Global ocean spectrophotometric pH assessment: consistent inconsistencies

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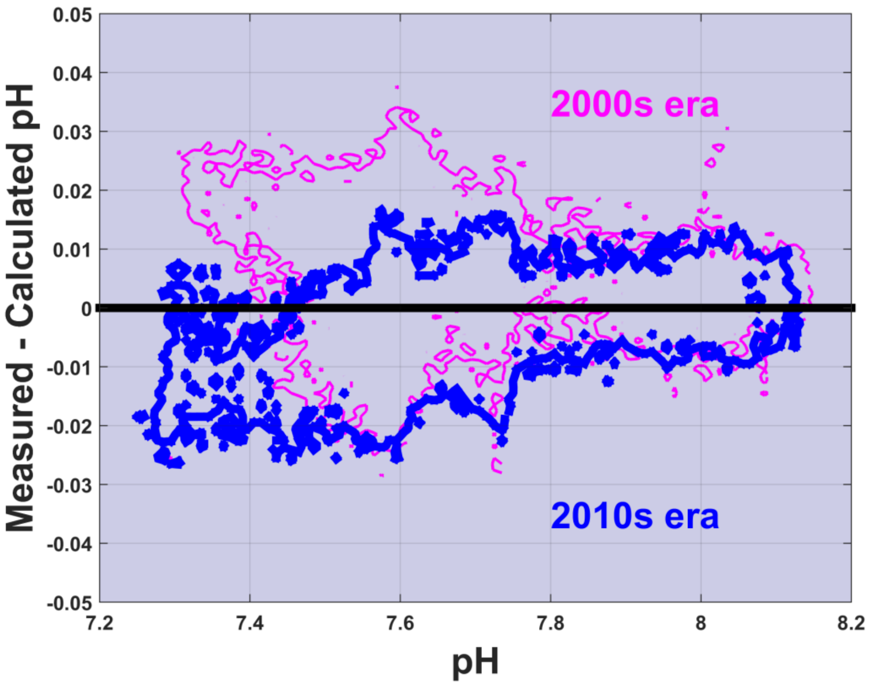
ABSTRACT

Ocean Acidification (OA)—or the decrease in seawater pH resulting from ocean uptake of CO_2 released by human activities—stresses ocean ecosystems and is recognized as a Climate and Sustainable Development Goal Indicator that needs to be evaluated and monitored. Monitoring OA related pH changes requires a high level of precision and accuracy. The two most common ways to quantify seawater pH are to measure it spectrophotometrically or to calculate it from Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC). However, despite decades of research, small but important inconsistencies remain between measured and calculated pH. To date, this issue has been circumvented by examining changes only in consistently-measured properties. Currently, the oceanographic community is defining new observational strategies for OA and other key aspects of the ocean carbon cycle based on novel sensors and technologies, that rely on validation against data records and/or synthesis products. Comparison of measured spectrophotometric pH to calculated pH from TA and DIC measured during the 2000s and 2010s eras, reveals that: 1) there is an evolution towards a better agreement between measured and calculated pH over time from 0.02 pH units in the 2000s to 0.01 pH units in the 2010s at pH>7.6; 2) a disagreement greater than 0.01 pH units persists in waters with pH<7.6, and 3) inconsistencies likely stem from variations in the spectrophotometric pH standard operating procedure (SOP). A reassessment of pH measurement and calculation SOPs and metrology is urgently needed.


Measured - Calculated pH
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
-0.03
-0.04
-0.05
7.2
7.4
7.6
7.8
8
8.2
pH
2000s era
2010s era

TEXT

INTRODUCTION

1.1. General background about ocean acidification

Human activities, fossil fuel combustion, cement production and land use change have released an enormous amount of CO_2 into the atmosphere with two main consequences: global warming[1] and Ocean Acidification (OA).[2] These two processes are occurring at unprecedented rates, with unknown consequences for ocean[1,3,4,5,6] ecosystems. Great concern about OA consequences for marine life and ocean resources has stimulated global coordination and synthesis efforts (e.g., Global Ocean Acidification Observing Network, GOA-ON; International Ocean Carbon Coordination Project, IOCCP; Ocean Acidification International Coordination Centre, OA-ICC).

Ocean pH is included within the inorganic carbon system as an Ocean Essential Variable. It has been recently declared a Climate Indicator by the World Metereological Organization and adopted as a Sustainable Development Goal Indicator (#14.3.1) by the United Nations General Assembly. Despite this importance, measurements of pH in the ocean are still scarce compared to the other CO_2 variable measurements such as Total Alkalinity (TA), Dissolved Inorganic Carbon (DIC) and partial pressure of CO_2 (pCO_2). Seawater pH was first defined and measured more than a century ago[7] and has been measured ever since on oceanographic expeditions[8] and open-ocean[9] and coastal[10] time series in order to detect OA and associated chemical and ecological changes.

The first potentiometric pH Spanish measurements were done in 1977 during the GALICIA IV[11] cruises, but it was only after the slow introduction of more precise spectrophotometric techniques[12] (see section 1.2) that pH data collection on repeat hydrographic sections started in the early 1990s.[13,14,15,16,17] However, no pH data were included in the first oceanographic data global consistency exercise, the Global Ocean Data Analysis Project (GLODAP);[18,19] only 40% of the total data included pH in Carbon in the North Atlantic (CARINA)[20] data product; and only 31% included pH data in the second GLODAP data product.[21,22] As a consequence, estimates of water column OA ascribed to anthropogenic input are generally indirectly derived avoiding the use of direct pH measurements.[23,24] As discrete and sensor-based (e.g., Ion Sensitive Field Effect Transistor, ISFET,[25,26] electrodes) pH measurements become more widespread, it is essential to insure high quality calibrations and inter-comparability among different observational platforms, from ships to new technologies (e.g. gliders and Argo floats).

1.2. Evolution and current status of ocean pH methodology and metrology

The reason behind the less frequent ocean pH measurements is both methodological and metrological as described and discussed in recent reviews.[8,27,28] Ocean pH was first measured potentiometrically and there are inherent caveats for this technique in seawater studies: the medium-high ionic strength of seawater precludes the use of conventional pH calibration standards.[27,29,30] Further complexity is added by the fact that pH can be defined on four different scales that differ by the chemical species concentration involved in their definition.[12,27,31,32] There are 0.1 pH unit differences between the different scales, differences that roughly equal the entire surface ocean change in pH from OA.[27,28,32]

Spectrophotometric approaches based on sulfonephthalein indicators emerged as an alternative to potentiometric pH measurements in the late 1980s.[12,33] These measurements should also be traced back to standard buffers, usually prepared in synthetic seawater and measured using Harned-cell measurements.[27,34,35,36] Urgent research is needed to develop standard equations to convert spectral absorptions to an International System Units traceable pH.[37]

The fast, precise and relatively inexpensive spectrophotometric method first described by Clayton and Byrne[12] (hereafter C&B93) was adopted as Standard Operational Procedure (SOP6b).[38] This method consists of adding a known volume of pH-sensitive indicator, usually m-cresol purple (mCP), to the seawater sample and the measurement of an absorbance ratio between specific wavelengths at a controlled temperature. C&B93[12] characterized the dissociation constant for Kodak mCP for a wide range of temperature and salinity, though the temperature dependence of the indicator optical properties was not initially assessed. From repeat measurements C&B93[12] ascribed a precision of 0.0004 units for this pH method. Assuming proper sample handling and preservation, along with a high quality spectrophotometer with good wavelength and absorbance accuracy, pH accuracy depends on: a) the quality of the Tris buffer experimentally used for characterizing the indicator, b) any differences between the behaviour of mCP in Tris buffer vs. seawater, c) the accuracy of the molar absorbance ratios and d) the accuracy of the assigned total scale Tris pH values. In this regard, a few years later, DelValls & Dickson[39] proposed an increase of 0.0047 pH units for pH measurements obtained through this method because C&B93[12] Tris buffers were based on Ramette et al.[40] After applying this correction, Clayton et al.[41] ascribed an accuracy to spectrophotometric pH values of 0.002 pH units based on an internal consistency exercise, though it has not always been accepted or applied.[42–48] Considering all uncertainties in the Tris buffers prepared in synthetic seawater that are used to calibrate measured pH, the final pH uncertainty is higher: ranging from 0.004[36,39] to 0.01,[49,50] when considering temperature corrections, as pH is seldom measured at in situ temperature.

Fourteen years after C&B93,[12] Yao et al.[51] studied the effect on the pH measurements of impurities in the mCP indicators. The most important impurities are compounds perturbing the absorbance properties of the dye. Common impurities result in an negative bias for measured pH that ranges from -0.003 to -0.02 pH units,[52] with the bias being larger at high pH values. This magnitude depends on the manufacturer (i.e., the type and quantity of impurities), but even varies from batch to batch of a single manufacturer. Initially Yao et al.[51] proposed an equation to empirically correct the effect of impurities based on calibrations against the Kodak indicator used by C&B93. Nevertheless, the equation was only suitable for pH measurements obtained with indicator from the manufacturer Sigma Aldrich. Given the range of manufacturers, the approach has recently evolved towards removing the impurities with high performance liquid chromatography (HPLC)[52] or flash chromatography[53] to produce purified mCP (PUR mCP). The optical properties of PUR vs. unpurified mCP (UNPUR mCP) were evaluated, and Liu et al.[52] proposed a new PUR mCP parameterization. This parameterization has been independently validated by several laboratories,[54,55] and even extended to wider temperature and salinity ranges, for fresh, estuarine and seawater[56] or even more extreme conditions, including seawater near the freezing point and brines with extreme salinity values.[55]

Liu et al.[52] proposed to correct UNPUR mCP pH measurements with empirical formulas, making PUR and UNPUR mCP paired pH measurements over a wide range of pH values, so as to obtain an UNPUR mCP batch and manufacturer specific correction. Alternatively, for the most common impurities absorbing at 434nm at high pH values, Douglas and Byrne[57] suggested an UNPUR mCP batch-specific correction at this wavelength, which would produce very similar PUR and UNPUR adjusted pH values. However, this approach can only be applied when the UNPUR mCP indicator manufacturer and lot are known and the UNPUR mCP indicator used are available for evaluation. In addition, PUR mCP is not yet commercially available and most labs currently rely on PUR mCP from Dr. Byrne's lab (University of South Florida). Not all laboratories can yet access and afford PUR mCP.

1.3. Measured vs. calculated pH

As commented before, although the manual C&B93[12] method for pH is accessible, relatively cheap and fast seaboard pH measurements on hydrographic sections are still scarce compared to more time consuming and expensive TA and DIC measurements. Within ideal conditions (properly sampled, presevered and analysed by well trained personnel) spectrophotometric pH measurements have a precision of about 0.0004 pH units and an ascribed accuracy of 0.004 pH units,[58,59] while calculated pH from DIC and TA (pH=f(DIC,TA)) was ascribed to have a mean uncertainty that ranges from 0.004 to 0.008 pH units[31], depending on the seawater characteristics,[60,61] and only considering the standard uncertainties of measured TA and DIC. If including the uncertainty in the first and second CO_2 dissociation constants,[49] at surface conditions, calculated $[H^+]$ uncertainty would be 3%[49], or 0.013 pH units. Given that long-term pH change assessment requires uncertainties of order 0.003 pH units,[62] it is clear that the field would benefit from consistent implementation of a well-defined pH methodology and metrology.

