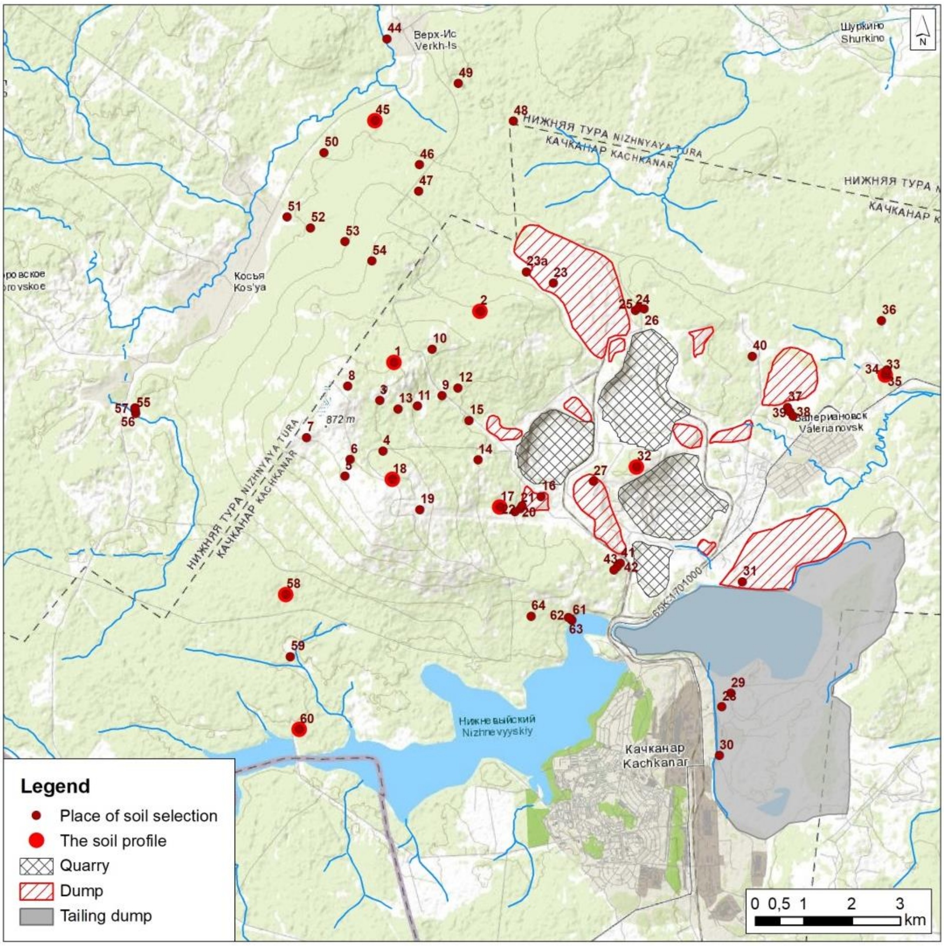

Fig. 2. The distribution of the sample plots (SP)

Low content of labile phosphorous could be noted for all the undisturbed mountain forest cambisols.

Calcisols were determined in the eastern and northern (Verkh-Is River) parts of the area. The soils with podzol features are formed in gentle slopes or poorly drained flat lands that receive additional moisture from water runoff. At heights of 328 m and 214–220 m in dark coniferous forests with moist conditions, gley podzols and calcisols are formed.

Calcisols are specified by high acidity and negligible content of exchangeable bases, accompanied with complete unsaturation of the medium part of the profile. Heavy texture and location within poorly drained lands provide consistent soil moisture, pseudoglazation, and partial accumulation of exchangeable bases relative to the upper part of the profile.

To sum up the data on undisturbed, natural soils of the investigated area, specific aspects of the pedogenic process should be noted. These are the prevalence of cambisols or mountain forest nonpodzolized soils accompanied by limited distribution of podzols. The morphology of the mountain soils is unique—it is negligibly differentiated and highly gravelly. Primitive accumulative soils of the upper parts of the slopes and mountain forest cambisols are formed due to xeromorphous pedogenesis and weathering conditions [25].

The close proximity of underlying dense rocks leads to insignificant soil differentiation and the absence of a clearly visible podzolic horizon. Reduced humidity of the mountain soils is due to water runoff and good rock permeability. These conditions make excessive moistening and reducing conditions impossible and provide for preserving iron in the soil profile. Iron stabilizes soil structure and preserves it from lessivage [26,27]. The intensity of weathering increases from the upper to lower relief components. Increases in moisture and soil depth down the slope lead to podsolization of forest cambisols. Such soils lose sandy fractions while the amount of coarse silt particles (0.05–0.01 mm) increases significantly. The distribution of clay fractions shows podzolic features, with their amounts decreasing in the podzolized horizon and increasing in the enrichment horizon. As the impact of mother rock on the soil disappears, it becomes similar to zonal calcisols [25].

