THE ASSESSMENT OF HEAVY METALS POLLUTION OF WATER BODIES AND SOIL IN THE ZONE OF ECOLOGICAL DISASTER (CITY KARABASH)

Smago metālu piesārņotāju ietekmes novērtējums uz ūdens tilpnēm un augsni ekoloģisko katastrofu zonās (Karabahas pilsēta)

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Abstract

The report gives intermediate results of research carried out as the start of the INTAS Project "Strategy development for long term pollution control in regions of extreme environmental risk (ENVRISK)" The work on the project is a logical continuation of the research by project INCO-Copernicus TOXICAL (Contract No ICA2-CT2001-0016) [Ref. to preceding Conference] [14]. The major goal of the work is to elaborate a strategy and methods of pollution assessment and monitoring of Argazinskoye water storage basin, which is a reserve of drinking water supply for he city of Chelyabinsk in order to take steps for mitigating the health risk of the population of the region.

The Russian project participants of the United Institute of Physics of the Earth, Russian Academy of Sciences, were presented with the following tasks.

- *Grading and summing up the available data on the geological and tectonic structure and heavy metal pollution of the region;*
- *To substantiate field observation stations network and points of sampling of soil, biomass and surface water for laboratory analysis of heavy metal content;*
- *Rating stations of monitoring surface water pollution by neutron logging in relation to ecological conditions of the region;*
- *To obtain data on areal distribution of heavy metals pollution of soils, underground water and biomass;*
- *To elaborate a model of major pollutants spreading with surface runoff and hydrology system of the region on the basis of GIS technologies;*
- *To work out recommendations for local authorities to minimize health risk of the population.*

Currently a map of sampling has been made, sampling techniques have been elaborated in compliance with effective norms (GOST), samples processing and partial chemical analysis have been carried out. Some results of the research are given below.

Keywords: *heavy metals, pollution control.*

The analysis and summarization of existing data on the work area and environmental pollution

At the first stage of work, the available initial data were analyzed and summarized on the pollution of the region and natural environmental features which determine ecologically dangerous elements distribution. The data available at present are structured in the following way (fig.1).

Eight blocks of initial data are presented in various formats. Those are digital data, mapping material, reports, tables and papers. At present, work is being conducted to formalize the collected data on the basis of GIS-technology. A part of the data has already been digitized, transformed into format *ArcView 3.2* and put in the server of GC RAS. The server can be accessed in Internet and the right of using those data is supposed to be given to the authorities and enterprises of the city.

The profiles on which samples were taken had been selected to the task of determining the dynamics of pollution distribution of the area in relation to prevailing direction of smoke emissions of the pipes of Karabash Copper Smelting Plant (Fig. 2). On the basis of the geological structure features, the overlap of the structure with loose sediments, and the

