Condition Assessment Industrially Contaminated Soils of Kuzbass by Bioindication

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Abstract. This work evaluates the state of the soil that has undergone negative changes as a result of technogenic impacts, the presence of pollutants - heavy metals, considers the assessment of the state of the soil by the bioindication method. Shell amoebae, which are unicellular organisms, as well as earthworms and plants, were used as bioindicators. We also studied the ratio of the concentration of heavy metals in the soil to the distance of these soils from the source of heavy metals, and the seasonal dynamics of changes in the content of heavy metals in the soil. Using the method of stripping voltammetry, results were obtained on the presence of heavy metals in soil, earthworms and plants.

1. Introduction

The biosphere is exposed to heavy metal pollution from human industrial activities. Most of the heavy metals entering the biosphere tend to accumulate in the soil. The amount of heavy metals entering the soil and their behavior patterns in different soil-geochemical conditions can help predict the environmental hazard of soil contamination with these metals.[1, 2] Thus, these pollutants affect the density and structural composition of the soil, and their accumulation leads to an ecological imbalance that adversely affects the environment. [3, 4, 5] Purpose of the study: to assess the ecological state of soils in the territories exposed to technogenic pollution near the ash dump of the thermal power plant.

2. Materials and methods

To determine the chemical composition of ash and slag waste, ash samples were taken. A total of 130 samples were taken. Chemical analysis was carried out using a KevexSpectrace X-ray fluorescence spectrometer, Quan'X. Soil sampling is carried out in accordance with the requirements for soil sampling for general and local contamination. When sampling soil, the sampling points were located along the "envelope" (four points in the corners of the site and one in the center). Four more pits were made around each of the five points. Thus, a pooled sample was composed of 25 spot samples. Plant samples were taken in the same areas as soil samples. To obtain a combined sample of plants weighing 1 kg of natural moisture, 10 point samples were taken. On the same sites, at each point measuring 10×10 meters, samples were taken from three sites measuring 25×25 cm. from a depth of 20 cm. Earthworms were counted by hand sampling from soil monoliths. When studying the road-path network, the number of earthworms was counted according to the levels of distance from the pollution object. Shell amoebas were counted in aqueous suspensions using a Biomed 3 light microscope and a Motic DM-BA300 digital microscope at 40 magnification. The mass concentrations of zinc, cadmium, lead and copper were measured by stripping voltammetry after preliminary sample preparation by means of wet mineralization.

3. Results and Discussion

In a chemical study of the composition of ash and slag waste, ash samples were taken. As a result of the study, the chemical composition of this material in percentage terms, containing oxides of chemical elements, was revealed. The results of the study are presented in Table 1.

Table 1. Average chemical composition of ash and slag waste

SiO_2	CaO	Al_2O_3	MgO	MnO	Fe_2O_3	FeO	K_2O	TiO_2	SO_3	BaO	P_2O_5
55.7 %	6.8 %	21.83 %	1.95 %	0.1%	7.4%	6.7 %	3.53 %	1.28 %	0.72 %	0.44 %	0.38 %

This method proved to be unable to show the presence of heavy metals in the composition of the test material. With the help of atomic emission spectrometry, the chemical composition of ash was more accurately studied, which nevertheless showed the content of such heavy metals as cadmium (Cd), zinc (Zn), lead (Pb), copper (Cu) and their content in soil 1.22; 88; 21; 43 mg / kg, respectively. It follows from the study that the analysis by atomic emission spectrometry made it possible to detect the presence of heavy metals in the ash and slag waste stored at the ash dump. [6, 7]

To determine the presence of heavy metals (Cd, Zn, Pb, Cu) in the composition of soils, three samples were taken from three territories different in distance from the ash disposal area. [8, 9] Using the method of stripping voltammetry, the presence of heavy metals in the composition of soils was detected. The data obtained from soil samples from three territories are shown in Table 2.

Table 2. Content of heavy metals in soil samples

	Cu, mg/kg	**Pb, mg/kg**	**Zn, mg/kg**	**Cd, mg/kg**
Sample 1 30m from the ash dump	29	27	61	14
Sample 2 150m from the ash dump	32	41	69	268
Sample 3 Background plot	4.6	6.6	22.2	0.1

It follows from the table that the highest content of heavy metals is present in the samples taken from the second site, located at a distance of 150 m from the ash disposal area. It should be noted that there is an increase in the concentration of heavy metals in the sample taken from the second site compared to the sample taken from the background site.

