



# Geogenic and Pedogenic Inheritance of Arsenic, Antimony, Selenium and Tellurium in Poorly Developed and Metamorphic Soils

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## Abstract

The content of arsenic, antimony, selenium and tellurium in soils from a territory with natural and man-caused load, located in the range of the Old Quaternary proluvial plume in the northeastern part of the Sofia valley, was studied. The contents have been determined by LA-ICP-MS, together with those of more than 45 chemical elements, for the purpose of future remediation and study of the impact of natural and man-made factors on the geochemical relationships of the elements in the specific soil environment. The studied soil types are Regosols and Cambisols, most of which have been changed and classified as Technosols (*IUSS Working Group WRB*, 2015, Teoharov et al., 2019, Stoykova, 2021) under the influence of industrial waste from the former Kremikovtzi metallurgical plant. Very high contents of the groups of elements Te - Se and As - Sb have been established, which are inherited from the soil - forming rocks with predominant, respectively syenite or ore material. The content of arsenic in Technosols is on average 4 times higher than the maximum permissible concentration of metalloid in industrial soils, and the arsenic in the control profile of Cambisols exceeds 1.5 times the norm for the maximum permissible concentration for arable land. The processes of overwetting, acidification and microbiological activity are the factors that influence the redistribution of the four elements in the soil environment. Contamination with agglomeration dust leads to the accumulation of antimony in the spolic horizon, where it is associated with a number of heavy metals. Its more metallic character is reflected in the statistically significant high positive correlation with iron -  $r(\text{Sb-Fe}) = 0.85$ , which shows only this element.

**Keywords:** arsenic, antimony, contamination, Cambisols, Regosols, selenium, tellurium, Technosols

## Introduction

Arsenic (As), antimony (Sb), selenium (Se) and tellurium (Te) are chalcophilic elements of the p-block of the Periodic Table, satellites (As, Sb) or analogues (Se, Te) of sulfur (Stefanova, 2005). In the primary endogenous environment they are concentrated in sulfides, related minerals and sulfosols, and in the exogenous environment, like sulfur, they are oxidized relatively easily (Stefanova, 2005, Plant et al. 2003, Fersman, 1939) and in the form of variously charged oxygen radicals compounds are involved in active soil metabolism. Soil macro and microbiome, including man, are directly influenced by the excess content of

these elements (Sadiq, 1995, Denys, 2009, Missen, 2020, Cuvardic, 2003). Their study is of interest to soil science not only because of their toxic effects on living organisms, but also because of the food needs of selenium, which is a trace element essential for organisms.

In the context of the specific geological and ecological situation on the territory of the former Kremikovtzi MP and beyond, the study of these four elements serves purely scientific interests, as processes can be identified - natural and technogenic, affecting their distribution in the soil environment. The soils subject to the present study were developed on proluvial rocks containing materials of diverse geological origin, naturally enriched in metals and metalloids, primarily gold (Stoykova, 2021). The proluvial rocks, shaped like proluvial cones connected in an extensive proluvial plume, are the result of drainage through ravines of two feeding provinces (tentatively called *western* and *eastern*) that operated during the Pleistocene. They are poorly fused gravels with sandy-clay matrix and alternating grains of sand, gravel and clay horizons. They contain rock fragments and deposited products of Paleozoic argillites, siltstones, lydites and others. with varying degrees of metamorphism, carbonate and clay-carbonate Triassic and Jurassic sediments (Angelov et al., 2008), potassium-alkaline magmatic rocks from the Buhovo-Seslavitzi pluton (Dyulgerov, 2005), ore rocks and ore minerals from the Buhovo uranium deposit (Kalaydzhiev, 1993). Due to their loose structure and proximity to the mountain slope, they are relatively easy to weather and should have lost much of their primary minerals. According to Stoykova (2021), the technogenic situation in the district and the reported alkalization also invariably influenced the geochemical relations of the elements sensitive to the parameters of the environment, such as arsenic, antimony, selenium and tellurium.

