© VITALY G. LINNIK, VITALY YU. KHOROSHAVIN,
OLGA A. POLOGRUDOVA
vlinnik_53@mail.ru, purriver@mail.ru, lab@utmn.ru

UDC: 538.214 : 551.43

NATURAL LANDSCAPES DEGRADATION AND CHEMICAL CONTAMINATION IN THE NEAR ZONE OF KARABASH COPPER–SMELTING INDUSTRIAL COMPLEX[*]

SUMMARY. Study results of the natural landscapes degradation of territory located in the zone of direct influence of the copper–smelting industrial complex of Karabash Town in Chelyabinsk Region reveal a very complicated ecological situation. The copper–smelting industrial complex in Karabash Town is the leader of Russian non-ferrous metallurgy. It has had an impact on the state of the region's environment over 100 years.

The study focuses on zoning of the territory of influence of the enterprise according to the degree of anthropogenic transformation of landscapes. On the leeward slopes of Mount Zolotaya, which is situated to the east of the plant, landscape–geochemical peculiarities have been studied, which determine the conditions of accumulation and migration of compounds of heavy metals, the content of heavy metals in the surface layer eluvial, deluvial and proluvial sediments. Spatial character of the mountainous countryside has caused the need for adaptation of the standard methods of research of migration and accumulation of heavy metals. In the sampling of soil a land area was chosen up to 50 x 50 cm. Using a shovel, samples were selected from the surface layer up to 5 cm deep. The chemical analysis of the samples showed that the content of Cu, Zn exceeds the allowable level by 36–40 times, the content of Pb by 166 times.

KEY WORDS. Heavy metals, technogenic contamination, migration of heavy metals, Southern Urals, Karabash Town.

Natural landscapes degradation caused by technological environmental impact presents a serious environmental problem in a number of areas of Russia. Enterprises that create the greatest ecological damage to the environment are copper–smelting industrial complexes, such as Pechenga–Nikel, Severo–Nikel and Karabashmed, located in the Southern Urals [1–3].

The scale and form of environmental contamination caused by copper–smelting industrial complexes are connected with the production method (copper smelting technology, composition and volume of emissions), atmospheric conditions of aerotechnogenic contaminant dispersal, landscape–geochemical conditions of pollutants migration.

---

[*] *The study was supported by The Russian Foundation for Basic Research, research project No. 12-05-10074-к.*

Since the time of Karabash copper–smelting industrial complex (KCC) foundation in 1910, two combined natural and technogenic zones have been formed in the surrounding 30km^2 territory: an industrial badland (IB) and a zone of tolerant condition of vegetation [4]. The indicator of tolerant condition of vegetation is dieback of birch forest. IB zone includes the area of KCC and the Karabash mountain range with the adjacent low-mountain areas. This territory is barren and has a poor soil cover as a result of intensive erosion processes. The geoenvironmental conditions of Karabash Town area were assessed in July 2012. This study presents the results of the initial assessment of technogenic contamination caused by KCC emissions of the western hillside of Mount Zolotaya, which is located in the sanitary protection zone.

The Karabash massif is situated at the juncture of the Southern and Middle Urals (at the northern closure of the Magnitogorsk megazone) forming a "greenstone belt" rich in ultrabasite. This territory presents Karabash ore district. The massif that is elongated, lens-shaped stretches in the northsouth direction for 6–7 km, widening at the latitude of Karabash Town up to 1.5 km [5]. The rocks of the massif are largely composed of antigorite serpentinites. On the eastern slope of Mount Zolotaya, multiple blocks of enclosing rock units can be found, and in the south-eastern part of the massif there are listvenite bodies.

Landscape conditions. The area of Karabash Town belongs to the mountain landscape province of the Southern Urals where grey and dark-grey wood soils are mostly found, and primary vegetation is pine-birch forests. The development of copper smelting industry changed the local landscape drastically. As a result of polluting air emissions, a considerable part of the territory became a treeless zone. The degradation of vegetation reached its maximum from the 1950s to the 1980s century. After the copper smelting production was stopped in 1989, birch saplings grew on the western hillside of Mount Zolotaya.

