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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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THE CONTENT AND DISTRIBUTION OF TRACE ELEMENTS IN SOILS DURING THE DEVELOPMENT OF OIL FIELDS IN THE REPUBLIC OF KALMYKIA

Abstract. The article presents the results of chemical analysis soils of drilling sites of the Sostinsky and Mezhozerny oil fields of the Republic of Kalmykia. The content of sodium ions is more than 2 times higher in both deposits. At the same time, the content of chlorides in some areas of the Mezhozerny field reaches its maximum. As a result, the soils are highly saline in terms of the degree of salinity and are mainly chloride-sulfate-sodium in terms of the type of salinity. In oil fields, oil spills lead to the accumulation of organic carbon many times, with the total content of organic matter exceeding up to 5 times. The increase in the content of petroleum products is greatest in water discharge and wellheads. Studies on the content of heavy metals in the soils of oil fields showed that the average content of elements does not exceed the maximum permissible concentration of substances. At the same time, the content of most heavy metals exceeds the background ones, for example, lead, cadmium up to 2 times, strontium up to 8 times, mercury up to 6-12 times. In comparison with the clarke of the lithosphere (according to Vinogradov), an ecological-geochemical specialization in cadmium is noted. In the soils of the Sostinsky deposit, in the series of distribution of heavy metals, the maximum value is typical for cadmium, and in the Mezhozernoye deposit for mercury. At the Sostinskoye deposit, higher than the background is characteristic of such elements as: lead, vanadium, copper, strontium, and at the Mezhozernoye deposit, the excess of the background is achieved for such elements as: cadmium, zinc, lead, vanadium, copper, chromium, strontium.

Key words: oil-contaminated soils, heavy metals, trace elements, oil products, drilling sites.

Introduction. Oil and gas technogenesis has become one of the most acute challenges of the 21st century. It covers vast areas of all inhabited continents of the Earth. Despite the improvement in the technology of extraction and its transportation, the problem of environmental pollution by oil products and associated heavy metals remains a major environmental problem. Unlike petroleum products, heavy metals are redistributed between individual components of the environment [1-3].

Monitoring and forecasting the state of the environment in the sphere of influence of the oil and gas complex is a prerequisite for taking timely measures to protect the natural environment from degradation. The content of heavy metals in the soil is a complex and informative indicator of the degree of soil pollution and can be used in environmental monitoring of technologically disturbed territories [4-6].

The territory of the Republic of Kalmykia is considered one of the main oil-producing regions in the Lower Volga region. There are 41 hydrocarbon deposits on the territory of the Republic of Kazakhstan, including 19 oil, 11 gas, 6 oil and gas and 5 oil and gas condensate. The deposits are located in the southeast of the Republic of Kalmykia in the Northwestern Caspian region.

The purpose of the study is to assess the changes in the chemical composition of the soils of the drilling sites of the fields under oil pollution; to determine the content of gross forms of heavy metals (HM), and to assess the degree of their pollution of soils in the studied areas.

Methods. The objects of study in this work were samples of soils and soil samples that were taken in the territory near the drilling sites of oil fields located in the southeastern regions of the Republic of Kalmykia - Sostinskoe and Mezhozerny.

The Republic of Kalmykia is located in the zone of steppes, semi-deserts and deserts. The climate is continental with the transition to a sharply continental climate. The region is the driest in the south of the European part of Russia. The soil cover of the area is formed in a hot climate and moisture deficit, it is a slightly undulating plain with a slope to the east, southeast with great diversity and high complexity. The relief of the area influences the formation of vegetation and soil cover.

Soil and soil samples were taken as the distance from the source of pollution: mouth, torch, oil storage tanks from a surface of 0-20 cm and from a depth of 20-30 cm.

Soil samples were taken as background samples at a distance of 1 km from the pollution source. During the work, more than 50 samples were selected and analyzed.

Studies were carried out on the content of water-soluble cations, anions, organic carbon, oil products, heavy metals (lead, cadmium, manganese, nickel, mercury, vanadium, zinc, copper, cobalt, strontium) in soils and soil grounds.

To carry out statistical processing of the data of the research results, geochemical indicators were determined, such as the concentration coefficient - Kc, the coefficient of the relative accumulation of trace elements in the soil - Kra, and the background concentration coefficient - Kbc.

