

CRITERIA DEVELOPMENT FOR DETERMINING PERMISSIBLE CONTENT OF PETROLEUM POLLUTION IN PERMAFROST SOILS

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Abstract

*The desk-top experiment on study the behavior of soil-plant system in conditions of petroleum pollution has been carried out. For this purpose, different amounts of petroleum (0.6 to 1.22%) added to the samples of permafrost sod-meadow soils of the Central Yakutia and after that seeds of wild plants: *Lepidium ruderae* L. and *Artemisia vulgaris* L. had been sowed into the contaminated soil. A non-linear alteration of the physiological characteristics of the plants with the increase the content of added petroleum had been detected that indicated the adaptive nature of these changes. Consequently, as the criteria for an assessing of permissible content of petroleum pollutant in soils is proposed to use the integral indicators: survival index of plants expressing changes in adaptive potential of the soil-plant system; index characterizing of intensity of petroleum pollution accumulation; geochemical data on soil bitumoids composition indicating the processes of petroleum pollution transformation. As result it had been defined the permissible content of petroleum pollution in the permafrost sod-meadow soils for the Central Yakutia which is equal 1 g per kg of soil.*

Key words: *permissible content of petroleum pollution, permafrost soils, adaptive potential of soil-plant system.*

1. INTRODUCTION

In connection with intensive development of oil and gas complex accidents leading to result in a release of petroleum and petroleum products in an environment increased. Light hydrocarbons of petroleum spill evaporate, heavier remain in soils. It is believed that petroleum has biogenic origin as there is a genetic link between petroleum and organic matter of sedimentary rocks. Probably because of this petroleum spillage into the ground is not an absolute evil. It is known that at low levels of petroleum pollution a soil is capable to heal itself and petroleum acts even a stimulating effect on plant growth. Therefore, it is important to determine a value of content of petroleum pollution in the soils which is extremely valid. It is especially important for evaluation of the quality of remediation works on cleaning territories from petroleum spills.

There is not possible to determine an uniform norm for permissible concentrations of petroleum pollution in the soils because it depends on many factors: the climatic and geographical conditions, terrain, soil type, pollutant type etc. For example Pikovskii (2003) believes that it is appropriate to normalize the petroleum pollution content depending on reaction of the soil itself on it. Probably the maximum permissible content of petroleum in the soils should be such amount when polluted soils retain the ability to heal it. An important question remains what are the criteria to assess the soil's ability to heal itself? Some authors Pikovskii (2003) and Ananieva (2002) believe that the best indicator of the stability of soil to petroleum pollutions is a condition of microbial communities. In presence the petroleum in the soil microbial community initially felt the shock, which sharply reduced its amount. Then hydrocarbon micro oxidizing flora activates on the petroleum substrate. Its strength and activity depends on many factors: soil type, petroleum pollution level, duration of contamination, air- water conditions, etc. Relationship between the level of petroleum pollution and amount of hydrocarbon oxidizing microorganisms, as well as the total number of soil micro flora has complex and non-linear character. As a consequence, it cannot establish a clear correlation to establish the permissible content of petroleum pollution in soils.

One of the indicators of toxicity of petroleum contaminated soil is its phytotoxicity. However, as indicated earlier our model experiments the dependence of germination of seeds on the content added petroleum into the soil has a distinctly non-linear Lifshitz (2008). This also makes it difficult to determine the level of pollution in which the soils still retain the ability to recover. Furthermore, at high levels of petroleum pollution of soils a high germination of seeds can be observed at low survival of seedlings.

Thus, by one or even several indicators of biological activity of soil it is difficult to determine the permissible content of petroleum pollution because there are no direct or inverse correlations between level

pollution and the studied indicators. Non-linear character these dependences show the adaptive nature of the soil changes occurring under the influence of the increasing stress factor - petroleum pollution. To determine the permissible content of petroleum, it is necessary to consider some integral characteristics of soils or soil-plant systems, which are connected with a mechanism of the system restructuring in response to the increase in the petroleum. Such an integral characteristic, apparently, would be the alteration of the adaptive potential of the soil-plant system to strengthen petroleum pollution.

