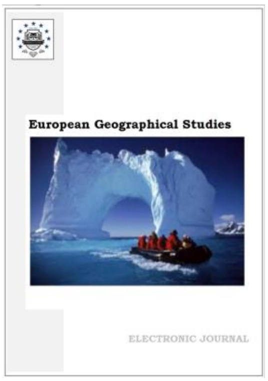
Published in the USA
European Geographical Studies
Has been issued since 2014.
E-ISSN: 2413-7197
2021. 8(1): 55-62

DOI: 10.13187/egs.2021.1.55
https://egs.cherkasgu.press



Pollution of Kvemo Kartli Region (Georgia) Soils by Heavy Metals

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Abstract

The expedition works were held in the territory of the Madneuli enterprise of Kvemo Kartli region in 2020, where brown soils are spread. In order to study the migration of heavy metals in the soil, taking into consideration the wind direction, the samples of soil was taken from 0-100 (0-10, 10-20, 20-40, 40-60, 60-80, 80-100) cm depths, in North from the source of pollution direction (Background) – weak winds direction, 500 m from the enterprise and in the direction of a strong wind in the West and 300 m from the enterprise. In the soil samples were determined general forms of heavy metals Cu, Zn, Pb, Mn, Ni, Cd, Co, As, Ag, Cr, Fe by Plasma-emission spectrometer at ICP-OES.

The quality of some heavy metal contamination of soil is revealed in connection with Clark; In contaminated areas, the relatively high concentrations of heavy metals are observed in the upper layers, which are due to the prevailing winds. in the samples taken from the north (background-weakest wind direction) heavy metal content were less. Specifically, from the background and contaminated areas the copper content with 0-10 cm layer 63.22 (1.4) and 324.13 (6.9) mg/kg; 80-100 cm depth decreases copper content and is 22.15 and 156.17 (3.3) mg/kg. Similar situation is in case of zinc.

Migration of heavy metals is reduced by increasing depth and approximately 1-5 times exceeding the relevant background importance.

In the samples taken from the background areas, some metals (cadmium, arsenic and silver) are high content, which is due to their existence in the soils of the region. At the same time, it is noteworthy that their Clark indicator is low and therefore 0.13; 1.7 and 0.07, which leads to increasing the Ratio concentration of these metals in relation to Clark.

As it appears from the data, the soil meets in the categories of copper, zinc and arsenic in the category of slightest pollution (<10) category; In cadmium and silver cases – in average pollution (10-30); And the concentrations of lead, manganese, nickel, cobalt and chromium do not exceed Clark.

Correlation links are investigated between the concentrations of different metals in the upper layers of the soil. The correlation coefficient is the largest between Cu and Zn concentrations. It is positive and equals 0.77, determination Coefficient (R^2) is 0.58 among the Cu-Zn concentrations. Correlation coefficient between Cu and Co concentrations are 0,62, determination coefficient of Cu-Co concentrations is 0.38. In all other cases the correlation coefficient is negligible and can be neglected.

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Keywords: Soil, heavy metals, pollution, concentration, correlation.

1. Introduction

In general, one of the most important sources of technological contaminants is mining enterprises that can play a negative role in environmental pollution processes and therefore it can be the risk factor in relation to the population's health.

For example in Georgia (Kvemo Kartli), in the Bolnisi municipality, is operating the polymetal mining enterprise in the south-east of Tbilisi.

Madneuli sulfide deposit is presented mainly in three types of ores – gold-copper-colachal, gold-barit-polymetal and gold-quartzit, which is processed by the flotation method (Gaphrindashvili et al., 2004). The works are carried out in an open career. This method is very cheap and profitable, but it can cause an environment, namely, the forests can be destroyed, the soils can be polluted and biodiversity. Priority pollutants of Madneuli enterprise are heavy metals – Cu, Zn, Pb, Mn, Ni, Cd etc, in particular it can occure in the environmental facilities in natural waters (Gvakharia et al., 1997, Shavliashvili et al., 2017) in soils (Vodyanitsky, 2017; Urushadze et al., 2007, Bakradze et al., 2018, Vodyanitsky, 2013, Khubutia, 2004) and therefore in food products. There is a threat to not only to the environment of the region, but also the health of the population and certain cities.

