Bulgarian Journal of Agricultural Science, 30 (No 4) 2024, 561–567

Sources of metals, metalloids and non-metals in surface horizons of soils near Aurubis-Pirdop copper smelter in Bulgaria

Irena Atanassova*, Maya Benkova, Lyuba Nenova, Tsetska Simeonova and Milena Harizanova

Agricultural Academy, "N. Poushkarov" Institute for Soil Science, Agrotechnology and Plant Protection, 1331 Sofia, Bulgaria

**Corresponding author:* i.d.atanassova@abv.bg

Abstract

Atanassova, I., Benkova, M., Nenova, L., Simeonova, Ts. & Harizanova, M. (2024). Sources of metals, metalloids and non-metals in surface horizons of soils near Aurubis-Pirdop copper smelter in Bulgaria. *Bulg. J. Agric. Sci., 30*(4), 561–567

A study was conducted to assess the sources of metals and other elements considered as pollutants and their relationship with general characteristics of the soils in the area of Aurubis-Pirdop copper smelter and refinery. In the early spring of 2023, soil samples were taken from the surface horizon (0-20 cm) of Alluvial-deluvial soils (Fluvisols) and Cinnamon Forest soils (Chromic Luvisols). The studied soils possess light texture, low content of clay 5.7-14.7% and vary in organic carbon (OC) from 0.5-2.9%. We observed exceeding of the maximum permissible levels (MPL) for the metals Cu, Pb and the metalloid As, and elevated contents for Mn, B and Se. Several groups of elements were distinguished on the basis of principal component and cluster analysis (PCA and CA). The metals Cu, Mg, Mo, Pb, Zn, Hg and the elements As, Se and Na were of anthropogenic origin and had elevated concentrations in the surface soils, especially Cu, Pb and As. The group of elements Al, Ba, Co, Cr, Fe, Mn, together with the % clay were of litho-pedogenic origin and revealed their belonging to the crystal lattice of the secondary soil minerals. The third, fourth and the fifth groups included B, Li, Mg, Ni, Mn and Na, mainly elements present as accessory components in soil minerals which have both anthropogenic and/or litho-pedogenic origin.

Keywords: metals; metalloids; non-metals; sources; smelter

Introduction

Aurubis Bulgaria copper smelter and refinery in Pirdop is the biggest facility for smelting and refining copper in South-Eastern Europe. The plant, was founded in 1958, and comprises a smelter, refinery, acid plant, precious and rare metal production. The plat activities are processing of copper concentrates, production of cathode copper, of copper anodes and as well as sulfuric acid and iron silicate.

The contamination of soils around the industrial plant with copper including acidic deposition was studied in Bulgaria by Tchuldjian (2008), Benkova & Atanassova (2015), Benkova et al. (2005a) and Benkova et al. (2005b). A survey indicates a wide range of Cu contamination of surface soils (from 100 to 2700 mg/kg soil). The concentrations of other elements such as Zn, Pb and As also exceed normal contents in soils (Atanassov et al., 2001).

It has been found that in a pot and mesocosm experiments with alfalfa grown on acidic soil from the vicinity of Pirdop-Zlatitsa, contaminated with heavy metals, that ameliorative effects lead to improvement of soil parameters (pH, humus), and the physiological status and yield of the crop with concomitant decrease in the contents of contaminants (Benkova et al., 2005a; Benkova et al., 2005b, Dimova et al., 2007). Benkova & Atanassova (2015) and Atanassova et al. (2019) studied soil acidity and amelioration of copper (Cu)-, zinc (Zn)-, and lead (Pb) – contaminated soils around industrial plants in Bulgaria, including Arubis-Pirdop Cu smelter and described the effects of applying organo-mineral ameliorants and coal ash on the solubility, speciation, and bioavailability of heavy metals in soil.