2. MATERIALS AND METHODS

To study the adaptive potential of the soil-plant system in conditions of petroleum pollution cameral experiments were conducted Lifshits (2011). The seeds of wild plants: *Lepidium ruderae* L. and *Artemisia vulgaris* L. were sowed in petroleum polluted meadow-plant soil (the Central Yakutia). The main characteristic of the soil is given in Lifshits (2011). The amount of added petroleum in the soil ranged from 0.06 to 1.22%. During the experiment were determined following the physiological characteristics of the plant: germination (on day 10), the seedling survival (on the 60th days, the end of the experiment).

Extracts of soil samples extracted with chloroform. Then the solution was filtered and distilled with using water bath. The extract was transferred to weighing bottles and brought to constant weight in a vacuum oven.

The chloroform extracts (bitumoids) studied by the infrared spectroscopy (FT-IR). The spectra were obtained on the FT-IR spectrometer "Protege 460" Company "Nicolet" in the broad range of 500–4000 cm⁻¹.

Group composition of the extracts: hydrocarbon components, resins was determined by adsorption column chromatography on silica gel. Asphaltenes precipitated from the extracts by excess of petroleum ether.

Gas chromatography-mass spectrometry (GC–MS) studies of the individual composition of the hydrocarbon fractions were carried out on the system that included the Agilent 6890 gas chromatograph with an interface to the Agilent 5973N high performance mass-selective detector. The chromatograph was equipped with a 30 m quartz capillary column with a diameter of 0.25 mm impregnated with an HP5MS phase. Helium was used as a carrier gas; the flow rate was 1 ml/min; evaporator temperature 320°C. The temperature rise was programmed in the temperature range 100–300°C at a rate of 6°C/min. The ionizing voltage of the source was 70 eV.

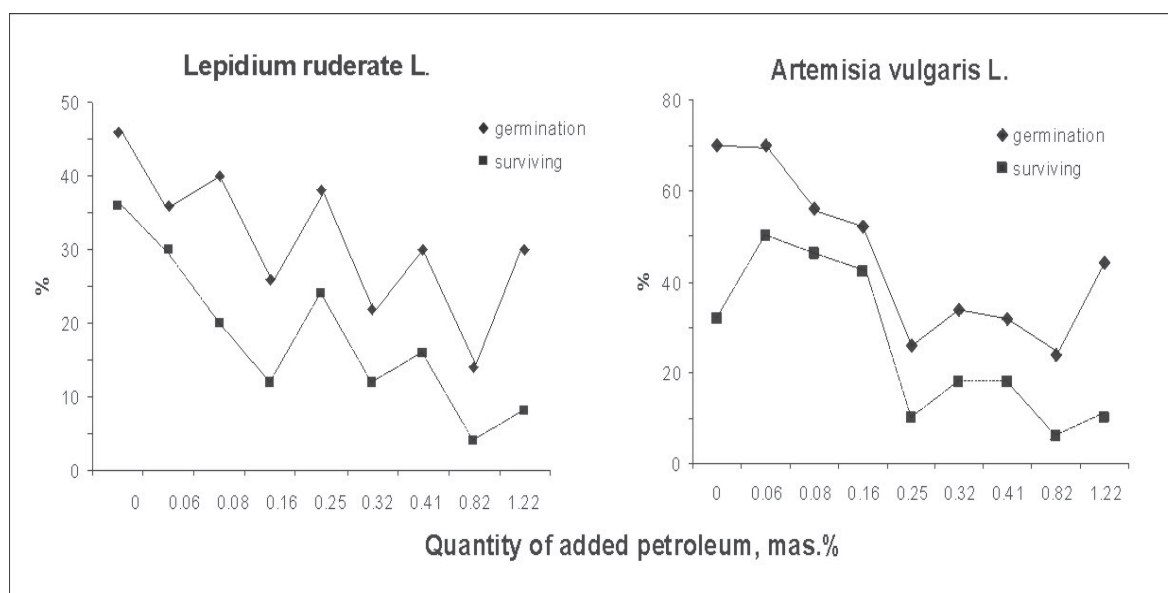


Fig. 1. Effect of quantity of added petroleum on the physiological characteristics of plants.

