Journal of Marine Systems 243 (2024) 103950

Contents lists available at ScienceDirect

Journal of Marine Systems

journal homepage: www.elsevier.com/locate/jmarsys

# Origin and evolution of the surface desalinated layer of the Kara Sea during the ice-free period

Uliana Kazakova *, Alexander Polukhin, Pavel Shabanov

*Shirshov Institute of Oceanology of RAS, Moscow, Russia*

ARTICLE INFO

*Keywords:*
Kara Sea
Surface desalinated layer
Total alkalinity
Silicates
Seasonal ice cover
Meltwater
Interannual variabilityvariability

ABSTRACT

This work focuses on the freshwater contribution (water from the Ob' and Yenisei rivers and ice meltwater) to the surface layer of the Kara Sea according to 2015–2020 expedition data. Salinity and hydrochemical data (total alkalinity and silicates) were used to calculate the proportion of freshwater in the desalinated layer of the Kara Sea. The ratio of the water fractions with the linear mixing of several sources was considered. Our results showed that riverine sources varied greatly, and the total contributions of the Ob' and Yenisei runoff ranged from 10 to 60%, while the contribution of ice meltwater did not exceed 25%. The relationship between the period of seasonal ice retreat in the Kara Sea and its proportion in the surface desalinated layer was revealed. The interannual variability in freshwater source composition varied greatly from the southwestern to the eastern part of the sea owing to wind forcing and seasonality in river discharge.

## 1. Introduction

A significant amount of continental runoff enters the Arctic Ocean. This ensures salinity stratification (Anderson et al., 2013). The presence of a halocline influences many large-scale processes (Osadchiev et al., 2020a; Osadchiev et al., 2023) that determine the climatic processes (Polukhin, 2019) in the Kara Sea. The influence of freshwater runoff on the surface layer of the Arctic Ocean is most pronounced in the estuarine and shelf seas. It is important to assess the contribution and variability of various freshwater sources to the surface layers of the Arctic seas. There has been an increase in river runoff (Peterson et al., 2002; Drake et al., 2018; Shiklomanov et al., 2021b) and a reduction in sea ice cover (Stroeve and Meier, 2018; Yamagami et al., 2022). Many studies have been devoted to the distribution of freshwater in the Arctic Ocean using their hydrochemical features (Aagard and Carmack, 1989; Anderson et al., 2004; Yamamoto-Kawai et al., 2005; Nedashkovsky, 2012; Newton et al., 2013). It is especially important to accurately and precisely forecast changes in the ecosystems of Arctic shelf seas.

River runoff, ice melting, atmospheric precipitation, and advection from adjacent sea areas (Pacific waters) are sources of freshwater throughout the Arctic Ocean (Aagard and Carmack, 1989; Carmack et al., 2016).

The study of the features of river runoff propagation is a fundamental problem, and related issues, such as the spatial variability of primary production (Demidov et al., 2018) and the distribution of anthropogenic pollutants (Miroshnikov et al., 2021) over the sea area, are among the most important. The catchment basins of Arctic rivers are situated in areas that experience significant anthropogenic pressure owing to economic activity in the Siberian region (Groisman et al., 2017; Slepneva et al., 2016). Therefore, the anthropogenic activity in this region directly affects the Siberian Arctic shelf seas. The effect of river runoff on marine waters is also evident from the removal of suspended and dissolved allochthonous matter (Miliman, 1990).

Approximately 55% of the total runoff from the Siberian rivers enters the Kara Sea (Gordeev et al., 1996; Shiklomanov et al., 2021b). One of the distinctive features of the Kara Sea is presence of a surface desalinated layer (SDL) (Rusanov and Vasil'ev, 1976; Aagard and Carmack, 1989; Zatsepin et al., 2010; Zavialov et al., 2015; Polukhin and Makkaveev, 2017; Osadchiev et al., 2020b). It is formed by the inflow of a large amount of river runoff and characterized by reduced density due to low salinity (Johnson et al., 1997), which leads to the presence of density stratification that hampers vertical mixing. The distribution of continental runoff and the ice cover regime of the Kara Sea are affected by the wind field, which determines the composition of the SDL in its different geographical areas (Zatsepin et al., 2010). The advection of water from the adjacent Pechora Sea (part of the Barents Sea) can affect the freshening of the southwestern part of the Kara SeaSea (Johnson et al., 1997).

* Corresponding author.
*E-mail address:* ulya_kazakova_2910@mail.ru (U. Kazakova).

https://doi.org/10.1016/j.jmarsys.2023.103950
Received 22 March 2023; Received in revised form 13 November 2023; Accepted 28 November 2023
Available online 1 December 2023
0924-7963/

The determination of freshwater sources of different origins in the Kara Sea SDL cannot be considered accurate if only salinity data are used. Various characteristics such as total alkalinity (TA), ratio of nutrients, different isotopes (for example, $\delta^{18}O$), heavy metals (Ba, Sr, etc.) were used to determine the genesis of freshwater (Anderson et al., 2004; Yamamoto-Kawai et al., 2005; Cooper et al., 2008; Sutherland et al., 2009; Dubinina et al., 2017). It is possible to identify the waters of the Ob' and Yenisei rivers and sea ice meltwater by TA and dissolved silicate content (Stunzhas, 1995; Makkaveev et al., 2010; Polukhin and Makkaveev, 2017) due to the distinctive geochemical features of the river catchment areas.

Freshwater is found throughout the surface layer of the Kara Sea, except in a few areas near the northern part of the Novaya-Zemlya Archipelago. Our results confirm that the waters of the Kara Sea result from the mixing of ambient seawater (of Atlantic origin) and river runoff (Hanzlick and Aagard, 1980; Dubinina et al., 2017). The amount of meltwater present in the SDL compared to river water does not depend on hydrological and meteorological processes because of the annual formation of seasonal ice throughout the sea from November to May (Stroeve and Meier, 2018).

A detailed study of the contribution of fresh waters of different origins will help to understand how the formation mechanism of the SDL in the Kara Sea has occurred in recent years, considering the changes in riverine discharge, wind forcing, and seasonal ice cover in recent decades.

## 2. Methods and data

### 2.1. Data

The Shirshov Institute of Oceanology of the Russian Academy of Sciences has been implementing the program "Ecosystems of the Seas of the Siberian Arctic" since 2007 (lead by Academician M.V. Flint). The purpose of the program is to study the current state of the Siberian marginal seas of the Arctic shelf, the connections of the shelf with the areas of the continental slope of the deep Arctic, and the interactions among the physical, chemical, and biological processes occurring in view of the changing ecosystems of these seas.

This work was based on data obtained from the expeditions of the Shirshov Institute of Oceanology to the Kara Sea from 2015 to 2020 (Table 1). Analysis of the contribution of various sources to the formation of the surface desalinated layer was carried out according to the data from 305 surface samples (Fig. 1).

Hydrological data (salinity and temperature) werewas obtained using a CTD complex SBE 911 (Seabird Electronics, USA) equipped with 22 12-L plastic Niskin bottles (General Oceanics, USA). Samples for the study of pH, nutrients, and TA were collected in plastic 0.5-L bottles and processed immediately. The sampling depth with Niskin bottles was 1–3 m below the surface, depending on the weather conditions (wave height). Sampling between stations was conducted using an onboard flow system along the course of the vessel. The depth of the water intake from the flow system was 3 m.

**Table 1**
Observation period.

| Year | Cruise | Measurements period | | Number of stations |
|---|---|---|---|---|
| | | beginning | ending | |
| 2015 (Flint et al., 2016) | 63rd cruise | August 28 | October 7 | 25 |
| 2016 (Sukhanova et al., 2018) | 66th cruise | July 15 | August 18 | 68 |
| 2017 (Flint et al., 2018) | 69th cruise | August 24 | September 27 | 54 |
| 2018 (Flint et al., 2019) | 72nd cruise | August 19 | September 17 | 56 |
| 2019 (Flint et al., 2020) | 76th cruise | July 7 | August 01 | 74 |
| 2020 (Flint et al., 2021) | 81st cruise | September 1 | September 20 | 28 |

TA was analysed by direct titration (the Bruyevich method) with visual determination of the titration endpoint (Pavlova et al., 2008). Accuracy of the measurement of TA is 5 μM. Dissolved inorganic silicates (Si) were determined by spectrophotometry using a blue silicon-molybdenum complex with an accuracy 0.02 μM (Parsons, 2013).

The contribution of meltwater to the formation of the surface layer was compared with data on the ice conditions in the Kara Sea. This information was obtained from survey ice maps of the Arctic Ocean (http://www.aari.nw.ru and https://nsidc.org). Information on the melting time, area of distribution, and integrity of the ice cover was used to analyse the distribution of meltwater. The wind reanalysis data (ERA5) were obtained from (Hersbach et al., 2020).

Notably, the coverage of the hydrological and hydrochemical data was uneven in the water area of the Kara Sea (Fig. 1).