Nearly 30 years after C&B93[12], the evolution of the pH methodology from manual to mainly automated systems along with the introduction of PUR mCP have been unable to resolve the clear pH dependent discrepancy between spectrophotometrically measured and calculated pH (ΔpH).[50,63,58] A recent work[58] evaluated the pH discrepancies from four transoceanic Pacific and Indian Ocean 2014-2016 cruises led by a single research group using PUR mCP. Unique adjustments to the CO_2 constants and the total boron to chlorinity ratio were proposed, alongside a contribution of 4-6 μmol.kg^{-1} from organic TA, that is mainly constant with depth and basin, in order to match the general consistency of these pH, TA and DIC measurements with our current knowledge on the acid-base seawater CO_2 system. These adjustments, although plausible for these cruises, might likely not be the ultimate solution for explaining pH measurements inconsistencies, thus leaving an open door to new approaches to tackle the ΔpH (measured pH minus pH calculated from TA and DIC) vs. pH inconsistency. In this work, we used the best publicly available CO_2 measurements and ancillary data with a global coverage using hydrographic sections from the 2000s Climate and Ocean – Predictability Variability and Change (CLIVAR) era to the 2010s Global Ocean Ship-Based Hydrographic Investigations Program (GO-SHIP) era, led by different research groups in order to:

- evaluate the CO_2 community improvements regarding pH, DIC and TA internal consistency with a focus on the pH measurement evolution,
- assess the magnitude and distribution of ΔpH focusing on the sources of uncertainty both in the pH method and calculated pH,
- evaluate the implications of these inconsistencies for current and future OA studies, and
- propose ways forward to tackle remaining complications for seawater pH.

2. MATERIAL AND METHODS

2.1 CO_2 and ancillary data

Two groups of data from hydrographic transoceanic sections were selected. In addition to CO_2 data we also used data relative to inorganic nutrients (phosphate and silicate), Apparent Oxygen Utilization (AOU) from dissolved oxygen and Dissolved Organic Carbon (DOC). Group 1 cruises (Table S1 & Figure 1) from the CLIVAR program were downloaded from the GLODAPv2.2016 data product.[21,22] These data are strictly quality controlled to assure the highest accuracy and consistency of CO_2 and ancillary data and, when flagged as fully-quality controlled, are expected to have a consistency better than 6 µmol.kg^{-1} for TA, 4 µmol.kg^{-1} for DIC and 0.005 pH units for pH.[21]

We selected Group 1 cruises from GLODAPv2.2016 based on the following criteria: 1) pH should be measured using a spectrophotometric technique[12] using UNPUR mCP; 2) pH, TA and DIC should be available, as well as the measured temperature, salinity, silicate and phosphate values required for carbonate system calculations; 3) quality flags for ancillary, pH, TA and DIC should equal 2, i.e., the measurement is acceptable in the original and product files; 4) secondary quality control (2QC) flags for pH, TA and DIC should equal 1, i.e., a crossover analysis or inter-cruise check was performed, and ΔDIC (measured DIC - DIC=f(pH,TA)) values for deep waters should be ±5 µmol.kg^{-1} (Figure S1). The GLODAPv2 strategy[64] to asses pH was to first carryout crossover analysis wherever possible, but since pH measurements are fewer than those of DIC and TA, an internal consistency analysis was adopted using the ΔDIC (measured DIC - DIC=f(pH,TA)) magnitude and distribution in deep waters. Then pH adjustments were proposed based on these analyses.

Group 2 cruises (Table S2 & Figure 1) correspond to the 2010s GO-SHIP program and contain TA, DIC and spectrophotometric pH. Group 2 cruise pH values were mostly obtained using PUR mCP, though some cruises were measured with UNPUR mCP and had methodological adjustments designed to make the values comparable to PUR mCP measurements. The same selection criteria as in Group 1 were also applied to Group 2 cruises selected from GLODAPv2. Three cruises that meet these criteria were included in GLODAPv2.2016[22] and eight were included in GLODAPv2.2019.[65] Five additional cruise datasets were added for this study: two P06 legs in the Pacific ocean, I09N in the Indian ocean, ARC01 in the Arctic ocean and the coastal Gulf of Mexico GOMECC2 datasets. These datasets were downloaded from CCHDO (https://cchdo.ucsd.edu) and their spectrophotometric pH measurements used PUR mCP.

This work presents the distribution and magnitude of ΔpH for original and corrected pH data in Group 1 and original pH data in Group 2. This a priori incongruence reveals useful information and will be assessed in the Results and Discussion section.

2.2 Thermodynamics calculations

All thermodynamic calculations were performed using the CO2SYS package for Matlab®,[66] with option 10 for the CO_2 constants[45] and option 1 for the total boron to chlorinity ratio (TB)[67] and sulphate constant (K_{SO4}),[68] as agreed by the GLODAPv2 team.[22,64] Measured phosphate, silicate, salinity, DIC, TA, temperature and pressure are inputs to the CO2SYS package. The contributions of borate (estimated from salinity), silicate and phosphate to TA are needed to estimate carbonate alkalinity by residual: organic alkalinity contributions are neglected in these routines.

Before exploring ΔpH vs. pH (hereinafter pH on the Total Scale at 25ºC and atmospheric pressure) results, it is crucial to understand the magnitude of systematic uncertainties affecting pH=f(DIC,TA) from TA and DIC measurements, CO_2 constants and the acid-base borate system. Random uncertainties are not considered in this work. At constant temperature, seawater pH is closely related to the TA/DIC ratio, which relates to the seawater buffering capacity.[69,70] The closer to one, the lower buffer capacity, i.e., waters with a low pH (i.e., a low TA/DIC ratio) are prone to larger acid-base changes when perturbed. We present our results as a function of pH following recent works[50,58] dealing with the pH inconsistency, although the TA/DIC ratio would be nearly equivalent at constant temperature.[71,72,61]

Uncertainties for calculated pH, pH=f(DIC,TA), are obtained by perturbing seawater properties by a range of values from zero up to about five times the total estimated standard uncertainty for the input variables according to Orr et al.[49] (2 μmol.kg^{-1} for TA and DIC, 0.0075 for pK_1, 0.015 for pK_2, 0.01 for pK_B, 2% for TB). If TA is overestimated (equivalent to positive values in the y-axis of Figure 2A, $\delta TA>0$, i.e., perturbed minus reference TA), calculated pH would be overestimated (equivalent to positive pH error isolines, or lines of constant perturbed minus reference pH, in Figure 2A). The wider separation between error isolines in Figure 2A at higher pH values means that calculated pH is less sensitive to TA uncertainties. Since DIC and pH are inversely correlated, the sensitivity of calculated pH to DIC uncertainties (Figure 2B) is nearly a mirror image of that from TA (Figure 2A). Uncertainties in TA or DIC greater than 2 μmol.kg^{-1} would cause an uncertainty in pH=f(DIC,TA) higher than 0.005 pH units.

Regarding the equilibrium constants (Figure 2D-F), pK_2 has the largest influence on pH=f(DIC,TA) at any pH (Figure 2E), though pK_1 may play a significant role at pH<7.6 (Figure 2D). Uncertainties in TB are more influential at high pH: a TB uncertainty of 2% would influence pH by 0.002 pH units (Figure 2C). A pK_B systematic uncertainty of 0.004[58] would cause an uncertainty lower than 0.001 pH units (Figure 2F).

3. RESULTS AND DISCUSSION

3.1 Distribution and magnitude of ΔpH

The ΔpH distribution is shown as a function of pH (Figure 3), the same reference variable as used in Figure 2. Group 1 data (Figure 3A) present trends in ΔpH vs. pH that vary by cruise (Figure S2), with 62% of ΔpH values within 0.01, and 40% within 0.005 with no clear patter with pressure (not shown). There are ΔpH values well above 0.01 and below -0.01 for waters with pH<7.6. Points with |ΔpH| > 0.01 represent 48% of the data in Group 1 and are usually found in high AOU (>200 µmol.kg^{-1}) waters above 2000 dbar. Extreme pH values <7.3 are only found in the hypoxic layer of the Oxygen Minimum Zone (OMZ) of the North Pacific Ocean at about 500 dbar.[73–75] The ΔpH distribution for GLODAPv2 adjusted Group 1 data (Figure 3B) scatters around zero with no clear trends (Figure S2 vs. S3), 80% of ΔpH values are within 0.01, and 56% within 0.005, therefore, pH, TA and DIC are internally consistent, as forced by the GLODAPv2 corrections.[22]

A more thorough inspection of the results in Figure 3A at low pH reveals that negative ΔpH values mostly correspond to US (expocode 35*) cruises while positive ΔpH values correspond to Japanese (expocode 49*) cruises (Figure S2 & Table S1). This fact implies a methodological bias in either pH, TA and/or DIC. With regard to pH methods: most Japanese labs in Group 1 measured pH with an identical automated system while the US labs used automated and manual pH methods. With regard to TA methods: US labs used a mixture of open and closed-cell potentiometric systems for TA, while Japanese labs used an automated open cell titration system or spectrophotometric determination. With regard to DIC methods: both US and Japanese groups used a coulometric procedure with different extraction units, which were usually calibrated with gas loops or Na_2CO_3 standards. In addition, DIC and TA were metrologically referenced to CO_2 Certified Reference Materials[76] and double checked with the crossover analysis, with most of the cruises flagged as good (Table S1). Without disregarding sampling issues for very high DIC (low pH) samples and a pH dependent incoherence in the pKs mostly affecting calculated pH at low pH (Figure 2D&E), we suspect that the lack of internal consistency in the original Group 1 pH, TA and DIC data points to some sort of incoherence in the pH measurements. More details will be given in section 3.2.

The more recent, automated spectrophotometric UNPUR and PUR pH measurements in Group 2 (Figure 4A) clearly present different ΔpH results for pH>7.6 waters, with 76% ΔpH values within 0.01 and 47% within 0.005, compared to waters with pH<7.6, where 56% of the ΔpH values are within 0.01 and 29% within 0.005. Most of the US cruises in Group 2, either using PUR or UNPUR mCP present a clear ΔpH vs. pH dependence, with negative ΔpH values at low pH (Figure S4).[63]

Assuming that DIC and TA are precise, metrologically referenced and accurate to less than 2 μmol.kg^{-1}, the significant ΔpH inconsistencies at pH<7.6 and the marked ΔpH vs. pH trend in both groups of CLIVAR and GO-SHIP cruises could be attributed to:

- uncertainties in the CO_2 system constants affecting calculated pH: uncertainty in pK_1 would have the largest, but relatively low, impacts on pH in low pH waters while uncertainty in pK_2 would affect across the pH range with a higher magnitude (Figure 2D&E). Section 3.3 further explores proposed corrections on the constants.

- uncertainties in measured pH: these could be derived from 1) sampling biases, for example degassing of very low pH waters could explain positive ΔpH values as measured pH would be overestimated; 2) underestimation of measured pH because of indicator impurities affecting the whole pH range, but causing larger impact on higher pH values; 3) instrumental problems related to the wavelength, bandpass, absorbance accuracy and precision,[54] affecting the whole pH range; and 4) the lack of certified reference material covering the whole pH range.

With regard to points 1&2, in the CO_2 intercomparison exercise performed in 2013[77] only 38% of the participating labs reached an agreement for pH within 0.005 from the reference value in the high (pH>7.6) and low (pH<7.6) pH ranges tested. The low pH range showed more scattered results, with 50% within 0.01, compared to 69% in the high pH range. Several reasons were hypothesised for those scattered pH results: the lack of available pH reference material for all pH ranges, lack of automation of the method, loss of CO_2 from the sample, particularly in the low pH range (i.e., sample handling) and the unavailability of PUR mCP for many labs. Only 26 pH values were reported in that exercise. A more recent CO_2 intercomparison exercise performed in 2017 (unpublished) compiles about 60 pH results, and again in the low pH range only 52% reached 0.01 agreement compared with 73% in the high pH range, separating by PUR and UNPUR mCP does not improve the results (E. Bockmon and A. Dickson personal communication). Section 3.2 further comments on the pH direct comparison between groups.