windrose, three profiles were chosen (Fig. 2). It should be noted that in those profiles a great thickness of loose sediments for a major part was composed of technogenic deposits.
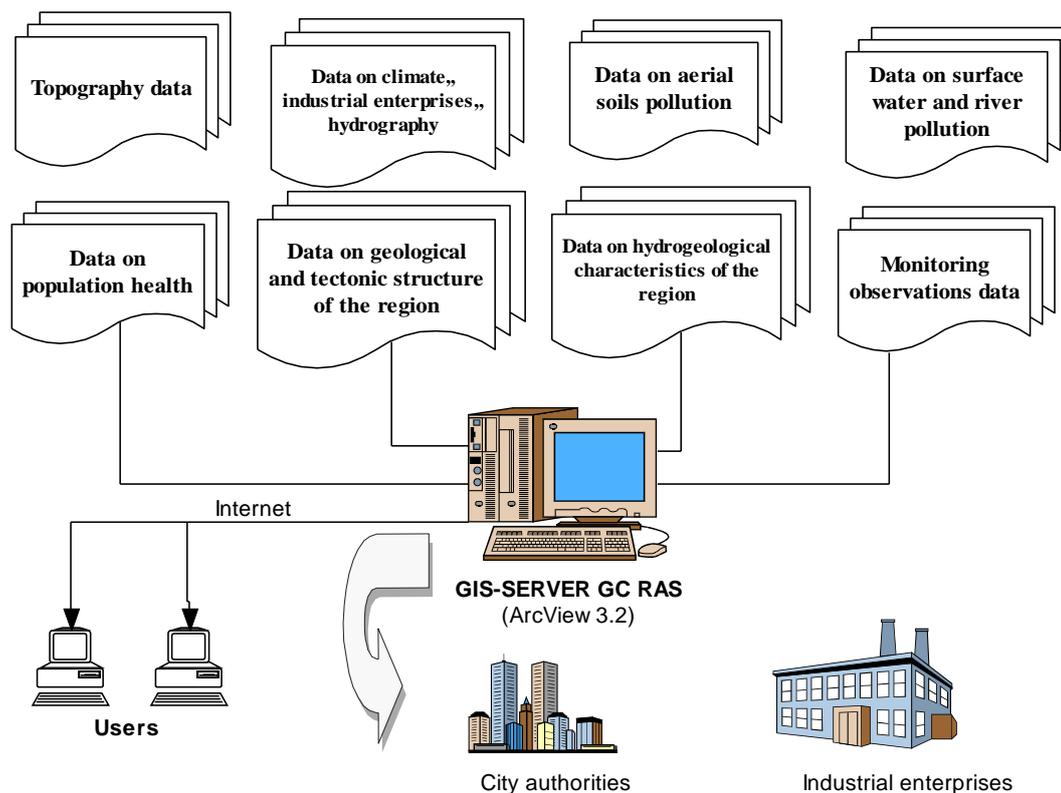

Fig. 1. The structure of data base on the city Karabash area

Selecting a site for sampling
Taking soil and biomass samples for laboratory analysis

For sampling a site is chosen that bounds Serebry lake and the Atkus river in the north, the central area of the city in the west, Bogorodsky pond and the Sal Yelga river in the east and the river Miass and the bank of Argazinskoye water storage basin in the east.

Sampling of soils and biomass (leaves of growing birch trees for biochemical analysis) is planned to be carried out on profiles 1, 2, 3 (See Fig. 2) crossing the investigated area from west to east in the northern, central and southern areas.

Profile 1 starts from Serebry lake dam and runs across the river Atkus up to its flow into Argazinskoye water storage basin. Height differences on the profile are up to 100 m. The length of the profile is ~6.5 km.

Profile 2 starts at the piedmont of the city of Karabash in the KCP pipes area and runs eastwards across the mountain and the abandoned gold mining area to the Argazinskoye water storage basin dam. The height differences of the profile reach 200 m. The length of the profile is ~4.5 km. Along the profile, dunite and peridotite serpentinous to a lesser or greater degree and serpentines with chlorite sericitic carbonaceos schist interlayers of a thickness up to 150 - 200 m are exposed. The area is drained with a series of   ravines of latitudinal orientation that were formed by temporary water flows in which bedrocks and rupture tectonics units can be observed. It is a feature of this profile that along the prevailing direction of the smoke of KCP pipes, the profile is located in the head part of the cone of KCP pipes smoke dispersion, that is marked on the ground with a kind of a black crust of a thickness of 0.5 - 0.7 mm overlapping natural outcrops of bedrocks. This crust is apparently a result of the transformation of the initial sulfate carbonaceous aerosol, which is the major component of industrial emissions.

