Почвознание агрохимия и екология, 59, 4/2025
Bulgarian Journal of Soil Science Agrochemistry and Ecology, 59, 4/2025

DOI: https://doi.org/10.61308/JZUT1154

Origin of critical raw materials in technogenically disturbed soils from the territory of a steel metallurgical plant in South-eastern Europe

Mariela Stoykova*, Irena Atanassova

Institute of Soil Science, Agrotechnology and Plant Protection "Nikola Pushkarov" – Sofia, Agricultural Academy
Corresponding author*: mariela_stojkova@abv.bg

Citation: Stoykova, M., & Atanassova, I. (2025). Origin of critical raw materials in technogenically disturbed soils from the territory of a steel metallurgical plant in Southeastern Europe. *Bulgarian Journal of Soil Science Agrochemistry and Ecology, 59*(4), 3-15.

Abstract

Six soil profiles with metamorphic and weakly developed structure, formed on old and young Quaternary proluvial and colluvial deposits, were studied. A comprehensive dataset was obtained for over 50 elements (including more than two-thirds of the CRMs), across 20 genetic horizons of various types - metamorphic, gleyed, and contaminated with agglomeration dust, coke, and other materials. Due to the growing interest and knowledge of these raw materials, this study has derived statistical relationships between many of them in the context of increased values of most. The soils are geochemically and technogenically enriched, reflecting both natural and anthropogenic influences. Three genetic and one technogenic geochemical associations were identified through XRD, LA-ICP-MS, statistical and geochemical analyses (PCA, Pearson's correlation, Concentration coefficients - CC). The plutonogenic association Hf–P–W–Nb–Ce/LREE–Sr–Bi–Ge+Ta–Th–Rb–Cs–Au, derived from the potassic-alkaline Buhovo–Seslavtsi pluton, shows strong correlations (r (P) = 0.46–0.86; r (W) = 0.50–0.98; r (Th) = 0.55–0.98). The ore-related association As–Mo–Co–Ni–Ga–Mn–Sb–Cu–Zn–U–V (r = 0.45–0.94) reflects proluvial material enriched with sulfide and uranyl-phosphate minerals. The lithophillyc association Ga–Y/HREE–Ce/LREE–Al–Ti–Sc–Si (r(Sc) = 0.63–0.88) represents a stable Al–Si–oxide-controlled system, while the technogenic Ba–Mn–Pb–Ag–Sr–Sb–Cu association (r(Ba) = 0.51–0.75; r(Pb) = 0.41–0.91) records up to 11-fold Pb and 4-fold Ba enrichment in surface horizons due to persistent metallurgical impact.

Key words: critical raw materials, rare earth elements, geochemical associations

Introduction

In our modern era, which increasingly relies on advanced technologies and digital infrastructure, the global interest in critical raw materials (CRMs) has intensified dramatically. These materials are essential for the manufacture of semiconductors, batteries, renewable energy systems, and defense technologies and underpin the progress and stability of contemporary economies (European Commission, 2023). Their importance extends beyond industrial value: the secure and sustainable supply of CRMs has become a key strategic priority for the European Union and other global economies, striving for technological sovereignty and green transition (Graedel et al., 2015).

Recent studies have examined the multifaceted challenges surrounding CRMs, encompassing not only geological exploration and extraction, but also refining, recycling, substitution, and the social dimensions of resource governance (Blengini et al., 2020). The intersection between technological demand and environmental responsibility raises complex questions about sustainability, circularity, and the ethical implications of resource use. Consequently, understanding the entire life cycle of these materials, from mining to remediation, is essential for assessing their long-term availability and minimizing their environmental footprint. Recent research increasingly focuses on the environmental pathways and geochemical behavior of critical raw materials (CRMs) in soils, especially near mining, metallurgical, and industrial areas. Elements such as Ta, Nb, Hf, and rare earth elements, can accumulate in soil profiles through atmospheric deposition or water-mediated transport, leading to potential alterations in soil chemistry and ecosystem function (Alloway, 2013). Their mobility, bioavailability, and speciation are largely controlled by soil properties such as pH, redox potential, organic matter content, and mineral composition (Kabata-Pendias, 2011). Understanding these interactions, is crucial for assessing both the environmental risks and the potential for secondary resource recovery from contaminated or technogenically altered soils (Reimann and de Caritat, 2017).

The present study is in this direction, the main subject of which is the study of the genesis, behavior and geochemical associations of some critical raw materials (Nb, Ta, Ge, V, Hf, Sc, Bi, Ga, W, Co, Ni, Cu, P, As, Sb) in soil environment, in the context of a naturally and anthropogenically loaded geochemical background and specific local soil-forming processes. Thus, the content of over 10 critical raw materials (obtained together with data for over 35 more chemical elements), analyzed by LA-ICP-MS, in soils from the site of the former Kremikovtsi metallurgical plant, was studied, and the study is based on a comprehensive approach, in which these elements are considered as a part of larger geochemical associations, but also as an individual geochemical objects.

The Kremikovtsi Metallurgical Plant area has long-standing anthropogenic and technogenic influence, expressed in three directions: 1) Deforestation, which ended about 200 years ago, and was documented in 1913 by Nikola Pushkarov; 2) Uranium mining (1939 – 1992), (Buhovo uranium ore field), which to this day is the cause of toxic contaminated waters, a product of poor liquidation of mine activities or infiltrates from uncontrolled old embankments in the depressions of the relief; 3. The metallurgical industry in the area (MK "Kremikovtsi", 1963 – 2009), which is the cause of secondary pollution, alkalization and accumulation of insoluble salts of a number of heavy metals (PCSURSF, 2021).

Deforestation, combined with mining in the area, has led to the systematic deposition of large amounts of redeposited and primary soil masses from the lower mountain, parts to the foot of the mountain during the spring and autumn rains. These masses, in addition to being infertile, are also naturally enriched not so much in uranium, as in a number of metals and metalloids from the mineralization accompanying the mining, e.g Pb, As, Sb, Co, Ni, Cd, Zn, Mo (Faitondjiev et al., 2000; Stoykova, 2020).

