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Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

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.

«ҚР ҰҒА Хабарлары. Химия және технология сериясы».

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CONTENT OF HEAVY METALS IN THE SEA WATER OF THE NORTHERN CASPIAN SEA

Abstract. The article presents the results of chemical analysis for the content of heavy metals in the waters of the fields in the northern part of the Caspian Sea. The content of heavy metals in water is a complex and informative indicator of the degree of water pollution and can be used in environmental monitoring of water bodies. An analysis was carried out on the content of eleven heavy metals at the Kashagan, Kalamkas Kairan and Aktoty deposits for the period from 2006 to 2019. All results were averaged with indication of their minimum, maximum and average values, and were also compared with the MPC of these heavy metals. Among the eleven heavy metals, only one metal is characterized by a content below the MPC, this is barium. The barium content was determined by sweat in all samples, but at the same time they did not exceed the MPC in all samples. A slight excess of the MPC is typical for such metals as cadmium, arsenic and zinc. Almost in all samples, except for one sample, cadmium was found, but at the same time it did not exceed 0.3 MPC. The maximum value was determined in samples from the Kashagan field. Arsenic was found only in 3.4% of samples, mainly in deep-water areas of the Kalamkas field, in which the content did not exceed 1.3 MPC. The zinc content was found in most samples with no excess of more than 0.3 MPC. The rest of the elements are high and highly high in content such as mercury, lead, vanadium, chromium, copper, nickel, and iron. The content of mercury was found in the samples over 1%, but with an excess of 10 to 47 MPC. The content of lead was found in the samples over ten percent, with an excess of 11 to 60 MPC. Vanadium was found in samples of about 20%, with an excess in the range of 2-6 MPC. Chromium was found in most samples with an excess of 3 to 29 MPCs at Kalamkas in 2014 and Kashagan in 2019. Copper content was found in samples of about 90%, with high concentrations at Kashagan in 2006 and 2010 up to 10-38 MPC. Nickel is found in most samples with a level of 0.9-1.1 MPC. The content of iron was found in more than 10 percent of samples with an excess of 15-60 MPC with a decrease of almost 3 times from 2006-2010 to 2011-2019.

Key words: seawater samples, heavy metals, North Caspian deposits, maximum permissible concentration (MPC), water pollution monitoring.

Introduction. The Caspian Sea is the largest inland undrained water on the planet, with all the characteristics of the ocean. The Caspian Sea is characterized by unpredictable long-term cyclical changes.

Nowadays, the condition of the Caspian Sea ecosystem is constantly changing under the influence of natural factors and human activities.

According to morphological and structural characteristics and natural geographical conditions, the Caspian Sea is usually divided into three parts: the North Caspian Sea, the Central Caspian Sea and the South Caspian Sea. The boundary between the North Caspian Sea and the Central Caspian Sea conditionally extends along the Mangyshlak rapids from Cape Tupkaragan to the bank of the Kulalinskaya River, and then to Chechnya. The border between central and southern is along the entrance of Absheron-at Zhiloy Island and Cape Kuli. The northern part with an area of more than 80,000 square kilometers is

shallow; the average depth is 5-6 m, and the maximum depth is 15-20 m. The North Caspian Sea is an area where rivers and seawater are actively mixed [1].

The Volga and Zhaik rivers are the largest sources of pollutants entering the North Caspian Sea. Nearly 90% of the total pollutants enter the Caspian Sea through river runoff. The Volga River accounts for about 80% of the total surface runoff into the sea. In some high water years, river runoff may be 75% of Beili sea volume [2,3]. Depending on the degree of pollution of the river waters, their contribution to the pollution of the northern ocean is also different. Compared with the last decades of the last century, the beginning of this century is characterized by the reduced concentration of petroleum products, synthetic surfactants and organochlorine pesticides in the water of the lower Volga River. However, the concentration of certain heavy metals (iron, zinc, nickel and copper) is still high [4,5].

The shallow depth and active mixing of water create conditions for the vertical distribution of nutrients. In the area under consideration, the stratification of seawater in terms of nutrients is not obvious; some signs of vertical differentiation were observed in the Kalamkas oil field, and a higher level of ammonium nitrogen was observed in the bottom horizon, which was found in Kashgar In the opposite relationship, the mineral forms of surface nitrogen and phosphorus are slightly dominant [6].