The forest growth conditions could be considered to be quite favorable. The absence of podsolization and the close location of soil-forming rocks, often crystalline, provide considerable amounts of nutrients, while the strong structure of the soils creates good air and water conditions. However, significant earth grades and deforestation can create the conditions for severe erosion and rapid loss of all the soil cover.

Most of the published papers with data for background content of microelements in soil were based only on the research of zonal soils. Besides, the investigated area is characterized as the area of a geochemical anomaly since the large mineral deposits, in particular iron ores with high vanadium content, have been found here.

Based on the above considerations, there is a need for the determination of a local background. The local background is the average modal value of the geochemical index (or indices) of a given geological space (geological feature) and statistically acceptable interval of its variation [23].

The soils of the area were thoroughly sampled for the determination of the background values of microelement content. The results of the calculations are given in Table 1. The data is shown for the elements, with application in the calculation of Total Chemical Pollution Index.

Table 1. Calculations of the geochemical background values in soils

Chemical element	Maximum value (mg/kg)	Minimum value (mg/kg)	Background value (mg/kg)	Standard deviation (mg/kg)	Variation coefficient (%)	Minimum anomaly value (mg/kg)
V	262.2	130.6	219.4	40.6	0.2	259.9
Mn	995.5	339.2	674.4	183.1	0.3	857.5
Ni	54.4	19.1	34.8	10.7	0.3	45.5
Cu	56.9	17.7	29.3	12.4	0.4	41.6
Zn	119.2	52.5	80.3	17.8	0.2	98.1
As	12.0	5.1	7.7	2.0	0.3	9.7
Cd	1.3	0.3	0.7	0.3	0.4	1.0
Pb	64.5	13.3	29.3	17.3	0.6	46.6

The maximum values for the content of the considered elements exceed the background values (Fig. 3). All the studied sample plots in the area of iron ore deposit were combined into 9 groups according to plant communities. For each of these groups, a geochemical series was constructed. We distinguish 5 groups according to the similarity of the geochemical series. Group 1 contains plot soils with mixed geochemical signature, where lithophiles (Mn and V), chalcophiles (Zn and Cu), and siderophiles (Ni) are prevalent. The mixed forest (SP 15, 17) with the series $\frac{Mn}{707} > \frac{V}{353} > \frac{Zn}{83} > \frac{Ni}{58} > \frac{Cu}{54} > \frac{Pb}{25} > \frac{As}{10} > \frac{Cd}{0.7}$ and the sparse spruce-birch forest (SP 19) with $\frac{Mn}{996} > \frac{V}{262} > \frac{Zn}{77} > \frac{Ni}{44} > \frac{Cu}{19} > \frac{Pb}{13} > \frac{As}{5} > \frac{Cd}{0.5}$ series fall under this group.

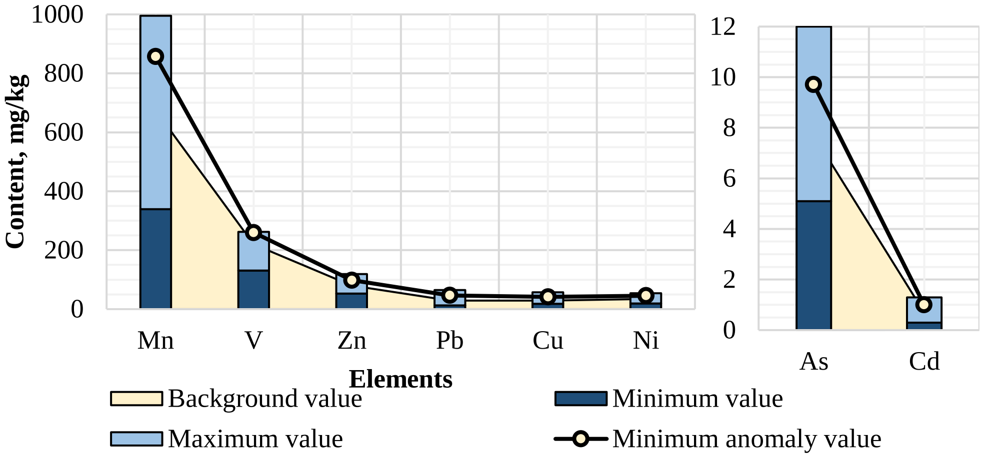

Fig. 3. The geochemical background values in soils

The geochemical series and mixed geochemical signatures of Group 2 and Group 1 are similar, but here we can see a greater content of Pb than Cu. For the spruce-birch krummholz (SP 6, 8) the following series is characterized: $\frac{Mn}{860} > \frac{V}{259} > \frac{Zn}{75} > \frac{Ni}{39} > \frac{Pb}{22} > \frac{Cu}{19} > \frac{As}{6.3} > \frac{Cd}{0.6}$. While the sparse coniferous forest (SP 18) has the following series: $\frac{Mn}{860} > \frac{V}{259} > \frac{Zn}{75} > \frac{Ni}{39} > \frac{Pb}{22} > \frac{Cu}{19} > \frac{As}{6.3} > \frac{Cd}{0.6}$.

