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MARINE CHEMISTRY

Dissolved Inorganic Carbon in the Estuarine Area of the Lena River: Results of Expeditions in 2015 and 2017

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Abstract—Transects near the estuarine area of the Lena River were studied on cruises 63 and 69 of the R/V *Akademik Mstislav Keldysh*, organized by the Institute of Oceanology, Russian Academy of Sciences, in 2015 and 2017, the program of which included hydrochemical studies. Based on the results, the components of the carbonate system were calculated, and their dynamics was studied in sea–river mixing zone. Despite the general similarity in the distribution of hydrochemical parameters, the patterns of variations in the content of dissolved inorganic carbon along the river–sea mixing line in 2015 and 2017 were significantly different. In 2015, the increase in the content of dissolved inorganic carbon along the river–sea mixing line was higher than can be provided by the oxidation of organic matter. In 2017, almost the entire influx of dissolved inorganic carbon into water could be controlled by the destruction of dissolved and/or particulate organic matter. The difference in the state of components of the carbonate equilibrium of waters and their dynamics may be the result of significantly higher runoff of particulate matter from the Lena River in 2015 than that in 2017.

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INTRODUCTION

The hydrochemical and hydrological regime of the Laptev Sea is formed under the influence of three major factors: river runoff, ice cover most of the year, and water exchange with the Arctic Basin. In addition, the hydrochemical characteristics of the Laptev Sea shelf are controlled by destruction of coasts and, which is especially important for the marine hydrochemical regime, destruction of subaqueous permafrost, resulting in the exposure of Pleistocene organic matter [16]; the runoff of organic carbon into the sea under coastal abrasion is estimated as 0.9×10^9 t per year [11].

The Lena is the largest river flowing into the Laptev Sea; other rivers flow into the Laptev Sea as well, the most significant of them being the Yana, Khatanga, Olenek, and Anabar. However, the Lena River delivers ~70% of runoff into the Laptev Sea [7]. The total annual removal of mineral salts in the Laptev Sea by the Lena River is ~49.2×10^6 t, which is ~1.3% of the world's river runoff. Naturally, Lena River runoff has a significant influence on the hydrogeochemistry of water in the southeastern Laptev Sea [24]. Because of this, Lena River runoff patterns draw the attention of scientists. This is especially important under the conditions of probable climate change. It is considered that the average Lena River runoff during the first decade of the 21st century increased by 11% (583 km^3), which has been caused by the increase in bulk precipitates and degradation rates of land permafrost in the river basin [28]. Therefore, a significant number of the integrated international expeditions were carried out in the estuarine area of the Lena River in the past two decades with the participation of researchers from the Siberian and Far Eastern branches of the Russian Academy of Sciences [28] and other scientific organizations.

The estuarine area of the Lena river was also studied during expeditions on R/V *Akademik Mstislav Keldysh* in 2015 and 2017. A diagram of the studies is shown in Fig. 1. The southern parts of transect approached the Trofimovskaya Channel, which on average provides 60% of the total river runoff [22]. The studies on the transect were carried out from September 8 to 15, 201,5 and twice in 2017, September 2–3 and 14; it can be stated that all studies were performed within the same summer–autumn low- and high-water seasons [22]. The average total runoff in this season (August–October) is 32% of the annual volume [22].

MATERIALS AND METHODS

During the studies in 2015 and 2017, samples were collected with 5 L plastic Niskin bottles, in accordance with GOST 51592-2000 "General Requirements for Sampling." Application of a case of Rosette bathome-

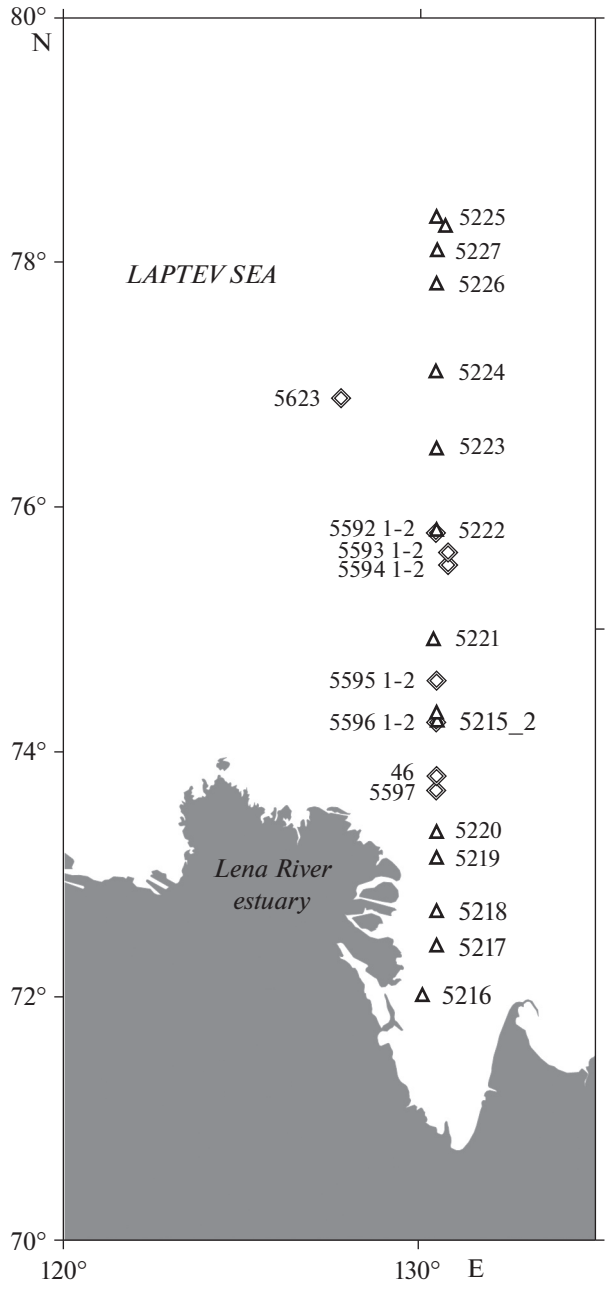

Fig. 1. Location of stations in estuarine area of Lena River, where our hydrochemical studies were performed in 2015 (triangle) and 2017 (rhomb).

ters equipped with a CTD probe allowed targeted sampling at the most significant horizons. The hydrochemical analyses on all expeditions were carried out by the standard methodologies [12, 13, 18] accepted in Russian oceanology. The use of common methods on all expeditions allows us to compare the studies of different years correctly. To analyze nutrients, we preliminarily used 0.45 μm filters for waters with a high SPM content, which often occurs in bays and gulfs, in river–seawater mixing zones. In the water samples with visible color, colorimetric measurement of mineral phosphorus and silicates were corrected for chromaticity of waters by methods [13, 18]. pH was estimated in NBS scale units normalized to in situ conditions [18]. Components of the carbonate system were calculated with the pH–Alk method using thermodynamic equations of carbonate equilibrium with concentration constants of carbonic acid dissociation [26]; waters with properties different from those of seawater were corrected [1, 25]. Universal, small-size, and autonomous transparency meters (PUM and PUM-A) were applied to measure the index of light attenuation by seawater.

In our studies, we were unable to obtain river water: in 2015, the minimum salinity in the marine part of the transect was 3.01 psu; during the first study in 2017, we obtained only a salinity of 13.40 psu; during the second study, the minimum recorded salinity was 6.61 psu. Determination of the endmembers for each parameter characterizing waters from different sources was chiefly responsible for the uncertainty in calculating the dynamics of chemical parameters in mixing zones. During the study, we were forced to apply regression analysis to determine the hydrochemical characteristics of river water. We used the regression equations for the alkalinity values and Si concentrations with salinity for different marine areas:

$$C = A_0 + SA_1, \quad (1)$$

where A_0 and A_1 are empirical coefficients, S is salinity, and C is the concentration of any conservative chemical parameter. The value of the constant A_0 can be interpreted as a parameter value at zero salinity; in this case, it indicates the alkalinity or Si content in river waters. Earlier, such approach was successfully applied in studying river water distribution over the water area of the Kara Sea [20].

