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Mass balance estimates of carbon export in different water masses of the Chukchi Sea shelf

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ABSTRACT

We construct mass-balance based estimates of carbon (C) export fractions from the water column across the Chukchi Sea shelf. Export is calculated as the difference between phytoplankton drawdown of dissolved inorganic C (DIC) and the accumulation of autochthonous particulate and dissolved organic C in the water column. Organic carbon (C_{org}) exports of $>50\%$ of DIC drawdown are ubiquitous across the shelf, even during, or shortly after, phytoplankton blooms, suggesting widespread and strong pelagic-benthic coupling. Export fractions on the shelf were generally greater in the less-productive Alaska Coastal Water than in the more productive Bering Shelf-Anadyr Water. Additionally, export fractions were greater in 2011 than in 2010, highlighting the significant spatial and inter-annual variability of the fate of C_{org} in this ecologically and biogeochemically important, and rapidly changing, ecosystem.

1. Introduction

The response of primary production to changes in sea ice cover is of central interest to the Arctic community (Schofield et al., 2010). Characterizing this response allows us to understand how climate change will influence Arctic marine ecosystems, as well as how the cycling of carbon (C) and nitrogen (N) in these systems will affect global C and N budgets. As an example, the Chukchi Sea shelf in the Pacific Arctic exhibited a 48% increase in net primary production (NPP) between 1998 and 2009 (Arrigo and van Dijken, 2011) (though see Yun et al., 2014 for evidence of lower primary production on the shelf in 2009). It has been suggested that more exposed open water, staying ice-free for longer, with greater biological productivity in the surface layer, leads to a greater air-sea flux of carbon dioxide (CO_2) (Bates and Mathis, 2009), and that any extra drawdown enhances the CO_2 sink, acting as a negative feedback on climate change.

Ultimately, however, any changes in net flux of CO_2 are only a significant feedback to climate change if the associated C removed from the atmosphere enters and remains in the deep ocean, where it is no longer in equilibrium exchange with the atmosphere, or is buried in the sediments. Even if primary production increases substantially on the shelf, if the resulting organic C is remineralized back to CO_2 in shallow waters and re-equilibrates with the atmosphere, the net effect on the C cycle is only an increase in the rate of ocean-atmosphere C cycling, but not an increase in the net oceanic storage of C. In the deep ocean, a fraction of C_{org} fixed by photosynthesis sinks below the mixed layer and is exported to depth, sequestering it from exchange with the atmosphere. The fraction of fixed C_{org} that is exported from the surface ocean through this 'biological pump' is a critical global determinant of the fate of anthropogenic CO_2 in the atmosphere (Ducklow et al., 2001).

On shallow (<150 m) continental shelves where the entire water column mixes in the winter due to sea ice formation, C_{org}

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export is not sequestered below the mixed layer. In shallow shelf systems, fixed C_{org} is either remineralized and exchanged with the atmosphere, accumulates in benthic sediments, or is transported off of the shelf. Many such continental shelves exhibit the capacity to "pump" atmospheric C to the deep ocean by advecting dense coastal C-rich water off the continental shelf, through a process known as the "continental shelf pump" (Tsunogai et al., 1999). There is evidence for an active continental shelf pump in the western Arctic Ocean, including the Chukchi Sea and East Siberian Sea shelves (Bates 2006; Anderson et al., 2010). Results from the Shelf-Basin Interactions (SBI) project show significant, but seasonally variable, rates of C export off the northeastern Chukchi Sea shelf (Moran et al., 2005; Lalande et al., 2007b; Lepore et al., 2007). Understanding the spatial variability of rates of C_{org} export from the vast productive Chukchi Sea shelf is critical to understanding the response of the C cycle to reductions in sea ice duration and extent in this region.

The Chukchi Sea is a shallow continental shelf sea located in the western Arctic Ocean, bounded on the southwest by the Chukotka Peninsula and on the southeast by northwestern Alaska. It has an average shelf depth of $\sim$50 m (Hameedi, 1978), and there is a pronounced shelf-break that runs northwest to southeast, separating the Chukchi Sea shelf from the Canada Basin (Weingartner et al., 2005). Pacific water flows onto the shelf from the Bering Strait (Fig. 1), originating from three distinct sources. The first is the nutrient-rich water from the Gulf of Anadyr and the second is water from the central Bering Sea shelf. These two water masses flow through the western portion of the Bering Strait (Hansell et al., 1993; Cooper et al., 1997; Weingartner et al., 2005), and mix in the southern Chukchi Sea to form Bering Sea Water (BSW, Coachman et al., 1975). The third Pacific water source is Alaskan Coastal Water (ACW), which is warmer and fresher than BSW and lower in nutrients. It is advected northward by the Alaskan Coastal Current (ACC) and flows through the eastern portion of the Bering Strait predominantly in summer (Paquette and Bourque, 1974; Weingartner et al., 2005).

It is believed that the BSW and ACW progress northward in the Chukchi Sea predominantly along three main pathways. One of these pathways is the ACC (Fig. 1, shown in light green), which comprises ACW, and two of these pathways comprise BSW: a central branch and a western branch. In the central branch, BSW follows a pathway through the Central Channel (between Herald and Hanna shoals) and in the western branch, BSW flows through Hope Valley into Herald Canyon (Fig. 1, shown in dark blue). As described in Pickart et al. (this issue) and shown in Fig. 1, some of the water in the western branch is diverted eastward north of Herald Shoal and joins the Central Channel branch. As this water encounters Hanna Shoal it then bifurcates and flows around each side of the shoal. In addition, some of the water in the Central Channel pathway appears to leak through gaps in the ridge between Hanna and Herald shoals. Ultimately much of the Pacific water entering through Bering Strait drains through Barrow Canyon, particularly during the summer months (Itoh et al., 2015; Gong and Pickart, 2015; Pickart et al., in press). Notably, the middle of Barrow Canyon exhibits high benthic biomass (Grebmeier, 2012). This is the location where high-nutrient Pacific winter water exits the shelf in late-summer (Itoh et al., 2015) and also where wind-driven upwelling can bring this water back into the canyon from the Canada Basin (Mountain et al., 1976; Aagaard and Roach, 1990; Pickart et al., 2013). An eastward flowing shelf-break jet flows along the northern edge of the Chukchi Sea (Pickart et al., 2005), which can spawn eddies that transport organic carbon off the shelf (Mathis et al., 2007a).

Sea ice retreats from south to north across the shelf, beginning in May each year. From 1979 to 1998, sea ice remained over the northern portion of the Chukchi shelf in summer. Since then, however, the ice has regularly been retreating past the shelf-break each summer, and, since 2007, it has retreated fully or nearly-fully off the shelf each year. In the Chukchi Sea, the mean open water area has increased by 1000 km^2 per year over the last decade, and the duration of the open water season has also significantly increased (Brown and Arrigo, 2012; Frey et al. 2015). There is some evidence that these patterns of retreat are due to changes in

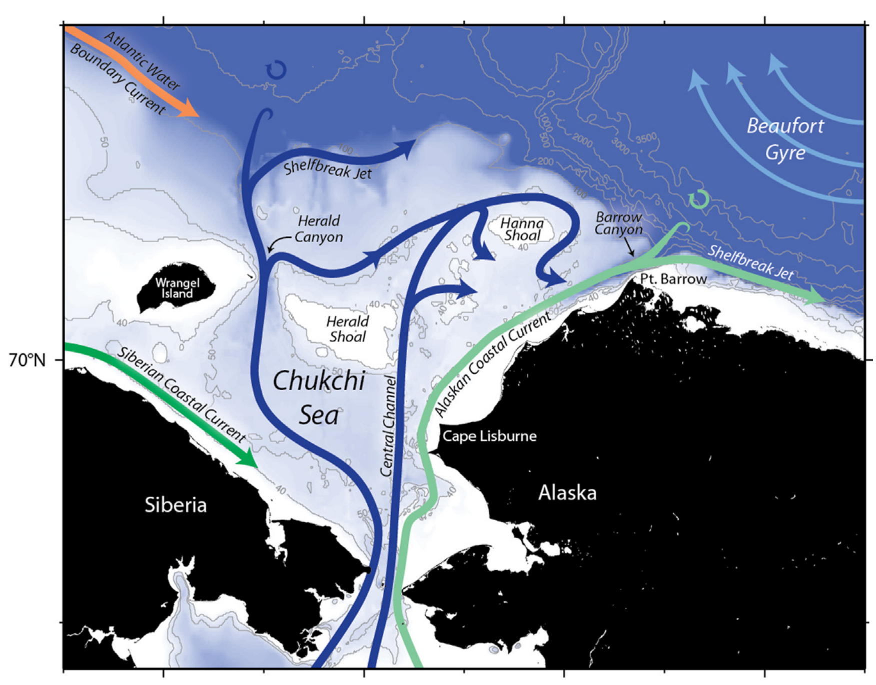

Fig. 1. Schematic circulation of the Chukchi Sea shelf region (after Brugler et al. 2014), including place names. Water enters the shelf through the Bering Strait. The Bering Sea Water (BSW) flow pathways, which progress across the shelf around Herald and Hanna Shoals, are shown in dark blue. The Alaska Coastal Current flow path, which follows the coast, is shown in light green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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annual mean heat flux through the Bering Strait (Shimada et al., 2006; Woodgate et al., 2012).