The complicated technogenic situation is due to the nearly 50 years of operation of the former Kremikovtzi metallurgical plant, which is a conglomeration of heavy industry plants, located on an area of 24,000 m<sup>2</sup>. Agricultural land around the plant has been the subject of many studies over the years. From them it can be concluded that the lands have high levels of heavy metals and arsenic around the plant, and with the removal of it only lead and arsenic remain exceeded (Faitondjiev et al., 2000; Shulin et al., 2007).

This publication is the only one that interprets the results for the content of arsenic, antimony, selenium and tellurium, as a group obtained together with data for more than 45 other chemical elements in soil profiles located near various factories inside the plant. External control profiles were also included in the study.

### **Materials and Methods**

Soils from 15 profiles in the area of Kremikovtzi MC have been studied, incl. 11 from the territory of the plant - with man-caused influence and 4 controls in different directions outside it. The profiles are divided into a total of 6 geographical positions. In turn, the eleven profiles with man-made impact are grouped into three groups depending on the type of pollution, as well as the local geographical location:

- o In the middle parts of the western proluvial cone, in a border area with modern proluvium, rich in deposited limestones and potassium-alkaline magmatic rocks, mainly syenites (Terrain group I) - Profiles 1, 2, 3, 4 + 13c, 14c,

- o In the upper parts of the eastern proluvial cone, rich in deposited limestone and ore matter - (Terrain group II) - Profiles 5, 6, 7, 8.

o In the middle parts of the eastern proluvial cone - (Terrain group III) - Profiles № 9, 10, 11.

A number of standard soil analyzes were performed on the 15 soil profiles. In view of the large database, five man-made influences were selected (Profiles № 3, 6, 7, 8 and 11) and one control profile - № 13c, the most representative for each of the initially separated groups, which were subjected to additional chemical and mineralogical research, incl. LA-ICP-MS. The results of the chemical analyzes are an interpretation based on the parameters

o Average content,

o Linear Brave correlation coefficient ( $r$ ). The statistical significance of the obtained coefficient is calculated by the formula  $|r| \geq 3 * \sigma_r$ , where  $\sigma_r = (1 - r^2) / \sqrt{n}$ , and “n” is the number of pairs in the correlation. After the calculations, it was determined that the correlation coefficients in the intervals (-1 ÷ -0.5) and (0.5 ÷ 1) (Rollinson, 1993) were statistically significant.

o Concentration coefficient (CC), calculated as the ratio between the content of the element in the specific horizon of the profile (Ke) to its content in the lowest horizon of the same profile (Kc) – Ke / Kc (Fersman, 1953; Stefanova, 2005). This coefficient makes it possible to identify accumulation and migration processes vertically, within the soil profile.

According to their genetic nature and the natural course of soil development, secondarily contaminated soils are divided into two groups: Cambisols - profile 3, profile 7, profile 13c and Regosols - profile 6, profile 8, profile 11. According to the changes that have taken place due to the influence of industrial materials, some of them are already classified as Technosols (Stoykova, 2021).

Morphologically, the studied soils are reddish in color (50% of all samples have a hue of 5 YR), with high fragmentation, naturally or artificially overlapped. Cambisols have well-formed genetic horizons, and Regosols have a layered profile structure. Soil-forming sediments are reached everywhere - alternating gravel, sand and clay layers. Vegetation in the technogenic profiles is scarce or absent, except for one secondary afforested with acacia profile (№ 1).

### Results and Discussion

According to the results obtained, the average content of the discussed elements in the studied soils is much higher, compared to selected reference values (Kabata-Pendias, 2011) - Te (56x) >> As (25x) > Se (24x) >> Sb (10x). The determined average contents are (in  $\mu\text{g} / \text{g}$ ) As – 170,66 (409.34 ÷ 24.63); Se – 10.56 (14.25 ÷ 6.15); Sb – 6.66 (13.93 ÷ 3.13) and Te – 4.49 (7.03 ÷ 2.14) (Table 1).

