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Internal Consistency of the inorganic carbon system in the Arctic Ocean

By

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Abstract

Highly accurate and precise measurements of the inorganic carbon system are crucial for monitoring and assessing the uptake of anthropogenic CO₂ by the ocean. The Arctic Ocean is an area of particular interest due to Arctic amplification of climate change. Internally consistent constants are essential for making high quality CO₂ system measurements and for calculating the full suite of carbon parameters. Temperatures and salinities in the Arctic are near or below the valid ranges of most carbon system constants, but the applicability has never been fully assessed in the Arctic. Using measurements of all four carbon parameters (total alkalinity, total CO₂, pH and *p*CO₂) made on the Arctic GEOTRACES/GO-SHIP cruise in summer 2015, we evaluate the internal consistency of six different sets of constants for surface waters at in-situ temperature. Five of the six sets of constants are generally internally consistent, but each is statistically significantly different from each other. Although differences among constants are generally within the uncertainty of the calculations, these results indicate caution should be used when comparing data using different constants as biases may result from the choice of constants. We also find significant uncertainty in converting measured pH to pH at in-situ temperature. The uncertainty in the pH temperature conversion limits our ability to determine the accuracy of pH measurements, particularly in polar regions. Measurements in marginal ice zones indicate that dissolution of semi-stable ikaite (CaCO₃) may bias total alkalinity measurements, and should therefore be analyzed immediately upon collection or filtered before storage.

Introduction

The Arctic Ocean is currently experiencing a period of rapid change (Hassol and Corell 2006; Cohen et al. 2014). Recent decades have shown warming (e.g., Serreze and Francis 2006; Vihma 2014), substantial sea ice loss (e.g., Maslanik et al. 2007; Wang and Overland 2009; Cohen et al. 2014), changes in freshwater input (Wu et al. 2005; McGuire et al. 2006, 2009), and various ecosystem shifts (e.g., Pabi et al. 2008; Arrigo et al. 2008; Fossheim et al. 2015), all of which are expected to continue into the foreseeable future. Many of these changes are contributing to large perturbations in the marine carbon cycle, as sea ice melt exposes an increasing area of surface waters undersaturated with respect to atmospheric CO₂ during summer months (Bates et al. 2006; Cai et al. 2010; Mathis et al. 2014). Warmer temperatures and increased freshwater inputs also affect CO₂ solubility.

Despite the relatively small area and volume of the Arctic Ocean (only 3% of the world's ocean surface area), it is predicted to have a disproportionate uptake of anthropogenic carbon (Tanhua et al. 2009; Olsen et al. 2015). Yasunaka et al. (2016) found the annual Arctic CO₂ uptake to be ~10% of the total (natural and anthropogenic) global uptake. Based on CFC/SF₆ distributions, the anthropogenic uptake rate is approximately twice the global average (Tanhua et al. 2009). The uptake will likely increase as sea ice coverage decreases. This high uptake potential is thought to be a result of high biological production in the marginal seas and low temperature (Anderson et al. 1998; Bates 2006). Confirming this disproportionate uptake and reducing the uncertainty requires large quantities of high quality measurements of the carbon system over time and across seasons. The often unwelcoming weather conditions prevalent in the Arctic, particularly during winter, make observations difficult and limited in space and time. In order to make the best use of the limited data sets, it is important to fully understand the quality

of the data and identify areas for improvement. The inorganic carbon system has two degrees of freedom, meaning only two carbon parameters must be measured in order to fully constrain the system, thereby allowing one to characterize the system without measuring all possible parameters. This is achieved using relationships between the measurable parameters and the dissociation constants of carbonic acid (Park 1969). The accuracy of these calculations is determined by the quality of the measured parameters and the accuracy of the dissociation constants.

Several studies since the derivation of these equations have determined the required dissociation constants (Hansson 1973; Mehrbach et al. 1973; Goyet and Poisson 1989; Roy et al. 1993; Millero et al. 2002, 2006; Mojica Prieto and Millero 2002) and many others have refit the original data (Dickson and Millero 1987; Millero 1995, 2010; Lueker et al. 2000) in order to formulate the older data to modern standards and understanding, or to combine several studies into a unified set of equations. Numerous studies have shown that constants determined in real seawater produce better internal consistency than those determined in artificial seawater (Lee and Millero 1995; Millero 1995, and references therein), this is likely a result of interactions with borate in real seawater. The most commonly used constants are those of Mehrbach et al. (1973) as refit by Dickson and Millero (1987) due to the recommendations of Wanninkhof et al. (1999) and Lee et al. (2000); however, these studies only looked at surface samples in equatorial to temperate oceans and did not contain pH data. Temperatures in the Arctic are often below zero, and only the constants of Goyet and Poisson (1989) were measured below zero; however, artificial seawater was used in their measurements. Differences among the various sets of constants are known to be largest at the low temperatures and salinities (Wanninkhof et al. 1999) experienced in the Arctic; however, which specific set produces the best internal consistency is

not currently known. Recently Chen et al. (2015) examined the internal consistency of carbon measurements in the Arctic and found the best agreement with the constants of Mehrbach et al. (1973) as refit by Dickson and Millero (1987), with several caveats; measurements were not internally consistent in areas of active sea ice melt, and differences between measured and calculated values were a function of temperature and salinity, indicating a bias in the constants under these conditions. The reason for poor internal consistency in areas of active ice melt was thought to be a result of CaCO_3 dissolution during sample storage, since total alkalinity was measured in the lab and not on board the ship (Chen et al. 2015).