With regard to point 3, except for the spectrophotometer model, no info about equipment calibration or maintenance is provided in the cruise reports, making it impossible to evaluate further. With regard to point 4, cruise reports rarely include pH measurements of Tris buffer solutions or pH measurements on CO_2 CRMs, both are usually used to evaluate long term reproducibility, not accuracy. In terms of accuracy, pH is not yet certified for CO_2 CRMs and measuring pH at 20 or 25ºC in Tris buffers can only constrain high pH values if Tris solution is properly prepared and calibrated.[34]

3.2 Direct original Group 1 and 2 pH comparison at crossover points

Discrepancies in pH measurements seem to be the main reason behind the ΔpH inconsistencies. However, the exact mechanism is unknown and the bias could be in the sampling, preservation, reagents (UNPUR or PUR mCP), equipment specifications, or a combination of some or all of them. Identifying and quantifying those biases could be attained by: 1) directly comparing all available spectrophotometric pH measurements from hydrographic sections in CCHDO in overlapping areas less affected by OA, along with a careful examination of the pH method metadata information; and/or 2) designing a specific intercomparison exercise focused on spectrophotometric pH. Option 1 is a massive task on top of the list for the future 2020 GLODAP release. Option 2 is one of the main objectives of the recently accepted Ocean Carbonate System Intercomparison Forum (OCSIF) working group started in summer 2019.

By means of our data base, we attempt to give insights using option 1: we identified 5 crossover locations (black points in Figure 1) and explored differences for TA, DIC and original pH data in deep waters with low temporal variability. For that purpose we used the scripts in Lauvset and Tanhua[78] to interpolate measured CO_2 variables into standard density ($sigma_4$) levels for each cruise and area using a Piecewise Cubic Hermite Interpolation scheme. After obtaining the mean profile per cruise and area, the mean difference profile between cruises and the corresponding mean difference for each variable within a given $sigma_4$ interval were calculated.

The results in the North Pacific Ocean are illustrative and discussed here, while the other crossover areas are supplementary and therefore detailed in the Supporting Information (Figure S5, S6 & S7). Two Group 1 (cruise 306, US P16N 2006, & cruise 502, Japanese P01 2007) using UNPUR mCP and two Group 2 (US P16N.2 2015 and Japanese P01 2014) using PUR mCP cruises overlap in the North Pacific Ocean (Figure 1). This region, is characterized by very low pH values (pH<7.6 for $sigma_4$>44.3, Figure 5E). Bottom waters below 4000 dbars and $sigma_4$>45.86 present a difference between cruises (306-502) for TA, DIC and pH of 1.7±2.1 $\mu mol.kg^{-1}$, -2.0±0.6 $\mu mol.kg^{-1}$ and -0.018±0.001, respectively in Group 1 (Figure 5A-F, Table S4), and -0.8±1.2 $\mu mol.kg^{-1}$, -2.4±0.2 $\mu mol.kg^{-1}$, -0.008±0.0005, respectively in Group 2 (P16N.2-P01) (Figure 5G-L, Table S4).

Clearly, DIC and TA for the two sets of cruises agree within 2 μmol.kg^{-1}, despite using different equipment and approaches, according to the cruise reports: DIC methods were both based on coulometry but each research group used different extraction units and coulometer models; US TA was determined by open cell potentiometry, and Japanese TA using a spectrophotometric procedure. In the case of pH, a clear discrepancy is evident, ≈0.02 pH units, in Group 1 (Figure 5E&F), accentuated in the layer with pH<7.4. In Group 2 the pH difference reduces to 0.01 pH units and is nearly constant with pH (Figure 5K&L).

Group 1 cruises used both UNPUR mCP (no information about manufacturer is given in the cruise reports, but the same C&B93[12] equation is used) with manual (US P16N) and custom-made automated (Japanese P01) techniques. Degassing of very low pH samples during the pH analysis during 2007 P01 could explain the ΔpH positive values (Figure S3) and the negative correction applied by GLODAPv2 (-0.015, cruise 502 in Table S1). The opposite is found for the 2006 P16N cruise: ΔpH negative values (Figure S3) and the positive correction applied by GLODAPv2 (0.013, cruise 306 in Table S1) indicating a pH underestimation, which is difficult to associate with sampling issues but could be the result of calibration issues in the spectrophotometer equipment.[54] Differences in measured pH in Group 1 are difficult to ascribe to indicator impurities, as those are expected to be largest at high pH,[51] opposite to what was found here (Figure 5F). In Group 2 both cruises used automated independent custom made spectrophotometric systems with PUR mCP (provided by Dr. Byrne in P16 and home made in P01, both used the same Liu et al.[52] pH equation), the pH difference between cruises is nearly constant and ≈0.01 pH units. The pH, DIC and TA data from 2014 P01 are consistent with ΔpH within 0.01 pH units and no GLODAPv2 recommended corrections, 2015 P16N presents ΔpH≈-0.04 pH units (Figure S4) and pH is corrected upwards (0.016, cruises 1043 & 1044 in Table

S2). Instrumental issues such as accuracy in the wavelength and absorbance of the spectrophotometer could be the cause,[54] but are impossible to evaluate post-cruise.

Overall, except for TA in the South Western Pacific Ocean, DIC and TA agree within 2 μmol.kg^{-1} for all crossovers locations (see Supporting Information), so they both appear to be measured by well established, precise and accurate methodologies. Spectrophotometric pH measurements present a problematic situation specially for pH<7.6, with very high discrepancies (≈0.02 pH units) between CLIVAR research groups using UNPUR mCP, and lower, but still significant discrepancies (≈0.01 pH units) when using PUR mCP in the GO-SHIP era. At higher pH values, >7.7, the discrepancies decrease to ≈0.008 pH units when comparing UNPUR to UNPUR (CLIVAR era) or UNPUR to PUR mCP pH (CLIVAR to GO-SHIP) cruises.

Given that OA observational studies associated with climate change[62] require an observational uncertainty better than 0.003 consistent over time, the ocean CO_2 research community needs to revisit the pH method procedure, sampling, preservation, reagents, equipment, equations, calibration, robustness and traceability to consensually accepted standards.[35,50,54] Rephrasing the pH SOP and reporting procedure is one of the main objectives of OCSIF working group.

3.3 Accounting for the ΔpH vs. pH inconsistency

Fong & Dickson[58] proposed systematic adjustments for pK_1, pK_2 and TB, along with a non-negligible contribution of organic alkalinity (4 to 6 μmol.kg^{-1}) homogeneously distributed in the water column of the Indian and Pacific oceans (cruises P16N, P16S, I09N and I08S in Group 2). Those adjustments would minimize and flatten the ΔpH vs. pH discrepancy. This section explores if those corrections are conceivable globally.

Organic TA refers to any organic molecule that accept protons under the conditions set in the definition of TA.[79] Organic TA can be considered an excess of measured TA compared to calculated TA, or ΔTA (Organic TA = ΔTA = TA measured - TA=f(pH,DIC)), when assuming no systematic errors in measured pH or DIC and that other thermodynamic inconsistencies are negligible.

Using original (i.e., without any of the adjustments proposed by Fong & Dickson[58]) pK constants and TB for Group 2 data, ΔTA values present a clear pH dependence with positive (negative) values at low (high) pH (Figure 4C), directly correlated with AOU (Figure 4E), which suggests that highly remineralized waters would present higher concentrations of organic TA (≈ΔTA). Surprisingly, this organic TA (≈ΔTA) would be inversely correlated with DOC and pressure, presenting negative values in the upper ocean which has high DOC values (Figure S8A&C). When adjusting the pKs constants and TB (pK_1 -0.0074, pK_2 +0.014 and TB -2.47%) according to Fong & Dickson,[58] ΔTA vs. pH would flatten (Figure 4D) at a mean value of 5.9 $\mu mol.kg^{-1}$, without showing any relation to AOU (Figure 4F), DOC or pressure (Figure S8B&D). Adding this organic TA of 5.9 $\mu mol.kg^{-1}$, the resulting Group 2 ΔpH distribution would flatten and center ΔpH distribution around zero (Figure 4B).

Adjustments on the constants are plausible considering corresponding standard uncertainties, but ignore the pH dependent impact of changing pKs and TB on pH=f(DIC,TA) (Figure 2). Those adjustments would flatten and minimize ΔpH with the existence of a constant and relative high organic TA in open ocean waters (Figure 4D&F), which in turn would also cancel out the correlation of ΔTA with DOC or pressure (Figure S8B&D). This picture is surprising as organic TA is usually associated with shallow coastal waters with high DOC, where the input of fresh organic matter contains a high fraction of humic and fulvic substances, which are proton acceptors.[80,81,82]

In the open deep ocean some DOC components able to accept protons, the so called Carboxyl-rich alicyclic molecules (CRAMS)[83] are associated with recalcitrant DOC[84] and with specific humic-like fluorescence peaks,[85,86] that are correlated with AOU.[87] Original ΔTA vs. AOU distribution for Group 2 data shows a linear positive relationship (Figure 4E), while if applying the corrections to pKs and TB, there is no such relation (Figure 4F). A nearly constant value of organic TA, 4-6 μmol.kg^{-1}, with no relationship with pressure, DOC, or AOU is difficult to explain. CRAMS constitute about 8-10% of DOC[83,88] with about 6 carboxilic acid functional groups for every 30 carbon atoms. Consequently, organic TA from CRAMS can be approximated as $0.10 \times 6/30 \times \text{DOC}$, which is about 1 μmol.kg^{-1} below 500 dbars and up to a maximum of 2-3 μmol.kg^{-1} in upper waters. Without modifying pKs but including this small contribution from organic TA, ΔpH centres to zero for $\text{pH}<7.6$, but at higher pH values ΔpH would be mainly positive (results not shown).

This discussion is intended as a reminder that the proposed pKs and TB corrections, with constant organic TA throughout the water column[58] are simply one combination of plausible uncertainties that could account for the majority of the pH dependent pH discrepancy for these cruises, and that these adjustments are not derived from first principles. The true coastal and deep ocean magnitude, distribution and biogeochemical relationships of organic TA, and its impact on CO_2 chemistry are still open questions.

3.4 Concerns about CO_2 calculations in the ocean

Rates of OA can be calculated from sustained, accurate and precise DIC and TA measurements. The pH experienced by ecosystems can be calculated from these measurements to within 0.01 pH units of directly measured spectrophotometric pH, except for waters with pH<7.6 (Figure 3A & 4A), here either calculated pH is overestimated on many cruises or measured pH is erroneously low.

Considering that waters with pH<7.6 constitute 34% of the samples in the upper 1500 dbars in Group 2, and are more sensitive to anthropogenic carbon accumulation,[24] urgent consensus both on pH measurements and calculations is needed, particularly in light of the revolutionary new era of biogeochemical observations, particularly for CO_2 variables,[89] by means of various autonomous platforms.[90,91,92] During the last 10 years rapid progress has been made in developing biogeochemical sensors that are sufficiently lower power, smaller, more precise, more accurate, more stable, and more pressure tolerant, and these new sensors have been installed on ships of opportunity, profiling floats and gliders. Commercially available sensors are ready for dissolved oxygen, particles, chlorophyll and nitrate[93,94] and more recently pH.[95,96] Key questions for oceanography and global change will be addressed with this new global ocean observing capability[94,97] only if data amongst platforms is consistent and comparable.

