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The Effect of Oil Pollution of the Gray Soils on Revegetation in the South of Kazakhstan

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ABSTRACT
To assess the level of soil contamination with oil and petroleum products, the criterion of the cenotic level as the nature of the phytocenosisformation was used. It was found that the bioindication reaction of vascular plants to oil pollution is the deterioration of quantitative and qualitative indicators of the native phytocenosis with possible self-recovery of the plant community at the threshold concentrations of petroleum products 6.0±0.3–8.0±0.5 l/m^2. Light fractions of oil products cause complete destruction of the existing plant community, and the new community is formed at the expense of the soil stock of seeds and drift ruderal plant species. Dark fractions of petroleum products cause structural changes in the species composition of the existing phytocenosis. The most resistant to oil pollution of the soil are the representatives of the Poaceae family, and the representatives of the families *Solanacee* and *Malvaceae* are eliminated from the phytocenosis. For 8 years of research, the projective cover of soil with vegetation is reduced to 92.6±6.3–99.6±0.4%.

Keywords: phytocenosis, oil pollution of soil, ruderal species, phytoindication.

INTRODUCTION

The South of Kazakhstan is one of the largest regions of the Republic, where enterprises of agro-industrial, mining – metallurgical and oil refining complexes are concentrated. Unfortunately, the increase in refining and transportation of petroleum products often leads to oil pollution. Vascular plants form the basis of phytocenosis of Southern Kazakhstan ecosystems different biotopes. Taking into account the extreme sensitivity of vascular plants and their communities to changing environmental conditions and, on the other hand, the high adaptability of plants to the new conditions of the created ecological situation, the use of their life for bioindication and bioremediation of oil-contaminated ecosystems is relevant. A number of studies are known where plants are used in the purification of oil-contaminated soils (Hutchinson t al. 2001, Merkel et al. 2004, Dzhura et al. 2008). Hence, for bioremediation of oil-contaminated soils, Al-Ateeqi S. (2014) offers the use of representatives of the local flora. Djura (2011) investigated the use of *Vicia faba L.,* Chaineau et al. (2005) and Marinescu et al. (2011) use of maize biomass in the purification of oil-contaminated soils. Special attention is paid to the role of rhizosphere microflora in the processes of biodegradation of petroleum hydrocarbons (Miya and Firestone, 2001, Joner and Leyval 2003, Merkel 2005, Mohsenzadeh et al. 2010, Tang et al. 2010). It was found that inoculation of maize seeds by rhizospheric microflora increases the resistance of plants to the toxic effects of petroleum products (Ajuzieogu et al., 2015). The use of vascular plants in bioindication of the environment ecological state is based on the study of their response to the action of anthropogenic factors. At the same time, the reactions of plants, manifested at the coenotic, organizational and cellular levels of their organization, as an integral indicator, most fully reflect the qualitative and quantitative parameters of the impact factor (Avetov, Shishkonakova, 2008).

The most commonly used indicative criterion is the germination rate of test plant seeds (Ekundayo et al., 2001, Banks and Schultz, 2005, Tang, et al., 2011, Cruz et al., 2013). In the research of Romaniuk et al. (2016) using plant seeds *Linum usitatissimum L., Helianthus annuus L., Fagopyrum vulgare St.* concentration limits of toxicity of oil products were established: concentration of 0.4–2.5% is menacing, 2.5–10.0% – pre-crisis, 10.0–15.0% – crisis and more than 15.0% – catastrophic. The indicative quality of plant communities in assessing the degree of ecosystems contamination with oil and petroleum products, showed that in the areas with chronic oil pollution dominated by species of perennial grasses with a predominance of the proportion of ruderal plant species.

At the same time, the bioindication methods of disturbed ecosystems using phyto-test properties of vascular plants are not widely used, which is explained by the lack of research results that take into account the zonal specifics of soil and climatic conditions. In addition, these studies are extremely relevant in the arid conditions of the South Kazakhstan Region (SKR), on the territory of which there are extensive areas contaminated as a result of the activities of the oil and gas industry.

MATERIALS AND METHODS OF RESEARCH

Local areas in the industrial zone of the oil refinery of “Petro KazakhstanOil Products” LLP (“PKOP”) were used as the object of research.

