Mobility of trace elements in virgin soils from the Bobov dol valley, Bulgaria

Ivona Nikova[1], Venera Tsolova[2]

[1] *Assist. prof. PhD Ivona Nikova,"N. Poushkarov" Institute of Soil Science, Agro technologies and Plant protection, Dept. "Soil chemistry", Shosse Bankya 7, 1080 Sofia, Bulgaria*

[2] *Prof. PhD Venera Tsolova, ,"N. Poushkarov" Institute of Soil Science, Agro technologies and Plant protection, Dept. "Soil chemistry", Shosse Bankya 7, 1080 Sofia, Bulgaria*

---***---

Abstract - *The content and mobility of trace elements are the ecological hallmarks of soils revealing their quality and safety. Since the mobilty of trace elements is one of the reliable indicators for soil toxicity the aim of this study is to assess the mobility of trace elements in virgin soils located in the vicinity of the Bobovdol Thermoelectric Power Plant operating with coal. Some of classical methods for sampling, morphogenetic diagnosis and chemical analysis of soils are applied [3, 4, 5, 6, 14, 15, 16, 17, 18, 21, 36, 37]. The local geochemical particularities and key soil features are also used to assess the mobility of Cu, Zn, Pb and Mn.*

The total content of trace elements in studied soils is lower than the background values found in the Bulgarian soils, and determines the non-toxic mobile concentrations of Cu, Zn, Pb and Mn. Organic and mineral colloids (silt and clay fractions) are the basic collectors and providers of mobile metal species although the soil type dependent bioavailability of studied metals had also been recognized.

The content of mobile zinc and manganese is the most strongly associated with pedogenesis and the superficial soil formation processes, providing their surface accumulation. The mobile content of Cu is extremely low (average of 0.04 mg/kg) and basically attached to the content of organic carbon and fine particles. Lead is usually allied with organic carbon but also occurs in fine soil fractions creating the soil type dependent bioavailable pools of Pb. It reacts antagonistically when organic carbon preferentially determines the mobility of Cu, Zn and Mn.

Key words: **mobility, trace elements, virgin soils, organic carbon, Bobov dol valley**

1. INTRODUCTION

Trace elements are chemically active ingredients of all soils. As mineral species they present in clay minerals, ferrous and manganese oxides, wherein form the depots of potentially mobile metal species [10, 11]. Metals also occur in the organic fraction, frequently as valency bound forms.

Heavy metals and metalloids can be involved in a series of complex chemical and biological interactions. The most important factors which affect their mobility are pH, sorbent nature, presence and concentration of organic and inorganic ligands, root exudates and nutrients. Furthermore, redox reactions, both biotic and abiotic, are of great importance in controlling the oxidation state and thus, the mobility and the toxicity of many elements, such as Cr, Se, Co, Pb, As, Ni and Cu [35].

Only a small portion of heavy metals and metalloids in soils is bioavailable. These amounts resulted in various processes such as precipitation-dissolution, sorption-desorption, complexation-dissociation, and oxidation-reduction. Not all the processes are equally important for each element and that is way it is crucial to study the reactions in soils that control the release of trace elements in order to manage the problems related to their deficiency and excess [13, 22].

The bioavailability of metals can be defined as an indicator showing the part of the element which is readily soluble and therefore, mobile and bioavailable mainly for plants and soil biota [25, 28]. In the case of soil contamination, the consumption of metals from terrestrial organisms is a complex and dynamic process involving all varieties of living organisms [1, 9]. The assessment of microelement availability in soils requires not only the knowledge of the amount of specifically adsorbed elements but also the types of surfaces which interact with these elements and the factors that contribute to their release from these surfaces [2].

It is known that bioavailability, leaching and toxicity of metals and metalloids in soils is primary related to the element chemical speciation. The speciation of trace metals in soils depends on both the preliminary processes of parent materials formation and the secondary processes during the soil evolution. Therefore, the total content of heavy metals is insufficient to assess their real toxicity because the type of compounds of heavy metals determine their behavior in the environment [32], potential mobility and bioavailability [19, 33].

Since the mobilty of trace elements is one of the reliable indicators for soil toxicity the aim of this study is to assess the mobility of trace elements in virgin soils located in the

vicinity of the Bobovdol Thermoelectric Power Plant (TPP) and its facilities. In the anthropogenically modified landscape of the Bobov dol valley this study allow to assess the toxicity level of soils caused by the accumulation of aerozoles and by-products of the Bobovdol Thermoelectric Power Plant opperating with coal.

