Biogeosciences
Discussions

Open Access

Intercomparison of carbonate chemistry measurements on a cruise in northwestern European shelf seas

M. Ribas-Ribas[1], V. M. C. Rérolle[1,2], D. C. E. Bakker[3], V. Kitidis[4], G. A. Lee[3], I. Brown[4], E. P. Achterberg[1,5], and T. Tyrrell[1]

[1]Ocean and Earth Science, National Oceanography Centre Southampton, University of Southampton, Southampton, UK
[2]National Oceanography Centre Southampton, Southampton, UK
[3]Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich Research Park, Norwich, UK
[4]Plymouth Marine Laboratory, Prospect Place, Plymouth, UK
[5]GEOMAR, Helmholtz Centre for Ocean Research, Kiel, Germany

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

BGD

11, 2793–2822, 2014

Intercomparison of carbonate chemistry measurements

M. Ribas-Ribas et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

Four carbonate system variables were measured in surface waters during a cruise traversing northwestern European shelf seas in the summer of 2011. High resolution surface water data were collected for partial pressure of carbon dioxide (pCO_2; using two independent instruments) and pH_T, in addition to discrete measurements of total alkalinity and dissolved inorganic carbon. We thus overdetermined the carbonate system (four measured variables, two degrees of freedom) which allowed us to evaluate the level of agreement between the variables. Calculations of carbonate system variables from other measurements generally compared well (Pearson's correlation coefficient always ≥ 0.94; mean residuals similar to the respective uncertainties of the calculations) with direct observations of the same variables. We therefore conclude that the four independent datasets of carbonate chemistry variables were all of high quality, and as a result that this dataset is suitable to be used for the evaluation of ocean acidification impacts and for carbon cycle studies. A diurnal cycle with maximum amplitude of 41 µatm was observed in the difference between the pCO_2 values obtained by the two independent analytical pCO_2 systems, and this was partly attributed to irregular seawater flows to the equilibrator and partly to biological activity inside the seawater supply and one of the equilibrators. We discuss how these issues can be addressed to improve carbonate chemistry data quality on research cruises.

1 Introduction

Accurate determination of the inorganic carbon system is a key requirement for ocean acidification studies, as it forms the basis for assessments of biogeochemical responses to changes in ocean carbonate chemistry as a result of rising atmospheric CO_2 concentrations. It is also essential for the determination of the air–sea fluxes of CO_2, calculation of carbon budgets and estimation of anthropogenic CO_2 concentrations in different water masses. When the carbonate system is overdetermined, it is

possible to test if the different variables are consistent with one another. This requires that more than two of the analytical variables (total dissolved inorganic carbon (C_T), total alkalinity (A_T), pH_T, or partial pressure or fugacity of CO_2 (pCO_2, fCO_2)) are determined.

Several at-sea intercomparison studies have taken place in recent years. Lamb et al. (2001) investigated 25 cruises in the Pacific Ocean where at least two of the four inorganic carbon variables were determined. They examined the consistency of the dataset using certified reference material analyses, precision of at-sea replicate analyses, agreement between shipboard analyses and replicate shore based analyses, comparison of deep water values at locations where two or more cruises overlapped or crossed, consistency with other hydrographic parameters and internal consistency with multiple carbon variables measurements. With these evidences they adjusted the carbonate data for inconsistencies to obtain a combined dataset. These workers found that C_T and A_T had an overall accuracy of $3\,\mu\mathrm{mol\,kg}^{-1}$ and $5\,\mu\mathrm{mol\,kg}^{-1}$, respectively.

Körtzinger et al. (2000) reported on a comprehensive shipboard, international intercomparison exercise which used one discrete and seven underway systems for the measurement of fCO_2. This exercise showed that underway fCO_2 can be determined to a high level of precision ($\pm 2\,\mu\mathrm{atm}$) with a variety of equilibrator and system designs. Johnson et al. (1999) compared C_T, fCO_2 and A_T measurements for the same intercomparison exercise than Körtzinger et al. (2000). These scientists found a systematic $9\,\mu\mathrm{atm}$ overestimation of fCO_2 values calculated from C_T and A_T measurements relative to observed fCO_2.

