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Numerical Modelling of RedOx Condition Dynamics at the Water-Sediment Interface in Sevastopol Bay

Yu. S. Gurova [1]*, E. V. Yakushev [2, 3], A. V. Berezina [2, 3],
M. O. Novikov [2], K. I. Gurov [1], N. A. Orekhova [1]

[1] *Marine Hydrophysical Institute of RAS, Sevastopol, Russia*
[2] *Shirshov Institute of Oceanology RAS, Moscow, Russia*
[3] *Norwegian Institute for Water Research, Oslo, Norway*
* *e-mail: kurinnaya-jul@yandex.ru*

Abstract

The paper aims at assessing the variability of characteristics of redox conditions in the water column and the surface layer of sediments under changing anthropogenic load using *in situ* observational data and results of numerical modelling (the case of Sevastopol Bay). A comprehensive analysis is carried out of the chemical characteristics of the water column and pore water as well as geochemical characteristics of the bottom sediments. It is confirmed that there is the previously determined violation of the natural hydrochemical regime due to phytoplankton blooms in summer and the location of a large amount of stormwater and municipal wastewater in the bay. Despite the saturation of waters with oxygen in the bottom layer (94–113 % sat.), suboxic conditions are registered in the surface layer of bottom sediments. This is explained by predominance of the fine-grained fraction and high content of organic carbon. Mathematical calculations were performed using the one-dimensional benthic-pelagic Bottom RedOx Model (BROM). The numerical modelling results were validated using in situ observational data. The results showed that the model reproduces the natural seasonal variations of hydrochemical parameters associated with phytoplankton blooms, the occurrence of high concentrations of organic matter and its oxidation by the dissolved oxygen. Two numerical experiments with decreased and increased concentrations of organic matter were conducted to assess the effects of varying amounts of the organic matter entering the bay. It was found that the increased load on the bay results in a decrease in the oxygen concentration (up to 12 μM) and the development of anaerobic conditions in the bottom layer of water. Reduced organic matter input promotes aerobic conditions in the water column and in the bottom water layer. However, for bottom sediments, such a reduction in the load is not sufficient given the level of excess organic matter accumulated in them. The pore waters still consume oxygen and nitrates heavily and produce reduced forms of iron and manganese.

Keywords: bottom sediments, pore waters, oxygen, organic carbon, modelling, Black Sea, Sevastopol Bay, BROM model

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Численное моделирование динамики окислительно-восстановительных условий на границе вода – донные отложения в Севастопольской бухте

Ю. С. Гурова [1]*, **Е. В. Якушев** [2, 3], **А. В. Березина** [2, 3],
М. О. Новиков [2], **К. И. Гуров** [1], **Н. А. Орехова** [1]

[1] *Морской гидрофизический институт РАН, Севастополь, Россия,*
[2] *Институт океанологии им П.П. Ширшова РАН, Москва, Россия*
[3] *Norwegian Institute for Water Research, Oslo, Norway*
* *e-mail: kurinnaya-jul@yandex.ru*

Аннотация
Цель работы – оценка изменчивости характеристик окислительно-восстановительных условий в водной толще и поверхностном слое отложений при изменяющейся антропогенной нагрузке с использованием данных натурных наблюдений и результатов численного моделирования на примере Севастопольской бухты. Выполнен комплексный анализ химических характеристик водной толщи и поровых вод, а также геохимических характеристик донных отложений. Подтверждено, что происходит установленное ранее нарушение естественного гидрохимического режима, связанное с цветением фитопланктона в летнее время и расположением в акватории бухты большого количества ливневых и коммунальных стоков. Несмотря на насыщение придонного слоя вод кислородом (94–113 % нас.), в верхнем слое донных отложений зафиксированы субкислородные условия. Это объясняется преобладанием мелкозернистой фракции и высоким содержанием органического углерода. Математические расчеты выполнялись с помощью одномерной бентосно-пелагической модели Bottom RedOx Model (BROM). С использованием данных натурных наблюдений проведена валидация результатов численного моделирования. Полученные результаты показали, что модель воспроизводит естественный сезонный ход гидрохимических параметров, связанный с цветением фитопланктона, появлением высоких концентраций органического вещества и его окислением растворенным кислородом. Для оценки последствий поступления различного количества органического вещества в акваторию бухты были проведены два численных эксперимента с уменьшением и увеличением его концентрации. Установлено, что увеличение нагрузки на акваторию бухты приводит к снижению концентрации кислорода (до 12 мкМ) и развитию анаэробных условий в придонном слое вод. Сокращение поступления органического вещества способствует формированию аэробных условий в водной

толще и придонном слое вод. Однако для донных отложений, с учетом уровня накопленного в них избыточного органического вещества, подобного снижения нагрузки недостаточно. В поровых водах все еще происходит интенсивное потребление кислорода и нитратов и образуются восстановленные формы железа и марганца.

Ключевые слова: донные отложения, поровые воды, кислород, органический углерод, моделирование, Черное море, Севастопольская бухта, модель *BROM*

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Introduction

Coastal ecosystems characterized by high biodiversity, play a significant role in the social and economic sphere. It is in the coastal water areas that the highest level of pollution is observed [1].

The anthropogenic load exerted on coastal water areas leads to the inflow of an additional amount of organic matter and nutrients into them. The consumption of oxygen for the oxidation of organic matter and other reduced compounds leads to a shift in the processes occurring due to the anaerobic oxidation of organic matter closer to the surface of bottom sediments. As a result, oxygen is exhausted in the upper layer of sediments, which results in the formation of anaerobic conditions [2]. An increase in the content of reduced compounds in the surface layer of sediments leads to an increase in their flow into the bottom layer of waters, due to which suboxic and anaerobic conditions are also registered in it [3].

The bays of the Sevastopol region are an example of the water areas of the Crimean shelf with the maximum anthropogenic load, in which the accumulation of organic matter in bottom sediments significantly prevails over its decomposition [4].

Of all the bays of the Sevastopol region, Sevastopol Bay stands out directly as the level of anthropogenic load on it has shown significant growth over the years [5–7]. This results in intensive silting of bottom sediments, accumulation of organic carbon in them, development of oxygen deficiency in bottom sediments and the bottom water layer, and further emergence of ecological risk zones.