Methods. Marine ecology research is based on field guidelines: baseline research and environmental impact assessment research. The concentration of certain pollutants was compared with the maximum allowable concentration (MPC) of fishery reservoirs (MPC's General List, 1990) [7].

In order to evaluate the impact of technical factors, we will conduct the environmental monitoring station [4] and the comprehensive marine research station contract water long-term monitoring process of the pollutant water physical and chemical parameter values and pollutant concentration obtained In order to evaluate the biological resource status of Kazakhstan part of the Caspian Sea (independent research, hereinafter referred to as "comprehensive marine research") 2010-2016 [8]. The complex marine research work area covers the entire Kazakhstan part of the North Caspian Sea.

Results. During 2006-2019, in the samples of seawater, a multicomponent complex of microelements consisting of 11 metals and arsenic (metalloid) was investigated. In 2009 (autumn) - 2010 (autumn), aluminum was not detected. In the samples of sea water, trace elements of 1-4 hazard classes were determined [9].

Cadmium. In 2006-2019, concentrations were below the limits of analytical detection, below the MPC were recorded in 100% of cadmium samples, except for the 1st detection of 1.56 mg/dm³ (0.2 MPC) at Kashagan in 2011 (figure 1). At the stations of integrated marine research, cadmium was only detected in 2010 and 2019 up to 0.3 MPC [10].

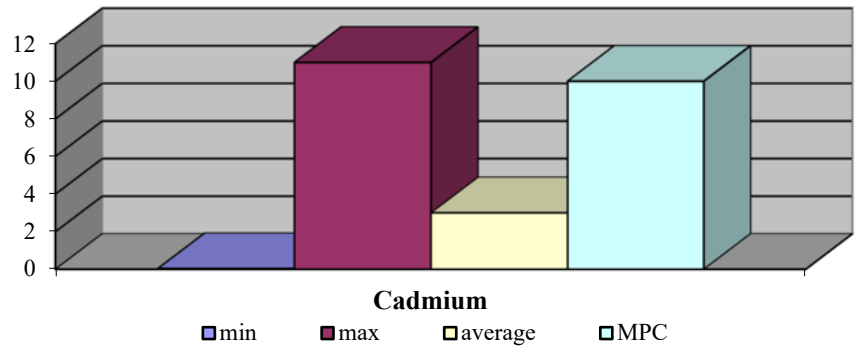

Figure 1 – Cadmium content in marine samples waters of the Northern Caspian

Arsenic was detected in 3.4% of samples in the range of 0.74-12.8 mg/dm³ (figure 2). In the monitoring site, an extensive joint distribution of Hg and As, stretching from Kalamkas to the coast, was found in 2008 (spring, autumn). During the pollution period (2008), As concentrations were in the range of 0.74-12.8 mg/dm³ (up to 1.3 MPC). At Kalamkas, a deeper-water area, the arsenic concentrations in the bottom horizon were slightly higher than in the surface one.