According to [6], the content of mineralization in the lower reaches of the Lena River is 16–456 mg/L. The content of mineralization in water of the Lena River was estimated as 80–100 mg/L during the high-water and flood periods and up to 160–500 mg/L in the low water period [10]. According to the results of expeditions by the Siberian and Far East Branches in 2005–2007, salinity in the estuarine area of the Lena River ranged within 0.1–8.4 psu in summer and 0.7–27.4 psu in winter [9, 29]. It is known that the winter concentrations of dissolved chemical elements and mineralization in water increase compared to those in the flood water period. This is due to the changes in the supply mode, in which groundwater plays a major role. Because of the extreme climate, Lena River runoff is characterized by very intense summer high water periods, a relatively poorly pronounced spring flood, and a very low water level in winter. This results from the change in river water supply: 50% of water in the lower reaches of the Lena River comes form snowmelt; 35%, from rainfall; and 15%, from ground subpermafrost waters [4]. Therefore, the chemical con-

Table 1. Results of regression analysis for river–sea mixing end points

Study	River mixing point				Sea mixing point			
	Alk, mg-eq/L	C_{tot}, g/L	Si, μM	P-PO_4, μM	Alk, mg-eq/L	C_{tot}, g/L	Si, μM	P-PO_4, μM
September 8–15, 2015	0.902	11.46	70.66	0.04	2.246	27.68	3.74	0.38
September 2–3, 2017	0.849	10.23	49.37	0.00	2.257	27.13	0.00	0.86
September 14, 2017	0.781	9.58	49.18	0.05	2.253	27.84	4.22	0.17

tent in winter runoff will be significantly (several times) higher than that in the flood water period. The warm season accounts for 75–95% of Lena River runoff. Hence, it will not yield a large error if for calculations we take the mineralization of the river water as 0.2 g/kg.

According to oceanographical chemical classification [14], surface seawater of the Laptev Sea is associated with to the northern land type (western part of the sea) and to the central type (eastern part of the sea). The average long-term salinity of these waters is 30.7 and 32.8 psu, respectively. During our expeditions in the estuarine area of the Lena River, the maximum salinity in the 0–10 m layer (30.15 psu) was recorded in 2015. A seawater salinity value of 32 psu was taken for calculation of water mixing. Table 1 gives the results from calculating the "river" and "sea" points of mixing. The values obtained for the "sea" point during different studies agree quite well with each other. The "river" point shows significant variations between the 2015 and 2017 studies. This is because the chemical composition of river runoff is not constant and strongly depends on the runoff volume. For Lena River water, 913 μmol/kg or 936 mg-eq/L is taken as the Alk value [8, 24]; this is close to the values obtained with the regression equation.

Using the equation of water mixing, we calculated the theoretical C_{tot} values and concentrations of phosphates and silicates for the transect. If these components were transported as a conservative admixture, their concentrations over the transect should be determined by the equation

$$C_i = C_2 + (C_1 - C_2)(S_i - S_2)/(S_1 - S_2), \qquad (2)$$

where C_i is the assumed C_{tot} value at mixing point i, S_i is the salinity at this point, C_1 and C_2 are the measured C_{tot} values at the endpoints of the mixing line, and S_1 and S_2 are the salinities at the endpoints of the mixing line.

The values obtained with the regression equations were selected as the endpoints of the river–sea mixing line (Table 1). We calculated the difference between the theoretical values obtained from Eq. (2) and the actually observed values of certain hydrochemical parameters. Under certain assumptions, this difference can be interpreted as changes in the flux occurring under the influence of various processes [5]. A decrease in the actually observed value compared to the calculated one can be explained by biological production or bonding as a result of processes at the river–sea biochemical barrier. The excess of the actually observed value over the calculated one may be due to the influx of elements from the decomposition of organic matter (OM) dissolved in water, contained in suspension or in the upper sediment layer. This can most likely be explained by the dissolution of mineral particles in suspension and sediments as well.

RESULTS AND DISCUSSION

The ratio of the total alkalinity to salinity Alk/S, called the specific alkalinity (SA), is one of the most widely used and reliable indicators of the presence of river water. If the Alk/S is >0.06–0.08, we can confidently assume the significant presence of river water [17]. According to the results of two studies in 2017, the SA ranged from 0.068 to 0.160 along the transect. The maximum presence of river waters is naturally recorded in the surface layer of the southernmost station of the transect. The range of SA variations in 2015 was wider (from 0.060 to 0.360), but this is explained by the longer transect than the one in 2017. The SA value indicates that the studied water area was more greatly influenced by continental waters. The position of the lower boundary of river water penetration (SA < 0.07) varied slightly over the entire study period, occurring at a depth slightly below 20 m. Similar to other rivers, Lena River water in the Laptev Sea spread above more saline and denser seawater. Depending on the river runoff volume and type of atmospheric processes, waters with lower salinity can be transported north to Kotel'nyi Island, east to the Dmitry Laptev Strait, and even to the Long Strait [8, 27, 29].

The salinity distribution along the transect is common for the estuarine front of a large river. We observe a so-called horizontal front, that is repeatedly disturbed by the meandering of the river's main discharge flow. As a whole, the salinity increases with depth and towards the marine part of the transect. The transects studied in 2017 covered only the central part of the transect studied in 2015 (Fig. 1). The main features in the salinity distribution remained the same (Fig. 2). The salinity values were close as well, if we consider only the part of the transect between 74° and 76° N, where all results overlap. The salinity in the surface

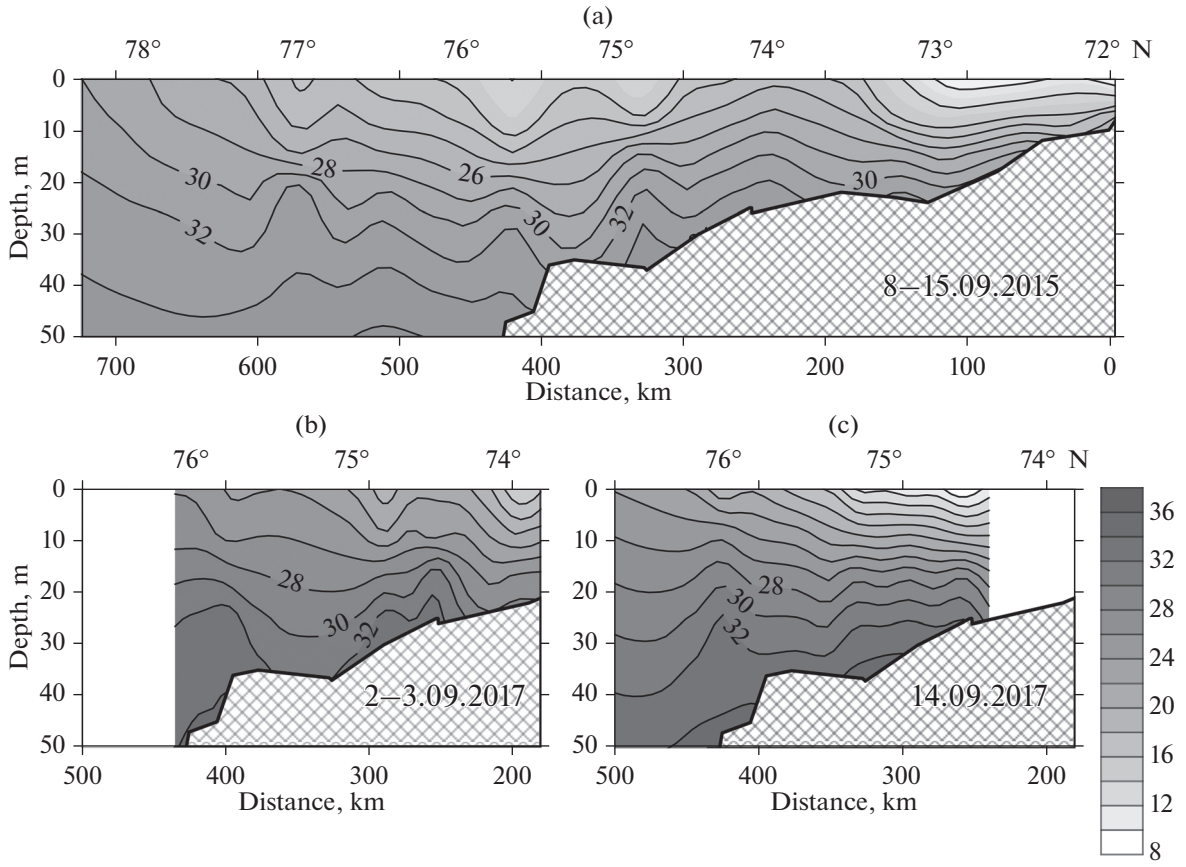

Fig. 2. Salinity (psu) distribution on transect in estuarine area of Lena River from results of studies on R/V *Akademik Mstislav Keldysh*. (a) September 8–15, 2015; (b) September 2–3, 2017; (c) September 14, 2017.

