Original paper

# Assimilation Capacity of Azov Sea Bottom Sediments with Respect to Copper and Zinc

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### Abstract

The work aims to assess the assimilation capacity of bottom sediments of the Sea of Azov with respect to copper and zinc by the level of their elimination into the geological depot as a result of sedimentation. The paper analyses metal concentrations in water and bottom sediments in 1991-2023. In 1998-2023, the average values of copper in sea water exceeded maximum permissible concentration (5 µg/L) and ranged 5.2-12 µg/L. The average concentration of copper in the bottom sediments of the Sea of Azov in 1991–1999 was 29.8 µg/g, in 2000–2010 it was 35.5  $\mu$ g/g and in 2011–2023 it was 9.3  $\mu$ g/g. The copper flux from the water to the bottom sediments of the open part of the sea ranged 14–381 t/year, whereas in Taganrog Bay it was 16-153 t/year. Sediment turnover periods of copper in the open sea and in Taganrog Bay averaged 0.5 and 1.6 years, respectively. The assimilation capacity of bottom sediments for copper in the open sea was 135.6 t/year and for Taganrog Bay it was 75.7 t/year. The zinc concentration in water exceeded its maximum permissible concentration (50 µg/L) in different years (up to 79 µg/L in Kuban-Akhtarsky and Kuban-Temryuksky districts). In the bottom sediments, the zinc concentration during the entire observation period was in the range of  $17.1-98 \ \mu g/g$  in the open sea and  $19.0-111 \ \mu g/g$  in the bay. The flux of sedimentation self-purification of water from zinc in the open sea was in the range of 175–902 t/year and in Taganrog Bay it was 76–407 t/year. The zinc turnover period in the open part of the sea varied within 0.7-39.8 years and in the bay, it was 0.1-4.8 years. The assimilation capacity of the bottom sediments with respect to zinc was 313.6 t/year for the open part of the sea and 169.1 t/year for Taganrog Bay. Determination of assimilation capacity of bottom sediments allows normalizing planned inputs of copper and zinc into the water area of the Sea of Azov.

**Keywords**: Sea of Azov, copper, zinc, pollution, heavy metal flux, accumulation coefficient, self-purification, copper flux, zinc flux, assimilation capacity

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# Ассимиляционная способность донных отложений Азовского моря в отношении меди и цинка

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#### Аннотация

Цель работы – оценить ассимиляционную способность донных отложений Азовского моря в отношении меди и цинка по уровню их элиминации в геологическое депо в результате седиментационных процессов. Анализировались концентрации металлов в воде и донных отложениях в 1991-2023 гг. В 1998-2023 гг. средние значения меди в воде моря превышали ПДК (5 мкг/л) и находились в диапазоне 5.2–12 мкг/л. Концентрация меди в донных отложениях Азовского моря в 1991–1999 гг. составляла в среднем 29.8 мкг/г, в 2000–2010 гг. – 35.5 мкг/г, в 2011–2023 гг. – 9.3 мкг/г. Поток меди из воды в донные осадки открытой части моря варьировал в пределах 14-381 т/год, в Таганрогском заливе – 16–153 т/год. Периоды седиментационного оборота меди в открытом море и в Таганрогском заливе в среднем составляли 0.5 и 1.6 лет соответственно. Ассимиляционная способность донных отложений в отношении меди составила в открытой части моря 135.6 т/год, в Таганрогском заливе – 75.7 т/год. Концентрация цинка в воде превышала ПДК (50 мкг/л) в разные годы (в Кубано-Ахтарском и Кубано-Темрюкском районах – до 79 мкг/л). В донных осадках концентрация цинка весь период наблюдений находилась в диапазоне 17.1-98 мкг/г в открытом море и 19.0-111 мкг/г в заливе. Поток седиментационного самоочищения вод от цинка в открытой части моря находился в интервале 175–902 т/год, в Таганрогском заливе – 76-407 т/год. Период оборота цинка в открытой части моря варьировал в пределах 0.7-39.8 года, в заливе - 0.1-4.8 года. Ассимиляционная способность донных отложений в отношении цинка составила 313.6 т/год в открытой части моря и 169.1 т/год в Таганрогском заливе. Определение ассимиляционной способности донных осадков позволяет нормировать плановые поступления меди и цинка в акваторию Азовского моря.