2. MATERIALS AND METHODS

The local geochemical particularities, profile distribution of elements and key soil features were simultaneously used with element fractionation to assess the mobility of Cu, Zn, Pb and Mn.

2.1 Geomorphological description of studied soils

Four soil types located in the lands of the villages of Goliamo Selo, Palatovo and Kamenik, Bulgaria have been studied. These soils are affected by anthropogenic activity to a different extent and are uncultivated at the time of the study. The location of the studied soils and the landscape views are shown on fig. 1, 2, 3, 4 and 5.
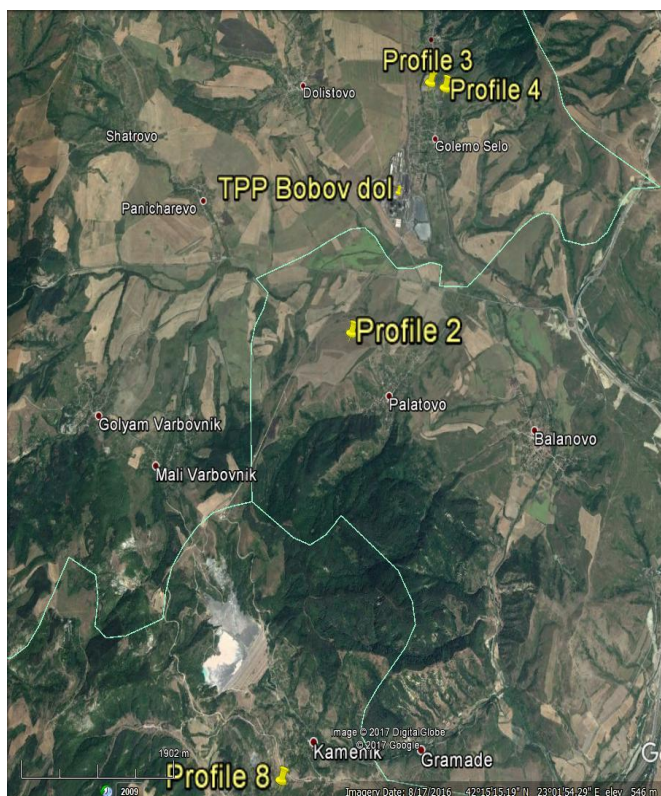

Fig – 1: Geographic location of the profiles

Profile № 2. **Pantotransportic Bathygarbic Technosol (Hypereutric, Loamic)**

The profile is situated in the reclaimed tailing pond "Suhoto dere" in the land of Palatovo village at 616 m.

Biological reclamation is carried out with meadow vegetation, which is further enriched with self-settled local plant species, incl. bushes. The relief of the surrounding area is low mountainous (figure 2). These soils are included in the study because they contain microelements of geogenic origin they are built by covering the tailing pond with 1.5 m of earth masses obtained from various excavation activities in the area. According to the regulatory framework in Bulgaria [30], these areas are reclaimed for recreational purposes only not for agriculture or forestry.

Fig – 2: Landscape view around profile 2

Profile № 3. Chernic Phaeozem (Loamic, Colluvic, Epivermic)

The soil is located on the territory of the village of Goliamo Selo at 520 m above sea level on non-carbonated diluvial-alluvial materials and weathered sandstones. It is covered with wild meadow and bushy vegetation. This soil province occupies lowlands and hills (figure 3).

Fig – 3: Landscape view around profile 3

Profile № 4. **Gleyic Fluvisol (Loamic, Pantohumic)**

The profile is situated on the above flood terrace of the Bobovdolska river in a plain, non arable area, at 515 m above sea level, in the land of the village of Staro Selo (figure 4).

Fig – 4: Landscape view around profile 4

It is formed on non-carbonate alluvial materials under the influence of meadow vegetation with the predominance of the moisture-loving species (*Typha angustifolia*). The ground water is very shallow (60 cm). The relief of the surrounding area is flat-hilly.

Profile № 8. Albic Luvisol (Loamic, Hypereutric, Pantohumic)

The profile is situated in a low mountainous relief on a slope with a slight incline to the east, at 652 m above sea level in the land of the village Kamenik. It is formed of non-carbonate materials with the participation of meadow and bushy vegetation (figure 5).

Fig – 5: Landscape view around profile 8

2.2 Methods

Soil survey in the Bobovdol valley was performed by advanced pedological methods for morphogenetic diagnosis of soils [21, 35, 37] and the actual sampling standards (3, 4, 5). The methodology in Guidance for Soil Description [18] is also used for description of soil profiles.

