MARINE CHEMISTRY

Volume of the Ob Bay Waters as a Factor of the Formation of the Hydrochemical Inhomogeneity

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Abstract—This report presents a new analysis of the results of two hydrochemical surveys over the Ob Bay in 2010 performed by the Institute of Fisheries and Oceanography (VNIRO) and the Institute of Oceanology (IO RAS). The unique world feature of the Ob River–Ob Bay system is shown. The water volume in the bay exceeds the average annual runoff of the Ob River, being somewhat under the total runoff of all the inflowing rivers. Because of this, the complete renovation of the waters in the bay requires a long time. The within-year distribution of the runoff is characterized by both the flood waters and those of the Ob River winter runoff characterized by much different hydrochemical parameters registered even in the course of summer surveys in the bay. This fact, but not the biological transformation of the waters, as assumed previously, is the primary cause of the variability of the water composition in the bay. The summer waters of the Ob River reach the seaward boundary of the bay only in the next spring, enter the Kara Sea with the spring flood, and form lenses of desalinated waters in the sea. The autumn expeditions by the IO RAS found that the waters in the lenses were quite similar to the autumn waters in the bay, although these were the Ob River waters of different years, which was disregarded formerly.

INTRODUCTION

The Ob Bay is one of the longest riverine estuaries in the world. It is of the great economic importance in the fields of transport, fishery, and the power industry (the presence of hydrocarbon deposits). In view of this, particular attention is drawn by the processes of the transformation of nutrients supplied by the Ob, Taz, and Pur rivers. It is assumed that the hydrochemical conditions are characterized by wide variability [2, 9, 15] being quite superior, e.g., to that in the Yenisei Gulf located just under the same natural conditions. As the most prominent characteristic of the hydrochemical variability in the bay and the adjacent areas of the Kara Sea, one may consider the content of silicon (Si) being both a nutrient and a tracer of the propagation of the riverine waters. Thus, according to the data by the Arctic and Antarctic Research Institute for the summer surveys of 1976–1991 in this area, the Si values amounted to 2–115 μM in the fresh (riverine) waters and varied within 40–130 μM in the seawater (extrapolated to zero salinity) [15]. By convention, this variability is mainly caused by the intense production–destruction processes in the Ob Bay: at the first stage, silicon is quite completely withdrawn from the water (up to 2–4 μM), and, at the second stage, silicon is supplied to the water as a result of the dye-off and rapid destruction of the freshwater phytoplankton under mixing of the riverine and marine waters. In this case, the Si content might increase to 100–130 μM [15].

At the same time, the surveys by the IO RAS in the Kara Sea during the same seasons (August–September) of 1993 and 2007 showed a simple and stable hydrochemical situation when the linear relationships between the alkalinity and salinity ($Alk–S$), as well as between the silicon and salinity ($Si–S$), were asserted well in desalinated lenses over a major part of the sea. It is significant that the same relationships were traced in the proper bay (although some of the points dropped out towards the decrease of the Alk and Si values). The conservatism as such in the character of the Alk and Si variability allowed one to propose that separated lenses formed with a contribution of the continental runoff (mainly by the Ob and Yenisei waters) might exist in the sea under favorable conditions [13, 21]. At that, it was implied that the basic composition of the Ob and Yenisei riverine waters varied slightly during a year and the stability of the finite term of the mixing of the riverine and marine waters. Really, these rivers are over 3000 km in length and, with the average flow rate of 0.5 m/s, the time lag of the flow from the river head to the mouth should amount to about three months. This seems to be sufficient for the seasonal variations of the properties characteristic for smaller rivers being pronouncedly smoothed at the downstream of great rivers [1]. This conclusion was criticized particularly by [15], which stated the notion that the identification as such of the waters in the Kara Sea was impossible because of the mentioned variability, its chaotic mode, and the wide range. Several expedi-

tions to the Ob Bay that also registered a wide variability of nutrients [4, 7, 11, 22] could not present an integrated view of the processes in the Ob Bay.

Two detailed hydrochemical surveys in the Ob Bay were performed in 2010 when specialists of the VNIRO and IO RAS using a OTA-777 lake pusher executed 117 stations (along 30 cross sections) covering the central and northern parts of the bay. At that, the surveys were carried out not only along the channel line but also near the coasts [8, 10]. The spatial and temporal variability of the nutrient concentrations registered in the bay appeared to be even wider than that noted earlier by [15]. Thus, extremely high concentrations of nutrients, especially of nitrates and silicon (up to 10 and over 200 µM, respectively) were found in the north of the bay. Their origin was commonly ascribed to the dying off of freshwater diatom plankton and its rapid destruction [8, 9].

In the authors opinion, to understand the variability of the concentrations of silicon and other nutrients in the Ob Bay, which is not found in the Gulf of Yenisei, as mentioned above, one must include the buffer effect of the water volume in the bay. Its rough estimation—750 km length, 60 km width, and 10 m depth—result in 450 km^3. This value exceeds the annual runoff of the Ob River, although it is less than the total runoff of all the rivers flowing into the bay. Evidently, the description of the nutrient variability should be one-sided with no including of a delay of the waters of the Ob and Taz rivers in the bay.

METHODS OF MEASUREMENTS

The procedures of the water sampling and determining the hydrochemical parameters are given in [8, 9]. The nutrients and oxygen were determined using the standard procedures accepted at the VNIRO [18]. The alkalinity value used below as a conservative parameter was measured by direct titration modified by Bruevich with the visual identification of the endpoint of the titration [20].

In view of the high concentration of particulate matter in the waters of the Ob Bay, the analyses were performed with a correction for the turbidity and the color of the waters. By the procedures in [18], the turbidity of the samples was taken into account by means of the comparison of the optical density of a sample to the same sample containing one reactant less and hence being not colored. By the procedure in [20], another technique—filtration of the samples and colorimetry against filtrates—was used. The question of the suitability of different approaches to account for the turbidity and color of the samples still seems to be debatable and requires further investigations. The present report does not concern this subject.

To measure the temperature and conductivity, an FSI probe was used. The salinity value was calculated with the standard "marine" equation being hardly suitable for riverine water characterized by quite another ionic composition. Because of this, the absolute values of the salinity might contain considerable errors, but they are applicable as relative values for comparison. The term "mineralization" is conventionally used for freshwater instead of "salinity," and the content of salts is expressed in mg/L. The present study uses the term "mineralization" for the values below 1000 mg/L and "salinity" for those over 1000 mg/L. However, this value should be expressed in g/L but neither in promille nor in PSU units.

ANALYSIS OF THE SURVEY DATA

Survey (1), July 29 to August 17, 2010. As evident from the estimation of the water volume in the bay, the occurrence of different-time waters (of the winter runoff and the flood) at the recession of the spring flood is beyond question. However, the possibility to distinguish these waters by their properties, which was not done before, firstly was not evident. In the course of the treatment of the survey results of 2010, study [9] and other publications proposed to divide the bay aquatic area into the southern merely "riverine" and northern "marine" part in which the mixed waters are seen. It was suggested to draw their boundary along the isohaline of 0.5 g/L. In our view, the waters must be subdivided not by one but by two conservative parameters (the mineralization M and alkalinity Alk) or rather by their ratio (see Fig. 1a for the waters of mineralization below 1 g/L and Fig. 1b for those of higher mineralization).

Figure 1a is crucial. If we consider all the data in common, the figure should only show the trend of the alkalinity increase with the growth of the mineralization and the inhomogeneity of the waters by these parameters. However, we subdivided the points into two groups: the flood (melt) waters (marked with squares) and the winter ground waters (the daggers). The value of $M = 100$ mg/L might be taken as the boundary between these groups. Nevertheless, just the relationship between the M and Alk values is the more important criterion. Really, the waters of the rivers of the Yamal Peninsula [3, 7] and of other northern rivers are characterized by snow feeding (meltwaters) for 50−80% and belong to the hydrocarbonate type of riverine waters with prevailing Na cations, as noted even in [1]. Their mineralization is within 30−180 mg/L, and the content of hydrocarbonate ions (alkalinity) amounts to 0.3−1.8 mg-equiv/L, which coincides well with our parameters for meltwaters, including the error of the calculation of the mineralization. The incidence of line 1 in Fig. 1a may be verified in the following way. The low-mineralized hydrocarbonate waters may be roughly considered as a solution of $NaHCO_3$ or of $Ca(HCO_3)_2$. In this case, the following approximate relationship should be fulfilled:

M (mg/L) ~ 82Alk (mg-equiv/L).

