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ASSESSMENT OF THE DEGREE OF SOIL CONTAMINATION OF THE COASTAL ZONE OF THE CASPIAN SEA IN THE AREA OF AKTAU SUBURB

The article presents an assessment of the degree of soil contamination of the coastal zone of the Caspian Sea in the suburbs of Aktau. It examines the content of heavy metals at research sites in 2021 compared to 2018. The studies were conducted in the period from April 18 to April 25, 2021. Samples were taken according to a well-known method in soil science, at a depth of 0-20 cm by the envelope method using a sampler. The determination of humus in soil samples was carried out using the Nikitin method with a colorimetric ending by Orlov-Grindel. Mobile forms of heavy metals were determined at research sites using an atomic absorption spectrometer (MGA-915). According to the results of the research, it was revealed that the soils of the surveyed territory differed in the alkaline reaction of solutions, the content of organic matter at a low level and low resistance to anthropogenic influences. The content of heavy metals such as cadmium, arsenic and nickel decreased in 2021. It was found that the values of cadmium in all samples have the same values, and the values of arsenic are reduced. During the comparison, it was found that these results have not changed much, and the decrease in the content of heavy metals in the soil indicates a decrease in the anthropogenic load on the environment, due to the suspension of activities in all areas during the pandemic.

Key words: monitoring, soil, pollution, heavy metals, Caspian Sea, coastal zone, soil analysis.

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Ақтау маңы ауданында Каспий теңізінің жағалау аймағы топырағының ластану дәрежесін бағалау

Мақалада Ақтау қаласының маңындағы Каспий теңізінің жағалау аймағы топырағының ластану дәрежесін бағалау ұсынылған. Ол 2021 жылғы зерттеу алаңдарындағы ауыр металдардың құрамын 2018 жылмен салыстырғанда қарастырады. зерттеулер 2021 жылдың 18-25 сәуірі аралығында жүргізілді. Сынамалар топырақтанудағы белгілі әдістеме бойынша, 0-20 см тереңдікте сынама алу арқылы конверт әдісімен алынды. Колориметриялық аяқталуы бар Никитин әдісі бойынша топырақ үлгілеріндегі гумустың анықтамасы Орлов-Гриндель бойынша жасалды. Атом-абсорбциялық спектрометрді (МГА-915) пайдалана отырып, зерттеу алаңдарында (ЖК) ауыр металдардың жылжымалы нысандары анықталды. Зерттеу нәтижелері бойынша зерттелген аумақтың топырақтары ерітінділердің сілтілі реакциясымен, Органикалық заттардың төмен деңгейімен және антропогендік әсерлерге төзімділігінің төмендігімен ерекшеленетіні анықталды. Кадмий, мышьяк және никель сияқты ауыр металдардың мөлшері 2021 жылы азайды. Барлық үлгілердегі кадмий мәндері бірдей мәндерге ие және мышьяк мәндері төмендегені анықталды. Салыстыру барысында бұл нәтижелер ерекше өзгермегені анықталды, ал топырақтағы ауыр металдардың азаюы пандемия кезінде барлық салалардағы қызметтің тоқтатылуына байланысты қоршаған ортаға антропогендік жүктеменің төмендегенін көрсетеді.

Түйін сөздер: мониторинг, топырақ, ластану, ауыр металдар, Каспий теңізі, жағалау аймағы, топырақты талдау.

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Оценка степени загрязненности почвы прибрежной зоны Каспийского моря в районе пригорода Актау

В статье представлена оценка степени загрязненности почвы прибрежной зоны Каспийского моря в пригороде города Актау. В ней рассматриваются содержание тяжелых металлов на исследовательских площадках 2021 года по сравнению с 2018г. Исследования были проведены в период с 18 по 25 апреля 2021 г. Пробы отбирались по известной методике в почвоведении, на глубине 0–20 см методом конверта при помощи пробоотборника. По методу Никитина с колориметрическим окончанием по Орлову-Гринделю было выполнено определение гумуса в почвенных образцах. На исследовательских площадках (ИП) с использованием атомно-абсорбционного спектрометра (МГА-915) были определены подвижные формы тяжелых металлов. По результатам исследований было выявлено, что почвы обследованной территории отличались щелочной реакцией растворов, содержанием органического вещества на низком уровне и низкой устойчивостью к антропогенным воздействиям. Содержание тяжелых металлов таких как кадмий, мышьяк и никель уменьшились в 2021 году. Было выявлено, что значения кадмия во всех пробах имеет те же значения, а значения мышьяка снижены. В ходе сравнения было обнаружено, что данные результаты особо не изменились, а снижение содержания в почве тяжелых металлов, свидетельствует о снижении антропогенной нагрузки на окружающую среду, в связи с приостановлением деятельности во всех областях во время пандемии.