These results leave open several important questions which we attempt to answer using data collected on the US GEOTRACES/GO-SHIP ARC01 cruise in the summer of 2015. On this cruise, which traveled from Dutch Harbor Alaska to the North Pole and back (Figure 1), pH, total alkalinity (TA), and total CO_2 (TCO_2) were collected on discrete full water column profiles, and $p\text{CO}_2$ was collected on surface water samples using an underway system. With the carbon system fully constrained in the surface, we are able to look into the system more fully than Chen et al. (2015) who only determined TA, TCO_2 , and $p\text{CO}_2$, and compare our results to theirs.

Methods

In the summer of 2015, the U.S. Coast Guard Cutter Healy conducted the U.S. GEOTRACES/GO-SHIP repeat hydrography cruise ARC01 (also called GN01; expocode 33HQ20150809) sampling in the Makarov and Canada Basins of the Arctic Ocean between August 9 – October 13 (**Figure 1**). Out of 66 stations occupied, 60 full depth profiles were sampled for TA, TCO_2 , pH, salinity, nutrients (phosphate, silicate, and nitrate), and oxygen. Of those stations, 54 had accompanying $p\text{CO}_2$ surface data from the ship's underway $p\text{CO}_2$ system.

It should be noted that after quality control, not all of those 54 stations have all four carbon parameters. All data are available on CDIAAC (http://cdiac.ornl.gov/oceans/RepeatSections/CLIVAR_Arctic_Ocean.html). The $p\text{CO}_2$ data are also available at www.ldeo.columbia.edu/CO2. For measurements with full water column profiles, deep water values were compared with previous occupations of sections of the cruise track in the Makarov Basin (AOS-1994; expocode 18SN19940724) and the Canada Basin (AOS-2005; expocode 77DN20050819), also available on CDIAAC at the above URL, to ensure quality and consistency of the data with other cruises. Deep values were only considered as a quality control check and were not used in the internal-consistency calculations since they are essentially modified Atlantic and Pacific waters which have been studied more extensively and $p\text{CO}_2$ was only measured in the surface waters.

Salinity, Temperature, and Nutrients

Discrete samples were collected from a 36-place rosette with a CTD package (SBE32 carousel, SBE3plus dual temperature sensor, and SBE4C dual conductivity from Sea-Bird Scientific, Bellevue, WA). Only the surface bottle was used in our calculations and ranged in depth from 3-8 m. Discrete nutrient samples (phosphate and silicate) were measured using a Seal Analytical continuous-flow AutoAnalyzer 3 (AA3) (Atlas et al. 1971; Hager et al. 1972; Gordon et al. 1993; Hydes et al. 2010). Bottle salinity was measured using a Guildline Autosol 8400B salinometer, calibrated using standard seawater (IAPSO SSW batch P158). If the bottle salinity was flagged as bad or questionable then CTD salinity was used for calculations instead. The average difference between bottle salinity and CTD salinity was 0.02, well below the required precision of 0.1 required for carbon system calculations (Dickson et al. 2007). Differences between the salinity from the rosette and the salinity from the $p\text{CO}_2$ system (measured by an

SBE21) was < 0.05 , with the exception of 2 stations, discussed later. Bottle salinity and nutrients were used to identify any miss-trips, and confirmed that all samples were tripped at the expected depth. The salinities ranged from 22.8 to 32.9. The temperature, also obtained from the CTD, ranged from -1.5 to 9.8°C . Differences between the CTD temperature and the temperature measured by the underway $p\text{CO}_2$ system was $< 0.1^{\circ}\text{C}$, except for the same 2 stations that showed large differences in salinity. This difference in temperature results in a difference in $p\text{CO}_2$ of < 1 μatm (Takahashi et al. 1993) and is therefore insignificant.

Total Alkalinity

The total alkalinity was measured using a custom designed closed cell HCl titration (Millero et al. 1993) run by an automated computer program. A Ross glass pH electrode (Orion, model 810100) and a double junction Ag, AgCl reference electrode (Orion, model 900200) were used to measure the electromotive force (EMF) throughout the titration. The potentiometric data were then fit using a Levenberg-Marquardt nonlinear least-squares algorithm to calculate the TA. The accuracy and precision of the measurements were monitored using certified reference material (CRM) provided by Dr. Andrew Dickson (Marine Physical Laboratory, Scripps Institute of Oceanography, La Jolla, California), and duplicate samples from the same Niskin bottle. Based on the CRM and duplicate measurements, the precision and accuracy are estimated to be ~ 2 $\mu\text{mol kg}^{-1}$. Further details of the methods and quality control measures can be found in Millero et al. (2016).