The next start-up of KCC caused a great increase in air pollutant emissions, which led to a new stage of inhibition of vegetation growth. In subsequent years due to the implementation of a KCC project aimed at recovery of copper smelting production exhaust gases, there appeared a tendency to restoration of vegetation cover [2].

Conditions of transmission of air pollutants. KCC is situated in Saymonovskaya Valley stretching in the north south direction and surrounded on all sides by small mountains. The pipes of KCC, which are up to 125 m high, are at the elevation of 375–380 m. The highest point of Mount Zolotaya is 611.9 m. Thus, the level of horizontal distribution of smoke plume is at the elevation of 500–510 m. A closed depression contributes to inversion, which is detrimental to the sanitary–hygiene environment of Karabash Town and its surroundings [3–4]. As a result the difference in sulphur content at the distance of 1 and 3 km from KCC is nonsignificant.

According to long-term climatic data on the territory of KCC the following distribution of atmospheric transfer is pointed out: 28%—east-bound transfer, 17%—northeast, 15%—north, 5%—northwest, 15%—southwest, 9%—south, 7%—southwest, 4%—west [6]. Therefore, the sector that forms the solid mass of Mount Zolotaya to the east of the industrial complex endures 60% of repeated wind direction (Figure 1).

Judging by orographic features of the region, the western (windward) slope of Mount Zolotaya is a classic orographic geochemical barrier which, according to A.I. Perelman's classification [7], refers to mechanical barriers. Consequently the main technological environmental impact falls on Mount Zolotaya.

Distribution strategy of sampling points. The choice of sampling points was influenced by the landscape features of the territory. Application of traditional methods of environmental and geochemical monitoring when a sample area 10 x 10 meters or 20 x 20 meters is selected and samples are taken with the help of the "envelope" method was unacceptable. In the process of assessment of technogenic contamination, the main requirement to the sample area is homogeneity (or quasi-homogeneity) in terms of pollution intensity.

However, the landscape conditions demanded to change the sampling procedure. The slopes of Mount Zolotaya are covered with eluvial and deluvial deposits.

The stones that are found on the mountain slopes have a dark coating due to permanent exposure to sulphuric acid which gives them a kind of a "chemical tan". As pollutants are deposited on the surface of the stones, to assess the composition of the sinking technogenic dust special methods are applied, such as dust sampling with sticky glass fixed at the bedrock exposure [6].

Due to the fact that it is not likely that the technogenic dust stays on the stones being washed away with precipitation, it tends to accumulate between stones or even under stones. That is why it was impossible to reliably estimate the deposition density the way it is usually done during snow survey. Open surfaces between separate stone blocks, where sampling of mineral part of soils could be done, were several millimetres or centimetres, which made us refuse the traditional sampling methods, for example, using a soil core sampler 6–10 cm in diameter.

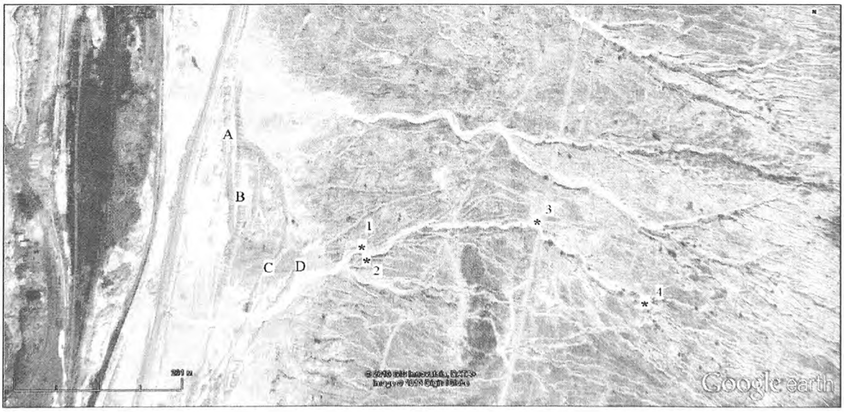

Figure 1: Sampling area (windward slope of Mount Zolotaya, Karabash Town) legend: *1 — No. of station; A, B, C, D—soil-saving dams.