Ключевые слова: Азовское море, медь, цинк, загрязнение, потоки тяжелых металлов, коэффициент накопления, самоочищение, поток меди, поток цинка, ассимиляционная способность

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# Introduction

Assessment of the water area self-purification ability by calculating the assimilation capacity (AC) of bottom sediments with respect to a particular pollutant can serve as a scientific and technical basis for finding ways to normalize the ecological state of marine ecosystems. Self-purification of the aquatic environment is a complex set of dilution, migration and redistribution of pollutants [1].

It was shown in <sup>1</sup> that from the point of view of self-purification, the AC could be understood as a transformable and irreversibly eliminated flux of pollution from the marine environment as a result of abiotic and biotic processes <sup>1</sup>.

According to V. N. Yegorov, on the one hand, the marine environment AC means the amount of pollutant that can be diluted in the water areas so that the concentration of pollutant in critical biotic components of ecosystems does not exceed maximum permissible values. On the other hand, the AC is a differential criterion, i. e. the marginal flux of pollution eliminated to aquatic or geological depots [2, p. 238]. This approach to the AC assessment was implemented in [3], where on the basis of estimates of ultimate elimination fluxes of radionuclides, mercury and chlororganic compounds from the aquatic environment into bottom sediments (geological depots) of Sevastopol Bay, the AC values of bottom sediments were obtained with respect to these pollutants. The authors obtained the AC values of bottom sediments with respect to the mentioned pollutants. In particular, the authors obtained that the AC of bottom sediments in relation to mercury is 32.7 t/year [3]. The methodology for calculating the maximum permissible flux was also used in [4] to assess the AC of bottom sediments in the Azov Sea concerning lead. A similar method of assessment of the AC of bottom sediments with respect to copper and zinc is applied in this work.

The Sea of Azov is a relatively small shallow water body, which experiences high anthropogenic load. Among the most significant pollutants entering the water area of the Sea of Azov are heavy metals including such essential trace elements as copper and zinc, which are necessary for the metabolism of hydrobionts in low concentrations but become toxic to them in higher concentrations.

The work aims to assess the assimilation capacity of bottom sediments of the open part of the Sea of Azov and Taganrog Bay with respect to copper and zinc by their elimination into the geological depot as a result of sedimentation.

In this process, the following objectives were addressed:

1. To study the dynamics of water and bottom sediments pollution of the sea proper and Taganrog Bay by copper and zinc for 1991–2023.

2. To study the dependence of copper and zinc concentration in bottom sediments on their concentration in water, taking into account the accumulation coefficient.

3. To assess annual fluxes of copper and zinc deposition from water to bottom sediments during the studied period.

4. To determine the sediment turnover period of copper and zinc in the aquatic environment.

This study continues the series of works commenced by paper [4].

<sup>&</sup>lt;sup>1)</sup> Polikarpov, G.G. and Egorov, V.N., 1986. [*Marine Dynamic Radiochemoecology*]. Moscow: Energoatomizdat, 176 p. (in Russian).

### Materials and methods

The data on copper and zinc concentration in water and bottom sediments in 2010–2023, provided by *Azovmorinformtsentr* branch of *Tsentrregionvodkhoz* within the cooperation with the Department of Ecology and Environment Management of Sergo Ordzhonikidze Russian State University for Geological Prospecting (MGRI) were used in this paper. To determine interannual trends, we also used the literature data on copper and zinc content in the water of the Sea of Azov in 1991–2009 [5, 6].

The maximum permissible concentration (MPC<sub>w</sub>) of copper in marine waters of fishery objects is 5  $\mu$ g/L, while that of zinc – 50  $\mu$ g/L. Zinc and copper are classified as hazard class 3 (moderately hazardous) and have a toxicological limiting indicator of harmfulness.<sup>2)</sup>.

Since no quality standards for bottom sediments have been established in the Russian Federation, assessment of the degree of contamination of the sediments under study can be carried out according to <sup>3)</sup> where maximum permissible concentration (MPC) of metals in bottom sediments is specified. Thus, MPC of copper is 73  $\mu$ g/g dry wt. and that of zinc is 620  $\mu$ g/g dry wt.

Water samples were taken for the analysis by PE-1220 sampling system according to standard GOST 31861-2012 and RD 52.24.309-2016 from the surface horizon (0–5 m) at 32 points (Fig. 1). Dissolved forms of metals were determined. Bottom sediments were sampled for the analysis at the same stations as water samples using a bottom sampler DCH-0.034 according to standard GOST 17.1.5.01-80 in the surface layer of soils (0–5 cm). Sampling and chemical analysis of water samples and bottom sediments was carried out according to standard methods.

