ISSN 0001-4370, Oceanology, 2017, Vol. 57, No. 1, pp. 48–57. © Pleiades Publishing, Inc., 2017.
Original Russian Text © P.N. Makkaveev, A.A. Polukhin, A.V. Kostyleva, E.A. Protsenko, S.V. Stepanova, Sh.Kh. Yakubov, 2017, published in Okeanologiya, 2017, Vol. 57, No. 1, pp. 57–66.

MARINE CHEMISTRY

Hydrochemical Features of the Kara Sea Aquatic Area in Summer 2015

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Received June 30, 2016; in final form, September 26, 2016

Abstract—During cruise 65 of the R/V *Akademik Mstislav Keldysh* in the Kara Sea, three transects were executed: one eastwards from the Novaya Zemlya Archipelago and two in the St. Anna and Voronin troughs. It was noted that the continental runoff affected the entire surveyed aquatic area, even at the northern extremity of the Novaya Zemlya Archipelago. The transect along the St. Anna Trough showed the presence of a slope frontal zone overlaid at the surface by a desalinated layer. The Voronin Trough was characterized by sliding of slope waters. The hydrochemical parameters show that the surveys were carried out during a recession of biological activity of the waters and that the peak bloom was over by that time. The hydrochemical structure of waters conformed to early autumn conditions, but before the beginning of intense cooling of surface waters.

DOI: 10.1134/S0001437017010088

INTRODUCTION

Cruise 63 of R/V *Akademik Mstislav Keldysh* continued hydrochemical studies of the Kara Sea performed by preceding expeditions of the Institute of Oceanology (IO RAS) since 1993 until the present [4, 5, 7–10, 20]. The main line of studies in the Kara Sea in 2015 was research of the propagation of transformed riverine runoff waters, as well as processes occurring on the continental slope. Moreover, studies started in 2007 in the bays of the Novaya Zemlya Archipelago were continued. Figure 1 shows the disposition of stations and sampling sites over the aquatic area of the Kara Sea. The key areas of surveys are marked as transects I, II, and IV. Transect III was situated in the aquatic area of the Laptev Sea and will be considered in another report [17]; a special publication will also deal with studies in the bays of the Novaya Zemlya Archipelago [16].

MATERIALS AND METHODS

The expedition in the Kara Sea included two stages: the first from August 30 to September 3 (transect I) and the second from September 19 to October 6, 2015 (transects II and IV). The samples were collected by means of 5-L plastic Niskin bottle samplers of Rosette equipment in accordance with GOST 51592–2000 *General Requirements for Sample Collection*. The samples for dissolved oxygen and ammonium nitrogen were fixed immediately after sampling. The samples for determining pH values and nutrients (silicates, phosphates, and nitrogen forms) were collected into 0.5-L plastic containers with no preservation. The pH and total titrated alkalinity (Alk) values, along with the concentrations of dissolved oxygen, nitrate, nitrite and total nitrogen, mineral and total dissolved phosphorus, and dissolved silicon, were determined in the onboard laboratory. The measurements were carried out within 6 h of the sampling time. Like on the preceding IO RAS expeditions, hydrochemical measurements were carried out by standard procedures used in Russian oceanological studies [12, 13, 15]. The use of a unified procedure by all expeditions provides a means for correct comparison of surveys of different years.

When surveyed in waters containing a great deal of particulate matter (in bays and bights, as well as in the mixing zone of riverine and marine waters), the samples for nutrients were filtered beforehand with 0.45-μm filters. The colorimetric data for mineral phosphorus and silicates in visually colored water samples were corrected for water coloration by appropriate procedures [13, 15].

RESULTS

The studies of the waters of continental origin. The abundance of riverine runoff supplied to the aquatic area of the Kara Sea causes a permanent presence of transformed continental waters in the surface layer of the aquatic area of the sea. These waters, characterized