Also, when studying the sites listed in Table 2, shell amoebas were found in their soils, including 10 different genera of these microorganisms, and 2 species of earthworms that live in this environment. Their presence or absence shows the ecological state of the habitat, that is, the soil. The found species of shell amoebae in the studied soils are presented in Table 3.

This table shows that the presence of shell amoebas in the soil is affected by the level of its contamination with heavy metals. The largest number of these microorganisms are found in the soil of the background plot, which indicates a more favorable habitat for them and a lower concentration of pollutants in the soil. Accordingly, the smallest number of shell amoebas is found in the second area - with the highest content of heavy metals. Each type of these microorganisms has a different resistance to contamination with heavy metals, and therefore not all species can be present at once in all studied areas subject to contamination, which is well observed in Table 3.

In contrast to the different presence of species of shell amoebas in the studied soils, individuals of earthworms were found only in an area of 30 m from the ash dump, and their number per sq. m. was 8 copies. However, at the next site (150m), a large number of nematodes were found in the soil sample taken. This indicates an increase in the unfavorable state of the soil, which follows from Table 2, which shows that the second site has the highest concentration of heavy metals. This environment is unfavorable for earthworms. This is influenced by the increased pollution of the territory.

Investigation of the seasonal dynamics of changes in the content of heavy metals in the soil at different distances from the ash dump. This study was conducted over five months from May to September 2020. Samples were taken from four different sites, including sites located near crops, at a distance of 1000 and 3000 meters from the source of pollution. The analysis of the abundance of shell amoebas and their species composition was carried out by direct microscopy of the aqueous suspension of the soil. The presence of heavy metals in the soil was revealed by the method of stripping voltammetry. The results of changes in the content of heavy metals in the soil, obtained as a result of the study, are presented in tables 4-7.

Table 3. Species composition of communities of shell amoebas in the studied soils

Types of shell amoebas	Plots		
	1	2	3
Difflugia compressa	-	+	+
Difflugia globulosa	-	-	+
Euglipha ciliata	-	-	+
Euglipha laevis	-	-	+
Corytion dubium	+	-	+
Corytion orbicularis	+	-	+
Cyclopyxis eurystoma v. parvula	+	+	+
Cyclopyxis kahli	+	+	+
Nebela collaris	-	-	+
Nebela tubulosa	+	-	+
Plagiopyxis declivis	+	+	+
Plagiopyxis penardi	+	+	+
Euglipha rotunda dorsalis	-	-	+
Heleopera petricola	+	-	+
Heleopera sylvatica	+	-	+
Hyalosphenia elegans	-	-	+
Hyalosphenia papilio	+	-	+
Trinema encheles	-	-	+
Trinema lineare	-	-	+
Trinema complanatum	-	-	+
Centropyxis elongata	+	+	+
Centropyxis spinosa	+	-	+
Centropyxis orbicularis	+	-	+
Centropyxis aerophila	+	+	+

Table 4. Seasonal dynamics of changes in the content of heavy metals in the soil at a distance of 100 m from the gold ditch

Date	**Cu, mg/kg**	**Pb, mg/kg**	**Zn, mg/kg**	**Cd, mg/kg**
02.05.2019	18	25	32	0.059
02.06.2019	21	26	35	0.059
02.07.2019	32	28	53	0.09
02.08.2019	56	27	59	0.12
02.09.2019	68	30	89	0.12

Table 5. Seasonal dynamics of changes in the content of heavy metals in the soil at a distance of 300 m from the gold ditch

Date	**Cu, mg/kg**	**Pb, mg/kg**	**Zn, mg/kg**	**Cd, mg/kg**
02.05.2019	0.9	0.9	1.5	0.0031
02.06.2019	0.9	1.2	1.5	0.0031
02.07.2019	1.2	1.2	2.8	0.061
02.08.2019	1.38	1.4	5.5	0.09
02.09.2019	4.4	1.5	6.1	0.09

Table 6. Seasonal dynamics of changes in the content of heavy metals in the soil at a distance of 1000 m from the gold ditch