The objective of the present study was to evaluate the sources of metals and relationships with soil characteristics in surface soil horizons near Aurubis copper smelter in Bulgaria with the general aim to ameliorate contamination of elements exceeding the MPL in the soils.

Materials and Methods

The dominant soil types in Zlatitsa – Pirdop area are Diluvial soils (Colluvisols), which occupy 72% of the total area. In addition to these, Diluvial (Gleyic) and Alluvial-diluvial (Fluvisols), 5%, Alluvial 2%, Cinnamon Forest soil (Chromic Luvisols) – 10% and undeveloped soils, 3% are also common in the area (Teoharov & Hristov, 2016). Atanassova et al. (2004) found that in a loamy sand soil (Distric Fluvisol) clay minerals are dominated by hydromica (55%), as well as chlorite and kaolinite.

Soil sample (0–20 cm) were taken in the spring of 2023 from arable plots in the vicinity of Aurubis-Pirdop copper smelter and refinery and possess light texture and low content of clay 5.7–14.7% in the 0–20 cm depth (Table 1). Soils are classified as sandy loam according to USDA Soil Taxonomy. The map of sampling points is presented on Figure 1. After drying and grinding, the soil samples were prepared for analysis. Soil texture was analyzed by the method of Kachinski, electrical conductivity (EC) was determined in soil:water (1:5) according to ISO 11265, soil pH/Eh were measured in a soil:water slurry of 1:2.5, total organic carbon (TOC) in the samples was determined by oxidation with $K_2Cr_2O_7/H_2SO_4$ by the Kononova method, cation exchange capacity (CEC) was assessed as sum of titratable acidity (pH 8.2) and extractable Ca, by saturation with K malate at pH 8.2 by the method of Ganev & Arso-

Table 1. Physico-chemical characteristics of the experimental soils, $CEC_{8,2}$ – cation exchange capacity, CEC_{SA} – strongly acidic cation exchanger, CEC_a – weakly acidic cation exchanger

Points No	**pH** /H_2**O**	$CEC_{8.2}$	CEC_{SA}	CEC_{WA}	**$H_{8.2}$**	Al	**Ca**	Mg	Base satur.	Clay	TOC
		cmol. kg^{-1}							%		
1	4.9	23.2	18.1	5.1	7.5	2.5	13.5	2.1	67.7	9.0	1.21
2	6.3	24.0	22.2	2.0	2.0	0.0	20.2	2.3	91.7	14.7	0.48
3	4.7	22.6	17.8	4.8	7.6	2.9	12.6	2.2	66.4	8.6	2.17
4	5.4	25.0	21.9	3.1	4.0	1.0	19.1	2.2	84.0	11.4	2.86
5	4.6	22.3	17.3	5.0	7.8	3.0	12.2	2.1	65.0	21.1	1.02
6	4.3	21.7	17.0	4.7	8.0	3.1	11.4	2.1	63.1	16.7	0.83
7	6.2	24.8	21.9	2.9	2.8	0.0	20.2	2.3	88.7	5.7	1.79
8	6.2	24.8	22.8	2.0	1.9	0.0	20.6	2.3	92.3	7.3	1.96
9	5.3	25.0	21.8	3.2	5.4	1.1	18.8	2.2	82.4	6.5	1.71

Table 2a. Contents of total (pseudo-total) forms of the analysed elements (means +/− SD (2-8%) in the studied soils around the Aurubis-Pirdop Cu smelter

Points No	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
	%	mg/kg		%	mg/kg				%
1	2.4	45.6	265.7	0.21	1.7	16.0	34.5	2645.0	4.02
2	2.5	56.1	112.5	0.29	0.5	14.6	38.5	100.8	4.14
3	2.4	56.5	146.3	0.28	0.3	11.7	32.9	641.9	2.83
4	2.3	66.1	124.0	0.30	0.5	12.8	33.1	965.7	2.91
5	2.8	74.6	167.6	0.21	0.5	17.5	38.4	340.9	3.39
6	2.6	77.0	157.3	0.22	0.4	15.2	37.5	318.7	3.17
7	2.3	104.2	103.0	0.23	0.4	15.6	31.1	962.0	3.33
8	2.5	97.1	136.5	0.30	1.9	14.9	33.8	1377.0	3.39
9	2.4	94.3	139.1	0.26	0.5	14.4	34.0	714.2	3.30
$MPL_{pH< 6,0*}$					1.5		200	80	
$MPL_{pH\ 6,0-7,4*}$					2.0		200	150	