3. RESULTS

The dependence of the physiological characteristics of plants upon the quantity of added petroleum is represented in Figure 1. As can see the dependences are complex non-linear. As for the assessment of adaptation processes are important not so much the absolute values of the physiological characteristics, but their relations,

we proposed the indicator namely the survival index (the ratio of survival of seedlings to their germination). As can be seen from Figure 2, for both types of plants the dependence of the survival index on the amount of added petroleum has the bimodal with trend to decrease. Each of two ranges of the maxima of these curves is responsible, apparently, for a particular survival strategy of plants.

At a small addition of petroleum to the soil up to 0.16% for *Lepidium ruderalis* L. and to 0.25% for *Artemisia vulgaris* L. at the region of the first maximum the survival index is close to or even higher than that for plants growing in the pure soil. Probably at this stage adaptation antioxidant and DNA reparation systems are including increasing the adaptive potential of plants (Kershengolts, 2002; Lifshitz, 2008).

The second peak where the amount of added petroleum is higher, survival index increases after the minimum but does not reach the magnitude of the first. For adaptation (a survival of the population) in these conditions, the plants appear to be activated following a “defence” mechanism associated with apoptosis and accelerated cell division. This leads to a significant depletion of energy and functional resources of plant organism and accelerated aging (Lifshits, 2011).

During further increase the amount of added petroleum (0.82%) populations of plants are trying to adapt in a toxic environment by increasing germination (see Figure 1). However, the majority of them are non-viable. Probably at this stage the SOS-reparations mechanism is involved (Kershengolts, 2002; Lifshitz, 2008). At this stage the mutations fix in the progeny. For the population as a whole it doesn't become important survival or the quality of life of the individual but the rapid reproduction with mutations fixation for finding viable forms in the new environment.

The chloroform extract of the soil samples characterizes the bituminous component of organic matter of soil. The permafrost sod-meadow soil was used in the experiment. The content of extracted bitumoid of the pure soil sample appeared more than 20 times less than for the petroleum contaminated soil samples. Consequently, in this experiment it is possible to assume that the value of bitumoid yield (or chloroform extract) of soils contaminated with petroleum will characterize the level of petroleum pollution, which was determined by weight percent.