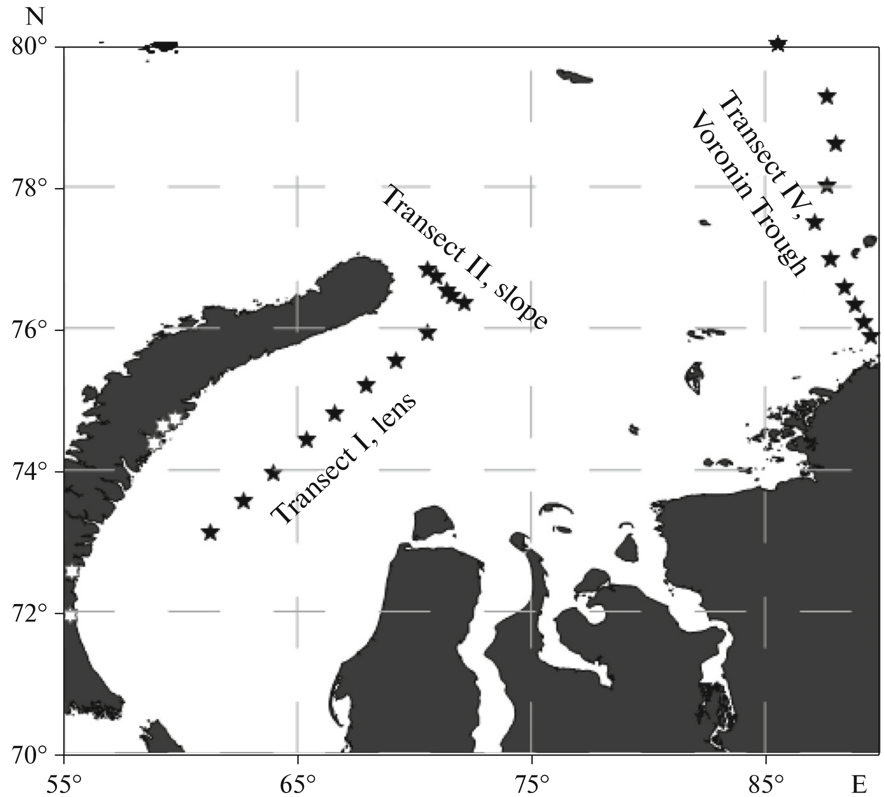

Fig. 1. Scheme of surveys in Kara Sea during cruise 63 of R/V *Akademik Mstislav Keldysh*.

by decreased salinity, increased turbidity, and peculiar chemical composition, form more or less steady structures on the sea surface. These structures are commonly called lenses [1, 18] or surface desalinated layers [2]. The identification of these waters, along with studies of their propagation over the aquatic area, have long been carried out [14]. By now, the Alk/salinity ratio (specific alkalinity, Salk) is considered as one of the key characteristics of the propagation of riverine runoff; these ratios of over 0.06–0.07 point uniquely to the presence of riverine waters.

The most pronounced occurrence of riverine waters was recorded in transect I, which was specially executed to study a lens of low-saline waters (Fig. 1). By the values of specific alkalinity in the transect, the influence of continental runoff was traced over the entire surface layer to depths of 10–15 m (Fig. 2a). The core of desalination in the transect conforms to station 5207. The considered effect of riverine runoff was also seen in transects II and IV. The transect II along the branch of the St. Anna Trough (the most distant from the coasts) showed the influence of riverine runoff mainly in the southern part (Fig. 2b). The thickness of the water layer subjected to the pronounced affect of continental runoff is about 10 m on average. The influence of riverine waters is less pronounced in the transect at the Voronin Trough but it manifests itself to the depth of 30 m in the northern part of the transect and deeper than 50 m in the southern part (Fig. 2c).

The presence of transformed riverine waters was recorded by all preceding IO RAS expeditions. The surface desalinated layer was characterized by an irregular chemical composition (table) depending on the degree of transformation, existence time, and, above all, the composition of runoff from the main rivers of the region, which can vary both interannually and interseasonally [10, 19]. However, it should be noted that, according to all the surveys, the Salk–salinity relationships fit the same curve, which might point to their common origin (Fig. 3a). This is also true for the dissolved silicon–salinity ratios (Fig. 3b).

As a rule, continental waters are very enriched in dissolved silicon compared to seawaters. The content of dissolved silicon (silicates) is commonly used as a tracer for the propagation of riverine waters. Therefore, the presence of continental runoff waters in transect I can be also identified by the distribution of dissolved silicon (Fig. 4). The maximum silicon content (39 μM) was recorded at station 5207. Similarly to Salk values, the influence of riverine waters was traced by the 10-μM isoline to depths of 10–15 m at stations 5203–5209. Deeper, a decrease in silicon content with increasing salinity was seen and the concentration of silicon was as low as 2–5 μM in the 15–20 m layer. At some of the stations (5200–5203), the silicon content