The Alk values are equal to 0.098 and 1.178 mg-equiv/L for the two endpoints of line 1. Hence, the
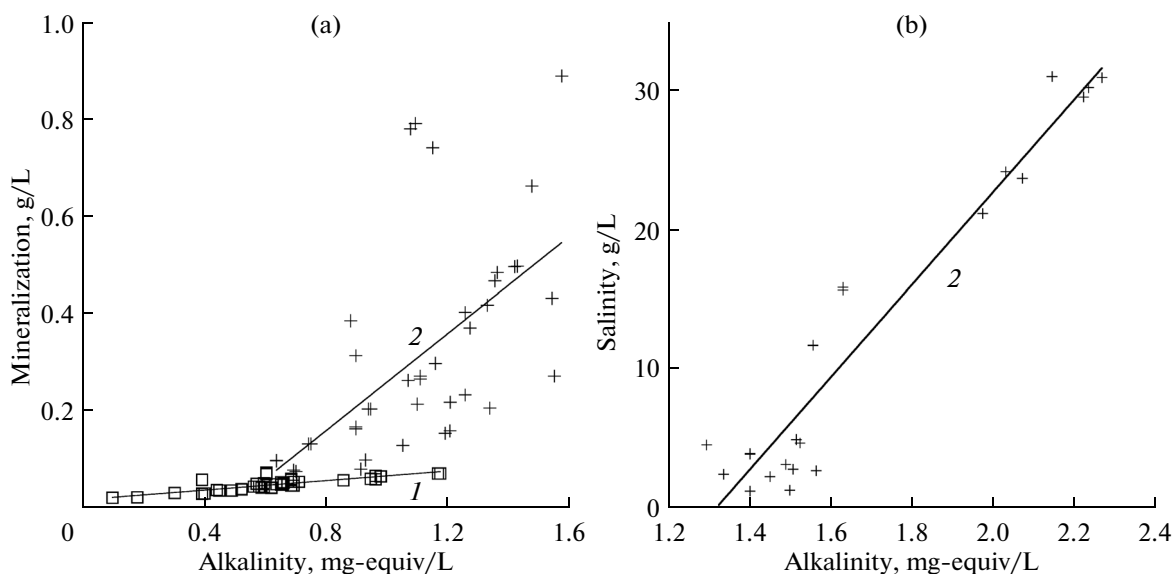
Fig. 1. Correlation of the mineralization and alkalinity (a) for the riverine part of the bay and (b) for the mixing zone of marine and fresh waters. The squares mean the stations with mineralization below 100 mg/L (see the text), and the daggers are the stations with mineralization within 0.1−1 g/L. The average correlation ratios are shown by lines *1* and *2*, respectively.

calculated values of the mineralization should be equal to 8 and 99 mg/L, respectively, and the measured concentrations should amount to 17 and 67 mg/L, or only doubled. However, the deviations from the equation for the meltwaters, especially in small rivers, might be caused not only by the variations in the ionic composition but also the presence of organic matter in the water (firstly, of humic substances). This latter affects the alkalinity in two ways: strong acids decrease the alkalinity value (often to zero in the rivers of the temperate zone), and weak acids increase the alkalinity values [23]. Nevertheless, in the considered case, the presence of meltwaters in the bay aquatic area during the first survey was registered unambiguously.

We assigned the other waters of mineralization over 1000 mg/L in Fig. 1a to the winter waters. In general, their distinguishing in the bay may present some difficulties. As seen from Fig. 1a, the waters were subdivided by the mineralization values as well as by the *M−Alk* ratios. Unlike the meltwaters, the winter waters are characterized by ground feeding, so they usually show higher mineralization and another ionic composition with a small hydrocarbonate fraction. The seasonal variability of the parameters of the water is also revealed in other great Siberian rivers, e.g., in the Lena River [5]. The most pronounced variations take place there before and during the flood. The average values for 15 years are $M = 325$ and 49 mg/L and $Alk = 1.7$ and 0.55 mg-equiv/L, respectively. In the latter case, the above relationship between them was also fulfilled; at that, the mineralization was determined here by the basic ion composition. Thus, although the ratio of the alkalinity and mineralization in riverine and, especially, in the melted waters is

affected by the content of organic matter, nevertheless, this ratio is still important and a suitable parameter to identify these waters.

Assuming that the *M−Alk* ratio allows us to distinguish the flood and winter waters, let us consider their location in the bay aquatic area. It is shown in Fig. 2, and, as expected, the location of the flood waters is further south than that of the winter waters, and both are moving northwards faster at the deep stream than near the coasts. The location of the meltwaters in the bay aquatic area (Fig. 2) allows one to mark out some of their peculiarities. It is known [17] that the waters of the Taz and Pur rivers are less mineralized than those of the Ob River; thus, in our case as well, the freshest fraction of meltwaters was located in the middle of the Taz Bay (station 9) and downstream at the right coasts (stations 19 and 19.1). The fact that stations 30 and 34 did not show the meltwaters is also reasonable because the water movement at the deep stream is faster than that at the coasts.

Naturally, the winter waters are located to the north of the meltwaters. These are the waters noted at stations 30 and 34, as well as at stations 37−52 and in the upper layers of stations 53−58, except for stations 56 and 57, i.e., all the stations at which the water mineralization was below 900 mg/L. As seen from Fig. 1a, their *Alk* values varied from 0.6 to 1.6 mg-equiv/L and tended to increase with the growth of the mineralization; also, no close correlation takes place here. This might be caused by the winter feeding of the rivers by the groundwaters of increased mineralization owing to the appearance of other ions (sulfate, chlorine, and magnesium) [1]; therefore, the simple *M−Alk* relationship is disturbed in these waters. It is easy to show
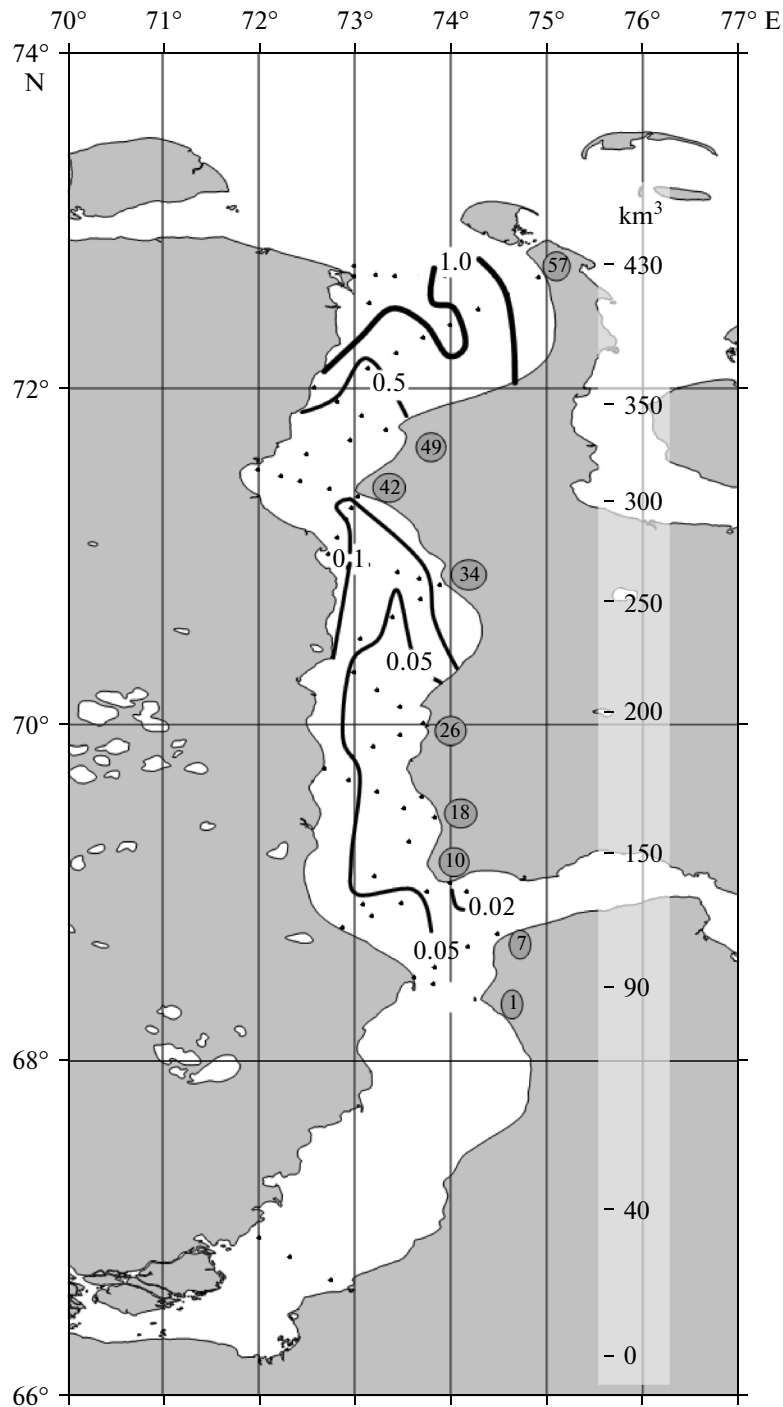
Fig. 2. Location of flood and winter waters (mineralization below 0.1 g/L and 0.1−1 g/L, respectively) distinguished in the Ob Bay by the mineralization−alkalinity ratio during survey (1). The gradation of the isolines is as follows: 0.02, 0.05, 0.1, 0.5, 1, and 5 g/L. The numbers at the left coast of the bay are the coastal station nos. On the right is the scale of the bay water volume increasing from the south (see the text). The scale of the X axis is doubled for obviousness.

