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**RELATIONSHIPS BETWEEN HEAVY METAL
AND METALLOID CONTENTS AND MAJOR SOIL
CHARACTERISTICS IN SOILS AROUND THE FORMER
KREMIKOVTSI METALLURGICAL PLANT FOLLOWING
ITS CLOSURE IN 2009**

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Abstract

Soils around the former metallurgical plant Kremikovtsi were subject of continued interest due to the environmental problems resulting from the plant's activities and especially heavy metal pollution. The aim of the present study was to investigate the contamination of the studied soils by metals and metalloids, several years after the closure of the plant (2009) and to relate their concentrations to basic soil parameters, pH, electrical conductivity, cation exchange capacity, clay content and total organic carbon, which will contribute to better assessment of their behaviour and remediation strategies. Total concentrations (aqua-regia) of the elements Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Zn and As were determined. Elevated levels of the heavy metals Pb, Cd, Zn, and the metalloid arsenic (As) were found at the studied sites. Lead (Pb) exceeded maximum permissible concentrations (MPC), regulated by Bulgarian legislation for arable lands between 2 and 15 times, cadmium (Cd) between 3 and 5 times, arsenic (As) between 3 and 6 times, and zinc (Zn) was

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higher than MPC in three of the sampled sites. Soil pH values were in significant correlation with EC ($R^{**} = 0.805$), CEC ($R^{**} = 0.781$), B ($R^* = 0.638$), Cu ($R^* = 0.669$), Fe ($R^{**} = 0.766$) and Mn ($R^{***} = 0.916$) contents. Aluminium, cadmium, lithium and lead concentrations were related to the content of the clay fraction in soil. Positive correlation was obtained in multiple regression models between Pb, Al, Cd, TOC and soil pH, and negative relationship was observed with electrical conductivity (EC). The obtained results showed complex relationships between soil characteristics and the metals and metalloids, which emphasize the need for their simultaneous assessment, remediation and careful use for agricultural purposes.

Key words: heavy metals, soil contamination, Kremikovtsi, relationship, soil characteristics

Introduction. Soils are considered a precious non-renewable natural resource, which needs to be preserved and restored by human activities. Many industries such as metallurgy, thermal power engineering, coal mining, etc., result in release of various contaminants into the atmosphere and their deposition onto the soil surface. The area around the former Kremikovtsi metallurgical plant (its activity was suspended in 2009) was a subject of multi-year investigations, due to the serious environmental problems that arose as a result of the smelter work and, especially the pollution with heavy metals [1-7]. The activity of the metallurgical plant, built more than 50 years ago, has caused diffuse aerosol and dust pollution, including technogenic carbonates in the humus horizon of the soils in the region. A large part of these carbonates represents weakly soluble compounds of heavy metals (Ba, Sr, Pb, etc.), which gradually and irreversibly accumulated in the soil environment, disrupting its natural balance [8]. An attempt to distinguish anthropogenic from geogenic metal sources in the study area was made by [3] who found that part of the pollution was due to dust emitted by the iron smelter, however, some metals in the area were of geogenic origin. In the study of [5], polluted soils from the region of Kremikovtsi were ameliorated with different organo-mineral mixtures (lime, phosphorite-glaucinite, peat, coal and iron-hydroxide) in the conditions of pot experiment and the effectiveness of amendments on bioavailability, solubility and speciation of Cu, Zn and Pb was assessed. Soluble (H_2O and 0.01M $CaCl_2$) and bioavailable (EDTA) extractable forms of heavy metals in soils from the industrial area of the Kremikovtsi metallurgical plant were analyzed and compared with natural uncontaminated leached Cinamonic forest soil [6]. The authors found higher fixation of copper in the technogenic soils possessing alkaline pH, compared to the control soil.

The aim of the present study was to investigate heavy metal and some metalloid pollution in the area of Kremikovtsi plant 14 years after its closure and analyze the relationships between the investigated elements with major soil characteristics (pH, CEC, EC, TOC and clay), which can help for further remediation strategies in the area.

