Original article **DOI:** 10.29039/2413-5577-2023-2-105-119

Lead contamination of water and sediments of the Taganrog Bay and the open part of the Sea of Azov in 1991–2020

M. V. Bufetova [1]*, **V. N. Egorov** [2]

[1] *Federal State Budgetary Institution of Higher Education "Sergo Ordzhonikidze Russian State University for Geological Prospecting", Moscow, Russia*

[2] *A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russia*

**e-mail: mbufetova@mail.ru*

Abstract

The paper analyzes the data on lead content in water and bottom sediments of the central part of the Sea of Azov and Taganrog Bay for 1991–2020. Studies have shown that in 1991–2009 the lead concentration in the water of the central part of the sea was below the maximum permissible concentration. Since 2010, the lead contamination in waters has been higher, but that in bottom sediments has been lower. It is shown that with an increase in the lead concentration in water its content in bottom sediments decreased, which is associated not only with saturation of the bottom sediment surface, but also with a decrease in the accumulation coefficient. Until 2006, in Taganrog Bay, except for small peaks in 1992–1998, the lead concentration in water was quite low. After 2006, its upward changes were noted, which generally did not exceed the maximum permissible concentration. The paper lists possible sources of increased lead concentration in the gulf and sea in 2010–2015. For 1991–2020, the lead concentration in the bottom sediments of Taganrog Bay varied in antiphase with changes in its content in the water and in all cases was below the permissible concentration normalized according to the Dutch Lists. The relationship between the accumulation coefficient and lead concentration in the bay water was characterized by a high coefficient of determination. The materials illustrate the sorption capacity of bottom sediments, which is an important component of their assimilation capacity for lead. The paper defines the maximum permissible flows of lead (59.6 t/year into the open part of the sea and 21.4 t/year into Taganrog Bay), which can be assimilated by water areas without affecting their biological and water resources. After analyzing the long-term data on the lead content in the water and bottom sediments of the central part of the sea and Taganrog Bay, the paper concludes that the bay can serve both as a lead pollution source and a barrier that either transports lead into the Sea of Azov or entraps it.

Keywords: Sea of Azov, lead, pollution, water, bottom sediments, marginal flows, rationing, assimilation capacity

Acknowledgements: The work was carried out under topic of A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS «Seismological and biogeochemical bases of homeostasis of marine ecosystems» (121031500515-8). The authors are grateful to Azovmorinformcenter for the data provided. The authors also express their gratitude to the reviewers for useful comments and to the editorial staff of the journal for competent, high-quality and well-organized editorial work.

For citation: 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. doi:10.29039/2413-5577-2023-2-105-119

Загрязнение свинцом воды и донных отложений Таганрогского залива и открытой части Азовского моря в 1991–2020 годах

М. В. Буфетова [1] *, В. Н. Егоров [2]

[1] *Российский государственный геологоразведочный университет имени Серго Орджоникидзе (МГРИ), Москва, Россия*
[2] *Институт биологии южных морей им. А. О. Ковалевского РАН, Севастополь, Россия*
* *e-mail: mbufetova@mail.ru*

Аннотация
Проанализированы данные о содержании свинца в воде и в донных отложениях центральной части Азовского моря и Таганрогского залива за 1991–2020 гг. Исследования показали, что в 1991–2009 гг. концентрация свинца в воде центральной части моря была ниже предельно допустимой концентрации. С 2010 г. наблюдался более высокий уровень загрязнения свинцом вод, но более низкий уровень загрязнения им донных отложений. Показано, что с увеличением концентрации свинца в воде его содержание в донных отложениях снижалось, что связано не только с насыщением поверхности донных отложений, но и с уменьшением коэффициента накопления. В Таганрогском заливе до 2006 г., кроме небольших пиков в 1992–1998 гг., концентрация свинца в воде была достаточно низкой. После 2006 г. были отмечены ее изменения в сторону увеличения, которые в целом не превышали предельно допустимую концентрацию. Перечислены возможные источники повышения концентрации свинца в заливе и в море в 2010–2015 гг. За период 1991–2020 гг. концентрация свинца в донных отложениях Таганрогского залива изменялась в противофазе с изменением его содержания в воде и во всех случаях была ниже допустимой концентрации, нормируемой по «голландским листам». Зависимость между коэффициентом накопления и концентрацией свинца в воде залива характеризовалась высоким коэффициентом детерминации. Материалы иллюстрируют сорбционную способность донных отложений, которая является важным компонентом их ассимиляционной емкости в отношении свинца. Определены предельно допустимые потоки свинца (59.6 т/год – в открытую часть моря и 21.4 т/год – в Таганрогский залив), которые могут ассимилироваться акваториями без ущерба для их биологических и водных ресурсов. После анализа многолетних данных о содержании свинца в воде и в донных отложениях центральной части моря и Таганрогского залива делается вывод, что залив может выполнять функции как источника загрязнения свинцом, так и барьера, пропускающего свинец в Азовское море или задерживающего его.

Ключевые слова: Азовское море, свинец, загрязнение, вода, донные отложения, предельные потоки, нормирование, ассимиляционная емкость

Благодарности: работа выполнена в рамках темы ФИЦ ИнБЮМ «Молисмологические и биогеохимические основы гомеостаза морских экосистем» (121031500515-8). Авторы благодарны филиалу «Азовморинформцентр» ФГБВУ «Центррегионводхоз» за предоставленные данные.