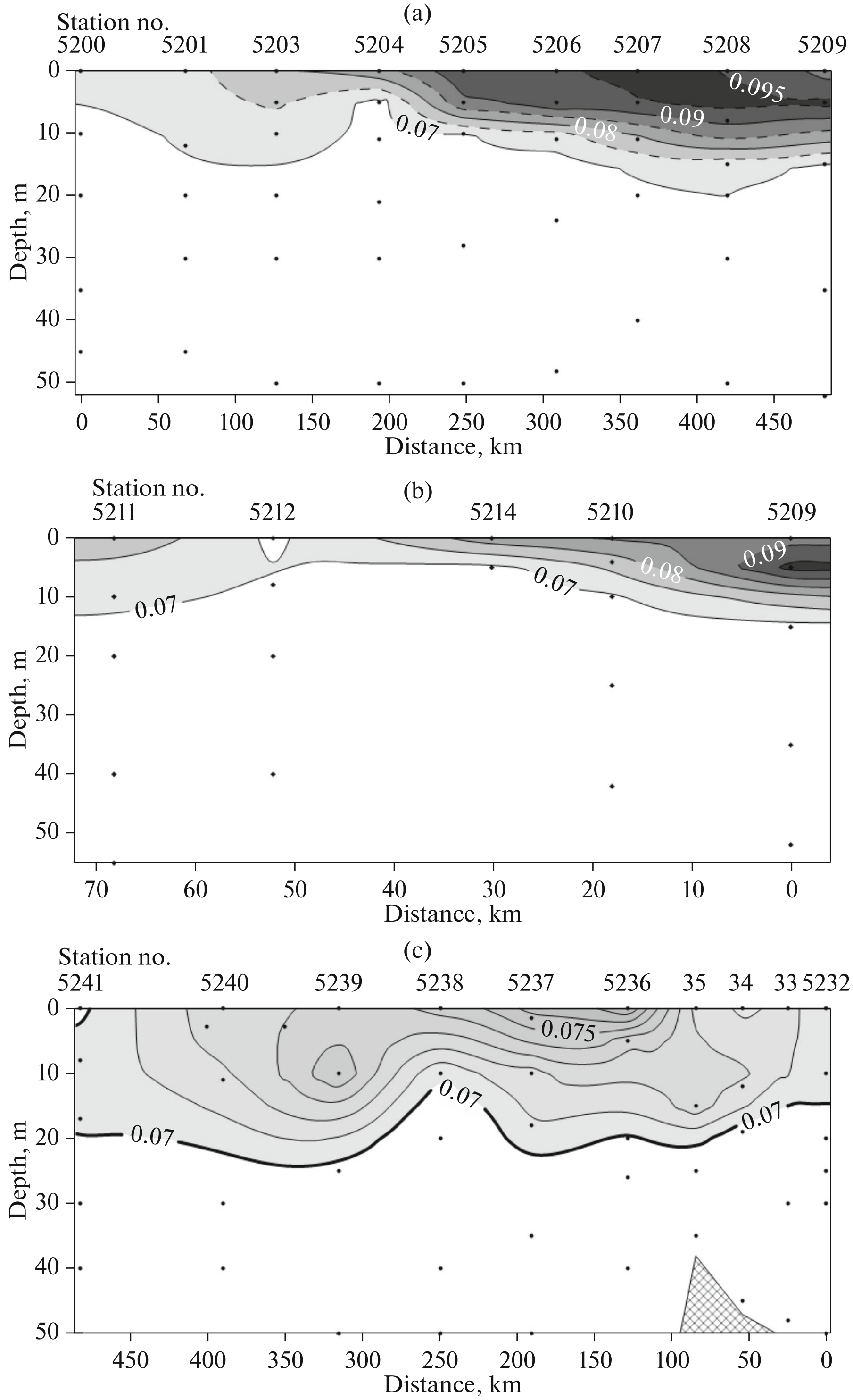

Fig. 2. Alkalinity–salinity ratios for upper 50-m layers of transects: (a) I, (b) II, and (c) IV.

was close to analytical zero at depths of 10–50 m. Furthermore, an increase in silicon content with depth took place (to 6–8 μM in the near-bottom layer). A similar distribution of dissolved silicon was also seen in transects II and IV, considered below.

The distribution of other nutrients (phosphates, nitrate and nitrite forms of nitrogen) was common for a warm season in this region (Fig. 5). The surface layer contained extremely little phosphates and nitrate nitrogen: less than 1 μM of nitrate nitrogen and, Hydrological and hydrochemical characteristics of surface desalinated water layer in Kara Sea from data of IO RAS expeditions

Obtained values	*T*, °C	*S*, psu	pH, NBS	Alk, mg-equiv/L	PO_4, μM	Si, μM	NO_2, μM	NO_3, μM	NH_4, μM	Salk
September 1993										
Minimum	1.57	10.188	8.003	1.397	0.05	8.4	0.00	0.00	0.05	0.074
Maximum	4.80	24.343	8.14	1.870	0.2	52.0	0.08	0.24	0.78	0.137
Average	2.92	16.713	8.05	1.587	0.14	31.7	0.0214	0.06	0.33	0.100
September 2007										
Minimum	4.88	25.369	8.08	1.997	0.14	10.9	0.00	0.00	0.17	0.075
Maximum	6.35	28.108	8.17	2.121	0.31	16.0	0.02	0.70	0.73	0.080
Average	5.66	26.397	8.12	2.050	0.21	14.3	0.01	0.28	0.40	0.078
September 2011										
Minimum	1.81	15.085	8.05	1.534	0.12	21.0	0.02	0.1	0.84	0.076
Maximum	4.93	25.73	8.13	1.944	0.77	38.1	0.31	5.96	1.09	0.104
Average	4.02	22.5	8.09	1.657	0.24	33.4	0.081	1.16	0.96	0.094
September 2013										
Minimum	3.17	19.000	7.87	1.676	0.07	2.37	0.00	0.00	0.34	0.074
Maximum	5.92	29.900	8.12	2.226	0.34	32.3	0.42	0.05	2.15	0.088
Average	4.67	25.250	7.99	1.984	0.19	14.2	0.13	0.034	0.87	0.079
August 2014										
Minimum	0.59	0.03	7.35	1.565	0	0.47	0.00	0.00	0	0.067
Maximum	8.68	34.69	8.34	2.182	47.36	77.23	0.17	6.5	7.5	0.172
Average	4.65	20.03	8.01	1.932	3.79	20.16	0.07	0.67	1.4	0.085
September 2015										
Minimum	5.75	16.400	7.85	1.542	0.05	8.3	0.10	0.03	0.60	0.073
Maximum	8.70	28.591	8.09	2.089	0.18	39.4	0.64	0.08	3.20	0.098
Average	7.35	20.128	7.99	1.732	0.14	28.4	0.41	0.04	1.34	0.088

sometimes, even down to analytical zero for phosphates. In view of the concentrations, phosphates might be a limiting factor of phytoplankton development. The concentrations of all nutrients increased in the near-bottom layer (Fig. 5), owing to the oxidation of organic matter supplied from the upper layers. This is also confirmed by saturation of waters by dissolved oxygen. The surface layer of transect I was saturated in oxygen for 100% exclusively at stations with maximum salinity (5200 and 5201). This value was 95% or less in the area of more intense effect of riverine runoff. This was probably because the intensity of the oxidation processes of organic matter supplied with continental runoff became comparable to that of the processes of organic matter synthesis, which is quite reasonable for the considered season (late summer–early autumn). The subsurface maximum of oxygen content, very characteristic of the Kara Sea [18], was found solely at station 5201. The deep layers undergo no oxygen deficiency, and the water mass is quite well aerated: the degree of saturation was 77% at the deepest point of the transect (250 m; Fig. 6).