Millero et al. (2002) noted that use of pH_T and C_T from field measurements from the Atlantic, Indian, Southern and Pacific oceans yielded calculated values of pCO_2 and A_T that were comparable with observed values. The standard errors (1σ) were $\pm 22.3\,\mu\mathrm{atm}$ in pCO_2 and $\pm 4.3\,\mu\mathrm{mol\,kg}^{-1}$ in A_T. Lueker et al. (2000) noted that observed values of pCO_2 above $500\,\mu\mathrm{atm}$ were higher than pCO_2 calculated from C_T and A_T by on average 3.35 %. This apparent discrepancy has not yet been explained satisfactorily (Dickson, 2010). It is possible that an unidentified acid-base system affects the calculation

of pCO$_2$ or that one or more dissociation constants for acid-base equilibria are not well parameterised at high pCO$_2$ (Dickson, 2010).

Hoppe et al. (2012) reported that, in experimental ocean acidification perturbation studies, the pCO$_2$ values calculated from C_T and A_T were typically about 30 % lower than those calculated from A_T and pH$_T$ or from C_T and pH$_T$. These authors did not have an explanation for the discrepancy. The pCO$_2$ maxima discussed by Hoppe et al. (2012) were up to 2500 µatm, well above the pCO$_2$ range typically observed in most open ocean and shelf sea settings.

The aims of our study were to evaluate the quality of our observations of inorganic carbon variables (their utility for assessing ocean acidification impacts) and to investigate differences between observed and calculated variables in the hope of identifying means of improving data quality. Our study differs from some previous work in two aspects: firstly, our study was undertaken in surface waters of shelf seas with large spatial variability, and secondly the data collection effort was not planned in advance as an intercomparison exercise which would have normally involved putting all the instruments in one laboratory, sampling from a single seawater supply and an unusually intense focus on every aspect of carbonate chemistry measurement. Instead, the instruments were in three different separate laboratories, with samples taken from four different seawater outlets and the operators conducting multiple tasks as part of the multidisciplinary research activities conducted on the cruise. Therefore the findings are more representative of a typical multidisciplinary research cruise.

2 Material and methods

The data used in this study were collected in the period 06 June to 07 July 2011 during the RRS *Discovery* research cruise D366 in northwestern European shelf seas. The cruise formed part of the UK Ocean Acidification Research Programme. Two variables of the carbonate system (pCO$_2$ and pH$_T$), plus salinity and sea surface temperature, were determined at a high temporal resolution (every 5 min for one pCO$_2$ system

(pCO$_2$-1), every 6 min for pH$_T$, and every 1 min for a second pCO$_2$ system (pCO$_2$-2)) in surface waters sampled from the underway continuous seawater supply (intake positioned at ca. 5 m depth). In addition, nutrients (nitrate plus nitrite, phosphate and silicate), C_T and A_T were sampled every 2 h from the underway supply, and also collected

5 in surface waters sampled by CTD casts (samples obtained from the sampling bottle closest to 5 m depth; typically between 2.0 and 8.2 m). Continuous temperature and conductivity data were obtained from the Sea-Bird Electronics SBE45 thermosalinograph (TSG) installed on the ship's underway supply. Discrete surface water samples for salinity (S) were collected every 4 h in order to calibrate the conductivity measure-

10 ments. Discrete salinity samples were analysed using a salinometer (Guildline Autosal 8400B). Photosynthetically Active Irradiance, radiation between 400 and 700 nm (PAR) was measured as part of the ship's meteorological parameters with a 2-pi sensor (Skye Instruments, model SKE 510) positioned at 10 m height.