Various systematic studies of the hydrological and hydrochemical parameters of waters [5, 6, 8–10], the spatial distribution of the geochemical characteristics of bottom sediments [11–13], and the level of their pollution [7, 14, 15] have been carried out for a long time in the bay water area. In addition to the characteristics of the solid phase of bottom sediments, the chemical composition of pore waters has also been actively studied [2, 13, 16].

Based on *in situ* measurements, important information about the current state of the water area was obtained. The use of the results of model calculations makes it possible to obtain a broader (in space and time) idea of possible changes in the characteristics of the ecosystem when the influencing factors change [17, 18].

Concerning Sevastopol Bay, both its hydrodynamic regime [19–21] and the distribution of pollutants in it [22, 23] are regularly modelled. However, no work has been carried out in the studied area to assess changes in redox conditions in bottom sediments and the bottom water layer on a space-time scale using mathematical modelling methods.

The paper aims at assessing the variability of characteristics of redox conditions in the water column and the surface layer of sediments under changing anthropogenic load using *in situ* observational data and numerical modelling (the case of Yuzhnaya Bay, which constitutes a part of Sevastopol Bay).

Area characteristics

Sevastopol Bay is a semi-enclosed water area with significantly limited water exchange between the bay and the open sea [24]. The water area of the bay is under constant anthropogenic pressure [10]. The average depth of the bay is 12.5 m. The formation of the hydrochemical structure of the Sevastopol Bay waters is significantly influenced by the river runoff in the eastern part and municipal wastewater, which transport an additional amount of organic matter into the water area (Fig. 1) [5, 13, 25]. For a long time, the bay was used for growing oysters, but now such use is impossible due to the depletion of bioresources and the increasing level of pollution [6]. Currently, the bay is one of the most polluted Black Sea coastal areas [4–7], with the maximum level of pollution in Yuzhnaya Bay. This bay is elongated in the meridional direction and is characterized by a large number of sources of municipal wastewater and stormwater and the location of ship repair facilities along its shores [7, 11, 26, 27] (Fig. 1).

According to [28], the hydrodynamic regime of the Yuzhnaya Bay ecosystem (Fig. 1) is characterized by difficult water exchange with the main water area of the bay and by water ventilation determined by the wind regime. With northerly and northeasterly winds, the waters are blocked in Yuzhnaya Bay. With southerly winds, waters polluted by municipal wastewater can be carried out of Yuzhnaya Bay and reach the northern shores of Sevastopol Bay [28].

Under certain conditions, bottom sediments also influence the characteristics of the bottom water layer of Yuzhnaya Bay [13]. The surface layer of bottom sediments (0–5 cm) in the bay is represented mainly by sandy silty and pelitic silts and, to a lesser extent, by silted shell rock [11–13]. Abrasion processes accumulate coarse-grained material at the outlet of the Sevastopol Bay and along the coastline.

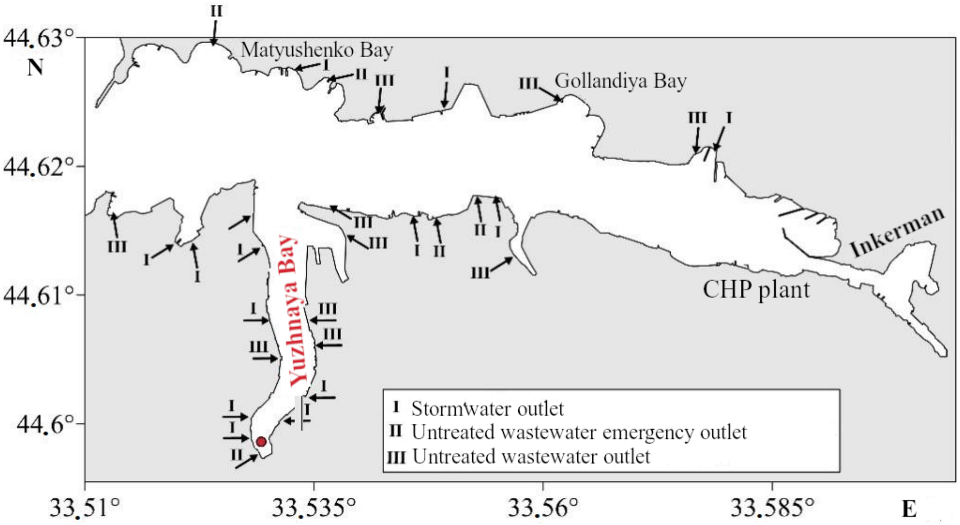

Fig. 1. Location of the bottom sediment column sampling station (red dot) as well as stormwater and emergency wastewater outlets [13]

In Yuzhnaya Bay, the rate of input of terrigenous material weakens, and fine-grained fractions accumulate here as a result of intensive input of organic matter (OM) and low water dynamics [11, 12]. In recent years, the proportion of the silt fraction in the surface layer of bottom sediments of the bay has been increasing, which can indicate silting of the bay [7]. The vertical distribution of C_{org} in Yuzhnaya Bay is heterogeneous and varies from 4.5 to 7 % dry weight [7].

In accordance with the hydrological and hydrochemical parameters of the waters of the bay and its physical and geographical characteristics, the seasonal distribution of hydrochemical components, in particular oxygen, is determined not only by the temperature regime and hydrodynamics of the waters, but also by a biological factor, namely, phytoplankton blooms [5]. At the same time, the saturation of the bottom layer of waters with oxygen, as a rule, does not reach 100 % during the year in the Yuzhnaya Bay apex. According to [5, 29], mass phytoplankton blooms both in the surface and in the bottom water layer are observed in July. The so-called summer maximum is typical for polluted water areas including Sevastopol Bay. The amount of phytoplankton decreases in the cold period of the year. Therefore, the Sevastopol Bay waters can be characterized in terms of phytoplankton biomass as conditionally clean in winter and polluted in summer [29].

Over the past 20 years, the supply of nutrients and organic matter to Sevastopol Bay has increased, which results in a decrease in oxygen concentration and pH, as well as acidification of the bay waters [6]. The results of the study [16] showed that the organic matter oxidation occurred mainly under anaerobic conditions.