To estimate fluxes F (t/year) of annual deposition of copper and zinc in bottom sediments, expression [2] was used

$$F = C_{\rm bs} S v_{\rm sed},\tag{1}$$

where  $C_{bs}$  is metal concentration in the surface layer of bottom sediments,  $\mu g/g$ ; S is area of the water area under consideration, km<sup>2</sup>;  $\nu_{sed}$  is sedimentation rate,  $g \cdot m^{-2} \cdot y ear^{-1}$ .

Sediment turnover period of heavy metal in the aquatic environment T (years) equal to the ratio of its volume in water to the deposition flux into bottom sediments reflects the time scale of sedimentation self-purification in waters [2]:

$$T = (C_{\rm w}S h_{\rm m}) / F, \quad \text{or} \quad T = (C_{\rm B}V) / F, \tag{2}$$

where  $C_w$  is metal concentration in water,  $\mu g/L$ ; V is volume of the analysed water area, km<sup>3</sup>;  $h_m$  is average depth of the analysed water area, m.

<sup>&</sup>lt;sup>2)</sup> Ministry of Agriculture of Russia, 2016. On the Approval of Water Quality Standards for Water Bodies of Commercial Fishing Importance, Including Standards for Maximum Permissible Concentrations of Harmful Substances in the Waters of Water Bodies of Commercial Fishing Importance: Order of the Ministry of Agriculture of Russia dated December 13, 2016, No. 552. Moscow: Ministry of Agriculture of Russia (in Russian).

<sup>&</sup>lt;sup>3)</sup> Warmer, H. and van Dokkum, R., 2002. Water Pollution Control in the Netherlands. Policy and Practice 2001: RIZA Report 2002.009. Neue Niederlandische Liste. Altlasten Spektrum 3/95. Lelystad, 77 p. Available at: https://edepot.wur.nl/674312 [Accessed: 2 March 2025].

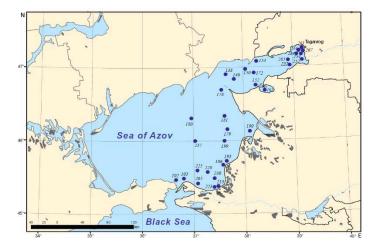


Fig. 1. Map of water and bottom sediments sampling in 2010–2023 (numbering of stations by *Azovmorinformcenter* branch of *Tsentrregionvodkhoz*)

Coefficients ( $C_a$ ) of accumulation of heavy metals by bottom sediments were calculated according to formula [2]:

$$C_{\rm a} = 1000 \ (C_{\rm bs}/C_{\rm w}).$$

Relationship between coefficient of accumulation of metals in bottom sediments ( $C_a$ ) and their concentration in water ( $C_w$ ) is described by equation of straight line on the graphs with a logarithmic scale on the ordinate axes ( $C_a - C_w$ ). This indicates that the processes of sorption interaction of bottom sediments with dissolved heavy metals in water are described by power function, which coincides with Freundlich adsorption equation:

$$C_{\rm a} = C_{\rm bo} / C_{\rm w} = a C_{\rm w}^{-n},$$
 (3)

where a is coefficient which corresponds to adsorption and depends on the nature of adsorbent and adsorbate, it is determined graphically; n is power exponent.

AC of bottom sediments of water areas is determined from relationship [2, p. 283]

$$Q = S v_{\rm sed} C_{\rm bs},\tag{4}$$

where *S* is area of the water area under consideration, km<sup>2</sup>;  $v_{sed}$  is sedimentation rate,  $g \cdot m^{-2} \cdot year^{-1}$ . Taking into account formula (3) and equation (4), expression  $C_{bs} = C_w C_a$  is transformed into a ratio that can be used for normalization according to ecotoxicological criteria (with  $C_w = MPC$ ):

$$Q = S v_{\text{sed}} C_{\text{w}} a C_{\text{w}}^{-n}, \tag{5}$$

where *S* is area of the water area under consideration, km<sup>2</sup>;  $v_{sed}$  is sedimentation rate,  $g \cdot m^{-2} \cdot year^{-1}$ ;  $C_w$  is metal concentration in water,  $\mu g/L$ ; *a* is coefficient which corresponds to adsorption and depends on the nature of adsorbent and adsorbate, it is determined graphically (highlighted in bold in the equation of the power function in Figs. 2, *e* and 3, *e*); *n* is power exponent.

Area	Total area, km <sup>2</sup> [7]	Volume, km <sup>3</sup> [7]	Average depth, m [7]	Average rate of sedimentation <sup>1</sup> ), $g \cdot m^{-2} \cdot year^{-1}$
Taganrog Bay	5600	25	4.9	700
Open sea	33,400	231	/	300

Parameters of the studied areas

The AC of bottom sediments in the open sea and in Taganrog Bay (Table) was calculated for the period of 1991–2023 for copper, for the period of 1993–2023 for zinc.

