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Article

Chemical and sanitary assessment of coal spoil heaps in the south of the Kuznetsk Basin

Ekaterina E. Vorobyeva*, Natalya V. Fotina, Lyudmila K. Asyakina, Mariya A. Osintseva, Alexandr Yu. Prosekov

Kemerovo State University, ul. Krasnaya 6, Kemerovo, 650000 Russia

**89515923860k@gmail.com*

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Abstract. Due to the large amount of pollution at coal spoil heaps, soil reclamation is slow and requires development and use of microbial preparations, selected based on assessments of the biochemical parameters of soil and the extent of its contamination. The material for this study was mine soils sampled in three different zones (Ka, Kb, Kc) of the Korchakol coal spoil heap. The studied sanitary and chemical indicators did not exceed the approximate permissible concentrations (APC) / maximum allowable concentrations (MAC), except for oil products (in the Ka, Kb, Kc zones, the excess averaged 2.2, 1.4, 1.2 times, respectively). The study found a direct correlation between the zinc content and the enzymatic activity of polyphenol oxidase, the level of Ni and peroxidase, as well as an inverse correlation between the As and Cu concentrations with invertase and nitrite reductase, respectively. The index of bacteria of the *Escherichia coli* group (coliform bacteria) in different zones exceeded the standard values by 61 and 171 times. Even though the sanitary indicators studied do not exceed permissible levels, they can slow down growth and development of plants. Thus, successful reclamation of mine soils requires introduction of biological preparations based on microorganisms that biotransform heavy metals and rhizobacteria.

Keywords: Kemerovo Region, Kuznetsk Basin, enzymatic activity of soils, heavy metals, organic pollutants, sanitary and biological indicators, reclamation of contaminated soils, rhizobacteria, remediation

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Introduction

The large Kemerovo Region (Kuznetsk Basin) ranks first in Russia for coal production (Vylegzhanin, 2015). Most of the Kuznetsk Basin coal is mined in the Kemerovo, Leninsk-Kuznetsk, Prokopyevsk, Mezhdurechensk, Kiselevsk and Belovo disctricts (Manakov et al., 2018). Coal mining, in particular open-pit coal mining, enrichment, and storage of coal, as well as coal waste disposal, leads to depletion of fertile soils and an increase in the toxicological indicators of soil (Drozdova et al., 2021; Ismagilov et al., 2018). When developing coal heaps, the fertile soil layer is removed, and mine soils become exposed.

Soil enzymes contribute to the breakdown of complex organic and inorganic compounds, and participate in the mineralization of nutrients and their inclusion in the cycle of carbon (invertase, cellulase), nitrogen (nitrite reductase, asparaginase, urease, protease), and phosphorus (phosphatase) (Assemien et al., 2019; Fan et al., 2021; Sobat et al., 2021; Yinping et al., 2018). In addition, enzymes are responsible for detoxification of pollutants (hydrogen peroxide (catalase) and complex organic substances (peroxidase, polyphenol oxidase)), and also contribute to the remediation of polluted soils (Kaushal et al., 2018; Khosrozadeh et al., 2022; Liu et al., 2021).

Coal mining leads to the destruction of the topsoil and the disruption of the flow of subsurface and groundwater, resulting in a decrease in the biodiversity of plants and microorganisms (Fan et al., 2021). Subsequently, soil nutrient content and enzymatic activity decrease, while pathogenic microorganisms and toxic compounds accumulate (Nakayama and Tateno, 2021). In particular, the low enzymatic activity of the soil may indicate high concentrations of various pollutants, including heavy metals and metalloids, which serve as inhibitors for many groups of enzymes. As a result, degradation processes begin in the soil, which lead to the depletion of nutrients, vegetation biodiversity and beneficial microorganisms (Samuel et al., 2017).

The process of soil remediation makes it possible to restore technogenically disturbed territories, for transfer to forest or agricultural use. To select the method of remediation, a sanitary assessment of the soil is necessary to determine the degree of its contamination, using two groups of sanitary indicators (Mathew et al., 2017):

1. sanitary-chemical: the content of heavy metals and metalloids, PAHs, phenols, oil products, etc. [1, 2];
2. sanitary biological[3]:

a) sanitary-bacteriological: coliform index, enterococci index, content of pathogenic enterobacteria *Salmonella* and *Shigella*;

b) sanitary-epidemiological: eggs and larvae of helminths, cysts of intestinal pathogenic protozoa, larvae and pupae of synanthropic flies.

The purpose of this study was to study chemical and sanitary indicators of the quality of mine soils in coal heaps in the south of the Kemerovo Region (Kuznetsk Basin) for further selection of a rational method for the remediation of technogenically disturbed landscapes.

Materials and methods

The objects of the study were mine soil samples taken from the surface layer of the outer spoil heap of the Korchakol Mine (K) (Fig. 1). The total area of the dump is 499000 m2, the height reaches 100 m, and the steepness of the slopes varies from 1°–2° to 35°. The dump is characterized by sandy-argillaceous loose rocks and sparse vegetation; the age of its individual sections is from 5 to 30 years. The heap area is part of the dark coniferous taiga natural zone, located in the continental climate zone. Biological reclamation was partially located at the heap; sites of spontaneous combustion were also observed.

Mine soil samples were taken in autumn (November) 2021 at sub-zero temperatures, before snowfall, in accordance with generally accepted methods[4] (sampling depth was 0–20 cm). Sampling was located in three zones of the surface layer of the Korchakol coal heap in five repetitions::

- Zone "Ka" (age – 5 years) is a mixture of waste – rocks from coal enrichment (at least 86%) and overburden rocks (up to 14%), there is no vegetation in this zone. Sampling point coordinates: N 53°42′ E 87°25′.
- Zone "Kb" (age –15 years) undergoing technical stage of reclamation (filling with clay); no vegetation recorded. Sampling point coordinates: N 53°41′ E 87°25′.
- Zone "Kc" (age – 20 years) is at the biological stage of technogenic land reclamation, including trees planted here (*Pinus sylvestris* L.), shrubs (*Hippophaë rhamnoides* L.), and herbaceous plants (*Trifolium pratense* L. and *Melilotus albus* L); all plants found are characterized by

[1] SanPiN 42-128-4433-87. Sanitary standards for permissible concentrations of chemicals in the soil.