Date	**Cu, mg/kg**	**Pb, mg/kg**	**Zn, mg/kg**	**Cd, mg/kg**
02.05.2019	0.68	0.56	1.09	chemical element not found
02.06.2019	1.18	6.27	1.18	0.0017
02.07.2019	1.49	6.48	2.57	0.036
02.08.2019	2.86	6.57	3.15	0.078
02.09.2019	3.75	6.57	5.5	0.09

Table 7. Seasonal dynamics of changes in the content of heavy metals in the soil at a distance of 3000 m from the gold ditch

Date	**Cu, mg/kg**	**Pb, mg/kg**	**Zn, mg/kg**	**Cd, mg/kg**
02.05.2019	0.58	0.43	1.1	chemical element not found
02.06.2019	0.69	0.4	1.05	0.0021
02.07.2019	0.68	0.52	1.38	0.0032
02.08.2019	3.1	2.1	1.94	0.09
02.09.2019	4.8	3.48	2.7	0.11

From these tables it follows that during the study period, the dynamics of changes in the content of heavy metals in the soil is positive. This is due to the fact that during the period when the research was carried out, the average daily temperature changed every month, and the rate of movement of heavy metals in the soil increased. The most pronounced concentration of heavy metals is in the area located 100 m from the ash disposal area, and, consequently, the largest change in the dynamics of the content of heavy metals.

Table 8. Seasonal change in the number of shell amoebas at different distances from the ash dump

	Sample 1	Sample 2	Sample 3	Sample 4
02.05.2019	1190±540	3286±680	10627±780	14484±390
02.06.2019	2110±340	3713±225	11610±370	17150±610
02.07.2019	2720±290	4185±310	12250±670	19650±480
02.08.2019	3060±475	5045±270	13000±520	22100±510
02.09.2019	3780±570	5465±233	13815±440	22590±230

x ± mt - mean ± confidence interval, at t> 0.95

From the data given in table 8, which were obtained as a result of research, it is worth noting that with an increase in the distance from the ash dump, the number of shell amoebas increases. In the area located 100 meters from the ash dump, the smallest number of shell amoebas is observed. This is facilitated by the most unfavorable habitat for them, which has the highest concentration of heavy metals in its composition.

Study of the content of heavy metals in earthworms at different distances from the ash dump. To assess the impact of heavy metals on earthworms, five samples were taken at five sites, different in distance from the ash dump. As a result, earthworms were found in only three samples. The presence of heavy metals in earthworms was determined by the method of stripping voltammetry. Table 9 presents data from studies of the content of heavy metals in earthworms from the sites where these worms were found.

Table 9. The content of heavy metals in earthworms

	Cu, mg/kg	Pb, mg/kg	Zn, mg/kg	Cd, mg/kg
30m	-	1.18	56	0.89
300m	-	1.9	980	0.085
1000m	-	0.85	248	1.76

The data shown in Table 9 shows that the earthworms found in different areas have different contents of heavy metals. Moreover, the taken distance from the ash dumps contributes to a favorable habitat for earthworms, otherwise the detection of individuals of earthworms would be impossible. The highest content was found in worms taken from a site located at a distance of 300 m from the ash dump. This is mainly due to the high content of zinc in this area, compared to the content of this element in the other two areas.

Study of the content of heavy metals in plants at various distances from the ash dump. In order to reveal the regularity of the distribution of the content of heavy metals in plants, five samples were taken from different territories, with different distances to ash outlets, including from territories near which crops are sown. The material was taken as samples - forbs, which were dried for the necessary analysis. The work was carried out in the summer of 2019. As a result, in all samples obtained from the studied areas, the content of heavy metals was found using the method of stripping voltammetry. The results of studies on the presence of heavy metals in plants are presented in Table 10.

Table 10. The content of heavy metals in plants

	Cu, mg/kg	Pb, mg/kg	Zn, mg/kg	Cd, mg/kg
30m	3.38	0.73	12	0.05
100m	2.63	0.36	11	0.019
300m	2.15	0.23	5.8	0.22
1000m	1.64	0.065	5.35	0.78
3000m	1.19	0.0061	2.3	1.2

From this table it follows that the concentration of heavy metals in plants is influenced by the distance from the ash disposal area to the given area where the plant samples were taken. The highest content of heavy metals is observed in the first section, located 30 meters from the ash dump.