### 2.2. Method of calculating the percentage contribution of water

The parts of water of different origins were calculated by solving a system of equations (Yamamoto-Kawai et al., 2005; Nedashkovsky, 2012; Polukhin and Makkaveev, 2017). This includes the salinity, TA, and dissolved silicate values of the observed surface waters and those presumably involved in the mixing process.

$$\begin{aligned} \alpha \times S_{sw} + \beta \times S_O + \gamma \times S_Y + \delta \times S_{mw} &= S \\ \alpha \times TA_{sw} + \beta \times TA_O + \gamma \times TA_Y + \delta \times TA_{mw} &= TA \\ \alpha \times Si_{sw} + \beta \times Si_O + \gamma \times Si_Y + \delta \times Si_{mw} &= Si \\ \alpha + \beta + \gamma + \delta &= 1\,\# \end{aligned} \tag{1}$$

where $S_{sw}$, $S_O$, $S_Y$, $S_{mw}$, $S$ are the salinity of sea water, freshwater of the Ob', freshwater of Yenisei, meltwater, and observed surface water, respectively; $TA_{sw}$, $TA_O$, $TA_Y$, $TA_{mw}$, $TA$ are the alkalinity of sea water, freshwater of Ob', freshwater of Yenisei, meltwater, and observed surface water, respectively; $Si_{sw}$, $Si_O$, $Si_Y$, $Si_{mw}$, $Si$ are the concentration of silicates in sea water, freshwater of Ob', freshwater of Yenisei, meltwater, and observed surface water, respectively; and $\alpha$, $\beta$, $\gamma$, $\delta$ are fractions of sea water, freshwater of Ob', freshwater of Yenisei, and meltwater, respectively.

We adopted this system of equations. Initially, the proportion of freshwater required for desalination of the sea surface layer was calculated using only salinity values. The second stage included the calculation of the proportions of freshwater with known endmember parameters (TA and Si). A linear relationship was observed between these parameters and salinity (Fig. 2). The dependence of alkalinity on salinity was high at 0.98. The lower values of the determination coefficient for dissolved silicate concentrations can be explained by their involvement in biogeochemical processes (Lisitzin, 1999) and their non-conservative behaviour in the river-sea system (Gordeev et al., 1996). Therefore, we did not consider the zone of influence of river runoff with a salinity of less than 10 psu when calculating the freshwater fractions; however, it was used to calculate the river source water concentrations. This was done to exclude the influence of biogeochemical processes on the silicate content and TA. Thus, the magnitudes of these parameters change linearly with increasing distance from the mouths of the Gulf of Ob' and the Yenisei Gulf.

In this regard, we consider a certain part of the sea surface layer where linear mixing is the main factor that determines the values of the hydrochemical parameters. TA and silicate are markers of river runoff in the Kara Sea (Gordeev et al., 2007; Cooper et al., 2008).

The source water salinity, alkalinity, and dissolved silicate concentrations of seawater and meltwater were assumed to be constant for the entire observation period (Table 2). The salinity of seawater was assumed to be equal to 34.8 psu. The salinity, TA, and Si of the

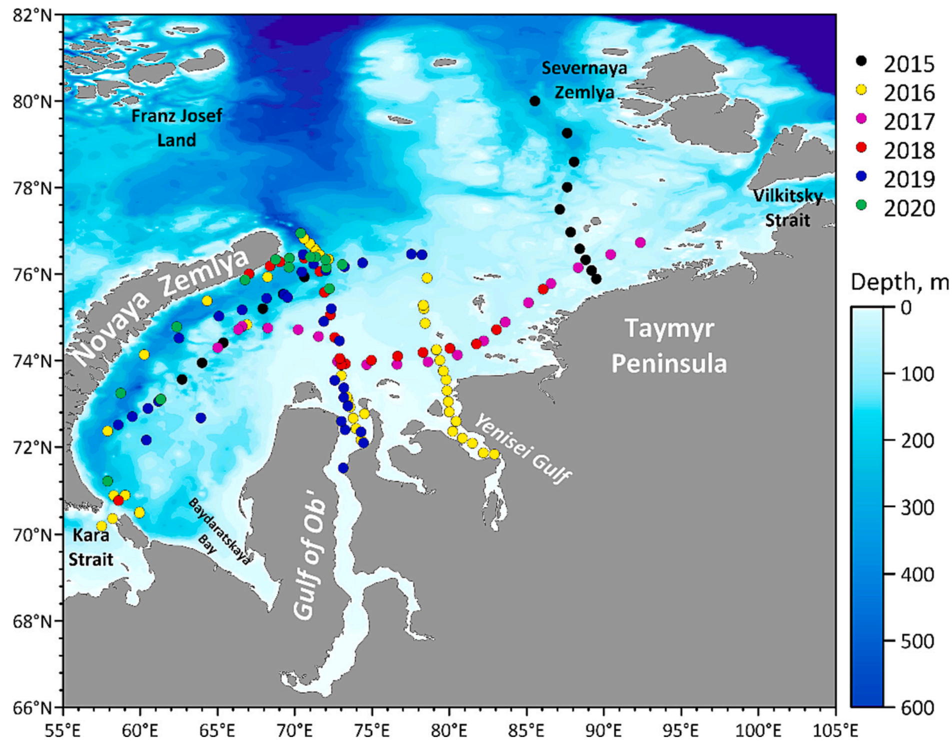


**Fig. 1.** Map showing the sampling stations of the sampling stations at the Kara Sea.

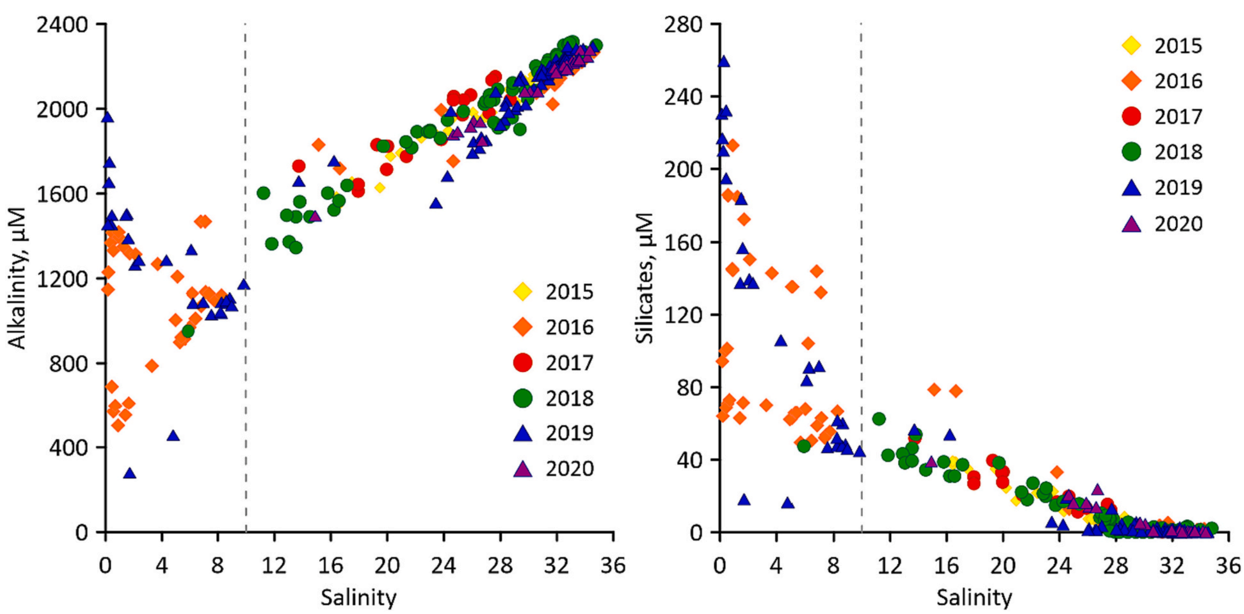


**Fig. 2.** Graphs showing alkalinity-salinity (left) and silicates-salinity (right) relationships for the period of 2015–2020.

meltwater were considered to be those of distilled water (Yamamoto-Kawai et al., 2005).

The waters of Ob' and Yenisei can be divided based on the absence of field observations in the freshwater part of the estuaries according to the values of alkalinity and silicates using regression analysis (Stunzhas, 1995). A regression analysis was performed for TA and Si.

$$Y = a \times X + b \tag{2}$$

where $X$ is salinity, $Y$ is alkalinity or dissolved silicate concentration, and $a$ and $b$ are empirical coefficients.

The value of the coefficient $b$ defines the TA or dissolved silicate concentration when salinity is equal to zero, which can be used as the runoff source water value in the mixing equation because there are no direct measurements in the rivers. The results of the regression analyses are presented in Table 2.

The error of the regression equation was calculated by the equation:

$$m_y = \pm \sigma_y \sqrt{1 - r^2} \tag{3}$$

where $\sigma_y$is the standard deviation and $r^2$ is the square of the correlation coefficient.