Hydrochemistry of the slopes. The processes occurring on the continental slope, especially the features of slope fronts in the hydrochemical structure of waters, were studied in two transects across branches of the St. Anna and Voronin troughs (transects II and IV). It is seen that precisely all of the surface waters of the transects were subjected to the pronounced impact of continental runoff, as mentioned above. Along with increased Salk values in surface waters on these transects (Figs. 2b and 2c), very increased concentrations of dissolved silicon were also recorded (Fig. 7). One can see that the layer with a considerable presence of riverine waters was thicker in transect IV located closer to the coasts. The area with a Salk coefficient of 0.078 was distinguished at central stations of the transect; all stations except nos. 5232, 5234, and 5241 were subjected to slight desalination. The core of a desalinated lens was found at stations 5236 and 5237. The

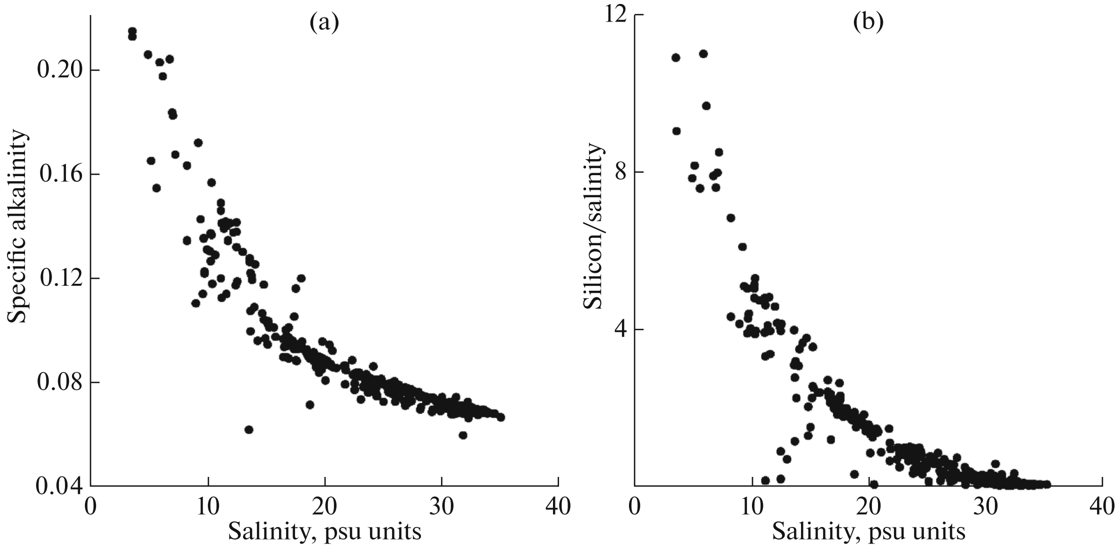

Fig. 3. Dependence of specific alkalinity (a) and silicon–salinity ratio (b) on salinity for transformed riverine water from survey data.

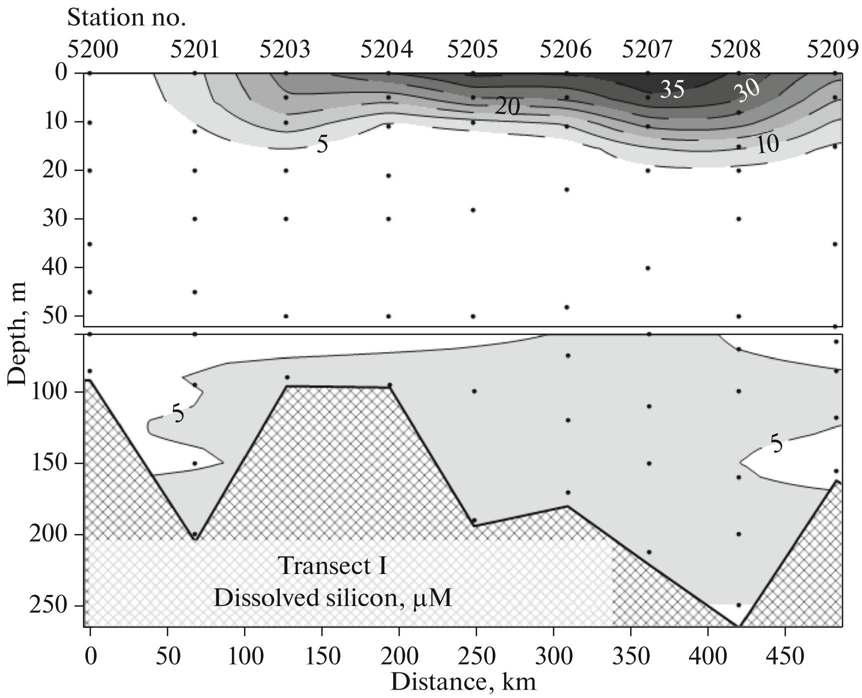

Fig. 4. Distribution of dissolved inorganic silicon (μM) on transect I.

core of desalinated water in transect II was located at station 5209 within the 5-m layer. Farther to the northwest, this layer degenerated and station 5212 showed a Salk value of 0.068, which indicated the presence of virtually pure marine waters. The Salk coefficient again reached more than 0.07 at station 5211, which testified to the presence of continental fresh waters.