Sea ice retreat strongly determines the variability of phytoplankton production on the Chukchi shelf (Grebmeier et al., 2010; Wang et al., 2013). Prior to the discovery of under-ice phytoplankton blooms (Arrigo et al., 2012), it was believed that phytoplankton production in the Chukchi began each year in late-May as the ice retreats, peaking around 10 June (Arrigo and van Dijken, 2011). Zooplankton grazing rates of these blooms are generally considered to be low (Sherr et al., 2009), allowing a large portion of the production to settle to the benthos without being grazed (Grebmeier, 2012).

Because of relatively low grazing rates in cold water at the onset of the blooms, the Chukchi shelf is characterized by significant pelagic-benthic coupling, as early season sea ice algal production and spring phytoplankton blooms support significant benthic production (Grebmeier et al., 1988; Grebmeier et al., 2006). The C_{org} from the blooms that reaches the sea floor fuels one of the most productive soft-bottom benthic ecosystems on the planet; levels of macroinfaunal biomass of 60 g C m^{-2} are found in southern portions of the Chukchi shelf (Grebmeier, 1993). Benthic production represents a significant food source for the Pacific walrus (*Odobenus rosmarus* divergens) (Fay, 1982) and summer-feeding gray whales (*Eschrichtius robustus*) (Clarke et al., 1989; Moore et al., 2003). As such, changes in sea ice may have significant implications for both pelagic and benthic ecosystems (Grebmeier et al., 2006; Wassmann and Reigstad, 2011; Grebmeier, 2012). Previous studies have suggested that there is no long-term accumulation of C_{org} on the shelf (Mathis et al., 2007b), and that a significant proportion of fixed C is likely transported off the shelf and into the Canada Basin after remineralization (Bates et al., 2005b).

The organic C produced by marine phytoplankton blooms also fuels benthic denitrification, the microbial enzyme-mediated conversion of fixed N to gaseous N_2 (Devol et al., 1997; Chang and Devol, 2009; Granger et al., 2011). Owing to the fact that the Pacific water traverses the shallow Chukchi shelf before being advected into the basin and ultimately exiting the Arctic through Fram Strait and the Canadian Arctic Archipelago, the rates of denitrification on the shelf play a globally significant role in N removal, stimulating intensive nitrogen fixation in the North Atlantic (Yamamoto-Kawai et al., 2006).

Photosynthesis by phytoplankton blooms on marginal continental shelves in the Arctic can substantially lower the water column partial pressure of carbon dioxide (pCO_2), driving a net air to sea flux of CO_2 during the seasonally ice-free season (Arrigo et al., 2010). Continental shelves in the Arctic are generally thought to be net "sinks" for atmospheric CO_2 (Chen and Borges, 2009), and the Chukchi Sea shelf has been demonstrated to be a strong and increasing CO_2 sink (Bates et al., 2006), though the strength of the sink itself may be decreasing (Cai et al., 2010). Satellite-derived estimates of total annual NPP in the Arctic Ocean are on the order of 500 Tg C yr^{-1} (Arrigo and van Dijken, 2011), which is thought to represent a significant net metabolic sink of atmospheric CO_2, on the order of 100–200 Tg C yr^{-1} (Arrigo et al., 2010). This represents 5–14% of the global C cycle balance (Bates and Mathis, 2009). Thus, in addition to fueling productive benthic ecosystems on the shelf itself, the fate of production in these shallow waters is also a significant potential determinant of the global N and C cycles.

In this study, we construct mass-balance based estimates of C_{org} export across the Chukchi Sea shelf, including central and southern portions of the shelf, using data collected during the NASA-sponsored program Impacts of Climate on the Eco-Systems and Chemistry of the Arctic Pacific Environment (ICESCAPE). As part of ICESCAPE, oceanographic cruises to the Chukchi Sea were carried out in summer 2010 and summer 2011. We assume that the nutrient-rich winter water on the shelf during each of the surveys represents pre-bloom conditions and, based on this assumption, we compute the C_{org} export of the nutrient-poor summer waters. Our objective is to understand how the amount of C_{org} exported from the water column varies across this ecologically significant continental shelf and to compare our estimates with those made previously in the region. Such understanding is critical for assessing the implications of changes in sea ice, water temperature, and increases in NPP for this highly productive ecosystem.

2. Methods

2.1. Study location and sampling

We assessed export of fixed C from the water column on the shallow Chukchi shelf during two consecutive summer field campaigns (15 June–21 July 2010 and 25 June–29 July 2011), conducted as part of the ICESCAPE project. Numerous transects were occupied across the shelf during each survey (Fig. 2). A total of 140 stations were occupied in 2010 and 173 stations in 2011. Seawater samples were taken from discrete depths throughout the water column at each station. Typical sampling depths included 2, 10, 25, and 50 m, the depth of maximum chlorophyll *a* (Chl *a*) concentration, and approximately 2 m above the seafloor. At stations on the continental slope, additional samples were typically taken at depths of 100, 150, and 200 m.

At each station, seawater was collected from 30 L Niskin bottles attached to a rosette that included a SBE 911+ conductivity-temperature-depth (CTD) sensor. The water samples collected from each depth at each station were analyzed for Chl *a* concentration, dissolved inorganic C (DIC) concentration, nitrate+nitrite (NO_3^-), ammonium (NH_4^+), phosphate (PO_4^{3-}), and dissolved silicate ($Si(OH)_4$) concentrations. From selected stations, samples were also analyzed for dissolved organic C (DOC) concentration, water oxygen stable isotope ratios ($\delta^{18}O$) and particulate organic C (POC) concentration. Salinity measurements were made at a minimum of two discrete depths at each station to calibrate the CTD-mounted conductivity sensor.

2.2. Sample analyses

Samples for fluorometric analysis of Chl *a* were filtered onto 25 mm Whatman glass fiber filters (GF/F, nominal pore size 0.7 μm), placed in 5 mL of 90% acetone, and extracted in the dark at 3 °C for 24 h. Chl *a* was then measured fluorometrically (Holm-Hansen et al., 1965) using a Turner Fluorometer 10-AU (Turner Designs, Inc.).

DIC samples were collected in 300 mL borosilicate bottles, poisoned with 100 μL mercuric chloride ($HgCl_2$), and stored in the dark until analysis using a gas extraction/coulometric detection system. Samples collected in 2010 were analyzed at the University of Alaska Fairbanks, and samples collected in 2011 were analyzed shipboard and at Bermuda Institute for Ocean Sciences.

POC was analyzed by filtering seawater onto pre-combusted 25 mm Whatman GF/F. The filters were fumed with hydrochloric acid (HCl), dried at 60 °C, and transferred to tin capsules (Costech Analytical Technologies, Inc.) for analysis on an Elementar Vario EL Cube elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) at the University of California, Davis.

