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Satbayev University

ХАБАРЛАРЫ

ИЗВЕСТИЯ

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STUDY OF HEAVY METALS AND ARSENIC CONTENT IN SOILS OF THE COASTAL ZONE OF THE CASPIAN SEA OF THE KAZAKHSTAN SECTOR

Abstract. The study of the content of heavy metals and arsenic in the soils of the Caspian coast is of great practical importance. It is necessary to monitor the ecological state of the soil and assess the degree of its pollution on the existing situation. The so-called background content of heavy metals and arsenic in the soils of the coast will serve as a reference point for the study of contaminated soils in the event of an emergency oil spill, and will also reliably determine the rate and degree of their contamination.

Generally accepted methods and methods were used in conducting the observations. Chemical contamination of soils according to the results of the study has not been established.

The concentrations of gross forms of heavy metals are also below the established standards of maximum permissible concentrations (MPC), with the exception of single exceedances of gross copper. The exception is arsenic, the content of which almost everywhere exceeds the values of MPC, the maximum concentrations of which reach 7.1 MPC. High concentrations of arsenic are a regional natural geochemical feature of the territory, which are noted in the results of a number of research works carried out in the Caspian region. A feature of the studied area is the extremely low content of mobile forms of heavy metals, the concentrations of which are hundredths of the MPC, including in areas where there was an excess of gross forms. The MPC indicators established by

regulatory documents often do not take into account the geochemical features of the province and, moreover, the local features of the soil cover formed in natural abnormal territories. In soils above geochemical anomalies, some elements may be contained in an amount comparable to that observed in technogenically heavily polluted soils, or even exceed it.

According to the results of laboratory analyses, it can be concluded that the influence of technogenic factors on the content of heavy metals and arsenic in soils has not been revealed.

Key words: heavy metals, arsenic, soil, Caspian coast, Kazakhstan sector.

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ҚАЗАҚСТАН СЕКТОРЫНЫҢ КАСПИЙ ТЕҢІЗІ ЖАҒАЛАУ АЙМАҒЫНЫҢ ТОПЫРАҚ ҚҰРАМЫНДАҒЫ АУЫР МЕТАЛДАР МЕН МЫШЬЯКТЫ ЗЕРТТЕУ

Аннотация. Каспий жағалауы топырақтар құрамындағы ауыр металдар мен мышьякты зерттеудің практикалық маңызы зор. Бұл топырақтың экологиялық жағдайын бақылау және оның ластану дәрежесін қазіргі жағдайға бағалау үшін қажет. Жағалау топырақтарындағы ауыр металдар мен мышьяктың фондық құрамы мұнайдың төтенше төгілуі жағдайында ластанған топырақты зерттеу кезінде тірек нүктесі болып, сонымен қатар олардың ластану қарқыны мен дәрежесін сенімді анықтауға мүмкіндік береді.

Бақылау жүргізу кезінде жалпы қабылданған әдістер мен тәсілдер қолданылды. Зерттеу нәтижелері бойынша топырақтың химиялық ластануы анықталған жоқ.

Ауыр металдардың жалпы түрлерінің концентрациясы, жалпы мыстың бір реттік асып кетуін қоспағанда, шекті рұқсат етілген концентрацияның (ШРК) белгіленген нормаларынан төмен. Максималды концентрациясы 7,1 ШРК жететін, тұрақты дерлік ШРК асатын мышьякерекшелікке ие. Мышьяктың жоғары концентрациясы аумақтың аймақтық табиғи геохимиялық ерекшелігі болып табылады, бұндай тұжырым Каспий маңы

аймағында жүргізілген бірқатар зерттеу жұмыстарының нәтижелерінде тіркелген. Зерттелетін территорияның ерекшелігі ауыр металдардың жылжымалы нысандарының өте төмен құрамы болып табылады, оның ішінде жалпы түрлердің асып кетуі байқалған жерлерде олардың концентрациясы ШРК жүзден бір бөлігін құрайды. Нормативтік құжаттарда белгіленген ШРК көрсеткіштері көбінесе провинцияның геохимиялық өзгешеліктерін, әсіресе табиғи аномалды аумақтарда қалыптасқан топырақ жамылғысының жергілікті ерекшеліктерін ескермейді. Геохимиялық аномалиялардағы топырақтарда кейбір элементтер техногендік жоғары ластанған топырақтарда байқалатын мөлшерде болуы немесе одан да асып кетуі мүмкін.

