Freshening of the western Arctic negates anthropogenic carbon uptake potential

Ryan J. Woosley,1* Frank J. Millero2
1Center for Global Change Science, Massachusetts Institute of Technology, Cambridge, Massachusetts
2Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida

Abstract

As human activities increase the atmospheric concentration of carbon dioxide (CO2), the oceans are known to absorb a significant portion. The Arctic Ocean has long been considered to have enormous potential to sequester anthropogenic CO2, and mitigate emissions. The frigid waters make CO2 more soluble, and as sea ice melts, greater surface area is exposed to absorb CO2. However, sparse data have made quantifying the amount of anthropogenic CO2 in the Arctic difficult, stimulating much debate over the basin’s contribution to CO2 sequestration from the atmosphere. Using three separate cruises in 1994, 2005, and 2015 in the Canada and Makarov basins, we analyze the decadal variability in anthropogenic CO2 uptake in the central western Arctic. Here we show, from direct carbon system measurements spanning two decades, that despite increased atmospheric CO2, total dissolved inorganic carbon has actually decreased, with minimal anthropogenic CO2 uptake. The reduction in dissolved CO2 results from a dilution of total alkalinity by increased freshwater supply, particularly river water. Changes in the freshwater budget of the western Arctic override its uptake potential, resulting in a weak sink, or possibly source of CO2.

The Arctic Ocean is experiencing large-scale changes in temperature, freshwater budgets, and carbon cycling, all of which impact the local and global climate. Despite this importance, there is a severe lack of data for the interior Canada and Makarov basins of the western Arctic Ocean. The data that do exist are concentrated in the summer and over the continental shelf (Key et al. 2015; Olsen et al. 2016). Such sparsity has led to large uncertainties in the Arctic carbon cycle (Schuster et al. 2013) and debates over the importance of the Arctic as a sink for anthropogenic CO2 now and into the future (Bates and Mathis 2009; Cai et al. 2010; Parmentier et al. 2013). The Arctic has been widely considered a reservoir to naturally sequester anthropogenic CO2, limited mainly by its perpetual sea-ice cover. The cold temperatures promote solubility and intense summertime biological production draws down the partial pressure of CO2 (pCO2) in the seawater, steepening the gradient between the ocean and atmosphere and stimulating a significant flux into the water (Omar et al. 2007). Potential future increases in Arctic sequestration might result from more surface area exposed to the atmosphere as sea ice melts, and possible increases in biological production in these ice free waters (Anderson and Kaltin 2001; Schuster et al. 2013). Others have postulated that the highly stratified waters will create a barrier to storage in deeper waters, thus limiting the CO2 the Arctic will take up (Cai et al. 2010). Regardless, a seemingly overlooked component critical to assessing Arctic CO2 uptake is the freshening of the Arctic due to increased inputs from both sea-ice melt and river runoff. Seawater is able to hold a significant amount of CO2 due to its high total alkalinity (TA) that buffers the water from changes in pH. Arctic freshwater in the form of river runoff or sea-ice melt has little to no TA (~ 1000 and < 300 μmol kg−1, respectively) and therefore can hold much less CO2. Freshening of the Arctic will reduce this buffering capacity and inhibit the uptake potential of the Arctic. The few who have considered the impact of increased river runoff predict it would increase the ability of the Arctic to take up anthropogenic CO2 (e.g., Bates et al. 2006; Steinacher et al. 2009). Such a view posits that rivers are a source of alkalinity to the ocean, but ignores the impacts of dilution. Because the Arctic is experiencing changes on multiple fronts, all of which can impact the Arctic’s ability to take up and store CO2, the net impact has remained uncertain.

To investigate long-term decadal scale changes in the Arctic Ocean carbon system, direct measurements were conducted in...

*Correspondence: rwoosley@mit.edu

Additional Supporting Information may be found in the online version of this article.

Author Contribution Statement: F.M. directed and designed the research. R.W. lead and helped carry out the analysis on board the 2015 cruise. R.W. performed all quality control and analysis of the data. Both R.W. and F.M. contributed to the writing and editing of the manuscript.
the summer of 2015. The cruise track was designed to be a repeat of two previous cruises, one completed in 2005 and the other in 1994. By repeating occupations across decades (Fig. 1), direct comparisons of the changes are possible. The three cruises were compared using an ensemble extended multilinear regression (ensemble eMLR) technique and theoretical calculations to determine the change in anthropogenic CO2 between occupations as well as other variability in the Arctic Ocean inorganic carbon system.

Methods

Measurements of the carbon system and other physical chemical parameters were made on board the U.S.C.G.C. Healy in the summer of 2015 (expocode 33HQ20150809, also referred to as ARC01 or GN01). Details about the cruise and methods used for the various measurements, including conductivity, temperature, depth (CTD), salinity, nutrients and oxygen, can be found at http://www.geotraces.org/images/stories/geotraces/Cruises/GN01/HLY1502_GN01.pdf. Detailed methods for the carbon system measurements are given later and in a technical report (Millero et al. 2016).

TA was measured with a custom-designed closed cell automated HCl titration system (Millero et al. 1993b). Samples were thermostated to 25 ± 0.1°C using a water bath (ThermoFisher, Model Haak A10). The accuracy and precision of the measurements were approximately 2 μmol kg⁻¹ of seawater, as determined by certified reference material (CRM) and duplicate measurements. Further details on the methods and quality control can be found in the technical report (Millero et al. 2016).

The pH was measured using a spectrophotometric method (Clayton and Byrne 1993; Lee et al. 1996) with purified meta-cresol purple indicator (Liu et al. 2011) provided by Dr. Robert H. Byrne (University of South Florida) and calibrated with 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS) buffers (Ramette et al. 1977; Millero et al. 1993a). Samples were collected in gas tight 50 mL boro-silicate syringes and thermostated to 25 ± 0.1°C using a water bath (NesLab, model RTE-10). An adjustment was applied for the indicator perturbation (Clayton and Byrne 1993). The accuracy was determined to be ±0.005 based on measurements of TRIS buffer.

Fig. 1 Cruise tracks for each of the three cruises, (a) 2015, (b) 2005, and (c) 1994. The color represents the total alkalinity in the surface (<20 m) at each station. There is a decrease of 100–150 μmol kg⁻¹ between the 2015 cruise and the older cruises. The westward variation in the northernmost track from 2005 was a result of unanticipated heavy sea ice. Figures were created using ocean data view (Schlitzer 2016).
The precision was determined to be ±0.0023 based on duplicate measurements and CRMs. Further details of the methods and quality control can be found in the technical report (Millero et al. 2016).