2. Materials and methods

Chemical analyzes were conducted in the accredited laboratory of the atmospheric air, water and soil analysis of the Environmental Pollution Monitoring Department of the National Environmental Agency of the ministry of Environment Protection and Agriculture of Georgia. For analysis, high tech equipment are used (soil depletion – Milestone – Start D Microwave System; pH meters-Milwaukee-mi 150; Plasma-emission spectrometer-ICP-OES and others). All stages of the monitoring is in accordance with the standards of the International Organization (ISO).

Features and statistical purposes of correlation coefficients between different metals concentrations are assessed by stiudent criteria:

$$t = \frac{r}{\sqrt{1-r^2}}\sqrt{n-2} \sim t_{n-2}$$

Where the R-correlation is a coefficient, and n-observations. If the stiudent parameter exceeds its critical importance at a specified level, or it is considered that the correlation coefficient is noteable, and if the criterion of Stiudent is less than its critical importance, then the correlation coefficient is not considered statistically and may be neglected.

3. Discussion

Wind rose of the Bolnisi municipality according to statistical materials of the Hydrometeorology Department of the National Environment Agency.

As shown in the Bolnisi municipality, the windshields of the West and the East in the Bolnisi municipality are less than the southern direction winds, and the winds of the north are negligible. Therefore, we have selected places where the most powerful is Western (contaminated) and North (Wallpaper) – weak wind directions.

It should be noted that as a result of drilling-explosive works on Madneuli deposit, large amount of can dust occures in the air, along with various heavy metals content, which can affect the territories of the villages, as well as the dust particles by the wind can distribute by long distances (about 30 km) and they are absorbted in the soil. In addition, at the place of ore is located Oreking devices and alkal squeres. Ore transportation is being carried out by cars which can cause Bypass roads pollution of Kazreti and can create additional dust. The dust content in the air is especially large in the summer season. Gold and copper mining enterprise works in continuous mode and frequency of dust separation from the enterprise depends on the intensity of explosions. The dust contains a large number of different kinds of harmful substances, including heavy metals that can be in the air. After some time they can be precipitated on the surface of the soil and can migrate in deep layers of soil. Thus, the high background content of heavy metals in the can increase in different depths.

Brown (Cambisoli) soils are widespread in study areas (Urushadze, 1997). In order to study the migration of heavy metals in the soil, taking into consideration the wind direction, the samples 0-100 (0-10, 10-20, 20-40, 40-60, 60-80, 80-100) cm depths, from the source of pollution In the direction of GPS N41º26'35 ", E-44º35'55 " (background), 500 m from the quarry to the N-41º22'60 ", E-44º23'42 " (contaminated) carrier 300 m (once in a year). In The soil samples were determined general form of heavy metals (Fomin, Fomin, 2001).

In Table 1 is given the background concentracions of heavy metals in contaminated areas of the soil depth 0-100 cm in June 2020.

We have compared the concentrations of heavy metals with the corresponding Clark (Bogdanov et al., 2013, Supatashvili, 2009) (Table 1). It is worth mentioning that all metal content is high in the upper layers and their concentration decreases in the depths.

Copper in the soil, moves to organic masses and minerals and will be binded by them. As a result, it is hardly shifted to the deep layers of soil and it is possible to appear in a small amount in groundwater. As the results of the analysis show from the background and contaminated (ore) place, the copper content in accordance with 0-10 cm layer 63.22 (1.4) and 324.13 (6.9) mg/kg; 80-100 cm depth decreases copper content and is 22.15 and 156.17 (3.3) mg/kg.

Zinc's background concentracions does not exceed the Clark value at any depth, and at the door – 0-10 cm depth is 376.27 (4.5) mg/kg; 80-100 cm depth decreases its concentration and equals – 231.32 (2.8) mg/kg.