Lithophiles (Mn and V) and chalcophiles (Pb and Zn) are prevalent in group 3. It should be noted that Mn content significantly varies from 371 mg/kg to 741 mg/kg. The soils of the spruce forest (SP 4) with the following series: $\frac{Mn}{371} > \frac{V}{131} > \frac{Zn}{98} > \frac{Pb}{56} > \frac{Ni}{39} > \frac{Cu}{31} > \frac{As}{13} > \frac{Cd}{1.3}$ have minimal content of Mn. The content of the elements is higher in the spruce-birch mixed forest (SP 14) with $\frac{Mn}{741} > \frac{V}{244} > \frac{Zn}{132} > \frac{Pb}{63} > \frac{Ni}{47} > \frac{Cu}{40} > \frac{As}{12} > \frac{Cd}{1.6}$ series, and the dark coniferous green moss forest (SP 9, 11–13) with $\frac{Mn}{643} > \frac{V}{209} > \frac{Zn}{92} > \frac{Pb}{44} > \frac{Ni}{32} > \frac{Cu}{31} > \frac{As}{9} > \frac{Cd}{0.9}$ series.

The spruce green moss forest forming group 4 has the following series: $\frac{Mn}{660} > \frac{V}{235} > \frac{Zn}{69} > \frac{Cu}{40} > \frac{Ni}{25} > \frac{Pb}{20} > \frac{As}{7} > \frac{Cd}{1}$. The sparse birch forest (group 5, SP 2), which has the following series: $\frac{V}{237} > \frac{Mn}{229} > \frac{Zn}{53} > \frac{Ni}{19} = \frac{Cu}{19} > \frac{Pb}{16} > \frac{As}{6} > \frac{Cd}{0.3}$, where V content is greatest but not exceeding Mn content in this site`s samples, has shown the biggest difference from other groups.

We calculated the Total Chemical Pollution Index for the territory of the iron ore deposit where pollutants exceed background values (Fig.4). This index was assessed relative to the background content of the elements in Ural soils (Z_c) [25].

As for the background content, the Ural soils demonstrate the following: we can observe excess content in one sampling plot (spruce-birch mixed forest), while some plots` content approach but do not exceed an allowable level (spruce forest, mixed forest, dark coniferous green moss forest).

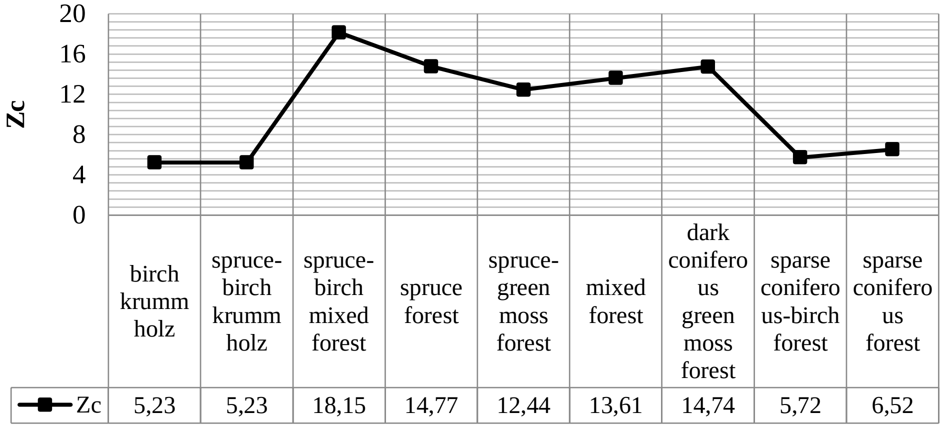

Fig. 4. Total heavy metal chemical pollution of soils from the iron ore deposit

The most important part of the research was the determination of the impact of mining waste dumps on soils. The heavy metal content in soils of sampled plots is shown in Fig. 5–9. The element content values were transformed to one order by raising to the power (the content of V, Ni, Cu, and Zn is equal to X mg/kg×10-1; the content of Mn is X mg/kg×10-2, Cd – X mg/kg×101; the content of As and Pb didn't change).

