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IMPACT OF BIOREMEDIATION TECHNIQUES ON HEAVY METAL DYNAMICS IN EXTREMELY HIGH-MOUNTAINOUS CONDITIONS

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Abstract. *In high mountain places, soil pollution has long-term effects, since natural self-purification is time-consuming because of the low temperatures. It is widely known that the process of petroleum product degradation in natural conditions has a biogeochemical nature, with a pivotal role played by the activity of a complex of specific microorganisms that facilitate complete pollutant mineralization. Due to this fact, the most effective environmental clean-up methods for oil pollution involve microbiological approaches, which essentially entail introducing active strains of hydrocarbon-degrading organisms into the ecosystem. The article aims to investigate the effectiveness of bioremediation methods for soil contaminated with petroleum products, focusing on heavy metals in particular. This paper examined changes in heavy metals in soil that had been contaminated by oil derivatives, both before and after treatment. The Kumtor's, is 4000 meters above sea level, and soils were examined for their As, Pb, Cu, Cr, and Ni levels. In addition, contaminated soil was treated in the warm season by bioaugmentation. A comparative analysis of heavy metal content in high-altitude soils has been conducted before and after bioremediation processes. The practical significance of the obtained results lies in their applicability in the development of effective techniques for cleaning soil from heavy metals, particularly in mountainous terrain.*

Keywords*: aerobic bacteria, phytotoxicity, adaptation, soil biological activity, toxic compounds.*

Introduction

Soil is a dynamic, multi-component system that has the properties of animate and inanimate nature. Air, water, solid rock, and living organisms interact in the soil. The soil consists of several layers, which differ in physical, chemical, biological, and mineralogical properties. Soil types are influenced by climate, topography, and the activity of living organisms. Soil is also the first protective layer of groundwater, filtering out organic and inorganic pollutants [1], [2]. The soil cover is a vital component of an ecosystem, and its proper functioning is essential for maintaining its balance. This underscores the necessity to support and optimize soil conditions and, when necessary, engage in intensive soil restoration. It's worth noting that soil resources are finite and, in cases of significant degradation, may often be irreversibly depleted and difficult to regenerate[3].

Pollution of soil and groundwater causes many problems in the environment. In this regard, the scale and destructiveness of contamination are mostly determined by the chemical composition of the pollutants and the characteristics of the soil cover. Of particular concern are heavy metals and petroleum products.

Concentrations of heavy metals in soil are increasing because of anthropogenic activities, mainly related to the technogenic process [4]. Heavy metals have properties such as toxicity, persistence, and lack of biodegradation. In any soil, heavy metals are contained in very small quantities, being a micronutrient for microorganisms, plants, and animals. At high concentrations, heavy metals can inhibit various cellular processes [5]–[8]. The results of numerous studies indicate that metals such as Pb, Cd, and Ni cause some diseases in humans and animals [9]–[11]. Metal pollution is becoming a serious and widespread environmental threat, especially in urban areas [12]. The main threat is considered their accumulation in the soil environment, microorganisms exhibit the capacity to form new compounds while existing in various chemical forms of substances remaining equally toxic [13]. Among the primary pollutants, it is worth highlighting Al, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn, and some radionuclides [14].

With the beginning of the development of the oil industry, oil has become a serious environmental pollutant. Oil pollution occurs during exploration, transportation, storage, and processing [15]. Soil contamination by petroleum products triggers several processes that affect biotic and abiotic factors. Specifically, the quantity of microorganisms and their level of activity play a significant role for plants [16]. A decrease in metabolic activity and the quantitative composition of microorganisms leads to the formation of a dense membrane, disrupting the normal processes of water and air circulation. Soil composition and structure, water content, type of organic matter, and composition and amount of contaminated petroleum products give the contaminated soil various physical and chemical properties. Oil derivatives can be biodegraded naturally, but the presence of heavy metals can slow down the biodegradation of oil [17]. In this paper, we used bioremediation method namely biomtisulation to clean up contaminated soil. Many scientists [16][18][19] clearly highlight the advantages of bioremediation method such as compliance with the principles of sustainable management, exclusion of hazardous chemical compounds, possibility of complete degradation of pollutants, significant economic effect at minimal cost, as well as the ability to adapt to each cleaning process depending on specific problems, conditions and expected results. This approach preserves the natural biological properties of the soil, creating optimal conditions for the formation of soil micro- and microbiota with high biological activity. As a result, optimal conditions for the functioning of the "soil – soil biota – plant" system components are formed [8][20][21]. These processes create prerequisites for effective bioremediation of heavy metal-contaminated soils and their quality regeneration, as well as preventive measures against biological and chemical soil degradation [2][4][22].