Для цитирования: *Буфетова М. В., Егоров В. Н.* Загрязнение свинцом воды и донных отложений Таганрогского залива и открытой части Азовского моря в 1991–2020 годах // Экологическая безопасность прибрежной и шельфовой зон моря. 2023. № 2. С. 105–119. EDN PFVZIY. doi:10.29039/2413-5577-2023-2-105-119

Introduction

Radioactive and chemical contaminants of various nature entering the marine environment are exposed to many biotic and abiotic factors. First of all, they are carried by currents in water areas. Due to the vertical component of the current velocity, advection and diffusion, pollution penetrates into deep waters. Simultaneously with migration due to mixing of waters, they are absorbed by living and inert components of ecosystems, and abiotic and biotic transformation of physicochemical forms and transfer to water and geological depots take place [1, p. 150; 2].

According to modern concepts [2], the ecotoxicological situation of water areas is largely determined by the interaction of suspended matter with heavy metals (HMs). Under the influence of sorption and metabolic processes, HMs are extracted by suspended matter from the water solution, acquire a density that differs from the specific mass of water, and are involved in biogeochemical cycles that determine not only their migration over water areas, but also their sedimentation entry into bottom sediments. The intensity of biogeochemical cycles depends on the concentrating ability of suspended matter characterized by accumulation coefficients (Co_a) [1]. In the Black Sea, suspended matter can accumulate such HMs as Co, Ni, Cu, Zn, As, Mo, Cd, and Pb, with Co_a equal to $(0.02–180)\cdot10^4$ units in terms of dry mass, and their pool can make 0.2–55.9 % of the total content in water [3]. The pool of mercury in the composition of the Black Sea suspended matter can exceed 98% of its content in the marine environment [4]. The pool of HMs (copper, zinc, mercury, lead) in the suspended matter of the Sea of Azov can reach 95.6% [5]. Hence it appears that the high concentrating ability of suspended matter is a significant factor in the biogeochemical self-purification of the aquatic environment.

It is commonly known that marine nature management is regulated by anthropocentric and ecocentric principles, which differ in the choice of the so-called weak link by which ecosystems are managed [6]. The anthropocentric approach is based on taking into account only the anthropogenic factor, while the ecocentric one proceeds from the objectivity of the existence of a single system within which the person and all living organisms interact with each other and with the environment. Therefore, not only the person can be the weak link in the ecosystem, but also its individual biotic components.

Consideration of this circumstance requires the development of new approaches in order to provide marine nature management activities. One of them is to implement the concept of sustainable development of water areas by maintaining a balance between consumption and natural reproduction. With regard to ecotoxicological problems, this concept is based on the consideration of the assimilation (ecological) capacity of the marine environment as a result of the impact of natural biogeochemical processes [1, 2, 7]. One of the promising ways to exploit this area is the development of biogeochemical criteria for the assessment of the self-purification flows of waters with subsequent regulation of the maximum permissible anthropogenic impact on marine ecosystems by factors of radioactive and chemical pollution of the marine environment.

Currently, human health-related environmental criteria, which correspond to the maximum permissible concentrations (MPC) of pollutants in water or in hydrobionts, are used as the main indicators of the marine environment quality. The quality standards for water bodies of commercial fishing importance, which include the Sea of Azov, were established by Order No. 552 of the Minister of Agriculture of the Russian Federation of December 13, 2016 "On the Approval of Water Quality Standards for Water Bodies of Fishing Importance, Including Standards for the Maximum Permissible Concentrations of Harmful Substances in the Waters of Water-Based Fishing Objects" [1)]. In accordance with this Order, lead belongs to the third hazard category with its MPC in sea water of 10 µg/L.

Concerning marine bottom sediments in the Russian territorial waters, there are currently no normatively fixed characteristics of their quality in terms of the level of pollutant concentration similar to MPC in the water column. However, it is possible to assess the degree of pollution of bottom sediments in a controlled area of the sea based on the compliance of the level of certain pollutants with the criteria for environmental assessment of soil pollution according to normative indicators adopted in other countries, e. g., the Dutch List [2)]. These indicators can be used for the simplified comparative characterization of different parts of the water area or for the assessment of interannual variability. Thus, in Russia, permissible concentrations according to the Dutch List are used in the *Marine Water Pollution* Annual Reports [3)]. According to the Dutch List, permissible concentration of lead in bottom sediments is 85 µg/g dry mass.

It should be noted that the ecotoxicological characteristics according to MPC and the Dutch List have the dimensions of the maximum permissible concentration of pollutants in water, hydrobionts and bottom sediments. These characteristics are diagnostic indicators only. On the other hand, biogeochemical criteria have the dimensions of self-purification flows of water [2]. Therefore, their use makes it possible to assess the maximum allowable water pollution flows based on the condition of maintaining the stationarity of the state of ecosystems due to the equality of flows of self-purification and pollution of the marine environment. At the same time, the fact should not be ignored that pollutants dissolved in water are

---

[1)] Ministry of Agriculture of the Russian Federation, 2016. *On the Approval of Water Quality Standards for Water Bodies of Fishing Importance, Including Standards for the Maximum Permissible Concentrations of Harmful Substances in the Waters of Water-Based Fishing Objects.* Order No. 552 of the Ministry of Agriculture of the Russian Federation of 13.12.2016 (in Russian).