Modification of methodology was required with due regard to specific landscape conditions. It was offered to use the method employed by the Russian Hydrometeorological Service to monitor atmospheric dust fallout. To do that, Typhoon Research and Production Association (Obninsk, Kaluga Region, Russia) uses a 0.3 m^2 gauze plate to analyse radioactive fallout. In the process of soil sampling a land area up to 50 x 50 cm was chosen, where samples were selected from the surface layer up to 5 cm deep.

Chemical test procedure. Determination of heavy metals in soil samples was conducted in accordance with the methods described in the Conservation normative document (Russia)—16.1:2.2:2.3:3.36-02 [8]. A weighed quantity of soil—0.1–0.5 gr (depending on the proposed amount of the determined elements) was placed into a porcelain crucible and calcined in an incinerator for two hours at T = (400–450)°C. Acidolysis with hydrofluoric acid was applied to analyse samples with a high content of silicic acid. The residual matter left after calcination was placed into a glass-carbon cup (or platinum cup) and 10–20 cm was treated with hydrofluoric acid (? = 1.19) and heated until the silicate component was decomposed and wet salts appeared. Then 5.0 cm^3 of chlorohydric acid was added to convert salts into chlorides and evaporate the matter. After 20.0 cm^3 0.5 M of chlorohydric acid was added the residue which was heated until the residue was dissolved. The solution was poured into a volumetric flask of 50 cm^3 until the mark 0.5 M HCl was reached.

The quantitative measurement of heavy metals was performed by applying the method of atomic absorption spectrophotometry with the use of the acetylene-oxygen flame.

Results and discussion. Complex researches into the negative impact of KCC industrial emissions undertaken in the early 1980s revealed a critical condition of the natural landscapes. According to published data [1] the volume of dust fallout in 1970 was 28.8 thousand tons, SO_2—364.5 thousand tons. In the early 90s after a decision to convert the production to recycling of secondary non-ferrous metals, the level of dust fallout and SO_2 dropped to 0.2 thousand tons and 0.62 thousand tons respectively in 1994.

Direct measurement of SO_2 in October 2000 [9] showed high concentration levels—up to 20,000 mg/m^3 directly in the under-flame zone at the distance of 1 km from the plant. However the concentration of SO_2 in the atmosphere of Karabash is not constant due to the changes in the speed and direction of wind.

Taking into account the fact that during the period of KCC intensive production the territory of the industrial badland was 30 km^2 [4] and all the dust was deposited there; we can calculate the daily input of dust into the environment. In the 70s the calculated dust load near Karabash could reach 2.6 tn/km^2 a day.

According to the results of snow sampling at the beginning of the 2000s [3] background atmospheric dust input in the Southern Urals was 10–15 kg/km^2 a day. These data coincide with similar values obtained during ecogeochemical snow sampling in Moscow Region in the early 80s—10 kg/km^2 a day [10]. In 1994 the calculated dust load in Karabash could be up to 18 kg/km^2 a day, which is slightly higher than the background fallout level for the Southern Urals and Moscow Region.

The chemical analysis of fallout in Karabash area showed that aerosols in the background territories consist of silicates, aluminum silicates and oxides, while technogenic particles present zincite (ZnO), anglesite ($PbSO_4$), pyrite (FeS_2), Cu-Zn-spinel ((Mg, Fe_2, Cu, Zn)O_4), galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$) [11].

Modern geoenvironmental conditions. According to historical data, at the beginning of the 20th century western slopes of Mount Zolotaya were covered with forest, and in some places there were open glades where local people picked berries. Parts of pine stumps found during the research conducted at the beginning of the 80s prove that in the past there was a pine forest on the slopes of Mount Zolotaya [1].

As the technogenic burden of KCC increased in the 40s of the last century the forests were cut down and degradation of soil cover started. With excess input of sulphur dioxide into the environment, there was no development of grassland vegetation in the cleared space or natural regeneration of the forest.