Sulfur dioxide SO_2 makes up from 47 to 93 % of the total KCP emissions and carbonaceous component content varies from 6 to 42%, thus in pipes emissions, the sulfate component is presented only by sulfuric acid and carbonaceous component is presented by a mixture of graphite and polyatomic compounds of hydrocarbon.
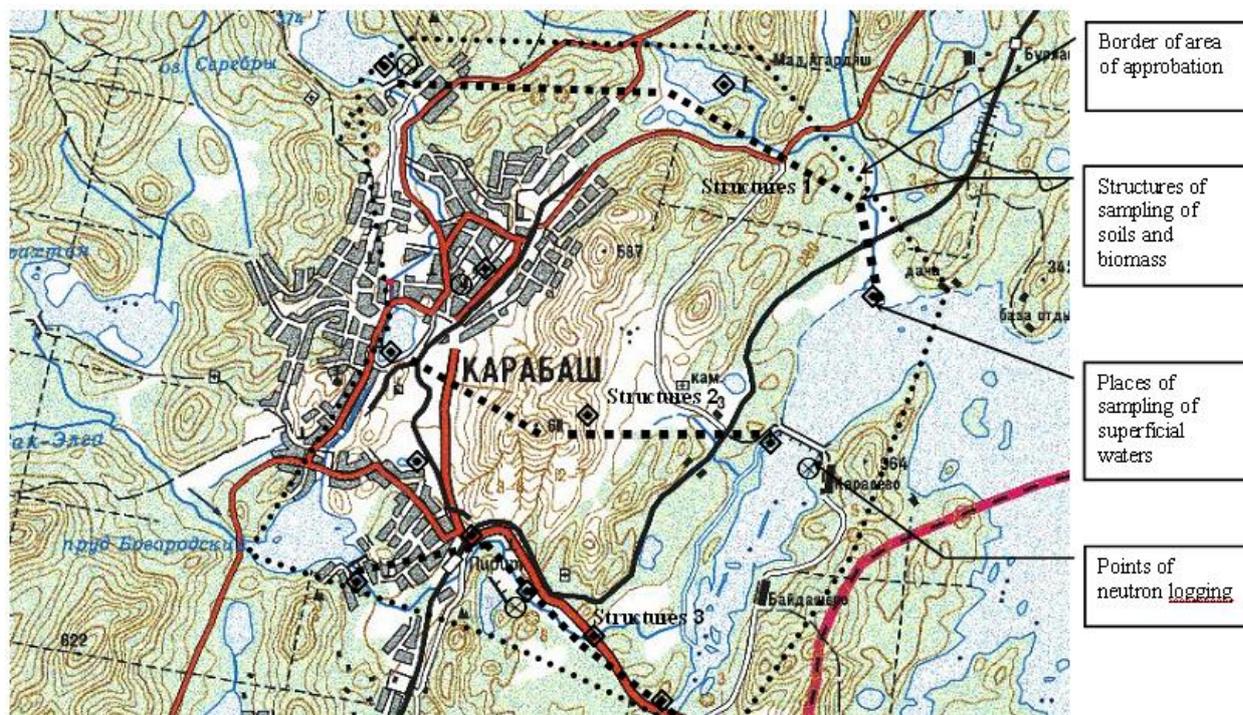

Fig 2.The scheme of procedure of field work and sampling

A copper gold placer Zolotaya gora is located in the east of the profile. This fact should be taken into consideration because recently specialists draw their attention to the contamination of the area with mercury, which from the 20s to 40s of the last century was applied to extract gold by amalgamation.

Profile 3 starts at Bogorodskiy pond and runs along the Sak-Yelga river across the dam of sludge settling pit where solutions from it can be drained to the Sak Yelga river and then by the Miass river to Argazinskoye water storage basin. The profile crosses a man-made pyrite deposit formed as a result of resedimentation of mining production waste.

Samples are taken with a step of 2 - 2.5 km. At the same time, geological and geomorphological observations and measurements of rocks fissuring directions will be conducted on the profiles.

Sampling surface water for laboratory analysis

On the whole, 12 points are planned for taking surface water samples. Samples are proposed to be taken from Serebry lake (1 sample), the river Atkus (1 sample), Argazinskoye water storage basin (1 sample), Bogorodskyi pond (1 sample), the river Sak Yelga (4 samples), acid water bodies (2 samples), springs situated in the Karabash city area.

Neutron logging for the determination of heavy metals content in the water

To determine heavy metals content with the use of neutron logging method four points are planned: Serebry lake, the mine «Tsentral'naya» area, the sludge settling pit, and Argazinskoye water storage basin.

Soil and water sampling

Soil is most complicated substance in ecological analysis, containing a lot of chemical compounds of various nature and especially organic matter. The amount of compounds in soils for which quantitative norms have been worked out in Russia is small as compared to the atmospheric air, the work zone air and water. For a major part those are heavy metals. Eight most dangerous toxic metals, such as cadmium, lead, arsenic, copper, tin and iron are among food components which are subject to control in international trade. The adverse effects of heavy metals on people health are well-known [1-4].