that the waters in Fig. 1a could not be a mixture of riverine and marine waters because the water of 900 mg/L mineralization and 1.6 mg-equiv/L *Alk* value could not be formed by mixing the seawaters of 30 g/L salinity and 2.4 mg-equiv/L *Alk* value and the riverine waters of about 600 mg/L mineralization and *Alk* values from 0.6 to 1.6 mg-equiv/L. The mineralization values in the marine and riverine waters require a 1% or less admixture of marine to riverine waters. Thus, all the waters of over 900 mg/L mineralization are purely riverine winter waters, mainly of the Ob River.

Table 1. Annual supply of waters to the Ob Bay

Sources of waters supplied to the bay	Runoff, km³/year
Ob River (the alignment of Salekhard)	398
Ob River (at the exit to the bay)	408
Nadym River	18.5
Pur River	32.9
Taz River	45.8
Small rivers of the Taz Bay	15.4
Small rivers in the south of the Ob Bay	8.4
Small rivers in the north of the Ob Bay	11.0
Total	540

The detailed survey of 2010 enables one to evaluate the volumes of different waters in the bay and to compare them to the known data on the runoff of the rivers to the bay. The published data on the volume of the Ob Bay are quite different: according to [19], the bay area is 44 500 km² and the water volume is 445 km³ and, according to [14], the bay area is 40 800 km² and the water volume is about 400 km³; i.e., these are very rough estimates in both cases based evidently on the average bay depth of 10 m. At that, it should be considered that the volume of waters in the bay varies by the seasons, as well as under positive and negative setups affecting much of the water level. Of our interest is the volume of freshwaters in the bay within the test area of 2010. This volume was estimated by the coordinates and depths measured in the sections from one to the other coast during both surveys. To generalize the results, the bay volume from the Ob River mouth to the Taz Bay, where no measurements were made in 2010, was also calculated. This volume was estimated from the area of this part of the bay assuming that its average depth is equal to 5 m [3, 14]. The resulting total volume of the bay was about 430 km³; the growing bay volume from the south is shown in the right of Fig. 2. We evaluated the error of this estimate as ±20 km³; however, the relative error for the volumes of different waters must be 2−3 times less.

The average data on the runoff of the Ob and other rivers for 1930−2004 are given in [3] (see Table 1). As seen from Table 1, the Ob River runoff near Salekhard amounts to 398 km³ with the maximum and minimum of 574 and 268 km³ in 1979 and 1967, respectively; the

constant of variation of the annual runoff is not high and amounts to 0.15. The data on the within-year distribution of the runoff are taken from [3] for the Ob, Taz, and Pur rivers and from [6] for the Shchuch'ya River (see Table 2). To calculate the within-year distribution of the runoff to the bay in km³, the authors combined the data into three groups: the Ob River runoff, the runoff of medium rivers (the Nadym, Taz, and Pur rivers), and the runoff of small rivers. As an example of the latter, the data on the Shchuch'ya River were used [6] (Table 2).

To determine the volume of freshwaters in the bay, one must evaluate the volume of the seawaters occurring there, which was quite low during the first survey. Assuming that the freshwaters in the mixing zone were 5 m in depth, the volume of seawaters amounted to about 62 km³. The calculation of the volume of the riverine waters disregarded their admixture to the seawaters because we believed that these waters were mixed with seawaters earlier, although this might probably be not entirely true. At that time, the volume of all the freshwaters amounted to 368 km³. Among them, the bay area we studied contained about 62 km³ of winter and 176 km³ of flood waters. In view of the last surveying of the north of the bay in mid-August, one may determine by means of Table 2. The month when the northernmost freshwaters were supplied to the bay. The calculations show that it took place in late January because 360 km³ of freshwaters should be supplied to the bay from February to mid August. Of this volume, 85 km³ were supplied during February−May, i.e., before the Ob River became free of ice; these waters must show the properties of winter waters. An additional 190 km³ (during the first survey) were supplied from late May to about mid July; these waters were characterized by the properties of thawed snow waters. In view of the roughness of our calculations, the correspondence of the water parameters with the time of their supply seems to be quite suitable.

After determining the location and volumes of the different-time waters in the bay, let us consider their hydrochemical distinctions. Figure 3a presenting the pH−Alk ratio shows that the pH values in the meltwaters changed by more than 1 (i.e., the concentration of hydrogen ions varied more than by tenfold) and correlated well with the alkalinity. This was caused by the

Table 2. Distribution of the riverine runoff by the months in % and in km³ according to [3, 17]