* Maximum Permissible Levels (MPL) according to Decree No 3. (2008)

Table 2b. Total (pseudo-total) contents of the analysed elements (means +/− SD (2–7%) in the studied soils around the Aurubis-Pirdop Cu smelter

Points No	Li	Mg	Mn	Mo	Na	Ni	Pb	Zn	As	Hg	Se
	mg/kg	%	mg/kg								
1	65.5	0.52	721.4	51.1	436.7	22.3	233.6	155.4	144.6	0.33	7.1
2	78.5	0.57	720.7	1.2	230.7	25.4	20.5	73.6	15.9	0.03	1.9
3	64.0	0.46	513.5	4.7	289.5	14.9	50.3	70.6	18.7	0.13	1.6
4	62.0	0.50	752.1	11.9	262.5	18.6	91.5	86.9	26.9	0.14	2.2
5	68.0	0.48	1334.6	3.4	297.7	25.3	38.0	80.2	13.0	0.06	1.4
6	66.7	0.48	1031.6	3.1	287.8	25.7	33.1	82.6	10.8	0.05	1.3
7	82.2	0.63	914.2	17.1	294.5	26.8	186.9	99.3	78.2	0.29	2.8
8	94.4	0.62	639.1	15.7	509.9	31.6	111.0	262.4	51.5	0.17	3.7
9	87.3	0.60	789.6	10.0	402.8	29.0	94.9	98.4	33.2	0.18	2.9
MPL $_{pH< 6,0*}$						90	60	200	25	1,5	
MPL $_{pH\ 6,0-7,4*}$						110	100	320	25	1,5	

* Maximum Permissible Levels (MPL) according to Decree No 3 (2008)

Fig. 1. Map of the sampling points in the area of Aurubis-Pirdop copper smelter point 1: N 42° 42′ 42.0″ E 24° 09′ 30.6″; point 2: N 42° 42′ 38.7″, E 24° 09′ 32.1″; point 3: N 42° 42′ 35.1″, E 24° 09′ 31.5″; point 4: N 42° 42′ 32.3″, E 24° 09′ 30.6″; point 5: N 42° 42′ 29.2″ E24° 09′ 24.6″; point 6: N 42° 42′ 29.2″ E 24° 09′ 20.2″; point 7: N 42° 42′ 16.2″, E24° 09′ 37.3”; point 8: N 42° 42′ 14.5″, E 24° 09′ 37.0″; point 9: N 42° 42′ 13.9″, E 24° 09′ 34.7″

va (1980). Analysis of the total contents of heavy metals was performed by decomposition with "aqua regia" (ISO 11466:1995) and ICP-OES determination (Agilent ICP-OES 5800) and results were compared with standard values stated in Decree No 3 (2008) (Tables 2a and 2b).

Principal component (PCA) and cluster analyses were performed by IBM SPSS Statistics 23 for Windows.

The soils possess acidic to slightly acidic soil reaction (pH 4.3–6.3), which is a prerequisite for increased mobility of heavy metals at the acidic sites and specific sorption in soils with pH 6.2–6.3. The electrical conductivity does not indicate high salt content of soil solution. Total organic carbon (TOC) ranged widely from 0.48% OC to 2.86% and is presented in Table 1.

