

MARINE
CHEMISTRY

The Influence of Geochemical Processes in the Near-Bottom Layer on the Hydrochemical Characteristics of the Waters of the Sea of Japan

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Abstract—According to the results of the international expedition aboard the R/Vs *Roger Revelle* and *Professor Khromov* in the summer 1999, areas with low oxygen contents (below 210 $\mu\text{M}/\text{kg}$) and those with increased contents of dissolved inorganic carbon and phosphates were found that roughly coincided with one another. These areas are located near the bottom on the southwestern slope of the Tsushima Basin in the region of the Korea Strait and on the continental slope in the region of the Tatar Strait in the northern part of the sea at about 46° N. The set of hydrochemical data points to a high geochemical activity in the near-bottom layer of the areas noted. This activity is confirmed by direct observations of the composition of the interstitial water in the sediments collected in the northern part of the sea during the expedition of R/V *Akademik M.A. Lavrent'ev* in 2003. It was supposed that the main cause of the increased geochemical activity is the runoff of suspended and dissolved matter from the Korea and Tatar straits. In the areas mentioned, the near-bottom waters are characterized by low values of the nitrogen–phosphorus ratio (below 10), which is geochemical proof of the denitrification process occurring under the conditions of high oxygen concentrations characteristic of the Sea of Japan. Based on the value of the annual production in the Sea of Japan, a rate of denitrification equal to 3.4×10^{12} gN/year was calculated. Hence, it is confirmed that the geochemical processes in the near-bottom layer have a direct influence on the spatiotemporal characteristics of the hydrochemical properties of the waters of the Sea of Japan.

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INTRODUCTION

The hydrochemical characteristics of the water masses in the Sea of Japan and their spatiotemporal variations were widely discussed in publications [3–6, 10–12, 20–23, 29, 40]. These reports noted some specific features of the hydrochemical conditions in the sea. Because of the shallow-water straits connecting the Sea of Japan with the neighboring basins (the East China Sea, the Sea of Okhotsk, and the Pacific Ocean), the waters deeper than 150 m are formed in the Sea of Japan proper. The features of the water mass formation and circulation result in the fact that the concentrations of the principal nutrients (nitrogen, phosphorus, silicon), total dissolved inorganic carbon (DIC), and alkalinity (TA) are considerably lower, while the concentrations of oxygen and freons are higher in the water of the Sea of Japan than those in the Sea of Okhotsk and the Pacific Ocean at the same depths. This difference is related to the high intensity of the vertical and horizontal water mixing in the Sea of Japan. Another important feature of the Sea of Japan consists of the pronounced interannual variability of the hydrochemical properties of the waters and, particularly, of the eutrophication trend mentioned, i.e., of the increase in the nutrient con-

centrations and decrease in the oxygen content [5, 12, 17, 18, 24, 28, 30]. The third feature is that the waters of the Sea of Japan are characterized by decreased values of the nitrogen–phosphorus ratio, which allows one to suppose a denitrification process in the waters of the Sea of Japan occurring under conditions of relatively high oxygen concentrations [35, 42].

According to the results of the expeditions of 1999 aboard the R/Vs *Roger Revelle* and *Professor Khromov*, several local sites of decreased oxygen content in the near-bottom layer were found [31, 32, 35, 40]. This study shows that the areas of decreased oxygen content are characterized by a high hydrochemical activity. In these areas, increased contents of phosphates and the normalized dissolved inorganic carbon ($\text{NDIC} = \text{DIC} \cdot 35/\text{S}$) and elevated partial pressures of carbon dioxide (pCO_2) are observed, and these are the centers of denitrification. The latter means that, at these sites, the nitrate nitrogen is transformed into inactive forms capable of escaping to the atmosphere (N_2 and N_2O).

Thus, the geochemical activity at the seawater–sediment interface allows us to look afresh on the mechanisms of the spatiotemporal variability of the hydrochemical properties of the waters of the Sea of Japan.