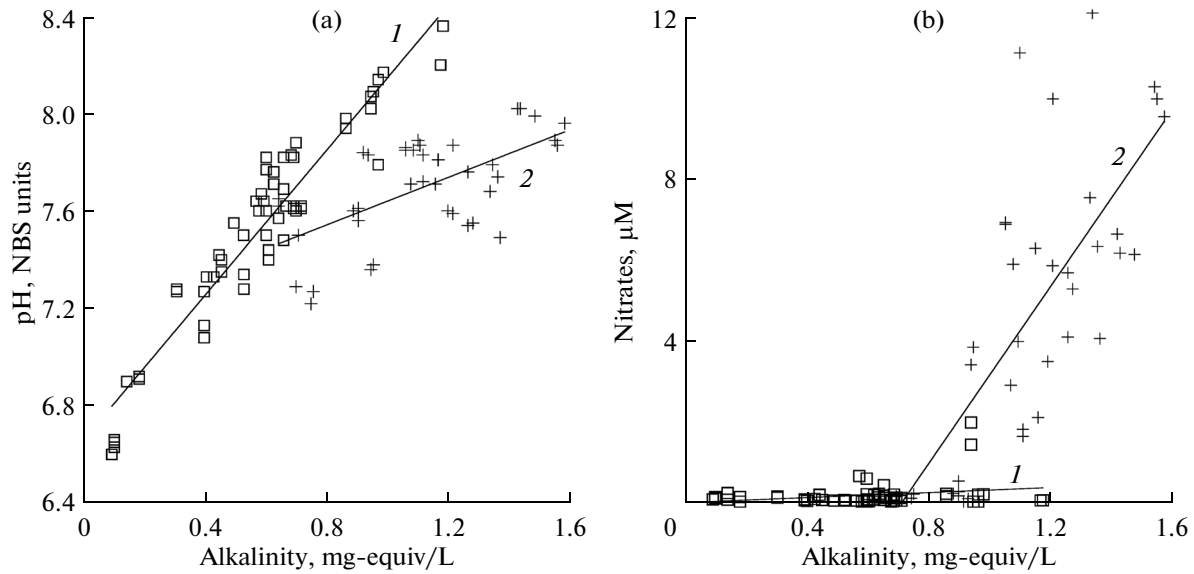| Rivers	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Total
Ob River	3.1	2.6	2.3	2.4	10.1	21.7	19.6	14.5	9.0	6.8	4.3	3.6	100%
Pur River	2.8	2.4	2.1	2.1	6.3	35.1	16.2	9.1	8.5	7.0	4.7	3.7	100%
Taz River	2.4	2.0	1.9	1.8	6.9	34.3	21.1	8.2	7.4	6.5	4.3	3.2	100%
Shchuch'ya River	0	0	0	0	5.1	38.3	23.0	10.7	14.1	6.2	1.5	1.1	100%
Ob River	12.6	10.6	9.4	9.8	41.2	88.5	80.0	59.3	36.7	27.7	17.5	14.7	408 km³
Middle rivers	2.5	2.1	1.9	1.9	6.4	33.7	18.2	8.4	7.7	6.6	4.4	3.4	97.2 km³
Small rivers	0	0	0	0	1.8	13.3	8.0	3.7	4.9	2.2	0.5	0.4	34.8 km³
Total	15.1	12.7	11.3	11.7	49.4	135.5	106.2	71.4	49.3	36.5	22.4	18.5	540 km³

Fig. 3. (a) pH−alkalinity ratios and (b) nitrate nitrogen−alkalinity ratios. See the notations in Fig. 1.
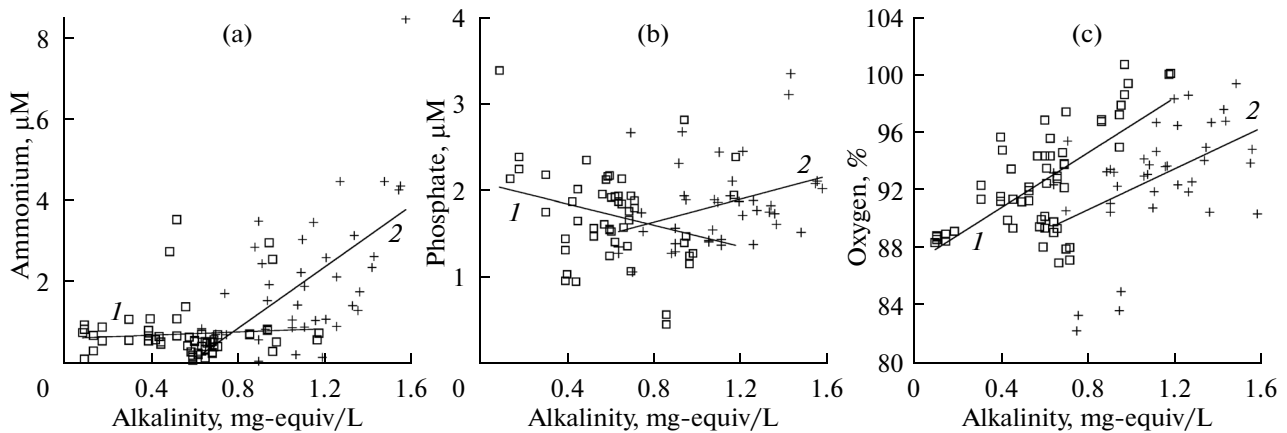

Fig. 4. Ammonium nitrogen−alkalinity ratios (a), phosphates−alkalinity ratios (b), and water saturation in oxygen (%)−alkalinity ratios (c). See the notations in Fig. 1.

fact that the pH values of these waters were mainly determined by the dissolved organic matter, which might have partially neutralized the alkalinity. The most acidic waters were registered at the mouth of the Taz Bay and near the right coast downstream of it, which is in agreement with the published data [17].

Figure 3b shows the relationship of the alkalinity and nitrate nitrogen (NO_3). It is seen that the meltwaters contain just no nitrates, and their content is quite high in the winter waters. A concentration of about 2 μM of nitrates was found here exclusively at a single station (station 32) near the boundary between the melted and winter waters. This complies with the data obtained by winter expeditions of different years, e.g., by [12]. Thus, it is seen from the pH−*Alk* and NO_3−*Alk* ratios that the flood and winter waters are greatly different in these two parameters. However, a clear distinction as such of

these waters is not characteristic for all the other hydrochemical parameters (sees Fig. 4). Thus, a distinction in the ammonium content takes place, although it is less pronounced than that of the nitrate nitrogen (Fig. 4a). Stations 20 and 21 dropped out of the general regularity. Just no distinctions between the winter and flood waters in phosphates and oxygen (in saturation %) were found (see Figs. 4b, 4c).

Now, in view of the occurrence of different-time waters in the bay, let us consider the variability of silicon ascribed conventionally, as noted above, to the biological transformation. The Si−*Alk* relationship for the two types of waters should be used once again. Figure 5a shows that the meltwaters are characterized by a low Si concentration (16−43 μM) tending to a small decrease with the growth of the *Alk* values. Probably, this is caused by photosynthetic activity because of the
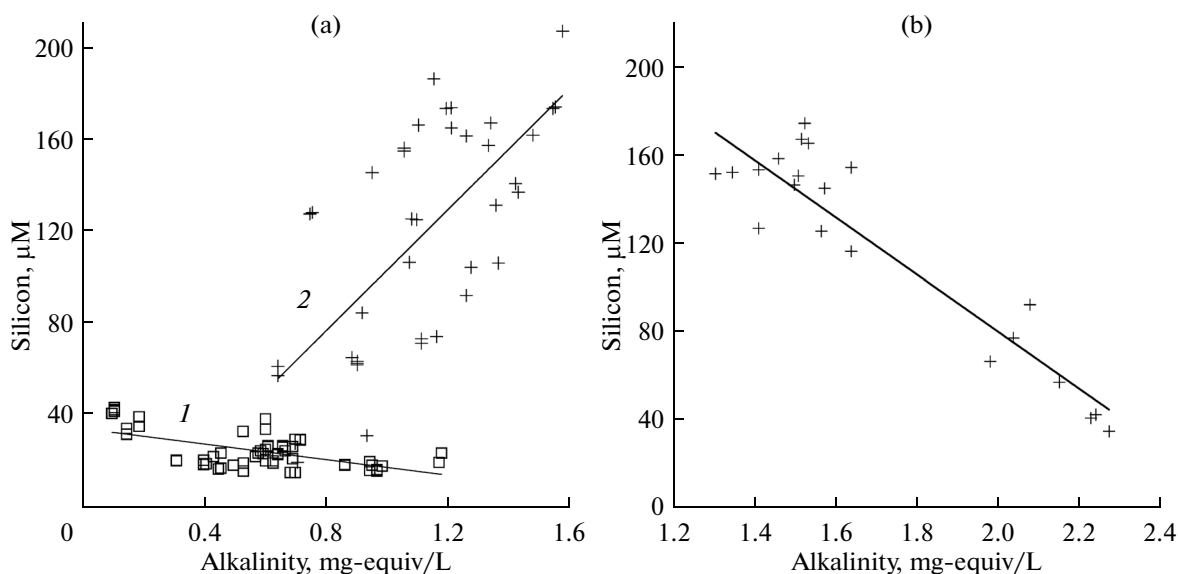
Fig. 5. Correlation of the content of dissolved silicon with the alkalinity for the riverine part of the bay (a) and for the area of the influence of seawaters (b). See the notations in Fig. 1.

simultaneous increase of the oxygen saturation of these waters (Fig. 4c). More interesting is the fact that the winter waters are characterized in general by a quite higher Si concentration tending to increase with the growth of the *Alk* values. This is not surprising because it is known that the groundwaters contain more Si than the surface waters [1, 17]. Moreover, the measurements of the silicon content in the Ob River nearby Salekhard on December 20, 2001, resulted in average values of 120 ± 10 μM, although the river during this time was not characterized by purely ground feeding owing to the supply of waters from the midstream of the river [12]. The above-mentioned surveys on the Lena River [5] also showed a considerable difference between the average Si values (117 and 53 μM before and during the flood, respectively). Thus, the high concentrations of silicon in the northern part of the bay during survey (1) are naturally explicable: these are the winter waters but not the products of the dying off and rapid destruction of freshwater phytoplankton, as asserted by [9, 15]. In our view, the occurrence of rapid destruction is also in conflict with the observations of a great abundance of freshwater diatoms in the sediments of the northern part of the Ob Bay and in the proper Kara Sea up to 73°−73.5° N [16].