2.1 Carbonate chemistry analysis

15 ### 2.1.1 Partial pressure of CO$_2$

Quasi-continuous measurements of pCO$_2$ in surface water and marine air were undertaken using two different instruments (hereafter pCO$_2$-1 and pCO$_2$-2). The pCO$_2$-1 and pCO$_2$-2 systems undertook 6187 and 26 671 measurements, respectively, of surface water pCO$_2$ during the cruise. For both systems, all calibration gases underwent

20 pre- and post-cruise calibration against certified primary standards from the National Oceanic and Atmospheric Administration (NOAA).

System 1: the system pCO$_2$-1 is an underway pCO$_2$ instrument (PML-Dartcom *Live* pCO$_2$) as described in detail by Hardman-Mountford et al. (2008), with the modified "vented" equilibrator introduced by Kitidis et al. (2012). The instrument was located in

25 a mid-ship chemistry laboratory. The system used a vented-showerhead equilibrator, with ambient light blocked out, to equilibrate seawater CO$_2$ with a headspace. In order to maintain atmospheric pressure in the equilibrator headspace, the unit was vented

M. Ribas-Ribas et al.

to a second equilibrator, which in turn was vented to the atmosphere via a 2 m coil of stainless steel tubing (1.5 mm internal diameter). The equilibrator was fitted with 2 platinum resistance thermometers (Pico Technology, model PT100) and a water-jacket supplied with seawater from the ship's underway seawater system. A seawater flow of 1.6 L min^{-1} was maintained across the equilibrator. The average warming between the ship's underway seawater intake and the equilibrator was $0.5 \pm 0.1\,°C$. Atmospheric measurements of CO_2 were taken from an intake located forward on the deck above of the ship's bridge. Both gas streams from the equilibrator headspace and the air inlet were dried in a Peltier cooler ($-20\,°C$). Mixing ratios of CO_2 and water in the marine air and equilibrator headspace were determined by infrared detection (LI-840, LI-COR). Measurements were referenced against secondary calibration gases from BOC Gases, UK with known CO_2 mixing ratios (0, 251.3 and 446.9 μmol CO_2 mol^{-1}) in synthetic air mixtures (21 % oxygen and 79 % nitrogen). The water was deemed to have spent 1 min in the ship's underway system before reaching the equilibrator and the pCO$_2$ measurements were thus backdated by 1 min.

System 2: the system pCO$_2$-2 is an underway pCO$_2$ system that was located in a container laboratory positioned on the aft-deck of the ship. The instrument setup and calibration procedures have been described by Bakker et al. (2007), with the exception of the vented equilibrator. The percolating packed bed-type equilibrator was identical to the one described in Schuster and Watson (2007). The equilibrator of transparent perspex was positioned next to the window of the container without blinds. Atmospheric samples were taken from an air inlet located forward on the deck above of the ship's bridge. Samples from the equilibrator headspace and marine air were partially dried by being passed through an electric cool box at about 2 °C, prior to analysis. Mixing ratios of CO_2 and water in the marine air and equilibrator headspace were determined by infrared detection with a LI-COR LI7000. The LI-COR was calibrated using secondary gas standards BOC Gases, UK with CO_2 mixing ratios of 2.4, 260.9, 364.2 and 473.1 μmol CO_2 mol^{-1} in an artificial air mixture (21 % oxygen, 79 % nitrogen). Throughout the cruise the seawater flow to the container laboratory was highly vari-

able due to being downstream of other large water usages on board, including large incubation tanks. To avoid flooding of the equilibrator and CO_2 analyser during sudden spikes in supply, the water flow was regulated to a maximum of $1.8\,L\,min^{-1}$. The water flow tended to gradually decrease to very low flow over 6 to 12 h. Two platinum resistance thermometers positioned in the upper and lower part of the seawater stream determined the temperature of the seawater in the equilibrator. Average warming of the seawater between the intake and the equilibrator was estimated as $0.5 \pm 0.4\,°C$. Large temperature deviations reflected the irregular seawater flow to the equilibrator. To make matters worse, the post-cruise temperature calibration of the PT100 sensors showed excessive drift of 4–5 °C relative to the pre-cruise calibration. The absolute calibration of the temperature sensors was therefore deemed unreliable. Equilibrator temperatures from 13 June (09:57) to 17 June (17:12) have been reduced by 0.7 °C, while equilibrator temperatures after 19 June (21:57) have been increased by 0.7 °C to remove negative temperature change. We determined that the CO_2 measurements were on water that was 3 min old following intake using a comparison of the intake and the equilibrator temperatures, and therefore back-dated the pCO_2 values by 3 min.