The aim of this research is to study and refine the origin of the critical raw materials, enriched in the soils of the area, and to assess and confirm through statistical software the relationships between them.

Materials and Methods

The study area is located in the northeastern periphery of the Sofia Basin, at the foot of the Sofia Stara Planina (Fig. 1). The soil cover is formed on proluvial and colluvial sediments of Pliocene age. In the western part, these sediments are enriched with fragments and redeposited syenite products, originating from the Buhovo–Seslavtsi potash-alkaline magmatic pluton, while in the eastern part, there are residual ore mineralization products, associated with the Buhovo uranium deposit.

The composition of the soil-forming materials includes widely distributed carbonate and clay-carbonate sediments of Triassic and Jurassic age, which are also part of the adjacent mountain slopes, as well as variously metamorphosed Paleozoic rocks, argillites, siltstones, lyddites and their redeposited fragments, which are widely involved in the construction of the soil substrate (Angelov et al., 2008; Dyulgerov, 2005; Kalaydzhiev, 1993).

These initial genetic characteristics of the soil-forming rocks determine the specific geochemical background with increased contents of a number of trace elements in the soils developed on them.

Topographically, the site of the plant is divided by a submeridional depression, in the western direction of which thick Cinnamonic Forest Soils (Cambisols) are developed on syenite soil-forming materials, and in the eastern direction on coarse-grained colluvial materials, enriched in ore matter, predominantly Regozems (Regosols) (according to IUSS Working Group WRB, 2022; Teoharov, 2019).

Morphologically, the studied soils are reddish in colour (nearly 50% of the samples have a 5YR hue), and are highly fragmented and partially naturally overlapped. Cambisols are distinguished by well-developed genetic horizons and significant thickness, and Regosols have a layered structure with successively alternating gravelly, sandy and clayey layers.

Vegetation cover is a determining factor for the direction and speed of soil formation, and is scarce or completely absent in the contaminated areas.

Bondev's (1991) studies show that the area around Kremikovtsi is characterized by mesophytic and mesoxerophytic microthermal vegetation in the area.

The study included 15 soil profiles, 11 of which were from the site of the plant, and 4 were controls, in different directions outside the plant. The profiles were constructed to a depth of up to 400 cm, which allows for the simultaneous diagnosis of the natural and anthropogenic factors determining the ecological state of the area. Standard soil analyses were carried out on the materials from all horizons of the 15 profiles, to determine textural composition, CEC, pH and SOM. The soil texture analysis was conducted using the Kachinsky method (Kachinsky, 1943), SOM was analyzed using the Kononova method (Kononova, 1966), and the physico-chemical properties were determined by the Ganev and Arsova method (Ganev and Arsova, 1980) (According to their acid-base reaction, the studied soils are slightly alkaline (mean: 7.54, median: 7.8), with some larger deviations of natural and technogenic origin (min - max: 3.8 - 9.2). The CEC is within 16.9 - 35.1; mean 24.78, median 24.1, with significantly higher values in the control profile. Total Carbon is low - in range 0.1 – 0.92 in the control profile (Stoykova, 2023).

Based on this database, the main elementary soil-forming processes controlling the behavior and geochemical fate of the elements were determined.

Of all 15 profiles, 6 representative (base) profiles were selected for additional chemical and mineralogical studies, wet silicate analysis, XRD and LA-ICP-MS. Thus, a rich database was collected on the content of over 50 macro- and microelements in soils from 20 soil horizons with different chemical, textural, physico-chemical and genetic characteristics, which allows the application of statistical methods to determine the relationships between them.

The interpretation of the results was carried out on the basis of average content, minimum and maximum values, median, Pearson's linear correlation coefficient (r). Concentration coefficient (CC) was also calculated, representing the

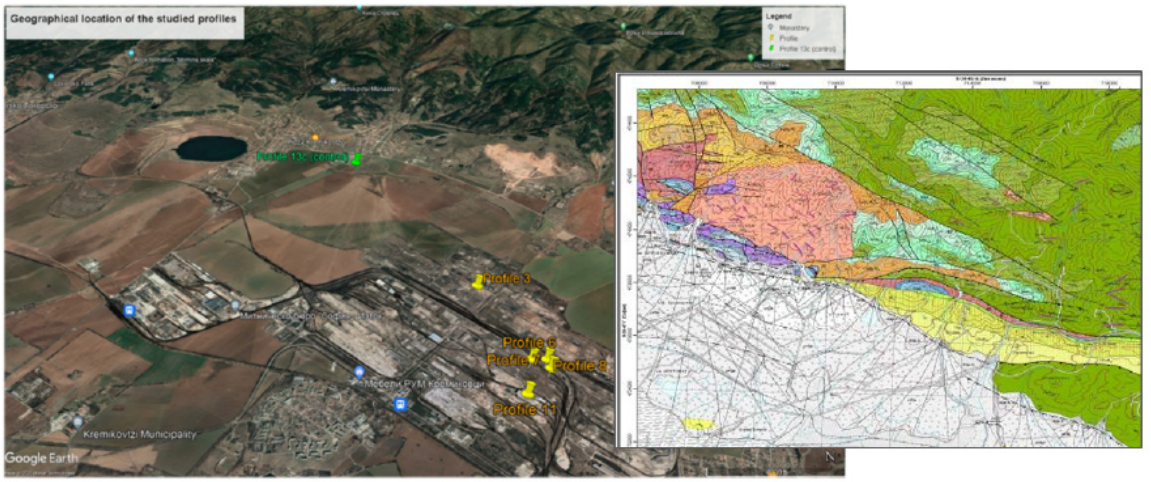

Fig. 1. Right: Geological map of the region. In pink - Buhovo-Seslavtsi pluton; green and orange - Paleozoic rocks; blue and violet - Triassic and Jurassic sediment; yellow - Neogene; gray - Quaternary (after Angelov et al., 2008, M 1:50000). Left: Geographical location of the studied profiles (Stoykova, 2023).

ratio between the element content in a given soil horizon (Ke) and its content in the lowest horizon of the same profile (Kc) – Ke/Kc (Fersman, 1953; Stefanova, 2005). This coefficient provides information about the degree of accumulation/migration of the elements relative to the soil-forming materials. Principal Component Analysis was used to determine the geochemical associations of elements according to their origin.