Seawater samples for DOC analysis were gravity-filtered directly from Niskin bottles through pre-combusted Whatman GF/F (0.7 μm pore size), collected into pre-cleaned (10% hydrochloric acid solution) 60 mL Nalgene High-Density-PolyEthylene (HDPE) bottles, and stored frozen immediately until analysis. DOC

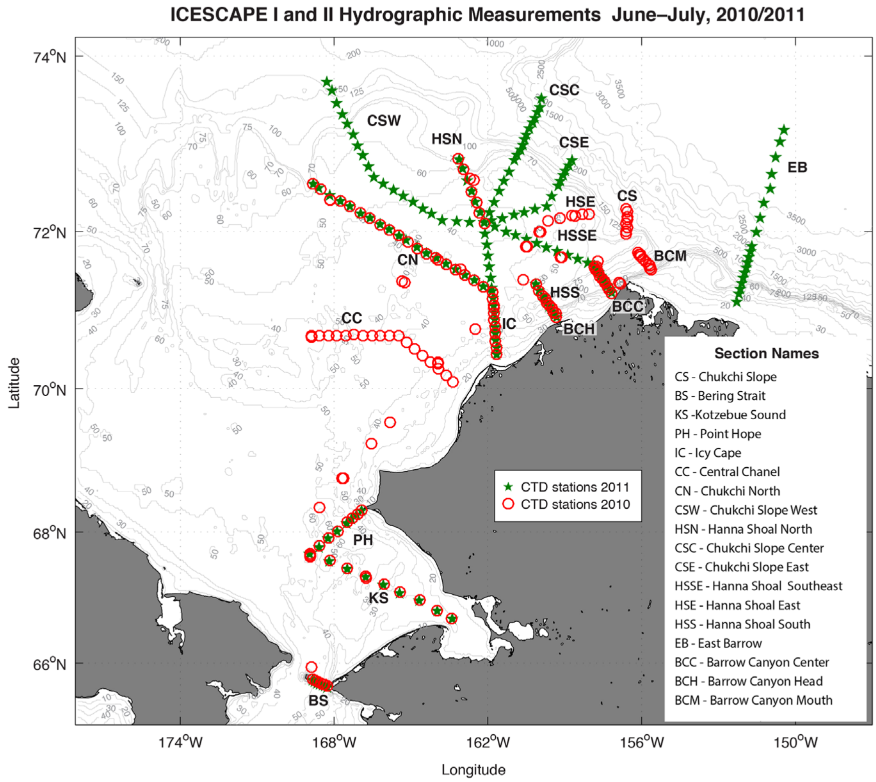

Fig. 2. Sampling transects of the ICESCAPE project are shown for 2010 and 2011.

analysis was conducted within three months of collection by high-temperature combustion using a Shimadzu total organic carbon TOC-V analyzer equipped with an autosampler (Benner and Strom, 1993, Shen et al., 2012) at the University of South Carolina. Blanks were negligible and the coefficient of variation between injections of a given sample was typically 0.6%. Accuracy and consistency of measured DOC concentrations was checked by analyzing a deep seawater reference standard (University of Miami) every sixth sample.

$\delta^{18}O$ samples were returned to the Chesapeake Biological Laboratory of the University of Maryland Center for Environmental Science in sealed vials with precautions undertaken to prevent evaporation (and isotopic fractionation). Water samples were analyzed by equilibration with CO_2 using a Thermo Fisher Gas Bench II peripheral linked to a continuous flow Delta V Plus isotope ratio mass spectrometer. Analytical precision was better than $\pm 0.1‰$ and was assessed by analysis of in-house water standards during sample analysis and calibration to international water isotope standards (V-SMOW, SLAP, GISP). Data were normalized as per recommendations of Paul et al. (2007).

Prior to the calculations of C_{org} export, all concentration values were salinity-normalized to a winter water salinity value of 33.1, following Bates et al. (2009), to account for dilution by sea ice melt at the surface.

2.3. Calculating particulate organic carbon export

C_{org} export from the summer waters of the shelf was estimated for each station using a mass balance approach, defined as the difference between the estimated drawdown of DIC and the accumulation of POC+DOC in the summer water from pre-growth winter water values. Thus, the C exported out of the water column is calculated as the amount of C_{org} that was fixed by phytoplankton, but is not present in the observed particulate or dissolved organic form in the water column. This mass-balance approach provides an estimate of an instantaneous amount of particulate organic C exported rather than a rate of export in units of time. We express this mass-balance derived C_{org} export estimate as an absolute mass (mmol C m^{-2}) and as a % export fraction, relative to the amount of inorganic C drawdown by photosynthesis. This approach also accounts for remineralization within the water column, as DIC drawdown is calculated using measured DIC concentrations that would include any remineralized C (DIC drawdown is thus equal to net community production (NCP)). Because we are interested in shelf-stations, we limited our analysis to stations with depths <150 m.

The equations for the amount of C_{org} exported from the water column, and the %C exported, at a given station, in units of mmol C m^{-2} is:

$$C_{exp} = \Delta DIC_i - (\Delta POC_i + \Delta DOC_i) \tag{1.1}$$

and

$$\%C_{exp} = (\Delta DIC_i - (\Delta POC_i + \Delta DOC_i))/\Delta DIC_i \tag{1.2}$$

where ΔDIC_i is the depth-integrated DIC deficit, ΔPOC_i is the depth-integrated POC (the delta indicates an accumulation from a baseline of close to 0), and ΔDOC_i is the depth integrated accumulation of DOC.

ΔDIC_i is defined as

$$\Delta DIC_i = DIC_{ww} * z - \left(\sum((DIC_{mz} + DIC_{mz+1})/2) * \Delta z\right) \tag{2}$$

where DIC_{ww} is the estimated pre-bloom, winter water DIC concentration in mmol C m^{-3}, DIC_{mz} is the measured, salinity-normalized DIC concentration of summer water at sampling depth z, DIC_{mz+1} is the measured salinity-normalized DIC concentration at the adjacent sampling depth, and Δz is the vertical difference (m) between sampling depths. It is assumed that, in pre-growth conditions, winter water DIC concentrations are generally uniform across the Chukchi Sea shelf. As such, our estimates of DIC_{ww} were taken as representative across all shelf stations, even if no remaining winter water was present at the time of sampling.

ΔPOC_i is defined as

$$\Delta POC_i = \sum ((POC_{mz} + POC_{mz+1})/2) * \Delta z \tag{3}$$

where POC_{mz} is the measured concentration of summer water POC in mmol C m^{-3} at depth z and POC_{mz+1} is the POC concentration of at the adjacent depth. POC is listed assumed to be close to zero prior to the onset of phytoplankton production.

Finally, ΔDOC_i is defined as

$$\Delta DOC_i = \sum (DOC_{mz} + DOC_{mz+1})/2) * \Delta z - DOC_{ww} * z \tag{4}$$

where DOC_{mz} is the measured summer water DOC concentration in μmol L^{-1} at depth z and DOC_{ww} is the mixing-model derived winter water concentration of DOC for that year.

ΔDIC_i, the water-column DIC deficit, represents a per-meter squared estimate of the difference between the amount of DIC that was in the water-column prior to phytoplankton growth, and the amount remaining in the water column at the time the sample was taken. Winter water DIC concentrations were estimated by first identifying all sampling depths with temperatures of ≤ -1.6 °C (Pickart et al., in press) and NO_3^- concentrations ≥ 10 μmol L^{-1} (to avoid including surface water), and then by calculating the mean salinity-normalized concentration of DIC for those locations in that year. Winter water defined as such was present at 51 individual depths at stations in water < 150 m deep in 2010 and at 102 individual depths at stations in water < 150 m deep in 2011. Our winter water samples had a mean salinity of 33.0 ± 0.2 in 2010 and 32.8 ± 0.3 in 2011 corresponding closely the value of 33.1, which is salinity of the upper halocline of the Arctic Ocean. In 2010, the mean winter water DIC concentration was 2229 ± 56 μmol C L^{-1}, with a maximum concentration of 2301 μmol C L^{-1}. In 2011, the mean winter water DIC concentration was 2272 ± 28 μmol C L^{-1}, with a maximum concentration of 2356 μmol C L^{-1}. These estimated winter water values are slightly lower than, but generally consistent with, shelf-wide winter water measurements made during the pre-bloom spring portion of the SBI project (Bates et al., 2005a). Because DIC_{ww} is an average of winter water values taken from stations for each year of the cruise, for a given station and depth, it is possible for the measured DIC in the summer water to exceed the calculated winter water DIC. If $DIC_{mz} > DIC_{ww}$, there was assumed to be no DIC deficit (relative to winter water) at that station and depth.

For the ΔPOC_i calculation, we assumed that there was no remnant POC in the water column prior to spring phytoplankton growth, since organic matter produced in previous years would have been either remineralized, transported off of the shelf, or deposited to the bottom.