Ключевые слова: мониторинг, почва, загрязнение, тяжелые металлы, Каспийское море, прибрежная зона, анализ почвы.

Introduction

The Caspian Sea is a highly productive reservoir, which is combined with the relative poverty of its biological diversity. A significant number of works are devoted to physical, hydrochemical and biological processes and the ecological state of the Caspian Sea [1].

Exploration and exploitation of oil fields is the most important component of pollution. Large-scale geological exploration works are being carried out, new oil and gas fields have been discovered and the flow rate of old ones is increasing. It is no coincidence that the levels of oil pollution in different parts of the Caspian Sea are already many times higher than the maximum permissible norms [2, 3].

In view of this, it is necessary to carry out high-quality predicted work based on geo-ecological monitoring in order to preserve the resources of the Caspian Sea and the coastal zone, these methods will give not only a point assessment, but also a spatial picture of the ecological state of the Aktau territories [4, 5].

Notwithstanding the significant studies of the Caspian Sea, at present some of the sea areas are not widely researched. Several application questions relate to these areas and require fundamental approach to solve some issues on the soil state and the coastal areas of the sea. This issue is quite popular abroad, especially in the United States of America and Germany. These countries were the first to take interest in soil covering and impact of different factors on it. During the last thirty years there has been a sharp reduction in scientific research on this issue. One of such areas is the eastern coast of the Middle Caspian Sea, especially a water area in the center of Mangistau oblast, Aktau city and surrounding territory. Thus, issues on studying the coastal and water areas of the Caspian Sea are actual and necessary.

Earlier there were no studies on a soil covering at Akshukyr village of Mangistau oblast for presence of heavy metals. These studies may serve as a basis for the measures contributing Environmental Quality Management.

Materials and research methods

Field research was conducted in the coastal zone near the village of Shapagatov. The research was conducted before the V Summit of the heads of the Caspian states of Kazakhstan, Russia, Azerbaijan, Turkmenistan and Iran, scheduled for August 12, 2018 in Aktau. Field research was conducted by the route method. 4 research sites (RS), RS-1, RS-2, RS-3 and RS-4 (background) were laid to monitor the state of soils in the area of the suburban territory of Aktau opposite the hydrological stations HS-14 – HS-17 (Fig. 1 and 2). Table 1 shows the coordinates of the soil sampling points.

Figure 1 – Map-scheme of the research sites of RS 1,2,3 for monitoring the state of soils

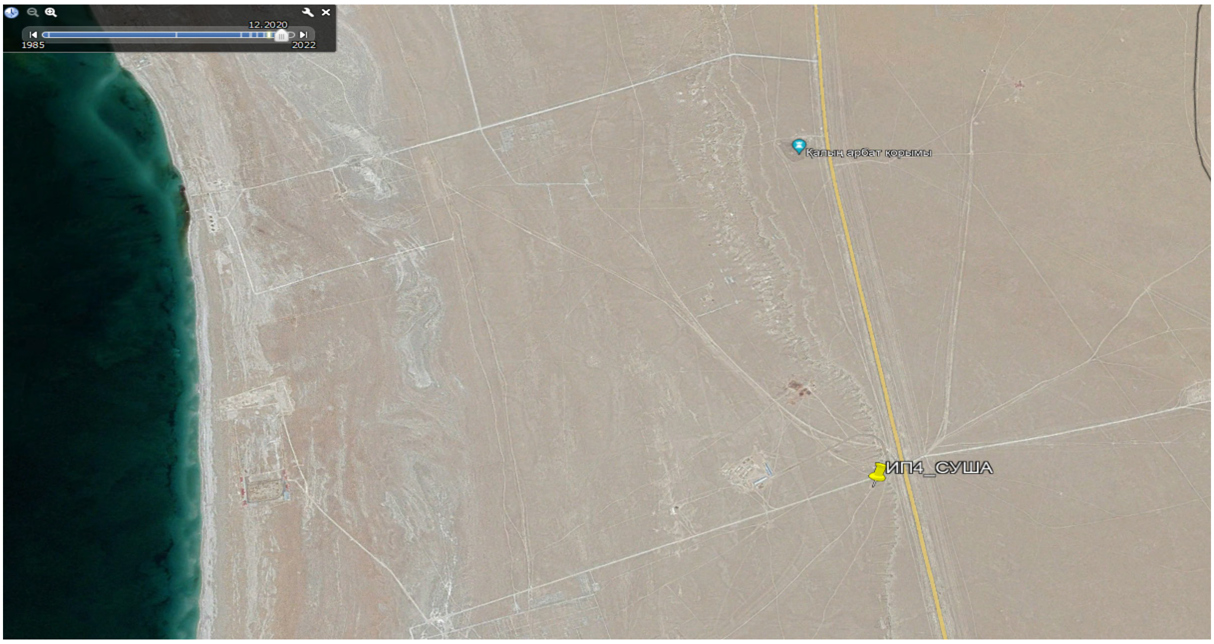

Figure 2 – Map-scheme of research sites RS-4 (background) for monitoring the state of soils