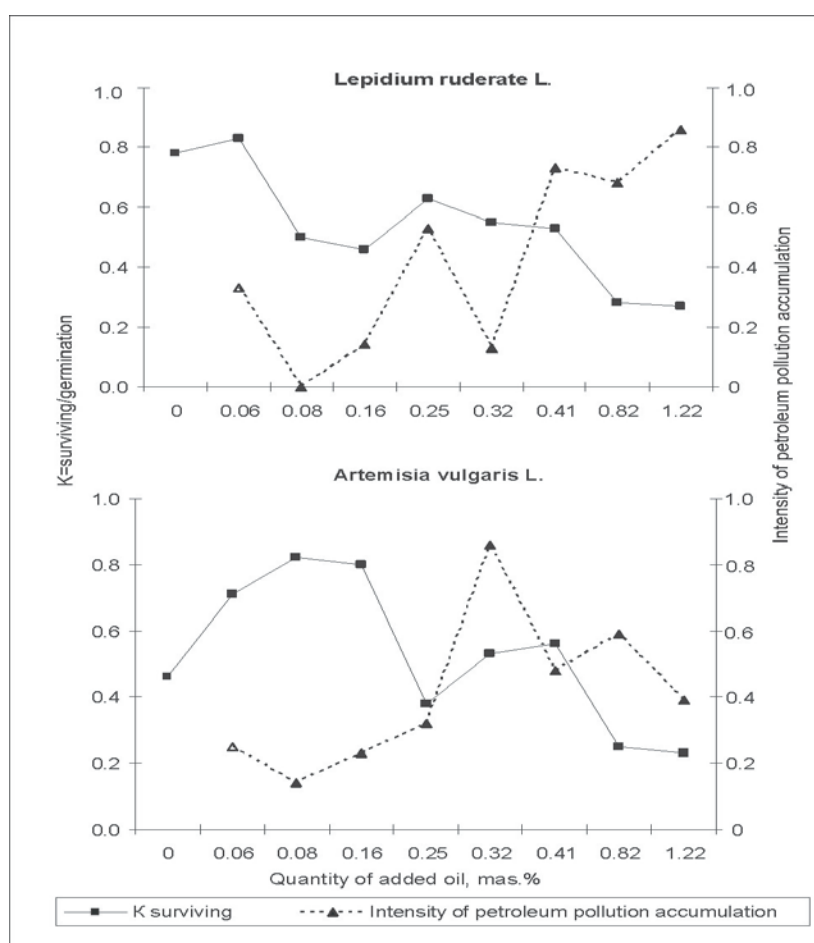


Fig. 2. Effect of quantity of added petroleum on the survival index of plants and the intensity of the petroleum pollution accumulation

The above data (Table) indicate that the contamination increases with increasing the amount of added petroleum to the soil. However, the dependence of the petroleum contamination of soils on the amount of added petroleum is not linear. In our work we proposed the index of intensity of petroleum pollution accumulation as the ratio between the increase of petroleum pollution and the increase of added petroleum which is dimensionless value, since both parameters are expressed in the same units (% wt.). The dependence of the intensity of the accumulation of petroleum pollution on the amount of added petroleum is shown in Fig. 2. As can see, it has a polymodal character. The first maximum on the curve intensity of accumulation of petroleum pollution in the case of *Artemisia vulgaris* L. is present at 0.32% petroleum addition, which corresponds to the residual contamination of soil 0.12% at the end of the experiment. In the case of *Lepidium ruderae* L. growing and 0.25% amount of added petroleum, residual contamination is equal 0.08%. Besides it has been observed the increase in the survival index of the plants after the minimum at the same petroleum adds (Fig 2).

Table Response to petroleum addition in geochemical characteristics of soil bitumoids

Quantity of added petroleum, % mass	<i>Lepidium ruderae</i> L.			
	Bitumoid yield, % mass	Composition of bitumoids, %		
		Hydrocarbons	resins	asphaltenes
0.06±0.01	0.021±0.001	39.1±2.0	49.1±2.5	11.8±0.6
0.08±0.01	0.020±0.001	46.6±2.3	49.7±2.5	3.8±0.2
0.16±0.01	0.030±0.001	47.2±2.4	51.0±2.6	1.8±0.1
0.25±0.01	0.080±0.001	58.7±2.9	39.6±2.0	1.8±0.1
0.32±0.01	0.088±0.001	58.7±2.9	40.2±2.0	1.1±0.1
0.41±0.01	0.157±0.001	71.5±3.6	28.2±1.4	0.4±0.1
0.82±0.01	0.436±0.001	77.0±3.9	22.7±1.1	0.3±0.1
1.22±0.01	0.778±0.001	79.3±4.0	20.5±1.0	0.2±0.1
	<i>Artemisia vulgaris</i> L.			
0.06±0.01	0.016±0.001	51.4±2.5	46.1±2.3	2.4±0.1
0.08±0.01	0.019±0.001	57.3±2.8	38.7 ±2.9	4.0±0.2
0.16±0.01	0.036±0.001	50.7±2.5	44.5±2.2	5.1±0.3
0.25±0.01	0.066±0.001	60.6±3.0	37.0±2.9	2.4±0.1
0.32±0.01	0.120±0.001	72.6±3.6	25.7±2.4	1.8±0.1
0.41±0.01	0.165±0.001	71.0±3.5	28.3±2.4	0.7±0.1
0.82±0.01	0.408±0.001	78.7±3.9	21.1±2.1	0.3±0.1
1.22±0.01	0.579±0.001	78.1±3.9	21.7±2.1	0.2±0.1