Of the four elements, the content of arsenic in soils is subject to state regulation, on the one hand as the most common of them, but also because of its anthropogenic contribution to the soil and its toxic properties, falling into it. The values obtained for this element exceed the trigger values from Regulation 3 / 1.08.2008 as follows: arsenic in Technosols is on average about 4 times above the maximum permissible concentration of metalloid in industrial soils (40  $\mu\text{g} / \text{g}$ , Regulation 3 / 1.08.2008), and the arsenic in the control profile exceeds 1,5 times the established norm for the maximum permissible concentration in arable land (25  $\mu\text{g} / \text{g}$ , Regulation 3 / 1.08.2008).

**Table 1.** Average contents of the studied elements, compared to world reference values (Kabata-Pendias, 2011), distributed by geographical area and by man-made pollution.

	Average in soils, ref. data	Average in this study	Mediana	Max	Min	Field group I	Field group II	Field group III	Control profile 13c, average
µg/g									
As	6.83	170.66	150.22	409.34	24.63	97.80	247.56	144.93	37.21
Se	0.44	10.56	11.09	14.25	6.15	11.82	10.75	7.26	11.56
Sb	0.67	6.66	6.23	13.93	3.13	8.27	7.02	5.89	4.04
Te	0.08	4.49	4.95	7.03	2.14	5.58	4.43	2.91	4.81

The content of Te and Se is inherited from proluvial rocks enriched in syenite fragments, and that of As and Sb is bound to soil-forming materials enriched in ore minerals and sulfosols, arsenides and antimonides, some of the minerals accompanying uranium mining (Kalaydzhev, 1993). This statement is based on the higher measured values for the two groups of elements in the profiles of the respective terrain groups, which are formed on different soil-forming rocks - Te and Se in profiles №№ 3 and 13c of terrain group I and As and Sb in profiles №№ 6, 7, 8, 11, part of terrain groups II and III (Table 1, Table 2). The mechanism of Te concentration in alkaline magmatic rocks is known to science. Such rocks are associated with the largest deposits of tellurium and gold, in the form of tellurides, which are generally part of the ore (sulfide) fraction of accessory minerals (Kostov, 1993). Selenium, following its chalcophilic nature, is also concentrated in this fraction, where it forms its own selenides or replaces sulfur in metal sulfides (Kostov, 1993).

Natural and technogenic soil-forming processes are imposed on these soil-forming rocks, which lead to redistribution of the studied elements within the soil profiles.

The over wetting process covers the entire volume of profile 8 (Reductic Technosols, colluvic), combined with a strongly acidic soil reaction in the intermediate horizons (Table 2).

This has mobilized all four elements ( $CCTe = 2.41$ ,  $CCSb = 1.55$ ,  $CCSe = 1.86$ ,  $CCAs = 2.43$ ) (Fig. 1), which are known to be reduced in a reducing environment. easily reduce to neutral or weakly negatively charged mobile forms such as  $HAsO_2^0$ ,  $H_2AsO_3^-$ ,  $HSbO_2^0$ ,  $SbO_2^-$ , Se (s), Te (s) (Sadiq, 1995, Denys, 2009, Missen, 2020, Plant et al., 2003) and hydrogen selenide anions ( $HSe^{2-}$ ) - and hydrogen selenide ( $H_2Se^0$ ), as a manifestation of the halogen nature of selenium (Cuvardic, 2003, Plant et al., 2003).

Antimony is an exception to the general trend in this example. The upward movement is to a lesser extent, and fixation is observed in the most acidic horizon  $AC_{III}$  (125 - 225 cm) and CC (1.55 and 1.53) for the surface and intermediate horizon, respectively. The behavior of antimony under these conditions reflects its metallic nature (expressed in the lowest energy of positive ionization  $Z^K$  among the four elements), by virtue of which in oxidation conditions it does not form charged oxygen radicals but solid mineral phases -  $Sb_2O_4$ ,  $Sb_2O_5$  (Stefanova, 2005). They are adsorbed and incorporated isomorphically into the

poorly soluble Fe-Mn oxide and hydroxide structures crystallizing during the drought and oxidation period, thus gradually accumulating (Denys, 2009).

