much this heavy metal is always toxic for animals and human. It is used for example in batteries, dyes and ceramics production and production of alloys. Significant quantity of lead derived from combustion of liquid fuel with lead additive (7).

In opposite to lead, zinc is active element in soils, and occur in exchangeable forms and in compounds with organic matter, too. It is necessary heavy metal for all living organisms. The main anthropogenic sources of zinc are metallurgy, chemical industry, pigments and paints production and municipal wastewater. Another important factor caused the pollution with Zn is agriculture (7; 8).

### **Research area**

Hungary with 93036 km<sup>2</sup> of area is typical lowland country. Terrains below 200 m a. s. l. occupy 68% of whole country. Sites above 400 m a. s. l., recognize as mountains practically, are only 2% of Hungarian territory (5).

The research area is situated on north Hungary, on the border between two, big regional units – Great Hungarian Plain and Northern Highlands (11). Apc city and its surroundings belong to the Zagyva's catchment. Zagyva (with 179 km length) created from several smaller rivers. Its source is located in northern part of Cserhát Mountains on 600 m a. s. l. It flows into Tisza near Szolnok (13).

Research area, according *M i d z i o* (11) called Palócföld, lies between Cserhát Mountains (with Karancs 729 m a. s. l.) from north-west and Mátra Mountains (with Kékes 1015 m a. s. l.). Both of mountain ranges is part of Carpatians Mountain there had place a Tertiary volcanic processes (in Miocene Age). Cserhát Mountains has

hilly character with single, higher heights. They are fragmented by numerous valleys. Cserhát Mountains are built mainly from a Tertiary sands and silts, and also volcanic stones, especially from andesite. Mátra Mountains as the highest mountain range of Hungary, is built from young volcanic stones, such as andesite, rhyolite, andesite's conglomerates, tuffs and its agglomerates (9; 13).

In connection with frequent flooding of Tisza river and its river tributaries, in large areas of Hungary silts and sands was accumulated. From these deposits developed so-called young alluvial soils, characterized by small content of humus (13).

Research area is characterized by very flat relief, with wide floodplain of Zagyva river. A quite small remnants of terrace lie several meters above floodplain's surface. An Holocene backswamps has been created in shallow depressions.

The research area is located within rural areas, on the border of two county (*Megye*): Nógrád and Heves. Zagyva's catchment have typical agricultural character that is connected with fertile and high quality soils, according map of Hungarian Institute of Surveying and Mapping (3) mainly alluvial soils, chernozems and forest brown soils. Forests dominate mainly on areas of Matrá and Cserhát Mountains. Near investigated multicultural site runs national road n° 21 (hun. *21-es főút*), about 67 km of length and relation of Hatvan-Salgótarján. The nearest single-track and not electrified railway (n° 81 Hatvan-Somoskőújfalu) extends across Zagyvaszántó. An industry of Zagyva's catchment is relatively weak-developed. A bigger cities (Hatvan, Jászberény, Szolnok) are located in the lower section of mentioned river (23; 25).



Fig. 1. Research area

As it is shown in Table 1, the content of heavy metals depends on soils types and soil texture, on examples of Hungarian soils (1). Lithosols are the richest in As. A high content of Cr, Cu and Zn accumulates in meadow soils and alluvial and sedimentary soils. The high accumulation of Pb is typical for salt-affected soils, lithosols, alluvial and sedimentary soils and meadow soils. The poorest in selected heavy metals soils type is skeletal soils. Deposits derived from clay have usually significant higher amount of heavy metals than soils from sand and loam.

Table 1

Average of elements content of Hungarian soils

Soil types/ soil texture	As (mg·kg <sup>-1</sup> )	Cr (mg·kg <sup>-1</sup> )	Cu (mg·kg <sup>-1</sup> )	Pb (mg·kg <sup>-1</sup> )	Zn (mg·kg <sup>-1</sup> )
Skeletal soils	4	8	13	11	27
Lithosols	8	19	17	24	49
Brown forest soils	6	19	17	17	43
Chernozem soils	6	21	21	16	51
Salt-affected soils	5	20	20	26	54
Meadow soils	7	23	24	23	62
Bog soils	6	15	19	15	32
Alluvial and sedimentary soils	5	21	25	23	69
Sandy soils	3	6	10	9	19
Loamy soils	7	17	18	16	44
Clayey soils	6	26	26	26	71

Source: (1)

As it is shown in Geochemical Atlas of Europe, edited by Forum of European Geological Surveys (FOREGS) (17), floodplain deposits are commonly rich in trace elements, especially in Cu and Zn. Additionally, near Apc region a local geochemical anomaly of copper occurs, with value 97 mg·kg<sup>-1</sup>. These deposits are quite poor in Ni (22-33 mg·kg<sup>-1</sup>) and Pb (28-35 mg·kg<sup>-1</sup>). Other values are presented in Table 2, below.

Table 2

The range of values for investigated trace elements according FOREGS

Element	The range of values (in mg·kg <sup>-1</sup> )
As	13-17
Cr	59-88
Cu	35-65
Ni	22-33
Pb	28-35
Zn	100-130

Source: (17)