The extremely high value of Si = 207 μM at station 54 in the layer of 0.5 m is worthy of special notice. Exclusively this station and none other was characterized by many extreme parameters: the alkalinity value of *Alk* = 1.58 mg-equiv/L was higher than that expected for the mineralization of 886 mg/L; the extremely high value of NH_4 = 8.5 μM; the increased pH value with the decreased O_2%. Thus, the water of station 54 (0.5 m) is not typical for the Ob Bay, and the Si values of 180−185 μM may be taken for now as the

maximum for the winter waters. The same conclusion concerning the maximum Si concentrations was drawn by the author [9], although the other high Si values were ascribed here to the decomposition of diatoms.

Let us turn to the consideration of the riverine waters with an admixture of seawater (see Fig. 1b). The southern boundary of the seawaters is difficult to verify using the *Alk*−mineralization relationship because of the scattering of the *Alk* values. This boundary was taken above as the mineralization of 1000 mg/L. At that, the admixture of seawaters of 30 g/L salinity was minor (1−4%) in the layers of salinity within 1−2 g/L as seen from Fig. 1b. However, the same figure shows that the points of low salinity do not lie exactly along the salinity−alkalinity mixing line but are widely scattered. In our view, this is in agreement with the possible wide variability of the mineralization in the winter waters as well. It is seen from Fig. 1b that line *2* (the salinity−*Alk* regression line) shows the minimum *Alk* value of about 1.35 mg-equiv/L, although the scattering of the points is quite wide. This points indirectly to the possibility of the *Alk* value in the preceding portion of the winter water being higher than that during survey (1). The scattering of the points of the salinity−*Alk* relationship are in agreement with Fig. 1a showing wide scattering of these values for the winter waters.

The Si concentration in the zone of mixing waters decreases owing to the dilution, so the boundary of the riverine and mixed waters is determined quite exactly using the Si−*Alk* graph (see Fig. 5b), while coinciding with the boundary drawn by the 1000-mg/L mineralization. The regression line in this figure shows that the average Si value at *Alk* = 1.2 mg-equiv/L amounts to about 180 μM, while coinciding with that noted above. The behavior of other nutrients in the mixing
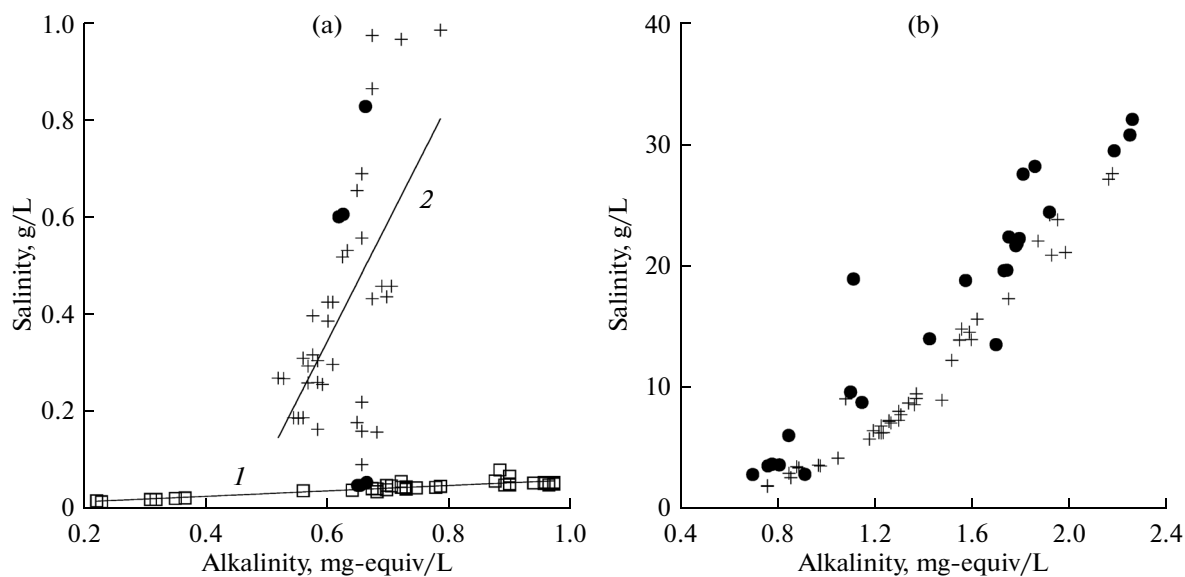
Fig. 6. Survey (2). The salinity−alkalinity ratio for the waters of mineralization below 1000 mg/L (a) and for the mixing zone of riverine and marine waters (b). See the notations in Fig. 1. The data of 2007 are also given (black circles).

zone shows in general the decrease of the concentrations with the growth of the salinity (as well as the decrease of $O_2\%$), but the scatter of the points is much wide. The analysis of these regularities is beyond the scope of this report.

Thus, the analysis of the mineralization−*Alk* relationship allowed us to distinguish during the survey (1) the different types of waters in the bay aquatic area: two purely riverine (flood and winter waters) and the mixture of winter and marine waters.

Survey (2) on September 18 to October 7, 2010. Now, consider the data of the autumn cruise. According to the logic used above, about 85 km³ of the winter waters should now be displaced out of the bay (see Table 2), and only flood and summer waters of the Ob and Taz rivers should occur there. These would be the biologically transformed waters being quite uniform in the *Alk*, *M*, and Si values with the average values of *Alk* = 0.8−1.0 mg-equiv/L, *M* = 400−500 mg/L, and Si = 40−60 μM. Nevertheless, the results of the IO RAS of 1993 and 2007 would be difficult to explain in this case.

However, the situation we should analyze in the same way as above in Fig. 1 appeared to be quite different. Figure 6a shows the *M*−*Alk* relationship for freshwaters, i.e., for those of mineralization below 1000 mg/L. One may see that the waters of low (less than 100 mg/L) and medium mineralization (100−1000 mg/L) are well distinguished again in the aquatic area of the bay. At that, the former showed still just the same *M*−*Alk* relationship as in Fig. 1a, and the latter show slightly varied *Alk* values of about 0.6−0.2 mg-equiv/L (below that in Fig. 1a). Figure 6b presents the *M*−*Alk* relationship for the mixing area of fresh and marine waters. Evidently, the extrapolated *Alk* value

for the waters of salinity below 5 g/L amounts also to about 0.6 mg-equiv/L; for more saline waters, it is somewhat higher (about 0.9 mg-equiv/L). This testifies that the average *Alk* value of 0.6 mg-equiv/L was formed not long before survey (2), being higher formerly. Thus, the three types of waters occur again in the bay aquatic area: one type is the mixture of riverine and marine waters and two types of riverine mineralization (below 1000 mg/L). These latter are even more distinct than those during survey (1).

Consider first the hydrochemical properties of these waters. Figure 7 shows the relationships between the Si, pH, and NO_3 values and the *Alk* value in the low-mineralized waters. It is seen that these three parameters increase synchronously with the *Alk* growth, which might be considered as the inhomogeneity of the summer waters, in which the content of nutrients increases with the growth of the *Alk* value. At that, the six left points on all these graphs belong to the three stations at the outlet of the Taz bay and show the minimum registered values of these parameters. The waters at the other stations are mixtures of the waters as such and the Ob River waters.