Materials and methods

A comprehensive analysis of the hydrological and hydrochemical characteristics of the water column and the physical and chemical characteristics of bottom sediments was carried out in May 2018 under quarterly expeditions of the Marine Biogeochemistry Department of the Marine Hydrophysical Institute of RAS onboard the small vessel "Hydrograph-4". Fig. 1 shows the location of the sea water and bottom sediment column sampling station in Yuzhnaya Bay.

Sea water samples from the surface and bottom horizons were taken with a bathometer.

The content of dissolved oxygen in water samples was determined by the method of Winkler volumetric titration modified by Carpenter [30]. This method makes it possible to obtain results with the accuracy of ±0.01 ml/L (±0.4 μM). The degree of oxygen saturation (%) was calculated using Weiss formula [31]

$$\ln C = A_1 + A_2\,(100/T) + A_3 \ln(T/100) + A_4\,(T/100) + \\ + S\,[B_1 + B_2\,(T/100) + B_3\,(T/100)^2],$$

where C – solubility of oxygen at total pressure of 1 atmosphere, taking into account the pressure of saturated water vapor, ml/L; $A(_{1,2,3,4})$ and $B(_{1,2,3})$ – constants ($A_1 = -173.4292$; $A_2 = 249.6339$; $A_3 = 143.3483$; $A_4 = -21.8492$; $B_1 = -0.033096$; $B_2 = 0.014259$; $B_3 = -0.0017$); T – absolute temperature, K; S – salinity, PSU.

Mineral forms of biogenic substances (phosphates, silicic acid, ammonium nitrogen) were analyzed by the photometric method on a spectrophotometer KFK-3KM after seawater samples were filtered through a membrane filter with a pore size of 0.45 μm (except for samples for determining the content of ammonium ions) 1). When determining the concentration of silicic acid, a correction was made for salinity, calculated by the following formula

$$C_{\text{tru}} = C_{\text{obs}} \cdot (1 + 0.0045S),$$

where C_{tru} – true silicic acid concentration; C_{obs} – observed silicic acid concentration; S – final salinity of the analyzed sample, PSU 1).

Ammonium nitrogen was determined using modified Sage-Solorzano method for sea water, which is based on a phenol-hypochlorite reaction using sodium nitroprusside and sodium citrate 2). To determine the amount of nitrates and nitrites on a flow autoanalyzer AutoAnalyzer AA II (*Bran+Luebbe*), the method of reducing nitrates to nitrites with copper-plated cadmium was used.

To determine the chemical composition of pore waters, bottom sediment columns were sampled using a Plexiglas tube, 6 cm in diameter, with a vacuum liquid trap.

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1) Bordovsky, O.K. and Ivanenkov, V.N., eds., 1992. *Modern Methods of Ocean Hidrochemical Investigations*. Moscow: IO AS USSR, 201 p. (in Russian).

2) UNESCO, 1987. *Thermodynamics of the Carbon Dioxide System in Seawater*. Paris: UNESCO, pp. 3–21.

When analyzing the chemical profile of the pore waters of bottom sediments, a polarographic method of analysis was used with a glass Au-Hg microelectrode [13, 32, 33]. An electrode saturated with silver chloride was used as a reference electrode, and a platinum electrode was used as an auxiliary one. Profiling of bottom sediment columns was carried out with a vertical resolution of 1 to 10 mm. The main advantage of the method is the ability to analyze the chemical composition of pore waters under conditions as close as possible to natural ones, without any sample destruction and additional sample preparation. For all the measurements, the determination error did not exceed 10 %.

The granulometric composition of bottom sediments was determined with the combined decantation and diffusion method. The separation of the silty and pelitic fraction (≤ 0.05 mm) was performed by wet sieving followed by gravimetric determination of the dry weight. Coarse-grained fractions (> 0.05 mm) were separated by the dry sieving method using standard sieves (GOST 12536-2014).

Carbon content (C_{org}) was determined coulometrically on an express analyzer AN 7529 according to the method adapted for marine bottom sediments. The standard deviation value for samples with C_{org} content less than 0.5 % was 0.03, and for samples with C_{org} more than 1.5 % it was 0.08 [34].

Mathematical model and input data

The one-dimensional benthic-pelagic Bottom RedOx Model (BROM) was used to calculate redox conditions and predict their possible changes in the water column and the surface layer of sediments of Yuzhnaya Bay [35].

BROM is integrated into the existing Framework for Aquatic Biogeochemical Modeling (FABM) and includes a 2D transport model 2DBP [36] and a biogeochemical module (BROM-biogeochemistry) [17, 37–41].

The biogeochemical module consists of several submodules that parameterize the processes in the ecosystem and the processes of transformation of the chemical elements considered in the model: nitrogen, phosphorus, carbon, silicon, iron, manganese, and sulfur. Within the framework of the model, OM is represented as particulate organic matter labile (POML) and dissolved organic matter labile (DOML), which can be oxidized by dissolved oxygen, being a part of various compounds.

The equations and parameters used in BROM are given in [35], and the block diagram of the model is shown in Fig. 2.

The temporal variability of the substance concentration is stipulated by its diffusion and sedimentation, taking into account the processes leading to the formation and consumption of this substance:

$$\frac{\partial \hat{C}}{\partial t} = \frac{\partial}{\partial z} D \frac{\partial \hat{C}_i}{\partial z} - \frac{\partial}{\partial z}\left(v_i \hat{C}_i\right) + \varepsilon_h\left(\hat{C}_{0i} - \hat{C}_i\right) + T_{birr(i)} + R_i,$$