Elements with high Kc values are typomorphic and determine the geochemical setting.

Results. To assess the degree of contamination of the soils of the drilling sites, the salt composition of soil samples taken on the territory of the oil sites was determined. As a result of studies of the salt composition of the soils of the studied areas, it was found that the soils are highly saline in terms of salinity and are mainly chloride-sulphate in terms of salinity. Salinization of oil fields is caused by spills of drilling fluids during well drilling, as well as spills of highly mineralized formation water during well operation. The highest salinization of soils of oil fields occurs with sodium ions and chloride ions. Increased salinity also occurs due to the strong alkalinity of soils in the arid zone.

The sodium content in the oil field ranges from 109.2 to 647.5 mg/kg. On the territory of the Sostinsky field, a high sodium content is observed near the wells and near the reservoir up to 312.75 mg/kg, while in the territory of the Mezhozerny field, a high sodium content is observed near the discharge of formation waters - 647.5 mg/kg. The average sodium content at the Sostinskoy deposit is approximately 2 times higher than the background values, and 2.5 times on the territory of the Mezhozerny field (figure 1).

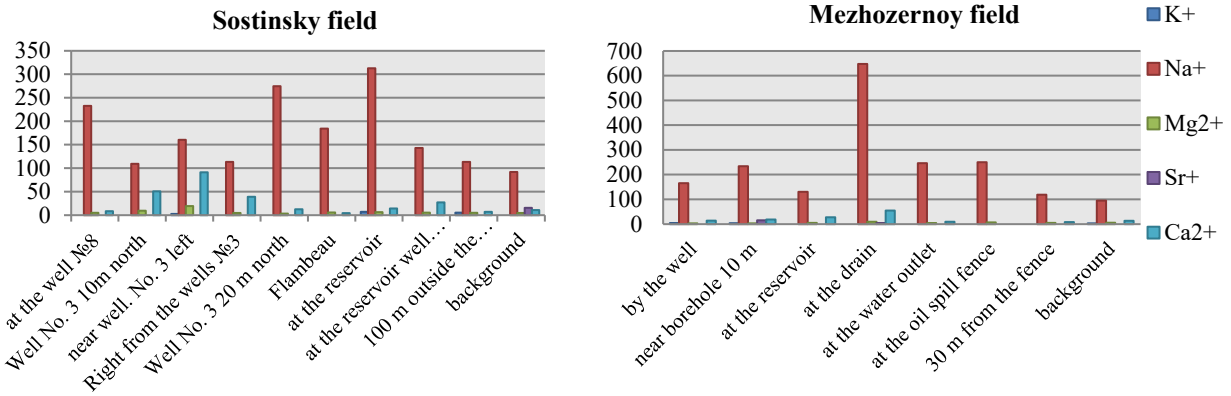

Figure 1 – Content of water-soluble cations in soils of deposits, mg/kg

The comparative content of chloride ions in the study areas varies within 94.1 - 3485.1 mg/kg. The highest chloride content is observed on the territory of the Mezhozernoy field, at the discharge of highly mineralized formation waters - 3485.1 mg/kg, a high chloride content is also observed at the reservoir, at the discharge of water and at the oil spill (figure 2).

