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ECOLOGICAL AND GEOCHEMICAL EVALUATION OF ENVIRONMENTAL POLLUTION WITHIN THE OPERATING AREA OF THE KARABASH COPPER-SMELTING PLANT

SUMMARY. As the result of the long-term operation of a major copper-smelting plant, an anthropogenic geochemical anomaly emerges in the Karabash region. Based on the analysis of field work results, the distribution of heavy metals and arsenic in soil, air, surface waters, and benthal deposits is evaluated within the operating area of this plant. No cardinal changes are discovered after comparing the results of the analysis with the data obtained before the plant modernization. Despite the major decrease in pollutant emissions, the atmosphere pollution index in the settlement area is 6.6, which indicates high pollution. The degree of polluting soil, surface waters, and benthal deposits with heavy metals remains rather high, while the soil regeneration process expected during the suspension of production in 1990-1998 slows down. However, the Karabash geological anthropogenic anomaly is both a natural test site and an anthropogenic one for the research of environment affected by the changed anthropogenic load.

KEY WORDS. Heavy metals, Karabash, surface waters, air, and soil pollution.

In the Southern Urals, the extensive growth of mining and metallurgical industries has greatly affected the local environment. The local anthropogenic geochemical anomalies are formed due to non-observance of basic ecological standards in mining and metallurgic plants. Such areas can be considered both natural and anthropogenic test sites to study the chemicals involved in the process of natural migration flows. The Karabash anthropogenic anomaly which has been formed within the operating area of a major copper-smelting plant is an example of such a test site, providing a unique opportunity to study the environment pollution and its rehabilitation under the anthropogenic load.

The amounts of pollutants that were released into the atmosphere during the operational period of the Karabash Copper-Smelting Plant (over 10 million tons of pollutants — SO_2, industrial dust, and heavy metal compounds), as well as crude industrial, mining, and domestic wastewaters flowing into the local fluvial system, have resulted in the strong pollution of soil, water bodies, benthal deposits, and air with toxic substances; the scale of pollution is a danger to people living there, it may cause the forest dieback near the city and land degradation. The production was suspended in 1989, and in 1995 the Russian Federation Ministry of Environmental Resources and Ecology recognized the environmental condition in this area as an ecological disaster zone. The production was restarted in 1998, and the plant has been in constant modernization ever since. However, the environment is still affected, although in a less degree, by the gas and dust releases from the plant, as well as by the waste and acid waters from abandoned mines.

The basis for ecological disaster solutions should be the objective evaluation of the actual environment condition in the region and its behavior in time. The purpose of this paper is to evaluate the heavy metal and arsenic distribution in the operational area of the Karabash Copper-Smelting Plant and to compare it with the data collected before the plant was modernized.

Karabash is located in a flat valley stretching from south-west to north-east. The mountain ranges up to 600 m high and the predomination of northern winds creates a complicated picture of industrial air pollutants distribution, while in windless weather, the pollutants settle down in the urban area. Being a natural orographic barrier, the mountain frame on the east of the city prevents a rapid outflow of emissions from the valley which results in smog formation.

According to the official data for 2002 (2-TP Air Form), the pollutant emissions amounted to 97,300 tons, 70% of which (67,600 tons) being sulphur dioxide. The 2003 research made by the Chelyabinsk Hydrometeorology and Environmental Monitoring Center [1] showed a high air pollution level. The maximum Pb concentration in the settlement area exceeded MAC 156.2 times as much. It was 192 MAC at the distance of 1 km from the flame and 97.6 MAC at the distance of 3 km. The maximum one-time SO_2 concentration was 11.5 MAC, and the annual average concentration exceeded MAC 2.2 times as much. Complex Air Pollution Index (API) calculated for the most crucial pollutants (plumbum, formaldehyde, sulphur dioxide, hydrogen fluoride, and suspended substances) was 21.

