ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ Satbayev University

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН Satbayev University

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STUDY OF THE BOTTOM SEDIMENTS OF RESERVOIRS OF URAL-CASPIAN BASIN

Abstract. Pollution entering the pond, especially heavy metals, is passed through the food chain to the person. In this chain, an important role is played by bottom sediments. Bottom sediments are of particular ecological interest among all parameters of the marine environment due to their important role in the processes of biological transformation. Today, it is very important to analyze the level of accumulation of heavy metals in bottom sediments. With an excess of their concentration, the problem is aggravated by the ability of heavy metals to accumulate and retain for a long time at all levels of the ecological pyramid, which can lead to longterm effects, since many metals are carcinogenic and mutagenic substances. The article presents the results of studies of the sediments on the content of heavy metals in reservoirs of the Ural-Caspian basin. Samples of the bottom sediments of the Ural (Zhayik), Kigach and the squares of the North-eastern Caspian were studied at different periods of the year. In the Ural River, the maximum permissible concentration is exceeded by the content of copper, chromium and lead. In the Kigach River, high levels of copper, chromium and nickel are present. In the bottom sediments of the North-eastern Caspian, the chromium content exceeds the maximum permissible concentration by several dozen times. In conclusion, I would like to note that studies carried out in various water bodies of the Ural-Caspian basin have shown the presence of toxic pollution in bottom sediments. Their concentration depends on the amount of runoff entering the reservoir. Although, at different points of the study, they show different values, the point is that they exist and play an important role in limiting the number of biological resources.

Key words: The Ural-Caspian Basin, the atomic absorption spectroscopy, the bottom sediments, heavy metals, maximum permissible concentration.

Introduction. In the marine environment of the Caspian, along with hydrocarbons, pollutants are heavy and transition metals - products of both natural origin (dissolved and sedimentary forms) and introduced as components of industrial wastes with river runoff (Kuliyev 2014).

Due to the diverse activities of mankind in recent decades, heavy metals (HM) have become common pollutants of aquatic ecosystems (Collective monograph 2001), and among the priority pollutants of freshwater ecosystems they occupy a special position (Komov & Tomilina 1999) in contamination of the biosphere and are of greatest interest for various environmental quality control services (Mudryi 1997). Migration of chemicals in water bodies is closely related to the transition of substances in the system «water - bottom sediments». Bottom sediments (BS) no longer interpreted only as a factor of improving the quality of water due to precipitation and sorption of various pollutants from the water mass, such as heavy metals, organic compounds of natural and anthropogenic origin and products of their degradation, radio nuclides, pesticides, etc. The accumulation of substances in bottom sediments of water bodies is a temporary fact of their elimination from the circulation and strengthen the self-purification of the aquatic environment, but pollution of aquatic ecosystems is still retained (Linnick 2006).

Under certain conditions, bottom sediments can act as a source of secondary contamination. This indicates that in the ecological assessment of the hydro ecosystem, bottom sediments are one of the most informative objects of study. This fact can be explained by the fact that our studies did not take into account the type of bottom sediments, and it is known that silty and clay bottom sediments keep heavy metals more firmly than sand deposits, which causes different degrees of metal accumulation (Stepanova 2006, Golinskii 2009).

About ten microelements are included in the list of toxicants especially dangerous for biota. Their danger

is associated, first of all, with the emergence of toxic risk zones in the water body. High concentrations of a number of toxic elements in BS pose an immediate danger to benthos and fish inhabiting the bottom layer. According to toxicological assessments of «stress indices», HMs rank second after pesticides. Particularly toxic are HM salts, which are decreasing toxicity can be arranged in a row (Brekhovskikh V.F. et al.2017):

$$Hg > Sb > Pb > Cr > Cd > Ni > Zn > Cu > Fe$$

In this regard, the monitoring of water quality and ecological state of natural water body and watercourse should include a comprehensive assessment of chemical concentrations in components of the ecosystem. Most metals are natural components of the environment, they participate in a variety of enzymatic reactions in the organisms' life, and their deficiency is sometimes as harmful as the excess (Shulkin 2007). The effect of sorption increases with the presence of clay particles with a diameter of about 20 microns. While changing the temperature conditions in the reservoir, pH, chemical oxygen consumption, concentration of sulfur compounds, bottom sediments can become a source of secondary pollution for water and hydrobionts: adding a toxicant to the reservoir even in the absence of a source of contamination.