**Table 2.** Content of the studied elements, iron, manganese, sulfur and values of the main soil indicators.

Horizon / Depth, cm	Fe	Mn	S	As	Se	Sb	Te	pH / H <sub>2</sub> O	CEC	Base-cation saturation, %	Total Carbon, %	Carbonates, %	Physical clay, %	
	%	mcg/g						cmol/kg		% CEC	%	%	%	
<b>Profile 3 <i>Spolic Technosols (Alcalic, Cambic, Chromic, Endoskeletal, Eutric, Toxic)</i></b>														
Asp <sub>1</sub>	30-0	very black mass, agglomeration powder												
Aek	25-0	concrete flooring												
Asp <sub>2</sub> k	0-50	13.25	9447.42	2726.75	79.10	10.35	13.93	4.68	8.4	22.3	100	0.63	1.97	9.1
B <sub>1</sub>	50-105	4.17	2117.42	1824.95	137.53	12.70	6.14	5.73	8	21.7	100	0.19	0.32	28.5
B <sub>2</sub> w	105-170								7.5	20.6	100	0.11	0.25	40.5
1C	170-235	3.00	1239.74	1202.65	63.56	10.31	6.43	5.38	7.6	20.9	100		0.17	22.7
2Cg	235-347	4.65	1859.27	1872.34	111.01	13.92	6.58	6.52	8.2	26.3	100		0.54	50.6
<b>Profile 6 <i>Spolic Technosols (Alcalic, Chromic, Colluvic, Epicalcic, Eutric, Toxic)</i></b>														
Asp <sub>1</sub>	30-0	granular and non-granular coke powder												
Asp <sub>2</sub> k	0-40	4.28	9333.53	2383.79	170.70	11.40	6.31	4.83	9.2	27.6	100	0.4	20.4	5.9
aC <sub>1</sub>	40-60	5.94	7918.97	1402.77	322.38	11.23	9.22	5.76	8	18.9	100		0	14.6
C <sub>1</sub>	60-110								7	18.2	96.2		0	18.4
C <sub>II</sub>	110-160	5.21	4014.86	1534.74	275.37	10.94	7.78	4.87	6.9	16.9	94.7		0	36
C <sub>III g</sub>	160-260	6.35	13075.71	2393.49	409.34	11.42	8.93	5.09	7.6	26.5	100		0.31	20.8
<b>Profile 7 <i>Spolic Technosols (Cambic, Chromic, Eutric, Gleyic, Toxic)</i></b>														
Asp	10-0	coal dust												
Ak	0-38	4.73	6042.74	2515.69	196.01	12.58	5.58	6.53	8	26.8	100	0.18	1.34	38.4
AB	38-68								7.3	22.5	96.9	0.09	0	47.9
Bw(g)	68-110	4.96	2736.36	1112.65	162.90	8.85	6.14	2.14	7.6	22	100		0	43.7
BC	110-165								7.9	22.6	100		0.94	33
C	165-210	4.58	2737.84	1695.98	227.42	12.53	5.58	5.14	7.7	20.5	100		1.64	20.4
<b>Profile 8 <i>Spolic Reductic Technosols (Chromic, Colluvic, Eutric, Gleyic, Toxic)</i></b>														
Asp	20-0	tar. tar fus. naphthalene												
AC <sub>I g</sub>	0-40	5.36	3409.46	1728.74	333.90	13.34	7.85	5.51	7.9	19.3	100	0.14	0.31	22.7
AC <sub>II</sub>	40-125								5.6	19.9	85.9	0.1	0.16	21.1
AC <sub>III</sub>	125-225	5.09	1841.76	941.62	240.12	8.02	7.76	2.16	3.8	19.2	67.7	0.11	0	36.9
AC <sub>IV g</sub>	225-400	4.91	2189.57	957.05	137.42	7.17	5.08	2.29	6.6	24.3	93		0	55.7
<b>Profile 11 <i>Spolic Technosols (Chromi., Colluvi., Eutric, Skeletic)</i></b>														
Asp <sub>1</sub>	20-0	loose sandy quartz substance												
Asp <sub>2</sub>	20-0	dark cast iron - slag												
Asp <sub>2</sub> k	0-30	5.26	4134.00	1443.99	108.41	8.35	4.95	3.35	8	25.7	100	0.23	1.74	38.4
AC <sub>I</sub>	30-115	4.89	2489.79	1178.28	126.05	7.29	4.68	2.82	7.9	24.6	100	0.2	0.39	42.2
C <sub>II</sub>	115-215	5.82	2854.41	987.06	200.32	6.15	8.05	2.55	7.2	24.1	94.6	0.13	0	19.1
<b>Profile 13c <i>Rhodic Eutric Cambisols (Clayic)</i></b>														
A	0-32	3.72	894.48	811.88	24.63	6.94	3.56	2.36	7.8	33.1	100	0.81	0.39	60.8
AB	32-67								7.7	30.3	100	0.89	0.39	70.5
B <sub>1</sub> w	67-116	3.88	1037.50	1502.27	36.36	13.50	3.13	5.03	7.8	32.5	100	0.63	0.46	73.7
B <sub>2</sub> w	116-151								7.8	33	100	0.66	0.39	67.4
B <sub>3</sub>	151-185								7.8	35.1	100	0.92	4.2	70.5
BCK	185-220	4.04	681.73	1652.07	50.64	14.25	5.43	7.03	8	31.4	100	0.28	6.44	55.7
C	220-260								8	31.8	100	0.3	0.74	49.8