The following methods of analysis are applied:

1. Pretreatment of soil samples for physico-chemical analysis according to [6].

2. pH (H_2O) determination - potentiometrically according to [14].

3. Determination of the total content of trace elements – soil mineralization with "aqua regia" [17] and measuring the contents by AAC on a Perkin-Elmer 2100 [15].

4. Determination of the content of easily soluble trace elements - by extraction of soil with 1 M NH_4NO_3 [16].

5. Cation exchange capacity – method of Ganev and Arsova [12]. This method determines the contribution of the permenent, preferential charges (on basal surfaces, T_{CA}) and variation charges (basically pH dependent exchange including the lateral surfaces, T_A) of soil colloids in the cation exchange capacity of soils by titration of soil extract (4 g of soil and several portions of 8 cm^3 of 1.0 n sodium acetate and 0.2 n potassium maleate with pH 8.25 to reach 100 cm^3) with 0.04 n sodium hydroxide solution in the presence of phenolphthalein to determine T_A and subsequent titration of the above eluate with 0.04 n complexon after dilution up to 200 cm^3 deionized water and addition of 10 cm^3 of triethanolamine (1: 1) and 2 cm^3 of 5.0 n potassium hydroxide solution (non-carbonate) to achieve pH 12-13 in the presence of chromium-blue to determine T_{CA}.

6. Particle size distribution – method of Kachinsky [20]. This method differs form the method described in ISO 11277:2009 mostly in samples pretreatment (NaOH is used here as a dispercing agent) and sieves mesh sizes. The following size of major fractions are recognized by Kachinsky: Sand – this fraction involves particles with 1.00 - 0.05 mm equivalent spherical diameter; Silt fraction – from 0.05 to 0.001 mm equivalent diameter and Clay <0,001 mm.

3. RESULTS AND DISCUSSION

The data on the content of microelements (trace metals) and their relation to the soil components shown in the tables confirm that pH, the content and cation exchange capacity of soil colloids (in particular the content of organic carbon, silt and clay fractions) have a very important role in the accumulation and the mobility of studied elements. Prevailing neutral pH (average value of 6.6) is one of the reasons for the uniform distribution of trace elements, their low solubility and low potential availability. In general, the content of trace elements is lower than the background values found in Bulgarian soils [31] and principally predetermines their low mobile concentrations. According to Prüeß's [28] critical values for soil phytotoxicity, based on 1 M NH_4NO_3 extract (1 mg/kg for Pb and Cu and 30 μg/g for Zn) the values obtained are non-toxic and ecologically safe.

The vertical distribution of trace elements in reference soils (profile 2) resembles the profile layered structure, while their mobile content depends on more factors (table 2). For example, the mobile quantities of zinc and manganese seem related to pedogenesis and the more intensive weathering and soil-forming processes in the surface 40 cm (namely organic matter accumulation and recycling) leading to their superficial accumulation. In genetically older soils (profiles 3, 4 and 8), the tendency towards surface accumulation is not well expressed, especially in terms of the total forms. Lead mobility does not seem affected by the primary soil-forming processes, but rather by the geospatial variations of the element total content appearing as a weak accumulation near the TPP (profiles 3 and 4) and significant dispersion of the concentrations in the South [34].

In profile 2 (Technosol) copper content and accumulation is influenced by pH and soil organic carbon, which distinguishes it from the other elements for which mineral colloids are the main collectors of total and exchangeable amounts of zinc, manganese and lead (table 2). These data reveal that implementation of other methods of analysis (optical spectroscopy or combined techniques) would give more information about the chemical speciation and linkage of copper in these genetically young soils (although they are formed by geological materials that are old in a geo chronological sense).

