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## The role of river runoff in the Kara Sea surface layer acidification and carbonate system changes

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## LETTER

## The role of river runoff in the Kara Sea surface layer acidification and carbonate system changes

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E-mail: [polukhin@ocean.ru](mailto:polukhin@ocean.ru)**Keywords:** Kara Sea, acidification, carbonate chemistry, continental runoff increase, carbon dioxide, aragonite

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**Abstract**

This study aims to perform the results of the investigation of the Kara Sea carbonate system (CS) changes and the factors that determine it. The important feature of the Kara Sea water structure is strong stratification caused mainly by the Ob' and Yenisey rivers discharge which is estimated as 81% of the total continental runoff to sea. Occurring climate changes, as an increase in the total volume of the Arctic Ocean water (due to melting of glaciers, sea ice decline and river runoff increase), air temperature and CO<sub>2</sub> concentration growth should affect greatly the Kara Sea CS. However, riverine water influence seems to be the main driver of future acidification of the Kara Sea water due to permafrost thawing as it stores a great amount of buried carbon. An increase of carbon (mainly inorganic) flow to the sea will lead to carbonate equilibrium shift, oxidation of organic matter and release of CO<sub>2</sub> that ultimately leads to a decrease in pH and therefore acidification. The area of the riverine plume depends on the amount of freshwater flowing into the sea and the conditions of the wind forcing. According to the data from Shirshov Institute cruises within the plume area aragonite saturation is below 1 that shows its state as acidified. Prevalence of pCO<sub>2</sub> values in the freshened surface layer over the atmospheric shows that atmospheric carbon dioxide, apparently, cannot serve as the main driver for the acidification of the surface waters of the Kara Sea. At the shallow shelf to the north of the Ob' Inlet mouth we observe acidification of the whole water column from surface to the bottom layer due to elevated riverine discharge and increase of flowing terrestrial carbon.

**1. Introduction**

The Kara Sea has been studied for a long time since the mid-30s of the 20th century. The researchers of the Soviet Union were tasked to assess the productivity of its waters as a fishing area. These studies have shown that the sea will never be of commercial importance due to physical and chemical properties (mainly strong stratification) of the sea and its influence on ecosystem biodiversity. The data obtained during these expeditions has served as the basis for fundamental studies of the Kara Sea state and processes occurring in its water area today. During 1995–2003 in the frame of several international projects (SIRRO, SPASIBA) there have been investigated physical and biogeochemical properties of the Kara Sea (Galimov *et al* 2006). Considering the climatic changes that have occurred for the last decades (Groisman and Soja 2009, Blunden and

Arndt 2016) the marine ecosystem has changed nowadays: in the south-western part of the sea there are observed invasive species of crab (Zalota *et al* 2018), and cod larvae (never performed in the species composition of ichthyoplankton) are found in the southern bays of the Novaya Zemlya archipelago (NZA).

One of the important results became the understanding of the role of stratification due to the large volume of fresh water flowing in its water area. According to modern data, 1400–1600 km<sup>3</sup> of fresh water annually enters its water area (Harms and Karcher 1999, Osadchiev *et al* 2017) due to the continental runoff of the Ob and Yenisei rivers, as well as many other small rivers. Previously a lot of attention was paid on physical characteristics of the river plume, disposition of frontal zones (Zavialov *et al* 2015) and physical conditions of the desalinated surface layer of

the Kara Sea (Zatsepin *et al* 2015). There is also a general trend towards a decrease in the ice cover in the Arctic (Vihma 2014), which is also reflected in the Kara Sea (Petoukhov and Semenov 2010). In consequence of this, the part of meltwater, desalinating the sea surface layer, also increases (Polukhin and Makkaveev 2017). Both of these factors, as shown in the paper (Fransson *et al* 2015), can positively or negatively affect the dynamics of acidification of Arctic waters and the Kara Sea in particular.

Global climate changes manifest most intensely in the Arctic Ocean, the result of which is, in particular, the process of acidification of its waters. For the Arctic region causes and consequences of acidification are described by many authors, and all the latest knowledge was unified in the AMAP report (AMAP 2013). In general, acidification is the process of increasing the concentration of hydrogen ions (i.e. lowering the pH value) under the influence of various factors. Inorganic carbon compounds are found in the ocean in the form of carbonic acid and its derivatives. These include carbon dioxide  $\text{CO}_2$ , carbonic acid  $\text{H}_2\text{CO}_3$ , bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  ions. These compounds are closely interrelated with each other and form a carbonate system (CS). Calcium carbonate, one of the main CS parameters, is poorly soluble and can dissolve and exist in it in appreciable quantities only in the presence of dissolved carbon dioxide. Thus, dissolving carbonates perform an important function—maintain balance in the system. In turn, an increase in the concentration of dissolved  $\text{CO}_2$  in seawater leads to a shift in equilibrium in the CS of the oceans and, as a consequence, an increase in its acidity (Horne 1969).

A lot of attention was devoted to the study of the process of acidification of the seas of the Arctic basin and its impact on the ecosystem (AMAP 2018). Especially the Canadian and American sectors of the Arctic are well studied (Bates *et al* 2009, Mathis *et al* 2011, Bates *et al* 2013, Robbins *et al* 2013, Azetsu-Scott *et al* 2014). The current acidification state of the East Siberian shelf seas (Laptev and East Siberian) is known from (Semiletov *et al* 2016, Pipko *et al* 2017). Based on the published data, the acidification process is quite intense in these seas. In the Canadian sector of the Arctic, water with  $\Omega_{\text{Ar}} < 1$  is already observed at considerable depths (Fabry *et al* 2009), and acidification of the waters of the East Siberian shelf occurs faster than predicted (Semiletov *et al* 2016).

River runoff is one of the main factors affecting the CS of marine waters, including the solubility of aragonite, due to the inflow of erosive carbon decomposing to  $\text{CO}_2$ , thus exacerbating ocean acidification. For the Kara Sea, this factor should be considered as one of the main drivers of acidification. There are several reasons for this thesis: catchment area of the Ob' and Yenisey Rivers, located in the West Siberia, is covered with organic-rich peatlands ( $\sim 70$  Pg of carbon is currently stored in permafrost) and it could be transferred to the

sea by great continental runoff ( $\sim 35\%$  of the total freshwater runoff that the Arctic Ocean receives) (Frey *et al* 2007). Thus, an inflow of organic matter only into the Kara Sea is more than into any other part of the Arctic Ocean (Opsahl *et al* 1999). Moreover, (Drake *et al* 2018) shows that as Yenisey runoff has increased by 2%/year for the last decades the flow of total alkalinity (and terrestrial carbon as well) is also increasing. In this case, the role of atmospheric carbon dioxide in the acidification of the Kara Sea waters may be less significant.