Dissolved inorganic carbon (DIC) was measured using the DIC analytical equipment (DICE), which is based on the single-Operator Multiparameter Metabolic Analyzer (SOMMA) system (Johnson 1992). This is a coulometric method where all DIC species are converted to CO$_2$ gas using 8.5% H$_3$PO$_4$. The evolved CO$_2$ is then carried to a titration cell with N$_2$ gas where it reacts quantitatively with a proprietary reagent to generate hydrogen ions. The H$^+$ are subsequently titrated with coulometrically generated OH$^-$. CO$_2$ is thus measured by integrating the total charge required to achieve this titration (Dickson et al. 2007). The system is calibrated with pure CO$_2$ (99.995%) at the beginning of each titration cell preparation. CRMs were also measured to evaluate accuracy and precision. The accuracy and precision were determined to be ~2.5 μmol kg$^{-1}$ based on CRM and duplicate measurements. This is slightly larger than typical for this system (<2 μmol kg$^{-1}$) and is thought to be the result of the inability to fully control the temperature and humidity of the laboratory space. Further details of the methods and quality control can be found in the technical report (Millero et al. 2016).

**Consistency with older data sets**

Data from two older cruise seasons were used in order to determine decadal trends. In the Canada Basin, the Arctic Ocean Section 2005 (expocode 77DN20050819), and in the Makarov Basin the Arctic Ocean Section 1994 (expocode 18SN19940724) were used. The cruises will be abbreviated AOS94 and AOS05. Both data sets are publicly available on the Ocean Carbon Data System (OCADS) (https://www.nodc.noaa.gov/ocads/) and Carbon Hydrographic Data Office (CCHDO) (https://cchdo.ucsd.edu) websites. Only stations where the cruise tracks overlapped are considered. The stations included in the analysis of each cruise are 6-35 for AOS94 and 5-43 for AOS05. ARCO1 is divided into two sections covering the two previous cruises. Stations 7-36 are used for comparison with AOS94, and stations 29-36 and 41-62 for comparison with AOS05. Stations 37-41 are not included due to deviations in the cruise track between occupations. In 2005 the ice over the Alpha ridge was too thick and the track had to be diverted around the ridge, while in 2015 the ice was thin enough to cross the ridge. This region of the section therefore has a slightly higher uncertainty than the rest of the sections.

In order to determine consistency between all data sets and to ensure trends are real and not artifacts, crossover analysis similar to the methods applied by GLODAPv2 (Key et al. 2015; Lauvset and Tanhua 2015; Olsen et al. 2016) were used. The unique characteristics and limited data in the Arctic required some modifications to be made to the crossover analysis methods. Due to the extremely small density gradient of deep waters, analysis was done vs. depth rather than density. The Arctic is a small ocean divided into several smaller basins through a system of ridges. The bathymetry of the Arctic plays the main role in determining the deep ocean circulation, and each basin therefore has its own geochemical signatures. As a result, stations very close together may come from different basins and therefore are not reliable crossover stations. Each crossover was examined manually to ensure the stations came from the same basin. Such considerations severely limited the number of crossovers available for each cruise as many of the possible crossovers occur near the North Pole where multiple basins are in close proximity. To help combat these limitations basin wide averages of deep waters (> 2000 m) were also considered. A concurrent cruise on the opposite side of the Arctic in 2015 was also included in the crossover analysis (expocode 06AQ20150817). Crossover between the two 2015 cruises show them to be consistent within the GLODAP recommendations (Ulfisbo et al. 2018). Given the improvements in methods over the last two decades and consistency between the 2015 cruises, these two cruises were considered the most accurate and no corrections were made to the 2015 cruise. For the older cruises, GLODAPv2 recommended corrections for all parameters except the carbon system were applied. Our own corrections were determined for TA and DIC. Due to the multitude of issues involved in comparing pH between cruises (Woosley et al. 2017) and because it was not directly measured on the 1994 cruise, pH was calculated from TA and DIC for AOS94 and AOS05. Measured pH values for the ARCO1 cruise were converted to in situ temperature using TA and measured pH. All calculations were done using the Matlab version 1.1 of CO2sys (Van Heuven et al. 2011). The carbon system corrections are additive and the nutrient and Chloroflorocarbon (CFCs) corrections are multiplicative. For AOS94 the following corrections were applied: DIC $-7$ μmol kg$^{-1}$, TA $-26$ μmol kg$^{-1}$, Si 0.9 CFC-11 1.05. For AOS05 the corrections were: DIC $-9$ μmol kg$^{-1}$ and TA +4 μmol kg$^{-1}$.

**Ensemble extended multilinear regression**

The extended multilinear regression (eMLR) approach (Friis et al. 2005) for determining anthropogenic CO$_2$, which was modified from the MLR method (Wallace 1995) has become a common technique for determining decadal changes in anthropogenic CO$_2$ ($\Delta$C$_{anth}$). We apply further modifications and use the ensemble eMLR (Carter et al. 2017). The approach assumes that natural processes (internal variability) affecting DIC also change other chemical/physical parameters, but those parameters are not affected by C$_{anth}$ uptake from the atmosphere (i.e., gas exchange). Therefore, multilinear functions (f) of various measured (e.g., salinity, nutrients) and derived (e.g., conservative temperature, apparent oxygen utilization) properties (P) are fit to determine the internal variability of DIC according to:

$$\text{DIC} = f(P)$$

MLRs are determined for each occupation of a section. The different fits are denoted by subscripts 1 for the older occupation, and 2 for the more recent occupation. The difference
between the two regressions from the properties at time 2, or residual DIC, is assumed to be the change in Cant (ΔCant) between the two occupations expressed as:

\[
\Delta C_{\text{ant}} = (f_2 - f_1) P_2
\]  

(2)

The assumptions and limitations of this method have been discussed in detail (Goodkin et al. 2011; Plancherel et al. 2013). One limitation is the determination of the best parameters to fit in order to produce the lowest possible error while not overfitting the data. The ensemble eMLR was introduced (Carter et al. 2017) to handle this issue. Rather than a semi-arbitrary decision on which parameters are best, a suite of possible parameters and combinations are regressed and then averaged to give the final result. The averaging acts to remove bias that any individual choice of P might have, lowering the overall uncertainty in the results. Also, rather than fitting the entire section using one regression or dividing the water column into arbitrary density bins, a moving window was used to select the measurements used at each regression point. For each sample location all points with a potential density ± 0.15 kg m\(^{-3}\) and within 200 m depth of the sample point were fit. All sample locations <25 m depth (the deepest mix layer depth of the sections) were excluded from the ensemble eMLR. A tighter density restriction of 0.1 kg m\(^{-3}\) was initially applied but many of the regressions had too few points to produce reliable results. No latitude window was placed on the sections because they only covered ~17° of latitude.

