

3-27-2021

CHEMICAL PROPERTIES OF ORDINARY CHERNOZEM UNDER OIL CONTAMINATION AND SALINIZATION UNDER THE CONDITIONS OF A LABORATORY EXPERIMENT (EVIDENCE FROM REPUBLIC OF BASHKORTOSTAN)

Elena Timofeeva PhD., Associate Professor

Moscow State University named after M.V. Lomonosov, Faculty of Soil Science, Moscow, Russia,
helentimofeeva17@gmail.com

Alisa Alexandrova Master

Moscow State University named after M.V. Lomonosov, Faculty of Soil Science, Moscow, Russia

Sadritdin Turabdzhanov Dr., Professor

Tashkent state technical university, Tashkent, Uzbekistan

Follow this and additional works at: <https://btstu.researchcommons.org/journal>



Part of the [Biomedical Engineering and Bioengineering Commons](#)

Recommended Citation

Timofeeva, Elena PhD., Associate Professor; Alexandrova, Alisa Master; and Turabdzhanov, Sadritdin Dr., Professor (2021) "CHEMICAL PROPERTIES OF ORDINARY CHERNOZEM UNDER OIL CONTAMINATION AND SALINIZATION UNDER THE CONDITIONS OF A LABORATORY EXPERIMENT (EVIDENCE FROM REPUBLIC OF BASHKORTOSTAN)," *Technical science and innovation*: Vol. 2021: Iss. 1, Article 4.

DOI: <https://doi.org/10.51346/tstu-01.21.1-77-0103>

Available at: <https://btstu.researchcommons.org/journal/vol2021/iss1/4>

This Article is brought to you for free and open access by Technical Science and Innovation. It has been accepted for inclusion in Technical science and innovation by an authorized editor of Technical Science and Innovation.

13. K. Rakhmatullayev, B.G. Zakirov. Extraction of indium iodide complex in the presence of dimethylpharmamide and its complexation with 1-(2-peridilazo) 2-naphthol in the organic phase. Bulletins of higher education institutions. Chemistry and Chemistry Technology 1979. Issue 6, Pages - 663-666 (in Russian).
14. K. Rakhmatullayev, A.S. Giyasov. Thallium Extraction (III) in the Presence of Chloride ions and Dimethylpharmamide and its Complexation in the Organic Phase. Bulletins of higher education institutions. Chemistry and Chemistry Technology 1984. T.27. Issue 9. Pages - 1028-1031 (in Russian).
15. I. V. Mironov, L. D. Tsvlodub. Electronic absorption spectra of thiourea complexes of monovalent copper, silver, and gold in an aqueous solution. 4, 1997, vol. 64, pp. 458-462.
16. S.Sasic, A.Antic-Jovanovic, M.Jeremic . An investigation of the equilibrium of mercury(II) thiocyanate complexes in DMF solutions via Raman spectra and factor analysis. J. Chem. Soc. Faraday Trans. 21, 1998, vol.94, pp.3255-3260.
17. Agarwal Arvind, A. N. Vishnoi. Chemical shifts of L[III] X-ray absorption edge of mercury and valence state of mercury ion in its compounds. Indian J. Phys. A N 2, 2000, vol.74, pp.127-129.
18. V. L. Talrose, R.D. Jacob, A.L. Burlingame, M.A. Baldwin. Laser desorption-ionization mass spectrometry of complex salts of cesium, mercury, and iodine. Chem. Phys. N 4, 2002, vol. 21, pp. 6-17. Castro Miguel, Cruz Julian, Otazo-Sanchez Elena, Perez-Marin Leone I. Theoretical study of the Hg {2+} recognition by 1,3-diphenyl-thiourea. J. Phys. Chem. A N 42, 2003, vol.107, pp.9000-9007.
19. Castro Miguel, Cruz Julian, Otazo-Sanchez Elena, Perez-Marin Leonel. Theoretical study of the Hg{2+} recognition by 1,3-diphenyl-thiourea. J. Phys. Chem. A N 42, 2003, vol.107,pp.9000-9007.
20. Eland John H. D., Feifel Raimund, Edvardsson David. Single and double photoelectron spectroscopy of atomic mercury. J. Phys. Chem. A N 45, 2004, vol.108, pp.9721-9725.

UDC 504.06

**CHEMICAL PROPERTIES OF ORDINARY CHERNOZEM UNDER OIL
CONTAMINATION AND SALINIZATION UNDER THE CONDITIONS OF A
LABORATORY EXPERIMENT (EVIDENCE FROM REPUBLIC OF
BASHKORTOSTAN)**

E. A. Timofeeva^{1*}, A.V. Alexandrova¹, S.M. Turabdzhano²

¹Moscow State University named after M.V. Lomonosov, Faculty of Soil Science
119234, Moscow, Leninskie gory 1, building 12

²Tashkent State Technical University named after Islam Karimov,
100095, University St. 2, Tashkent, Uzbekistan

***Abstract.** The Republic of Bashkiria, Russia, is both an agricultural and crude producing region. Soil pollution and as the related process soil salinization are often caused by crude production. One of the most fertile soils - chernozems, represent more than a third of the soil cover of the Bashkortostan Republic. The research crucial task is to study chernozem salinization caused by petroleum pollution, it aims to research the chemism of soil salinization upon condition that*

crude oil and stratal waters flow into the soil simultaneously. The practical implementation of the proposed research is comprehension that we need to regulate the negative human impact on the soil. The research results can give a rise to regulations drafting that control residual oil, petroleum and salts content in soil after the soil remediation. The purpose of the research is evaluation of oil-contaminated Bashkortostan ordinary chernozem chemical properties in a simulation experiment. The laboratory-scale experiment simulates Bashkortostan ordinary chernozem oil contamination and salinization; we achieved varying degrees of soil salinity (from non-saline to highly saline soil); the soil salinization chemism is neutral from sulfate in «clean» soil to chloride in highly saline soil. The research shows that with an increase of soil oil pollution from 0 to 1 g/kg, the salts content increases within one gradation of salinity, and with an increase in soil oil pollution up to 3 g/kg occurs the supposed decrease in the salts content, possibly due to the «sealing» of some of the ions inside the soil aggregates by oil. Significant differences were found for soil pollution with oil over 1 g/kg and soil salinity over 0.3%. Chlorine and sodium ions are distributed on a like-to-like basis. The sulfate content declines with soil salinity increase. This may be caused by sulfates predisposition to form a strong inner-sphere complexes with clay minerals of the soil.