### **Results and discussion**

Copper. The most powerful source of anthropogenic input of copper into the environment – up to 75% of the total – is non-ferrous metal production [8]. This trace element is intensively transported with atmospheric fluxes. Up to 13% of the total concentration of copper in surface waters of the seas is the share of dry deposition with wind dust and atmospheric precipitation [5]. River runoff of the Don and Kuban rivers is also a significant source of copper intake. Thus, according to the results of studies [9], in the lower reaches of the Don River copper concentration exceeded MPCw for fresh waters of fishery objects everywhere, and in [10] it ranged from 1–14  $\mu$ g/L (average value 3.5  $\mu$ g/L). Partially copper comes with the products of coastal abrasion, which causes its high content in the Taganrog Bay coastal zone [11]. In addition, copper can enter the ecosystem of the Sea of Azov with diffuse wash-off of mineral fertilizers and chemical plant protection products from agricultural lands located on the catchments of the Don and Kuban rivers [12], as well as with wastewater from industrial, household and municipal services enterprises [5, 9–11]. Thus, according to generalized data, the discharge of copper as part of wastewater into the Sea of Azov within the boundaries of the Rostov Region, according to data from the federal statistical report according to form 2-TP (Vodkhoz) for 2023, is 64.7 kg (data from the Water Resources Department of the Rostov Region, Don Basin Water Administration, Rostov-on-Don).

Copper concentrations in the water of the Sea of Azov exceeded MPC<sub>w</sub> in different years. In 1991–1995, its concentration in the water of the open part of the sea and Taganrog Bay decreased (Fig. 2, a), and then an increasing trend of

copper contamination of water in both areas was observed. In 2010–2017, the annual average concentration of copper in the open sea exceeded MPC<sub>w</sub> and ranged from 5.2 to 8.1  $\mu$ g/L. According to the results of the 2020–2023 surveys, the annual average values of copper in the open sea and in Taganrog Bay exceeded MPC<sub>w</sub> and were 9.5 and 6.2  $\mu$ g/L, respectively.

The physical and chemical composition of bottom sediments provides information on the accumulation and distribution of heavy metals over a longer period of time than water analysis, which characterizes its quality only at a given moment [13]. The sorption of ions and compounds of heavy metals by suspended matter and bottom sediments plays a special role among in-water processes, which, in the opinion of many researchers, are determinant, making the greatest contribution to the self-purifying capacity of a water body. The intensity of sorption depends on the pH and Eh values of the medium, the presence of clay particles, ligands, humic acids, ferromanganese oxides and a number of copper-binding cations [14].

The spatial distribution of copper in bottom sediments of the Sea of Azov was characterized by mosaic and variability. Thus, copper concentration was in the range of  $21.0-37.0 \ \mu g/g dry$  wt. (average  $29.8 \ \mu g/g dry$  wt.) in 1991-1999,  $33.0-42.0 \ \mu g/g dry$  wt. (average  $35.5 \ \mu g/g dry$  wt.) in 2000-2005 and further decreased with an increase in some years (Fig. 2, *b*). According to the data, no values exceeding the MPC value were observed during the specified periods. In 2011-2023, offshore concentrations ranged from 1.4 to  $30 \ \mu g/g dry$  wt. (average  $9.3 \ \mu g/g dry$  wt.) and those in Taganrog Bay were from 4.1 to  $40 \ \mu g/g dry$  wt. (average  $15.2 \ \mu g/g dry$  wt.). The highest concentrations of copper in bottom sediments were recorded in the areas of clay silt development, namely, in the central, north-western and western parts of Taganrog Bay, Yasen Bay, southern and central parts of the sea as well as on the Kuban River seashore.