The increased concentration of heavy metals in plants indicates their increased concentration in the soil. This is a pattern. Plants by their nature feel the need to obtain trace elements, which can be heavy metals, but in turn heavy metals pose a danger of soil contamination. It should also be noted from the data in the table that on plots 4 and 5, which are sown, the presence of heavy metals was found, the content of which slows down the growth and lowers the productivity of agricultural crops located in the study areas. [10].

4. Conclusion

Based on the results of the work done, the following conclusions can be drawn:

- Ash and slag waste contains heavy metals, the presence of which was detected by atomic emission spectrometry.
- The composition of the soil located at a distance of 30-150 m from the ash dump is susceptible to contamination with heavy metals, the concentration of which changes depending on the increase or decrease in the distance.
- Shell amoebae show changes in the number of species in a particular area, which make it possible to use these unicellular organisms as bioindicators for assessing the state of soil with different levels of heavy metal contamination.
- The seasonal dynamics of changes in the content of heavy metals in the soil was revealed in the period from May to September 2020, which turned out to be positive. And the factor influencing this dynamics was revealed.

• The content of heavy metals in earthworms and plants in the studied areas, their role in soil bioindication, and the dependence of the concentration of heavy metals in them on the increase in distance from ash dumps were revealed.

References

[1] Westra, L., Bosselmann, K., & Fermeglia, M. (2020). Ecological integrity in science and law. *Ecological integrity in science and law* (pp. 1-264) doi:10.1007/978-3-030-46259-8

[2] Ecological Biochemistry: Environmental and Interspecies Interactions Krauss, G. -., & Nies, D. H. (2015). Ecological biochemistry: Environmental and interspecies interactions. *Ecological biochemistry: Environmental and interspecies interactions* (pp. 1-413) doi:10.1002/9783527686063

[3] Il'yaschenko D.P., Chinakhov D.A., Chinakhova E.D., Kirichenko K.Yu., Verkhoturova E.V. Assessment of Negative Influence of Manganese in Welding Fumes on Welder's Health and Ways to Reduce it. FME Transactions (2020) 48, 1, 75-81. doi:10.5937/fmet2001075I.

[4] Chinakhov D.A., Grigorieva E.G., Mayorova E.I., Solodsky S.A., Torosjan V.F. Dependence of Manganese Content in the Weld Metal on the Velocity of Active Shielding Gas Flow. IOP Conf. Series: Materials Science and Engineering. 253(2017) 012034. doi:10.1088/1757-899X/253/1/012034

[5] Lazutina, T. V., Tempel, Y. A., Tempel, O. A., & Lazutin, N. K. (2017). Aspects of production ecologization of machine-building enterprises as part of the system approach. Paper presented at the *IOP Conference Series: Earth and Environmental Science, 66*(1) doi:10.1088/1755-1315/66/1/012027

[6] Malchik, A. G., Litovkin, S. V., Rodionov, P. V., Kozik, V. V., & Gaydamak, M. A. (2016). Analyzing the technology of using ash and slag waste from thermal power plants in the production of building ceramics. Paper presented at the *IOP Conference Series: Materials Science and Engineering, 127*(1) doi:10.1088/1757-899X/127/1/012024

[7] Mal'Chik, A. G., Litovkin, S. V., & Rodionov, P. V. (2015). Investigations of physicochemical properties of bottom-ash materials for use them as secondary raw materials. Paper presented at the *IOP Conference Series: Materials Science and Engineering, , 91*(1) doi:10.1088/1757-899X/91/1/012081

[8] Ayres, R. U. (1992). Toxic heavy metals: Materials cycle optimization. *Proceedings of the National Academy of Sciences of the United States of America, 89*(3), 815-820. doi:10.1073/pnas.89.3.815

[9] Pahlsson, A. -. B. (1989). Toxicity of heavy metals (zn, cu, cd, pb) to vascular plants - A literature review. *Water, Air, and Soil Pollution, 47*(3-4), 287-319. doi:10.1007/BF00279329

[10] Lambers, H., & Oliveira, R. S. (2019). Plant physiological ecology. *Plant physiological ecology* (pp. 1-699) doi:10.1007/978-3-030-29639-1