Lead affects blood formation and nervous system, gastrointestinal tract and kidneys. In acute mercury poisoning kidneys and mucous coat are affected. Strong methyl mercury poisoning affects central nervous system, which may result in ataxia, convulsions, speech disorders, blindness, loss of hearing and even death. Cadmium is one of the strongest carcinogens causing lung cancer. Typical diseases caused by cadmium are hypertonia, renal failure, pulmonary emphysema. In difficult cases, mineral composition of bones is affected. Nickel combinations cause diseases of nasopharynx, lungs, malignant tumors, dermatitis and eczema. Chromium and its compounds cause allergic eczema and dermatitis, chronic ulcus, cancer of respiratory tract and lungs. Copper excess may lead to toxicosis, gastroenteric disturbances and kidneys damage. Arsenic causes both sharp and chronic poisonings. Arsenic chronic poisoning causes weight loss, gastrointestinal disturbances, periphery neurosis, conjunctivitis and skin melanoma, which can grow into cancer. Besides metals can interact strengthening or weakening the influence of one another on living organisms.

Data of researchers of Urals showed, that in Karabash, children with increased metal content (lead, arsenic, cadmium) in their hair make 60.26% and 20.6% children show increased content of all the above-mentioned elements.

Table 1.

Metal content in the hair of children of 4 - 5 living at different distance from Karabash Copper Smelting Plant (KCSP) [5]

Element mkg/gm	Distance from the metallurgy workshop of KCSP					
	0,5 km	1km	1,5km	Control city Chebarkul	Allowable level	Background level
Lead	56,6	44,8	28,4	7,16	9	2-4
Cadmium	3,4	2,86	2,12	0,44	1	1-2
Arsenic	2,7	1,4	1,62	1,4	5	0,5-1
Nickel	102.8	104,2	H/o	2,47	10	2
Zinc	58	47	47,4	388,5		
Copper	Not found	Not found	Not found	11,64		

Water quality for household and drinking needs is also a key problem in Karabash, because research carried out by scientists from Urals showed that consuming water from local wells is one of the major factors of oncology risk and the cause of a wide spectrum of other diseases, the level of which is the highest in Karabash. These data were taken as a starting point to set up this research aimed at determining heavy metals content in the water and soils of Karabash.

Soil is one of the most important objects of the environment, giving more than 90% of foodstuffs and raw material for manufacturing various products. As distinct from other objects of the environment like water and air where processes of self-purification go on, the

soil shows insignificant ability of self-purification. The soil is a large-capacity acceptor for heavy metals. They are solidly sorbed and they interact with the soil humus, forming combinations that are difficultly soluble. Thus toxic metals are accumulated in the soil. Besides, in the soil, substances getting into it permanently migrate and are transported at large distances under various effects. Heavy metals polluting the soil may come into the water, plants and organisms of animals.

From literature, maximal metal content is observed at a distance of 1 - 5 km from the source of pollution (near zone). Metal content there may exceed background levels by 1 or 2 orders. As we move father from the pollution source, metal content decreases and at a distance of 15 - 20 km it approaches background level. The depth to which heavy metals penetrate in the contaminated soils commonly does not exceed 20 cm, if pollution is great the depth is up to 160 cm. Hg and Zn show the greatest ability of migration; commonly they are distributed evenly in the soil layer at a depth of 0 - 20 cm. Lead is accumulated in the surface layer (0-2.5 cm); cadmium fills the intermediate place between them [2].

In the research on the soils, an important stage is sampling that the methods recommend to carry out in compliance with GOST 17.4.4.02.84 [6]. The standard is intended for monitoring the general and local pollution of soils in the areas of various pollution sources. Point samples are taken with the use of envelop method diagonally or in another way on the basis that each sample is a part of soil typical of genetic horizons. The integrated sample is prepared of point samples. To determine matter distributed on surface (heavy metals) point samples are taken in layers at a depth of 0 - 5 cm and 15 - 20 cm and of a weight up to 1.0 kg (0.5 kg is allowable).