Зертханалық талдау нәтижелері бойынша топырақтағы ауыр металдар мен мышьяктың құрамына техногендік факторлардың әсері анықталмағандығы туралы қорытынды жасауға болады.

Түйін сөздер: ауыр металдар, мышьяк, топырақ, Каспий жағалауы, қазақстандық сектор.

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ИССЛЕДОВАНИЕ СОДЕРЖАНИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ И МЫШЬЯКА В ПОЧВАХ ПРИБРЕЖНОЙ ЗОНЫ КАСПИЙСКОГО МОРЯ КАЗАХСТАНСКОГО СЕКТОРА

Аннотация. Изучение содержания тяжелых металлов и мышьяка в почвах побережья Каспия имеет большое практическое значение. Оно необходимо для контроля за экологическим состоянием почв и оценки степени ее загрязнения на существующее положение. Так называемое фоновое содержание тяжелых металлов и мышьяка в почвах побережья послужит точкой отсчета при исследовании загрязненных почв в случае аварийного разлива нефти, а также позволит достоверно определить темпы и степень их загрязнения.

При проведении наблюдений были использованы общепринятые методики и методы. Химическое загрязнение почв по результатам исследования не установлено.

Концентрации валовых форм тяжелых металлов также ниже установленных нормативов предельно-допустымих концентрации (ПДК), за исключением единичных превышений валовой меди. Исключение составляет мышьяк, содержание которого практически повсеместно превышает значения ПДК, максимальные концентрации которого достигают 7,1 ПДК. Высокие концентрации мышьяка являются региональной природной геохимической особенностью территории, которые отмечаются в результатах ряда исследовательских работ, проводимых в Прикаспийском регионе. Особенностью исследуемой территории является крайне низкое содержание подвижных форм тяжелых металлов, концентрации которых составляют сотые доли ПДК, в том числе на участках, где наблюдалось превышение валовых форм. Установленные нормативными документами показатели ПДК зачастую не учитывают геохимические особенности провинции и, тем более, локальные особенности почвенного покрова, сформированного на природных аномальных территориях. В почвах над геохимическими аномалиями некоторые элементы могут содержаться в количестве, сопоставимом с тем, какое наблюдается в техногенно сильно загрязненных почвах, или даже превосходить его.

По результатам лабораторных анализов можно сделать вывод, что влияния техногенных факторов на содержание в почвах тяжелых металлов и мышьяка не выявлено.

Ключевые слова: тяжелые металлы, мышьяк, почва, побережье Каспия, казахстанский сектор.

Introduction. The Caspian Sea is the largest closed reservoir on the planet with huge reserves of oil, gas and biodiversity. At least about 330 species living in the Caspian Sea are endemic. At the same time, this unique reservoir is a very fragile and vulnerable ecosystem. The main aspects of current environmental problems in the region are associated with serious pollution of oil and heavy metals and, as a result, a decrease in biodiversity levels, floods and fluctuations in water levels.

Currently, ecosystems of the Caspian Sea are undergoing changes under the influence of natural factors and human activities (Sokolskiy et al., 2021; Kenzhegaliev et al., 2021; Kenzhegaliev et al., 2021:16; Baibotayeva et al., 2021; Kenzhegaliev et al., 2019:14).

In the fall of 2019, scientists of the Atyrau University of Oil and Gas named after Safi Utebayev, together with the Kazakhstan Agency for Applied Ecology LLP, in accordance with the Contract UI163260 (Ground part) with NCOC N.V. company carried out field and analytical work within the framework of the implementation of «The National Plan for oil spill prevention and response in the

sea and inland water bodies of the Republic of Kazakhstan» and «The National Plan for oil spill preparedness and response at sea, inland water bodies and in the safety zone of the Republic of Kazakhstan» (Report NCOC N.V., 2019).