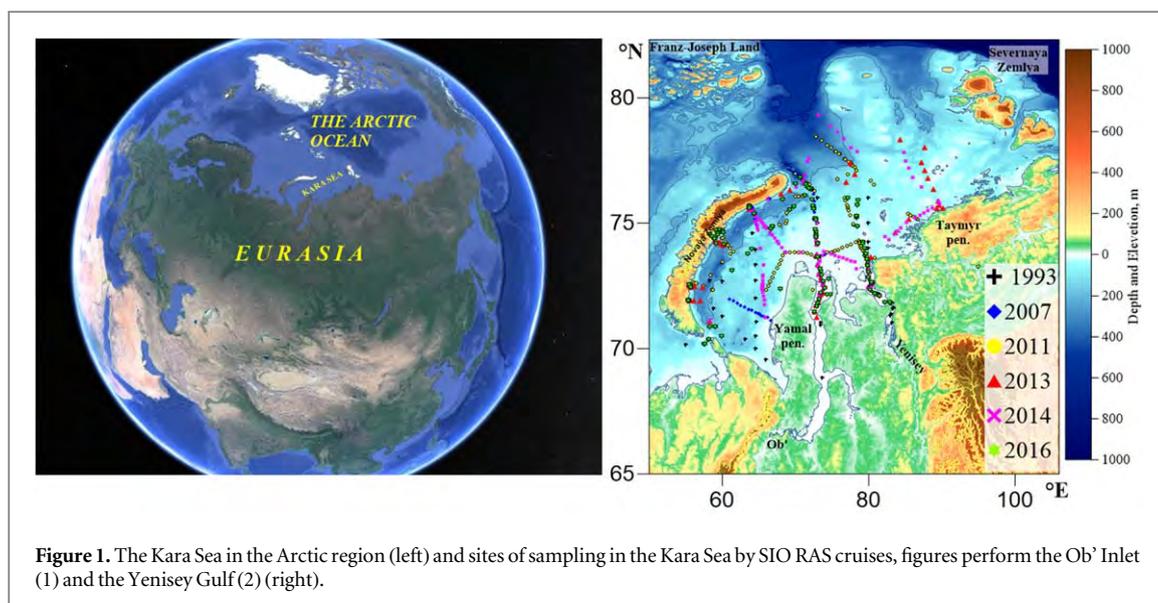
## 2. Data and methods

Since 1993, Shirshov Institute of Oceanology (SIO) has completed 9 complex research expeditions to the Kara Sea. Most of the data received in the SIO cruises was collected by the same team, including the author of the study, using the classical hydrochemical techniques (DOE Handbook of Methods for Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water 1994, Parsons 2013) and it has underwent manual and machine verification. The main emphasis in hydrochemical research was aimed at providing biological studies with abiotic environmental parameters. Published works give characteristics of the distribution of various parameters in a particular (mostly autumn) season (Makkaveev *et al* 2010, 2015a, 2017). At the same time, the CS parameters of the Kara Sea waters remained practically neglected being used only as a tracer of river waters or as indicators of processes of organic matter oxidation.

The data used in the study was obtained in scientific cruises held by SIO RAS to the Kara Sea in 1993, 2007, 2011, 2013, 2014, and 2016 (Lisitzin and Vinogradov 1994, Flint 2010, 2015, Flint and Poyarkov 2015, Flint *et al* 2016). Sites layout is shown on figure 1.

Altogether, we have 378 sites with both vertical and surface samplings covering practically all parts of the sea. Cruises in 1993, 2007, 2011, 2013, were held in September–October; 2014 in August; 2016 in July–August.

Samplings on hydrological stations were carried out with 5 l plastic bathometers in accordance with ISO 51592-2000 'General requirements for water sampling'. Samples for determination of pH, nutrients and alkalinity were collected in plastic 0.5 l bottles without preservation and processed immediately. The pH value (NBS scale) was determined on the ionomer 'Ekoniks Expert 001' with a glass composite pH electrode by CJSC 'Akvilon' (Moscow, Russia), for calibration we have used buffer solutions ISO 8.135-74 (techniques are the same as in (Dickson 1993)). Analysis of total alkalinity ( $A_T$ ) was conducted by direct titration (the Bruyevich method) with a visual determination of the titration end point. This method, developed in 1930s, shows very good correlation



(Pavlova *et al* 2008) and high measurement accuracy in comparison with other methods of total alkalinity determination (Edmond 1970, DOE Handbook of Methods for Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water 1994, Dickson *et al* 2003). Dissolved Inorganic Carbon (DIC), aragonite saturation ( $\Omega_{Ar}$ ) and partial pressure of carbon dioxide ( $pCO_2$ ) were calculated using temperature, salinity,  $A_T$  and pH data with 'Program Developed for CO<sub>2</sub> System Calculations' by (Lewis and Wallace 1998). Temperature and salinity were measured directly with CTD-profiler (usually SBE19+ or similar by SeaBird Electronics, USA).

Data on Ob' and Yenisey discharge was obtained from A Shiklomanov from University of New Hampshire, USA, (period 1993–2010) and Arctic Great Rivers Observatory (A-GRO, <https://arcticgreatrivers.org/data/>) project (period 2011–2017).

The maps on distribution of salinity and aragonite saturation were prepared with Golden Software Surfer 15, data was extrapolated with the kriging method. Graphs are performed with Golden Software Grapher 13.