Key words: *oil contamination, salinization, ordinary chernozem, calcic chernozem, Bashkortostan, rationing*

INTRODUCTION. Accidental spills of crude and commercial oil, petroleum products, drilling wastewater, oilfield wastewater cause a number of physical, physico-chemical, chemical and biological transformations in the soil: from changes in the water-air regime, chemical composition and composition of the soil adsorption complex to morphological changes in the genetic horizons as a whole, moreover, structural and functional changes take place in the soil biocenosis. Taken together, all these processes lead to a soil fertility decrease, disruption of its ecosystem functions, and various ingredients in the composition of oil and petroleum products (salts, heavy metals, hydrocarbons), getting through the soil into plants, can reduce the quality of agricultural products.

The volume of Russia's crude production is over 500 million tons annually, the accident losses of crude oil are about 3-5%, as a result about 25 million tons of petroleum enter the environment annually. According to the the Ministry of the Russian Federation for Civil Defense, Emergencies and Elimination of Consequences of Natural Disasters report, the area of oil-contaminated soils in Russia estimates 71.5 thousand hectares [1].

Unfortunately, despite the active development of alternative energy sources, the demand for oil is not decreasing, therefore, its flow into the environment with accidental losses is also growing. Thus, according to the forecast of the International Energy Agency, the world demand for primary energy resources may increase in 2005–2030 by 55%, and demand will reach 17.7 billion tons of oil equivalent [2].

In Uzbekistan one of the urgent problems is the study of the state of contaminated soils for further remediation, especially in the desert zone, where the problem of accompanying salinization becomes acute. Desert territories (the Uzbekistan's Republic of Karakalpakstan, Kashkadarya and Surkhandarya regions), which occupy most of the area in Uzbekistan, have a huge national economic potential. These extremely arid areas provide excellent pasture resources; cotton, vegetables and fruits are grown on irrigated lands, at the same time Uzbekistan's largest oil production enterprises and petroleum refineries are located here, thus oil fields, oil pipelines, oil refineries, oil storage facilities are the main potential sources of oil

pollution. [3] The production and processing of oil and oil products is also carried out in Bukhara and Fergana regions, where the three Uzbekistan's largest petroleum refineries are located. Fergana Valley is famous for the largest oil spill in Central Asia. On March 2, 1992, an oil blowout occurred at the Mingbulak field. As a result, huge lands were polluted and set-aside. The problem of oil pollution of soils in the Fergana Valley remains relevant up to the present day. Estimates show that soil contamination in the area of the Mingbulak field varies from 0.57 to 312 g/kg of oil [4].

The Bashkortostan is both an agricultural and oil-producing region. More than a third of the soil cover of the Republic is represented by chernozems - fertile soils that form up to 60% of the workable soil of Bashkiria [5]. At the same time, the area of oil-contaminated land is several tens of thousands of hectares. Shkapovskoe, Tuimazinskoe and Arlanskoe fields are the most prone to oil pollution [1].

At the moment the Russian regulatory has not defined the maximum permissible concentrations for the content of petroleum products in the soil. Until recent times, the only regulation was the «Procedure for determining the land pollution damage estimation from chemical substances», which fixes six levels of soil pollution with petroleum (from less than 1 g/kg to over 5 g/kg). However, these figures do not take into account regional soil characteristics. Therefore, in recent years, there is a tendency to develop regional standards, which have their own specifics, despite the fact that they are based on generic procedure requirements for the development and implementation of standards for the permissible residual petroleum content in soils after remediation and other restoration works [7].

As is known, soil oil pollution is often accompanied by soil salinization [6]. In total, both of these processes are the leading degradation processes that determine the ecological state of lands. In order to regulate this type of human impact, many oil-producing regions (the Republic of Tatarstan, the Chuvash Republic, the Stavropol Territory and others) initiate the development of relevant standards. Table 1 shows the values of the permissible residual content of oil, petroleum products and salts from the regulatory legal acts of a number of regions of Russia (Table 1). As Table 1 shows in the Russia's regions, where the permissible residual petroleum content standards in the prevailing soil types are implemented, the type of land use and the natural zone are taken into account, since these conditions affect the degree of negative impact on the soil. The standard values for the permissible residual oil content range from 0.4 g/kg to 10 g/kg. This range of values is explained by the individual characteristics of each soil type, its ability for self-healing after pollution. Generally, for more southern regions with neutral soils this standard values are higher (for example, for chernozems), the further north the region is located and the more acidic the soil, the lower the standard values (for example, for sod-podzolic). However, it can be noted that for the tundra gley soils of the Nenets Autonomous District, these standards are quite high (5-10 g/kg), and this fact is possibly related to the commodity-based regional economy specific, and not to the characteristics of soil or climatic conditions. The standards for the salt content after the remediation of oil-contaminated soils are developed so far only for the Republic of Tatarstan, the Chuvash Republic - at the level of 0.15% and the Stavropol Territory - at the level of 0.5%, since water-soluble salts are also often present in these soils in natural conditions.

Regional standards of some regions of the Russian Federation for the permissible residual content of oil and petroleum products and salts.

Regional standards of some regions of the Russian Federation for the permissible residual content of oil and petroleum products and salts.

Region	Soil	Oil content standard, g/kg	Salts content standard, %	Legal act
Republic of Tatarstan	Typical chernozem (forest-steppe, forest fund)	5	0.15	Order dated October 28, 2016 No. 1201-p
	Dark-gray forest (forest-steppe, forest fund)	5	0.15	
	Dark-gray forest (forest-steppe, agricultural lands)	2.8	0.15	
Chuvash Republic	Dark-gray forest (forest-steppe, southern taiga, agricultural lands)	3	0.15	Decree dated January 24, 2013 No. 6
Stavropol Territory	Technogenically transformed soils (org. carbon 0.5-1%, agricultural lands)	2.5	0.5	Order dated December 20, 2010 No. 468
	Chernozems of all subtypes	5	-	
Nenets Autonomous District	Peat-bog soils (subarctic floodplain of Pechora, agricultural lands)	2	-	Decree dated December 15, 2011 No. 293-p
	Tundra gley (southern taiga, agricultural lands)	10	-	
	Tundra gley (northern taiga, agricultural lands)	5	-	
Sakhalin Region	Peat-bog soils (coniferous forests, agricultural lands)	6	-	Decree dated June 20, 2018 No. 279
	Podzolic (coniferous forests, agricultural lands)	2	-	
Perm Territory	Sod-podzolic (agricultural lands)	2.4	-	Decree dated December 20, 2018 No. 813-p
	Sod-podzolic (forest fund)	1.5	-	
Krasnoyarsk Territory	Swamp-podzolic (forest fund)	1.9	-	Decree dated June 9, 2012 No. 269-p
	Tundra gley (forest fund)	2	-	
	Flood plain bogged	0.4	-	

Analysis of foreign regulatory documents shows some simplification of the environmental regulation system in the field of assessing soil oil contamination, which often does not consider the type of soil, however, the characteristics of the permissible content of pollutants in the soil are worked out in details, depending on the fractional composition of

petroleum products and the presence of individual pollutants in them. Meanwhile, there is not an unambiguous approach to the issues of rationing by types of economic use in foreign works, and the norms of permissible oil concentrations in soil are given, as a rule, only for residential areas (Table 2) [7].