layer (0–10 m) varied from 15.8 to 22.4 psu in 2015; the salinity ranges within this layer in the first and second transects of 2017 were 18.3–25.7 and 6.6–24.9 psu, respectively (Figs. 2b, 2c). Considering the concentrations of dissolved inorganic carbon (C_{tot}) and dissolved silicon (Table 1), we can assume that in the periods of our studies, runoff in 2015 was lower than in 2017.

All studies were carried under conditions of decreasing biological activity, when oxidation of organic matter predominated over its production. The dissolved oxygen concentration in the 2015 transect ranged from 4.99 to 8.04 mL/L with the minimum in the bottom layers of the river part of the studied region. The dissolved oxygen concentration in water did not exceed 97% along the entire transect, even on the surface [19]. In the bottom water of the river part of the mixing zone, where the vertical salinity gradient was the highest, the oxygen concentration at the bottom decreased to 64% (Fig. 3a). According to the results of both studies in 2017, the dissolved oxygen concentration ranged from 5.24 to 8.5 mL/L. The minimum oxygen content was recorded in the bottom layer of the stations within the river part of the transect, whereas the maximum oxygen concentrations were observed at the lower boundary of the thermocline (approximately at the 20 m horizon with a typical sharp decrease in temperature) in the marine part of the transect.

The vertical structure of the dissolved oxygen distribution varied slightly over the two weeks between studies in 2017, as well as between studies in different years. The oxygen saturation of water along the 2017 transect varied from 61.6 to 99.8%. The bottom layer of the southern stations of the transect is characterized by substantial undersaturation in oxygen, most likely resulting from the active oxidation of organic matter removed with river runoff.

The pH distribution is characterized by the minimum values in the bottom layers within the river part of the mixing zone and by an increase in the values with intensification of the influence of seawater (Fig. 4). The maximum pH value was recorded in the marine part of the transect at the upper boundary of the temperature jump, where a high dissolved oxygen concentration was often observed as well. However, the absolute value varied rather significantly in different studies. In 2017, pH in the layer 0–50 m ranged within 7.32–7.99. In 2015, the pH values were higher: from 7.80 to 8.13 during the first study and from 7.60 to 8.39 during the second study. Such increase in pH in 2017 can partially be explained by the slight increase in dissolved oxygen

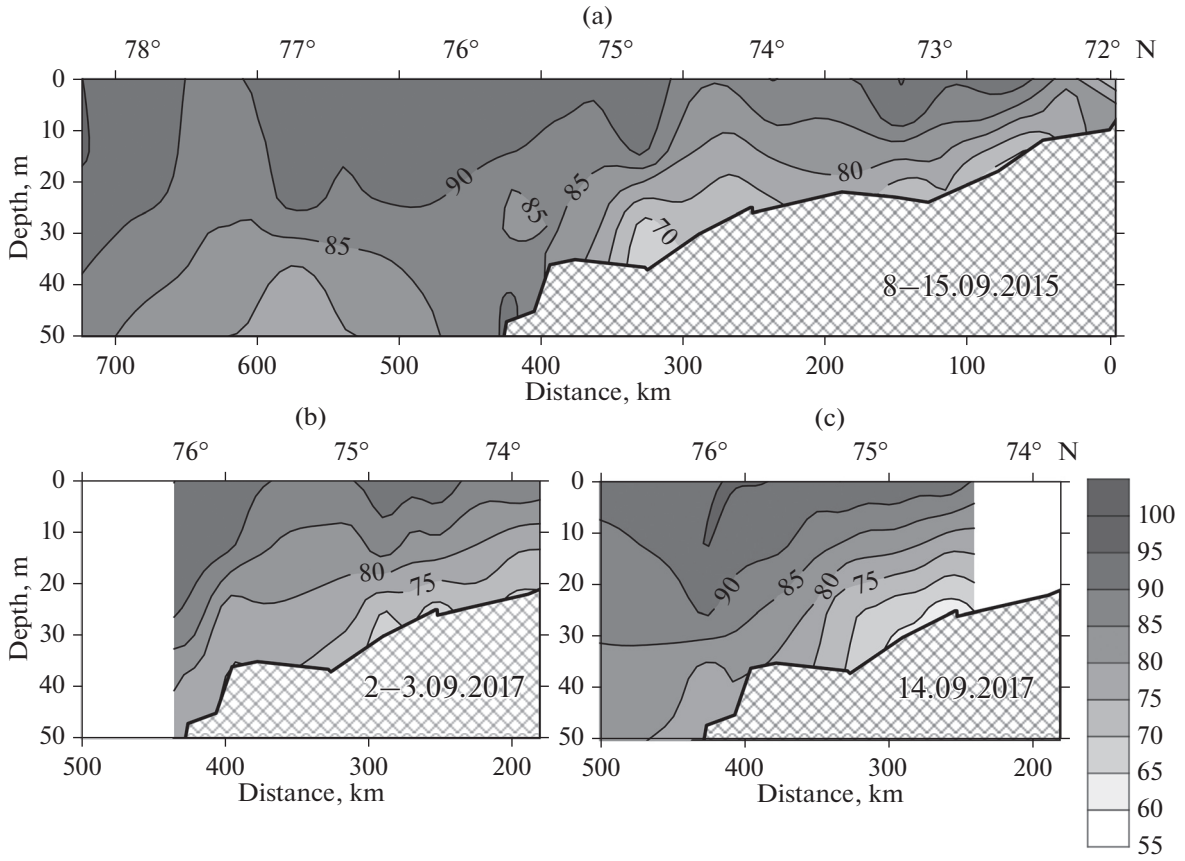

Fig. 3. Oxygen saturation of waters (%) on transect in estuarine area of Lena River from results of studies on R/V *Akademik Mstislav Keldysh*. (a) September 8–15, 2015; (b) September 2–3, 2017; (c) September 14, 2017.

concentration in comparison with that in 2015. The water temperature in the 0–10 m layer varied from 3 to 4.8°C in 2015, from 2.1 to 4.3°C during the first study in 2017, and from 2.1 to 4.6°C during the second study in 2017. Such a change in the temperature of the surface layer could hardly have affected the pH value. Most likely, the processes of OM oxidation in water were more intense than in 2017. This is reflected in the value of the partial pressure of carbon dioxide (pCO_2) along the transect (Fig. 5).

pCO_2 was often <400 ppm in the upper 20-m layer of the marine part of the transect during the first study in 2017 and in the upper 5-m layer during the second study, which is possible with a low activity of oxidizing processes or if there is equilibrium between the OM synthesis and oxidation processes. The highest pCO_2 value was recorded in bottom waters of the southern part of the transect. The maximum partial pressure (1130 ppm) was observed during repeated works on the transect, in the bottom layer of the southernmost station (Fig. 5b). This value provides evidence for the active oxidation of OM delivered with continental runoff. Such values were not observed during the first study, which indicates the smaller influence of river runoff on the water area during the first study of the transect. In 2015, the range of pCO_2 on the transect was 515–2030 ppm. Even in surface waters, pCO_2 was significantly higher than that in equilibrium with the atmosphere. The highest pCO_2 values (>2000 ppm) were recorded in bottom waters of the river part of the transect (Fig. 5a).