Total CO₂

The total carbon dioxide was measured using the dissolved inorganic carbon analytical equipment (DICE) which is based on the original SOMMA systems (Johnson 1992). The

instrument converts all carbonate species to $\text{CO}_{2(\text{gas})}$ by adding 8.5% H_3PO_4 . The evolved gas is then carried to a titration cell where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions, which are subsequently titrated with coulometrically generated OH^- (Dickson et al. 2007). The precision and accuracy of the measurements were determined using CRMs and duplicate samples from the same Niskin bottle as was done with TA. Based on these measurements the accuracy and precision are estimated to be $\sim 2.5 \mu\text{mol kg}^{-1}$. Further details on the methods and quality control can be found in Millero et al. (2016).

pH

The concentration of hydrogen ion (pH) was determined spectrophotometrically using purified m-cresol purple indicator dye (batch 7, provided by Robert H. Byrne, University of South Florida, St. Petersburg, FL). The automated system is similar to that described in Carter et al. (2013). Measurements were made on the seawater scale using the equations for purified indicator (Liu et al. 2011) and the fluoride and sulfate dissociation constants of Dickson and Riley (1979) and Dickson (1990a) respectively. Measurements were made at a temperature of either 20 or 25°C. Precision was monitored throughout the cruise using CRMs, duplicate samples from the same Niskin bottle, and TRIS buffers. Based on these measurements the precision of the pH measurements is estimated to be ~ 0.0014 . Further details on the methods and quality control can be found in Millero et al. (2016).

Converting pH to in situ temperature can be problematic. The most common method is to calculate it using thermodynamic relationships and either TA or TCO_2 . The results of these calculations are therefore dependent on the choice of carbonate constants used, which is what we are trying to evaluate. Empirical equations have been developed for use when only pH is known (Millero 1995; Lui and Chen 2017). However, both also rely on the set of constants used to

determine them (Millero 1995; Lui and Chen 2017). Millero (1995) also relies on a constant ratio of TA/TCO₂ which is changing as a result of anthropogenic carbon uptake. Comparisons of pH at the in situ temperature using the two empirical equations and values calculated using TA and pH₂₅ and the various constants were made. The values calculated using CO₂sys generally agreed with each other to ± 0.003, except for Millero et al. (2002) which averaged 0.025 pH units higher than the other values. For this reason the Millero et al. (2002) values were excluded from this comparison. The average of the values calculated from the other five sets of constants were then compared to the empirical equations. The values calculated using the equation of Millero (1995) averaged 0.0170 ± 0.0024 pH units higher than the average values calculated using CO₂sys. This is not completely unsurprising given the limits of the equation, although other work shows it to work reasonably well for temperature differences <~5°C (Millero et al. 2002, 2016). The values calculated using Lui and Chen (2017) averaged 0.0033 ± 0.0041 pH units higher than the CO₂sys calculated values. Although not entirely unreasonable, the noise in the values is high relative to values calculated from CO₂sys. Based on these results, the pH was converted to in situ temperature by calculating it using CO₂sys, pH at measured temperature, and TA for each of the constants and then averaging the results (excluding Millero et al. (2002), as explained above). Using the average value helps to remove biases that may result from a single set of constants, but does not eliminate the reliance of the pH on the accuracy of the constants, and therefore limits our ability to assess the accuracy of pH measurements.

*p*CO₂

The partial pressure of carbon dioxide (*p*CO₂) was determined using an underway system attached to the ship's uncontaminated seawater line, with a water intake located at ~5 m depth. Seawater was continually pumped into the 30 L shower type air-water equilibrator, and the

equilibrated air was then dried and pumped into the non-dispersive infra-red CO₂ gas analyzer (Sutherland et al. 2015). The system was calibrated approximately every 75 minutes with 5 different standard air-CO₂ gas mixtures (pure N₂, 254.8, 391.6, 504.9 and 738.3 ppm mole fraction CO₂) which were calibrated by the Earth System Research Laboratory of NOAA (Boulder, CO). The *p*CO₂ was computed assuming that CO₂ was an ideal gas and that mixing of CO₂ and air was also ideal. In order to match the *p*CO₂ values with the corresponding in-situ temperature, the time of measurement was adjusted by 3 ~ 6 minutes to account for the time lag between the water intake and the *p*CO₂ system. The temperature difference between measured and in-situ temperature was less than 2°C throughout the expedition. The *p*CO₂ value was corrected to the in-situ temperature using the effect of temperature at constant chemistry of ($\partial \ln p\text{CO}_2 / \partial T$) = 0.0433 – 8.7 × 10⁻⁵ T (°C) (or 4.29 % *p*CO₂ °C⁻¹ at 5 °C), which was based on the direct measurements of *p*CO₂ of a North Atlantic surface water sample in a temperature range of 2 to 25 °C (Takahashi et al. 1993). The overall accuracy and precision of the *p*CO₂ values were estimated to be ± 2 μatm.

In order to make the data comparable with the other carbon parameters they must be aligned in space and time. Using the time and location that the surface bottle was closed on the CTD, all *p*CO₂ data points measured from 0 to 15 minutes after the bottle closed and within 2 km of the bottle closure location were used. At 6 stations, there was no underway *p*CO₂ measurement corresponding to the rosette samples, mainly as a result of standards being run during that time period. The resulting *p*CO₂ values were then averaged at each station. The mean value for each station was used in all calculations and comparisons. The number of points averaged for each station ranged between 1 and 6 based on the above merge criteria. The average number of points was 5, and the mode was 6. The standard deviation of the points used at each

station was generally less than 1 μatm , with the largest being 2.7 μatm . The standard deviation at all but three stations was within the estimated precision of the $p\text{CO}_2$ measurement (2 μatm), confirming the validity of the merge criteria. For all measurements and calculations, $p\text{CO}_2$ is used rather than fugacity ($f\text{CO}_2$), because of the ambiguity of non-ideality of CO_2 in wet air. However, at the range of $p\text{CO}_2$ measured in this study, the differences between $p\text{CO}_2$ and $f\text{CO}_2$ are within the precision of the measurements.