According to the similar research executed by the Chelyabinsk Hydrometeorology and Environmental Monitoring Center in 2006-2007, i.e. after the new melting chamber and the sulfuric production unit had been put into operation, the API was 10.3 while the maximum daily Pb and Cu concentrations exceeded MAC 61.7 and 3.4 times as much, respectively. The maximum one-time SO_2 concentration was 3.4 MAC [2].

According to the similar research executed in 2011 [3], the air pollution level is still high: the API is 6.6 (Fig.1). Unfortunately, all of these researches lacked a crucial parameter — observation continuity.

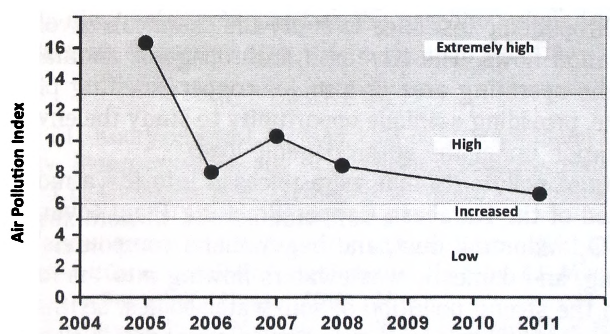

Fig. 1. Changes in the complex Air Pollution Index (API), calculated for the most crucial pollutants

According to official statistics, the plant modernization resulted in essential decrease in air pollution — sulphur dioxide reduced more than 4 times as much, inorganic dust reduced more than 10 times as much. However, it should be noted that in Canada where the main SO_2 emission sources are non-ferrous smelters, the all-Canada SO_2 emission was 2,379 tons in 2000 and was expected 2,244 tons in 2010 [4] which is several fold less than that of the Karabash Copper-Smelting Plant alone in spite of the significant emission decrease in recent years.

The field research of the environment changes in the conditions of changing anthropogenic load were carried out in 2009-2011 around the town of Karabash (the Chelyabinsk Region, the Southern Urals, Russia).

Soil samples were taken from the surface soil (up to 10 cm depth) and dried in the open air. Water samples were taken from the surface into acid-washed 100 ml containers after filtering.

The chemical analysis was carried out in V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry and in the Institute of Microelectronics Technology of the Russian Academy of Science. The atomic absorption method, the inductively-coupled plasma mass spectrometry, and cold-vapor atomic absorption were applied.

The Karabash anthropogenic ecosystem is the result of long-lasting exposure to mining, metallurgic, concentrating, and joint industries. Chemicals and their compounds in the smoke and gas emissions have been settling in soils, which has led to their profound changing and forming various intensive toxic-metal anomalies.

The main soil types in this area are grey and dark-grey forest soils. In natural conditions, these soil types are characterized by sub-neutral or weak acid soil reaction with pH of 5.8-6.7 and low Ca and Mg contents. The humus content does not exceed 4-4.5%. All of the above determines low buffering capacity of such soil types, their complexing capacity is too weak to fix heavy metals brought by aerial flows, and thus they are unable to resist the anthropogenic load.

In spite of the emission abatement, the ecological situation in the region caused by more than 100 years of the plant operation remains severe. During this period, active degradation processes (soil erosion and vegetation cover extinction) have been predetermined.

During the period of the plant operation, two natural-anthropogenic zones have been formed — the impact zone (6-8 km in radius) and the buffer zone.

In the impact (desert) zone, the effect of pollution and deforestation has destroyed the basic mechanism providing the soil stability and has catalyzed the development of sheet and linear erosion on the hillslopes. This zone is characterized by the absence of natural vegetation and the high level of heavy metal pollution.

