

Water mass classification on a highly variable arctic shelf region: origin of Laptev Sea water masses and implications for the nutrient budget

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Key points

Principle component analysis allows classification of highly variable Laptev Sea water masses

Imported waters dominate the nutrient budget in the central Laptev Sea in years with weak polynya activity

Enhanced local polynya activity changes the nutrient budget significantly

Abstract

Large gradients and inter annual variations on the Laptev Sea shelf prevent the use of uniform property ranges for a classification of major water masses. The central Laptev Sea is dominated by predominantly marine waters, locally formed polynya waters and riverine summer surface waters. Marine waters enter the central Laptev Sea from the northwestern Laptev Sea shelf and originate from the Kara Sea or the Arctic Ocean halocline. Local polynya waters are formed in the Laptev Sea coastal polynyas. Riverine summer surface waters are formed from Lena river discharge and local melt. We use a principal component analysis (PCA) in order to assess the distribution and importance of water masses within the Laptev Sea. This mathematical method is applied to hydro-chemical summer datasets from the Laptev Sea from five years and allows to define water types based on objective and statistically significant criteria. We argue that the PCA derived water types are consistent with the Laptev Sea hydrography and indeed represent the major water masses on the central Laptev Sea shelf. Budgets estimated for the thus defined major Laptev Sea water masses indicate that freshwater inflow from the western Laptev Sea is about half or in the same order of magnitude as freshwater stored in locally formed polynya waters. Imported water dominates the nutrient budget in the central Laptev Sea; and only in years with enhanced local polynya activity is the nutrient budget of the locally formed water in the same order as imported nutrients.

1. Introduction

Climatic changes are clearly visible within the Arctic Ocean environment, e.g. in the decline of the summer sea-ice cover. Changes such as the freshwater content of the Arctic Ocean (Rabe et al., 2011) This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/2017JC013524

have been linked to the freshwater supply and release from the Siberian shelf areas (Thibodeau et al., 2014). The retreat of sea-ice and changes of the freshwater budget in response to Arctic warming have already significantly affected Arctic marine productivity (e.g. Arrigo and van Dijken, 2015). Yet, the availability of nutrients that ultimately limits or amplifies primary productivity is not well understood. The warming of the Arctic region has also caused an increase of river discharge (Peterson et al., 2002), leading to enhanced upper water stratification and a reduction of vertical mixing (e.g. Rabe et al., 2011). This in turn results in a decrease of nutrient supply from the subsurface to the surface layer, significantly affecting primary producers (e.g. diatoms). The Arctic rivers at the same time are a source of nutrients themselves, even though their nutrient contribution was recently proposed to have only little impact beyond estuarine mixing zones (Le Fouest et al., 2013) and the incorporation of nutrients into the shelf bottom water is of critical importance for its further occurrence on the shelf (Thibodeau et al., 2017). The exact nutrient supply paths and changes of biogeochemical cycling as a consequence of sea-ice loss, increasing freshwater discharge from Arctic rivers and other environmental parameters in the Siberian Arctic, affecting the nutrient budgets, have yet to be investigated in great detail. The Laptev Sea hydrography is determined by large gradients and strong inter annual variations (Bauch et al., 2009). A definition of uniform ranges that may serve for a classification of the major water masses for different years is therefore not possible. Consequently it is difficult to detect climatic changes in the hydrography of the shelf areas even though these changes are clearly visible within the Arctic Ocean environment, e.g. in the decline of the summer sea-ice cover. Despite these difficulties it is important to understand and to detect climatic changes in the highly variable but climatically critical Laptev Sea system as bottom waters from the Laptev Sea maintain parts of the Arctic Ocean halocline (Bauch et al., 2011a,b). Here we use a principal component analysis (PCA) in order to allow a useful and objective classification of Laptev Sea water masses across different years and thus provides a basis to objectively identify long term changes. A PCA has been used for an analysis of lower halocline waters from the Laptev Sea shelf break (Bauch et al., 2016) and has also been applied for the Beaufort shelf area (Moore et al., 1992).

As the freshwater cycle and sea-ice processes on the Laptev Sea shelf are expected to be altered with the ongoing climate change we expect our analysis to be useful for evaluating ongoing changes in water mass distribution on the freshwater and nutrient budgets.

2. Methods

Samples for $\delta^{18}\text{O}$ analyses at the Laptev Sea shelf were collected in summer 1994, 2007, 2010, 2011, 2013 and 2014 during TRANSDRIFT expeditions (Fig. 1) and complimented with 1995 data, collected during Polarstern expedition ARK XI. (Frank, 1996). In all cases water samples were taken

with a conductivity-temperature-depth (CTD)-rosette with an accuracy of at least ± 0.002 S/m in conductivity and $\pm 0.005^\circ\text{C}$ in temperature.

Accuracy for all presented $\delta^{18}\text{O}$ is equal or better than $\pm 0.04\text{‰}$ (Bauch et al., 2010, 2011a+b, 2013). $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ ratios were calibrated with Vienna Standard Mean Ocean Water (VSMOW) and are reported in the usual δ -notation (Craig, 1961). A subset of the stable isotope data from the Laptev Sea shelf were published before (Thibodeau et al., 2014; Thibodeau and Bauch, 2016).

Based on $S/\delta^{18}\text{O}$ mass balance calculations fractions of river water and sea-ice meltwater are derived following Bauch et al. (1995; 2011a). It is assumed that each sample is a mixture between fractions of marine water (f_{mar}), river runoff (f_r), and sea-ice meltwater (f_{SIM}). The mass balance is governed by the following equations:

$$\begin{aligned} f_{\text{mar}} + f_r + f_{\text{SIM}} &= 1, \\ f_{\text{mar}} * S_{\text{mar}} + f_r * S_r + f_{\text{SIM}} * S_{\text{SIM}} &= S_{\text{meas}}, \\ f_{\text{mar}} * O_{\text{mar}} + f_r * O_r + f_{\text{SIM}} * O_{\text{SIM}} &= O_{\text{meas}}, \end{aligned}$$