One can see that the distribution of dissolved silica in the surface layer (Fig. 7) was similar to that of the Salk values. The maximum silicate content in transect II was recorded at station 5209. Station 5212 showed values of about analytical zero, which is peculiar for waters in the northern Kara Sea not subjected to riverine runoff impact. The maximum silicon content in surface waters of transect IV (11.5 μM) was found at station 5236, with a decrease down to 1.0–1.5 μM in surface waters of the northern and southern parts of the transect. Below the surface desalinated layer, that of decreased silicon content was seen in both transects.

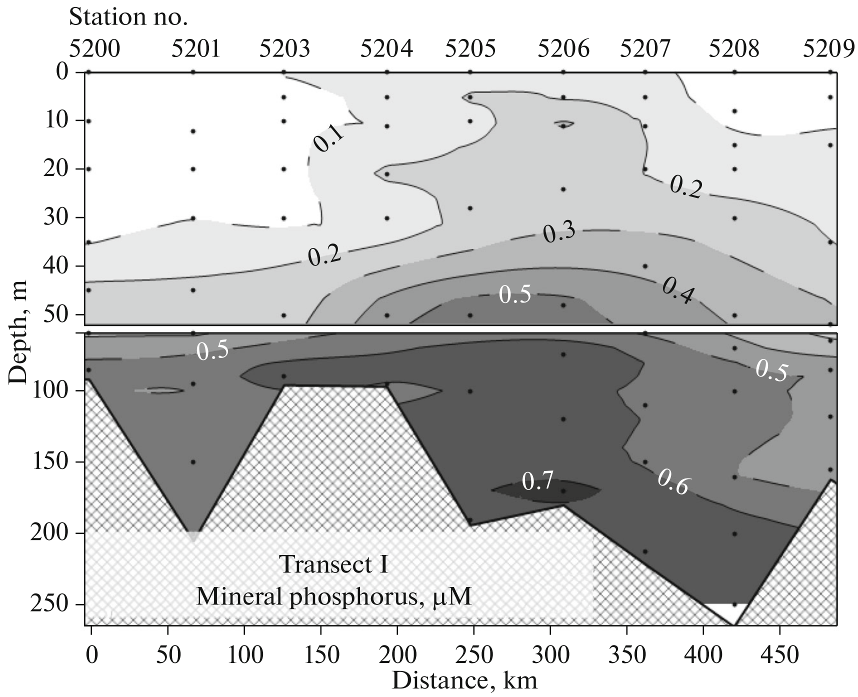

Fig. 5. Distribution of dissolved inorganic phosphorus (μM) on transect I.

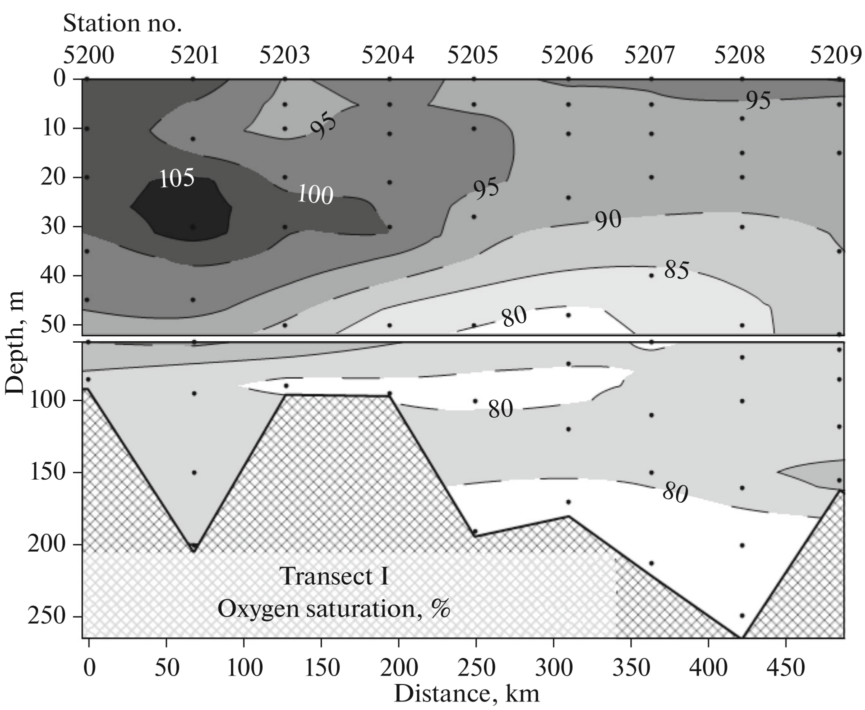

Fig. 6. Saturation of waters in dissolved oxygen (%) on transect I.