Fig. 5 shows the content of heavy metals in soils affected by mine waste dump 6 with the following series: $\frac{Mn}{623} > \frac{V}{259} > \frac{Cu}{112} > \frac{Zn}{73} > \frac{Ni}{47} > \frac{Pb}{16} > \frac{As}{6.1} > \frac{Cd}{0.5}$.

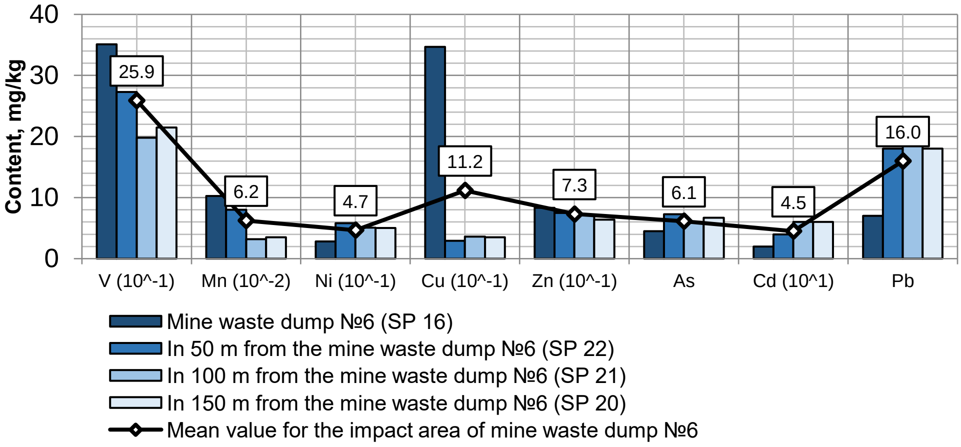

Fig. 5. Heavy metal content in soils affected by mine waste dump Nr. 6

We can observe the decrease in the content of V, Mn, and Zn with increasing distance between sample plots and the mine waste dump (50, 100, and 150 m), as shown in Fig. 3. High content of Cu is noted only in the plot on the territory of the mine waste dump itself. Ni, As, Cd, and Pb tend to increase in content with increasing distance from the dump. We can state, therefore, that the impact of mine waste dump 6 leads to an increase in lithophile (Mn and V) and chalcophile (Zn and Cu) concentrations.

Fig. 6 shows the content of heavy metals in soils affected by mine waste dump 4 with the following series: $\frac{Mn}{623} > \frac{V}{259} > \frac{Cu}{112} > \frac{Zn}{73} > \frac{Ni}{47} > \frac{Pb}{16} > \frac{As}{6.1} > \frac{Cd}{0.5}$.

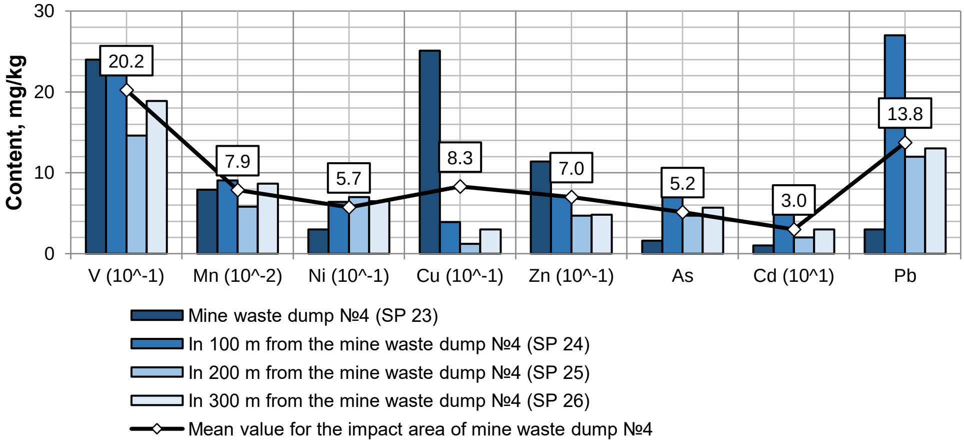

Fig. 6. Heavy metal content in soils affected by mine waste dump Nr. 4

The pattern of heavy metal distribution relative to mine waste dump 4 shown in Fig. 6 is similar to that for dump 6 (Fig. 5). With increasing distance from the mine waste dump, a reduction in V, Mn, Cu, Zn, and Pb content is observed. The greatest difference is seen for Cu.

Fig. 7 shows the data for heavy metal content in several sampling plots, including mine waste dump 1, 7, and the site that is 200 m from the quarry. Geochemical patterns for the soils of the dumps 1 and 7 are different only in the content of Ni and Zn.