Table 2.

Comparison of the concentrations of the permissible residual content of oil and petroleum products in soils in different countries, mg / kg.

Country	Land use type						With account of soil texture	Standardized substances	References
	Agricultural lands	Industrial areas	Human settlements	Play-grounds	Protected areas	Excluding land use			
Germany	-	12	4	2	10	-	-	Benzo(a)pyrene content	[8]
Netherlands	-	-	-	-	-	1000	-	Petroleum products content	[9]
Canada	130	310	30	-	30	-	More than 75 microns	Hydrocarbons: C ₆ -C ₁₀	[10]
	449	760	149	-	149	-		C ₁₁ -C ₁₆	
	260	660	260	-	260	-	Less than 75 microns	C ₆ -C ₁₀	
	900	1490	900	-	900	-		C ₁₁ -C ₁₆	
Czech	-	1000	500	-	750	-	-	Hydrocarbons (total)	[11]
	-	5	0,8	-	1	-	-	C ₆ H ₆	
USA	-	-	-	-	-	950	Coarse gravel	Petrol	[12]
	-	-	-	-	-	2200		Diesel	
	-	-	-	-	-	2800	Coarse sand	Petrol	
	-	-	-	-	-	6500		Diesel	
-	-	-	-	-	7500	Fine sand/silt	Petrol		
-	-	-	-	-	17000		Diesel		
Kazakhstan	-	-	-	-	-	100	-	Petroleum products of the Zhetybai field	[13]
	-	-	-	-	-	10	-	Petroleum products of the Kalamkasskoye field	
Belarus	50	500	100	-	50	-	-	Petroleum products content	[14]

Talking about the assessment of soil salinity, internationally, the criteria for assessing the specific electrical conductivity of filtrates from water-saturated soil pastes are widely used, which were developed by the USDA Salinity Laboratory in the 1950s [15]. In Russia, it is traditional to use the water extraction method, which is based on the extraction of the total salts content from the soil with excess water in a ratio of 1: 5 (the ratio can be expanded to 1:10 or more, for organogenic soils - to 1:25). Thus, using the method of water extracts, information is obtained on the total amount of water-soluble salts, their mass fraction in the soil, and the method of soil pastes provides information on the concentration of salts in the soil close to real conditions, but not their total content. The category of saline includes soils containing readily soluble salts or their ions in at least one horizon of the soil profile in quantities exceeding the

toxicity threshold - the maximum allowable amount of salts that does not cause oppression of plants. The values of this threshold within the framework of international approaches are: by the amount of toxic salts obtained by the method of water extracts from 0.05-0.15% - correspond to non-saline soils, and over 1% - to very saline; by the specific electrical conductivity of filtrates from water-saturated soil pastes, where below 2 mS / cm are non-saline soils, and above 16 mS / cm are very saline soils [16-17].

At present, various technologies are developed for the remediation of oil-contaminated soils. Biological remediation technologies are especially noteworthy, and they are divided into two large groups: in-situ (at the location) and ex-situ (with soil removal). In order to choose a suitable technology, it is necessary to possess the information on the pollution scale, on the period in which the territory needs to be reclaimed, on the geophysical characteristics of the territory, on the costs of carrying out remediation measures using one technology or another. For example, the existing bio-bulk technology is the only ex-situ one that has advantages over in-situ technologies, since it meets following requirements: 1) it is carried out in a shorter time, 2) it is cheaper, since it is carried out over a large area and repeats bio ventilation / enhanced bioremediation technologies, but has a big drawback - it requires soil removal. In addition to the fact that in-situ technologies do not require soil removal, they have a number of disadvantages: 1) in-situ processing takes longer time; 2) lack of processing uniformity due to the soil variability and aquifer properties; 3) the effectiveness of the land restoration process is more difficult to verify; 4) sometimes extracted groundwater may need additional processing; 5) when using in-situ biotechnology, toxic compounds can pass into groundwater; 6) the temperature regime affects the final result: on the one hand, biodegradation will slow down with a decrease in temperature, therefore, in northern climatic conditions, bioremediation may be ineffective for most of the year, on the other hand, with an increase in temperature, the solubility of oxygen decreases, which reduces the rate decomposition of oil and petroleum products. The phytoremediation technology has a number of advantages: the most "natural" technology, does not disturb the soil cover, and is effective over large areas. However, the downsides is that one can note its low efficiency at high concentrations of the pollutant, limitation on the depth of remediation and efficiency mainly for volatile organic pollutants. If we compare the technology of bio-bulk with other ex-situ technologies, then: 1) land farming is a short-term technology, but ineffective for high concentrations of pollutants, during processing, volatile components evaporate rather than decompose, which leads to an air quality deterioration and is especially dangerous for large areas; 2) processing in bioreactors is an effective but rather expensive technology [18].

There is no standard for the permissible residual content of petroleum products and salts in the soil in the Republic of Bashkortostan due to insufficient knowledge of the physic-chemical properties of soils during oil contamination and accompanying salinization, primarily due to the specific of the extracted oil and formation waters. So, modeling these processes and studying changes in soil properties during contamination, as well as studying the effect of oil pollution and salinization on the growth and development of plants, is an important stage for developing a standard for the permissible residual content of oil, petroleum products and salts after soil remediation in this region, which is a necessary measure to regulate the anthropogenic impact on soil. The establishment of regional standards for the residual content of petroleum products and salts in the soils of the Republic of Bashkortostan after remediation and other restoration works is required to optimize the costs of remediation and to calculate the damage for land pollution.

MATERIAL AND METHODS. The object of the study is the unpolluted ordinary chernozem (according to the classification of 1977 [19]) of the Republic of Bashkortostan, which was sampled in the Ufa region of the republic, north of the village of Dmitriyevka. The total number of samples taken was 100 pieces, the weight of each sample was 300 - 500 g. For sampling and determination of the soil type, a 10x10m test site was laid, sampling was carried out on a grid from a depth of 0-10 cm. During the study, the soil profile of ordinary chernozem was described and the name was given: ordinary chernozem (according to the classification of Russian soils in 1977 [19]); Migration-segregation carbonate-bearing chernozem, medium-thick, high-carbonate, medium-loamy (according to the Russian soil classification in 2004 [20]); Calcic Chernozems (Loamic, Aric) (according to WRB 2014 [21]).

Also, a description of the local flora of the territory near the soil cut, was made. There is a cereal-forb meadow, represented by the following species: *Poa pratensis*, *Taraxacum officinale*, *Tanacetum vulgare*, *Veronica sp.*, *Galium mollugo*, *Cirsium vulgare*, *Hypericum perforatum*, *Arctium lappa*.