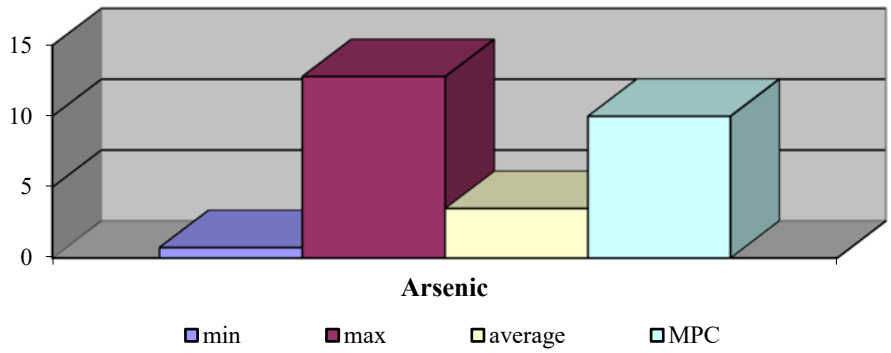

Figure 2 – Arsenic content in marine samples waters of the Northern Caspian

Mercury was detected in 1.1% of samples in the range of 0.07-3.7 mg/dm³ (figure 3). In the same year (2008), Hg concentrations were in the range of 0.07-3.23 mg/dm³. At Kalamkas, the mercury content (0.07-0.25 mg/dm³) was detected in the surface and bottom layers. At Kashagan, the field of mercury contamination covered only the surface layer, the center of concentration of relatively high Hg concentrations (1.46 - 3.23 mg/dm³) was in the area of islands A and EPC3. In all other water samples during 2006-2016 As and Hg were absent, except for occasional detections of As (3.36-4.76 mg/dm³) and the only Hg detection of 3.7 mg/dm³ at Kashagan in 2016. As concentrations are below the MPC in 100% of the samples. *Hg* concentrations ≥ 0.5 mg/dm³ in seawater are classified as extremely high pollution levels. The sources of As, Hg input to the water area in 2008 are unknown. The joint appearance and disappearance of pollutants could be provoked both by a single source and autonomous ones. It can be noted that arsenic and mercury, being biocides, can be part of biocidal polymers for anti-fouling and / or anti-corrosion coatings (corrosion inhibitors).

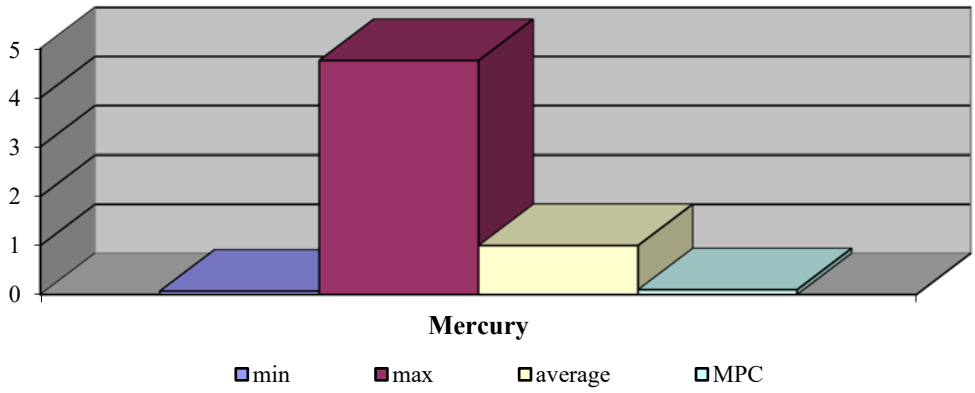

Figure 3 – Mercury content in marine samples waters of the Northern Caspian

Lead was found in significant quantities in 6.4% of samples in the range of 0.17-43.6 mg/dm³. The average long-term lead content at Kashagan and Kalamkas is within 0.2-0.3 MPC (figure 4). At Kairan and Aktoty, lead was not found in 100% of the samples. At Kalamkas, lead was detected in 2007, within the MPC in all samples. At Kashagan in 2012, the zone of relatively high lead concentrations was adjacent to the artificial islands A, D, EPC3. In the water area of the field pipelines, the lead detection zones were located in the marginal areas: near the northern border of Kashagan and higher concentrations (1.7-2.2 MPC) - in the landfall area. According to independent comprehensive marine studies, lead concentrations did not exceed the MPC level [11,12].

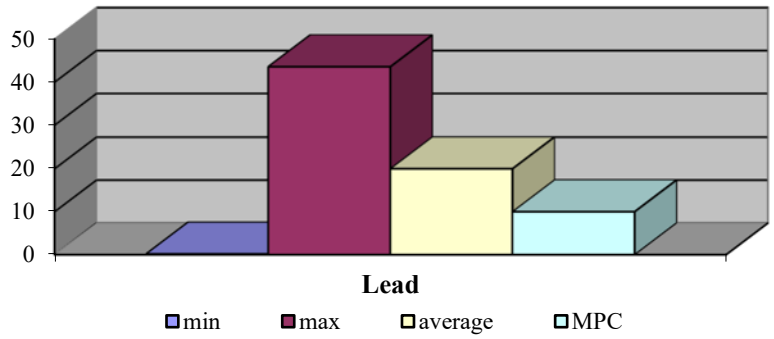

Figure 4 – Lead content in marine samples waters of the Northern Caspian

Vanadium was found in the range of 0.2-240 mg/dm³ in 18% of the samples (figure 5). The long-term average concentration of vanadium in 2011-2016 was significantly lower than that in 2006-2010. The currently recorded concentration range is 2-5 mg/dm³ (2-5 MPC), which is probably determined by the natural geochemical background. In the autumn of 2008, extremely high concentrations of vanadium (129-222 mg /dm³) were discovered in the western part of the Kalamkas mine. In Kashagan, high concentrations of vanadium were mainly detected in 2006 (up to 120 mg/dm³) and 2008 (up to 139 mg/dm³).