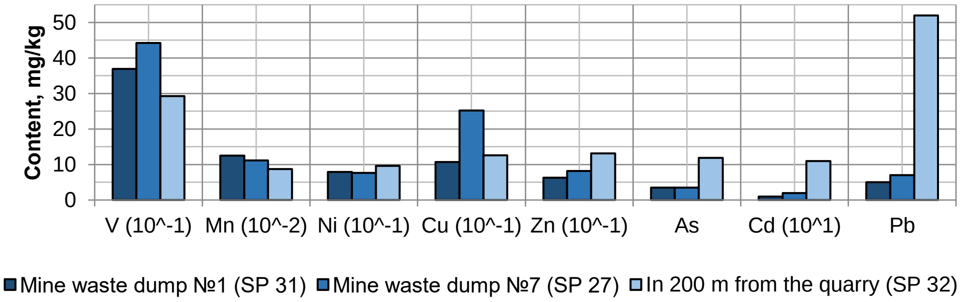

Fig. 7. Heavy metal content in soils affected by mine waste dumps Nr.1 and Nr.7 (soils taken 200 m from the quarry)

The following two geochemical series for the impact area of mine waste dump 1 and for mine waste dump 7 have mixed character in general, with prevalence of lithophiles (Mn and V) and chalcophiles (Zn and Cu): $\frac{Mn}{1253} > \frac{V}{369} > \frac{Cu}{107} > \frac{Ni}{79} > \frac{Zn}{63} > \frac{Pb}{5} > \frac{As}{3.5} > \frac{Cd}{0.1}$ and $\frac{Mn}{1119} > \frac{V}{442} > \frac{Cu}{252} > \frac{Zn}{82} > \frac{Ni}{76} > \frac{Pb}{7} > \frac{As}{3.5} > \frac{Cd}{0.2}$.

The distribution of heavy metals in soils affected by mine waste dump 2 is shown in Fig. 8. As the distance from the mine waste dump increases, a reduction in V, Mn, Ni, and Zn is observed. The content of Cu, As, Cd, and Pb tends to increase as the distance from the mine waste dump increases.

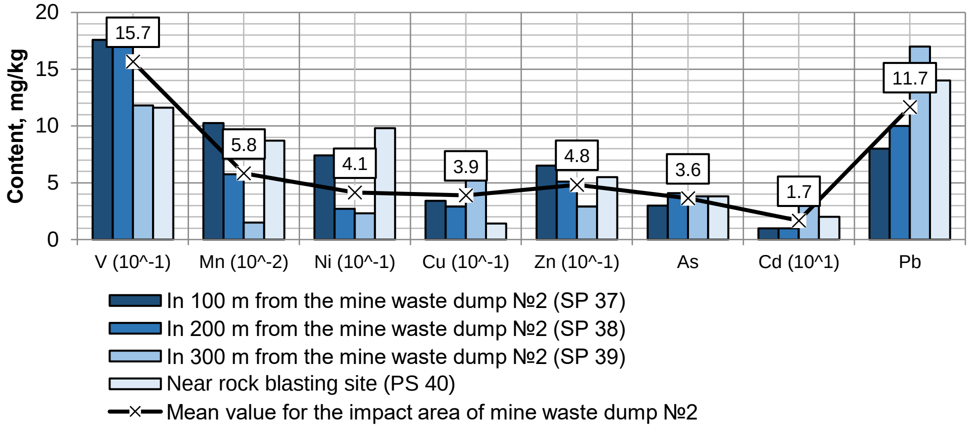

Fig. 8. Heavy metal content in soils affected by mine waste dump Nr.2

The following geochemical series for the impact area of mine waste dump 2 has primarily lithophiles, but their content is significantly less than in the impact areas of other dumps: $\frac{Mn}{583} > \frac{V}{157} > \frac{Zn}{48} > \frac{Ni}{41} > \frac{Cu}{39} > \frac{Pb}{12} > \frac{As}{3.6} > \frac{Cd}{0.2}$. It should also be noted that there is a steep increase in the content of several elements near the rock blasting site. The geochemical series for this area is the following: $\frac{Mn}{871} > \frac{V}{116} > \frac{Ni}{98} > \frac{Zn}{55} > \frac{Cu}{14} = \frac{Pb}{14} > \frac{As}{3.8} > \frac{Cd}{0.2}$. Here, we can see the large content of lithophiles and chalcophiles, in particular Mn, Ni, and Zn.

The southern deposit (Fig. 9) does not affect accumulation of heavy metals in soils in a notable way. The content of all the elements decreases as the distance from the deposit increases. The following series $\frac{Mn}{535} > \frac{V}{176} > \frac{Zn}{49} > \frac{Ni}{41} > \frac{Cu}{18} > \frac{Pb}{13} > \frac{As}{4.1} > \frac{Cd}{0.2}$ for the impact area of the southern deposit is lithophilous, with Mn and V most prevalent: $\frac{Mn}{535} > \frac{V}{176} > \frac{Zn}{49} > \frac{Ni}{41} > \frac{Cu}{18} > \frac{Pb}{13} > \frac{As}{4.1} > \frac{Cd}{0.2}$.