Description of the laboratory experiment. The selected samples of chernozem were placed in individual plastic containers of 250-750 ml, dried to air-dry state and ground in a mill to 1 mm. In total, 100 containers were prepared with various variants of experiment. In the framework of the laboratory experiment, soil samples were contaminated with petroleum products and salted with drilling mud. An oil-contaminated sample, are prepared from non-contaminated soil, was used to contaminate the bulk of the soil. At first, the oil capacity of chernozem was determined, which was 23.0%. Next, the required amount of oil was calculated, which must be spent to contaminate all 100 samples, then, taking into account the oil capacity, one contaminated sample was prepared, which was mixed until complete homogenization several times over several days. Then a weighed portion was taken from a contaminated soil sample and mixed with a "clean" soil sample, in accordance with the variants of the experiment in four-fold repetition (Table 3). It should be noted that the uniqueness of the conducted laboratory experiment is the maximum possible approximation of the experimental conditions in the laboratory to the natural environmental conditions, and the simulated pollution and salinization - to how it occurs in real conditions. In our case, when introducing oil into the soil to simulate pollution, oil-contaminated samples of the same soil were used, which, in comparison with similar experiments (the introduction of a pollutant using oil-contaminated sand or the introduction of oil in a solution with hexane or benzene) made it possible to avoid the introduction of third-party components. So, in the case of the introduction of oily sand, there is a change in the granulomere composition of the soil (Stimulation of microbial destruction of oil in the soil by introducing bacterial associations and mineral fertilizers in laboratory and field conditions, I. Nechaeva, A. Filonov, 2009), and with the introduction of hexane / benzene, additional hydrocarbon-containing components of light oil are directly introduced (Influence of oil pollution on the properties of leached chernozem under the conditions of a laboratory experiment, S. Trofimov, A. Fokin, 2008).

The second feature of setting up this laboratory experiment is its scale, repetitions allow us to use methods of statistical data processing.

For soil salinization, a brine solution of formation water was used, sampled in the Republic of Bashkortostan. The composition of the main investigated components of the solution is presented in table 3:

Table 3.

Chemical composition of the saline solution

Evaporated residue, %	Na ⁺ , mg/l	Cl ⁻ , mg/l	SO ₄ ²⁻ , mg/l
25,38	4515,7	6243,4	324,1

The solution of formation water was poured into the soil samples, based on the required content, corresponding to the variant of the experiment presented in table 4.

Table 4.

Variants of the experiment of the laboratory experiment

Petroleum products content, g/kg of soil	Total salts content (evaporated residue), %				
0	0	0,05	0,15	0,30	0,50
1	0	0,05	0,15	0,30	0,50
2	0	0,05	0,15	0,30	0,50
4	0	0,05	0,15	0,30	0,50
5	0	0,05	0,15	0,30	0,50

After contamination, the soil was moistened with distilled water and thoroughly mixed with a spatula until homogenized. The conditions for the experiment were as follows: the soil was in a state of black steam, there was no drainage, the activity of microorganisms was not suppressed; humidity was not maintained at a constant level, while the soil was flooded with distilled water based on the incoming average annual precipitation rate of 500 mm / year - typical for the Republic of Bashkortostan; the temperature for the entire period of the experiment was about 20°C. Sampling for analysis was carried out one month after the start of the experiment.

In the course of the laboratory experiment, all the samples were moistened from time to time, and the weight of the samples and the amount of added water were constantly recorded, therefore, to determine one or another indicator, the weighed portion of the soil was taken in a wet form, and after the analysis, a recalculation was carried out taking into account soil moisture.

To determine the evaporated residue, water-soluble sodium, chloride and sulfate ions, we used the method of water extracts with a soil: water ratio of 1:5. After the weighed portions were poured with water, they were thoroughly shaken, the resulting suspension was settled for a day, then filtered, since the extracts were turbid, they were centrifuged using an Eppendorf Centrifuge 5804 at a speed of 7500 rpm for 15 minutes.

Next, there was a process of filtration through a blue ribbon filter. The obtained extract filtrates were analyzed. The determination of the evaporated residue was carried out by standard methods in accordance with GOST 26423-85 «Methods for determining the specific electrical conductivity, pH, and dense residue of the aqueous extract». The determination of sulfate ions was carried out by the photometric method (Theory and practice of chemical analysis of soils. Edited by L.A. Vorobieva. - M. GEOS, 2006). The determination of chloride ions was carried out by the method of argentometric titration (according to Mohr) according to GOST 26425-85

«Soils. Methods for the determination of the chloride ion in an aqueous extract». Sodium was determined by the method of flame photometry in accordance with GOST 26427-85 «Soils. Method for determination of sodium and potassium in water extract». Determination of petroleum products was carried out according to PNDF 16.1: 2: 2.2: 2.3: 3.64-10 «Quantitative chemical analysis of soils. Methods for measuring the mass fraction of petroleum products in soil samples, grounds, bottom sediments, silts, sewage sludge, production and consumption waste by the gravimetric method».

RESULTS AND DISCUSSION. Actual oil and salt content after model pollution. The actual salinity values are shown in the table below (Table 5) and are presented as medians of 25 unique values of combinations (in four-fold repetition). The upper number is the combination number, the number below it is the value of the total salt content, %. The gray column shows the median content of oil products (in twenty-fold repetition) corresponding to the numbered combination of salinity and oil pollution.

Table 5.

Actual values of the content of petroleum products and salts during the laboratory experiment (medians)

Petroleum products content, g/kg of soil	Total salts content (evaporated residue), %				
	0	1	6	11	16
	0,04	0,15	0,31	0,51	0,82
0,6	2	7	12	17	22
	0,11	0,10	0,45	0,82	0,95
1,0	3	8	13	18	23
	0,17	0,30	0,27	0,47	0,151
2,5	4	9	14	19	24
	0,20	0,21	0,48	0,55	0,85
3,1	5	10	15	20	25
	0,13	0,24	0,44	0,44	1,09

Figure 1 illustrates the content of petroleum products and salts in the soil after 1 month of the laboratory experiment. The abscissa shows the combination number, so that the oil content increases sequentially in combination; the combinations are circled in ovals. It can be seen from the graph that with an increase in the oil content inside a combination homogeneous in salinity, an increase in salinity is observed, since during the experiment it was found that the oil used was also salted:

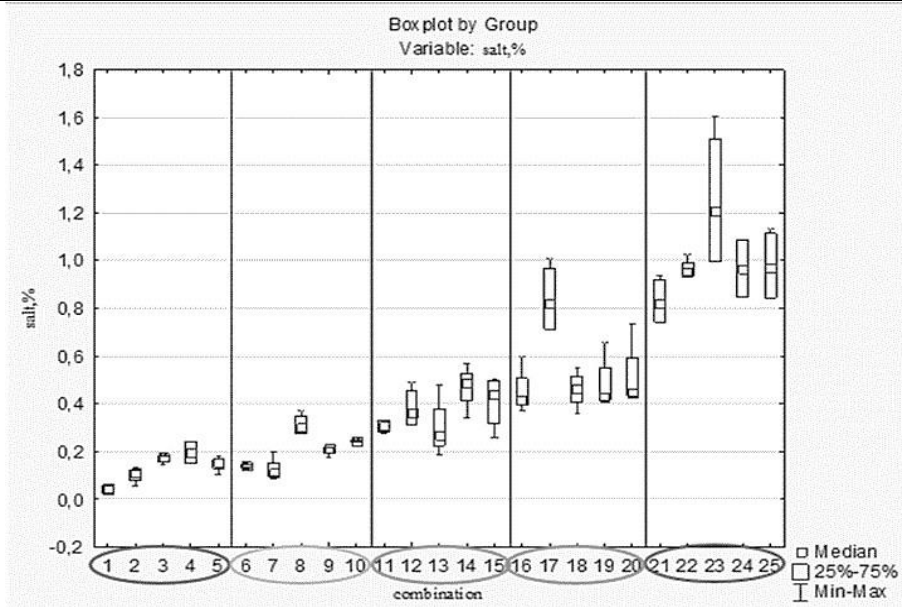


Figure 1. Oil and salt content in the soil after 1 month of the laboratory experiment

Taking into consideration that the medians of the obtained values practically do not differ from the mean, the LSD test (the least significant difference) was performed to detect differences. The graphs below (Fig. 2,3,4) show an inflection towards a decrease in the content of salts with an increase in the concentration of oil pollution, where, based on the setting of the experiment, the maximum amount of salts was introduced. The variances of the mean values also allowed this test to be carried out. Due to the fact that the LSD analyzes the average values, the table below shows exactly the average salinity values (in oil is still the medians):

Table 6.

LSD-test for detecting significant differences in salt reduction in visible inflections in the graph

Petroleum products content, g/kg of soil	Total salts content (evaporated residue), %				
	0,04	0,14	0,31	0,45	0,83
0	c	c	b	b	b
0,6	0,17	0,13	0,38	0,840	0,97
1	b	c	ab	a	b
2,5	0,10	0,31	0,30	0,46	1,25
3,1	a	a	b	b	a
	0,20	0,21	0,47	0,48	0,97
	a	b	a	b	b
	0,15	0,24	0,41	0,51	0,98
	ab	b	ab	b	b

Table 6 shows a section of the visible inflection on the graph (Fig. 2) towards a decrease in the content of the mass fraction of salts. Different letters (a and b) within the column indicate the found differences.

When the soil is contaminated with oil over 1 g / kg and the accompanying salinization is over 0.3%, soil particles are enveloped by oil, it can lead to the phenomenon of «sealing» salt ions inside soil aggregates, salts do not immediately come out into the soil solution, but it happens gradually as the oil degrades. [22] To confirm this conclusion, further research is required, this experiment will continue.

The degree and chemism of soil salinity under the conditions of a laboratory experiment. Summary table 7 shows the degree and chemism of ordinary chernozem salinity in all variants of the experiment. The pH of the aqueous extracts of chernozem was 7.0; therefore, the salinity chemism was determined as neutral. As in the graph above, here - the values within the oval characterize combinations of homogeneous salinity with an increase in oil content in it. It can be seen that, due to its salinity – oil affects the chemism of soil salinization, changing the natural sulfate chemism to chloride. The degree of salinity within the «homogeneous» salinity combination increases due to the increase in oil too. In general, it was possible to achieve a variation in the degree of soil salinity from «non-saline» to «very highly saline».

Table 7.

Varying the degree of soil salinity during the experiment according to the variants of the experiment, g/kg.

Variant of experiment	Chemism	Salinity	Salt, %	Oil, g/kg
	Neutral			
1	sulfate	non-saline	0,04	0,00
2	sulfate	non-saline	0,11	0,52
3	sulfate	non-saline	0,17	1,00
4	chloride	low	0,20	1,33
5	chloride	low	0,13	2,65
6	sulfate-chloride	low	0,15	0,00
7	sulfate-chloride	non-saline	0,10	0,58
8	sulfate-chloride	medium	0,30	1,26
9	sulfate-chloride	medium	0,21	1,75
10	chloride	medium	0,24	2,46
11	sulfate-chloride	medium	0,31	0,00
12	chloride	high	0,45	0,56
13	chloride	medium	0,27	1,25
14	chloride	high	0,48	2,70
15	chloride	high	0,44	2,87
16	chloride	high	0,51	0,00
17	chloride	high	0,82	0,72
18	chloride	high	0,47	0,61
19	chloride	high	0,55	2,73
20	chloride	high	0,44	5,03
21	chloride	high	0,82	0,00
22	chloride	very high	0,95	0,43
23	chloride	very high	1,51	0,80
24	chloride	high	0,85	2,67
25	chloride	very high	1,09	3,03

Change in salts content by gradation, which depends on the gradation of the petroleum products impact. Below is the dependence of the total salt content on the level of oil pollution in ordinary chernozem (Fig. 2):