where f_{mar} , f_r , and f_{SIM} are the fractions of marine water, river runoff, and sea-ice meltwater (SIM) in a water parcel, and S_{mar} , S_r , S_{SIM} , O_{mar} , O_r and O_{SIM} are the corresponding salinities and $\delta^{18}\text{O}$ values of the endmembers (Tab. 1). S_{meas} and O_{meas} are the measured salinity and $\delta^{18}\text{O}$ of the water samples. Technically f_r refers to meteoric water, which includes local precipitation, but as river runoff dominates in the study area we refer to river runoff for simplicity. For the freshwater endmembers a $\delta^{18}\text{O}$ of -20‰ is chosen for river water and for sea-ice -2‰ $\delta^{18}\text{O}$ and 4 salinity (see also Bauch et al., 2010, 2011b). The $\delta^{18}\text{O}$ value of Lena River water is $\sim -20\text{‰}$ (Bauch et al., 2005), while the $\delta^{18}\text{O}$ value of Ob and Yenisey rivers is $\sim -18\text{‰}$ (Bauch et al, 2003). Therefore the chosen $\delta^{18}\text{O}$ freshwater endmember reflects river water in areas where the Lena River dominates e.g. in the south eastern Laptev Sea, while in areas where river water from the Kara Sea dominates the calculated river water fractions will be underestimated by $\sim 10\%$ e.g. in the north western Laptev Sea.

All fractions are net values reconstructed from the $\delta^{18}\text{O}$ and salinity signatures of each sample, and reflect the time-integrated effects on the sample volume over the residence time of the water in the Arctic Ocean. Negative SIM fractions (f_{SIM}) reflect the amount of water removed by sea-ice formation and are proportional to the addition of brines to the water column. SIM fractions may be negative during summer season sampling if the winter sea-ice formation signal exceeds the summer melt signal. Based on a $\delta^{18}\text{O}$ measurement precision of 0.04‰ , the error in calculated fractions is about 0.2% for both sea-ice meltwater and river water fractions. An additional systematic error or shift depends on the exact choice of end-member values. When end-member values are varied within the estimated uncertainties (Tab. 1), both fractions are shifted by up to $\sim 1\%$, but results are always qualitatively preserved even when tested with extreme end-member variations (see Bauch et al., 2011b).

Principal Components (PCs) and Empirical Orthogonal Functions (EOFs) were calculated using function PRINCOMP of the MATLAB software package. Analysis was conducted for data of temperature (T), salinity (S), f_{SIM} , f_r , silicate (Si), phosphate (P) and nitrate (N) from the Laptev Sea shelf (with depth range 0-375 m) for summer datasets from 1994, 2007, 2010, 2011, 2013, 2014 and three stations from 1995 (one from Kara Sea and two from in front of Shokalskiy Strait region). We included f_{SIM} , f_r , instead of $\delta^{18}O$ as calculated fractions are much easier to directly interpret and incorporate the exact relation between $\delta^{18}O$ and salinity measurements; this would not be the case if fractions were calculated later from average values for water types. The results when including $\delta^{18}O$ instead of f_{SIM} , f_r differ only marginally. Data were organized as a matrix in which the columns are T, S, f_{SIM} , f_r , Si, P, N, and the rows are the samples, i.e. 1159 values, for all 200 available stations. The T, S, f_{SIM} , f_r , Si, P and N data were normalized using the data means and standard deviations in order to avoid influence of different scales of input data. EOF decomposition was made for normalized data and EOFs as well as PCs were obtained. North's "rule of thumb" was applied to estimate reliability of obtained EOFs (North et al., 1982). According to this test, the first three EOFs are statistically significant as the distances between them is larger than the sampling errors. The first three EOFs describe over 90% of total data variance within our dataset. Each EOF is a combination of values T, S, f_{SIM} , f_r , Si, P and N, and the PCs tabulate the contribution of each of these combination to a sample in principal component space.

A cluster analysis (Ward, 1963) was applied to the PCs in order to use an objective method to identify similarities between samples. PCs phase portrait (Fig.2) together with cluster analysis (Ward, 1963) allowed us to distinguish 8 clusters, which we associate with 8 water masses. In cluster analysis the measure of the distance between the nodes was introduced through the Euclidean metric. The points with minimal linkage distance were combined into groups (clusters), where T, S, f_{SIM} , f_r , Si, P and N values has minimal difference. Points that were placed in the same cluster by Ward's method are usually also located close to each other in the PC1 versus PC2 scatter plot.

Budgets of clusters were calculated for volumes, nutrients, f_r and f_{SIM} on the base of vertical cluster distribution by calculating a vertical integral for each station. Then gridding of integral values over the investigated area was conducted using Krigging method and an average value of volume or amount of property was calculated for each cluster.

3. Results

Strong interannual variations are reflected in S and $\delta^{18}O$ ranges with wider ranges in 2007 and 2010 compared to 2011, 2013 and 2014 (Fig. 3a). Accordingly derived fractions of river water and distributions within the Laptev Sea show strong inter annual differences (Fig. 3b) with extremely high river fractions in the southern Laptev Sea in 2007 and 2010 but a wider spread of less extreme, but still relatively high river water fractions towards the north in 2011, 2013 and 2014.

Salinity ranges of PCA clusters suggest that C1-C5 represent shelf and surface waters, while C6-C8 are within the salinity range of LHW (Tab. 2). C1 may be directly associated with Lena River water as it occurs near the delta area only (Fig. 4). C2 occurs east of 126°E and is linked to C1 but spreads further north from the delta area (up to 77°N). C5 and C8 are largely found in the western part of the Laptev Sea. C5 is fresher than C8 and spreads further onto the shelf, while C8 is found in the northern part of the sections towards the east (Fig. 4). C4 occurs predominantly in the very east at 140°E, but is also found in the central Laptev Sea. C3 and C7 are primarily found in the central and eastern Laptev Sea. While C3 spreads further to the west at the surface, C7 is found below the surface layer. C6 is found sporadically in the central Laptev Sea at the bottom only.

4. Discussion

The clusters derived for PCA of all samples are based on statistical significance. But how solid is their meaning within the hydrography of the Laptev Sea? We argue that PCA clusters indeed describe water masses or types even though the physical properties of these water masses have a wide range and standard deviations (Tab. 2) determined by considerable inter annual variation. Nevertheless cluster analysis identifies water masses or types with statistical significance.