Soil

The studies were performed with the typical gray soils, dominant on the territory of South Kazakhstan, characterized by low humus content and poorly expressed macrostructure. In most cases, the humus layer is represented by a fulvate composition. The physico-chemical properties of the gray soils are characterized by low absorption capacity (9–10 mg. EQ. in light gray soils, 12–15- in typical and up to 18–20 mg. EQ. the dark), alkaline reaction and base saturation. The number of exchange ions K+ and Na+ is about 2–5% capacity. Soil density ranges from 0.5 to 1.7 dv.

Preliminary studies have shown that the distribution of heterotrophic, hydrocarbon-oxidizing microorganisms and micromycetes along the soil horizons is heterogeneous and depends on the molecular weight of oil hydrocarbons. It was found that in the soils contaminated with AI 92 gasoline and fuel oil containing asphaltenes and maltenes, the greatest amount of soil microflora is concentrated in the horizon of 10–20 cm and 20–30 cm, where, in all likelihood, favorable conditions for the development of soil microflora are created: gas-air regime, humidity, optimum biogenic elements and the absence of direct insolation (Sattarova and Issayeva, 2015). The highest titer of microorganisms was observed in soil samples contaminated with AI 92 gasoline, which is explained by the easy availability of gasoline hydrocarbons for the metabolic processes of heterotrophic and hydrocarbon-oxidizing microflora. Taxonomic analysis revealed the dominant species of hydrocarbon-oxidizing microorganisms as Micrococcus varians, M. luteus, Rhodococcus-erytropolis, Pseudomonas putida, Azotobacterch-roococcum, from which active strains-destructors of petroleum hydrocarbons were subsequently isolated (Issayeva et al., 2017).

Oil products

The studies examined petroleum products obtained from the Kumkol oil field with the following indicators: pour point 10 °C, content of silica-gel resins 19.2%; carbene-carbides 5.82%; asphaltenes 5.4%; paraffin 7.5%; sulfur 0.064%. At a temperature of 20 °C, it has a density of 0.850 g/cm^3. Kinematic viscosity, at 20 °C, cSt – 6.8–7.2; at 50 °C, cSt – 2.8–3.8. Acidity, mg KOH – 1.3–1.8. Coking ability, % wt. – 1.4–1.6, content of chloride salts, mg/l – 24 – 66, water content, %wt. – 0,1 – 15. Sulfur content, % by weight – 0.3 – 0.4. Solidification temperature, with heat treatment, +10 +12 °C; without heat treatment, +11 +14 °C. The fractional composition is represented by gasoline, ligroin, kerosene gas, and oil fractions. Kumkol oil field is particularly light type 0: up to

200 °C distilled at least 30%, up to 300 °C distilled at least 50%. The oil of the Kumkol field is acidic, and the fractions extracted from it are acidic, respectively. The high acidity of oil is due to the increased content of naphthenic acids in them. On the basis of the group chemical composition, the oil is paraffin with a content of 18.5–19.4% of the mass of paraffin with a low content of asphaltenes and mechanical impurities.

Light fractions: diesel fuel fractions are low-sulfur, acidity of less than 3%. At a temperature of 200 °C has a density-0.804 g/cm^3.The high content of n-alkanes (24%) can be regarded as a promising raw material for the production of liquid paraffins.

Dark fractions: fuel oil is characterized by the actual freezing point between 25–42 °C. At a temperature of 20 °C has a density -0.890–0.899 g/cm^3. The viscosity at 80 °C is not more than 16, a sulfur contentnot exceeding 0.5%, solids of not more than 1%.

Determination of species composition of phytocenosis

To determine the species composition of plants the plant determinants was used (Illustrated determinant of plants of Kazakhstan, 1969; Flora of Kazakhstan, in 9T, 1961). Sampling of plants was carried out by route-reconnaissance method followed by Desk processing of the collected material. The frequency of occurrence of terrestrial plant species was determined by the Drude scale (Bykov, 1983).

The study of the dynamics of recovery of the phytocenosis

The dynamics of recovery of phytocenosis of oil-contaminated areas of LLP "PKOP" was studied in three analyzed areas: A. contaminated with light fractions, B. contaminated with dark fractions of oil products, C. areas with replaced soil. The dynamics of changes in the weight content of petroleum products in the soil and the number of plant species in the plant community were studied during 2012–2017.