Table 1. Determine heavy metals in the soil 0-100 cm in depth, June, 2020

№	location	pH	Cu	Zn	Pb	Mn	Ni	Cd	Co	As	Ag	Cr	Fe
			mg/kg										%
1	background 0-10 cm	7	63.22/1.4	71.51	16.17	624.68	17.39	2.25/17.3	8.36	15.13/8.9	1.16/16.6	6.79	1.32
2	---„--- 10-20 cm	7.2	57.45/1.2	62.42	9.42	497.25	16.25	2.04/15.7	8.06	11.63/6.8	1.05/15.0	6.60	1.21
3	---„--- 20-40 cm	7.5	39.21	53.40	5.43	443.61	15.17	1.88/14.5	7.45	10.27/6.0	0.96/13.7	5.15	1.19
4	---„--- 40-60 cm	7.4	39.12	51.66	3.11	389.78	14.12	1.51/11.6	6.34	9.86/5.8	0.55/7.9	5.12	1.05
5	---„--- 60-80 cm	7.6	27.78	49.35	1.56	365.43	13.27	1.15/8.9	5.44	7.77/4.6	0.25/3.6	4.81	0.94
6	---„--- 80-100 cm	7.7	22.15	42.16	1.23	347.75	12.82	0.45/3.5	4.27	4.91/2.9	0.10/1.4	4.28	0.56

7	Near the mining 0-10 cm	7.2	324.13/6.9	376.27/4.5	18.14	712.33	19.53	3.06/23.5	10.64	17.65/10.4	1.89/27.0	10.72	1.77
8	---„--- 10-20 cm	7.4	288.62/6.1	323.41/3.9	16.78	591.41	18.60	2.75/21.2	9.86	15.88/9.3	1.75/25.0	9.54	1.28
9	---„--- 20 40 cm	7.3	185.65/4.0	333.17/4.0	15.18	555.48	16.48	2.21/17.0	9.52	15.47/9.1	1.52/21.7	8.23	0.95
10	---„--- 40-60 cm	7.3	261.87/5.6	272.11/3.3	13.26	432.27	15.24	1.88/14.5	7.17	13.56/8.0	1.33/19.0	6.65	0.81
11	---„--- 60-80 cm	7.5	192.21/4.1	247.05/3.0	8.11	422.49	14.66	1.56/12.0	5.44	8.21/4.8	1.20/17.1	4.68	0.60
12	---„--- 80-100 cm	7.6	156.17/3.3	231.32/2.8	5.46	402.72	13.18	1.32/10.2	3.19	5.31/3.1	0.54/7.7	4.47	0.44
Clarks-Clarks of elements of the Earth's crust according to Vinogradov			**47**	**83**	**16**	**1000**	**58**	**0.13**	**18**	**1.7**	**0.07**	**83**	**3**

It should be mentioned the high content of some metal (cadmium, arsenic and silver) in the samples taken from the background was observed, which is naturally in the region's soils. At the same time, it is noteworthy that their Clark indicator is low 0.13; 1.7 and 0.07, which leads to increasing the concentration of these metals in relation to Clark. In particular, the cadmium content in the background is 2.25 (17.3) and career – 3.06 (23.5) mg/kg 0-10 cm depth, and in the depths of 80-100 cm depth, its concentration is reduced to 0.45 (3.5) and 1.32 (10.2) mg/kg.

There is a similar situation in case of arsenic. Its content varies in the background ranges 15.13 (8.9) – 4.91 (2.9) to the entire depth of the mg/kg of the profile and 17.65 (10.4) – 5.31 (3.1) within mg/kg. While silver in the upper horizon of the background plot is 1.16 (16.6) mg/kg, gradually decreases in the depths and 80-100 cm is 0.10 (1.4) mg/kg; And near carier – 1.89 (27.0) – 0.54 (7.7) mg/kg.

Concentrations of lead, manganese, nickel, cobalt and chromium are not exceeding the values of Clark.

Element concentracions were compered with Clarks. The soil is considered a slightly contaminated, if the ratio is less than 10; On average, if the ratio varies from 10-30 pongs and strongly contaminated, if this size exceeds 30 (Gvasalia, 2014).

As it appears from the data, the soil meets in the categories of copper, zinc and arsenic in the category of slightest pollution (<10) category; In cadmium and silver cases – in average pollution (10-30); And the concentrations of lead, manganese, nickel, cobalt and chromium do not exceed Clark.

Below are the concentrations of heavy metals mg/kg, and the ratio of Clark.