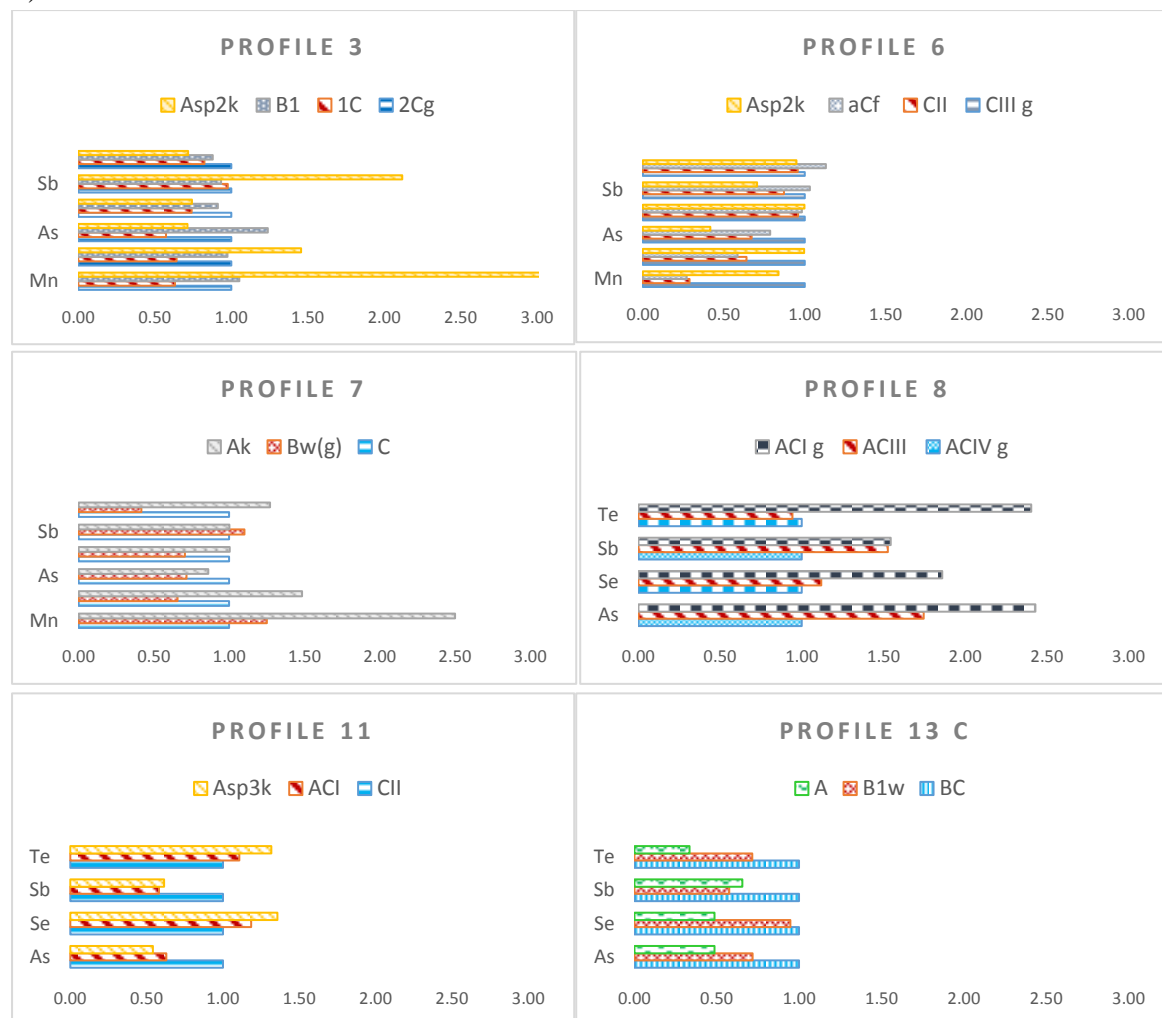
**Table 3.** Concentration coefficients (CC) of the investigated elements, calculated as the ratio between the values in each of the horizons to the values in the lowest horizon of the profile.