Calculations

Calculation of the various carbon parameters using different carbonate dissociation constants are easily facilitated with the readily available CO2sys program (Pierrot et al. 2006). All calculations were done using CO2sys version 2.1 in Excel. For all calculations, the HSO_4^- dissociation constants of Dickson (1990a), the fluoride dissociation constant of Dickson and Riley (1979), the borate dissociation constants of Dickson (1990b), and the boron concentration of Lee et al. (2010) were used. The measured dissolved silicate and phosphate concentrations were also used as input parameters. Using paired sets of the four carbon parameters, the other two parameters were calculated at in situ temperature and atmospheric pressure for each of the six sets of dissociation constants Dickson and Millero (1987), Lueker et al. (2000), Mojica Prieto and Millero (2002), Millero et al. (2002), Millero et al. (2006), and Millero (2010), which will be referred to as DM87, L00, MPM02, M02, M06 and M10, respectively, for simplicity. Only constants measured in real seawater were considered as those made in artificial seawater are known to be biased, especially for pH (Millero 1995; DelValls and Dickson 1998; Wanninkhof et al. 1999). It should be noted that both DM87 and L00 are refits of Mehrbach et al. (1973) and the main difference is that DM87 forced their values into the pure water value, while L00 did

not. This may cause differences at low salinities (< 20). DM87 was also determined on the seawater scale, and L00 on the total scale. The difference between the measured and calculated values were then determined; $\Delta_{\text{param}} = \text{measured parameter} - \text{calculated parameter}$, where param is either pH, TA, TCO₂, or *p*CO₂. The averages and standard deviations for all of the calculations are given in Table 1 and Figure 2. The input parameters for each calculation are shown in parentheses.

In order to determine if the different constants produced statistically significantly different results, a correlated t-test was used. The calculation was done using the statistical analysis program JMP Pro version 13.1 (SAS Institute Inc., Cary, NC). All possible pairs of constants were compared; however, only comparisons with the constants of DM87 will be presented, because they are the most commonly used and have been previously recommended (Wanninkhof et al. 1999; Lee et al. 2000).

Results

As seen in Table 1 and Figure 2, overall the parameters appear to be generally internally consistent, with a few notable exceptions. Two points, station 8 and 62, had very large $\Delta p\text{CO}_2$ values. Comparisons of the CTD temperature and salinity with the sea surface temperature and salinity showed large differences. The differences in salinity were greater than 2, and differences in temperature were greater than 1.6°C. This is compared to the other stations which average differences of < 0.1 in both temperature and salinity. Internal consistency for the other three parameters are all reasonable. The mixed layer depth at these two stations was less than 10 m which likely explains the differences in temperature and salinity. These factors indicate that the poor internal consistency for *p*CO₂ for these two points is the result of different waters being

sampled for $p\text{CO}_2$ than the other parameters, and not issues with the calculations or analysis. These two points have therefore been excluded from all calculations involving $p\text{CO}_2$. The extremely shallow mixed layer of these stations, both of which occurred in the MIZ, indicate the heterogeneity that can be experienced in Arctic surface waters.

For pH, all sets of constants except M02 had a mean delta of $\leq |0.006|$ pH units. This is well below the relative uncertainties of the calculations of 0.3-0.6%, as determined by McLaughlin et al.(2015) and similar to estimated errors in pH measurements in field studies (Lamb et al. 2002). The standard deviations of the means are all also less than the estimated uncertainties of the calculations (McLaughlin et al. 2015). The constants of DM87 produced the deltas closest to zero. Only the constants of M02 produced deltas higher than the estimated 0.02 pH unit absolute uncertainty of pH measurements (McLaughlin et al. 2015). The constants of M02 are discussed in more detail later.

For $p\text{CO}_2$, all sets of constants except one had a mean delta $\leq |6.2|$ μatm . These are all significantly less than the 3-12% relative uncertainty of the calculations (McLaughlin et al. 2015). The standard deviation of the means is also less than the 3% uncertainty. Most of the means are close to the 2 μatm precision of the measurements (Sutherland et al. 2015). The constants of M02 had significantly larger means for calculations involving pH, although still close to the relative uncertainty. The constants of M02 are discussed in more detail later. The constants of M87 and L00 produced the deltas closest to zero.

For TCO_2 and TA, all sets of constants except for M02 and some calculations involving pH and $p\text{CO}_2$, had a mean delta of $\leq |5|$ $\mu\text{mol}\cdot\text{kg}^{-1}$, and standard deviations ~ 5 $\mu\text{mol}\cdot\text{kg}^{-1}$ except for calculations involving pH and $p\text{CO}_2$ which had standard deviations ~ 30 $\mu\text{mol}\cdot\text{kg}^{-1}$. These are

less than the $\sim 10 \mu\text{mol kg}^{-1}$ relative uncertainty for calculations involving TA or TCO_2 and the $\sim 140 \mu\text{mol kg}^{-1}$ relative uncertainty for pH and $p\text{CO}_2$ as input parameters (McLaughlin et al. 2015). The only calculation that approaches the estimated relative uncertainty is the calculation using pH and $p\text{CO}_2$ and the constants of M02, which will be discussed later. Most of the calculations produced values within the estimated absolute uncertainty in TA and TCO_2 of $\sim 10 \mu\text{mol kg}^{-1}$ (McLaughlin et al. 2015). The constants of M87 and L00 produced the deltas closest zero.