Results and Discussion

Total contents of metals, metalloids and non-metals and their sources

Total metal contents for Cu, as well as for Pb and As at the sampling points of the studied soils exceeded the national regulation standards (Decree No 3, 2008, Tables 2a and 2b). Mn was above the normal range in agricultural soils of Bulgaria, but in the range observed worldwide (Atanassov et al., 2001; Kabata-Pendias & Pendias, 2001). The elements Mg, Mo, Na, Ni and Hg are also in the normal range found in soils. According to Brdar-Jokanović (2020), the majority of the world's agricultural soils contain 5–30 ppm total B, and the maximum amount of the element that should not affect

Table 3. Correlation matrix between the studied elements and some key soil properties, OC %, % humus, clay content %

	pH	clay	AI	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	Li	Mg	Mn	Mo	Na	Ni	Pb	Zn	As	Hg	Se	OC%
pH	1.00	-.531	-.444	.451	-.550	.540	.197	-.062	-.311	.007	.331	.778	.897	-.365	-.011	.179	.500	.209	.352	.119	.215	.125	.124
clay	-.531	1.000	.835	-.332	.097	-.331	-.301	.424	.873	-.500	.116	-.468	-.604	.712	-.423	-.486	-.071	-.629	-.408	-.499	-.735	-.471	-.553
AI	-.444	.835	1.00	-.048	.174	-.398	-.022	.603	.823	-.396	.156	-.079	-.361	.701	-.366	-.049	.274	-.544	-.048	-.409	-.617	-.341	-.620
B	.451	-.332	-.048	1.00	-.543	.017	-.029	.218	-.352	-.193	-.304	.729	.678	.238	-.250	.288	.702	.094	.304	-.127	.141	-.211	.206
Ba	-.550	.097	.174	-.543	1.00	-.565	.536	.345	.155	.716	.363	-.396	-.379	.045	.760	.437	-.168	.469	.220	.649	.406	.726	-.242
Ca	.540	-.331	-.398	.017	-.565	1.00	.047	-.726	-.239	-.194	-.213	.294	.227	-.684	-.340	-.003	-.106	-.311	.211	-.367	-.256	-.226	.502
Cd	.197	-.301	-.022	-.029	.536	.047	1.00	.267	-.112	.778	.423	.349	.318	-.298	.693	.859	.366	.549	.920	.649	.472	.788	.020
Co	-.062	.424	.603	.218	.345	-.726	.267	1.00	.451	.129	.530	.177	.187	.765	.243	.211	.600	.224	.179	.292	.101	.240	-.619
Cr	-.311	.873	.823	-.352	.155	-.239	-.112	.451	1.00	-.448	.446	-.180	-.361	.515	-.352	-.279	.177	-.620	-.245	-.416	-.730	-.298	-.800
Cu	.007	-.500	-.396	-.193	.716	-.194	.778	.129	-.448	1.00	.279	-.018	.150	-.340	.972	.677	-.029	.884	.593	.928	.844	.956	.239
Fe	.331	.116	.156	-.304	.363	-.213	.423	.530	.446	.279	1.00	.226	.328	.021	.415	.161	.369	.257	.193	.459	.137	.519	-.709
Li	.778	-.468	-.079	.729	-.396	.294	.349	.177	-.180	-.018	.226	1.00	.906	-.164	-.072	.543	.836	.125	.584	.048	.152	.105	-.043
Mg	.897	-.604	-.361	.678	-.379	.227	.318	.187	-.361	.150	.328	.906	1.00	-.197	.145	.427	.741	.401	.493	.293	.407	.272	.030
Mn	-.365	.712	.701	.238	.045	-.684	-.298	.765	.515	-.340	.421	-.164	-.197	1.00	-.236	-.264	.295	-.205	-.306	-.224	-.288	-.322	-.431
Mo	-.011	-.423	-.366	-.250	.760	-.340	.693	.243	-.352	.972	.415	-.072	.145	-.236	1.00	.569	-.020	.906	.457	.973	.851	.972	.076
Na	.179	-.486	-.049	.288	.437	-.003	.859	.211	-.279	.677	.161	.543	.427	-.264	.569	1.00	.502	.522	.884	.539	.524	.683	.146
Ni	.500	-.071	.274	.702	-.168	-.106	.366	.600	.177	-.029	.369	.836	.741	.295	-.020	.502	1.00	.095	.525	.064	.037	.117	-.361
Pb	.209	-.629	-.544	.094	.469	-.311	.549	.224	-.620	.884	.257	.125	.401	-.205	.906	.522	.095	1.00	.435	.955	.979	.859	.239
Zn	.352	-.408	-.048	.304	.220	.211	.920	.179	-.245	.593	.193	.584	.493	-.306	.457	.884	.525	.435	1.00	.451	.392	.569	.170
As	.119	-.499	-.409	-.127	.649	-.367	.649	.292	-.416	.928	.459	.048	.293	-.224	.973	.539	.064	.955	.451	1.00	.907	.946	.030
Hg	.215	-.735	-.617	.141	.406	-.256	.472	.101	-.730	.844	.137	.152	.407	-.288	.851	.524	.037	.979	.392	.907	1.00	.806	.337
Se	.125	-.471	-.341	-.211	.726	-.226	.788	.240	-.298	.956	.519	.105	.272	-.322	.972	.683	.117	.859	.569	.946	.806	1.00	.017
OC	.124	-.553	-.620	.206	-.242	.502	.020	-.619	-.800	.239	-.709	-.043	.030	-.431	.076	.146	-.361	.239	.170	.030	.337	.017	1.00