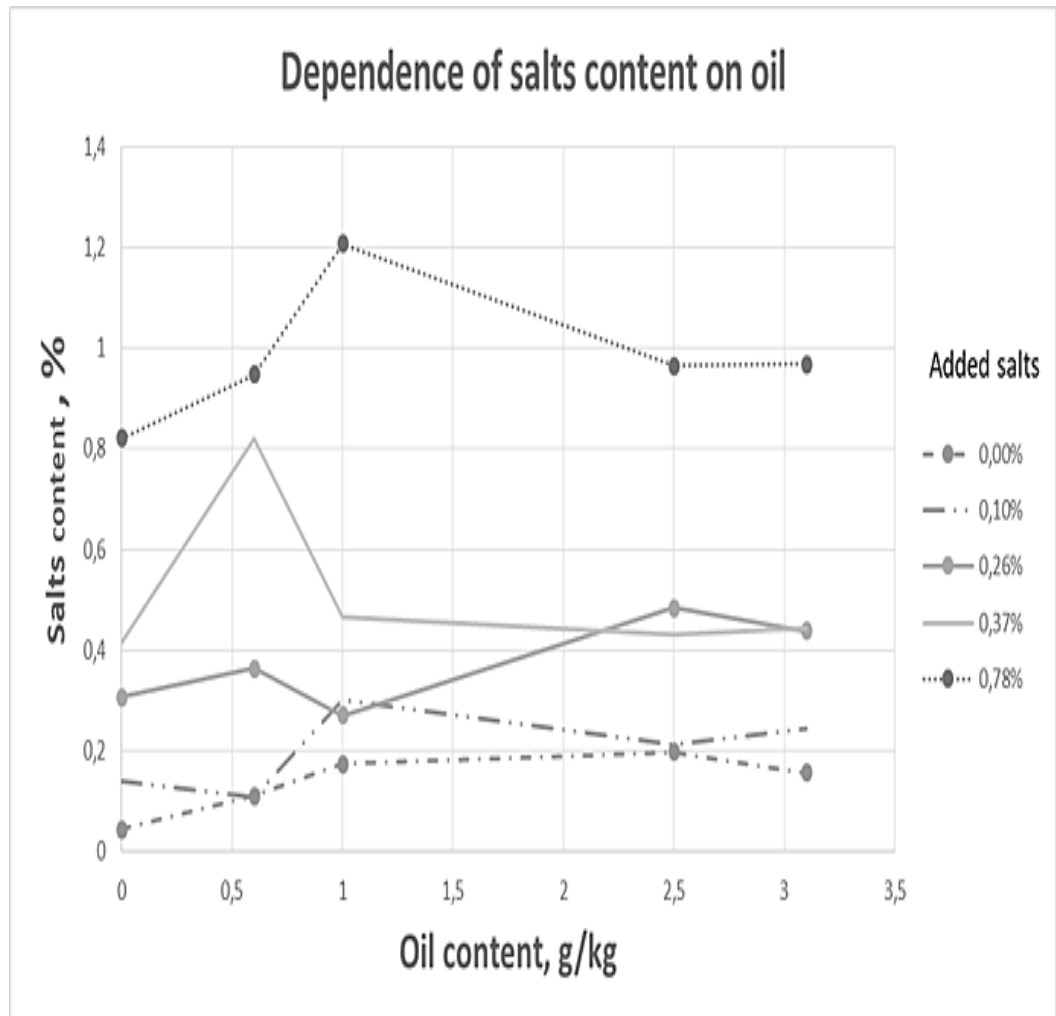


Figure 2. Graph of the dependence of the total salt content on the content of petroleum products

As noted above, with an increase in the oil content, the salt content inside the combination at first increases (since the oil is also salted), but then, within the same combination, we can trace a slight decrease in the salt content, which occurs, possibly, due to the «sealing» of the part ions inside soil aggregates, and it does not allow them to go into solution.

The same picture is observed separately for sodium and chlorine ions - since they form the main pool of salts (Fig. 3.4):

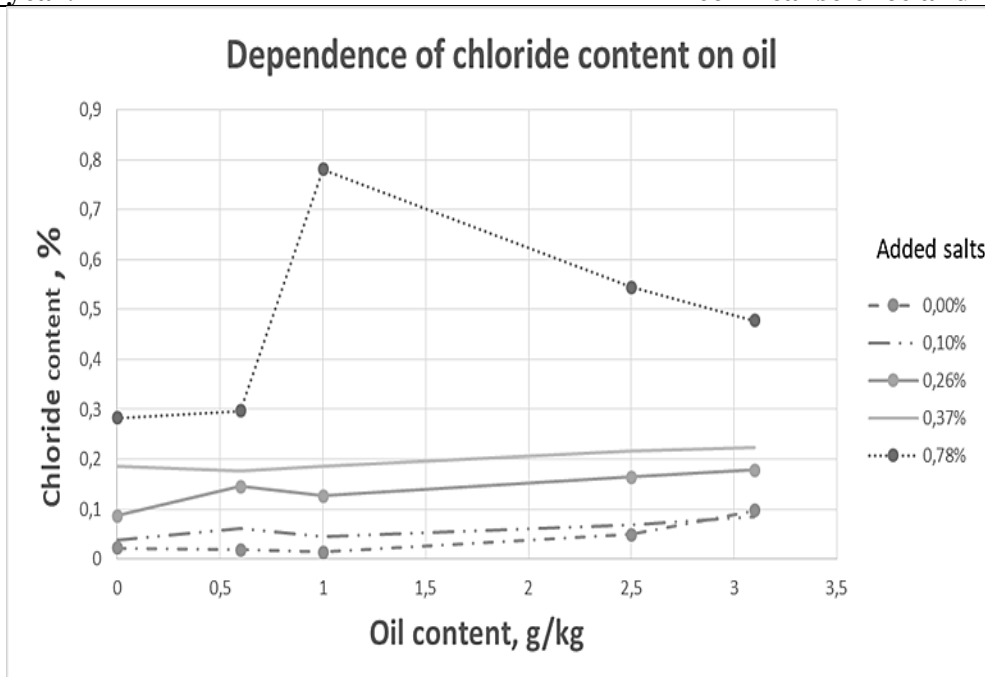


Figure 3. Dependence of the content of chloride ions on the content of petroleum products

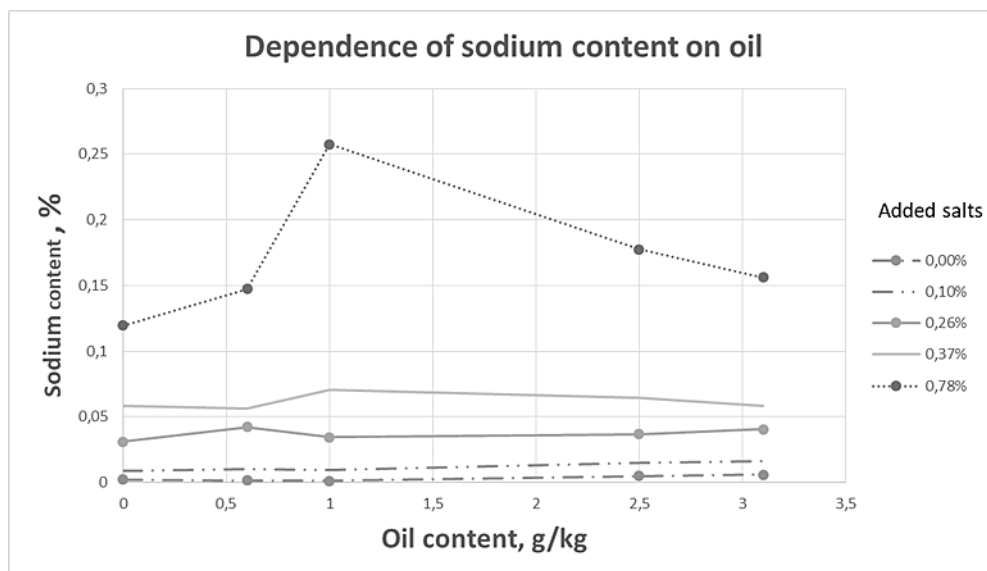


Figure 4. Dependence of the content of sodium ions on the content of petroleum products

For sulfates, a completely otherwise relationship is observed (Fig. 5): on the whole there are more of them in clean soil and their amount lowers with increasing pollution. Moreover, according to the absolute values of sulfates in clean soil, initially there is more than chlorides and sodium. This situation is possibly related to the fact that sulfates are prone to the formation of inner-sphere complexes (the formation of exclusively outer-sphere complexes is characteristic of chloride ions) with clay minerals of the soil. And also the phenomenon of negative adsorption is described for chlorides, and under conditions of oil pollution, there are more chlorides in the solution, and less sulfates, therefore, due to competitive interactions,

sulfates can exhibit the possibility of forming inner-sphere complexes and bind to clay minerals of the soil [22-24].