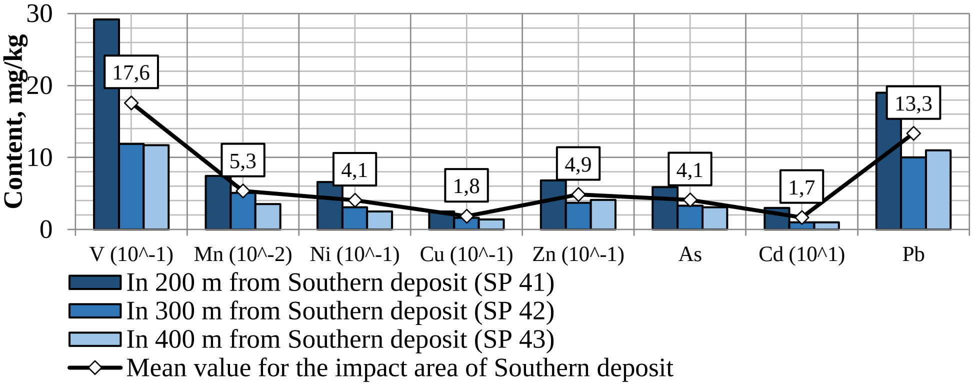

Fig. 9. Heavy metal content in soils affected by of Southern deposit

The total pollution of soils with heavy metals (Fig. 10) exceeds the permissible level (16) in the territory under the influence of the quarry (200 m from the quarry), in the territory of mine waste dumps 6 and 7. We can suggest maximum levels of heavy metal contamination in the sites closest to mine waste dumps, and there is a decrease in those levels when moving away from these dumps.

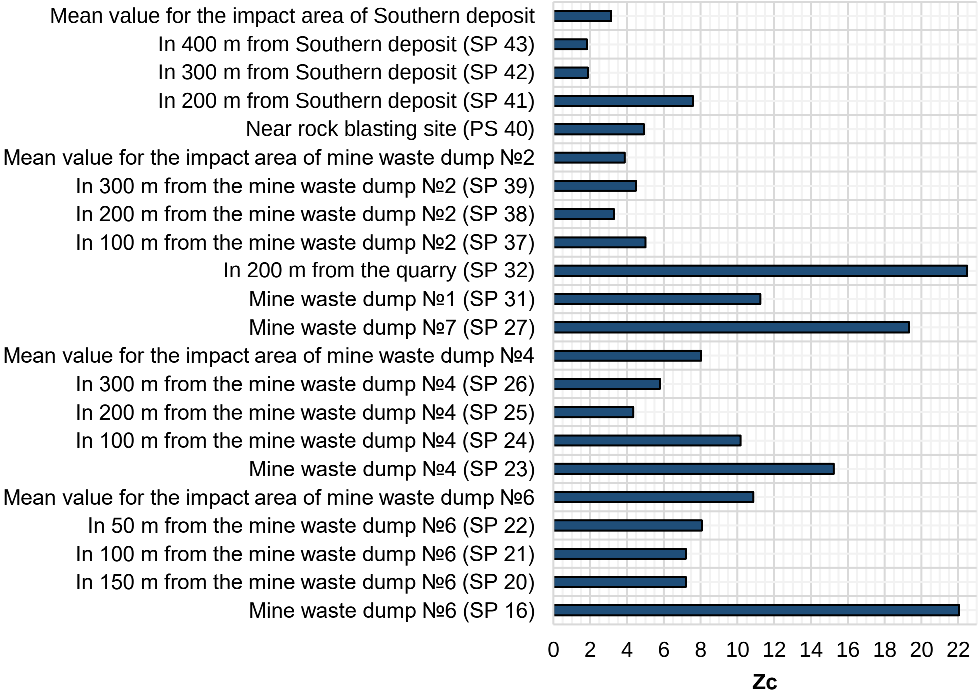

Fig. 10. Total chemical pollution of soils with heavy metals

Fig. 11 shows the content of heavy metals affected due to gold mining. We note a steep increase in heavy metal content compared to the other mine waste dumps. The following average series for the gold mining affected territory has mixed accumulation patterns with prevailing lithophiles and siderophiles:

$$\frac{Mn}{2624} > \frac{Ni}{650} > \frac{V}{143} > \frac{Zn}{64} > \frac{Cu}{42} > \frac{Pb}{11} > \frac{As}{9} > \frac{Cd}{0.2}.$$

