MARINE CHEMISTRY

The Features of the Hydrochemical Regime in Ob Inlet during the Open Water Time

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Abstract—The hydrochemical features of Ob Inlet in the open-water time were characterized using the data of the surveys during two seasons of different water content. The inlet was subdivided into the "riverine," "marine," and intermediate areas being different in the factors determining their hydrochemical regime. The processes occurring in each of the distinguished areas were considered in detail. Special attention was paid to the hydrochemical features in the mixing area of the fresh and saline waters (the frontal zone) within the periods of the maximum and minimum biological activity in the aquatic area of Ob Inlet.

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INTRODUCTION

In 2010, two complex expeditions to the Ob Inlet were performed by the specialists of the Russian Federal Research Institute of Fisheries and Oceanography and the Shirshov Institute of Oceanology (VNIRO and IO RAS, respectively) [8]. The surveys were carried out from the deck of the leasehold push boat OTA-777 and covered the most part of the aquatic area of Ob Inlet from Cape Parusnyi at 68°21' N to the seaward end of the bay at 72°40' N. The performed studies had no parallel in the number of traced parameters and in the thoroughness of the surveys of the aquatic area of Ob Inlet (120 integrated stations and 22 additional ones for hydrological probing only). The small draught of the vessel allowed us to go beyond the surveys along the fairway and to research in detail the entire aquatic area including its coastal shallow-water parts, unlike previous integrated expeditions [9, 17]. These surveys were different from numerous marine and coastalmarine expeditions [3, 4, 12, 18, 19] in the large coverage of the bay aquatic area and in the very wide variety of the determined parameters. Moreover, most of the previous surveys were carried out in August and September, when this region was available for the passage of R/Vs from the direction of the Kara Sea. The small dimensions of the vessel and its basing at the Labytnangi port allowed us to carry out the surveys just following the ice floating immediately after the bay's clearing of ice during the high-water time (July 29 to August 17, 2010) and just before the beginning of freeze up (September 18 to October 7, 2010).

THE METHODS OF THE STUDIES

At each of the integrated stations, the water samples were collected using Van Dorn 5-L bottle samplers to determine the contents of the dissolved oxygen, the silicon, the mineral phosphorus, the nitrates, the nitrite and ammonium nitrogen, the organic forms of nitrogen and phosphorus, the values of the pH and the total titratable alkalinity (Alk), and the iron content. The sampling was carried out from two more layers depending on the vertical structure of the waters. The water samples were processed to obtain all the considered hydrochemical parameters in the onboard laboratory according to the standard procedures [15, 16] immediately after the collecting at the stations.

The water-dissolved oxygen was determined by titration using Winkler's procedure modified by Chernyakova [16]. The nutrients (the nitrate, the nitrite, and the total and ammonium nitrogen; the total and mineral phosphorus; and the silicon) were determined by means of colorimetry using the standard procedures [15, 16]. To determine the iron content, we used Stocky's ferrozine technique modified by Rozanov [14]. The Alk values were measured by the direct titration procedure modified by Bruevich with the visual indication of the titration endpoint. The pH values were measured by potentiometry in the units of the NBS practice scale. In view of the high content of the particulate matter in the waters of Ob Inlet, the measurements included corrections for the turbidity and coloration of the waters [15]. The components of the carbonate system (the total dissolved organic carbon, the carbonate and bicarbonate ions, and the dissolved carbon dioxide) were calculated using the pH-Alk procedure [20]. The mineralization of the water was determined by the conductivity using a probe.

Evidently, the obtained value characterized rather the relative variations rather than the absolute content of salts in the water.