A safety zone of dry land has been investigated - a land zone extending for five kilometers from the shoreline of the sea towards the land, which may be contaminated due to an oil spill at sea or a source of sea pollution. The coastline is based on -27 mBS, from the average annual sea level over the past decade. The offshore coastal zone has been studied taking into account the location of plant biotopes, but not less than 5 km from the shore.

The purpose of the studies is to identify areas and zones of priority protection of environmentally sensitive zones along the coast of the Kazakhstan sector of the Caspian Sea from the border with the Russian Federation (RF) to the Tupkaragan Bay to determine priorities for oil spill response (Kenzhegaliyev, 2010; Gilazhov et al., 2020; Johnston, 2003; Pogrebov, 2010).

When conducting research, ground observation stations in the coastal zone above the water edge were examined. Sampling stations are located perpendicular to the shoreline and are designated as profiles (sections). Along the entire northern and eastern coasts of the Kazakhstan sector of the Caspian Sea (KSCS) on the profiles there are 3 ground stations from SP01 to SP19, one of which is at the water edge and further along the profile - 2 stations at a distance of 1000 and 5000 meters. From SP20 to SP28, 2 stations were examined along the profile (15 and 150 meters).

In total, 75 coastal stations were subjected to observation (in the table). The planned length of the research route along the seacoast from the border of the Russian Federation to the Tupkaragan Bay was more than 1200 km, the distance between the profiles was no more than 20 km.

Table - Number of stations, coordinates and components to be determined

№	Station	Latitude	Longitude	№	Station	Latitude	Longitude
1.	SP01	46° 29' 13.962" N	49° 51' 48.257" E	39.	SP11-1000-On	46° 50' 31.672" N	52° 42' 3.547" E
2.	SP02	46° 35' 24.994" N	50° 1' 47.909" E	40.	SP12-1000-On	46° 44' 15.696" N	53° 3' 8.027" E
3.	SP03	46° 41' 12.847" N	50° 14' 40.212" E	41.	SP13-1000-On	46° 37' 35.996" N	53° 2' 6.152" E
4.	SP04	46° 48' 24.273" N	50° 34' 26.099" E	42.	SP14-1000-On	46° 29' 26.751" N	53° 1' 18.426" E
5.	SP05	46° 51' 36.628" N	50° 43' 39.469" E	43.	SP15-1000-On	46° 18' 14.531" N	53° 0' 30.620" E
6.	SP06	46° 56' 55.834" N	51° 2' 7.915" E	44.	SP16-1000-On	46° 11' 23.786" N	52° 54' 14.192" E