[2)] Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer, 2000. *Dutch Target and Intervention Values (2000) (the New Dutch List). Annexes. Circular on Target Values and Intervention Values for Soil Remediation*. P. 8. Available at: https://www.yumpu.com/en/document/read/44815398/dutch-target-and-intervention-values-2000-esdat/13 [Accessed: 26 June 2023].

[3)] Korshenko, A.N., ed., 2022. *Marine Water Pollution. Annual Report 2021*. Moscow: Nauka, 230 p. (in Russian).

transported through water areas and in depth only in the direction of decreasing gradients in the fields of their distribution in water as a result of the impact of hydrodynamic processes, and pollutants as part of suspended matter can migrate through any water areas. These processes take place on different scales of space and time. Therefore, it is necessary to take into account the periods of averaging the characteristics of hydrodynamic and biogeochemical processes.

The purpose of the work was to study the lead content in water and bottom sediments of the central part of the Sea of Azov and Taganrog Bay for 1991–2020. In this work, the studies were carried out with the mid-annual averaging of the parameters. At the same time, the following problems were solved:

1) to determine the trends and level of lead pollution of the waters of Taganrog Bay and the open part of the Sea of Azov (the sea proper) based on the results of monitoring studies from 1991 to 2020;

2) to study the dependence of lead concentration in bottom sediments on its concentration in the water of the Sea of Azov;

3) to assess the assimilation capacity of bottom sediments in relation to lead in the open part of the Sea of Azov and Taganrog Bay;

4) to find out whether Taganrog Bay is a source of lead pollution of the open part of the Sea of Azov.

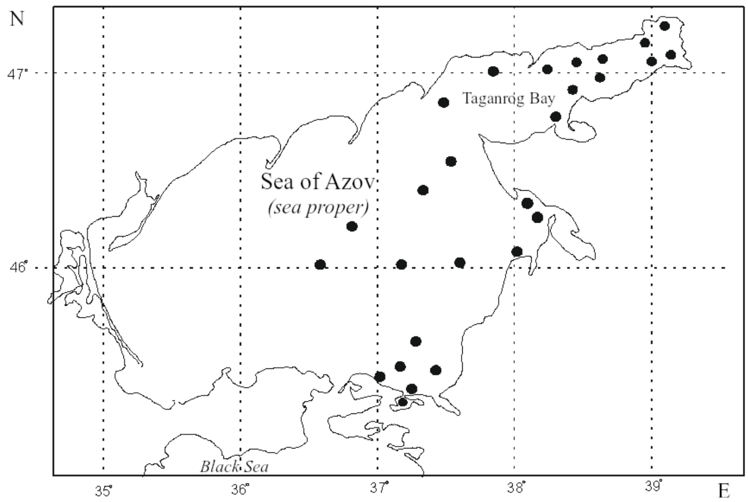
Materials and methods

The data on lead concentration in water and bottom sediments in 2010–2020 provided by the *Azovmorinformcenter* branch of *Centerregionvodkhoz* State Organization under cooperation with the Department of Ecology and Environment Management of the Federal State Budgetary Institution of Higher Education "Sergo Ordzhonikidze Russian State University for Geological Prospecting", were used in this work. Water samples for analysis were taken by the PE-1220 sampling system in accordance with GOST 31861-2012 and RD 52.24.309-2016 from the surface horizon at 32 points (Fig. 1). The studies were carried out in the central and eastern parts of the Sea of Azov and in Taganrog Bay. Water samples were taken in spring (March–April), summer (June–July), autumn (September–October) and winter (December). Outboard works were performed according to standard methods. Chemical analysis of water samples concerning lead content was carried out in accordance with the method PND F 14.1:2:4.140-98, with the sensitivity lower limit of 0.0002 mg/dm^3.

Samples of bottom sediments were taken for the analysis at the same stations as water samples using a bottom sampler DCh-0.034 according to GOST 17.1.5.01-80 in the surface layer of soils (0–2 cm). Samples of bottom sediments were taken annually in the summer. Chemical analysis of samples of bottom sediments for lead content was carried out in accordance with the M-MVI-80-2008 method, with the lead sensitivity lower limit of 0.0005 mg/g.

The lead content in water and in bottom sediments was measured with the AAS KVANT-Z.ETA device.

To determine interannual trends, retrospective data on the lead content in water and bottom sediments of the Sea of Azov from 1991 to 2006 were additionally used [8]. In this work, the studies were carried out in accordance with



F i g . 1 . Map of sampling of water and bottom sediments in 2010–2020

guideline FR.1.31.2005.01514 – this method preceded the method PND F 14.1:2:4.140-98, according to which lead concentrations were determined by the *Azovmorinformcenter* branch of *Centerregionvodkhoz* State Organization. With this consideration in mind, the data from monograph [8] were used in our work for comparison.

Mathematical processing of analytical data was carried out using the standard *Excel* package.

In the work, two areas were identified in the Sea of Azov: Taganrog Bay and the open part of the Sea of Azov (the sea proper), which is associated with their morphometric and hydrological features. The parameters of the districts used in the calculations are presented in the following table.

Parameters of the studied areas

Area	Total area, km^2 [9]	Average sedimentation rate [4], $g \cdot m^{-2} \cdot year^{-1}$
Taganrog Bay	5600	700
Open part of Sea of Azov	33400	300

[4] Sorokina, V.V., 2006. [*Peculiarities of Terrigenous Sedimentation in the Sea of Azov in the Second Half of the 20th Century*]. Ph.D. Thesis. Rostov-on-Don, 216 p. (in Russian).