Because Fig. 6a allowed one to conclude that the alkalinity during survey (2) was of about the same value over most of the bay, being a low-informative parameter, the distribution of the hydrochemical parameters in medium-mineralized waters might be presented as the relationship of the nutrients and mineralization. Figures 8a, 8b, and 9 show the pH−*M*, NO_3−*M*, and Si−*M* relationships, respectively. It is seen that low- and medium-mineralized waters represented as such are also well distinguished, but the former show much wider variability then the latter. Quite the contrary, during survey (1), the waters of medium mineraliza-
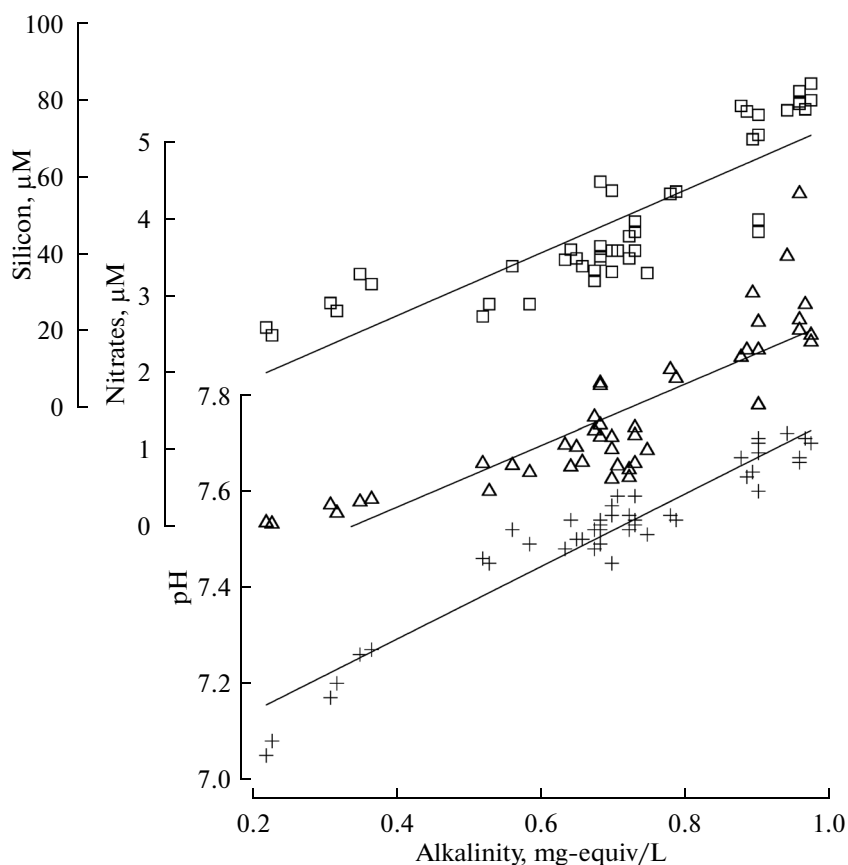
Fig. 7. Ratios of the Si, pH, and NO_3 values to the *Alk* value in the low-mineralized waters according to survey (2).

tion were less uniform than the low-mineralized waters. The origin of the low-mineralized waters was considered above. These are the summer waters of the Ob River and Taz Bay but before they might be mixed and transformed. The most difficult problem is how the medium-mineralized waters were formed. Easily, it should be assumed, as in [2, 8], that these are the same waters that were observed during survey (2), i.e., a mixture of purely riverine and marine waters, and their concentrations of nutrients were changed owing to biotransformation. However, it was shown above that the waters of 100−1000 mg/L mineralization according to survey (1) were constituted of riverine winter waters with no admixture of seawater. Therefore, the general explanation as such is not respective.

To find the explanation, consider the location of these waters in the bay shown in Fig. 10. It is seen that both the northern and southern boundaries of the medium-mineralized waters shifted considerably to the south as if they were dammed with saline waters. These latter became more abundant in the northern part of the bay compared to the first survey (Fig. 2). The volumes of all three types of waters and their average hydrochemical parameters are given in Table 3. It turned out that the volume of the high- and medium-mineralized waters increased, while that of the low-

mineralized waters (below 100 mg/L) decreased. The result as such is expectable in view of the possibility of the supply of seawaters to the bay with the decrease of the runoff of the riverine waters. However, this is contrary to the assumed changing of the waters owing to their simple displacement out of the bay. Moreover, why do the medium-mineralized waters show quite constant values of all the parameters but mineralization as such?

In our view, the weather factor must be included first of all. The winds over the bay were of northern and northeastern direction during the month before survey (2), thus providing a pileup of seawater. This is typical of the bay [6], whereas the time of survey (1) was characterized by typical winds of southern and southwestern directions causing negative setups of water, thereby intensifying the currents. Moreover, a pileup transforms the system of currents and promotes the horizontal mixing of the waters.

This was reflected in the features of the distribution of the parameters in the course of surveys (1) and (2). During survey (1), the flow was characterized by a pronounced jet mode, and the waters retained their characteristics after coming out of the Ob River bed to the Ob Bay. During survey (2), the low-mineralized waters were mainly constituted by the summer Ob waters with
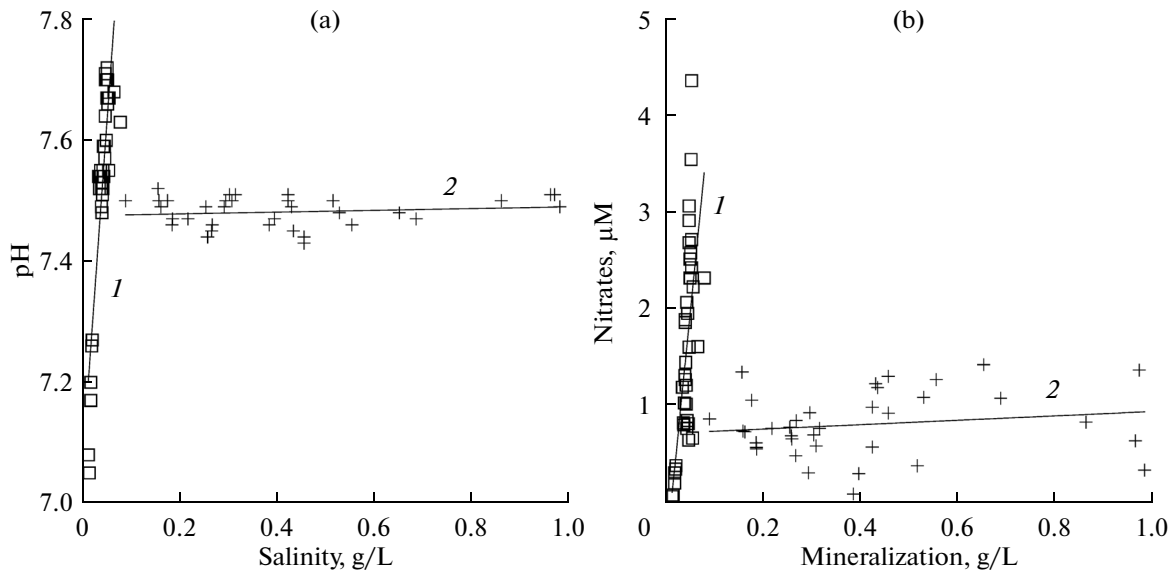
Fig. 8. Ratios of the pH and nitrate nitrogen values to the mineralization (a and b, respectively) for the riverine waters according to survey (2). See the notations in Fig. 6.
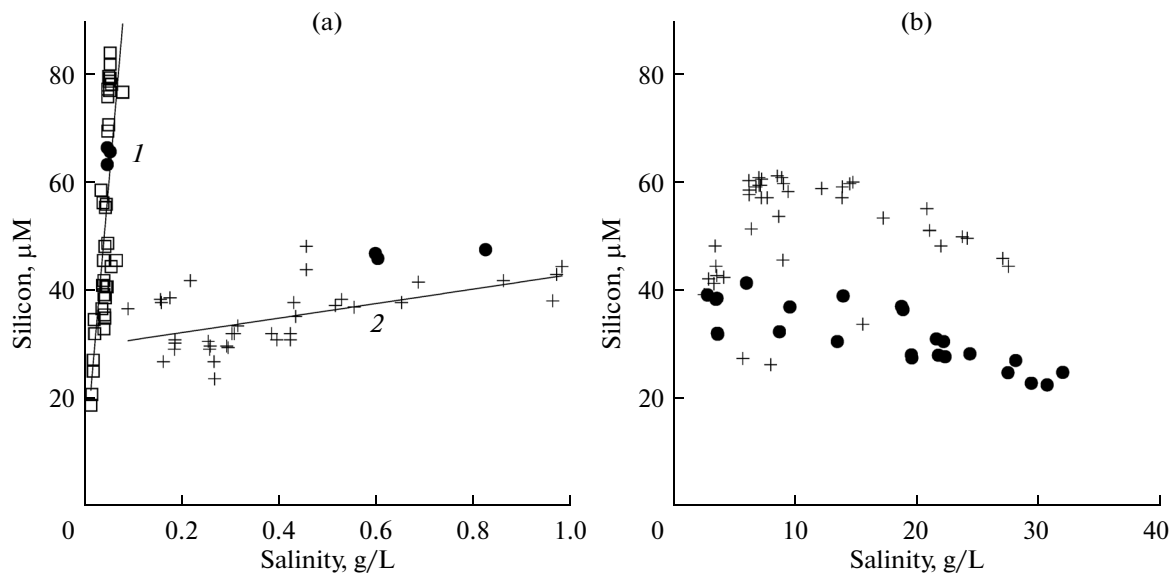