DOC concentrations in Arctic waters are strongly influenced by the input of DOC from riverine sources (Dittmar and Kattner, 2003), and the Chukchi Sea shelf is no exception, with the majority of riverine DOC entering the Chukchi Sea shelf originating from the Yukon River and passing through the Bering Strait (Anderson 2002). Allochthonous riverine DOC is thought to be relatively resistant to degradation and is present year-round in waters on the Chukchi Sea shelf (Mathis et al., 2005; Cooper et al., 2005). Thus, accumulation of autochthonous DOC derived from phytoplankton drawdown of inorganic C, which is the DOC accumulation that we wish to include in our mass balance calculation, must be calculated relative to background concentrations that are present year round, and these background concentrations vary with the mix of source waters across the shelf.

In particular, on the Chukchi Sea shelf, DOC concentrations are strongly correlated with salinity, reflecting a conservative mixing of water sources. Thus, the amount of DOC at a given location on the shelf is a function of the amount of freshwater that is derived from meteoric water in the water column relative to the amounts of Atlantic basin water and sea ice melt water (Cooper et al., 2005). To assess the background concentrations of DOC, we first used a three-component mixing model approach described by Cooper et al. (2005) and Mathis et al. (2007b) to determine the fraction of runoff water present at each station.

Measurements of salinity and oxygen stable isotopes in water are used to determine the relative fractions of the three different water components (sea ice melt, Atlantic basin water and runoff water of meteoric origin) at each station and depth on the Chukchi Sea shelf. These fractions were estimated by solving three coupled equations:

$$f_{sim} + f_{runoff} + f_{Atlantic} = 1 \tag{5.1}$$

$$f_{sim} * \delta^{18}O_{sim} + f_{runoff} * \delta^{18}O_{runoff} + f_{Atlantic} * \delta^{18}O_{Atlantic} = \delta^{18}O_{observed} \tag{5.2}$$

$$f_{sim} * Salinity_{sim} + f_{runoff} * Salinity_{runoff} + f_{Atlantic} * Salinity_{Atlantic} = Salinity_{observed} \tag{5.3}$$

where f is the fraction of each component, "sim" denotes water from sea ice melt, "runoff" denotes freshwater from meteoric water, and "Atlantic" denotes the core Atlantic water in the Arctic Ocean basin. We assume that Atlantic water in the Arctic Ocean basin has a salinity of 34.8 and a $\delta^{18}O$ value of +0.3‰ (Ekwurzel et al., 2001). Based upon measurements of sea ice during ICESCAPE cruises, we set the salinity of sea ice to 4, with a $\delta^{18}O$ value of –1‰ (Logvinova et al., 2015). Because freshwater on the Chukchi Sea shelf comes from meteoric water transported north from Bering Strait (Weingartner et al., 2005), we chose a runoff end-member of $\delta^{18}O$ of −21.35‰, which corresponds to the most up-to-date data for waters collected solely within Bering Strait (Cooper et al. 2006, and unpublished data). The salinity for the freshwater-fraction is set to 0.

Using measured salinity and $\delta^{18}O$ data for 2010 and 2011 and Eqs. (5.1), (5.2), and (5.3), we estimated the fractions of melted sea ice, Atlantic water and freshwater derived from meteoric water (runoff) for all samples where isotopic measurements were made (n=513 in 2010; n=640 in 2011).

We calculated DOC_{ww} for use in Eq. (4) from $\delta^{18}O$-derived data using two approaches. In the first approach, we used the relationship between runoff fraction and DOC to calculate a DOC_{ww} value for each individual station, following Mathis et al. (2007b). In this manner, for a given station and depth, DOC_{ww} is equal to the background DOC concentration for the given mix of sea-ice melt, runoff, and Atlantic water. ΔDOC_i is then measured as the accumulation above that background value.

In the second approach, average runoff fractions were calculated for stations and depths with winter water (defined as described above). Using the relationship between runoff fraction and DOC concentration (shown in Fig. 3), we then calculated DOC_{ww} from the average runoff fraction for all winter water stations.

Consistent with previously published data from the Chukchi Sea, autochthonous DOC accumulation represented only a small fraction of NCP (Mathis et al., 2007b). In 2010, using the first approach, DOC accumulation represented an average of 5% of DIC drawdown, with a maximum increase of 11 μmol L^{-1} DOC from autochthonous production. Using the second approach, DOC accumulation was an average of 7% of DIC drawdown. Likewise, in 2011, these fractions were 12% and 7.5%, respectively, with a maximum increase of 22 μmol L^{-1} DOC from autochthonous production in surface waters at one station. Previously published estimates for DOC accumulation as a fraction of NCP for this region

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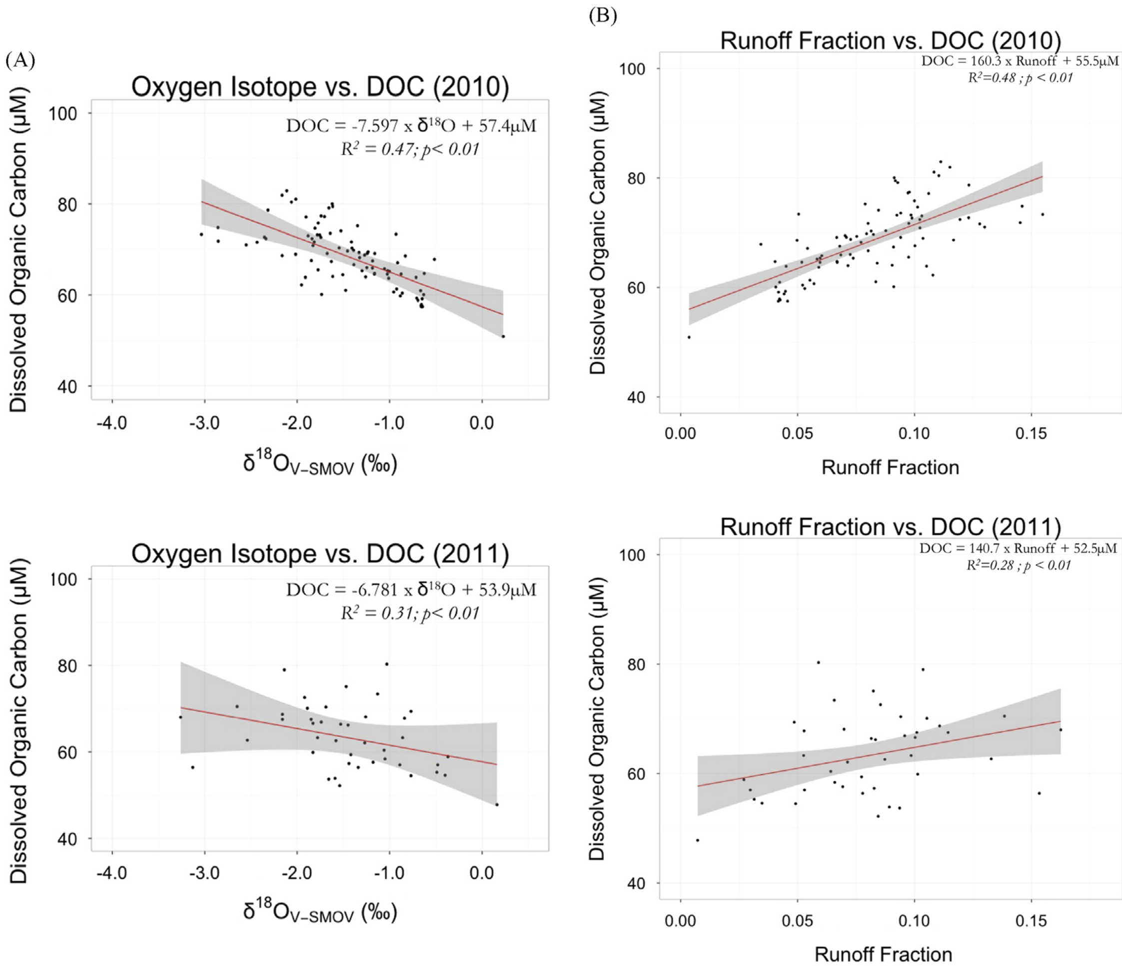

Fig. 3. Regression for 2010 and 2011 of (A) seawater $\delta^{18}O$ versus DOC and (B) three-component mixing model-derived runoff fractions versus DOC. The best fit linear model is shown in red, with a 99% confidence interval for the model's position shown in gray. The equation and R^2 for each model is given and both models are significant at the $p<0.01$ level. Background DOC concentrations on shelf waters follow a mixing line of Atlantic origin water, sea ice melt, and meteoric water. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

