= MARINE CHEMISTRY ====

# Hydrochemical Structure of the Waters in the Eastern Part of the Laptev Sea in Autumn 2015

S. V. Stepanova<sup>*a*</sup>, \*, A. A. Polukhin<sup>*a*</sup>, and A. V. Kostyleva<sup>*b*</sup>

<sup>a</sup>Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow, 117997 Russia <sup>b</sup>Shirshov Institute of Oceanology (the Southern Department), Russian Academy of Sciences, Gelendzhik, 353470 Russia \*e-mail: s.stepanova87@gmail.com

Received September 21, 2016

Abstract—The study of the Laptev Sea was a part of a comprehensive program for investigating Arctic seas during the cruise 63 of the R/V *Akademik Mstislav Keldysh*. On a transect along  $130^{\circ}$  E (September 8–14, 2015) from the estuary area of the Lena River on the traverse of the city of Tiksi to the continental slope (over 700 km), water samples were taken to study the hydrochemical structure of waters and the influence of the Lena River flow. From the obtained data, it was found that the effect of fresh water on the sea surface layer was very high and can be traced to a great distance from the river delta. An unconservative distribution of some hydrochemical parameters in the mixing zone was recorded. The concentration of nutrients in the surface layer, and a high turbidity can serve as limiting factors in the development of the phytoplankton community.

#### DOI: 10.1134/S0001437017010180

### INTRODUCTION

The large volume of continental runoff, harsh climate, free water exchange with the Arctic Ocean, and year-round existing ice of a large part of the water area influence the hydrochemical conditions of the Laptev Sea. This primarily affects the spatiotemporal variability of the hydrochemical characteristics. The sea is distinguished by a large contrast and heterogeneity of the hydrochemical structure.

Lena River runoff definitely has a large effect on the hydrochemical structure of the sea. According to [14], the relative contribution of the Lena River to the overall fresh continental runoff into the Arctic Ocean is approximately 20% (525 km<sup>3</sup>/year). As a result, the river flow, similarly to the Kara Sea, spreads over large distances.

This research presents the main results of hydrochemical studies in the estuary area of the Lena River in September 2015. The main objective of hydrochemical investigations was to characterize the abiotic component of ecosystems (dissolved oxygen, basic nutrients, and inorganic carbon compounds) during biological studies.

### MATERIALS AND METHODS

Hydrochemical investigations were carried out in September 2015 (cruise 63 of the R/V *Akademik Mstislav Keldysh*). The transect was at  $130^{\circ}3'$  E between  $72^{\circ}$  and  $78^{\circ}$  N. In total, 14 stations were set up on the transect, with the use of bathometers in a Rosette cassette also equipped with a CTD probe (temperature and salinity data provided by the head of the hydrological team, Cand. Sci. (Phys.–Math.) S.A. Shchuka). The layout of stations is shown in Fig. 1.

The hydrochemistry team carried out a wide range of works to determine the main hydrochemical parameters in water samples: dissolved oxygen, pH, total alkalinity, and contents of mineral phosphorus, total phosphorus, dissolved silica, nitrite nitrogen, nitrate nitrogen, ammonia nitrogen, and total dissolved nitrogen. Using the pH and total alkalinity values, the team calculated the parameters of the carbonate water system (total dissolved inorganic carbon, the concentration of carbonate ion, and the content and partial pressure of carbon dioxide) using the pH–*Alk* method [13]. The dydrochemical parameters were determined in the onboard laboratory using standard methods adopted in Russian oceanology [4, 5].

#### **RESULTS AND DISCUSSION**

The hydrochemical structure of the waters depended closely on the temperature distribution (Fig. 2). There was a thin (less than 5 m) strongly desalinated layer below 10 psu, and the temperature was  $6-8^{\circ}$ C at stations 5216–5219. In the surface layer between stations 5219 and 5220, a clearly visible boundary separated this layer from waters with salinity higher than 18–20 psu and a temperature of 2–4°C. The boundary defined the area of direct influence of river flow, located between stations 5224 and 5228 (24 psu isohaline). This area was over the edge of the shelf; the from-



Fig. 1. Location of stations in Laptev Sea transect.