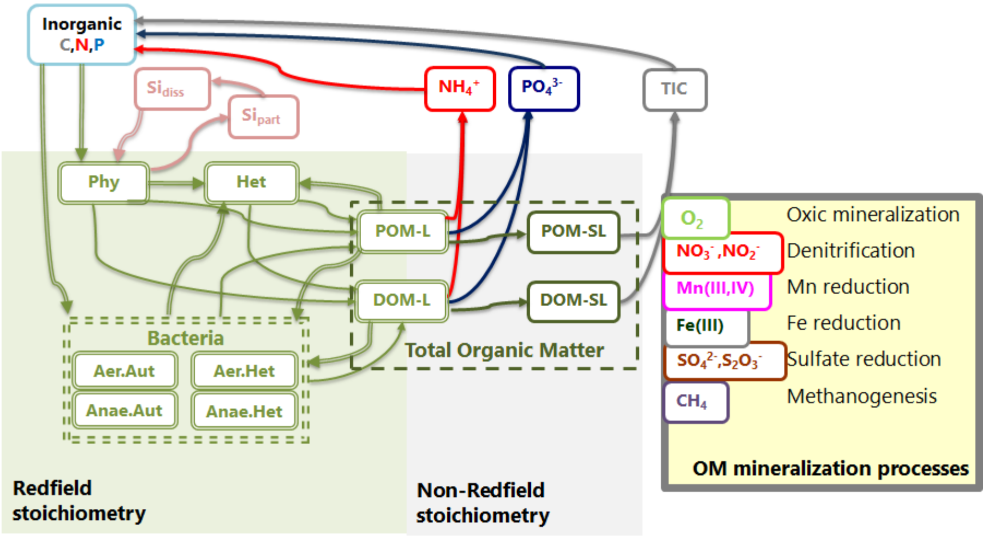


Fig. 2. Block diagram of the biogeochemical module provided in the Benthic RedOx Model (BROM)

where $\hat{C}_i$ – concentration, mmol·m^{-3} total volume, *i*-th state variable; $D(z, t)$ – vertical diffusion coefficient; v_i – sedimentation rate; $\varepsilon_h(z, t)$ – specific rate of climatic concentration relaxation $\hat{C}_{0i}(z,t)$; $T_{birr(i)}$ – trend stipulated by bioirrigation (non-zero for solutes in the bottom water column only); R_i – sources minus wastewaters.

Sedimentation rate v_i is non-zero for weighted (undissolved) variables only and is determined at each time step by the biogeochemical module [36].

The vertical grid in the BROM transport is divided into the water column, the bottom boundary layer, and bottom sediments. The grid spacing in the water column is 2 m. For the bottom water layer (1 m above the sediment surface), the grid spacing decreases towards the water–bottom boundary from 20 cm to 17 mm for the fluffy layer. For the upper layer of deposits, the grid spacing increases geometrically downward from the boundary of the fluffy layer from 1.5 mm to 20 mm. The result is represented by a complete grid with non-uniform spacing and maximum resolution near the water-bottom boundary. In this vertical grid, temperature, salinity, and biogeochemical concentrations are determined at the centers of the layers, while diffusion coefficients, sedimentation rates, and net fluxes are determined at the boundaries between the layers [36].

The results of the calculation of the Princeton Ocean Model (POM) adapted for the bays of the Sevastopol region were used as input data in the BROM hydrophysical module [19].

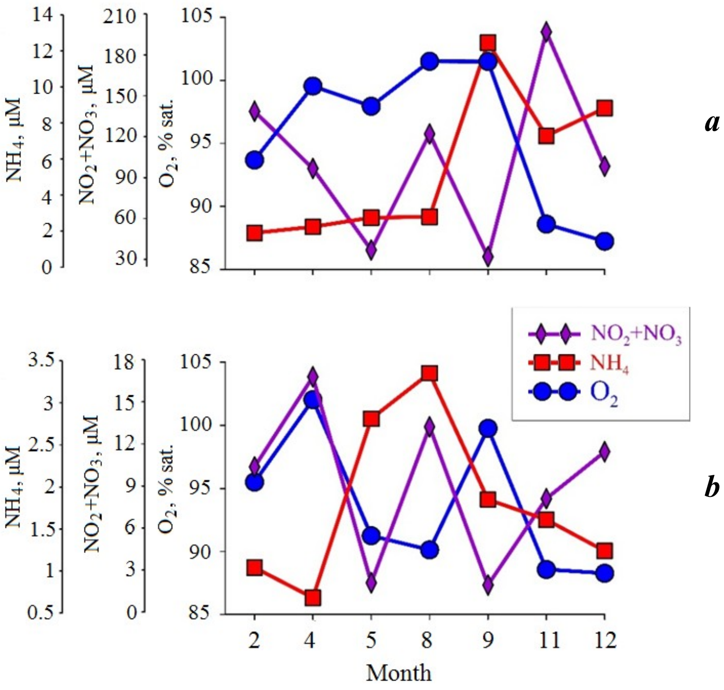
Results and discussion

Chemical composition of bottom water layer

The concentrations of hydrochemical parameters in the surface and bottom water layers for the period from February 2017 to February 2022 are shown in Fig. 3.

For the surface water layer, high values of the degree of saturation of water with oxygen (98–102 %) are observed from April to September, while from November to February, these values decrease (87–94 %). Such a decrease in the oxygen content is explained by the fact that in cold weather, due to the absence of phytoplankton blooms, oxygen is probably consumed for the oxidation of organic substances entering the bay [5].

It is known from literary sources that the maximum values of ammonium ion concentrations and the sum of nitrates/nitrites are noted in the apex of Yuzhnaya Bay both in the surface and in the bottom water layer [5, 6]. This is explained by the presence of stormwater and municipal wastewater in the apex of the bay (Fig. 1). Analysis of the data obtained confirmed the change in the intra-annual course of hydrochemical parameters [5, 6], which takes place for the waters of



F i g 3 . Temporal variability of hydrochemical characteristics in the surface (*a*) and bottom (*b*) water layers in Yuzhnaya Bay in 2017–2022

Sevastopol Bay, as well as significant difference in their concentration in the surface and bottom layers [6] (Fig. 3). The decrease in the concentration of the sum of nitrates/nitrites in the warm period of the year is explained by their consumption by phytoplankton, and in the autumn and winter seasons their concentrations increase.