Discussion

From a cursory look at Table 1, it would appear that the constants of D87 or L00 produce the most internally consistent values. However, except for M02, the values of all constants appear to be within the expected relative uncertainty of the calculations (McLaughlin et al. 2015) and measurement uncertainties (Dickson et al. 2007). The question now becomes, are the differences between the constants statistically significant? As described in the methods, a correlated t-test was used to compare the means of the calculations of the different constants with each other. All of the means were compared with the means of DM87, as these are generally the recommended constants for surface waters (Wanninkhof et al. 1999) and the most commonly used. All possible pairs were analyzed, but the results were similar to the comparisons with DM87 so only comparison with DM87 will be discussed further. The results of the correlated t-tests are given in Table 2. The means of all calculations were found to be statistically different from DM87 at the 95% confidence level. These results indicate that each set of constants has some bias relative to the constants of DM87, although in most cases it is smaller than the relative and absolute uncertainties. The sample size of these calculations is admittedly small, but caution

should be used when comparing results calculated using different sets of constants, and such biases should be considered in error estimates. It is also important to always clearly document all constants used for calculations. More work is needed to determine and untangle the causes of the apparent differences in the constants.

As noted above, the constants of M02 produced considerably poorer internally consistent results than the other constants. Although the standard deviation of the results are similar to the other constants, many of the means are considerably far from zero, particularly those involving pH. The M02 constants are unique relative to the other constants in the technique that was used to determine them. All the other constants were determined from laboratory experiments of real seawater. M02 instead used field measurements to back calculate K_1 and K_2 . The constants of M02 were determined over a wide range of salinity and temperature that includes the range of values of this study; however, the majority of the data were at 20°C and pH values were determined by multiple methods (both spectrophotometric and potentiometric). The reason for the offsets needs further evaluation, but may be caused by the use of the less precise potentiometric pH measurements on one of the datasets used in the determination (Millero et al. 2002), and limited data as a function of temperature. The use of different pH scales and the uncertainties of converting between them may also contribute.

The Arctic, particularly the marginal ice zone (MIZ) where some of the samples were collected, has relatively low temperatures and salinities, and is at the lower end of the range in which many of these constants are valid. To determine if any of the deltas were a function of temperature or salinity, the deltas were plotted against both temperature and salinity and a line was fit to the data. None of the slopes for any sets of constants were found to be statistically significant at the 95% confidence level, except a few involving the M02 and MPM02 constants.

Nearly all have R^2 values < 0.1 . For M02 and MPM02, the calculation of $p\text{CO}_2(\text{TCO}_2, \text{pH})$ and the calculation of $\text{pH}(\text{TCO}_2, p\text{CO}_2)$, as a function of temperature, had $R^2 \sim 0.2$ and the slopes were statistically significant. As a function of salinity for M02, those same calculations had $R^2 \sim 0.4$ and also had statistically significant slopes. Although the sample size is small, it appears that the constants of M02 and to a lesser degree MPM02 may have biases at low temperature and salinities. The reason for the issues at low temperature are likely related to the conversion of the measured pH to in situ pH. As discussed in the methods, this conversion is one of the largest uncertainties in measurements of pH, and the most difficult to deal with. It should be emphasized that part of the reason for M02 having larger offsets is that it was excluded from the conversion to in situ pH, as described in the methods. Given the large absolute uncertainties in pH (McLaughlin et al. 2015), it cannot be ruled out that the results of M02 are, in fact, more accurate than the other constants. Calculations using M02 that do not involve pH have similar means to the other constants, further indicating the need for better understanding of the temperature dependence of pH, particularly as pH sensors become more common on floats and other autonomous platforms.

Recently, Chen et al. (2015) looked at the internal consistency of the carbon system in the Arctic, with a study area similar to that of ours. There are two significant differences. First, they did not measure pH, so the carbon system was not as overly determined as ours, and second, both TA and TCO_2 were measured upon return to the lab rather than on board the ship. Their results are generally in good agreement with ours. They too found the constants of DM87 and L00 to have the means closest to zero (Chen et al. 2015). One of the interesting results of their work was that areas with light ice cover, or the MIZ, had relatively poor internal consistency with measured $p\text{CO}_2$ being $\sim 20\text{-}25 \mu\text{atm}$ higher than calculated $p\text{CO}_2$. They attributed this to possible

changes in TA between collection and analysis, as a result of CaCO_3 dissolution (Chen et al. 2015). Since all of our TA samples were analyzed within 12 hours of collection, we are able to test this hypothesis to a limited degree. Our results show no relationship between ice cover and $\Delta p\text{CO}_2$ ($R^2 < 0.01$). Also, calculations of $p\text{CO}_2$ in the MIZ using TCO_2 and pH are not significantly different from calculations that do involve TA. The sample size is very small ($N = 15$), but indicates that either CaCO_3 (ikaite) was not present in our samples, or that it did not dissolve during analysis. More work is needed to confirm which is true, but regardless of the cause, samples from the MIZ should either be analyzed immediately on board or filtered before being stored for analysis on land.