Fig. 2. Distribution of temperature and salinity in transect.

tal zone, distinguished not only by the hydrophysical, hydrochemical, and biological characteristics, was adjacent to it. The presence of more saline waters was recorded at station  $5215_2$ ; as a result, the desalinated region was divided into two parts. This was due to the intrusion of more saline waters or, more likely, to orographic upwelling of waters. The depth of the transition layer of the hydrophysical parameters varied greatly from station to station, but it generally it increased from south to the north with the increasing influence of marine waters from 3-4 to 15 m. In the bottom layer, the salinity reached 30 psu at stations 5216-5219 and 33 psu at stations  $5215_2-5225$ ; deeper than the 20 m horizon, the temperature was below 0°C. Exceptions

OCEANOLOGY Vol. 57 No. 1 2017

were deep stations 5225-5227, where the temperature of the layer from 140 m to 1 km was above 0°C, and in the core of the water mass, the temperature was +1.55°C (300 m horizon). At the deep stations after the transition layer, the salinity distribution gradually increased from 33.5 to 34.8 psu; in the core of the warm water mass, salinity increased to 34.9 psu. Below, in the bottom layer, the salinity was 34.94 psu. Such a water structure in deep layers assumes the presence of waters of Atlantic origin, flowing from the North Atlantic through the Barents and Kara seas along the slope of the continental shelf [10–12].

The influence of a river flow, to a greater or lesser extent, reflects on the distribution of all hydrochemi-



Fig. 3. Distribution of dissolved silicon in transect.

cal parameters, especially the total alkalinity (*Alk*) and dissolved silicon values, which are a good tracer elements of river waters [7, 9].

In the study area, the dissolved silicon content ranged from 2.2 to  $-66.6 \,\mu\text{M}$  (Fig. 3). The highest concentrations of silicon (over 50 µM) were recorded in the surface waters of the southern stations of transect close to the Lena River delta (stations 5216-5219). Lower, in the transition layer of the hydrophysical parameters, the silicon concentration decreased to  $30 \mu M$ , and lower toward the bottom it decreased to  $25 \,\mu$ M. With the increasing influence of marine waters, the silicon concentration decreased along the entire profile, and the structure of the vertical distribution of silicon also varied. The silicon distribution acquires the features of the mixing zone of river and marine waters: the silicon maximum was on the surface; the subsurface layer was characterized by high gradients; the layer with the silicon minimum was located lower; and a slight increase in silicon concentrations was recorded in the bottom. At station 5215 2, the silicon distribution had more uniform character, without welldefined gradient layer; possibly, it was connected with the rise of the bottom waters in this location of the water area. In general, for dissolved silicon, the influence of the river flow is well traced in the surface layer to station 5226. Stations 5225 and 5227 are both marine because of the silicon concentration, which did not exceed  $10 \,\mu\text{M}$  throughout the water column.

The total alkalinity distribution in the transect was similar to that observed in the same season (September) in 2011 [3]. According to the total alkalinity distribution (Fig. 4), the influence of the river flow in surface waters also was recorded at station 5226. The quantity of total alkalinity in the transect ranged from 1.0 to -2.4 mg-equiv/L. At stations 5216-5219, where the influence of the river flow was the highest, the total alkalinity value in surface waters was less than 1.40 mg-equiv/L, and the minimum value of 1.07 mg-equiv/L was recorded at station 5216. At stations 5220-5226, the alkalinity value ranged from 1.60 to -2.00 mg-equiv/L, generally increasing from south to north with decreasing influence of the river flow. The vertical distribution of the Alk value was violated in the area of station 5215 2, where a rise in water was observed. The 1.80 mg-equiv/L isoline approaches the surface here. At marine stations 5225 and 5227, the alkalinity value in the surface layer was more than 2.00 mg-equiv/L; however, desalination was recorded (continental runoff or melt water) in the surface layer (salinities of 30.15 and 28.56 psu, respectively). In the transition layer of hydrophysical parameters, the total alkalinity value increased to 2.20 mg-equiv/L, then there was a slight increase in Alk to the bottom.

It should be noted that the presence of a total alkalinity maximum (2.43 mg-equiv/L) in the bottom layer in the area of station 5221 coincided with the maxima of ammonia nitrogen and total and mineral phosphorus, and the minimum of the absolute and relative oxygen contents (see below). The formation of such a maximum is most likely related to massive sedimentation and decomposition of organic matter in this area. Usually, the total alkalinity value is considered a quite conservative parameter that depends little on biological processes. However, as a result of



Fig. 4. Distribution of total alkalinity in transect.

decomposition of organic matter, the content of total inorganic carbon increases and the influence of other components of the total alkalinity are intensified, for example, ammonia, which can lead to increased total alkalinity.