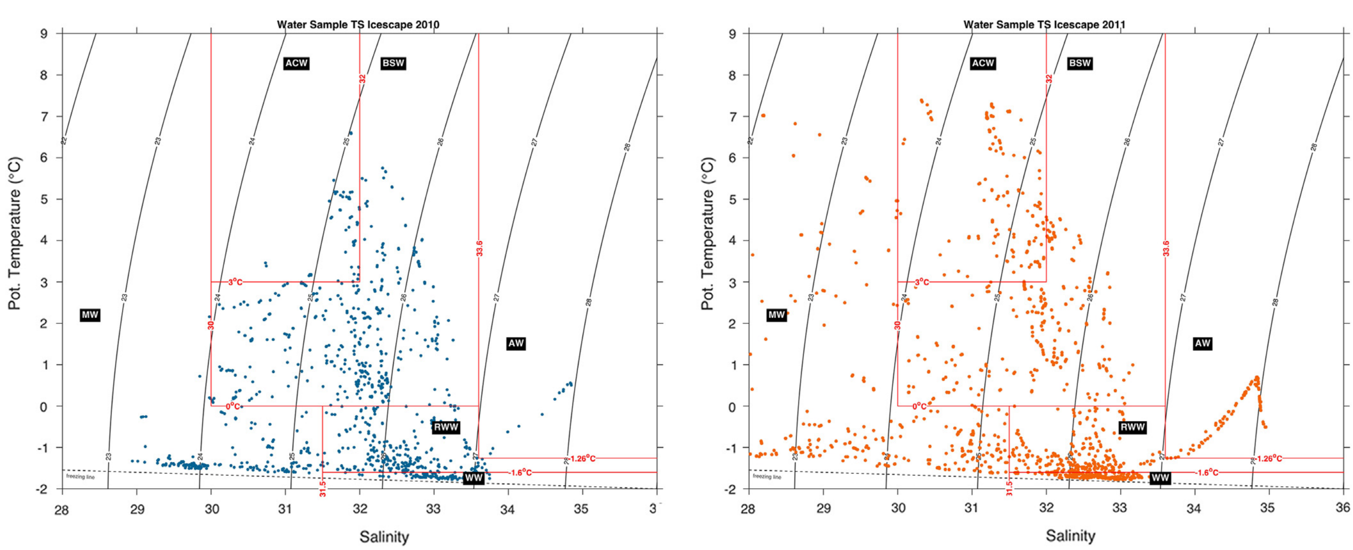

Fig. 4. Temperature vs. salinity diagram for all depths and all stations sampled in 2010 and 2011. The boxes denote the approximate boundaries of the different water masses. ACW is Alaska Coastal Water, BSW is Bering Sea Water, RWW is Remnant Winter Water, WW is recently ventilated Winter Water, AW is Atlantic Water, and MW is Melt Water.

were ~10%, with increases of up to ~14 μmol L^{-1} (Mathis et al., 2007b).

In order to estimate DOC accumulation at stations where no DOC measurements were made during the ICESCAPE cruises, we took advantage of the small fraction of NCP that DOC accumulation represents and assumed a value of 7% of DIC drawdown in 2010 and 12% of DIC drawdown in 2011. Post-hoc comparisons of the calculated export fraction at stations where data were available

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revealed close agreement between the approach using an assumed percentage value and using the mixing-model derived value ($r^2=0.98$, slope = 1 in 2010 and $r^2=0.87$, slope = 0.8 in 2011). It should be noted that, regardless of the method used to estimate DOC accumulation, the overall conclusions derived from the results are not changed because of the uniformly low levels of autochthonous DOC production on the shelf.

2.4. Separating stations by flow path/region

As noted above, the summer waters of the Chukchi Sea shelf can be divided into warmer, nutrient-poor ACW, and colder, nutrient-rich BSW (e.g. Weingartner et al., 2005). The difference between these water masses is pronounced in sections from the ICESCAPE cruises (Fig. 4, see also Lowry et al. 2015). Additionally, other waters are found on the shelf in the summer. This includes the recently ventilated winter water (WW) discussed above, which is taken here to be colder than −1.6 °C, as well as remnant winter water (RWW), melt-water (MW), and Atlantic Water (AW). The RWW is winter water that has been warmed by solar heating and/or by mixing with summer waters.

We separate our analysis of C export from summer water on the Chukchi Sea shelf between stations that contained ACW in surface water and stations that had BSW or any other water mass in surface waters, when occupied. Separations were made based on the T-S diagram shown in Fig. 4. Thus, all stations were considered either as “ACW stations” or “non-ACW stations”. The vast majority of “non-ACW” stations had either BSW or MW when occupied. Water from the shelf flows through Barrow Canyon (BC) as it advects off of the shelf (Weingartner et al., 2005, Pickart et al., 2005, Fig. 1). For each year we analyzed a set of stations, with both non-ACW and ACW, from transects located in this hydrographically complex BC region. Station designations (ACW, non-ACW) and the subset of BC stations are shown in Fig. 5A and B for 2010 and 2011, respectively.

In 2010, POC data used to calculate C export were obtained from 79 stations located on the continental shelf (< 150 m depth). Two stations were located near the head of Kotzebue Sound, where no ACW was observed in 2010. These two stations, likely subject to localized influences, were hydrographically distinct from stations with ACW or any other water-mass and were removed from the analysis. Of the 77 remaining stations, 32 stations were ACW stations, while 45 had non-ACW (either BSW or MW) when occupied. In 2010, a total of 13 stations were located on the Barrow Canyon Head, Barrow Canyon Center, or Barrow Canyon Mouth transects, which we consider to be in the BC hydrographic region. Of these, 8 stations exhibited ACW and 5 exhibited non-ACW.

In 2011, POC data used to calculate C export were obtained from 79 stations located on the continental shelf (< 150 m depth). Of these 79 stations, 36 stations had ACW, while 43 had non-ACW (either BSW or MW). In 2011, a total of eight stations were located in the Barrow Canyon transects. Of these, seven stations exhibited ACW and one exhibited non-ACW.

All statistical analyses were performed using the R statistical software (https://www.r-project.org). *P* -values for comparisons between years or regions represent results of two-tailed *t*-tests, unless otherwise specified.

3. Results

3.1. Runoff fractions and DOC

We first present results from our mixing model approach used to estimating DOC_{WW}, needed to calculate export fractions. In 2010, the average runoff fraction was 8.6%, with a range from 0% (in AW) to 15.7% runoff (at several ACW stations). In 2011, the average runoff fraction for all stations was 8.5%, with a range from 0% (in AW) to 20% runoff (at several ACW stations). As expected, DOC concentrations were negatively correlated with $\delta^{18}O$ (Fig. 3A) and were strongly and positively correlated with runoff fraction (Fig. 3B) in both years across the shelf. Using these relationships, the DOC concentration of shelf water, if it had no runoff water, would be 55.5 μmol L^{-1} for 2010 and 52.5 μmol L^{-1} for 2011. For near-average Arctic river water with a $\delta^{18}O$ value of −20‰, the