Table – 1: Content of trace elements in the studied soils (mg/kg, %)

Horizon depth	pH	Cu			Zn			Mn			Pb		
		Total	Mob.*	%**	Total	Mob.	%	Total	Mob.	%	Total	Mob.	%
Profile 2. Pantotransportic Bathygarbic Technosol													
AC 0-5	5,7	15.0	0.03	0.20	51.0	0.13	0.25	235.0	3.93	1.67	19.5	0.70	3.59
C1 5-40	6,7	16.0	0.03	0.19	55.5	0.10	0.18	260.0	1.65	0.63	22.0	0.65	2.95
C2 40-69	6,9	23.5	0.03	0.13	68.0	0.08	0.11	280.0	0.33	0.12	18.5	0.50	2.70
C3 69-97	7,2	24.5	0.05	0.20	60.0	0.08	0.13	255.0	0.30	0.12	18.0	0.90	5.00
C4 97-130	7,2	32.0	0.03	0.09	32.5	0.08	0.23	150.0	0.10	0.07	11.5	0.40	3.48
M***	6.74	22.2	0.03	0.16	53.4	0.09	0.18	236.0	1.26	0.52	17.9	0.63	3.55
SD	0.55	6.95	0.01	0.05	13.26	0.02	0.06	50.67	1.61	0.68	3.90	0.19	0.89
Profile 3. Chernic Phaeozem													
Ah 0-5	5,8	19.5	0.05	0.26	52.0	0.13	0.24	300.0	6.10	2.03	24.5	0.40	1.63
A1 5-46	6,0	18.0	0.03	0.17	53.0	0.15	0.28	245.0	2.88	1.18	24.0	0.40	1.67
Btu1 46-88	6,3	17.5	0.03	0.17	59.0	0.13	0.21	275.0	1.70	0.62	24.0	0.50	2.08
Btu2 88-133	7,2	20.0	0.03	0.15	60.5	0.08	0.12	830.0	0.15	0.02	23.0	0.50	2.17
C 133-165	7,3	18.5	0.03	0.16	56.5	0.10	0.18	480.0	1.00	0.21	20.0	0.40	2.00
M	6.52	18.7	0.03	0.18	56.2	0.12	0.21	426.0	2.37	0.81	23.1	0.44	1.91
SD	0.62	1.04	0.01	0.04	3.68	0.03	0.06	243.71	2.31	0.81	1.82	0.05	0.25

Mob.* – mobile element content, mg/kg; %** - relative element content; M*** – arithmetic mean

Table – 1: Content of trace elements in the studied soils (mg/kg, %)

Horizon depth	pH	Cu			Zn			Mn			Pb		
		Total	Mob.*	%**	Total	Mob.	%	Total	Mob.	%	Total	Mob.	%
Profile 4. Gleyic Fluvisol													
Ah 0-4	6,9	20.5	0.08	0.37	53.5	0.13	0.23	480.0	1.73	0.36	23.5	0.40	1.70
Ag1 4-27	7,1	16.0	0.05	0.31	45.5	0.13	0.27	465.0	0.58	0.12	22.0	0.33	1.50
Ag2 27-60	7,3	14.0	0.03	0.21	45.5	0.08	0.16	485.0	0.55	0.11	22.0	0.33	1.50
Ag3 60-100	7,4	16.0	0.05	0.31	48.0	0.08	0.16	500.0	2.30	0.46	21.0	0.50	2.38
M	7.18	16.63	0.05	0.30	48.13	0.10	0.21	482.5	1.29	0.26	22.13	0.39	1.77
SD	0.41	2.75	0.02	0.06	3.77	0.03	0.06	14.43	0.87	0.17	1.03	0.08	0.42
Profile 8. Albic Luvisol													
Ah 0-12	6,4	25.0	0.05	0.20	52.5	0.10	0.19	310.0	2.80	0.90	15.5	0.60	3.87
AE 12-43	6,5	17.0	0.08	0.44	48.0	0.23	0.47	340.0	3.70	1.09	7.0	0.65	9.29
Bts 43-74	6,5	31.0	0.05	0.16	47.5	0.13	0.26	295.0	3.70	1.25	4.5	0.35	7.78
Bt 74-115	6,5	15.0	0.03	0.20	47.5	0.13	0.26	310.0	5.95	1.92	10.0	0.28	2.80
M	6.48	22.0	0.05	0.25	48.88	0.14	0.30	313.75	4.04	1.29	9.25	0.47	5.93
SD	0.04	7.39	0.02	0.13	2.43	0.06	0.12	18.87	1.34	0.44	4.73	0.18	3.09

In profile 3 (Chernic Phaeozem) there is a high correlation between the total content of copper and manganese, which reveals the importance of manganese oxides and oxy-hydroxides and their geochemical activity for Cu accumulation (Table 3). However, in this profile, the main source of mobile copper and manganese is the organic carbon, although the mobile copper content depends also on its total content. To some extent that is typical of mobile zinc too, but the mineral colloid are the more important factor for Zn bioavailability.