Soil sampling. When studying the soil, an important stage is sampling, recommended in accordance with GOST 17.4.4.02.84. This standard is necessary to control soil pollution, both general and local in areas affected by industrial enterprises, agricultural and transport sources of pollution. Sampling and soil analysis were carried out according to the approved methodology "Soil sampling for chemical analysis" [6, 7], from a depth of 5-20 cm, once during daylight on sites from one horizon (the weight of the soil sample is 1 kg). Soil samples were dried to an air-dry state at room temperature, removing large lumps and inclusions. The soil was ground in a mortar, sifted through a sieve (d = 1 mm). After spreading the soil in an even layer of 1 cm, point samples were taken with a spatula from at least four places and mixed to form a combined sample. The studies were carried out with a soil extract, which was prepared according to the standard method. Soil samples were taken at test sites RS-1,2,3 and 4 (background). The mixed sample consisted of 5 soil samples taken by an envelope of 5 points. An average sample of 300-400 grams was taken. In general, the samples are mixed samples with 20 points, that is, 5 points for 4 RS. Preparation of samples for the determination of heavy metals was carried out based on the laboratory of the department.

Table 1 – Location, coordinates, distance from the sea coastline, spring 2021

Station №	Location	Width	Longitude	Distance from the coast, m
RS -1	District of the village Akshuqyr	43°48'1»	51°1'59»	303,65
RS-2	District of the village Akshuqyr	43°49'5»	51°2'14»	1635,1
RS-3	District of the village S. Shapagatova	43°49'0»	51°1'29»	2135
RS-4	District of the village S. Shapagatova	43°55'19»	51°2'0»	9578

1. RS-1 is laid 20 km from Aktau in the village Akshuqyr, at a distance of 303.65 meters from the coastline of the sea.
2. RS-2 – at the highway, Aktau-F-Shevchenko, at a distance of 1635.1 m, from RS-1, in the area of open fertilizers and a warehouse of road-building materials.
3. RS-3 – in the area of private buildings at a distance of 2135 m, from RS-2.
4. RS-4 (background), at a distance of 9578 meters from RS-3, where the impact of harmful emissions from construction and production is practically not traced.

Determination of humus in the soil. Soil samples were studied by the following methods: color was determined by the Mansell scale, humus was determined by Tyurin, granulometric composition by Kachinsky, gross nitrogen was determined by Kjedal, mobile compounds of potassium and phosphorus – by Chirikov, mobile compounds for carbonate soils were determined by Machigin. Also, the following were determined by conventional methods: volume mass, solid phase density, hydrolytic acidity, the amount of absorbed bases. Determination of the amount of humus was carried out by the Nikitin method with a colorimetric ending according to Orlov-Grindel, which is based on wet salinization of organic soil compounds.

Determination of heavy metals in the soil. The soil samples were studied for the heavy metal content applying MGA-915A atomic spectrometry (Russia) in the Ecology Department laboratory in the Mangistau oblast as per the methodology. [8].

Since the heavy metal (HM) content in the soil was significant, the mobile forms of the following elements were determined: Pb, Ni, Cr, Hg, V, Cu, Fe, Zn [9]. Certain concentrations of heavy metals (HM) were compared with the available maximum permissible concentrations (MPC).

Methods of geoinformation technologies (GIT). The cartographic material of the research area was made using satellite images and using GIS programs (Google Maps, SAS Planet). Editing of schematic maps, diagrams and graphs are performed using CorelDRAW 11 and Paint programs.

Research Results and Discussion

Being as a complicated mechanism, the upper soil covering regulates the interaction between the spheres such as biosphere, lithosphere, and atmosphere, at the same time the Earth soil surface is not a target exposure only, but also has negative impact on a human body. The most intensive load is noticeable at studying the upper horizon of the soil since they have tendency to accumulate heavy metals [10]. The soil has an important role as a cleaner and a buffer, since it sustains emissions and wastes, being able to accumulate pollutants such as heavy metals, pesticides, hydrocarbons.