The silicon concentrations were 1–2 μM to depths of 50 m and decreased below 1 μM in the seaward parts. A gradual and monotonic increase in silicon content towards the bottom was recorded deeper than 50 m.

As expected, the hydrological characteristics in transect II revealed the slope frontal zone, which was also observed by preceding expeditions [21]. The front extended between stations 5210 and 5214, somewhat closer to the latter. The frontal zone within the upper 20-m layer was most probably removed by transformed waters of continental runoff. Residues of these waters were found in the northern seaward part of the

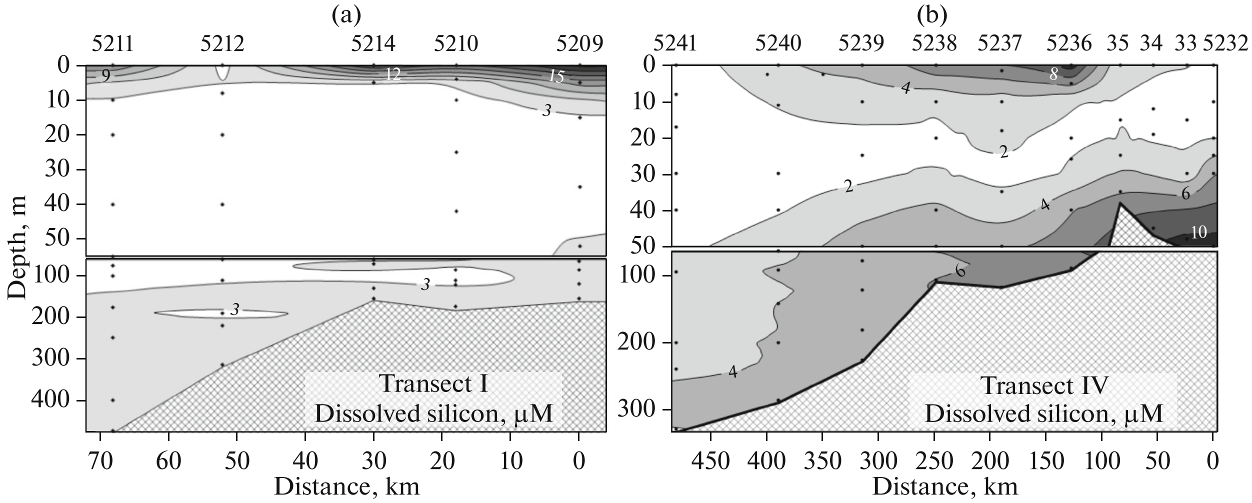

Fig. 7. Distribution of dissolved inorganic silicon (μM) on transects II (a) and IV (b).

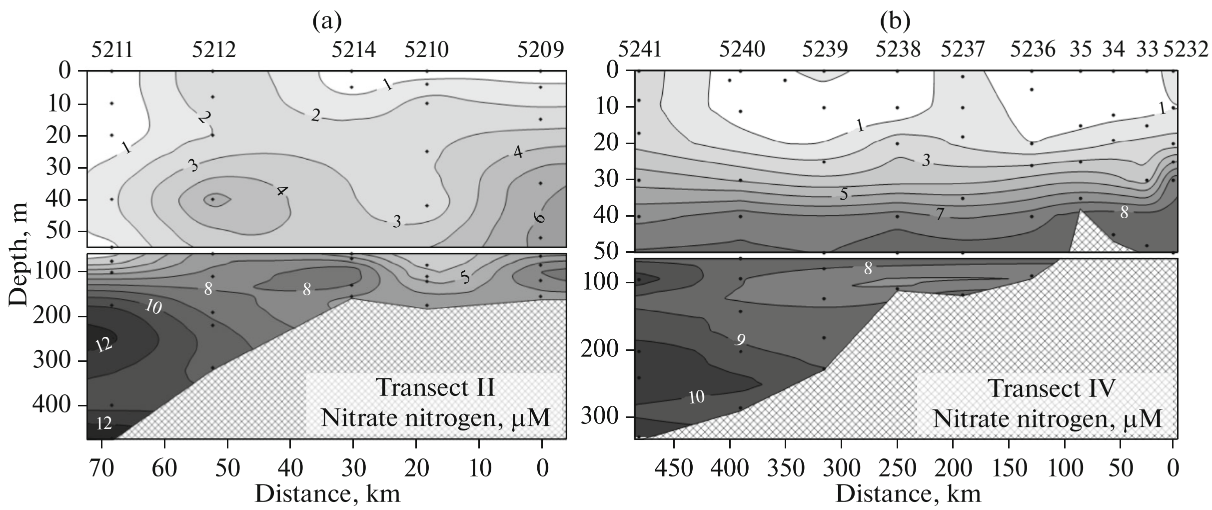

Fig. 8. Distribution of nitrate nitrogen (μM) on transects II (a) and IV (b).

transect. Pronounced variations of temperature and salinity peculiar to frontal zones were seen from a depth of about 30 m. It should be noted that this frontal zone was less pronounced in its hydrochemical rather than hydrophysical and biological parameters. Variations in the characteristics such as the concentrations of mineral forms of nitrogen and dissolved oxygen, as well as of oxygen saturation, if manifested at all, were within the sensitivity of the detection method. Upon passage to the seaward part of the transect, the dissolved silicon content somewhat decreased. Conversely, the pH and alkalinity values increased, as well as the dissolved oxygen content.