RESULTS

The hydrological and hydrochemical characteristics of Ob Inlet were considerably different during the first and second surveys. Pronounced variations were also observed along the bay. We had supposed to subdivide the Ob Inlet into two large areas in view of their hydrological and hydrochemical parameters [5, 6, 7], the boundary between these areas is quite mobile and depends on the season and on the runoff volume:

—the "riverine" area (to $71^{\circ}20'$ N during the open-water period in 2010) with no contact with the saline seawaters, in which the processes are determined by the riverine runoff;

—the "marine" area (to the north from 72° N), i.e., a part of the mixing (frontal) zone of the saline waters from the Kara Sea and the freshwater riverine runoff being limited from the south by the mineralization value of 0.5 g/L.

Between the two areas, the intermediate zone is located, which is subjected to periodic impacts from the frontal zone (by wind-induced pile ups and tides). The mineralization value here is higher than in the riverine and lower than in the marine area and varies within 0.1-0.5 g/L.

In turn, the riverine area may be subdivided into two parts up- and downstream of the confluence of the Ob and Taz inlets characterized by quite different hydrological and hydrochemical characteristics.

Hydrochemical characterization of the "riverine" part of Ob Inlet. The hydrochemical regime of the riverine part of Ob Inlet in the summer time are determined by the great volume of the runoff. The so-called streamy structure of the flow was much pronounced, in which individual water streams retained the peculiarities of their chemical composition for quite a long distance over the Inlet. With complete mixing from the bottom to the surface within each of the streams, the transverse mixing is minor. This effect is most pronounced in the expansion of the Taz River waters, which are traced along the eastern coast of the Inlet even to 71°30' N.

The Ob River waters in the southern part of the Inlet (before the confluence with the Taz River waters) were relatively warm $(11-15^{\circ}C)$. The content of dissolved oxygen (Figs. 1a, 1b) was pronouncedly low for this period (6.8–7.2 mL/L). The oxygen saturation amounted to 88–90% in both the surface and the bottom layers.

The Taz River waters inflowed to the Ob Inlet were cooler. The content of oxygen (from 7.4 to 7.7 mL/L) and the saturation degree (90–94%) were higher than those in the Ob River waters. To the north from the mixing zone of the Ob and Taz waters, the oxygen con-

tent increased to 8.0 mL/L owing to the decrease of the surface water temperature to 3–4°C. However, the oxygen saturation was still below 100%. This was caused by the intense utilization of oxygen for the oxidation of great amounts of organic matter and iron compounds supplied with the runoff [6, 7]. In this case, the waters at the western shallow-water coasts of the bay were warmer $(7.0-8.2^{\circ}C)$ than those at the eastern coasts (below 5° C), providing here more favorable conditions for the active photosynthesis processes [5]. As a result, the water's saturation in dissolved oxygen at the western coasts amounted to its maximum values for this area (98.0-99.8%). At the same time, this value was 92% or below at the eastern coasts. The Ob and Taz waters were also much different in the values of the total alkalinity (Alk). The lowmineralized Taz waters (below 0.02 g/L) showed very small Alk values (below 0.1 mg-equiv/L). The content of dissolved inorganic carbon was about 2.2-2.4 mg/L, i.e., considerably lower than that in the Ob waters (6– 12 mg/L). Moreover, the Taz waters were more acid than those of the Ob River. The pH values amounted to 6.6-6.9 NBS units against 7.6-8.1 NBS in the Ob waters (Fig. 2). This is caused, first, by the peculiarities of the drainage basins of the rivers and second, by the quite small buffer capacity of the Taz waters owing to their low alkalinity. Before the confluence of the inlets, the Alk value in the Ob waters amounted to 0.92-0.98 mg-equiv/L and pH value of over 7.8. Immediately before the "marine" area (the frontal zone), where the Ob and Taz waters were completely mixed, the Alk and pH values amounted to 0.6 mg-equiv/L and 7.6-7.7, respectively. This was close to the average long-term values for the Ob River runoff [10, 11].