Materials and methods. The area, that is a subject of the present investigation is located in the north-eastern part of Sofia field on a wide flat-hilly plume of Alluvial-proluvial materials of heterogeneous composition. As a consequence of the rich carbonate composition of the soil forming materials, the red coloured soils in the region (2.5 YR – 5 YR) possess predominantly alkaline reaction, while the trace element composition was represented by the elements Pb, Ba, Rb, Cu, Au, U, etc. and the metalloids As, Se, etc. The representative soil types in the area are Rhodic-Chromic Cambisols with an increased content of gravel (up to 10%). Other common soil types, determined by the proximity to the mountain, are Regosols, Fluvisols, Dystric-Eutric Cambisols, Leptosols, etc. [7]. Soil samples were taken from ten sites at a depth of 0–20 cm from the lands of the villages Gorni Bogrov, Yana and Buhovo and covering territories with different relief (Fig. 1).



Fig. 1. Map of the experimental points

Soil samples from the sites 1; 1.1; 1.2, situated close to the village of Gorni Bogrov were classified as Alluvial-meadow soils (Fluvisols), deep, sandy-loam, stony with alluvial deposits. The type of the land use was field sown with alfalfa (*Medicago sativa*). The soils from the village of Yana Site 2; 2.1; 2.2; 2.3 were classified as Diluvial soils, moderately deep, medium-sandy and stony with deluvial deposits. The type of land use was field sown with rapeseed (*Brassica napus*). The soil from Site 3, Buhovo village, was Diluvial-meadow soil (Fluvisols), shallow, sandy-loam, stony, diluvial deposits, designated as meadow. Sites 3.1; 3.2 also situated close to the village of Buhovo were shallow Leached Cinnamonic forest soils, sandy-loam moderately eroded (Chromic Luvisols) with carbonate-free hard rocks, the vegetation was mixed (black pine, oak, cherry plums, rosehips, clover, wild strawberries, etc).

Soil texture and especially the composition of clay fraction strongly influences the mobility of heavy metals. Light soil texture determines low sorption capacity that generally increases metal transport. Other factors such as the amount of soil

T a b l e 1

Physico-chemical characteristics of the investigated soils

Sites	pH (H ₂ O)	EC mS.cm ⁻¹	CEC	Tsa	Twa	H _{8.2}	V	TOC	Clay
1.	7.8	0.321	26.8	–	–	0	100	1.44	3.3
1.1	5.6	0.119	23.8	19.6	4.2	4.5	81.1	1.80	8.7
1.2	5.7	0.133	23.6	20	3.6	4.0	83.1	1.72	7.9
2.	8.0	0.241	29.0	–	–	0	100	1.22	4.5
2.1.	7.3	0.175	26.6	25.8	0.8	0.6	97.7	1.34	9.5
2.2.	7.3	0.175	26.8	27.6	0.8	0.6	97.8	1.56	10.3
2.3.	7.3	0.168	29.0	28.5	0.5	0.4	98.6	1.51	10.8
3.	6.9	0.209	23.0	21.8	1.2	1.0	95.7	1.16	3.8
3.1.	6.2	0.119	25.1	23.6	1.5	1.3	94.8	1.36	8.8
3.2.	6.3	0.112	25.0	23.5	1.5	1.3	94.8	1.44	8.2

EC – electrical conductivity; CEC – cation exchange capacity; Tsa, Twa – strongly acidic and weakly acidic cation exchange sites [9]; H_{8.2} – titratable acidity at pH_{8.2}; V – base saturation; TOC – total organic carbon; Clay particles < 0.001 mm

organic carbon, pH, the presence of carbonates and bicarbonates also influences to a great extent the behaviour of metals [5]. Regarding the soil texture studied soils can be defined as sandy-loam or medium sandy with alluvial and deluvial deposits. The fractions of coarse, medium and fine sand are predominant. The clay content varied within the range 3.3–10.0% (Table 1) and particles < 0.01 mm were within the range 13.0–38.3%. The soil reaction (pH H₂O) varied from moderately acidic in sites 1.1. and 1.2., situated in Gorni Bogrov to slightly alkaline in sites 2., 2.1., 2.2. and 2.3. which were closely located to the walls of the industrial plant in the territory of the village of Yana. Cation exchange capacity (CEC) varied in a narrow range from 23.6 to 29.0 cmol.kg⁻¹. The base saturation (V%) was high between 81.8 and 100%.