Conclusions

By over determining the inorganic carbon system we were able to evaluate the internal consistency of the measurements. Evaluations of six different sets of carbon constants found that each set produced similar, although statistically significant different results. The constants of M87 and L00 produced calculated values that were closest to the measured values. Contrary to other claims (Lamb et al. 2002), this does not necessarily mean that these sets of constants are more accurate than the others, only that they are more internally consistent; biases may still exist in the constants, the measurements, or both.

The constants of M02 produced Δ values much larger than the other constants when pH was used in the calculation. There is some indication that the Δ pH and $p\text{CO}_2$ values are a function of temperature and salinity (although the sample size is too small to be definitive), indicating that they may not be suitable for use in the cold, relatively fresh waters of the Arctic. One of the largest uncertainties in the inorganic carbon system is the dependence of pH on

temperature, particularly at low temperatures. This uncertainty is highlighted by our results. We show that conversion of pH from measured temperature to in situ temperature is highly dependent on the choice of constants, and at least for Arctic waters, do not agree with empirical relationships of temperature. Given the large changes occurring in the Arctic at present, this issue deserves further attention. This can be achieved by field and laboratory studies on the temperature dependence of pH, both of real seawater samples and buffers. Improvements in the accuracy of pH measurements will also be required. Until such work can be done it is important to carefully evaluate the choice of constants one uses, clearly detail all constants used in calculations, and make data available in publications and databases so that data can be re-evaluated once improvements are made.

Our results were also able to build on earlier work which showed poor internal consistency in MIZ waters (Chen et al. 2015). They hypothesized that areas of active or recent ice melt may contain ikaite, a semi-stable form of CaCO_3 , which then dissolved between collection and analysis. Our samples were analyzed immediately on board, and did not show poor internal consistency in the MIZ indicating either that their hypothesis is correct or that our samples contained no ikaite. We therefore recommend samples of TA collected in the MIZ either be analyzed immediately on board, or filtered before storage.

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Figure 1. Surface $p\text{CO}_2$ at station locations for the ARC01 cruise in summer 2015.

Figure 2. Means and standard deviations of the internal consistency calculations. Note the break in the scale for the pH, $p\text{CO}_2$ calculations, and that some of the error bars are off scale for those calculations. All values used in this figure can be found in *Table 1*. The salinities ranged from 22.8 to 32.9. The temperature ranged from -1.5 to 9.8°C .

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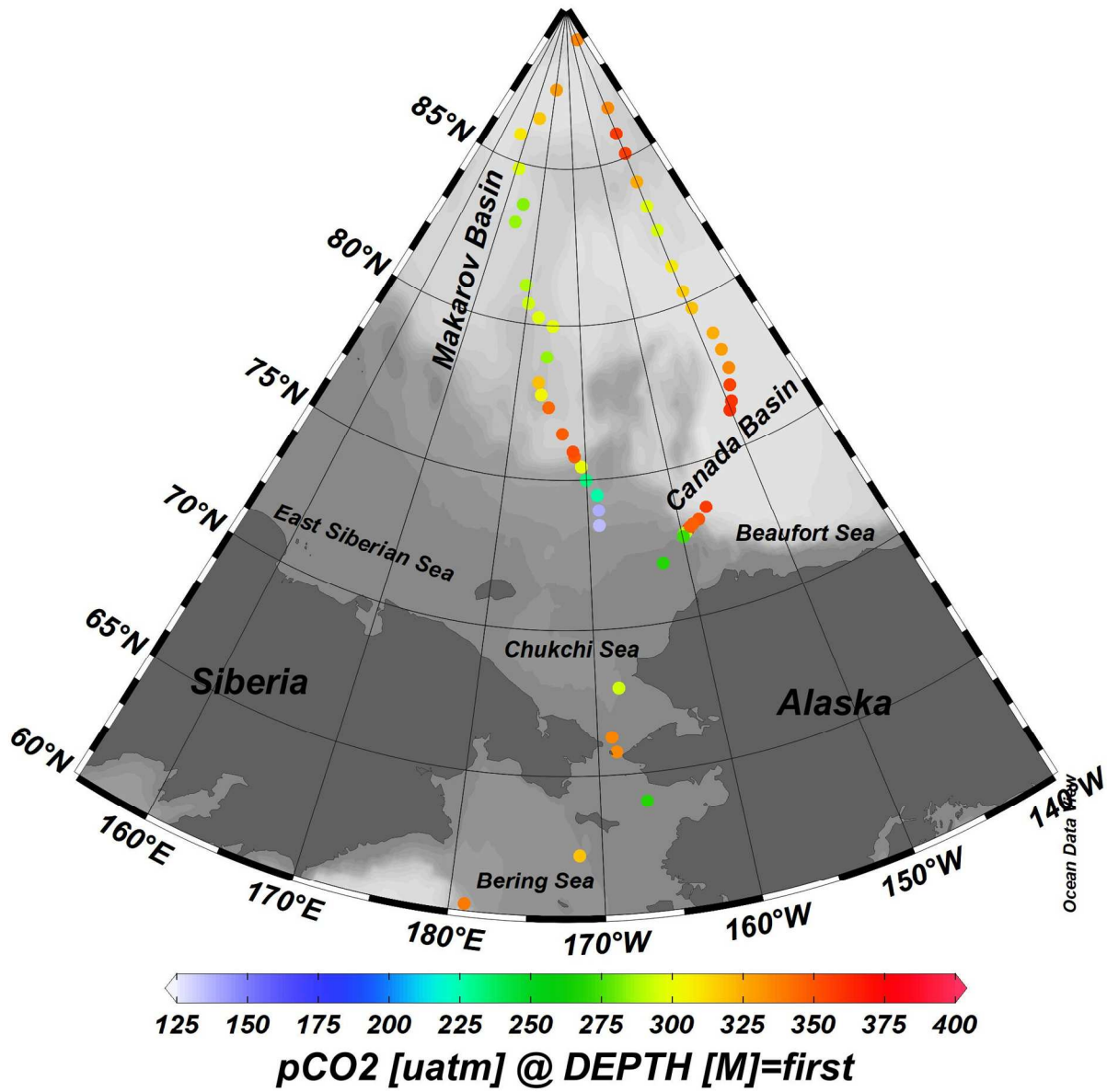