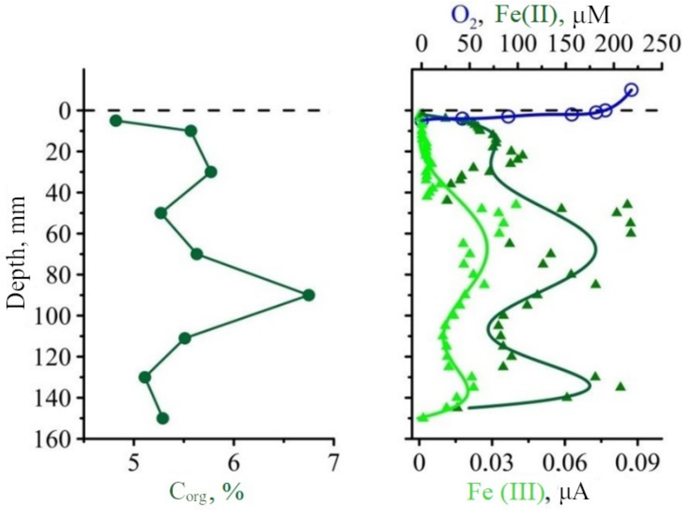
The maximum concentrations of ammonium ions were determined in the warm period of the year: in the surface layer in September, and in the bottom layer from May to September. According to [5, 6], this is explained by the processes of bacterial destruction of organic matter, as well as the intensification of the processes of stormwater and municipal wastewater in the summer.

Geochemical composition of bottom sediments

The surface layer (0–5 cm) of bottom sediments in the apex of Yuzhnaya Bay is formed mainly by silty material (78 %), consisting of 51 % of the pelitic and aleurite fraction and 27 % of the aleurite and pelitic fraction. The proportion of fine-grained material increased with depth. The C_{org} content in the surface layer was 4.82 %, and its vertical distribution was distinguished by the presence of several concentration peaks at a depth of 30 and 90 mm (Fig. 4, *a*).

Chemical composition of pore waters

In the apex of Yuzhnaya Bay, oxygen penetrated into the bottom sediments to a depth of 4 mm, its average concentration was 132 μM (up to 79 % sat.). The characteristics of pore waters were determined by processes involving dissolved forms of iron (Fe(II, III)), with their maxima in the 40–60 mm and 130–140 mm layers (Fig. 4, *b*). The average Fe(II) concentration was 398 μM.



a ***b***

F i g . 4 . Vertical distribution of C_{org} (*a*) and pore water components (*b*) in the bottom sediments of Yuzhnaya Bay

The analysis of the pore waters of bottom sediments showed that, despite sufficient saturation of the bottom water layer with oxygen (94–113 % sat.), suboxic conditions formed in the upper layer of bottom sediments. This is explained by the predominance of the fine-grained fraction (> 75 %) and high C_{org} content (> 4 %).

To predict the variability of the redox conditions in the bottom sediments and bottom water layer of Yuzhnaya Bay on a space-time scale, the numerical modelling results were validated and a series of model experiments was carried out, suggesting a change in the amount of OM in the water area of the bay.

Validation of numerical calculations

To validate the numerical modelling results, *in situ* observational data obtained for the water column (O_2 concentrations) and bottom sediments (concentrations of O_2, Fe(II), Mn(II), H_2S, C_{org}) during expeditions along Sevastopol Bay (Yuzhnaya Bay) in 2017–2020, were used. To compare the numerical results with *in situ* observations, the BROM model was run with a vertically uniform initial distribution of parameters. After reaching a quasi-stationary state with seasonal fluctuations of the studied parameters, the results were compared with *in situ* observations. In order to adequately reproduce seasonal dynamics of biogeochemical characteristics and to adapt the model parameters to local conditions, the model was run several times. The validation results are shown in Fig. 5, 6.

The modelling took into account biogeochemical processes occurring under various redox conditions, which determine the mechanisms of OM mineralization (aerobic oxidation, denitrification, reduction of manganese and iron, and sulfate reduction). Most of the results of model calculations generally corresponded to the concentrations of the measured parameters in the water column, bottom sediments, and pore waters (points in Fig. 5).

Two numerical experiments were conducted to assess the effects of changes in the OM entering the bay for the distribution of hydrochemical characteristics in the water area of the bay. The first experiment assumed an increase in the OM concentration by a factor of two compared to the concentration observed in the water area of the bay. It was established that the seasonal course of biogeochemical processes was disturbed (Fig. 7). An increase in OM inflow can result from an increase in the impact of stormwater and emergency discharges of wastewater entering the water area of the bay (see Fig. 1).

A sharp increase in the amount of OM (DOML, DOMR) activates the process of oxygen consumption for its oxidation and disrupts the seasonal course of oxygen. If OM excessive supply of occurs in February, then in June suboxic conditions are formed in the bottom water layer (the oxygen concentration decreases up to 12 μM) [42], and in August such conditions also arise in the water column. In September, hydrogen sulfide appears in the upper layer of sediments, and conditions in the bottom layer of waters change to anaerobic ones. The return to the original conditions of the bay ecosystem is slow and lasts for several months.