### 3. Results

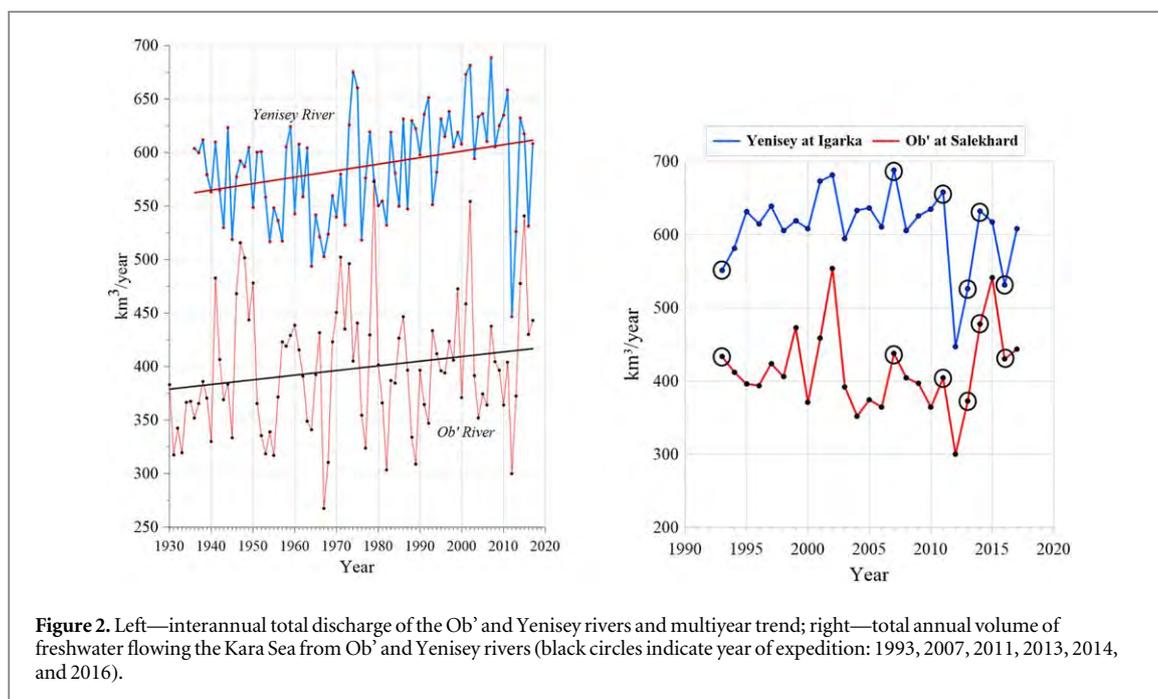
#### 3.1. River runoff

It was mentioned above that river runoff should play a crucial role in acidification of the Kara Sea surface layer owing to increased export of terrestrial carbon through permafrost melting that would generate the acidification. It is well-known that continental discharge to the Arctic Ocean is continuously increasing (Peterson *et al* 2002) and the discharge of the Ob' and Yenisey Rivers is not an exception (Drake *et al* 2018). According to the discharge data from A-GRO project annual discharge is continue to increase (figure 2 right). There has been investigated interannual

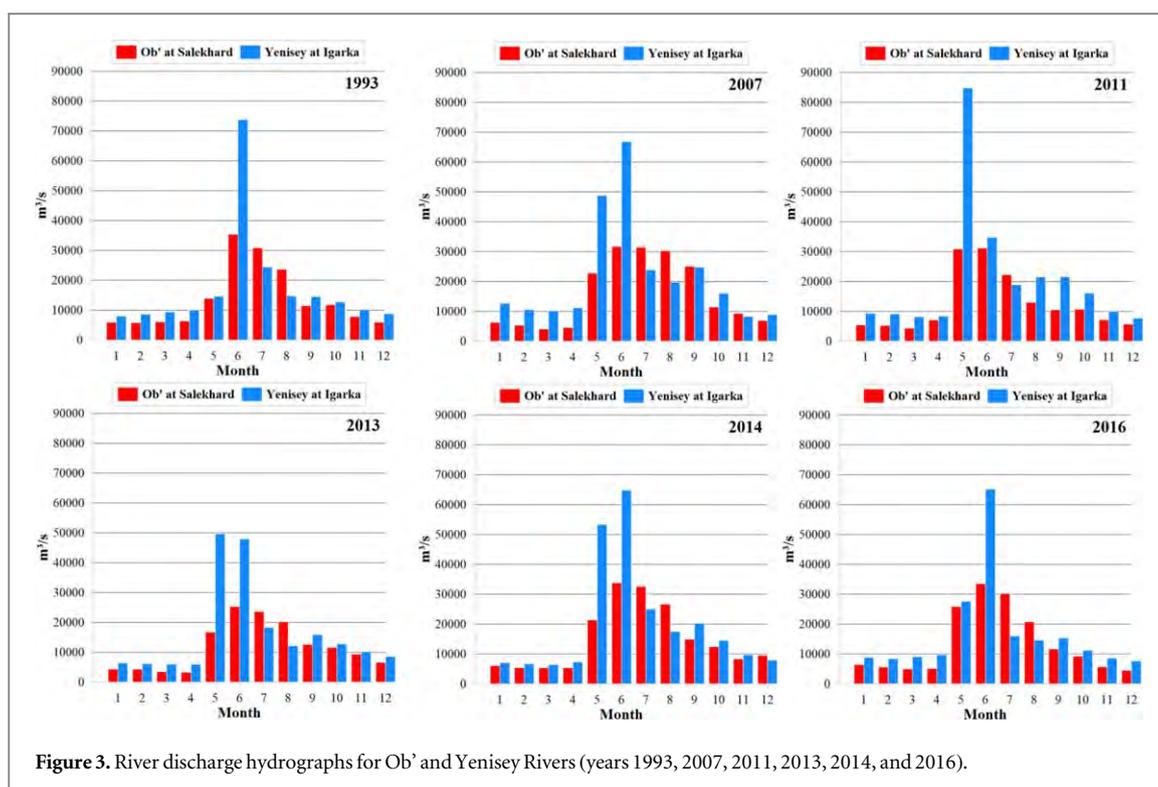
discharge of Ob' and Yenisey Rivers for the period 1993–2017 (figure 2 left). Total discharge of Yenisey and Ob' to the Kara Sea is estimated as 620 and 429 km<sup>3</sup> respectively (Gordeev *et al* 1996). The data shows that the lowest amount of fresh water flowed into the sea in 2012 was 447 km<sup>3</sup> and 300 km<sup>3</sup> for Yenisey and Ob' respectively representing 72% and 69% of average outflow. It should be also mentioned that at the same year sea ice coverage in the Arctic was the lowest for the 1979–2012 observing period (Vihma 2014). If we take into account only the years of expeditions, the most total water discharge has been observed on Yenisey in 2007 (688.5 km<sup>3</sup>) and on Ob' in 2014 (477.5 km<sup>3</sup>) and the least total water discharge has been observed on Yenisey in 2013 (526 km<sup>3</sup>) and on Ob' in 2013 as well (372 km<sup>3</sup>).

Considering the hydrographs of both rivers over the years of interest a number of important features should be noted (figure 3). For example, high water period usually occurs on Yenisey in June (except 2011 when it has occurred in May) and does not exceed several weeks. The discharge is 2 times lower over the summer months. Meanwhile, on the Ob' the flood is stretched for several summer months with a constantly high flow volume for the Ob' River. It should be noticed that after the flood period (in June) on the Yenisey discharge of the Ob' prevails during other summer months. Low water period on both rivers is characterized by a comparable amount of discharge.

It is known that most freshwater discharge on the Ob' and Yenisey Rivers is occurring through the summer months (Bowling *et al* 2012). For the May–September (so-called 'high-water period') it was calculated part of discharge that flowing to the Kara Sea from the Ob' and Yenisey. On average, over a multi-year period, the proportion of runoff (per calendar year) during the high-water period for both rivers was 75%. However, we can see that the value is decreasing over the long-term period (figure 4 left) for both



**Figure 2.** Left—interannual total discharge of the Ob' and Yenisey rivers and multiyear trend; right—total annual volume of freshwater flowing the Kara Sea from Ob' and Yenisey rivers (black circles indicate year of expedition: 1993, 2007, 2011, 2013, 2014, and 2016).