[2] SanPiN 1.2.3685-21. Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors for humans.

[3] SanPiN 2.1.3684-21. Sanitary and epidemiological requirements for the maintenance of territories of urban and rural settlements, for water bodies, drinking water and drinking water supply, atmospheric air, soils, residential premises, operation of industrial, public premises, organization and implementation of sanitary and anti-epidemic (preventive) measures.

[4] GOST 17.4.4.02–2017. Protection of Nature. Soils. Methods for taking and preparing samples for chemical, bacteriological, helminthological analysis.

Fig. 1. A satellite image from Google Maps of the coal heap of the Korchakol Open-Pit Mine. Ka, Kb, Kc – sampling zones.

a small height. Sampling point coordinates: N 53°41′ E 87°24′. N 53°41′ E 87°24′.

The formation of a fertile soil layer requires a certain content of readily available carbon, as well as the C/N ratio and the redox potential of soils, therefore, at the initial stages of the study, the following enzymes were selected: invertase, nitrite reductase, peroxidase, polyphenol oxidase (Antonov and Chmuzh, 2016; Kochkina, 2016; Li et al., 2020).

Invertase activity was determined using the Sun et al.'s (2021) method. Sucrose solution (Russia, SigmaTek), acetate buffer, copper reagent (5% $CuSO_4$*5H_2O (Russia, Yugreaktiv) + solution 25 g Na_2CO_3 (Russia, LenReaktiv), 25 g Rochelle salt (Russia, SigmaTek), 20 g $NaHCO_3$ (Russia, LenReaktiv), 200 g Na_2SO_4 (Russia, Yugreaktiv) in 1 liter of distilled water, in a ratio of 1:25), sodium hydrogen phosphate (Russia, "SigmaTek") and a molybdenum reagent (1 l 20% H_2SO_4 solution (Russia, LenReaktiv) + 5% ammonium molybdate solution (Russia, Yugreaktiv)) were used for the analysis.

Nitrite reductase activity was determined using the method of Liu et al. (2020). Calcium carbonate (Russia, LenReaktiv), sodium nitrite solution (Russia, Yugreaktiv), glucose solution (Russia, SigmaTek), distilled[5] water, aluminum alum, Griess reagent (Russia, LenReaktiv).

Peroxidase activity was determined using the method of Sun et al. (2021). The analysis was performed using hydroquinone solution (Russia, SigmaTek), hydrogen peroxide solution (Russia, Ecos-1), ethyl alcohol (Russia, Kemerovo Pharmaceutical Factory).

Polyphenol oxidase activity was determined using Qianxi. et al.'s (2022) method using hydroquinone solution (Russia, SigmaTek).

The optical density of all samples after thermostatting was measured using a UNICO spectrophotometer (Model 1201) (Russia, ProPribory).

Recent publications show that the main pollutants present in the coal of the Kemerovo Region are zinc, copper, nickel, arsenic, and mercury (Fotina et al., 2021; Osipova et al., 2015; Zhuravleva et al., 2015). Therefore, these heavy metals were selected to control the sanitary and chemical state of the study area. Content of these substances was determined according to standard methods[6, 7, 8]. In addition, in accordance with regulatory documents, the presence

[5] GOST 6709–72. Distilled water. Specifications.

[6] M-MVI-80-2008. Method for performing measurements of the mass fraction of elements in samples of soils, soils and bottom sediments using atomic emission and atomic absorption spectrometry methods.

[7] MU 31-11/05. Quantitative chemical analysis of soil samples, greenhouse soils, sapropels, silts, bottom sediments, solid wastes. Method for performing measurements of mass concentrations of zinc, cadmium, lead, copper, manganese, arsenic, mercury by inverse voltammetry (stripping analysis) using analyzers of the TA type.

[8] PND F 16.1:2:2.2.80-2013. Quantitative chemical analysis of soils. Method for measuring the mass fraction of total mercury in samples of soils, grounds, including greenhouse soils, clays and bottom sediments using an atomic absorption method using a RA-915M mercury analyzer.

of benzo(a)pyrene, phenols and oil products was analyzed[9, 10, 11], as well as sanitary-bacteriological and epidemiological indicators[12].

All sanitary-chemical and sanitary-biological parameters were determined in triplicate. For statistical processing was the Statistica for Windows v. 12.0 ("StatSoft, Inc.") software was used.

Results and discussion

The results of granulometric and physico-chemical analyzes of the studied soils of rocks are presented in Tables 1 and 2. It was found that according to the granulometric composition, the soils of rocks of the Ka, Kb, Kc zones belong to light loam, medium clay, and heavy loam, respectively. The soils of the Kb zone have a slightly alkaline reaction of the medium (8.6), while the soils of the Ka and Kc zones have a pH close to neutral (7.4 and 7.5, respectively). The studied samples are characterized by a low level of humidity, which may indicate an insufficient ability of coal heaps to retain water. The studied samples were characterized by a high degree of saturation with bases, so the restored soils do not need liming. In all samples, a low content of organic matter is observed, therefore, in order to improve fertility during reclamation, additional sources of humic acids will be required. In addition, a low content of total nitrogen, calcium and magnesium was found, suggesting the need for mineral fertilizers.

Since inorganic and organic pollutants seriously affect the biochemical parameters of the soil, the assessment of enzyme activity makes it possible to assess the state of the soil (Dadenko et al., 2013). The results of determining the enzymatic activity of the studied rock soil samples are presented in Table 3; the average values of these indicators are shown in Figs. 2–4.