Determining the contribution of riverine waters of different origins (Ob' and Yenisei) is possible because of the differences in the chemical

**Table 2**
Parameters of various freshwater sources according to the regression equation and regression coefficient error.

| Year | End-member | TA, μM | *ΔTA* | Si, μM | *ΔSi* | *n* |
|---|---|---|---|---|---|---|
| 2015 | Ob' | 801 | ±27 | 54.1 | ±1.4 | 16 |
| | Yenisei | 910 | ±37 | 77.7 | ±4.3 | 10 |
| 2016 | Ob' | 1148 | ±85 | 94.4 | ±11.8 | 13 |
| | Yenisei | 1240 | ±19 | 145.3 | ±0.8 | 19 |
| 2017 | Ob' | 880 | ±20 | 47.6 | ±6.7 | 21 |
| | Yenisei | 1376 | ±35 | 86.3 | ±3 | 33 |
| 2018 | Ob' | 721 | ±61 | 78.3 | ±3.5 | 19 |
| | Yenisei | 1196 | ±27 | 50.2 | ±3.5 | 34 |
| 2019 | Ob' | 1455 | ±38 | 83.1 | ±6.1 | 12 |
| | Yenisei | 1199 | ±19 | 86.6 | ±0.8 | 18 |
| 2020 | Ob' | 807 | ±18 | 64.1 | ±3.4 | 12 |
| | Yenisei | 888 | ±12 | 69.4 | ±1.3 | 16 |
| | Sea water | 2315 | | 2 | | |
| | Melt water | 134 | | 0 | | |

composition of these waters (Polukhin and Makkaveev, 2017). The distribution of the Si-TA ratio shows that groups of points related to a specific source of riverine water can be clearly traced (Fig. 3).

This was also noted for the ratios of alkalinity to salinity and silicate salinity. The values of the regression coefficients for TA and Si coincided with field observations in the freshwater part of the estuaries within the regression coefficient error (in 2016 and 2019). Notably, the values of alkalinity and silicates varied significantly from year to year. At the same time, they were comparable with previously obtained results. In Anderson et al. (2004), the alkalinity values of the Ob' and Yenisei are 1300 and 1200 μM, respectively. Polukhin and Makkaveev (2017) obtained the values of alkalinity and silicates of river water using regression analysis. The values of these parameters of both the Ob' and the Yenisei vary from 500 to 1000 μM for TA and from 30 to 100 μM for silicates in different years.

In comparison with the PARTNERS data for the 2003–2005 period from July to September (Peterson Bruce et al., 2016) in the Ob' (at Salekhard),) TA varied from 693 to 1005 μM and silicates varied from 88.4 to 135.7 μM (mean values 850 and 90 μM, respectively); in the Yenisey (at Dudinka) TA varied from 629 to 1057 μM and silicates varied from 64.2 to 139 μM (mean values 875 and 110 μM, respectively). The difference between our data and the PARTNERS data can be explained by the fact that they sampled directly at the mouth of the river, while we worked with already transformed riverine waters: the Gulf of Ob' has a length of 800 km, the Yenisei Bay is about 300 km, and obviously the composition of the water is subject to changes as a result chemical and biological processes.

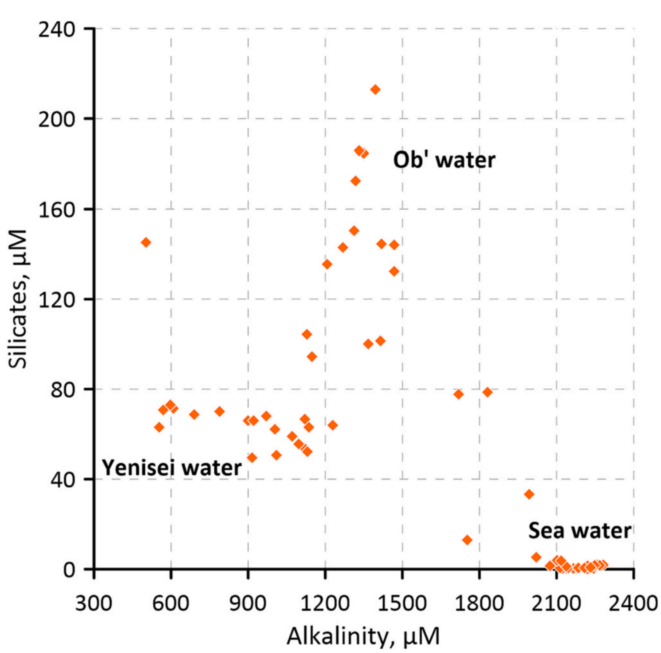


**Fig. 3.** Silicates-Alkalinity ratio for the surface layer of the Kara Sea in 2016.

One of the circumstances that complicates the calculation of freshwater components in the SDL is the determination of the parameter values of the source freshwater (riverine characteristics). The hydrochemical parameters of riverine waters were used individually for each year under consideration, which partially considers the interannual variability of the hydrochemical regime of both the Ob' and Yenisei rivers. However, the absence of observations in winter and the fact that observations were obtained in different seasons make it difficult to assess the seasonal parameter variability of river water related to biological activity and hydrological regime. Consequently, this makes it difficult to estimate the percentage contribution of waters of different origins. One of the factors determining the composition of river water in the open sea is the size and volume of river estuaries and the biochemical processes in the frontal zones of estuaries (Pivovarov, 2001). For more accurate results, it is also necessary to consider the hydrochemical features of the meltwater formed during the melting of sea ice for each period considered (Nedashkovsky et al., 2009).

## 3. Results and discussion

As a result of the calculations, the contribution of each freshwater part (the Ob' and Yenisei rivers and meltwater) involved in the formation of the SDL of the Kara Sea was assessed for 2015–2020.

### 3.1. Contribution of riverine waters

The contribution of riverine water varied greatly and depended on the type of continental runoff propagation (Fig. 4). According to scholars (Pivovarov, 2001; Kubryakov et al., 2016; Polukhin and Makkaveev, 2017), there are three types of continental runoff propagations: western, eastern, and central. However, recent results (Osadchiev et al., 2023) have shown that the existence of river plume in the Kara Sea (which exists throughout the year) prevails over the propagation of river runoff in the context of the SDL formation process. However, we are certain that the type of propagation (as well as the SDL structure) is strongly connected to wind forcing, as shown below.

The propagation of riverine runoff over the sea during the study period exhibited a centralized distribution pattern. In 2015, 2017, and 2020, riverine water was observed in the far north, almost reaching the north-eastern shore of the Novaya Zemlya Archipelago. In 2016 and 2018, the eastern type was observed, which was explained by the deflecting force of the Coriolis moving riverine water from Ob' and Yenisey along the coast towards the Vilkitskiy Strait to the Laptev Sea (Makkaveev et al., 2020; Osadchiev et al., 2020a, 2020b). The wind conditions before the expeditions confirmed this statement (Fig. 5). This was demonstrated by the magnitude of the percentage contribution of riverine waters to the SDL in the eastern Kara Sea in 2015, 2017, and 2018 (Fig. 4).

The contribution of riverine water was minimal in 2016, 2018, and 2020 in the southwestern part of the sea off the coast of Novaya Zemlya. In other years, a greater riverine water contribution (up to 60%) was observed. This was due to the central and western propagation of continental runoff under the influence of south-eastward wind (Kubryakov et al., 2016).

Fig. 5 shows the wind forcing over the Kara Sea according to the ERA5 reanalysis during the maximum discharge of the Ob' and Yenisei rivers. In June 2015, 2016, 2018, and 2019, the northward winds moved the riverine plume of Ob' and Yenisei origin to the central part of the sea extending to 76°N. In 2017, the most powerful winds from the north near the eastern shore of Novaya Zemlya created a border of river plume propagation westward. In 2020, the most intensive wind forcing