This study investigated the effects of oil spills and soil bioremediation techniques on soil As, Pb, Cu, Cr, and Ni levels.

Materials and Methods

Soils contaminated with oil were studied in the soil cover of the territory located at an altitude exceeding 4000 meters above sea level (Kumtor). The object under study place is located in a partially glaciated permafrost zone on the north-western slope of the Ak-Shyirak Range in the Tien Shan Mountains. The climate of the area where the enterprise is located is alpine, and continental, with long cold winters and short cool summers. At this place, soil samples were taken from four oil-contaminated sites, and control samples were taken 500 meters from these sites in summer. The soil samples were taken in the autumn also for comparison content of considered metalloids and metals in polluted soils. Collected samples were treated with biostimulation for 3 months (08/06-30/09)

The samples were collected from a restricted area. Therefore, we could only collect a few samples. Soil samples were collected using the envelope method. Analyses were performed on an ICP-AES OPTIMA 5300DV atomic emission

During experimental research, 60 g/m² of mineral fertilizers were applied as amendments in a ratio of N: P: K=16:16:16. This composition included 16% inorganic nitrogen, 16% pentoxide phosphorus, and 16% potassium oxide, manually mixed in samples of contaminated soils before addition. Special attention was given to supporting a group of previously identified local bacterial strains, including Pseudomonas fluorescens P1, Rhodococcus Rhodococcus R3, and Flavobacterium K1 [18,19].

On the surface undergoing biostimulation a mixture of 30 milliliters was introduced and subsequently mixed. Throughout each study, a moisture level of 80% was maintained. The soil used in the experiments was tilled every 14 days to ensure proper aeration processes.

Through the application of systemic analysis, the research managed to focus on the effectiveness of bioremediation methods and their appropriateness for use in purifying oil-contaminated soils from heavy metals. This method involves a comprehensive search for optimal solutions regarding risk management, and variability in approaches to practical implementation of regenerative and preventive measures while relying on indicators of expected method effectiveness.

Results and discussion

The concentration of metals and metalloids in the soil of Kumtor is demonstrated in Table 1.

Elements	Concentration (mg/kg)									
	Control site		Site #1		Site #2		Site #3		Site #4	
	08.06	30.09	08.06	30.09	08.06	30.09	08.06	30.09	08.06	30.09
Al	20674	16803	7515	6416	6606	7489	8244	6649	6992	7641
Ca	21599	23556	18524	17569	16706	17334	19334	16642	17519	17540
Fe	33002	31143	25755	25297	23402	28057	27109	25179	26466	27599
K	2597	2382	1248	1180	1086	1505	1358	1339	1214	1478
Mg	11674	10539	5365	5001	4860	5599	5718	5192	5068	5636
P	738	371	723	356	611	362	761	349	710	346
Ti	674	219	266	225	227	223	278	232	261	241
Mn	693	652	520	524	479	587	591	593	547	628
Na	249	268	203	174	161	128	163	143	207	155
Ba	143	133	216	203	193	277	235	227	219	272
As	17	18	14	16	13	15	17	16	15	16
Pb	21	21	12	16	10	13	14	13	12	14
Cr	39	34	16	17	15	18	18	15	14	21
Cu	30	27	35	58	34	40	38	38	34	39
Ni	33	31	21	23	18	24	23	22	21	25
Co	15	14	10	11	10	11	11	9	11	12
Sr	72	23	48	14	45	21	53	16	46	18
V	43	40	18	16	18	19	17	19	19	18
Y	12	2	7	3	6	4	7	2	7	3
Zn	101	84	75	65	66	74	73	67	69	79
Zr	4	2	7	4	6	2	7	3	7	1

Table 1. The concentration of elements in sampling sites at Kumtor

The average concentration of As, Pb, Cr, Cu, and Ni in summer is 15.2, 13.8, 20.4, 34.2, and 23.2 mg/kg, respectively. For the month average concentration of considered metalloids and metals increased As 1.07, Pb 1.12, Cr 1.03, Cu 1.18, and Ni 1.08 times.