CC	Te	Sb	Se	As
<b>Prof. 3</b>				
Asp <sub>2</sub> k	0.72	2.12	0.74	0.71
B <sub>1</sub>	0.88	0.93	0.91	1.24
1C	0.83	0.98	0.74	0.57
2Cg	1.00	1.00	1.00	1.00
<b>Prof. 6</b>				
Asp <sub>2</sub> k	0.95	0.71	1.00	0.42
aC <sub>f</sub>	1.13	1.03	0.98	0.79
C <sub>II</sub>	0.96	0.87	0.96	0.67
C <sub>III g</sub>	1.00	1.00	1.00	1.00
<b>Prof. 7</b>				
Ak	1.27	1.00	1.00	0.86
Bw(g)	0.42	1.10	0.71	0.72
C	1.00	1.00	1.00	1.00
<b>Prof. 8</b>				
AC <sub>I g</sub>	2.41	1.55	1.86	2.43
AC <sub>III</sub>	0.94	1.53	1.12	1.75
AC <sub>IV g</sub>	1.00	1.00	1.00	1.00
<b>Prof. 11</b>				
Asp <sub>3</sub> k	1.32	0.61	1.36	0.54
AC <sub>I</sub>	1.11	0.58	1.19	0.63
C <sub>II</sub>	1.00	1.00	1.00	1.00
<b>Prof. 13c</b>				
A	0.34	0.66	0.49	0.49
B <sub>1</sub> w	0.72	0.58	0.95	0.72
BC	1.00	1.00	1.00	1.00

Another factor for the reduced mobility of Sb is the high content of As in the soil, which plays a limiting role at 60 - 230  $\mu\text{g} / \text{g}$  As (Kabata-Pendias, 2011), and in the considered profile the values for arsenic are in the range 137 - 334  $\mu\text{g} / \text{g}$ . The mechanism of upward movement of arsenic, antimony, selenium and tellurium, which in acidic environment are strongly adsorbed by soil colloids as negatively charged oxygen radicals (Sadiq, 1995, Denys, 2009, Missen, 2020, Cuvardic, 2003, Plant et al., 2003) is debatable. The measured acidity of pH 3.8 creates conditions for the destruction of soil colloids, which in the season of wetting, attracting with them the adsorbed ions rise and accumulate in the surface horizon. Confirmation of this thesis is the accumulation of physical clay in this horizon, which is more than the one below (Table 2), as well as the presence of pyrite and manganese stains (Stoykova and Teoharov, 2021).