We will compare the distribution of clusters and parameters on selected sections (Fig. 4) to demonstrate that clusters are not mere statistical artifacts but indeed represent a useful classification of water masses within the physical world that may serve to analyze the Laptev Sea hydrology across inter annual differences.

Water mass classification:

We hypothesize that **current-year water** with low salinity and high river water content that is found in the southeastern Laptev Sea near the Lena River delta is represented by C1 and C2.

Coastal polynya water with relatively high salinity and formed locally in the coastal polynyas of the southeastern Laptev Sea is represented by C3, C4 and C7. C6 is defined by a few bottom samples and represents **Coastal polynya water** with a signal of bottom resuspension.

Inflowing water entering the central Laptev Sea from the west may originate in the Arctic Ocean halocline or might pass from the Kara Sea through Vilkitski Strait. C5 and C8 represent **inflowing water** from the western Laptev Sea.

This allotment is based on the distribution and average properties of clusters (Fig. 4 and Tab. 2). The differences between clusters within the three general water masses current-year water, coastal polynya water and inflowing waters are mainly determined by distribution and consequential further modification, e.g. different nutrient consumption or influence of local melt near the surface or subsurface. The distribution of clusters C1 and C2 is limited to the southeastern Laptev Sea (Fig. 6c). Only in 2011 when atmospheric conditions caused an extreme offshore distribution of the annual Lena

River plume (Fig. 3) is C2 also found in the central Laptev Sea (Fig. 6b). Both clusters have extremely low salinities and the highest fractions of river water and are a mixture of surface waters and Lena River discharge. While absolute brine fractions are similar to other water masses in the eastern and central LS, brine fractions are relatively low compared to river fractions. This indicates that this water consists mainly of current-year's river discharge. As C2 is not directly exposed to the surface the ratio between brine and river is about 1:7, while net f_{SIM} values in C1 are close to zero due to local summer surface melt.

Water mass types C3, C4, C6 and C7 are influenced by sea-ice formation in combination with a high river water content and are most likely modified by the southeastern Laptev Sea coastal polynyas. The SE Laptev Sea coastal polynyas are driven by wind forcing and brine released during sea-ice formation is added to the water column. Due to high river water content at the surface, brine as well as river water is transported into the bottom layer (Bauch et al., 2012). Therefore SE-Laptev Sea polynya water has the highest brine content together with the narrowest ratio between brine and river fractions and accordingly shows the strongest deviation from the direct 2-component mixing line between river and marine waters (see Fig. 3). Indication for this modification is the ratio between brine and river fractions with about 1:3 for C3, C4 and 1:2 for C6, C7. The difference between clusters is mainly determined by distribution and consequential exposure at the surface (C3) or location at subsurface (C4). As a consequence nutrients are depleted within C3, while nutrients are preserved in C4 as this depth must be below the photic zone. C3 is typically present in the SE-Laptev Sea but also in the NW-Laptev Sea at the surface in several years (except 2014 and 2010 when C3 seems to be replaced by C5 in the NW-LS). Distribution of C4 is in the SE-Laptev Sea below low salinity water masses (C1+C2) that are rich in light absorbing components (Bauch et al., 2013). C7 and C6 have the highest salinities and the highest brine relative to river water content. Thus these waters masses must be formed at the surface with relatively low river water fractions compared to C3 and C4, e.g. in an area relatively remote from the delta or within the SE-Laptev Sea polynya at the end of winter when there is potentially less river water near the surface. C7 is mainly found east of 126°E in the SE-Laptev Sea (Fig. 6 a+b). C6 is found sporadically at the bottom and high nutrient levels indicate local signal of bottom resuspension or respiration (Fig. 6b).

Clusters C5 and C8 are waters that spread into the central and northern Laptev Sea from the west consistent with the general circulation in the central Laptev Sea (Bauch et al., 2013). These waters from the western Laptev Sea may originate from the Arctic Basin and from the Kara Sea via a transport through Vilkisky Strait (Janout et al., 2015) and waters may spread also onto the central Laptev Sea shelf (Janout et al., 2016). Both clusters have relatively high salinities and their occurrence is mainly in the northwestern part of the central Laptev Sea (Fig. 6a). With average salinities of ~ 33.75 , C8 is within the salinity range of LHW and represents a component of LHW that may originate in the western Laptev

Sea or Kara Sea (Bauch et al., 2016). When comparing to other datasets (e.g. Bauch et al., 2016) it is important to remember that cluster names are not universal and watermasses need to be compared by properties that will always deviate due to averages on different sample assemblages. Cluster C5 is found at the surface and shows relatively low brine values with a ratio of brine to river water of 1:6; indicating an influence of melt water within this water mass. The ratio of brine to river water in cluster C8 is with 1:2, considerably lower and indicates a transformation of these waters by winter polynya activity and a transport of river water by brines released during sea-ice formation.

LS budget analysis based on PCA derived water masses: Implications for freshwater budgets and nutrient supply and storage

We calculated budgets for volumes, nutrients, f_r and f_{SIM} (Fig. 7) in order to assess the relative importance of Laptev Sea water masses, i.e. the relative importance of inflowing marine waters from the western Laptev Sea (C5 and C8) and locally formed polynya waters (C3, C4, C7).

The volumes of inflowing marine waters of water masses show little inter annual variations, while the volume of polynya waters shows a 2-3 fold increase in 2011-2014 relative to volumes in 2007 and 2010 (Fig. 7).

Ice production in the Laptev Sea south-eastern coastal polynya was higher in winters previous to 2011 and 2013-2014 (~3 m of ice/winter) compared to 2007 and 2010 (~0.5m of ice/winter) (Preußner et al., 2016). These enhancements in ice production within the SE coastal polynya are in conformity with a 2-3 fold increase in volumes of polynya waters in the same years. Also the budgets of f_r and f_{SIM} in these years are 2-3 fold and thus in proportion to the increase in volume of polynya water. Also the nutrient budgets are much higher for those years but the increases are considerable higher than the volume increase. For P and N the budgets are ~5-10 fold higher than in years with lower polynya activity. We therefore conclude that the polynya plays an important role in pumping of nutrients into intermediate and bottom depth on the shelf. Away from the surface consumption of nutrients is hampered with limited or missing light and nutrients within the intermediate and bottom layer of the shelf are either slowly incorporated into the photic zone of the shelf again or exported with the shelf bottom water into the halocline of the Arctic Ocean (Bauch et al., 2011).

