Features of CU and MN accumulation by bottom sediments of the Caspian Sea

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Abstract. The main sources of chemical elements for aquatic organisms are sea water and bottom sediments, and the levels of chemical elements in organisms depend on the level of these elements in the environment. The Caspian Sea is a special biogeochemical province with geochemical barriers in the area of mixing of river and sea waters, therefore, the study of its biogeochemical background, the peculiarities of the chemical composition of bottom sediments is the relevance of the work. The aim of this work was to reveal the content of manganese and copper in the bottom sediments of the Caspian Sea. The study revealed low concentrations of copper and relatively high manganese in the bottom sediments of the Caspian Sea, which is primarily due to the parent rocks of the Caspian lowland, which are poor in Cu, but rich in Mn.

The results of biogeochemical analysis of bottom sediments of the ecosystem of the Caspian Sea serve as material for resolving the issue of the role of biogenic transformation of microelements in the cycle of substances.

1. Introduction

At present, the issues of geochemical ecology are relevant, which consider the processes of interaction between organisms and the environment through the biogenic migration of chemical elements. Chemical bonds of any organism with the environment in the biosphere are carried out through biogeochemical food chains of organisms - chemical elements of soil, water, air, and depend on the adaptation of organisms to the environment [1]. The main sources of chemical elements for hydrobionts are seawater and bottom sediments, and the levels of chemical elements in organisms depend on the level of elements in the environment [2].

The Caspian Sea is a lake with an oceanic bed, the age of which is about 10 million years. Parent rocks, river flows and atmospheric precipitation determine the chemical composition of the components of the ecosystem of the Caspian Sea. In this regard, the Caspian Sea is a special biogeochemical province with geochemical barriers in the area of mixing river and seawaters [3-4], therefore, the study of its biogeochemical background, as well as the features and patterns of migration of chemical elements from the abiotic to the biotic part is of relevance work.

Previously, studies of the content of some chemical elements in the soils of the Volga-Caspian basin [5-9] were carried out, while various types of bottom sediments in the northern and middle parts of the Caspian Sea were not studied.

Based on the above, the purpose of this work was to determine the concentrations of manganese and copper in various types of bottom sediments and to assess the effect of the biogeochemical barrier on the content of these elements in the soils of the northern and middle parts of the Caspian Sea.
2. Materials and methods
The objects of study were silt, sandy and shell bottom sediments of the Caspian Sea. The collection of material was carried out in the northern and middle parts of the Caspian Sea in the period from 2011 to 2019.

The determination of the concentration of manganese and copper in soils was carried out using the atomic absorption method. A soil sample in the amount of 10-20 g was dried to a dry-air state. After that, the sample was crushed and sieved. Weighed a weighed portion of the sieved sample of at least 0.25 g, transferred into a glass heat-resistant beaker, and added 10 ml of concentrated nitric acid of the "high purity" grade. Then the sample was boiled in a sand bath for at least 20 minutes. After cooling the solution, 10 ml of concentrated hydrogen peroxide was added dropwise to it, and then it was boiled for about 30 minutes until the sample was completely dissolved. After cooling, the sample was filtered. A blank sample was prepared in parallel with the test sample.

To determine manganese and copper, an MGA-915 MD atomic absorption spectrometer with electro thermal atomization was used. The concentration of chemical elements was determined in mg / kg dry weight.

3. Results and discussion
Comparative analysis of the media in various indications of the Northern and Middle parts of the Caspian Sea indicates a higher sorption capacity of metal by silts (8.2 ± 0.4 and 16.4 ± 1.2 mg / kg in the Northern and Middle parts of the Caspian Sea). It is noted that in the studied territories in the silty bottom sediments, the element is 2 higher than in the sandy ones (4.3 ± 0.4 and 10.7 ± 0.4 mg / kg in the Northern and Middle parts of the Caspian Sea). Perhaps this is because organic matter does not stay in the sand [10]. Dissolved organic substances form complexes with copper, which play an important role in the biological consumption of some metals from water [11]. Thus, the highest values of copper accumulation in the Northern and Central parts of the Caspian Sea were recorded in the silty type of soil, and the lowest in the sandy one.

The averaged data on the content of the studied chemical element in various types of bottom sediments indicate that the level of copper accumulation in the soils of the Northern part is 2 times lower than in the Central part of the Caspian Sea (6.18 ± 1.12 and 11.94 ± 2.4 mg / kg dry matter).

It was previously shown that, compared with the concentrations of other chemical elements in the soils of the Northern and Middle parts of the Caspian Sea, comparatively low values of the copper content in them were revealed [12], which is due to the parent rocks of the Caspian lowland and is associated with its deficiency in the soils of the Astrakhan region [13-14] and, accordingly, weak copper accumulation in the soils of the studied areas of the Caspian Sea.

Based on the values of the calculated concentration clarkes for bottom sediments in the Northern and Middle parts of the Caspian Sea, copper has a low biophilicity, since its concentration is lower than in the lithosphere (20 mg / kg according to AP Vinogradov [2]).

It is known that the parent rocks of the Caspian lowland are represented mainly by manganese-containing clays [10]. The content of manganese in the soils is quite high, especially in the northern part of the Caspian Sea, where it enters with river runoff.

Among the studied types of bottom sediments, both in the northern and middle parts of the Caspian Sea, the highest manganese content was found in silty soils (215.02 ± 1.06 and 72.04 ± 1.48 mg / kg dry matter, respectively). One of the ways that manganese is transported into bottom sediments is that organisms (in skeletons or soft tissues) absorb Mn. After their death, detritus reaches the bottom together with the skeletal parts and is buried, first, in silt [2].

Shell bottom sediments of the studied parts of the Caspian Sea (North and Middle) contained the minimum concentrations of the element (8.65 ± 0.35 and 4.34 ± 0.55 mg / kg dry matter, respectively). In the bottom sediments of the northern part of the Caspian Sea, the concentration of manganese is higher than in those in the middle part. This is due to the fact that in the mixing zone of river and sea waters there is a loss of many chemical elements, including manganese [11], therefore, in comparison
with the northern part, the content of manganese in the muddy bottom sediments of the Middle Caspian Sea is more than 3 times less, while in sandy and shell soils - 2 times.

Calculated clarke of manganese concentration relative to clarke according to A.P. Vinogradov [2] (850 mg / kg) for all types of bottom sediments indicate that these types of soils do not possess the ability to accumulate the element. Low clarke values of manganese concentration indicate the absence of ecosystem pollution with this metal.

Comparing the revealed concentrations of manganese in bottom sediments of the northern and middle parts of the Caspian Sea with the clarke according to A.P. Vinogradov, it can be noted that its concentration is much lower than in the lithosphere, therefore this element is also characterized by a relatively low biophilicity.

4. Conclusion
The study revealed low concentrations of copper and relatively high manganese in the bottom sediments of the Caspian Sea, which is primarily due to the parent rocks of the Caspian lowland, which are poor in copper, but rich in manganese. Comparatively high concentrations of manganese in the bottom sediments of the Caspian Sea indicate that it comes mainly with river runoff. Manganese is deposited in the soils of the Northern part of the Caspian Sea, and copper is deposited in the soils of the Central Caspian Sea.

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