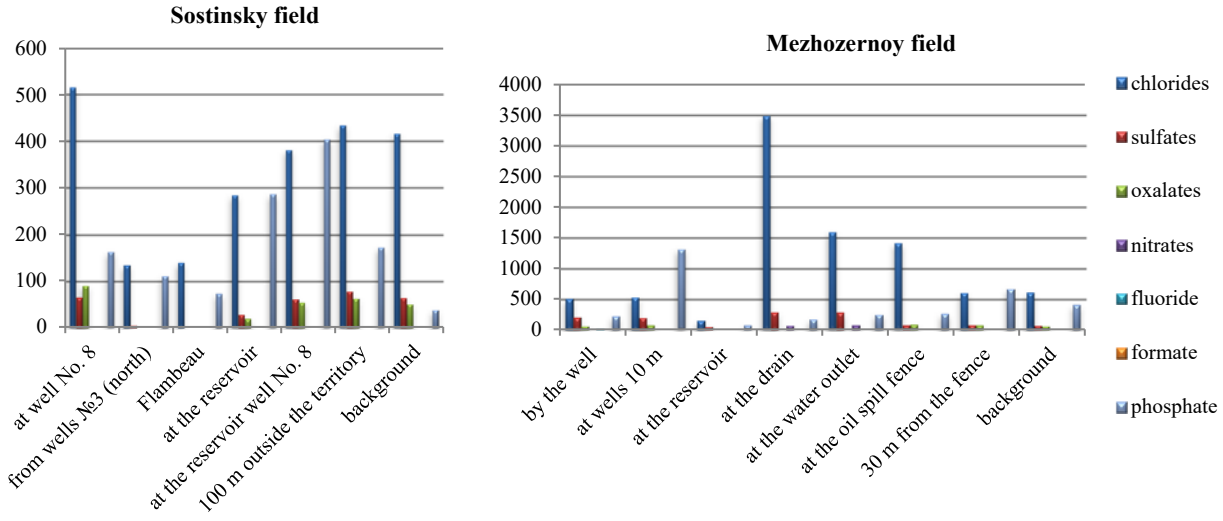

Figure 2 – The content of water-soluble anions in the soil on the territory of the studied deposits, mg/kg

The degree of salinity is greatly influenced by the chemical composition of formation waters. Many researchers have shown that the content of chlorine and sodium ions is mainly determined in the composition of salinization by drilling and formation waters. They account for 95% of the salt composition [7,8].

As a result of the restructuring of the main soil-geochemical parameters with oil pollution, the distribution of organic carbon in the soil changes. In case of oil spills at oilfield areas, such as wellheads, wells, technogenic carbon is introduced, which is sorbed in the soil and causes an increase in its total content [9, 10]. In such areas, the total organic carbon content is many times higher than the background values, sometimes tens of times.

According to the obtained data of the research results, it was revealed that the content of organic matter in the analyzed soil samples from the studied deposits varies from 0.42 to 12.7%. Compared to the background content, there is an excess in the territories of the fields 1.5-5.5 times higher than the background. The concentration of organic matter decreases with distance from the source of pollution.

The content of oil products is in the range from 61.9 ± 24.8 to 5475.0 ± 1368.8 ppm. The regularity of the increase in the concentration of oil products on the territory of the Sostinsky field can be traced from 100 m beyond the territory to the wells. On the territory of the Mezhozernoy field, the highest concentration of oil products is observed on the territory at the water outlet and at the wellheads.

In the soils of the studied deposits, we analyzed the soils for the content of heavy metals - Cd, Zn, Pb, V, Mn, Ni, Cu, Cr, Co, Sr, Hg, by atomic adsorption spectrometry.

The obtained values of the content of heavy metals in the soils of oil fields on the territories of the Sostinsky and Mezhozernoy fields showed that the Cd content is in the range from 0.17 to 0.99 mg/kg and 0.12-0.92 mg/kg, respectively. In all samples, the background values were exceeded. So, on the territory of the Sostinsky field, the cadmium content in the wells is 2 times higher, on the territory of the Mezhozernoy field, a significant excess of background indicators was observed by 8-13 times.

Determination of the Pb concentration in the soils of the studied deposits showed that its content varies within 0.8-6.4 mg/kg. High values were found near well No. 3 - 7.5 mg/kg in the Sostinsky field. On the territory of the Mezhozernoy field, an excess of the background concentration was noted throughout the entire territory, the highest concentration near the well - 6.4 mg/kg.

The strontium content in the selected samples significantly exceeds its background values. In the soils of the Sostinsky deposit, the range of its concentration was 11.1-61.8 mg/kg. In the samples near the well No. 8 and outside the territory of the field, its maximum concentrations were found 50.8-61.8, which is 8 times higher than the background value. In the samples from the Mezhozernoy field, an excess of up to 5 times was found in samples taken from the well, from the water drain and the oil spill.

The Hg content in soil samples is in the range of 2.7-79.0 mg/kg. A high content of mercury was found in the sample taken from the well and from the oil spill of the Mezhozernoy field, which is 6-12 times higher than the background value.