7.	SP07	47° 0' 45.127" N	51° 26' 39.224" E	45.	SP17-1000-On	46° 4' 32.187" N	53° 3' 2.305" E
8.	SP08	46° 54' 18.370" N	51° 40' 16.525" E	46.	SP18-1000-On	45° 36' 57.004" N	52° 45' 1.867" E
9.	SP09	46° 50' 20.580" N	51° 58' 14.904" E	47.	SP19-1000-On	45° 27' 13.226" N	52° 35' 19.361" E
10.	SP10	46° 46' 14.384" N	52° 15' 29.596" E	48.	SP01-5000-On	46° 31' 12.937" N	49° 49' 9.077" E
11.	SP11	46° 50' 4.662" N	52° 41' 37.498" E	49.	SP02-5000-On	46° 37' 25.723" N	49° 59' 11.220" E
12.	SP12	46° 44' 18.837" N	53° 2' 21.140" E	50.	SP03-5000-On	46° 43' 54.167" N	50° 14' 18.989" E
13.	SP13	46° 37' 36.900" N	53° 1' 19.158" E	51.	SP04-5000-On	46° 51' 5.704" N	50° 34' 45.393" E
14.	SP14	46° 29' 22.697" N	53° 0' 31.901" E	52.	SP05-5000-On	46° 54' 16.962" N	50° 44' 13.063" E
15.	SP15	46° 18' 23.878" N	52° 59' 45.872" E	53.	SP06-5000-On	46° 59' 27.965" N	51° 0' 46.668" E
16.	SP16	46° 11' 21.138" N	52° 53' 27.709" E	54.	SP07-5000-On	47° 3' 23.745" N	51° 25' 51.240" E
17.	SP17	46° 4' 34.658" N	53° 2' 15.899" E	55.	SP08-5000-On	46° 56' 4.956" N	51° 43' 14.290" E
18.	SP18	45° 37' 5.703" N	52° 44' 17.398" E	56.	SP09-5000-On	46° 52' 2.196" N	52° 1' 18.759" E
19.	SP19	45° 27' 16.676" N	52° 34' 33.590" E	57.	SP10-5000-On	46° 48' 55.363" N	52° 15' 55.580" E
20.	SP20	45° 24' 46.943" N	51° 58' 47.311" E	58.	SP11-5000-On	46° 52' 19.698" N	52° 43' 47.815" E
21.	SP21	45° 20' 57.747" N	51° 26' 29.983" E	59.	SP12-5000-On	46° 44' 3.080" N	53° 6' 15.556" E
22.	SP22	45° 11' 51.236" N	51° 15' 35.283" E	60.	SP13-5000-On	46° 37' 32.328" N	53° 5' 14.121" E
23.	SP23	44° 58' 19.045" N	51° 2' 54.820" E	61.	SP14-5000-On	46° 29' 42.914" N	53° 4' 24.546" E
24.	SP24	45° 3' 36.958" N	50° 19' 36.304" E	62.	SP15-5000-On	46° 17' 37.095" N	53° 3' 29.569" E
25.	SP25	45° 0' 51.709" N	50° 1' 24.878" E	63.	SP16-5000-On	46° 11' 34.328" N	52° 57' 20.136" E
26.	SP26	44° 51' 35.198" N	50° 4' 1.646" E	64.	SP17-5000-On	46° 4' 22.251" N	53° 6' 7.916" E
27.	SP27	44° 38' 41.285" N	50° 18' 31.507" E	65.	SP18-5000-On	45° 36' 22.158" N	52° 47' 59.701" E
28.	SP28	44° 25' 30.416" N	50° 14' 33.512" E	66.	SP19-5000-On	45° 26' 59.376" N	52° 38' 22.429" E
29.	SP01-1000-On	46° 29' 37.762" N	49° 51' 16.436" E	67.	SP20(-150)	45° 24' 42.087" N	51° 58' 47.534" E

30.	SP02-1000-On	46° 35' 49.145" N	50° 1' 16.586" E	68.	SP21(-150)	45° 20' 53.009" N	51° 26' 31.507" E
31.	SP03-1000-On	46° 41' 45.107" N	50° 14' 35.908" E	69.	SP22(-150)	45° 11' 48.999" N	51° 15' 41.383" E
32.	SP04-1000-On	46° 48' 56.505" N	50° 34' 30.843" E	70.	SP23(-150)	44° 58' 15.270" N	51° 2' 59.131" E
33.	SP05-1000-On	46° 52' 8.666" N	50° 43' 46.477" E	71.	SP24(-150)	45° 3' 32.108" N	50° 19' 36.717" E
34.	SP06-1000-On	46° 57' 26.220" N	51° 1' 51.512" E	72.	SP25(-150)	45° 0' 48.609" N	50° 1' 30.153" E
35.	SP07-1000-On	47° 1' 16.872" N	51° 26' 29.783" E	73.	SP26(-150)	44° 51' 36.953" N	50° 4' 8.017" E
36.	SP08-1000-On	46° 54' 37.737" N	51° 40' 54.417" E	74.	SP27(-150)	44° 38' 40.073" N	50° 18' 38.099" E
37.	SP09-1000-On	46° 50' 40.910" N	51° 58' 51.660" E	75.	SP28(-150)	44° 25' 30.147" N	50° 14' 40.282" E
38.	SP10-1000-On	46° 46' 46.580" N	52° 15' 34.789" E				

In the autumn of 2019, studies were conducted at 50 stations.