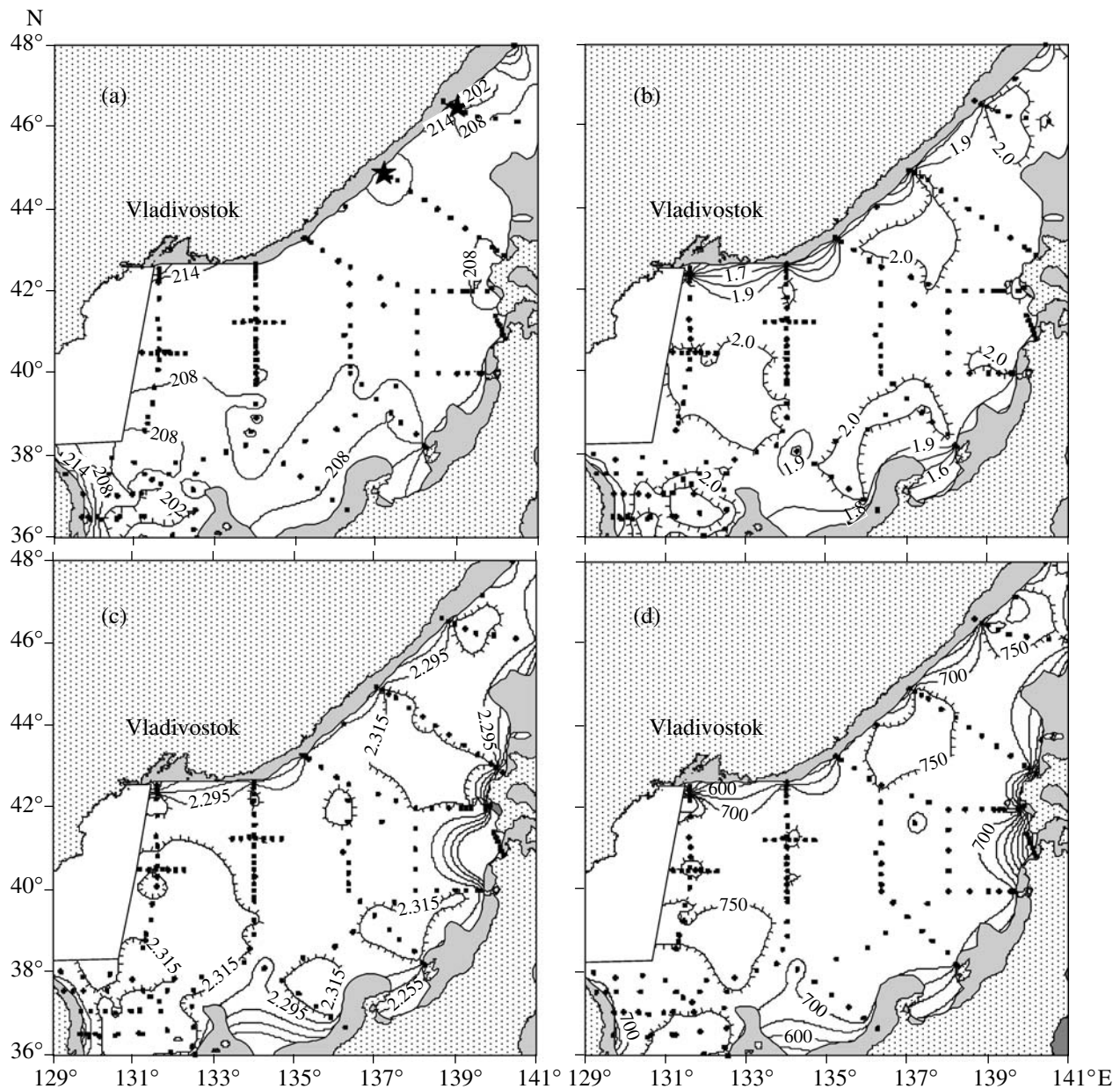


Fig. 1. Distribution of the hydrochemical parameters in the Sea of Japan in the summer of 1999: (a) oxygen in the layer of the minimum, (b) phosphates in the layer of the maximum, (c) normalized total inorganic carbon in the layer of the maximum, and (d) carbon dioxide partial pressure in the layer of the maximum. The asterisk shows the locations of sampling of bottom sediments (a). The areas shallower than 500 m are shaded.

THE DATA

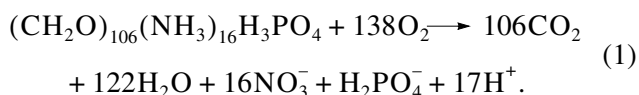
In the summer of 1999, in the Sea of Japan, aboard the R/Vs *Roger Revelle* and *Professor Khromov*, extensive hydrochemical surveys were performed including measurements of the salinity; pH values; and concentrations of oxygen, freons, nitrites, nitrates, silicates, phosphates, and alkalinity. The sampling for hydrochemical tests was accompanied by hydrological exploration using the standard physical parameters (conductivity, temperature, pressure, and turbidity).

The surveys were performed uniformly over the entire aquatic area of the Sea of Japan excluding the region neighboring North Korea. Using the pH and alkalinity values, the partial pressure of carbon dioxide in the seawater and the content of dissolved inorganic carbon were calculated. The dissociation constants for carbonic acid were taken from [7]. A detailed description of the measurement procedures, including the maps and sections for both the physical and chemical properties of the water masses according to the results of these expeditions, was published in [37].

This study also used the results of chemical analyses of interstitial waters from the sediments sampled on the continental slope at one of the sites of low oxygen content in the near-bottom layer (46° N) as well as at the background station about 45° N (Fig. 1a). The sediments were collected in October 2003 during cruise 32 of R/V *Akademik M.A. Lavrent'ev*. The interstitial water was analyzed for dissolved calcium, magnesium, total alkalinity, chlorides, and sulfates; measurements of the pH values in the sediments were made as well. Detailed procedures of the chemical tests of the interstitial water from the sediments were presented in [41].