This effect is also enhanced when the water content of the year decreases and the level of flood waters decreases, which was noted in the middle reaches of the Ural River from 2006 to 2014. Settling in the river, heavy metals accumulate in the bottom sediments and in living organisms inhabiting the reservoir (Miller et al., 2012). Thus, we clarify that the physico-chemical properties of sediment largely determine the intensity of accumulation of mercury compounds, as they are clusters of soil particles, mining (maternal) breeds of vegetable, animal debris and clay on the bottom of the pond, which, subjected to processes of destruction are becoming porous structure with a large number of active sites on the surface capable of attaching ions of mercury as well as holding them (Bespamyatov & Krotov 1985).

Sediments of the Northern Caspian have a coarse-grained character of aleurite (silt composed of quartz) mixed with crumb of shellfish, as well as terrigenous and oolitic sands. In the Ural furrow of the Northern Caspian, the bottom sediments are of fine-grained character: limestone silt, mixed with shell sand. The type of bottom sediments and granularity are dependent on the depth: the smaller the depth, the more coarse-grained deposits (Meliakina E.I., et al., 2006).

Sediments are of particular environmental interest among all parameters of the marine environment due to the important role in the processes of biological transformation. Their composition and structure are largely determined by the characteristics of the formation and sedimentation, which in the North-East of the Caspian sea are characterized by high content of carbonates and the high mobility of the material due to the transport of water masses (Kostianoy & Kosarev 2005; Ogar et al. 2014).

Disruption of the equilibrium state in the pore water – solid phase system as a result of external influences (acidification of the aquatic environment, erosion of BS, etc.) can lead to a noticeable increase in the flow of trace elements into the water mass. This change in concentration occurs over a short period of time, which is typical for the most typical emergency situations in the reservoir. (Brekhovskikh V.F. et al.2017, p.104). The content of heavy metals in bottom sediments of the Northern and Southern parts of the Caspian Sea is widely represented today in the publications of scientists dealing with this problem (Brekhovskikh et al. 2017, Hosseini, et al., 2018, Nasrollahzaden et al., 2015; Alizaden et al., 2018).

Studies on the level of toxicological contamination of bottom sediments North-East of the Caspian sea and reservoirs of the Ural-Caspian basin are not so numerous, mostly work 10-20 years ago. The aim of our research is to determine the content of heavy metals in the bottom sediments of the Ural-Caspian basin using more modern methods of sample preparation.

Materials and methods. Toxicological studies were conducted in autumn 2015 and spring, summer, autumn 2016. Sampling of bottom sediments for the analysis of metals, petroleum products was carried out at 15 stations, 6 of them are located in the estuary of Ural river, 3 – Kigach river (eastern branch of the estuary of the Volga) at 6 stations the North-Eastern part of the Caspian sea were surveyed.

Determination of heavy metals in bottom sediments is carried out by atomic absorption method using a spectrometer «M Γ A-915», method with electrothermal atomization in a graphite cuvette, intended for the quantitative determination of the content of various metals. The proportion of the prepared sample was 10 μ L Preparation of samples – by mineralization at elevated pressure on "Minotaur-2" with micro-wave heating method. The dosage of the prepared sample was 10 MKL (Methodology, 2014).

To compare the indicators of heavy metals in surface water bodies and in drinking water, water samples were also taken from the tap. Sampling dates from the Ural River and from the tap are the same.

Concentration of heavy metals was determined by the atomic absorption MGA-915 spectrometer intended for quantitative determination of heavy metal concentrations (Methodology PND F 2009).

Results and discussion. To study the dynamics of the coming pollution produced by sampling of bottom sediments of rivers Ural and Kigach River in six workstations studies and analyzed the content of heavy metals.

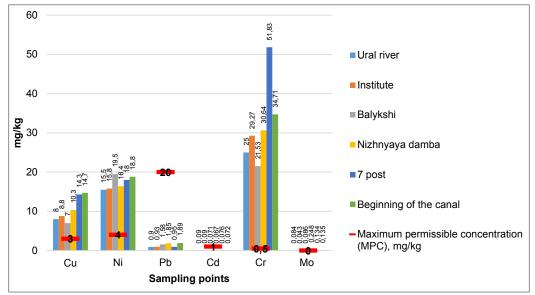


Figure 1. The heavy metals content in the bottom sediments of the Ural River in the autumn, 2015.

In 2016 sediments in the Ural River were chosen at the end of May from the shores of the reservoir. Compared to the fall 2015(Fig. 1), the content of metals is much less, with the exception of lead, which increased 2 times, but remained within the MPC (Fig. 2). The copper content at stations "Balykshi" and "Start channel" is higher than in the other stations of the study.