After collecting soil samples in the early spring of 2023, they were air dried, ground and prepared for further chemical and physico-chemical laboratory analyses. Total organic carbon (TOC) in the samples was determined by oxidation with K₂Cr₂O₇/H₂SO₄ according to the method of Kononova, 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 [9]. Electrical conductivity (EC) was determined in soil:water (1:5) according to (ISO 11265:2002). Soil pH was measured in a soil:water slurry of 1:2.5. Texture was analyzed by the sedimentation method of Kachinski. Total forms of heavy metals were analyzed by aqua regia digestion of soil (ISO 11466:1995) and ICP-OAS Agilent 5800 VDV determination. Statistical analyses were performed by STATGRAPHICS Centurion 18.

Results and discussion. Total forms of heavy metals (Al, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, and Zn) and As and B were presented in Table 2a and 2b. The obtained results were compared with the maximum permissible concentrations for arable lands (MPC) regulated by Bulgarian legislation [10].

According to the Bulgarian legislation [10] some of the investigated elements exceeded several folds the maximum permissible concentrations (Table 2a and 2b). As it was found in previous studies [1-5,7] lead (Pb) was the main pollutant in the region. Its concentrations exceeded (MPC) for arable lands between two- and fifteen-fold in all of the investigated sites (Table 2b). The origin of elevated

T a b l e 2

a. Metal concentrations, incl. B (aqua regia) in soils from Kremikovtsi region (means $\pm$ 1-12% SD)

Sites	Al	B	Ba	Cd	Co	Cr	Cu	Fe
	mg/kg							
1.	21000.0	116.6	836.0	2.8	15.0	62.8	110.1	63600.0
1.1	26623.8	70.4	474.7	7.8	20.5	45.8	68.2	39118.7
1.2	22894.4	90.6	485.0	8.1	19.6	41.4	68.1	38884.9
2.	19000.0	118.4	2210.2	2.8	23.2	40.4	83.9	49000.0
2.1.	24849.6	74.3	2499.4	9.4	20.5	46.4	97.7	46822.8
2.2.	23308.0	93.8	2458.9	9.6	21.7	44.2	99.3	47744.2
2.3.	28091.3	103.8	2431.4	9.5	22.9	48.8	98.9	47935.6
3.	20000.0	119.9	1492.8	2.0	20.3	40.4	71.7	40400.0
3.1.	23770.5	92.8	1710.0	7.8	25.8	43.6	87.7	41739.3
3.2.	21602.0	77.8	2486.0	9.3	23.8	34.6	93.5	42678.6

b. Metal concentrations, incl. As (aqua regia) in soils from Kremikovtsi region (means $\pm$ 1-12% SD)

Sites	Li	Mn	Mo	Ni	Pb	Zn	As
	mg/kg						
1.	42.1	3643.9	3.1	43.6	248.7	143.3	69.2
1.1	58.2	2332.8	3.9	53.3	899.2*	236.7	111.7
1.2	53.0	2246.1	3.4	50.8	608.6**	232.6	110.9
2.	42.3	4474.0	4.1	61.6	272.9	384.2	108.6
2.1.	54.5	3675.1	4.2	53.2	799.4	212.5	132.4
2.2.	51.3	3786.1	4.6	56.3	685.6	234.5	117.1
2.3.	62.1	3878.2	3.9	60.0	800.0***	243.4	95.8
3.	50.7	2607.6	3.9	54.5	208.1	258.6	98.2
3.1.	56.7	2231.8	4.6	62.4	520.2	217.5	119.1
3.2.	62.9	2545.8	5.0	64.6	506.7	360.5	154.9