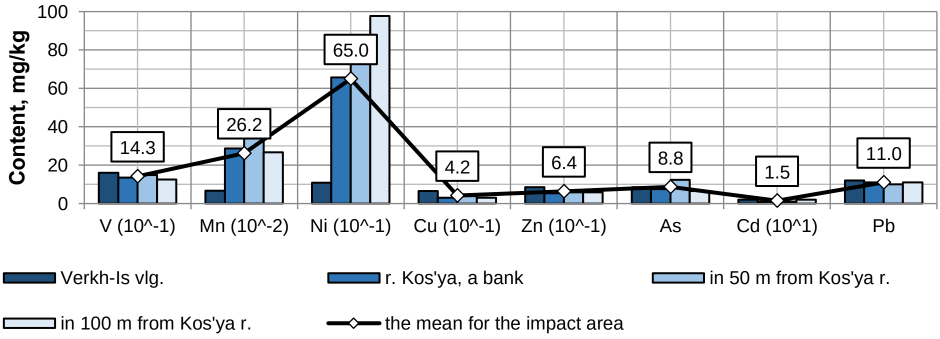

Fig. 11. Heavy metal content in soils affected by gold mining

The largest level of total soil pollution with heavy metals (Fig. 12) was found near the Kosya River (50 and 100 m away). Exceedance of this index was not revealed in the site near. Verkh-Is settlement, while other sites were found to be far beyond that level.

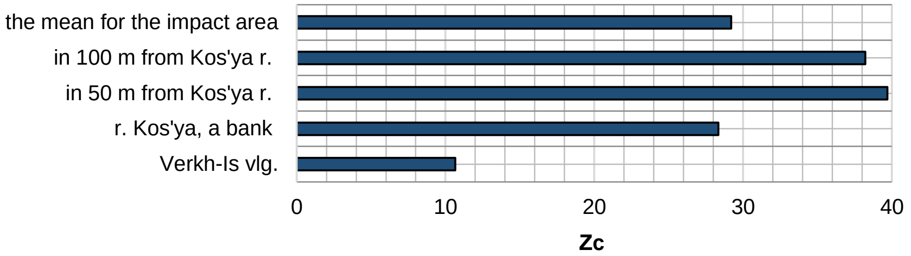

Fig. 12. Total heavy metal chemical pollution of soils affected by gold mining

The analysis of the influence of gold mining on the elementary composition of soil revealed that the content of Mn and Ni increased considerably.

We also discovered moderately hazardous pollution of Ural soils with V, Ni, Zn, and As, which is connected with an increase in their natural levels.

In addition to samples from natural soils, the samples from disturbed lands were also assessed. The largest total pollution index was observed for dumps formed by dredging operations of gold mining in the past (gold mining waste dumps). These dumps are unremediated windrows with heights of 1.5 m. The surface of the windrows is partially covered with grass. A fine-grained soil with 20 cm thickness accumulated in the swale features. Today, these areas are occupied by secondary mixed forests.

Moderately hazardous pollution was also observed in the grounds of the overburden waste dumps 4 and 6, which were formed as the result of mining of the deposit.

We found an insignificant exceedance of the MAC (Minimal Allowable Level; less than 2 MAC) for Mn and of the TAC (tentative allowable concentration; less than 2 TAC) for Cu, Zn, Cd, and Pb in natural soils, which is caused by natural features of the area. The natural background for V and As exceeds the MAC, which led to the exceedance of the regulation values of V in all samples and As in the majority of samples. The natural background is close to the TAC value for Ni, which is the reason why the regulation value was exceeded in a large amount of samples.

4 Conclusion

The mining of iron ore deposits occurs in territories where cambisols are prevalent (mountain and forest cambisols) or in mountain and forest non-podzolized soils with limited distribution of podzols. The morphology of mountain soils is unique—they are negligibly differentiated or differentiated in a way that they cannot be clearly distinguished, and they are highly gravelly. Primitive accumulative soils of the upper parts of the slopes and mountain forest cambisols are formed due to xeromorphous pedogenesis and weathering conditions.

The average geochemical series for all the phytocenosises could be presented as the following: $\frac{Mn}{676} > \frac{V}{242} > \frac{Zn}{83} > \frac{Ni}{36} > \frac{Cu}{33} > \frac{Pb}{32} > \frac{As}{8} > \frac{Cd}{0.7}$. This series is characterized by high concentrations of V, Zn, Ni, Pb, and As, and quite low concentrations of Mn. Gold mining of the area creates the following mixed geochemical series with high content of Mn and Ni across the territory of the deposit: $\frac{Mn}{2624} > \frac{Ni}{650} > \frac{V}{143} > \frac{Zn}{64} > \frac{Cu}{42} > \frac{Pb}{11} > \frac{As}{9} > \frac{Cd}{0.2}$.