Figures 1-5 show change in heavy metals concentrations of soil (0-100 cm depth) and is comparable to Clarks's. As shown from the figures, background indicators in the case of copper, zinc and cadmium are much less than a career (contaminated). Their maximum concentrations are recorded at 0-10, 10-20 and 20-40 cm depths. According to our opinion, this is due to the intimidated wind And severe metals accumulation and migration in the upper layers of soils. Their concentration is minimal in 80-100 cm depth. In the case of silver and arsenic, high concentrations of these metals in the background area, as mentioned, are due to their relatively high content in the region's soils.

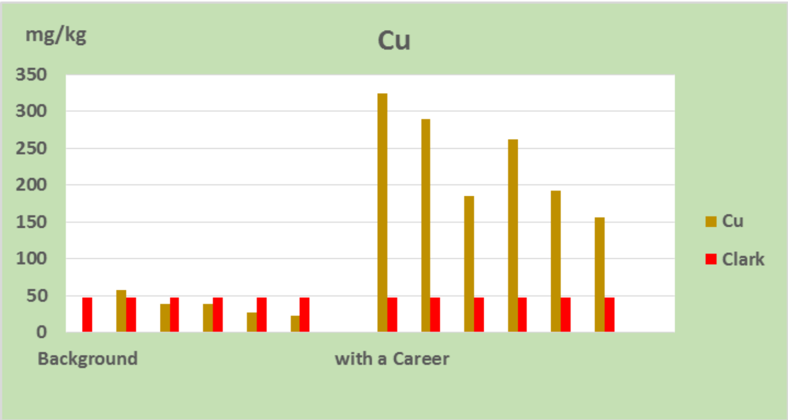

Fig.1. Copper concentration change in the soil 0-100 cm depth, 2020