In our previous works (Stoykova, 2023; Stoykova and Teoharov, 2022), the behavior of Sr, Ba, Cs and Rb, as well as Sb, As, Te and Se, was assessed, but in this study they were considered simultaneously with other trace elements.

As a result of the high concentrations of a number of toxic elements, both types of contaminated soils have changed their taxonomic affiliation, and are classified as Technosols (IUSS Working Group WRB, 2022; Stoykova, 2021; Teoharov, 2019).

The statistical analysis is based on data from 6 profiles (5 from the plant site and one control, outside the plant) for concentrations of metals and rare earth elements in a total of 20 genetic horizons at depths, ranging from 0 – 30 cm to 225 – 400 cm, and was conducted with free JASP Statistical Software. The data for each element are considered together as one dataset for all profiles, including the control one, since despite the recent technogenesis, the soil-forming materials and the centuries-old processes are the same.

Free statistical software does not allow analysis of more cases then number of variables, in our case 20, so additional correlation matrices were derived, with PCA components included in them, correlated with additional elements, to complete the overall association.

Results and Discussion

Due to the composition of the adjacent mountain range, these relatively young materials, on which the steel plant was built, are naturally enriched with a number of metals and metalloids, including CRMs. The presence of the Buhovo uranium ore deposit and the potash-alkaline Buhovo-Seslavtsi pluton affects the local geochemical background, making it particularly specific, with increased alkalinity, including heavy alkali and alkaline earth metals, increased gold contents up to 80 times (x) above the average reference value, tellurium - 56 times, arsenic - 25 times, selenium - 24 times, antimony - 10 times and many others: Au (80x) > Te (56x) > As (25x) > Se (24x) > > Sb (10x) >

Tl (9x) > Pb (6x) > Ag (6x) > W (4x) > Ba (4x) > Zn (4x) > U238 (3x) > Th232 (3x) > Rb (3x) (Kabata-Pendias, 2011; Stoykova, 2021).

The elementary natural and technogenic soil-forming processes, determined as a result of the morphological and physicochemical properties of the soil profiles, are the following:

Cambic alteration/Siallitization (Profile 3, Profile 7, Profile 13c), Gleyic conditions (Profile 6, Profile 7), Stagnic gleyic conditions (Profile 8), Humus accumulation (Profile 13c) geomorphic (residual) enrichment due to selective erosion of the fine fractions and, respectively, residual accumulation of minerals from the accessory minerals and ore fractions (Profile 13c, Profile 3, Profile 11), agglomeration dust contamination (Profile 3), coke dust and granules contamination at pH 9.2 (Profile 6), coal dust pollution (Profile 7), quartz sand and slag contamination from blast furnace production (Profile 11).

Under these conditions, the origin of the elements and the influence of the primary soil-forming processes that have occurred, as well as secondary technogenic pollution, on the behavior of critical raw materials has been determined through statistical (derived from JASP software) and geochemical (calculation of the concentration coefficient) methods, based on a comprehensive approach, in which these are considered as part of larger geochemical associations, but also as individual geochemical objects. It is important to highlight that these relationships (Pearson's correlations, PCA) are a summary of all values of the trace elements. In this sense, in the indicated associations, there are elements with statistically low relationships between themselves, but with higher with a third term of the series, which additionally indicates the direction and degree of connectivity between them, also indicates the subsequent sub-grouping, already through the Concentration coefficient (CC, Fig. 2), which well demonstrates the vertical distribution and element relationships in the profile.

Therefore, three main genetic associations and several secondary ones were determined, based on a common origin in the host minerals and a common source, as well as one of them, based on the impact of Technogenesis (Table 1, Table 2).

We speculate that the Old Quaternary proluvium and colluvium (enriched with ore elements)/overlapped, contribute to the increased content of As, Mo, Co, Ni, ±Ga, Mn, Sb, Cu + Zn, U, V, etc. (PC1, Table 1, Table 2 A) in the Regoslos, which are predominantly developed on them in the eastern part of the technological site. According to the mine documentation cited by Kalaydziev (1993), the main ore minerals are torbernite $Cu(UO_2)(PO_4)_2.12H_2O$ and otunit $Ca(UO_2)_2(PO_4)_2.10\text{-}20H_2O$. Uranyl phosphates and uranyl silicates such as casolite, sodiite, uranocyrite, devindite, bassetite, sabugalite, containing additional cations – Ba, Pb, Fe, Al, are also less common. Accompanying are sulfides of Fe, Cu, Zn, Pb, Ni, Co, as well as nickel, iron and copper arsenides – nickeline NiAs, rammelsbergite $NiAs_2$, tennantite $Cu_{12}As_4S_{13}$, arsenopyrite FeAsS, etc.

Thus, according to the cited author, the inherent geochemical background is based on increased content of As, Sb, S, Co, Ni, Cu, Zn, Pb, Mo, Ba, etc. Vanadium (part of CRMs), in the genetic association deduced by us, is also present – with high correlation dependencies with the others, which is naturally justified by the close geochemical connections between uranium and vanadium. Vanadium is associated with uranyl-phosphate deposits by co-precipitation with the uranyl ion (UO_2^{2+}), forming uranyl-vanadate minerals such as carnotite and tivenite, and in the oxidation zones it forms stable vanadate anions (VO_4^{3-}), which isomorphically replace PO_4^{3-} (Burns, 2005; Kabata-Pendias, 2011).

Phosphorus, also a part of CRMs, typomorphic for the region as a component of the ore mineralizations in the Buhovo uranium deposit, but also genetically linked to the potash-alkaline magma body (as noted above), has no statistically significant correlation with the metals from the accompanying mineralization, but has retained that with uranium (P-U r = 0.56) (Table 2 B).