The dissolved oxygen concentration in the transect varied from 4.99 to 8.04 mL/L with a minimum in the bottom layers of the river part of the study area. Oxygen saturation of the water, observed on the entire transect, did not rise above 97% (Fig. 5). Thus, even on the surface, the oxygen concentration did not reach equilibrium with the oxygen concentration in the atmosphere. In the bottom layers at the beginning of the transect (stations 5116-5219), where saline marine waters penetrate, the percentage of oxygen falls to 64%; it can be concluded that in the studied transect, oxidation of organic matter prevails over production. In view of the large amount of suspension that was removed with continental runoff and prevented penetration of sunlight into the upper active layer of the sea, such an oxygen distribution was not unusual and it was observed in the same season on other expeditions [6].

The pH distribution has features in common with the dissolved oxygen distribution: minimum values were observed in the bottom layer at stations closest to the delta (7.32 at station 5216); under the influence of marine water, the pH value increased on average to 7.9 NBS units.

Except for silicon, the contents of other nutrients were low. A distinctive feature of the distribution of mineral phosphorus and nitrate nitrogen was an increase in the content of these parameters in the bottom horizons, in the area of influence of continental runoff (stations 5216–5222). The content of mineral phosphorus in the transect varied from 0.07 to 1.22  $\mu$ M (Fig. 6). In the surface layer, its content ranged from 0.09 to  $-0.16 \mu$ M, and it limited phytoplankton development. It should be noted that the presence of an intermediate maximum of mineral phosphorus at depths of 500–1000 m may be associated with the presence of Atlantic waters [10–12].

The distribution of total dissolved phosphorus in the transect is similar to the distribution of mineral phosphorus: in the surface layer, the maximum was in the bottom horizons in the zone of influence of river flow, the intermediate maximum was at depths of 500-1000 m, the maximum was in deep stations, and there was a slight increase to the bottom. Its content was  $0.18-1.7 \mu$ M. In both parts of the river plume (south and north of the intrusion of more saline waters), relatively high values of organic phosphorus (calculated as the difference between total and mineral phosphorus) were recorded, and the concentration at almost all stations was 1.5-2 times higher than the mineral concentration. In the surface waters at deep stations, such differences were not observed. The mineral phosphorus values were close to the total phosphorus values at all horizons; at station 5215 2, it was typical of the bottom water in the transect.

The nitrate nitrogen content ranged from 0.14 to 17.33  $\mu$ M (Fig. 7). The maximum content of nitrates (5.2  $\mu$ M) was observed in the surface layer at station 5215\_2. Also, a high nitrate nitrogen content was observed at stations subjected to the strongest



Fig. 6. Distribution of mineral phosphorus in transect.

influence of river runoff (stations 5216–5219), where it was 2.6–4.2  $\mu$ M. Outside this zone (north of station 5215\_2), the nitrate concentration ranged from 0.15 to -2.3  $\mu$ M; it was lower than the limiting values for the development of phytoplankton communities.

Ammonium nitrogen characterized the oxidation of organic matter, since it was the first in the chain of

oxidation of organic nitrogen to mineral nitrogen. The maximum concentration of ammonium nitrogen was found in the bottom layer at station 5216 and reached 2.15  $\mu$ M (Fig. 8). The second maximum, as mentioned above, was observed in the bottom layer at stations 5221–5222. Another local maximum occurred in the selected frontal area, above the edge of the shelf at station 5226 (1.83  $\mu$ M).



Fig. 7. Distribution of nitrate nitrogen in transect.



Fig. 8. Distribution of ammonia nitrogen in transect.

Data analysis confirms the hypothesis that the increased contents of ammonium and nitrate nitrogen (especially in the bottom layer) were associated with the oxidation and decomposition of dead organic matter, not with removal of these elements directly from the river flow. The nitrite nitrogen concentration o the entire transect was close to analytical zero; the maximum was 1.1  $\mu$ M at the 4 m horizon of station 5218 and was most likely related to the oxidation of rapidly decaying organic matter carried from the Bykovskaya channel of the Lena River delta.

OCEANOLOGY Vol. 57 No. 1 2017

The maximum total nitrogen values were recorded in the bottom layer closest to stations 5216-5218 of the Lena River delta. Here, the concentration reached 100  $\mu$ M; it was higher than that observed for the mixing zones in Ob' and Yenisei bays [1, 2] in September. The surface layer maximum at  $5212_2$  station confirms the assumption that bottom waters rise here.

## CONCLUSIONS

Data obtained as a result of field studies in September 2015 made it possible to assess the impact of continental runoff of the Lena River on the hydrochemical structure of shelf waters and the continental slope of the Laptev Sea.

Calm weather during the works contributed to the conservation of the highly stratified water structure formed during active removal of continental waters during the flood, as well as additional desalination by melt waters.