Key data

One of the objectives of the study was to determine the impact of Taganrog Bay on lead pollution of water and bottom sediments in the open part of the Sea of Azov. Its solution was carried out on the basis of a comparison of lead concentrations in water and bottom sediments of Taganrog Bay and the open part of the Sea of Azov (Fig. 2 and 3).

HMs, including lead, can enter the Sea of Azov from both natural and anthropogenic sources. One of the main ones is the flow of such large and small rivers as Don, Kuban, Mius, Yeya, Beisug, Kagalnik, etc. [10, 11]. An important role in sea pollution belongs to the cities located on the coast and in the delta of the Don River – Azov, Taganrog, Yeysk, Primorsko-Akhtarsk, Temryuk – as a result of the discharge of insufficiently treated wastewater. It is also worth noting the impact of ports, shipping, landfills, and soil dumping [5), 6)]. Lead can come with atmospheric precipitation [8, 10–12] and also as a result of coastal abrasion.

The lead content in the water of the central part of the sea and Taganrog Bay increased in 2010–2015, which can have been associated with the development of industrial production in this region (thus, in 2010–2012, the following facts can be taken into account: the construction of a port complex near the city of Primorsko-Akhtarsk, of the Taman transshipment complex; the implementation of the Temryuk and Akhtarsk project for the extraction of oil and gas condensate; an increase in the capacity of the Taganrog Metallurgical Plant, the Taganrog Boiler Plant "Krasny Kotelschik" and the Taganrog Automobile Plant with an increase in emissions and discharges of pollutants).

According to the data presented in Fig. 2, *a*, it can be seen that in 1991–2009 the lead concentration in the water of the open part of the Sea of Azov was significantly below the MPC. Since 2010, there have been higher levels of lead pollution in waters, but lower levels of sediment pollution (Fig. 2, *b*). The dependence of lead concentration in bottom sediments on the change in the average annual values of its specific content in surface waters with a sufficient degree of probability (R^2 = 0.6) lay on a straight line on a logarithmic scale along the ordinate axes (Fig. 2, *c*), which allowed it to be described by the following exponential function:

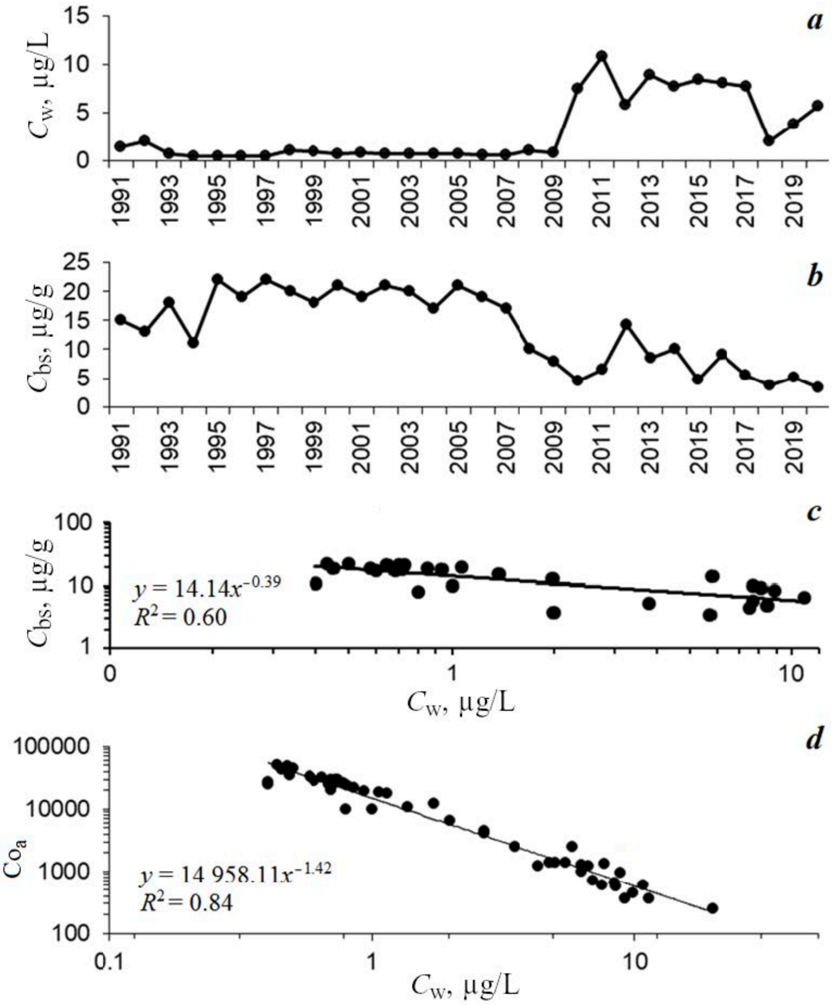
$$C_{\mathrm{bs}} = 14.14 \cdot C_{\mathrm{w}}^{-0.39}, \qquad (1)$$

where C_{bs} – concentration of lead contained in the upper layer of bottom sediments; C_{w} – lead concentration in the liquid phase.