Other calculated correlation coefficients are: statistically significant for As are in the range r (As) = 0.56 – 0.94, for Co: r(Co) = 0.46 – 0.94, for Ni: r(Ni) = 0.45 – 0.94. The three elements with the lowest dependencies in the listed association,

Table 1. Principal Component Analysis (PCA), performed by JASP statistical software

Component Loadings				
Elements	PC1	PC2	PC3	Uniqueness
As	0.971			0.069
Mo	0.947			0.085
Co	0.938			0.078
Ni	0.917			0.038
Ga	0.615		0.906	0.088
Mn	0.603		-0.549	0.228
Sb	0.556		-0.649	0.100
Hf	-0.459	0.629		0.182
Cu	0.423		-0.690	0.243
P		0.999		0.067
W		0.858		0.054
Nb		0.854		0.069
Ce/LREE		0.651	0.727	0.139
Sr		0.600	-0.533	0.143
Bi		0.589		0.605
Ge		0.502		0.683
Y/HREE		-0.463	0.672	0.232
Al			0.919	0.172

close to the significance limit, are Ga, Sb and Cu, which clearly describes their - multiple origin.

When compared with the geochemical association statistically derived by us (PC1+Zn, U, V), it is found that Pb, Ba, Sb and to some extent Cu (the last 3 CRMs) have lost their genetic connections with the remaining trace elements in the association (with low correlation coefficients), as their modern geochemistry is most strongly influenced by the technogenic metallurgical activities of the Kremikovtsi plant (Table 2 A, B).

The old and young Quaternary proluvium, containing a syenite fraction, contribute to the increased content of Hf, P, W, Nb, Ce/LREE, Sr, Bi, Ge + Ta, Th, Rb, Cs, Au (PC2, Table 2 C), etc. (over half of them CRMs), in the Cinnamonic Forest soils (Cambisols), which are predominantly developed on them (Stoikova, 2021). The correlation coefficients of P with all listed elements are in the range r(P) = 0.46 – 0.86, for W: r(W) = 0.5 – 0.98 (with Th), for Th: r(Th) = 0.55 – 0.98, etc. This geochemical association is naturally genetically predetermined, if we proceed from the rare petrology of the potassic-alkaline Buhovo–Seslavtsi magmatic pluton, whose multiphase composition is enriched in elements with large ionic radii (LILE) — in μg/g: Rb – 341.3, Cs – 16.1, Sr – 591, Ba – 1716 (min 1149 – max 2284) (Dyulgerov, 2005). It is also enriched in elements with high ionic potential (HFSE), such as P^{5+}, Zr^{4+}, Hf^{4+}, Nb^{5+}, Ta^{5+}, Th^{4+}, U^{6+}, and REE^{3}, forming their own accessory minerals, as well as Au–Te–Bi–Ag–As–Mo–W ore deposits in the late magmatic and postmagmatic hydrothermal stages of magmatism (Dyulgerov, 2005; Kamenov, 2003).

In the soils, we observe that all elements of the primary geochemical association PC2 (Table 1) have preserved their genetic relationships in the soils with the exception of As (part of CRMs)

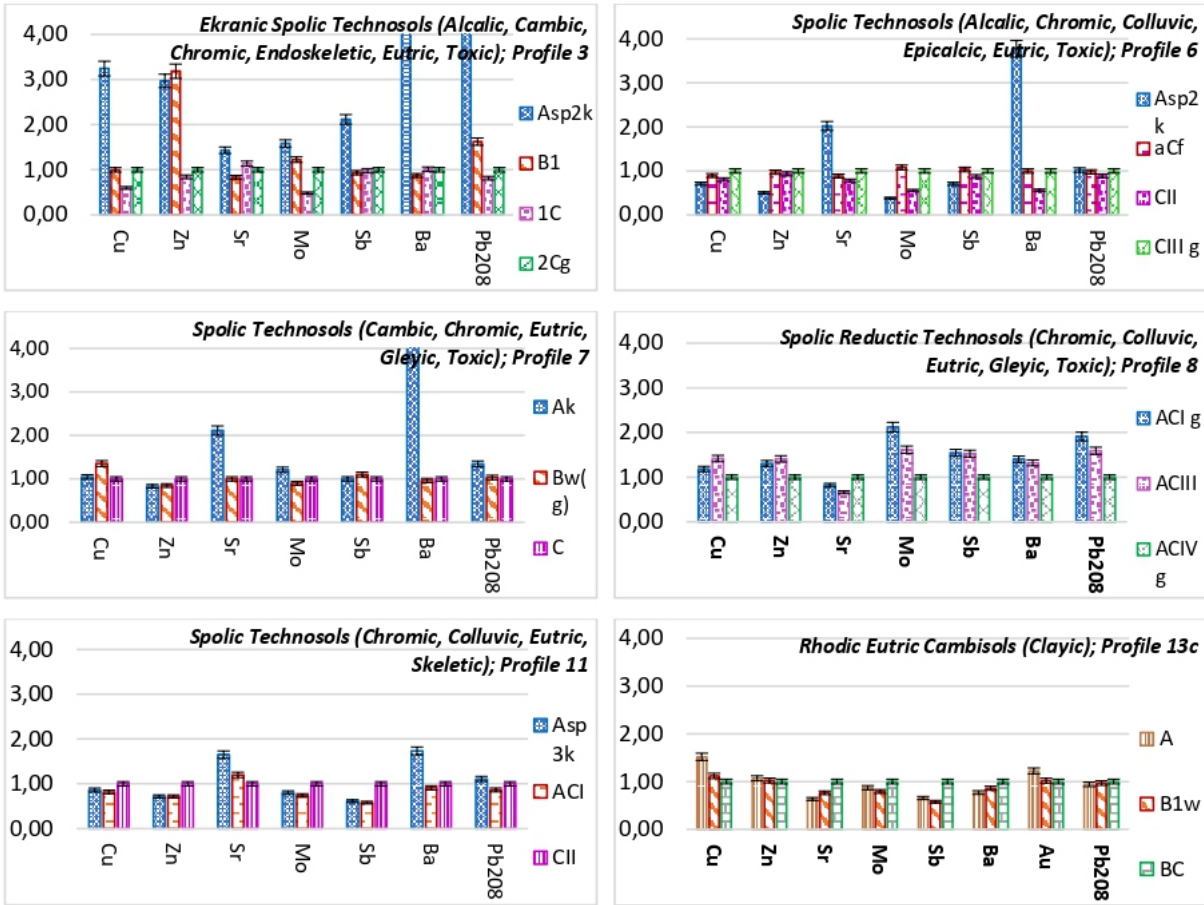

Fig. 2. Concentration coefficients (CC) of technogenically accumulated elements, calculated as the ratio between the values in each of the horizons to the values in the lowest horizon of the profile