Calculations based on formula (1) showed that the sedimentation flux of copper deposition into bottom sediments ranged in different years from 14 to 381 t/year (average 217 t/year) in the open sea and from 16 to 153 t/year (average 95 t/year) in Taganrog Bay (Fig. 2, c). Periods of sediment turnover of copper in the sea proper and in Taganrog Bay calculated by formula (2) at different concentrations of copper in water amounted to 0.5 and 1.6 years on average, respectively (Fig. 2, d). The dependence of the coefficient of copper accumulation by bottom sediments on its content in the aquatic environment shows moderate relationship and is described by equation of straight line in logarithmic scales along the ordinate axes (Fig. 2, e). When these data were approximated by the power function equation, the following was obtained for the open part of the sea:  $C_a = 33,831 C_w^{-1.569}$ , for Taganrog Bay:  $C_a = 30,976 C_w^{-1.293}$ . It is shown that the parameters of these equations are indicators of the AC of bottom sediments with respect to copper. They can be used for the purposes of ecological standardization taking into account sanitary and hygienic norms. If we assume  $C_w = MPC_w$ , then  $C_a$  of copper for the open part of the sea is 2708 and that for Taganrog Bay is 3866. To assess the AC of bottom sediments of the open part of the Sea of Azov, substituting corresponding values into expression (5) and taking into account the dimensionality, we obtain Q = 135.6 t/year and for Taganrog Bay Q = 75.7 t/year.

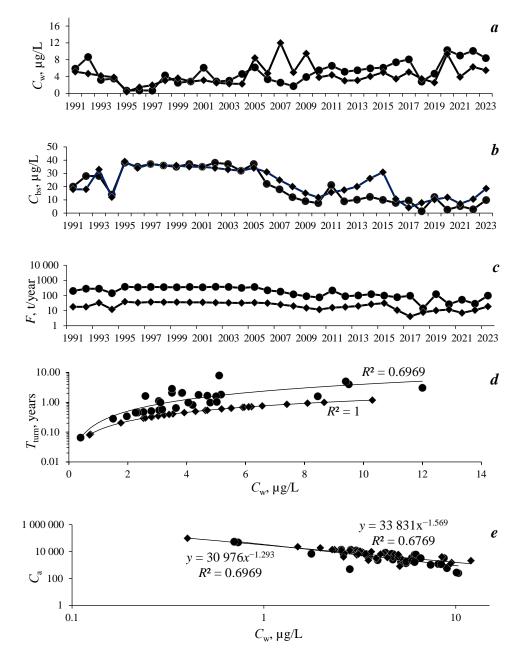


Fig. 2. Characteristics of copper distribution in open sea (•) and Taganrog Bay (•): concentration in water,  $\mu g/L(a)$ ; concentration in the surface layer of bottom sediments,  $\mu g/g$  dry mass (*b*); flux of copper deposition into bottom sediments, t/year (*c*); period of sediment turnover of copper in water, years (*d*); dependence of the change in the coefficient of copper accumulation in bottom sediments on its concentration in water (*e*)

It should be noted that in addition to sedimentation, sediment is agitated at the water-bottom interface. At high values of dynamic velocity near the bottom, this sediment is agitated and then reenters the water. This is especially important for the Sea of Azov because of its shallow water and the tendency of the upper layer of bottom sediments to resuspend. Taking into account the results of [15, 16] and our own data, it was assumed in our study that the settling rate of particles after agitation was 7.5 mm/s (aleurite) and 0.04 mm/s (silt). Thus, the period of gravitational return of suspended sediments from the surface layers of the sea to the bottom sediments at a depth of up to 15 m will not exceed 28–30 h, i. e. it will be estimated on a daily time scale. In our case, annual average time scale of the study was considered. Therefore, the effect of turbulence was taken into account integrally when assessing the rate of sedimentation processes.

Zinc. Zinc enters natural waters as a result of the breakdown and dissolution of rocks and minerals (ZnS – sphalerite, ZnO – zincite, ZnSO<sub>4</sub>×7H<sub>2</sub>O – goslarite, ZnCO<sub>3</sub> – smithsonite, etc.) as well as with wastewater from mining and processing plants and electroplating shops, production units of parchment paper, mineral paints, viscose fibre [17]. For example, zinc discharge into the Sea of Azov as part of wastewater from enterprises of the Rostov Region was 570 kg in 2023 (according to form 2-TP (*Vodkhoz*)). Zinc is one of the vital elements for the biota. Hormonal metabolism, immune reactions, stabilization of ribosomes and cell membranes of hydrobionts are impossible without zinc participation.<sup>4)</sup>. Zinc content in unpolluted water bodies is usually 0.5–15  $\mu$ g/L. Zinc occupies an intermediate position between mercury and copper, on the one hand, and lead and cadmium, on the other hand, in terms of toxic effects on the biota, affecting significantly the behavioural and reproductive functions of fishes <sup>1)</sup>.