At the small additions the transformation of pollutants occurs rapidly due to the high activity of soil enzymes of microbial and plant origin as well as the activation of antioxidant and DNA repair systems (Kershengolts, 2002; Lifshitz, 2008). Under the influence of more high petroleum additions, presumably, the next adaptation strategy begins to realize in plants consisting in activation of apoptosis and increase of cell division.

The results for the study of group composition of bitumoids (see Table 1) showed that with a growing percentage of added petroleum the quantity of hydrocarbon fractions becomes higher and asphalt-resin components - lower. This is probably due to the fact that the enzymes of soil-plant systems can not already affect on the

transformation of petroleum hydrocarbons thus the bitumoids become closer to topped petroleum. The high proportion of hydrocarbons in bitumoids is observed in case of both species of plants at 0.25% of added petroleum and above.

The IR-spectra analysis of soil bitumoids also shows that at small petroleum additions (0.16%) the oxygen-containing structures predominate over hydrocarbon (Figure 3). In this case as can see the intensity of absorption bands $1710\text{--}1735\text{cm}^{-1}$ is more above versus the bands 1605 , 1380 , 1460 , 887 , 815 , 750 cm^{-1} . This indicates an intensive process of transformation of petroleum hydrocarbons under the influence of growing plants. At the higher petroleum additives the type of the IR-spectra became more close to the IR-spectra of petroleum as result the soil-plant system can't to cope with petroleum pollution.