and Mo, which show insignificant correlation and even negative relationship with the rest of the above listed series (PC2) (Table 1, Table 2 A, B) – As r(As) = -0.56 (with Ta) - -0.02 and Mo r(Mo) = - 0.55 (with Ta) – 0.01. The reason can be sought in the long evolution of the Cinnamonic Forest soils, that is, in their absolute and relative age, defining them as mature soils, with a soil substrate that began its accumulation even before the last Ice Age (Teoharov, 2019), and in this sense, without interruption of soil-forming processes for hundreds of thousands of years.

According to Birkeland (1999), the formation of a well-developed B horizon may require 10^4–10^5 years. The variable oxidation states of arsenic +5, +3, -3 allow it to be more easily transformed when environmental conditions change, especially during the characteristic periodic partial waterlogging at the foot of the mountain slope, where it is reduced to neutral or slightly negatively charged mobile forms such as $HAsO_2^0$, H_2AsO^{3-} (Sadiq, 1995). The local soil microbiome, which has evolved for hundreds or thousands of years in the elevated levels of this metalloid, probably also uses the variable nature of arsenic and has adapted, including it in its metabolism. Microorganisms - fungi and bacteria - are known to biologically transform metalloids through reactions such as oxidation, reduction and methylation, leading to the formation of soluble or volatile organic compounds (Fatoki, 1997, Bentley and Chasteen, 2002). Additionally, arsenic and molybdenum in the studied area, due to its very close genetic relationship with uranium ores (Dahlkamp, 2010), is statistically related to

Table 2. Pearson's Correlations, performed by JASP statistical software; Coefficients > |0.45| correspond to a p-value < 0.05, indicating the statistical significance of the coefficient

Pearson's Correlations (A)											
Variable	As	Mo	Co	Ni	Ga	Mn	Sb	Cu	Zn	U	V
As	—										
Mo	0,89	—									
Co	0,94	0,84	—								
Ni	0,94	0,93	0,91	—							
Ga	0,40	0,27	0,41	0,45	—						
Mn	0,56	0,74	0,56	0,57	-0,18	—					
Sb	0,42	0,53	0,35	0,28	-0,29	0,62	—				
Cu	0,39	0,50	0,46	0,33	-0,41	0,65	0,83	—			
Zn	0,88	0,77	0,88	0,85	0,20	0,45	0,37	0,53	—		
U	0,66	0,66	0,57	0,57	0,26	0,51	0,56	0,29	0,48	—	
V	0,79	0,62	0,80	0,83	0,57	0,13	-0,07	0,12	0,84	0,25	—

Pearson's Correlations (B)										
Variable	As	Co	Ni	Zn	U	Sb	Mo	Ba	Pb	P
As	—									
Co	0,94	—								
Ni	0,94	0,91	—							
Zn	0,88	0,88	0,85	—						
U	0,66	0,57	0,57	0,48	—					
Sb	0,42	0,35	0,28	0,37	0,56	—				
Mo	0,89	0,84	0,93	0,77	0,66	0,53	—			
Ba	-0,1	-0,1	-0,2	-0,1	0,08	0,52	0,08	—		
Pb	0,19	0,22	0,09	0,32	0,21	0,83	0,34	0,75	—	
P	-0,02	-0,11	-0,18	-0,25	0,55	0,43	0,01	0,14	0,13	—

Pearson's Correlations (C)												
Vari-able	P	Au	W	Cs	Rb	Sr	Ta	Hf	Nb	Bi	Th	Ce/ LREE
P	—											
Au	0,63	—										
W	0,77	0,63	—									
Cs	0,78	0,54	0,76	—								
Rb	0,82	0,64	0,94	0,89	—							
Sr	0,59	0,64	0,78	0,33	0,64	—						
Ta	0,66	0,4	0,84	0,6	0,77	0,56	—					
Hf	0,58	0,45	0,84	0,53	0,72	0,62	0,96	—				
Nb	0,77	0,52	0,94	0,75	0,89	0,66	0,96	0,92	—			
Bi	0,57	0,6	0,5	0,44	0,48	0,42	0,35	0,38	0,43	—		
Th	0,86	0,65	0,98	0,81	0,94	0,74	0,87	0,85	0,96	0,55	—	
Ce/ LREE	0,46	0,27	0,5	0,66	0,52	0,14	0,59	0,56	0,68	0,26	0,6	

Table 2. Continue

Pearson's Correlations (D)											
Variable	P	Au	W	Rb	Cs	Sr	Ta	Nb	Bi	As	Mo
P	—										
Au	0,63	—									
W	0,77	0,63	—								
Rb	0,82	0,64	0,94	—							
Cs	0,78	0,54	0,76	0,89	—						
Sr	0,59	0,64	0,78	0,64	0,33	—					
Ta	0,66	0,4	0,84	0,77	0,6	0,56	—				
Nb	0,77	0,52	0,94	0,89	0,75	0,66	0,96	—			
Bi	0,57	0,6	0,5	0,48	0,44	0,42	0,35	0,43	—		
As	-0,02	-0,09	-0,53	-0,29	-0,07	-0,46	-0,56	-0,53	-0,23	—	
Mo	0,01	0,17	-0,45	-0,26	-0,11	-0,3	-0,55	-0,51	-0,23	0,89	—