Chemical analysis of samples and the discussion of results

Samples were taken on the profiles given above, and partial chemical analysis was carried out to determine the content of hazardous elements in them. At present several methods defined by GOSTs Russia are applied in Russia to determine heavy metals.

The major method is atomic absorption. It is based on extracting metals and their compounds from the soil and measuring atomic absorption with spectrophotometer with the use of lamps with hollow cathode. Metals content was determined with the use of atomic absorption spectrometer Z-8000 produced by Hitachi Company with graphite thermal atomizer in accordance with "The methods of making measurement of metal mass content with the use of atomic absorption spectrometry technique with flameless atomization and Zeeman effect" [10].

To make preliminary chemical analysis 6 samples of soils corresponding to numbers 1, 2, 3, 4, 18 and 16 of profile 2 were selected and chemical analysis of water samples was made as well. The content of copper, zinc, lead, cadmium and arsenic was determined in water and soil samples.

The results of chemical analysis of soil and water samples obtained from atomic absorption spectrometry are given in Tables 2 and 3.

Since maximum permissible cadmium content in soil has not been defined yet, rough permissible concentrations are given in the Table.

Background values of elements content in rocks and soils of Karabash are taken average from data of the Ministry of Ecology (1993) and data by Granovsky (1994). They are related to the peculiarities of rocks composition in Urals. Chemical analysis data on soils taken at a distance of 3 km from KCSP showed that all the samples contain heavy metals in amounts many times exceeding acceptable.

Profile no. 2 starts immediately near the Copper Smelting Plant and soil samples no. 4, 3, 2 and 1 were taken at a distance of 1 km from it. The nearest is sample no. 4, next are samples nos. 3, 2 and 1. Samples nos. 18 and 16 are taken at a distance of up to 2 km from the

Plant. Of all the samples, sample 4 is the dirtiest with all the above-mentioned metals. Chemical analysis data on soils taken at a distance of up to 3 km from the KCSP showed that all the samples contain heavy metals in amounts many times exceeding maximum permissible norms. Immediately near KCSP (Sample 4), soils overloaded with heavy metals (cadmium content exceeds background level 72 times, lead content is 24 times as much, arsenic 140 times, copper 600 times and zinc 90 times exceeds background content) may be considered as industrial raw material of those metals.

Table 2.

Heavy metals content in soil samples of profile 2

Place of water sampling	Copper,Cu mkg/g	Zink, Zn, mkg/g	Lead, Pb, mkg/g	Cadmium, Cd mkg/g	Arsenic, As mkg/g
*Background content in soil	60	80	20	0,2	0,15
Maximum permissible concentrations	3,0	23,0	6,0	-	2,0
Rough permissible concentrations	30-132	110-220	65-130	1-2	
Soil 1	1611,4	666,9	78,7	5,54	4,95
Soil 2	1100,8	985,6	61,78	6,22	1,21
Soil 3	572,6	140,3	38,55	5,16	2,13
Soil 4	3711,8	1778,0	480,6	36,78	207,6
Soil 16	1551,7	604,8	393,9	22,71	90,77
Soil18	1870,0	612,8	406,2	20,29	101,63

Table 3.

Heavy metal content in water samples

Place of water sampling	Copper, Cu mg/l	Zinc, Zn mg/l	Lead, Pb mg/l	Cadmium, Cd mg/l	Arsenic, As mg/l
Maximum permissible concentrations	1,0	1,0	0.03	0,001	0,05
1 Serebry Lake	0,009	0,292	0,004	0,005	0
2 Mine Central	0	0,178	0,	0,009	0,001
3 Zolotaya Gora	0, 03	0,605	0,	0,007	0,015
4 Ryzhyi Brook	58,68	2,446	0	0,136	0,018
Гx-5, Bridge	0,03	2,47	0,0004	0,058	0,005
Гx-7, water well no. 3	0,02	0,79	0,0012	0,034	0,001
*water pipe	<0,01	< 0,02	<0,01		< 0, 01

On the average (of 6 samples), those metals content exceeds maximum permissible concentrations (MPC) at a distance of 3 km from KCSP as follows: copper makes 579 MPC, zinc is 35 MPC, cadmium makes 16 rough permissible concentrations, arsenic is 34 MPC. Peak excess of lead content is 80 MPC and of arsenic it is 104 MPC.