In 2011 the distribution of river water over the central Laptev Sea was most pronounced and we may assume that consumption of nutrients was additionally hampered by turbid river water over a wider area than in all other years. This may explain relatively high nutrient levels in all clusters (polynya waters and imported waters from the NW Laptev Sea) in 2011.

Influence of the atmospheric circulation

In order to explain high interannual variability in volumes of polynya waters and imported marine waters we compare budgets with regional atmospheric circulation patterns. Considering the short time

series of available data we performed Spearman correlations between volumes of Polynya waters and inflowing waters from the western Laptev Sea with atmospheric circulation patterns i.e. summer (JAS) and winter (NDJFM) Arctic Oscillation (AO) and Arctic Dipole (AD) indices together with summer meridional (V) and zonal (U) wind components over the eastern part of the Kara Sea and winter wind components over the Laptev Sea. Atmospheric circulation patterns were retrieved from NOAA websites: <http://www.cpc.ncep.noaa.gov> (for AO) and <http://www.beringclimate.noaa.gov> (for AD). Wind component data were taken from www.esrl.noaa.gov/psd/ as [CDC Derived NCEP Reanalysis Product at Surface Level](#). Statistically significant coefficients were obtained for the volume of Polynya waters with winter wind U-component over the Laptev Sea (-0.9) and for “Kara Sea waters” with winter AO and AD (-0.7 and -0.9 respectively). These connections may be explained as follows: easterly winds over the Laptev Sea region contribute to an enhanced polynya activity and formation as well as spreading of polynya waters over the Laptev Sea shelf. At the same time enhanced easterly winds over the Arctic seas that occur during positive phases of AO and AD indexes are leading to a reduction of the outflow of waters through Vilkitsky Strait (Janout et al., 2015) and, thus, to a reduction of imported marine waters into the central Laptev Sea. In 2011 when a dramatic increase of the volume of Polynya waters occurred (Fig. 7), several factors i.e. increased Polynya activity in winter and blocking-favorable winds over the Kara Sea in summer combined that led to the enhanced formation and unobstructed distribution of polynya waters over the central Laptev Sea.

5. Conclusions:

The large gradients and strong inter annual variations on the Laptev Sea shelf prevent an application of uniform ranges for a classification of the major water masses for different years. We use a principal component analysis (PCA) in order to assess the distribution and importance of water masses within the Laptev Sea shelf area. We show that the PCA derived water types are consistent with the Laptev Sea hydrography and represent the major water masses on the central Laptev Sea shelf i.e. (i) predominantly marine inflowing waters that originate from the Kara Sea or the Arctic Ocean basin and enter the central Laptev Sea from the northwestern Laptev Sea, (ii) locally formed coastal polynya waters were modified by winter processes in the southeastern Laptev Sea coastal polynya and (iii) current year water that is riverine summer surface water that is formed from the Lena river discharge and local melt. Despite prominent ranges in physical properties of these water types the mathematical method of cluster analysis performed on PCA of samples allows definition of water types based on objective and statistically significant criteria.

Budgets for freshwater and nutrients in the major Laptev Sea water masses indicate that freshwater inflow from the western Laptev Sea is about half or in the same order of magnitude as freshwater stored in locally formed polynya waters. We find that imported water dominates the nutrient budget

in the central Laptev Sea; and only in years with enhanced local polynya activity the nutrient budget of the locally formed bottom water is in the same order of magnitude as imported nutrients.

The coastal Laptev Sea polynya is clearly important for the Laptev Sea nutrient budget. With an export of shelf waters to the Arctic Ocean halocline (Bauch et al., 2009, 2011) the Laptev Sea coastal polynya therefore also influences the nutrient budget of the Arctic Ocean halocline. The importance of this nutrient export remains to be determined but it is likely that this influence will change as we may assume that polynya openings and activity might be more frequent in the future with thinner and more mobile ice cover in the Arctic Ocean and shelves. It is an important but open question in which direction the arctic system and the maintenance of the halocline will develop with a changing climate.

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8. Figures:

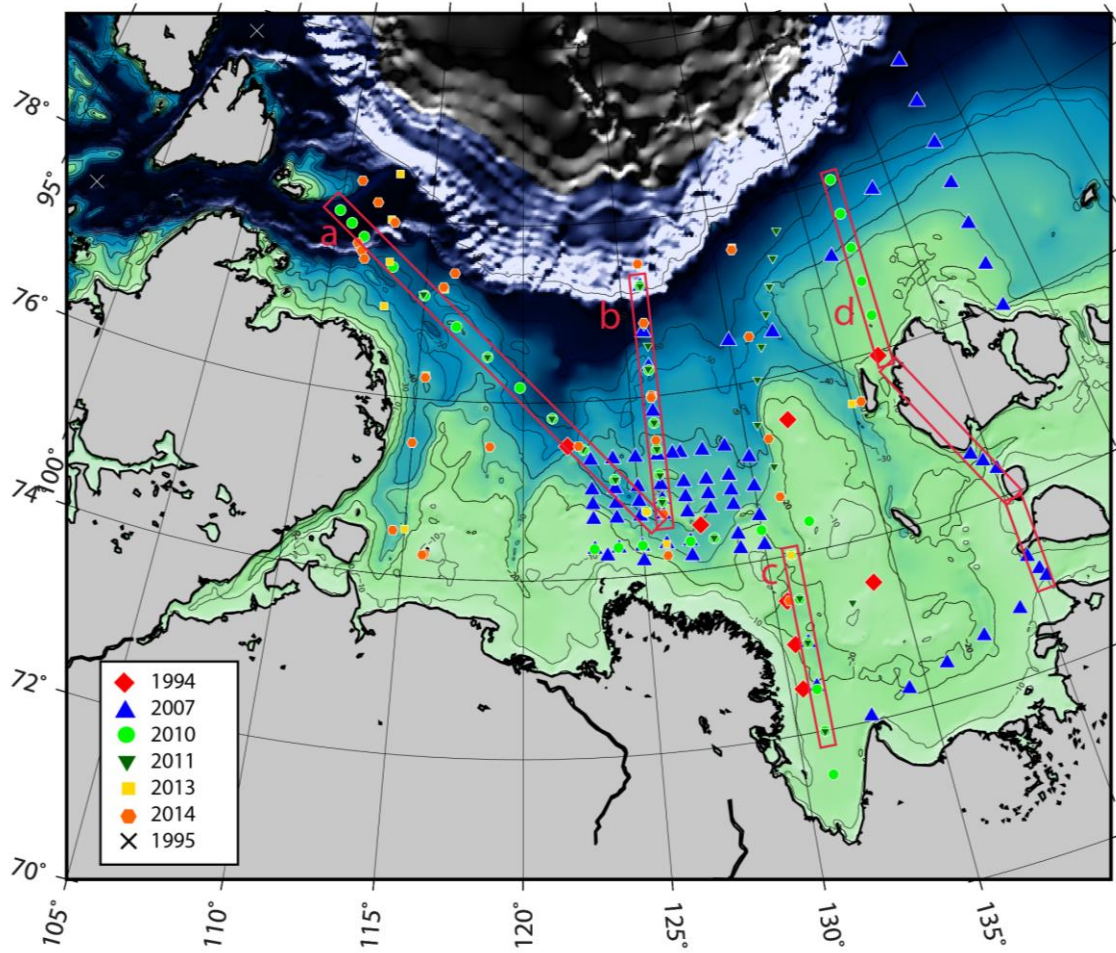


Figure 1: Map of the Laptev Sea and station distribution for different years according to color code. Also indicated are position of sections (a-c) shown in Fig. 6 and (a-d) shown in Fig. 4.

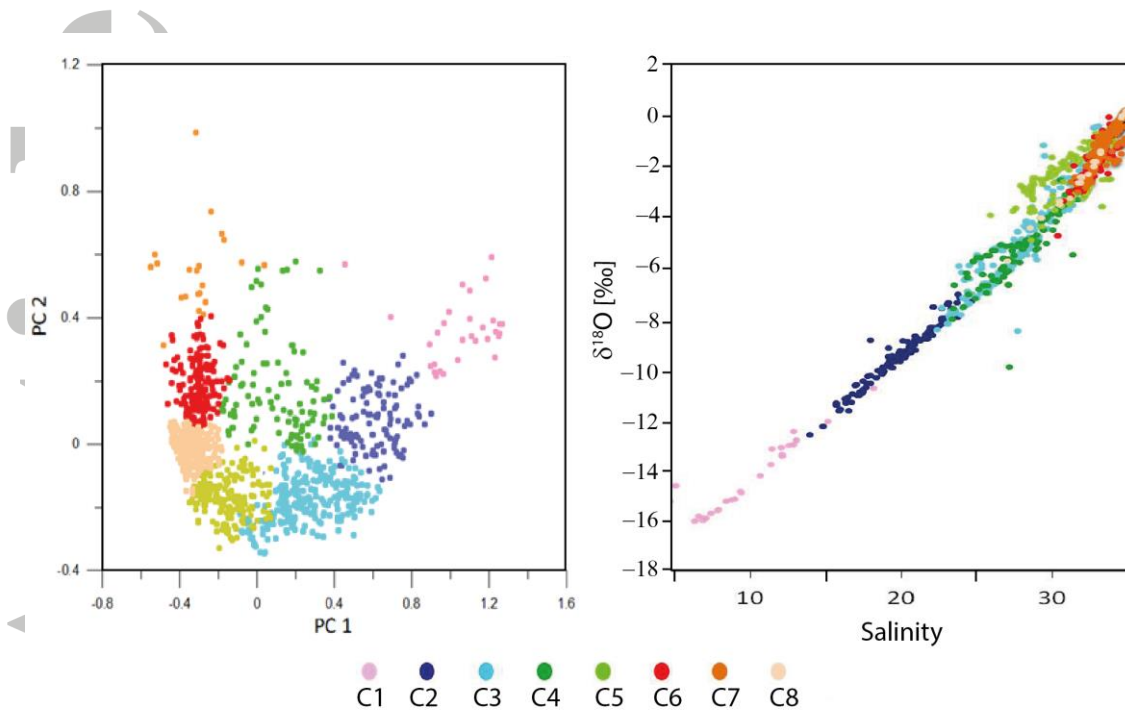


Figure 2: Phase portrait of PC1 versus PC2 (left) and $\delta^{18}\text{O}$ versus salinity (right hand side) with colors for clusters.

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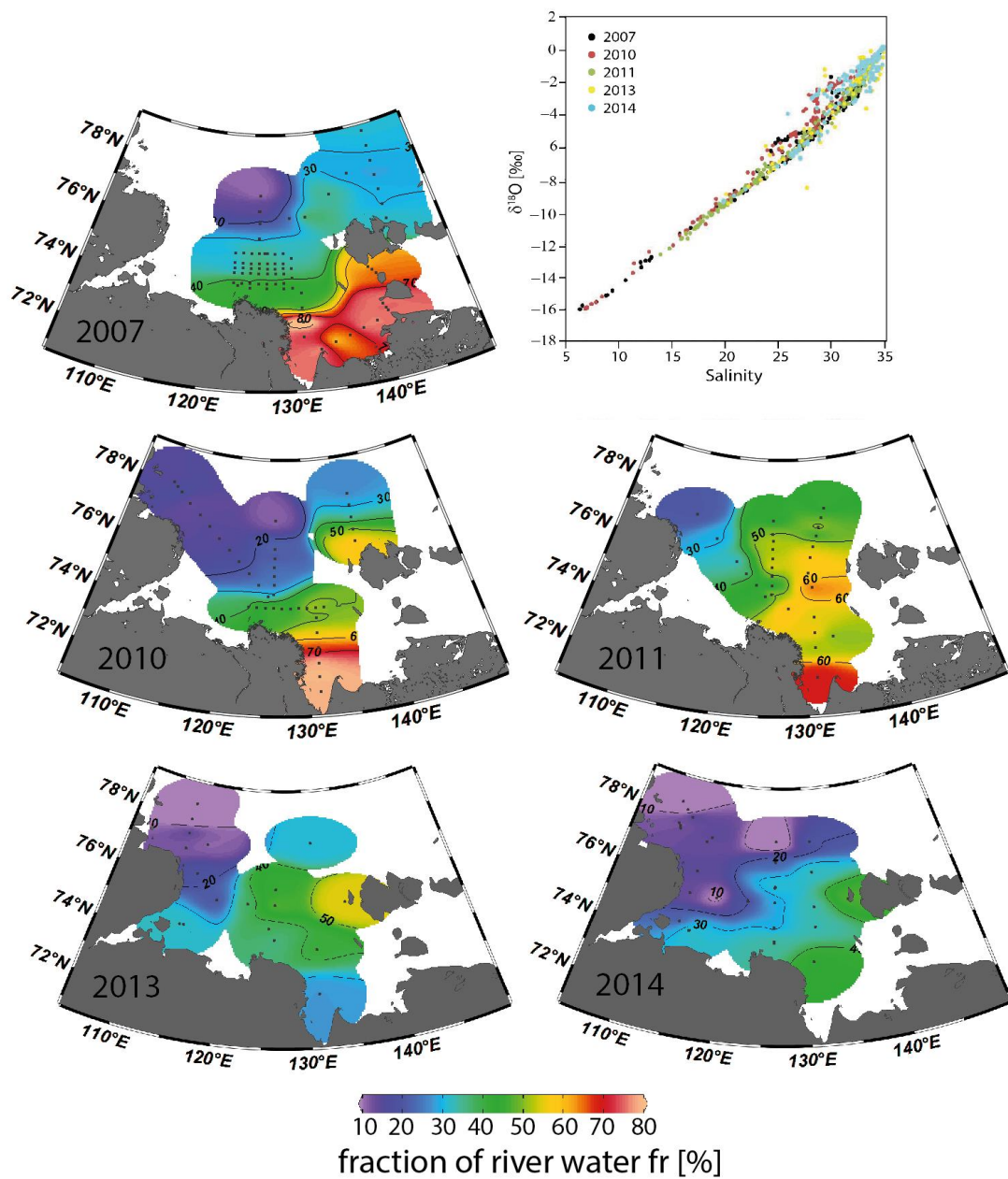