Pearson's Correlations (E)									
Variable	Al	Ga	Ce/LREE	Y/HREE	Ti	Si	Sc	Nb	Fe^{3+}
Al	—								
Ga	0,79	—							
Ce/LREE	0,42	0,50	—						
Y/HREE	0,56	0,51	0,26	—					
Ti	0,49	0,40	0,85	0,60	—				
Si	0,76	0,53	0,41	0,61	0,68	—			
Sc	0,76	0,88	0,63	0,67	0,64	0,63	—		
Nb	-0,02	-0,02	0,68	-0,45	0,42	0,03	0,02	—	
Fe^{3+}	-0,66	-0,47	-0,51	-0,46	-0,57	-0,65	-0,49	-0,13	—

Pearson's Correlations (F)							
Variable	Ba	Mn	Pb	Ag	Sr	Sb	Cu
Ba	—						
Mn	0,62	—					
Pb	0,75	0,64	—				
Ag	0,51	0,29	0,55	—			
Sr	0,71	0,20	0,41	0,51	—		
Sb	0,52	0,62	0,83	0,46	0,37	—	
Cu	0,52	0,65	0,91	0,51	0,10	0,83	—

the other genetic association (PC1).

The third genetic association is: Ga-Y/HREE-Ce/LREE-Al (PC3, Table 1) to which, through Pearson's correlation coefficient, we added Ti, Sc, Si (Table 2, E) (all elements are part of the CRMs list). This is a typical geochemical association of elements, controlled by the Al–Si mineral matrix and the adsorption of free oxides, especially in the specific case, where there is an established Cambic soil process and free iron oxides, giving the soil its red color.

All elements of the association are concentrated together in pedogenic environments due to similarities in their ionic radii and valence (Al, Ga, Sc, Y, HREE, LREE - especially Ce^{3+}), and correspondingly sorption and co-precipitation on amorphous Fe/Al oxides and hydroxides and SiO_2 (Al, Ga, Y, HREE, Ce^{3+}, Eu, Sc, Ti partially), and isomorphic substitution with secondary aluminosilicates (Al, Ga, Si, Y, HREE, partially LREE, Sc) or participation in insoluble accessory minerals (Ce^{4+}, Ti, partially Y and HREE, less often Sc and Ga) (Kabata-Pendias, 2011, Stefanova, 2005, Aide, 2019). Scandium (Sc), in this association, is the only one with statistically significant relationships with all of the others (in range r(Sc) = 0.63 – 0.88), because it has a transient, amphoteric geochemical character, stable both in the aluminosilicate matrix and in Ti–Fe–REE minerals, which in our study makes it a connecting link between the lithophillic and accessory subsystems of the association (Stefanova, 2005, Kabata-Pendias, 2011, Teitler et al., 2022). The obtained results for the dual behavior of scandium in the soil environment, do not fully overlap with the results of Jeske and Gworek, (2013), according to whose results Sc is extremely concentrated in the residual accessory fraction (from 71 – 83 % of the total content), but in natural brown, lessive and rusty soil profiles (the literal nomenclature of soils from the reference source is cited), and three times lower average values, compared to the soils from our study (data not yet published).

In Table 2 (E), Nb, as a typical representative of the association of "accessory" elements, and Fe, as part of the characteristic Al/Fe oxide composition in the clay fraction of Cambisols and red Regosols, are added to this association, thus clearly revealing all genetic relationships and differences between the elements.

It is found that from the indicated association, only Ce and Ti have a positive genetic relationship with Nb (titanium, at the border of significance). This is because Ce^{3+}, unlike Y/HREE, is able to oxidize to Ce^{4+}, which makes it more closely related to Ti–Fe oxides (similar to Nb) (Kabata-Pendias, 2011, Aide, 2019). A large share of the total content of Ce and Ti is in its primary form (in rutile, ilmenite and monazite) despite the active processes in the area. The relationship with niobium appears to be divisive for Y/HREE and Ce/LREE. The significant negative relationship between Y/HREE and Nb (r Y/HREE – Nb = -0.45) on the one hand, and the significant relationship of Y/HREE with Si, Al, Ti compared to Ce, demonstrate that while part of the cerium is fixed in the oxide phase, Y/HREE entirely remains sorbed in alluminosilicates and hydroxides, reflected in a weak correlation between Y and Nb. Increased binding of yttrium to aluminosilicates is discussed in Jeske and Gworek, (2013), in whose studies yttrium is only about 1/3 in the residual fraction, 1/3 bound to organic matter and 1/3 in mobile forms and bound to the inorganic matrix.

The positive relationships of Ti and Ce with both Nb and Si and Al (cerium slightly below the significance limit; Table 2 E), and the absence of correlation between Nb and Al/Si, clearly indicate the intermediate role of titanium and cerium in the geochemical system. They appear to be a connecting link between the HFSE elements (Nb, Ta) and the lithophile phases (Si–Al), through their participation in both accessory Ti-, Nb-, Ce- minerals and secondary Al–Si phases. The question of which systems Ce and Ti participate together with Sc remains debatable, since the correlation of the latter with Nb does not indicate a common link and origin, i.e. with the accessory fraction of the nearby alkaline pluton. The answer probably lies in the dual origin of scandium, genetically related to the upper ore (PC1) association, (Sc and V r = 0.6).

Thus, it was determined that two mutually complementary geochemical systems are mani-

fested in the latter geochemical association - a secondary, lithophile (sorption-clayey), which is controlled by Al-Si-Ti-Ga-Sc-Y-HREE, and reflects processes of weathering, sorption and residual accumulation, and a residual, accessory (Ce-Ti) inherited from the mineral composition of the pluton, which is stable and weakly active pedogenetically.

The highlighted similarity with Al suggests that the elements follow the main pedogenic element in the secondary Al/Fe oxides as well, being sorbed on the surface or included in them, but the correlation coefficients do not support this assumption, if we look at the relationships with Fe in these soils, which are even statistically significant inversely proportional (Table 2, E). This, of course, does not exclude the mechanisms of sorption of these trace elements, but the processes of technogenesis are the strongest of all, which shape the behavior of iron in this region of active metallurgical activity, and this is reflected in the statistical calculations. Table 2 (F) presents the trace elements from the deduced and representative for the region technogenic geochemical association, Ba, Mn, Pb, Ag, Sr, Sb, Cu, whose main members are Pb and Ba (with the highest correlation coefficients with the others and among themselves). The correlation coefficients for Ba with all the elements of the association are within the range (r(Ba) = 0.51 – 0.75), and those for Pb r(Pb) = 0.41 (with Sr) – 0.91.