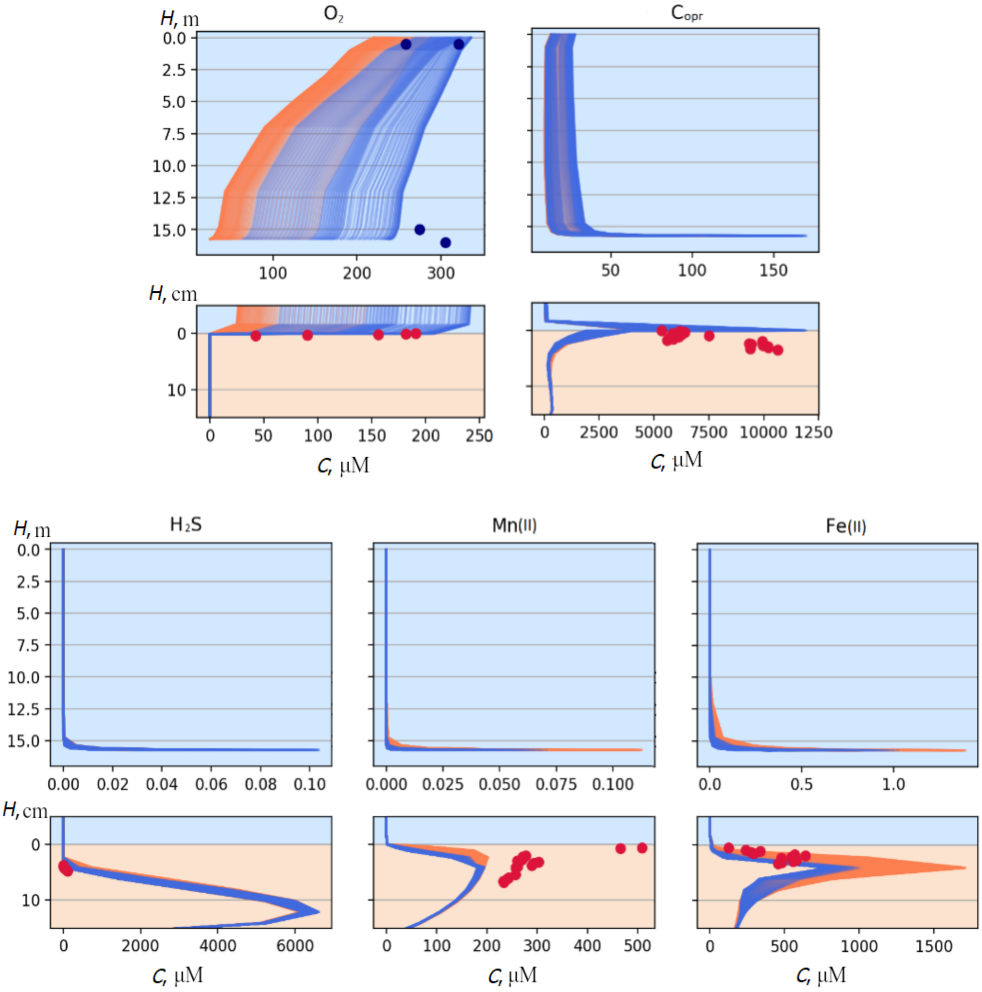


Fig. 5. Calculated seasonal changes of vertical profiles of the concentration of dissolved oxygen (O_2), organic carbon (C_{org}), hydrogen sulfide (H_2S), reduced iron (Fe(II)), reduced manganese (Mn(II)) and data from *in situ* observations in the water column (upper panels) and in the bottom layer of waters and bottom sediments (lower panels). The orange and blue lines are simulated warm and cold seasons, red and blue dots are *in situ* data in warm and cold seasons

For the second numerical experiment, the OM concentration was reduced by a factor of two compared to the observed concentration in the bay (Fig. 8).

It was found that with a decrease in the load on the bay, the seasonal course of biogeochemical parameters was preserved. The intensity of phytoplankton blooms decreases, and the period of blooms stretches out from March to October. When oxygen is consumed for OM oxidation, suboxic conditions do not arise either in the bottom water layer or in the water column. The minimum oxygen

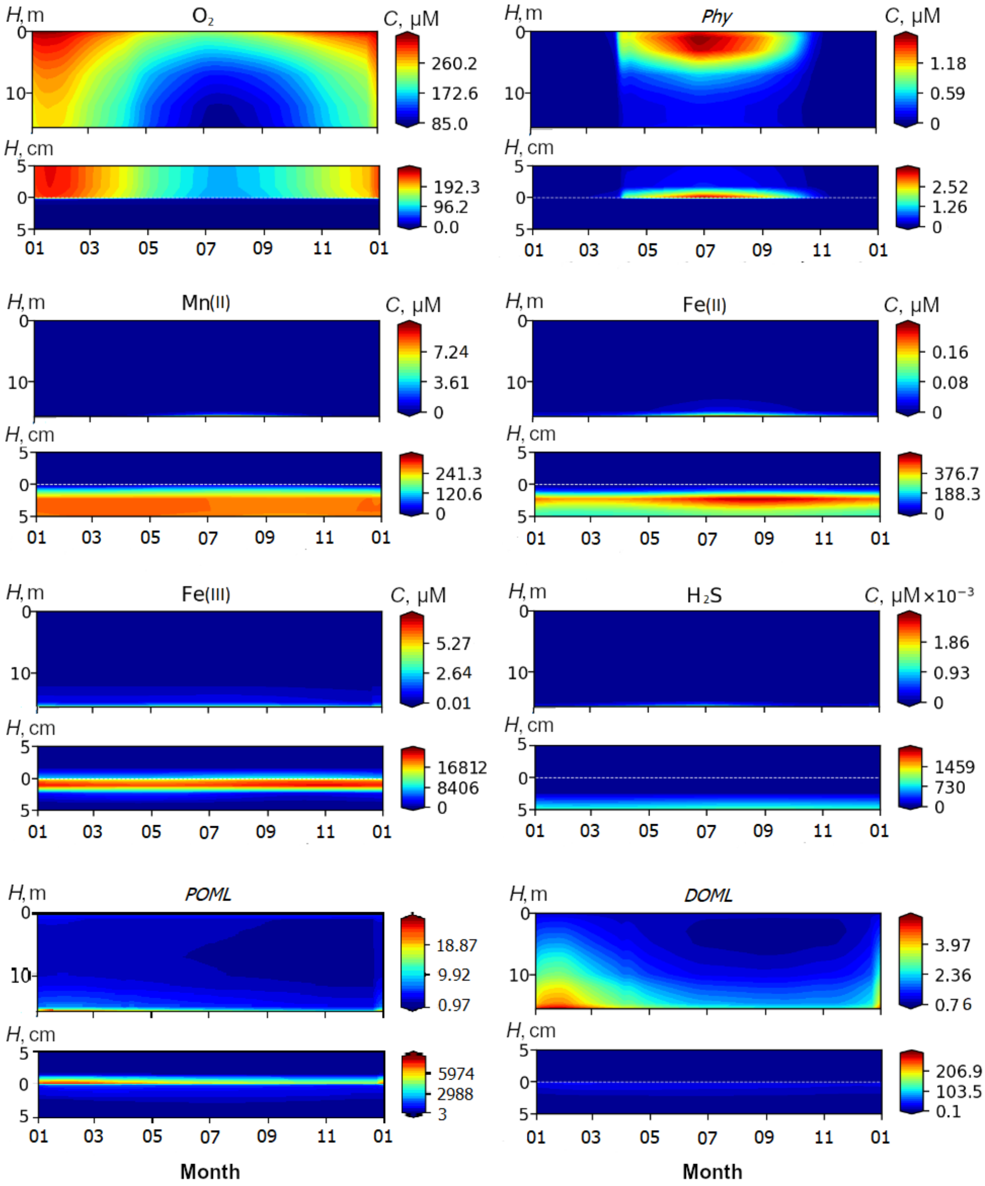


Fig. 6. The results of numerical calculations of seasonal dynamics of the BROM model variables in the water column (upper panels) and in the bottom layer of waters and bottom sediments (lower panels) when adapting the model to the waters of Yuzhnaya Bay. *Phy* – phytoplankton