**Figure 3.** River discharge hydrographs for Ob' and Yenisey Rivers (years 1993, 2007, 2011, 2013, 2014, and 2016).

ivers. Accordingly, the proportion of winter runoff has increased over the long-term period. This is observed, for example, on the Lena River as well (Yang *et al* 2002). Winter runoff on Eurasian rivers is characterized by very low discharge and speed values. This contributes to the fact that in winter the content of many chemical elements in riverine water increases according to A-GRO water quality datasets. Average annual values of  $A_T$  in the waters of the Ob' and Yenisey for the 2004–2016 period prove that DIC input to the Kara Sea is also increasing (figure 4 right).

Thus we can state that increase of  $A_T$  in the Ob' and Yenisey rivers water on the background of increase of total (annual) riverine discharge and its 'low-water' part leads to growing flow of DIC to the Kara Sea shelf.

### 3.2. Salinity, aragonite saturation and pCO<sub>2</sub> distribution in the surface layer

In September 1993, according to the data,  $\Omega_{Ar}$  values have varied from 1.03 to 2.48 in the surface layer (figure 5(B)). The lowest values observed in the Ob'

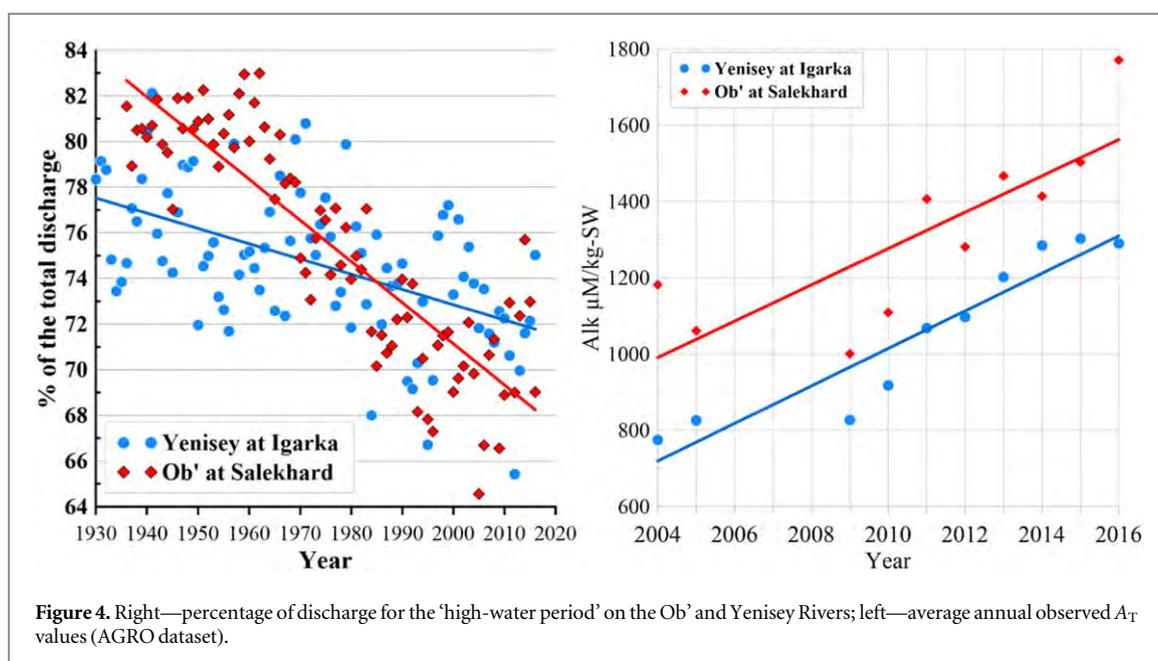


Figure 4. Right—percentage of discharge for the 'high-water period' on the Ob' and Yenisey Rivers; left—average annual observed  $A_T$  values (AGRO dataset).

Inlet and the northern part of the Yenisei Gulf where salinity varies from 0 to 10 psu (figure 5(A)). The influence of freshwater manifests in the central part of the sea with  $\Omega_{Ar}$  value  $< 1$ . Strong horizontal salinity gradient differs central part ( $S = 15\text{--}25$  psu) from south-western part ( $25\text{--}32$  psu) where  $\Omega_{Ar}$  more than 2. Maximum values of  $\Omega_{Ar}$  (2.4) are observed over the southern part of Novozemelskiy Trough. In general propagation of freshwater observed during the cruise has covered the shallow part of the Kara Sea shelf with aragonite saturation below 1. The important factor of the runoff propagation comes the wind forcing on the study area (Polukhin and Makkaveev 2017).

In 2007 investigated area has covered a part of Ob'-Yenisei shelf, the southern part of St. Anna Trough and south-western part. The  $\Omega_{Ar}$  values varied from 0.01 in the Ob' Inlet to 3.21 in the southern part of St. Anna Trough (figure 5(D)). The lowest value was observed in the Ob' Inlet and reflects the influence of riverine water. The highest value (3.21) shows the influence of marine water in the northern part of the research area. According to salinity data, riverine influence manifested overall studied area except for local regions in the north (near NZA) and south (near Yamal shore) where salinity exceeds 25 psu (figure 5(C)). However, most parts of freshwater have been propagating to the east from the investigated area due to the wind forcing (Kubryakov *et al* 2016). Average values of salinity and  $\Omega_{Ar}$  in the surface were 21.65 and 1.51 respectively and perform the physical process of mixing of marine water and continental runoff. A small area near NZA shore with  $\Omega_{Ar}$  value below 1.2 and salinity below 18 psu accents influence of riverine plume presumably of Yenisey origin (Polukhin and Makkaveev 2017). The main part of desalination belongs to melted ice water (Polukhin and Makkaveev 2017).

In 2011 study site has covered central and western parts of the sea. The range of  $\Omega_{Ar}$  value was from 0.04 to 2.74 (figure 5(F)) and salinity from 0 to 33 psu (figure 5(E)). The lowest values of salinity were observed in the northern part of the Yenisei Gulf, surface water with  $\Omega_{Ar} < 1$  has spanned a wide area in the central Kara Sea shelf towards the Taymyr Peninsula. This propagation of riverine water reflects in salinity distribution as well. Then to the north from the continental shore water with low aragonite saturation meet marine water forming a strong frontal zone with high salinity gradient. We can also state propagation of freshwater to the east in accordance with Pan-Arctic Riverine Coastal domain theory by (Carmack *et al* 2015). The highest  $\Omega_{Ar}$  value (2.74) was observed in the very southern part of St. Anna Trough where salinity slightly exceeded 33 psu.

In September 2013 distribution of salinity and  $\Omega_{Ar}$  in the surface layer has the more or less repeated situation of 2011 (figure 5(H)). The area with low (below 25 psu) salinity and  $\Omega_{Ar}$  (below 1) was narrower, the northern part was mostly influenced with marine water with high  $\Omega_{Ar}$  value (3.02) and salinity 30–33 psu (figure 5(G)). We can also register a precise frontal zone between riverine and marine waters at the shallow central part of the shelf where salinity has varied intensively from 15 to 25 psu. Location of the freshened surface layer in quite small part of the shelf is explained by strong wind forcing from the north.