Table – 2: Correlations between the content of elements and mobility sources contents in profile 2

Para-meter	Cut	Cum	Znt	Znm	Mnt	Mnm	Pbt	Pbm	pH	<0.001	<0.01	C, %
Cut	1.00											
Cum	0.18	1.00										
Znt	-0.45	0.28	1.00									
Znm	-0.83	-0.38	-0.06	1.00								
Mnt	-0.63	0.21	0.97	0.12	1.00							
Mnm	-0.81	-0.33	-0.01	0.99	0.14	1.00						
Pbt	-0.91	0.01	0.72	0.52	0.86	0.50	1.00					
Pbm	-0.45	0.78	0.45	0.23	0.50	0.26	0.54	1.00				
pH	0.84	0.18	-0.21	-0.93	-0.34	-0.96	-0.59	-0.40	1.00			
<0.001	-0.84	0.01	0.73	0.61	0.80	0.66	0.81	0.51	-0.82	1.00		
<0.01	-0.92	0.14	0.61	0.71	0.73	0.73	0.88	0.70	-0.85	0.93	1.00	
C, %	0.61	-0.23	-0.82	-0.07	-0.90	-0.04	-0.88	-0.51	0.15	-0.56	-0.62	1.00
T8,2	-0.82	0.22	0.86	0.41	0.94	0.43	0.94	0.66	-0.60	0.91	0.92	-0.84
TCA	-0.74	0.33	0.89	0.31	0.95	0.34	0.90	0.71	-0.53	0.88	0.88	-0.85
TA	-0.78	-0.75	0.19	0.75	0.34	0.72	0.62	-0.20	-0.66	0.58	0.53	-0.29

Another characteristic of these soils is the expressed (categorical) antagonism between the mobile forms of lead

and the other mobile elements, which probably is the result of the clear association of lead (total content) with the organic matter which also predominantly determines the mobility of the other elements.

the soil solution. Whereas pH and clay fraction play a significant role for accumulation of copper, zinc and manganese, the organic carbon is the source of their mobile forms.

Table – 3: Correlations between the content of elements and mobility sources contents in profile 3

Para-meter	Cut	Cum	Znt	Znm	Mnt	Mnm	Pbt	Pbm	pH	<0.001	<0.01	C, %
Cut	1.00											
Cum	0.43	1.00										
Znt	0.07	-0.64	1.00									
Znm	-0.66	0.20	-0.72	1.00								
Mnt	0.71	-0.29	0.68	-0.94	1.00							
Mnm	0.09	0.90	-0.85	0.60	-0.63	1.00						
Pbt	-0.01	0.43	-0.28	0.51	-0.39	0.57	1.00					
Pbm	0.04	-0.41	0.88	-0.48	0.47	-0.57	0.20	1.00				
pH	0.62	-0.27	0.56	-0.94	0.91	-0.62	-0.72	0.21	1.00			
<0.001	0.43	-0.32	0.51	-0.85	0.76	-0.63	-0.87	0.09	0.96	1.00		
<0.01	-0.69	-0.61	-0.15	0.38	-0.34	-0.32	-0.51	-0.42	-0.12	0.08	1.00	
C, %	0.23	0.84	-0.58	0.45	-0.42	0.88	0.85	-0.16	-0.60	-0.73	-0.63	1.00
T$_{8,2}$	-0.81	0.00	-0.30	0.85	-0.86	0.35	0.58	0.00	-0.94	-0.86	0.25	0.35
T$_{cA}$	-0.09	-0.64	0.61	-0.61	0.49	-0.80	-0.92	0.18	0.72	0.86	0.43	-0.94
T$_A$	-0.30	0.46	-0.57	0.81	-0.72	0.72	0.91	-0.13	-0.93	-0.99	-0.20	0.82

Table – 4: Correlations between the content of elements and mobility sources contents in profile 4