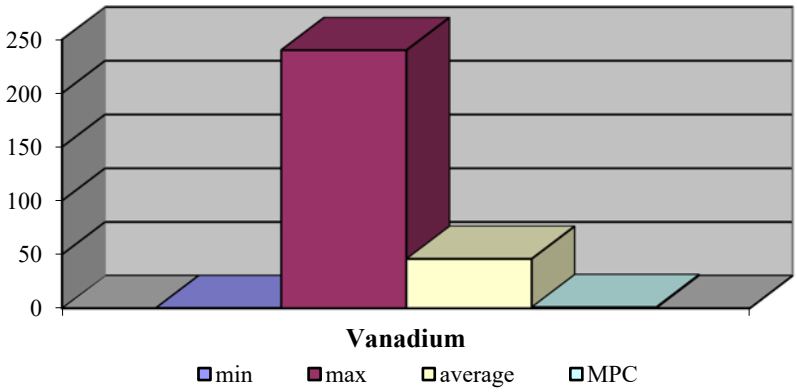

Figure 5 – Lead content in marine samples waters of the Northern Caspian

The total *chromium* content found in 94% of the samples was 0.1-1.059 mg/m³. The average annual concentration of chromium in 2011-2019 has decreased compared with the concentration in 2006-2010. The long-term average chromium concentration in the Kairan and Aktoty regions of Kalamkas is low, at 3-4 mg/dm^3. In the fall of 2008, in Kalamkas, an abnormally high chromium content of 583 mg/dm^3 was recorded; in 2016, the concentration recorded at various monitoring stations was 15-75 mg/dm^3. The dynamics are shown in figure 6.

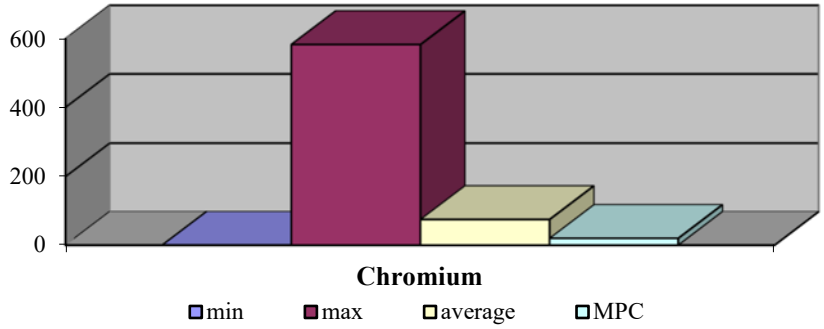

Figure 6 – Chromium content in marine samples waters of the Northern Caspian

The *zinc* content found in 90% of the samples was 0.35-154 mg/dm^3 (figure 7). From 2006 to 2016, the annual average zinc concentration remained at a fairly stable level at all observation points at 0.1-0.3 MPC. According to a comprehensive marine research, the zinc concentration is lower than the MPC level [11,12].

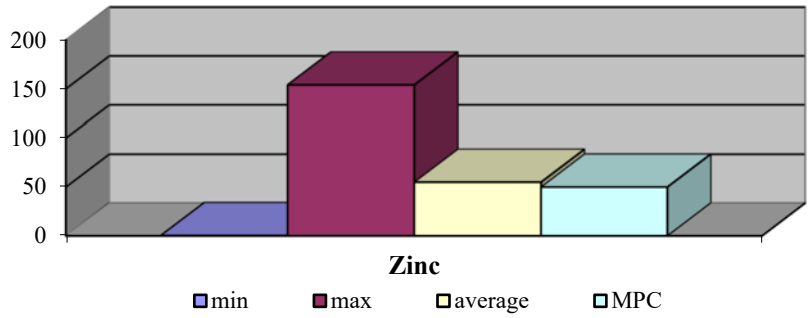

Figure 7 – Zinc content in marine samples waters of the Northern Caspian

The *copper* content found in 88% of the samples was 0.5-192 mg/dm³. The high concentration of copper (123-172 mg/dm³) in Kashgan State can be traced back to 2006. According to independent comprehensive marine research [Bio-Confirmation, 2010-2015, 2016], the average copper content in seawater is 0.5-7.1 mg/dm³. The maximum concentration level of this element was recorded in 2010, reaching 34 mg/dm³, and the value was lower than the MPC level in the rest of the time. From 2011 to 2016, at all observation points, the copper concentration usually did not exceed 10 mg/dm³. The distribution of copper concentration can be seen in figure 8. In the fall of 2015, in the waters of the on-site pipeline, the recorded copper concentration was very different (129 mg/dm³).