The heavy metals in sandy soils are easily escaped, seeping into the underground water. Some numbers of heavy metals are contained in the sandy and sabulous soil-forming rocks [11, 12]. Low analyzed samples show that sandy rocks own ultra-high filtration capacity.

Reductive-oxidative properties of the soil influences metals' mobility in the soil covering and the level of their oxidation at condition where there are reclamation processes.

Negative impact of the heavy metals on the soil covering due to anthropogenic activity depends on different sources of impact. The most dangerous pollution by the heavy metals coming from oil processing and chemical companies' activity [13-16]. It is known that around 95% of toxins come in as an anthropogenic dust, and around 20% with atmospheric residue, and the rest is in the form of dry fallout. Moreover, the anthropogenic sources of pollution of the soil by the heavy metal include organic and mineral fertilizers and sewage water [17-20].

According to the results of monitoring in Table 2, shows the physico-chemical properties of soils.

On the way to the airport of the city, brown desert soils predominate in the soil samples at the studied sites in the village of Akshuqyr, and the depth of the upper saline horizon is mainly saline or saline soils. Table 2 shows that the content of the humus in the upper horizon of the soil varies between 1.19 and 2.63%. The content of biogenic elements is low. Total phosphorus in the upper surfaces of the soil varies between 473.4 and 2003.8 mg/kg. The content of carbonates ranges from 1.78 to 3.13%, and the total nitrogen content varies between 0.24-0.41 The exchange capacity in the soil samples depends on the granulometric content, the heavier the content, the higher the capacity. The exchange capacity value varies between 9.65 and 32.19 mg-eq/100g of the soil. Stable predominance of exchangeable magnesium (40-80% of the exchange capacity) is observed in the soil-absorbing complex.

Water suspensions in the soil reacts as slightly alkaline or close to neutral (pH 6.88-7.42). As per the results of the survey, it was found out that the soil of the territory under survey was different by the alkaline reactions of the solutions, by a low content of the organic matter and weak resistance to anthropogenic impact.

Table 2 – Physical and chemical properties of soils of research sites

Physico-chemical characteristics of soils	Research sites (soil condition monitoring)			
	RS-1 2021	RS-2 2021	RS-3 2021	RS-4 (background) 2021
Humus, (%)	1,19	1,41	1,48	2,63
Total nitrogen, (%)	0,24	0,36	0,41	0,28
Phosphorus (gross), mg/kg	1662	473,4	516,15	2003,8
Carbonates, (%)	3,13	1,78	1,84	2,77
Exchange capacity, mg-eq/100 g of soil	9,65	22,89	24,89	32,19
Exchange calcium, mg-eq/100 g of soil	1,7	4,2	5,2	1,4
Exchangeable magnesium, mg-eq/100 g of soil	7,12	17,2	18,5	11,8
Exchange sodium, mg-eq/100 g of soil	0,63	0,95	0,98	16,29
Sum of salts	0,59	1,07	1,33	0,24
pH	7,42	7,52	7,63	6,87

At present the study of the upper surface of the soil for presence of the heavy metals is of great practical value. Rated level of the maximum allowable concentration is important, since the presence of the heavy metals exceeding MAC has a negative impact. These results of monitoring surveys are the basis for full assessment of the soil covering and can be applied for the development of work plan on reduction of the heavy metal concentration level. [21].

The main pollutants at the industrial zone territory are: Koshkar-ata tailings pit, transportation and industrial facilities.

Table 3 presents a comparative analysis of soils for heavy metals.

Table 3 – The content of heavy metals in the soils of the study sites, mg/kg

Substance	Research sites (2018,2021) in the soil monitoring area								
	RS-1 (*n* = 4) 2018	RS-1 (*n* = 4) 2021	RS-2 (*n* = 4) 2018	RS-2 (*n* = 4) 2021	RS-3 (*n* = 4) 2018	RS-3 (*n* = 4) 2021	RS-4 (Background) 2018	RS-4 (Background) 2021	MPC, mg/kg
Cu	3,2	2,1	4,7	2,0	3,6	3,2	2,1	2,8	**3,0**
Ni	3,6	1,45	5,3	1,5	3,8	1,85	2,5	1,46	**4,0**
As	2,9	0,54	4,9	0,57	4,2	0,53	7,3	0,59	**2,0**
Cd	3,6	0,012	9,4	0,018	4,1	0,022	3,7	0,02	**5,0**
Cr	4,3	2,0	5,3	1,98	3,5	3,1	2,8	2,65	**6,0**
Pb	5,9	0,23	6,17	0,29	4,1	0,31	6,3	0,071	**32,0**

Figure 3 – Diagrams of HM concentrations in soils in the area of Akshuqyr village (suburb of Aktau) on RS-1, 2, 3 and 4 (background), depending on the distance