The precision of both pCO_2 systems was 1.0 µatm established using standard gases. We estimate different accuracies for the two systems. Accuracy of system pCO_2-1 is 4 µatm Accuracy of system pCO_2-2 experienced problems with its temperature sensors and therefore had an estimated accuracy of 10 µatm. The pCO_2 was computed from the CO_2 mixing ratios and the ship's barometric pressure corrected from 18 m height to sea level, and corrected for seawater vapour pressure (Weiss and Price, 1980). Sea surface pCO_2 data were corrected to sea surface temperature to account for the warming between the seawater intake and the equilibrators (Takahashi et al., 1993). The accuracy of the temperature measurements inside the equilibrator was 0.02 °C and 5 °C for pCO_2-1 and pCO_2-2, respectively.

pCO_2-1 measurements were backdated by 1 min and pCO_2-2 measurements by 3 min to account for the travel time of the seawater between the seawater intake and the respective equilibrators (Sect. 2.1.1). The time offsets were chosen objectively as

those producing the minimum standard deviation between paired equilibrator and intake temperatures.

2.1.2 pH_T

Surface water pH_T was measured continuously with an automated instrument located in the mid-ship chemistry laboratory and connected to the ship's underway seawater supply. The pH_T system undertook 29 950 measurements. The surface distribution and the processes that controls pH_T in this cruise has been described by Rérolle et al. (2014). The instrument, described by Rérolle et al. (2013), was based on a colorimetric method using Thymol Blue as pH indicator (Clayton and Byrne, 1993; Rérolle et al., 2012). pH_T was determined on the total scale. Measurements were made every 6 min with a precision of 1 mpH (Rérolle et al., 2013). Three bottles of Tris pH buffer provided by Dr Andrew Dickson (Scripps Institution of Oceanography, Marine Physical Laboratory, University of California San Diego, USA) were analysed at the beginning, middle and end of the cruise to check the accuracy of the pH_T measurements, which was 4 mpH. The Thymol Blue extinction coefficients were determined in the laboratory following the cruise, applying the salinity and temperature ranges observed during the cruise and the indicator's dissociation constant from Zhang and Byrne (1996). Measurements at sea were made at the seawater temperature plus 0.2 °C. The temperature increase was due to warming between the seawater intake and the pH instrument.

2.1.3 Dissolved inorganic carbon and total alkalinity

Samples for C_T and A_T analysis were collected from the underway seawater supply (322 samples in total) and shallow depths sampled (64 samples) using Ocean Test Equipment bottles on the CTD frame following procedures detailed in Bakker et al. (2007). All samples were fixed with 50 µL of saturated mercuric chloride (HgCl$_2$) solution per 250 mL seawater. The samples were analysed in duplicate on replicate 250 mL samples bottles. Two VINDTAs 3C (Versatile Instrument for the Determination

of Titration Alkalinity; Marianda) were used to determine C_T and A_T, with Certified Reference Materials (batch 107) analysed in duplicate for C_T and A_T at the beginning, middle and end of each use of a coulometric cell. One VINDTA was used for surface water samples and the other one for CTD casts. For consistency, we checked offsets between the surface samples and CTD samples which were less than 30 min apart. Because underway sampling was often stopped when we were on station, only 19 stations could be checked. The average offsets between CTD and surface water samples from the continuous supply were 0.3 and 0.5 $\mu mol\,kg^{-1}$ for C_T and A_T, respectively. This is below the accuracy of the method and so we merged the data from the two types of sampling and the two VINDTA 3C instruments. The concentration of C_T was determined using coulometric analysis (Johnson et al., 1987). Analysis for A_T was carried out by potentiometric titration with hydrochloric acid to the carbonic acid end point (Dickson, 1981). The accuracy of the C_T and A_T measurements were 2.0 and 1.5 $\mu mol\,kg^{-1}$ and the precision 1.7 and 1.2 $\mu mol\,kg^{-1}$, respectively.