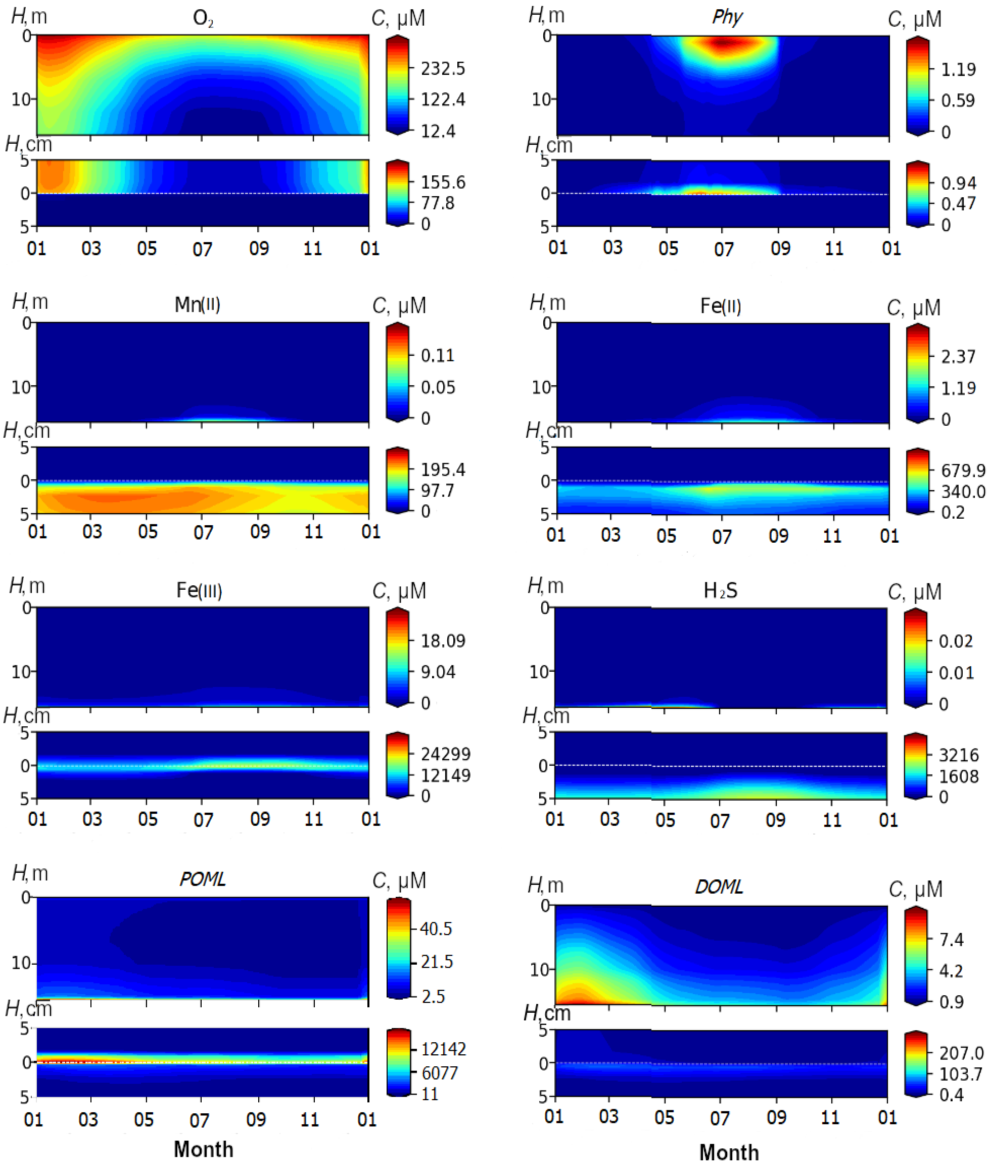


Fig 7. The results of numerical calculations of seasonal dynamics of the BROM model variables in the water column (upper panels) and in the bottom layer of water and bottom sediments (lower panels) with an increase in the content of organic matter. *Phy* – phytoplankton