To assess the distribution and accumulation of toxicants in soils, an analysis of variance was carried out. To determine the nature of technogenic pollution, the values of the concentration coefficients Kc (the ratio of the content of an element in the soil to the content in the lithosphere), the coefficient of the relative accumulation of trace elements in the soil Kcr (the ratio of the content of a trace element in the soil to the background level in the Republic), the coefficient of background concentration Kb (the ratio of trace elements to the background concentration) [8].

According to the data obtained, it was revealed that when compared with Clark according to Vinogradov, all elements Kc <1, except for cadmium. Cadmium is a trace element, and in soils depleted in humus, the processes of cadmium migration are enhanced [11,12]. This is likely the reason for the increased concentrations of cadmium in the soils of the region [13].

The following series of HM distribution was formed in the soils of the Sostinsky field: Cd> Co> Zn> Ni> Mn> Pb> V> Cu> Cr.

In the soils of the Mezhozernoye field: Hg> Cd> Co> Cu> Zn> Ni> V> Pb> Mn> Cr.

The obtained ANOVA data are presented in table.

ANOVA of the results of determination of heavy metals

Element	K_c	K_{cr}	K_{cb}	Shares of MPC
Sostinsky field				
Cd	1.1	0	1.45	0.55
Zn	0.37	0	0.32	0.31
Pb	0.19	0.19	1.064	0.099
V	0.17	–	1.03	0.115
Mn	0.21	0.40	0.90	0.138
Ni	0.27	0.65	0.80	0.185
Cu	0.04	1.0	1.43	0.065
Cr	0.03	0.082	0.46	0.063
Co	0.42	0	0.75	0.66
Sr	0	0	4.20	0.055
Hg	0.03	0.04	0	2.8
Mezhozernoy field				
Cd	0.84	0	6.0	25.2
Zn	0.31	0.54	11.0	0.25
Pb	0.18	0.175	6.36	0.093
V	0.19		1.94	0.13
Mn	0.16	0.31	0.93	0.11
Ni	0.30	0.72	1.0	0.20
Cu	0.36	1.47	2.94	0.096
Cr	0.068	0.175	1.25	0.14
Co	0.44	–	0.95	0.7
Sr	–	–	2.48	0.11
Hg	0.108	0.144	0.00034	10.29

Kcr is the coefficient of regional concentration indicating elements that are strong pollutants in the soils of the study areas. According to the data obtained, it is possible to trace a series on the territory of the Sostinsky field: Cu> Ni> Mn> Pb> Cr> Hg, on the territory of the Mezhozernoy field: Cu> Ni> Zn> Mn> Pb> Cr> Hg.

For comparison with the background content of elements, we calculated the background concentration coefficient - Kcb. An excess of the background is observed for such elements: lead, vanadium,

copper, strontium, at the Sostinskoy field, and at the Mezhozernoy field, the following turned out to be higher than the background: cadmium, zinc, lead, vanadium, copper, chromium, strontium. Accordingly, the following rows were formed [14]:

Sr> Cd> Cu> V> Pb> Mn> Ni> Co> Cr> Zn> Hg;

Zn> Pb> Cd> Cu> Sr> V> Cr> Ni> Co> Mn> Hg.

To identify the features of the distribution of heavy metals in the studied soils of the deposits, a geochemical spectrum was built, the spectra were plotted according to the concentration or dispersion clark of elements. The regional concentration coefficient - Kcr is the ratio of the average content of an element in soils of oil fields to its background in the Republic of Kalmykia (figure 3).