### Materials and methods

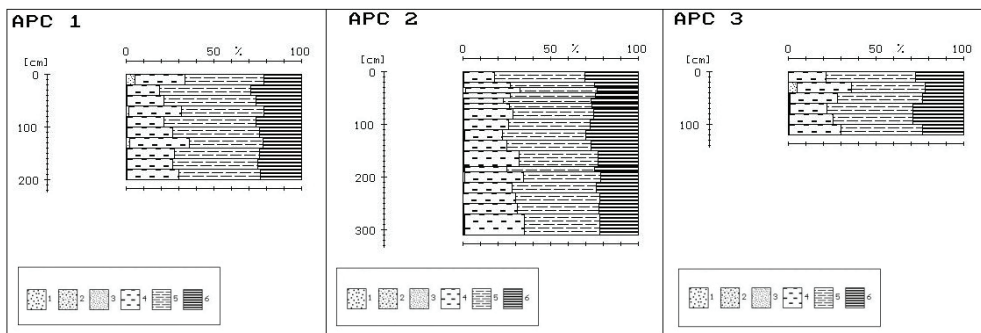
The main geoarchaeological research in Hungarian territory were carried on floodplain area where as a results of earlier work identified artifacts of Neolithic, Bronze and Roman cultures. From this place made three drilling on variable depth by use hand-auger Eijkelkamp. The picked profiles marked in turn: Apc 1 (N 47°48',093; E 19°40',178) from 200 cm depth, Apc 2 (N 47°48',062; E 19°40',147) from 310 cm depth and Apc 3 (N 47°48',115; E 19°40',196) from 120 cm depth. In case of Apc 1 the collecting of samples was limited by groundwater level by which materials situated below 200 cm was outwashed with a water intensively. Samples was taken usually on each 20 cm. The total number of cores is 33, it means 10, 17 and 6 from Apc 1, Apc 2 and Apc 3, respectively. Each samples were cleaned and described by organoleptic method. The material in 100-250 g per samples was picked up to folic bag and additive protected in black bags. After transport, samples were stored in laboratory room and air-dried. Because of the advantage of clayey fraction, dry samples became very compact and hard, therefore they had to be crushed to receive loose material. Such prepared samples were used to further analysis. The grain size analysis had made on laser particle size analyzer Mastersizer 3000. The basic analysis were performed by use: potentiometric method for determination of pH value, Scheibler's method for determination of carbonates content and Tiurin's method for determination of organic carbon content. The determination of 20 elements and percentage of Light Elements group (LE) had realized on mobile XRF spectrometer BAS® Delta type.

## Results and discussion

During drilling in Apc 1 on 120-140 cm of depth (sample n° 7) discovered the level of paleosol which distinguished from overlying levels by a little darker colour. The dominant colour of almost all samples was dark grey. Light yellow tinge was characteristic for parent rock layers which emerged out in Apc 2 on 270-310 cm of depth and in Apc 3 even from 80 cm below ground level.

Grain size analysis shown an advantage of clay fraction in case of all samples. A quite high share of silt was noted (from above 20% to over 40%). Content of sand is usually very small, no more than 10%. During field works has noted very individual cases of small pebbles on variable depth.

Figure below (Fig.2) have been generated by GRANULOM Programme, after the introduction of input data from laser analysis. As shown, the whole profiles are built from weakly sorted clayey deposits with admixture of silt. That material had been accumulated by floods of Zagyva river. Mean diameter of this samples oscillate between  $6,58 \Phi$  (0,01 mm) and  $7,56 \Phi$  (0,052 mm).



An explanation for Fig. 2: Fraction: 1 – coarse sand, 2 – medium sand, 3 – fine sand, 4 – silt, 5 – coarse clay, 6 – fine clay

Fig. 2. The results of grain size analysis for Apc profiles

The reaction of tested samples are weakly basic or basic. They have high or very high of carbonates content, often more than 15-20%, and even 44,02% in one sample of Apc 3. The content of organic carbon is low, and some samples values of that parameter do not reach 0,5%. All data connected with basic geochemical characteristics are summarized below, in Tab. 3.

On the same table (Tab. 3) put together the elementary statistic parameters for As, investigated heavy metals and also three macroelements (K, P and Fe). The visible notation (\*) next to some values shows exceedances of acceptable level of some elements concentration, established by Hungarian standard (6).

Table 3

## The geochemical data for Apc profiles

Profile	Parameter	Minimum	Mean	Maximum	Standard deviation	Median
Apc 1	pH in H <sub>2</sub> O	7,31	7,45	7,52	0,06	7,45
	pH in KCl	6,58	6,93	7,12	0,20	6,99
	%CaCO <sub>3</sub>	1,35	11,33	25,40	8,32	7,62
	%C-c <sub>org</sub>	0,78	0,99	1,38	0,18	0,96
	K (%)	1,37	1,47	1,69	0,10	1,45
	Fe (%)	3,57	4,03	4,62	0,32	4,00
	P (mg·kg <sup>-1</sup> )	318,00	521,14	762,33	163,89	471,21
	As (mg·kg <sup>-1</sup> )	9,50	12,35	14,33	1,87	13,17
	Cr (mg·kg <sup>-1</sup> )	64,00	79,50*	92,00*	8,78	80,00*
	Cu (mg·kg <sup>-1</sup> )	28,67	36,86	45,00	4,28	36,67
	Ni (mg·kg <sup>-1</sup> )	33,25	40,44*	43,67*	3,41	41,67
	Pb (mg·kg <sup>-1</sup> )	16,00	19,66	21,33	1,51	20,00
Zn (mg·kg <sup>-1</sup> )	83,67	99,46	120,00	10,28	98,50	
Apc 2	pH in H <sub>2</sub> O	7,41	7,63	7,95	0,13	7,59
	pH in KCl	6,76	7,06	7,38	0,18	7,03
	%CaCO <sub>3</sub>	1,03	7,98	22,39	6,78	5,98
	%C-c <sub>org</sub>	0,16	1,05	1,66	0,45	1,20
	K (%)	1,23	1,44	1,82	0,13	1,43
	Fe (%)	3,02	3,89	4,61	0,49	3,98
	P (mg·kg <sup>-1</sup> )	128,00	352,52	793,33	160,41	323,00
	As (mg·kg <sup>-1</sup> )	8,25	11,85	16,50*	2,14	11,33
	Cr (mg·kg <sup>-1</sup> )	<5,00	70,49	111,00*	27,97	76,00*
	Cu (mg·kg <sup>-1</sup> )	23,50	37,82	44,00	4,81	39,67
	Ni (mg·kg <sup>-1</sup> )	28,25	39,33	49,00*	6,26	40,40*
	Pb (mg·kg <sup>-1</sup> )	15,33	19,20	23,33	2,69	19,75
Zn (mg·kg <sup>-1</sup> )	57,25	95,88	115,67	15,02	97,60	
Apc 3	pH in H <sub>2</sub> O	7,36	7,68	7,87	0,20	7,74
	pH in KCl	7,03	7,48	7,77	0,27	7,53
	%CaCO <sub>3</sub>	7,18	21,95	44,02	16,52	18,59
	%C-c <sub>org</sub>	0,00	0,83	1,83	0,73	0,77
	K (%)	1,04	1,29	1,53	0,23	1,28
	Fe (%)	2,47	2,86	3,34	0,36	2,87
	P (mg·kg <sup>-1</sup> )	577,67	1194,49	1994,67	570,25	1024,00
	As (mg·kg <sup>-1</sup> )	9,33	10,46	11,75	1,05	10,50
	Cr (mg·kg <sup>-1</sup> )	<5,00	39,33	90,00*	41,06	35,50
	Cu (mg·kg <sup>-1</sup> )	21,67	29,33	39,25	7,97	28,04
	Ni (mg·kg <sup>-1</sup> )	16,67	25,92	33,75	6,09	26,00
	Pb (mg·kg <sup>-1</sup> )	11,33	16,79	24,00	4,68	16,58
Zn (mg·kg <sup>-1</sup> )	56,67	73,65	89,75	13,49	74,17	