crops is 25 ppm. Increased above the normal content ranges in soils were Se and B, as well (Brdar-Jokanović, 2020; Xing et al., 2015). As far as boron is concerned in this study, we detect much higher concentrations than normally found in Bulgarian soils (Stoyanov et al., 1999). Selenium concentrations were also higher than the normal range in agricultural soils, and this increase is often attributed to its presence as a by-product in copper smelting slag (Desai et al., 2016).

Statistical analysis

We applied Principal Component Analysis (PCA) for the studied soils from Aurubis-Pirdop smelter area by examining 23 variables. The PCA explained data variability in the process of factor reduction to unrelated components similarly to Atanassova et al. (2019) and Micó et al. (2006). The analysed variables were: pH, clay, Al, B, Ba, Ca, Cd Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Zn, As, Hg, Se and % OC. The correlation matrix and the component matrix are presented in Table 3 and Table 4. Five factors with eigenvalues > 1 were extracted when analyzing the data, explaining 38.8%, 23.08%, 19.39%, 8.61% and 7.07% of the total variance 96.9 % (Table 4). This table contains component loadings, describing correlations between the variable and the component. The 1st component was loaded by Cu, Mg, Mo, Na, Pb, Zn, As, Hg, Se, and % OC with lower loadings (coefficients) (Table 5). The 2nd component was loaded by % clay, Al, Ba, Co, Cr, Fe, Mn, the 3rd component, by B, Li, Mg, Ni, the 4th by Ca, and the 5th component was positively but insignificantly loaded by OC, Zn, Cd, Al, B.

It is very well distinguished that the 1st component is loaded by elements which are present at concentrations exceeding the maximum permissible levels MPL, most probably having an anthropogenic input (from the smelter). A proof of the anthropogenic and more recent input of Cu and Pb, lies in the fact that organic carbon (OC) contents are not significantly correlated with these metals, which in principle, show high affinity and correlation to soil organic matter (SOM). The 2nd component is loaded by the major structural elements of the aluminosilicates, while the 3rd component highly correlates with metals present as accessory minerals in soils or as isomorphic substitutes in secondary or primary minerals. The 4th and 5th components are loaded by common variables, reflecting dual sources or a couple of sources for these variables.

