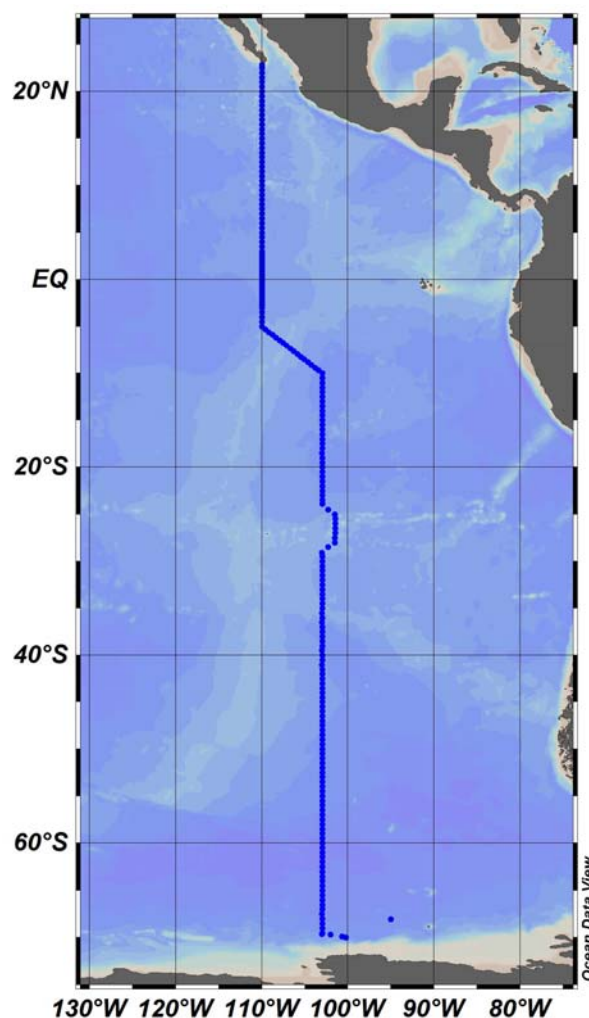


Global Ocean Repeat Hydrography Study: pH and Total Alkalinity Measurements in the Pacific Ocean

P18 Leg 1 and Leg 2

Nov 2016 – Feb 2017



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1. Introduction

The P18 cruise began with leg 1 departing from San Diego, CA and traveling to Hanga Roa, Easter Island and leg 2 departing from Hanga Roa and heading south towards Antarctica, finally ending in Punta Arenas, Chile. This cruise is part of a decadal series of repeat hydrography sections jointly funded by the NOAA [Climate Program Office](#) and the [National Science Foundation Division of Ocean Sciences](#) as part of the Climate Variability and Predictability Study (CLIVAR) CO₂ Repeat Hydrography Program, which was updated in 2007 to the Global Ocean Ship-based Hydrographic Investigations Program ([GO-SHIP](#)). The repeat hydrography program focuses on the need to monitor inventories of CO₂, heat and freshwater and their transports in the ocean. Earlier programs under WOCE, JGOFS, and CLIVAR have provided baseline observational fields for these parameters. The new measurements will reveal much about the changing patterns on decadal scales. The program serves as a structure for assessing changes in the ocean's biogeochemical cycles in response to natural and/or human-induced activity.

The NOAA ship R/V *Ronald H. Brown* departed San Diego, CA on November 19, 2016, after a long delay. The ship proceeded south principally along a 110°W, at about 10°S the track turned toward 103°W line for the remainder of the cruise (making a slight diversion to avoid the Easter Island EEZ). The cruise roughly followed the previous occupations conducted in 1993/94 and 2007/08. The ship conducted a full-depth CTD/rosette/LADCP cast approximately every 0.5° of latitude, with closer spacing over topographic features. The first leg of P18 ended on December 23, 2016 in Easter Island, Chile. After a week wrap-up for leg 1 the second leg departed on December 30, 2016 at approximately 25°S continuing south along the 103°W line toward Antarctica. The 2nd leg continued to provide half-degree stations to 70°S and then underway sampling every 4 hours between the last station and the Chilean coast. The cruise ended on February 3, 2017 in Punta Arenas, Chile. The full cruise track is shown in the figure on the cover. Underway measurements of surface seawater (temperature, salinity, CFCs, O₂, TA, pH, TCO₂) and atmospheric measurements (pCO₂) were also made along the cruise track. The complete coordinates of the waypoints can be found in Appendix A.

Fifty-five scientists from 14 academic institutions and 3 NOAA research facilities participated in this cruise (Appendix B). Our group measured total alkalinity (TA), total CO₂ (TCO₂) and pH by potentiometry and pH by spectrophotometry. The final dataset for all measured parameters is freely available at the Ocean Carbon Data System (OCADS, <https://www.nodc.noaa.gov/ocads/>, formally CDIAC). This report only covers the Total Alkalinity and pH measurements and quality control measures. Although potentiometric TCO₂ and pH measurements were made, they are not reported to OCADS since higher precision and accuracy methods were also used for those parameters.

2. Description of Variables and Methods

Total alkalinity (TA) and pH are the main variables determined by our group. The use of a closed cell titration for TA allows us to also determine the TCO₂ and pH by potentiometry, which provides a check on our systems. These values are not reported to

OCADS since this method provides lower precision of TCO_2 and pH than other methods used on the cruise. A detailed description of the methods is found below.

2.1 Total Alkalinity Analyses

Total alkalinity can be conceptually thought of as the sum of the excess bases in seawater, principally carbonate and bicarbonate, with small contributions from borate and other bases. The standard method for determination is through potentiometric titration with hydrochloric acid. Details of the sampling collection and analysis are given below.

2.1.1. Sampling

Samples for total alkalinity were drawn from the 10 L Niskin bottles into 500 cm³ borosilicate bottles using silicone tubing that fit over the petcock. The tubing both helped avoid contaminating dissolved organic carbon (DOC) samples and allowed samples to be filled from the bottom, entraining little to no bubbles. Bottles were rinsed a minimum of two times and filled from the bottom, overflowing at least half of the volume. Approximately 15 cm³ of water was withdrawn from the flask by arresting the sample flow and removing the sampling tube, thus creating a small expansion volume and a reproducible headspace. The sample bottles were sealed at a ground glass joint with a glass stopper. The samples were thermostated at 25°C before analysis. At most stations, duplicate samples were taken near the surface, the bottom, and the oxygen minimum layer.

2.1.2. Analyzer Description

The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point, $\text{pH}_{\text{equiv}} \approx 4.5$ at 25°C in one kilogram of sample. The method utilizes a multi-point hydrochloric acid titration of seawater according to the definition of total alkalinity [Dickson, 1981]. Potentiometric titrations of seawater using a closed cell give values of TA, dissolved inorganic carbon (DIC or TCO_2) and pH, which is determined from the initial EMF.

Two titration systems, A and B, were used for measuring TA. Each system used a Metrohm 665 or 765 Dosimat titrator, an Orion 720A pH meter and a custom designed plexiglass water-jacketed closed titration cell [Millero *et al.*, 1993b]. The seawater samples were equilibrated to a constant temperature of $25 \pm 0.1^\circ\text{C}$ with a water bath (Thermo Haak A10). The water-jacketed cell has a volume of $\sim 200 \text{ cm}^3$. Each cell has a fill and drain valve that is electronically activated to increase the reproducibility of the volume of sample. A typical titration recorded the EMF after the readings became stable (deviation less than 0.09 mV) and then enough acid was added to change the voltage a pre-assigned increment ($\sim 13 \text{ mV}$). A full titration (~ 25 points) takes about 20 minutes. The electrodes used to measure the EMF of the sample consisted of a ROSS glass pH electrode (Orion, model 810100) and a double junction Ag, AgCl reference electrode (Orion, model 900200).

An integrated program controls the titration, data collection, and the calculation of the carbonate parameters (TA, pH, and TCO_2) [Millero *et al.*, 1993b]. The program is

patterned after those developed by several others [Dickson, 1981; Johansson and Wedborg, 1982; Dickson *et al.*, 2007]. The program uses a Levenberg-Marquardt nonlinear least-squares algorithm to calculate E^0 , pH, TA, TCO_2 and pK^*_1 from the potentiometric titration data. A diagram of the system is shown in Appendix C.

2.1.3 Reagents

A single 50 L batch of ~ 0.25 M HCl acid was prepared in 0.45 M NaCl by dilution of concentrated HCl, AR Select, Mallinckrodt, to yield a total ionic strength similar to seawater of salinity 35.0 ($I \approx 0.7$ M). The acid was standardized and verified with alkalinity titrations on certified reference material (CRM). The calibrated normality of the acid used was 0.24361 ± 0.0001 N HCl. The acid was stored in 500-ml glass bottles sealed with Apiezon® M grease for use at sea.

2.1.4 Standardization

The volumes of the cells used were calibrated to ± 0.03 cm³ in port in San Diego, California before the start of the cruise by multiple titrations using Certified Reference Material (CRM) provided by Dr. Andrew Dickson, Marine Physical Laboratory, La Jolla, California. The certified values for the batches used are given in **Table 1** Error! Reference source not found. Calibrations of the burette of the Dosimat with water at 25°C indicate that the systems deliver 3.000 cm³ (the approximate value for a titration of seawater) to a precision of ± 0.0004 cm³, resulting in an error of ± 0.3 $\mu\text{mol}\cdot\text{kg}^{-1}$ in TA. The reproducibility and precision of measurements are checked using low nutrient surface seawater collected from the ship's flowing seawater system and CRMs. CRMs were utilized in order to account for instrument drift and to maintain measurement precision. Duplicate samples were collected from the same Niskin bottle and provided additional quality assurance. Duplicates were either measured on the same instrument, A or B, or measured one on each system.

Table 1. The assigned values of CRM batch 129, 149, and 159 provided by A. Dickson of SIO.

	Batch 129	Batch 146	Batch 159
<i>Parameter</i>	<i>Assigned Value</i>	<i>Assigned Value</i>	<i>Assigned Value</i>
Salinity	33.361	33.122	33.572
Total Alkalinity	2237.32 ± 0.52	2214.11 ± 0.68	2213.59 ± 0.59
Total Dissolved Inorganic Carbon	2016.65 ± 0.32	2002.92 ± 0.67	2027.14 ± 0.68
Phosphate	0.34	0.34	0.64
Silicate	4.1	1.8	5.5
Nitrite	0.00	0.01	0.00
Nitrate	0.83	0.22	3.4

*Al concentration in $\mu\text{mol Kg}^{-1}$, except salinity which is unitless.

2.2 Discrete pH Analyses

The pH is measured using an indicator dye and a spectrophotometer. In seawater there are several different definitions or scales for pH which complicates the measurement [Waters and Millero, 2013]. The three main scales used are the free scale (pH_F) which only includes the concentration of the free proton ($[\text{H}^+]_F$), the total scale (pH_T) defined as:

$$\text{pH}_T = [\text{H}^+]_F + [\text{HSO}_4^-] \quad (1)$$

and the seawater scale:

$$\text{pH}_{\text{sws}} = [\text{H}^+]_F + [\text{HSO}_4^-] + [\text{HF}] \quad (2)$$

The subscripts F, T, and SWS are used to distinguish between the different scales. All values reported here are on the seawater scale unless mentioned otherwise.

2.2.1 Sampling

At each station, samples were drawn directly from the Niskin bottles on the rosette into 50 cm^3 glass syringes using polycarbonate Luer-lock 3-way valves that fit directly on the petcock of the Niskin bottle. The syringes were rinsed a minimum of two times and filled while taking care not to entrain any bubbles. After collection the syringe was checked for bubbles and any found were ejected. The samples were thermostated at 25°C before analysis and measured within 6 hours of collection.

2.2.2 Analyzer Description

Measurements of the pH of seawater, on the total scale (pH_T) were first made using multi-wavelength spectrophotometric techniques and equations of *Clayton and Byrne* [1993] and *Liu et al.* [2011], which were calibrated using TRIS buffers [*Ramette et al.*, 1977]. The values were then converted to the seawater scale (pH_{sw}) using the dissociation constants of H_2SO_4 [*Dickson*, 1990] and HF [*Dickson and Riley*, 1979]. The Sulphonphthalein indicator m-cresol purple (mCp) was used to make the pH measurements using the methods of *Clayton and Byrne* [1993] as modified by *Lee et al.* [1996] and *Liu et al.* [2011]. The system is patterned after the standard operating procedure developed by the U.S. Department of Energy (DOE) [*Dickson et al.*, 2007] and is similar to the system devolved by *Carter et al.* [2013]. The automated system performs discrete analysis of pH on samples approximately every 7 minutes using a total of 40 cm^3 of sample. The syringes are stored in a water bath at 25°C to maintain a constant temperature. A refrigerated circulating temperature bath (Neslab, model RTE-10) regulates the temperature of the sample at $25 \pm 0.05^\circ\text{C}$. A microprocessor controlled syringe pump (Kloehn V6) with a 10 cm^3 syringe and sampling valve aspirates and injects the seawater sample into the 10 cm micro-volume optical cell (Starna Cells, Inc.) at a precisely controlled rate. The syringe pump rinses and primes the optical cell with 20 cm^3 of sample and the software permits 80 seconds for temperature stabilization. An Agilent 8453 UV/VIS spectrophotometer measures background absorbance of the sample. The automated syringe pump and sampling valves aspirates $\sim 9.08 \text{ cm}^3$ seawater and $\sim 0.02 \text{ cm}^3$ of indicator and injects the mixture into the cell. After the software permits 80 seconds for temperature stabilization, a Fluke 1523 digital platinum resistance thermometer measures the temperature, the spectrophotometer acquires the absorbance at 434, 578, 730, and 488 nm, and the pH_{sws} is calculated. The full spectra from 190-900 nm at 1 nm intervals are also archived. A diagram of the system is shown in appendix D.