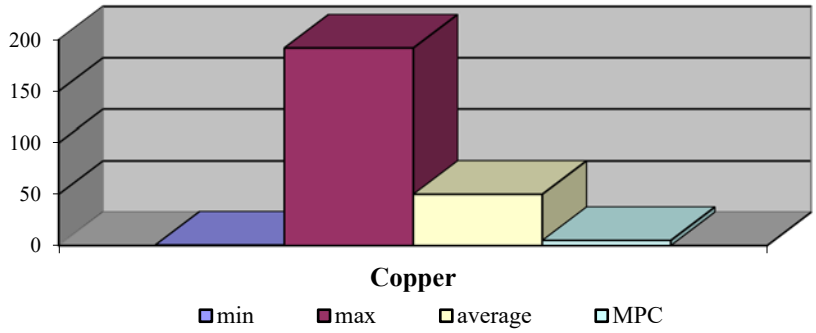

Figure 8 – Copper content in marine samples waters of the Northern Caspian

The *nickel* content found in 93% of the samples was 0.16-44,2 mg/dm³ (figure 9). The average annual nickel concentration from 2006 to 2016 remained at the level of 0.9-4.1 MPC.

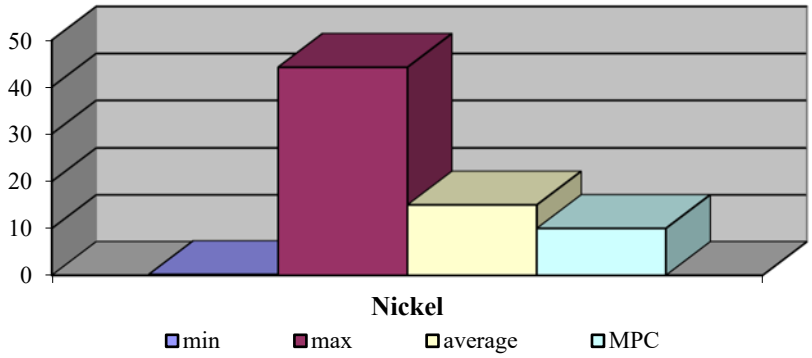

Figure 9 – Nickel content in marine samples waters of the Northern Caspian

The *barium* content in 94% of the samples was in the range of 1-442 mg/dm³. The maximum value was recorded in the waters of the on-site pipeline in the spring of 2016. The annual average dynamics of barium at the observation site is similar to that of nickel. No more than the maximum allowable concentration was detected in 100% of the samples (figure 10).

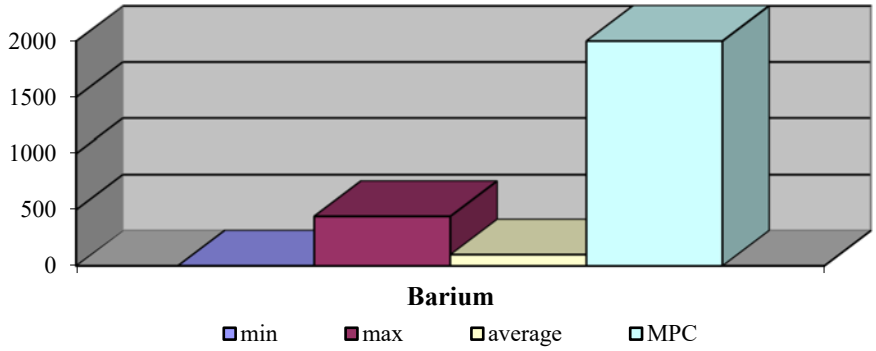

Figure 10 – Barium content in marine samples waters of the Northern Caspian

The total *iron* content found in 11% of the samples was 0.7-3112 mg/dm³ (figure 11). From 2011 to 2019, the annual average iron concentration in Kashagan State dropped three times compared with the annual average concentration from 2006 to 2010.