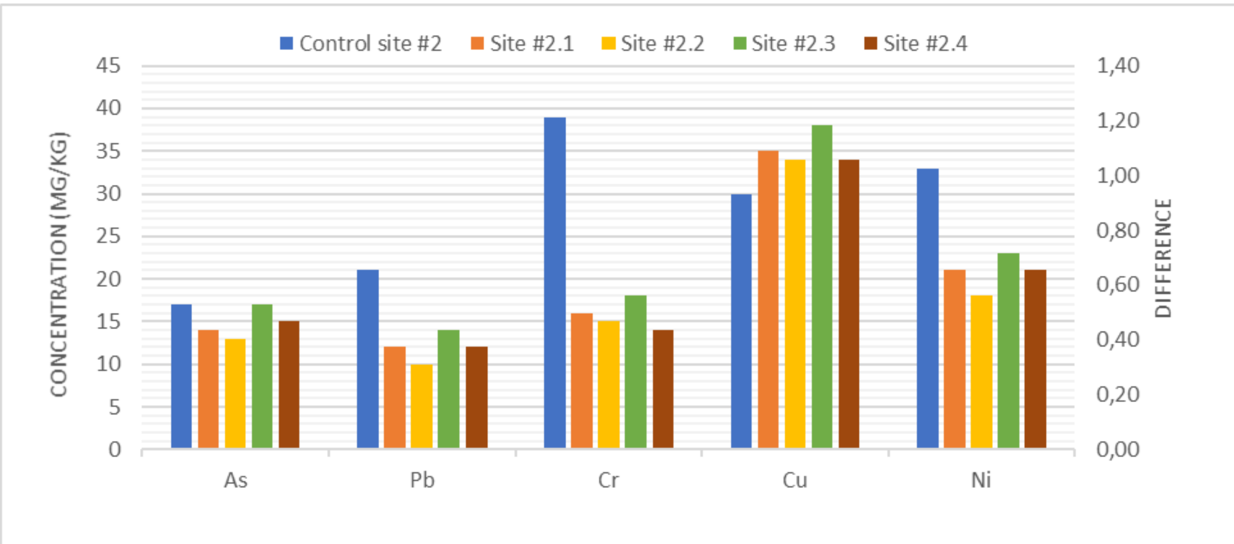

Figure 1. Content of considered metalloids and metals in polluted soils and for comparison, control sample in summer

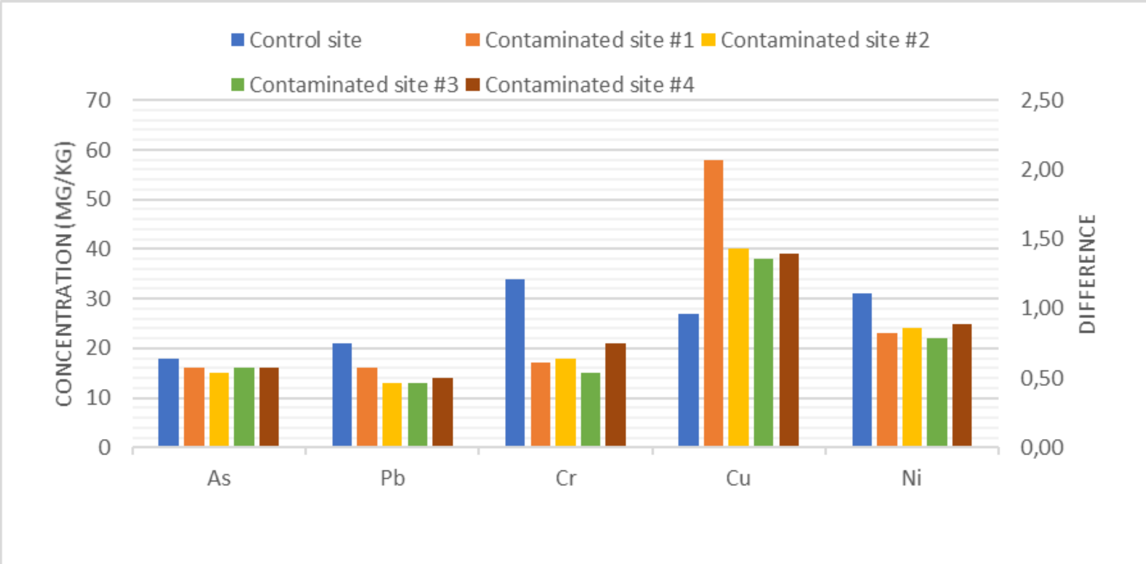

Figure 2. Content of considered metalloid and metals in polluted soils and for comparison control sample in autumn

Figure 1 and Figure 2 show the difference between soil polluted with oil derivatives and non-polluted sites. We see As, Pb, Cr, and Ni in polluted sites have lower concentrations, and only copper has high concentrations. The concentration of chromium in polluted sites is lower almost twice.