Six different parameters were chosen as independent variables for the regressions, apparent oxygen utilization (AOU), absolute salinity (Sa), Conservative Temperature (CT), nitrate (NO\(_3\)\(^-\)), silicate (Si), and TA* (TA* = TA + 1.26 * [NO\(_3\)\(^-\)] – 66.4 * Sa; Carter et al. 2014). TA* is a combination of potential alkalinity and normalized alkalinity that attempts to account for the influences of both organic matter and precipitation/evaporation cycling on total alkalinity. TA was originally used but found to produce extremely large positive and negative ΔCant in areas of large density gradients. TA* was found to handle these large gradients better. The other parameters were chosen based on their availability, known influence on carbon cycling, and reliability as determined by their use in other studies (Waters et al. 2011; Woosley et al. 2016; Carter et al. 2017; Ulfsbo et al. 2018). A minimum of three parameters were used in each regression, giving a total of 42 possible combinations of regression parameters. The mean of all regressions is used to produce the final ΔCant estimates. Regressions were carried out in Matlab using the “robustfit” regression routine with a bisquare outlier test and default tuning constant (4.685). Before being regressed, all parameters were normalized by the mean of the measured values from all cruises. An average of 280 measurements per regression was used, with a minimum of nine. The ARC01 cruise tended to have fewer measurements per regression due to the compressed density structure of the upper waters. For the Canada Basin, one regression was more than two standard deviations from the mean, indicating overfitting of the data, and was excluded from further analysis.

One notable difference between our methods and Carter et al. (2017) is that for regressions without AOU they made an additional correction by doing a separate regression for AOU in order to correct for biological processes not accounted for in those regressions. We found this to be unnecessary for several reasons. First, doing multiple regressions on the same data complicates analysis and could potentially add additional sources of error. Second, the AOU regressions use some of the same parameters as the DIC regressions, by fitting the data twice there is a significant risk of over fitting the data or double counting biological processes. Third, comparisons of our regressions with and without AOU did not show significant differences in the estimated column inventory means of anthropogenic CO\(_2\) (0.10 ± 0.27 and 0.20 ± 0.23 mol CO\(_2\) m\(^{-2}\) yr\(^{-1}\) with AOU and without AOU, respectively, for the Canada Basin and 0.21 ± 0.15 and 0.24 ± 0.13 mol CO\(_2\) m\(^{-2}\) yr\(^{-1}\) with and without AOU, respectively, for the Makarov Basin, Table 1).

In order to align the coefficients and physical/chemical properties (AOU, nutrients, etc.) between occupations and calculate ΔCant using Eq. 2 the regression coefficients and measured/derived properties were gridded onto a regular 2-D depth-latitude grid. First, properties were gridded vertically from 0 to 500 m every 5 m and every 50 m from 500 m to the bottom. Coefficients were gridded vertically between 25 and 500 m every 5 m and every 50 m from 500 m to the bottom depth. Both properties and coefficients were gridded at each station using the cubic Hermite piecewise polynomial linear interpolation (Carter et al. 2014). Data from the mixed layer are excluded from the coefficient interpolation as gas exchange with the atmosphere can influence the coefficients in nonlinear ways. Instead, the value at the base of the mixed layer (25 m) was assumed to be the same as the mixed layer and extended to the surface. The coefficients and properties were then linearly interpolated every 0.25° latitude along the sections using a Delaunay Triangulation. No extrapolations were made. The gridded results were then used for all further calculations. All section plots created from the gridded results use the cmocean colormaps for colorbars (Thyng et al. 2016).

Using the gridded coefficients and properties, the ΔCant at each point was calculated following Eq. 2. For waters from the upper halocline (σ_0 = 24.8 [Rudels 2012]) and deeper, density was used to align the regressions from the two cruises. For a given point from ARC01, all points at the given latitude in the older section with a σ_0 ± 0.1 kg m\(^{-3}\) of the 2015 point were averaged and used in Eq. 2. For waters less dense than the upper halocline there was no corresponding density in the older cruise, therefore depth had to be used to align the points from the two cruises. After ΔCant was calculated for each individual regression on the two sections the results of all 42 regressions were averaged to produce the mean ΔCant for
Table 1. Mean and standard deviation of the column inventories for regressions with and without a given parameter along with the $p$ value showing that none of the means are statistically different except for CT. Although CT is statistically different there is not enough information to subjectively weight or remove any regressions. Removing the regressions without CT would change the overall mean, but would not impact the results or conclusions.

| Parameter | With parameter | Without parameter | $p$ |
|-----------|----------------|-------------------|-----|
|          | Mean | Std | Mean | Std |      |
| S$_a$    | 0.14 | 0.24 | 0.12 | 0.29 | 0.78 |
| CT       | 0.28 | 0.20 | -0.09 | 0.17 | <0.01 |
| AOU      | 0.10 | 0.27 | 0.20 | 0.23 | 0.18 |
| NO$_3$   | 0.14 | 0.26 | 0.13 | 0.26 | 0.92 |
| Si       | 0.15 | 0.26 | 0.11 | 0.25 | 0.70 |
| TA$^*$   | 0.19 | 0.26 | 0.05 | 0.24 | 0.08 |
| All regressions | 0.13 | 0.25 | -    | -    | -    |

For the theoretical calculations of changes in DIC, the Matlab version 1.1 of CO2sys (Van Heuven et al. 2011) was used. The input variables were TA and pCO$_2$. The change in atmospheric pCO$_2$ was determined from the Mauna Loa pCO$_2$ record (Keeling et al. 2005; http://scrippscpco2.ucsd.edu/data/atmospheric_co2/primary_mlo_co2_record) using the monthly average during each cruise.

Water mass fractions

The water mass fractions were determined using water mass decomposition methods (Jones et al. 2008; Newton et al. 2013). The water masses were divided into four fractions, Atlantic (Atl), Pacific (Pac), river (Riv), and sea-ice melt (SIM) using salinity, TA, and the Arctic Nitrate Phosphate tracer (ANP; Newton et al. 2013). Knowing the end members for each fraction, the fractions for a given point can be determined by solving the following system of equations:

$$TA_{Atl}f_{Atl} + TA_{Pac}f_{Pac} + TA_{Riv}f_{Riv} + TA_{SIM}f_{SIM} = TA_m$$

$$S_{Atl}f_{Atl} + S_{Pac}f_{Pac} + S_{Riv}f_{Riv} + S_{SIM}f_{SIM} = S_m$$

$$ANP_{Atl}f_{Atl} + ANP_{Pac}f_{Pac} + ANP_{Riv}f_{Riv} + ANP_{SIM}f_{SIM} = ANP_m$$

$$f_{Atl} + f_{Pac} + f_{Riv} + f_{SIM} = 1$$

where m is the measured value and Eq. (6) is the mass balance. TA was used instead of $\delta^{18}$O because the data for the older cruises are not publicly available, and the data for the 2015 cruise have not yet been released. The base MATLAB code for water mass decomposition was provided by Andrew Babbin (Massachusetts Institute of Technology). Comparisons of fractions determined from TA and $\delta^{18}$O have been shown to have good agreement (Newton et al. 2013) with differences arising...
from the choice in endmembers, and slight differences in the definitions of the freshwater fractions. When TA is used, the $f_{\text{Riv}}$ includes only river water inputs, while $\delta^{18}O$ determines the meteoric fraction ($f_{\text{Met}}$) that includes river inputs as well as precipitation. When TA is used, precipitation becomes part of the SIM fraction. The values used for the endmembers are given in Table 2. For the 2005 cruise previous studies have already determined the fractions (Jones et al. 2008; Newton et al. 2013). Our results show near quantitative agreement for the upper 250 m with Jones et al. (2008), which used TA, and good agreement for the upper 500 m with Newton et al. (2013), which used $\delta^{18}O$.