Z_c values in soils around the iron ore deposit are changing from permissible to moderately hazardous. It was revealed that regulation values of V, As, and Ni were exceeded, which could be explained by the increased geochemical background in the area. An increased Cd and Pb content relative to background was observed for Ural soils near the quarry.

References

1. V.I. Vernadsky, *Chemical Structure of the Earth's Biosphere and its Environment* (Nauka, Moscow, 2001) (in Russian)
2. V.A. Alekseenko, *Ecological Geochemistry* (Logos, Moscow, 2000) (in Russian)
3. V.A. Alekseenko, A.V. Suvorinov, V.A. Alekseenko, & A.B. Bofanova, *Metals in the Environment. The Soils of Geochemical Landscapes of Rostov Region* (Logos, Moscow, 2002) (in Russian)
4. V.A. Alekseenko, S.A. Buzmakov & M.S. Panin, *Geochemistry of Environmental: monograph for schools* (Perm state university, Perm, 2013) (in Russian)
5. S.A. Buzmakov, Y.V. Khotyanovskaya, Applied Geochemistry, **113**, 104443 (2020)
6. S.A. Buzmakov Vestn. Perm. Gos. Univ., Biol., **2**, 133–138 (2004). (in Russian)
7. S.A. Buzmakov, Geographical bulletin, **4(23)**, 46–50 (2012). (in Russian)
8. L. Angelovičová, L. Bobuľská & D. Fazekašová, Carpathian J. of Earth and Environmental Sciences, **10(1)**, 193–201 (2015)
9. A. Kelepertsis, A. Argyraki,, & D. Alexakis, Geochemistry: Exploration, Environment, Analysis, **6(4)**, 349–355 (2006)
10. V.I. Golik, O.N. Polukhin, A.N. Petin & V.I. Komachshenko, Mining J., **4**, 91–98 (2013). (in Russian)
11. R.A. Wuana, & F.E. Okieimen, ISRN Ecology, **2011**, 1-21 (2011).
12. Adriano, D.C., *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals* (Springer, New York, 2003)
13. G.A. Teplaya, Astrakhan bull. of ecol. education, **1(23),** 182-192 (2013). (in Russian)
14. V.V. Ivanov *The geochemistry of the dispersed elements Ga, Ge, Cd, In and TI in hydrothermal deposits* (Nedra, Moscow, 1966)
15. S.E. Deryagina, O.V. Astaf'eva & A.N. Medvedev, Nature management economics, **1**, 24-30 (2013) (in Russian)
16. V.I. Golik, V.I. Komachshenko & A.V. Polikov, Izvestiya of the Tula State University. Sciences of Earth., **1**, 100–110 (2016) (in Russian)
17. G. A. Vostroknutov, *Temporary methodological guideline on conducting geochemical surveys during geo-ecological works* (Ekaterinburg, 1991) (in Russian)
18. Yu.E. Sayet, B.A. Revich & E.P.Yanin, *Environmental Geochemistry* (Nedra, Moscow, 1990) (in Russian)
19. R.S. Zubareva & V.P. Firsova *On soil characteristics in spruce forests of the mountain band in the Middle Ural region. Soils and hydrologic regime of Ural forests* (UF AN SSSR, Sverdlovsk, 1963) (in Russian)
20. *Methodological recommendation for identification of degraded and polluted lands*, (Russian Federal Environmental Informational Agency, Moscow, 1996) (in Russian)
21. *SanPiN 2.1.7.1287-03. Sanitary and Epidemiological Requirements with Respect to Soil Quality* (Moscow, 2003) (in Russian)
22. *SanPiN 4266-87. Methodological instructions for assessing the degree of danger of soil contamination with chemicals* (Moscow, 1987) (in Russian)
23. S.V. Grigoryan, A.P. Solovrv & M.F.Kuzin, *Instruction on Methods of Geochemical Prospecting of Ore Deposits* (Nedra, Moscow, 1983). (in Russian)
24. B.A. Lebedev, *Agrochemical characteristics of the USSR soils* (Nauka, Moscow, 1964) (in Russian)
25. A.P. Solovov & A.A. Matveev, *Geochemical prospecting methods of ore deposits* (Moscow State University Publ., Moscow, 1985) (in Russian)
26. V. P. Firsova *Soils of Sverdlovsk oblast and their changes under the influence of forestry practices. Institute of plant and animal ecology*, (RAS, Sverdlovsk, 1969. (in Russian)
27. I.S. Urusevskaya, Eurasian Soil Science, **40(11)**, 1145-1157 (2007). (in Russian)