At present there is no standard value of maximum permissible concentration for cadmium. However even rough permissible values are 37 times exceeded at most (37 rough permissible concentrations).

High content of toxic metals in soils results in their migration into groundwater and water bodies in spring floods, rainfall and snow melt.

Water is a mobile structure. The processes of exchange and self-purification go on much faster in water than in soils. Nevertheless chemical analysis data showed anomalous content of toxic metals in the water bodies of the region.

Previously (*) we carried out chemical analysis of water of the water pipe of city Karabash. The result of the analysis showed iron content of 0.78 mg/l. Physicians made the conclusion that the water is not fit for drinking because iron content is 2.6 times as much as maximum permissible concentration. Cadmium content was not determined in the research.

We consider it significant that in all sampling places cadmium content was in excess ranging from 5 to 136 times. Serebry lake is a water intake of drinking water. However cadmium content there 5 times exceeds MPC.

As it was mentioned above, cadmium is most dangerous of all metal pollutants of food; it is transported with blood and is accumulated in liver and kidneys. The half-cycle of biological life is long, approximately 40 years.

Heavy metals concentrations many times exceeding MPC in soils and water bodies caused a considerable degrading of the population of the region.

Taking into consideration the fact that soils and water bodies of city Karabash are overloaded with metals hazardous for population health, local authorities must start work of cleaning out and reclamation and assign the metallurgists of KCSP with the task of detailed studies of technological processes and introducing new safe technologies.

References

1. Beliaev M. P., Gneushev M. I., Glotov Ya. K., Shamov O. I. Handbook of maximum permissible concentrations of harmful matter in foodstuffs and environment. Moscow, 1993.
2. Dmitriev M. P., Kaznina N. I., Penegina I. A. Sanitary and chemical analysis of pollutants in the environment. M., Chimiya. 1987, p. 368.
3. Yufit S. S. Poisons around us. Lectures. Moscow, Publishing House James. 2001.
4. Drugov Yu. S., Rodin A. A. Preparation of samples in the ecological analysis. S-Pb., Anatolia. 2002.
5. The assessment of changes in population health related to ecological effects in city Karabash. The Center of State Sanitary Epidemiological Surveillance. Chelyabinsk, 1999.
6. GOST 17.4.4.02-84. Soil. Methods of taking and preparing samples for chemical, bacteriological and helminthologic analysis. M. Izd Standartov, 1985, p. 11. GOST 17.4.3.01-83 CMEA standard 3847-82. Soils. General requirements to soil sampling. Official edition. M., Izd. Standartov, 1984.
7. Recommending methods of assessment the pollution degree of the atmospheric air of settlements from pollutants content in the snow cover and in the soil. M., Minzdrav SSSR, 1960, p. 16.
8. Guide of sanitary and chemical research of soil (Norms). M., Minzdrav RF, 1993, p. 145. List of maximum permissible concentrations and rough acceptable quantities of chemical agents in the soil. M., Minzdrav RF., 1993.
9. Control of chemical and biological parameters of the environment. Encyclopedia "Ecometry". Saint Petersburg, State Standard of RF. Publishing House Cristmas+", 1998, pp. 260 - 262 and 414 - 430.
10. Methods of defining chemical agents, maximum permissible concentrations (MPC) of chemical agents in the soil. M., Izd. Minzdrava SSSR, 1985, pp. 3 - 31.
11. Prais V., Analytical atomic absorption spectroscopy. Translated from English, Ed. L'vov B. V., M., Mir, 1976, 355 p.
12. Handbook. The control of chemical and biological parameters of the environment. Ed. Isaev L. K., S-Pb., 1988.
13. Karyakin A. V., Gribovskaya I. F. Methods of optical spectroscopy and luminescence in the analysis of natural and waste water. M., Khimiya, 1987, 304 p.
14. Sobolev G.A., Morozov V.N., Ponomarev A.V., Tatarinov V.N. The Development of Technology of Ground Waters Pollution in Real Time Regime. International conference. Traditions and innovations in sustainable development of society. Rezekne. 2002. P.107-114.