Some of the stations were unavailable for research: fire in the SP01 section area, flooded salt marshes - SP07, surge phenomena in the SP15-SP19 section and worsening weather conditions (blizzard, snow) on the coast of northern Buzachi (SP20). The total length of the research route along the seacoast was - 2762 km. Also, the location of some profiles and the number of ground observation stations were changed in accordance with the real landscape of the coastline, the nature of the soils (flooded salt marshes), fire.

The hydrometeorological measurements, vegetation observations, soil sampling and morphological descriptions of soil horizons were carried out directly on the ground, and subsequent analysis of soil samples was carried out in laboratory conditions.

Materials and basic methods. Generally accepted methods and methods were used during the observations.

The soil samples were taken to determine the content of heavy metals and petroleum products at a typical site for the surveyed area, where a test site with a size of 10m x 10m was laid, and spot samples were taken at the corners and in the center of the site. Samples were taken in layers from 0-5 cm and 5-20 cm depths in accordance with the requirements of the following regulatory documents: GOST 17.4.3.01-83 «Nature protection. Soils. General requirements for soil sampling» and GOST 17.4.4.02-84 «Nature protection. Soils. Sampling methods and preparation of samples for chemical, bacteriological, and helminthological analyses», «Instructions for sampling when controlling soil pollution with oil and petroleum products. Basic requirements. 2006» and NCOC N.V. field work

guidelines: «Background environmental studies and production environmental monitoring: field work. Revision of A01. December of 2016» HSE-H34-PR-0001-000.

Research results. The criteria for assessing soil pollution are currently MPCs of chemical elements established by regulatory sanitary and hygienic documents. MPC of chemicals in soil, approved by Order of the Minister of National Economy of the Republic of Kazakhstan dated June 25, 2015, No. 452 «On approval of Hygienic Standards for environmental safety (soil)». MPCs of pollutants missing in the specified order were used from RND 03.1.0.3.01-96 «Procedure for standardization of production waste generation and disposal volumes».

The results of laboratory analyses showed that the concentrations of most elements determined in soils along the Caspian Sea coast are within the established MPC standards.

The content of gross forms of lead and zinc in all sampled soil samples is mainly tenths of the established MPC standards.

Maximum concentrations of gross lead in the surface layers of 0-5 cm and 5-20 cm at the level of 16.3-14.9 mg/kg (0.51-0.47 MPC) were noted in the soils of the SP08 and SP14 stations, respectively.

The fluctuation of concentrations in the upper soil horizons, except for the recorded maximum values, is 1.04-13.4 mg/kg (0.03-0.42 MPC), which is also a low indicator of the content of the element in soils. The lead content not exceeding the lower detection range of the laboratory method of 0.07 mg/kg is noted in isolated cases (Figure 1).

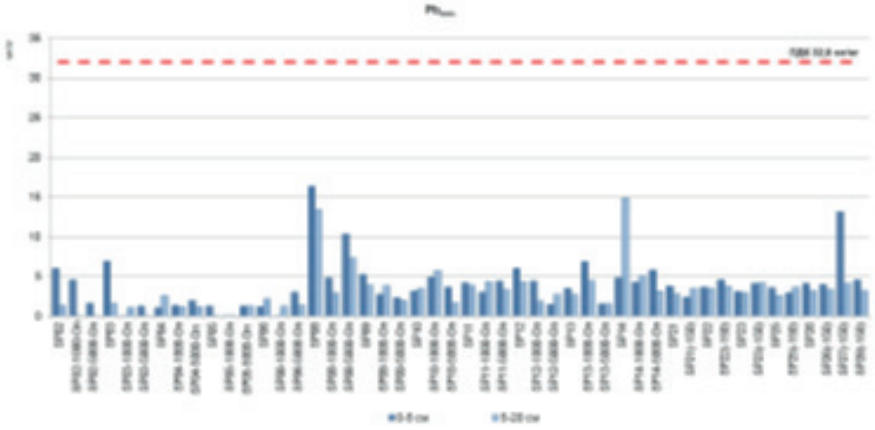

Figure 1 –The gross lead content in the soils of observation stations, autumn 2019.