\* the exceedance of threshold limit value of selected heavy metals in Hungarian soils (7)

For each element the limit of detection (LOD) was established according technical parameters of used spectrometer (24). LOD's values is shown in Table 4.

Table 4

Limit of detection for investigated elements

Element	LOD's value
K	0,0035%
Fe	0,001%
P	50 mg·kg <sup>-1</sup>
As	2 mg·kg <sup>-1</sup>
Cr	3 mg·kg <sup>-1</sup>
Cu	5 mg·kg <sup>-1</sup>
Ni	5 mg·kg <sup>-1</sup>
Pb	3 mg·kg <sup>-1</sup>
Zn	3 mg·kg <sup>-1</sup>

Source: (24)

The graphs for macroelements are shown in Fig. 3, and for heavy metals in Fig. 4-6.

The concentration of potassium is always higher than 1%, and its distribution in profiles is not very varied. The characteristic peaks are visible on level of paleosol in Apc 1 (1,69%) and in Apc 2 on 20-30 cm of depth (1,82%). Potassium content in Apc 3 is significant lower in deeper layers of deposits than in topsoil and shallower layers of subsoils.

The content of iron is between 2,47% (Apc 3\_4) and 4,62% (Apc 1\_7). Such as in case of previous element, for Apc 1 core the highest concentration recorded on paleosol's level. In Apc 2 a bigger accumulation of Fe observed in shallower layers of subsoil, and second decrease of content on 230-250 cm of depth. Another situation is in Apc 3 where the higher accumulation of iron occurs.

The distribution of phosphorus concentration in profiles shows a significant variation. In Apc 1 a big accumulation of this element is visible in deeper layers of deposits, it means below 120 cm. In second profile sample Apc 2\_1 apparently stands out with content almost 800 mg·kg<sup>-1</sup>. The course of graph for that profile is characterized by frequent fluctuations. In Apc 3 the highest concentration of P noted in 20-40 cm below ground level (1994,67 mg·kg<sup>-1</sup>) and 40-60 cm below ground level (1786,33 mg·kg<sup>-1</sup>).

An average content of arsenic, established individually for each profiles, are similar to each other (Tab. 3). These values are sometimes less than 10 mg·kg<sup>-1</sup>. Only in Apc 2 in samples n° 5 (50-60 cm of depth) and n° 6 (60-70 cm of depth), are recorded not large exceedances of acceptable value of As in Hungarian soils, set on 15 mg·kg<sup>-1</sup> (6). Exceedances are 2% (0,33 mg·kg<sup>-1</sup>) and 10% (1,5 mg·kg<sup>-1</sup>) for sample n° 5 and n° 6, respectively. In another cases standard is kept at an appropriate level. These re-

sults usually is in range of As concentrations for Apc region according FOREGS (17). In Apc 1 (Fig.4) the highest content of As observed on 40-60 cm depth (sample n° 3). The distribution of values of this metalloid is characterized by low fluctuations from topsoil to 120 cm of depth. Below that level marked a big decrease of arsenic content. As previously mentioned, the highest peak in distribution of values for Apc 2 (Fig.5) distinguishes significant amongst other cases. The second part of graph, i.e. 90-270 cm, is characterized by decidedly smaller values than first part (0-80 cm). A topsoil in Apc 3 (Fig. 6) contains the most amount of As in this profile. In this case recorded two decrease: the first on 20 cm of depth, and the second on 80 cm of depth.