Fig. 9. Silicon–salinity ratio for the riverine waters (a) and for the mixing zone of the riverine and marine waters (b) according to survey (2). See the notations in Fig. 6.

an admixture of the Taz waters (as testified to by their volume). It is seen from Table 3 that the averaged parameters of the medium-mineralized waters of survey (2) might have been formed by those of the low-mineralized waters of survey (1) by the addition of about 1% saline waters ($S = 30$ g/L, $Alk = 2.4$ mg-equiv/L). The supply of seawaters with these parameters to the area of low-mineralized waters is difficult to conceive of because these waters are much separated spatially. The other mechanisms of salinization seem to be more probable: the carry-over of more saline waters from shoals to the deep stream, the wind-induced formation of streams in the surface layer, the transfer of salts by the air owing to the splitting, and the supply of salts from the underlying more saline layer under turbulent mixing. The latter way is the most reasonable and prevalent because this was registered at many of the northern stations during both surveys. However, it is characterized by the vertical gradient of the salinity, whereas the medium-mineralized waters of survey (2) showed just no gradient as such. Hence, the former ways of salinization are more probable here, although this question is still much unclear.
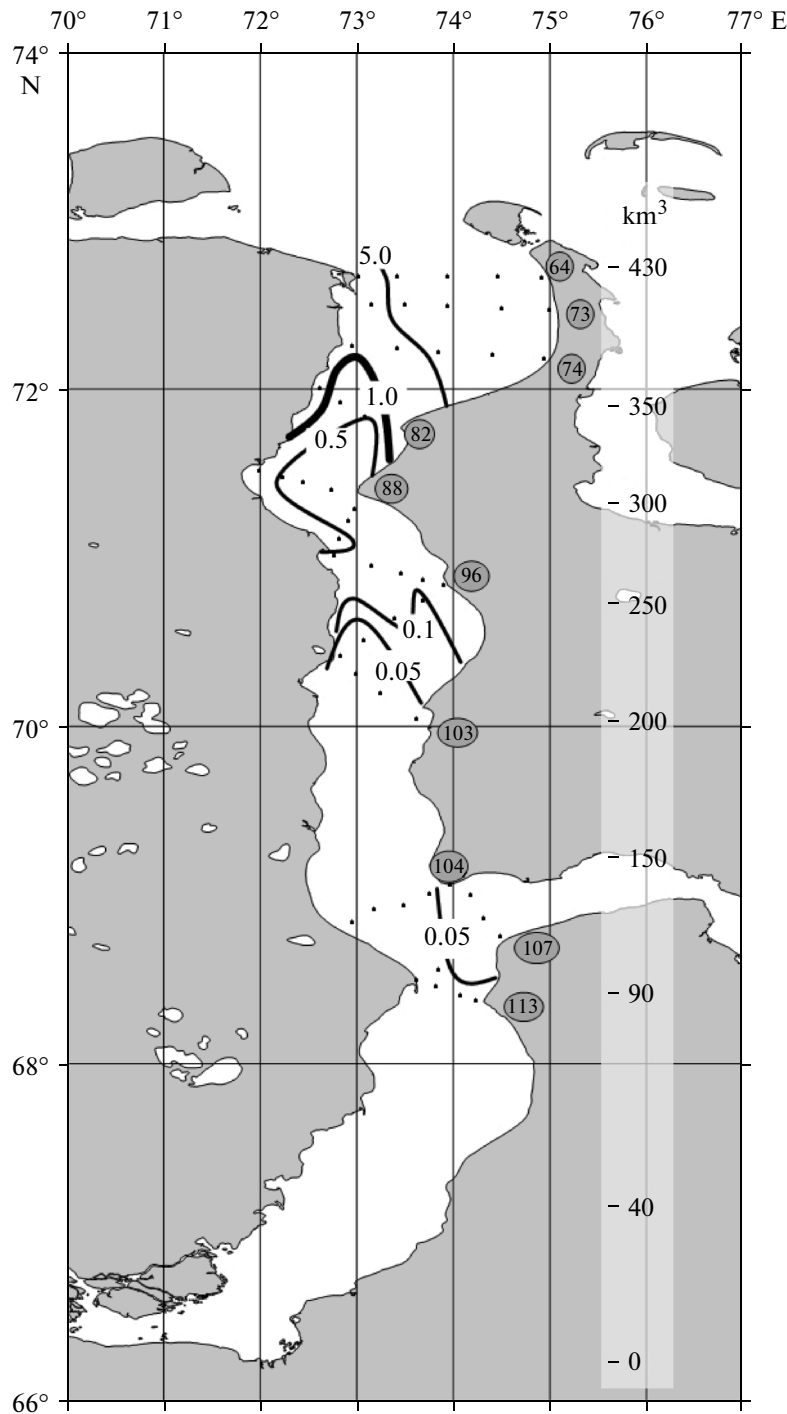
Fig. 10. Location of waters of different mineralization in Ob Bay according to survey (2). See the notations in Fig. 2.

Nevertheless, one may note that all these processes were intensified by winds and might have been started about a month before survey (2). In this case, the waters of higher salinity began admixing with the melt-waters and, respectively, their fraction should exceed that of purely marine waters. However, it is still difficult to calculate even roughly the properties of the

water formed as such. Moreover, the nonconservativity of the alkalinity owing to the oxidation of the organic matter might also be a complicating factor. By latitude, two opposite processes take place: while moving northwards, the *Alk* value decreased owing to oxidation but increases because of the considerable admixture of seawaters. Later on, besides the nutri-

Table 3. Volumes of different types of waters and their mineralization, average hydrochemical parameters, and standard deviations according to surveys (1) and (2)

Types of waters	Volume, km^3	Mineralization, mg/L	pH value	*Alk*, mg-equiv/L	O$_2$, %	Si, µM	NO$_3$, µM
Survey (1)							
Low-mineralized	176	47 ± 19	7.53 ± 0.36	0.60 ± 0.24	89.7 ± 14	30 ± 16	0.2 ± 0.4
Medium-mineralized	100	350 ± 210	**7.71** ± 0.21	1.17 ± 0.22	92.9 ± 4	133 ± 43	5.0 ± 3.4
Highly mineralized	62	12.3 ± 11 g/L	7.63 ± 0.14	1.69 ± 0.33	84.4 ± 9.4	120 ± 46	4.7 ± 1.9
Survey (2)							
Low-mineralized	130	42 ± 14	7.53 ± 0.18	0.72 ± 0.22	87.3 ± 0.6	53 ± 20	1.51 ± 0.96
Medium-mineralized	118	400 ± 240	7.42 ± 0.02	0.63 ± 0.06	86.1 ± 1	35 ± 6	0.84 ± 0.35
Highly mineralized	90	10.3 ± 7 g/L	7.56 ± 0.06	1.36 ± 0.39	88.2 ± 5.8	50 ± 10	2.1 ± 0.7

ents, the variations of the ions of the basic saline composition, being more conservative parameters than the alkalinity, should be of great importance to determine the processes of the formation of the waters.