### Changing CO$_2$

Rather than an increase in DIC as would be predicted due to atmospheric CO$_2$ uptake, measurements unexpectedly show large decreases of 50 to $>100 \, \mu$mol kg$^{-1}$ in the upper 100 m (Fig. 2a,c). The uptake of CO$_2$ from the atmosphere does not change TA (Millero 2007), yet there are also significant changes in TA (Fig. 2b,d) of similar magnitude. Changes are not limited to the carbon system. Physical parameters also show large changes (e.g., increased temperature and decreased salinity) exemplifying the complex dynamics of the Arctic Ocean. Such alteration has not yet been seen in other ocean basins and make analyzing the Arctic data uniquely complex. Similar work in the Atlantic (Woosley et al. 2016) and Pacific (Waters et al. 2011; Carter et al. 2017) found changes in temperature (T), salinity (S), and TA to be too small (to date) to have significant impacts on the carbon system. Yet, the Arctic is a small confined basin (~3% of the global ocean surface area) subject to large freshwater inputs from Canadian and

### Table 2.

Endmember values used to determine the water mass fractions. The Pacific TA endmember was determined from measured values in the Bering Strait in 1994 and 2015, and the Atlantic ANP endmember was the average value of deep water (>2000 m).

|               | Salinity | TA (μmol kg$^{-1}$) | ANP (fraction) |
|---------------|----------|---------------------|----------------|
| Atlantic      | 34.92    | 2292$^*$            | 0.13           |
| Pacific       | 32.5     | 2200                | 1              |
| River         | 0        | 1048$^†$            | 0              |
| Sea-ice melt  | 4        | 263$^‡$             | Surface        |

$^*$Newton et al. (2013).
$^†$Cooper et al. (2008).
$^‡$Anderson (2004).

*Fig. 2* Measured changes in DIC (a and c) and TA (b and d) for the Canada Basin (top) and Makarov Basin (bottom). The upper ~100 db show significant decreases in both parameters, indicating large scale changes in the carbon system aside from uptake of anthropogenic CO$_2$ from the atmosphere.
Russian rivers (~10% of global river input; Aagaard and Carmack (1989), with substantial amounts of sea ice. Such conditions prime the Arctic to respond rapidly to climate forcing by CO2.

The ensemble eMLR used to estimate $\Delta C_{\text{ant}}$ is only able to detect the direct uptake of anthropogenic CO2 resulting from the burning of fossil fuels, cement production, and land use change; it is unable to detect anthropogenic CO2 caused by secondary effects because such effects are attributed to internal variability. Therefore, any changes in other parameters, such as changes in biological productivity or freshwater inputs, resulting from climate change or ocean acidification are not encompassed in $\Delta C_{\text{ant}}$. Such secondary effects can act to either increase or decrease the sequestration power of the oceans. Based on the increase in atmospheric CO2, increases in surface seawaters of ~10–20 and 20–40 $\mu$mol kg$^{-1}$ would have been expected for 10 and 20 years, respectively. In the Canada Basin (Fig. 3a), the vast majority of the surface shows less than expected or slightly negative $\Delta C_{\text{ant}}$. In the Makarov Basin (Fig. 3c), the upper ~100 m also has very low to negative $\Delta C_{\text{ant}}$, with intermediate waters (100–300 m) closer to expected values. Ice cover blocking gas-exchange might explain low values; however, intermediate waters (50–150 m) are rapidly ventilated (~4–7 years [Ekwurzel et al. 2001]), and ice-free waters are only slightly higher than ice covered waters. Gas exchange and large-scale circulation alone cannot explain the low and even negative values. The inorganic carbon system has four degrees of freedom, two within the carbon concentrations themselves, and two more from temperature and salinity as state variables. This means there are four possible ways in which to perturb the carbon equilibria. For most of the world’s oceans, only one factor has changed sufficiently to influence the carbon system. In essence, only pCO2 is being forced, while temperature, salinity, and TA remain nearly constant. Conversely, in the Arctic, temperature and pCO2 are increasing, and salinity and TA are decreasing rapidly enough to impact the carbon system.

The seemingly counter-intuitive results, whereby the Arctic displays near zero to negative anthropogenic uptake despite an anthropogenic increase of CO2 in the atmosphere; therefore, low Arctic uptake must be attributed to other anthropogenic or natural variations in the system. Such variations can be investigated by isolating changes in temperature, salinity, TA, and pCO2. We tested how changes in temperature,

![Gas Exchange Only](image1)

![Gas Exchange Plus TA, T, S](image2)

![Canada Basin](image3)

![Makarov Basin](image4)

**Fig. 3** Change in DIC resulting only from direct uptake of anthropogenic CO2. (a) 2005–2015 and (c) 1994–2015 determined from the ensemble eMLR method (mean $\Delta C_{\text{ant}}$). Predicted change in DIC resulting from measured changes in TA, temperature (T), salinity (S), and gas exchange. (b) 2005–2015 and (d) 1994–2015. See decadal CO2 changes section for details of the calculations. Note the different scales between the left and right hand panels. The Canada Basin displays 10 years of changes while the Makarov Basin comprises 21 years. See supplemental material for predicted changes only as a result of TA.
salinity, and TA impact DIC through a series of theoretical calculations. First, we calculated DIC by holding temperature, salinity, and TA constant at the 2005 or 1994 levels. The pCO2 was increased by the same amount as the atmospheric concentration between occupations (21 and 42 μatm for 2005 and 1994, respectively). This serves as the base case where the carbon system is only forced by anthropogenic CO2. Next, we calculated DIC using the temperature, salinity, and TA measured in 2015 along with the theoretically increased pCO2. This case represents the possible DIC fluctuations resulting from all four variables changing simultaneously. The difference between these two cases comprises the net impact of temperature, salinity, and TA on the carbon system (Fig. 3b,d). If gas exchange dominated in the Arctic, as in the Pacific and Atlantic, then Fig. 3b,d would look very similar to Fig. 3a,c. Instead the differences, especially in the surface, indicate gas exchange is relatively minor and changes in TA, temperature, and salinity effects dominate. Similar calculations that individually separate TA, temperature, and salinity (Supporting Information Fig. S1) determine that TA is the dominant factor while temperature and salinity changes are comparatively minor. Although unlikely that there would be a uniform increase in pCO2 across the sections, the theoretical calculations match quite well with the measured changes (Fig. 2), with the theoretical changes generally being larger than the measured change. The results also indicate that decreases in TA can in fact result in negative ΔC_{amt} or release of anthropogenic CO2 to the atmosphere. The reason the Arctic can be a surprising source of CO2 results from the loss of buffering capacity when TA is lowered, shifting the carbonate equilibria (Millero 2007) toward aqueous CO2. This means that increases in pCO2 come from carbonate and bicarbonate already in the seawater, rather than the uptake of new CO2 from the atmosphere. The overall result is a net loss of CO2 dissolved in seawater. Such a change would not be detectable by traditional CO2 flux studies (Olsen et al. 2003; Bates et al. 2006; Yasunaka et al. 2016) where TA is rarely measured and implicitly assumed to be constant.