Completing the description of the transect II, we can assert that the flow of Barents Sea waters was traced at the seaward part of the transect, which was confirmed by hydrophysical surveys, as well as by the species composition of zooplankton peculiar to the waters of the Barents Sea. Nitrate nitrogen concentrations of 3 μM in the upper 20-m layer can also be considered indirect evidence of the presence of Barents Sea waters (Fig. 8). Mineral nitrogen and phosphorus in the upper 50-m layer of the transect were contained in the amounts which might be limiting factors of the development of phytoplankton. The concentration of phosphates was within 0.1–0.3 μM, while the phosphate content below 0.5 μM should prevent the development of phytoplankton. The content of nitrate nitrogen was below 1 μM in the seaward part of the transect. Evidently, a deficiency of nutrients caused the oxygen unsaturation in the upper productive layer of the sea, although less pronounced than that in the transect I. Deeper than 50 m, the growth of concentrations was recorded for all the forms of nutrients.

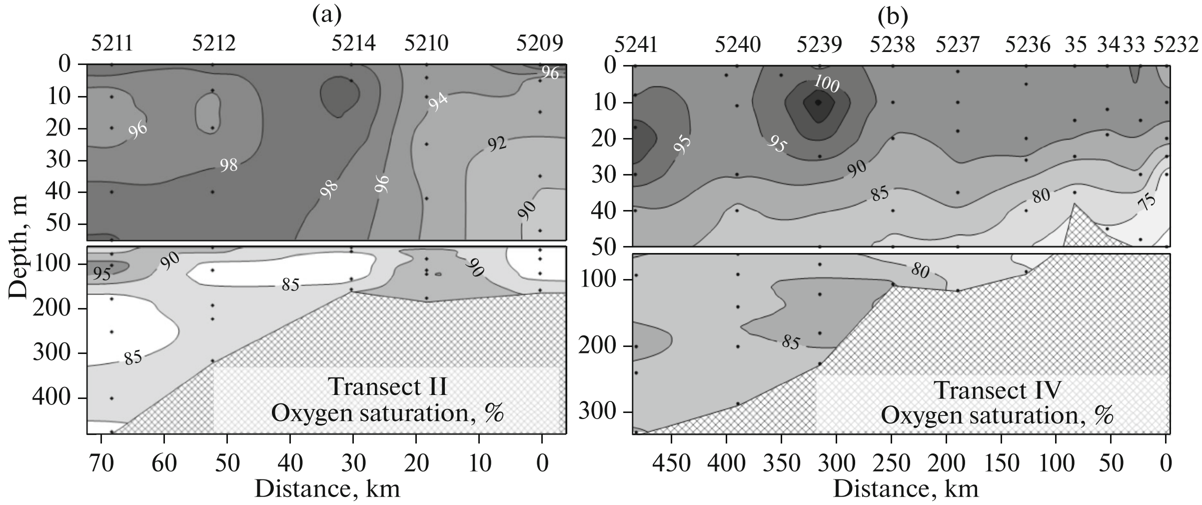

Fig. 9. Distribution of degrees of water saturation with dissolved oxygen (%) on transects II (a) and IV (b).

The hydrochemical characteristics make it possible to suppose that the time of intense photosynthesis was over. The oxidation of organic matter, if not yet intense, prevailed in the upper layer. The initiated oxidation process was confirmed by the distribution of ammonium nitrogen. Concentrations over 1 μM in the southern part of the transect at stations 5209, 5210, and 5214 point to the oxidation of organic nitrogen into mineral forms; ammonium nitrogen is the initial form of this process. Nevertheless, despite the deeper northern part of transect II compared to transect I, the oxygen saturation of deep layers was 85% or more.

The hydrochemical structure of transect IV from the shallow coastal area near the Taimyr Peninsula northwards to the Voronin Trough (Fig. 1) shows some peculiar distinctions compared to transect II. The area affected considerably by freshwaters and distinguished by the surface layer at central stations of transect IV was characterized by an increased total nitrogen content, which indicates a high concentration of organic nitrogen supplied with continental runoff. The surface layer at station 5241 in the seaward part of the transect was characterized by a slight decrease in the Salk value with decreased salinity, which might have been caused by the considerable content of meltwaters in this part of the transect. It is interesting that the same station showed an increased nitrate nitrogen content (2.5 μM) compared to the other parts of the upper 20-m layer (Fig. 8), whereas a nitrate nitrogen concentration below 1 μM in the surface layer at other stations might be a limiting factor for the development of phytoplankton.