*Exceeds MPC 15 times; **exceeds MPC 10 times; ***exceeds MPC 7 times

concentrations of lead is generally associated with the dust emitted by the iron smelter. The other serious pollutant found in the soils of “Kremikovtsi” region was arsenic (Table 2b). Its concentrations exceeded MPC between 3- and 6-fold. Arsenic is known as a harmful element as its elevated concentrations lead to reduction of soil biodiversity, loss of crop productivity and could be a potential risk to human health [11]. The sources of arsenic could be both of geogenic or anthropogenic origin. Mining activities are closely related to a huge release of As [12]. In the region of “Kremikovtsi” the increased content of As was also attributed to inheritance from proluvial soil forming rocks [7], while other technogenic processes were considered subordinate. In a 2 km soil long transect, situated at increasing distance from Kremikovtsi smelter, heavy metal concentrations were investigated in soil depth profile by [3], who did not distinguish categorically anthropogenic from geogenic sources of contamination. In the present research Cd concentrations varied between 2.0 and 9.3 mg/kg exceeding MPC between 3- and 5-fold (Table 2a). Cadmium is easily available to plants and is one of the most toxic pollutants that enter the food chain. The elevated concentrations of Cd and the other contaminants represent a serious risk for the quality of agricultural crops grown in the region. Cadmium availability depends on soil characteristics, mainly pH, hydrous oxides and free carbonates; wherever Cd contamination occurs, Zn contamination was present, as well [13]. The data obtained (Table 2b) showed that Zn concentrations were not very high, only at sites 1.2, 2.2. and 3.2. did they exceed MPC. From the combined soil contamination with Cd and Zn, it could be assumed that the source of these pollutants was of anthropogenic origin. The content of Ba in soils largely reflects its concentration in parent rocks, and most often it ranges from 10 to 1500 mg/kg [14]. Although in Bulgaria the content of barium in soil is not regulated, in some countries, such as Canada, the maximum concentration for arable land is set at 750 mg/kg [15]. At high concentrations, Ba is considered toxic to plants and animals, and its toxicity to organisms depends on its bioavailability [16]. In our study high Ba concentrations were observed up to 2499.4 mg/kg, most probably due to increased concentration of this element in the parent rock, and partly to anthropogenic loading, since the highest concentrations were recorded at the sites located closest to the plant. Barium is often concentrated in manganese soil minerals [14] and in the presence of sulphates and carbonates, barium tends to precipitate, making it less available to plants [17]. The concentrations of Fe and Mn in uncontaminated leached Cinamonic forest soil from the area of Kremikovtsi (close to the village of Seslavtsi) were found to be on average 35.4 g/kg (Fe) and 923.0 mg/kg (Mn) [6]. The data obtained in the present study showed increased contents of iron by 10–80% compared to uncontaminated soil, and for Mn the increase was about 3–4 times, showing also anthropogenic enrichment. The obtained results indicate complex contamination of the investigated soils with heavy metals, at some of the sites several times above MPC. The origin of contamination is linked with the activity of the “Kremikovtsi”

steal works, but studies of our team showed that the geogenic enrichment of the whole region was also represented.

In view of assessing the relationships between basic soil characteristics pH, EC, CEC, clay and TOC and metals and metalloids concentrations, regression analysis was performed including metals, As and B and main soil characteristics. The major results of statistical analysis are presented in Table 3.

T a b l e 3

Significant correlations between major soil parameters and some heavy metals and metalloids

Soil parameters	<i>R</i>	<i>p</i> -value	Soil parameters	<i>R</i>	<i>p</i> -value
pH/EC	0.805	0.005	EC/Li	−0.841	0.002
pH/CEC	0.781	0.008	EC/Pb	−0.636	0.048
pH/B	0.638	0.047	EC/As	−0.736	0.015
pH/Cu	0.669	0.034	CEC/pH	0.781	0.008
pH/Fe	0.766	0.010	CEC/Cu	0.669	0.034
pH/Mn	0.916	0.000	CEC/Mn	0.903	0.000
EC/pH	0.805	0.005	TOC/Pb	0.684	0.029
EC/Clay	−0.722	0.018	Clay/EC	−0.722	0.018
EC/B	0.755	0.012	Clay/Al	0.806	0.005
EC/Cd	−0.746	0.013	Clay/B	−0.699	0.025
EC/Co	−0.652	0.041	Clay/Cd	0.964	0.000
EC/Cr	0.672	0.033	Clay/Li	0.753	0.012
EC/Fe	0.841	0.002	Clay/Pb	0.892	0.001