Figure 2 shows that invertase activity increases as the reclamation works progress: its average value for rock soils taken from the surface layer of the Korchakol coal heap in the Kc zone is almost twice as high as the same indicator for the Ka zone. This could result from the mine soils of the Ka zone containing a small amount of polysaccharides, while the root systems of vegetation in the Kc zone contributes to an increase in their concentration. Thus, it can be concluded that the native microflora of this area mainly uses polysaccharides as a carbon source.

The study of the nitrite reductase activity of the soils of the Korchakol coal heap showed that in the Kc zone this parameter is 1.5 times higher than in the Ka zone (Fig. 3). This may indicate an increased need for nitrogen caused by the biological processes of microorganisms and plants.

The data presented in Fig. 4 show a significant decrease in the peroxidase and polyphenol oxidase activities of the soil in the Kc zone compared to the Ka and Kb zones (by 3.5 and 3.2 times, respectively). This can be because the content of organic pollutants decreases in the mine soils from the Ka zone to the Kc zone (Table 4), which, in turn, affects the production of the above enzymes. However, these pollutants were not completely degraded; this can be established by the fact that enzyme activity is still observed in the area of the biological stage of reclamation.

Inorganic and organic pollutants in high concentrations have a toxic effect on plants and microorganisms. Therefore, to determine a consortium of microorganisms that remediate contaminated sites, it is necessary to assess the degree of contamination. The results of the study of the soils of the Korchakol coal dump in terms of sanitary and chemical indicators are presented in Table 4. APC/MAC and average values of pollutant concentrations in the studied areas are shown in Figs. 5 and 6.

We found that high concentrations of zinc, copper, nickel, arsenic are observed in the soils of the Korchakol heap (Fig. 5), which is consistent with the data of other studies (Akinina et al., 2017; Fotina et al., 2021). It is known that an increased content of zinc can lead to slower plant growth and cause leaf chlorosis (Jain et al., 2020), because of Zn-chlorophyll derivatives, which cannot perform photosynthesis (Küpper and Andresen, 2016). A high copper concentration negatively affects photosynthesis, the absorption of phosphorus from the soil, and also promotes the synthesis of reactive oxygen and lipid peroxidation in plants. This leads to high oxidative stress, which can cause plant death (Angulo-Bejarano et al., 2021). Excessive nickel concentrations can provoke a decrease in biomass growth, inhibit the formation of lateral roots, disrupt the nutrient balance in the plant, and lead to leaf chlorosis (Hassan et al., 2019). Finally, an increased content of arsenic can lead to a decrease in germination and yield of plants, growth of shoots, roots and leaves, slow down the process of photosynthesis, and also cause plant death due to oxidative stress (Martins et al., 2019; Zhang et al.,

[9] FR.1.31.2008.01725. Method for measuring the mass fraction of benzo(a)pyrene in soils, soils and sewage sludge using high performance chromatography.

[10] PND F 16.1:2.3:3.44-05. Quantitative chemical analysis of soils. Method for performing measurements of the mass fraction of volatile phenols in soil samples, sewage sludge and waste using the photometric method after stripping with water vapor.

[11] PND F 16.1:2.2.22-98. Quantitative chemical analysis of soils. Methodology for measuring the mass fraction of oil products in mineral, organogenic, organo-mineral soils and bottom sediments using IR spectrometry.

[12] SanPiN 2.1.3684-21. Sanitary and epidemiological requirements for the maintenance of territories of urban and rural settlements, for water bodies, drinking water and drinking water supply, atmospheric air, soils, residential premises, operation of industrial, public premises, organization and implementation of sanitary and anti-epidemic (preventive) measures.

Table 1. Granulometric analysis of soils of the surface layer of the Korchakol coal heap.

Size of mechanical particles, mm	% of total particles		
	Zone Ka	Zone Kb	Zone Kc
Over 10.0	0	0	0
10.0–5.0	0	0	0
5.0–2.0	0	0	0
2.0–1.0	0	0	0
1.0–0.5	0.4	1.9	0.1
0.5–0.25	0.2	0.2	0.2
0.25–0.1	0.3	0.1	0.3
0.1–0.05	55.4	14.6	10.4
0.05–0.01	22.7	38.7	39.3
0.01–0.002	15.8	27.6	28.4
Less than 0.002	5.2	16.9	21.3

Table 2. Physico-chemical parameters of soils of the surface layer of the Korchakol coal heap.

Indicator	Zone		
	Ka	Kb	Kc
pH of water extract	7.4 ± 0.1	8.6 ± 0.1	7.5 ± 0.01
Hygroscopic humidity, %	2.10 ± 0.09	5.16 ± 0.23	4.34 ± 0.21
Organic matter, %	1.15 ± 0.04	3.48 ± 0.15	4.08 ± 0.20
Degree of saturation with bases, %	98.40 ± 4.52	99.14 ± 4.85	99.66 ± 4.73
Total nitrogen, %	0.17 ± 0.01	0.21 ± 0.01	1.2 ± 0.04
Calcium, mmol/100 g	0.45 ± 0.02	0.58 ± 0.02	0.79 ± 0.02
Magnesium, mmol/100 g	0.55 ± 0.02	0.64 ± 0.03	0.99 ± 0.04

2021). Also note that zinc and arsenic belong to the first hazard class, while copper and nickel to the second[13].

The MAC of benzo(a)pyrene was not exceeded in any of the studied samples (Fig. 6). The content of oil products in the studied soil of the Ka sample (mean value 160.872 mg/kg) was more than double the background value, but, for the heap of the Kc zone subject to biological reclamation, this parameter is almost equal to the background content (86.544 mg/kg) (Fig. 5).

The content of phenols in the studied samples did not exceed 1 mg/kg (Fig. 6). Phenolic pollution of soils can be caused by both biogenic and technogenic factors. The complex nature of this type of pollution, as well as the chemical and typological diversity of soils inhibits using fixed MAC for the total content of phenols. Based on the published data, at a concentration of phenolic substances from 1 to 5 mg/kg, the pollution level is interpreted as medium (Ieronova and Bezukhova, 2014). Thus, the studied mine soils in all zones have a low level of contamination with phenolic substances.