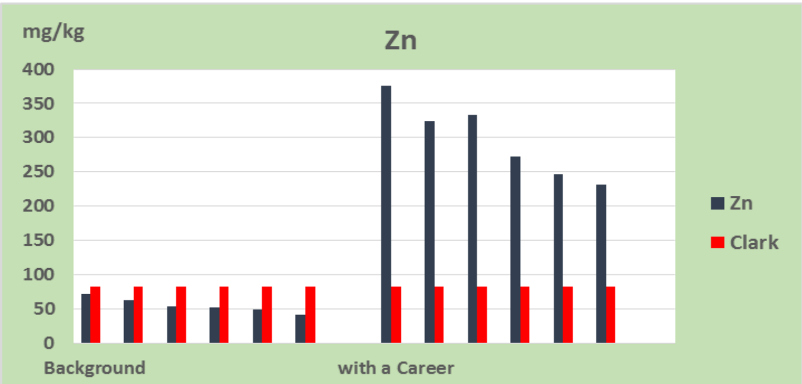

Fig. 2. Change of zinc concentration in the soil 0-100 cm depth, 2020

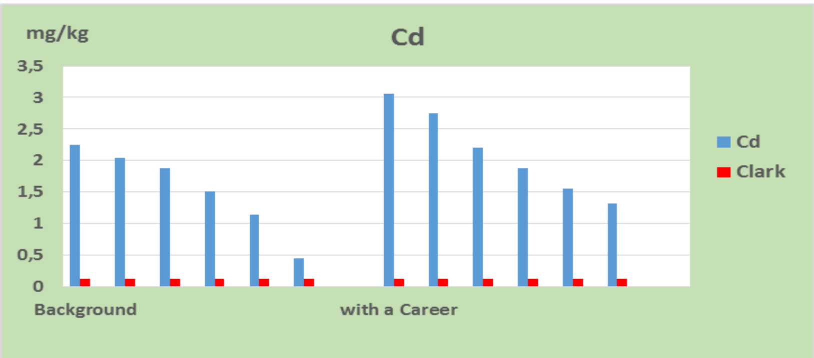

Fig. 3. Change of cadmium concentration Soil 0-100 cm depth, 2020

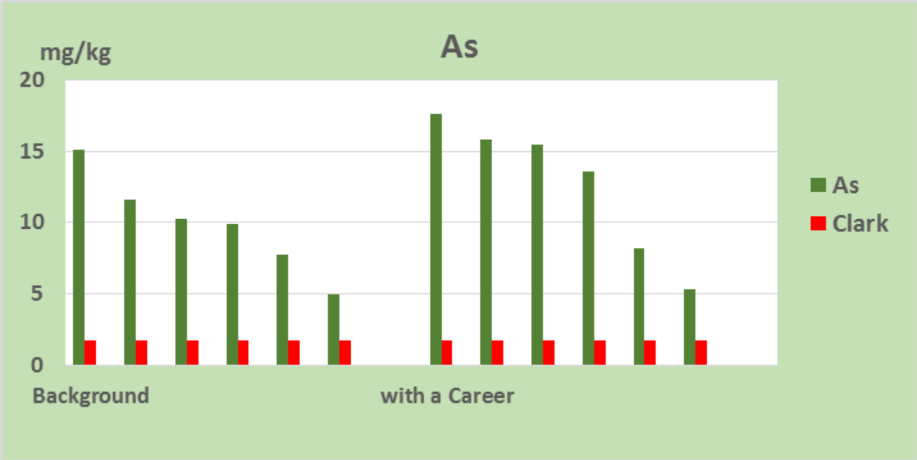

Fig. 4. Change of arsenic concentration Soil 0-100 cm depth, 2020

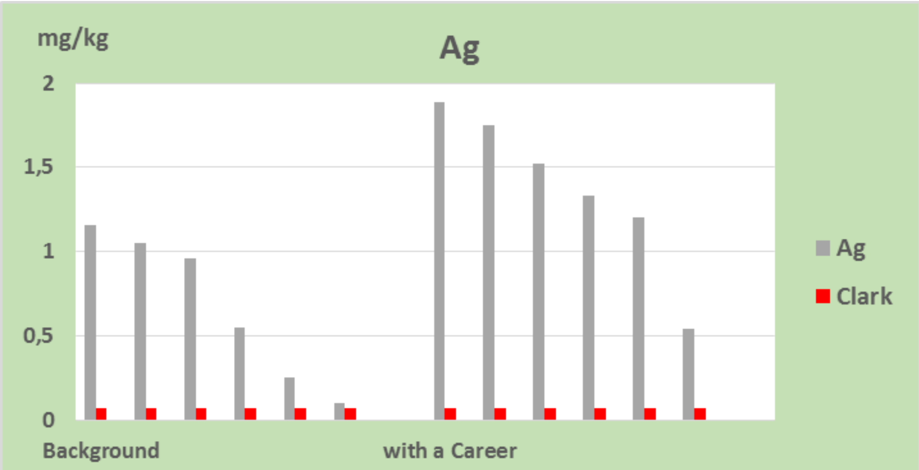

Fig. 5. Change of silver concentration Soil 0-100 cm depth, 2020

Figures 6, 7 show change in the concentrations of heavy metals in the soil 0-100 cm depth in 2020, where it is clear that high concentrations of heavy metals are marked in the upper layers of soil and in the background areas as well and near cariers.

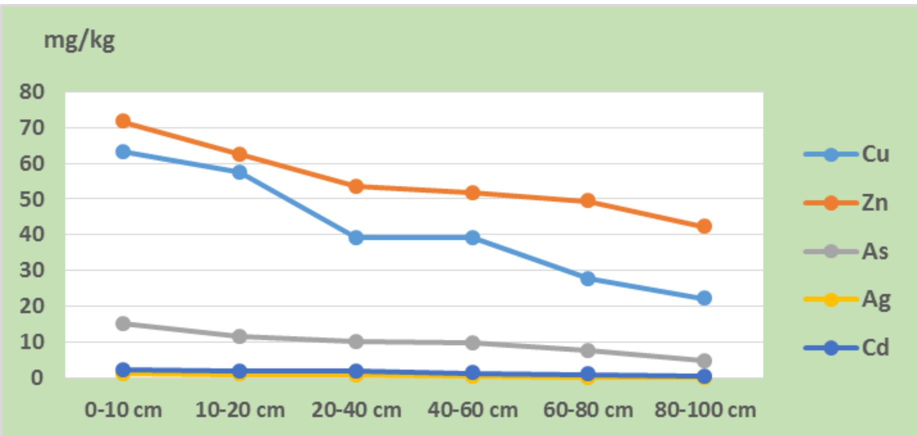

Fig. 6. Change of heavy metals concentration in the soil profile in background locations, June 2020