A 300 mL batch of mCp indicator was used for the entire cruise. The solid purified indicator was obtained from Dr. Robert H. Byrne (University of South Florida, St. Petersburg, FL). The indicator was prepared and calibrated to have an $R \approx 1.6$ in the lab before the cruise.

The addition of indicator slightly perturbs the pH of the sample. To account for this an indicator correction must be made. This is done by making additional measurements on a subset of the samples (approximately 1 per station), in which the sample is measured a second time using twice the amount of indicator. It was insured that the entire pH range was adequately covered over the course of the cruise. The change in the absorbance ratio (ΔR) was then determined by fitting the measurements to the following equation:

$$\Delta R = A + BR \quad (3)$$

where R is the absorbance ratio from a single addition of indicator. The corrected absorbance ratio (R_{corr}) is then calculated using:

$$R_{\text{corr}} = R + (A + BR) * (A_{488} - A_{730}) \quad (4)$$

The absorbance at the isosbestic point (488 nm) is used instead of the volume of the indicator, as was done by *Clayton and Byrne* [1993], because it is more precise than assuming a constant volume of indicator has been added. For P18 the value of $A = 0.0312$ and $B = -0.0409$.

3. Accuracy and Precision of Measurements

The accuracy and precision of both measurements was checked using several different methods. For TA CRMs were used to determine accuracy. For pH there is no certified standard, but CRMs were also measured and compared to the values calculated from the certified TA and TCO_2 values. The precision of the total alkalinity was checked using low nutrient surface seawater collected in 20 L batches as needed from the ship's flowing seawater system. A TRIS buffer was also used to check the precision of the pH samples. For both total alkalinity and pH, duplicates were measured on each station to check precision. Details of the results are given in the following sections.

3.1 Total Alkalinity Accuracy and Precision

Several methods were used to determine the accuracy and precision of the total alkalinity measurements. A comparison of measured values of TA made on CRMs during the cruise are given in **Table 2**. The differences between the measured values of TA, TCO_2 and pH are shown in **Figure 1-Figure 3**. Values of TCO_2 and pH from CRM bottles obtained from the DIC group after their analysis are not reported due to probable loss of CO_2 after opening. This consists of all bottles from batch 159.

The precision in the measured values of TA, TCO_2 and pH are reasonable. The average measured value for TA is in good agreement with the assigned value. The measured values of TCO_2 are higher than the assigned value as found in previous studies [*Millero et al.*, 1993b].

Table 2. Comparison of the measured TA ($\mu\text{mol}\cdot\text{kg}^{-1}$) with the values of CRM from Cell A and B during the cruise.

P18 TA CRM Results					
<i>Batch</i>	<i>Cert. Value</i>	<i>Mean</i>	<i>Stdev</i>	<i>Number</i>	Δ (<i>Meas</i> – <i>CRM</i>)
Cell A					
129	2237.32	2234.69	1.11	5	-2.63
146	2214.11	2215.33	1.95	48	1.22
159	2213.59	2211.39	2.45	57	-2.2
All			2.78	110	-0.73
Cell B					
129	2237.32	2236.14	3.32	6	-1.18
146	2214.11	2215.24	2.11	50	1.13
159	2213.59	2212.04	2.43	50	-1.55
All			2.81	106	0.02

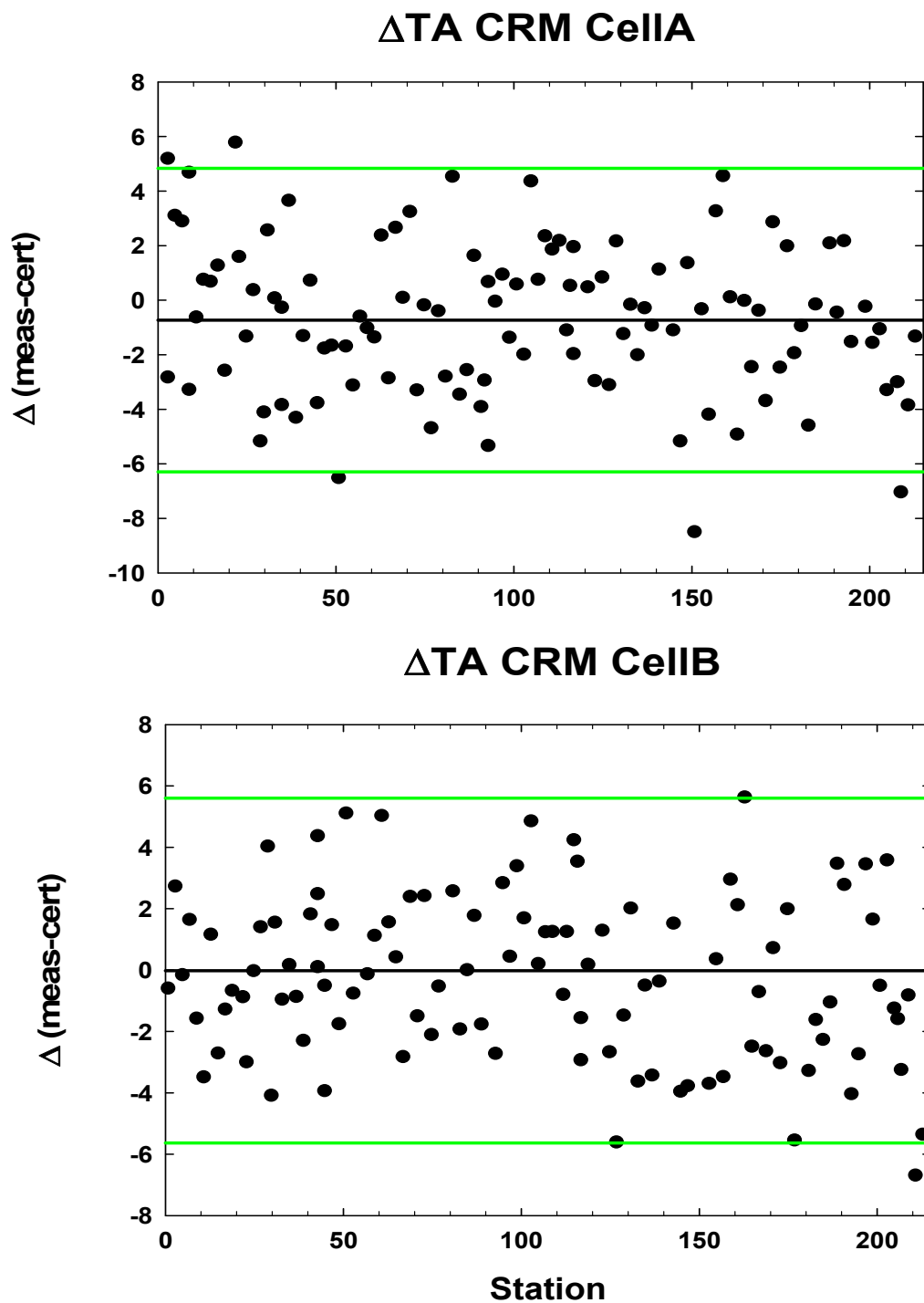


Figure 1. The difference (Δ) between the measured TA ($\mu\text{mol}\cdot\text{kg}^{-1}$) and the certified values of batches 129, 146, and 159 (see Table 1). The green lines are 2 standard deviations from the means (black lines, see).

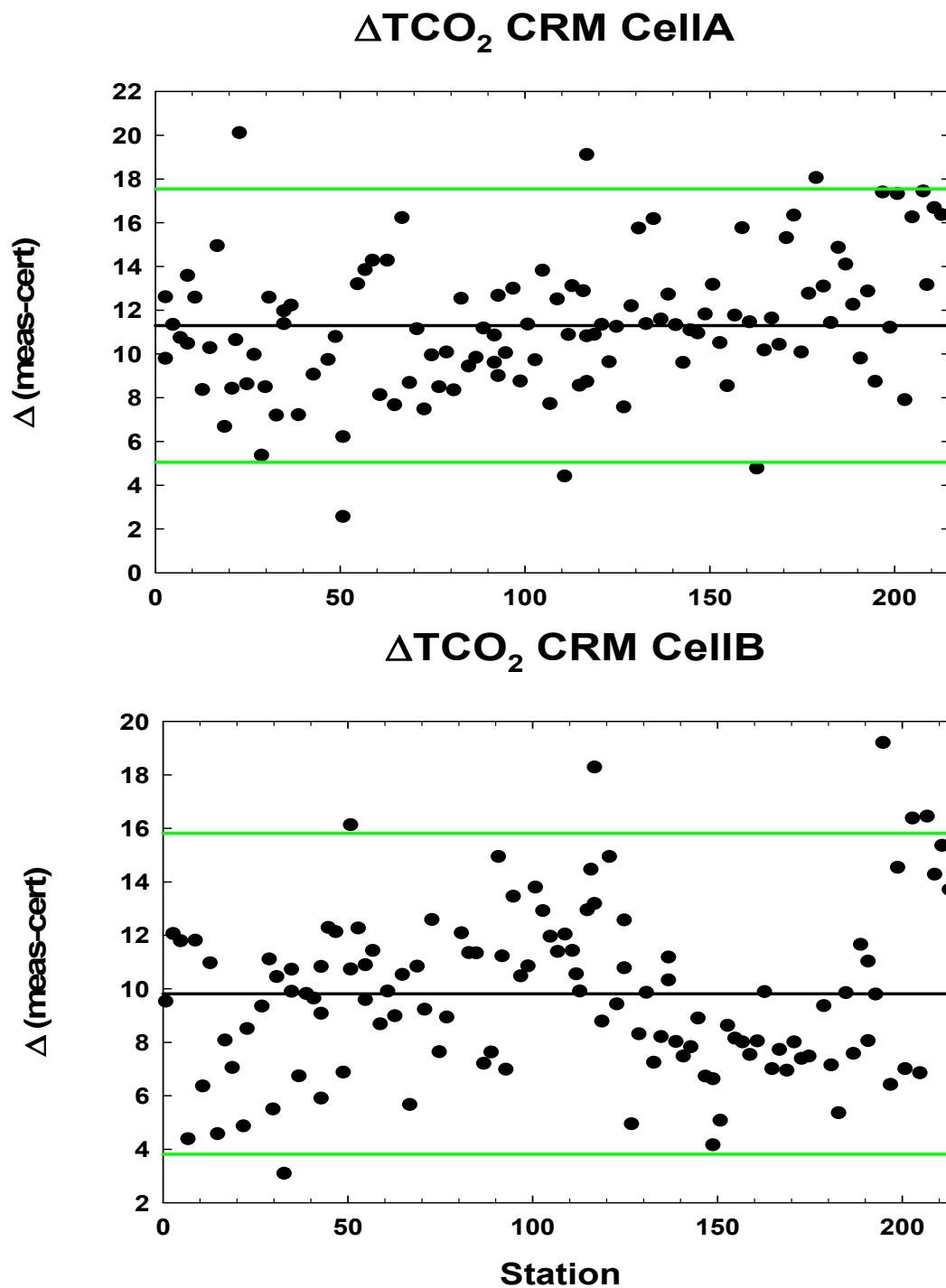


Figure 2. The difference between the measured potentiometric TCO_2 ($\mu\text{mol}\cdot\text{kg}^{-1}$) and the certified reference value. The standard deviations are ± 3.12 and ± 3.00 $\mu\text{mol}\cdot\text{kg}^{-1}$ for cell A and B, respectively. The green lines are 2 standard deviations from the means (black lines).