The amount of mercury in the soils of the Korchakol coal dumps did not exceed MA^{C14} (Fig. 6), which does not contradict published data (Zhuravleva et al., 2015). This is due to the impact of reclamation measures that contribute to the purification of soils from pollutants.

Correlation coefficients (*r*) and significance coefficients (*p*) were calculated to reveal the relationship between metal content and enzyme activity. The sig-

[13] MU 2.1.7.730-99. Guidelines. Soil, cleaning of populated areas, household and industrial waste, sanitary protection of the soil. Hygienic assessment of soil quality in populated areas.

[14] SanPiN 1.2.3685-21. Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors for humans.

Table 3. Enzymatic activity of soils of the surface layer of the Korchakol coal heap (mean ± SE).

Indicator	Zone					
	Ka		Kb		Kc	
Invertase activity, mg of sucrose, split 1 g of soil for 1 hour	Ka_1	2.197 ± 0.062	Kb_1	3.865 ± 0.102	Kc_1	4.295 ± 0.164
	Ka_2	2.284 ± 0.074	Kb_2	4.253 ± 0.115	Kc_2	5.218 ± 0.231
	Ka_3	2.140 ± 0.063	Kb_3	4.154 ± 0.123	Kc_3	4.124 ± 0.185
	Ka_4	2.161 ± 0.085	Kb_4	4.647 ± 0.098	Kc_4	5.081 ± 0.193
	Ka_5	2.185 ± 0.053	Kb_5	3.846 ± 0.075	Kc_5	4.768 ± 0.205
Nitrate reductase activity, mg reduced NO_2^- per 1 g of soil in 24 hours	Ka_1	0.380 ± 0.012	Kb_1	1.536 ± 0.086	Kc_1	2.378 ± 0.063
	Ka_2	0.316 ± 0.007	Kb_2	1.974 ± 0.092	Kc_2	2.643 ± 0.086
	Ka_3	0.410 ± 0.018	Kb_3	1.246 ± 0.066	Kc_3	2.014 ± 0.051
	Ka_4	0.597 ± 0.025	Kb_4	2.211 ± 0.094	Kc_4	2.936 ± 0.069
	Ka_5	0.451 ± 0.021	Kb_5	2.675 ± 0.083	Kc_5	3.476 ± 0.094
Peroxidase activity, mg of formed 1.4-p-benzoquinone per 1 g of soil in 30 min	Ka_1	1.545 ± 0.068	Kb_1	0.856 ± 0.035	Kc_1	0.568 ± 0.014
	Ka_2	1.427 ± 0.053	Kb_2	0.921 ± 0.029	Kc_2	0.294 ± 0.006
	Ka_3	1.638 ± 0.077	Kb_3	1.058 ± 0.051	Kc_3	0.316 ± 0.011
	Ka_4	1.402 ± 0.061	Kb_4	0.716 ± 0.026	Kc_4	0.842 ± 0.023
	Ka_5	1.430 ± 0.064	Kb_5	0.693 ± 0.034	Kc_5	0.169 ± 0.004
Polyphenol oxidase activity, mg of formed 1.4-p-benzoquinone per 1 g of soil in 30 min	Ka_1	1.101 ± 0.031	Kb_1	1.145 ± 0.046	Kc_1	0.564 ± 0.009
	Ka_2	1.213 ± 0.048	Kb_2	0.956 ± 0.032	Kc_2	0.429 ± 0.016
	Ka_3	1.167 ± 0.056	Kb_3	0.843 ± 0.028	Kc_3	0.683 ± 0.017
	Ka_4	1.054 ± 0.025	Kb_4	1.058 ± 0.041	Kc_4	0.267 ± 0.003
	Ka_5	1.182 ± 0.057	Kb_5	0.732 ± 0.036	Kc_5	Kc_5

nificance coefficient in all cases was less than 0.05. Samples of soils of the surface layer of the Korchakol coal heap showed a high direct relationship between zinc content and polyphenol oxidase activity (r = 0.84), as well as nickel content and peroxidase activity (r = 0.83). The obtained direct dependence contradicts previously published data (Pleshakova et al., 2010; Rusyaeva et al., 2019; Tang et al., 2022) and indicates the possible presence of other factors that reduce the effect of metals. These factors may include the following: amount of substrate, C/N ratio in soil, soil pH, microbiome composition, mass fraction of humus, amount of mineral compounds, humidity (Dadenko et al., 2013; Soldatov et al., 2020; Tovstik and Olkova, 2021; Xu et al., 2020). High inverse correlation was observed between the contents of copper and nitrite reductase (r = −0.92), as well as arsenic and invertase (r = −0.84). This dependence is consistent with the data of other studies (Black et al., 2019; Dadenko et al., 2013; Govarthanan et al., 2018).

Growth and development of plants and useful microflora are affected not only by the concentration of heavy metals and organic pollutants, but also by the sanitary and biological indicators of the soil[15], data on which for the surface layer of the Korchakol coal dump are presented in Table 5. According to the results of the research, there are no enterococci, pathogenic enterobacteria, eggs and larvae of helminths (viable), cysts of pathogenic protozoa, larvae and pupae of synanthropic flies in the samples. Bacteria of the Escherichia coli group (ECG) were also not found in soil samples from the Ka zone; at the same time, in zones Kb and Kc, the ECG (coliform) index exceeds the norm[16] by about 61 and 171 times, respectively. Apparently, the Kb and Kc zones have optimal conditions for the growth of microorganisms; at the same

[15] MU 2.1.7.730-99. Guidelines. Soil, cleaning of populated areas, household and industrial waste, sanitary protection of the soil. Hygienic assessment of soil quality in populated areas.