Biogeochemical sensors placed on Argo profilers usually require post-deployment calibration when compared to direct discrete measurements at the deployment site and often require adjustments to account for of temporal drift.[98] In the case of dissolved oxygen some sensors can measure the atmospheric oxygen content which is nearly constant and used as reference. Deep nitrate, pH and oxygen sensor measurements can be adjusted to predicted values from linear [63,99,100,101] or neural networks[102,103] algorithms predictions but are reliant on high quality discrete measurements such as those from the CLIVAR and GO-SHIP programs. Critically, there are insufficient consistently-measured pH data to train these algorithms globally, so pH values calculated from TA and DIC are currently used alongside pH measurements. CO_2 system measurement intercomparability is therefore important for the calibration of pH sensors operating on the Argo array. In this regard, compared to GLODAPv2.2016[22] the GLODAPv2.2019[65] update kept the same DIC consistency in 4 μmol.kg^{-1}, improved the consistency of TA from 6 to 4 μmol.kg$^{-1,}$ but widened the uncertainty for pH from 0.005 to 0.01 pH units.

Some examples below using Argo pH measurements illustrate our concerns when using adjusted pH as an input for estimating other CO_2 variables:

1) Juranek et al.[104] obtained algorithms for pH as a function of discrete oxygen or nitrate plus temperature data, however, this discrete pH actually was pH=f(DIC,TA) and not directly measured spectrophotometric pH. The reason behind this choice may have been that original pH measurements (cruise 306 in the North Pacific Ocean, Table S1) should be corrected upwards by 0.013 pH units according to an internal consistency analysis. In addition, ΔpH show a clear dependence with measured pH (Figure S3, cruise 325020060213), as also remarked in Williams et al.[105] Algorithms for pH by Juranek et al.[104] predicted calculated pH in the North Pacific, while Williams et al.[101] used directly measured spectrophotometric pH data in the Pacific sector of the Southern ocean. Given the results presented here, clear differences between measured spectrophotometric pH and pH=f(DIC,TA) indicate an important issue that the scientific community needs to address.

2) Williams et al.[105] proposed using adjusted Argo pH data along with estimated TA to calculate surface pCO_2, which is a reasonable option for surface waters where the error from

direct pH measurements on calculated pCO_2 is low, as it is the impact from TA or $pK_{1.}$[31] Biases in Argo pH are adjusted with an algorithm obtained from discrete temperature, salinity, oxygen and spectrophotometric pH measurements from 2011 S04P and 2014 P16S (both included in our analysis, cruise 295 in Table S1 and 1036 in Table S2, respectively), and A12/PS89 cruise data. Most of the cumulative offsets between cruise and Argo pH at 1500 dbar are negative (their Table 1), so Argo pH is increased. As far as we understand, a further offset (+0.0054 pH units) is added to the Argo adjusted pH based on comparing spectrophotometric pH and pH=f(DIC,TA) from the cruises P16S & S04P at 1500 dbar. However if using surface instead of deep pH=f(DIC,TA) the pH offset would instead be negative and even an order of magnitude higher (about -0.015 pH units) because the ΔpH is pH dependent (Figure S3, cruise 320620110219 and Figure S4, cruise P16S). We therefore contend such adjustments should be applied in a pH dependent fashion rather than as a fixed offset.

3) Recent work by Takeshita et al.[96] gives a more detailed assessment of surface underway pCO_2 along the A13.5 cruise (Table S2) as a function of Argo pH and estimated TA. Different discrete pH values (spectrophotometric pH measurements, pH=f(DIC,TA), pH=f(pCO_2,TA), pH=f(pCO_2, DIC)) are used to adjust the surface Argo pH. The authors note the better agreement between pCO_2=f(Argo pH,TA) when Argo pH is calibrated with pH=f(pCO_2,DIC or TA), instead of surface discrete spectrophotometric pH. They claim this is due to the use of UNPUR mCP that underestimates pH at high pHs, even when reported spectrophotometric pH is supposed to be corrected to PUR mCP.

The CO_2 community is on the cusp of a new era with the implementation of BioGeoChemical Argo and other autonomous CO_2 measurements which require calibration with high quality discrete measurements. Long term monitoring of OA requires a very high level of precision and accuracy for all carbon system parameters, yet despite decades of research small but important inconsistencies remain. Consensus is clearly required on how to calibrate and adjust float pH data to ensure the highest accuracy of data and comparability among different studies and data sets from diverse platforms. Different methods can lead to different biases and uncertainties which may hide trends or lead to misinterpretation of data. Although improvements in spectrophotometric pH measurements have been made since the CLIVAR era, there are still discrepancies that will require further research to resolve. A clearly detailed spectrophotometric pH SOP including accuracy control is urgently needed.

FIGURES

Figure 1. Global map with the hydrographic cruises included in Group 1 (red dots), Group 2 (cyan dots) and those included in both (blue dots). Analyzed crossover areas discussed in Section 3.2 are shown as black circles.

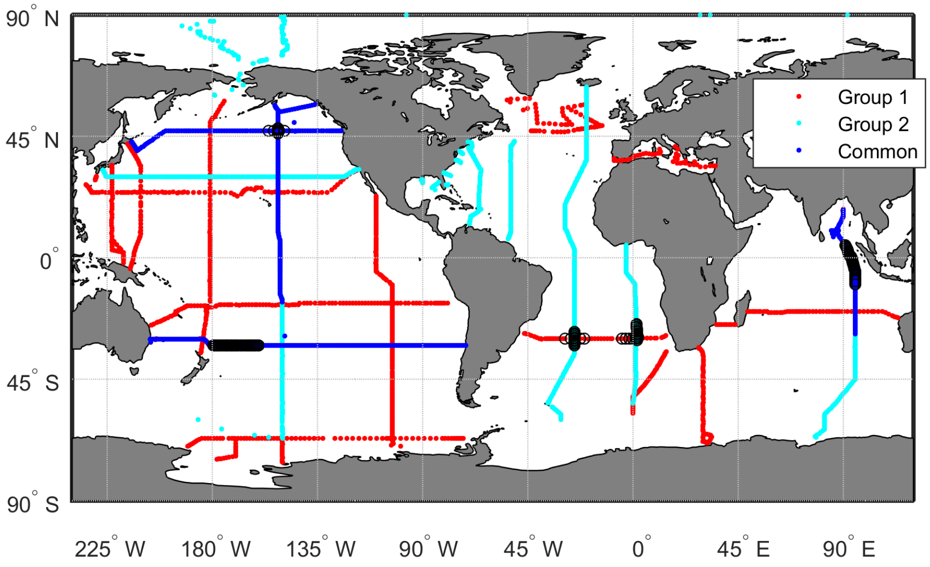


Figure 2. Sensitivity of calculated pH (pH=f(DIC,TA)) as a function of pH, to errors in the input variables A) TA, B) DIC, C) the total boron to chlorinity ratio (TB), D) the pK$_1$ CO$_2$ constant, E) pK$_2$ CO$_2$ constant and F) the borate constant pK$_B$. The respective errors (δ), as well as the pH sensitivity isolines, correspond to the modified minus the reference values. All the calculations were performed on the Total Scale, at 25ºC, 35 salinity and atmospheric pressure. δTA and δDIC in µmol.kg^{-1}, δTB in %, other constants in logarithmic scale.

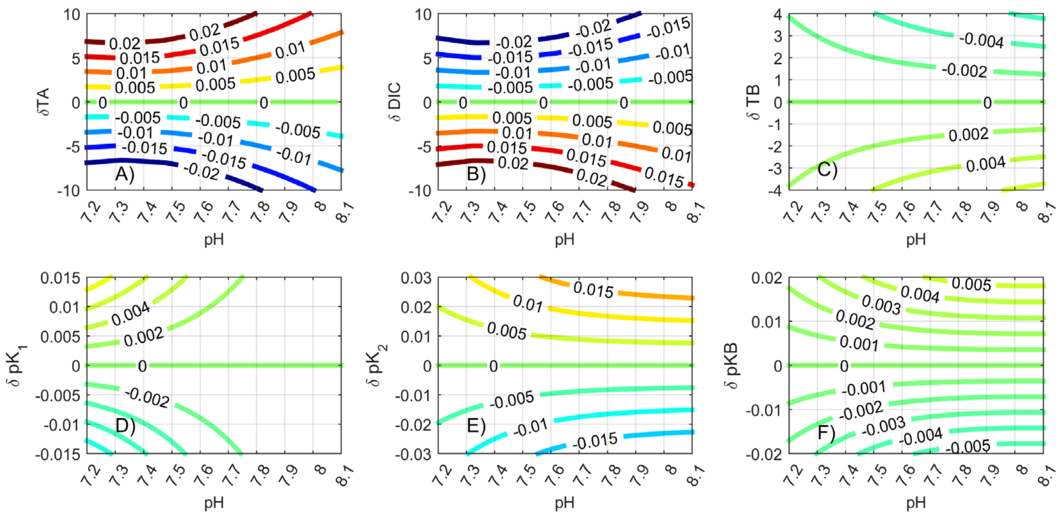


Figure 3. Two-dimensional histograms for Group 1 data showing the number of data points falling within bins of ΔpH (y-axis, ΔpH, i.e., measured pH minus pH calculated, pH=f(DIC,TA)) versus pH (x-axis); A) original GLODAPv2.2016 pH data and B) corrected GLODAPv2.2016 pH data. z-axis shows the histogram frequency in logarithmic scale. The pH is on the Total Scale, at 25ºC and atmospheric pressure.

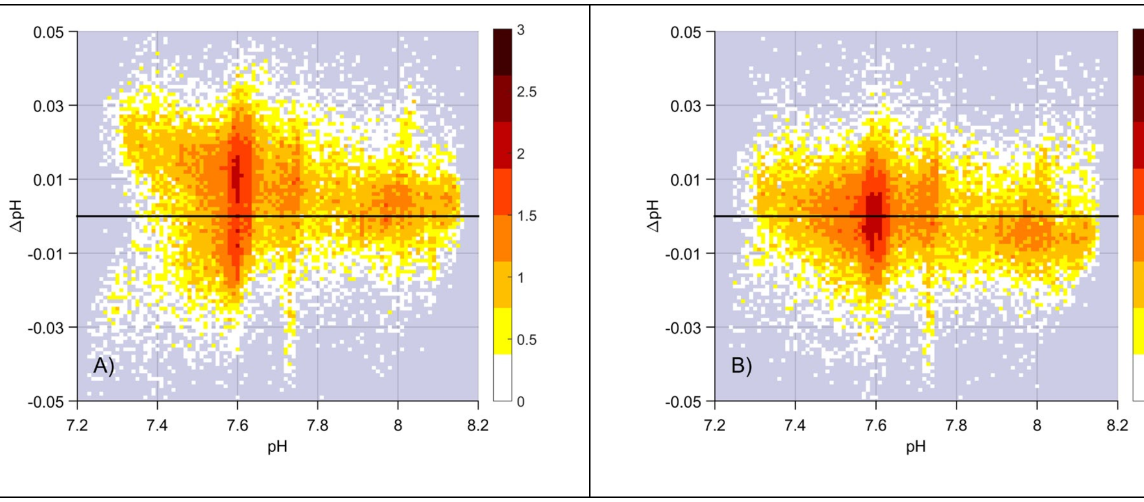


Figure 4. Group 2 data, original (left column) and modified, following Fong & Dickson,[58] (right column) pKs and TB values, two-dimensional histograms showing the number of data falling within bins of (A&B) ΔpH (y-axis, ΔpH, i.e., measured pH minus pH calculated, pH=f(DIC,TA)) vs. pH (x-axis); (C&D) ΔTA (y-axis, ΔTA, i.e., measured TA minus TA calculated, TA=f(pH,DIC)) vs. pH (x-axis); (E&F) ΔTA (y-axis) vs. AOU (x-axis). z-axis shows the histogram frequency in logarithmic scale. The pH is on the Total Scale, at 25ºC and atmospheric pressure, TA & AOU in µmol.kg^{-1}. Note: calculated pH in B) contains an organic TA contribution of 5.9 µmol.kg^{-1}, in D & F no organic TA is considered.