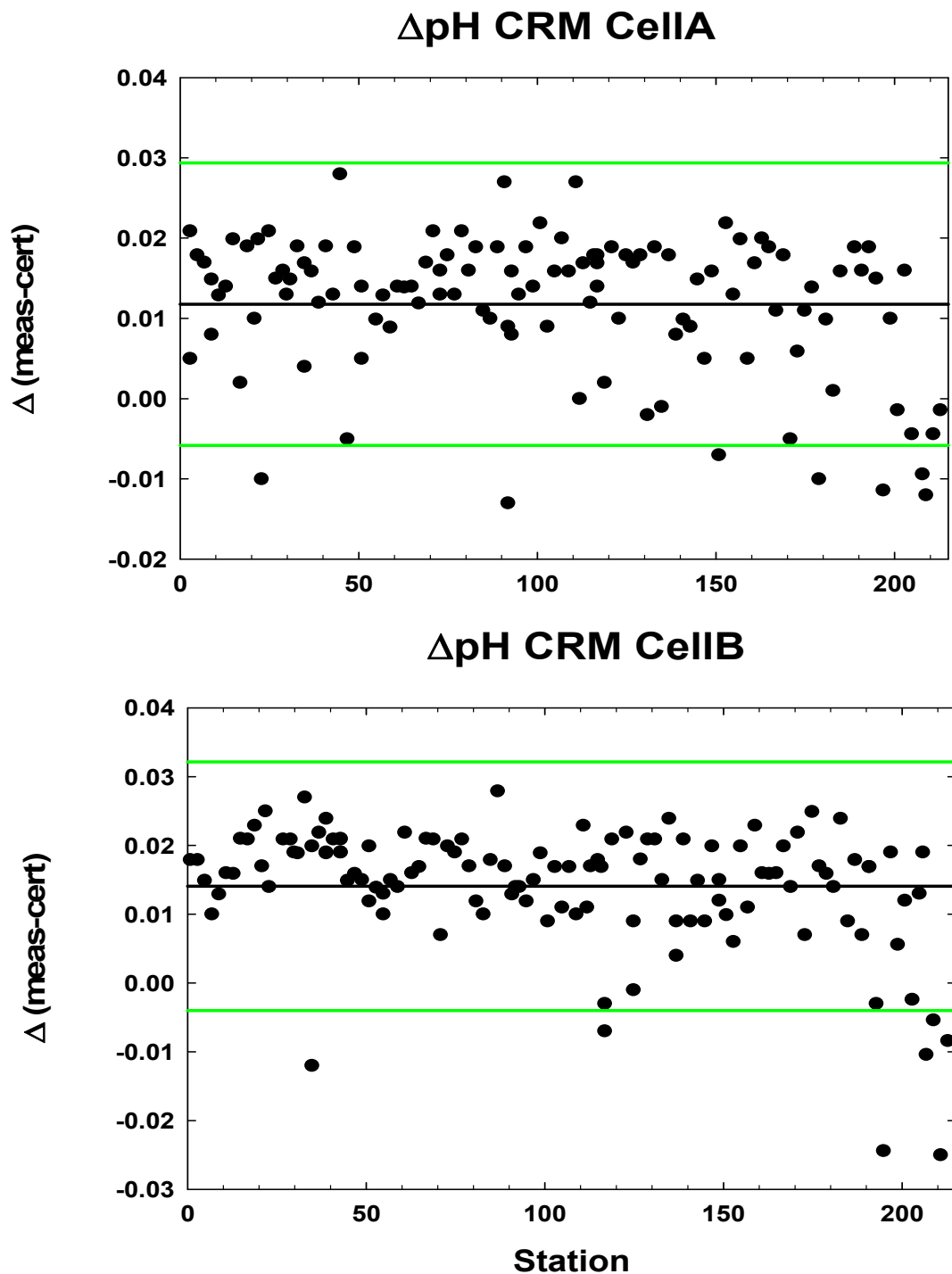


Figure 3. The differences between the measured potentiometric pH and values calculated from the certified TA and TCO_2 . The standard deviations are ± 0.0088 and $\pm 0.0090 \mu\text{mol}\cdot\text{kg}^{-1}$, respectively for the Cell A and Cell B. The green lines are 2 standard deviation from the means (black lines).

For P18 the offset in Cells A and B was ~ 0.009 . This has been found in earlier studies and is probably related to the non-Nernstian behavior of the electrodes or absorption of atmospheric CO_2 once the bottle is open. Thus, an adjustment was made to all potentiometric pH values by calibrating the cell with known CRM pH values calculated from the TA and TCO_2 CRM values. The average difference between the titration pH and the CRM value (**Figure 3**) were used to correct for the potentiometric pH measurements of the samples.

Seven batches of low nutrient surface seawater were used on P18. The precision (standard deviation) was approximately $2 \mu\text{mol}\cdot\text{kg}^{-1}$ for most batches with some closer to $1 \mu\text{mol}\cdot\text{kg}^{-1}$.

The reproducibility of the measurements was also checked by comparing the results of both systems on seawater sampled from the same Niskin bottle. The results of measurements for the duplicate samples, both measured on the same instrument, and one on each system (Cells A and B) are given in **Table 4** and **Figure 4** **Figure 6**. The measurements of TA with the same Niskin bottle measured on each cell agreed to less than $\pm 3 \mu\text{mol}\cdot\text{kg}^{-1}$ (stdev), while those where both were measured on the same cell agreed to less than $\pm 2 \mu\text{mol}\cdot\text{kg}^{-1}$. The TCO_2 was slightly higher at $\pm 2\text{-}3.5 \mu\text{mol}\cdot\text{kg}^{-1}$. The values of pH agreed to about ± 0.007 . These results are typical precisions for at sea measurements using this method.

Table 3. Comparison of duplicate measurements of TA ($\mu\text{mol}\cdot\text{kg}^{-1}$), TCO_2 ($\mu\text{mol}\cdot\text{kg}^{-1}$) and pH determined from the closed cell TA titration systems.

		Cell A	Cell B	Cell (A-B)
TA ($\mu\text{mol}\cdot\text{kg}^{-1}$)	Mean	0.56	0.19	-0.24
	Stdev	1.87	1.89	2.79
	N	195	176	198
TCO_2 ($\mu\text{mol}\cdot\text{kg}^{-1}$)	Mean	1.43	0.23	2.26
	Stdev	2.33	2.31	3.65
	N	192	187	204
pH	Mean	-0.003	-0.0001	-0.002
	Stdev	0.006	0.0046	0.007
	N	193	188	205

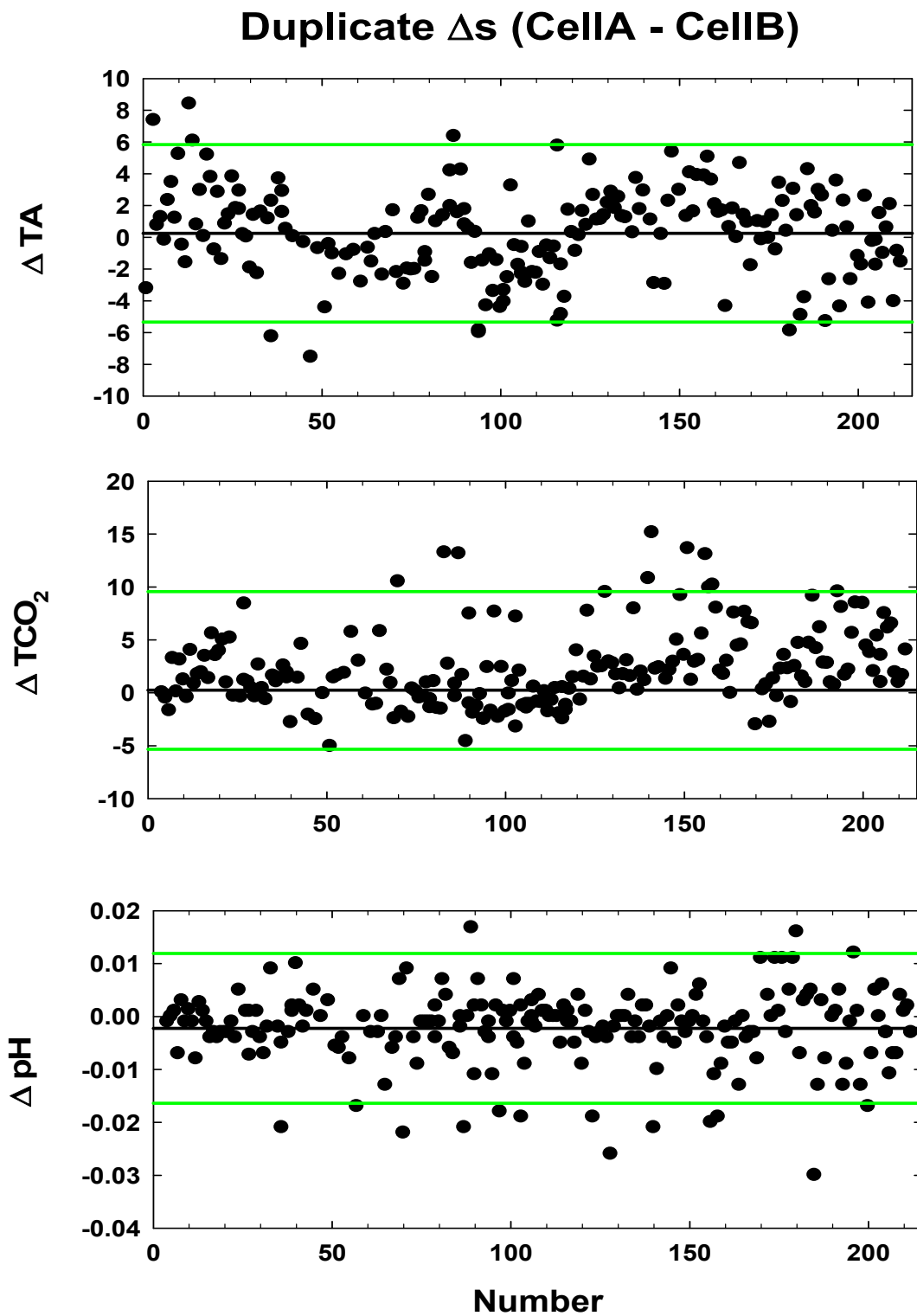


Figure 4. Precision of TA ($\mu\text{mol}\cdot\text{kg}^{-1}$), TCO₂ ($\mu\text{mol}\cdot\text{kg}^{-1}$) and pH duplicate measurements between Cells A and B. The green lines are 2 standard deviations from the means (black lines).

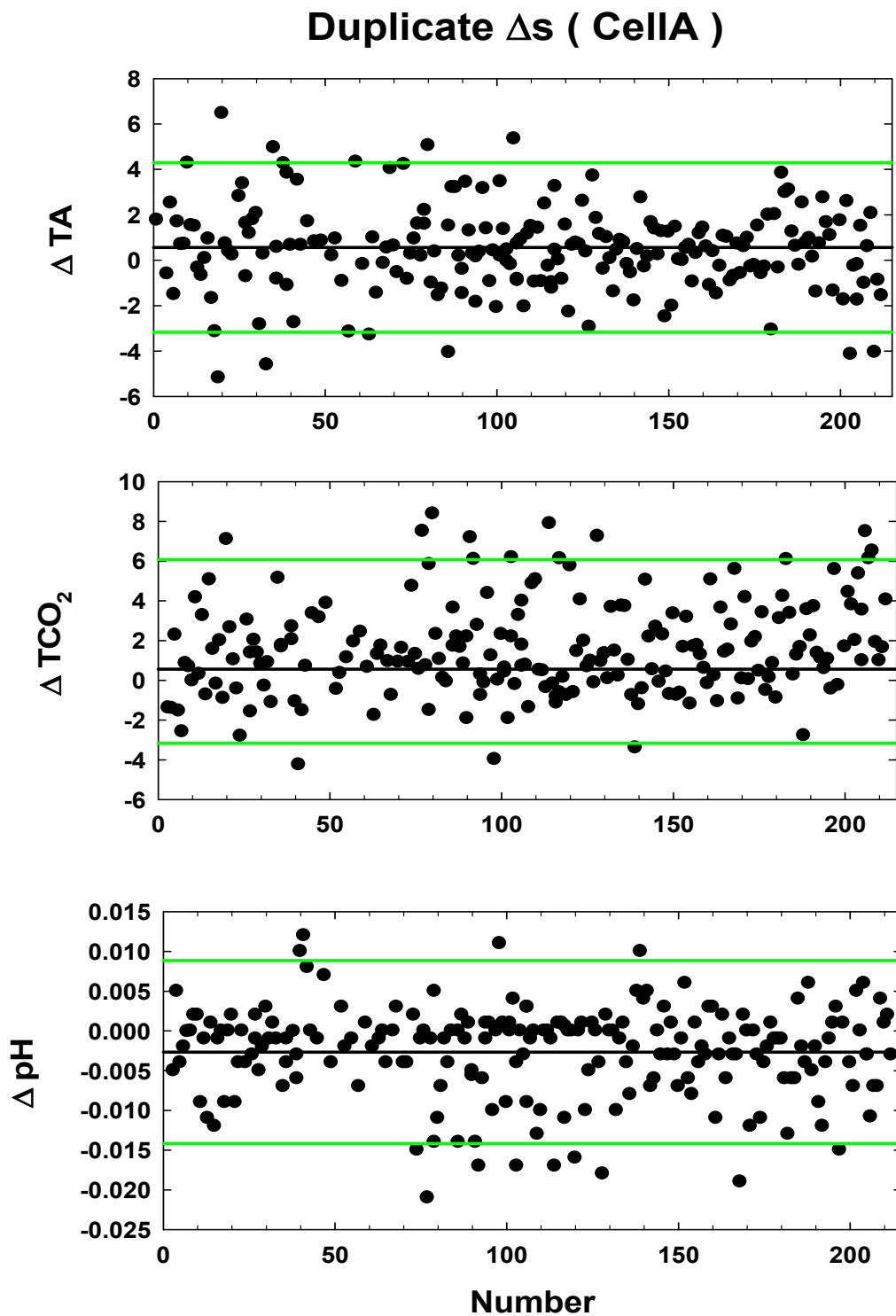


Figure 5. Precision of TA ($\mu\text{mol}\cdot\text{kg}^{-1}$), TCO₂ ($\mu\text{mol}\cdot\text{kg}^{-1}$) and pH duplicates on Cell A. The green lines are the 2 standard deviations from the means (black lines).