[16] SanPiN 2.1.3684-21. Sanitary and epidemiological requirements for the maintenance of territories of urban and rural settlements, for water bodies, drinking water and drinking water supply, atmospheric air, soils, residential premises, operation of industrial, public premises, organization and implementation of sanitary and anti-epidemic (preventive) measures.

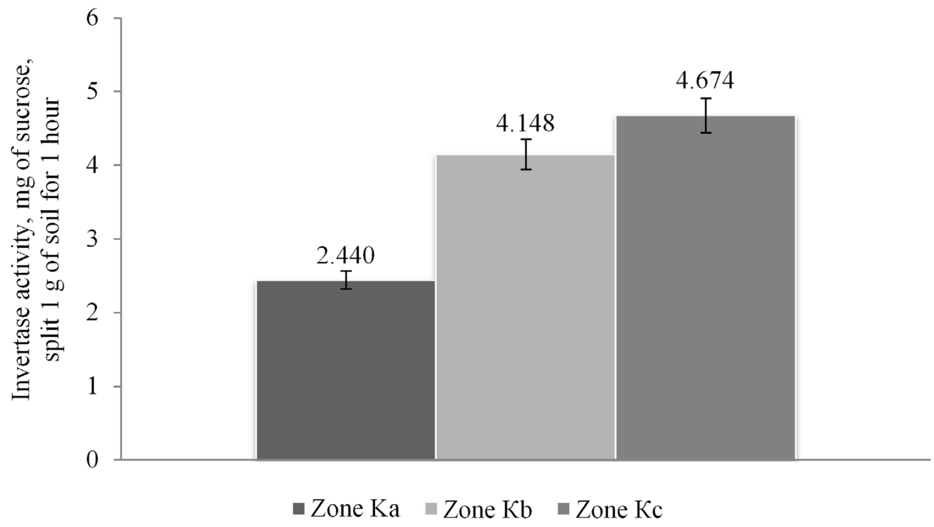

Fig. 2. Invertase activity of soils in the surface layer of the Korchakol coal heap (mean ± SE).

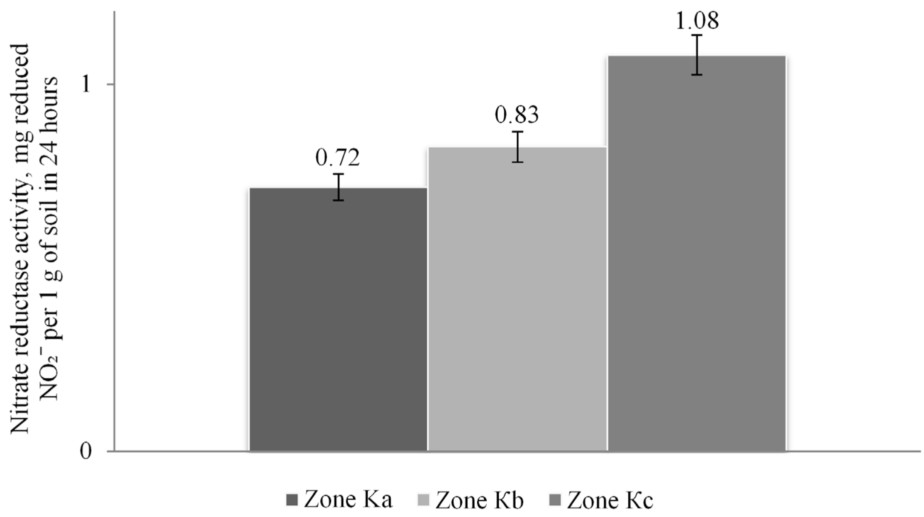

Fig. 3. Nitrite reductase activity of soils in the surface layer of the Korchakol coal heap (mean ± SE).

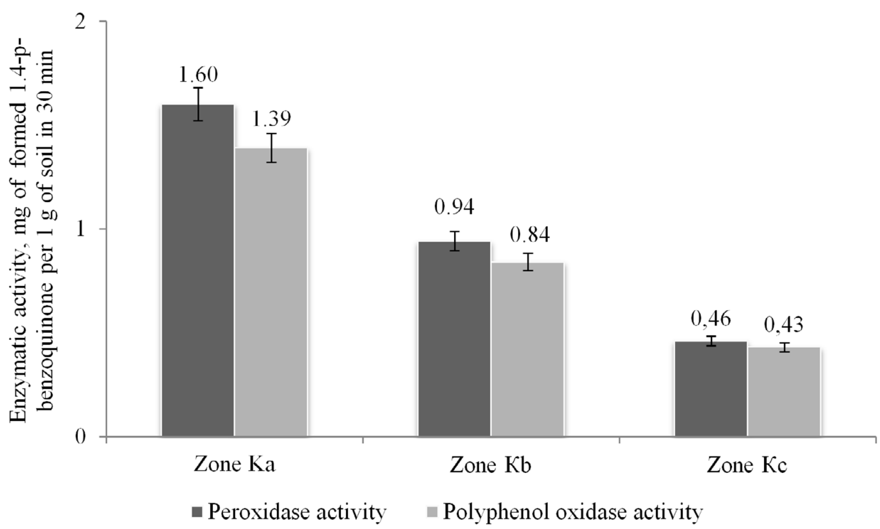

Fig. 4. Peroxidase and polyphenol oxidase activity of soils of the surface layer of the Korchakol coal heap (mean ± SE).

Table 4. Sanitary and chemical indicators of soils of the surface layer of the Korchakol coal heap; “n/n” – the indicator is not standardized.