In the Sea of Azov, the 1993-2006 period is characterized by low annual average zinc concentrations in the range of  $2.2-12.2 \mu g/L$  in the open sea and 2.2-22.3 µg/L in Taganrog Bay (Fig. 3). In 2007-2014, a gradual increase in the annual average concentration was observed up to  $38 \mu g/L$  in the open sea and 27 µg/L in Taganrog Bay. In 2020–2023, zinc content was 21.5 µg/L in the open sea and 6.9  $\mu$ g/L in Taganrog Bay (Fig. 3, *a*). Zinc concentration in several water samples exceeded MPCw in different years, mainly in Kuban-Akhtarsky and Kuban-Temryuksky districts (up to 79 µg/L), which is explained by the influence of the towns of Primorsko-Akhtarsk and Temryuk, metal removal with the Kuban River water, polluted discharges from rice paddies and runoff from adjacent fields as well as removal of contaminants with storm water of residential areas [18]. In the water sample taken in the Taganrog Bay central part on 16.10.2014, zinc concentration of 750 µg/L was recorded. Such an abnormally high value can be related to severe flooding on 24.09.2014 in Taganrog Bay and the Don estuary when the water level rose by 251 cm. The Don River waters are a significant source of zinc input into Taganrog Bay. In [10], the data on the content of dissolved forms

<sup>&</sup>lt;sup>4)</sup> Moore, J.W. and Ramamoorthy, S., 1984. *Heavy Metals in Natural Waters*. Springer, 268 p. https://doi.org/10.1007/978-1-4612-5210-8

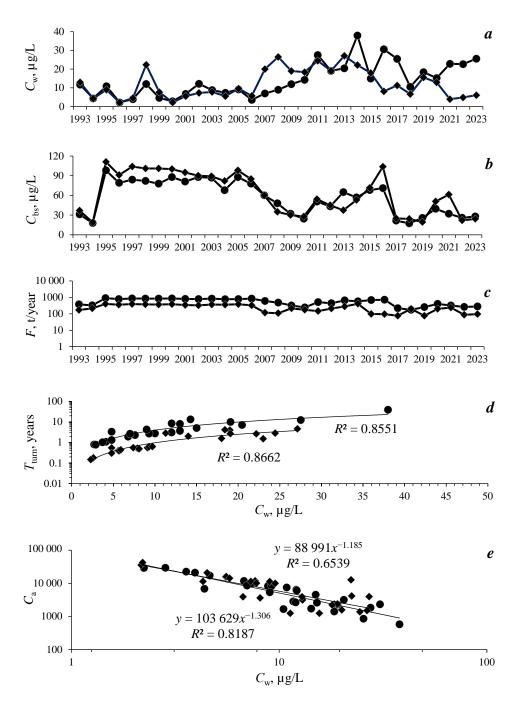


Fig. 3. Characteristics of zinc distribution in the open sea (•) and Taganrog Bay (•): concentration in water,  $\mu g/L$  (*a*); concentration in the surface layer of bottom sediments,  $\mu g/g$  dry mass (*b*); flow of zinc deposition into bottom sediments, t/year (*c*); period of sediment turnover of zinc in water, years (*d*); dependence of the change in the coefficient of zinc accumulation by bottom sediments on its concentration in water (*e*)

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of zinc in the lower reaches of the Don River are given. Thus, zinc concentration ranged from 1 to  $10 \,\mu$ g/L (average value 5.6  $\mu$ g/L) [18].

In bottom sediments, zinc concentrations did not reach MPC for the entire observation period and ranged from 17.1 to 98.0  $\mu$ g/g in the sea proper and from 19.0 to 111.0  $\mu$ g/g in the bay (Fig. 3, *b*). Higher zinc values correspond to the zone of clay silt distribution.

The results of assessment of zinc deposition fluxes in bottom sediments using formula (1) indicate (Fig. 3, c) that the flux of sedimentation self-purification of waters from this trace element was 175–902 t/year (with an average of 601 t/year) in the open sea and 76–407 t/year (average 256 t/year) in Taganrog Bay. Fig. 3, d shows that the sediment turnover period of zinc was 0.7–39.8 years in the open sea and 0.1–4.8 years in Taganrog Bay (Fig. 3, d). Fig. 3, d demonstrates that the dependence of changes in coefficients of the accumulation of zinc by bottom sediments at different concentrations of zinc in water is described with a sufficient degree of adequacy by equation of straight line in logarithmic scale along the ordinate axes (Fig. 3, e). For the open part of the sea, it was  $C_a = 103,629 C_w^{-1.306}$  and for Taganrog Bay, is was  $C_a = 88,991 C_w^{-1.185}$ . If we assume  $C_w = MPC_w$ , then  $C_a$  is 626 for the open part of the sea and 863.1 for Taganrog Bay.

The AC of bottom sediments with respect to zinc calculated by relation (5) was 313.6 t/year for the open part of the sea and 169.1 t/year for Taganrog Bay.