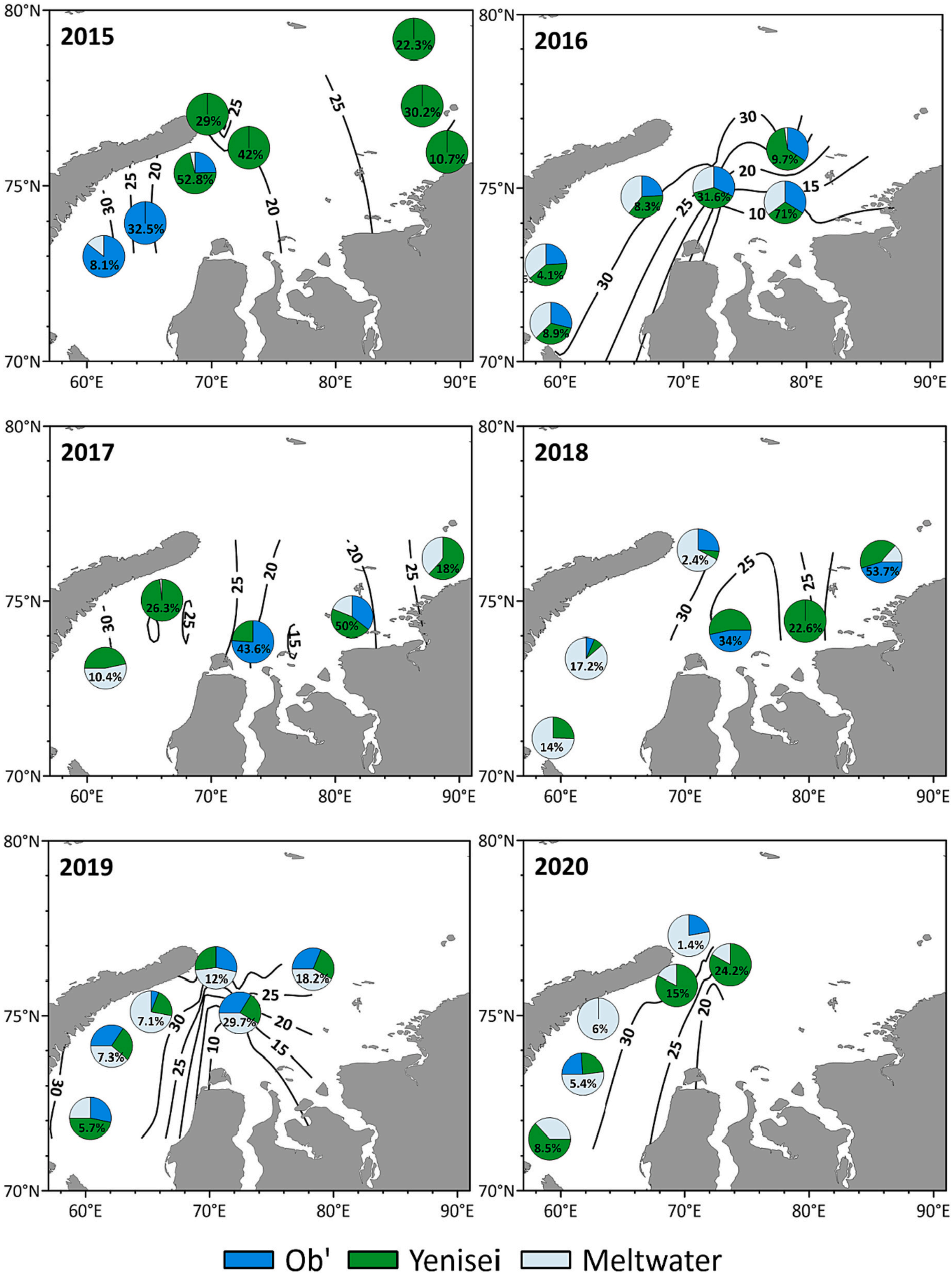


**Fig. 4.** Percentage contribution of various sources to the SDL and salinity distribution on the surface of the Kara Sea in 2015–2020. Figures in circles show the total percentage of fresh water.

occurred west of the Yamal Peninsula, forming conditions for riverine water propagation to the central and eastern parts of the sea.

In most cases under consideration (except for 2016 and 2019), we note the predominance of the Yenisei water over the Ob' River water, which is due to the seasonality of the hydrological regimes of the Ob' and Yenisei rivers (Zatsepin et al., 2010; Polukhin and Makkaveev, 2017; Shiklomanov et al., 2021a) (Fig. 6). In 2015, 2017, 2018, and 2020, the proportion of Yenisei waters exceeded that of Ob' waters. On average, the total contribution of the Ob' and Yenisei ranged from 10 to 60% over the investigated area. According to Polukhin (2019), more

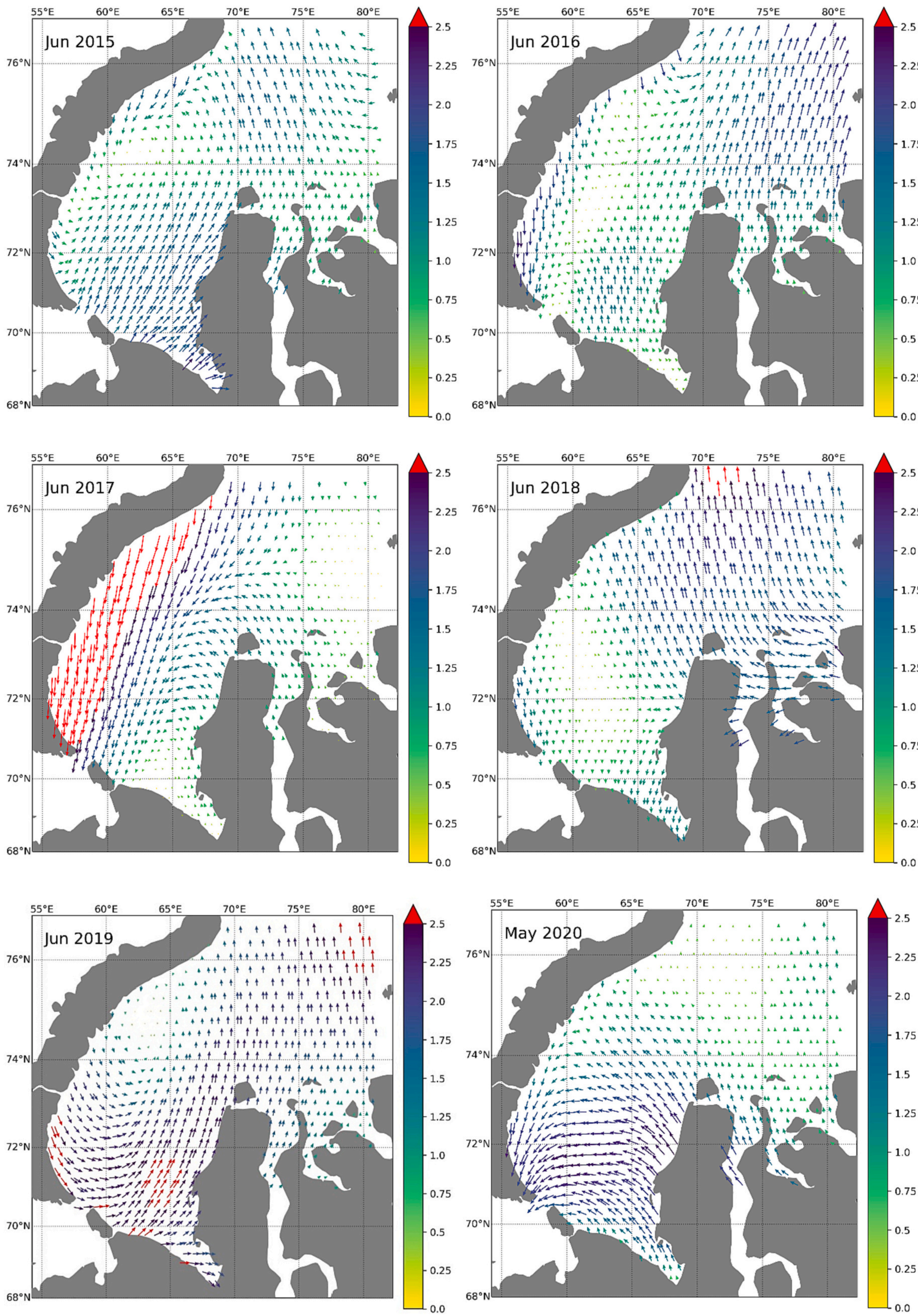


**Fig. 5.** Reanalysis (ERA5) of monthly average wind speed for different periods for Ob' and Yenisei discharge maximums.