Indicator	MAC[17]/ APC[18]/	Zone: Ka		Zone: Kb		Zone: Kc	
Zinc (gross content), mg/kg	110[18]	Ka_1	60.187 ± 2.759	Kb_1	53.452 ± 2.156	Kc_1	48.556 ± 1.956
		Ka_2	61.234 ± 3.015	Kb_2	52.363 ± 2.349	Kc_2	47.234 ± 1.894
		Ka_3	60.568 ± 2.963	Kb_3	52.951 ± 2.448	Kc_3	48.191 ± 2.056
		Ka_4	59.894 ± 2.565	Kb_4	54.184 ± 2.128	Kc_4	49.352 ± 2.148
		Ka_5	60.819 ± 3.003	Kb_5	53.079 ± 2.356	Kc_5	47.848 ± 1.920
Copper (gross content), mg/kg	66[18]	Ka_1	22.341 ± 0.987	Kb_1	15.906 ± 0.623	Kc_1	10.740 ± 0.415
		Ka_2	22.644 ± 1.004	Kb_2	15.231 ± 0.587	Kc_2	10.327 ± 0.276
		Ka_3	23.104 ± 1.216	Kb_3	16.361 ± 0.713	Kc_3	11.167 ± 0.348
		Ka_4	22.377 ± 0.855	Kb_4	14.815 ± 0.346	Kc_4	10.078 ± 0.500
		Ka_5	22.185 ± 0.783	Kb_5	14.557 ± 0.469	Kc_5	9.856 ± 0.281
Nickel (gross content), mg/kg	40[18]	Ka_1	24.128 ± 1.005	Kb_1	18.751 ± 0.865	Kc_1	13.841 ± 0.516
		Ka_2	24.896 ± 1.225	Kb_2	19.141 ± 0.921	Kc_2	14.026 ± 0.631
		Ka_3	24.314 ± 1.119	Kb_3	19.759 ± 0.934	Kc_3	14.338 ± 0.522
		Ka_4	25.373 ± 1.342	Kb_4	20.239 ± 0.756	Kc_4	15.124 ± 0.684
		Ka_5	24.184 ± 0.989	Kb_5	20.016 ± 1.005	Kc_5	14.959 ± 0.348
Arsenic (gross content), mg/kg	5[18]	Ka_1	4.313 ± 0.121	Kb_1	3.043 ± 0.124	Kc_1	1.995 ± 0.085
		Ka_2	4.658 ± 0.203	Kb_2	3.531 ± 0.110	Kc_2	2.262 ± 0.114
		Ka_3	4.066 ± 0.043	Kb_3	3.919 ± 0.098	Kc_3	2.738 ± 0.099
		Ka_4	4.237 ± 0.109	Kb_4	3.235 ± 0.086	Kc_4	2.515 ± 0.054
		Ka_5	4.210 ± 0.098	Kb_5	4.149 ± 0.146	Kc_5	3.127 ± 0.123
Mercury (gross form), mg/kg	2.1[17]	Ka_1	0.052 ± 0.003	Kb_1	0.036 ± 0.002	Kc_1	0.015 ± 0.001
		Ka_2	0.059 ± 0.002	Kb_2	0.024 ± 0.001	Kc_2	0.023 ± 0.001
		Ka_3	0.065 ± 0.004	Kb_3	0.041 ± 0.002	Kc_3	0.018 ± 0.001
		Ka_4	0.054 ± 0.002	Kb_4	0.034 ± 0.001	Kc_4	0.023 ± 0.001
		Ka_5	0.045 ± 0.002	Kb_5	0.046 ± 0.001	Kc_5	0.031 ± 0.002
Benz(a)pyrene, mg/kg	0.02[17]	Ka_1	0.020 ± 0.005	Kb_1	0.014 ± 0.001	Kc_1	
		Ka_2	0.019 ± 0.006	Kb_2	0.013 ± 0.001	Kc_2	
		Ka_3	0.018 ± 0.002	Kb_3	0.013 ± 0.001	Kc_3	≤0.010
		Ka_4	0.019 ± 0.007	Kb_4	0.015 ± 0.001	Kc_4	
		Ka_5	0.017 ± 0.005	Kb_5	0.011 ± 0.001	Kc_5	
Oil products, mg/kg	73.6[19]	Ka_1	161.234 ± 8.012	Kb_1	105.349 ± 5.107	Kc_1	86.348 ± 4.210
		Ka_2	160.319 ± 7.942	Kb_2	106.217 ± 4.234	Kc_2	88.102 ± 3.861
		Ka_3	161.075 ± 8.105	Kb_3	104.315 ± 4.751	Kc_3	86.318 ± 4.105
		Ka_4	161.237 ± 7.346	Kb_4	105.284 ± 5.106	Kc_4	85.294 ± 3.756
		Ka_5	160.496 ±7.812	Kb_5	106.101 ± 5.245	Kc_5	86.657 ± 4.208
Phenol, mg/kg	н/н	Ka_1	0.915 ± 0.041	Kb_1	0.759 ± 0.027	Kc_1	0.218 ± 0.015
		Ka_2	0.751 ± 0.036	Kb_2	0.613 ± 0.021	Kc_2	0.134 ± 0.009
		Ka_3	0.824 ± 0.042	Kb_3	0.598 ± 0.019	Kc_3	0.259 ± 0.013
		Ka_4	0.917 ± 0.046	Kb_4	0.716 ± 0.025	Kc_4	0.187 ± 0.008
		Ka_5	0.862 ± 0.035	Kb_5	0.653 ± 0.026	Kc_5	0.210 ± 0.016

[17, 18] SanPiN 1.2.3685-21. Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors for humans.

[19] The background content of oil products for the city of Novokuznetsk is presented (Zagryaznenie..., 2021).