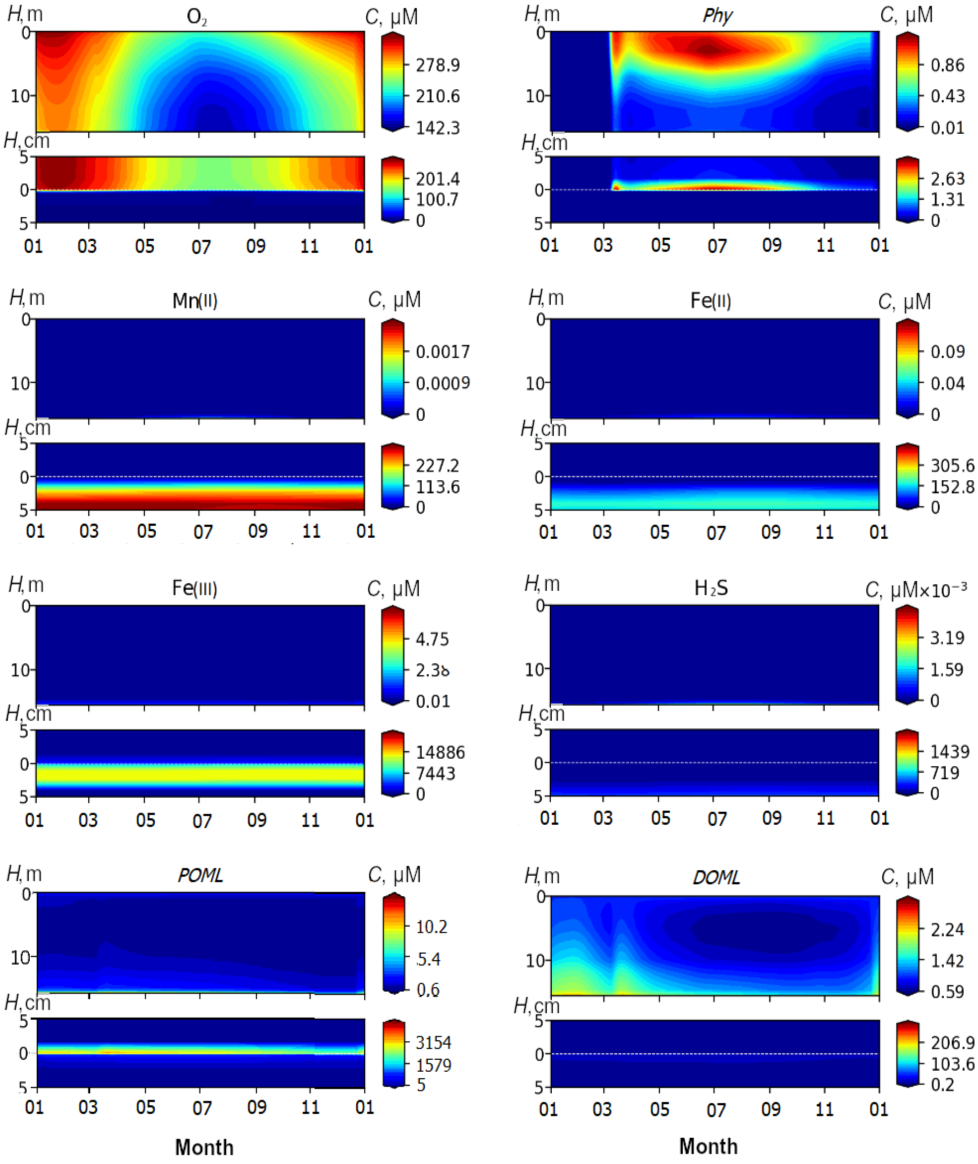


Fig. 8. Results of numerical calculations of seasonal dynamics of variables of the BROM model in the water column (upper panels) and in the bottom layer of waters and bottom sediments (lower panels) with a decrease in the content of organic matter. *Phy* – phytoplankton

concentration (142 μM) in the bottom water layer, which corresponds to aerobic conditions, is observed in July. However, in bottom sediments, despite the presence of oxygen in the bottom water layer, suboxic conditions are fixed, and this fact confirms the presence of reduced forms of iron and manganese in pore waters.

Conclusion

Based on observations and modelling, it is shown that the redox conditions in bottom sediments depend mostly on seasonal changes in the oxygen content in the bottom water layer, the particle size distribution of sediments, and the OM entering them. At the same time, bottom sediments, being a source of secondary water pollution, can also determine the hydrochemical characteristics and redox conditions in the bottom water layer.

It is shown that the BROM model used in the work to assess the redox conditions in the bottom sediments and the near-bottom water layer of Yuzhnaya Bay reproduces the seasonal course of hydrochemical parameters properly. The modelled increase in the load (a doubling of the OM concentration) on the bay water area leads to the OM accumulation and decrease in the oxygen concentration (up to 12 μM), as well as to the seasonal oxygen cycle violation in the bottom water layer. The results of numerical experiments showed that if the OM average annual concentration on the surface increased from 107 to 195 μM, anaerobic conditions developed in the bottom water layer.

The change in the load on the bay water area, which consisted in a twofold decrease in the OM entering the bay, contributed to the fact that the oxygen concentration did not fall below 142 μM throughout the year, and aerobic conditions were preserved in the water column and bottom water layer. However, such a load reduction is not sufficient for bottom sediments. Taking into account the level of accumulated pollutants determined by high concentrations of organic carbon in the surface layer of sediments (> 4 %), the oxygen is still insufficient for OM oxidation, and reduced forms of iron and manganese are still formed in the pore waters, which indicates the development of suboxic conditions in bottom sediments.

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About the authors:

Yulia S. Gurova, Junior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), **ORCID ID: 0000-0002-9826-4789**, **ResearcherID: AAB-5628-2019,** *kurinnaya-jul@yandex.ru*

Evgeniy V. Yakushev, Chief Research Associate, Shirshov Institute of Oceanology RAS (36 Nahimovskiy Ave., Moscow, 117997, Russian Federation), Dr.Sci. (Phys-Math.), **ORCID ID: 00000-0001-5008-9611**, **ResearcherID: M-5470-2019**, *evgeniy.yakushev@gmail.com*

Anfisa V. Berezina, Leading Engineer, Shirshov Institute of Oceanology RAS (36 Nahimovskiy Ave., Moscow, 117997, Russian Federation), **ORCID: 0000-0001-9356-8807**, **ResearcherID: AAK-7150-2021**,*fisa4247@gmail.com*

Matvey O. Novikov, Engineer, Shirshov Institute of Oceanology RAS (36 Nahimovskiy Ave., Moscow, 117997, Russian Federation), **ORCID ID: 0000-0003-3124-3702**, **ResearcherID: AGP-2782-2022**, *novikov.mo@ocean.ru*

Konstantin I. Gurov,Junior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), **ORCID ID: 0000-0003-3460-9650, ResearcherID: L-7895-2017**, *gurovki@gmail.com*

Natalia A. Orekhova, Head of Marine Biogeochemistry Department, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), Ph.D. (Geogr.), **ORCID ID: 0000-0002-1387-970X, ResearcherID: I-1755-2017**, *natalia.orekhova@mhi-ras.ru*

Contribution of the authors:

Yulia S. Gurova – problem statement, analysis of calculation results, article text and graphic material preparation

Evgeniy V. Yakushev – mathematical model development, performance of calculations, discussion of results, critical analysis and revision of the text

Anfisa V. Berezina – performance of calculations, graphic material preparation

Matvey O. Novikov – correction of the mathematical model

Konstantin I. Gurov – sampling, analysis of geochemical characteristics of bottom sediments, article text and graphic material preparation

Natalia A. Orekhova – analysis of pore water chemical composition, critical analysis and revision of the text

All the authors have read and approved the final manuscript.