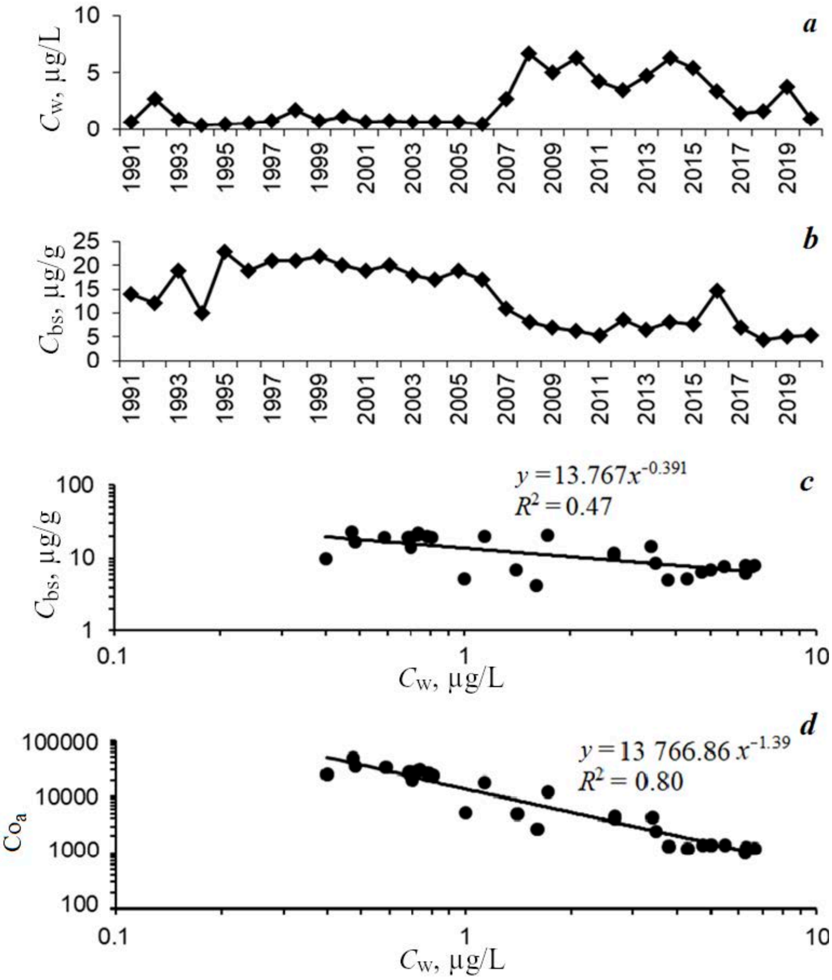
Fig. 2, *d* shows the dependence of the change in Co_{a} on the value of C_{w} based on the results of observations in 1991–2020. Statistical analysis materials showed

5) Bespalova, L.A., 2006. [*Ecological Diagnostics and Assessment of Sustainability of the Landscape Structure of the Sea of Azov*]. Ph.D. Thesis. Rostov-on-Don, 271 p. (in Russian).

6) Latun, V.V., 2005. [*Impact of the Operation of Shipping Channels on the Ecosystem of Taganrog Bay*]. Ph.D. Thesis. Rostov-on-Don, 209 p. (in Russian).



F i g . 2 . Characteristics of lead distribution in the open part of the Sea of Azov: concentration in water, µg/L (*a*); concentration in the surface layer of bottom sediments, µg/g dry mass (*b*); dependence of the lead concentration in bottom sediments on its concentration in water (*c*); dependence of the change in the coefficient of accumulation of lead by bottom sediments on lead concentration in water (*d*)



F i g . 3 . Characteristics of lead distribution in Taganrog Bay: concentration in water, µg/L (*a*); concentration in the surface layer of bottom sediments, µg/g dry mass (*b*); dependence of the concentration in bottom sediments on the concentration in water (*c*); dependence of the change in the coefficient of accumulation of lead by bottom sediments on lead concentration in water (*d*) that the correlation between Co_a and C_w with reliability characterized by the coefficient of determination $R^2 = 0.84$, could be described by the exponential function equation:

$$Co_a = 14958\ C_w^{-1.42}. \quad (2)$$

Correlation (1) showed that with an increase in lead concentration in water ($C_в$), its concentration in bottom sediments (C_{bs}) decreased. The study of this effect showed that a decrease in the value of C_{bs} with an increase in C_w was associated not only with the saturation of the surface of bottom sediments, but also with a decrease in their Co_a, taking into account the dimensional matching $Co_a = 1000C_{bs}/C_w$.

Fig. 3, *a* shows that except for small peaks in 1992–1998, the lead concentration in the water of Taganrog Bay was quite low until 2006. After 2006, its oscillatory changes were noted with an increase of concentration in water, which in general did not exceed the MPC of 10 μg/L. In 1991–2020 (Fig. 3, *b*), the lead concentration in the bottom sediments of Taganrog Bay, as a rule, changed in antiphase with the change in its content in the water, and in all cases it was below the MPC rationed according to the Dutch List. The dependence between C_{bs} and C_w lay on a straight line with determination characterized by the corresponding coefficient $R^2 = 0.47$. The exponential function equation obtained according to Fig. 3, *c*, was as follows:

$$C_{bs} = 13.767 \cdot C_w^{-0.391}. \quad (3)$$

The dependence between Co_a and C_w on a logarithmic scale along the ordinate axes (Fig. 3, *d*) was also described by a straight line, characterized by the coefficient of determination $R^2 = 0.8$. When approximating these data by the exponential function equation, we obtained:

$$Co_a = 13766 \cdot C_w^{-1.39}. \quad (4)$$

Obviously, materials shown in Fig. 2, *c*, *d* and 3, *c*, *d*, illustrate the ability of bottom sediments to concentrate lead under the combined impact of biotic and abiotic factors of the marine environment. The determination of the biogeochemical mechanisms responsible for the formation of the types of exponential dependence between C_w and C_{bs}, as well as between C_w and Co_a, requires the study of sorption, metabolic, and trophic interactions of living and inert matter included in bottom sediments under conditions of changes in salinity, pH, temperature, and hydrodynamic characteristics of the water. The above mentioned parameters were not registered in 1991–2020 as a part of the monitoring carried out by *Centerregionvodkhoz* State Organization.