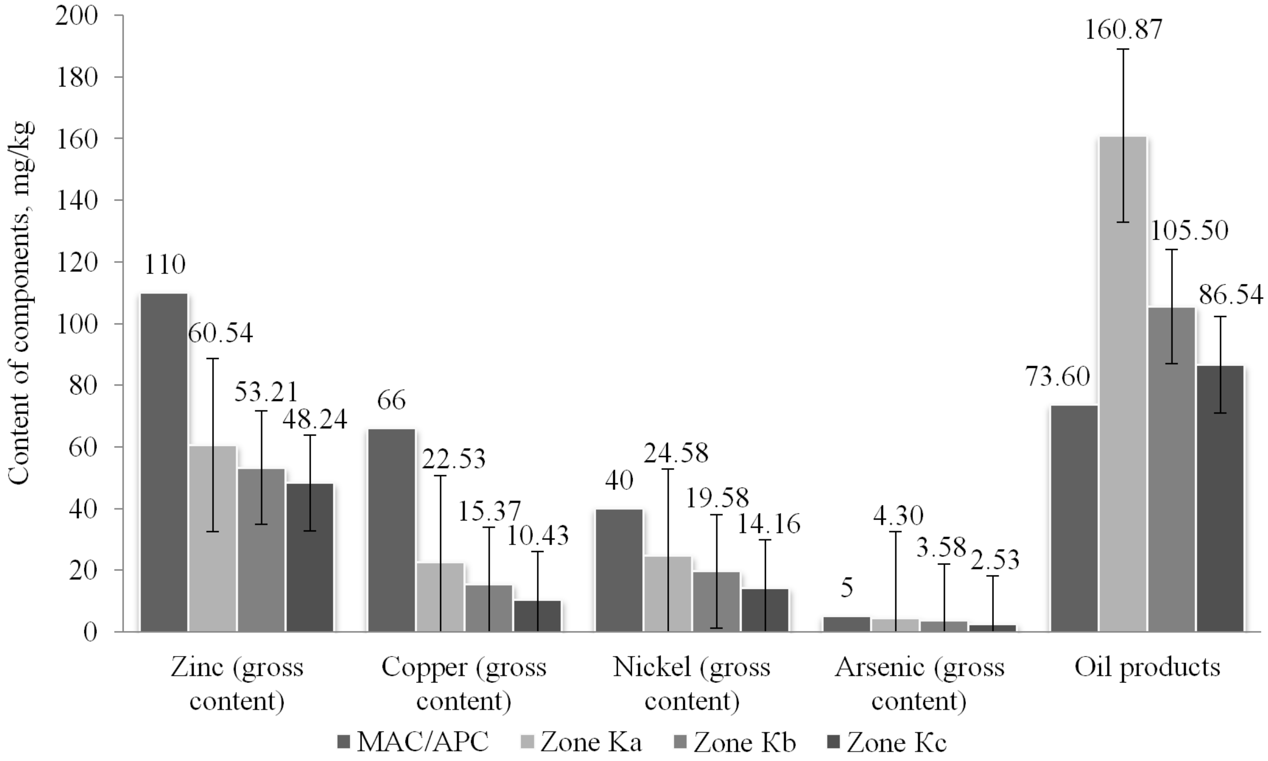

Fig. 5. The content of heavy metals/metaloids and oil products in the rock soils of the surface layer of the Korchakol coal heap (mean ± SE).

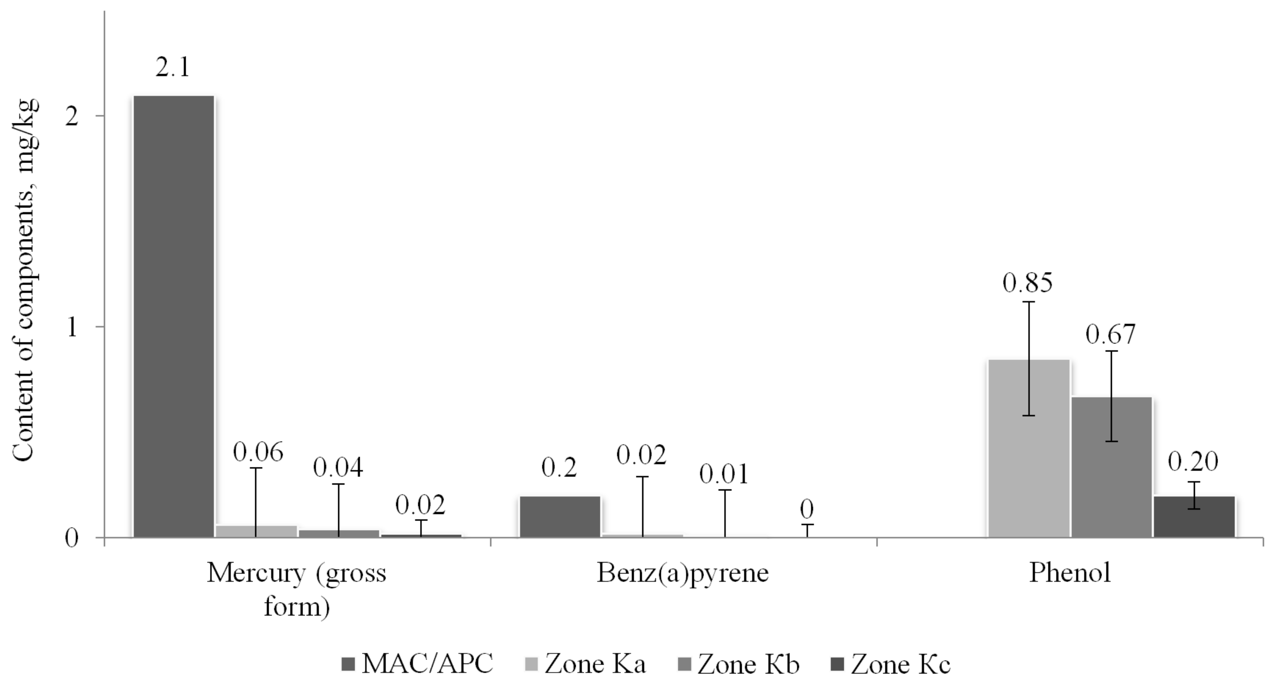

Fig. 6. The content of mercury, benzo(a)pyrene, phenols in the soils of rocks of the surface layer of the Korchakol coal heap (mean ± SE).