Similarly to other transects in the Kara Sea, the oxygen saturation of the surface layer was below 100%. The low oxygenation of water combined with an ammonium nitrogen content about 1 μM demonstrates the prevalence of the destruction of organic matter and the completion of the time of intense photosynthesis. Water oxygenation over 100% was recorded fragmentarily within the 10–20 m layer (Fig. 9). Probably, these were residues of the effect described back in 1995 by Stunzhas based on results of an expedition of R/V *Dmitrii Mendeleev* to the Kara Sea in 1993 [18], as well as by other authors. The effect consisted in the onset of an intense phytoplankton bloom in spring under the ice of the Kara Sea with fast oxygenation of the underice water layer. With ice melting and a supply of fresh flood waters from Siberian rivers, this oxygen-supersaturated layer of denser seawater was overlain by a lighter freshwater layer, as though it became "conserved." This layer could have exist for several months and was recorded and described repeatedly by recent IO RAS expeditions to the Kara Sea.

Of interest is also a considerable increase in the concentrations of dissolved mineral phosphorus (over 0.6 μM) and silicon (to 10 μM) in near-bottom waters of the southern part of transect IV (stations 5232–5236). This was probably the effect of water creep (cascading), quite common in the Arctic [3]. This is also confirmed by layering in the silicon and nitrate nitrogen distribution in waters deeper than 50 m at the central and northern parts of transect IV (Figs. 7b and 8b).

By means of repeatedly executed stations 5205 and 5214, it was possible to trace the variability of the hydrochemical structure of waters (the time intervals between measurements at the stations was 23 and 20 days, respectively, i.e., on a synoptic scale). Station 5205 was affected by powerful continental runoff, and key transformations of the hydrological and hydrochemical structure of water proceeded in the upper 10-m layer. The profiles of all considered parameters began to level off three weeks after the former measurements. However, complete mixing was hampered by pronounced stratification of a water mass peculiar to the studied area of the Kara Sea, and occurring under the action of continental runoff to the sea surface layer.

Another situation was observed at station 5214, located on transect II and characterized by quite weak action of continental runoff on the surface layer. While the water mass was stratified during a previous survey, with a pronounced layer of decreased salinity, complete leveling of the profile of the hydrological and hydrochemical parameters was observed 20 days later. Some of these parameters showed no significant changes over the entire profile (e.g., alkalinity and silicon) and others decreased in absolute values (phosphates and nitrates).

DISCUSSION AND CONCLUSIONS

All the surveyed areas of the sea were subjected to the action of continental runoff. A pronounced effect was recorded even at the seaward part of transect II near the northern extremity of the Novaya Zemlya archipelago. Earlier [14], the ingress of transformed riverine waters was seen in the Kara Sea even much farther to the north. It is possible to say that, considering the boundary of the river mouth area by the conventional definition [11], almost the entire Kara Sea should be regarded as the mouth area of the Yenisei and Ob rivers [6]. The propagation of desalinated waters over the aquatic area is determined by weather conditions, as well as the runoff volume and time distribution. Thus, in the course of the considered expedition, the dynamics of the surface desalinated layer under wind action resulted in leveling of the slope front in surface waters, and the frontal zone was recorded only below the halocline.

Despite the abundance of riverine runoff, the waters were characterized by low photosynthetic activity. Water oxygenation over 100% was mainly recorded in subsurface waters as a relic of early bloom. A significant decrease in the dissolved silicon content (utilized by common species of phytoplankton) under the water layer of decreased salinity might probably be caused by the mentioned effects. To depths of about 50 m, the concentrations of nutrients (phosphates and nitrate nitrogen) were low. The appearance that waters subjected to voluminous runoff of continental waters were depleted in nutrients (excluding silicon) was observed quite frequently in the Arctic seas. This might have resulted from several causes. First, the bulk of nutrients are utilized in water mixing zones (estuarine fronts), which belong as a rule to the most productive areas. Second, the nutrients supplied by high-latitude rivers and passing through the mixing zone might probably be in forms poorly assimilated by phytoplankton. Third, the presence of a desalinated layer intensifies the water stratification and hinders the supply of nutrients to the zone of intense photosynthesis from deeper layers of the aquatic area. A more general cause of low bioactivity in waters during the considered surveys might be in end of the main peak of bloom and the prevalent oxidation of organic matter.

Repeated measurements of the hydrochemical parameters at some of the stations have shown that the density stratification caused by the occurrence of the surface desalinated layer might retard or even stop the transformations of the hydrochemical structure of waters under the impact of weather processes on a synoptic time scale. Moreover, it is the "locking" effect of the desalinated layer that caused the occurrence of the above-mentioned relic-bloom layer. The presence of transformed riverine waters is quite stable with time. In addition, the 2014 surveys demonstrated that a lens of transformed riverine water occurred east of the Yamal Peninsula for at least two months despite considerably complex weather conditions.

The hydrochemical characteristics of the surveyed region instead conformed to the season of transition from summer to autumn, or to early autumn, when bioactivity is already decreasing and no intense cooling of the surface layer has begun. Water cooling frequently causes the autumn peak of the phytoplankton bloom, intensified by the supply of nutrients from deeper layers. The bloom as such becomes possible if convective mixing processes are intensified quite early, i.e., with sufficient insolation. The vast propagation and thickness of the surface desalinated layer during the year of the surveys might prevent transformations of the hydrochemical and biological structure of waters for quite a long time.

ACKNOWLEDGMENTS

Field studies were supported by the Russian Science Foundation (project no. 14-50-00095) and the Russian Foundation for Basic Research (project no. 14-05-05005 Kar-a; processing and analysis of materials were supported by the Russian Science foundation (project no. 14-17-00681).

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Translated by A. Rylova