RESULTS AND DISCUSSION

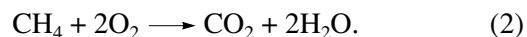
Oxygen is not only a key biochemical parameter but it is also used for the classification of water masses [25, 33] and as an indicator of physical processes in the ocean, e.g., of the aeration of deep and near-bottom waters [27, 36], and of the climatic variability of the ocean [12, 24, 28, 30]. Therefore, knowledge of both the mechanisms of water saturation with oxygen and of the processes of oxygen utilization is of importance. The vertical decrease in the oxygen concentration with depth is caused by the aerobic oxidation of organic matter proceeding due to the vital activity of bacteria; this may be presented by the following scheme:



In Eq. 1, the Redfield stoichiometry for organic matter was used. However, the decrease in the oxygen concentration with depth is not uniform over the sea. When drawing the maps and cross-sections of the oxygen distribution according to the results of the international expedition of 1999, areas of decreased oxygen content were found [4, 31, 32, 35, 40]. A detailed description of the sites of the oxygen minimum is given in [31, 35]. The most pronounced are two sites of decreased oxygen content (below 210 $\mu\text{M}/\text{kg}$): one is located at the southwestern slope of the Tsushima Basin and the other is on the continental slope in the northern part of the sea at about 46° N (Fig. 1a). The areas of minimum oxygen content are located in the near-bottom layer. This is well seen from the distribution of oxygen in the meridional section across the Sea of Japan from Vladivostok to the Korea Strait (Fig. 2a) and in the latitudinal section in the northern part of the sea at about 46° N (Fig. 2c). Moreover, the existence of the minima is independent of the season [4, 31, 40]. Because the minimum concentrations of oxygen are found in the near-bottom layer, they are evidently caused by the geochemical processes at the seawater–bottom sediment interface [4, 31, 35, 40]. However, the reason for their location is still unknown. One of the hypotheses of the potential cause consists in the fact that gas hydrates are found at these sites [4, 35, 40]. Their partial decomposition causes a methane gas flow from the sediment

mass up to the water–sediment interface. This flow entrains reduced substances (products of the diagenesis). At the water–sediment interface, the bacterial oxidation of reduced matter proceeds, thus, resulting in a decrease in the oxygen concentration. At that, the concentration of dissolved inorganic carbon (DIC) must be increased to cause the growth of the carbon dioxide partial pressure (pCO_2). In fact, the maps of the distribution of the maximum DIC contents (Fig. 1c) and of those of the pCO_2 values (Fig. 1d) showed patterns generally similar to the distribution of the minimum oxygen concentrations.

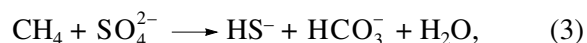
The formal equation of the reaction of the methane bacterial oxidation by dissolved oxygen is very simple:



From Eq. (2) it follows that the oxidation of methane by dissolved oxygen causes an increase in the DIC and pCO_2 values. Meanwhile, this process does not affect the alkalinity and nutrient concentrations (excluding their utilization and production by the vital activity of microorganisms). Indeed, when drawing maps of the distribution of the maximum concentrations for the sum of nitrates and nitrites ($\text{NO}_3^- + \text{NO}_2^-$), silicates, phosphates, and the total alkalinity, no correlations were found between the distributions of the alkalinity, silicates, and the sum of nitrates and nitrites, on the one hand, and the oxygen minimum, on the other. This result provides an argument in favor of the gas hydrate hypothesis of the cause of the location of the oxygen minima. Moreover, publications present independent geological and geophysical data on the prospects of gas hydrate existence in the areas of the Tatar [1] and Korea straits [19].

During cruise 32 of R/V *Akademik M.A. Lavrent'ev*, an attempt at a direct discovery of gas hydrates at the continental slope in the northwestern part of the Sea of Japan was made. To do so, two cores of the bottom sediments were collected: one in the area of the oxygen minimum (station 33, 46°28.808' N, 139°0.294' E) and the other (background) 230 km to the southwest (station 38, 44°52.611' N, 137°10.388' E) (Fig. 1a). However, the results showed that both of the cores of gray (reduced) sediments contained no gas hydrates.

We carried out chemical analyses of the interstitial water in the samples collected; the results are presented in Fig. 3. The data point to an intense process of early diagenesis in both of the cores, which is exhibited in the sulfate reduction (the decrease in the sulfate ion concentration and the alkalinity increase) and in the decrease in the calcium and magnesium concentrations over the cores. The diagenesis in the sediments may proceed both under the influence of the methane leaked through the sediment mass and as a result of the bacterial decomposition of the organic matter in the sediment [9, 16]:



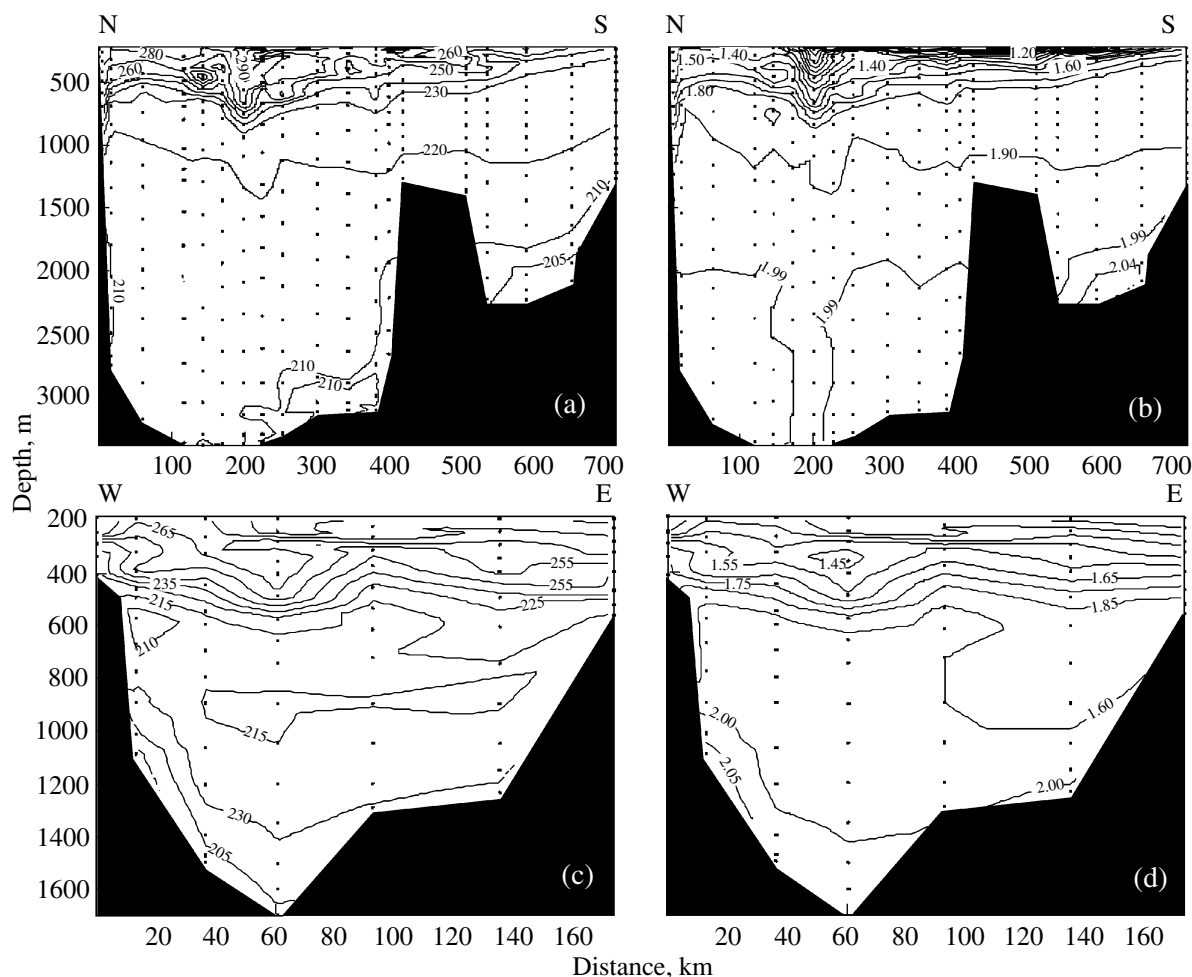
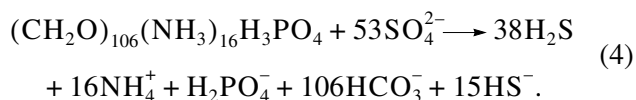


Fig. 2. Distributions of (a, c) oxygen and (b, d) inorganic phosphorus in the Sea of Japan (a, b) over the meridional section in the eastern part at $\sim 131^{\circ} 30' E$ and (c, d) over the latitudinal section in the northern part of the sea at $\sim 46^{\circ} N$ in the summer of 1999.



Because an increase in the phosphate concentrations was found at the sites of a local oxygen decrease (Figs. 1a, 2b, 2d), this allows one to suppose that, in the sediments treated, the diagenesis of organic matter takes place (Eq. 4). This assumption was also advanced earlier [30, 35], being confirmed by the results of [2], which showed that the sediments on the continental slope of the Sea of Japan are enriched with organic carbon to concentrations as high as 1.5–2%. However, sediments enriched with organic carbon are abundant throughout the entire perimeter of the sea. Therefore, an assumption was additionally made about the correlation of the sites of the oxygen minima with the areas of intense slope currents. At these sites, the sediments enriched in organic carbon are roiled, which results in a more rapid oxidation of the organic matter contained in the sediments and in a corresponding decrease in the oxygen concentration [18, 34, 35]. However, the results

of the turbidity measurements show that the roiling of the bottom sediments takes place at many stations and no direct correlation is found between the decrease in the oxygen concentration and the increase in the turbidity.

Below, we propose another way to explain the hydrochemical anomalies in the near-bottom layer that follows from the mechanism of denitrification in coastal marine basins characterized by high oxygen concentrations.

Due to the high concentration of dissolved oxygen, reaction (1) is dominant over the entire water mass of the Sea of Japan. This is confirmed by the increase in the organic matter oxidation products (nitrates, phosphates, silicates, and DIC) with depth. However, in the areas of local oxygen minima, an increase of phosphates but not of nitrates is observed. This allows one to suppose that, at these sites, a denitrification process takes place. From the most general considerations, the denitrification proceeds within the boundary area between the oxic and anoxic conditions of the environment [15]. Evidently, this area may be formed at the