In 2014, the riverine plume has covered a large area from  $65^\circ$  to  $90^\circ$  eastern longitude and  $75^\circ$  northern latitude due to wind forcing and high freshwater discharge (figure 2) mainly from the Ob' Inlet (Polukhin and Makkaveev 2017). Salinity in the central part of the sea was 9–12 psu (figure 5(I)),  $\Omega_{Ar}$  value within the plume was lower 1.2 (figure 5(J)), and large surface layer area even below 1. We can also allocate

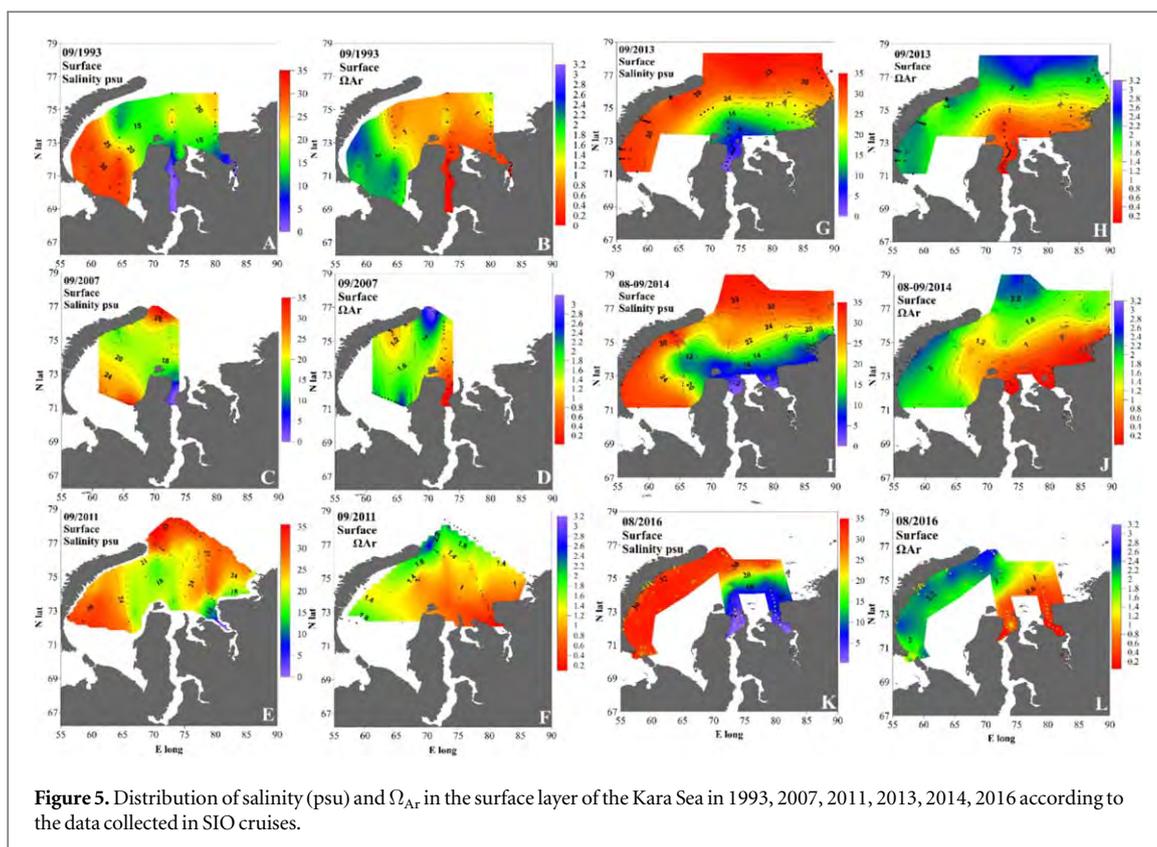


Figure 5. Distribution of salinity (psu) and  $\Omega_{Ar}$  in the surface layer of the Kara Sea in 1993, 2007, 2011, 2013, 2014, 2016 according to the data collected in SIO cruises.

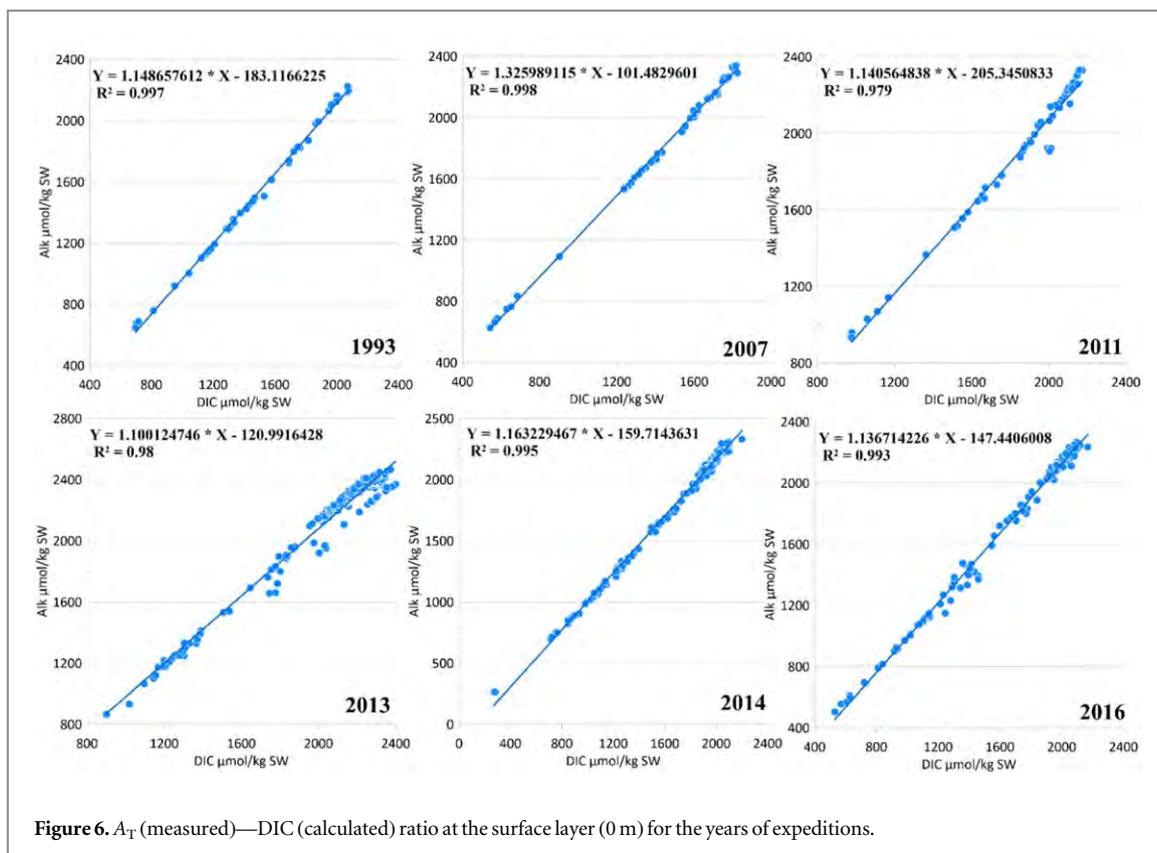


Figure 6.  $A_T$  (measured)—DIC (calculated) ratio at the surface layer (0 m) for the years of expeditions.

two areas with high  $\Omega_{Ar}$  (2.6) values along NZA coastline and in St. Anna Trough where we have also observed the highest salinity values (more than 30–32 psu).