Upon detailed study of the concentration coefficients indicating the vertical migrations of the elements, additional information can be derived that in the 5 soil profiles from the Kremikovtsi site, barium (CRMs), and lead contents, maximazied in the surface contaminated horizons, strontium (CRMs) in four of them. In the control profile (13c), all three metals are predominant in the soil-forming sediments (Fig. 2). The reason is the technogenic alkalization in the area, registered by Faytondzhiev, (2000), expressed in a progressive accumulation of carbonates in the surface soil horizons (Stoykova, 2023).

The highest calculated concentration coefficient (CC) is for lead in Profile 3, contaminated with sinter dust, in which the heavy metal in the surface horizon is 11 times higher than its content in the soil-forming materials. Barium is more than 4 times higher, copper more than 3 times higher, and antimony more than 2 times higher. Antimony and copper (part of CRMs) fall in this association due to their active accumulation in this spolic horizon, as well as in the superficial lighter horizons/layers of the partially gleyed Profile 8 (Fig. 2). Sinter contamination (Profile 3) is associated, in addition to secondary enrichment of Pb, Ba, Sr, Cu, Sb, Mo (Fig. 2).

Conclusions

Soil profiles with metamorphic and weakly developed morphology, formed on old and young Quaternary proluvial and colluvial sediments, were studied, in order to determine the origin and geochemical pathway of a number of enriched macro and microelements. The study is based on data on the concentration of over 25 elements from the nomenclature, adopted by the EU list of Critical Raw Materials, sampled from 20 genetic horizons from depths, varying according to the profiles from 0-30 to 225 - 400 cm, on 6 soil profiles - 5 technogenic and one control. Statistical interpretation of data via PCA, Pearson's correlation was performed by JASP Statistical Software, and mean content, median, minimum and maximum value and Concentration coefficients - CC were calculated using Excel.

Three genetic geochemical associations of CRMs were determined in the studied technogenically altered Cambisols and Regosols, with a predominantly alkaline reaction, sparse vegetation and significant technogenic impact that slowed down the processes of soil formation.

The geochemical association As–Mo–Co–Ni–Ga–Mn–Sb–Cu–Zn–U–V (PC1) in the Regozems (Regosols) reflects the influence of the Quaternary proluvial and colluvial material, enriched with ore minerals (uranyl phosphate, uranyl silicates, sulfides, sulfosols, arsenides, determining their increased concentrations. The high correlations between the main elements (As r(As) = 0.56–0.94, Co r(Co) = 0.46–0.94, Ni r(Ni) = 0.45–0.94, P–U r = 0.56) indicate stable genetic relationships in

the association, while Pb, Ba, Sb and Cu are not correlated due to technogenic influences from the Kremikovtsi metallurgical complex.

The geochemical association Hf–P–W–Nb–Ce/LREE–Sr–Bi–Ge+Ta–Th–Rb–Cs–Au (PC2) in the Cinnamonic Forest Soils (Cambisols) reflects the genetically inherited mineral specificity of the potassic-alkaline Buhovo–Seslavtsi pluton, enriched with LILE and HFSE elements. The correlation coefficients between the main elements are high – for P r(P) = 0.46–0.86, for W r(W) = 0.50–0.98 (with Th), and for Th r(Th) = 0.55–0.98, which indicates stable genetic relationships, preserved in the process of pedogenesis. The exceptions are As (r(As) = –0.56 to –0.02) and Mo (r(Mo) = –0.55 to 0.01), whose separate dynamics is explained by their mobility, the long evolution of soils and their closer genetic relationship with the ore association in the area (PC1).

The genetic association Ga–Y/HREE–Ce/LREE–Al–Ti–Sc–Si shows stable relationships between elements in a lithophillic system, with Sc having statistically significant correlations with all the elements (r(Sc) = 0.63–0.88), and Ce and Ti exhibiting positive relationships with Nb, as a part of the accessory phase. The significant negative relationship Y/HREE–Nb (r = –0.45), and the added correlation Sc–V (r = 0.6), outline the dual lithophillic and accessory control on the geochemical system, and emphasize the role of scandium as a connecting link between the both subsystems and even between the both associations PC2 and PC3.

The defined technogenic association Ba–Mn–Pb–Ag–Sr–Sb–Cu is dominated by Pb and Ba, with the highest correlations (r(Ba) = 0.51–0.75; r(Pb) = 0.41–0.91). In the surface contaminated horizons, the content of Pb is up to 11 times, of Ba, 4 times, Cu, 3 times, and Sb,– 2 times higher than that in the soil-forming materials, which clearly shows the irreversible technogenic accumulation due to metallurgical activity and alkalization of the soils in the area.

Acknowledgements

This work has been carried out in the framework of the National Science Program "Critical and strategic raw materials for a green transition and sustainable development", approved by the Resolution of the Council of Ministers № 508/18.07.2024, and funded by the Ministry of Education and Science (MES) of Bulgaria.

Conflict of interest

The authors declare that they do not have any financial or non-financial conflict of interest with regard to this manuscript.

References

Aide, M. (2019). Lanthanide Soil Chemistry and Its Importance in Understanding Soil Pathways: Mobility, Plant Uptake, and Soil Health. *IntechOpen.* doi: 10.5772/intechopen.79238.

Alloway, B. J. (2013). *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability*. Springer, Dordrecht.

Angelov, V., Antonov, M., Gerdjikov, S., Petrov, P., Tanatsiev, S., Kiselinov, H., Marinova R., & Valev, V. (2008). Geological map of Bulgaria M 1: 50000, m. pp. K-34-48-B (Elin Pelin). Research Institute of Geology and Geophysics JSC, MGU "St. Ivan Rilski ", S.