Table 4. Factors extracted and represented % of variance

Component	Initial Eigenvalues		
	Total	% of Variance	Cumulative %
1	8.915	38.759	38.759
2	5.308	23.078	61.837
3	4.460	19.392	81.230
4	1.980	8.610	89.839
5	1.626	7.068	96.908

In this study we observed a negative correlation between OC and the clay content (Table 3), probably due to the fact that OC is mainly contained in particulate organic matter, rather than in organo-mineral associations, because the sampled soils possess comparatively low clay content (11.2 +/− 5%) on average.

The element Mn was found in one group with Al, Cr and Fe, because it readily substitutes for Fe^{2+} and Mg^{2+} in minerals. The distribution of MnO_2 in soil is closely related to the contents of Fe_2O_3 (Ure & Berrow, 1982). In a previous study of Technogenic coal mine reclaimed soils, the total Mn (incl. MnO_2) was found in high degree of association with some transition metals, in particular with Co, Ni, Cu, Zn, Pb, etc. (Atanassova et al., 2018). In this study a positive, although insignificant correlation was found between Mn and Fe (R= 0.421) (Table 3). Atanassova et al. (2018) have observed a dual origin of Mn, due to the fact that, except lithogenic sources, this element has also biogenic sources, because of involvement in electron transport in photosynthesis and enzymatic reactions.

Table 5. Component matrix

	Component				
	1	2	3	4	5
pH	.372	-.596	.505	.154	-.419
clay	-.741	.594	.130	.091	.078
AI	-.530	.599	.443	.101	.341
B	.130	-.473	.639	-.528	.253
Ba	.431	.799	-.315	.118	.158
Ca	-.036	-.775	-.053	.589	.044
Cd	.774	.249	.202	.414	.316
Co	.109	.697	.610	-.308	-.028
Cr	-.592	.602	.354	.377	-.079
Cu	.906	.289	-.275	.041	.102
Fe	.312	.503	.392	.385	-.587
Li	.373	-.435	.794	.072	.015
Mg	.539	-.442	.659	-.088	-.269
Mn	-.440	.536	.386	-.545	.105
Mo	.868	.411	-.253	-.026	-.078
Na	.768	.069	.288	.171	.492
Ni	.248	.003	.944	-.069	.078
Pb	.910	.137	-.143	-.321	-.139
Zn	.707	-.049	.373	.317	.462
As	.896	.341	-.151	-.120	-.191
Hg	.900	.015	-.202	-.361	-.110
Se	.909	.357	-.111	.128	-.084
OC %	.261	-.648	-.476	-.174	.386

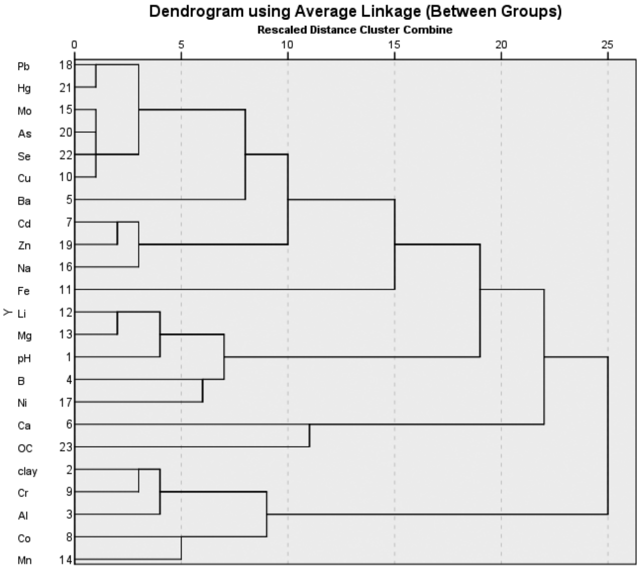

Fig. 2. Dendrogram of the 23 measured parameters

The Cluster analysis supports our findings from the PCA and displays grouping of variables containing members of similar characteristics and/or sources (Figure 2). The dendrogram contains two main clusters, the 1st containing the phyllosilicate structural elements of lithogenic origin contained mainly in the clay fraction, the 2nd main group was subdivided into a couple of sub-groups: one consisted of Fe, and the other of the elements Li, Mg, B, Ni in accessory minerals, whose presence is pH correlated. The anthropogenic heavy metals and Na comprise the rest of the sub-groups, while OC is linked with Ca, which is often implicated in soil organic carbon stabilisation.

