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Influence of Lead-Zinc Slags of the Shymkent City on the Environment

Yerbol Salim¹, Akmaral Issayeva^{2*}, K. Kidirbayeva³, A. Zhumadulayeva², G. Dossybayeva¹, N. Bozhbanbaeva⁴, S. Ashirbayeva²

- ¹ South Kazakhstan Medical Academy, Al-Farabi Square 1, Shymkent 160001, Kazakhstan
- ² Research Institute of Ecology and Biology, Shymkent University, Zhybek Zholy St 131, Shymkent 160031, Kazakhstan
- ³ M. Auezov South Kazakhstan University, Tauke Khan Ave 5, Shymkent, Kazakhstan
- ⁴ Asfendiyarov Kazakh National Medical University, Tole Bi Street 94, Almaty 050000, Almaty, Kazakhstan
- * Corresponding author's e-mail: akissayeva@mail.ru

ABSTRACT

Due to the rapid pace of urbanization, the lead-zinc slags previously located outside the settlement turned out to be within the city of Shymkent and began to pose a serious threat to the environment. Therefore, the purpose of the study was to investigate the impact of lead-zinc slags on the environment of Shymkent. It has been revealed that the fields of ruderal plant species are inversely correlated with the lead content in the soil, for phyto-indication of the state of soils, the most informative indicators are the phytocenotic composition and the projective covering of soils with vegetation. At the same time, the proportion of annual species in the control is $53.5 \pm 5.6\%$; with an increase in the toxic load, their role gradually weakens, reaching from 14496.0 ± 105.1 mg/kg Pb²⁺ to $5.2 \pm 0.4\%$. It was found that *Dodartia orientalis, Centaurea squarrosa Willd., Plantago lancetofolium* are hyperaccumulators of lead ions, while electron microscopic images showed that lead ions accumulate in the intercellular space of plants, forming significant conglomerates of 10-75 nm. The negative influence of lead-zinc waste has been established, which leads to the accumulation of lead in the blood of children and, as a consequence, is the cause of various diseases. The maximum lead content in the amount of 103 micrograms / dl was found in the blood of children in the area of the city, located 800-1000 m from the slag storage site. Developing hypochromic anemia in children indicates its toxic origin. It was revealed that 90% of children have such pathologies as biliary dyskinesia, dental carries, small anomalies of heart development.

Keywords: lead-zinc slags, lead ions, environment, phytoindication, accumulation, children's health.

INTRODUCTION

Understanding the processes of distribution of metals in the environment and their increasing concentrations at the local level is one of the urgent environmental tasks. The anthropogenic input of heavy metals into the environment has increased dramatically over the last century, which is due not only to the continuously growing volumes of metal production, but also to erosion processes occurring in the areas of storage of mineral and man-made waste (Masindi, V., Muedi, K.L. 2018). The distribution of chemical elements in natural environments is determined by many factors. In the absence of an external anthropogenic load, the content of chemical elements and their compounds in natural substrates depends on their composition, as well as natural conditions that cause the accumulation and migration of substances. Among them, meteorological, landscape-geochemical conditions, and water migration under hypergenic conditions are decisive. The distribution of elements in media is also determined by physico-chemical processes: diffusion, infiltration, mechanical transfer, biochemical (Tleukeyeva E., et al., 2022) and chemical reactions. Under natural conditions, with the current relative equilibrium of processes occurring in nature, the rate of change in the contents of elements is practically unnoticeable.

In industrial areas, under the conditions of intense anthropogenic pressure on the environment, the natural balance in all geospheres is disturbed (ElAti-Hellal, M., Hellal, F., 2021). Violation of the soil cover in an industrial area is carried out, first of all, by mechanical means - by changing the natural landscape during the construction of production facilities: communications, structures, tailings dumps, ash dumps, etc. At the same time, a technogenic landscape is formed with different properties compared to the natural one. Pollution of natural environments under technogenic conditions occurs in several ways. Part of the pollutant in the form of dust and gas emissions is carried by air currents and settles to the ground, forming technogenic scattering halos. Such halos with concentrations exceeding the natural background can have significant sizes, depending on the intensity of emissions and atmospheric conditions of the area. Chemicals, falling on the soil cover, accumulate or migrate depending on the landscape and geochemical conditions of the area (Rastmanesh, F. et al., 2018). The facts of accumulation of heavy metals in plants have been established (Memon, A. et al., 2000, Viehweger, K. 2014, Shawon, M.A.A., et al., 2021) and animal organisms (Pandey, G. et al., 2014, Aksorn, S. et al., 2022). The unfavorable environmental situation in most regions of Kazakhstan can be characterized by three important generalizations:

- new foci of anthropogenic socio-economic stress have formed around industrial facilities, spreading their harmful effects on the environment over long distances;
- these foci are technogenic anomalies, which, in terms of the severity of the harmful effects on the health of large populations, significantly exceed the pathogenetic influence of climatogeographic and geochemical provinces;
- 3) the population living in the territories affected by these foci differs significantly in terms of health status, prevalence and pronounced indicator and environmentally caused pathology of adults and children, mortality rates and average life expectancy.