According to the results of all our studies, the total concentrations of dissolved inorganic carbon (C_{tot}) were almost the same, of course, given that in 2015, the transect was longer and came closer to the mouth of the channel. The range of C_{tot} values was 13.6–29.6 mg/L, with an average of 23.8 mg/L. In 2017, the ranges of C_{tot} were 16.7–27.3 (with an average of 23.7) mg/L and 12.7–17.4 (with an average of 22.6) mg/L during the first and second studies, respectively. The C_{tot} distribution in the transect in 2015 and 2017 is very similar. We observed an increase in concentration with depth and towards the marine part of the transect (Fig. 6).

Based on the results of all three studies, the average concentration of inorganic carbon on the transect was almost constant (~23 mg/L). The variation in the range of the values observed in the three studies was more significant, which is naturally explained by the lengths of transects. Based on the line of water mixing,

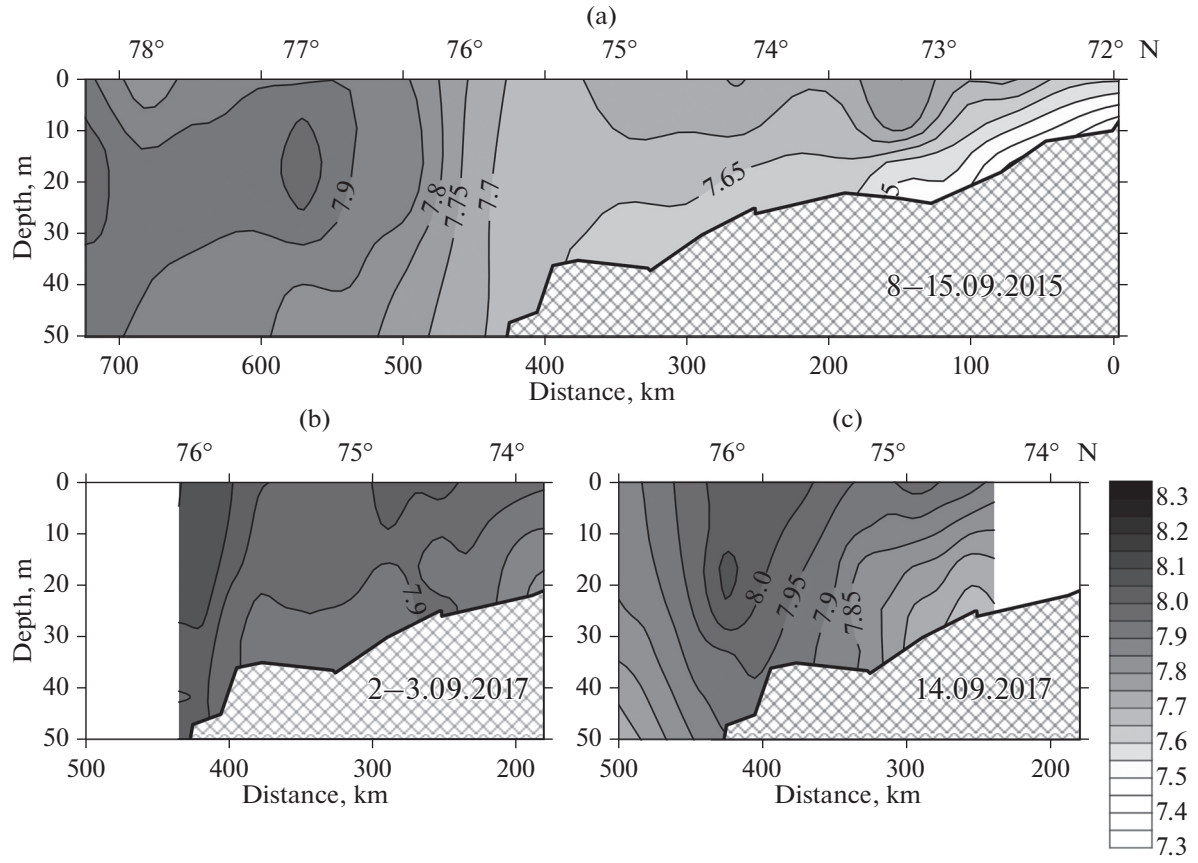

Fig. 4. pH (units of NBS scale) on transect in estuarine area of Lena River from results of studies on R/V *Akademik Mstislav Keldysh*. (a) September 8–15, 2015; (b) September 2–3, 2017; (c) September 14, 2017.

we calculated the difference between the theoretical and actually observed total concentrations of dissolved inorganic carbon (ΔC_{tot}), dissolved inorganic phosphorus, (ΔP) and dissolved silicon (ΔSi).

The spatial distribution of ΔC_{tot} differed significantly in our different studies (Fig. 7). In 2015, ΔC_{tot} ranged from –388 to 199 μM with an average of 9 μM. Efflux of carbon was observed in the bottom layer of the river part of the transect. Absorption of carbon was recorded on the surface in individual "spots" (Fig. 7a). Similar values were obtained in the first study of 2017: from –53 to 103 μM with an average of 7 μM. The second study of 2017 showed a much narrower range of 1.5–8 μM with an average of only 0.8 μM. Carbon was absorbed in the marine part of the transect. Since the degree of oxygen saturation was always <100%, the decrease in C_{tot} is probably not controlled by absorption during the formation of new OM. Most likely, the drop in carbon content was due to an "organoelemental bottleneck," where OM and iron and aluminum oxyhydrates flocculated and precipitated into bottom sediments [3].

The distribution of variations in the contents of dissolved inorganic phosphorus (ΔP) and dissolved silicon (ΔSi) along the transect was similar as well. A positive ΔSi value is always observed in bottom waters, in which dissolved Si is released from the upper part of sediments. Absorption is recorded in almost all surface waters. In 2015, ΔSi varied from –14.0 to 24.1 μM, with an average over the transect of 1.6 μM. In both studies of 2017, ΔSi ranged from –6 to 13 μM. The average ΔSi value was 2 μM in the first study and close to 0 in the second study. As mentioned above, the low oxygen concentration and degree of its saturation allow us to explain with high probability the decrease in Si in surface waters by its consumption at the river–sea geochemical boundary.

The dynamics of dissolved inorganic phosphorus (ΔP) is similar to that of ΔSi in the river part of the transects. In the marine part, there are significant differences between ΔP and ΔSi. This most likely results from the higher lability of phosphorus. In 2015, ΔP ranged from –0.2 to 0.8 μM, with an average over the transect close to 0. During both studies in 2017, ΔP varied from –0.8 to 0.5 μM. The average ΔP value was close to 0 in the first study and ~0.15 μM in the second study.

In order to estimate the main factors regulating variations in C_{tot} over the transect more reliably, we can use the value of apparent oxygen utilization (AOU),