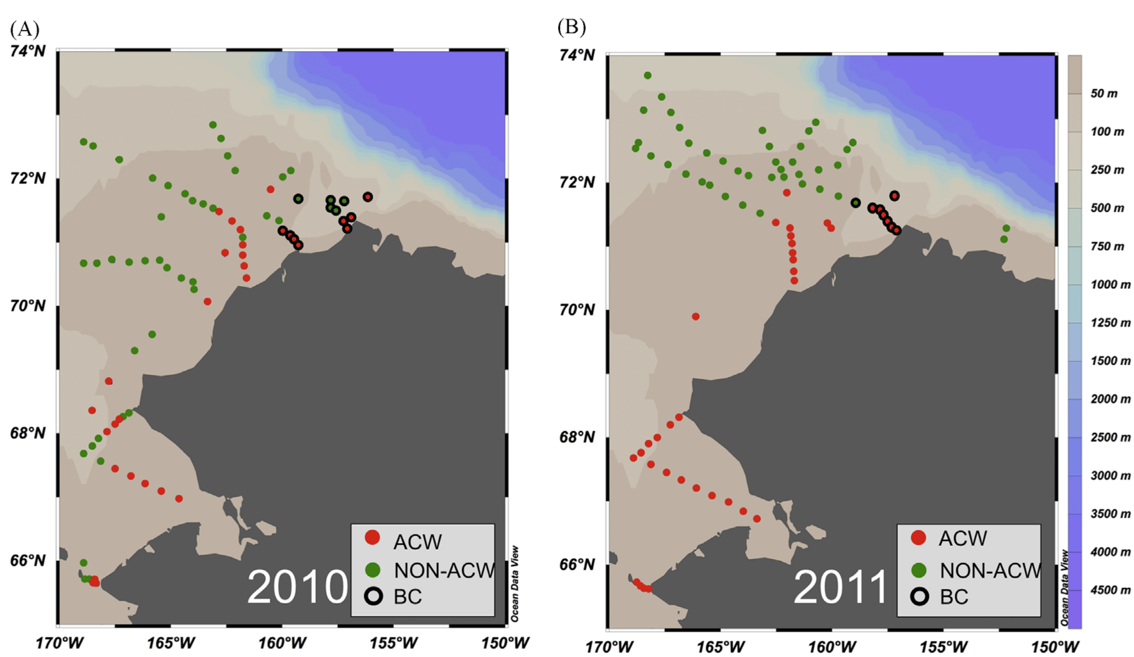

Fig. 5. (A) 2010 and (B) 2011 stations for which mass-balance estimates were made using available DIC, POC and DOC data. ACW stations are shown in red. Non-ACW stations are shown in green. Barrow Canyon (BC) stations have dark circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Table 1
Estimated carbon export %, DIC deficit and POC accumulation by flow path for 2010 and 2011. Ranges represent one standard deviation around the mean.

2010 (n=77)	ACW (n=32)	Non-ACW (n=45)	Barrow Canyon subset (n=13)
C Export %	65.6 ± 24.4%	37.6 ± 27.7%	36.9 ± 30.5%
DIC deficit	4423 ± 2694 mmol C m^{-2}	2962 ± 1972 mmo C m^{-2}	2824 ± 2245 mmo C m^{-2}
POC accumulation	882 ± 542 mmo C m^{-2}	1591 ± 1115 mmo C m^{-2}	1298 ± 707 mmo C m^{-2}
2011 (n=79)	**ACW (n=36)**	**Non-ACW (n=43)**	**Barrow Canyon subset (n=8)**
C Export %	75.5 ± 7.0%	47.9 ± 26.0%	67.2 ± 10.8%
DIC deficit	5447 ± 2025 mmol C m^{-2}	3149 ± 1677 mmo C m^{-2}	4790 ± 3514 mmo C m^{-2}
POC accumulation	645 ± 358 mmo C m^{-2}	1063 ± 664 mmo C m^{-2}	788 ± 352 mmo C m^{-2}

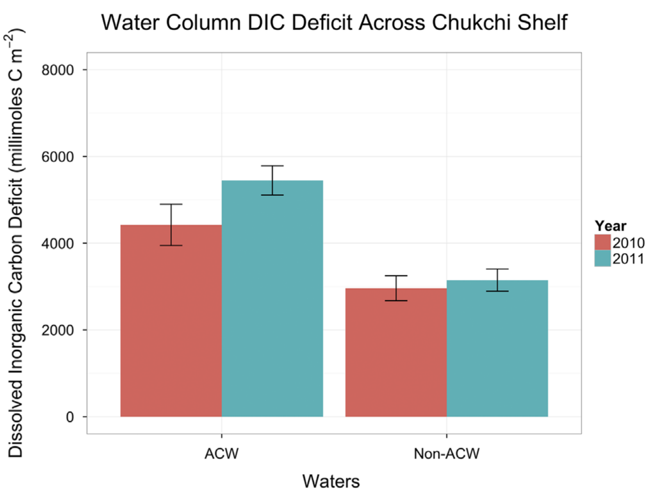

Fig. 6. Dissolved inorganic carbon deficit (mmol C m^{-2}) by cruise year and by water mass. Error bars are standard errors.

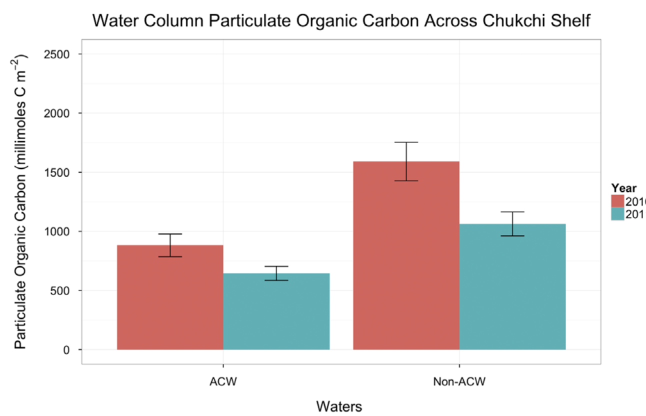

Fig. 7. Estimates of water column particulate organic carbon (mmol C m^{-2}) by cruise year and by water mass. Error bars are standard errors.

apparent meteoric DOC concentration using the 2010 DOC:δ^{18}O relationship would be 219 μmol L^{-1}, and using the 2011 relationship would be 190 μmol L^{-1}. In 2010 and 2011, the average winter water, mixing-model-derived DOC concentrations were 68.8 μmol L^{-1} and 63.7 μmol L^{-1} DOC, respectively.

3.2. *Mass balance estimates*

3.2.1. *DIC deficits*

The mean DIC deficit in the Chukchi Sea shelf water column across all stations at the time of sampling was 3516 ± 2391 mmol C m^{-2} in 2010 and 4197 ± 2164 mmol C m^{-2} in 2011. In both 2010 and 2011, ACW exhibited significantly greater DIC deficits than non-ACW ($p < 0.05$, see Table 1 and Fig. 6). ACW DIC deficits were greater in 2011 than in 2010 by approximately 1000 mmol C m^{-2}, but these differences were not statistically significant ($p > 0.05$). This same trend held for BC stations, while DIC deficits in the canyon were unchanged between years in non-ACW (not shown).

3.2.2. *POC accumulation*

The mean POC accumulation in the Chukchi Sea shelf water column across all stations at the time of sampling was 1296 ± 977 mmol C m^{-2} in 2010 and 872 ± 582 mmol C m^{-2} in 2011. In both 2010 and 2011, POC accumulation in non-ACW was approximately double that in ACW ($p < 0.01$, see Table 1 and Fig. 7). For both ACW and non-ACW stations, POC accumulation was significantly greater in 2010 than in 2011 ($p < 0.05$). Accumulation of POC at the BC stations in 2010 was 50% greater than in 2011 (Table 1).

3.2.3. *Carbon export*

The mean mass-balance estimate of C$_{org}$ exported from the water column across all stations at the time of sampling was 48.2 ± 30.0% (n=77, range 0–89%) and 60.4 ± 24.0% (n=79, range 0–83%) of total DIC drawdown in 2010 and 2011, respectively. Spatially averaged mass-balance estimates of the amount of C exported from the water column at the time of sampling were significantly greater in 2011 (2874 mmol C m^{-2}) than in 2010 (2036 mmol C m^{-2}) ($p < 0.05$). In both 2010 and 2011, there was a general trend of decreasing C$_{org}$ export fractions from south-to-north across the shelf (Fig. 8A and B).

In both 2010 and 2011, mean mass-balance estimates of C$_{org}$ export from the water column were significantly lower in non-ACW than in ACW ($p < 0.01$; Table 1 and Fig. 9). Among ACW stations, export percentages were greater in 2011 than in 2010 ($p < 0.05$). There was no difference in export fractions between 2010 and 2011 among non-ACW. Stations located in BC showed inter-annual variability in the estimated export fractions. In 2010 (n=13 stations), BC had export fractions of 36.9 ± 30.5% of DIC drawdown, which was significantly lower than in 2011 (n=8 stations), when the export fractions were estimated to be 67.2 ± 10.8%.