Statistical analysis of the results

Experiments were carried out five times in repetition, calculate the standard deviation at 0.95>P>0.80. Statistical processing was performed using the statistical software package Microsoft Excel on a "Pentium-IV" PC. By the number of measurements and in general diagnostic group determined the arithmetic mean (Schabenberger O. and Pierce F.J., 2002).

RESEARCH RESULTS AND DISCUSSION

The criterion of the cenotic level as the nature of the phytocenoses formation in local areas contaminated with various petroleum products was chosen due to the fact that regular monitoring of this process has not been carried out to date. This, in turn, is due to the lack of established by the state standard of the Republic of Kazakhstan (GOST RK) values of maximum permissible concentrations (MPC) of oil and petroleum products in the soil. For this reason, the official data of the statistical office of SKR reflect only the volume of oil-contaminated areas (more than 200 hectares), established by the results of inspections carried out in the territories of large oil producing and processing enterprises. The official statistics do not take into account the territories of small enterprises whose activities are related to the use of petroleum products or their sale, which, together, make a significant contribution to the pollution of the environment with oil and petroleum products. Against the background of the lack of control over the pollution of the environment with oil and oil products, the methods of oil-contaminated ecosystems phyto-indication based on the use of vascular plants are becoming increasingly important.

Due to the fact that the degree of oil-contaminated areas phytocenosis degradation depends on the type of oil product and its quantitative indicators, as a result, the dynamics of oil-contaminated ecosystems vegetation restoration, differing in soil type, nature of oil product, history of pollution and species composition of the phytocenosis can also vary significantly.

In the course of a preliminary study of the production zone of LLP "PKOP" it was found that in the territory of tank farms there are areas with historical pollution of oil products light and dark fractions in the amount of 6–8 l/m^2, formed as a result of accidental spills in 2010–2017. On the part of the contaminated area, the upper oil-contaminated soil layer was replaced with pure soil.

As a result of studies of the changes dynamics in the amount of petroleum products in the soil, it was found that in 2010 at the first analyzed site

A, despite the initial dose of 6–8 l/m^2, the content of light fraction in the horizon of 0–10 cm of soil did not exceed 1.2±0.1%, in 2016 this indicator decreased tenfold to 0.1±0.01%. This is due to the volatility of the light fraction of petroleum products. However, as a result of the acute toxic effect of the initial volley doses, the former vegetation cover of the site was completely destroyed, with the exception of certain species – *Cynodon dactylon L.* and *Centaurea squarrosa Willd*., which survived the buds of underground shoots and tap roots. Therefore, in the further dynamics of vegetation restoration, the main role was played by the soil stock of seeds and drift plant species. Thus, in subsequent years, the increase in species composition of the phytocenosis occurred at the expense of ruderal species of plants like *Sisymbriumaltissimum L., S. Loeselii, Euclidiumsyriacum L., Erigeron canadensis, Capsélla bursa-pastoris, Poaannua, Xanthium strumarium L., Bromus tectorum L.*

In contrast, at site B there was a low dynamics of decline in petroleum products, 5.7±0.21% in 2010 and 2.1±0.20% in 2017, due to the high content of heavy fractions of petroleum products, which are slowly degraded in the natural environment. The initial salvo pollution significantly reduced its species composition. At the same time, the deterioration of the water-air regime of the soil and the decrease in the share of the soil stock of seeds largely restrained the dynamics of increasing the species composition of the formed phytocenosis. At the time of volley pollution, first of all, the species occupying the lower tier of a grass stand and having weak root system were lost. Thus, in 2010 75.9±5.4% of the phytocenosis of the site B were perennial life forms, plants of the previous growing – *Rumexconfertus, Centaurea by Willd., Cynodondactylon L. Pers., Agropyrontricophorum (Link.) Richt.,Centaureaiberica Trev., Cirsiumarvense*, etc. The formation of the polluted biotope by new species occurred gradually through the settlement of ruderal species such as *Poaannua, Veronica repens L., Polygonumaviculare, Xanthium strumarium L., C. bursa-pastoris* and *Arabidopsis toxophylla.*

Restoration of phytocenosis on two analyzed sites led to an increase in the degree of projective coverage. As shown by the results of the assessment, the indicators of the degree of projective cover change abruptly, and on the site b gradually. This can be explained by the fact that the light fractions of petroleum products on site A, infiltrating into the soil, despite the acute toxic effect, quickly evaporate. Dark fractions of petroleum products have a chronic toxic effect due to changes in soil properties. In 2012–2017, there is a gradual slowdown in the development of phytocenosis, as evidenced by the stabilization of the projective cover indicators.