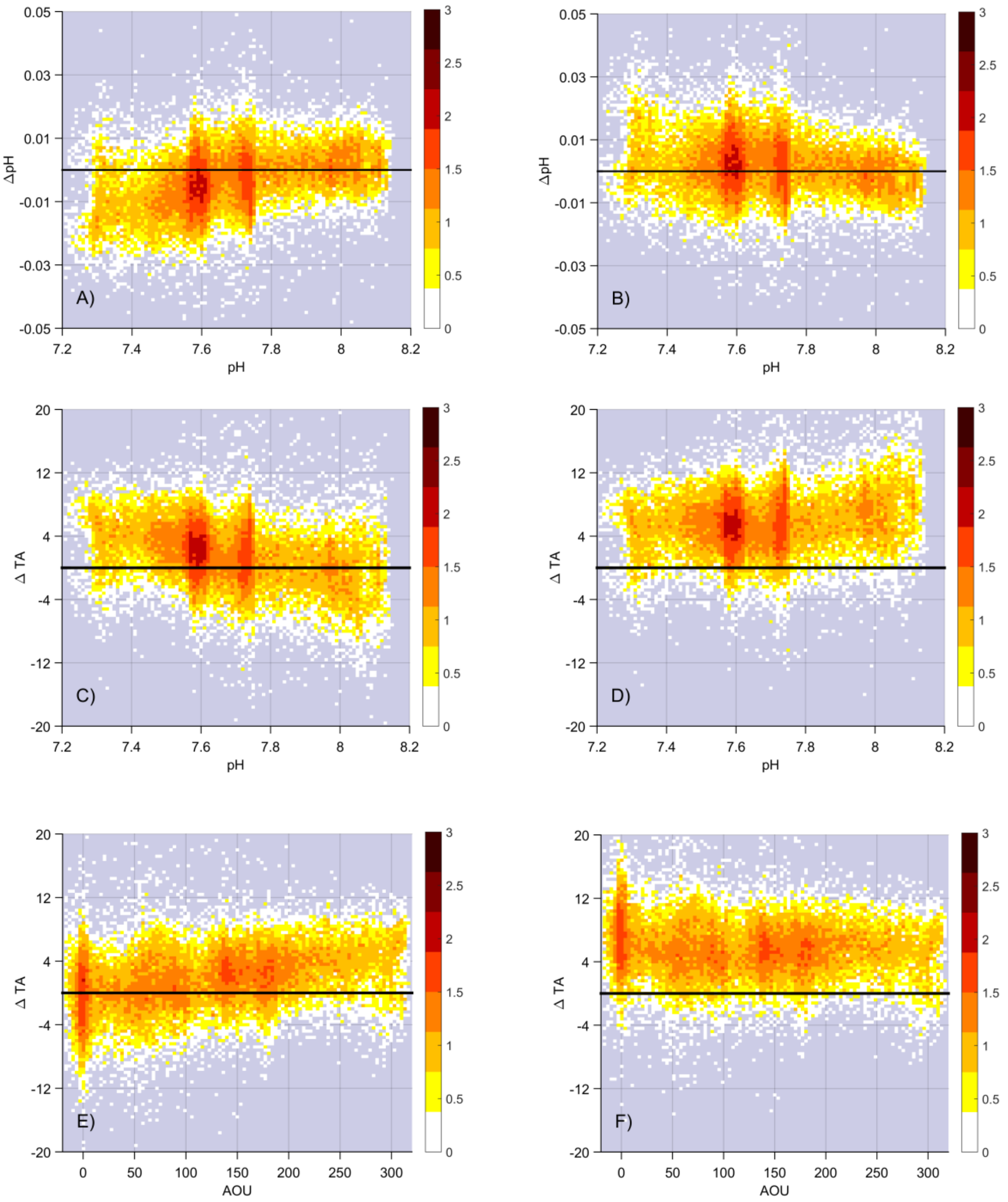
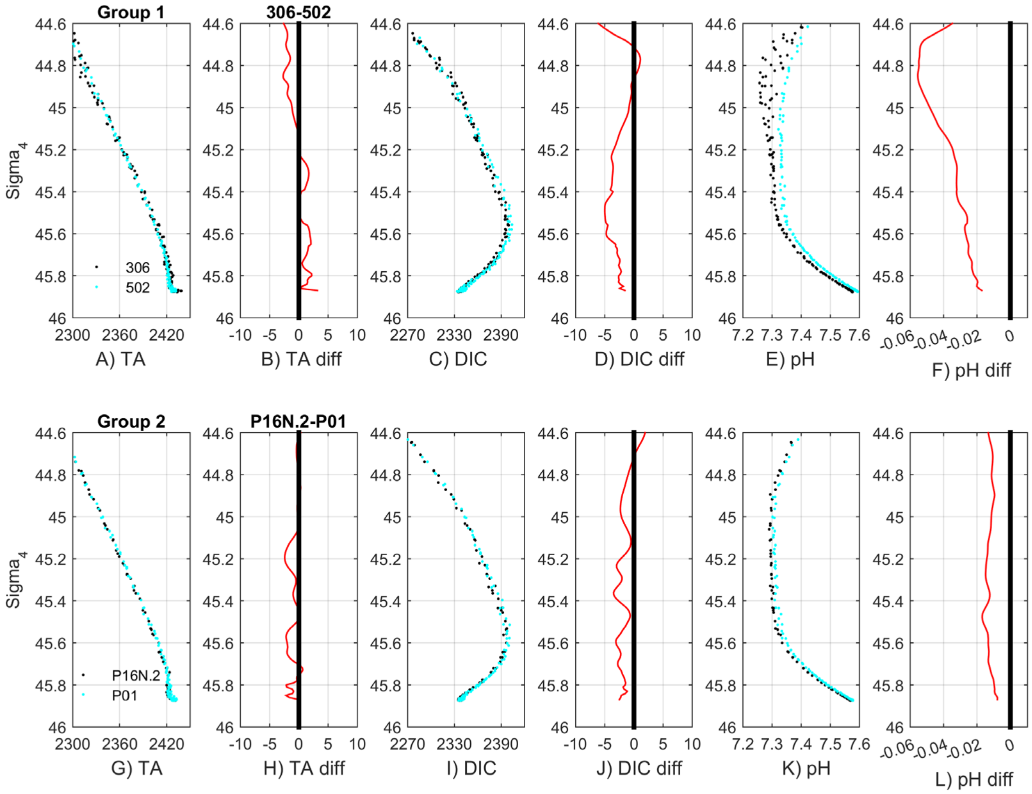


Figure 5. North Pacific Ocean crossover analysis for Group 1 (upper row, cruises 306 and 502) and Group 2 (lower row, cruises P16N.2 and P01) comparing samples for (A&G) TA, (C&I) DIC and (E&K) original pH; and the corresponding mean difference profiles between cruises for (B&H) TA, (D&J) DIC and (F&L) pH. The pH is on the Total Scale, at 25ºC and atmospheric pressure; DIC and TA are in µmol.kg^{-1}.



TABLES.

No tables.

ASSOCIATED CONTENT

Supporting Information.

The following file is available free of charge.

Tables with metadata information about the cruises in Group 1 (Table S1), Group 2 (Table S2), CO_2 thermodynamic constants used (Table S3) and crossover analysis (Table S4). Figures with more information about Group 1 and 2 measured minus calculated DIC (Figure S1) and pH (Figures S2, S3 and S4). Figures showing the results for crossovers in the South Pacific (Figure S5), South Atlantic (Figure S6) and North Indian (Figure S7) oceans. Figure with more information about Group 2 measured minus calculated TA with different constants (Figure S8). (PDF).

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CCHDO, CLIVAR and Carbon Hydrographic Data Office, https://cchdo.ucsd.edu/; CLIVAR, Climate and Ocean Variability, Predictability and Change; CSIF, Carbonate System Intercomparison Forum, https://www.us-ocb.org/ocean-carbonate-system-intercomparison-forum/; GOA-ON, Global Ocean Acidification Observing Network, http://goa-on.org/home.php; GO-SHIP, Global Ocean Ship-Based Hydrographic Investigations Program; OA-ICC, Ocean

Acidification International Coordination Centre, www.iaea.org/services/oa-icc; IOC-UNESCO, Intergovernmental Oceanographic Commission of the United Nations Educational, Scientific and Cultural Organization, http://www.unesco.org/new/en/natural-sciences/ioc-oceans/; IOCCP, International Ocean Carbon Coordination Project, www.ioccp.org

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Global ocean spectrophotometric pH assessment: consistent inconsistencies

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Supporting Information.

Table S1. Relevant metadata for Group 1 cruises, all used UNPUR mCP. Total number of data 38,171. Adjustments proposed by GLODAPv2[1] are additive. This manuscript uses original and corrected data.

EXPOCODE	GLODAPv2 Cruise Nº	Alias	Chief Scientist	Carbon PIs	pH method	DIC adjustment	TA adjustment	pH adjustment
06MT20030723	56	MT59/2, SFB 460	M. Rhein	D. Wallace	Automated (Friis)[2]	0	3	0.000
49NZ20030803	486	BEAGLE_2003, CLIVAR P06_2003	M. Fukasawa, S. Watanabe	A. Murata	Automated (Nippon ANS)	0	0	-0.013
49NZ20031106	487	BEAGLE_2003, CLIVAR A10_2003	Y. Yoshikawa	A. Murata	Automated (Nippon ANS)	0	0	0
49NZ20031209	488	BEAGLE_2003, CLIVAR I03/I04_2003	M. Fukasawa	A. Murata	Automated (Nippon ANS)	0	7	0.000
49NZ20050525	495	MR05-02, CLIVAR P10_2005	T. Kawano	A. Murata	Automated (Nippon ANS)	0	0	-0.005
49NZ20051031	497	MR05-05 Leg 1, CLIVAR P03E, Leg 2, CLIVAR P03C	T. Kawano, A. Murata, I. Kaneko	A. Murata	Automated (Nippon ANS)	0	0	-0.013
325020060213	306	CLIVAR P16N_2006	C. Sabine Leg 1, R. Feely Leg 2	C. Sabine, R. Feely, F. Millero, R. Wanninkhof	Manual	0	0	0.013
33RR20070322	353	CLIVAR I09N_2007	J. Sprintall	R. Feely, C. Sabine, F. Millero	St 89-123 automated, St 124-199 manual	0	0	0.000
49NZ20070724	502	MR07-04, CLIVAR P01_2007	T. Kawano	A. Murata	Automated (Nippon ANS)	0	0	-0.015
49NZ20071008	504	MR07-06 Leg 1, CLIVAR P01W/P14N	T. Kawano	A. Murata	Automated (Nippon ANS)	0	0	-0.015
49NZ20071122	505	MR07-06 Leg 2, CLIVAR P14C	A. Murata	A. Murata	Automated (Nippon ANS)	0	0	-0.009
33RO20071215	345	CLIVAR P18_2007	J. L. Bullister, G. C. Johnson	R. Feely, F. Millero, R. Wanninkhof	Manual	0	0	0
33RR20080204	354	CLIVAR I06S_2008	K. Speer	R.Feely, A.Dickson	Automated (Carter)[3]	0	0	-0.020
35MF20080207	385	CLIVAR A12, BONUS GoodHope	S. Speich	M. González-Dávila, B. Delille	Automated (QUIMA)[4]	0	0	-0.014
318M20091121	273	CLIVAR P06_2009	A. M. Macdonald, R. Curry	R. Wanninkhof, F. Millero	Automated	0	0	-0.010
49NZ20090410	507	Leg 1, CLIVAR P21W; Leg 2, CLIVAR P21E	A. Murata, H. Uchida	A. Murata	Automated (Nippon ANS)	0	0	-0.011
49UP20100706	609	CLIVAR P09_2010, RF10-05	T. Nakano	H. Kamiya	Automated?	-4	0	0.000
06MT20110405	64	M84_3	T. Tanhua	M. Álvarez, L. Mintrop, T. Tanhua	Manual	--	0	0.000
320620110219	295	CLIVAR S04P_2011	J. Swift	R. Feely, C. Sabine, F .Millero, A. Dickson	Automated	0	0	0.009

Table S2. Relevant metadata for Group 2 cruises. Total number of data 34,035. Adjustments proposed by GLODAPv2[1,5] are additive. This manuscript uses original data.