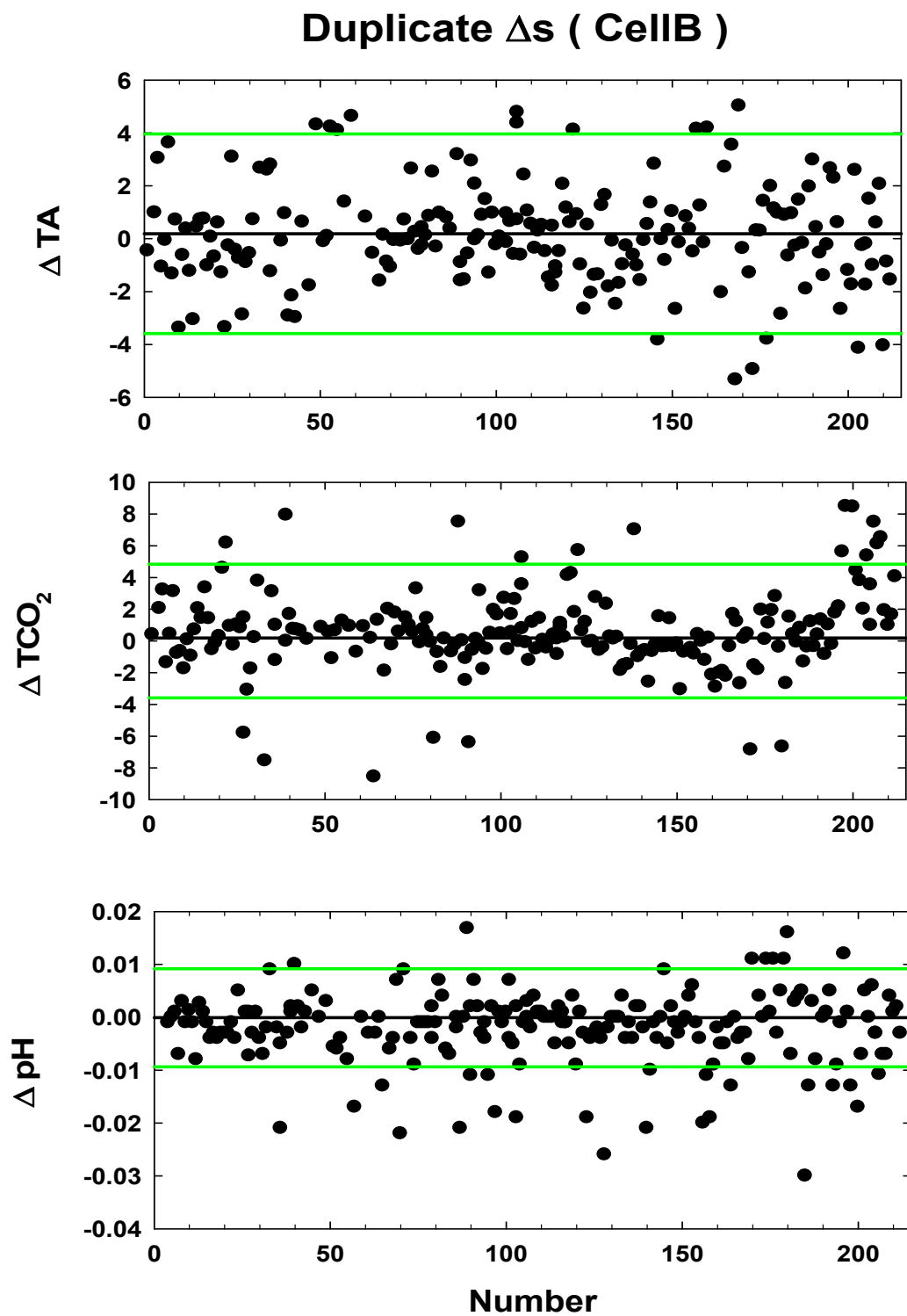


Figure 6. Precision of TA ($\mu\text{mol}\cdot\text{kg}^{-1}$), TCO_2 ($\mu\text{mol}\cdot\text{kg}^{-1}$) and pH duplicates on Cell B. The green lines are the 2 standard deviations from the means (black lines).

The NOAA group also measured TCO₂ using the more precise and accurate SOMMA method, which uses coulometry. The difference in the corrected potentiometric values of TCO₂ with the values determined by SOMMA is shown in **Figure 7**. The mean difference is $5.65 \pm 3.77 \mu\text{mol}\cdot\text{kg}^{-1}$ (N = 4963). The offset of the mean from zero indicates the constant offset correction determined from the CRM values does not fully correct for the bias in the potentiometric TCO₂ measurements.

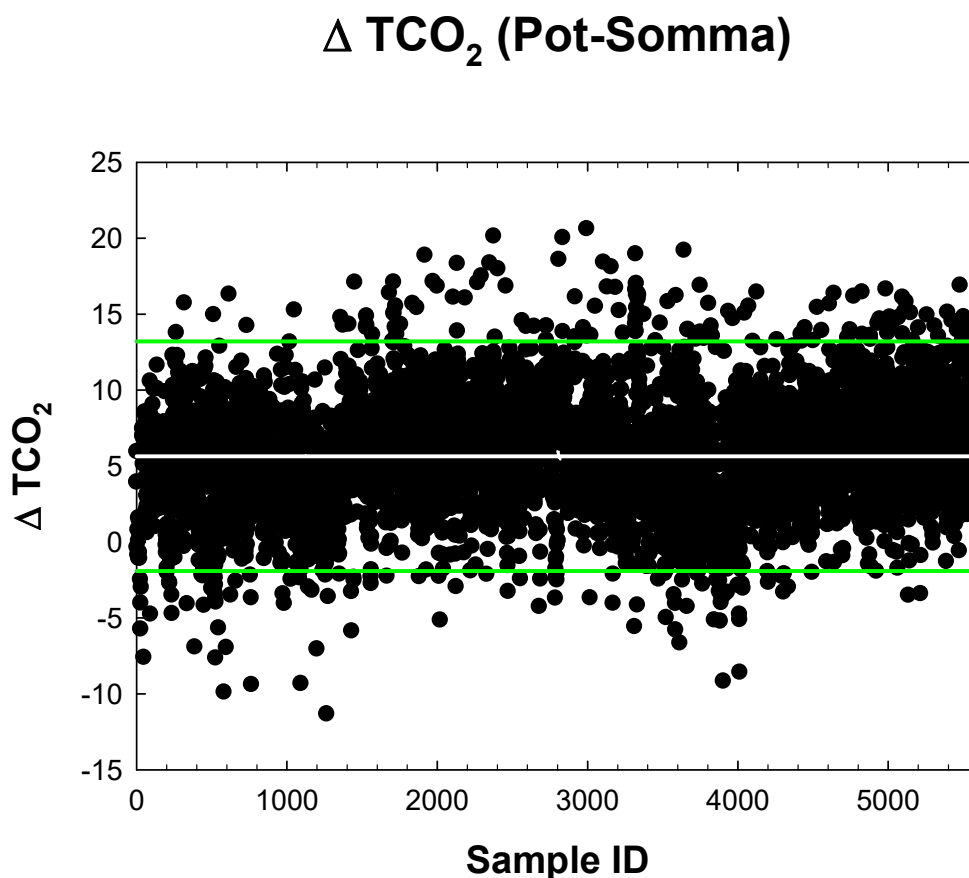


Figure 7. Difference between the TCO₂ ($\mu\text{mol}\cdot\text{kg}^{-1}$) measured by SOMMA and potentiometry. The green lines are the 2 standard deviations from the mean (white line).

4. Discrete pH Accuracy and Precision

The reproducibility of the spectrophotometric pH system was monitored throughout the cruise by making measurements on CRM, TRIS buffer, and duplicates of the same sample. The results are given in **Table 4**. Batch 129 was found to have an unstable pH and the results are not included here. The cause of the instability in Batch 129 is unknown but may be a result of contamination of CO₂ during the long storage time (it was bottled in 2013). The standard deviation of the measurements from Batch 146 is reasonable, and within the uncertainties. The CRM measurements from Batch 146 are shown in **Figure 8**.

An 8 L batch of TRIS buffer was prepared in the lab before the cruise according to the recipe of [Millero *et al.*, 1993a]. This does not include any fluoride so values are reported on the total scale. The TRIS was stored in 500 cm³ borosilicate bottles sealed with ground glass stoppers and Apiezon® M grease. The Measurements of TRIS buffer throughout the cruise are shown in **Figure 9**. Measurements of the TRIS buffer were made in the lab before the cruise (8.0940 ± 0.0007 , N=4). The TRIS measurements during the cruise are higher than those on the cruise, indicating a small but measurable change in the buffer between preparation in the lab and measurement on the cruise. The standard deviation of the TRIS is lower than that of the CRMs, which might be expected for a buffered solution.

Typically, two duplicate samples from the same Niskin bottle were measured for each sample. The mean and standard deviation of the absolute value of the difference is given in **Table 4**, and is typical for this method. The difference between the first and second measurement (i.e. no absolute value) of the duplicate sample is shown in **Figure 10**.

Table 4. Accuracy and precision of spectrophotometric pH measurements using CRM and TRIS buffer.

	pH	Stdev	N
CRM 146	7.8952	± 0.0045	96
TRIS ^a	8.0970	± 0.0026	98
\Delta Duplicates	0.0015	± 0.0011	372

^a The TRIS does not include any Fluoride so value is reported on the total scale.

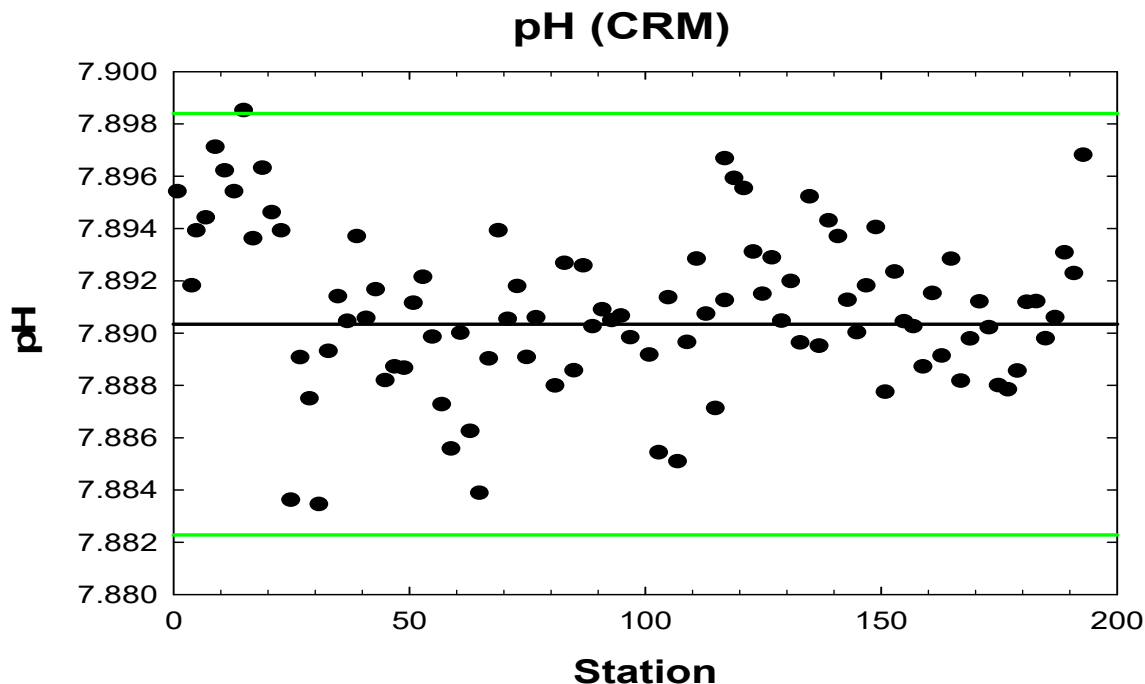


Figure 8. Measurements of pH from CRM Batch 146 measured every other station throughout the cruise. The greens lines are 2 standard deviations from the mean (black line).

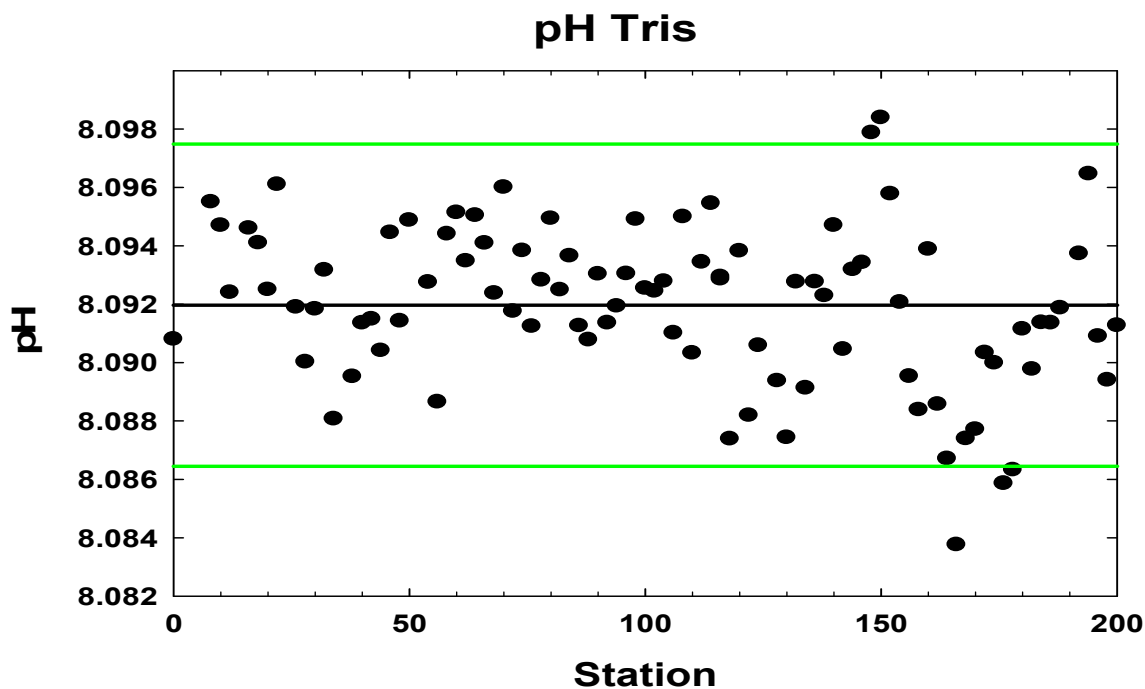


Figure 9. The pH measurements of TRIS buffer made at every other station throughout the cruise. The green lines are 2 standard deviations from the mean (black line).