The zinc content varies widely, ranging from 9.8 to 58.2 mg/kg (0.09-0.53 MPC) in various horizons. The maximum amount is observed in the surface

soil horizons of the SP08 station, where zinc concentrations reach 0.61-0.72 MPC (66.6-79.0 mg/kg) in the sampling horizons 0-5 and 5-20 cm. In 45% of the analyzed samples, the zinc content in the upper soil horizons is below the detection limit of the method (<0.7 mg/kg), (Figure 2).

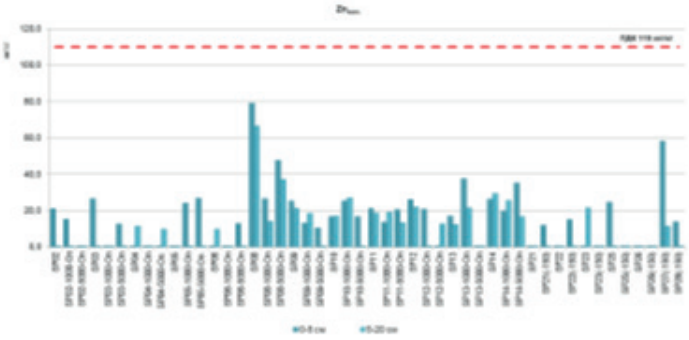

Figure 2 – The gross zinc content in the soils of observation stations, autumn 2019.

Analysis of data on the content of pollutants in the soils of the northeast coast of the Caspian Sea revealed an almost widespread excess of the normative indicators of gross forms of arsenic and copper (in isolated cases).

Isolated cases of exceeding the MPC of gross copper are noted in the soils of the SP08 station at a depth of 0-5 and 5-20 cm, amounting to 38.4 mg/kg (1.67 MPC) and 29.9 mg/kg (1.30 MPC), respectively, in other soil samples the copper concentrations do not exceed the tenths of MPC, the fluctuations of which are 1.10-15.2 mg/kg (0.05-0.66 MPC) (figure 3).

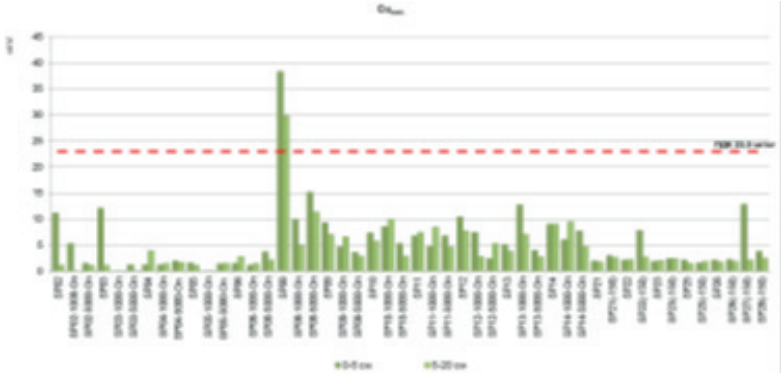

Figure 3 - Gross copper content in the soils of observation stations, autumn 2019.

The concentrations of gross arsenic in soils are in a wide range of fluctuations, which in the surface horizons of soils is mainly 1.03-13.56 mg/kg (0.52-6.78 MPC). As the maximum level of arsenic content, it is worth to highlight the highest indicators recorded in the soils of the SP22 and SP23 stations (-150)