EXPOCODE	GLODAPv2 Cruise Nº	Alias	Chief Scientist	Carbon PIs	pH method	DIC adjustment	TA adjustment	pH adjustment
33RO20100308	346	A13.5	J. Bullister, R. Key	R. Wanninkhof, R. Feely, A.Dickson	Corrected to PUR Automated	0	0	0
33AT20120324	329	A22	R. Curry	R. Wanninkhof, R. Feely, F. Millero	PUR Automated	0	0	0
33AT20120419	330	A20	M. McCartney	R. Wanninkhof, R. Feely, A. Dickson	PUR Automated	0	0	0.012
33RO20120721	-	GOMECC2	R. Wanninkhof, M. Wood, L. Barbero	E. Peltola, A. Joesoef, X. Liu and colaborators	PUR Manual	-	-	-
318M20130321	1035	P02	J.Swift, S.Yoshida Leg 1, S. Mecking, G. Voet Leg 2	R. Feely, A. Dickson	PUR Automated	0	0	0.010
33RO20130803	1041	A16N	M. O. Baringer, J. L. Bullister	R. Wanninkhof, F. Millero, R. Feely	UNPUR Automated	0	0	0
33RO20131223	1042	A16S	R. Wanninkhof, L. Barbero	R. Wanninkhof, F. Millero, R. Feely	UNPUR Automated	0	0	0
320620140320	1036	P16S	L. Talley, B. Carter	R. Feely, A. Dickson	PUR Automated (Carter)[3]	0	0	0
49NZ20140717	1053	P01	H. Uchida	A. Murata	PUR Automated (Nippon ANS)	0	0	0
33RO20150410	1043	P16N.1	J. Cross, S. Siedlecki	S. Alin, R. Wanninkhof, A. Dickson	PUR Automated (Carter)[3]	0	0	0.016
33RO20150525	1044	P16N.2	A. Macdonald, S. Mecking	S. Alin, R. Wanninkhof, A. Dickson	PUR Automated (Carter)[3]	0	0	0.016
33HQ20150809	-	ARC01	D. Kadko, W. Landing	F. Millero, R. Woosley	PUR Automated	0	0	0
33RR20160208	1046	I08S	A. Macdonald, V. Menezes	R. Wanninkhof, A. Dickson, R. Feely	PUR Automated (Carter)[3]	0	0	0
33RR20160321	-	I09N	L. Barbero, C. Rodriguez	R. Wanninkhof, A. Dickson	PUR Automated (Carter)[3]	-	-	-
320620170703	-	P06a	S. Mecking, I. Rosso	R. Wanninkhof, A. Dickson, R. Feely	PUR Automated (Carter)[3]	-	-	-
320620170820	-	P06b	K. Speer, L. Schulze	F. Millero, R. Wanninkhof, A. Dickson, R. Feely	PUR Automated (Carter)[3]	-	-	-

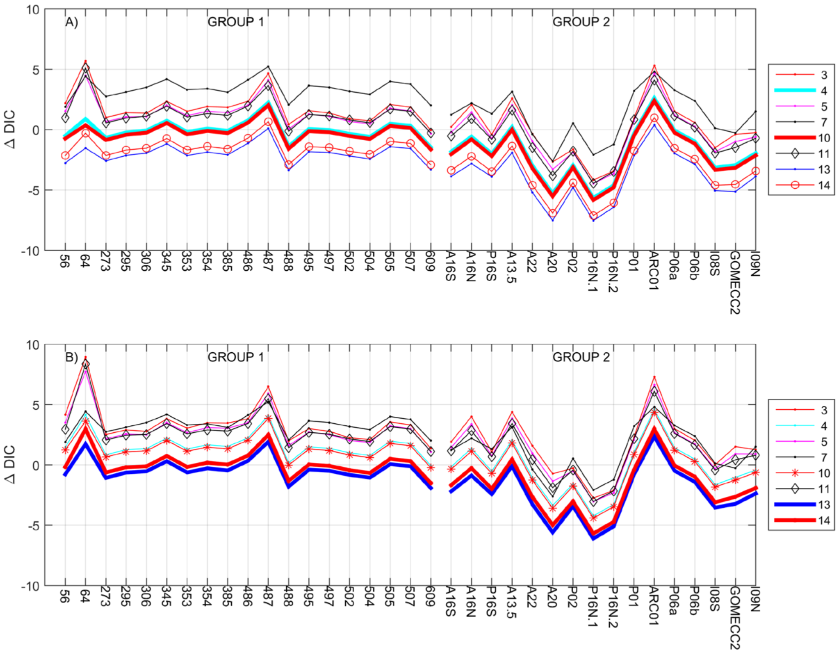
Table S3. Summary of the CO_2 dissociation constants used in the present work.

Authors	**Acronym**	**K1K2 CO2SYS option**	**Temperature range (ºC)**	**Salinity range**	**Scale**	**Seawater**
Hansson[6] refit by Dickson & Millero[7]	H87	3	2-35	20-40	Seawater (SWS)	Artificial
Mehrbach[8] refit by Dickson & Millero[7]	M87	4	2-35	20-40	SWS	Artificial
Hansson[6] & Mehrbach[8] refit by Dickson & Millero[7]	HM87	5	2-35	20-40	SWS	Artificial
Peng et al.[9]	P87	7	2-35	19-43	NBS	Real
Lueker et al.[10]	L00	10	2-35	19-43	Total	Real
Mojica-Prieto & Millero[11]	MM02	11	0-45	5-42	SWS	Real
Millero et al.[12]	M06	13	0-50	1-50	SWS	Real
Millero[13]	M10	14	0-50	1-50	SWS	Real

Table S4. Summary of crossover analysis reported in Section 3.2. The crossover areas are shown in Figure 1. For each cruise in Figures 5, S5, S6 & S7, the table shows the mean ± standard deviation for TA, DIC and pH measurements at given sigma$_4$ intervals, and the corresponding number of samples (N). The differences between cruises are calculated from the mean difference profile for each property showed in the crossover Figures. TA and DIC in µmol.kg^{-1}, pH on the Total Scale at 25ºC and atmospheric pressure.

Crossover Area	**Cruises**	**TA**	**DIC**	**pH**
North Pacific Ocean Sigma$_4$>45.86	306 - Group 1 US RSMAS P16N 2006 Manual UNPUR mCP (N=21)	2,429.1 ± 3.8	2,338.5 ± 0.7	7.564 ± 0.010
	502 - Group 1 Japanese P01 2007 Automated UNPUR mCP (N=27)	2,427.4 ± 1.7	2,340.5 ± 1.3	7.582 ± 0.009
	306 - 502 difference	1.7 ± 2.1	-2.0 ± 0.6	-0.018 ± 0.001
North Pacific Ocean Sigma$_4$>45.86	P16N.2 - Group 2 US SIO 2015 Automated PUR mCP (N=14)	2,426.5 ± 3.4	2,336.8 ± 0.8	7.559 ± 0.009
	P01 - Group 2 Japanese 2014 Automated PUR mCP (N=25)	2,427.2 ± 2.2	2,339.2 ± 0.7	7.567 ± 0.009
	P16N.2 - P01 difference	-0.8 ± 1.2	-2.4 ± 0.2	-0.008 ± 0.001
South Western Pacific Ocean Sigma$_4$>45.96	273 - Group 1 US RSMAS P06 2009 Automated UNPUR mCP (N=42)	2,367.4 ± 0.7	2,262.5 ± 0.8	7.625 ± 0.002
	P06a - Group 2 US SIO 2017 Automated PUR mCP (N=128)	2,362.5 ± 0.2	2,262.5 ± 0.3	7.607 ± 0.000
	273 - P06a difference	4.5 ± 0.2	-0.4 ± 0.1	0.019 ± 0.001
Eastern South Atlantic Ocean Sigma$_4$>45.8	487 - Group 1 Japanese A10 2003 Automated UNPUR mCP (N=21)	2,346.0 ± 6.3	2,207.2 ± 4.8	7.713 ± 0.006
	346 - Group 2 US SIO A13.5 2010 Automated corrected to PUR mCP (N=42)	2,343.8 ± 6.2	2,206.3 ± 3.6	7.711 ± 0.006
	487-346 difference	0.8 ± 1.3	-0.3 ± 0.8	0.002 ± 0.001
Western South Atlantic Ocean Sigma$_4$>45.85	487 - Group 1 Japanese A10 2003 Automated UNPUR mCP (N=38)	2,346.9 ± 8.0	2,214.9 ± 17.0	7.696 ± 0.022
	1042 - Group 2 US RSMAS A16S 2013 Automated UNPUR mCP (N=42)	2,347.8 ± 7.6	2,218.6 ± 16.2	7.685 ± 0.023
	487 - 1042 difference	-0.3 ± 1.2	-2.1 ± 2.0	0.008 ± 0.003
Northern Indian Ocean Sigma$_4$>45.94	353 - Group 1 US RSMAS I09N 2007 Manual UNPUR mCP (N=60)	2,397.4 ± 1.5	2,287.3 ± 3.1	7.628 ± 0.006
	I09N - Group 2 US SIO 2016 Automated PUR mCP (N=53)	2,396.4 ± 3.5	2,287.7 ± 3.0	7.620 ± 0.002
	353 - I09N difference	1.0 ± 2.0	-0.4 ± 0.2	0.008 ± 0.004

Figure S1. Mean value of measured minus calculated DIC (ΔDIC, µmol.kg^{-1}) for corrected Group 1 and original Group 2 data below 2500 dbar. Calculated DIC is a function of pH and TA using eight CO2SYS Matlab® K_1 and K_2 options (Table S3), with A) option 1[14,15] and B) option 3[15,16] for TB and K_{SO4}. Group 1 and 2 cruises are respectively identified with their GLODAPv2 cruise number (Table S1), and with the alias (Table S2)



As commented in Section 2.2, an additional criteria fulfilled by Group 1 and 2 is that the mean ΔDIC (= measured DIC - DIC=f(pH,TA)) below 2500 dbar should be within ±5 µmol.kg^{-1} (Figure S1). Using CO2SYS package for Matlab®[17] with option 10 for the CO_2 constants[18] and option 1 for the total boron to chlorinity ratio (TB)[14] and sulphate constant (K_{SO4}),[15] all cruises fulfil this criteria (Figure S1A).

To satisfy our scientific curiosity, we computed mean ΔDIC values below 2500 dbar for Group 1 and 2 using eight CO2SYS Matlab®[17] K_1 and K_2 options (Table S3), combined with option 1[14,15] and 3[16,15] for TB and K_{SO4}. Most of the considered options yield ΔDIC within ±5 µmol.kg^{-1} (Figure S1), but minimum values are obtained by means of using K_1 and K_2 options 4 (M87, Table S3) and 10 (L00, Table S3) and option 1 for TB[14] and K_{SO4}[15] (Figure S1A). Similar results are obtained with K_1 and K_2 options 13 (M06, Table S3) and 14 (M10, Table S3) with option 3 for TB[16] and K_{SO4}[15] (Figure S1B). In Group 2, as also noted by the GLODAPv2 2016 and 2019 teams, cruises 330 (A20-2012), 1035 (P02-2013), 1043 (P16N.1-2015) and 1044 (P16N.2-2015) pH should be increased (Table S2) in order to increase ΔDIC mean deep values, which are near the -5 µmol.kg^{-1} limit (Group 2, Figure S1A). Those corrections are not applied in this work.