Despite the magnitude of the changes in TA and DIC described here, such variation is not well documented. This is likely due to a lack of data, and little effort to monitor for TA changes. One study does note a decrease in TA in the mid-2000s (Miller et al. 2014), but largely overlooks the potential impact on anthropogenic CO2. Modeling studies have predicted TA will decrease in the future (Steinacher et al. 2009; Carter et al. 2016). Carter et al. (2016) predicted TA changes of a much smaller magnitude and not until after 2050. Steinacher et al. (2009) modeled changes beginning in the year 2000, but of much smaller magnitude than we measured. The surface TA values in 2015 were not predicted to occur until 2050–2070, and the surface DIC values in 2015 were lower than they predicted for 2100 (Steinacher et al. 2009). This is despite assuming river TA and DIC to be zero, which would bias their modeled changes high. Notably, Steinacher et al. (2009) predicted that such changes in TA and DIC would lower the pCO2, resulting (along with other climate change factors) in a 40% increase in anthropogenic CO2 uptake, the opposite of what we found. Other works (e.g., Bates et al. 2006; Bates and Mathis 2009) generally do not consider changing TA, but when they do note it, they predict it will increase the Arctic uptake potential. The Arctic basin has been biased from high-quality carbon measurements, particularly TA, being extremely limited and mostly focused over the shelf (Bates 2006; Bates and Mathis 2009; Key et al. 2015; Olsen et al. 2016). The majority of the data that do exist are limited to surface underway pCO2 (Olsen et al. 2003; Yasunaka et al. 2016). Here instead, the cruises in the Canada and Makarov basins have produced the only data currently available that completely transect the two basins, measured the full water column, and have the high quality, high density carbon measurements required to observe the full system.

**Arctic freshening**

Globally, TA is thought to be generally constant over decadal timescales (Carter et al. 2014, 2016); however, there are several ways in which TA can change. Changes in production or dissolution of calcium carbonate minerals are slow and would likely take decades to detect (Carter et al. 2016). Changes in net precipitation/evaporation affect TA through dilution/concentration, but such changes tend to be very localized, and can easily be accounted for by normalizing TA to salinity (Woosley et al. 2016). Increases in other freshwater inputs such as river runoff and sea-ice melt would dilute TA, and both are known to be increasing in the western Arctic (Jones et al. 2008; Yamamoto-Kawai et al. 2009; Newton et al. 2013; Carmack et al. 2016; Proshutinsky et al. 2019; Zhong et al. 2019). Surface ocean waters entering the Arctic from the Pacific have a TA around 2200 μmol kg\(^{-1}\), and deeper Atlantic derived waters are ~2300 μmol kg\(^{-1}\). Rivers have variable TA, but in the western Arctic, the flow weighted average is ~1050 μmol kg\(^{-1}\) (Cooper et al. 2008), and sea-ice melt is much lower, ~200 μmol kg\(^{-1}\) (Anderson 2004). The integrated inventories of river run off, sea-ice melt/formation, and Atlantic and Pacific water for each cruise were determined for the upper 500 m (Fig. 4) using water mass fraction decomposition. There were clear increases in river runoff for both sections, in line with previous studies (Jones et al. 1998, 2008; Yamamoto-Kawai et al. 2009; Newton et al. 2013; Carmack et al. 2016). The upper 100 m saw general increases in river run off of ~3–10% (Supporting Information Fig. S2). Sea-ice melt inventories changed much less, generally within the uncertainty. The upper 25–50 m do show, however, increases of ~5% in many parts of the Canada Basin, and ~10% in the Makarov Basin (Supporting Information Fig. S3). Sea ice is formed and mostly melted with the Arctic Ocean so it is not a direct freshwater input, and acts mainly to redistribute freshwater within the Arctic, with a limited amount of export to other oceans. Sea-ice melt also makes up a smaller fraction of the freshwater
balance, meaning it has less potential to dilute TA and is a small factor on basin scales. River runoff appears to be the main contributor to the observed decadal decreases in TA and DIC, and the low amounts of ΔC_{antr} although changes in sea-ice melt can be locally significant. The methods used define ΔC_{antr} as only anthropogenic CO\(_2\) uptake from the atmosphere, attributing secondary effects such as increased freshwater resulting from melting glaciers (Gardner et al. 2013) to natural variability. The theoretical calculations in turn, do not attempt to untangle natural variability from anthropogenic changes in freshwater cycling. While there is ample evidence that climate change is impacting the input of freshwater to the Arctic (e.g., Gardner et al. 2013; Proshutinsky et al. 2019) our methods are unable to quantify how much of the river input is anthropogenic vs. natural variability. If all of the changes were assumed to be anthropogenic, the western Arctic is actually a source of anthropogenic CO\(_2\) to the atmosphere.

Comparison to other basins

The column inventory is a convenient way to compare results from different transects and ocean basins as it integrates the full water column and normalizes the inventory on a per annum basis. The results of the Canada and Makarov basins are now directly comparable (Fig. 5). The basin-wide mean and standard deviations are 0.13 ± 0.26 and 0.22 ± 0.14 mol CO\(_2\) m\(^{-2}\) yr\(^{-1}\) in the Canada and Makarov basin, respectively. By contrast, the global average inventory is about 0.5 mol CO\(_2\) m\(^{-2}\) yr\(^{-1}\) and values in the North Atlantic can be as high as 2 mol CO\(_2\) m\(^{-2}\) yr\(^{-1}\) where deep water formation occurs (Woosley et al. 2016). For the entire Canada Basin, the uncertainty spans negative inventories, meaning even the sign of the signal is uncertain. Multiplying the column inventories by the area of basins (334, 224 km\(^2\) and 1,524,664 km\(^2\) for the Makarov and Canada Basin, respectively [Robbins et al. 2013]) and converting from moles to tera-grams, results in an uptake of 0.88 and 2.34 Tg C yr\(^{-1}\) for the Makarov and Canada Basin, respectively. This is significantly lower than the 6–19 Tg C yr\(^{-1}\) (Bates 2006; Bates and Mathis 2009) estimated for the entire central Arctic (which includes the Makarov, Canada, and Eurasian basins). Their results are largely based on scaling results from the Chukchi Sea to the entire Arctic. In light of our results, theirs is likely a significant overestimate for the central Arctic, and predictions of a 20% annual increase between 2002 and 2012 are unlikely to have come to fruition (Bates et al. 2006).