Elements	Concentration (mg/kg)									
	Control site		Site #1		Site #2		Site #3		Site #4	
	08.06	30.09	08.06	30.09	08.06	30.09	08.06	30.09	08.06	30.09
Al	12.4	0.3	2.6	1.2	2.6	0.6	1.0	1.2	2.1	1.3
Ca	148	461	156	71	151	222	168	112	158	100
Fe	5.70	0.13	1.51	0.76	1.69	0.51	0.50	0.85	1.35	0.68
K	6	4	19	18	20	39	24	21	21	19
Mg	17	49	22	10	22	18	25	13	23	14
Mn	0.1	0.1	0.6	<0.1	0.6	0.7	0.4	0.2	0.5	0.1
Na	26	28	79	49	66	14	56	16	101	25
Ba	0.1	0.2	0.1	0.2	0.2	0.2	0.2	n/a	0.2	0.1
Cu	1.89	0.05	0.20	0.19	0.11	0.16	0.09	0.14	0.08	0.11
As	<0.2									
Pb	<0.1									
Cr	<0.04									
Ni	<0.025									

Table 2. Concentration of water-soluble forms of elements at Kumtor

Table 2 shows the concentration of water-soluble forms of elements, the concentration of copper in polluted sites is lower than in non-polluted sites. In autumn, the content of copper decreased 37.8 times in the control site, and in site #1 decreased from 0.2 mg/kg to 0.19 mg/kg. However, on other sites, we observe an increase in the content of copper.

As shown in Table 3, the concentration of oil contaminants in study location sites has decreased due to applied bioremediation techniques. By the biostimulation method, the decrease of oil on the third site amounted to 2.4 times.

Sampling date	Oil derivatives (mg/kg)			
	Site #1	Site #2	Site #3	Site #4
08.06.2019	2960	2320	2620	1620
30.09.2019	1300	980	1340	1600

Table 3. Oil contamination of soil at study location sites

Figure 3. Changes in the content of metals and metalloids due to treatment

After using bioremediation techniques, we observed that the concentration of oil-based contaminants decreased, which is shown in Figure 3.

The obtained results indicate a reasonable effectiveness of bioremediation, with biostimulation showing superiority in terms of outcomes among the applied methods. This fact is partially explained by the enhancement of the natural microbial population in the environment through biostimulation, thereby increasing their ability to degrade pollutants.

Conclusions

The purification of the soil environment from oil and petroleum products remains an ongoing issue in terms of ecological safety. Contaminations of this type have a destructive impact on natural microbial ecosystems, local flora, and fauna, leading to the withdrawal of significant land areas from use. Heavy metals act as factors in the chemical and biological degradation of the “soil-biota-plant” system.

A conceptual approach to the regeneration of land resources should involve a set of organizational and technical measures for environmentally balanced and economical anthropogenic activities, with a priority on the use of organic resources. The study examined the consequences of contamination of the soil cover with heavy metals due to oil product spills on the local ecological situation.

As a result of the conducted research, it was possible to analyze the distinctive features and advantages of the proposed bioremediation methods compared to other approaches for soil restoration.

Conclusions were drawn regarding the highest effectiveness of the biostimulation method (reduction of oil pollution by 2.4 times after application on soil samples).

The research justified the feasibility and safety of using biological remediation methods for landscape regeneration, utilizing modern innovative opportunities in the biotechnological field. It was established that the methods proposed in the study are capable of improving the ecological condition of the soil by activating its natural biological potential, simultaneously neutralizing negative processes of heavy metal pollution, and providing optimal conditions for the formation of a soil ecosystem. This situation, in turn, creates optimal conditions for the proper functioning of the components of the "soil-soil biota-flora" system, preventing chemical and biological degradation of the soil cover, regenerating landscapes, and preserving their resource potential.

The research identified priority directions for further studies, emphasizing the need to systematize scientific research and practical information regarding the effectiveness of the practical application of bioremediation methods on heavy metal-contaminated soils. Further exploration of the possibilities of modern progressive biological remediation methods is seen as promising and reasonable for practical application. These methods could achieve significant results in terms of soil regeneration and preventive protection against contamination by toxic substances with minimal intervention in ecosystem processes.

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