The question in the Introduction concerning the way in which the simple linear relationships Si−*M* and *Alk−M* might be observed during the cruises by the IO RAS seems now to be quite easy. As shown above, the northern part of the bay is characterized by the processes averaging the concentrations of the nutrients and resulting in average *Alk* values of about 0.6−0.7 mg-equiv/L, as seen from Fig. 6a and well agreeing with the results of the expeditions by the IO RAS [13]. The waters formed as such (*Alk* ~ 0.6−0.7 mg-equiv/L and Si ~ 60 µM) would approach the seaward boundary of the bay and reach it before beginning the next flood in June (runoff of about 160 km^3, Table 2). These waters should be carried over to the sea and might become a base of a desalinated lens of the Ob River water. To the autumn of the same year (when the IO RAS usually an opportunity to perform a cruise), much various winter and flood waters would also be displaced from the bay, and a leveled averaged view should be seen there, as that during survey (2), especially with widely spaced stations. At that, the waters in the bay and in the desalinated lens would be similar to each other. Because of this, the preceding conclusions concerning the possibility to distinguish the Ob Bay waters in the Kara Sea [13, 21] seem to be true despite the overlooked significant fact that these were waters of different years.

CONCLUSIONS

The presence of water of quite different compositions in the bay, such as the winter and flood waters, must be taken into account when considering the environmental conditions in the bay. As we know, this was overlooked until recent times.

The replacement of different waters in the bay gives the impression that the variability of the nutrient concentrations might be caused by intense biological processes of C$_{org}$ production and destruction [9, 15]. According to [9]: "the primary production in the 'riv-

erine' part of the bay estimated as 2−3 g C/(m^2 day) is produced exclusively based on the before-vegetation resource of nutrients. At that, mineral nitrogen is the limiting element. By the values of the primary production, the entire Ob Bay may be assigned to the most productive coastal aquatic areas of the World Ocean." However, in view of the above-shown occurrence of waters of different ages in the bay, we think that the estimation of the primary production using the dynamics of the nutrients should be incorrect and considerably overvalued.

We suppose that the replacement of waters of different geneses but not the utilization of nutrients by phytoplankton is the main cause of the variations of the content of nutrients both over the bay area and with time (between the two surveys).

The new studies of the Ob Bay, including the surveys in July−August and even from the ice cover in the preceding months, might considerably clarify the replacement of the waters in the bay and their productivity.

REFERENCES

1. O. A. Alekin, *General Hydrochemistry* (Gidrometeoizdat, Leningrad, 1954) [in Russian].

2. K. V. Artamonova, S. A. Lapin, O. N. Luk'yanova, P. N. Makkaveev, and A. A. Polukhin, "The features of the hydrochemical regime in Ob inlet during the open water time," Oceanology (Engl. Transl.) **53** (3), 317−326 (2013).

3. D. B. Babich, D. Yu. Bol'shiyanov, A. A. Zaitsev, et al., "Regional peculiarities in formation of estuary-delta systems of Arctic coast of Siberia," in *Estuary-Delta Systems of Russia and China,* Ed. by V. N. Korotaev (GEOS, Moscow, 2007), pp. 112−240.

4. I. A. Gangnus, O. N. Luk'yanova, and N. V. Arzhanova, "Time-spatial variability of hydrochemical regime of the Ob Inlet," in *Int. Sci. Conf. "Marine Studies of Polar Regions in the International Polar Year 2007/08"* (Arkt. Antarkt. Nauchno-Issled. Inst., St. Petersburg, 2010), p. 55.

5. V. V. Gordeev, *Geochemistry of the River-Sea System* (Izd. I.I. Matushkina, Moscow, 2012) [in Russian].

6. V. V. Ivanov, "Hydrological regime of lower reaches and estuaries of the West Siberian rivers and a problem of assessment of changes caused by territorial redistribution of water resources," Probl. Arkt. Antarkt., No. 55, 20–43 (1980).

7. V. V. Kuznetsov, I. M. Efremkin, N. V. Arzhankin, et al., "Current condition of the ecosystem of the Ob Inlet and its importance for fishery," in *Problems of Commercial Oceanology* (VNIRO, Moscow, 2008), Vol. 5, No. 2, pp. 129–154.

8. S. A. Lapin, "Hydrological characterization of the Ob Inlet in the summer and autumn seasons," Oceanology (Engl. Transl.) **51** (6), 925–934 (2011).

9. S. A. Lapin, Candidate's Dissertation in Geography (VNIRO, Moscow, 2012).

10. S. A. Lapin, E. L. Mazo, and P. N. Makkaveev, "Integrated research on the Gulf of Ob (July to October 2010)," Oceanology (Engl. Transl.) **51** (4), 711–715 (2011).

11. A. P. Lisitsyn and M. E. Vinogradov, "International high altitude expedition in the Kara Sea (49th cruise of R/V *Dmitry Mendeleev*)," Okeanologiya (Moscow) **34** (5), 643–651 (1994).

12. P. N. Makkaveev, V. V. Gordeev, P. A. Sunzhas, et al., "Assessment of hydrochemical outflow of the Ob River during winter according to research works in December of 2001," in *Ecological and Biochemical Studies in the Ob River Basin*, Ed. by V. V. Zuev et al. (Tomsk, 2002), pp. 8–20.

13. P. N. Makkaveev, P. A. Sunzhas, and P. V. Khlebopashev, "The distinguishing of the Ob and Yenisei waters in the desalinated lenses of the Kara Sea in 1993 and 2007," Oceanology (Engl. Transl.) **50** (5), 698–705 (2010).

14. V. N. Mikhailov, *Estuaries of Russian Rivers and Adjacent Countries: Past, Present, and Future* (GEOS, Moscow, 1997) [in Russian].

15. S. V. Pivovarov, *Chemical Oceanography of the Arctic Seas of Russia* (Gidrometeoizdat, St. Petersburg, 2000) [in Russian].

16. E. I. Polyakova and Kh. Kassens, "Diatoms of Siberian Arctic seas," in the *System of the Laptev Sea and Adjacent Arctic Seas*, Ed. by Kh. Kassens (Mosk. Gos. Univ., Moscow, 2009), pp. 427–447.

17. *Nature of Yamal*, Ed. by L. N. Dobrinskii (Nauka, Yekaterinburg, 1995) [in Russian].

18. *Manual on Chemical Analysis of Marine and Fresh Waters during Environmental Monitoring of Fishery Reservoirs and the Regions of the World Ocean Prospective for Commercial Fishery*, Ed. by V. V. Sapozhnikov (VNIRO, Moscow, 2003) [in Russian].

19. I. V. Samoilov, *River Estuaries* (Geografiz, Moscow, 1952) [in Russian].

20. *Modern Hydrochemical Methods for Oceanological Studies*, Ed. by O. K. Bordovskii and V. N. Ivanenkov (Inst. Okeanogr., Akad. Nauk SSSR, Moscow, 1992) [in Russian].

21. P. A. Sunzhas, "Division of Yenisei and Ob waters in the Kara Sea according to alkalinity and silicon," Okeanologiya (Moscow) **35** (2), 215–219 (1995).

22. M. V. Flint, "Cruise 54th of the research vessel *Akademik Mstislav Keldysh* in the Kara Sea," Oceanology (Engl. Transl.) **50** (5), 637–642 (2010).

23. P. Ya. Tishchenko, K. Wallmann, N. A. Vasilevskaya, et al., "The contribution of organic matter to the alkaline reserve of natural waters," Oceanology (Engl. Transl.) **46** (2), 192–199 (2006).

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