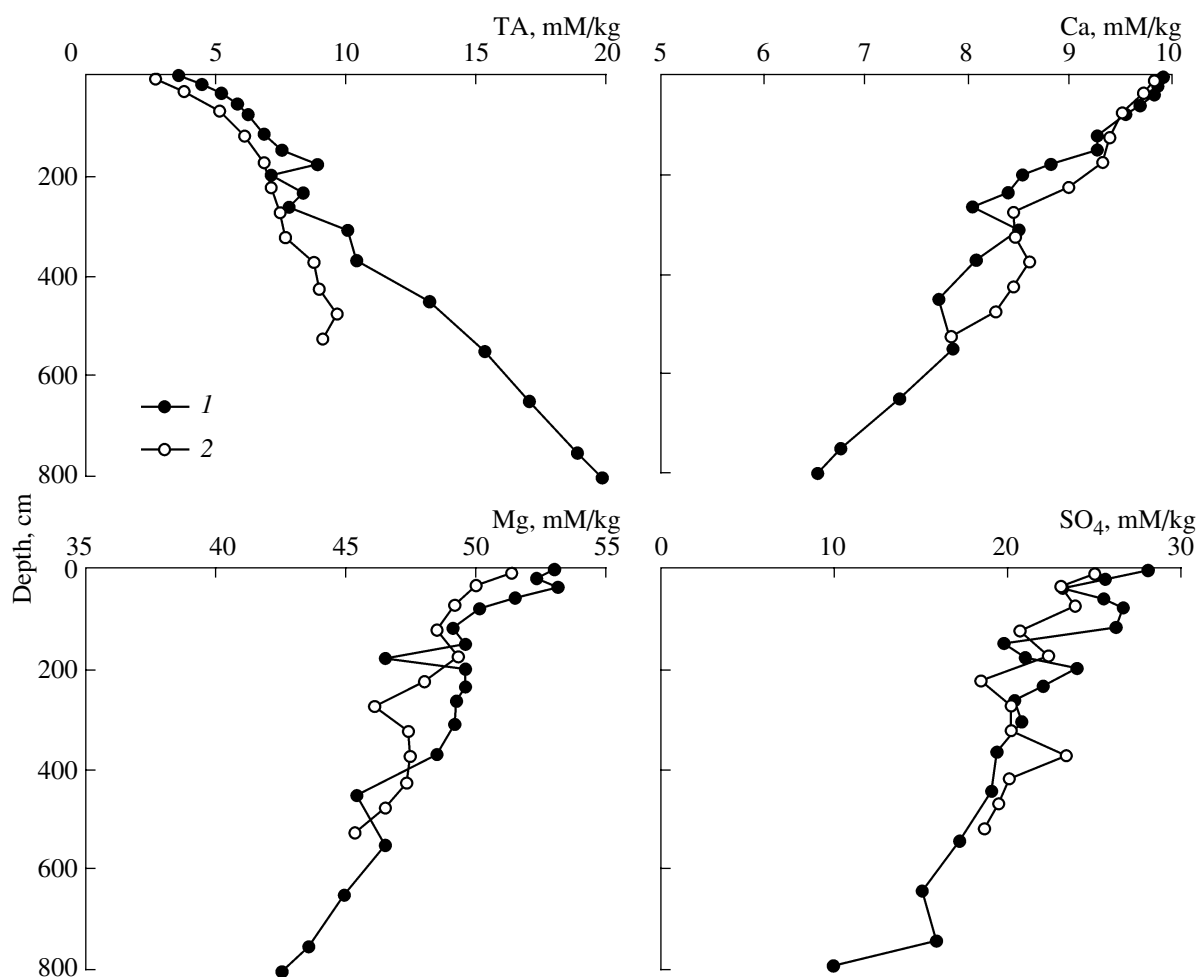
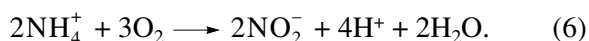
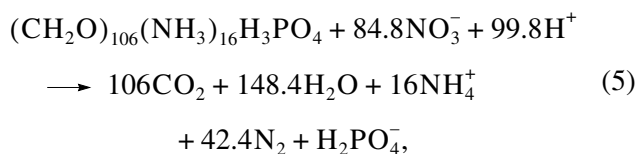
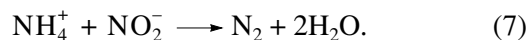


Fig. 3. Alkalinity (TA), dissolved calcium (Ca), dissolved magnesium (Mg), and sulfates (SO_4^{2-}) in the sediments of the Sea of Japan (1—station 33, $46^\circ 28.808' \text{ N}$, $139^\circ 0.294' \text{ E}$; 2—station 38, $44^\circ 52.611' \text{ N}$, $137^\circ 10.388' \text{ E}$).

water–sediment interface if the sediment is enriched with organic matter. In fact, in this kind of boundary area, two opposite processes take place: (a) the flux of the oxidized form of nitrogen (nitrite) is directed to a reduced environment, where it is reduced to molecular nitrogen (denitrification) by taking part in the oxidation of organic matter, and (b) the flux of the reduced form of nitrogen (ammonium) from the sediment is directed to an oxidized environment, where it should be oxidized into nitrite (nitrification) or into nitrate under favorable conditions [14–16]. Schematically, these processes may be presented as follows [16]:



The product of the denitrification reactions (5) is molecular nitrogen, which may finally leave the marine environment and enter the atmosphere. The reaction of nitrification (6) proceeds by means of nitrifying bacteria and may cause an increase not only in nitrite but also in nitrate ions due to the further process of oxidation with bacteria. Indeed, traces of nitrite ion were found in the near-bottom layer on the southwestern slope of the Tsushima Basin [35]. Nitrite is an intermediate product of the metabolism of bacteria, which themselves utilize it for their vital activity; therefore, nitrite cannot be accumulated in significant amounts. It was recently found that the anaerobic oxidation of ammonium by nitrite ion may take place in the upper layers of the sediments, which, along with the reaction of denitrification (5), also produces molecular nitrogen [38, 39]:



Although reactions (5) and (7) are substantially and formally different, they both lead to the inactive molecular form of nitrogen; therefore, in the text below, they will

be combined under the common term denitrification. The significance of the denitrification process for the waters of the Sea of Japan may be seen from the tangent of the inclination angle of the simple relationship between the sum of nitrates and nitrites and the concentration of phosphates over the entire water mass. From Fig. 4 it follows that the inclination angle is equal to 12.65. This value is less than the Redfield value ($N : P = 16$). Because, for the Sea of Japan, the nitrogen to phosphorus ratio in the organic matter is equal to 16.6 [42], the value obtained for the ratio of the inorganic forms of nitrogen and phosphorus (12.65) clearly points to the formation of molecular nitrogen, which may be caused by reactions (5) and (7). In Fig. 4, two areas may be distinguished where the increase in the phosphate concentration is not accompanied by a corresponding growth in the sum of nitrates and nitrites. These are the initial part with a wide scattering of points corresponding to the euphotic layer and the short final segment related to the near-bottom layers. In this study, we are interested in the latter part, i.e., in the near-bottom layers. To ascertain the areas of denitrification, empirical equations of the dependence of the sum of the nitrate and nitrite concentrations on the concentration of phosphorus were calculated for each of the stations:

$$[N] = a_i + b_i[P] + c_i[P]^2, \quad (8)$$

where a_i , b_i , and c_i are the empirical coefficients for station i . To obtain the empirical relationships, the layers from a depth of 200 m to the bottom were used (the results for the upper 200 m were ignored). From relationships (8), nitrogen–phosphorus ratios were obtained:

$$d[N]/d[P] = b_i + 2c_i[P]. \quad (9)$$

At each of the stations, for the layers below 200 m, the nitrogen–phosphorus ratios were calculated using empirical relations (9). The distribution of these ratios in the near-bottom layers points to two areas of intense denitrification generally coinciding with those of the oxygen minimum (Fig. 5). One of these areas is the southwestern part of the Tsushima Basin; the other is the region neighboring the Tatar Strait. Figure 6 presents the distribution of the nitrogen–phosphorus ratio over the meridional section from Vladivostok to the Korea Strait and over the latitudinal section in the northern part of the sea from the continental slope to the La Perouse Strait. The areas of low $N : P$ ratios in the sections confirm the process of intense denitrification in the near-bottom layer on the slope near the Korea Strait and at the continental slope about $46^\circ N$.

We suppose that the distribution maps of the concentrations of oxygen and dissolved inorganic carbon, the carbon dioxide partial pressure, the phosphates, and the nitrogen–phosphorus ratios presented in Figs. 1, 2, and 4–6 give additional geochemical evidence for the denitrification process in the Sea of Japan. The classical notion of denitrification proceeding at the water–sediment interface is always associated with high rates of sediment fluxes of organic and mineral matter [15]

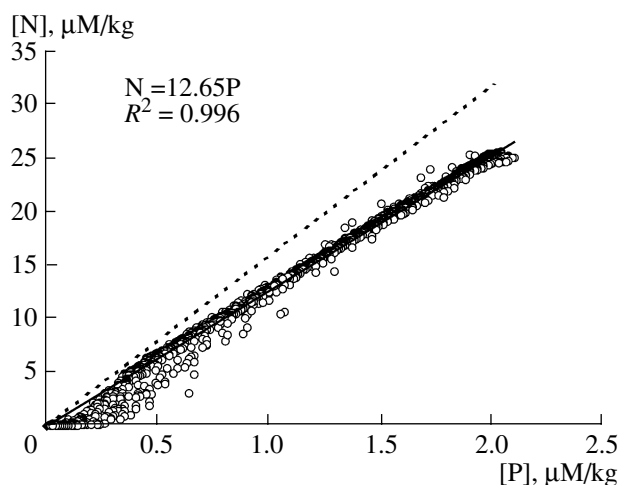


Fig. 4. Correlations between the concentrations of organic forms of dissolved nitrogen ($[NO_3^-] + [NO_2^-]$) and phosphorus for the waters of the Sea of Japan in the summer of 1999. The dotted line shows Redfield's value of the nitrogen to phosphorus ratio ($[N] : [P] = 16 : 1$).

causing a pronounced decrease in the oxygen content (concentrations of <0.1 ml/l) [14]. At oxygen concentrations that low, bacteria begin to use nitrate ions instead of dissolved oxygen as electron acceptors, thus, producing molecular nitrogen. The activity of bacteria results in denitrification. A significant role in this process is played by heavy metals, primarily iron and manganese, the presence of which increases the activity of bacteria [26]. This type of denitrification is characteristic of near-shore areas subjected to the influence of rivers supplying not only great amounts of terrigenous suspended organic matter but also mineral particles containing heavy metals. These areas are also characterized by extremely high productivity.