Compared to the pH values and the total alkalinity. the nutrients were distributed more uniformly. The distribution of the dissolved forms of nitrogen and silicon to the north from 69° N to Cape Khonarasalya $(71^{\circ}20' \text{ N})$ was mainly determined by the intense development of diatom algae, which constituted here 95% of the total phytoplankton mass. The concentration of dissolved silicon in the major part of the riverine area of the bay was relatively low (within 15- $60 \,\mu\text{M}$). The bulk of the silicon was utilized by diatom algae during the photosynthesis (Figs. 3a, 3b). In general, the waters of the riverine area of the bay were characterized by decreased contents of the mineral forms of nitrogen as well. The concentration of nitrate nitrogen in the main flow of the Ob River waters ranged from analytical zero to 1.0 µM; the content of ammonium nitrogen was also low. At the same time, a large number of organic forms of nitrogen and phosphorus were registered. Their concentrations varied from 40 to 50 μ M and from 0.5 to 1.4 μ M, respectively. The high concentrations of phosphates (0.4– $3.0 \,\mu\text{M}$) and trivalent iron (10–40 μM) were caused by great amounts of phosphorus and iron in the particulate matter (probably, a specific feature of the Ob River waters owing to the numerous marshes in the



Fig. 1. The distribution of the dissolved oxygen (mL/L) over the aquatic area of the Ob Inlet: (a) in the surface layer during the summer period; (b) in the near-bottom layer during the summer period; (c) in the surface layer during the autumn period; (d) in the near-bottom layer during the autumn period.

drainage basin). This is also responsible for the similarity in the general patterns of the phosphorus and iron distribution in the riverine area of the inlet.

In the autumn time, under the pronounced decrease of the runoff in the riverine area, the mixing proceeds even over the entire width of the river, unlike the summer conditions of the extremely limited transverse mixing. The considerable wind mixing resulted in the more uniform distribution of the dissolved oxygen and nutrients over most of the "riverine" aquatic area. This is also confirmed by the uniform distribution of the water temperature over the entire aquatic area of Ob Inlet [5, 7].

The content of dissolved oxygen (Figs. 1c, 1d) in the autumn varied within a narrow range (8.0-8.3 mL/L) and the saturation decreased to 88% on average compared to the summer values. This was caused by the decrease of the photosynthesis activity and the high

intensity of the destruction processes. The concentrations of the mineral forms of nutrients as a whole increased: to $30-70 \ \mu\text{M}$ for the dissolved silicon (Figs. 3c, 3d), to $0.5-3.0 \ \mu\text{M}$ for the nitrate nitrogen, and to $1.0-3.9 \ \mu\text{M}$ for the mineral phosphorus. At the same time, no pronounced variations took place in the contents of the organic matter and iron compared to the summer surveys. This conformed to the results of the preceding studies by the VNIRO and IO RAS performed during the autumn period [3, 4, 12].

Hydrochemical characteristics of the "marine" and intermediate areas of Ob Inlet. The influence of the saline seawaters is well pronounced to the north from $71^{\circ}20'$ N. By the results of the surveys, the signs of the marine impact (e.g., the increase of the alkalinity value in the near-bottom layer) were registered well southward of the location of the frontal zone.



Fig. 2. The distribution of the pH values over the aquatic area of the Ob Inlet: (a) in the surface layer during the summer period; (b) in the surface layer during the autumn period.

The "marine" area of Ob Inlet was considerably different from the "riverine" area by the features of the hydrochemocal parameters distribution and processes within these areas. The mixing zone of the riverine and marine waters was pronouncedly stratified in the summer time: the upper part of the cross profile was constituted by the riverine freshwater, and the saltish and saline waters were located below with the upper boundary, which rose gradually from the south to the north [6, 7]. During the summer bloom in the inlet, a significant mass of the freshwater diatom phytoplankton in this zone died off under the contact with the seawater. One may suppose that this was one of the causes of the growth of the content of the mineral

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Fig. 3. The distribution of the dissolved silicon (μ M) over the aquatic area of the Ob Inlet: (a) in the surface layer during the summer period; (b) in the near-bottom layer during the summer period; (c) in the surface layer during the autumn period; (d) in the near-bottom layer during the autumn period.

forms of all the nutrients. The concentrations in the surface layer were as high as 206 μ M for silicon (Fig. 3a), 11 μ M for nitrates, 8–9 μ M for ammonium nitrogen, and 2.5 μ M for phosphates. A high content as such of the nutrients, especially of silicon, was not registered early, because, as mentioned above, the preceding expeditions were carried out during the recession of the flood and strong decreasing of the phytoplankton bloom [7].