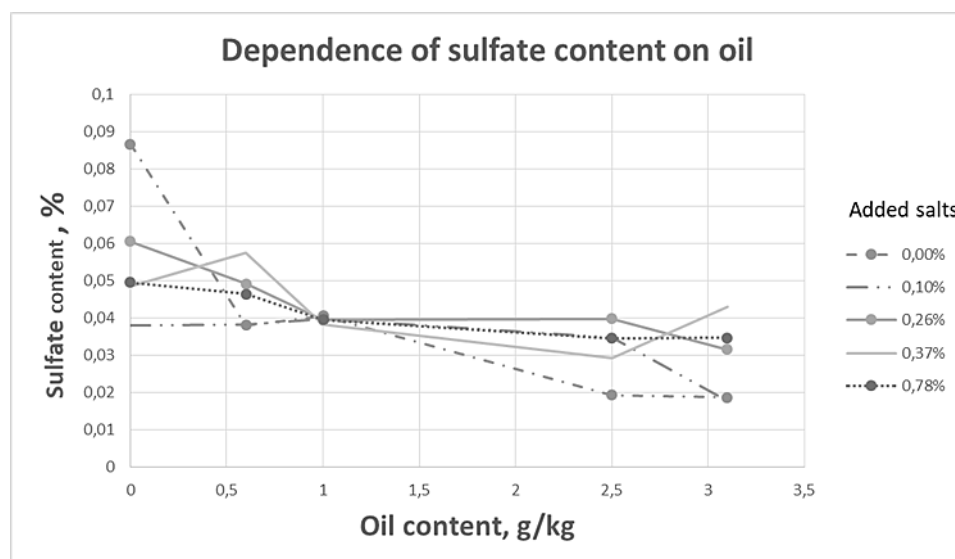


Figure 5. Dependence of the content of sulfate ions on the content of petroleum products

CONCLUSION. The Republic of Bashkortostan is both an agricultural and oil-producing region. A third of the soil cover of the Republic is represented by chernozems - fertile soils that form up to 60% of the workable soil of Bashkiria. The study of the accompanying salinization during oil contamination of soils, especially chernozems, is an urgent task.

As a result of accidental spills of crude and commercial oil, petroleum products, drilling wastewater, oilfield wastewater, which are increasing from year to year, a number of negative transformations take place in the soil - its physical, physico-chemical, chemical and biological properties change. At the same time, when oil enters the soil, it causes soil salinization, as well as the enveloping of soil particles, due to which the salts do not immediately come out into the soil solution, but gradually - as the oil degrades. In this case, there is a long-term toxic effect on vegetation. In addition, the oil envelops the roots of plants, impairing the flow of moisture and inhibiting their development, while being itself a potent toxicant [22-25].

The features of the dynamics of oil contamination and accompanying salinization require further study, which is planned to be performed subsequently both within the framework of the experiment after a year of exposure to oil and its ingredients in black steam conditions, and in the field experiment.

1) In the course of setting up a laboratory experiment, it was possible to achieve a variation in the degree of salinity of the samples from non-saline to highly saline; salinity chemism is neutral with variation from sulfate in «clean» soil to chloride in highly saline soil.

2) With an increase in oil contamination from 0 to 1 g / kg, the salt content increases within one gradation of salinity, and then with an increase in oil contamination to 3 g / kg, seeming decrease in the salt content occurs, possibly due to the «sealing» of some of the ions inside the soil aggregates, this fact does not allow them to go into solution, and, as a result, salts are determined in smaller quantities. Significant differences were found for soil contamination with oil over 1 g / kg and accompanying salinization over 0.3%. Since chlorine and sodium ions form the main pool of salts, they give a similar picture of the distribution pattern.

3) The amount of sulfates decreases with increasing salinity. This may be due to the predisposition of sulfates to the formation of strong inner-sphere complexes with clay minerals of the soil, while the phenomenon of negative adsorption is described for chlorides. Under conditions of oil pollution and accompanying salinization, the amount of chlorides increases; this, presumably, can contribute to the formation of inner-sphere complexes by sulfates due to the occurrence of competitive interactions, while chlorides remain in solution.

This research was performed according to the Development program of the Interdisciplinary Scientific and Educational School of M.V. Lomonosov Moscow State University «Future Planet and Global Environmental Change».

References:

- [1] Akhmetov, R.M., Khusainov, Sh.M., Leshan, I.Iu. (2011). Tekhnogennaya degradaciya pochv neftedobyvayushchih rajonov yuzhnogo predural'ya [Technogenic degradation of soils of oil-extracting areas southern predural], *In Izvestiya Samarskogo nauchnogo centra rossijskoj akademii nauk [Bulletin of the samara scientific center of the russian academy of sciences]*, Samara, 13(5-2), 39-42.
- [2] Haustov, A.P., Redina, M.M., (2015). Perspektivy razvitiya issledovaniy processov transformacii uglevodorodnyh zagryaznenij okružhayushchej sredy [Prospects for development of research processes of transformation of hydrocarbon environmental pollution], *In Innovatika i ekspertiza: nauchnye trudy [Innovatics and expertise: scientific works]*, Moscow, 2(15), 194-200.
- [3] Zhabbarov, Z.A., (2017). Zagryaznenie stepnyh pochv yuzhnyh regionov Uzbekistana nef'tyu i nefteproduktami i ih rekultivaciya: avtoref. dis. ... kand. biol. nauk [Contamination of steppe soils in the southern regions of Uzbekistan with oil and petroleum products and their remediation: Author's thesis], Tashkent. DOI:10.13140/RG.2.2.28412.69761.
- [4] Abdrahmanov, T.A., Zhabbarov, Z.A., Kamilova, D.K., Zhuraeva, U., (2006). Metody i tekhnologii vosstanovleniya zemel', zagryaznennyh nef'tyu i nefteproduktami [Methods and technologies for recovery of contaminated by oil and petroleum products lands], *In Politematicheskij setevoj elektronnyj nauchnyj zhurnal Kubanskogo Gosudarstvennogo Agrarnogo Universiteta [Polythematic network electronic scientific journal of Kuban State Agrarian University]*, 19, 106-109, available at: <http://ej.kubagro.ru/2006/03/pdf/>
- [5] Khaziev, F.Kh., (2011). Issledovanie pochv v Respublike Bashkortostan [Research of soils in the Republic of Bashkortostan], *In Vestnik Akademii nauk Respubliki Bashkortostan [Bulletin of the Academy of Sciences of the Republic of Bashkortostan]*, Ufa, 16(2), 34-45.
- [6] Li, C.R., (2009). Ecological effects and bioremediation of petroleum-contaminated soil, Shaanxi: Chang'an University.
- [7] Ahmadiev, M.V., Rudakov, L.V., Orlov, A.A., Mil'man, Ya.L., Graf, I., (2013). Problemy normirovaniya dopustimogo sodержaniya nefteproduktov v prirodnyh pochvah na primere rossijskogo i nemeckogo zakonodatel'stva [Problems of standardizing the permissible content of petroleum products in natural soils on the example of Russian and German legislation], *Modernizaciya i nauchnye issledovaniya v transportnom komplekse: materialy mezhdunar. nauch.-prakt. konf. [Modernization and scientific research in the transport complex: materials of the international. scientific-practical conf.]*. Perm, 50-58.
- [8] Federal soil protection and contaminated sites ordinance, (1999). Federal Law Gazette, Berlin, P. 1554.