The gravelly-sandy composition of the soil-forming sediments and the primitive structure of the polluted Regosols presented in profile 8 are a prerequisite for facilitating the rise of seasonal groundwater at the foot of the mountain slope and thus covering the entire soil profile from glaciation processes. On the same soil-forming materials in the near profile 7 a cambic soil-forming process takes place, which leads to a concentration of antimony only

in the cambic partial carbon horizon (CC = 1.1), again as a manifestation of its metallic properties, in association with iron, which is also maximum there (Table 2, Table 3, Figure 1).



**Figure 1.** Bar charts of the Concentration coefficients (CC) of Te, Sb, Se and As in this study.

A general trend is shown by the four elements in their redistribution in Rhodic Cambisol, presented in the uncontaminated control profile 13c, as the concentration coefficients (CC) indicate their downward movement along the profile and their secondary accumulation in the BCk horizon. Their downward movement is facilitated by the alkaline soil reaction (avg. pH 7.8), in which negatively charged oxygen radicals of metalloids are more mobile (Sadiq, 1995, Denys, 2009, Missen, 2020, Cuvardic, 2003, Plant et al. 2003). In the surface A-horizon their concentration is the lowest, with coefficients  $CC_{As} = 0.49$ ,  $CC_{Se} = 0.49$ ,  $CFSb = 0.66$ ,  $CCTe = 0.34$ . Antimony is again an exception, as it relatively accumulates in the A horizon, relative to the intermediate  $B_{1w}$  horizon ( $CC = 0.58$ ). This pronounced general tendency to impoverish the upper soil horizons in the unpolluted profile is in contrast to the erratic distribution of the four elements in the technogenic contaminated profiles (Figure 1). Technogenesis has influenced in such a way that in all contaminated profiles no microorganisms were identified, which are known to be an important factor in the processes of conversion of metalloids in the soil (Fatoki, 1997, Kabata-Pendias, 2011).

Microorganisms are known - fungi and bacteria, that biologically transform metalloids through reactions such as oxidation, reduction and methylation, leading to the formation of soluble or volatile organic compounds (Fatoki, 1997, Plant et al., 2003, Bentley and Chasteen, 2002). Methylation is also known to be a common mechanism by which cells metabolize metalloids and is key to the synthesis of volatile compounds leading to depletion of soil elements (Fatoki, 1997, Doran and Alexander, 1977, Missen, 2002, Bentley and Chasteen, 2002, Denys, 2009). In this sense, it could be reasonably argued that soil microorganisms, in the control example, but in the whole study, through their absence or presence are a leading factor in the distribution of arsenic, selenium, antimony and tellurium in soil profiles. Possible future remediation activities could be based on the pronounced biological sensitivity of these elements.

In profile 3 (Technosols, cambic), contaminated with agglomeration dust, rich in heavy metals in the form of technogenic salts (sulfates and carbonates) and Fe-Mn oxides and hydroxides and pH 8.4, only antimony has a CC above 1, i.e. it accumulates relatively in the surface horizon, and this is its highest concentration coefficient (CC) for all profiles – 2.12. Under these conditions, antimony is a companion of Mn, Fe, Pb, Mo, Cu and others technogenic pollutants (Stoykova, 2021), attached to Fe-Mn oxide and hydroxide structures, exhibiting their pronounced metallic properties, compared to other elements (Stefanova, 2005, Denys, 2009).