3.3. *Export relationship with chlorophyll concentration*

We defined stations as having a phytoplankton "bloom" if a discrete water column measurement was > 1 μg Chl *a* L^{-1} (Lalande et al., 2011). Stations where the near-surface discrete measurement (generally at 2 m depth) was > 1 μg Chl *a* L^{-1} were defined as having an active surface bloom, while stations with < 1 μg Chl *a* L^{-1} at the surface, but with at least one Chl *a* measurement > 1 μg Chl *a* L^{-1} at some greater depth were classified as having a sub-surface or sinking older bloom. Among all stations in 2010, there were 27 stations with active surface

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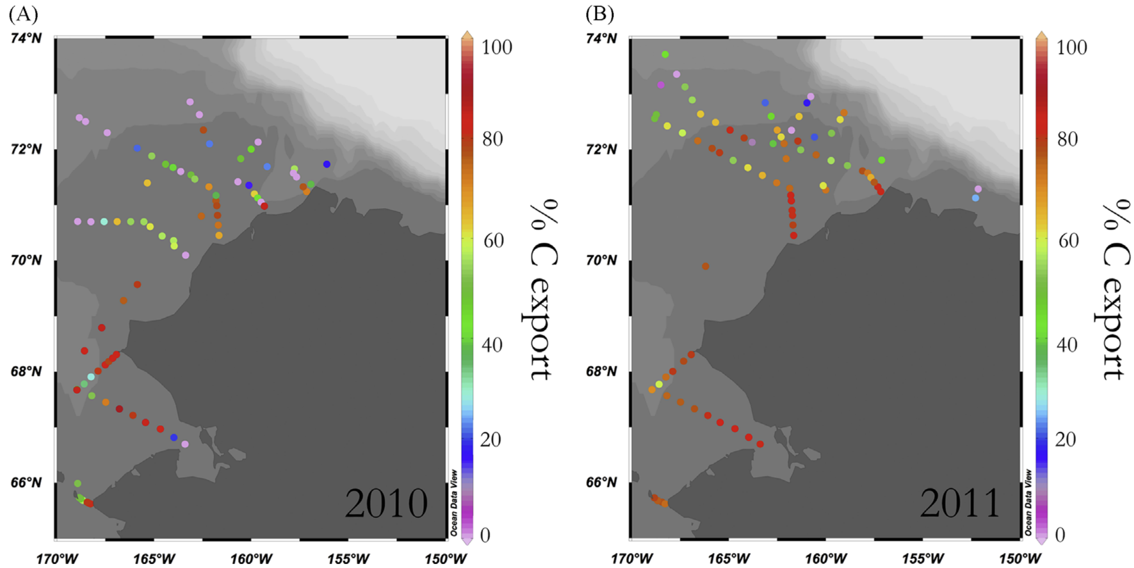

Fig. 8. Carbon export fraction estimates across the Chukchi Sea shelf in (A) 2010 and (B) 2011.

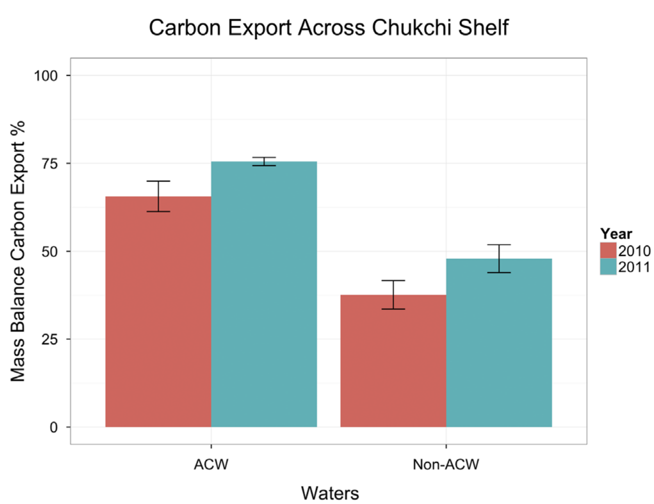

Fig. 9. Estimates of carbon export % by year and by water mass. Error bars show standard error estimates.

blooms, 39 stations with sub-surface or sinking older blooms, and 13 stations with no surface or sub-surface bloom. For 2010, the average C_{org} export fraction for stations with active surface blooms, sub-surface/sinking blooms, and no blooms was 29.5%, 54.1%, and 70.1%, respectively. In 2010, all stations that showed no sign of an active or recent bloom were in ACW, while all non-ACW stations exhibited evidence of a bloom, either at the surface or sub-surface. For 2011, the average C_{org} export fraction for stations with active surface blooms, sub-surface/sinking blooms, and no blooms was 51.1%, 59.1%, and 69.3%, respectively. In sum, for non-ACW stations with active blooms, or those that experienced recent blooms that were sinking at the time of sampling, C_{org} export fractions still ranged between 25% and 60% of drawdown by photosynthesis.

4. Discussion

Primary production that sinks out of the water column in the shallow marginal seas of the Pacific Arctic is both ecologically and globally biogeochemically important. In addition to the mass balance approach used here, a variety of other approaches for estimating the fraction export of C from this shallow shelf system have been used. These include $^{234}Th/^{238}U$ disequilibria (Moran et al., 2005; Lepore et al., 2007; Lalande et al., 2007b) and drifting sediment traps (Lalande et al., 2007a) from BC and East Hanna Shoal made as part of the SBI project, and NO_3^- utilization approaches, which relate the *f*-ratio (ratio of new production to total production) to C export (Hansell et al., 1993; Codispoti et al., 2013). Mathis et al. (2007b) employed a mass balance approach to estimate DOC and POC production as a fraction of total NCP in the northeastern Chukchi region, and Mathis et al. (2009) used a mass balance approach to estimate the fraction of NCP exported for this same region. Our approach estimates an instantaneous export fraction rather than an export rate, and our results are consistent with previously published ranges of C export fractions for the region (Table 2).

Most previous approaches have either focused on a particular region (BC and the east side of Hanna Shoal, e.g. Moran et al., 2005; Lepore et al., 2007; Mathis et al., 2007b, 2009) or have taken a much broader, synthetic approach across the western Arctic region (Hansell et al.,1993; Codispoti et al., 2013). While Codispoti et al. (2013) does include winter measurements of nutrients in Bering Strait, all NO_3^--utilization and mass balance-based approaches on the Chukchi shelf suffer from the challenge of a paucity of winter water nutrient data for the region, meaning that annual budgets involve the significant assumption that winter water nutrient values are relatively uniform across years and across the shelf in order to perform temporal extrapolations. Our results are similar in magnitude to a previous study by Mathis et al. (2007b) that also used a mass-balance estimate approach to assess the fraction of NCP exported from the water column (Table 2). Our mixing-model derived winter water DOC concentrations were approximately 65 μM DOC, consistent with the pre-bloom concentration of ~70 μmol L^{-1} DOC near Barrow Canyon (Mathis et al., 2007b), and our mixing model-derived estimates of the background DOC concentration in water with no runoff fraction are consistent with those reported by Cooper et al. (2005). The slope and intercepts of the relationship between DOC and $\delta^{18}O$ in summer 2010 and 2011 are similar to those from the May-June portion of the 2002 SBI cruise (Cooper et al., 2005), with some variation due to the fact that summer 2010 and 2011 data include changes to DOC concentrations due to autochthonous production during the growing season.

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Table 2
Comparison with published estimates of carbon export on the Chukchi Sea Shelf.

Sources	*Mean export of PP estimates*	*Approach*	*Regional coverage*
Hansell et al. (1993) Data synthesis	40–50%	*f*-ratio using NO_3^- utilization	Chukchi Sea shelf, single value
Moran et al. (2005) Summer 2002	32% (20% exported off shelf)	$^{234}Th/^{238}U$ disequilibrium and sediment traps	Northeastern Chukchi Sea shelf-and Barrow Canyon
Lepore et al. (2007) Summer 2002	15%	$^{234}Th/^{238}U$ disequilibrium and sediment traps	Northeastern Chukchi Sea shelf-and Barrow Canyon
Lepore et al. (2007) Summer 2004	38%	$^{234}Th/^{238}U$ disequilibrium and sediment traps	Northeastern Chukchi Sea shelf-and Barrow Canyon
Mathis et al. (2007b) Summer 2002	70%	Mass balance estimate as export production of NCP	Northeastern Chukchi Sea shelf-and Barrow Canyon
Mathis et al. (2009) Summer 2002	75%	Mass balance estimate as export production of NCP	Northeastern Chukchi Sea shelf
Mathis et al. (2009) Summer 2004	64%	Mass balance estimate as export production of NCP	Northeastern Chukchi Sea shelf
Codispoti et al. (2013) Data synthesis	20%	*f*-ratio using NO_3^- utilization	Chukchi Sea shelf, single value
This study summer 2010	48.2 ± 30.0%	Mass balance using DIC deficit and organic carbon accumulation	Regionally specific values across Chukchi Sea shelf
This study summer 2011	60.4 ± 24.0%	Mass balance using DIC deficit and POC/DOC accumulation	Regionally specific values across Chukchi Sea shelf

Taken as a whole, our results suggest that, given the assumption of a uniform mass of winter water, with constant pre-bloom DIC concentrations across the shelf, export percentages of over 50% of the DIC drawn down by phytoplankton production are common across the shelf. Our results also highlight that there is significant variability of C_{org} export fractions across the shelf. In both 2010 and 2011, export fraction ranged from 0% to roughly 80% across the shelf, meaning that, at some locations, nearly all the fixed C was exported out of the water-column, while at others, most of it remained in the water column in one form or another.