- [9] Mc Gill, W.W., (1997). Soil restoration following oil spills: review, *J. Can. Petrol. Technol.*, 16(2), 60-67.
- [10] Canada-Wide Standard for Petroleum Hydrocarbons (PHC) in Soil, (2008). Winnipeg, P.8, available at: www.ccme.ca/files/Resources/csm/phc_cws/phc_standard_1.0_e.pdf
- [11] Soil and groundwater pollution criteria. Annex to the Newsletter [Kriteria zničšteni Zemin a podzemni vody. Priloha Zdravodaje MZP CR roč 6], (1996). 8 p.
- [12] A Guide to the Assessment and Remediation of Underground Petroleum Releases, (1996). 2nd Edition, API Publication 1628, Washington, D.C. API.
- [13] Joint order of the Minister of Health of the Republic of Kazakhstan dated January 30, 2004 No. 99 and the Minister of Environmental Protection of the Republic of Kazakhstan dated January 27, 2004 No. 21-p «On approval of the standards for maximum permissible concentrations of harmful substances, harmful microorganisms and other biological substances that pollute the soil» [Sovmestnyj prikaz Ministra zdravoochraneniya Respubliki Kazahstan ot 30.01.2004 g. №99 i Ministra ochrany okruzhayushchej sredy Respubliki Kazahstan ot 27.01.2004 g. №21-p «Ob utverzhdenii normativov predel'no dopustimyh koncentracij vrednyh veshchestv, vrednyh mikroorganizmov i drugih biologicheskikh veshchestv, zagryaznyayushchih pochvu»].
- [14] Decree of the Ministry of Health of the Republic of Belarus «On approval of maximum permissible concentrations of petroleum products in lands (including soils) for various categories of lands» dated 12.03.2012 No. 17/1 [Postanovlenie Ministerstva zdravoochraneniya Respubliki Belarus' «Ob utverzhdenii predel'no dopustimyh koncentracij nefteproduktov v zemlyah (vklyuchaya pochvy) dlya razlichnyh kategorij zemel'» ot 12.03.2012 g. №17/1], (2012).
- [15] Soil description manual, Russian translation [Rukovodstvo po opisaniyu pochv, Russkij perevod], (2012). Food and Agriculture Organization of the United Nations [Prodovol'stvennaya i sel'skohozyajstvennaya organizaciya Ob"edinennyh Nacij], Rome, 101 p.
- [16] Bazilevich, N.I., Pankova, E.I., (1972). Opyt klassifikacii pochv po sodержaniyu toksichnyh solej i ionov [Experience in soil classification by the content of toxic salts and ions], In *Byullyuten' Pochvennogo instituta im. V.V. Dokuchaeva* [Bulletin of the Soil Science Institute. V.V. Dokuchaev], 5, 36-40.
- [17] Allison, L.E., Bernstein, L., Bower, C.A., Brown, J.W., Fireman, M.J., Hatcher, T., Hayward, H.E., Pearson, G.A., Reeve, R.C., Richards, L.A., Wilcox, L.V., (1954). *Diagnosis and improvement of saline and alkaline soils: USDA Agriculture handbook*, Government Printing Office, Washington D.C., 60, 160 p.
- [18] Stupin, D. Iu., (2009). Zagryaznenie pochv i novejšie tekhnologii ih vosstanovleniya [*Soil contamination and the latest technologies for their restoration*]. St. Petersburg, Lan', 432 p.
- [19] Ivanova, E.N., Egorov, V.V., Fridland, V.M., Rozov, N.N., Nosin, V.A., Frieв, T.A., (1977). *Klassifikaciya i diagnostika pochv SSSR* [Classification and diagnostics of soils in the USSR]. Moscow, «Kolos», 221 p.
- [20] Shishov, L.L., Tonkonogov, V.D., Lebedeva, I.I., Gerasimova, M.I., (2004). *Klassifikaciya i diagnostika pochv Rossii* [Classification and diagnostics of soils in Russia]. Smolensk, Ojkumena, 342 p.
- [21] IUSS Working Group WRB, (2015). World Reference Base for Soil Resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports, 106, FAO, Rome.

- [22] Trofimov, S.Ia., Fokin, A.D., Dorofeeva, E.I., Salpagarova, I.A., Kosheleva, Iu.P., Rudenko, A.N., Vasil'konov, E.S., Uzkih, O.S., (2008). *Viyanie neftyanogo zagryazneniya na svoystva chernozema vyshchelochnogo v usloviyah model'nogo eksperimenta [Effect of oil pollution on a leached chernozem properties in a laboratory experiment]*, In *Vestnik Moskovskogo universiteta. Seriya 17. Pochvovedenie [Moscow University Bulletin. Series 17. Soil Science]*, Moscow, 1, 34-38.
- [23] Pigna, M., Violante, A., (2003). Adsorption of Sulfate and Phosphate on Andisols, *In Communications in Soil Science and Plant Nutrition*, 34 (15-16), 2099-2113
- [24] Geelhoed, J.S., Hiemstra, T., Van Riemsdijk, W., (1997). Phosphate and sulfate adsorption on goethite: Single anion and competitive adsorption, *In Geochimica et Cosmochimica Acta*, 61(12), 3773-3797.
- [25] Hutchinson, T.C., Freedman, W., (1978). Effects of experimental crude oil spills on subarctic boreal forest vegetation near Norman Wells, N.W.T., Canada, *In Canadian Journal of Botany*, 56(19), 2424-2433.