During the experiment, an estimate of the lower limit of detection of these heavy metals was obtained: copper – 0.2 mg/kg, lead – 0.07 mg/ kg and chromium – 1.98 mg/kg with an initial weight of 5 g, the volume of the working solution is 50 ml. according to our own research in the village of Akshuqyr. No high concentration of heavy metals was found in all soil samples. The main array of values for the copper content in the soils of the city is in the range from 2 to 3.2 mg/kg according to the analyses of 2022. Chromium concentrations throughout the study area are much lower relative to the MPC (Cr – 6). A slight excess of the MPC of lead (up to 6.17) was detected only on one test area of RS-2 laid on the territory of highways located in the zone of constant exposure to automobile emissions – the roadside on the outskirts of the village.

And there is also a noticeable trend of a decline in the amount of heavy metals, over the years, apparently, due to the pandemic, the supply of heavy metals to the soil cover has decreased. Impurity index by the heavy metals of the soil, for instance by Zinc is less than 1.0 which means that the soil is pure. It should be here noted that the content of the existing heavy metals is much lower than maximum allowable concentration.

In Figure 3, you can clearly see how these content indicators have changed compared to 2018. It can be seen that the content of metals such as cadmium, nickel and lead is significantly overestimated by the test area of RS-2.

Thus, based on the comparison it was clear that the values have changed. Data on Cd, Ni, As content reduced in 2021. As per the values received, the presence of heavy metals in the soil covering ramps down every year, due to reduction of the anthropogenic load on the environment, because of the limits in the activities in most of companies during the pandemic.

The most direct and critical impact on the accumulation of the heavy metals, especially lead, in the soil covering is done by the exhaust gases [22]. Considering that the Koshkar-ata tailings pit is located near the populated area of Akshukyr village, it impacts directly on the accumulation of the chemical elements.

GOST 17.4.02.-83 introduced the classification division of heavy metals into 3 hazard classes:

Class 1 (especially toxic) – arsenic, cadmium, mercury, selenium, lead, zinc;

Class 2 (toxic) – boron, cobalt, nickel, molybdenum, antimony, chromium, copper;

Class 3 (low–toxic) – barium, vanadium, tungsten, manganese, strontium.

Accordingly, we found six heavy metals: cadmium, nickel, chromium, lead, copper and arsenic. Three of them belong to hazard class 1 and are particularly toxic. Such heavy metals are arsenic, cadmium, lead. The rest belong to hazard class 2 and are toxic. These are the remaining: nickel, chrome, and copper. Low-toxic heavy metals of hazard class 3 were not detected.

Conclusion

Based on the received results, we may conclude that the content of the heavy metals does not exceed maximum allowable concentration level. These surveys were performed in the designated laboratory, where the content of the heavy metals in the soil samples were defined for the following metals Cd, Cr, Cu, Ni, Pb, As. It was found out that in 2018 the content of the heavy metals was increased in the soil. Akshukyr village soil showed the presence of the heavy metals, thus, it was confirmed that near-by facilities have a negative impact on them. The soil pollution level by the heavy metals is average.

Of the metals under consideration, according to the degree of accumulation in the soil cover, lead prevails and a slight excess of MPC. The total index of soil contamination with heavy metals (Zc) is less than 1.0, which indicates that the soil is not polluted.

Based on the Table 2, the content of the humus at the upper surface of the soil varies between 1.19 and 2.63%. The content of gross phosphorus in the upper surface of the soil is within 473.4 to 2003.8 mc/kg. The content of carbonates ranges from 1.78 to 3.13%, and the total nitrogen content varies between 0.24-0.41%. The exchange capacity in the soil samples depends on the granulometric content, thus, when the granulometric content is heavy, the exchange capacity is high.

As per the survey results, it was found out that the soil of the area under survey is different by alkaline reaction of the solution, by the low content of the organic matter and by the weak resistance to the anthropogenic impacts. Compared to 2018, there is a decrease in copper in soils, its excess by 0.2 MPC was noted at RS-3, this is evidenced by a decrease in emissions from vehicles during the pandemic. The conducted studies showed that the contents of copper, nickel, zinc, arsenic, cadmium, chromium and lead at RS-3 were subject to the greatest pollution compared to other research sites in the area of private buildings, due to the influence of harmful emissions from construction and production. There is a decrease in chromium and copper by almost 2.5 times at RS-2, which may indicate the suspension of the storage of new road construction materials during the pandemic. The decrease is also noticed in the content of the heavy metals in soil samples: cadmium, arsenic and nickel, which is also a consequence after the pandemic.

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