Figure 1.

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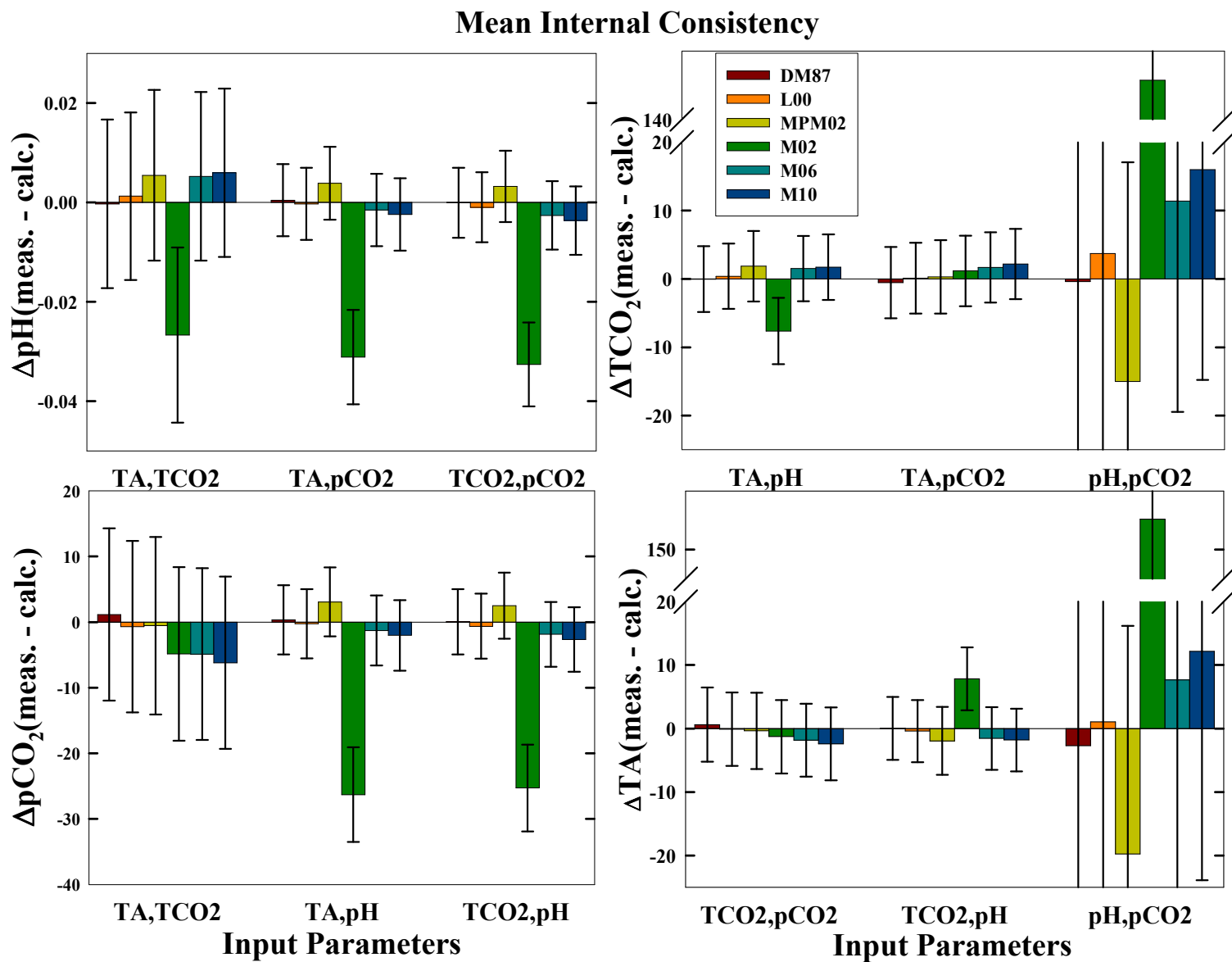


Figure 2

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Table 1. Mean and standard deviations of the differences between measured and calculated values for each set of constants. Abbreviations for the constants are DM87 (Dickson and Millero 1987), L00 (Lueker et al. 2000), MPM02 (Mojica Prieto and Millero 2002), M02 (Millero et al. 2002), M06 (Millero et al. 2006), and M10 (Millero 2010).

Table 2. T-test results for comparisons of each constant with DM87. Mean difference (constant - DM87) and standard error of the difference for each calculation and set of constant. All differences are significant at 95% confidence interval

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Table 1.