**Table 4. Correlation coefficients (*r*) between test elements, reference macroelements and soil fractions.**

	Fe	Mn	S	As	Se	Sb	Te	coarse and medium sand	fine sand	silt	clay
Fe	1	0.56	0.48	0.12	-0.09	0.85	-0.04	0.29	-0.40	-0.36	-0.42
Mn		1.00	0.70	0.56	0.10	0.62	0.19	0.57	-0.28	-0.49	-0.63
S			1.00	0.20	0.61	0.46	0.65	0.45	-0.18	-0.30	-0.48
As				1.00	0.10	0.42	0.09	0.53	-0.21	-0.18	-0.56
Se					1.00	0.03	0.92	0.09	0.02	0.06	-0.09
Sb						1.00	0.14	0.53	-0.15	-0.46	-0.72
Te							1.00	0.24	0.06	-0.11	-0.21

All the presented features are reflected in the derived correlation coefficients between the discussed p-elements and some benchmark macroelements - iron, manganese and sulfur. Confirmation of the strong attachment of antimony to iron and manganese are the calculated high values of the correlation coefficient -  $r(\text{Sb-Fe}) = 0.85$ ,  $r(\text{Sb-Mn}) = 0.62$  (Table 4). Man-made pollution with agglomeration dust also has a share in the formed large positive dependence with iron. Statistically significant, but weaker, is the relationship between arsenic and manganese ( $r(\text{As-Mn}) = 0.56$ ). This dependence, as well as the Sb-Mn correlation, are a reflection of the influence of coarse-grained soil-forming materials on polluted Regosols containing ore. The same is reflected in the statistically significant positive indicators for the relationship between the three elements (Mn, As, Sb) and the large soil fraction. The highest calculated correlation coefficient is between selenium and tellurium -  $r(\text{Se-Te}) = 0.92$ . This indicator, together with statistically significant values for a positive correlation between the



two elements and sulfur, illustrates the primary influence of the halogen geochemical nature of these elements, as well as the influence of proluvial soil-forming materials rich in syenite and ongoing overwetting processes. Arsenic and antimony are also mobilized in these processes, but, although positive, their indicators for correlation with sulfur are not statistically significant.

### Conclusion

After interpreting analytical data from 20 soil samples from Regosols and Cambisols, modified in Technosols, extremely high values for arsenic, antimony, selenium and tellurium content were determined compared to selected reference values - Te (56x) >> As (25x) > Se (24x) >> Sb (10x). The determined average contents are (in  $\mu\text{g} / \text{g}$ ) As – 170,66 ( $409.34 \div 24.63$ ); Se – 10.56 ( $14.25 \div 6.15$ ); Sb – 6.66 ( $13.93 \div 3.13$ ) and Te – 4.49 ( $7.03 \div 2.14$ ). It was specified that the increased contents in these soils are the result of inheritance from proluvial soil-forming rocks, fed by two provinces - with predominant syenite or mineral-rich composition, and soil-forming and technogenic processes are subordinate. The natural soil-forming factors that affect the distribution of these related elements are the overwetting and the state of the soil microbiome. Contamination with agglomeration dust is the cause of antimony accumulation in the spolic horizon. Antimony, the only one, shows a deviation from the common geochemical trends for the four elements, as reflected in the statistically significant large positive dependence with iron -  $r(\text{Sb-Fe}) = 0,85$ . The determined very high natural content of the metalloid arsenic in the studied soils, including the arable ones, compared to the normatively determined maximum values in Bulgaria, is of public importance. The content of arsenic in Technosols is on average about 4 times above the maximum permissible concentration of metalloid in industrial soils ( $40 \mu\text{g} / \text{g}$ ), and the arsenic in the control profile exceeds 1.5 times the established norm for the maximum permissible concentration in arable land ( $25 \mu\text{g} / \text{g}$ ). Due to the high biological sensitivity of the four elements, possible future remediation activities could be based on microbiological and organic treatment in situ, following the necessary preliminary laboratory experiments.

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