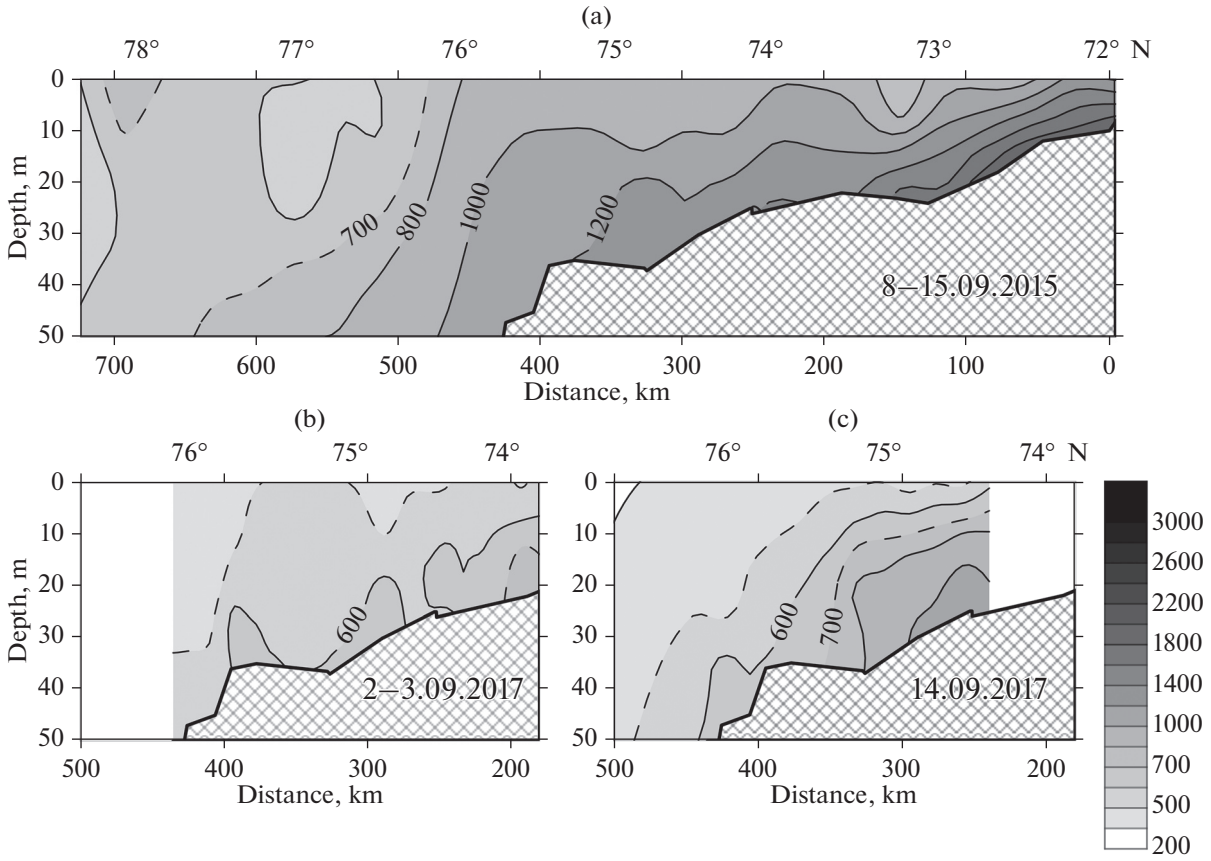

Fig. 5. pCO_2 (ppm) on transect in estuarine area of Lena River from results of studies on R/V *Akademik Mstislav Keldysh*. (a) September 8–15, 2015; (b) September 2–3, 2017; (c) September 14, 2017.

which is the difference between the equilibrium and real oxygen concentrations in water. The value of oxygen concentration in equilibrium with the atmosphere O_{eq} (μM) was calculated using an equation from [29]. Excess oxygen (AOU < 0) testifies to the predominance of production processes over destruction processes; its deficiency (AOU > 0) indicates the increasing role of destructive processes. Based on the studies in 2015 and 2017, the AOU range was almost the same, from 2–15 to 260–290 μg-at/L, with an average value of ~100 μg-at/L. The highest AOU values were recorded in the bottom layer on the stations in the river part of the transect; the lowest values were observed in the middle and marine parts of the transect (Fig. 8). Interestingly, the decrease in AOU in the central part of the transect coincided with a decrease in salinity, i.e., the presence of river waters affected to a higher degree in this area.

The apparent carbon utilization (ACU) is determined in a similar way:

$$ACU = [DIC_{eq}] - [DIC_{real}], \quad (3)$$

where DIC_{eq} is the concentration of inorganic carbon corresponding to the partial pressure of carbon dioxide in equilibrium with the atmosphere (the accepted value is 400 μatm) and to the measured Alk value; DIC_{real} is the concentration of C_{tot} calculated from the measured pH and alkalinity values.

The ACU value indicates the balance between production and destruction processes: if ACU > 0, production predominates; if ACU < 0, OM oxidation predominates [21]. According to the 2015 data, ACU was negative along the entire transect, even in the places where mixing equation (2) could have yielded a decrease in C_{tot}. This is consistent with the low value of saturation in dissolved oxygen and the positive AOU value along the entire transect. The lowest ACU value (<0.2 mM) was recorded in bottom waters of the river part of the transect (Fig. 9a), where the highest efflux of dissolved carbon into water can be expected. The range of ACU values in the transects of 2017 (Figs. 9b and 9c) is much narrower, even with allowance for the small length of the transects. The most intense efflux of carbon into water (ACU < –0.1 mM) was also observed in bottom waters of the river part of transects. It is very interesting that ACU becomes positive and reaches 0.05 mM at the most marine station (no. 5623) of the transect studied on September 14, 2017, where seawater with a salinity of >32 psu and a negative temperature is observed. Theoretically, absorption of C_{tot} from

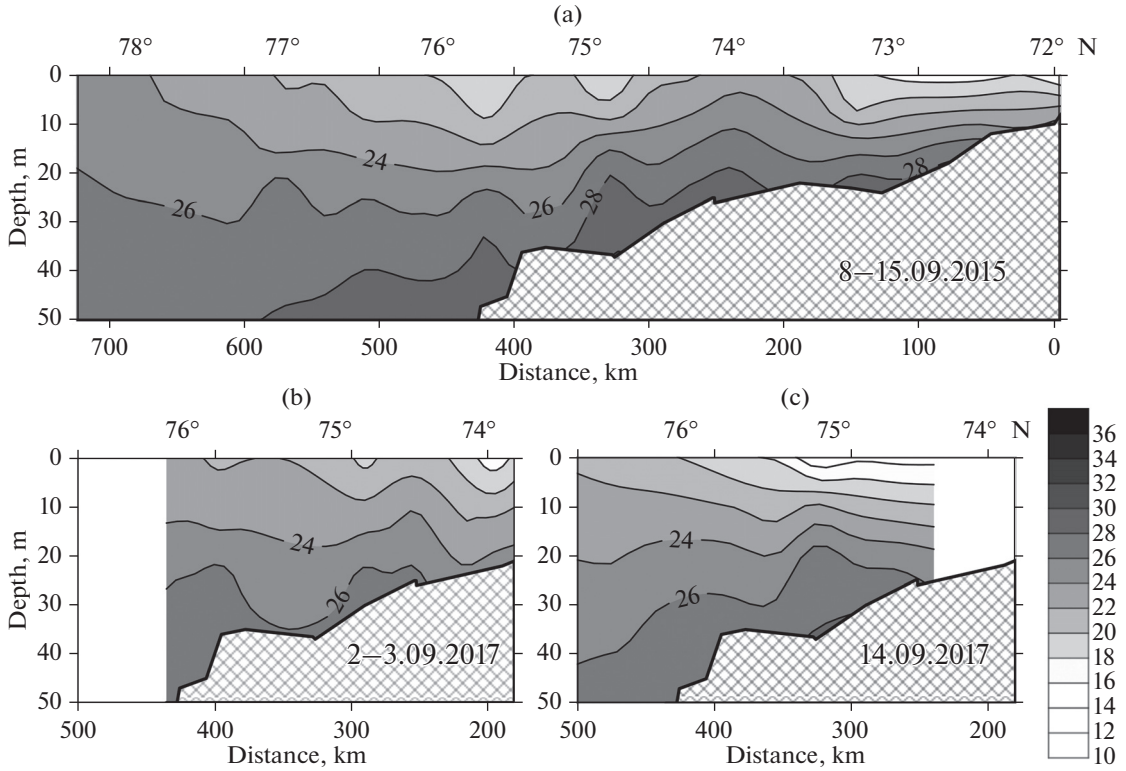

Fig. 6. Concentration of C_{tot} (mg/L) on transect in estuarine area of Lena River from results of studies on R/V *Akademik Mstislav Keldysh*. (a) September 8–15, 2015; (b) September 2–3, 2017; (c) September 14, 2017.