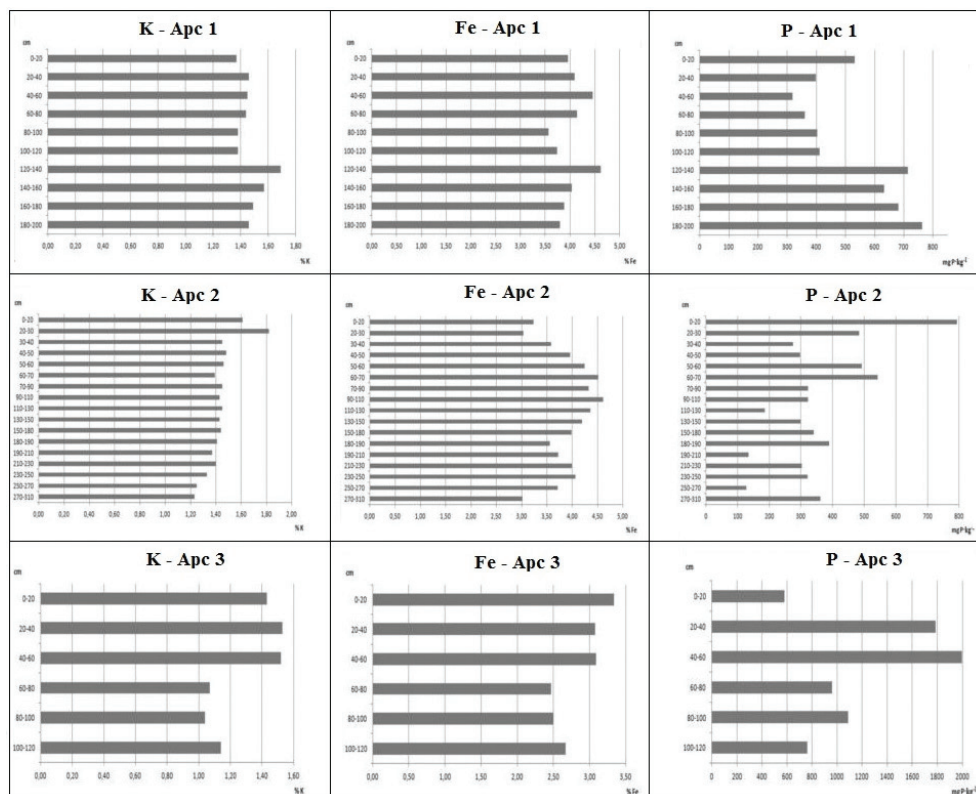


Fig. 3. The concentration of macroelements for Apc profiles

Chromium is that heavy metal of which content in Apc profiles shows a strong variability. It is characterized by high values of standard deviation (Tab. 3). Most of levels is significant improvement of Cr, but in some cases concentration of that heavy metal is lower than the limit of detection (below  $3 \text{ mg} \cdot \text{kg}^{-1}$ ) in sample n° 2 and sample n° 17 of Apc 2, and sample n° 4, 5 and 6 of Apc 3. Exceedances of acceptable content of chromium, i.e. sum of Cr ( $\Sigma\text{Cr}$ ) equal to  $75 \text{ mg} \cdot \text{kg}^{-1}$ , were noted in seven

samples of Apc 1, nine samples of Apc 2 and one sample of Apc 3 (6). These exceedances have values usually bigger than 5%. For sample n° 9 (110-130 cm) it is even 48% more than established standard ( $111 \text{ mg}\cdot\text{kg}^{-1}$ ) (Tab. 2). Similar values are presented in Geochemical Atlas of Europe (17), but in five cases they are smaller than Apc's results. The distribution of values for Cr from Apc 1 (Fig. 4) is characterized by two increases and two decreases, occurring alternately. The highest contamination of Cr observed on 40-60 cm of depth (sample n° 3). The content of chromium is lower in first sample (from topsoil) than in tenth sample (from sill of the profile). In Apc 2 (Fig. 5) the contamination of Cr is significant in topsoil, but it is not much higher than acceptable value ( $75 \text{ mg}\cdot\text{kg}^{-1}$ ) and lower significantly than maximum content on 110-130 cm of depth. The characteristic of this graph is a big diversity of presented values which is deepened by presence of values below the limit of detection on the beginning and the end of distribution. The similar situation occurs in Apc 3 (Fig. 6) where these values are represented by three last sample.

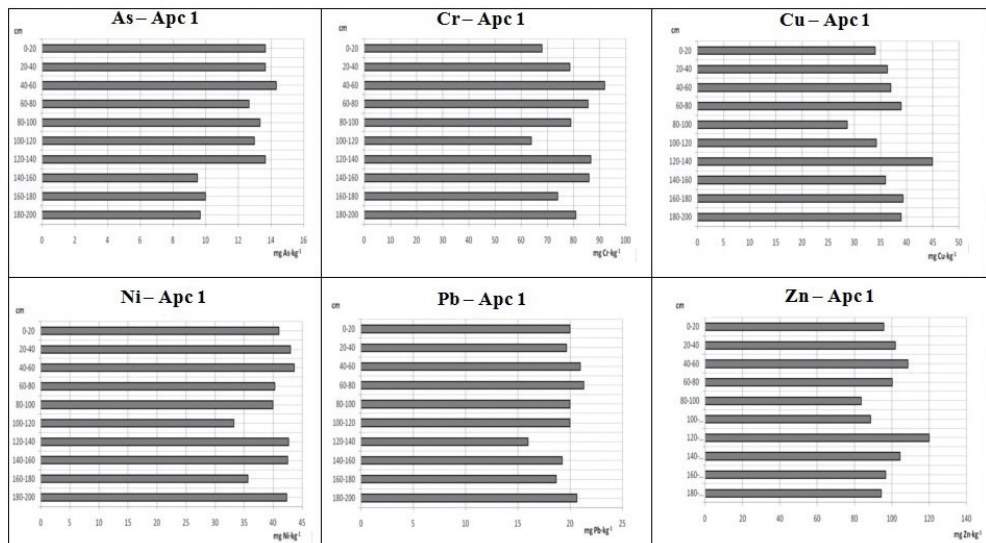


Fig. 4. The concentration of trace elements in Apc 1

The threshold limit value of copper for Hungarian soil is  $75 \text{ mg}\cdot\text{kg}^{-1}$  (6), and range of values established by FOREGS is  $35\text{-}65 \text{ mg}\cdot\text{kg}^{-1}$  (17). Therefore, exceedances for that heavy metal is not observed, especially as the content of Cu reaches maximal  $45 \text{ mg}\cdot\text{kg}^{-1}$ , but never falls below  $20 \text{ mg}\cdot\text{kg}^{-1}$ . Values of average of content for Apc 1 and Apc 2 are similar, and the highest differentiation occurs in Apc 3 (Tab. 3). In Apc 1 (Fig. 4) the Cu amount are increasing from topsoil to 80-100 cm. After that level observed a big downgrade and immediately afterwards a violent rise to the highest content ( $45 \text{ mg}\cdot\text{kg}^{-1}$ ) on 120-140 cm of depth. A similar situation in Apc 2

(Fig. 5) with growth of copper content from topsoil could be noticed, but to 70-90 cm of depth (sample n° 7). The significant decline is visible from 230-250 cm of depth. The topsoil of Apc 3 (Fig. 6) is characterized by the highest amount of Cu. The graph shows strong declining tendency.