The buffer zone can be divided into two subzones — the birch-forest subzone with dead soil cover and the degenerated-forest subzone. The birch-forest subzone with dead soil cover is determined by the morphological criterion of birch condition; birch is the species which is the most resistant to the copper-smelting smoke. The inner part of the buffer zone bordering with the impact zone is exposed to surface fumigation; thus the trees in this zone grow low and crippled with chlorosis signs, while in the outer part, the trees are taller and healthy in shape. No natural regeneration can be observed at the distance of 4 km from the plant. The whole zone is characterized by coniferous species damage, their complete absence on vast territories, and the formation of predominantly deciduous forests within natural regeneration. The area of degenerated forests equals 260 km^2.

The investigation of the Karabash settlement area (located mainly in the buffer zone and partially in the impact zone) carried out in 1990-1991 [5], stated the high contents of chemicals of hazard classes I, II, and III. The geochemical association based on the results of the analysis of 622 samples was $Hg_{148}Cu_{87}Sb_{43}Ag_{40}Pb_{37}As_{20}Bi_{19}Zn_{13}Ni_{1.7}$, and the average total pollution index for the area of 34 km^2 was Z_C =418, which is considered an ecological disaster zone according to [6].

In 2011, the analysis of the soil samples taken at various distances from the emission source within the buffer zone also showed extremely high concentrations of a number of chemicals (Table 1) and the multiple MAC excess for As, Cu, Pb, Cd, Hg, and Zn. The total pollution index for these soil samples Z_C was 463 and 252 which exceeds the values corresponding to an ecological disaster zone by several times.

Table 1

The chemical composition of soils and forest floor at various distances from the emission source, mg/km

	4 km north		2 km south A_1	MPC [7]	TAC (for acidic soils) [8]	Hazard class
	Forest floor (A_0)	A_1				
pH		3.71	3.75			
C		0.53	3.10			
As	558	77.67	493	2.0	5	2
Ba	563	303	1.373			3
Cd	100	2.83	12.7		1.0	2
Co	7.4	15.2	51.4			2
Cr	12.5	48.25	313.0			3
Cu	12.165	997	4.340	33	66	3
Fe	25.665	21.710	4.750			3
Hg	4.5	0.88	2.28	2,1		1
Mg	1.765	5.763	26.440			
Mn	2.517	93	2.426	1.500		3
Ni	42	30.2	280		40	3
Pb	9.609	339	900	32	65	2
S	6.842	5.810	6.278	160		
Sb		2.26	9.57	4.5		2
Se		1.29	5.15			2
Sr	38.4	45.70	81.96			2
V	39.0	59.0	77.5	150		
Zn	17.215	554	1.877	55	110	3
Z_C		252	463			

The forest floor which can be considered a pollutant accumulator is a prominent pollution indicator (Table 1). The less the distance from the pollution source is, the thicker the forest floor is, and its total matter in the buffer zone is four times greater than in the baseline area. This is caused by the fact that the anthropogenic impact slows down the biochemical processes, and if the pollution is high, it inhibits or completely stops the organic substance destruction in the forest floor. Moreover, the particle-size distribution of the forest floor changes, there are no traces of live ground cover close to the Karabash Plant.

However, even high total concentrations of heavy metals in the soil do not always indicate the potential ecological and toxicological hazard of anthropogenic pollution. In grey forest soils, the contents of the exchange Cu and Pb, the most ecologically destructive forms due to their bond with fine-dispersed Fe and Mn hydroxide fraction, are 2-4% of the total concentrations. The exchange Zn and Cd are the most hazardous, their fraction is 7-28% [9]. Nevertheless, all these elements in such high concentrations are potentially hazardous.

The land waters in the plant operation area differ essentially from the natural waters. Although in this area, the bed-rock has a high acid-neutralizing potential, the chemical composition of waters indicates the anthropogenic pollution.

The Government land-water quality control in the mid-1990s was carried out by the Chelyabinsk Hydrometeorology and Environmental Monitoring Center; samples were taken systematically from the Sak-Elga River (the mouth), the Atkus River (the mouth), and the Arghazin Pool (upstream). Nowadays the land-water quality is monitored only in the Arghazin Pool (upstream).