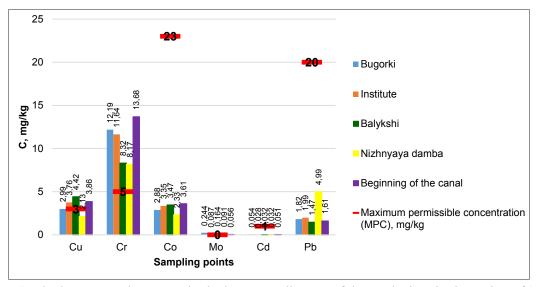


Figure 2. The heavy metals content in the bottom sediments of the Ural River in the spring of 2016.

Almost all heavy metals come from the upper reaches of the Ural river. The lead content in the sediments of the Ural river is in the range of 1.47-4,99 mg/kg. The content of cadmium on the coast of the river less than in the middle, as indicated by the data. The concentration of chromium is also much less than in the sediments of the middle of the river, which gives grounds to conclude about anthropogenic revenues contaminants. In the Ural River the conditions on the content of chromium in the bottom sediments is dressed up.

Spring research of bottom sediments in the river Kigach 26.04.2016 during the floods, from samples at two points of the "Kamyshinka". Data on the content of heavy metals in bottom sediments of the river Kigach to both objects of study show almost similar data. Compared with the last period (Tulemisova, et al., 2016) there are some changes in the direction of deterioration. The copper content in both points Kigach River exceed the MPC almost 2.6 times, cobalt is also a significant concentration compared to cadmium and molybdenum (Fig. 3).

The chromium content in the bottom sediments of the Kigach River is also high, as does the nickel content in the spring, apparently the introduction of industrial effluents into the reservoir.

The chromium content in the bottom sediments of the Kigach River is also high, as does the nickel content in the spring, apparently the introduction of industrial effluents into the reservoir. Same investigations showed that these metals can be deposited and magnified in the sediment and aquatic biomass (Hosseini M, et al., 2018) and reach a harmful level in the upper trophic leves. Concentration of lead, although within the limits of sanitary standards, but more than in the bottom sediments of the Ural River (Fig. 3). River water contains chemical elements in various forms: simple and complex ions, neutral molecules, and colloidal and suspended particles of various sizes. Different methods are used for their identification, which makes the interpretation of the data difficult. Contamination of the Volga aquatic systems is manifested mainly in an excess of HMs (Cu, Pb, and Cd) in suspended matter over the global background values, most notably in the flood period (Lychagin, et al., 2018).

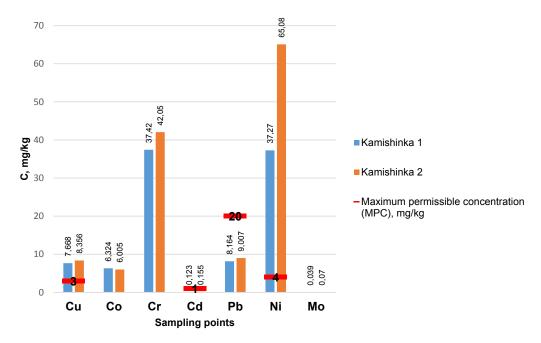


Figure 3. The heavy metals content in the bottom sediments of the Kigach River, spring.

After the floods, summer studies showed still high concentrations of chromium, cobalt and copper. In the studied stations "Pesok" and "Kamyshinka" of Kigach River approximately the same order values for content of heavy metals in the sediments were detected. In summer the content of lead, cadmium and copper decreased slightly to the MPC limits (Fig. 4).

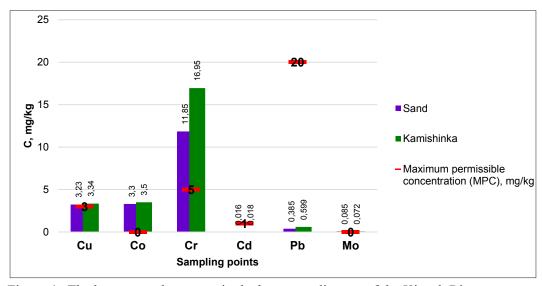


Figure 4. The heavy metals content in the bottom sediments of the Kigach River, summer.

With an excess of their concentration, the problem is aggravated by the ability of heavy metals to accumulate and retain for a long time at all levels of the ecological pyramid, which can lead to long-term effects, since many metals are carcinogenic and mutagenic substances. *North-Eastern Caspian*.