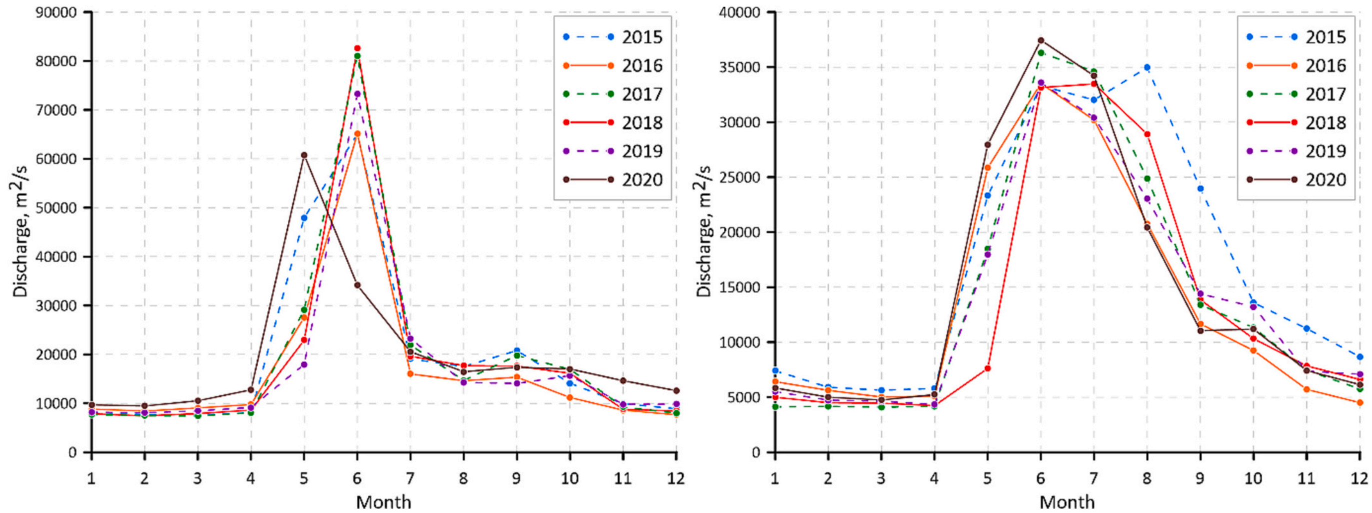


**Fig. 6.** Average monthly discharge of Yenisei (left) and Ob' (right) in 2015–2020. https://www.arcticrivers.org/

than 70% of the total discharge reached the sea during a high-water period and the subsequent two months. The flood peak in Yenisei was observed in June 2015–2019 and May 2020. Subsequently, in July and August, the discharge of Ob' exceeded that of Yenisei. The high-water period on the Ob' River had a larger temporal dimension and lasted from May to the beginning of August; therefore, the Ob' water was added to the SDL of the Kara Sea later, after the Yenisei water had already been partly transformed. This can be clearly observed in 2016 and 2019 (Fig. 4).

In the southwestern part of the sea in the Kara Strait, riverine waters (up to 5%) were observed in the surface layer in 2016, 2018, and 2020, although they rarely reached so far into this part of the sea. Most likely, the presence of a small proportion of riverine water in this area is explained by propagation through the strait of the Pechora Sea, the desalinated part of the Barents Sea where the Pechora River flows (Rogozhin et al., 2023).

### 3.2. Meltwater in the desalinated layer

During 1979–2022, the sea ice extent (SIE), area, thickness, age, and volume declined dramatically (Peng and Meier, 2017). Despite the observed tendencies, the Kara Sea ice area interannual variability remained high. For example, the sea ice area ranged from 192,000 to 381,000 km$^2$ in the Kara Sea during 2015–2020. The seasonal evolution of sea ice significantly affects Kara Sea salinity patterns through the duration of the open water season (Shiklomanov et al., 2021a, 2021b).

Using the NOAA/NSIDC climate data record of the passive microwave sea ice concentration dataset, version 4, G02202 (Meier et al., 2021), we estimated the total SIE for the southwest and central parts of the Kara Sea and found that three years (2015, 2016, and 2020) were characterized by significantly lower SIE than the 2017–2019 values. Fig. 7 shows the temporal (coloured markers, day of the year) and spatial distribution of open water season start dates (coloured round markers, day of year) and locations where the meltwater fraction (categorical marker types describe the fraction value) was measured during the marine cruises for 2015–2020. During the research period (July–October 2015–2020), meltwater dcontributes to the desalination of the surface layer (Fig. 4).

We suggest two reasons for the influence of sea-ice meltwater on the calculation results. First, the meltwater is closer to the estuaries. However, a large percentage of meltwater in the estuaries in 2016 was due to the presence of meltwater in the river catchment. Second, the higher the sea ice meltwater, the less time passed between the measurement and the beginning of the active seasonal ice retreat. This means that an early melt onset in combination with later August or early September sampling reduces the chance of identifying sea ice meltwaters (2015, 2020). In these cases, the impact of freshwater input from sea-ice melt is probably minimal. In turn, the later melt onset and earlier sampling time provides high melt water fractions in samples, especially in estuaries and within the riverine influence area, i.e.,. river plumes (2016, 2019).

Meltwater was observed in the southwestern part of the sea and ranged from 1 to 15% during the observed periods. The southwestern part of the sea is scharacterized by an earlier release from ice relative to other parts of the sea (Zhang et al., 2018). The impact of ice was particularly apparent in 2018, when, according to our data, up to 20% of the desalinated layer was meltwater.

The largest amount of meltwater was observed in 2016 (up to 50%); in other years, the contribution of meltwater did not exceed 20%. The exceptions were the estuary part of the Yenisei Gulf, where the contribution of meltwater was approximately 58%, and the bays of the Novaya Zemlya archipelago, where meltwater made the greatest contribution compared to other sources due to glacial runoff. The results obtained were in good agreement with the data obtained for this area for 1993–2014 (Polukhin and Makkaveev, 2017), who reported the presence of 30% meltwater in the SDL.

In 2016, a high proportion of meltwater was observed in the Yenisei Gulf (Fig. 4), most likely associated with the hydrological regime of the river and the removal of meltwater from the river catchment areas after the flood peak in late July–early August (Fig. 6), although not with the melting of sea ice. The contribution of meltwater reaches maximum values at the mouth of the Yenisei Gulf and is approximately 65%.

The sea area was ice-free during the research period of 2015 and 2018. The ice cover was near the southwestern part of the Severnaya Zemlya archipelago by the beginning of research in 2016, 2019, and 2020, where it was the longest observed period in this part of the sea (Duan et al., 2020).

Ice of insignificant thickness was observed west of the Vilkitsky Strait and near the Kara Strait in 2017. Meanwhile, during the observations in 2019 (early July), ice cover was also observed in the southwestern part of Baydaratskaya Bay and residuals of the Novozemelsky ice massif (which had disappeared by the beginning of the expedition) were observed. In almost all years when ice cover was observed at the beginning of the investigation period, the sea was ice free by the end of August, except in 2020, when the ice cover disappeared in the second week of September.

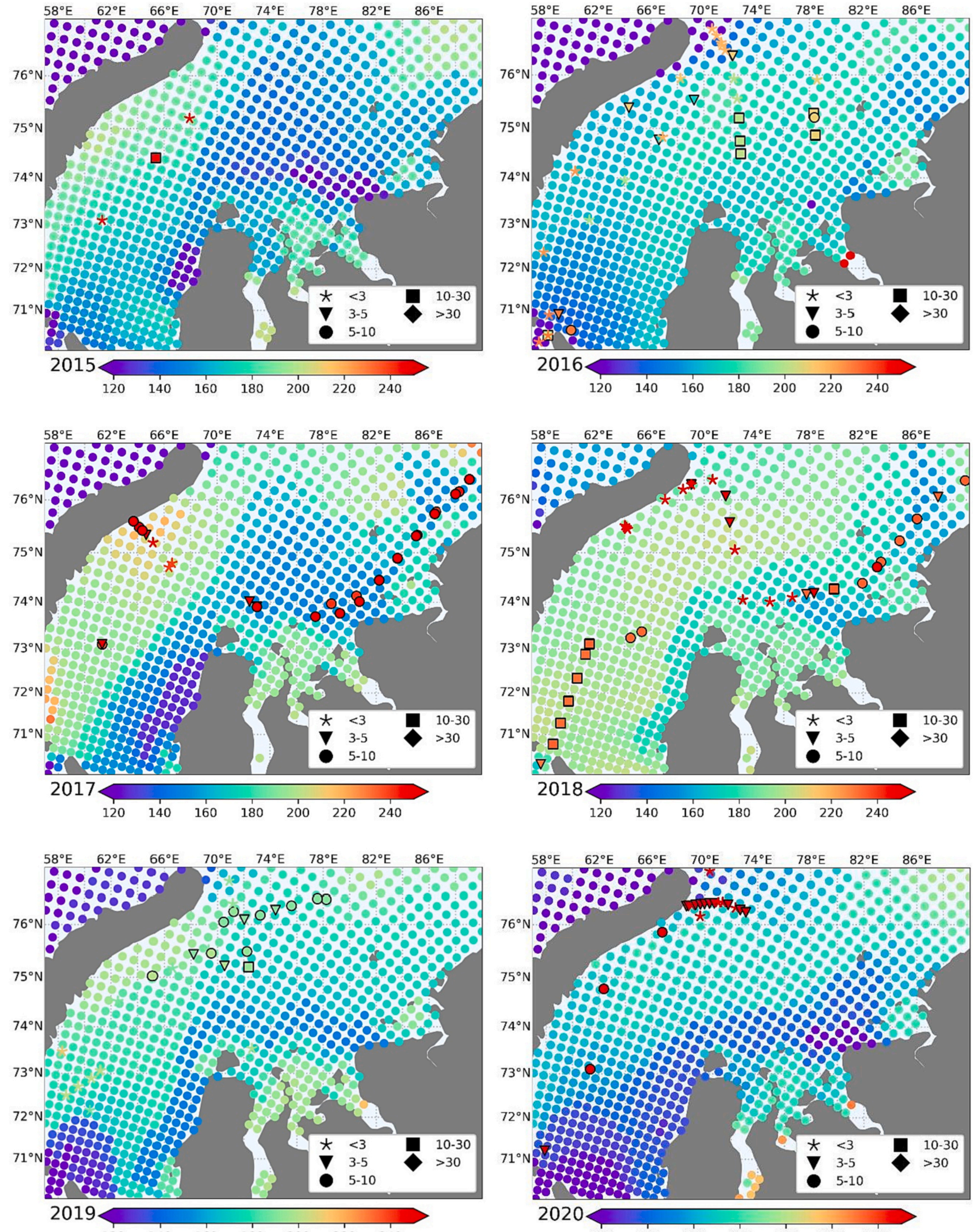


**Fig. 7.** Ice melting time and meltwater content (%) in the Kara Sea (the colour of the icons indicates the sampling time, day of the year).