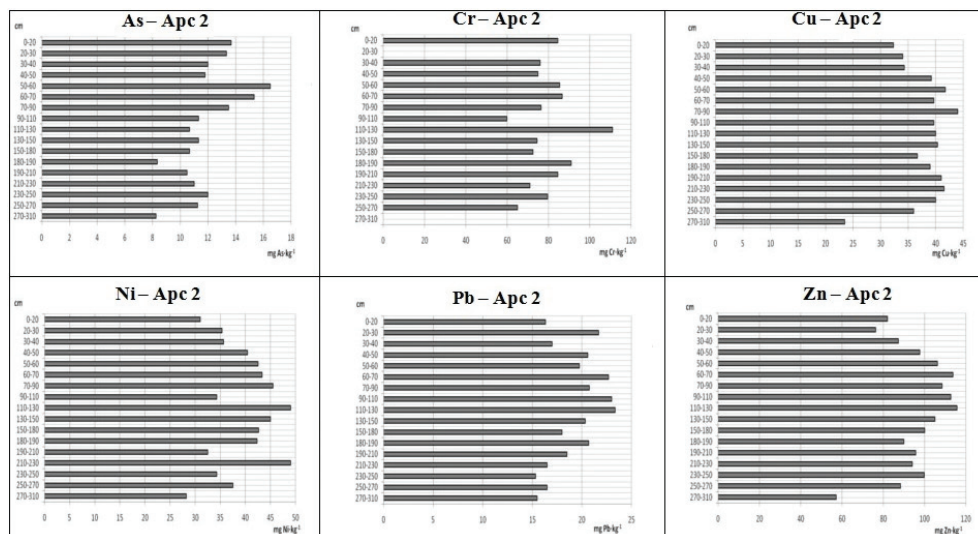


Fig. 5. The concentration of trace elements in Apc 2

The content of nickel in investigated deposits often exceeds the threshold limit value, determined on  $40 \text{ mg} \cdot \text{kg}^{-1}$  (6), especially in samples of Apc 1 (8 samples on 10 samples) and Apc 2 (9 samples of 17 samples). In opposite to Cr amount, these exceedances are not so large, to 22,50% at most. In almost all cases gained results are higher than FOREGS values (17). The range of Ni concentration is between  $33,25$  and  $43,67 \text{ mg} \cdot \text{kg}^{-1}$ , and  $28,25$  and  $49,00 \text{ mg} \cdot \text{kg}^{-1}$  for Apc 1 and Apc 2, respectively. The content of that heavy metal in Apc 3 is significant smaller than in other profiles. Both in case Apc 1 and Apc 2 (Fig. 4-5), nickel concentration increases from topsoil, but in Apc 2 an increasing tendency keeps longer. On distribution of values for Apc 1 marks a very deep decrease to  $33,25 \text{ mg} \cdot \text{kg}^{-1}$  (for sample n° 6, on 100-120 cm of depth). After that could observe two big growths and one decline, occurring alternately. The run of values for Apc 2 (Fig. 5) reveals more fluctuations and two maxima on 110-130 cm and 210-230 cm points. Such as arsenic and heavy metals described previously, a deep downgrade is observed in floor of the profile. Except for one increase of Ni content, the concentration of this element in Apc 3 (Fig. 6) diminishes with a fall of depth significantly.

In floodplain deposits of Apc surroundings the total content of lead stays below of the standard considerably, established on  $100 \text{ mg} \cdot \text{kg}^{-1}$  (6). Similar situation is shown

by comparison with values from Geochemical Atlas of Europe (17). Means of Pb concentration for each profiles do not exceed  $20 \text{ mg}\cdot\text{kg}^{-1}$ , and maximal value from all samples is  $24 \text{ mg}\cdot\text{kg}^{-1}$  in Apc 3 (sample n° 1) (Fig. 6). For Apc 1 (Fig. 5) the run of the graph from 0 to 100 cm depth is quite regular, apart from a one decrease of value on 80-100 cm of depth. The second part of graph is characterized by one sudden decrease to  $16 \text{ mg}\cdot\text{kg}^{-1}$  and even greater increase of Pb concentration. The main feature of the graph of Apc 2 (Fig. 18) is occurrence a lot of value fluctuations. The highest content of Pb is  $23,33 \text{ mg}\cdot\text{kg}^{-1}$  on 110 cm of depth (sample n° 9). The deeper samples (150-270 cm of depth) are characterized by relatively lower Pb amount than topsoil and shallower layers of subsoil. In Apc 3 (Fig. 6) could observe an enrichment of topsoil in lead and violent decline with a fall of depth.

Such as copper and lead, the content of zinc does not exceed the threshold limit value for Hungarian soils, it means  $200 \text{ mg}\cdot\text{kg}^{-1}$  (6). Apc's results for Zn in most cases stay below of the FOREGS' values (17). The highest value for all three profiles is  $120 \text{ mg}\cdot\text{kg}^{-1}$  in Apc 1 on 120-140 cm of depth (Fig. 4). The distribution of values in this profile is characterized by two increases and two decreases, occurring interchangeably. In Apc 2 (Fig. 5) can observe the growth of Zn concentration from topsoil to 60 cm depth. Afterwards the significant tendency to fall of content occurs. This decline is the most visible from 230 of cm depth when content of Zn falls below  $60 \text{ mg}\cdot\text{kg}^{-1}$ . The highest value creates a very indistinct peak ( $115,67 \text{ mg}\cdot\text{kg}^{-1}$ ). The decreasing tendency, typical for another distributions of heavy metals values in Apc 3 (Fig. 6), proceeds also in case of zinc. The small growth is visible in 40-60 cm of depth, and also in 100-120 cm of depth.