Studies of bottom sediments of the North-east Caspian were carried out by sampling in squares 12,25 in the pre-estuarine space of the Ural River and the Kigach River at 62,87 at the end of the flood. In general, the toxicological state of the water area of the North-east Caspian is diverse. The content of copper (Cu) in bottom sediments in significant amounts was found in square 12, but was not found in the foreheads of the Kigach river. Molybdenum, cadmium and lead are identified in small quantities in all the investigated sections of the sea. However, the cobalt content increased in all the squares of the North-east Caspian (Fig. 5). Obviously, this is the effect of the river's discharge during floods, yet the source of supply must be discovered. Perhaps, these are historical pollution of bottom sediments accumulated over the years.

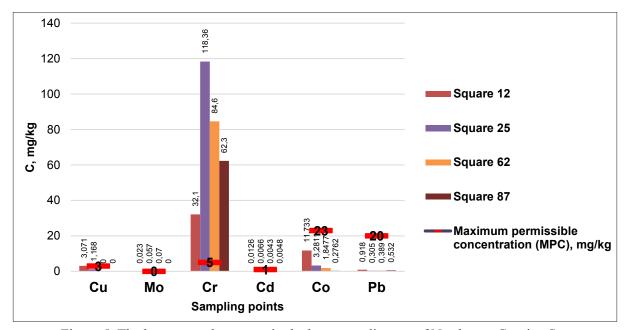


Figure 5. The heavy metals content in the bottom sediments of North-east Caspian Sea

Therefore, different points show different contents of heavy metals. According to (De Mora et.al. 2004), the studies of the content of heavy metals in bottom sediments in waters of the Caspian sea conducted in 2004, the content of chromium was 103,0 mg/kg, on the contrary the research of Agip KCO (2006-2010) (Review of the Potential for Environmental Impacts in the North Caspian ERM, 2008) showed the maxi-mum content of chromium was in the range 78,0 mg/kg. This is quite comparable with our data flood studies of chromium in squares 25, 62 (Fig. 5), which is the most maximum value for the entire measurement period. So in autumn of 2015 (Tulemisova et al. 2016), determined maximum value was in square of 25, 26 in the North-east Caspian.

The content of pollutants in bottom sediments are not regulated (Kenzhegaliev et al. 2019), but in the post-Soviet space, it was compared with the MPC for soil. Average concentration of all metals in the area Island D is higher than in the area of Island A. In all seasons we did not find any excess of the MPC for all pollutants, except for one case of chrome content stations at the level of one MPC.

The content of molybdenum (Mo) and cadmium (Cd) increased slightly compared to the previous period (Fig. 6). Concentration of lead from the investigated areas of the sea is lower in square 12 and above 25 in comparison with the flood period. The chromium content as the previous research period has high values several times higher than the MPC, this time in the square of 12 (Fig. 6).

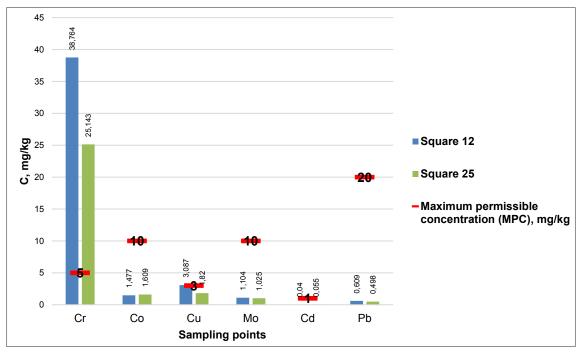


Figure 6. The heavy metals content in the bottom sediments of the North-east Caspian Sea in July, 2016.

In general, the condition on heavy metals in the sediments is satisfactory. In conclusion, it should be noted that studies conducted in various water bodies of the Ural-Caspian basin showed the presence of toxic contaminants in the bottom sediments. Their concentration depends on the amount entering the drainage basin (Tulemisova et al. 2015). Although, at different points in the study, they show different mea-nings, the fact is that they exist and play an important role in limiting the number of bioresources.

Conclusions. The elemental composition of bottom sediments reflects the biogeochemical situation in a particular subregion of the biosphere; therefore, the content of metals in the soils of various water bodies varies greatly. As noted by V. I. Vorobyov, the absence of clarke norms for soils of fishery reservoirs, norms similar to the MPC values for water, significantly complicates the assessment of both their supply with microelements and the assessment of their pollution. To prevent, control and reduce transboundary impact, the maximum permissible concentrations of emissions from point sources (dis-charges) should be based on the concept of best available technology.