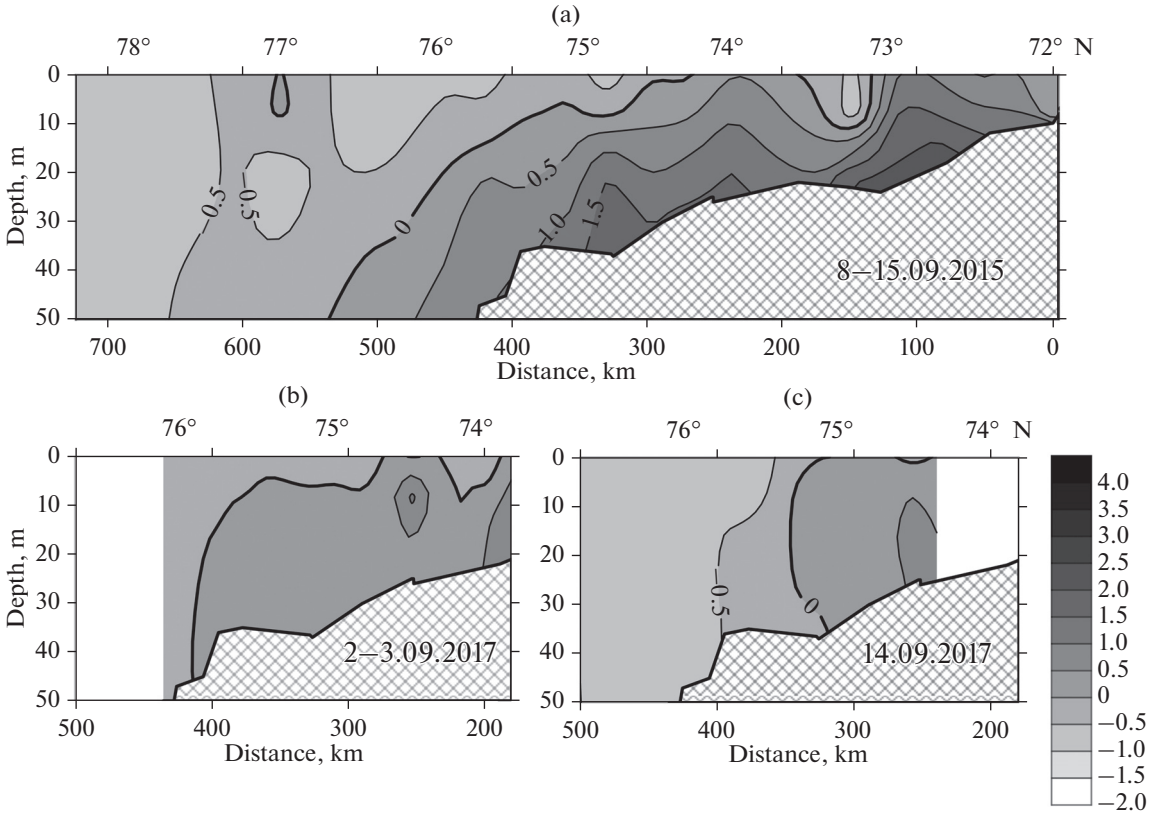

Fig. 7. Concentration of ΔC_{tot} (mg/L) on transect in estuarine area of Lena River from results of studies on R/V *Akademik Mstislav Keldysh*. (a) September 8–15, 2015; (b) September 2–3, 2017; (c) September 14, 2017.

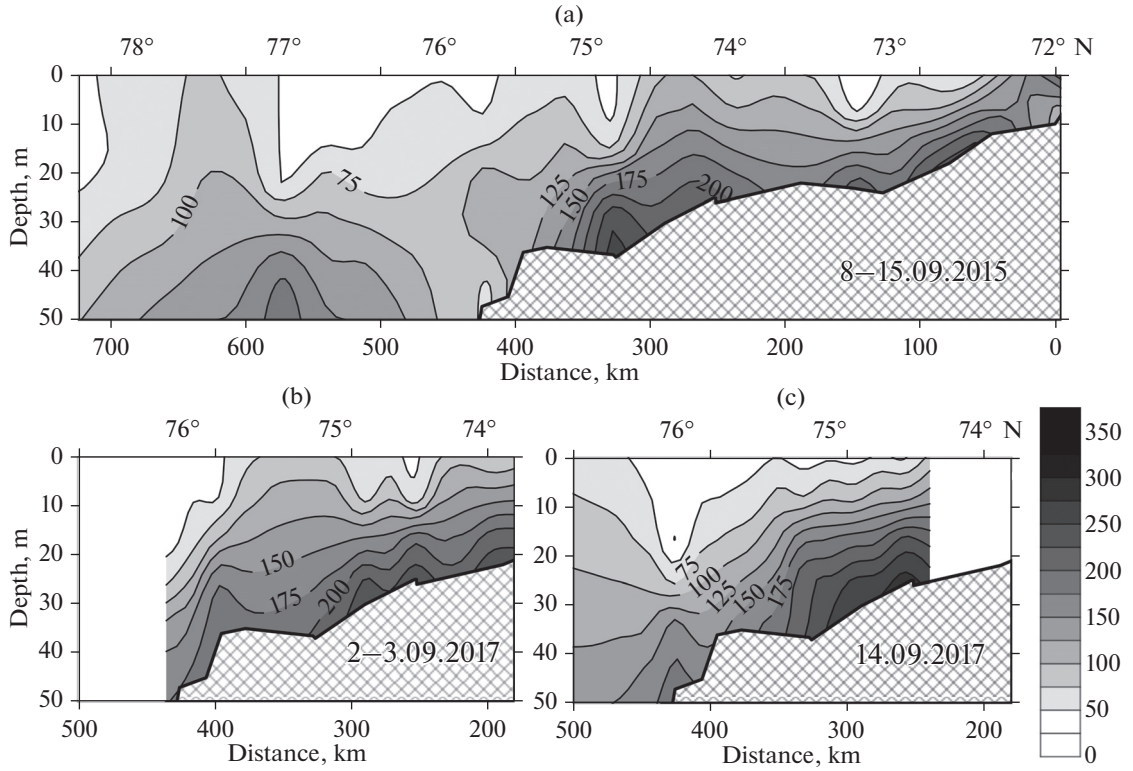

Fig. 8. Apparent oxygen utilization AOU (μM) on transect in estuarine area of Lena River from results of studies on R/V *Akademik Mstislav Keldysh*. (a) September 8–15, 2015; (b) September 2–3, 2017; (c) September 14, 2017.