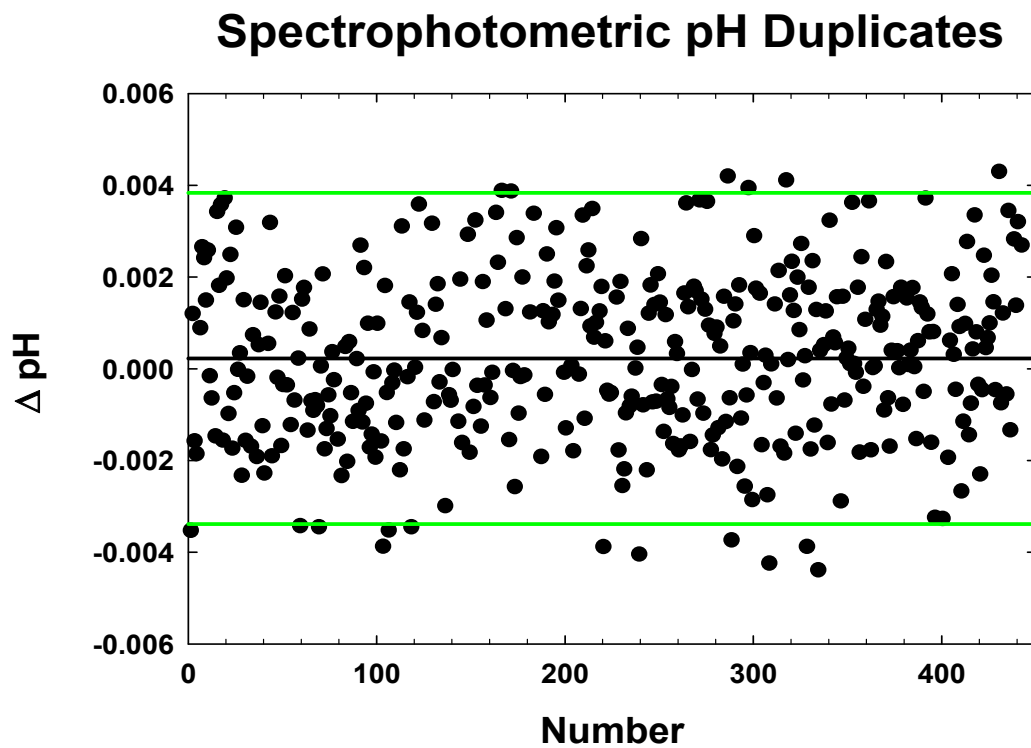


Figure 10. Precision of spectrophotometric pH measurements based on duplicate measurements. The green lines are 2 standard deviations from the mean (black line).

The pH values obtained by the two different methods (spec and potentiometric) were compared. The differences in the corrected potentiometric values of pH with the values determined by spectrophotometry are shown in **Figure 11**. The mean difference is -0.0024 ± 0.0095 ($N = 5326$). Although there appears to be a bias between the two methods it is within the uncertainty of the potentiometric measurements.

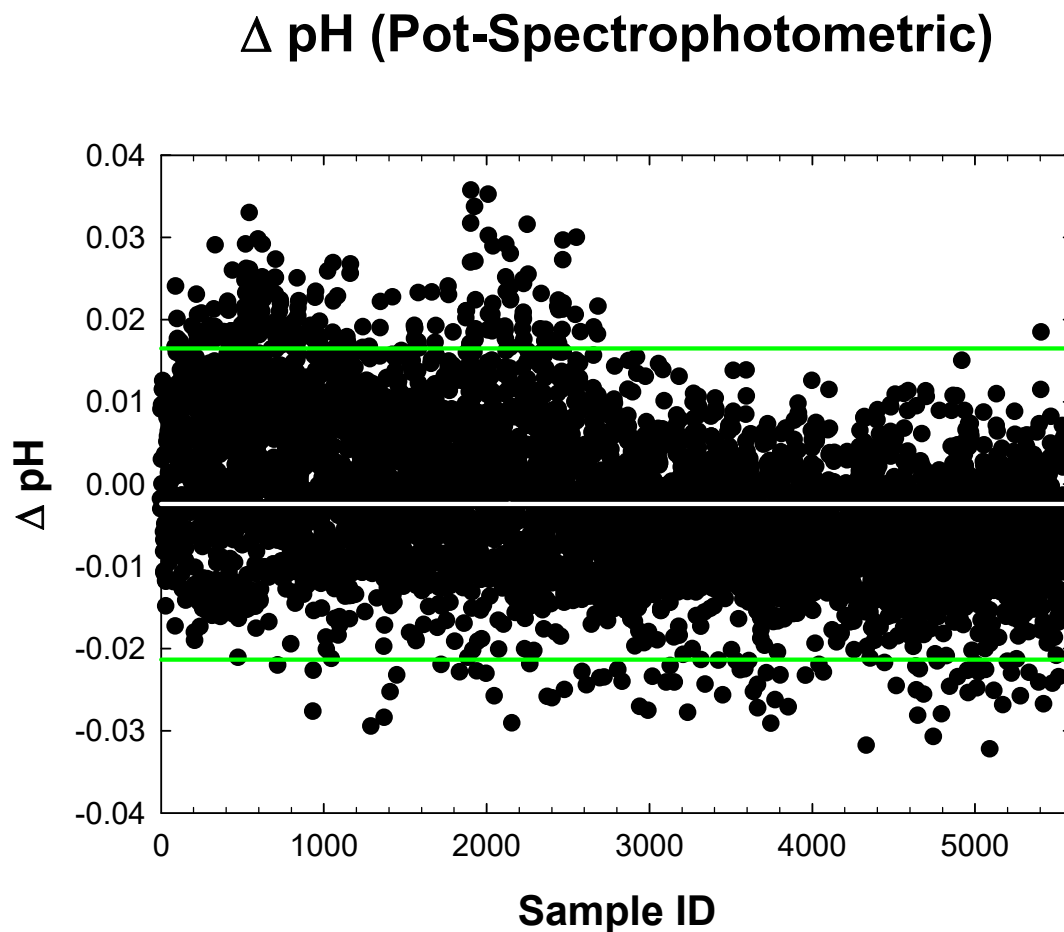


Figure 11. Difference between the pH measured by spectrophotometry and potentiometry. The green lines are 2 standard deviations from the mean (white line).

5. Internal Consistency

The carbonate system is characterized by four parameters: total alkalinity, total carbon dioxide, pH and partial pressure of CO₂ (pCO₂). Knowing two of these parameters, one can calculate the other two. If more than two parameters are known, a comparison of calculated and measured values can be used to examine the internal consistency of the system (i.e. how well measurements agree with theory). We have examined the internal consistency of our pH and TA measurements with the SOMMA values of TCO₂ measured by NOAA. The SOMMA data used for these calculations are the preliminary results submitted at the end of the cruise and not the final data. We used the Excel version 2.1 of CO₂sys program [Pierrot *et al.*, 2006] using the carbonic acid constants of Mehrbach *et al.* [1973] as refit by Dickson and Millero [1987] and Borate concentrations of Lee *et al.* [2010] for all calculations.

Since three parameters were measured on this cruise, each parameter was calculated using the other two. The results of these calculations are summarized in **Table 5** and the deviations are shown in **Figure 12** **Figure 14**.

Table 5. Difference between measured and calculated values of TA, pH, and TCO₂ (SOMMA).

Internal Consistency Summary				
Parameter	Input	Mean	Stdev	Number
ΔTA	pH, TCO ₂	-0.21	4.22	4898
ΔTCO_2	TA, pH	0.14	4.07	4898
ΔpH	TCO ₂ , TA	-0.0004	0.0103	4898

Δ TA (Measured-Calculated)

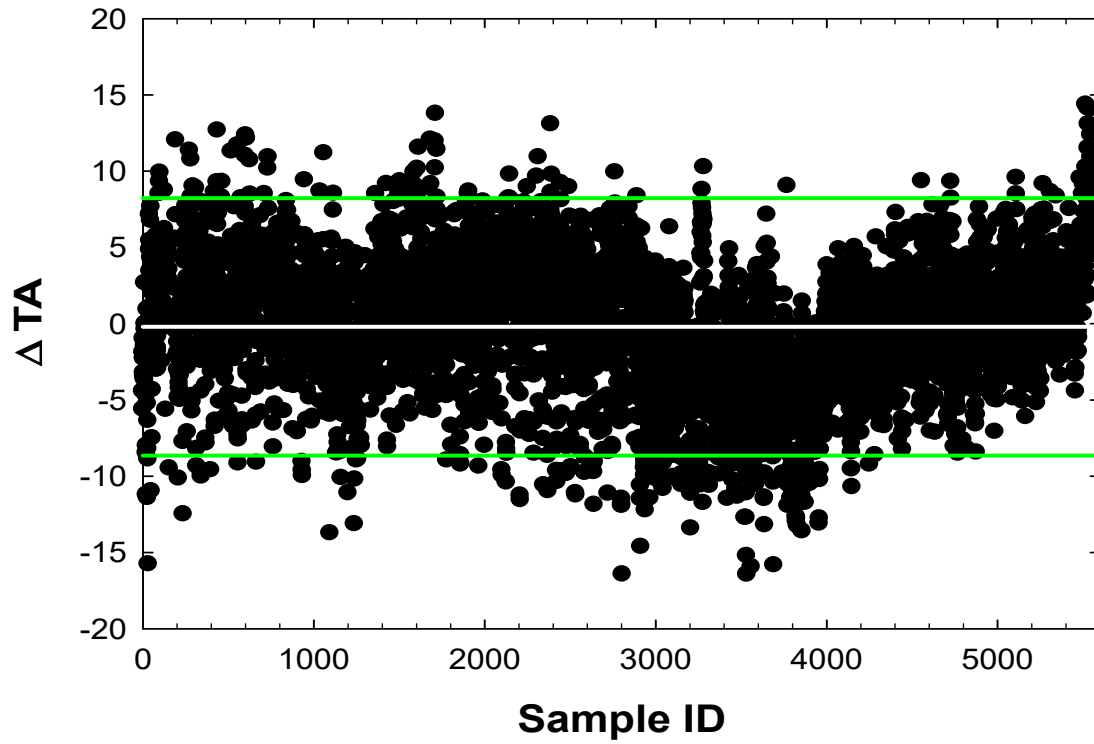


Figure 12. Difference between the measured and the calculated TA values. The green lines are 2 standard deviations from the mean (white line).

ΔTCO_2 (Measured-Calculated)

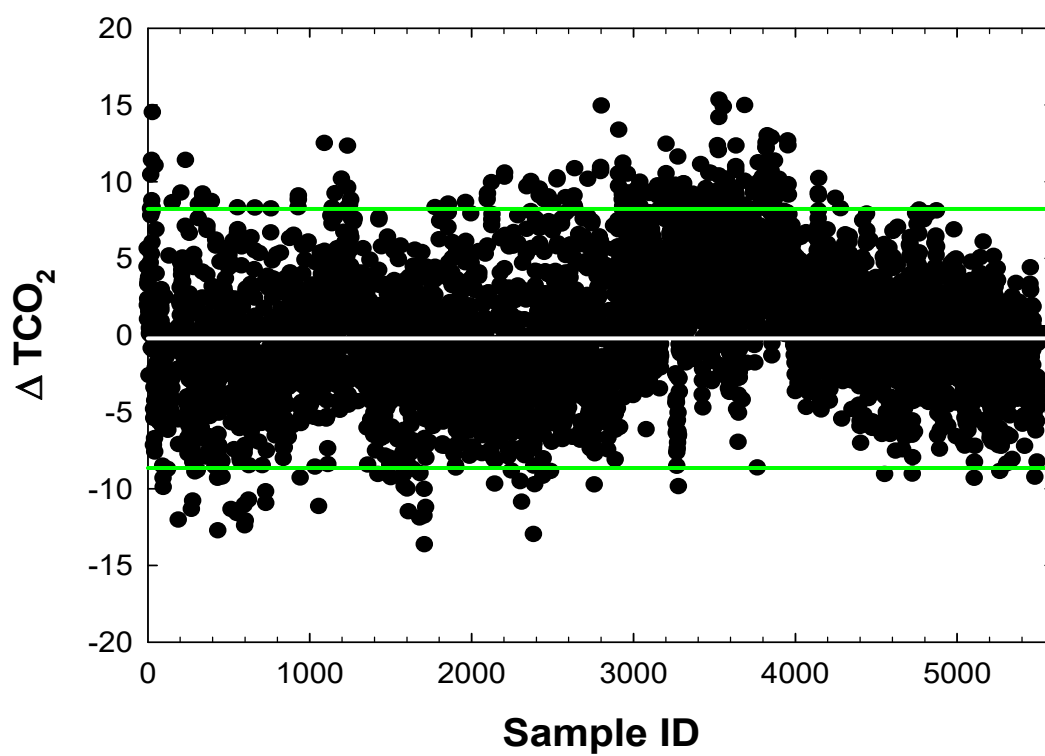


Figure 13. Difference between the measured and the calculated TCO_2 values. The green lines are 2 standard deviations from the mean (white line).