Figure S2. Measured minus calculated pH (ΔpH) vs. pH for uncorrected data included in Group 1. Calculated pH is a function of DIC and TA using CO2SYS Matlab® K_1 and K_2 option 10 (Table S3), combined with option 1[14,15] for TB and K_{SO4}. Blue dots are all data for Group 1, red dots the data for each cruise, which are identified with the corresponding expocode (Table S1) in each plot. The pH is on the Total Scale at 25ºC and atmospheric pressure.

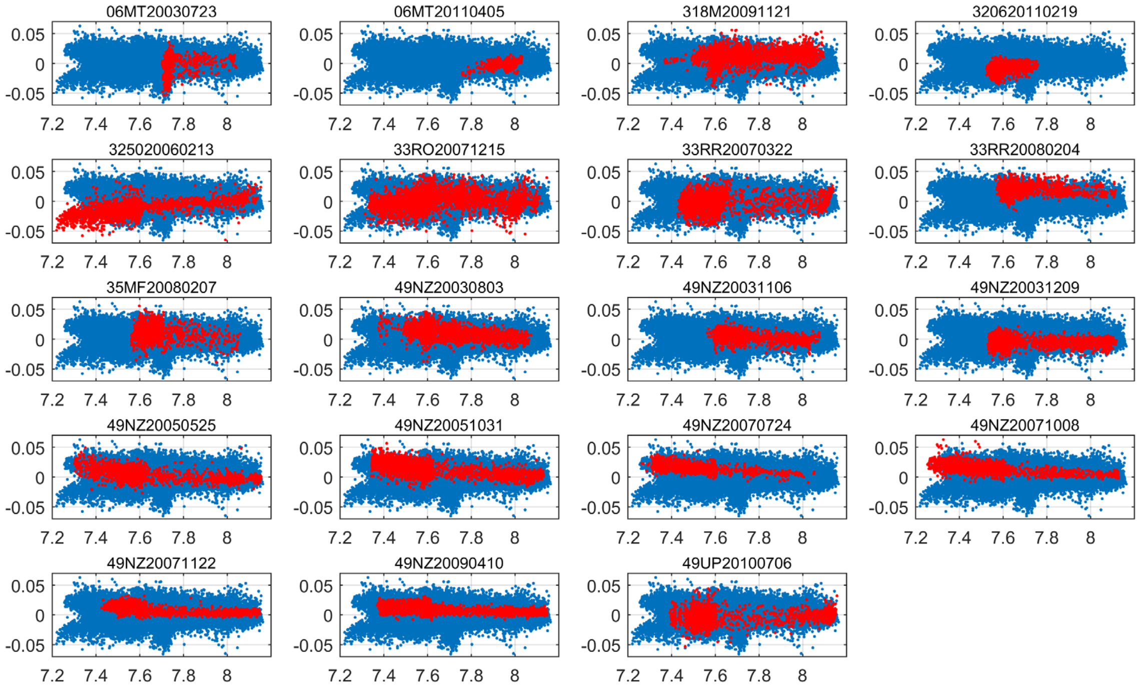


Figure S3. Measured minus calculated pH (ΔpH) vs. pH for corrected data included in Group 1. Calculated pH is a function of DIC and TA using CO2SYS Matlab® K_1 and K_2 option 10 (Table S3), combined with option 1[14,15] for TB and K_{SO4}. Blue dots are all data for Group 1, red dots the data for each cruise, which are identified with the corresponding expocode (Table S1) in each plot. The pH is on the Total Scale at 25ºC and atmospheric pressure.

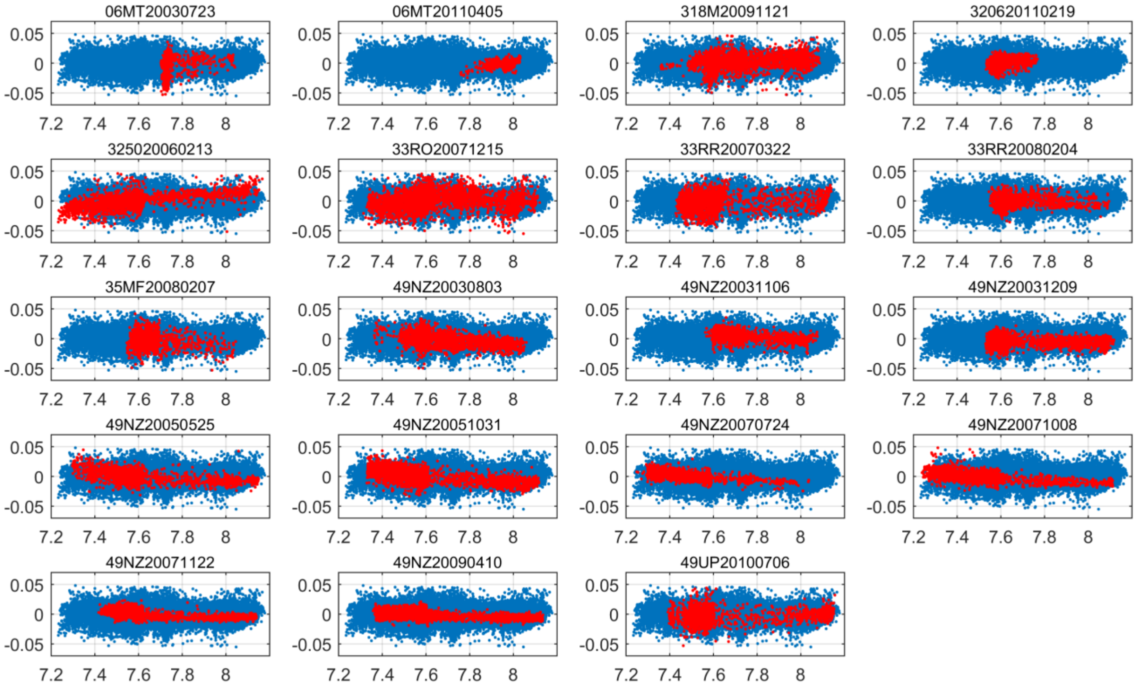


Figure S4. Measured minus calculated pH (ΔpH) vs. pH for original data in Group 2. Calculated pH is a function of DIC and TA using CO2SYS Matlab® K_1 and K_2 option 10 (Table S3), combined with option 1[14,15] for TB and K_{SO4}. Blue dots are all data for Group 2, red dots the data for each cruise, which are identified with the corresponding alias (Table S2) in each plot. The pH is on the Total Scale at 25ºC and atmospheric pressure.

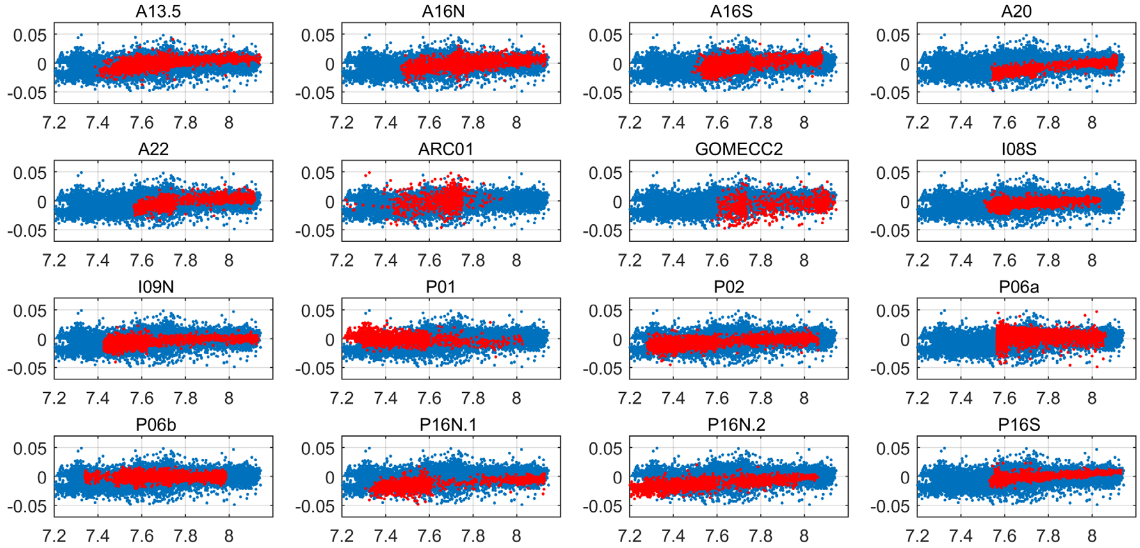
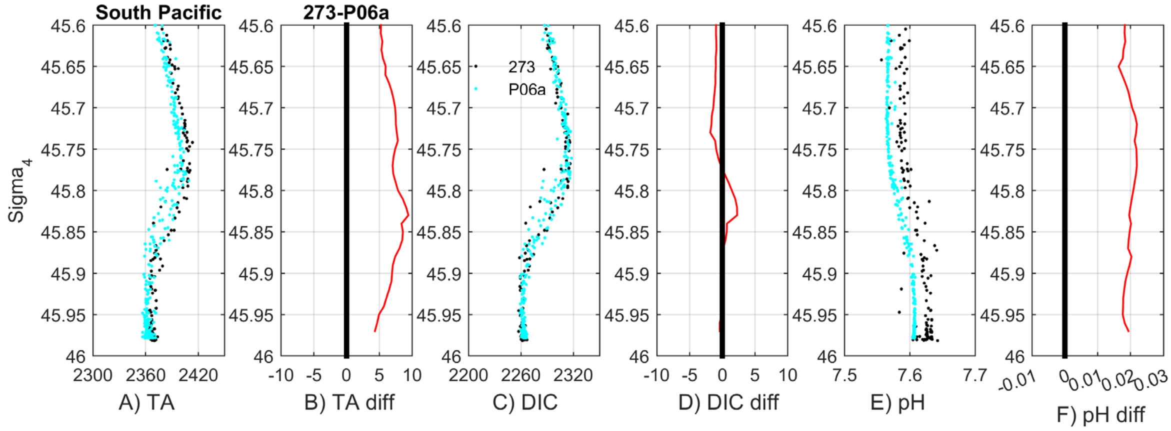
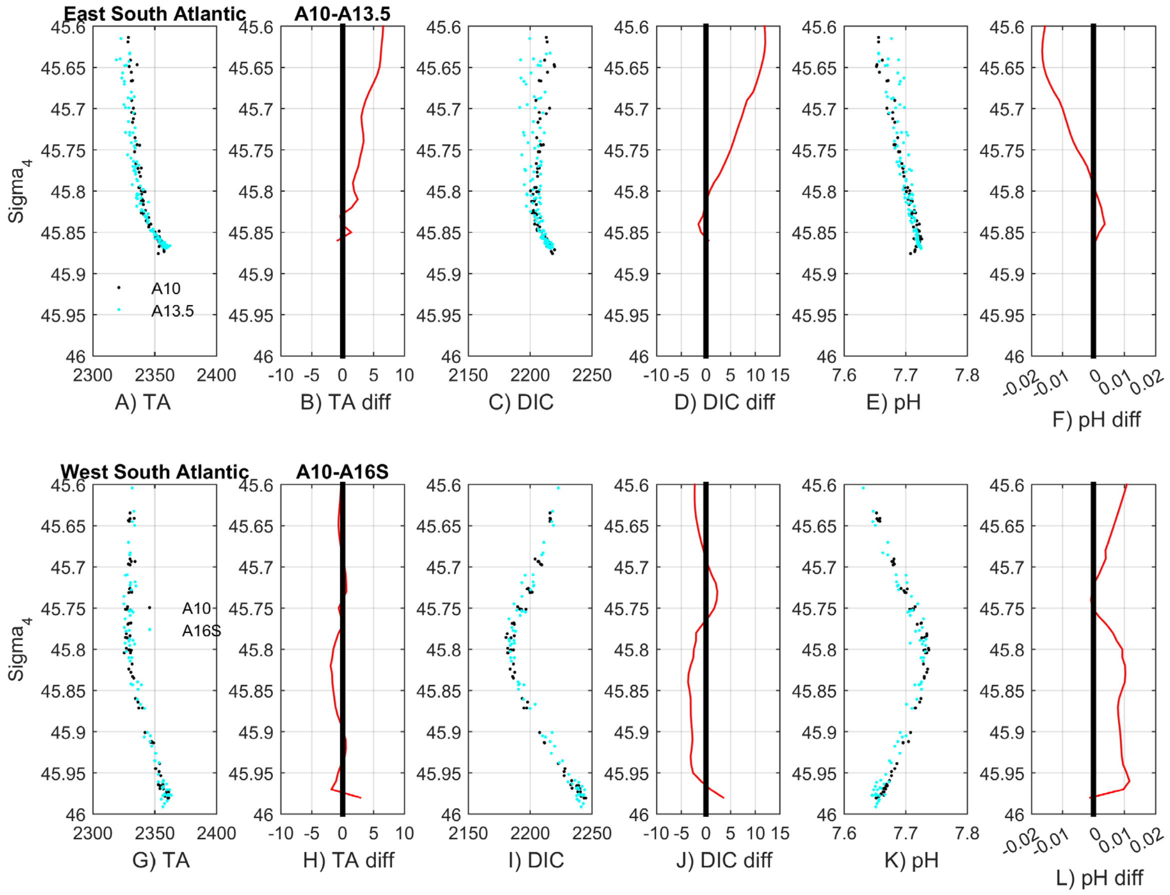