### 3.3. Interannual variability of freshwater sources contribution to the SDL

Depending on the factors affecting the distribution of river runoff (mostly seasonality of discharge and wind forcing), very different patterns in the SDL structure could be observed during different observation periods in the same area. We chose three sites located in the southwestern, central, and eastern parts of the sea, where sampling was conducted annually from 2015 to 2020 (Fig. 8).

In the southwestern part of the Kara Sea riverine waters have been present in the surface layer in almost all years. The Ob' River water was observed in all years (1–11%) (Fig. 8), and the presence of the Yenisei River water was observed in 2016 (2%), 2019 (2%), and 2020 (1%). The ice meltwater was less than 6% in all years except 2017.

In the central Kara Sea, the contribution of freshwater sources to SDL formation varied significantly. In 2015 and 2016, the waters of the Ob' River predominated from all fresh sources (25–42%), in 2017–2018, the waters of Yenisei (28–46%) were dominant. In 2019, the share of meltwater (12%) exceeded that of other freshwater sources. The proportionpart of meltwater in 2016 was quite high, up to 20%, which is explained by the melting of sea ice (or inflow of continental runoff during the high-water period in spring–early summer with chemical parameters close to those ofthe melted sea ice).

According to the NSIDC data, most of the Kara Sea was already free from seasonal ice cover at the time of the observations in July. Considering the interannual variability in the structure of the SDL, two types can be clearly distinguished: the predominance of Ob' waters (2015 and 2016) and the predominance of Yenisei waters (2017–2018). In Osadchiev et al. (2017), this structure occurs by the process of superimposing the warmer and fresher waters of Yenisei on saltier and colder waters from the Gulf of Ob'. As a result of this process a two-layer SDL structure is formed; the waters of Yenisei overlie the waters from the Ob'. The amount of continental runoff is determined by the hydrological regime and seasonality of discharge on both rivers.

Under the influence of the Coriolis and wind forcing, river water moves to the east, forming a narrow coastal current (Makkaveev et al., 2020; Osadchiev et al., 2020a). In the eastern part of the sea, the main source of freshwater to the SDL is the waters of Yenisei, whose contribution does which contribution not exceed 25%. Meltwater was observed in the surface layers in 2018 (3.5%).

## 4. Conclusion

Investigating the contributions of various freshwater sources to the formation of the surface-desalinated layer of the Kara Sea requires a complex approach. Using concentrations of TA, silicates, and salinity data (simple, common, and inexpensive analysis),) it was possible to determine the origin of freshwater involved in the formation of the SDL of the Kara Sea and its evolution in the 21 century. The type of continental runoff propagation is an important characteristic when assessing the contributions of various sources to the formation of the Kara Sea surface layer. The inflow of freshwater into the Kara Sea and the subsequent cross-shelf exchange with adjacent seas and the Arctic Ocean are important factors in the changing hydrological cycle of the entire Arctic Ocean (Anderson et al., 2013).

The main difference from previous international programs (SIRRO, SPASIBA, PARTNERS), which aimed to study river and sea geochemical

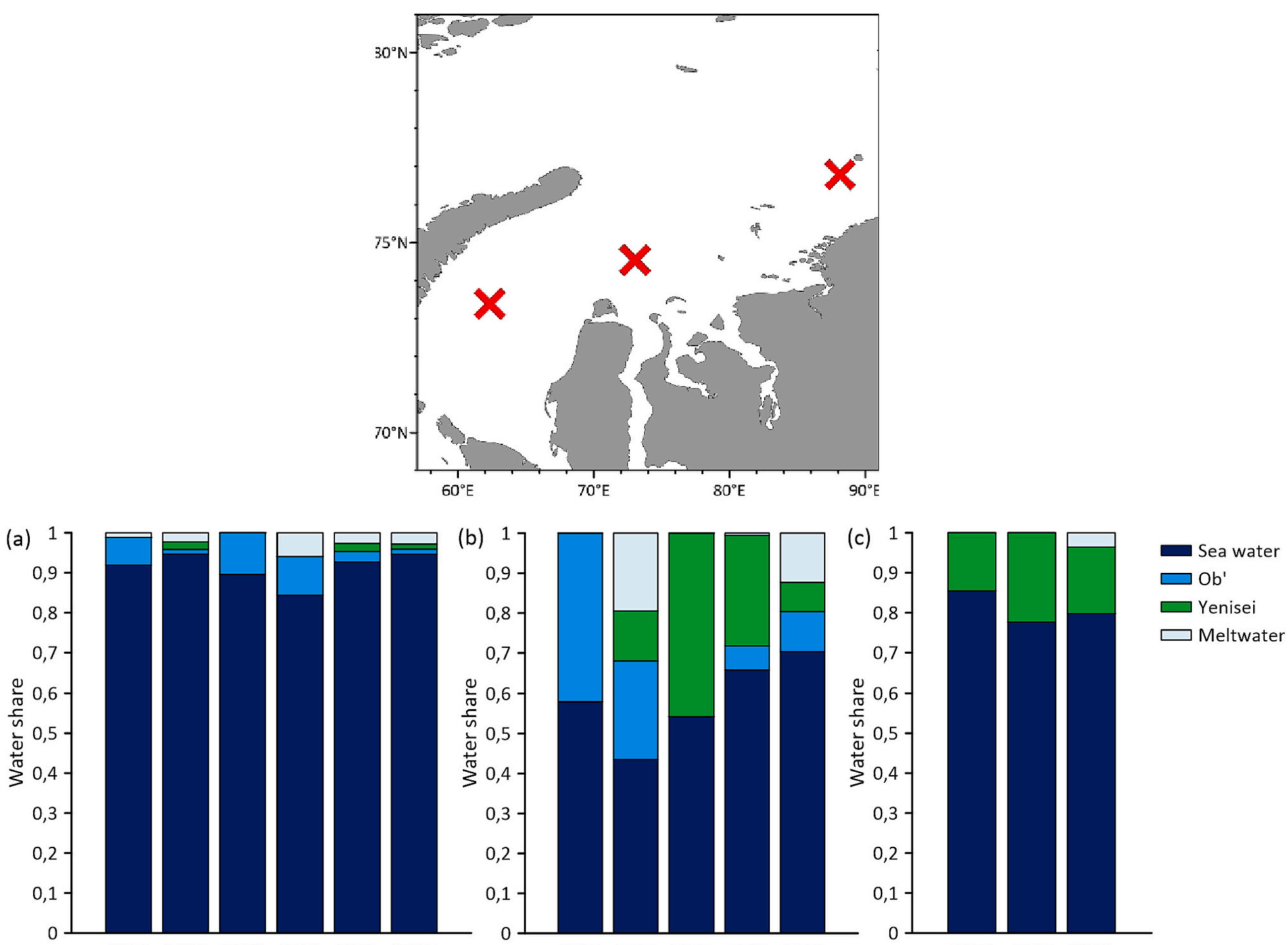


**Fig. 8.** Percentage contribution of waters of different origin in the (a) southwestern, (b) central and (c) eastern parts of the Kara Sea.

interactions in the Kara Sea, is the understanding of the changes that have occurred in the chemical composition of the Ob' and Yenisei rivers over the last two decades. Our unique data on TA and Si concentrations in the mouth areas of the Gulf of Ob' and Yenisei Gulf, as well as the adjacent shelf, demonstrate the biogeochemical changes in river discharge and its great seasonal variability.

Our calculations showed that, in most of the cases under consideration, the contribution of the Yenisei waters prevailed over the contribution of the Ob' waters to the SDL from 2015 to 2020. It is interesting to note that such calculations for the periods 1993 and 2007–2014 have revealed the reverse situation, when, in most cases, the waters of the Ob' prevailed over the waters of the Yenisei in the surface layer (Polukhin and Makkaveev, 2017). This may be related to the general restructuring of Eurasian climate, particularly in Western Siberia (Groisman and Soja, 2009; Groisman et al., 2017).

The highlight of this study is the estimation of the total SIE for the southwest and central parts of the Kara Sea. We state that the sea ice meltwater part in the SDL is as higher (according to our calculations) as less time has passed between the beginning of the expedition and the seasonal ice cover retreat. It can be assumed that the proportion of meltwater is sharply reduced a few weeks after the ice smelted. The largest amount of meltwater was observed in 2016 (25%).