4.1. What drives spatial and temporal variability in C export?

4.1.1. North–south gradient

Progressing northward across the shelf, fractions of C_{org} export generally decreased in both years. Some of this geographic variability could result from the timing of sampling relative to the timing of phytoplankton production. For example, at some more northern stations, phytoplankton were actively blooming at the time of sampling, and lower export fractions at these stations likely correspond with areas of greater water-column POC accumulation, which had neither been remineralized nor had time to sink.

In both years, all stations with active phytoplankton blooms at the surface had the lowest export fractions, followed by stations with sub-surface or sinking/senescent blooms, while stations without any Chl *a* accumulation at any depth had the greatest C_{org} export fractions, averaging around 70% in both years. Any locations where phytoplankton had not yet bloomed should exhibit low DIC deficits and low water column POC (i.e., winter-like conditions). In both 2010 and 2011, there were almost no stations that had both low DIC deficits and low water-column POC accumulation, suggesting that those stations with higher export fractions, but no Chl *a* in the water column, likely experienced a bloom prior to sampling. Evidence for this is further supported by the high O_2 concentrations at many of these stations (Lowry et al., 2015).

4.1.2. Differences between 2010 and 2011

In ACW, regardless of whether or not phytoplankton were actively blooming, export fractions were significantly greater in 2011 than in 2010 ($p < 0.01$). This difference was driven by significantly greater water column POC in 2010 compared with 2011 ($p < 0.01$), while DIC deficits were not significantly different between the two years. POC accumulation across all stations represented an average of 46% of the DIC deficit in 2010, while in 2011 POC only accounted for 28% of DIC deficit across all stations. The differences in average POC accumulation between 2010 and 2011 are likely due, in part, to the fact that in 2011 there were twice as many post-bloom stations sampled as in 2010, owing to the slight difference in seasonal timing of the cruises in the two years. However, among stations with active surface blooms, C_{org} export fractions were still significantly greater in 2011 (~50%) than in 2010 (~30%), suggesting that there is some inter-annual variability in the amount of C exported from the water column. These differences might be explained by differences in total NPP, changes in grazing pressure, or changes in phytoplankton species composition.

4.1.3. ACW vs. non-ACW differences

In both 2010 and 2011, ACW had significantly greater C_{org} export fractions than non-ACW. This variability of export fractions between the ACW and non-ACW could potentially be an artifact of the winter water value assumptions used in our mass-balance calculation method. DIC deficits may be artificially inflated by the assumption of cross-shelf uniform winter water DIC values. If winter DIC values were significantly lower in ACW than was assumed here, then DIC deficits would be smaller than those calculated, and C_{org} export fractions lower. To examine this possibility, we calculated export fractions for ACW stations assuming the average DIC deficit of non-ACW. This recalculation reduced estimated export fractions calculated for ACW stations (from 65.6% to 59.8% in 2010 and from 75.5% to 58.8% in 2011), but these recalculated values were still significantly higher than for non-ACW stations in both years. Thus, C export fractions remained greater in ACW stations than in non-ACW, even if we assume that the ACW exhibited the same DIC drawdown as non-ACW.

Pre-bloom DIC concentrations in ACW would need to be significantly lower, around 2050–2100 μmol L^{-1} (rather than 2230–2270 μmol L^{-1}), in order for ACW to have the same calculated C export fraction as non-ACW (assuming POC accumulation remained unchanged). While such low pre-bloom DIC values may be possible (it is unknown given the lack of early season sampling in this region), our data nonetheless suggest that substantial export percentages (> 50%) of any production that does occur in the ACW on the Chukchi Sea shelf are commonplace. The differences between the C_{org} export fractions in the ACW and non-ACW are fundamentally driven by the much lower accumulation of POC in the ACW. It should be noted that even though export percentages are much higher in the ACW than in the BSW flow paths, the amount of C exported from the water column in summer non-

ACW, in terms of mol C m^{-2}, is two and half times greater on average than the amount exported from the ACW, due to the much higher rates of production in non-ACW.

4.1.4. Barrow Canyon

Following the trend for other regions, export fractions in the vicinity of BC were greater in 2011 than in 2010, due to very low POC accumulation in the water column in 2011. Barrow Canyon is thought to be a particularly productive region due to regular upwelling of deep basin waters (e.g. Aagaard and Roach, 1990) and the fact that a number of winter water flow pathways across the Chukchi shelf converge there (e.g. Gong and Pickart, 2015; Lowry et al., 2015). Overall, observed export fractions in 2010 were more consistent with those observed in the region during the SBI project (Moran et al., 2005; Lepore et al., 2007), than the mass balance estimates made in 2011. All estimates exhibited large variability, which may be due to the inclusion of stations from a broad area around BC, but generally confirmed that BC is an important region of C export for the entire shelf system (Lalande et al., 2007a).

4.2. Conclusions

Our results demonstrate that strong pelagic-benthic coupling, with export percentages of $>50\%$ of fixed C_{org}, is common across the eastern Chukchi Sea shelf. In non-ACW with active blooms, or those that experienced recent blooms that were sinking at the time of sampling, export fractions still ranged between 25% and 60%, indicating an extremely rapid transfer of C_{org} from phytoplankton to the benthos, even during blooms. In both 2010 and 2011, ACW stations tended to have significantly higher fractions of C_{org} export than non-ACW stations, suggesting that the majority of fixed C quickly reaches the benthos in the ACW as well. Averaged across both years, stations with evidence of an earlier bloom, but where little Chl *a* and POC remained in the water column, had an average export percentage of 70% of NCP, with a POC accumulation around 20% and DOC accumulation around 10%. These percentages (70%, 20%, and 10%) for export, POC, and DOC, are identical to those reported by Mathis et al. (2007b) for the northeastern Chukchi Sea shelf. Nearly a decade later, as total NPP of the Chukchi Sea shelf appears to be increasing (e.g. Arrigo and van Dijken, 2011), the highly productive regions of Chukchi Sea shelf ecosystem appear to be behaving similarly in terms of the rapid removal of fixed C from the water column. Notably, the less productive regions of the shelf exhibited very similar patterns of export to the more productive regions.

Continued changes in seasonal sea ice dynamics, including earlier retreat, are likely to have profound influences on both the timing and magnitude of phytoplankton production on the shelf (Grebmeier, 2012). The duration of seasonal sea ice cover on the Chukchi shelf has been decreasing in recent years and annual primary production has been increasing (Arrigo and van Dijken, 2011). Over two years of sampling at roughly the same time of year in this region, the variability in the fraction of C_{org} exported was most strongly controlled by the variability in the amount of POC in the water column, with less depth-integrated POC, and thus greater export fractions, in 2011 than in 2010. In particular, at stations where phytoplankton were blooming or had recently bloomed, export fractions were significantly lower in 2010 than in 2011, suggesting more rapid pelagic-benthic coupling in 2011. On the one hand, seasonally ice-free waters on the Chukchi Sea shelf have been associated with greater particulate organic matter flux relative to ice-covered waters (Lalande et al., 2007a). On the other hand, if sea ice retreats early enough, at a time of year when waters are colder, grazing rates may be very low and export (of ungrazed phytoplankton biomass) may increase (Grebmeier, 2012). More work, including modeling efforts, and more years of data are needed to assess the long-term effects of changing sea ice retreat timing on the export of C from Chukchi Sea shelf waters.

Our results also demonstrate strong spatial and inter-annual variability in C export. Thus, while across the shelf $>50\%$ C_{org} export is common, eventually reaching values as high as 70% of DIC drawdown at the end of the phytoplankton growing season, there may be regions with much lower or much higher rates and these regions may change from year to year, perhaps depending on production, grazing rates, and sea ice dynamics and water temperature. While our results are at the high end of previous estimates of C_{org} export on the shelf, they are consistent with our understanding of the strong pelagic-benthic coupling of this system, and using a mass-balance approach, they take regenerated production from the water column (but perhaps not from the benthos) into account. Better estimation of pre-bloom winter water DIC concentration variability across the shelf will help constrain future estimates of export production, and will also shed light on the ultimate fate of the C_{org} after it has been exported to the benthos.

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