Recent work in the eastern Arctic covering a similar time period (1996–2015) did not find such low ΔC_{antr} (Ulfsbo et al. 2018). Their results (0.5–0.69 mol CO\(_2\) m\(^{-2}\) yr\(^{-1}\)) align more closely with the global average. The differences between the basins is not surprising. The majority of Arctic river runoff enters from Russian and North American rivers into the Leptev, East Siberian, and Beaufort Seas (Carmack et al. 2016) and most of the sea ice loss occurs over the Canada and Makarov basins (Frey et al. 2015). Importantly, the eastern Arctic study explicitly assumes constant TA (Ulfsbo et al. 2018). The general circulation in the Arctic (namely the Beaufort Gyre) may have confined much of the increased river runoff to the western Arctic, not yet propagating into the eastern Arctic. If this is true, the impacts of lowered TA may eventually spread into the other Arctic basins and into the north Atlantic.

The implications of our results are broad. First, studies using only surface pCO\(_2\) (Mckinley et al. 2016) and wind speeds (Bates 2006; Schuster et al. 2013; Yasunaka et al. 2016) to estimate fluxes of CO\(_2\) likely overestimate the uptake of CO\(_2\) for large portions of the Arctic. Changes in pCO\(_2\) that are
attributed to gas exchange are likely the result of shifting equilibria due to decreases in TA rather than uptake of anthropogenic carbon from the atmosphere. Second, attributing causes to changes in the Arctic becomes much more difficult. Only a small fraction of the measured change was attributed to atmospheric uptake by conventional methods. Changes in freshwater and biological productivity attributed to internal variability by the ensemble eMLR method are likely to be at least partially attributable to secondary anthropogenic changes in the carbon system. The Arctic is changing so rapidly that secondary effects from freshening, thought to not be detectable for several more decades, are already dominating over the primary effects. Assumptions used in previous studies for analyzing carbon data in the Arctic are no longer valid. Models of future Arctic carbon cycling and climate change will need to be reevaluated.

Ocean acidification

An additional impact of the shifting carbon system is a decrease in pH, termed ocean acidification. Both the Canada and Makarov basins show decreases of greater than \(-0.05\) for most of the upper 500 m (not shown). The expected rate of acidification from gas exchange is \(-0.018\) per decade (Waters et al. 2011). The western Arctic appears to be decreasing by more than double the expected rate (Qi et al. 2017). The decreased pH results not from uptake of CO\(_2\) from the atmosphere, but as a result of increased freshwater lowering TA and shifting the carbon system equilibria (Semiletov et al. 2016). Determining the exact rate of acidification in the Arctic is particularly challenging due to limitations of the data (Woosley et al. 2017) and because these methods too require an assumption of constant TA (Woosley et al. 2016; Ulfso et al. 2018). Therefore, exact determination of ocean acidification rates is beyond the scope of this work. However, it is clear that despite the low amounts of \(\Delta C_{\text{ant}}\), the western Arctic is still experiencing some of the highest rates of acidification with broad impacts for the organisms that live there. This is particularly true for calcium carbonate producing organisms, where the saturation state (an indication of the favorability for CaCO\(_3\) formation) for the upper 200 m straddles the equilibrium point between saturation and undersaturation—precipitation vs. dissolution (Luo et al. 2016).

Future of the Arctic

The results presented here bring the present and future potential CO\(_2\) uptake of the Arctic into question. The rates of change in all four carbon system parameters in the Arctic due to freshening by increased river inputs are substantial. If the freshwater inputs continue to increase, they will continue to override the potential for the cold productive waters to take up anthropogenic CO\(_2\) and the Arctic will remain a weak sink or even a source for CO\(_2\) into the future. Importantly, the disproportionate role that the Arctic has been predicted to have (Bates and Mathis 2009; Parmentier et al. 2013) in sequestering CO\(_2\) will not materialize. Although there are strong indications that river runoff is increasing due to human activities (Gardner et al. 2013), if the increased freshwater were a temporary event, recovery time will be substantial. The only way for the waters to regain their buffering capacity is for the freshwater to be flushed out of the Arctic and replaced by seawater, which requires a significant reduction of freshwater inputs and would take several decades. The rates of change in the Arctic carbon cycle are unprecedented, and the impact of freshening immense, even compared to other modern ocean basins. It is therefore of vital importance to monitor and study all of the relevant processes involved in control the carbon system of the Arctic.
**Data Availability**

All data used in this study are publicly available through the NOAA National Centers for Environmental Information, Ocean Carbon Data System (OCADS) at https://www.nodc.noaa.gov/ocads/ and the CLIVAR and Carbon Hydrographic Data Office at https://cchdo.ucsd.edu.

**References**

Aagaard, K., and E. C. Carmack. 1989. The role of sea ice and other fresh water in the Arctic circulation. J. Geophys. Res. 94: 14485. doi:10.1029/JC094iC10p14485

Anderson, L. G. 2004. Variability in river runoff distribution in the Eurasian Basin of the Arctic Ocean. J. Geophys. Res. 109: C01016. doi:10.1029/2003JC001773

Anderson, L. G., and S. Kaltin. 2001. Carbon fluxes in the Arctic Ocean- potential impact by climate change. Polar Res. 20: 225–232. doi:10.1111/j.1751-8369.2001.tb00060.x

Bates, N. R. 2006. Air-sea CO2 fluxes and the continental shelf pump of carbon in the Chukchi Sea adjacent to the Arctic Ocean. J. Geophys. Res. 111: C10013. doi:10.1029/2005JC003083

Bates, N. R., and J. T. Mathis. 2009. The Arctic Ocean marine carbon cycle: Evaluation of air-sea CO2 exchanges, ocean acidification impacts and potential feedbacks. Biogeoosciences 6: 2433–2459. doi:10.5194/bg-6-2433-2009

Bates, N. R., S. B. Moran, D. A. Hansell, and J. T. Mathis. 2006. An increasing CO2 sink in the Arctic Ocean due to sea-ice loss. Geophys. Res. Lett. 33: 1–7. doi:10.1029/2006GL027028

Cai, W.-J., and others. 2010. Decrease in the CO2 uptake capacity in an ice-free Arctic Ocean basin. Science 329: 556–559. doi:10.1126/science.1189338

Carmack, E. C., and others. 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. 121: 675–717. doi:10.1002/2015JC003140

Carter, B. R., J. R. Toggweiler, R. M. Key, and J. L. Sarmiento. 2014. Processes determining the marine alkalinity and calcium carbonate saturation state distributions. Biogeoosciences 11: 7349–7362. doi:10.5194/bg-11-7349-2014