Evidently, the bulk of the auto- and allochthonous organic matter of the Sea of Japan is mineralized according to schemes (5) and (7). At present, one cannot say for certain that the increased value of the $N : P$ ratio for the entire water mass of the sea is caused exclusively by the denitrification in the near-bottom layer. As noted above, the initial segment in Fig. 4 is characterized by low $N : P$ ratios (about 3), but this cannot be explained by denitrification, because it refers to the upper layer of the sea with a high oxygen content. The nature and intensity of the processes causing the decrease in the $N : P$ ratio in the upper layer of the sea require further studies.

The areas neighboring the Korea and Tatar straits belong to the most productive regions of the Sea of Japan. Here, increased contents of suspended and dissolved organic matter are registered, which are supplied, respectively, from the East China Sea subjected to the Yangtze River runoff and from the Tatar Strait also affected by an intense continental runoff including the Amur River waters. According to the estimations of

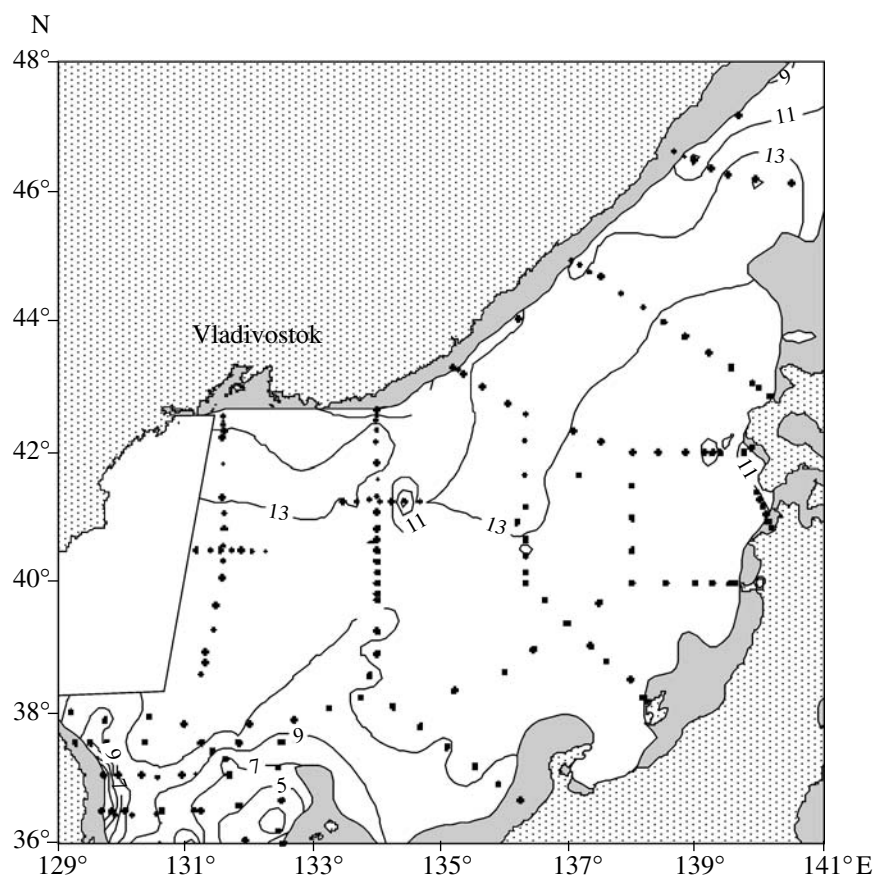


Fig. 5. Distribution of the nitrogen–phosphorus ratio in the near-bottom water layer of the Sea of Japan in the summer 1999. The areas shallower than 500 m are shaded.

[2], the total amount of the suspended matter supplied to the Sea of Japan via the Korea Strait and the Strait of Nevelskoy is equal to 18 and 0.1–0.2 million tons per year, including more than 60% of the organic form. The riverine runoff provides an additional amount of allochthonous organic matter.

A rough estimation of the nitrogen amount removed annually from the biogeochemical cycle due to denitrification may be made from the mass balance of organic matter. Assuming the stationary state of the system, i.e., the case when the fluxes of the organic matter primary production (PP) and organic matter import (F_i), including the terrigenous component, riverine runoff, and the supply from the straits, are balanced by the expenditure components F_m (mineralization of organic matter), F_d (accumulation in the sediment), and F_e (export to neighboring basins), we obtain the relationship

$$PP + F_i = F_m + F_d + F_e. \quad (10)$$

The most important terms in Eq. 10 are the primary production and the organic matter mineralization. For example, the burial of organic matter in the sediment amounts to 0.4–1.5% and the allochthonous runoff of organic matter into the Sea of Japan is below 5% of the total production [2]. Meanwhile, the uncertainty in the

estimation of the main flux (annual production of the Sea of Japan) is considerably higher [8]. Therefore, it was assumed that $PP \approx F_m$, the organic matter synthesized conforms to the Redfield formula, and the N : P ratio for the mineral forms equals 12.65. The annual flux of denitrification for the Sea of Japan amounts to 3.4×10^{12} gN/year assuming that the annual production is equal to 260 million t of dry mass per year [2]. Evidently, the nitrogen removed from the biogeochemical cycle is returned to the environment with riverine and terrigenous runoffs, as well as due to the activity of nitrogen-fixing bacteria.