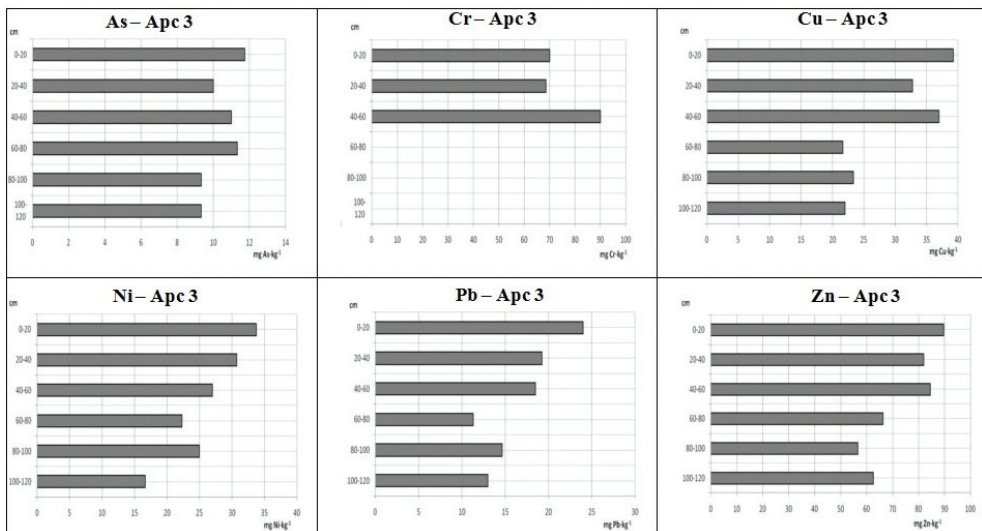


Fig. 6. The concentration of trace elements in Apc 3

The Fig. 7 and Fig. 8 below shows the level of exceeding of established standards for Cr and Ni. This problem was described earlier, but it is worth remembering that an increased concentration of the above-mentioned elements (excluding As) is common in Apc 1 and Apc 2. Only in sample of Apc 3 (Apc 3\_3) the Cr content is higher by 20% from the acceptable limit (6).

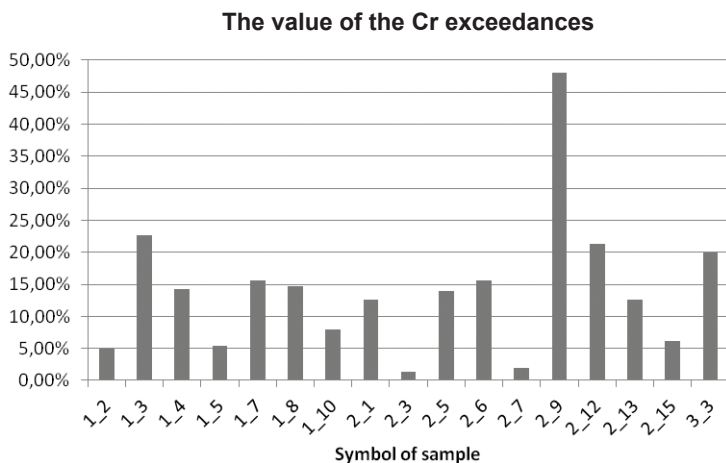


Fig. 7. The value of Cr exceedances in all three profiles

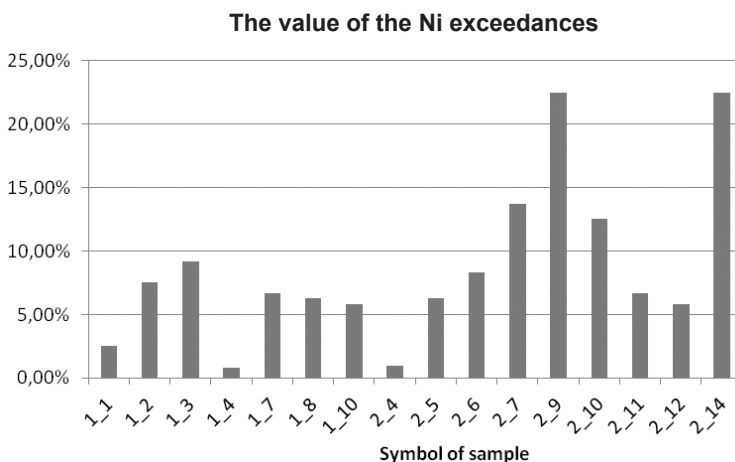


Fig. 8. The value of Ni exceedances in Apc 1 and Apc 2

In factor analysis which has been conducted for data from Apc profiles distinguished on three main factors explaining 75,22% of variability. The marked loadings was established on value  $> ,700000$ . In this analysis was used normalized Varimax

method, made by Statistica 10 Programme. Factor 1 is represented by Cr, Cu, Ni, Zn, Fe as positive values, and pH in KCl and CaCO<sub>3</sub> as negative values. This group can be interpreted as natural background, connected with strongly concentration of heavy metals in volcanic stones of Matrá and Cserhát Mountains. Another parameters belong to factor limiting accumulation of described trace elements. Within factor 2 solely participation of silt and participation of clay is representative, and in case of factor 3 – pH in KCl and organic carbon. It is very good visible a big dependence between lithology of deposits (content of clay) and concentration of C<sub>org.</sub> and concentration of studied heavy metals.

Table 5

The results from the factor analysis

Parameter	Factor 1	Factor 2	Factor 3
As	0,215030	0,067982	0,640823
Cr	0,767115	0,116185	0,315268
Cu	0,868020	-0,030828	0,277929
Ni	0,837642	0,095437	0,242597
Pb	0,569952	0,160758	0,516317
Zn	0,869752	0,080617	0,343970
Fe	0,903561	-0,007844	0,233579
K	0,437995	0,064054	0,564072
P	-0,771570	0,188867	0,074092
pH in H <sub>2</sub> O	-0,364249	-0,094034	-0,826663
pH in KCl	-0,867837	-0,035607	-0,236901
CaCO <sub>3</sub>	-0,758022	-0,006925	-0,393287
C <sub>org.</sub>	0,280251	0,166396	0,849674
% of sand	-0,176032	-0,593994	0,563118
% of silt	0,060403	-0,886245	-0,296273
% of clay	-0,019031	0,984634	0,103584
Expl. Var	6,348658	2,245964	3,440993
Prp. Totl	0,396791	0,140373	0,215062

Lot of geochemical research on Hungarian territory was conducted on Tisza River Valley and its surroundings. Györi et al. (4) analyzed the content of Zn, Cd and Pb and compared values from 2000 and 2011. The value for Pb amount of this site is higher than in case of Apc's profiles, because it reaches more than 40 mg·kg<sup>-1</sup>. This situation changes from 140 cm of depth - Apc's profiles is characterized by higher concentration of zinc. Scientists suppose that the increase of Zn and Pb is connected with periodical floods which caused the mobilization of contaminations.