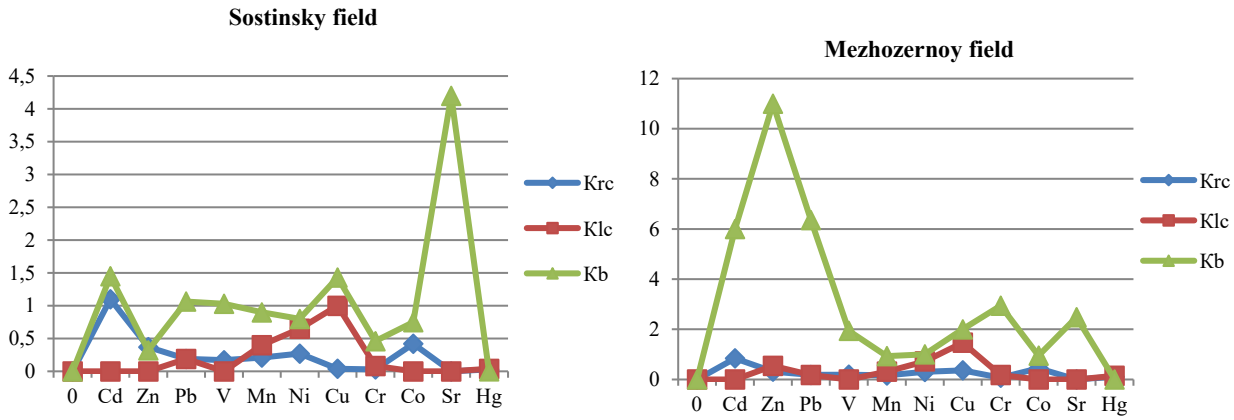

Figure 3 – Geochemical spectra of HM in the soil of the studied territories
(Krc-to the regional clarke, Klc - to the lithosphere clarke, Kb-to the background)

On the basis of the analyzes of the accumulation of heavy metals in the analyzed soil samples from the territories of the deposits, their ecological and geochemical specialization was revealed. In comparison with the clark of the lithosphere (according to Vinogradov), the ecological and geochemical specialization in cadmium on the territory of the Sostinsky field. In comparison with the regional clark, a high accumulation of copper was noted in the soils.

Conclusion. According to the results based on the determination of the chemical composition of the soils of the drilling sites of the studied deposits, it was determined that the soils are highly saline and, by the type of salinity, mainly chloride-sulfate-sodium. Studies of water extracts to determine the main ions of salinizing areas of deposits showed that the main cations that salinize the soil are sodium, potassium, magnesium, calcium, and of the anions, the main ions of salinization are chlorides, sulfates, phosphates. wells, as well as at the drain of water, the concentrations of which exceed the background content by several times.

Measurements to determine the content of organic matter (oil products and organic carbon) in soil samples showed that the content of organic matter exceeds the background content and a decrease in concentration is observed with distance from the wells.

2. Studies on the content of heavy metals in the soils of oil fields have shown that the average content of elements does not exceed the maximum permissible concentration of substances. In comparison with the clarke of the lithosphere (according to Vinogradov), there is an ecological and geochemical specialization in cadmium on the territory of the Sostinsky deposit. In comparison with the regional clark, a high accumulation of copper was noted in soils.

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ҚАЛМАҚ РЕСПУБЛИКАСЫНДА МҰНАЙ КЕН ОРЫНДАРЫН ИГЕРУ КЕЗІНДЕГІ ТОПЫРАҚТАҒЫ МИКРОЭЛЕМЕНТТЕРДІҢ ҚҰРАМЫ МЕН ТАРАЛУЫ