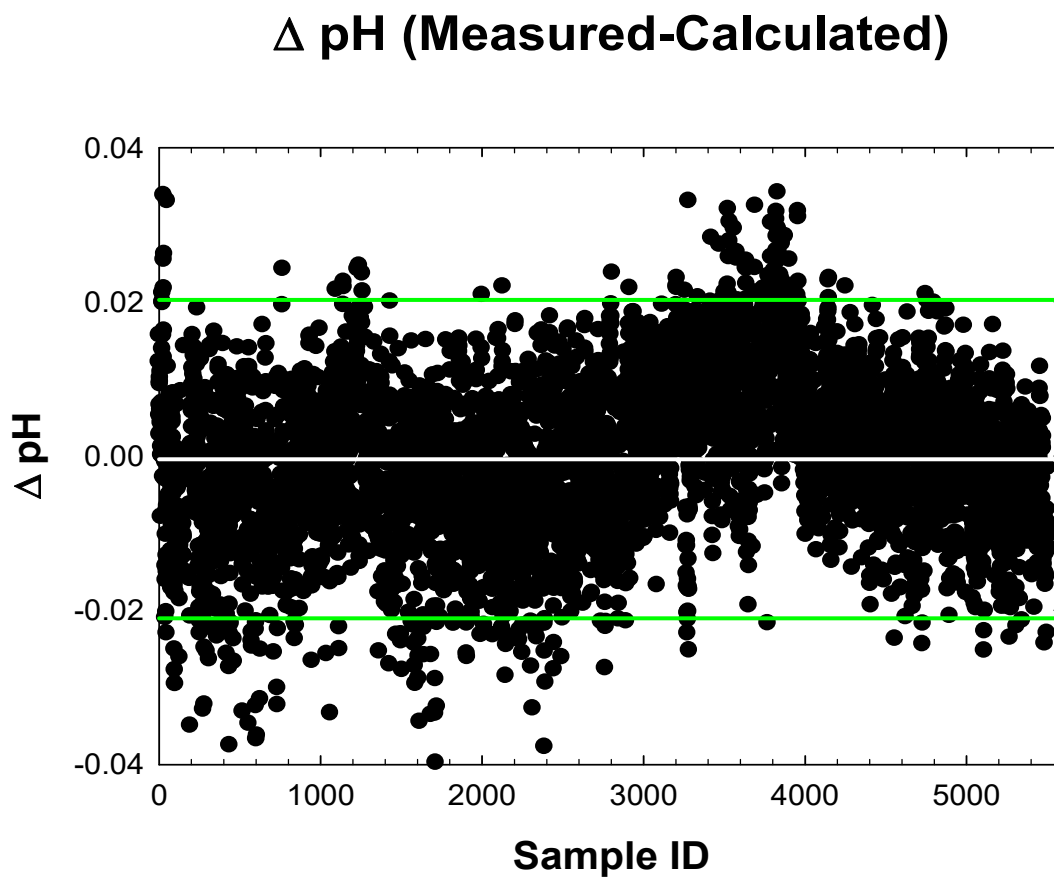


Figure 14. Difference between the measured and the calculated pH values. The green lines are 2 standard deviations from the mean (white line).

6. Distribution of the Carbon Parameters in Seawater Along the GO-SHIP P18 Track

The section profiles of spec. pH and TA are shown in **Figure 15**. The pH is on the seawater scale at 25°C. All sections were made using Ocean Data View [Schlitzer, 2016].

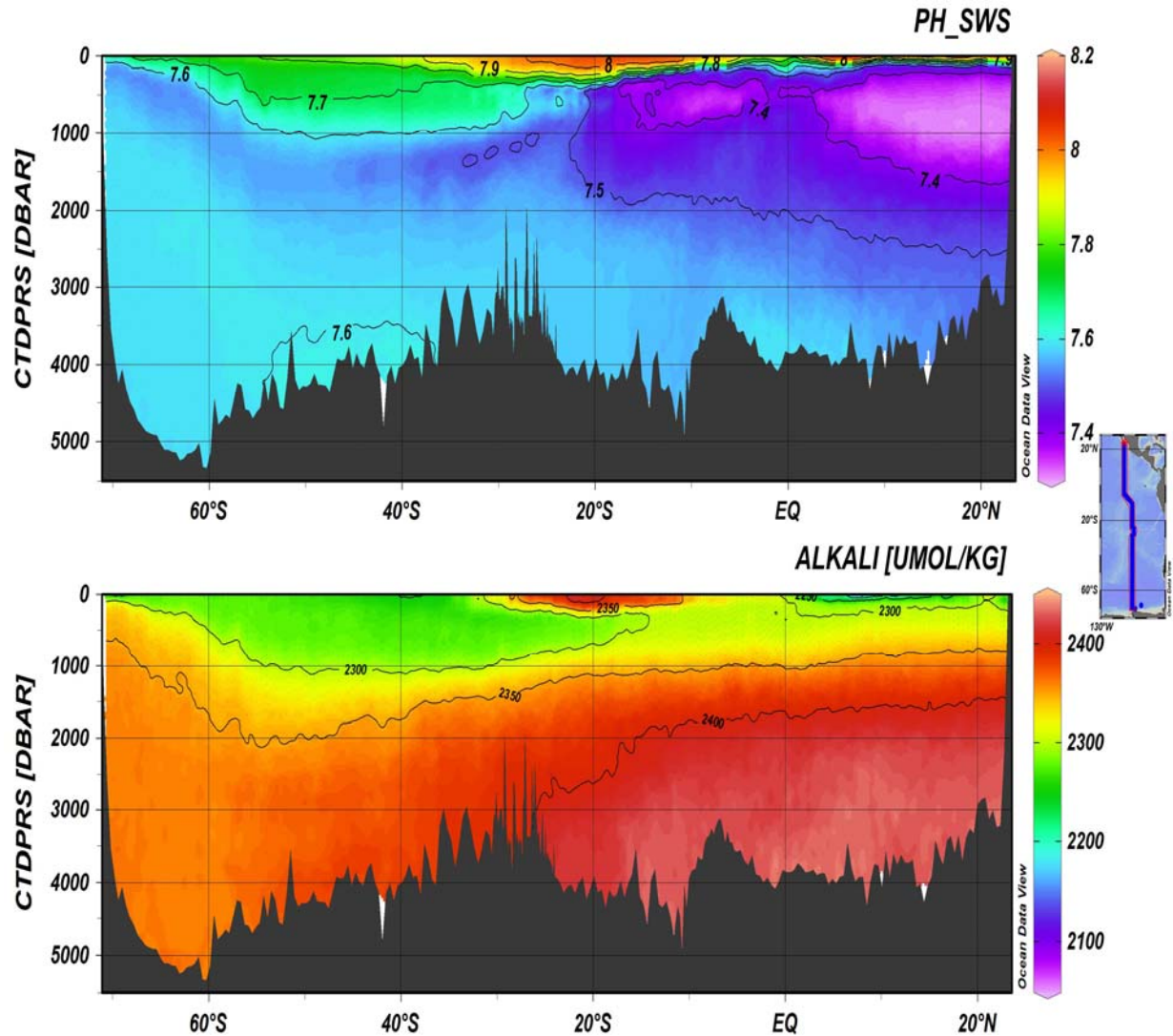


Figure 15. Entire cruise section of the pH (top) and Total Alkalinity (bottom).

7. Decadal Changes of the Carbon Parameters

The P18 line has now been occupied 3 times over the last 20 years. The first time was in 1994 as part of WOCE, then again in 2007-8 as part of CLIVAR, and finally this cruise in 2016-17 at part of GO-SHIP. Only the CLIVAR and GO-SHIP occupations will be considered here. The locations of the stations may not be exact repeats, but most are within several nautical miles. Differences in the salinity and oxygen measurements in the upper 1000 m collected along the P18 track in 2016-17 and 2007-8 are shown in **Figure 16**. Changes may be a result of changes in evaporation/precipitation, ocean circulation, or biologic processes. Differences below 1000 m are not significant. The differences in the measured pH and TA values between the two repeat sections for the full water depth are shown in **Figure 17**. Sections of only the upper 1000 m are shown in **Figure 18**. The greatest changes in pH (-0.05-0.1) occur at depths above 1000 m, as would be expected due to variation in biological productivity and anthropogenic input of CO₂, while generally TA remains nearly constant within $\pm 5 \mu\text{mol}\cdot\text{kg}^{-1}$ across the entire cruise section (with max differences of $\sim 10 \mu\text{mol}\cdot\text{kg}^{-1}$). Some areas in the surface show an increase in pH. These areas correspond to increases in oxygen indicating it may be caused by changes in biological activity.

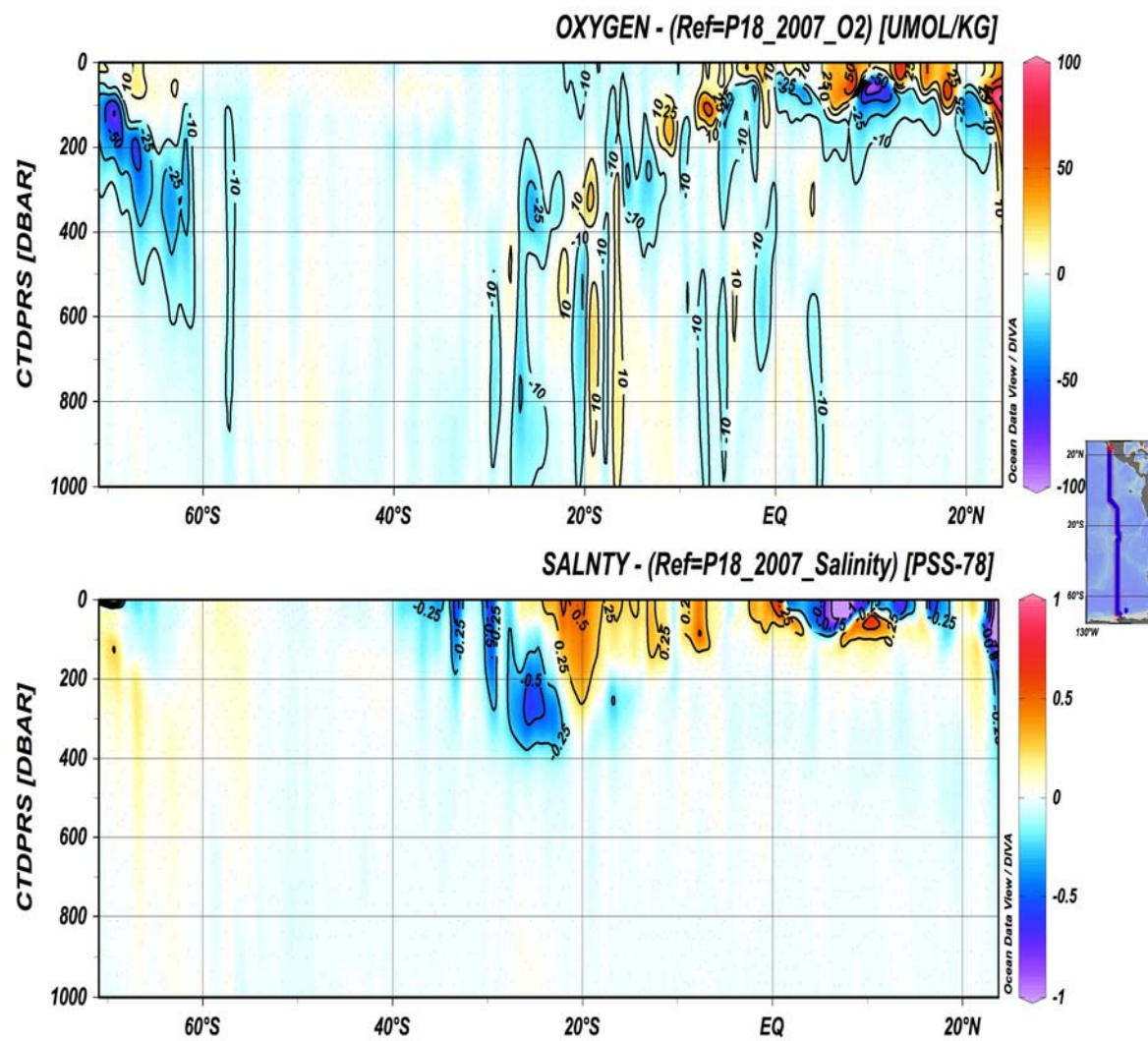


Figure 16. Decadal changes in oxygen and salinity in the upper 1000m measured during the P18 cruises between 2007-8 and 2016-17.