Carter, B. R., T. L. Frölicher, J. P. Dunne, K. B. Rodgers, R. D. Slater, and J. L. Sarmiento. 2016. When can ocean acidification impacts be detected from decadal alkalinity measurements? Global Biogeochem. Cycles 30: 595–612. doi:10.1002/2015GB005308

Carter, B. R., and others. 2017. Two decades of Pacific anthropogenic carbon storage and ocean acidification along GO-SHIP sections P16 and P02. Global Biogeochem. Cycles 31: 1–22. doi:10.1002/2016GB005485

Clayton, T. D., and R. H. Byrne. 1993. Spectrophotometric seawater pH measurements: Total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Res. Part I Oceanogr. Res. Pap. 40: 2115–2129. doi:10.1016/0967-0637(93)90048-8

Cooper, L. W., J. W. McClelland, R. M. Holmes, P. A. Raymond, J. J. Gibson, C. K. Guay, and B. J. Peterson. 2008. Flow-weighted values of runoff tracers (δ18O, DOC, Ba, alkalinity) from the six largest Arctic rivers. Geophys. Res. Lett. 35: L18606. doi:10.1029/2008GL035007

Dickson, A. G., C. L. Sabine, and J. R. Christian. 2007. Guide to best practices for ocean CO2 measurements. PICES Special Publication.

Ekwurzel, B., P. Schlosser, R. A. Mortlock, R. G. Fairbanks, and J. H. Swift. 2001. River runoff, sea ice meltwater, and Pacific water distribution and mean residence times in the Arctic Ocean. J. Geophys. Res. Ocean. 106: 9075–9092. doi:10.1029/1999JC000024

Frey, K. E., G. W. K. Moore, L. W. Cooper, and J. M. Grebmeier. 2015. Divergent patterns of recent sea ice cover across the Bering, Chukchi, and Beaufort seas of the Pacific Arctic region. Prog. Oceanogr. 136: 32–49. doi:10.1016/J.POCLEAN.2015.05.009

Fiis, K., A. Körtzinger, J. Pätsch, and D. W. R. Wallace. 2005. On the temporal increase of anthropogenic CO2 in the subpolar North Atlantic. Deep Sea Res. Part I Oceanogr. Res. Pap. 52: 681–698. doi:10.1016/J.DSR.2004.11.017

Gardner, A. S., and others. 2013. A reconciled estimate of glacier contributions so sea level rise: 2003 to 2009. Science 340: 852–857. doi:10.1126/science.1234532

Goodkin, N. F., N. M. Levine, S. C. Doney, and R. Wanninkhof. 2011. Impacts of temporal CO2 and climate trends on the detection of ocean anthropogenic CO2 accumulation. Global Biogeochem. Cycles 25: GB3023. doi:10.1029/2010GB004009

Johnson, K. M. 1992. Single-operator multiparameter metabolic analyzer (SOMMA) for total carbon dioxide (CT) with coulometric detection. Operator’s manual, Brookhaven National Laboratory.

Jones, E. P., L. G. Anderson, and J. H. Swift. 1998. Distribution of Atlantic and Pacific waters in the upper Arctic Ocean: Implications for circulation. Geophys. Res. Lett. 25: 765–768. doi:10.1029/98GL004646

Jones, E. P., L. G. Anderson, S. Jutterström, L. Mintrop, and J. H. Swift. 2008. Pacific freshwater, river water and sea ice meltwater across Arctic Ocean basins: Results from the 2005 Beringia expedition. J. Geophys. Res. 113: C08012. doi:10.1029/2007JC004124

Keeling, C. D., S. C. Piper, R. B. Bacastow, M. Wahlen, T. P. Whorf, M. Heimann, and H. A. Meijer. 2005. Atmospheric CO2 and 13CO2 exchange with the terrestrial biosphere and oceans from 1978 to 2000: Observations and carbon cycle implications, p. 83–113. In A history of atmospheric CO2 and its effects on plants, animals, and ecosystems. Springer-Verlag.
Key, R. M., and others. 2015. Global Ocean data analysis project, version 2 (GLODAPv2), ORNL/CDIAC-162, NDP-P093, carbon dioxide information analysis Center, Oak Ridge National Laboratory, US Department of Energy.

Lauvset, S. K., and T. Tanhua. 2015. A toolbox for secondary quality control on ocean chemistry and hydrographic data. Limnol. Oceanogr. Methods 13: 601–608. doi:10.1002/lom3.10050

Lee, K., F. J. Millero, and D. M. Campbell. 1996. The reliability of the thermodynamic constants for the dissociation of carbonic acid in seawater. Mar. Chem. 55: 233–245. doi:10.1016/0304-4203(96)00064-3

Liu, X., M. C. Patsavas, and R. H. Byrne. 2011. Purification and characterization of meta-cresol purple for spectrophotometric seawater pH measurements. Environ. Sci. Technol. 45: 4862–4868. doi:10.1021/es200665d

Luo, Y., B. P. Boudreau, and A. Mucci. 2016. Disparate acidification and calcium carbonate desaturation of deep and shallow waters of the Arctic Ocean. Nat. Commun. 7: 12821. doi:10.1038/ncomms12821

McKinley, G. A., D. J. Pilcher, A. R. Fay, K. Lindsay, M. C. Long, and N. S. Lovenduski. 2016. Timescales for detection of trends in the ocean carbon sink. Nature 530: 469–472. doi:10.1038/nature16958

Miller, L. A., R. W. Macdonald, F. Mclaughlin, A. Mucci, M. Yamamoto-Kawai, K. E. Giesbrecht, and W. J. Williams. 2014. Changes in the marine carbonate system of the western Arctic: Patterns in a rescued data set. Polar Res. 33: 20577. doi:10.3402/polar.v33.20577

Millero, F. J. 2007. The marine inorganic carbon cycle. Chem. Rev. 107: 308–341. doi:10.1021/cr0503557

Millero, F. J., J.-Z. Zhang, S. Fiol, S. Sotolongo, R. N. Roy, K. Lee, and S. Mane. 1993a. The use of buffers to measure the pH of seawater. Mar. Chem. 44: 143–152. doi:10.1016/0304-4203(93)90199-X

Millero, F. J., J.-Z. Zhang, K. Lee, and D. M. Campbell. 1993b. Titration alkalinity of seawater. Mar. Chem. 44: 153–165. doi:10.1016/0304-4203(93)90200-8

Millero, F. J., R. J. Woosley, A. R. Margolin, and F. Huang. 2016. Global ocean repeat hydrography study: pH, total alkalinity, and total CO2 measurements in the Arctic Ocean. CDIAC, Oak Ridge National Laboratory.