Another group of scientists (19) investigated sandy-silty flood deposits from Boroszló-kert (near Gulács). Their results of Cu, Ni and Zn content are similar to Apc's data.

The important research along Tisza carried in 2001, (16). In most of cases, the Zn, Pb and Cu contamination is considerable higher than in Apc's profiles. Within that area the highest concentration is  $567 \text{ mg}\cdot\text{kg}^{-1}$ ,  $123 \text{ mg}\cdot\text{kg}^{-1}$  and  $162 \text{ mg}\cdot\text{kg}^{-1}$  for Zn, Pb and Cu, respectively. Samples from Tisza river valley contain much less chromium, and have a similar concentration of nickel. The specific content of heavy metals along Tisza is highly connected with Romanian polymetallic ores which had released a huge amount of contaminations into river.

Another research was conducted by Yun (21). As it could notice, in this case the values of mean for Zn, Pb, As and Cu is higher than in deposits of Zagyva's floodplain.

In Tisza River Valley the geochemical research was carried out by Tamás & Far-sang (20). The content of Pb, Zn and Cu, especially in three oxbows is distinctly higher than in Apc profiles. These values reached even  $86,55 \text{ mg}\cdot\text{kg}^{-1}$  of Pb,  $274,50 \text{ mg}\cdot\text{kg}^{-1}$  of Zn and  $80,50 \text{ mg}\cdot\text{kg}^{-1}$  of Cu. Authors conclude that bigger enrichment in heavy metals of floodplain oxbows sediments is due by the increased mobility of these elements. On the other hand, Szabó & Babka (18) suppose that Tisa's floodwaters could refresh the water of oxbow lakes located outside dyke, and therefore its deposits can be depleted in heavy metals.

In the Reck-Lahoca mining area (on Matrá Mountains region) Rukezo's research (15) were conducted on water samples, stream sediment samples and tailings samples of Lahoca. This place was used to sourcing of copper, silver and gold between 1852-1998. Water samples is characterized by low level of arsenic and heavy metals, excluding an increased concentration of Cu. However, the concentration of studied elements in stream sediments and tailings samples are much higher that is the most visible in case of Cu, As and Zn. It is connected with the several kind of mineralization of volcanic stones, it mainly epithermal mineralization of Au-Cu, and skarn type of Cu-Zn. Therefore, deposits of the nearest surroundings of Matrá Mountains can contain a bigger amount of mentioned elements. Similar situation is shown within Gyögyösoroszi base metal mine, but samples of the tailing point in significant degree are polluted with Pb and Zn, especially (2). Nevertheless, mine industry of Matra Mountains' region could not have a very big role in elements' input to floodplain deposits because its relatively small values.

Factors, approved by various group of scientists as significant, could also reflected in deposits from investigated site. The raised concentration of heavy metals in topsoil that is the most visible in Apc 3 in case of Cu, Pb, As, Zn and Ni, can be connected with modern human activity (agriculture). Ancient activity can also some influence on changes of geochemical features. One of possible factors of strongly marking the high content of Cu, Zn and Fe in level of paleosol is occurrence of Neolithic settlement which had inhabited on Zagyva's terrace that deposits have been taken during periodic floods and accumulated on floodplain area. What is interesting, the run of distribution of copper, zinc and iron content is enough similar, so an occur-

rence of these heavy metals is dependent each other. A big significance for chemistry of paleosol could be connected with agriculture development in this time, as evidenced by relative big accumulation in macroelements, such as K and P. Therefore some amount of heavy metals not only from that area, but also from whole Zagyva's catchment was launched and displaced with fine material. Might a significant importance for heavy metals enrichment has volcanic stones from which Matrá and Cserhát are built. Natural features of investigated deposits, such as a high participation of clayey fraction determines the distribution of Cu, Zn and Ni, especially. Although an investigated deposits is characterized by small concentration of organic matter, but it can absorb of heavy metals and arsenic affecting the bigger enrichment in described elements, especially in topsoil and shallower layers of subsoil. In view of the quite low content of Pb, the proximity of route and relatively well-developed railway system of Zagyva's catchment is practically irrelevant. Regarding to concentration of trace elements an influence of industry is not taken into account because of significant distance of research area from major urban centers.

### **Summary and conclusions**

The conducted geochemical analysis shown that values of Cr and Ni concentration often exceeded the threshold limit established for these metals. According factor analysis such content of chromium is caused by the natural features of deposits. In the same group of factors (factor 1) are also Zn, Cu, Ni and Fe. Nickel and lead did not marked, because values in any groups did not exceed  $>700000$ . Another parameters which is representative for Factor 2 and Factor 3 has a big role in heavy metals accumulation in deposits (participation of clay fraction and content of organic carbon). Factors such as phosphorus concentration, pH and content of carbonates could significantly reduce the activity of trace elements and its bioavailability.

By analyzing the distribution of heavy metals in each profiles, it can be noticed some correctness, the same as the main factors which could potential cause an accumulation heavy metals and arsenic in deposits. They are distinguished below, in the order of most to least important:

1. The periodic floods – one of the most important factor which causes the mobilization of all of heavy metals, practically. It is also strongly connected with other factors.
2. The volcanic origin of Matrá and Cserhát Mountains – this kind of stones is always significantly enriched on arsenic and heavy metals. A particulate material from these areas could be transported with water on lower located land. This factor can have the biggest meaning in case of As, Zn, Cu, Pb and Fe.
3. A big participation of clayey fraction – it binds strongly almost all of heavy metals. It could be the most important reason of significant concentration of Cr and Ni, and partly another elements in these deposits.