It should be noted that lead entering the Sea of Azov with river runoff, with slope runoff from the coast and from atmospheric precipitation, is carried by currents along the sea area and vertically. According to reference data [3)], surge phenomena up to 4–6 m high, manifesting themselves on a time scale up to 12 h, and seiches up to 1 m with a period of some minutes to several hours, are observed in the Sea of Azov. At an average current velocity of 60–80 cm/s, a relatively uniform distribution of impurities over the sea area is ensured on a weekly time scale and in depth on an hour scale. However, under strong winds, detachment of bottom sediments is observed. The frequency of waves with a height of over 2 m, causing detachment of the bottom sediment, is 13%. In general, the non-stationarity of the hydrodynamic characteristics of the Sea of Azov can be estimated on a time scale of no more than one month and a half. The size spectrum of suspended particles in the Sea of Azov ranges from 1 to 300 microns, and their sedimentation to the bottom proceeds on time scales from minute to week in accordance with the Stokes' Law and Bernoulli's Principle. A review of the hydrodynamic and sedimentation features of the Sea of Azov as a whole indicates that the average annual estimates of pollution of its waters and bottom sediments with lead are acceptably adequate.

According to modern concepts, bottom sediments can be considered as a sorbent interacting with lead dissolved in water. The degree of their sorption saturation is usually reflected by the Freundlich equation. In accordance with the designations adopted in this paper, the Freundlich equation has the following form:

$$C_{bs} = A \cdot C_w^n, \tag{5}$$

where A and n – parameters ($n < 1$).

Comparison of correlations (1) and (3) with expression (5) showed that with identical common notation of these equations, parameter n in equations (1) and (3) had a negative sign. This means that the Freundlich equation of form (5) does not reflect the sorption saturation of bottom sediments with lead or that the sorption saturation does not prevail over other factors not currently taken into account.

Consideration of relations (2) and (4) showed that a significant (R^2 = 0.84 and R^2 = 80) decrease in Co_a of lead has a significant effect on the concentrating ability of bottom sediments in accordance with a power function of form (5), but with a negative sign of exponent n. Comparison of correlations (1) and (3) showed that the relative error of parameter A incongruence in them was 7.9, and n – 2.1 %. With the variability of the data characterized by the coefficients of determination, respectively, R^2 = 0.84 and R^2 = 80, this indicates the identity of correlations (2) and (4). The former was obtained from the results of monitoring of the open part of the Sea of Azov with a sedimentation rate of 300 $g \cdot m^{-2} \cdot year^{-1}$, and the latter – according to the study of Taganrog Bay with a sedimentation rate of 700 $g \cdot m^{-2} \cdot year^{-1}$. Hence it appears that the regularities of changes in the concentrating capacity of bottom sediments with respect to lead do not depend on the intensity of sedimentation.

At the same time, it should be noted that materials shown in Fig. 2, *c*, *d* and 3, *c*, *d*, illustrate the regularities of change in the sorption (C_{bs}) and concentrating (Co_a) capacity of bottom sediments on the scale of the entire observation period. Therefore, these dependences are significant indicators of the assimilation capacity of bottom sediments in relation to pollutants. The assimilation capacity of bottom sediments in water areas is determined from the correlation [2]:

$$Q_{as} = S \cdot V_{sed} \cdot C_{bs}, \tag{6}$$

where S – area of the water area under consideration, km^2; V_{sed} – specific sedimentation rate, g·m^{-2}·year^{-1}.

Formula (6) is applicable when rationing the maximum permissible flows of pollution of water areas with HMs according to the Dutch List (with C_{bs} = MPC$_{bs}$). Taking into account that $C_{bs} = C_w \cdot$ Co$_a$, with due regard to formulas of forms (2) and (4), equation (6) is transformed into the following correlation:

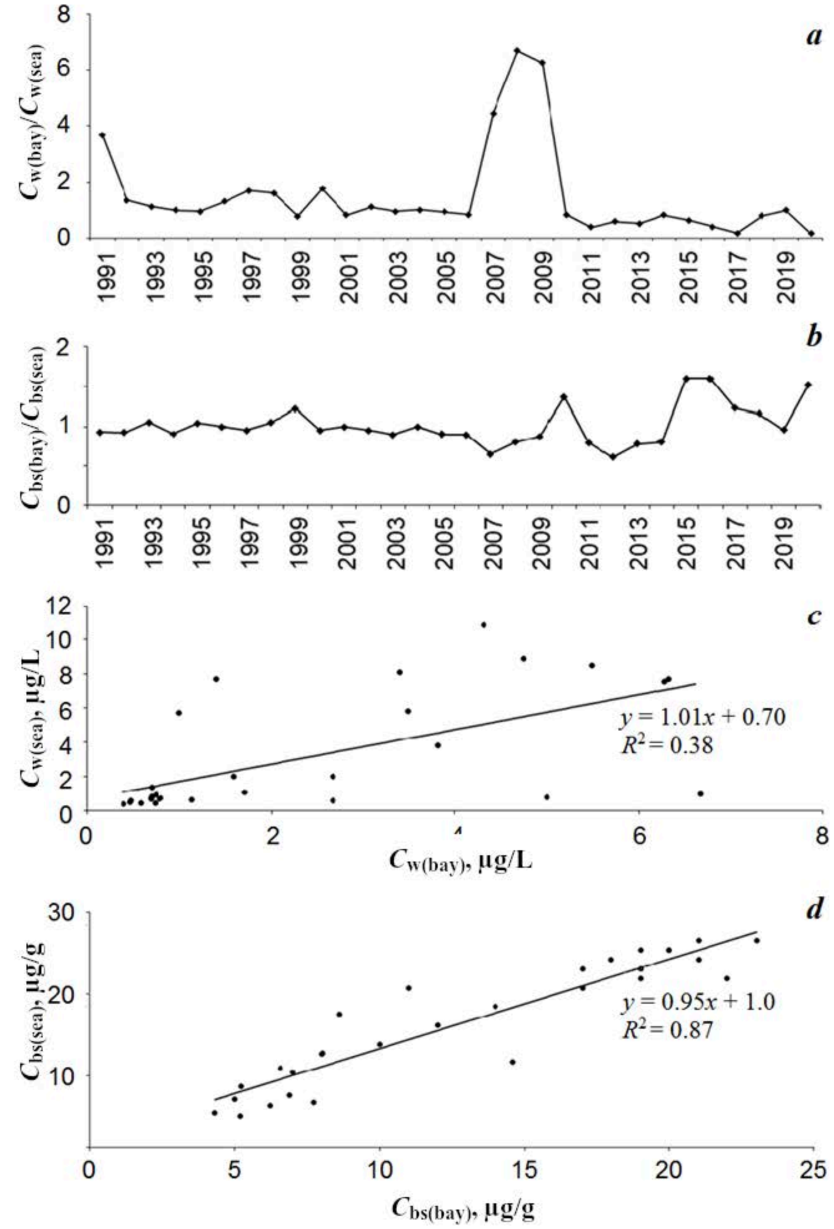
$$Q_{as} = S \cdot V_{sed} \cdot C_w \cdot A \cdot C_w^{-n}, \tag{7}$$

which can be used for rationing according to ecotoxicological criteria (with C_w = MPC).

With MPC$_w$ = 10 µg/L, the rationed maximum allowable flow of lead into the open part of the Sea of Azov calculated by correlation (7), was 59.6 t/year, and for Taganrog Bay, taking into account correlation (7), it was 21.4 t/year.

It can be seen from Fig. 4 that over the entire observation period from 1991 to 2020, except for 2007–2009, lead concentrations in the waters of Taganrog Bay and the open part of the Sea of Azov almost coincided. The same was noted for bottom sediments (Fig. 4, *b*). However, consideration of the dependences between the lead content in the water of the sea $C_{w(sea)}$ and bay $C_{w(bay)}$ revealed a weakly manifested relationship (R^2 = 0.38) between these two parameters. At the same time, the dependence between the lead content in the bottom sediments of the sea $C_{bs(sea)}$ and bay $C_{bs(bay)}$ was highly significant statistically (R^2 = 0.87). These data indicated that suspended matter with a higher lead content entering Taganrog Bay was transported as a result of hydrodynamic processes to the open part of the Sea of Azov and deposited in this water area as part of bottom sediments.

Calculations of the lead input resulted from water exchange through the Dolzhansky Strait (with average long-term values of the annual water outflow into the sea and the annual water inflow into the bay) performed in [13], showed that, e. g., in 2017, 302–1184 tons of lead could have arrived from the Sea of Azov to Taganrog Bay, and from Taganrog Bay to the sea proper – 131–827 tons. Thus, the sea proper acted as a source of pollution of Taganrog Bay. In 2007–2009, on the contrary, Taganrog Bay was a source of water pollution of the open part of the sea: lead concentrations in the bay were significantly higher than in the open part of the sea, e. g., in 2008, 6.67 µg/L in the bay and 0.8 µg/L in the open sea. Thus, Taganrog Bay can serve both as a source of pollution and a barrier that either transports HMs, including lead, into the Sea of Azov or entraps them [14].



F i g . 4 . Change in the ratio of lead concentrations in water of Taganrog Bay and in the open part of the Sea of Azov $C_{w(bay)}/C_{w(sea)}$ (*a*) and in bottom sediments of Taganrog Bay $C_{bs(bay)}/C_{bs(sea)}$ (*b*); dependence between lead concentrations in water of Taganrog Bay and the open part of the Sea of Azov (*c*) and in bottom sediments (*d*)

Conclusion

In general, for the period from 1991 to 2020, fluctuations in the average annual lead concentrations both in water and in bottom sediments of the open part of the sea and Taganrog Bay are not environmentally significant. The lead content in the water of the central part of the sea and Taganrog Bay increased in 2010–2015, which can have been associated with the development of industrial production in this region (thus, in 2010–2012, the following facts can be taken into account: the construction of a port complex near the city of Primorsko-Akhtarsk, of the Taman transshipment complex; the implementation of the Temryuk and Akhtarsk project for the extraction of oil and gas condensate; an increase in the capacity of the Taganrog Metallurgical Plant, the Taganrog Boiler Plant "Krasny Kotelschik" and the Taganrog Automobile Plant with an increase in emissions and discharges of pollutants).