Para-meter	Cut	Cum	Znt	Znm	Mnt	Mnm	Pbt	Pbm	pH	<0.001	<0.01	C, %
Cut	1.00											
Cum	0.98	1.00										
Znt	0.95	0.90	1.00									
Znm	0.68	0.70	0.42	1.00								
Mnt	-0.14	-0.14	0.15	-0.80	1.00							
Mnm	0.48	0.54	0.61	-0.18	0.72	1.00						
Pbt	0.76	0.65	0.70	0.70	-0.48	-0.13	1.00					
Pbm	0.25	0.33	0.39	-0.36	0.80	0.97	-0.38	1.00				
pH	-0.42	-0.54	-0.12	-0.83	0.67	0.04	-0.19	0.10	1.00			
<0.001	0.78	0.65	0.88	0.33	0.04	0.27	0.86	0.03	0.17	1.00		
<0.01	0.68	0.53	0.69	0.52	-0.32	-0.12	0.97	-0.36	0.04	0.92	1.00	
C, %	0.96	0.89	0.92	0.70	-0.25	0.27	0.91	0.01	-0.31	0.88	0.86	1.00
T$_{8,2}$	0.78	0.88	0.58	0.80	-0.35	0.39	0.38	0.25	-0.86	0.22	0.19	0.63
T$_{cA}$	0.18	0.34	0.16	-0.08	0.46	0.79	-0.50	0.86	-0.35	-0.31	-0.59	-0.10
T$_A$	0.54	0.46	0.36	0.84	-0.82	-0.48	0.89	-0.68	-0.43	0.54	0.81	0.71

In summary, lead is associated with organic carbon, but it has not a significant contribution to the extraction of lead in

In Gleyic Fluvisol (profile 4), the relationship between total and mobile forms of copper, zinc and manganese is best

expressed, but again except lead (Table 4). This confirms the logical and quintessential links between the elements and the mineral colloids, essentially for copper and zinc. The exchangeable forms of the last elements pronounced as a adsorption on weaky acid positions of mineral colloids are their main mobile forms. The mobility of manganese and lead, conversely, is related to the strongly acid positions of mineral colloids. There is a lack of correlation in profile 4 between the total manganese and the fine particles, which can be explained by the accumulation of manganese in the larger mechanical fractions, and especially in the heavy and non-visible minerals which are richer in manganese [7, 8, 26] although the transportation and sizing of minerals by water may also be responsible for allocation of the elements.

Soil formation in Albic Luvisol (profile 8) goes under the influence of leaching and metamorphism, which are the likely factors of the few positive correlations between the elements found here (Table 5).

Table – 5: Correlations between the content of elements and mobility sources contents in profile 8

Para-meter	Cut	Cum	Znt	Znm	Mnt	Mnm	Pbt	Pbm	pH	<0.001	<0.01	C, %
Cut	1.00											
Cum	0.04	1.00										
Znt	0.23	0.04	1.00									
Znm	-0.47	0.79	-0.44	1.00								
Mnt	-0.68	0.70	-0.04	0.87	1.00							
Mnm	-0.62	-0.63	-0.65	-0.01	-0.07	1.00						
Pbt	-0.17	-0.27	0.87	-0.48	0.01	-0.21	1.00					
Pbm	-0.06	0.82	0.56	0.49	0.70	-0.74	0.32	1.00				
pH	-0.05	-0.45	0.84	-0.67	-0.21	-0.15	0.97	0.13	1.00			
<0.001	0.27	-0.95	0.01	-0.89	-0.89	0.43	0.19	-0.83	0.39	1.00		
<0.01	-0.26	-0.48	0.74	-0.57	-0.08	0.03	0.97	0.09	0.97	0.36	1.00	

Table – 5: Correlations between the content of elements and mobility sources contents in profile 8

Para-meter	Cut	Cum	Znt	Znm	Mnt	Mnm	Pbt	Pbm	pH	<0.001	<0.01	C, %
C, %	0.14	0.24	0.98	-0.23	0.17	-0.71	0.83	0.72	0.75	-0.21	0.66	1.00
$T_{8,2}$	-0.05	-0.40	-0.91	0.04	-0.35	0.73	-0.75	-0.84	-0.64	0.39	-0.57	-0.98
T_{CA}	0.29	0.14	-0.96	0.33	-0.19	0.93	-0.99	-0.68	-0.93	0.01	-0.97	-1.00
T_A	-0.21	-0.23	0.98	-0.41	0.11	-0.96	1.00	0.62	0.96	0.08	0.99	1.00

The most expressed relationships are observed between the total zinc and lead content and between the clay fractions and the organic matter, which also determines the high significance of pH for their accumulation. The organic matter is a source of mobile lead, whereas its link with copper is not explicit. In fact, copper does not form clear positive correlations, either with the studied soil factors or with the other elements. The lack of correlation with the basic soil factors gives us reason to suppose that copper is interlinked with iron which is already found for the surface horizons of a variety of soils from the valley [33].