In general, the distribution of the hydrochemical parameters in the mixing zone of the riverine and marine waters may be traced in section 15, which may be considered, to a certain approximation, as a lengthwise section of the frontal zone (Fig. 4c). As seen from the figure, the maximum content of silicon within the water mass was registered above the bar, where the decomposition of organosilicon compounds reached its peak. The maximum concentration of silicon $(206 \,\mu\text{M})$ was found at the surface and decreased towards the bottom to $140-160 \,\mu\text{M}$. Northward of the bar, where the lower layers are formed by the Kara Sea waters of salinity up to 32%, the concentration of silicon decreased to $65 \,\mu\text{M}$ as the result of the limited water exchange between the well-stratified layers (Fig. 4b). The obtained data confirm the early studies by the Arctic and Antarctic Research Institute, which showed that the bulk of the frameworks of the diatom algae are dissolving after the die off before reaching the bottom [1, 2, 13].

The section well presents the distribution of oxygen in the frontal zone as well (Fig. 4a). In the southern part, where the effect of the halocline was the minimum, the water mass was characterized by the uniform distribution of the dissolved oxygen (8.2– 8.7 mL/L; only in the lower 3-m layer formed by saline water (about 11‰) did its content fall to 6.8 mL/L.

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Fig. 4. The distributions along section 15 in the mixing zone of the riverine and marine waters during the summer period: (a) the dissolved oxygen, mL/L; (b) the silicon, μM ; (c) the location of section 15.

Northwards, the effect of halocline increased gradually, resulting in the decrease of the content of dissolved oxygen from 8.5 mL/L at the surface to 6.3 mL/L at the bottom.

Considering the processes in the frontal zone during the summer high-water period, it is significant that the interaction of saline marine and fresh riverine waters proceeds most intensively along the coasts of the inlet. Thus, a pronounced southward intrusion of saline waters was registered at Cape Drovyanoi $(72^{\circ}40' \text{ N})$ during the summer surveys. At that, the water layer was mixed from the surface to the bottom, and the salinity value was over 20%. This effect was also revealed in the uniform vertical distribution of all the hydrochemical parameters, and their values were more characteristic for seawaters.

One must note that the winds of the northern quadrant are prevailing in the Ob Inlet area during summer period, which results in frequent pileups. In this case, the waters from the "marine" area (the frontal zone), being enriched in nutrients, are expand southwards beyond 72° N and exert a significant influence on the hydrochemical parameters of the intermediate area we distinguished. The influence as such was primarily found by the increased content of silicon, as well as of nitrate nitrogen and mineral phosphorus, both in the surface and in the near-bottom layers.

In the autumn time, the biological activity in the bay's aquatic area decreased considerably; respectively, the biomass of the diatom phytoplankton decreased sharply as well [6, 7]. As a result, the process of the water's enrichment in nutrients stopped in the frontal zone. The content of silicon, as well as of the mineral forms of the other nutrients, decreased and became a little different from the values registered at that time in the "riverine" part of Ob Inlet. The concentrations were not more 50 μ M for the silicon, 2.5 μ M for the nitrate nitrogen, and 1.5 μ M for the mineral phosphorus.