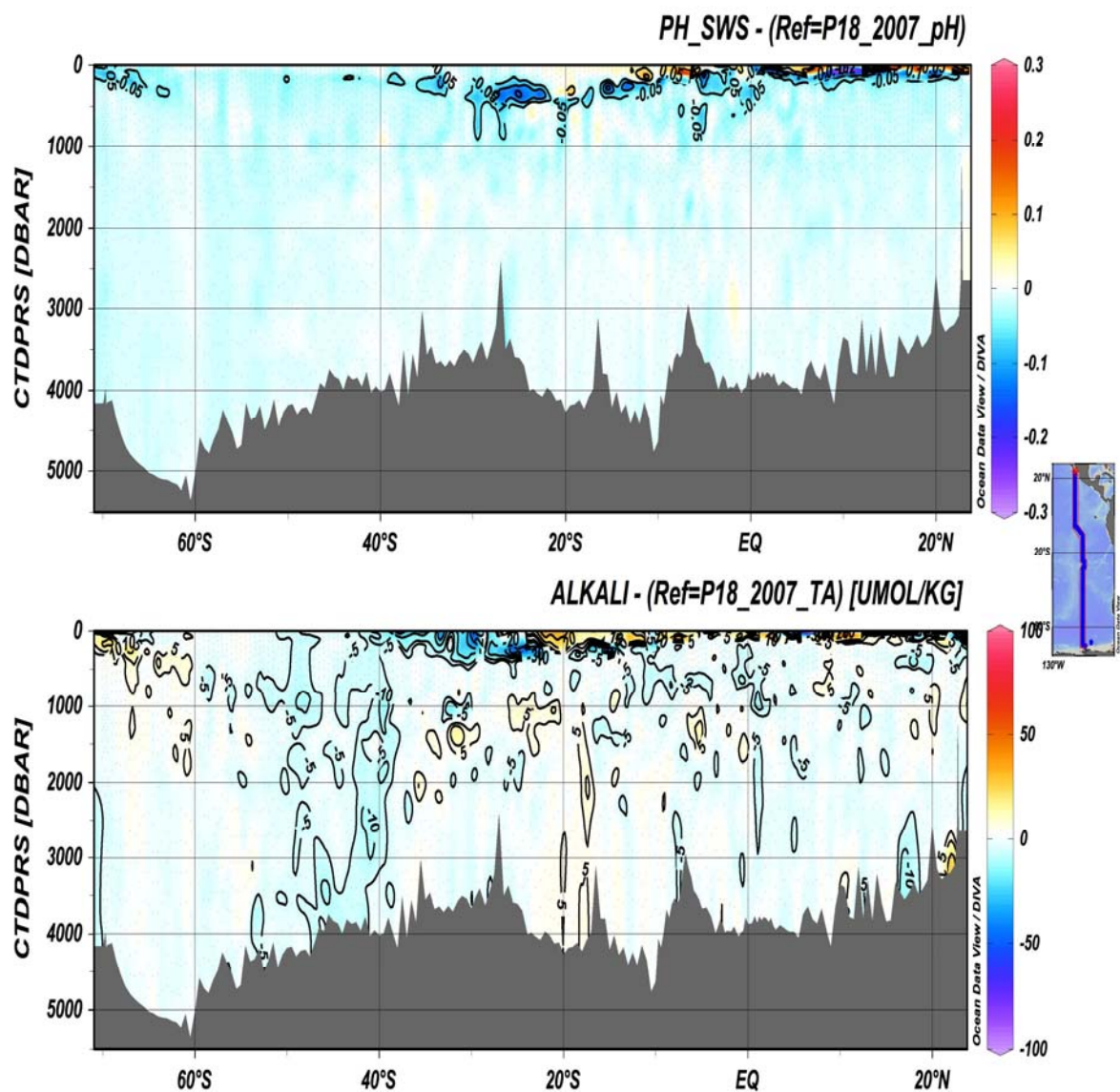


Figure 17. Decadal changes in pH (top) and Total Alkalinity (bottom) between the 2007-8 and 2016-17 occupations of P18.

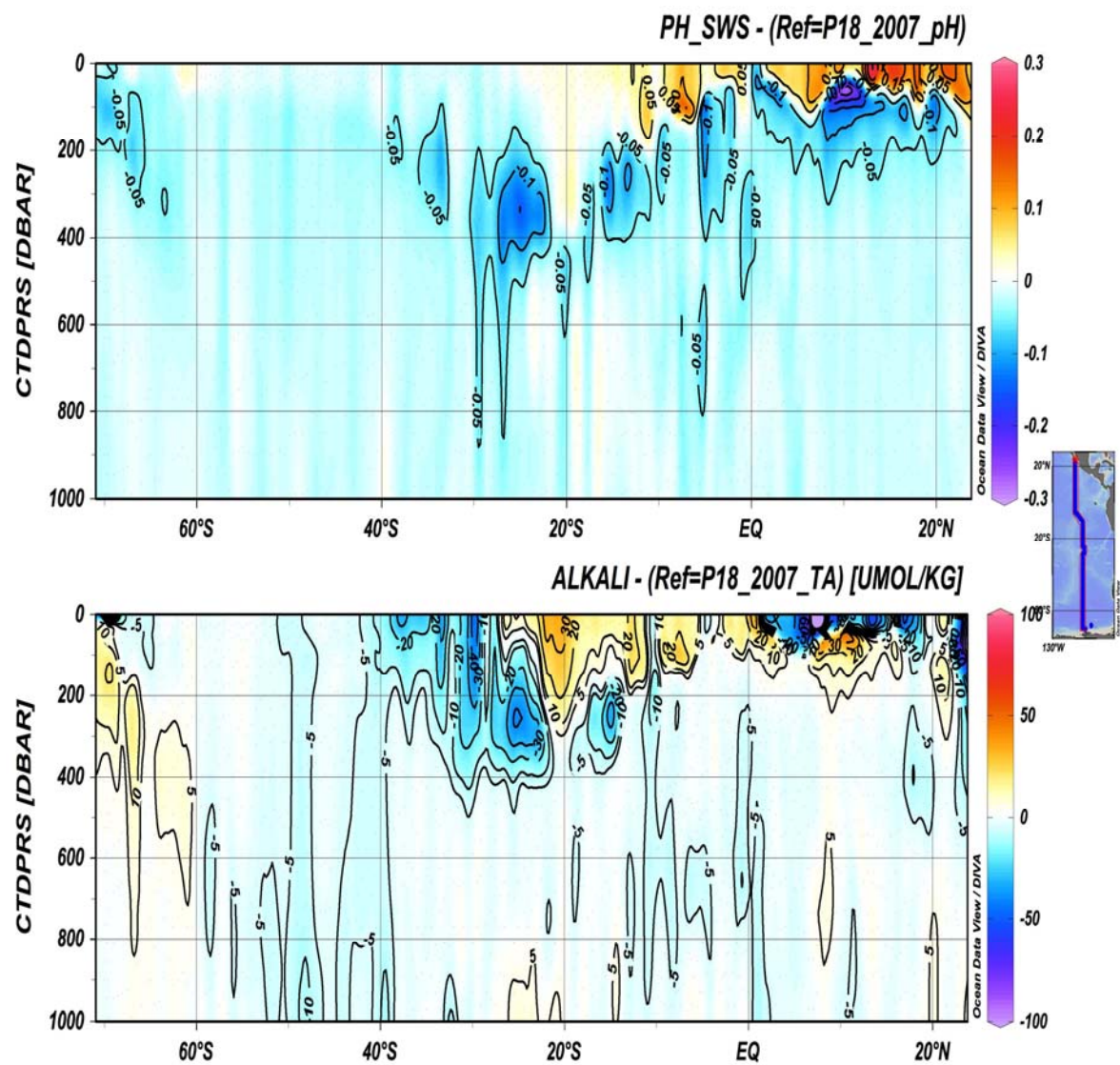


Figure 18. Decadal changes in the upper 1000m for pH (top) and Total Alkalinity (bottom).

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Appendices

Appendix A. Waypoint coordinates and bottom depth of the P18 2016/17 cruise.

P18				
Station	Date	Latitude	Longitude	Depth
1	11/24/2016	22.6880	-109.9982	2642
2	11/24/2016	22.8687	-110.0007	217
3	11/24/2016	22.7717	-110.0000	1256
4	11/25/2016	22.5022	-110.0005	3071
5	11/25/2016	22.0028	-109.9998	3182
6	11/25/2016	21.4988	-110.0002	3219
7	11/25/2016	20.9995	-110.0008	3293
8	11/25/2016	20.5002	-109.9990	3159
9	11/26/2016	19.9998	-109.9997	2541
10	11/26/2016	19.5002	-110.0002	3270
11	11/26/2016	19.0002	-109.9997	3416
12	11/26/2016	18.5070	-109.9997	3474
13	11/27/2016	18.0067	-109.9990	3315
14	11/27/2016	17.5192	-109.9983	3486
15	11/27/2016	16.9995	-110.0000	3551
16	11/27/2016	16.5048	-109.9992	3398
17	11/28/2016	16.0008	-110.0005	3327
18	11/28/2016	15.5012	-110.0012	3840
19	11/28/2016	15.0112	-110.0007	3799
20	11/28/2016	14.4997	-109.9995	3554
21	11/29/2016	14.0000	-109.9993	3160
22	11/29/2016	13.4997	-110.0003	3839
23	11/29/2016	13.0097	-110.0003	3289
24	11/29/2016	12.5137	-110.0012	3813
25	11/30/2016	12.0002	-109.9998	3261
26	11/30/2016	11.4998	-110.0005	3788

P18

Station	Date	Latitude	Longitude	Depth
27	11/30/2016	10.9993	-110.0000	3765
28	12/1/2016	10.5002	-110.0007	3177
29	12/1/2016	10.0003	-109.9997	3338
30	12/1/2016	9.5068	-109.9995	3621
31	12/1/2016	9.0000	-109.9987	4158
32	12/2/2016	8.5155	-109.9985	3927
33	12/2/2016	8.0057	-110.0010	3667
34	12/2/2016	7.5070	-110.0005	3843
35	12/2/2016	7.0222	-109.9997	3794
36	12/2/2016	6.5237	-109.9990	3641
37	12/3/2016	6.0025	-109.9987	3728
38	12/3/2016	5.5217	-109.9992	4048
39	12/3/2016	5.0000	-110.0000	3942
40	12/3/2016	4.5000	-110.0002	3958
41	12/4/2016	4.0492	-110.0002	3919
42	12/4/2016	3.5350	-109.9990	3870
43	12/4/2016	3.0272	-110.0003	3928
44	12/4/2016	2.7500	-110.0013	1440
45	12/5/2016	2.5005	-109.9998	3781
46	12/5/2016	2.2590	-110.0005	930
47	12/5/2016	2.0177	-110.0007	3796
48	12/5/2016	1.7515	-110.0005	871
49	12/5/2016	1.4997	-110.0003	3820
50	12/6/2016	1.2645	-110.0005	851
51	12/6/2016	1.0117	-110.0002	3850
52	12/6/2016	0.7588	-110.0008	909
53	12/6/2016	0.5263	-109.9998	3839
54	12/6/2016	0.2503	-109.9997	890
55	12/7/2016	0.0010	-110.0007	3861

P18

Station	Date	Latitude	Longitude	Depth
56	12/7/2016	-0.2487	-110.0025	829
57	12/7/2016	-0.4930	-110.0008	3952
58	12/7/2016	-0.7478	-109.9992	1363
59	12/7/2016	-0.9997	-109.9995	4019
60	12/8/2016	-1.2485	-110.0002	1351
61	12/8/2016	-1.4993	-109.9993	3890
62	12/8/2016	-1.7433	-110.0017	1440
63	12/8/2016	-1.9983	-109.9995	3948
64	12/8/2016	-2.2500	-110.0002	960
65	12/9/2016	-2.5007	-109.9998	3967
66	12/9/2016	-2.7492	-109.9998	1461
67	12/9/2016	-2.9993	-110.0012	3809
68	12/9/2016	-3.4972	-110.0010	3984
69	12/9/2016	-3.9882	-110.0008	3869
70	12/10/2016	-4.4947	-110.0008	3644
71	12/10/2016	-4.9728	-110.0005	3644
72	12/10/2016	-5.2788	-109.6065	3550
73	12/10/2016	-5.5860	-109.1862	3472
74	12/11/2016	-5.8753	-108.7680	3438
75	12/11/2016	-6.1773	-108.3548	3256
76	12/11/2016	-6.4622	-107.9517	3125
77	12/11/2016	-6.7507	-107.5422	3026
78	12/11/2016	-7.0587	-107.1220	3178
79	12/12/2016	-7.3408	-106.7232	3528
80	12/12/2016	-7.6452	-106.2965	3591
81	12/12/2016	-7.9400	-105.8817	3519
82	12/12/2016	-8.2377	-105.4745	3613
83	12/13/2016	-8.5233	-105.0698	3789
84	12/13/2016	-8.8157	-104.6562	3690

P18

Station	Date	Latitude	Longitude	Depth
85	12/13/2016	-9.1193	-104.2417	3975
86	12/13/2016	-9.4080	-103.8220	4176
87	12/14/2016	-9.7022	-103.4213	4089
88	12/14/2016	-9.9987	-103.0013	4631
89	12/14/2016	-10.4987	-103.0007	4758
90	12/14/2016	-10.9988	-103.0008	4347
91	12/15/2016	-11.4648	-103.0003	4144
92	12/15/2016	-11.9705	-103.0002	4442
93	12/15/2016	-12.4997	-102.9997	4228
94	12/15/2016	-12.9985	-103.0010	4411
95	12/16/2016	-13.4670	-103.0002	4172
96	12/16/2016	-13.9818	-103.0005	4276
97	12/16/2016	-14.4978	-103.0005	3995
98	12/16/2016	-14.9973	-103.0012	4261
99	12/17/2016	-15.4685	-103.0000	3781
100	12/17/2016	-15.9955	-103.0012	3808
101	12/17/2016	-16.4975	-103.0010	3145
102	12/17/2016	-16.9982	-103.0007	3972
103	12/18/2016	-17.4977	-103.0008	4082
104	12/18/2016	-17.9907	-103.0008	4237
105	12/18/2016	-18.4707	-103.0008	4104
106	12/18/2016	-18.9990	-103.0010	4147
107	12/19/2016	-19.4930	-103.0003	4159
108	12/19/2016	-19.9808	-102.9995	4284
109	12/19/2016	-20.4982	-103.0005	4104
110	12/19/2016	-20.9978	-103.0027	4125
111	12/20/2016	-21.4832	-103.0008	4010
112	12/20/2016	-21.9832	-103.0008	3964
113	12/20/2016	-22.4813	-103.0035	4062