In 2016 continental runoff was allocated in quite narrow Ob'-Yenisey shelf zone due to features of wind

forcing (Kubryakov *et al* 2016). We have observed a freshened layer from 0 to 10 psu (figure 5(K)) and  $\Omega_{Ar}$  0–0.8 (figure 5(L)) up to 140 km long from the Ob' Inlet and Yenisey Gulf mouths, than area with salinity 10–25 psu and  $\Omega_{Ar}$  0.8–1.2 up to 120 km long, and

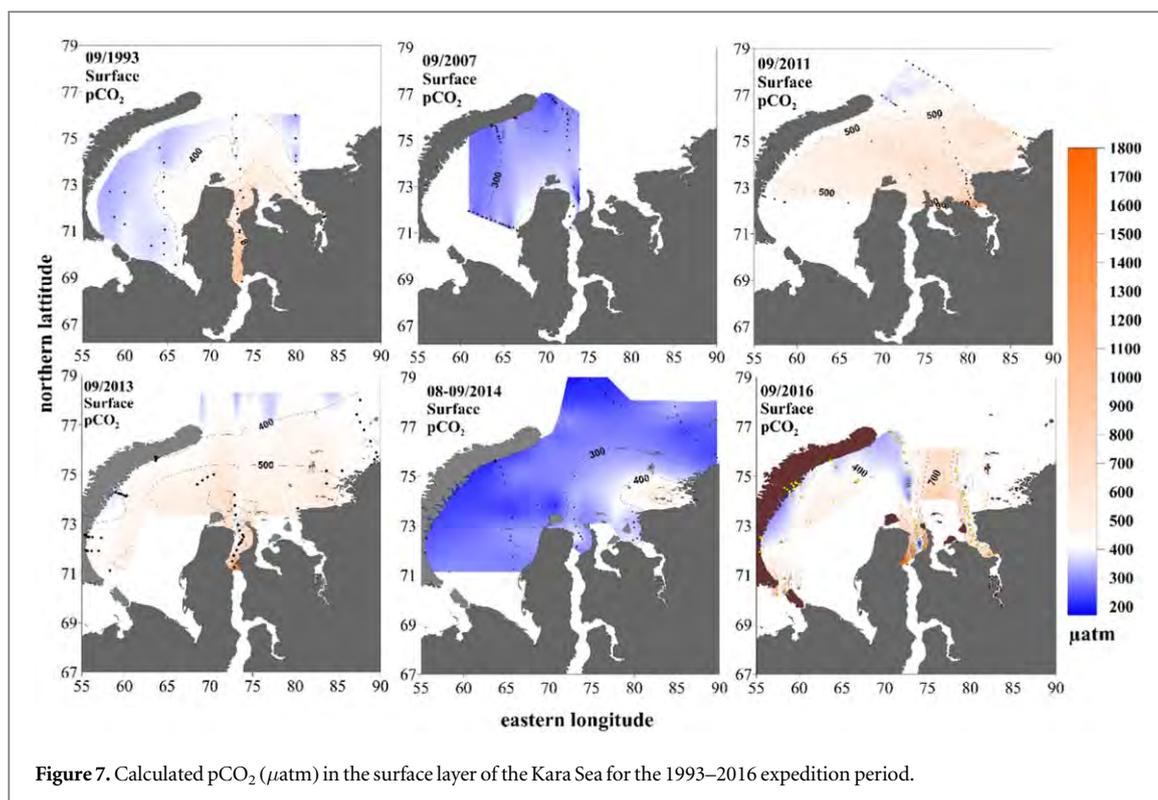


Figure 7. Calculated  $p\text{CO}_2$  ( $\mu\text{atm}$ ) in the surface layer of the Kara Sea for the 1993–2016 expedition period.

then a high-gradient belt separating riverine plume from the open sea with salinity 30–32 psu and  $\Omega_{\text{Ar}}$  2–2.2 and even 2.6 in the southern part of St. Anna Trough. In most part of the freshened area,  $\Omega_{\text{Ar}}$  values were much lower 1.

Using  $A_{\text{T}}\text{-DIC}$  ratio in the surface layer (figure 6) there have been calculated  $A_{\text{T}}$  values for the riverine end-point of the mixing line. It has varied from 101  $\mu\text{M}$  (in 2007) to 205  $\mu\text{M}$  (in 2011) and is showing sufficiently low  $T_{\text{A}}$  for the riverine waters. Thus, a significant effect of river runoff on the parameters of the CS of the surface waters of the Kara Sea can be confirmed.

Expedition data shows that except 2007 and 2014 most part of the surface layer over the investigated area was oversaturated with carbon dioxide (figure 7). Sometimes this area was limited by the central shelf zone (as in 1993) but in most cases it has covered large areas outside the central shelf zone, in the deep south-western part of the sea.

According to NOAA Earth System Research Laboratory (NOAA ESRL, <https://esrl.noaa.gov/gmd/>) data, average partial pressure of  $\text{CO}_2$  on Ny-Alesund (Svalbard) and Tiksi (Lena River, Russia) stations has grown from 390 to 415 ppm over the last decade.  $p\text{CO}_2$  values in the surface layer allow to estimate direction of  $\text{CO}_2$  fluxes over the Kara Sea. It seems that except 2007 and 2011  $\text{CO}_2$  flow was directed from the sea to the air over the investigated area. Thus, carbon dioxide was probably not the main cause of acidification of the Kara Sea surface layer.