Fig. 3: a) $\delta^{18}\text{O}/S$ plot with colors for different years b) distribution maps of derived river water fractions f_r .

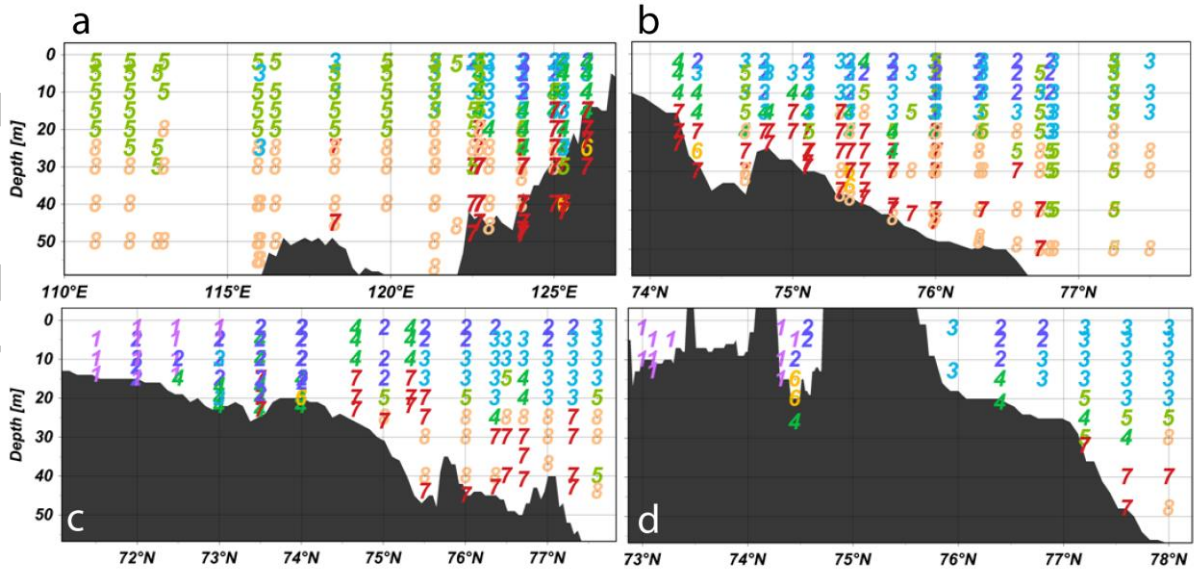


Figure 4: Vertical distribution of clusters/water masses. Position of sections (a-d) are indicated in Fig.1 with section (c) extended northward to ~78°N.