Bentley, R., Chasteen, T. G. (2002). Microbial Methylation of Metalloids: Arsenic, Antimony, and Bismuth. *Microbiology and Molecular Biology Reviews, 66* (2), 250-271.

Birkeland, P. W. (1999). *Soils and Geomorphology* (3rd ed.). Oxford University Press.

Blengini, G. A., EL Latunussa, C., Eynard, U., Torres de Matos, C, Wittmer, D., … & Pennington, D. (2020). Study on the EU's list of Critical Raw Materials – Final Report 2020. European Commission, Publications Office of the European Union. https://rmis.jrc.ec.europa.eu/uploads/CRM_2020_Report_Final.pdf (last access 12.09.2025).

Bondev, I. (1991). *The Vegetation of Bulgaria. Map and Explanatory Text*. Sofia, BAS (Bg).

Burns, P. C. (2005). The Crystal Chemistry of Uranium. In P. C. Burns and R. J. Finch (Eds.), *Uranium: Mineralogy, Geochemistry and the Environment* (pp. 23–90). Washington, DC: Mineralogical Society of America. (Reviews in Mineralogy, Vol. 38).

Ganev, S., & Arsova, A. (1980). Methods for determining the strongly acidic and the slightly acidic cation exchange in soil. *Soil Science and Agrochemistry, 15*(3), 22-33.

Dahlkamp, F. J. (2010). *Uranium Deposits of the World: Asia*. Springer-Verlag Berlin Heidelberg.

Dyulgerov, M. (2005). *Potassium Alkaline Magmatism from Stara Planina, Bulgaria: Petrological study of Buhovo-Seslavtsi, Svidnia and Shipka plutons*, Autoreph. Sofia University, University of Paris XI, Sofia (Bg).

European Commission. (2023). Critical Raw Materials

Act. COM(2023) 160 final, Brussels.

Faitondjiev, L., Stanislavova, L., Thculdjian, H., & Georgiev, B. (2000). Changes in soils of the Region of Kremikotzi. Sofia. *Soil Science Agrochemistry and Ecology, 4*, 3-10.

Fatoki, O. S. (1997). Biomethylation in the natural environment: A review. *South African Journal of Science 93*(8), 366-370.

Fersman, A.E. (1953). *Selected works, vol. II.* M., USSR Academy of Sciences (Ru).

Graedel, T. E., Harper, E. M., Nassar, N. T., and Reck, B. K. (2015). On the materials basis of modern society. *Proceedings of the National Academy of Sciences, 112(*20), 6295-6300, https://doi.org/10.1073/pnas.1312752110.

IUSS Working Group WRB. (2022). World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps. 4th edition. International Union of Soil Sciences (IUSS), Vienna, Austria.

Jeske, A. and Gworek, B. (2013). Distribution and mobility of scandium and yttrium in selected types of soils in Poland. *Chemical Speciation and Bioavailability, 25*(3), 216-222.

Kabata-Pendias, A. (2011). *Trace elements in soils and plants – 4th edition.* NW, CRC Press.

Kachinsky, N.A. (1943). *Methods of mechanical and microagregatic analysis of soil.* Publ. House Acad. Sci. Moscow, USSR.

Kalaydzhiev, S. (1993). Structural control of uranium deposits in the area of the Iskar Gorge. *Journal of Bulg. geol. Soc. 54*(1), 13-20.

Kamenov, B. (2003). *Magmatic petrology.* University Publishing House of Sofia University "St. Kl. Ohridski", Sofia (Bg).

Kononova, M.M. (1966) *Soil Organic Matter: Its Nature, Its Role in Soil Formation and in Soil Fertility, 2nd Ed.* Pergamon Press Ltd., Oxford, UK.

PCSURSF. (2021). Program for Conservation, Sustainable Use And Restoration of Soil Functions on the territory of Sofia-city district, 2020-2030. Institute of Soil Science, Agrotechnology and Plant Protection „Nikola Pushkarov", MEW (Bg).

Reimann, C., & de Caritat, P. (2017). *Chemical Elements in the Environment: Factsheets for the Geochemist and Environmental Scientist*. Springer, Berlin.

Sadiq, M. (1995). *Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations.* WRED, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, SA.

Stefanova, M.T. (2005). *Fundamentals of geochemistry*. SU "St. Kliment Ohridski ", Sofia (Bg).

Stoykova, M. (2020). Alkalisation of Technosols from the territory of the "Kremikovtsi" MW. "*International seminar of Ecology – 2019" 18 - 19 April 2019. Institute of Biodiversity and Ecosystem Research – Bulgarian Academy of Sciences, Sofia, Bulgaria, Farrago, 6(1), 66-72.*

Stoykova, M. (2021). *Characteristics of soils with geochemical and technogenic loading, formed on old Quaternary sediments*. Abstract of the Ph. D. Thesis, ISSAPP "N. Poushkarov" (Bg).

Stoykova, M. (2023). Technogenic and Geochemical Diagnostics of Soils, Distributed on the Territory of the "Kremikovtsi" Metallurgical Plant. *Bulgarian Journal of Soil Science, 8*(1), 22-32, https://doi.org/10.5281/zenodo.8216516.

Stoykova, M., & Teoharov, M. (2022). Geogenic and pedogenic inheritance of arsenic, antimony, selenium and tellurium in poorly developed and metamorphic soils. *Bulgarian journal of soil science, Sofia, 7*(1), 3-12, doi: 10.5281/ZENODO.6780095.

Teitler, Y., Favier, S., Ambrosi, J.-P., Sevin, B., Golfier, F., and Cathelineau, M. (2022). Evaluation of Sc Concentrations in Ni-Co Laterites Using Al as a Geochemical Proxy. *Minerals, 12*(5), 615, https://doi.org/10.3390/min12050615.

Teoharov, M. (Ed.) (2019). *Genetic and applied classifications of soils and lands in Bulgaria*. Bulgarian Soil Science Society, Sofia, Avangard (Bg).

Received: 24th October 2025, ***Approved***: 30th October 2025, ***Published***: December 2025