The set of hydrochemical data allows us to conclude that the sites of local natural minima of oxygen are associated with denitrification. We ascribed the location of these sites to the additional flux of organic matter and heavy metals. This additional flux may be provided by intense continental runoff.

In [5], it is noted that, due to the features of the water circulation in the Sea of Japan, the hydrochemical properties, including the interannual variability, are caused, first of all, by the waters supplied from the East China Sea via the Korea Strait. These waters are not moved as transit masses across the Sea of Japan to the Pacific Ocean and the Sea of Okhotsk but participate in the for-

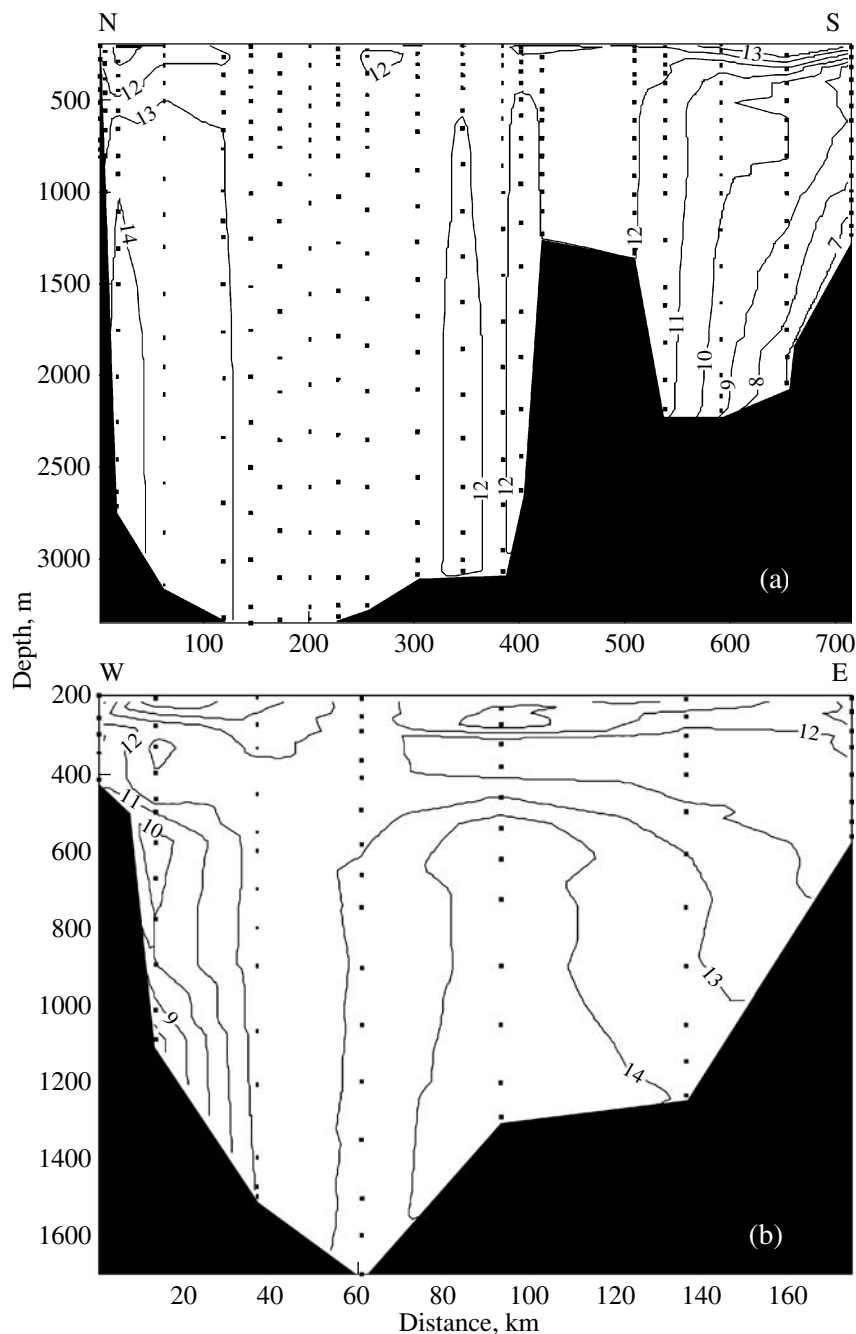


Fig. 6. Nitrogen–phosphorus ratio (a) over the meridional section in the eastern part of the sea at $\sim 131^{\circ}30'$ E and (b) over the latitudinal section in the northern part of the sea at $\sim 46^{\circ}$ N in the summer of 1999.

mation of deep waters in the Sea of Japan [42]. Since the waters of the East China Sea are now subjected to eutrophication [13], this must affect the waters of the Sea of Japan as well. The results of this study point to the fact that, besides the waters of the East China Sea, an important role in the variability of the hydrochemical properties of the waters in the Sea of Japan is played by the biogeochemical processes in the region of the Tatar Strait. We assume that the early diagenesis processes of organic forms of suspended matter in the

regions of the Korea and Tatar straits are responsible not only for the water denitrification in the Sea of Japan but also for the interannual variability of the oxygen content. The precipitation of suspended matter to depths of 1500–2000 m with the following diagenesis and spreading of the diagenesis products provides a direct affect on the spatiotemporal variations of the hydrochemical characteristics of the waters in the Sea of Japan.

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