### 3.3. Vertical distribution of Salinity and $\Omega_{\text{Ar}}$ in the mixing zone of the Ob' Inlet and the adjacent shelf

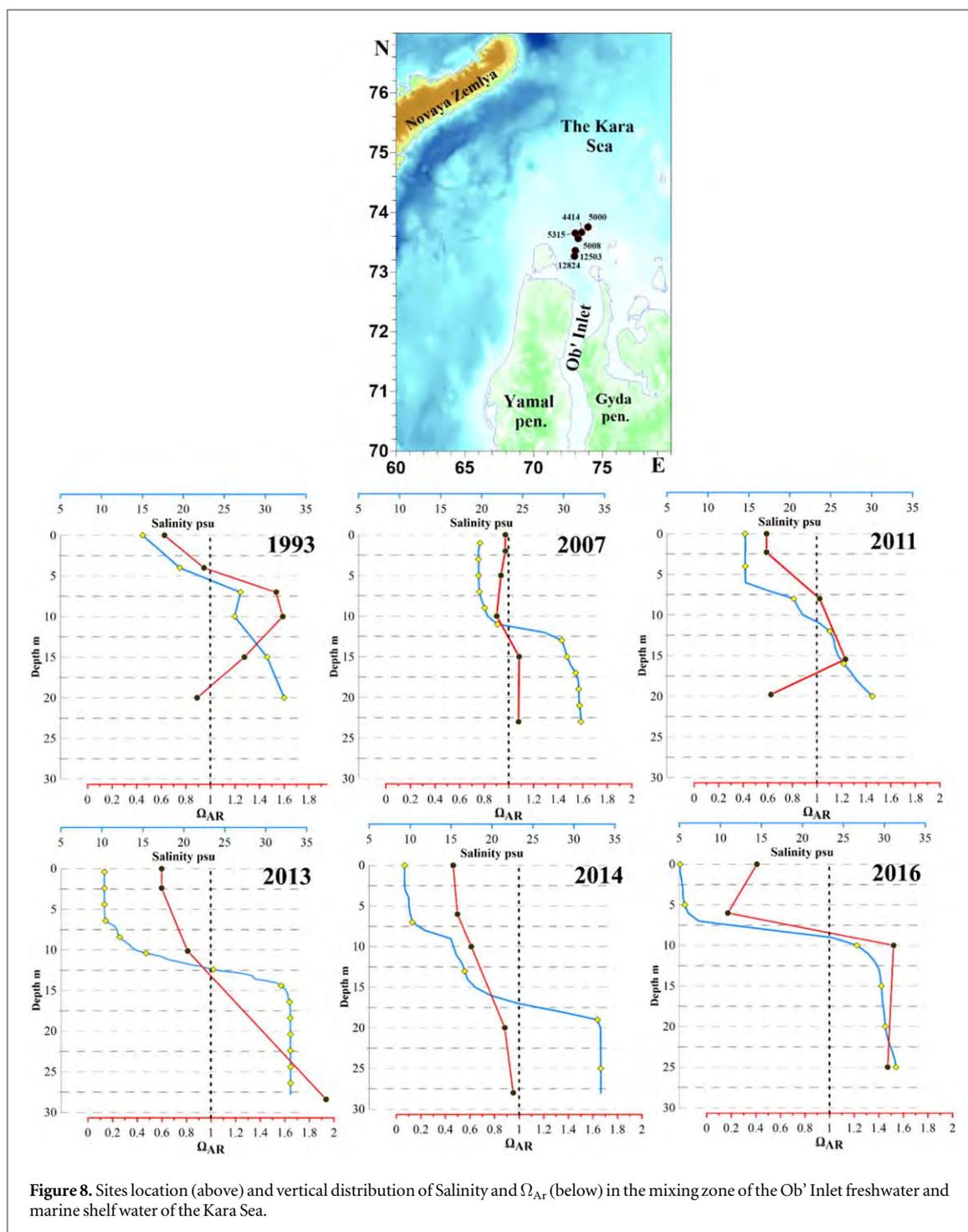
To assess the effect of river runoff from the Ob' Inlet on the distribution of saturation of the water column with aragonite, there were selected sites where samplings have been performed in each of the presented years (figure 7 above).

Vertical distribution of salinity and  $\Omega_{\text{Ar}}$  reveals strong salinity gradient (figure 8) and acidification of 5 m surface layer on site 4414 (coordinates 73.66°N and 73.5°E) in 1993. We have also observed  $\Omega_{\text{Ar}}$  below 1 in the bottom layer on the site. It could happen owing to OM (organic matter) flowing from the Ob' Inlet and its oxidation with emission of  $\text{CO}_2$  that reduces pH.

On site 5000 (coordinates 73.75°N and 73.9°E, on September 2007) vertical distribution of salinity shows 10 m freshened layer and  $\Omega_{\text{Ar}}$  below 1 reveals acidification effect of the Ob' discharge (figure 8). Moreover, even from pycnocline to the bottom  $\Omega_{\text{Ar}}$  does not exceed 1.2 that shows a strong effect of runoff on the bottom layer at the shallow shelf.

On site 5008 (coordinates 73.56°N and 73.24°E, on September 2011) the salinity gradient was allocated at 7.5 m depth, and  $\Omega_{\text{Ar}}$  did not exceed 1 except 15 m depth (figure 8). Thereby riverine inflow has affected the whole water column up to the bottom layer.

At the site 12 503 (coordinates 73.34°N and 73.02°E, on September 2013) freshwater influence was noticeable up to 10 m depth (figure 8) where the strong salinity gradient begins and  $\Omega_{\text{Ar}}$  was less than 1. However, near the bottom  $\Omega_{\text{Ar}}$  increased up to 2 due to the flow of marine water from the open sea



**Figure 8.** Sites location (above) and vertical distribution of Salinity and  $\Omega_{AR}$  (below) in the mixing zone of the Ob' Inlet freshwater and marine shelf water of the Kara Sea.

shelf as we can observe the classic for the Kara Sea two-layers vertical structure with strong salinity gradient (3 psu m<sup>-1</sup>).

On site 12 824 (coordinates 73.27 °N and 72.97 °E, 21 August 2014) vertical structure was divided into three parts (figure 8). First is 7.5 m are the homogeneous mixed layer with salinity 10 psu and  $\Omega_{AR}$  0.4. After a strong gradient (3.3 psu m<sup>-1</sup>) there comes another 5 m layer with salinity 15–17 psu and  $\Omega_{AR}$  0.6. The bottom layer has 10 m depth with salinity 33 psu, but  $\Omega_{AR}$  is still below 1. Thus the whole water column on the site with strong salinity gradients and affected

by great continental runoff is related to the mostly acidified area of the Kara Sea.

Chosen site 5315 (coordinates 73.65 °N and 73 °E, 23 July 2016) is characterized by the 2-layer vertical structure. Upper mixed 7.5 m layer with salinity about 5 psu and  $\Omega_{AR}$  0.2–0.4 continues high-gradient halocline (8.8 psu m<sup>-1</sup>) and is replaced by bottom layer with salinity about 30 psu and  $\Omega_{AR}$  1.4–1.6 (figure 8). Evidently, such a difference between two layers in aragonite saturation was occurred owing to very strong salinity gradient and wind forcing that allocate riverine plume in the limited space.