Conclusion

The study reflects areal distribution and sources of metals, metalloids and some non-metals in the vicinity of a copper smelter and refinery in Bulgaria. We observed exceeding of the MPL for the metals Cu, Pb and the metalloid As. Elevated were also the concentrations of Mn and the non-metals B and Se. Several groups of elements were distinguished on the basis of principal component and cluster analysis. The 1st group of elements Cu, Mg, Mo, Na, Pb, Zn, As, Hg, Se were of anthropogenic sources and had elevated concentrations in the surface soils, especially Cu, Pb and As. The metals, e.g. Cu and Pb were positively, although insignificantly correlated with organic carbon. The group of elements Al, Ba, Co, Cr, Fe, Mn, together with the % clay were of litho-pedogenic origin and revealed their belonging to the clay-crystal lattice of the secondary soil minerals. The third, fourth and the fifth groups included B, Li, Mg, Ni, Mn and Na, mainly elements present as accessory components in soil minerals, which might have a couple of sources, both anthropogenic and litho-pedogenic.

Acknowledgements

The study was funded by the National Science Fund, Ministry of Education and Science, Project No КП-06-Н66/2.

References

Atanassov, I., Terytze, K. & Atanassov, A. (2001). Background values for heavy metals, PAHs, and PCBs in the soils of Bulgaria. *International Workshop"Assessment of the Quality of Contaminated Soils and Sites in Central and Eastern European Countries (CEEC) and New Independent States"*. Sept. 30-Oct. 3, 2001, Sofia, Bulgaria.

Atanassova, I., Benkova, M., Raichev, T. & Jyzefaciuk, G. (2004). Analysis of a technogenically degraded soil using a rapid method for clay fraction separation. In: *Modern physical physicochemical methods and their applications in agroecological research*. G. Józefaciuk, R. Walczak (Eds), Centre of Excellence for Applied Physics in Sustainable Agriculture Agrophysics, Nikola Poushkarov ISS, Institute of Agrophysics PAS, 7-11 (Pl).

Atanassova, I., Benkova, M., Banov, M., Simeonova, Ts., Nenova, L. & Harizanova, M. (2018). Geochemical associations in technogenic soils (technosols) of contrasting hydrological characteristics from the region of maritsa-iztok coal mine in Bulgaria. *Bulg. J. Agric. Sci., 24* (Suppl. 2),18-26.

Atanassova, I., Benkova, M., Simeonova, Ts., Nenova, L., Banov, M., Doerr, St. & Rousseva, S. (2019). Influence of soil water repellency on heavy metal mobility and PAHs extractability in coal ash reclaimed Technosols. *Journal of Environmental Protection and Ecology, 20*(4), 1667-1679. ISSN 13115065 (Bg).

Benkova, M., Rousseva, S., Raytchev, T., Sokolovska, Z., Hajnos, M. & Jozefaciuk, G. (2005a). Impact of different ameliorants on some characteristics of acid soil polluted with heavy metals. I. Effect on the humus state. *In: Physicochemical management of acid soils polluted with heavy metals.* T. Raytchev, G. Józefaciuk, Z. Sokolovska, M. Hajnos (Eds.), Centre of Excellence for Applied Physics in Sustainable Agriculture Agrophysics, "Nikola Poushkarov" ISS, Institute of Agrophysics PAS, 32-46, ISBN 83-89969-00-9. (Pl).