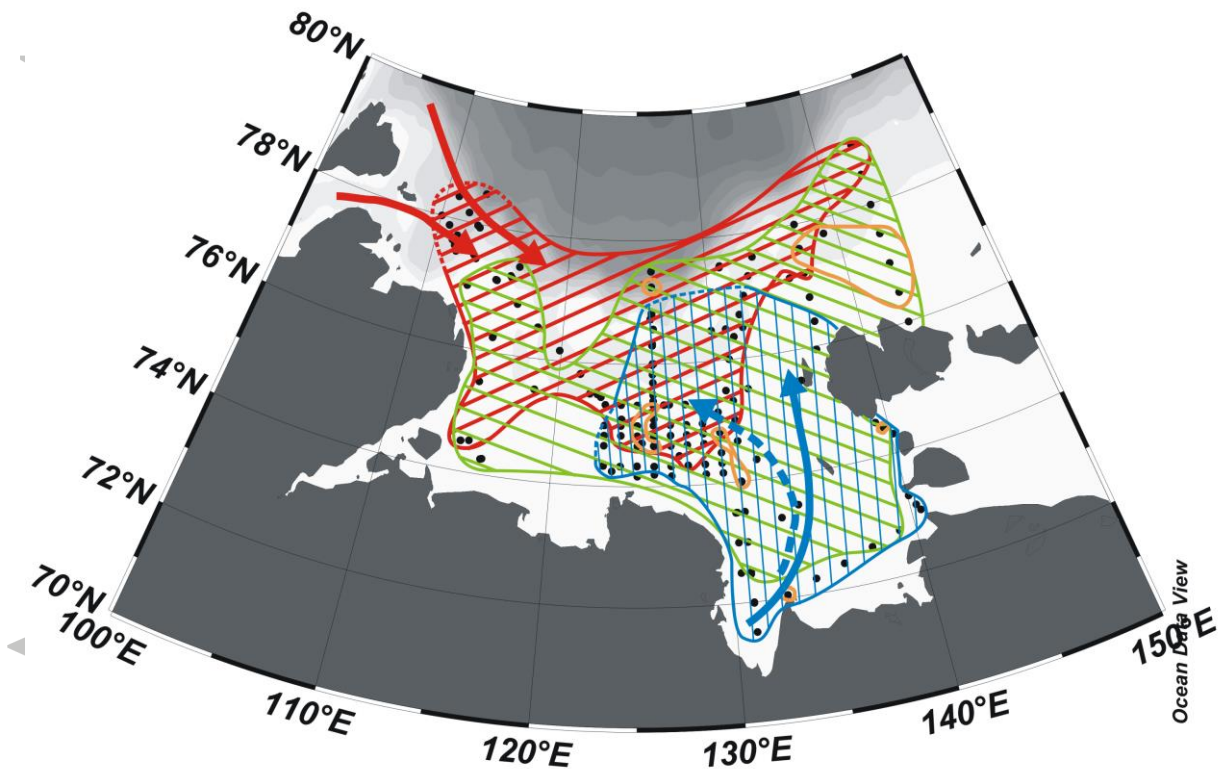


Figure 5: Spatial distribution of water masses types Inflowing Waters (red; C5 and C8), Polynya Water (green; C3, C4 and C7) and River Water (blue; C1 and C2).

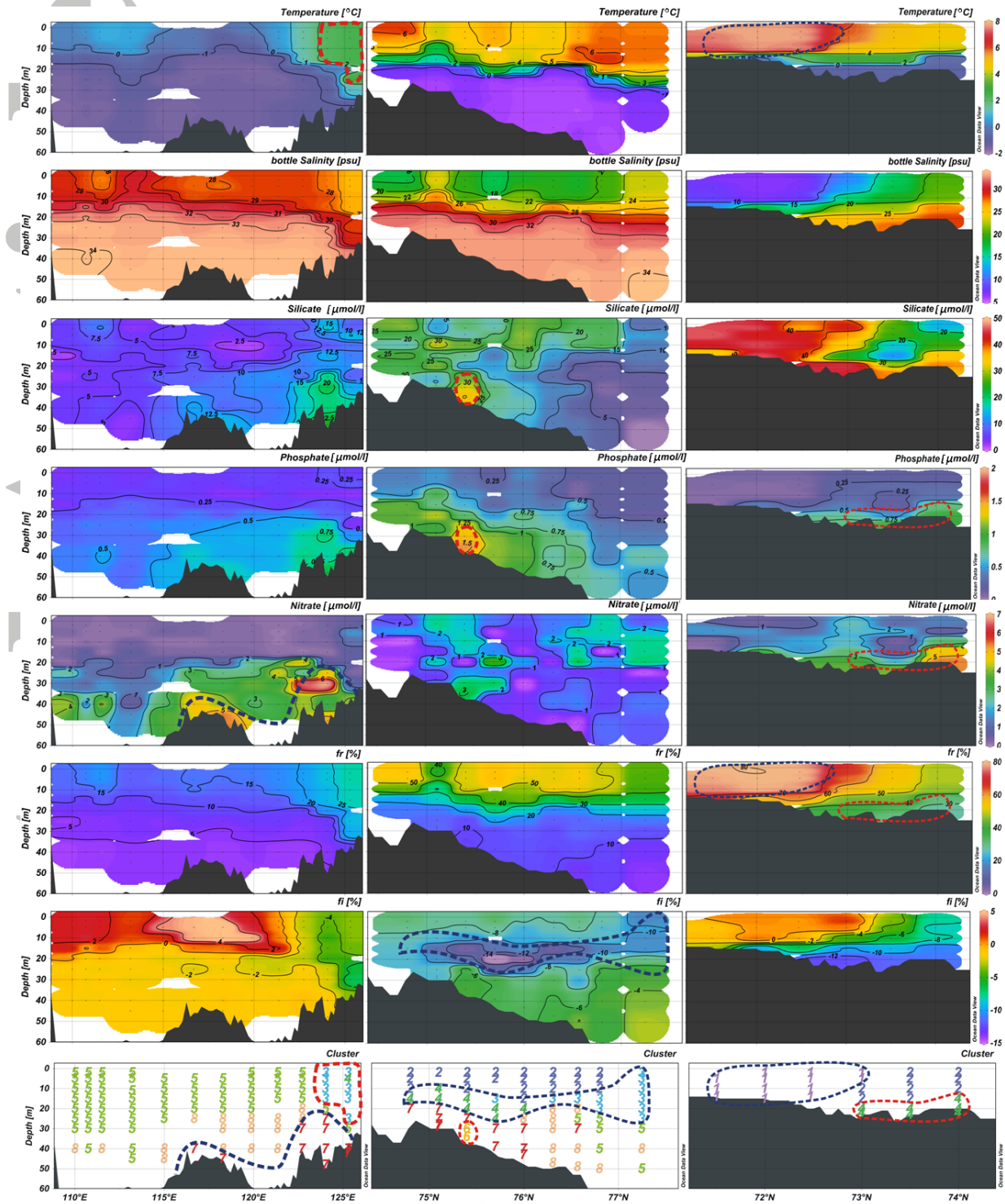


Fig. 6: Parameters and clusters for years (a) 2010 across the western to central Laptev Sea (b) 2011 along 126°E and (c) 2010 along 130°E (left to right). Positions of sections are indicated in Fig. 1.