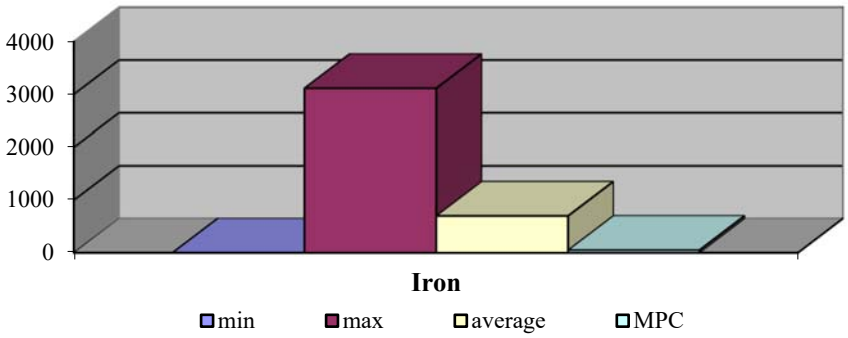

Figure 11 – Iron content in marine samples waters of the Northern Caspian

According to the published data [Caspian Sea, 1994], the HM content in the northern water of the Caspian Sea has the following characteristics: copper – 8 mg/dm^3, zinc-23 mg/dm^3, lead-1.3mg/dm^3, cadmium-0.5 mg/dm^3.

The current annual average copper concentration (7 mg/m^3) is no different from the concentration at the end of the last century. The concentrations of zinc (14-18 mg/dm^3) and lead (2-4 mg/dm^3) are very close to historical data [13].

Conclusion. Due to the inhomogeneity of natural geochemical conditions, the shift of the center of gravity of man-made loads and various operations, the distribution of metal content varies in space and time. Therefore, in the dynamic changes of the metal content index, in the last few years of the period under consideration Among them, the concentration level has a downward trend. Generally speaking, the metal content of seawater in the contract area can be considered satisfactory. The average concentration of metals such as cadmium, zinc, barium, total iron and arsenic did not exceed the standard. Except for vanadium and copper, the average annual concentration of metals is within the MPC range. In Kashagan in the spring of 2014, an abnormally high concentration of chromium (400 mg/dm³), iron (1672 mg/dm³), and nickel (138 mg/dm³) was found in a sample. The observation area is characterized by initial (background) contamination of copper (1.3 MPC) and vanadium (2-6 MPC). In 2008, a wide area with increased mercury and arsenic, vanadium, and total chromium content was discovered. In the Kailan and Aktoti deposit areas, isolated cases exceeded the maximum allowable concentrations of lead, total chlorine and lead along the pipeline in Kashagan, Kalamkas. During the study period, the long-term average average concentration of nickel stabilized at the level of 0.9-1.1 MPC.

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КАСПИЙ ТЕҢІЗІНІҢ СОЛТҮСТІК БӨЛІГІ АЙДЫНЫНДАҒЫ АУЫР МЕТАЛДАР ҚҰРАМЫ

Аннотация. Мақалада Каспий теңізінің солтүстік бөлігіндегі кен орындары суларындағы ауыр металдардың құрамына химиялық талдаудың нәтижелері келтірілген. Судағы ауыр металдардың мөлшері судың ластану дәрежесінің күрделі және ақпараттық көрсеткіші болып табылады және су нысандарының экологиялық мониторингінде қолданылады. Қашаған, Қаламқас Қайран және Ақтоты кен орындарында 2006 жылдан 2019 жылға дейінгі кезең ішінде он бір ауыр металл құрамына талдау жүргізілді. Барлық нәтижелер олардың минималды, максималды және орташа мәндерін көрсету арқылы орташаланды, сонымен қатар осы ауыр металдардың ШРМ-мен салыстырылды. Он бір ауыр металдың ішінде тек бір ғана барий металының құрамы ШРМ-ден төмен. Барий құрамы барлық сынама бойынша анықталды, бірақ сонымен бірге олар барлық сынамадағы ШРМ-ден аспады. ШРМ шамадан тыс артық болуы кадмий, күшяк және мырыш сияқты металдарға тән. Барлық сынама бойынша, бір сынаманы қоспағанда, кадмий анықталды, ол 0,3 ШРМ-ден аспады. Максималды мән Қашаған кен орнының сынамаларында анықталды. Мышьяк тек 3,4% сынамадан табылды, негізінен Қаламқас кен орнының терең сулы учаскелерінде, оның құрамы 1,3 ШРМ-ден аспады. Мырыш мөлшері 0,3 ШРМ-ден аспайтын көптеген сынамада анықталды. Қалған элементтер құрамы бойынша сынап, қорғасын, ванадий, хром, мыс, никель және темір сияқты жоғары және өте жоғары. Сынама құрамы сынамадан 1%-дан жоғары, бірақ 10-дан 47-ге дейінгі шекті деңгейден асып кеткен. Сынамада қорғасын мөлшері он пайыздан асып, 11-ден 60-ға дейін ШРМ артық болған. Ванадий шамамен 20% сынамадан табылды, оның мөлшері 2-6 ШРМ аралығында. Хром 2014 жылы Қаламқаста және 2019 жылы Қашағанда 3-тен 29-ға дейінгі ШРМ-ден асатын сынаманың көпшілігінде анықталды.