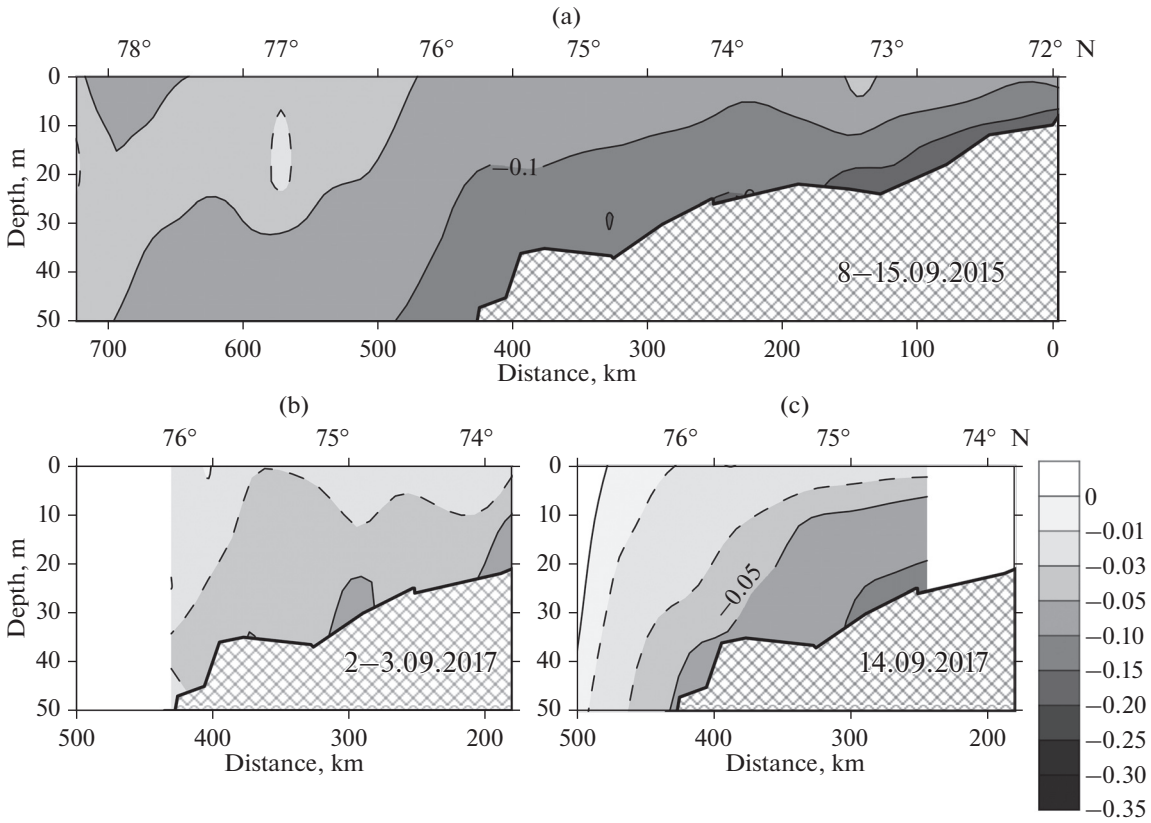

Fig. 9. Apparent carbon utilization ACU (mM) on transect in estuarine area of Lena River from results of studies on R/V *Akademik Mstislav Keldysh*. (a) September 8–15, 2015; (b) September 2–3, 2017; (c) September 14, 2017.

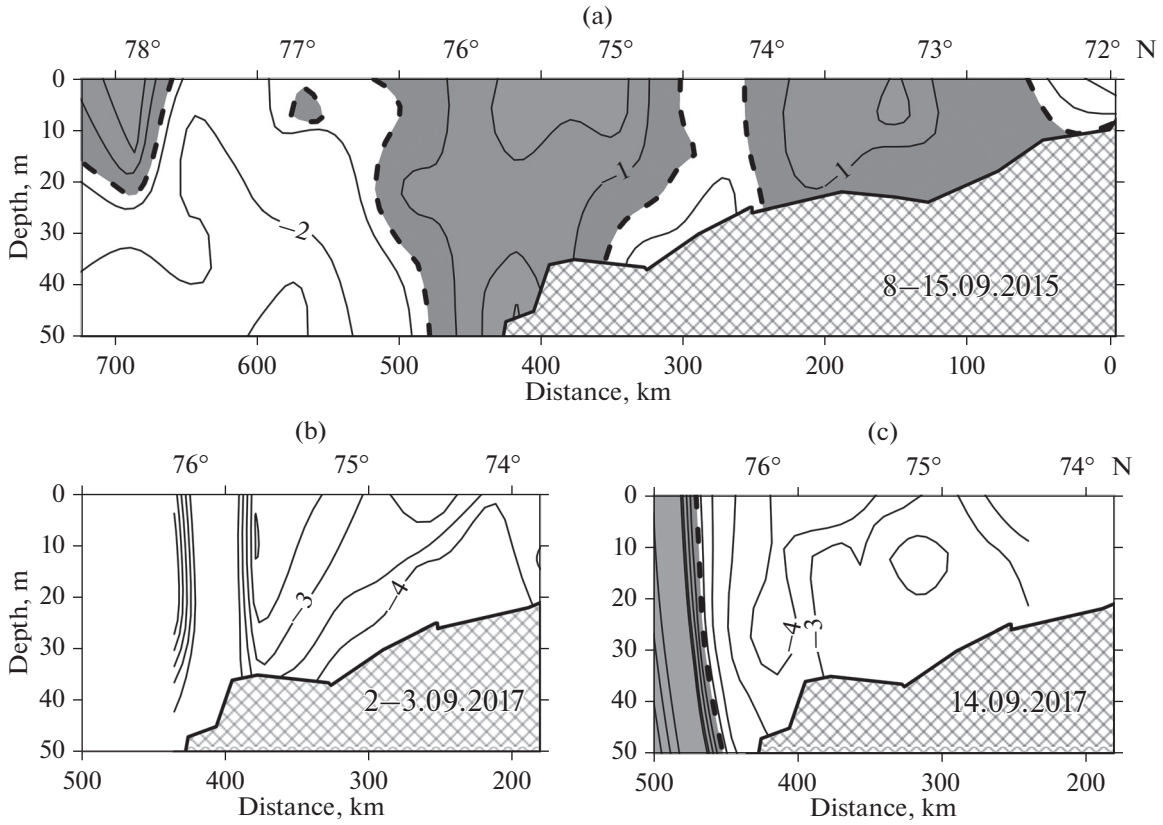

Fig. 10. Ratios of AOU and ACU values on transect in estuarine area of Lena River, based on results of studies on R/V *Akademik Mstislav Keldysh*. (a) September 8–15, 2015; (b); (c) September 14, 2017. AOU/ACU > −1.3 (see explanation in text) is shown by dark color; dashed line is an isoline of −1.3.

water is probable there as well. Based on mixing equation (2), extraction of carbon from water could have occurred at this station; ΔC_{tot} ranged from −1.7 to −1.2 mgC/L (Fig. 7).

Phytoplankton extraction of nutrients and carbon from seawater and corresponding oxygen production occur in certain stoichiometric proportions [2]. A decrease in the oxygen concentration (increase of AOU) and increase in the total dissolved inorganic carbon (ACU) should be related by a linear ratio AOU/ACU ≈ −1.3 [20]. If this ratio is ≤ −1.3, then variations in the dissolved carbon concentration in water can entirely be explained by oxidation or synthesis of OM. Figure 10 shows the distribution of the AOU/ACU ratio along the transect. The shaded parts of the transect show areas with variations in C_{tot} wider than can be expected by the stoichiometric model. It is evident that in 2015, water in which C_{tot} variations could not be explained only by the introduction of carbon during OM oxidation occupied more than half the transect. AOU/ACU > −1.3 in the river part of the transect was recorded over the entire water column, with salinity decreasing at the surface.

We can suggest that in 2017 oxidation of OM influenced the change in the content of dissolved carbon to a greater extent. Increase in the AOU/ACU ratio was observed in the marine part of the transect only. Such difference in distribution and dynamics of dissolved carbon most likely results from change in the volume of runoff and, consequently, its chemical composition. Probably, in 2015, river waters were characterized by higher carbon and nutrient contents (Table 1) than in 2017. The low concentration of dissolved materials is typical of the high runoff period, e.g., flood or high water. With allowance for the period of studies, we carried out our studies in 2015 just before the winter low water period, when the runoff volume is small, and the concentrations of dissolved chemical elements increase due to the increasing role of groundwater supply. At the same time, we can assume that the efflux of dissolved material due to degradation of permafrost rocks was higher during the study in 2015. This may be the reason for significantly higher pCO_2 in 2015 than in 2017.

Variation in the SPM content may be the reason for such a difference as well. The average SPM content in the lower reaches of the Lena River is 39 g/m^3 [3]. This is one of the highest SPM contents among the large Arctic rivers. With allowance for the discharge volume, the SPM content removed by the Lena River is the highest among the rivers of the region and reaches

20.7×10^9 t/yr [3]. In addition, the average concentration of C_{org} in Lena River SPM is estimated as 4.4% [15], which is higher than the average concentration of C_{org} in other rivers of the region. Naturally, the content and temporal dynamics of SPM strongly influence the chemistry of waters in the river–sea zone, especially the carbonate water system. As is evident from the data on the light attenuation coefficient (LAC), which directly depends on the SPM content, a three-layer structure of the Lena River profile is observed with a very sharp boundary exactly corresponding to changes in temperature and salinity. High LAC values were recorded in the surface and bottom layers. Such a structure is observed at a distance of 150–450 km from the coast. However, the LAC value was higher in 2015 than in 2017. In 2015, the LAC in the upper, lower, and bottom layers was extremely high (up to 12 m^{-1}). In 2017, the LAC varied from 0.6 to 3.0 m^{-1} at the surface and slightly exceeded 9 m^{-1} in bottom waters at river stations of the transect. We can suggest that at the time of our studies, discharge of SPM was much higher in 2015 than in 2017.