The soil pH values were in significant positive correlations with EC ($R^{**} = 0.805$), CEC ($R^{**} = 0.781$), the content of B ($R^{*} = 0.638$), Cu ($R^{*} = 0.669$), Fe ($R^{**} = 0.766$) and Mn ($R^{***} = 0.916$), Table 3. It is known that iron and manganese oxides are major mineral components of soil and a strong adsorbent of trace elements. The distribution and the amounts of different Mn compounds in soil are largely determined by the origin of parent rock, soil-forming processes, biological cycling of substances, seasonal fluctuations of water level and the redox gradient [18]. Most of the studied soils have a neutral and slightly alkaline soil reaction, which is a prerequisite for accumulation of poorly soluble iron and manganese oxides in the surface soil layer.

According to [14], Pb distribution in mineral soils shows a positive correlation with the fine granulometric fraction. This fact is explained by the slow oxidation of Pb sulphides during the weathering process, its ability to form carbonates and to be adsorbed by soil organic matter, clay minerals and hydroxides. In the present research a very good correlation was established between lead concentrations and clay soil fraction $R^{***} = 0.892$ ($p \leq 0.001$) (Table 3). Lead was also in relatively strong correlation with the total organic carbon (TOC) in soil, $R^{**} = 0.684$ ($p \leq$

0.01). The association of Pb with soil organic matter is also confirmed in our previous studies [2] and [4,19]. Positive correlations were found between the clay fraction and Al, Cd, Li and Pb, as well. As Pb is one of the main pollutants in the area, its association with Cd, Al and Li suggests a common source of pollution, namely the activity of the former metallurgical plant.

In addition to the simple correlation analysis, multiple regression analysis was performed for Pb, with the data for Al, Cd, Li, clay and TOC. The regression analysis obtained a multiple linear regression equation, $R^2 = 0.917$:

$$(1) \quad \text{Pb} = -1007.12 + 459.81 \text{ Al} + 31.11 \text{ Cd} + 194.68 \text{ TOC}.$$

The equation very well represents the positive correlation of Pb with Al, Cd, and TOC. This is well grounded by assuming preferential Pb adsorption by soil minerals and the organic carbon [20], while the positive correlation with Cd indicates a similar anthropogenic source of these metals.

In addition, a regression analysis was also performed for Pb, As and Cd, the major pollutants in the soils, and pH, EC, CEC and TOC as the important variables for Pb contents. The results for Pb are presented by a linear multiple regression equation with $R^2 = 0.792$.

$$(2) \quad \text{Pb} = -1839.98 + 945.72 \text{ TOC} - 3658.63 \text{ EC} + 243.74 \text{ pH}.$$

The model explains the positive correlation between Pb in soil with TOC and soil pH, and the inverse relationship with electrical conductivity (EC), indicating that salt increase in soil solution would lead to enhancement of Pb solubility and decrease of Pb contents. The association of Pb with soil organic carbon, has also been categorically observed in the studies of [1,4].

Conclusions. Elevated concentrations of Pb, Cd, Zn and As in ten sites from the area of the former Kremikovtsi metallurgical plant, situated close to the villages of Gorni Bogrov, Yana and Buhovo were detected in our recent studies. Lead (Pb) exceeded the maximum permissible concentrations for arable lands between 2 and 15 times, cadmium (Cd) between 3 and 5 times, arsenic (As) between 3 and 6 times, and Zn was above the MPC in three of the sampled points. The relationships between the main soil characteristics and metal and metalloids concentrations revealed that the activity of the metallurgical plant in the past was the main source of contamination in the area, but geogenic enrichment in soil was also an influential factor. Aluminium, cadmium, lithium and lead concentrations closely correlated with the content of the clay fraction in soil. The soil pH values were in significant positive correlation with EC, CEC, B, Cu, Fe and Mn contents. There was a significant positive correlation between Pb in soil and the total organic carbon (TOC), $R^* = 0.684$. Multiple regression models significantly explain the link between the contents of Pb in the contaminated soils with TOC, pH, Al and Cd. The results obtained complete the information about the long-lasting soil

contamination in the area of Kremikovtzi metallurgical plant, 14 years after its closure, and provide clues for remediation techniques, that might influence major soil characteristics which are responsible for immobilization or release of heavy metals and metalloids in soil.

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