Newton, R., P. Schlosser, R. Mortlock, J. Swift, and R. MacDonald. 2013. Canadian Basin freshwater sources and changes: Results from the 2005 Arctic Ocean section. J. Geophys. Res. Ocean. 118: 2133–2154. doi:10.1002/jgrc.20101

Olsen, A., R. G. J. Bellerby, T. Johannessen, A. M. Omar, and I. Skjelvan. 2003. Interannual variability in the wintertime air–sea flux of carbon dioxide in the northern North Atlantic, 1981–2001. Deep Sea Res. Part I Oceanogr. Res. Pap. 50: 1323–1338. doi:10.1016/S0967-0637(03)00144-4

Olsen, A., and others. 2016. The Global Ocean data analysis project version 2 (GLODAPv2) – An internally consistent data product for the world ocean. Earth Syst. Sci. Data 8: 297–323. doi:10.5194/essd-8-297-2016

Omar, A. M., T. Johannessen, A. Olsen, S. Kaltin, and F. Rey. 2007. Seasonal and interannual variability of the air–sea CO2 flux in the Atlantic sector of the Barents Sea. Mar. Chem. 104: 203–213. doi:10.1016/J.MARCHEM.2006.11.002

Parmentier, F.-J. W., T. R. Christensen, L. L. Sorensen, S. Rysgaard, A. D. McGuire, P. A. Miller, and D. A. Walker. 2013. The impact of lower sea-ice extent on Arctic greenhouse-gas exchange. Nat. Clim. Chang. 3: 195. doi:10.1038/nclimate1784

Plancherel, Y., K. B. Rodgers, R. M. Key, A. R. Jacobson, and J. L. Sarmiento. 2013. Role of regression model selection and station distribution on the estimation of oceanic anthropogenic carbon change by eMLR. Biogeosciences 10: 4801–4831. doi:10.5194/bg-10-4801-2013

Proshutinsky, A., and others. 2019. Analysis of the Beaufort gyre freshwater content in 2003–2018. J. Geophys. Res. Ocean 124: 9658–9689. doi:10.1029/2019JC015281

Qi, D., and others. 2017. Increase in acidifying water in the western Arctic Ocean. Nat. Clim. Chang. 7: 195–199. doi:10.1038/nclimate3228

Ramette, R. W., C. H. Culberson, and R. G. Bates. 1977. Acid-base properties of tris(hydroxymethyl)aminomethane (Tris) buffers in sea water from 5 to 40°C. Anal. Chem. 49: 867–870. doi:10.1021/ac50014a049

Robbins, L. L., and others. 2013. Baseline monitoring of the Western Arctic Ocean estimates 20% of Canadian Basin surface waters are undersaturated with respect to aragonite. PLoS One 8: e73796. doi:10.1371/journal.pone.0073796

Rudels, B. 2012. Arctic Ocean circulation and variability - advection and external forcing encounter constraints and local processes. Ocean Sci. 8: 261–286. doi:10.5194/os-8-261-2012

Schlitzer, R. 2016. Ocean data view, DOI: 10.1098/rsta.2015.0288.

Schuster, U., and others. 2013. An assessment of the Atlantic and Arctic Sea-air CO2 fluxes. Biogeosciences 10: 607–627. doi:10.5194/bg-10-607-2013

Semiletov, I., and others. 2016. Acidification of East Siberian Arctic shelf waters through addition of freshwater and terrestrial carbon. Nat. Geosci. 9: 361–365. doi:10.1038/ngeo2695

Steinacher, M., F. Joos, T. L. Fröhlicher, G.-K. Plattner, and S. C. Doney. 2009. Imminent ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-model. Biogeosciences 6: 515–533. doi:10.5194/bg-6-515-2009

Thyng, K. M., C. A. Greene, R. D. Hetland, H. M. Zimmerle, and F. DiMarco Steven. 2016. True colors of oceanography: Guidelines for effective and accurate colormap selection. Oceanography 29: 9–13. doi:10.5670/oceanog.2016.66

Ulfisbo, A., E. M. Jones, N. Casacuberta, M. Korhonen, B. Rabe, M. Karcher, and S. M. A. C. van Heuven. 2018. Rapid changes in anthropogenic carbon storage and ocean acidification in the intermediate layers of the Eurasian Arctic
Ocean: 1996-2015. Global Biogeochem. Cycles 32: 1254–1275. doi:10.1029/2017GB005738
Van Heuven, S., D. Pierrot, E. R. Lewis, and D. W. R. Wallace. 2011. MATLAB program developed for CO2 system calculations ORNL/CDIAC-105b.
Wallace, D. W. R. 1995. Monitoring global ocean carbon inventories. OOSDP Background Report No. 5.
Waters, J. F., F. J. Millero, and C. L. Sabine. 2011. Changes in South Pacific anthropogenic carbon. Global Biogeochem. Cycles 25: GB4011. doi:10.1029/2010GB003988
Woosley, R. J., F. J. Millero, and R. Wanninkhof. 2016. Rapid anthropogenic changes in CO2 and pH in the Atlantic Ocean: 2003–2014. Global Biogeochem. Cycles 30: 70–90. doi:10.1002/2015GB005248
Woosley, R. J., F. J. Millero, and T. Takahashi. 2017. Internal consistency of the inorganic carbon system in the Arctic Ocean. Limnol. Oceanogr. Methods 15: 887–896. doi:10.1002/lom3.10208
Yamamoto-Kawai, M., F. A. McLaughlin, E. C. Carmack, S. Nishino, K. Shimada, and N. Kurita. 2009. Surface freshening of the Canada Basin, 2003–2007: River runoff versus sea ice meltwater. J. Geophys. Res. 114: C00A05. doi:10.1029/2008JC005000
Yasunaka, S., and others. 2016. Mapping of the air–sea CO2 flux in the Arctic Ocean and its adjacent seas: Basin-wide distribution and seasonal to interannual variability. Polar Sci. 10: 323–334. doi:10.1016/J.POLAR.2016.03.006
Zhong, W., M. Steele, J. Zhang, and S. T. Cole. 2019. Circulation of Pacific winter water in the Western Arctic Ocean. J. Geophys. Res. Ocean. 124: 863–881. doi:10.1029/2018JC014604

Acknowledgments
The authors wish to thank the scientists and crew of the U.S.C.G.C. Healy and the U.S. GEOTRACES program, as well as the scientists and crew for the 1994 and 2005 expeditions. We are grateful to Andrew Margolin and Fen Huang for helping to measure the pH, DIC, and TA in 2015. We also wish to thank Andrew Babbin for providing the base code required to do the water mass decomposition analysis, and his editorial assistance in preparing this manuscript. We thank Marcie Henderson for her assistance in proof reading the manuscript. We are grateful to Siv Lauvset for developing the secondary CO2 quality control algorithm and assistance in adapting it to the unique conditions of the Arctic. Finally, we thank two anonymous reviewers for their many constructive comments. Funding for this project was provided by the National Science Foundation (Award No. 1436748), the Climate Observation and Monitoring Division of the Climate Program Office of the National Oceanic and Atmospheric Administration and the U.S. repeat hydrography cruises currently under the auspices of U.S. GO-SHIP.

Conflict of Interest
The authors declare no competing interests.