	DM87		L00		MPM02		M02		M06		M10		N
	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	
$\Delta\text{pH}_{(\text{TA},\text{TCO}_2)}$	-0.0003	0.0170	0.0013	0.0169	0.0055	0.0172	-0.0267	0.0176	0.0053	0.0170	0.0060	0.0170	45
$\Delta\text{pH}_{(\text{TA},\text{pCO}_2)}$	0.0005	0.0073	-0.0003	0.0072	0.0039	0.0073	-0.0311	0.0095	-0.0015	0.0073	-0.0024	0.0073	47
$\Delta\text{pH}_{(\text{TCO}_2,\text{pCO}_2)}$	-0.0001	0.0071	-0.0010	0.0070	0.0032	0.0072	-0.0326	0.0084	-0.0026	0.0069	-0.0036	0.0069	43
$\Delta\text{pCO}_2_{(\text{TA},\text{TCO}_2)}$	1.2	13.1	-0.7	13.1	-0.5	13.5	-4.8	13.2	-4.9	13.1	-6.2	13.1	48
$\Delta\text{pCO}_2_{(\text{TA},\text{pH})}$	0.3	5.3	-0.3	5.3	3.1	5.2	-26.3	7.2	-1.3	5.3	-2.0	5.4	46
$\Delta\text{pCO}_2_{(\text{TCO}_2,\text{pH})}$	0.0	5.0	-0.6	5.0	2.5	5.0	-25.3	6.6	-1.9	4.9	-2.7	4.9	43
$\Delta\text{TCO}_2_{(\text{TA},\text{pH})}$	0.0	4.8	0.4	4.8	1.9	5.2	-7.6	4.9	1.5	4.8	1.7	4.8	45
$\Delta\text{TCO}_2_{(\text{TA},\text{pCO}_2)}$	-0.6	5.2	0.1	5.2	0.3	5.4	1.2	5.2	1.7	5.1	2.2	5.1	48
$\Delta\text{TCO}_2_{(\text{pH},\text{pCO}_2)}$	-0.4	31.4	3.7	31.1	-15.0	32.1	145.7	30.8	11.4	30.8	16.0	30.8	43
$\Delta\text{TA}_{(\text{TCO}_2,\text{pCO}_2)}$	0.6	5.8	-0.1	5.8	-0.4	6.0	-1.3	5.8	-1.8	5.7	-2.4	5.7	48
$\Delta\text{TA}_{(\text{TCO}_2,\text{pH})}$	0.0	5.0	-0.4	4.9	-2.0	5.3	7.8	5.0	-1.6	4.9	-1.8	4.9	45
$\Delta\text{TA}_{(\text{pH},\text{pCO}_2)}$	-2.7	35.5	1.1	35.4	-19.7	35.9	155.2	34.2	7.6	36.0	12.2	36.0	46

Table 2.

	L00		MPM02		M02		M06		M10	
	Mean Diff.	Std Error	Mean Diff.	Std Error	Mean Diff.	Std Error	Mean Diff.	Std Error	Mean Diff.	Std Error
$\Delta\text{pH}_{(\text{TA},\text{TCO}_2)}$	0.0016	0.0002	0.0058	0.0005	-0.0264	0.0005	0.0056	0.0004	0.0063	0.0004
$\Delta\text{pH}_{(\text{TA},\text{pCO}_2)}$	-0.0007	0.0000	0.0034	0.0001	-0.0316	0.0009	-0.0020	0.0002	-0.0029	0.0002
$\Delta\text{pH}_{(\text{TCO}_2,\text{pCO}_2)}$	-0.0009	0.0000	0.0033	0.0001	-0.0325	0.0006	-0.0026	0.0002	-0.0036	0.0002
$\Delta\text{pCO}_2_{(\text{TA},\text{TCO}_2)}$	-1.86	0.10	-1.70	0.40	-6.01	0.11	-6.05	0.15	-7.36	0.16
$\Delta\text{pCO}_2_{(\text{TA},\text{pH})}$	-0.61	0.03	2.74	0.08	-26.64	0.64	-1.62	0.18	-2.37	0.19
$\Delta\text{pCO}_2_{(\text{TCO}_2,\text{pH})}$	-0.69	0.02	2.45	0.11	-25.32	0.64	-1.92	0.17	-2.70	0.18
$\Delta\text{TCO}_2_{(\text{TA},\text{pH})}$	0.42	0.05	1.90	0.21	-7.60	0.06	1.55	0.10	1.77	0.09
$\Delta\text{TCO}_2_{(\text{TA},\text{pCO}_2)}$	0.67	0.03	0.88	0.21	1.73	0.04	2.26	0.05	2.75	0.06
$\Delta\text{TCO}_2_{(\text{pH},\text{pCO}_2)}$	4.11	0.15	-14.60	0.60	146.15	1.89	11.77	1.12	16.39	1.21
$\Delta\text{TA}_{(\text{TCO}_2,\text{pCO}_2)}$	-0.72	0.04	-1.00	0.24	-1.90	0.06	-2.48	0.06	-3.04	0.07
$\Delta\text{TA}_{(\text{TCO}_2,\text{pH})}$	-0.42	0.05	-1.98	0.23	7.79	0.07	-1.59	0.10	-1.81	0.09
$\Delta\text{TA}_{(\text{pH},\text{pCO}_2)}$	3.77	0.19	-17.04	0.45	157.92	1.64	10.34	1.22	14.86	1.30