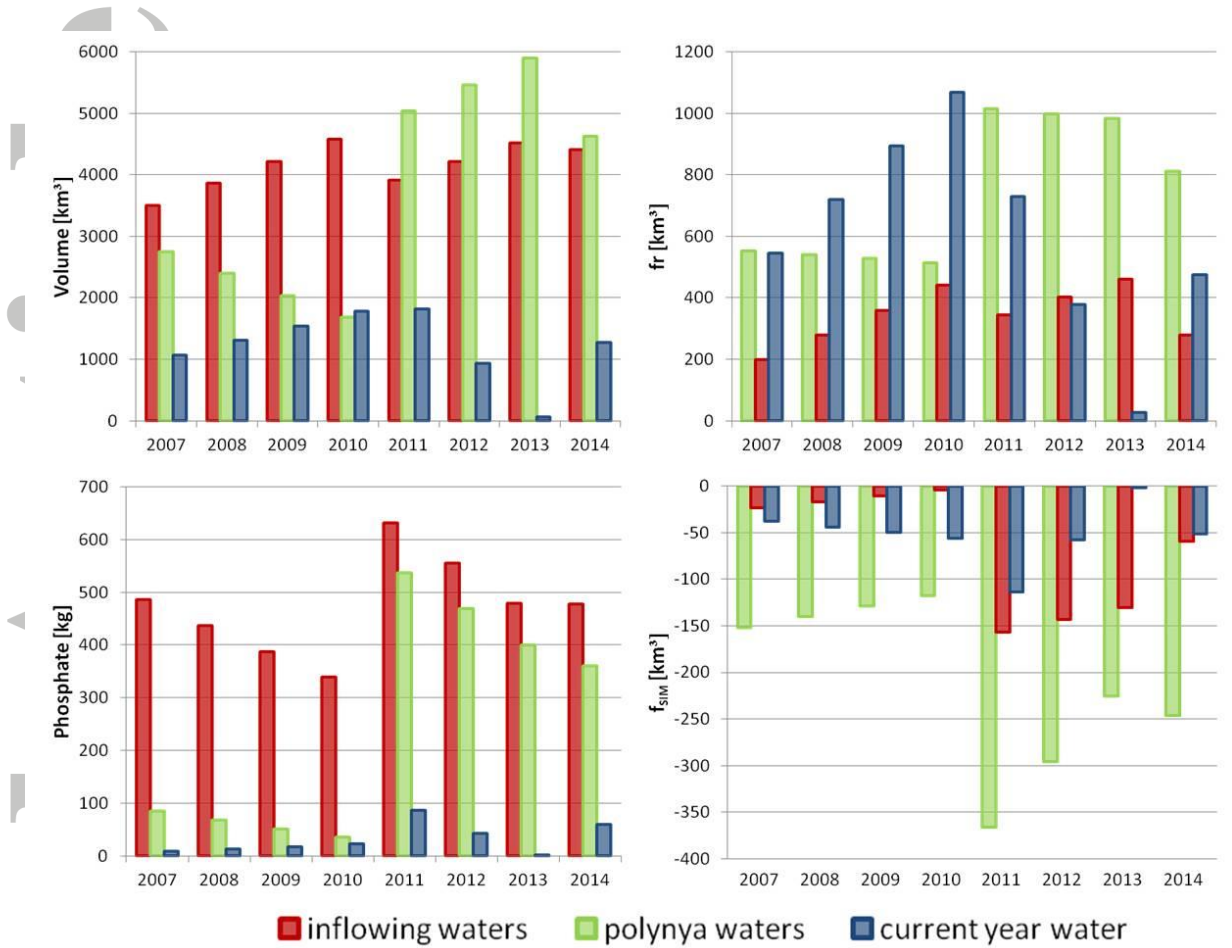


Fig. 7: Budgets of (a) volumes, (b) phosphate, (c) river water and (d) sea-ice meltwater for Inflowing waters (red; c5 and c8), Polynya Water (green; c1 and c2) and Current-year Water (blue; c3, c4 and c7). Budgets were calculated separately for each cluster within the area of 110-137.5°E; and 72-78°N and then combined in accordance with our water mass classification. Depth of Integration for deeper stations was cut off at 50m. The total area for the budgets is 328,833 km² (land excluded).

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9. Tables:

Tab. 1: End-Member Values Used in Mass Balance calculations^a

End-Member	Salinity	$\delta^{18}\text{O}$ (‰)
River water (f_r)	0	-20(1)
Sea-ice meltwater (f_{SIM})	4(1)	-2(1)
Marine water (f_{mar})	34.92(5)	0.30(1)

^aNumbers in parentheses are the estimated uncertainties within the last digit in our knowledge of each end-member value.

Table 2: Average properties for water masses distinguished by cluster analysis for the Laptev Sea. The standard deviation is given in parentheses.

	Depth [m]	T [°C]	Salinity [psu]	Phosphate [$\mu\text{mol/kg}$]	Silicate [$\mu\text{mol/kg}$]	Nitrate [$\mu\text{mol/kg}$]	f_i [%]	f_r [%]	$\delta^{18}\text{O}$ [‰]	f_i/f_r
c1	7 (5)	6.0(1.8)	9.8 (3.2)	0.2 (0.1)	41.6 (7.2)	0.8 (0.9)	-0.3 (5.3)	72.4 (6.7)	-14.4 (1.4)	na
c2	7(5)	5.0(1.2)	19.8 (2.3)	0.3 (0.1)	20.1 (6.2)	1.6 (1.1)	-7.3 (2.3)	49.6 (5.8)	-9.5 (1.2)	1:7
c3	10(6)	4.3(1.7)	27.9 (2.5)	0.3 (0.1)	8.4 (3.6)	0.9 (1.1)	-8.4 (3.9)	27.4 (8.9)	-5.0 (1.7)	1:3
c4	14(8)	1.5(1.8)	28.0 (2.3)	0.7 (0.2)	19.6 (8.1)	2.2 (1.7)	-9.6 (5.7)	28.3 (7.4)	-5.1 (1.4)	1:3
c6	52(67)	-1.0(0.7)	31.9 (2.0)	1.4 (0.3)	26.5 (8.4)	12.1 (4.6)	-5.8 (2.9)	13.7 (7.9)	-2.3 (1.5)	1:2
c7	31(13)	-1.4(0.4)	32.9 (0.7)	0.9 (0.2)	14.8 (4.6)	4.3 (3.0)	-5.5 (2.6)	10.5 (3.8)	-1.7 (0.7)	1:2
c5	18(12)	-0.2(1.1)	31.4 (2.0)	0.3 (0.1)	4.7 (2.5)	0.8 (1.1)	-1.9 (4.4)	11.8 (5.2)	-2.1 (1.0)	1:6
c8	69(72)	-1.3(0.5)	33.7 (0.8)	0.6 (0.1)	6.9 (2.2)	4.4 (2.8)	-2.9 (2.7)	5.9 (4.4)	-0.9 (0.8)	1:2