Мыс құрамы шамамен 90% сынамадан табылды, 2006 және 2010 жылдары Қашағанда жоғары концентрациясы 10-38 ШРМ аралығында. 0,9-1,1 ШРМ деңгейіндегі көптеген сынамада никель кездеседі. Темір мөлшері 10 пайыздан астам, 2006-2010 жылдардан бастап 2011-2019 жылдар аралығында 3 есеге дейін азаюы негізінде 15-60 ШРМ-ден асатын сынамадан табылды.

Түйін сөздер: теңіз суының сынамалары, ауыр металдар, Солтүстік Каспий кен орындары, шекті концентрация мөлшері (ШКМ), судың ластануын бақылау.

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СОДЕРЖАНИЕ ТЯЖЕЛЫХ МЕТАЛЛОВ В АКВАТОРИИ СЕВЕРНОЙ ЧАСТИ КАСПИЙСКОГО МОРЯ

Аннотация. В статье приведены результаты химического анализа на содержание тяжелых металлов вод месторождений северной части Каспийского моря. Содержание тяжелых металлов в воде является комплексным и информативным показателем степени загрязнения воды и может быть использовано в экологическом мониторинге водных объектов. Проведен анализ по содержанию одиннадцати тяжелых металлов на месторождениях Кашаган, Каламкас Кайран и Актоты за период с 2006 по 2019 годы. Все результаты были усреднены с указанием их минимального, максимального и среднего значений, а также сравнивались с ПДК данных тяжелых металлов. Среди одиннадцати тяжелых металлов только один металл характерен содержанием ниже ПДК, это барий. Содержание бария было определено почти во всех пробах, но при этом они не превышали ПДК во всех пробах. Незначительное превышение ПДК характерно для таких металлов, как кадмий, мышьяк и цинк. Почти во всех пробах, кроме одной пробы обнаружен кадмий, но при этом он не превышал более 0,3 ПДК. Максимальное значение было определено в пробах месторождения Кашаган. Мышьяк был обнаружен только в 3,4% проб, в основном на глубоководных участках месторождения Каламкас, в которых содержание не превышало 1,3 ПДК. Содержание цинка найдено в большинстве проб с непревышением более 0,3 ПДК. Остальные элементы характеризуются высоким и сильно высоким содержанием, такие как ртуть, свинец, ванадий, хром, медь, никель и железо. Содержание ртути найдено в пробах более 1%, но с

превышением от 10 до 47ПДК. Содержание свинца обнаружено в пробах более десяти процентов с превышением от 11 до 60 ПДК. Ванадий обнаружен в пробах около 20%, с превышение в интервале 2-6 ПДК. Хром найден в большинстве проб с превышением от 3 до 29 ПДК на Каламкасе в 2014 и Кашагане в 2019 годах. Содержание меди обнаружено в пробах около 90%, с высокими концентрациями на Кашагане в 2006 и 2010 годах до 10-38 ПДК. Никель обнаружен в большинстве проб с уровнем 0,9-1,1 ПДК. Содержание железа обнаружено в более чем в 10 процентах проб с превышением 15-60 ПДК с сокращением почти в 3 раза с 2006- 2010 годов к 2011-2019 годам.

Ключевые слова: пробы морской воды, тяжелые металлы, месторождения Северного Каспия, предельно допустимая концентрация (ПДК), мониторинг загрязнения воды.

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