4. CONCLUSION

The total content of trace elements in studied soils is lower than the background values found in Bulgarian soils, and determines the non-toxic mobile concentrations of Cu, Zn, Pb and Mn. Prevailing neutral pH also contributes to the uniform distribution of the trace elements, their low solubility and low potential availability. Organic and mineral colloids (silt and clay fractions) are the basic collectors and providers of mobile metal species although the soil type dependent bioavailability of studied metals had also been recognized.

The content of mobile zinc and manganese is most strongly associated with pedogenesis and the superficial soil formation processes (intensive weathering resulting in pH decrease, organic matter accumulation and recycling), providing their surface accumulation. Except acidity, the reducing conditions in Gleyic Fluvisol also increase the mobility of manganese.

The mobile content of Cu is extremely low (average of 0.04 mg/kg) and uniformly distributed along profile depths. It is basically attached to the content of organic carbon and fine particles content. Geochemical activity of manganese (mostly oxides and oxy-hydroxides) and affinity for Cu

during the formation of Chernic Phaeozem results in their simultaneous accumulation and synergism of mobile forms.

Lead is usually allied with organic carbon but also occurs in fine soil fractions. In Gleyic Fluvisol and Albic Luvisol the organic carbon is very fine sized and is also present in the fine fractions creating the soil type dependent bioavailable pools of Pb. This element reacts antagonistically with other mobile forms when organic carbon preferentially determines the mobility of Cu, Zn and Mn (as in Chernic Phaeozem).

REFERENCES

[1] Angelova Violina R., Radka V. Ivanova, Jivko M. Todorov, and Krasimir I. Ivanov, Lead, Cadmium, Zinc, and Copper Bioavailability in the Soil-Plant-Animal System in a Polluted Area. TheScientificWorldJOURNAL (2010) 10, 273–285. DOI 10.1100/tsw.2010.33

[2] Atanassova I., Labile forms of heavy metals and organic compounds in soil adsorbent – indicators of bioavalability and ecochemical perturbations. DSc Thesis, "N. Poushkarov" ISSAPP, 2012, 237 p.

[3] BDS ISO 10381-1:2005. Soil quality - Sampling - Part 1: Guidance on the design of sampling programmes.

[4] BDS ISO 10381-2:2005. Soil quality - Sampling - Part 2: Guidance on sampling techniques.

[5] BDS ISO 10381-4:2005. Soil quality - Sampling – Part 4. Guidance on the procedure for investigation of natural, near-natural and cultivated sites.

[6] BDS ISO 11464: 2012. Pretreatment of samples for physico-chemical analysis.

[7] Boneva K., Second National Conference on Soil Science, Sofia,1978.

[8] Dhery D., Zuirin N., Agrochemistry, vol.2, 1965

[9] Dinev, N., Ecological monitoring and risk assessment in heavy metal contaminated soils. DSc Thesis, ISSAPP N. Poushkarov", Sofia, 2012, 322 p. (in Bulgarian)

[10] Ehrlich. H. L, Geomicrobiology, Marcel Dekker, New York, lett.1.,517, 2002.

[11] Gadd, J.M., Transformation and mobilization of metals, metalloids, and radionuclides by microorganisms. In: A. Violante, P.M. Huang, G.M. Gadd. (eds). Biophysico-Chemical Processes of Metals and Metalloids in Soil Environments. Wiley-Jupac Series, Vol 1 John Wiley & Sons, Hoboken, 2008, NY pp: 53-96.

[12] Ganev, S., A. Arsova, Method for determining the strongly acid and weakly acid cation exchange in soil. Soil Sci. Agrochem., 15(3), 1980, 22–33 (In Bulg.).

[13] Huang, P.M, Germida, J.J., Chemical and biochemical processes in the rhizosphere: metal pollutants. In: P.M. Huang, J.-M. Bollag, N. Senesi (eds). Interactions between Soil Particles and Microorganisms: Impact on the Terrestrial Ecosystem. John Wiley & Sons, New York, 2002, pp: 381-438.

[14] ISO 10390: 2010. Soil quality - Determination of pH.

[15] ISO 11047: 2015. Soil quality - Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc - Flame and electrothermal atomic absorption spectrometric methods.

[16] ISO 11466: 1995. Soil quality - Extraction of trace elements soluble in aqua regia.

[16] ISO/DIN 19730:2012. Soil quality - Extraction of trace elements from soil using ammonium nitrate solution.

[17] ISO 11466: 1995. Soil quality - Extraction of trace elements soluble in aqua regia.