Benkova M., Filcheva, E., Raytchev, T., Sokolovska, Z,. Hajnos, M. & Jozefaciuk, G. (2005b). Impact of different ameliorants on some characteristics of acid soil polluted with heavy metals. II. Effect on the soil aggregate stability. *In: Physicochemical management of acid soils polluted with heavy metals.* T. Raytchev, G. Józefaciuk, Z. Sokolovska, M. Hajnos (Eds.), Centre of Excellence for Applied Physics in Sustainable Agriculture Agrophysics, Nikola Poushkarov ISS, Institute of Agrophysics PAS, 46-59, ISBN 83-89969-00-9. (Pl).

Benkova, M. & Atanassova, I. (2015). Effectiveness of Lime and Glauconite-Phosphorite Containing Organo-Mineral Ameliorants in Heavy-Metal-Contaminated Soil. *In Phosphate in soil: Interaction with Microelements, Radionuclides and Heavy Metal*. H. Magdi Selim (Ed.), *CRC Presss*, 293-320.

Brdar-Jokanović, M. (2020). Boron Toxicity and Deficiency in Agricultural Plants. *Int J Mol Sci., 21*(4),*1424*. doi: 10.3390/ijms21041424. PMID: 32093172; PMCID: PMC7073067.

Decree No 3 (2008). For Standards of Acceptable Content of Harmful Substances in the Soil. State Gazette, 71. (Bg).

Desai, B., Tathavadkar, V., Basu, S. & Vakil, K. (2016). Behavior of selenium in copper smelting slag. *In Advances in Molten Slags, Fluxes, and Salts,* proceedings of the 10th International Conference on Molten Slags, Fluxes and Salts, *Springer International Publishing*, 677-685.

Dimova, L., Dimitrov, D. & Benkova, M. (2007). Effect of different types of ameliorants on heavy metal export with crop production on contaminated alluvial-delluvial soils. *Soil Science, Agrochemistry and Ecology, 4,* 26-32 (Bg).

Ganev, S. & Arsova, A. (1980). Methods for determination of strongly acidic and weakly acidic cation exchange in the soil. *Soil Science and Agrochemistry, 3,* 22-33 (Bg).

ISO 11265: Soil Quality – Determination of the Specific Electrical Conductivity, 1994.

ISO 11466:1995. Soil Quality. Extraction of Trace Elements Soluble in Aqua Regia.

Kabata-Pendias, A. & Pendias, H. (2001). Trace Elements in Soils and Plants. *CRC Press,* Boca Raton, FL., 403.

Micó, C., Recatalá, L., Peris, M. & Sánchez, J. (2006). Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere, 65*(5), 863-872.

Stoyanov, D., Damyanova-Kirilova, I. & Atanasova, I. (1999). Characteristics of the boron regime of soils in Bulgaria*. Soil Science, Agrochemistry and Ecology, 4-5,* 115-122 (Bg).

Tchuldjian, H. (2008). Detoxification of Soils, Polluted Jointly by Heavy Metals, Acid Wastes and Acid Precipitations. In: *Soil Chemical Pollution, Risk Assessment, Remediation and Security. Springer Netherlands*, 1-12.

Teoharov, M. & Hristov, B. (2016). Soils in Zlatitsa-Pirdop field and the surrounding area. In: *Geochemical and Agroecological Problems of and Surroundings. Bulgarian Soil Science Society Publishing House,* 175 (In Bilgarian).

Ure, A. & Berrow, M. (1982). The Elemental Constituents of Soils. In: *Bowen HJM (ed) Environmental chemistry*. Royal Society of Chemistry, London, 94–203.

Xing, K., Zhou, S., Wu, X., Zhu, Y., Kong, J., Shao, T. & Tao, X. (2015). Concentrations and characteristics of selenium in soil samples from Dashan Region, a selenium-enriched area in China. *Soil Science and Plant Nutrition*, *61*(6), 889-897.

Received: **March, 30, 2023**; *Approved*: **July, 26, 2023;** *Published:* **August, 2024**