#### 4. Discussion and conclusion

The greatest freshwater coverage with  $\Omega_{Ar}$  below or equal 1 was observed in 1993. According to ArcticGRO project dataset (figure 3) period of high-water on the Yenisei is occurring in late May–early June and has the only and heavy peak. While the high-water period of the Ob' River is stretched in time from June until August. The flood on the Yenisei in 1993 was one of the most powerful for the last 25 years and this could be the explanation of highly acidified surface layer observed in 1993. The estimated  $\Omega_{Ar}$  for the entire investigated area of the sea has grown from 0.95 in 1993 to 1.4 in 2016. However, it is not connected with the volume of total discharge that has entered the Kara Sea (figure 2) that year because in the future years the inflow was higher but the acidified area of the surface layer was smaller. Propagation of riverine plume in the Kara Sea is strongly depends on the wind forcing (Kubryakov *et al* 2016, Osadchiev *et al* 2017, Polukhin and Makkaveev 2017). The highest total discharge of Yenisey was observed in 2007 (688 km<sup>3</sup>) but at the same time, Ob' discharge was at the average rate (437 km<sup>3</sup>). With corresponding wind forcing most part of the riverine plume has propagated to the east of both estuaries and observed acidified surface area was located near the Ob' Inlet mouth. With the lowest flow volume on both rivers, as in 2013 and 2016, the plume is localized in the central part of the sea. In 2014, there was a high flow of the Ob' and comparable to the average on the Yenisey, which led to the propagation of river flow to the west from the mouth of the Ob' Inlet, thereby increasing the area with low  $\Omega_{Ar}$ . We can state that the varying total discharge and wind forcing both characterize propagation of riverine plume. Thereby it changes the acidified area of the surface layer of the Kara Sea.

Despite the complex vertical structure in areas prone to strong continental runoff, strong salinity, and hence density, gradients that lead to stratification, possible (due to little scrutiny on the problem (Zatsepin *et al* 2015)) bottom currents, the aragonite saturation below 1 is observed not only (as expected) in the surface layer, but also at a depth of 20–30 m. Investigation of the biggest freshwater basins, the Ob' Inlet and the Yenisei Gulf, shows the increase of pCO<sub>2</sub> especially in the bottom layer (Makkaveev *et al* 2015b) thus performing an additional driver of acidification. This means that the organic matter transferred to the sea by rivers, which, oxidizing, releases carbon dioxide, which also reduces the solubility of aragonite, enhances the acidification. According to (Frey *et al* 2007) West Siberia where are located basins of both Ob' and Yenisey Rivers is covered by the largest on Earth net of peatlands which store about 70Pg of carbon in permafrost. Air temperature rise performed over Eurasia in (Groisman *et al* 2017) could lead to permafrost thawing and increase in OM transferred to the Kara Sea by Ob' and Yenisey.

The main factors affecting the acidification of the Kara Sea waters could be divided into 2 parts (atmospheric and hydrospheric, or external and internal for the Kara Sea system) but all together are influenced by the global climate change. Atmospheric (external) factors are air temperature and CO<sub>2</sub> concentration increase observed in the Arctic (Groisman *et al* 2017). Air temperature rise leads to surface layer temperature increase (Steele *et al* 2008), the decrease of CO<sub>2</sub> absorption into the water and thereby pH increase. The growth of atmospheric CO<sub>2</sub> leads to its increase in the surface waters of the sea. However, our data is indirectly showing that during expeditions in 1993, 2011, 2013, and 2016 CO<sub>2</sub> flux was directed from the sea to the air. This fact differs from similar observations in other Arctic seas (like in Pipko *et al* 2017). Hydrospheric (internal) factors are river discharge increase and sea ice loss. NSIDC data states the great decrease (12%/decade (Comiso 2012)) of ice coverage in the Arctic region for the last 40 years (Vihma 2014, Groisman *et al* 2017). Ice thawing induces freshening of the surface layer, more CO<sub>2</sub> absorption due to low temperature and consequently decrease of pH. Likewise, new water areas free of ice open and that leads to expansion of the space where CO<sub>2</sub> dissolves. It should be noted that sea ice loss occurring in the Arctic Ocean can provide a positive effect (Fransson *et al* 2015) on aragonite saturation in the surface layer of the Kara Sea. The most important feature of the Kara Sea is the giant continental runoff and strong stratification created by it. Many authors state the growth of total discharge from Arctic rivers (Peterson *et al* 2002, Holmes *et al* 2013, Holmes *et al* 2015, Groisman *et al* 2017, Drake *et al* 2018). It will entail the amplification of freshening (and stratification), the decrease of pH in the area affected by the fresh water and increasing flow of terrestrial carbon. Besides, more organic matter from peatlands and thawing permafrost will flow the Kara Sea and increase CO<sub>2</sub> in seawater as well. If we add up all the effects generated by main considered features of the climate changes in the Arctic then we get lowering the pH of the waters of the Kara Sea and, accordingly, its further acidification.

Existing model calculations show a significant impact of global climate change on the whole CS of the oceans including ocean acidification (Cao *et al* 2014b). It is also demonstrated well how extremal increase of atmospheric CO<sub>2</sub>, comparable to that is already observed in the Ob' Inlet estuarine area (Makkaveev *et al* 2015a, 2015b), pull up aragonite saturation horizon from the deep ocean to the shelf depths (Cao *et al* 2014a) and what are the consequences for the ecosystem. Modeling examinations of the CS parameters in the bottom layer have revealed negative trends in pH and aragonite saturation for the entire Kara Sea shelf by 2040 (Wallhead *et al* 2017).

In conclusion, it should be stated that the acidification state of the Kara Sea waters is not so extreme as for example the East-Siberian Sea (Semiletov *et al* 2016).

From the other side climate changes in the Arctic region (sea ice loss, warming of the near-surface air layer as well as upper layer of the ocean, increase of riverine discharge) will lead to decrease of pH and undersaturation (Bellerby 2017) with respect to aragonite, one of the main tracers of acidification process, in the Kara Sea as well.

We know that a decrease in pH and aragonite saturation due to the influx of organic matter with river runoff (also increasing annually due to warming in Western Siberia), which oxidizes and releases CO<sub>2</sub>, leads to the acidification of the Kara Sea. However, it is also known that the intensity of this process can be masked, for example, by increasing the surface temperature and atmospheric CO<sub>2</sub> (Salisbury and Jönsson 2018). Therefore, it is worthwhile to study in detail the variability of hydrophysical parameters and atmospheric CO<sub>2</sub> variability in order to estimate more accurately the intensity of the acidification process in the Kara Sea and its impact on its entire ecosystem (Salisbury *et al* 2008).

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## Data availability statement

The data that support the findings of this study may be available from the corresponding author upon reasonable request. These include processed data used to create figures. The raw data are not publicly available for legal and/or ethical reasons.

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