[18] IUSS Working Group WRB, World Reference Base for Soil Resources. 2nd edition. World Soil Resources Reports, № 103. FAO, Rome, 2006. ISBN 92-5-105511-4

[19] Kabata,C and Singh, B, Fractionation and Mobility of Copper, Lead, and Zinc in Soil Profiles in the Vicinity of a Copper Smelter Journal of Environmental Quality Vol. 30 No. 2, 2001, p. 485-492

[20] Kachinsky, A., Mechanical and micro-aggregates composition of soil, methods for its determination. Russian Academy of Sciences, Moscow, 191 p., 1985.

[21] Koinov V. et al, Soil map of Bulgaria in M 1: 400 000. Sofia, Publ. BAS, 1968.

[22] Krishnamurti, G.S.R, Naidu, R., Chemical speciation and bioavailability of trace metals.. In: A. Violante, P.M. Huang, G.M. Gadd (eds). Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environments. Wiley Interscience, New York, 2008, pp: 419-466.

[23] Krishnamurti, G.S.R., Naidu, R., Solid-solution speciation and phytoavailability of copper and zinc in soils. Environ. Sci. Technol. 36, 2002, 2645-2651.

[24] Krishnamurti, G.S.R., Pigna, M., Arienzo, M., Violante, A., Solid-Phase Speciation and

Phytoavailability of Copper in a Few Representative Soils of Italy. Chem. Spec. & Bioav. 19, 2007, 57-67.

[25] Meyer, J.S., The utility of the terms "bioavailability" and "bioavailable fraction" for metals. Mar. Environ. Res. 53, 2002, 417–423.

[26] Mirchev St., Chemical composition of soils in Bulgaria. Sofia, 1971.

[27] Morel, F.M.M., Principles of Aquatic Chemistry, first ed. Wiley, New York, USA, 1983.

[28] Peijnenburg, W., Jager, T., Monitoring approaches to assess bioaccessibility and bioavailability of metals: matrix issues. Ecotoxicol. Environ. Safety 56, 2003, 63–77.

[29] Prüeß, A., Vorsorgewrte und Prufwerte fur mobile und mibilisierbare potentiell okotoxische Spurenelenente in Boden. Graner Wendlingen: Verlag Ulrivh E., 1992.

[30] Regulation 26 about Reclamation of Disturbed Areas, Improvement of Low-productive Lands, Excavation and Utilization of Humus Layer. State Journal 89/1996, amended, State Journal 30/2002 (Bg).

[31] Regulation 3 about the Rates of Levels of Pollutants in Soil. State Journal 36/1979, Amended, State Journal 71 /2008 (Bg).

[32] Salomons, N and Forstner, U, Environment technology, Lett. 1, 517,1980.

[33] Tsolova V., M. Hristova, J. Bech, N. Pascual, M. Banov. Pb, Cu and Zn geochemistry in reclaimed soils (Technosols) of Bulgaria. Journal of Geochemical Exploration, 144, 2014, 337–344. IF2014 - 2.4.doi:10.1016/j.gexplo.2014.02.019

[34] Tsolova, V., I. Nikova, A. Zdravkov, K. Ruskov, V. Kolchakov., Soils in the Bobovdol valley: genetic, geochemical and ecological characteristics. AA, ISSAPP "N. Pouskarov", UMG "St. I. Rilski", Sofia, 2016, 160 p. PublishScieSet-Eco, Sofia.

[35] Violante A., V. Cozzolino, L. Perelomov, A.G. Caporale, and M. Pigna, Mobility and bioavailability of heavy metals and metalloids in soil environments. J. Soil. Sci. Plant Nutr. 10 (3): 268 – 292, 2010.

[36] Yolevski M. and A. Hadjianakiev, Agro-cultivation of Soils in Bulgaria, Advanced Systemic List. The code of groups and soil varieties. MAF, ISSAPP "N. Poushkarov, Sofia. 1976, 89 p.

[37] Yolevski M., N. Ninov, Sl. Kostanov, G. Gjurov, A. Hadzhianakiev, E. Angelov, I. Kabakchiev, K. Bonev, T. Andonov, J. Staykov, E. Fotakieva, P. Treikyashki, N. Todorova, P. Zhelyazkov, B. Hristov, Soil Classification scheme in the Republic Bulgaria . Publ. N. Poushkarov, Sofia, 42 pp., 1980.

BIOGRAPHIES

Assist. prof. PhD Ivona Nikova,"N. Poushkarov" Institute of Soil Science, Agrotechnologies and Plant protection, Dept. "Soil chemistry", Sofia, Bulgaria