Industrial genotoxic pollutants can pose a danger not only to the persons in professional contact with them, but also to the people living in areas of sources of these hazards (Rodriguez Villarreal et al., 2019; Buyun et al., 2020). If tens and hundreds of thousands of people are exposed to the negative effects of mutagens and carcinogens under production conditions, then in the second case, all residents of industrial regions are exposed to a similar, albeit less intense pressure of mutagens.

In this regard, the purpose of the study was to study the influence of lead-zinc slags on the environment of Shymkent.

OBJECT AND METHODS OF RESEARCH

The object of the study was the territory of the Abai district of Shymkent – one of the megacities of Kazakhstan with a population of 1118.0 thousand people. On the territory of this area, lead-zinc slags of JSC Yuzhpolmetall (YPM) have been stored since 1950 (Figure 1), the total volume of which amounted to 2.2 million tons. However, in recent years, due to the use of these slags for the production of building materials, its volume has decreased to 1.8 million tons.

Chemical analysis of soils for the content of heavy metal ions was carried out at a distance of 500, 1000, 1500 and 2000 meters from the territory of JSC "YPM" and 100, 500, 1000, 2000 and 5000 meters from the landfill, in all directions of parts of the world. The dynamics of migration of heavy metals along the horizons of the soil profile was analyzed based on the results of chemical analyses of the soil samples taken at depths of 10, 20, 30 and 40 cm. The territories located 8000 meters from the analyzed sites were selected as a control.

The content of heavy metals was determined according to the GOST methods. Video recording of the materials was carried out on a JEOL 2000 scanning electron microscope.

To determine the species composition of plants, the relevant literature was used (Illustrated Determinant of Plants of Kazakhstan, 1969; Flora of Kazakhstan, in 9t, 1961). Plant sampling was carried out using the route survey method, followed by in-house processing of the collected herbarium material under laboratory conditions.

Statistical processing of the obtained results was carried out by calculating the arithmetic mean and the value of the standard deviation at 0.95 > P > 0.80. All determinations were carried out in 3 and 5-fold repetition. The data was processed using an IBM Pentium personal computer based on Excel application software packages (Welham, S et al., 2014).



Figure 1. Storage location of lead-zinc slags in Shymkent (42.312523, 69.535100): a) top view, scale 1:100; 1 – The territory under lead-zinc slags; 2 – School District No. 9, 3 – The historical center of the city, 4 – residential sector; b) Top view, scale 1:1000; c) side view

RESULTS AND DISCUSSION

Due to the processes of urbanization, the storage site of toxic waste of Yuzhpolymetal JSC turned out to be within the city limits of Shymkent, due to the processes of wind and water erosion, waste began to pose a serious threat to the environment and public health. For 50 years in Shymkent, the work of the Shymkent Lead plant was accompanied by a massive influx of lead into the atmospheric air, which settled on the soil with dust particles, entered plants and contributed to the development of an unfavorable environmental situation. Currently, the emissions into the atmospheric air from the enterprise have significantly decreased, but the "lead" problem remains. This is due to the intensive pollution of the soil cover, which is the source of metal intake into adjacent environments and the human body.

The territory and sanitary protection zone of the enterprise are tightly adjacent to the residential quarters of the city. The waste of lead-zinc production is stored three kilometers from the production area, on the other side of the river. The results of chemical analysis showed that as the lead-zinc slag is removed from the storage site, the content of heavy metals in the kidney decreases (Table 1).

The studies of the dynamics of migration of heavy metals along the soil profile revealed that $70.0 \pm 5.9\%$ of the total established volume of acid-soluble forms of lead and cadmium are concentrated in 0–10 cm of the soil horizon, confirming the studies of Seraj, F., Rahman, T. (2018). The concentration of heavy metals in the lower 10–20 and 20–40 cm horizons of the soil, amounted to $45.0 \pm 3.7\%$ and $20.0 \pm 2.1\%$ of the established total volume of heavy metal ions, respectively. The content of heavy metals in the soil, within the limits of MPC values, is set at a depth of 50.0-60.0 cm.