It is determined that the dependences of the change in the concentration and coefficients of lead accumulation in bottom sediments on the change in its concentration in the water of Taganrog Bay and the open part of the Sea of Azov are described with a high degree of statistical significance by an exponential function equation. It is shown that the parameters of this equation represent the indicators of the assimilation capacity of bottom sediments in relation to lead. They can be used for the purposes of environmental regulation, taking into account sanitary and hygienic standards.

It is found that an increase in the lead concentration in the suspended matter of the Taganrog Bay led to an increase in its concentration in the suspended matter of the open part of the Sea of Azov.

Analysis of long-term data on the lead content in water and in bottom sediments of the central part of the sea and Taganrog Bay makes it possible to conclude that Taganrog Bay can serve both as a lead pollution source and a barrier that either transports lead into the Sea of Azov or entraps it.

REFERENCE

1. Polikarpov, G.G. and Egorov, V.N., 1986. [*Marine Dynamic Radiochemoecology*]. Moscow: Energoatomizdat, 176 p. (in Russian).
2. Egorov, V.N., 2019. *Theory of Radioisotope and Chemical Homeostasis of Marine Ecosystems*. Sevastopol: IBSS, 356 p. doi:10.21072/978-5-6042938-5-0 (in Russian).
3. Pospelova, N.V., Egorov, V.N., Proskurnin, V.Yu. and Priymak, A.S., 2022. Suspended Particulate Matter as a Biochemical Barrier to Heavy Metals in Marine Farm Areas (Sevastopol, the Black Sea). *Marine Biological Journal*, 7(4), pp. 55–69. doi:10.21072/mbj.2022.07.4.05
4. Stetsiuk, A.P. and Egorov, V.N., 2018. Marine Suspensions Ability to Concentrate Mercury Depending on its Contents in the Shelf Water Area. *Monitoring Systems of Environment*, 13, pp. 123–132. doi:10.33075/2220-5861-2018-3-123-132
5. Bufetova, M.V., 2022. Assessment of the Ability of Suspended Matter in the Sea of Azov to Concentrate Heavy Metals. *Ecological Safety of Coastal and Shelf Zones of Sea*, (1), pp. 55–65. doi:10.22449/2413-5577-2022-1-55-65
6. Alexakhin, R.M. and Fesenko, S.V., 2004. Radiation Protection of the Environment: Anthropogenic and Ecocentric Principles. *Radiation Biology. Radioecology*, 44(1), pp. 93–103 (in Russian).

7. Izrael, Yu.A. and Tsyban, A.V., 2009. *Anthropogenic Ecology of Ocean*. Moscow: Flinta; Nauka, 529 p. (in Russian).
8. 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).
9. 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).
10. 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).
11. Fedorov, Yu.A., Mikhaylenko, A.V. and Dotsenko, I.V., 2012. [Biogeochemical Conditions and their Role in Mass Transport of Heavy Metals in Aquatic Landscapes]. In: MSU, 2012. [*Landscape Geochemistry and Soil Geography: Proceedings of the All-Russian Scientific Conference (on the Occasion of Sentenary of the Birth of M. A. Glazovskaya). Moscow, 4–6 April 2012*]. Moscow: MGU, pp. 332–334 (in Russian).
12. Mamykina, V.A. and Khrustalev, Yu.V., 1966. Abrasion and Accumulation Processes of Recent Sedimentation in the Azov Sea. *Okeanologiya*, 6(3), pp. 451–457 (in Russian).
13. Bufetova, M.V., 2019. Assessment of Income and Elimination of Heavy Metals in the Taganrog Bay of the Sea of Azov. *Ecological Safety of Coastal and Shelf Zones of Sea*, (2), pp. 78–85. doi:10.22449/2413-5577-2019-2-78-85 (in Russian).
14. Vishnevetskiy, V.Yu. and Ledyaeva, V.S., 2012. Experimental Studies of the Dynamics of the Concentration of Heavy Metals in Surface Water in the Taganrog Bay. *Engineering Journal of Don*, (4–1), 5 p. (in Russian).

Submitted 7.02.2023; accepted after review 23.03.2023;
revised 03.05.2023; published 26.06.2023

About the authors:

Marina V. Bufetova, Associate Professor of the Department of Ecology and Nature Management, Faculty of Ecology, Sergo Ordzhonikidze Russian State Geological Exploration University (MGRI) (23 Miklukho-Maklaya St., Moscow, 117997, Russian Federation), Associate Professor, Ph.D. (Geogr.), **SPIN-code: 9133-4070, ORCID ID: 0000-0002-6247-1698**, *mbufetova@mail.ru*

Victor N. Egorov, Research Supervisor, A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Av., Sevastopol, 299011, Russian Federation), Academician of RAS, Dr.Sci. (Biol.), Professor, **SPIN-code: 6595-6759, ORCID ID: 0000-0002-4233-3212**, *egorov.ibss@yandex.ru*

Contribution of the authors:

Marina V. Bufetova – problem statement, processing, analysis and description of the study results, discussion of the results, conclusion drawing, article text and graphic material preparation

Victor N. Egorov – qualitative analysis of the results and their interpretation, discussion of the results, article text preparation, conclusion drawing

All the authors have read and approved the final manuscript.