The interannual changes of various freshwater sources in the SDL are characterized by weak variability, mainly related to seasonal sea ice retreat in the southwestern part of the Kara Sea (Dumanskaya, 2014). The interannual variability of freshwater sources composition in the central part of the sea is characterized by a clear predominance of Ob' or Yenisei water. In the eastern part of the sea, towards the Vilkitskiy Strait, a relatively stable amount of Yenisei water is present in the SDL, and the presence of meltwater up to 4% is observed.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

We have added data to supplementary materials in the end of the article

## Acknowledgments

The work was carried out within the framework of the state assignment of the Shirshov Institute of Oceanology (theme № FMWE-2023-0002), president grant for young scientists MK-3506.2022.1.5. Sea ice data processing and analysis were conducted with financial support from Russian Science Foundation Grant No. 22-77-10031. We thank Academician M.V. Flint for organising the expeditions and colleagues from our laboratory for carrying out the sample analysis during the cruises. S. Shchuka provided temperature and salinity data, as well as the captain and crew of the R/V Akademik Mstislav Keldysh for their selfless work at sea.

This article is dedicated to Dr. Science Petr Makkaveev (1955–2020), the former Head of the Laboratory of Biohydrochemistry in Shirshov Institute of Oceanology RAS. He has been an outstanding scientist and pioneer in the study of the chemical composition of the freshwater that formed the SDL of the Kara Sea since 1993. His ideas are at the heart of this work, and we always remember with gratitude the time we worked with and learned from him.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmarsys.2023.103950.

## References

Aagard, K., Carmack, E.C., 1989. The role of sea ice and other freshwater on the Arctic circulation. J. Geophys. Res. 94, 485–498.

Anderson, L.G., Jutterstrom, S., Kaltin, S., 2004. Variability in river runoff distribution in the Eurasian Basin of the Arctic Ocean. J. Geophys. Res. Atmos. 109, 10–16. https://doi.org/10.1029/2003JC0011773.

Anderson, L.G., Andersson, P.S., Björk, G., Peter Jones, E., Juttersröm, S., Wåhlström, I., 2013. Source and formation of the upper halocline of the Arctic Ocean. J. Geophys. Res. Oceans 118, 410–421. https://doi.org/10.1029/2012JC008291.

Carmack, E.C., Yamamoto-Kawai, M., Haine, T.W., Bacon, S., Bluhm, B.A., Lique, C., Melling, H., Polyakov, I.V., Straneo, F., Timmermans, M.-L., Williams, W.J., 2016. Freshwater and its role in the Arctic marine system: sources, disposition, storage, export, and physical and biogeochemical consequences in the Arctic and global oceans. J. Geophys. Res. Biogeo. 121, 675–717. https://doi.org/10.1002/2015JG003140.

Cooper, L.W., McClelland, J.W., Holmes, R.M., Raymond, P.A., Gibson, J.J., Guay, C.K., Peterson, B.J., 2008. Flow-weighted values of runoff tracers ($\delta^{18}$O, DOC, Ba, alkalinity) from the six largest Arctic rivers. Geophys. Res. Lett. 35, L18606. https://doi.org/10.1029/2008GL035007.

Demidov, A.B., Sherbestov, S.V., Gagarin, V.I., 2018. Estimation of annual Kara Sea primary production. Oceanology. 58 (3), 369–380. https://doi.org/10.1134/S0001437018030049.

Drake, T.W., Tank, S.E., Zhulidov, A.V., Holmes, R.M., Gurtovaya, T., Spencer, R.G.M., 2018. Increasing alkalinity export from large Russian arctic rivers. Environ. Sci. Technol. 52, 8302–8308. https://doi.org/10.1021/acs.est.8b01051.

Duan, C., Dong, S., Wang, Z., 2020. Estimates of sea ice mechanical properties in the Kara Sea. Pure Appl. Geophys. 177, 5101–5116. https://doi.org/10.1007/s00024-020-02543-8.

Dubinina, E.O., Kossova, S.A., Miroshnikov, A.Yu., Fyaizullina, R.V., 2017. Isotope (δD, $\delta^{18}$O) composition and the freshwater input to the Kara Sea. Oceanology. 57 (1), 38–48. https://doi.org/10.7868/S003015741701004X.

Dumanskaya, I.O., 2014. Ice Conditions of the Seas of the European Part of Russia. IG–SOCIN, Moscow.

Flint, M.V., Poyarkov, S.G., Rimsky-Korsakov, N.A., 2016. Ecosystems of the Russian Arctic-2015 (63rd cruise of the research vessel Akademik Mstislav Keldysh). Oceanology. 56 (3), 459–461. https://doi.org/10.1134/S0001437016030061.

Flint, M.V., Poyarkov, S.G., Rimsky-Korsakov, N.A., 2018. Ecosystems of the Siberian Arctic Seas-2017 (cruise 69 of the R/V Akademik Mstislav Keldysh). Oceanology 58 (2), 315–318. https://doi.org/10.1134/S0001437018020042.

Flint, M.V., Poyarkov, S.G., Rimskii-Korsakov, N.A., et al., 2019. Ecosystems of the Siberian Arctic seas 2018 (cruise 72 of the R/V Akademik Mstislav Keldysh). Oceanology. 59, 460–463. https://doi.org/10.1134/S0001437019030056.

Flint, M.V., Poyarkov, S.G., Rimsky-Korsakov, N.A., Miroshnikov, A.Y., 2020. Ecosystems of Siberian Arctic Seas-2019: spring processes in the Kara Sea (cruise 76 of the R/V Akademik Mstislav Keldysh). Oceanology. 60 (1), 134–137. https://doi.org/10.1134/S0001437020010105.

Flint, M.V., Poyarkov, S.G., Rimsky-Korsakov, N.A., et al., 2021. Ecosystems of Siberian Arctic seas–2020: the Kara Sea (cruise 81 of the R/V Akademik Mstislav Keldysh). Oceanology. 61, 292–294. https://doi.org/10.1134/S0001437021020041.

Gordeev, V.V., Martin, J.M., Sidorov, I.S., Sidorova, M.V., 1996. A reassessment of the Eurasian River input of water, sediment, major elements, and nutrients to the Arctic Ocean. Am. J. Sci. 296, 664–691.

Gordeev, V.V., Beeskow, B., Rachold, V., 2007. Geochemistry of the Ob and Yenisey estuaries: A comparative study. Berichte zur Polar-und Meeresforschung. 565 (235 p).

Groisman, P., Soja, A.J., 2009. Ongoing climatic change in Northern Eurasia: justification for expedient research. Environ. Res. Lett. 4, 045002 https://doi.org/10.1088/1748-9326/4/4/045002.

Groisman, P., Shugart, H., Kicklighter, D., Henebry, G., Tchebakiva, N., Maksyutov, S., Monier, E., et al., 2017. Northern Eurasia future initiative (NEFI): facing the challenges and pathways of global change in the twenty-first century. Progress Earth and Planetary Science. 4, 41. https://doi.org/10.1186/s40645-017-0154-5.

Hanzlick, D., Aagard, K., 1980. Freshwater and Atlantic water in the Kara Sea. J. Geophys. Res. 85, 4937–4942. https://doi.org/10.1029/JC085IC09P04937.

Hersbach, H., Bell, B., Berrisford, P., et al., 2020. The ERA5 global reanalysis. Q J R Meteorol Soc. 146, 1999–2049. https://doi.org/10.1002/qj.3803.

http://www.aari.nw.ru.

https://nsidc.org.

Johnson, D.R., McClimans, T.A., King, S., Grenness, Ø., 1997. Fresh water masses in the Kara Sea during summer. J. Mar. Syst. 12, 127–145.

Kubryakov, A., Stanichny, S., Zatsepin, A., 2016. River plume dynamics in the Kara Sea from altimetry based lagrangian model, satellite salinity and chlorophyll data. Remote Sens. Environ. 176, 177–187. https://doi.org/10.1016/j.rse.2016.01.020.

Lisitzin, A.P., 1999. The Continental-Ocean Boundary as a Marginal Filter in the World Oceans. Biogeochemical cycling and sediment ecology. Springer, Dordrecht, pp. 69–103.

Makkaveev, P.N., Stunzhas, P.A., Khlebopashev, P.V., 2010. On determination of the Ob and Enisey River waters in the semifresh lenses at the Kara Sea in 1993 and 2007. Oceanology. 50 (5), 1–8.

Makkaveev, P.N., Polukhin, A.A., Shchuka, S.A., Stepanova, S.V., 2020. Transport of continental runoff through the Vilkitskiy Strait in September 2017 and 2018. Oceanology. 60 (3), 355–363. https://doi.org/10.31857/S0030157420030053.