P18

Station	Date	Latitude	Longitude	Depth
114	12/20/2016	-22.9962	-103.0020	4044
115	12/21/2016	-23.4957	-103.0000	3971
116	12/21/2016	-23.9650	-103.0000	3907
117	12/21/2016	-24.4737	-103.0047	3598
117	1/1/2017	-24.4737	-103.0047	3766
118	1/1/2017	-24.9930	-101.5150	3600
119	1/1/2017	-25.4873	-101.5008	3577
120	1/2/2017	-25.9907	-101.5020	3399
121	1/2/2017	-26.4862	-101.5012	3504
122	1/2/2017	-27.0003	-101.4988	2400
123	1/2/2017	-27.4993	-101.4992	3215
124	1/3/2017	-27.9902	-101.5012	3396
125	1/3/2017	-28.4988	-102.3287	3614
126	1/3/2017	-29.0985	-102.9997	3316
127	1/3/2017	-29.5005	-103.0007	3521
128	1/4/2017	-29.9815	-103.0012	3658
129	1/4/2017	-30.4997	-103.0000	3552
130	1/4/2017	-31.0010	-103.0013	3489
131	1/4/2017	-31.4963	-103.0012	3569
132	1/5/2017	-31.9892	-103.0013	3696
133	1/5/2017	-32.4983	-103.0013	3623
134	1/5/2017	-32.9982	-102.9975	3716
135	1/5/2017	-33.4997	-103.0002	3629
136	1/6/2017	-34.0010	-102.9992	3662
137	1/6/2017	-34.4952	-102.9983	3462
138	1/6/2017	-34.9995	-102.9975	3570
139	1/6/2017	-35.4987	-103.0002	3147
140	1/7/2017	-35.9843	-102.9987	3913
141	1/7/2017	-36.4968	-102.9982	3532

P18

Station	Date	Latitude	Longitude	Depth
142	1/7/2017	-36.9865	-102.9973	4070
143	1/7/2017	-37.4990	-102.9982	3517
144	1/8/2017	-37.9703	-103.0010	4193
145	1/8/2017	-38.4973	-103.0015	4033
146	1/8/2017	-38.9988	-103.0015	3878
147	1/8/2017	-39.5000	-103.0037	3986
148	1/9/2017	-40.0003	-103.0007	4013
149	1/9/2017	-40.4983	-103.0017	3929
150	1/9/2017	-40.9985	-103.0023	4075
151	1/10/2017	-41.4980	-103.0000	3780
152	1/10/2017	-41.9667	-103.0002	3932
153	1/10/2017	-42.4747	-103.0010	3825
154	1/10/2017	-42.9977	-103.0012	3865
155	1/11/2017	-43.4768	-103.0002	3799
156	1/11/2017	-44.0000	-103.0003	3996
157	1/11/2017	-44.4970	-103.0005	3860
158	1/11/2017	-44.9912	-102.9998	3891
159	1/12/2017	-45.4607	-103.0008	3739
160	1/12/2017	-45.9782	-102.9988	3969
161	1/12/2017	-46.4990	-102.9962	3913
162	1/12/2017	-47.0002	-102.9985	4136
163	1/13/2017	-47.4733	-102.9982	4301
164	1/13/2017	-47.9788	-103.0000	4245
165	1/13/2017	-48.5013	-102.9975	4233
166	1/14/2017	-48.9987	-102.9987	4272
167	1/14/2017	-49.4730	-102.9995	4215
168	1/14/2017	-49.9667	-102.9997	4177
169	1/14/2017	-50.4993	-103.0005	4263
170	1/15/2017	-50.9990	-103.0005	4449

P18

Station	Date	Latitude	Longitude	Depth
171	1/15/2017	-51.4872	-102.9985	4121
172	1/15/2017	-51.9993	-102.9988	4394
173	1/16/2017	-52.4988	-102.9985	4490
174	1/16/2017	-52.9848	-102.9983	4215
175	1/16/2017	-53.4965	-102.9980	4345
176	1/17/2017	-53.9972	-102.9987	4374
177	1/17/2017	-54.4598	-102.9992	4216
178	1/17/2017	-54.9642	-102.9990	4687
179	1/17/2017	-55.4930	-102.9983	4722
180	1/18/2017	-55.9783	-102.9970	4535
181	1/18/2017	-56.4650	-102.9963	4426
182	1/18/2017	-56.9667	-102.9995	4232
183	1/18/2017	-57.4987	-102.9975	4102
184	1/19/2017	-57.9805	-103.0003	4672
185	1/19/2017	-58.4885	-102.9993	4784
186	1/19/2017	-58.9990	-102.9988	4736
187	1/20/2017	-59.4985	-102.9978	4568
188	1/20/2017	-59.9990	-102.9992	5040
189	1/20/2017	-60.4877	-102.9998	5366
190	1/21/2017	-60.9718	-103.0002	5056
191	1/21/2017	-61.4727	-102.9997	5231
192	1/21/2017	-61.9730	-103.0000	5178
193	1/21/2017	-62.4997	-102.9990	5151
194	1/22/2017	-62.9850	-102.9988	5117
195	1/22/2017	-63.5163	-102.9805	5107
196	1/22/2017	-63.9998	-102.9995	5094
197	1/23/2017	-64.4960	-102.9928	5057
198	1/23/2017	-64.9793	-102.9997	5024
199	1/23/2017	-65.4708	-102.9988	4973

P18

Station	Date	Latitude	Longitude	Depth
200	1/23/2017	-65.9905	-102.9993	4929
201	1/24/2017	-66.4642	-102.9997	4876
202	1/24/2017	-66.9960	-102.9992	4806
203	1/25/2017	-67.4998	-103.0240	4717
204	1/25/2017	-67.9952	-103.0005	4566
205	1/25/2017	-68.4998	-103.0025	4376
206	1/26/2017	-68.9908	-103.0085	4131
207	1/26/2017	-69.5038	-102.9957	4149
208	1/26/2017	-69.6083	-103.0272	4219
209	1/27/2017	-69.6912	-102.0252	3997
210	1/27/2017	-69.9023	-100.6733	4161
211	1/27/2017	-69.9998	-100.2412	4167
212	1/29/2017	-68.0655	-95.0013	4520

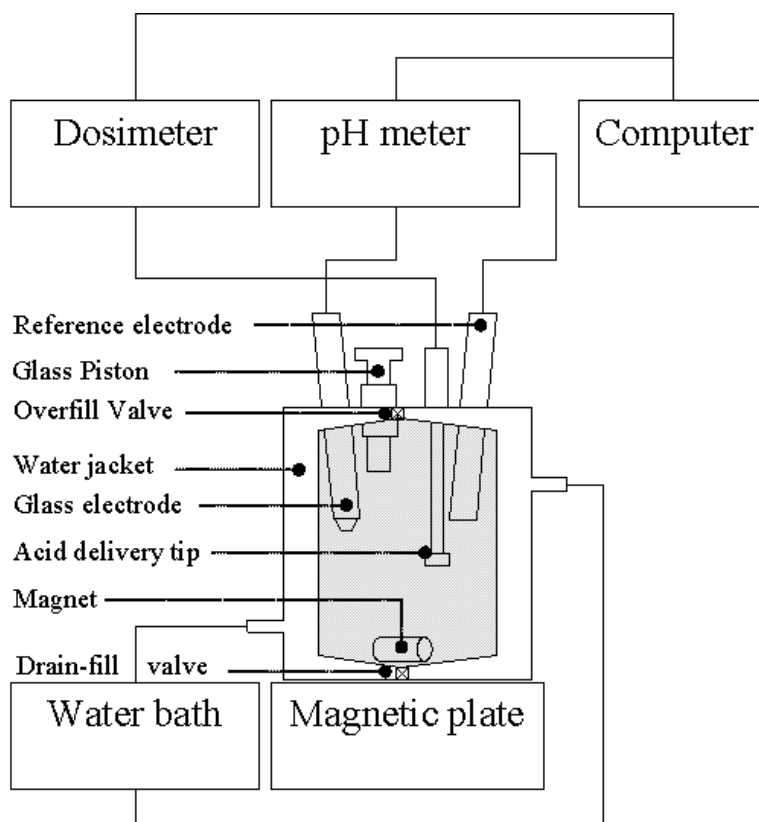
Appendix B. Scientific Personnel.

Scientific Personnel Carbon Group P18_2016 Leg I	
Role	Name (affiliation)
Chief Scientist	Carter, Brendan (PMEL)
Co-Chief Scientist	Annie Bourbonnais (WHOI)
Data Management	Remy Okazaki (PMEL)
CTD Processing	Kristy McTaggart (PMEL)
CTD/Salinity/LADCP/ET	Andrew Stefanick (AOML)
CTD/Salinity/LADCP	James Hooper (AOML)
Dissolved O2	Samantha Ladewig (RSMAS)
Dissolved O2	Alexander Sidelev (RSMAS)
Nutrients	Charles Fischer (AOML)
Nutrients	Eric Weisgarver (PMEL)
Total CO2 (DIC)	Robert Castle (AOML)
Total CO2 (DIC)	Remy Okazaki (PMEL)
Total Alkalinity	Ryan Woosley (RSMAS)
Total Alkalinity	Fen Huang (RSMAS)
pH	Andrew R. Babbín (RSMAS)
pH	Alexandra Fine (RSMAS)

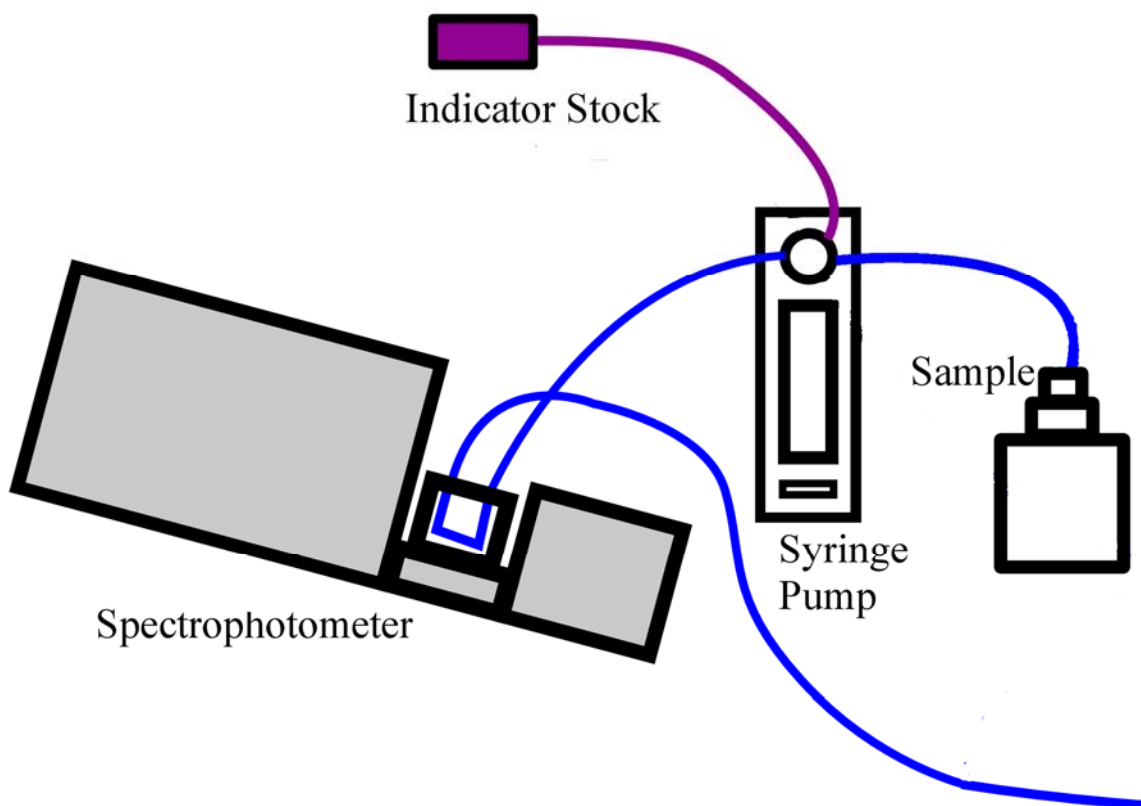
Appendix B. Scientific Personnel... continued.

Scientific Personnel Carbon Group P18_2017 Leg II	
Role	Name (affiliation)
Chief Scientist	Rolf Sonnerup (UW)
Co-Chief Scientist	Sarah Purkey (Lamont-Doherty Earth Observatory)
Data Management	Remy Okazaki (PMEL)
CTD Processing	Kristy McTaggart (PMEL)
CTD/Salinity/LADCP/ET	James Hooper (AOML)
CTD/Salinity/LADCP	Paige Logan (UW)
Dissolved O2	Christopher Langdon (RSMAS)
Dissolved O2	Emma Pontes (RSMAS)
Nutrients	Charles Fischer (AOML)
Nutrients	Eric Weisgarver (PMEL)
Total CO2 (DIC)	Charles Featherstone (AOML)
Total CO2 (DIC)	Andrew Collins (PMEL)
Total Alkalinity	Ryan Woosley (RSMAS)
Total Alkalinity	Fen Huang (RSMAS)
pH	Andrew R. Babbin (RSMAS)
pH	Alexandra Fine (RSMAS)

Appendix C. Diagram of an automated total alkalinity system



Appendix D. Diagram of a manual pH system.



Appendix E. Data format description.

FIELD NAME	DESCRIPTION	UNITS
Lat	Latitude	°N
Lon	Longitude	°E
Depth	Depth	m
P	Pressure	db
S	Salinity	S _p
T	Temperature	°C
θ	Potential Temperature	°C
pH _{pot}	Potentiometric pH	
pH _{spec}	Spectrophotometric pH	
TA	Total Alkalinity	μmol·kg ⁻¹
TCO ₂	Total Inorganic Carbon Dioxide	μmol·kg ⁻¹
NTA	Normalized TA to a salinity of 35	μmol·kg ⁻¹
NTCO ₂	Normalized TCO ₂ to a salinity of 35	μmol·kg ⁻¹