Floristic analysis of the studied territories showed that the plant community of the control area (8000 meters from the source of pollution) is represented by 103 species of higher plants, which are representatives of 17 families. The dominant position in the community is occupied by the families Poaceae (22 species, 32.9%), Asteraceae (14 species, 16.5%) and Fabaceae (10 species, 18.7%). This is followed by Convolvulaceae (7 species, 6.2%), Brassicaceae (5 species, 5.1%), Polygonaceae (4 species, 4.2%) and Solanaceae (3 species, 3.1%). The remaining families are represented by 1-3 species of annual and perennial forms of herbaceous plants. The projective coverage of the soil surface is 96.7%. In the areas with increased doses of metals, there was a sharp decrease in both the projective coverage of the soil surface by vegetation and the species composition of the community. Therefore, if in the zone with the degree of soil contamination by lead - 18 MPC, 86 plant species were found, which is 17.5 ± 1.2 species fewer than in the control, then in the zone where the degree of soil contamination by lead is 49 MPC, there are only 53 species. Accordingly, the projective cover of the soil with vegetation in these areas was 75.6 \pm 4.5 and 63.8 \pm 14.8%. The plant communities established for different zones of soil contamination vary both in the number of species and in the phytocenotic composition of the groups. If meadow plant species predominate in the communities of the control area and the area with the lowest toxic load (up to 6.0 MPC), then the proportion of ruderal species increases in the direction of the toxic gradient growth. In the same direction, according to life forms, there is a pattern of the predominance of perennial plant species. In the control, the proportion of annual species is 53.5 \pm 5.6%, and with an increase in the toxic load, their role gradually weakens; on various toxicity backgrounds, their proportion ranges from $37.4 \pm$ 3.4% to $5.2 \pm 0.4\%$.

Table 1. Characteristics of soil pollution in Shymkent with heavy metal ions (average figures for 2011–2021)

| Sampling location | Heavy metal content, mg/kg | | |
|--|----------------------------|------------------|------------------|
| | Cd+2 | Pb ⁺² | Zn ⁺² |
| 0.5 km from JSC "YPM" | 11.8±1.1 | 350.6±10.3 | 54.3±4.7 |
| 0.9 km from JSC "YPM" | 13.3±1.1 | 455.6±12.7 | 66.3±3.3 |
| 4 km from JSC "YPM" (Central Park) | 5.3±0.2 | 256.3±13.9 | 37.9±3.9 |
| 7 km from JSC KP "YPM" (Ordabasy square) | 2.3±0.1 | 125.3±15.2 | 29.7±1.2 |
| 8 km from JSC KP "YPM" (School No. 9) | 2.2±0.2 | 112.8±9.8 | 26.8±1.0 |
| MPC values, mg/kg | 0.5 | 32.0 | 21.0 |

It was found that the dominant group of the plant community of the site, the soils of which contain 453.0 MPC, consisted of the following plant species: *Dodartia orientalis, Alhagipse udalhagi, Cynodon dactylon* (L.) Pers, *Psoraleum drupaceae, Plantagolan cetofolium, Agropyron tricophorum, Convolvulus arvensis, Polygonum aviculare, Capparis spinosa, Centaurea squarrosa* Willd., *Lactuca tatarica, Gallium verum, Peganum garmala.* The loss of annual species greatly simplifies the cenotic composition of the plant community of impact pollution zones.

The cenotic group, which forms the basis of the plant community of the territory with an average and high level of pollution, is formed by dominant species, which are characterized by a long-term, short- and long-stem, root-spraying root system. The large representation of rod-rooted biomorphs in the communities of the impact zone is determined by the peculiarities of their root system. This life form is characterized by a well-developed main root that penetrates to a great depth in the soil, which contributes to the removal of the absorption zone from the toxic soil horizon and acts as one of the mechanisms of plant protection at the organizational level. The weakening of the process of seed reproduction of annual species and the strong simplification of the cenotic composition of the community significantly affects the projective cover of the soil with vegetation. It was found that the largest amount of lead ions accumulates in the biomass of such species as Dodartia orientalis, Centaurea squarrosa Willd., Plantago lancetofolium. It was found that

lead ions in the biomass of D. orientalis, selected from the area around the landfill of JSC "YPM", are enclosed in large conglomerates of insoluble salts of organic acids. The dimensions of these formations are equal to the volume of dozens of cells of the main tissue, and are 10-75 nm. Presumably, these salts began to form in the intercellular space and, as their volume increased, the walls of neighboring cells gradually moved apart, which contributed to the formation of local places of their clusters (Figure 2). At the same time, it was found that the largest amount of lead accumulates in the roots, which is confirmed by studies by other scientists, as, for example, in the case of arsenic accumulation in rice roots (Sibuar et al., 2022).