Meier, W.N., Fetterer, F., Windnagel, A.K., Stewart, J.S., 2021. NOAA/NSIDC Climate Data Record of Passive Microwave Sea Ice Concentration, Version 4 [Data Set].

National Snow and Ice Data Center, Boulder, Colorado USA. https://doi.org/10.7265/efmz-2t65. Date Accessed 08-05-2022.
Miliman, J.D., 1990. Fluvial sediments in coastal seas: flux and fate. Nature and Resources (UNESCO). 26 (4), 12–22.
Miroshnikov, A.Yu., Badukov, D.D., Flint, M.V., Repkina, T.Yu., Asadulin, En, E., Sharapov, A.M., Komarov, Vl.B., Usacheva, A.A., 2021. Relief of the Kara Sea bottom and sediment sorption properties as pollution accumulation factors. Oceanology. 61 (5), 714–726.
Nedashkovsky, A.P., 2012. Hydrochemical variability in the surface mixed layer along the trajectory of the Drifting Station "north pole 35". Oceanology. 52 (4), 498–508.
Nedashkovsky, A.P., Khvedynich, S.V., Petrovsky, T.V., 2009. Alkalinity of sea ice of the high-latitude Arctic (based on observation on Drifting Station "north pole – 34") and assessment of the role of the Arctic Sea ice in $CO_2$ exchange. Oceanology. 49 (1), 61–69.
Newton, R., Schlosser, P., Mortlock, R., Swift, J., MacDonald, R., 2013. Canadian Basin freshwater sources and changes: results from the 2005 Arctic Ocean section. J. Geophys. Res. 118, 2133–2154. https://doi.org/10.1002/jgrc.20101.
Osadchiev, A.A., Izhitskiy, A.S., Zavialov, P.O., Kremenetskiy, V.V., Polukhin, A.A., Pelevin, V.V., Toktamysova, Z.M., 2017. Structure of the buoyant plume formed by Ob and Yenisei river discharge in the southern part of the Kara Sea during summer and autumn. J. Geophys. Res. Oceans 122, 5916–5935. https://doi.org/10.1002/2016JC012603.
Osadchiev, A.A., Pisareva, M.N., Spivak, E.A., Shchuka, S.A., Semiletov, I.P., 2020a. Freshwater transport between the Kara, Laptev, and east-Siberian seas. Sci. Rep. 10, 13041. https://doi.org/10.1038/s41598- 020-70096-w.
Osadchiev, A.A., Frey, D.I., Shchuka, S.A., Tilinina, N.D., Morozov, E.G., Zavialov, P.O., 2020b. Structure of the freshened surface layer in the Kara Sea during ice-free periods. J. Geophys. Res. Oceans 126. https://doi.org/10.1029/2020JC016486 e2020JC016486.
Osadchiev, A., Zabudkina, Z., Rogozhin, V., Frey, D., Gordey, A., Spivak, E., Salyuk, A., Semiletov, I., Sedakov, R., 2023. Structire of the Ob-Yenisei plume in the Kara Sea shortly before autumn ice formation. Front. Mar. Sci. 10, 1129331. https://doi.org/10.3389/fmars.2023.1129331.
Parsons, T.R., 2013. A Manual of Chemical & Biological Methods for Seawater Analysis. Elsevier.
Pavlova, G.Y., Tishchenko, P.Y., Volkova, T.I., et al., 2008. Intercalibration of Bruevich's method to determine the Total alkalinity in seawater. Oceanology 48, 438. https://doi.org/10.1134/S0001437008030168.
Peng, G., Meier, W.N., 2017. Temporal and regional variability of Arctic Sea-ice coverage from satellite data. Ann. Glaciol. 59, 191–200. https://doi.org/10.1017/aog.2017.32.
Peterson Bruce, J., Holmes Robert, M., McClelland James, W., Rainer, Amon, Tim, Brabets, Lee, Cooper, John, Gibson, Gordeev Viacheslav, V., Christopher, Guay, David, Milburn, Robin, Staples, Raymond Peter, A., Igor, Shiklomanov, Striegl Robert, G., Alexander, Zhulidov, Tanya, Gurtovaya, Sergey, Zimov, 2016. PARTNERS project Arctic River biogeochemical data. Arctic Data Center. https://doi.org/10.18739/A2166T.
Peterson, B.J., Holmes, R.M., McCelland, J.W., Vörösmarty, C.J., Lammers, R.B., Shiklomanov, A.I., Rahmstorf, S., 2002. Increasing river discharge to the Arctic Ocean. Science. 298, 2171–2173. https://doi.org/10.1126/science.1077445.
Pivovarov, S.V., 2001. Chemical Oceanography of the Arctic Seas of Russia (Study Guide). SPb. Gidrometeoizdat.
Polukhin, A., 2019. The role of river runoff in the Kara Sea surface layer acidification and carbonate system changes. Environ. Res. Lett. 14 (10), 105007 https://doi.org/10.1088/1748-9326/ab421e.
Polukhin, A.A., Makkaveev, P.N., 2017. Features of the continental runoff distribution over the Kara Sea. Oceanology. 57 (1), 25–37. https://doi.org/10.7868/S0030157417010142.
Rogozhin, V., Osadchiev, A., Konovalova, O., 2023. Structure and variability of the Pechora plume in the southeastern part of the Barents Sea. Front. Mar. Sci. 10, 311. https://doi.org/10.3389/fmars.2023.1052044.
Rusanov, V.P., Vasil'ev, A.N., 1976. Distribution of river waters in the Kara Sea according to Hydrochemical determination data. Trudy Arctic and Antarktic. Nauchno-Issled. Inst. 323, 188–196.
Shiklomanov, A.I., Holmes, R.M., McClelland, J.W., Tank, S.E., Spencer, R.G.M., 2021a. Arctic Great Rivers Observatory. https://arcticrivers.org/data. Date accessed 05-05-2022.
Shiklomanov, A., et al., 2021b. River freshwater flux to the Arctic Ocean. In: Yang, D., Kane, D.L. (Eds.), Arctic Hydrology, Permafrost and Ecosystems. Springer, Cham. https://doi.org/10.1007/978-3-030-50930-9_24.
Slepneva, L.R., Tsyrenov, D.D., Kokorina, A.A., Slepneva, J.V.E., Munkueva, I.S., 2016. Socio-economic development of regions of Russia: assessment of the state and directions of improvement. Int. J. Econ. Financ. Issues 6 (2), 179–187.
Stroeve, J., Meier, W.N., 2018. Sea Ice Trends and Climatologies from SMMR and SSM/I-SSMIS, Version 3 [Indicate subset used].. NASA National Snow and Ice Data Center Distributed Active Archive Center, Boulder, Colorado USA. https://doi.org/10.5067/IJ0T7HFHB9Y6.
Stunzhas, P.A., 1995. Separation of the waters of the Yenisei and the Ob in the Kara Sea by alkalinity and silicon. Oceanology. 35 (2), 215–219.
Sukhanova, I.N., Flint, M.V., Sakharova, E.G., Fedorov, A.V., Makkaveev, P.N., Nedospasov, A.A., 2018. Phytocenoses of the Ob estuary and Kara Sea shelf in the late spring season. Oceanology. 58 (6), 802–816. https://doi.org/10.1134/S0001437018060139.
Sutherland, D.A., Pickart, R.S., Peter Jones, E., Azetsu-Scott, K., Jane Eert, A., Olafsson, J., 2009. Freshwater composition of the waters off Southeast Greenland and their link to the Arctic Ocean. J. Geophys. Res. 114, C05020. https://doi.org/10.1029/2008JC004808.
Yamagami, Y., Watanabe, M., Mori, M., et al., 2022. Barents-Kara Sea-ice decline attributed to surface warming in the Gulf stream. Nat. Commun. 13, 37–67. https://doi.org/10.1038/s41467-022-31117-6.
Yamamoto-Kawai, M., Tanaka, N., Pivovarov, S., 2005. Freshwater and brine behaviors in the Arctic Ocean deduced from historical data of δ18O and alkalinity (1929–2002 AD). J. Geophys. Res. Oceans 110 (C10). https://doi.org/10.1029/2004JC002793.
Zatsepin, A.G., Zavialov, P.O., Kremenetskiy, V.V., Poyarkov, S.G., Soloviev, D.M., 2010. The upper desalinated layer in the Kara Sea. Oceanology. 50 (5), 698–708.
Zavialov, P.O., Izhitskiy, A.S., Osadchiev, A.A., Pelevin, V.V., Grabovskiy, A.B., 2015. The structure of thermohaline and bio-optical fields in the upper layer of the Kara Sea in September 2011. Oceanology. 55, 461–471. https://doi.org/10.1134/s0001437015040177.
Zhang, P., Wu, Y., Simpson, I.R., Smith, K.L., Zhang, X., De, B., Callaghan, P., 2018. A stratospheric pathway linking a colder Siberia to Barents-Kara Sea Sea ice loss. Sci. Adv. 4 (7), eaat6025. https://doi.org/10.1126/sciadv.aat6025.