Table 5. Sanitary and biological indicators of soils of the surface layer of the Korchakol coal heap; “n/a” – not allowed; “n/d” – not detected.

Indicator	Norm[20]	Zone					
		Ka		Kb		Kc	
ECG Index	1–9	Ka_1	n/d	Kb_1	643.98 ± 31.50	Kc_1	1598.54 ± 63.23
		Ka_2		Kb_2	453.21 ± 20.28	Kc_2	1456.29 ± 65.29
		Ka_3		Kb_3	567.30 ± 28.18	Kc_3	1673.67 ± 82.51
		Ka_4		Kb_4	482.49 ± 21.02	Kc_4	1435.83 ± 69.37
		Ka_5		Kb_5	631.25 ± 30.65	Kc_5	1549.11 ± 65.67
Enterococci Index	1–9	Ka_1	n/d	Kb_1	n/d	Kc_1	n/d
		Ka_2		Kb_2		Kc_2	
		Ka_3		Kb_3		Kc_3	
		Ka_4		Kb_4		Kc_4	
		Ka_5		Kb_5		Kc_5	
Pathogenic enterobacteria *Salmonella* sp. and *Shigella* sp.	n/a	Ka_1	n/d	Kb_1	n/d	Kc_1	n/d
		Ka_2		Kb_2		Kc_2	
		Ka_3		Kb_3		Kc_3	
		Ka_4		Kb_4		Kc_4	
		Ka_5		Kb_5		Kc_5	
Viable eggs and larvae of helminths	1–9	Ka_1	n/d	Kb	n/d	Kc_1	n/d
		Ka_2		Kb_2		Kc_2	
		Ka_3		Kb_3		Kc_3	
		Ka_4		Kb_4		Kc_4	
		Ka_5		Kb_5		Kc_5	
Cysts of pathogenic protozoans	1–9	Ka_1	n/d	Kb_1	n/d	Kc_1	n/d
		Ka_2		Kb_2		Kc_2	
		Ka_3		Kb_3		Kc_3	
		Ka_4		Kb_4		Kc_4	
		Ka_5		Kb_5		Kc_5	
Larvae and pupae of synanthropic flies	n/a	Ka_1	n/d	Kb_1	n/d	Kc_1	n/d
		Ka_2		Kb_2		Kc_2	
		Ka_3		Kb_3		Kc_3	
		Ka_4		Kb_4		Kc_4	
		Ka_5		Kb_5		Kc_5	

[20] SanPiN 2.1.3684-21. Sanitary and epidemiological requirements for the maintenance of territories of urban and rural settlements, for water bodies, drinking water and drinking water supply, atmospheric air, soils, residential premises, operation of industrial, public premises, organization and implementation of sanitary and anti-epidemic (preventive) measures.

time, the general sanitary-chemical state of the Ka zone inhibits the development of the natural microbiome.

Conclusion

In the direction from the Ka zone to the Kc zone, the activity of invertase and nitrite reductase increased; peroxidase and polyphenoloxidase activities, on the contrary, decreased. This may indicate that the technical and biological stages of reclamation have a positive effect on the enzymatic activity of rock soils, but it remains small. Also, in these territories, the values of all studied sanitary and chemical indicators are consistently decreasing; the content of pollutants does not exceed the established APC. Thus, it can be assumed that the ongoing reclamation contributes to the restoration of anthropogenically disturbed soils. At the same time, the concentration of pollutants remains significant, and they can negatively affect the vital activity of plants growing in the vicinity of the coal spoil heap, so in the future additional measures will be required to clean the soil from heavy metals.

Statistical analysis of biochemical and sanitary-chemical parameters of rock soils of the Korchakol coal heap revealed a significant negative correlation between copper content and nitrite reductase activity; between arsenic levels and invertase activity. At the same time, zinc and polyphenol oxidase, as well as nickel and peroxidase, show a direct correlation with each other. In the future, it is planned to study the dependence of the enzymatic activity of these territories on the amount of the substrate (phenol, aromatic compounds, PAHs and alcohols), the composition of the microbiome, humus, and the amount of mineral compounds. In addition, it is necessary to assess the impact of heavy metals on the microbiome of rock soils. In this case, it will be necessary to take into account their duration of exposure to pollutants, since the negative impact of these elements manifests itself in the long term (Ivanova et al., 2020).

In the study of sanitary and bacteriological indicators of the surface layer of the coal dump, it was found that the coliform index in the Kb and Kc zones exceeds the established norm for the permissible level of soil contamination by more than 60 times. Probably, these zones have more favorable conditions for the development and vital activity of the microbiota compared to the Ka zone. It is also planned to take samples in the spring to monitor the state of the heap[21].

At the moment, soil samples of the surface layer of the Korchakol coal heap have been analyzed for agrophysical, agrochemical, biochemical and sanitary indicators; in addition, microorganisms were isolated from the soils. Based on the results obtained and further research, it is planned to select certain types of plants and microorganisms for the remediation of technogenically disturbed lands. When developing a microbial preparation, first of all, it is necessary to select the most promising strains that biotransform heavy metals. This is necessary to increase the survival of plant cultures used in the biological stage of recultivation (Saha et al., 2021). Particular attention should be paid to strains capable of neutralizing zinc and arsenic, which pose the greatest threat in contaminated areas[22]. Also, for better plant survival, it is necessary to introduce rhizobacteria (Saha et al., 2021) and bacterial producers of substances with antimicrobial activity that can suppress the metabolism of ECG to reduce the risk of infection of agricultural products (Lukin and Marchuk, 2011). Thus, conducted and planned studies will be used in the future to develop a biological product that is best suited for the remediation of the studied area (Tretyakova, 2018).

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ORCID

E.E. Vorobyeva 0000-0001-6362-7589
N.V. Fotina 0000-0002-7655-0258
L.K. Asyakina 0000-0003-4988-8197
M.A. Osintseva 0000-0002-4045-8054
A.Yu. Prosekov 0000-0002-5630-3196

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