Serebry Lake is the least polluted as it is only exposed to air pollution. Only the fishery standards for Zn, Mn and Cu are exceeded here, although the amounts of Cd, Pb, Zn, Cu, and Hg in the upper layer of the benthal deposits exceed the baseline level by hundreds.

The waters in the Karabash and Bogorodsky ponds are characterized by neutrality, high mineralization, and high Zn, Mn, Cd, and Ni concentrations, that is typical for wastewaters from mining and metallurgic plants. The benthal deposits of the Karabash Pond also contain extremely high amounts of Pb, Ni, Cu, Cd, and As. Unfortunately, the Chelyabinsk Hydrometeorology and Environmental Monitoring Center stopped testing the water in these ponds in 2006. The results of the tests carried out in 2002-2005 are presented in Table 2.

Table 2

The evaluation of surface water pollution within the area of the Karabash Copper-Smelting Plant, mg/l

	Serebry Lake	Karabash Pond*		Bogorodsky Pond*		Sak-Elga River*		Miass River	MAC [10]
	2010	2002	2005	2002	2005	2002	2006	2010	
pH	6.5	7.59	7.41	7.55	7.2	5.88	5.90		
Sulfates		139.7	173	51.9	90.3	318	327		100
As	0.015							0.0034	0.05
Cd	0.0002		0.044		0.004		0.008	0.004	0.005
Cu	0.012	0.018	0.234	0.006	0.049	2.94	0.62	0.026	0.001
Fe_{total}	0.163	0.41	0.44	0.20	0.21	1.56	1.69	0.24	0.1
Mn	0.135	0.94	1.049	0.092	0.212	4.07	2.70	0.083	0.01
Ni	0.002	0.054	0.069	0.019	0.018	0.16	0.18	0.013	0.01
Pb	0.012		0.064		0.012		0.013	0.012	0.006
Zn	0.111	8.87	8.311	0.182	0.723	37.28	5.20	0.071	0.01

* Annual average values, according to the data of the Chelyabinsk Hydrometeorology and Environmental Monitoring Center.

The main sources of the Sak-Elga River pollution are the Ryzhy Stream and the pyritic silts in the flood plain. The Rizhy Stream waters form at the pit bottom of the plant and consist of the wash water of the preparation plant and the streams from the sides of Zolotaya Mountain. Its waters are alkaline at the upstream, while passing the tailings they acidify up to pH 2-3.5, and when the stream falls into the

Sak-Elga River they contain great amounts of sulfate ion, ferrum, copper, zinc, and other chemicals. The whole flood plain of the Sak-Elga River before it flows into the Miass River is rich in pyrites that form a dead massive over 100 ha in the mouth. It has no soil cover and is a secondary source of pollution. Thus, the Sak-Elga River is a recipient of almost all sorts of pollution from the plant, the abandoned mines, the industrial and domestic wastewaters from the town. No regular tests are carried out at the river nowadays.

Unfortunately, the slump in regular testing does not provide an opportunity to evaluate the changes in the surface water condition. Nevertheless, the testing continuing upstream the Argazin Pool demonstrated the increase in the occurrence of multiple MAC excess for Cu, Zn, and Mg in 2010-2011. The main source of pollution in this part of the pool is the Miass River which receives the waters of the Sak-Elga River 3 km before flowing into the pool. Our data obtained from the water samples prove this fact (Table 2).

Thus, the evaluation of the pollution within the operational area of the Copper-Smelting Plant after its essential modernization demonstrate that the air pollution remains rather high while the soil and vegetation regeneration process (expected during the suspension of production in 1990-1998) slows down. The pollution level for the soil and benthal deposits also remains extremely high.

However, the Karabash geological anthropogenic anomaly is both a natural test site and an anthropogenic one for the research of the degradation and regeneration of the environment affected by the changed anthropogenic load.

To carry out a more sophisticated investigation of the changing situation, we should arrange extensive ecological and chemical screening, as well as continuous air and water monitoring in the Karabash territory.

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