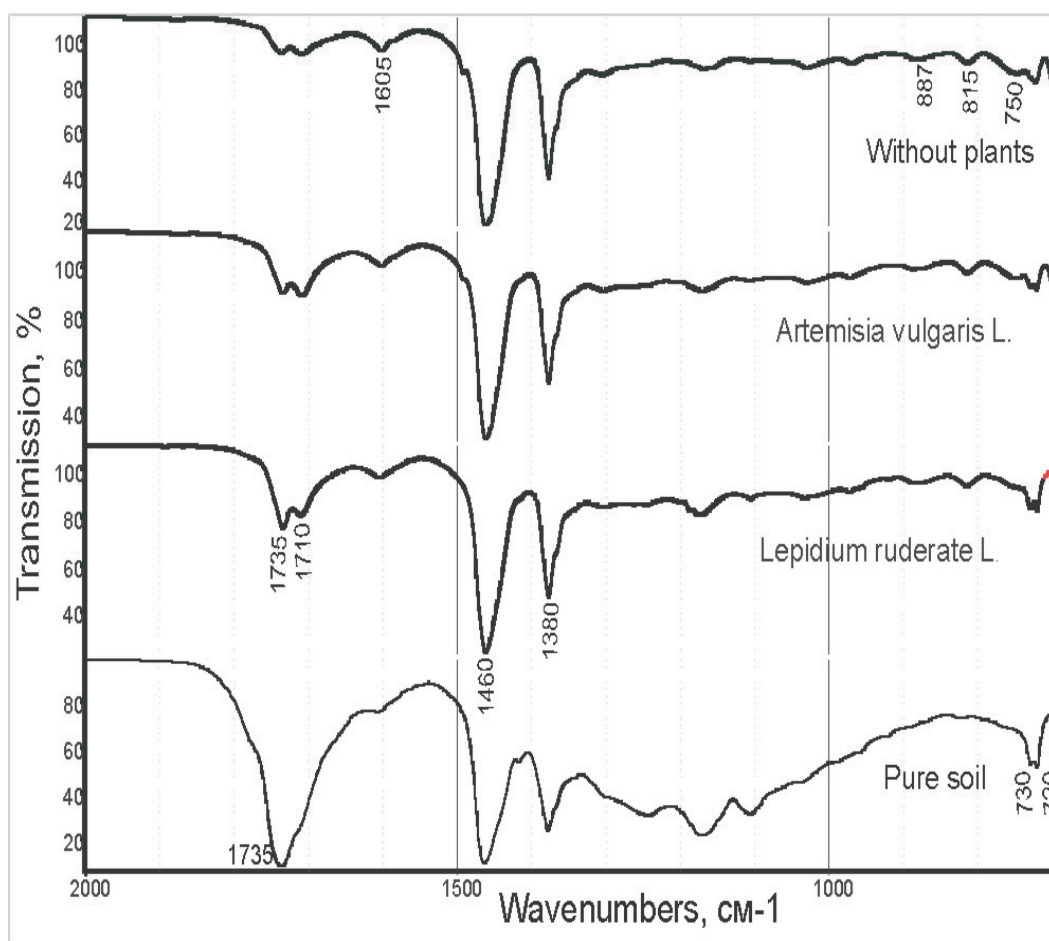


Fig. 3. The infrared spectra of chloroform bitumoids of the soil samples with 0.16% addition of petroleum and the pure soil sample

The mass-chromatograms of hydrocarbon fractions of bitumoids of polluted soil samples with 0.16% addition of petroleum are given on Figure 4. As can see in the case of plants growing more hydrocarbons begin to be involved in the biodegradation process. These hydrocarbons are the relatively low-molecular n-alkanes, isoprenoids, 12-13-metilalkanes. However, at the additions of petroleum 0.25% and above the distribution of individual hydrocarbons is getting close to topped petroleum.

According to the above as permissible petroleum pollution content in the permafrost sod-meadow soil in the Central Yakutia can be recommended the value 0.12% for *Artemisia vulgaris L.* growth and 0.08% for *Lepidium ruderalis L.* growth, or an average of 1 g/kg of soil. At these petroleum pollution contents in soils plants still retain relatively a high adaptive potential. Over these concentrations the adaptive potential of plants rapidly declines, there is observed an accumulation of pollutants, the soil bitumoids acquire petroleum character.