CONCLUSIONS

The distribution of hydrochemical parameters in 2015 (cruise 63 of the R/V *Akademik Mstislav Keldysh*) and in 2017 (cruise 69 of the R/V *Akademik Mstislav Keldysh*) has many common features. This is mostly related to the main factor controlling the hydrological and hydrochemical regimes of the region: Lena River runoff. The significant influence of continental runoff extends to the entire upper active layer of the transect. The depth of the density jump layer ranged widely from one station to another, but, on the whole, it progressively increased northward from 3–4 to 15 m with the increasing influence of seawater. According to the results of all studies, the presence of more saline water is observed in the central part of the transect at the surface. This fact may be explained by intrusion of more saline waters or orographic upwelling. As is evident from the results of all studies, the similarity in the hydrochemical structure is also explained by the fact that all studies proceeded at almost the same time: the end of the autumn–summer and beginning of the winter periods.

According to the results of all our studies, oxidation of OM predominated over its synthesis processes in water. Oxygen saturation of water with did not reach 100% anywhere. At the same time, we did not observe so called "stagnant" waters 30–50% saturated with oxygen, typical of the bottom structural zone of the southeastern part of the Laptev Sea affected by river runoff [7].

Calculation of the AOU and ACU values shows that the increase in the concentration of dissolved inorganic carbon along the river–water mixing line in 2015 was higher than could have been provided by OM oxidation. In 2017, introduction of almost all dissolved inorganic carbon into the water could have resulted from the destruction of dissolved and particulate OM. LAC measurements show that during our studies, SPM in Lena River runoff was much higher in 2015 than in 2017. This was reflected in the state of the carbonate equilibrium components in water and their dynamics.

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REFERENCES

1. A. S. Bychkov, G. Yu. Pavlova, and V. A. Kropotov, "Carbonate system," in *Chemistry of Sea Water and Authigenic Mineral Formation* (Nauka, Moscow, 1989), pp. 49–111.
2. M. E. Vinogradov, V. B. Tseitlin, and V. V. Sapozhnikov, "Primary production," Zh. Obshch. Biol. **53** (3), 314–327 (1992).
3. V. V. Gordeev, *Geochemistry of the River–Sea System* (Matushkina I.I., Moscow, 2012) [in Russian].
4. A. N. Zubakina, "Specific hydrochemical regime of the estuary area of the Lena River," Tr. Gos. Okeanogr. Inst. **143**, 69–76 (1979).
5. P. N. Makkaveev, "Dissolved inorganic carbon in waters of Kara Sea and estuaries of the Ob' and Yenisei rivers," Okeanologiya (Moscow) **34**, 668–672 (1994).
6. A. M. Nikanorov, V. V. Ivanov, and V. A. Bryzgalo, *Rivers of Russian Arctic under Anthropogenic Impact* (NOK, Rostov-on-Don, 2007) [in Russian]. ISBN 978-5-8431-0092-6
7. S. V. Pivovarov, *Chemical Oceanography of the Arctic Seas of Russia* (Gidrometeoizdat, St. Petersburg, 2000) [in Russian].
8. I. I. Pipko, S. P. Pugach, O. V. Dudarev, A. N. Charkin, and I. P. Semiletov, "Carbonate parameters of the Lena River: Characteristics and distribution," Geochem. Int. **48**, 1131–1137 (2010).
9. I. I. Pipko, S. P. Pugach, I. P. Semiletov, and A. N. Salyuk, "Carbonate characteristics of waters of the Arctic Ocean continental slope," Dokl. Earth Sci. **438**, 858–863 (2011).
10. *Resources of Surface Waters of Soviet Union*, Vol. 17: *Lena-Indigirka Area*, Ed. by A. V. Shestakov (Gidrometeoizdat, Leningrad, 1967) [in Russian].
11. E. A. Romankevich and A. A. Vetrov, *Carbon Cycle in the Arctic Seas of Russia* (Nauka, Moscow, 2001) [in Russian].
12. *Handbook on Chemical Analysis of Sea Water, RD 52.10.242-92* (Gidrometeoizdat, St. Petersburg, 1993) [in Russian].
13. *Handbook on Chemical Analysis of Marine and Fresh Waters during Ecological Monitoring of Fishery Reservoirs and Regions of the World Ocean, Prospective for Commercial Fishery*, Ed. by V. V. Sapozhnikov (VNIRO, Moscow, 2003) [in Russian].

14. V. P. Rusanov, "Hydrochemical characteristic of surface waters of the Arctic basin," in *Biology of the Central Arctic Basin* (Nauka, Moscow, 1980), pp. 15–35.
15. V. S. Savenko, *Chemical Composition of Suspended Sediments of the World Rivers* (GEOS, Moscow, 2006) [in Russian].
16. I. P. Semiletov, "The failure of coastal frozen rock as an important factor in the biogeochemistry of the Arctic shelf water," Dokl. Earth Sci. **369**, 1140–1143 (1999).
17. A. A. Smirnov, "Inflow of river waters into the Kara and Laptev seas," Tr. Arkt. Nauchno-Issled. Inst. **72** (2), 92–104 (1955).
18. *Modern Hydrochemical Analysis of Ocean*, Ed. by O. K. Bordovskii and V. N. Ivanenkov (Shirshov Scientific Research Institute of Oceanology, Academy of Sciences of Soviet Union, Moscow, 1992) [in Russian].
19. S. V. Stepanova, A. A. Polukhin, and A. V. Kostyleva, "Hydrochemical structure of the waters in the eastern part of the Laptev Sea in autumn 2015," Oceanology (Engl. Transl.) **57**, 58–64 (2017).
20. P. A. Stunzhas, "Separation of waters of the Yenisei and Ob rivers in the Kara Sea by alkalinity and silicon content," Okeanologiya (Moscow) **35**, 215–219 (1995).
21. P.P. Tishchenko, P.Ya. Tishchenko, V.I. Zvalinskii, and A.F. Sergeev, "The carbonate system of Amur Bay (Sea of Japan) under conditions of hypoxia," Oceanology (Engl. Transl.) **51**, 235–246 (2011).
22. *Estuary and Delta Systems of Russia and China: Hydrological and Morphological Processes, Geomorphology, and Prospective Development*, Ed. by V. N. Korotaev, (GEOS, Moscow, 2007) [in Russian].
23. V. V. Gordeev and I. S. Sidorov, "Concentrations of major elements and their outflow into the Laptev Sea by the Lena River," Mar. Chem. **43**, 33–45 (1993).
24. V. V. Gordeev, J.-M. Martin, I. S. Sidorov, et al., "A reassessment of the Eurasian river input of water, sediment, major elements, and nutrients to the Arctic Ocean," Am. J. Sci. **296**, 664–691 (1996).
25. P. N. Makkaveev, "The total alkalinity in the anoxic waters of the Black sea and in sea-river mixture zones," in *Joint IOC-JGOFS CO_2 Advisory Panel Meeting* (UNESCO, Paris, 1998), Suppl. 5.
26. F. J. Millero, "Thermodynamics of the carbon dioxide system in oceans," Geochim. Cosmochim. Acta **59** (4), 661–677 (1995).
27. I. I. Pipko, I. P. Semiletov, S. P. Pugach, et al., "Interannual variability of air-sea CO_2 fluxes and carbon system in the East Siberian Sea," Biogeosciences **8**, 1987–2007 (2011).
28. I. P. Semiletov, N. E. Shakhova, I. I. Pipko, et al., "Space-time dynamics of carbon and environmental parameters related to carbon dioxide emissions in the Bior-Khaya Bay and adjacent part of the Laptev Sea," Biogeoscinces **10**, 5977–5996 (2013). doi 10.5194/bg-10-5977-2013
29. R. F. Weiss, "The solubility of nitrogen, oxygen and argon in water and seawater," Deep-Sea Res. **17**, 721–735 (1970).

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