at the level of 14.06 mg/kg (7.03 MPC) and 14.24 mg/kg (7.12 MPC) in the selection horizons 5-20 and 0-5, respectively. Minimal concentrations of arsenic are observed in the soils of the SP02 stations in the horizon of 5-20 cm and SP06-1000-On horizon of 0-5 cm, the indicators of which are below the detection limit of the laboratory method (< 0.07 mg/kg). Arsenic concentrations in soils below the MPC level (1.03-1.91 mg/kg), marked by laboratory analyses in 20% of samples, are mainly distinguished at stations on the north coast located within the SP02- SP06 profiles. The eastern part of the coast, characterized by SP08-SP28 profile stations, is characterized by a widespread excess of arsenic MPC at the level of 2.03-14.24 mg/kg (1.01-7.12 MPC), except for SP10-5000-On (5-20 cm) and SP13-5000-On (0-5 cm) stations, where it is not observed. In particular, the territories of the coast of the Tupkaragan Peninsula, Buzachi and Kulaly Island (SP21 - SP28 profiles) are distinguished with the highest arsenic content in the soils, where its concentrations in individual upper soil horizons are represented by the maximum values recorded by the results of studies (Figure 4).

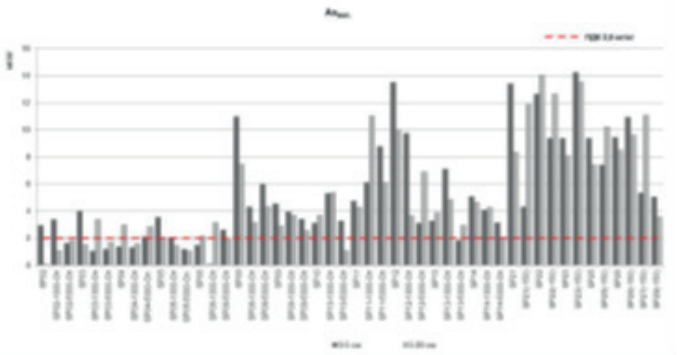

Figure 4 - Gross arsenic content in the soils of observation stations, autumn 2019.

Discussion. In the northeast Caspian region, NCOC N.V. has repeatedly carried out environmental studies, the results of which prove the natural high content of arsenic reaching the level of 10.0 MPC in soils and make it possible to attribute abnormal concentrations of arsenic to the regional geochemical feature of the territory (Report LLP «Kazekoproekt», 2017; Report LLP «Kazekoproekt», 2018; Report Sh.Yessenov, 2019). Similar studies were carried out in the Caspian region and are outlined in the joint work of «The Caspian State University of Technology and Engineering named after Sh. Esenov» and «The Tyumen Industrial University», which also confirm the anomalous feature of the increased arsenic content in coastal soils, noted at 10.0 MPC (Kenzhetaev et al., 2018; Kenzhetaev et al., 2019).The scientists of The Kazakh Research Institute of Soil Science and Agrochemistry named after U.U.Uspanov, on the basis of field route studies and the establishment of genetic properties of soils in the

coastal zone of the Northern Caspian region, developed a scale of soil stability to anthropogenic effects. Maps of soil resistance to mechanical disturbances and petrochemical pollution have been drawn up. Geoinformation technologies and remote sensing materials were used in mapping (Erokhina et al., 2018).

Conclusion. Based on the results of laboratory tests, it can be concluded that the influence of technogenic factors on the content of heavy metals and arsenic in soils was not detected.

Chemical contamination of soils according to the results of the study has not been established.

Concentrations of gross forms of heavy metals are also below the established MPC standards, except for single excess of gross copper. The exception is arsenic, the content of which almost everywhere exceeds the MPC values, the maximum concentrations of which reach 7.1 MPC. High concentrations of arsenic are a regional natural geochemical feature of the territory, which are noted in the results of a few research works carried out in the Caspian region.

A feature of the study area is the extremely low content of mobile forms of heavy metals, the concentrations of which make up hundredths of the MPC, including areas, where excess of gross forms was observed.

The MPC indicators established by regulatory documents often do not take into account the geochemical features of the province and, moreover, the local features of the soil cover formed in natural abnormal areas. In soils above geochemical anomalies, some elements can be contained in an amount comparable to that observed in technologically strongly contaminated soils, or even exceed it. As a result, there can be situations, in this case with arsenic, when the background content of elements in the soil, due to their concentration in the mother rock and soil formation conditions, exceeds the current MPC standards.

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