Аннотация. Мақалада Қалмақ Республикасының Состинский және Межозерное мұнай кен орындарының бұрғылау учаскелері топырағындағы химиялық талдау нәтижелері келтірілген. Топырақтағы ауыр металл мөлшері топырақтың ластану дәрежесінің күрделі және ақпараттық көрсеткіші болып саналады және технологиялық бұзылған территориялардың экологиялық мониторингінде қолданыла алады. Натрий иондарының мөлшері екі кен орнында да 2 еседен жоғары. Сонымен қатар хлорид мөлшері Межозерное кен орнының кейбір аудандарында максималды деңгейге жетеді. Нәтижесінде топырақтың тұздану дәрежесі бойынша аса тұзды, ал тұздану типі бойынша негізінен хлорид-сульфат-натрий болып келеді. Тұздану дәрежесіне қабат суының химиялық құрамы үлкен әсер етеді. Көптеген зерттеушілер хлор мен натрий иондарының мөлшері негізінен бұрғылау және қабат суымен тұздану құрамында анықталатынын көрсетті. Мұнай кен орындарында мұнайдың төгілуі органикалық көміртектің бірнеше рет жиналуына себеп болады, жалпы органикалық заттар мөлшері 5 есеге дейін асады. Мұнай өнімдері құрамының көбеюі су ағызу мен ұңғыма сағасында көп кездеседі. Мұнай кен орындары топырағындағы ауыр металл құрамына жүргізілген зерттеулер элементтердің орташа құрамы заттардың ШРМ-ден аспайтындығын көрсетті. Сонымен бірге, ауыр металдардың көп мөлшері фоннан асып түседі, мысалы, Состинское кен орнында кадмий 2 есеге дейін және Межозерное кен орнында 8-13 есе; екі кен орнында қорғасын 2 есе артады; стронций Состинское кен орнында 8 есеге дейін және Межозерное кен орнында 5 есеге дейін; Межозерное кен орнында сынап 6-12 есеге дейін көбейеді. Литосфера кларкімен салыстырғанда (Виноградов бойынша) кадмийдің экологиялық-геохимиялық ерекшелігі атап өтіледі. Состинский кен орнының топырағында, ауыр металдардың таралуында максимум мәні кадмийге, ал Межозерное кен орнында сынапқа тән. Аймақтық кларкпен салыстырғанда топырақта мыстың жоғары жинақталатыны байқалды. Состинское кен орнында фоннан жоғары қорғасын, ванадий, мыс, стронций сияқты элементтерге тән, ал Межозерное кен орнында фон кадмий, мырыш, қорғасын, ванадий, мыс, хром, стронций сияқты элементтер үшін асып түсті.

Түйін сөздер: мұнаймен ластанған топырақ, ауыр металдар, микроэлементтер, мұнай өнімдері, бұрғылау алаңдары.

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СОДЕРЖАНИЕ И РАСПРЕДЕЛЕНИЕ МИКРОЭЛЕМЕНТОВ В ПОЧВОГРУНТАХ ПРИ ОСВОЕНИИ НЕФТЯНЫХ МЕСТОРОЖДЕНИЙ РЕСПУБЛИКИ КАЛМЫКИЯ

Аннотация. В статье приведены результаты химического анализа почвогрунтов буровых площадок Состинского и Межозерного месторождений нефти Республики Калмыкия. Содержание тяжелых металлов в почве является комплексным и информативным показателем степени загрязнения почв и может быть использовано в экологическом мониторинге техногенно-нарушенных территорий. Содержание ионов натрия превышают на обоих месторождениях более чем в 2 раза. При этом содержание хлоридов на некоторых территориях Межозерного месторождении достигает максимума. Вследствие чего почвы по степени засоленности являются сильно засоленными и по типу засоления являются в основном хлоридно-сульфатно-натриевые. На степень засоления большое влияние оказывает химический состав пластовых вод. Многими исследователями показано, что в составе засоления буровыми и пластовыми водами определяется в основном содержание ионов хлора и натрия. На нефтепромыслах разливы нефти приводят к накоплению органического углерода во много раз, при превышении общего содержания органических веществ до 5 раз. Увеличение содержания нефтепродуктов наибольшее в сливах воды и устьях скважин. Исследования содержаний тяжелых металлов в

почвах нефтяных месторождений показали, что средние содержания элементов не превышают предельно-допустимые концентрации веществ. В то же время содержание большинства тяжелых металлов превышают фоновые, например: кадмия до 2 раз на Состинском месторождении и в 8-13 раз на Межозерном месторождении; свинца в 2 раза на обоих месторождениях; стронция – до 8 раз на Состинском месторождении и в 5 раз – на Межозерном месторождении; ртути – до 6-12 раз на Межозерном месторождении. В сравнении с кларком литосферы (по Виноградову) отмечается эколого-геохимическая специализация по кадмию. В почвах Состинского месторождения в ряду распределения тяжелых металлов максимальное значение характерно для кадмия, а на Межозерном месторождении – для ртути. В сравнении с региональным кларком в почвогрунтах отмечено высокое накопление меди. На Состинском месторождении выше фона характерно таким элементам, как: свинец, ванадий, медь, стронций, а на Межозерном месторождении превышение фона достигнуто для таких элементов, как: кадмий, цинк, свинец, ванадий, медь, хром, стронций.

Ключевые слова: нефтезагрязненные почвы, тяжелые металлы, микроэлементы, нефтепродукты, буровые площадки.

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