Figure S5. South Pacific Ocean crossover analysis between Group 1 Nº273 P06 (2009) and Group 2 P06a (2017) cruises comparing samples for (A) TA, (C) DIC and (E) original pH. The corresponding mean difference profiles between 273 and P06a cruises for (B) TA, (D) DIC and (F) pH are also shown. The pH is on Total Scale at 25ºC at atmospheric pressure; DIC and TA in µmol.kg^{-1}.



Here we compare two US repeat P06 cruises, in 2009 (Group 1 cruise 273, RSMAS automated UNPUR mCP) and 2017 (Group 2 cruise P06a, SIO automated PUR mCP). For sigma$_4$>45.96 waters the mean differences (273-P06a) for TA, DIC and pH are 4.5±0.2 µmol.kg^{-1}, -0.4±0.1 µmol.kg^{-1}, 0.019±0.001, (Table S4), respectively. While 2017 P06a is considered internally consistent (Figure S4 & Table S2), GLODAPv2.2016[1] recommended a pH adjustment of -0.01 for cruise 273 (Table S1, Figure S3). Both cruises used automated pH systems, and the same spectrophotometer model (but not the same system). The 0.02 pH units discrepancy at a mean deep water pH of ≈7.6, cannot be definitively ascribed to a particular reason (e.g., biases in sampling and preservation, equipment calibration or the PUR to UNPUR mCP dichotomy).

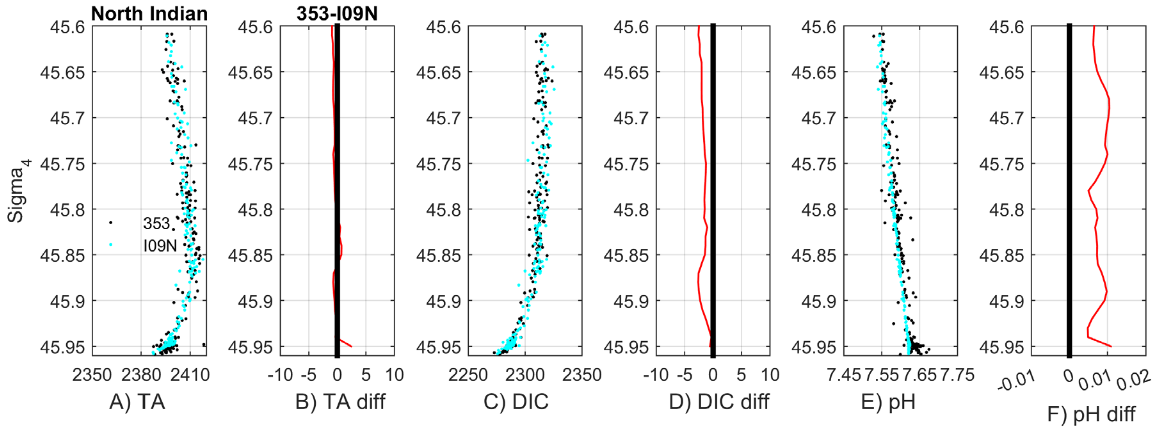
Figure S6. South Atlantic Ocean crossover analysis for Group 1 (Nº487, A10) & 2 (A13.5&A16S) cruises. Upper row shows the Eastern end (cruises A10-2003 and A13.5-2010) and the lower row the Western end (cruises A10-2003 and A16S-2013), comparing samples for (A&G) TA, (C&I) DIC and (E&K) original pH. The corresponding mean difference profiles between cruises for (B&H) TA, (D&J) DIC and (F&L) pH are also shown. The pH is on Total Scale at 25ºC at atmospheric pressure; DIC and TA in µmol.kg^{-1}.



In the Eastern South Atlantic (Figure 1) we compare a Japanese cruise (Group 1 cruise 487, CLIVAR A10 2003, automated UNPUR mCP) with a US cruise (Group 2 cruise 346, GO-SHIP A13.5 2010, automated SIO corrected to PUR mCP). Mean differences for TA, DIC and pH between A10 and A13.5 for sigma$_4$>45.8 waters are 0.8±1.3 µmol.kg^{-1}, -0.3±0.8 µmol.kg^{-1}, 0.002±0.001, respectively (Table S4), at a mean deep water pH of ≈7.7. The pH measured in both cruises agrees, the original A13.5 UNPUR mCP pH data was corrected to PUR dye using a pH dependent offset estimated by fitting a 2nd order polynomial to the Acros Organics dye data in Figure 2A by Liu et al.[19]

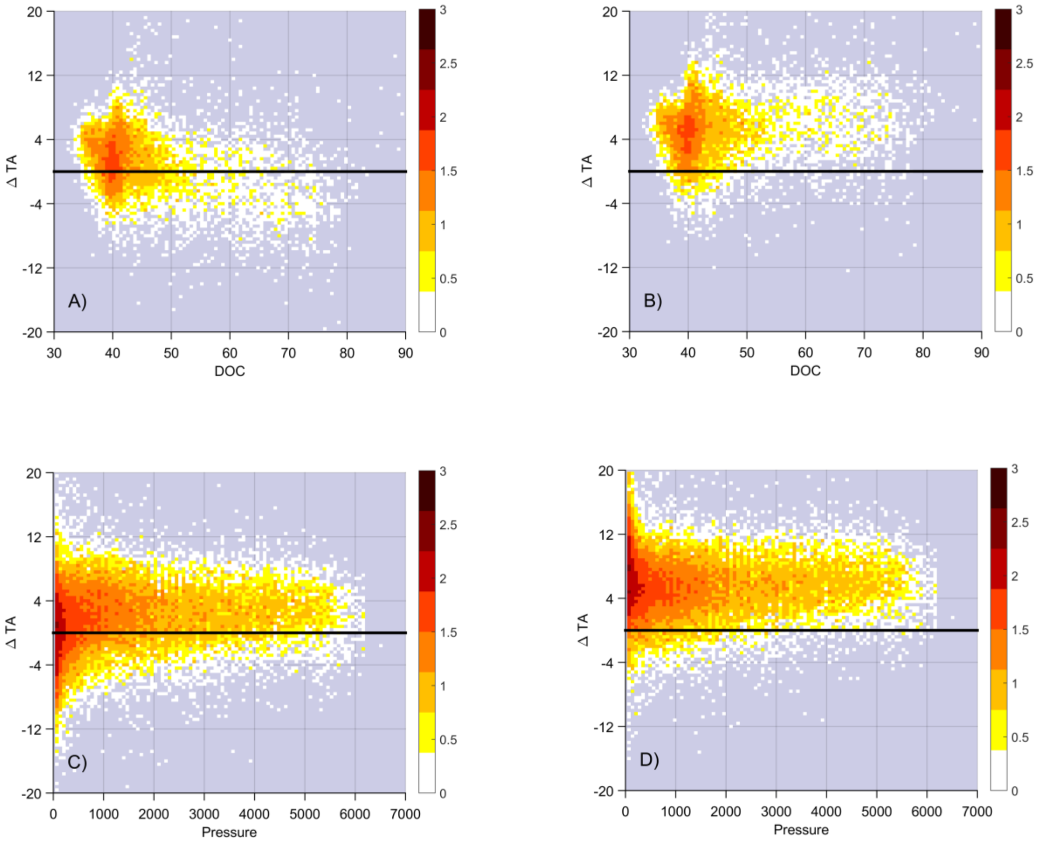
In the Western South Atlantic (Figure 1) we compare the same Japanese cruise (487, CLIVAR A10 2003, automated UNPUR mCP) with another US cruise (1042, GO-SHIP A16S 2013, automated RSMAS UNPUR mCP). Mean differences for TA, DIC and pH between A10 and A13.5 for sigma$_4$>45.85 waters are -0.3±1.2 µmol.kg^{-1}, -2.1±2.0 µmol.kg^{-1}, 0.008±0.003, respectively (Table S4), at a mean deep water pH of ≈7.7. The pH differences, given the TA and DIC agreement point to sampling and/or methodological issues with pH measurements, including the interference of mCP impurities.

Figure S7. North Indian Ocean crossover analysis between Group 1 Nº353 I09N (2007) and Group 2 I09N (2016) cruises comparing samples for (A) TA, (C) DIC and (E) original pH. The corresponding mean difference profiles between 353 and I09N cruises for (B) TA, (D) DIC and (F) pH are also shown. pH Total Scale at 25ºC at atmospheric pressure; DIC and TA in µmol.kg^{-1}.



In this area (Figure 1) we compared two US I09N repeated cruises ten years apart (Group 1 cruise 353, CLIVAR I09N 2007, RSMAS manual UNPUR mCP, and Group 2 I09N 2016, SIO automated PUR mCP). Mean differences for TA, DIC and pH between 2007 and 2016 for sigma$_4$>45.94 waters are 1.0±2.0 µmol.kg^{-1}, -0.4±0.2 µmol.kg^{-1}, 0.008±0.004, respectively (Table S4), at a mean deep water pH of ≈7.6. As in the Western South Atlantic, the two cruises agree for TA and DIC. UNPUR pH is higher than PUR pH which is striking and point to sampling and/or methodological issues with pH measurements, including the interference of mCP impurities.

Figure S8. Group 2 data, original (left column) and modified (right column) pKs and TB values according to Fong & Dickson,[20] two-dimensional histograms showing the number of data falling within bins of discrepancy between measured and calculated, f(pH,DIC), TA (y-axis, ΔTA) vs. (A&B) DOC (x-axis) and (C&D) pressure (x-axis). z-axis shows the histogram frequency in logarithmic scale. TA & DOC in μmol.kg^{-1}, pressure in dbars.



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