The obtained calculated AC values of bottom sediments can be used for normalization of copper and zinc discharges into the ecosystem of the Sea of Azov.

## Conclusions

According to the data for the 30-year period of studies, it was established that annual average concentrations of copper in dissolved form in water in different years exceeded MPC<sub>w</sub> for water bodies of fishery importance by 1.5-2 times both in the open sea and in Taganrog Bay. In some samples, copper concentration values reached 4–5 MPC<sub>w</sub>, mainly in the Kuban-Akhtarsky district and in the eastern part of Taganrog Bay. In the open sea, annual average copper concentrations for the last five years were slightly higher than in the bay. Annual average zinc concentrations in the water of the Sea of Azov did not exceed MPC<sub>w</sub> for the entire study period. Higher values in the open sea were recorded in the Kuban-Akhtarsky and Kuban-Temryuksky districts, in Taganrog Bay – in the area of the Mius Liman and in the zone of influence of the town of Yeysk.

The content of copper and zinc in the bottom sediments of the Sea of Azov did not reach MPC, with the highest values of these metals recorded in the areas of clay silt distribution.

Data on sedimentation rates and concentrations of copper and zinc in bottom sediments made it possible to assess the fluxes of sedimentation self-purification of water from these metals. Deposition fluxes lead to a decrease in the content of pollutants in water, i.e. the effect of the flux is aimed at compensating for the causes of the flux. Thus, the flux of metals deposited in bottom sediments demonstrates the manifestation of the Le Chatelier–Braun principle under natural conditions. Copper deposition flux averaged 217 t/year in the open sea and 95 t/year in Taganrog Bay. Zinc flux from water to bottom sediments averaged 601 t/year in the open sea and 256 t/year in Taganrog Bay.

Sediment turnover periods reflect the time scale of sedimentation self-purification of waters. This parameter for copper averaged 0.5 years in the open sea and 1.6 years in Taganrog Bay. The zinc turnover period averaged 7.7 years in the open sea and 1.8 years in Taganrog Bay.

The study of the trend of changes in the coefficient of copper and zinc accumulation by bottom sediments showed that the increased intensity of sedimentation self-purification of waters at low concentrations of copper and zinc in water was provided by high (with  $C_a > n \cdot 10^4$  units) concentrating ability of bottom sediments. With increasing degree of water pollution by copper and zinc, the value of Kn decreased; accordingly, the contribution of sedimentation processes to water selfpurification also decreased.

The AC values of bottom sediments expressed through flux dimensions can be accepted as quantitative criteria for normalization of the maximum permissible amount of pollutants entering the water area, at which their concentration in water will not exceed MPC<sub>w</sub>. Thus, for the normal functioning of the ecosystem, no more than 135.6 t/year of copper and 313.6 t/year of zinc should enter the open part of the Sea of Azov, while in Taganrog Bay, the input limits are 75.7 t/year for copper and 169.1 t/year for zinc.

#### REFERENCES

- 1. Goldberg, G.A. and Zats, V.I., 1991. *Modelling of Selfpurification Processes of the Shelf Zone Sea Water*. Sevastopol: IBSS, 59 p. (in Russian).
- 2. Egorov, V.N., 2019. *Theory of Radiousotope and Chemical Homeostasis of Marine Ecosystems*. Sevastopol: IBSS, 356 p. (in Russian).
- Egorov, V.N., Gulin, S.B., Malakhova, L.V., Mirzoeva, N.Y., Popovichev, V.N., Tereshchenko, N.N., Lazorenko, G.E., Plotitsina, O.V., Malakhova, T.V., Proskurnin, V.Y., Sidorov, I.G., Stetsyuk, A.P. and Gulina, L.V., 2018. Rating Water Quality in Sevastopol Bay by the Fluxes of Pollutant Deposition in Bottom Sediments. *Water Resources*, 45(2), pp. 222–230. https://doi.org/10.1134/S0097807818020069
- Bufetova, M.V. and Egorov, V.N., 2023. Lead Contamination of Water and Sediments of Taganrog Bay and the Open Part of the Sea of Azov in 1991–2020. *Ecological Safety of Coastal and Shelf Zones of Sea*, (2), pp. 105–119. https://doi.org/10.29039/2413-5577-2023-2-105-119
- Klenkin, A.A., Korpakova, I.G., Pavlenko, L.F. and Temerdashev, Z.A., 2007. [*Ecosystem* of the Sea of Azov: Anthropogenic Pollution]. Krasnodar: OOO "Prosveshcheniye-Yug", 324 p. (in Russian).
- Korablina, I.V., Sevostyanova, M.V., Barabashin, T.O., Gevorgyan, J.V., Katalevsky, N.I. and Evseeva, A.I., 2018. Heavy Metals in the Ecosystem of the Azov Sea. *Problems of Fisheries*, 19(4), pp. 509–521. https://doi.org/10.36038/0234-2774-2018-19-4-509-521
- Goptarev, N.P., Simonov, A.I., Zatuchnaya, B.M. and Gershanovich, D.E., eds., 1991. [*Hydrometeorology and Hydrochemistry of Seas of the USSR. Vol. 5. The Sea of Azov*]. St. Petersburg: Gidrometeoizdat, 236 p. (in Russian).
- 8. Putilina, V.S., Galitskaya, I.V. and Yuganova, T.I., 2013. Sorption When Groundwater Contaminating by Heavy Metals and Radioactive Elements. Copper. Novosibirsk: GPNTB SO RAN. Iss. 100, 95 p. (in Russian).