The results of environmental quality studies by the Center for Health Protection and Ecoprojection (CSE), together with the Institute "BlackSmidt", Idaho (USA) in 1998 found that in terms of lead content in the soils of industrial zones and in the blood of children, the city of Shymkent ranks first among the industrialized cities of Kazakhstan. In 250 chemical analyses conducted in various districts of Shymkent, it was found that in the territories of the city adjacent to JSC "YPM", the concentration of lead in the soil and air is 3564.9 mg/kg and 5.0 mcg/m³, respectively, and its maximum value at certain points reaches 24900.0 mg/ kg and 31.4 mcg/m³, respectively (Investigation of soil, 1998). Of the studied children attending the kindergartens in the area of the stable influence of lead-zinc slags, 66% were found to exceed the values of the MPC of lead in the blood for the



Figure 2. Lead-containing salts in *Dodartia orientalis* stem tissues: a) REM photo of a cut stem; b) sample IR-spectogram

child's body. At the same time, the established concentrations, at a norm of 10 micrograms /dl, were 3-4 times higher than in other cities of Kazakhstan studied. The maximum content in the amount of 103 micrograms / dl was found in the blood of children in the Gagarin Street area (800-1000 m from the slag storage site). On the basis of on the conducted studies, 5 territories of the city of Shymkent adjacent to JSC "YPM" have been established, where the lead content in the blood of children ranges from 50 to 60 micrograms / dl. In the children of kindergartens and schools located in a zone of 3-5 km from the plant, this indicator varied from 16 to 48 micrograms/ dl. The studies of the influence of lead-zinc slags on children's health have shown that on the territory of school No. 9, which is located at a distance of 8000 m from the source of pollution, lead concentrations exceed 12 times the MPC, cadmium - 1.5 times and chromium - 1.5 times. In adolescents living in the territory adjacent to school No. 9, in 53% of cases, an excess of lead in the blood up to $13.0 \pm$ 2.1 mcg / dl was detected. In 47%, the indicators were within the upper limits of permissible values $(10.0 \pm 0.2 \text{ mg/dl}).$

Examination of the cells of the upper respiratory tract of the nasal mucosa and buccal epithelium of the cheeks of preschool children (5–7 years old) revealed that 45% had a decrease in the number of normal epithelial cells and increased the number of phagocytized apoptotic bodies in girls by 6.7 times, in boys by 3.1 times. The high contamination of the microflora of the oral cavity, on average, was exceeded by 4.3 times. It is known that lead is a strumogen, i.e. it is able to influence the exchange of iodine, which was found in 52% of children with severe iodine deficiency, manifested in a decrease in its concentration in the blood to $4.8 \pm 0.22 \text{ mcg} / \text{dl}$ (physiol. limits 5-12 mcg/dl; $8.5 \pm 0.5 \text{ mcg/dl.}$).

One of the specific indicators of the effect of lead on hematopoiesis is the determination of reticulocytes. The results of the study showed that their content was within $0.61 \pm 0.01\%$ and is at the lower limit of the norm (0.5-1.2%). At the same time, it was revealed that the process of reticulocyte maturation (according to the reticulocyte production index – RPI) was significantly reduced to 0.28 ± 0.4 (at a norm of 1), which is the cause of anemia in children. Developing hypochromic anemia indicates its toxic origin. During an in-depth medical examination of children, it was revealed that only about 10% of children are relatively healthy, the most common pathologies are biliary dyskinesia, dental caries, small anomalies of heart development.

CONCLUSIONS

The results obtained show that lead-zinc slags located in the border of the city of Shymkent have a negative effect on the environment, while, as a result of erosion processes, the highest concentration of lead and cadmium ions accumulates in the upper horizons of soils (0-40.0 cm), which are the root-inhabited layer for most types of vegetation of the ephemeroid semisavanna of southern Kazakhstan. It was found that the indicators of the share of ruderal plants inversely correlate with the lead content in the soil, and for the phyto-indication of the soil state, the most informative indicators are the phytocenotic composition of the plant community and the projective cover of the soil with vegetation. At the same time, lead ions accumulate in the intercellular space, forming significant conglomerates. The negative influence of lead-zinc waste has been established, which leads to the accumulation of lead in the blood of children and, as a consequence, is the cause of various diseases in 90% of Shymkent children.

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