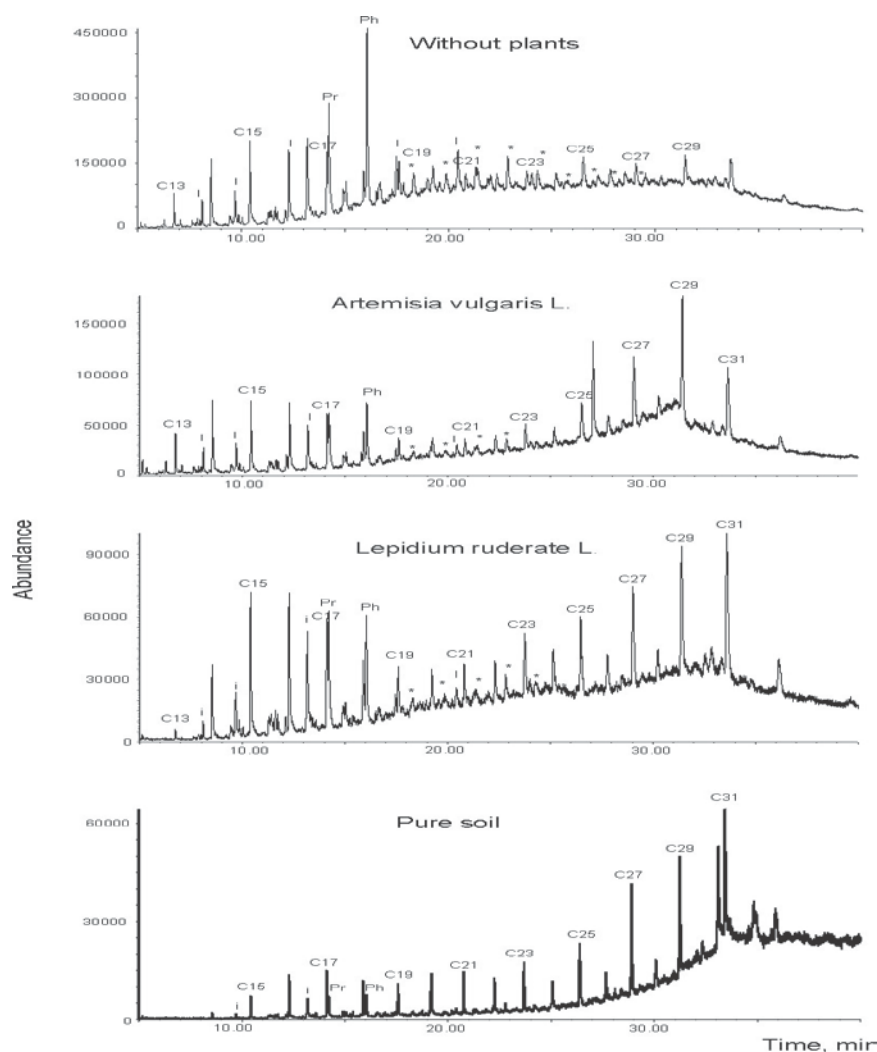


Figure 4. The mass-chromatograms of hydrocarbon fractions of soil bitumoids with 0.16% addition of petroleum in soil and pure soil sample. (C₁₅–C₃₁ – n-alkanes, Pr – pristane, Ph – phitane, i – isoprenoids, * – 12-13-metilalkanes).

4. CONCLUSIONS

Experiments have shown that to determine the permissible content of petroleum in the soil it seems necessary to study the adaptive potential of plants growing on the petroleum polluted soils as well as the processes of transformation of petroleum pollution in the soil-plant system.

The results showed as the criteria for the assessing of permissible residual petroleum pollution content can be, apparently, recommended the following integral indicators:

- survival index of plants expressed changes in adaptive capacity of the soil-plant system;
- index characterizing of intensity of petroleum pollution accumulation;
- geochemical characteristics of soil bitumoids characterizing the processes of petroleum pollution transformation.

REFERENCES

Ananieva N.D, Blagodatskaya E.V Demkina T.S. (2002) Stability estimate microbial complexes to natural and anthropogenic influence. Soil Science, 5, 580 [in Russian].

Kershengolts B.M. Sharoiko V.V., Nureeva G.V. (2002). Effect of lead cations (II) and some herbal complexes BAA on the activity and stability of the plant genome. Siberian Journal of Ecology. 2, P.127-135 [in Russian].

Lifshitz S.H., Kershengolts B.M., Chalaya O.N., Zueva I.N., Shashurin M.M., Glyaznetsova Ju. S. (2008) Study of the ability of the model system oil polluted permafrost soil the Yakutia - plants to restore. Chemistry for Sustainable Development. 16, N 5, 537-545 [in Russian].

Lifshits S.H., Chalaya O.N., Shashurin M.M., Glyaznetsova Yu.S., Zueva I.N., Kershengolts B.M. (2011) Transformation of oil pollution and the formation of an adaptive response in plants model experiment with permafrost soil of the Yakutia. Chemistry for Sustainable development. 9, 169-178 [in Russian].

Pikovskii Yu.I., Gennadiev A.N., Chernyansky S.S., Sakharov G.N. (2003) Problem diagnosis and regulation of soil contamination petroleum and petroleum products. Soil science. 9, 1132-1140 [in Russian].