The fall of the volume of the riverine runoff during this period, as well as the intense wind mixing, resulted in the more uniform distribution of the dissolved oxygen and nutrients. On the surface the riverine waters of the halved volume of the runoff were drawn near the



Fig. 5. The distributions along section 19 in the mixing zone of the riverine and marine waters during the autumn period: (a) the dissolved oxygen, mL/L; (b) the silicon, μM ; (c) the nitrate nitrogen, μM ; (d) the locations of sections 17 and 19.

western coast. The remaining "marine" aquatic area, being beyond the zone of the active impact of the riverine runoff during this season, was occupied with the water of salinity increasing from 6 to 9% in the upper mixed layer. Thus, one may ascertain that the mixing zone of the riverine and marine waters in the autumn time is subdivided distinctly into two unequal areas (the western and eastern), which are different in the character of the distribution of all the hydrochemical parameters [5, 7]. This is seen well from the distribu-

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Fig. 6. The distributions along section 17 in the mixing zone of the riverine and marine waters during the autumn period: (a) the dissolved oxygen, mL/L; (b) the silicon, μM ; (c) the nitrate nitrogen, μM .

tion of the dissolved oxygen, silicon, and nitrate nitrogen (Figs. 5a, 5b, 5c), which is presented in section 19 along nearly $72^{\circ}15'$ N in the southern part of the mixing zone (Fig. 5d). The western area was characterized by a higher content of dissolved oxygen (8.2– 9.0 mL/L) and by its saturation value (92-98%), as well as by decreased concentrations of silicon and nitrate nitrogen. The eastern area was characterized by high salinity, and the content of dissolved oxygen decreased to 7.8-8.2 mL/L. The higher concentra-

tions of silicon and nitrate nitrogen in this part of the inlet were probably related to the decomposition of the organic matter formed and supplied during the preceding period.

In the northern part of the mixing zone (section 17 along 72°40′ N, Fig. 5d), because of the dispersion of the riverine flow, the boundary between the described areas became less pronounced and was distinguished only by the silicon distribution (Fig. 6b). The distribution of the content of dissolved oxygen (Fig. 6a), nitrate nitrogen (Fig. 6c), mineral phosphorus, and iron became more uniform resulting from the considerable mixing.

CONCLUSIONS

The hydrochemical regime of the Ob Inlet is determined by the combination of the current hydrological and biological processes. At that, two areas of the bay are well distinguished. Their hydrochemical conditions show peculiarities being characteristic exclusively for each of them: the "riverine" area, where the freshwater riverine runoff determines all the parameters, and the "marine" area, in which the conditions are determined by the character of the interaction of the saline and fresh waters. Between these areas, the intermediate zone is distinguished, which is exposed to the periodical impact of the "marine" area. The location of the boundaries of these areas may vary considerably, both seasonally and annually.

During the high-water period, when the hydrological conditions of the bay were close to the riverine mode, a peak of the development of the diatom phytoplankton was registered in the "riverine" area. In turn, a great amount of nutrient mineral forms was formed during the same period in the mixing zone of the riverine and marine waters (in the "marine" area) under pronounced stratification owing to the massive dying off of the freshwater diatoms in the layer over the halocline. First, this is silicon supplied to the Kara Sea in fourfold concentrations compared to the common values registered by the autumn expeditions (40- $50 \,\mu\text{M}$). This may specify our notion concerning the amount of silicon supplied to the sea in view of the wide seasonal variability of its content in the Ob River waters.

Under the low runoff during the autumn period, the hydrochemical conditions are the most affected by the mixing process, thus resulting in the equalization of the values of all the hydrochemical parameters. This is also provided by the attenuation of the biological activity before the beginning of freeze up.

The peculiarities of the hydrological regime and hydrometeorological conditions in the Ob Inlet result in the fact that the hydrochemical regime in its freshwater area during the high-water time, is similer to rivers; particularly, the nonuniform of the chemical composition over the cross section. During the period of the low runoff, the conditions are similar to those in lakes and water storage basins, especially under northern winds "locking" the water runoff to the sea.

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