The upper active layer of the sea was undersaturated with oxygen; this may be due to the high turbidity of incoming inland waters and the beginning of oxidation of riverine organic matter. The content of nutrients, except for silicon, was low in the upper active layer. The content of mineral phosphorus and nitrate nitrogen was below the level limiting photosynthesis.

The accumulation of nutrients (mineral phosphorus and nitrate nitrogen), which are the limiting elements of phytoplankton growth in the study area, occurred largely owing to the decomposition of organic matter in deep-sea waters below the photosynthesis layer (recycling of nutrients), not the removal of river waters.

At the deepest stations in the 300-1000 m layer, we recorded a local increase in mineral phosphorus associated with movement of waters of Atlantic origin along the slope to the east. It was confirmed by a temperature above 0°C in this layer.

We should mention an "anomalous" distribution of most hydrochemical parameters at station 5215\_2, which was the division between the two parts of the Lena plume. Thus, there are increased total and nitrate nitrogen contents, low ammonium nitrogen values, and higher total alkalinity values in the surface layer compared with other transect stations. This distribution of nutrients was due to the rise of bottom water observed at this station.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 14-05-05005, and Russian Science Foundation, grant no. 14-50-00095, processing and analysis of hydrophysical data, grant no. 14-17-00581, processing and analysis of hydrochemical materials.

#### REFERENCES

- P. N. Makkaveev, Z. G. Melnikova, A. A. Polukhin, S. V. Stepanova, P. V. Khlebopashev, and A. L. Chultsova, "Hydrochemical characteristics of the waters in the western part of the Kara Sea," Oceanology (Engl. Transl.) 55, 485–496 (2015).
- P. N. Makkaveev, P. A. Stunzhas, Z. G. Mel'nikova, P. V. Khlebopashev, and S. K. Yakubov, "Hydrochemical characteristics of the waters in the western part of the Kara Sea," Oceanology (Engl. Transl.) 50, 688–697 (2010).
- 3. I. I. Pipko, S. P. Pugach, and I. P. Semiletov, Characteristic features of the dynamics of carbonate parameters in the eastern part of the Laptev Sea," Oceanology (Engl. Transl.) **55**, 68–81 (2015).
- 4. *RD* 52.10.242-92: *Manual for Chemical Analysis of Water* (Gidrometeoizdat, St. Petersburg, 1993) [in Russian].
- 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 (Russian Scientific Research Inst. of Marine Fisheries and Oceanography, Moscow, 2003) [in Russian].
- N. I. Savelieva, A. N. Salyuk, and L. N. Propp, "Peculiar features of the thermohaline and hydrochemical water structure in the southeastern Laptev Sea," Oceanology (Engl. Transl.) 50, 869–876 (2010).
- A. A. Smirnov, "Inflow of the river waters into the Kara and Laptev seas," Tr. Arkt. Nauchno-Issled. Inst. 72 (2), 92–104 (1955).
- Modern Hydrochemical Analysis of Ocean, Ed. by O. K. Bordovskii and V. N. Ivanenkov (Shirshov Scientific Research Inst. of Oceanology, Academy of Sciences of Soviet Union, Moscow, 1992) [in Russian].
- 9. 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).
- I. A. Dmitrenko, I. V. Polyakov, S. A. Kirillov, et al., "Seasonal variability of Atlantic water on the continental slope of the Laptev Sea during 2002–2004," Earth Planet. Sci. Lett. 244 (3–4), 735–743 (2006).
- I. A. Dmitrenko, I. V. Polyakov, S. A. Kirillov, et al., "Toward a warmer Arctic Ocean: Spreading of the early 21st century Atlantic Water warm anomaly along the Eurasian Basin margins," J. Geophys. Res. 113, C05023 (2008). doi 10.1029/2007JC004158
- I. A. Dmitrenko, S. A. Kirillov, L. B. Tremblay, et al., "Impact of the Arctic Ocean Atlantic water layer on Siberian shelf hydrography," J. Geophys. Res. 115, C08010 (2010). doi 10.1029/2009JC006020
- DOE Handbook of Methods for the Various Parameters of the Carbon Dioxide System in Seawater; Version 2, ORNL/CDIAC-74, Ed. by A. G. Dickson and C. Goyet (U.S. Department of Energy, Washington, DC, 1994).
- V. V. Gordeev, J. M. Martin, I. S. Sidorov, and M. V. Sidorova, "Assessment of the Eurasian river input of water, sediment, major elements, and nutrients to the Arctic Ocean," Am. J. Sci. 296, 664–691 (1996).

Translated by Z. Litvinenko

OCEANOLOGY Vol. 57 No. 1 2017