In addition, it was found that the restoration of vegetation is a gradual change in the ratio of the dominant families. Thus, if at the beginning of the study *Poaceae, Asteraceae* and *Fabaceae* dominated on site A, in accordance with Table 1, the share of cereals increases in subsequent years.

In the first years, in addition to the above families, ruderal species of families *Brassicaceae, Polygonaceae, Amaranthaceae, Convolvulaceae, Malvaceae, Plantaginaceae* and *Solanaceae* were identified in the oil-contaminated areas. In the future, there is a loss of species from the community of families *Solanaceae* and *Malvaceae.* The decrease in the Fabaceae percentage in subsequent years is explained by the stabilization of the carbon-nitrogen ratio in the soil due to the volatilization of light fractions of petroleum products. Projective cover by 2017, achieves of 99.6±0.4%.

The analysis of the proportion of families in the projective cover on site B showed that if at the beginning of the studies in 2010 the representatives of the *Asteraceae*family dominated, represented mainly by invasive species, in 2017 there was a predominance of *Poaceae*, the main part of which falls on *C. dactylon L. Pers*. and *P. annua*. Projective coverage by the end of the study is 98.2±0.9%.

Table 1. The ratio of the leading families in the experimental plots on the projective cover in 2010 and 2017%

Family	Site A		Site B	
	2010	2017	2010	2017
Poaceae	5	64	18	49
Asteraceae	15	10	19	16
Poligonaceae	5	4	5	3
Fabaceae	13	7	12	6
Brassicaceae	7	5	10	5
Solanaceae	4	0	0	0
Convolvulaceae	6	1	5	0
Plantaginaceae	5	2	0	0
Malvaceae	2	0	0	0
Amaranthaceae	5	3	0	0
Ranunculaceae	0	0	5	1
Boraginaceae	0	0	8	4
Other	0	0	18	16

A completely different dynamics of the recovery of the phytocenosis had been installed on site C. After replacement of the contaminated soils to clean, there is a gradual colonization by plants of the biotope, at the same time, a large role have plant seeds contained in the soil used for filling, and introduction of ruderal species. In 2010, the herbage of the studied site was formed by 16 species of annual ruderal and segetal species of vegetation. Among them, the annual representatives of the family *Brassicaceae* – 19.5±1.4%, *Poaceae* – 5.6±0.3%, *Asteraceae* – 18.6±1.1%, *Fabaceae* – 4.7±0.3% and *Boraginaceae* – 4.6±0.1% were dominant. This is due to the fact that the soil was imported in mid-spring, and the grass was formed by spring species that have a soil stock of seeds. Young seedlings of biennial and wintering plant species died in violation of the horizon of the soil and its transportation. In subsequent years, the growth of the species composition of the phytocenosis was influenced by the introduction of plant species, as a result of which in 2012 there were 35 species of annual and perennial plants in the community. In subsequent years, loss of individual plant species such as *Stellaria media*, *Fumaria officinalis, Euphorbia helioscopia* and *Veronica repens erectus* was noted. By 2017, the predominance of the main dominant families: *Poaceae, Fabaceae* and *Asteraceae* was noted in the species structure of the phytocenosis of the site C, and the projective soil cover was 92.6±6.3%.

CONCLUSIONS

An indicator sign of vascular plants for oil pollution, manifested at the cenotic level, is the deterioration of quantitative and qualitative indicators of native phytocenosis. Self-healing of the plant community is possible at threshold concentrations of 6.0±0.3–8.0±0.5 l/m^2. It is revealed that soil contamination with gasoline causes the complete death of the existing plant community, and a new community is formed due to the soil stock of seeds and introduced ruderal plant species. Soil contamination with heating oil causes only degradation of the species composition of the existing phytocenosis. The dominant part of the restored phytocenoses consists of representatives of the *Poaceae* family, including *Cynodondactylon L. Pers*. and *Poaannua*, which provide good biomass and easily cultivated types of cereals, promising as phytosiderates or feed for farm animals. The representatives of the families *Solanaceae* and *Malvaceae*were the most sensitive to oil contamination of the soil. By the end of the study, the projective cover of the soil with vegetation ranged from 92.6±6.3 – 99.6±0.4%.

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