4. The concentration of organic carbon – it absorbed a trace elements easily, but because of a little accumulation in deposits it could have a much lower importance than the participation of clayey fraction. Probably it have a bigger role in topsoil and paleosol.
5. The agriculture – an increased concentration of Cu, Pb, As, Zn and Ni is rather significant, but solely limited to topsoil or shallower layers of subsoil. This factor can have a much less importance than natural factors, mentioned above.
6. An ancient activity – the influence of this activity on Zagyva's floodplain probably are recorded in deeper layers. A raised concentration of Cu and Zn could be caused by human activity in Neolithic and Bronze Age partially, but cannot be recognized as a determining factor.
7. The communication and industry – these factors are practically irrelevant.

### Literature

1. De Vries W., Groenenberg J. E., Muráyi A., Curlík J., Šěfcik P., Römken P. F. A. M., Reinds G. J., Bril J., Modin A. K., Sverdrup H. U., Alloway B. J., Long-term of inadequate management practices on the sustainability of agricultural soils, Netherlands: Alterra-rapport 816, Alterra, Wageningen, 2003.
2. Földessy J., Böhm J., Fredriksson C., Mádai V., Banik J., Closure of the Gyögyösorszi base metal mine, Hungary – preliminary technical – geochemical assessment, Hungary: University of Miskolc Faculty of Engineering and Earth Science – source: <http://fold1.ftt.uni-miskolc.hu/~foldfj/toka.pdf>
3. Földmérési és Távérzékelési Intézet, Magyar Népköztársaság: Heves M.-Nógrád M.-Pest M.-Szolnok M. 76-Gyöngyös, 1: 100 000, Budapest: Földmérési és Távérzékelési Intézet, 1985.
4. Györi Z., Boros N., Szabó E. B., Sipos P., Heavy metal distribution of floodplain soils and pastures of the Tisza river, Visegrád: 4th International Symposium on Trace Elements in the Food Chain November 2012, Eur. Chem. Bull. 2012, **1(10)**: 407-409.
5. Gyula B. & Antal N., Magyarország földrajza a középiskolák számára, Budapest: Nemzeti Tankönyvkiadó, p. 12 - [www.tanugyelo.hu/file/220/mo\\_foldrajza.pdf](http://www.tanugyelo.hu/file/220/mo_foldrajza.pdf)
6. JOINT DECREE No. 10/2000 (VI.2.) KöM-EüM-FVM-KHVM of the ministers of environmental protection, public health, agriculture and regional development, and of traffic, communication and water management on the limit values necessary to protect the quality of groundwater and the geologic medium.
7. Kabata-Pendias A., Pendias H., Biogeochemia pierwiastków śladowych, Warszawa: Wydawnictwo Naukowe PWN, 1993.
8. Kabata-Pendias A., Szteke B., Pierwiastki śladowe w geo- i biosferze, Puławy: Instytut Upraw Nawożenia i Gleboznawstwa – Państwowy Instytut Badawczy, 2012.
9. Kaiser M., Magyarország földtani térképe. L-34-4 Gyöngyös, skála 1: 100 000, Budapest: Magyar Állami Földtani Intézet, 2003.
10. Małeck i J., Gruszczyński T., Mobilność chromu w strukturze artezyjskiej Doliny Krynki w świetle wyników modelowania pola filtracji, Warszawa: Biuletyn Państwowego Instytutu Geologicznego, 2012, **452**: 167-180.

11. Midzio J., *Krajobrazy węgierskie*, Warszawa: Wydawnictwa Szkolne i Pedagogiczne, 1979.
  12. Migaszewski Z., Gałuszka A., *Podstawy geochemii środowiska*, Warszawa: Wydawnictwa Naukowo-Techniczne, 2007.
  13. Pécsi M., Sárfalvi B., *Węgry*, Warszawa: Państwowe Wydawnictwo Naukowe.
  14. Perelman A., *Geochemia krajobrazu*, Warszawa: Państwowe Wydawnictwo Naukowe, 1971.
  15. Rukező G., *Drainage geochemistry of the Recsk-Lahoca mining area, Matrá-Mountains-Hungary*, ITC, 2003.
  16. Sakan S., Gržetić I., Đorđević D., *Distribution and fractionation of heavy metals in the Tisa (Tisza) river sediments*, *Env. Sci. Pollut. Res.*, 2007, **14(4)**: 229-236.
  17. Salminen R. (ed.), *Geochemical Atlas of Europe Part 1. Background Information, Methodology and Maps*, Espoo: Forum of European Geological Surveys, 2005 (Internet version: <http://weppi.gtk.fi/publ/foregsatlas/index.php>)
  18. Szabó Sz., Babka B., *Water chemical condition of oxbow lakes of Upper-Tisza. The function and importance of FLAPP-project in Upper-Tisza valley, cross-border, Hungary: Debrecen*, 2007.
  19. Szabó Sz., Posta J., Gosztonyi G., Mészáros I., Prokisch J., *Heavy metal content of flood sediments and plants near river Tisza*, *AGD Landscape & Environment*, 2008, **2(2)**: 120-131.
  20. Tamás M., Farsang A., *Evaluation of environmental condition: water and sediment examination of oxbow lakes*, *AGD Landscape & Environment*, 2011, **5(2)**: 84-92.
  21. Yun L., *Possibilities of assessing heavy metal contamination of soil in the Sajó River flood plains (Hungary) using reflectance spectroscopy*, *International Institute for Geo-Information Science and Earth Observation ITC*, 2003.
  22. Zglobicki W., *Geochemiczny zapis działalności człowieka w osadach stokowych i rzecznych*, Lublin: Wydawnictwo Uniwersytetu Marii Curie-Skłodowskiej, 2008.
  23. <http://hu.wikipedia.org/wiki/Zagyva>
  24. [http://northernani.com/wp-content/uploads/2014/08/Mining\\_LOD\\_DELTA\\_Professional.pdf](http://northernani.com/wp-content/uploads/2014/08/Mining_LOD_DELTA_Professional.pdf)
  25. <http://pl.wikipedia.org/wiki/>
  26. <https://www.google.pl/maps/>
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