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- Matishov, G.G., Stepan'yan, O.V., Har'kovskii, V.M., Startsev, A.V., Bulysheva, N.I., Semin, V.V., Soier, V.G., Kreneva, K.V., Glushchenko, G.Y. and Svistunova, L.D., 2016. Characteristic of Lower Don Aquatic Ecosystem in Late Autumn. *Water Resources*, 43(6), pp. 873–884. https://doi.org/10.1134/S009780781606004X
- Garkusha, D.N., Fedorov, Yu.A. and Predeina, L.M., 2022. Spatiotemporal Dynamics of Copper and Zinc Concentrations in the Lower Don Water. *Russian Meteorology and Hydrology*, 47(3), pp. 232–240. https://doi.org/10.3103/S1068373922030098
- 11. Khrustalev, Yu.P., 1999. The Fundamental Problems of the Sedimentogenesis Geochemistry in the Azov Sea. Apatity: Publishing house of the KSC RAS, 247 p. (in Russian).
- Bufetova, M.V., 2020. Analysis of Changes in the Coefficient of Bottom Accumulation of Heavy Metals from their Concentration in the Water of the Sea of Azov. *Scientific Notes of V.I. Vernadsky Crimean Federal University. Geography. Geology*, 6(2), pp. 193–206 (in Russian).
- Davydova, O.A., Korovina, E.V., Vaganova, E.S., Guseva, I.T., Krasun, B.A., Isaeva, M.A., Martseva, T.Y., Mulyukova, V.V., Klimov, E.S. and Buzaeva, M.V., 2016. Physical-Chemistry Aspects of Migratory Processes of Heavy Metals in Natural Aqueous Systems. *Bulletin of South Ural State University. Series Chemistry*, 8(2), pp. 40–50. https://doi.org/10.14529/chem160205 (in Russian).
- Saeva, O.P., Yurkevich, N.V., Kabannik, V.G. and Kolmogorov, Y.P., 2013. Determining the Effectiveness of Natural Reactive Barriers for Acid Drainage Neutralization Using Sr-Xrf Method. *Bulletin of the Russian Academy of Sciences: Physics*, 77(2), pp. 214–216. https://doi.org/10.3103/S1062873813020305
- 15. Martyanov, S.D., Ryabchenko, V.A. and Rybalko, A.E., 2011. Modelling of Sediment Resuspension in the Neva Bay. *Proceedings of the Russian State Hydrometeorological University*, 20, pp. 13–26 (in Russian).
- Gerasyuk, V.S. and Berdnikov, S.V., 2021. Experimental Estimation of the Deposition Rate of Water Suspended Particulate Matter in the Mouth of the Don River and in Taganrog Bay. *Oceanology*, 61(5), pp. 687–696. https://doi.org/10.1134/S0001437021040056
- 17. Putilina, V.S., Galitskaya, I.V. and Yuganova, T.I., 2013. Sorption When Groundwater Contaminating by Heavy Metals and Radioactive Elements. Zinc. Novosibirsk: GPNTB SO RAN. Iss. 102, 99 p. (in Russian).
- Bufetova, M.V., 2024. Dynamics of multi-year variability of copper and zinc content in the Azov Sea water (1991–2023). In: IBSS, 2024. Study of Aquatic and Terrestrial Ecosystems: History and Modernity: Book of Abstracts of the 3<sup>rd</sup> International Scientific and Practical Conference, 2–7 September, 2024, Sevastopol, Russian Federation. Sevastopol: IBSS, pp. 198–199 (in Russian).

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