The western slope of Mount Zolotaya is characterized by intensive erosion processes which result in a dense erosional pattern. Thus erosion processes are a significant mechanism for translocation of heavy metals delivered to the slopes of Mount Zolotaya through emissions from KCC.

At the moment the effects of erosion processes on the slopes of the mountain are disastrous, which poses a constant threat of the local highway washout during spring snowmelt. Due to the absence of vegetation and soil cover, gullies are quickly filled with melt water which flows downhill towards the Sak-Elgi River. On the way to the river there is a highway. In Figure 1 the effects of erosion processes are clearly seen as well as the results of erosion control measures taken by the administration of Karabash Town. The measures involve building 3–4 erosion-preventive structures just before the road. As a result of the erosion control measures, in the lower part of the slopes melt water lakes appear where heavy metals washed down the slopes of Mount Zolotaya are concentrated.

Chemical erosion. Dissolving in raindrops sulphur dioxide produces sulphuric acid solutions. Sulphuric acid acidifies soils making a destructive effect on plants and animals. Figure 2 presents an example of chemical erosion of rocks as a result of sulphuric acid fallout.

Traces of sulphuric acid fallout were found in all points of landscape description, with a slight decrease in the degree of chemical erosion further away from KCC.

Sulphur dioxide erodes the surface of stone creating micro cavities 1–2 cm deep, and in some cases there was complete erosion of rocks 10–15 cm deep.

Chemical elements distribution. Sampling points on the western slope of Mount Zolotaya are located at the absolute altitude of 350–391 m, which is lower than the height of emissions from KCC pipes. It is well known that in case of industrial enterprises with high pipes the highest level of pollutant fallout is observed much further away from the source of industrial emissions. Close to the industrial complex, in the under-flame zone, pollutant deposition rate is not the highest. However this trend is broken because of orographic features of the area surrounding KCC, which is a different research subject.

Figure 2: Chemical erosion of deluvial deposits on the western slope of Mount Zolotaya.

Location of sampling points (Table 1) was determined by the following considerations: station 1 and station 2 are situated at the same distance from the source of emissions; station 1 is located in the centre of the bottom of an erosional form built by proluvial sediments, while station 2 is on the edge of an erosional form constructed by bedrock diluvium. Station 1 characterizes transit conditions of accumulation of heavy metals delivered both by means of atmospheric emissions and transfer of erosion material from the top part of the erosional pattern. Station 2 controlled station 1 as it controlled the part of slope with insignificant lateral migration.

Station 3 is located at the elevation of 371 m on a flat segment of a convex slope that does not show signs of lateral migration, and the sample was taken from a local depression 3 by 3 metres in size and 5–10 cm deep. Station 4 is situated at the maximum distance from the source of emissions at the elevation of 391 m in the zone of water catchment discharge on the ~ 500 m^2 slope where the material gets along 6–7 erosion channels (up to 10–15 cm).

Table 1

Chemical elements distribution (mg/kg) in superficial deposits of Mount Zolotaya (Karabash)

No. of station	H (m)	Cu	Cd	Zn	Pb	Ni	Mn	Cr
1	350 m	482	4.3	1189	304	40	474	190
2	352 m	537	7.6	1014	770	39	391	171
3	371 m	2263	13.5	3593	4977	46.5	464.5	256
4	391 m	787	7.5	1535	1209	49.7	598	178
MAC		55	2.0	100	30	85	1500	100

The maximum level of contamination of Mount Zolotaya with Cu (station 3.2263 mg/kg) is close to the level of soil contamination around Nkana copper–smelting industrial complex (Zambia) where contamination reaches 2200 mg/kg [12]. As for the concentration of other heavy metals, station 3 registers the maximum concentration level, which confirms validity of this sampling point as the measurement standard of atmospheric heavy metal input. Station 1 registers the lowest concentration of all heavy metals (except Ni, Mn, Cr) as this is a transit zone of chemical subtraction. The highest level of heavy metals pollution exceeds allowable levels of Cu, Zn, Pb by 41, 35.9, 166 times respectively.