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ЖАЙЫҚ-КАСПИЙ БАССЕЙНІ ӨЗЕНДЕРІ СУ ТҮБІ ШӨГІНДІЛЕРІН ЗЕРТТЕУ

Аннотация. Су объектісіне түсетін ластаушы заттар, әсіресе ауыр металдар, адамдарға қоректік тізбек арқылы келеді. Бұл тізбекте су түбі шөгінділері маңызды рөл атқарады. Су түбі шөгінділері биоло-гиялық трансформация процестеріндегі маңызды рөліне байланысты теңіз ортасының барлық параметрлері арасында ерекше экологиялық қызығушылық тудырады. Бүгінгі күні ауыр металдардың су түбі шөгінді-лерінде жинақталу деңгейіне талдау жасау өте маңызды. Олардың концентрациясының асып кетуімен ауыр металдардың экологиялық пирамиданың барлық деңгейлерінде жинақталуы және ұзақ уақыт сақталуымен мәселе қиындай түседі, бұл ұзақ мерзімді эффектілерге әкелуі мүмкін, өйткені көптеген металдар канцеро-гендік және мутагендік заттар болып табылады. Мақалада Жайық-Каспий бассейнінің су қоймаларындағы шөгінділерде ауыр металдардың құрамын зерттеу нәтижелері келтірілген. Жылдың әр кезеңінде Жайық, Қиғаш өзендері мен Солтүстік-Шығыс Каспийдің квадраттарының су түбіндегі шөгінділердің үлгілері зерт-телді. Жайық өзені шөгінділері құрамында мыс, хром және қорғасынның ШРК артық мөлшері байкалған, Қиғаш өзенінде мыс, хром және никельдің мөлшері жоғарылаған. Солтүстік-Шығыс Каспийдің су түбі шөгінділерінде хром

мөлшері ШРК-дан бірнеше ондаған есе асып түседі. Қорытындылай келе, Жайық-Каспий бассейнінің әр түрлі су айдындарында жүргізілген зерттеулер, су түбі шөгінділерінде уытты ласта-ну бар екенін көрсеткенін атап өткіміз келеді. Олардың концентрациясы су қоймасына түсетін ағынның мөл-шеріне байланысты. Зерттеудің әр түрлі нүктелерінде олар әртүрлі нәтижелер көрсеткенімен, мәселе олар-дың қол жетімділігінде және биологиялық ресурстардың санын шектеуде маңызды рөл атқаратындығында.

Түйінді сөздер: Жайық-Каспий бассейні, атомды-абсорбциондық спектрометрия, су түбі шөгінділері, ауыр металдар, шекті рауалды концентрация.

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ИССЛЕДОВАНИЕ ДОННЫХ ОТЛОЖЕНИЙ ВОДОЕМОВ УРАЛО-КАСПИЙСКОГО БАССЕЙНА

Аннотация. Загрязнения, поступающие в водоем, особенно тяжелые металлы, через пищевую цепочку передаются человеку. В этой цепи немаловажную роль играют донные отложения. Донные отложения представляют особый экологический интерес среди всех параметров морской среды вследствие важной роли в процессах биологической трансформации. На сегодняшний день весьма актуально анализ уровня накопления тяжелых металлов в донных отложениях. При избытке их концентрации проблема усугубляется способностью тяжелых металлов накапливаться и длительное время удерживаться на всех уровнях экологической пирамиды, что может привести к отдаленным эффектам, так как многие металлы являются канцерогенными и мутагенными веществами.

В статье приводятся результаты исследований донных отложений на содержание тяжелых металлов в водоемах Урало-Каспийского бассейна. Исследованы пробы донных отложений рек Урал (Жайык), Кигач и квадратов Северо-восточного Каспия в различные периоды года. В реке Урал наблюдается превышение ПДК по содержанию меди, хрома и свинца, в реке Кигач - повышенное содержания меди, хрома и никеля. В донных отложениях Северо-Восточного Каспия содержание хрома превышает ПДК в несколько десятков раз. В заключение хочется отметить, что исследования, проведенные в различных водоемах Урало-Каспийского бассейна, показали наличие токсичных загрязнений в донных отложениях. Концентрация их зависит от количества, поступающего в водоем стока, хотя в различных точках исследования они показывают разные значения. Суть в том, что они имеются и играют не последнюю роль в лимитации численности биоресурсов.

Ключевые слова: Урало-Каспийский бассейн, атомно-абсорбционная спектрометрия, донные отложения, тяжелые металлы, предельно допустимые концентрации.

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