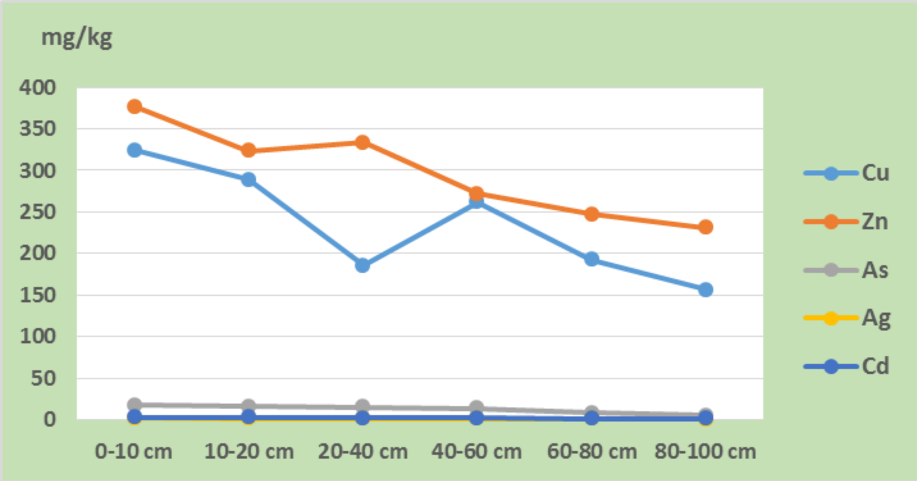

Fig. 7. Change of heavy metals concentration in the soil profile of the Career, June 2020

Correlation connections between the concentrations of different metals were investigated for the top layers of soil. The results are in correlated matrix (Table 2).

Table 2. Correlation matrix

	Cu	Zn	Pb	Cd	Co
Cu	1	0,77	-0.12	0.016	0.62
Zn	0,77	1	0.098	-0.57	0.26
Pb	-0.12	0.098	1	-0.10	0.28
Cd	0.016	-0.57	-0.10	1	0.45
Co	0.62	0.26	-0.28	0.45	1
Sample amount	10	10	10	10	10

Table 2 shows that the correlation coefficient is the largest between Cu and Zn concentrations. It is positive and equals 0.77, the connection between these two elements is directly proportionate and high; There is also positive and high correlation between Cu and Co concentrations and are 0,62.

That's the two couples Cu-Zn, and Cu-Co, meets Stiudents criteria $P < 0.05$. In all other cases the correlation coefficient is negligible and can be neglected.

The Determination Coefficient (R^2) is 0.58 among the Cu-Zn concentrations, which means that Zn's concentracion change 58 % is due to Cu-concentracion change. The determination coefficient of Cu-Co concentrations is 0.38, which means that the change of Co 38 % is due to Cu-changes.

4. Conclusion

1. In the polluted areas of Bolnisi municipality, on the basis of 0-100 cm depth, the analysis of samples revealed the relatively high concentrations of heavy metals in the upper soil layers, which is due to the prevailing wind through the factory of heavy metals and accumulated in the soil. And the northern (wind-weak, wind direction) areas in the samples heavy metals were much less content.
2. Migration of heavy metals in the soil samples taken from the baseline and contaminated place is reduced by increasing depth and approximately 1-5 times exceeding the relevant background importance.
3. The quality of soil pollution is established in connection with Clark. As it appears from the data, the soil is in a small pollutant category due to copper, zinc and arsenic; The content of cadmium and silver is especially distinguished from the metals, which are significant in the background locations. In terms of pollution they are in medium pollution category. And the lead,

manganese, nickel, cobalt and chromium concentrations do not exceed Clark indicators and there is no soil contamination with these elements.

4. Correlation connections are investigated between the concentrations of different metals in the upper layers of the soil. The correlation coefficient is a noted between Cu and Zn, and Cu and Co concentrations.

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