In Lake Serebry located 5 km away from KCC [13], the concentration of Cu, Zn exceeds the maximum level of contamination on Mount Zolotaya by 2.3 and 1.3 times respectively, but at the same time the Pb concentration is lower—the slope of Mount Zolotaya is 4.5 times "dirtier". Lower heavy metal concentration values on the slope of Mount Zolotaya are obviously determined by the preponderance of transfer over accumulation.

Conclusions. The research conducted on the western slope of Mount Zolotaya allowed us to define the degree of technogenic degradation on the territory of aerotechnogenic anomaly. A zone of chemical erosion of eluvial and deluvial sediments as a result of sulphur dioxide deposition, has been identified which is revealed in the formation of microcavities on the surface of rock fragments. Contamination with Cu, Zn exceeds the allowable level by hundreds of times, Pb, Cr — by tens of times.

REFERENCES

1. Chernenkova, T.V. Reaction of Silva to Industrial Pollution. Moscow: Nauka (2002): 191.

2. Kalabin, G.V., Moiseyenko, T.I. Ecodynamics of Technogenic Provinces of Mining Production: from Degradation to Reconstruction. *Reports of the Academy of Sciences. Vol. 437. No. 3.* (2011): 398–403.

3. Udachin, V.N. Ecogeochemistry of Mining Technogenesis in the Southern Urals. *Author's Abstract of Doctoral Thesis.* Tomsk (2012): 48.

4. Makunina, G.S. Degradation and Chemical Properties of Soils in Karabash Technogenic Anomaly. *Pedology. No. 3.* (2002): 368–376.

5. Rykus, M.V., Bazhin, E.A., Savelyev, D.E., Snachev, V.I. Geology and Geochemical Properties of Ultrabasites and Gabbroids in the Suture Zone of the Southern and Middle Urals (Kyshtym area). *Oil and Gas Engineering. Vol. 7. No. 1.* (2009): 72–80.

6. Makunina, G.S. Geoenvironmental Characteristics of Karabash Technogenic Anomaly. *Geoecology, Geological Engineering, Geohydrology, Geocryology. No. 3.* (2001): 221–226.

7. Perelman, A.I. Geochemistry. Moscow: Vyshaya Shkola (1979): 423.

8. PND F 16.1:2.2:2.3:3.36-02. Conservation Normative Document (Russia) 16.1:2.2:2.3:3.36-02. *Methods of Estimation of Gross Concentration of Cu, Cd, Zn, Pb, Ni, Mn, Co, Cr in Soils, Bottom Deposits, Sewage Sludge and Waste by Means of Flame Atomic Absorption Spectrometry.*

9. Udachin, V.N., Williamson, B.J., Purvis, O.W., Spiro, B., Dubbin, W., Herrington, R.J., Mikhailova, I. Assessment of Environmental Impacts of Active Smelter Operations and Abandoned Mines in Karabash, Ural Mountains of Russia. *Sust. Devel. Vol. 11.* (2003): 1–10.

10. Linnik, V.G., Saet, Yu.E., Smirnova, R.S. Operational Mapping of Geochemical Fields for Monitoring. *Environmental Development Modeling Process. Issue 13.* Moscow: All-Union Institute for Systems Research (1986): 71–77.

11. Udachin, V.N., Dzheydzhy, M., Aminov, P.G., Lonshchakova, G.F., Filippova, K.A., Deryagin, V.V., Udachina, L.G. Chemical Composition of Precipitation in the Southern Urals. *Natural and Technical Sciences. No. 6.* (2010): 304–311.

12. Ettler, V., Mihaljevič, M., Kříbek, B., Majer, V., Šebek, O. Tracing the Spatial Distribution and Mobility of Metal. *Metalloid Contaminants in Oxisols in the Vicinity of the Nkana Copper Smelter, Copperbelt Province, Zambia.* Geoderma. 164 (2011): 73–84.

13. Udachin, V.N., Deryagin, V.V., Kitagava, R., Aminov, P.G. Isotopic Geochemistry of Lake Bottom Sediments in the Southern Urals for Estimation of Mining Technogenesis Scale. *Tyumen State University Herald. № 3.* (2009): 144–149.