The final datasets have been submitted to the British Oceanographic Data Centre (http://www.bodc.ac.uk/projects/uk/ukoa/data_inventories/cruise/d366/).

2.2 Nutrients

Analyses of nitrate and nitrite, phosphate and silicate were undertaken using a segmented flow auto-analyser (Skalar San+) following methods described by Kirkwood (1989). Samples were stored in 25 mL polycarbonate vials and kept refrigerated at approximately 4 °C until analysis (conducted within 12 h after sampling). Nutrient concentrations were used for calculations of the carbonate chemistry system.

2.3 Carbonate chemistry calculations

We applied the CO2SYS programme (Lewis and Wallace, 1998; Van Heuven et al., 2011) to all possible pairs of pH_T, pCO_2, C_T and A_T measurements to calculate the other variables, using the carbonate equilibria constants described by Mehrbach

et al. (1973) and refitted by (Mehrbach et al., 1973); Dickson and Millero (1987) and sulphate constants by Dickson (1990). For the borate constants, we used Uppström (1974), but also compared against results calculated using Lee et al. (2010) (Sect. 3.3).

2.4 Intercomparison

5   The sampling frequency of pCO$_2$-1 and pH$_T$ was around 5 min, but the measurements were not synchronised and were undertaken simultaneously (within 1 min) on only 208 occasions. However, it was possible to interpolate pH$_T$ determinations (with a maximum interval of 5 min) and thereby obtain analyses at comparable times.

  Data from the underway temperature, salinity, PAR, pCO$_2$ and pH$_T$ measurements
10   were retrieved at the times of nutrient, C_T and A_T measurements.

  Statistical analyses were used to determine the level of agreement between observed and calculated carbonate system variables:

– Pearson's correlation coefficient (r): a measure of the degree of linear dependence between two variables.

15 – Mean Residual (MR): average difference between two variables, e.g. between the observed values and the values calculated from measurements of a pair of other carbonate variables; MR will be negative if the observed values are on average lower than the calculated values.

– Root Mean Square Error (RMSE): square root of the mean of the squared differ-
20   ences between the observed and calculated values.

  Some properties of individual variables (as opposed to comparisons) are also used in Sect. 3:

– Accuracy is an expression of the lack of bias and relates to the degree of agreement of a measured value with the true value (as determined using a certified
25   reference material). Accuracy is a property of a single type of measurement.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Uncertainty characterizes the range of values within which the true value is asserted to lie with some level of confidence. Uncertainty is derived from inaccuracy and imprecision of measurements, and also from propagation of errors for calculated variables.

In this study, calculated uncertainties were determined by a Monte Carlo approach. The carbonate chemistry variable values that were input into the CO2SYS program (MATLAB version) (Van Heuven et al., 2011) were first adjusted by adding artificial random errors (normally distributed according to the central limit theorem) with a mean of zero and standard deviation equal to the accuracy of measurement. This Monte Carlo approach has previously been used by Juranek et al. (2009) to calculate calcium carbonate saturation state uncertainties.

In this paper we use accuracy and calculated uncertainties as benchmarks. We use them to give an idea of how close a match it is reasonable to expect between observed and calculated values. We compare values of both with MRs and RMSEs to evaluate if the calculated variables are in "good" agreement with the measured variables. For example, if the MR between measured and calculated (from A_T and pCO_2-1) C_T is $-1.7\,\mu\text{mol}\,\text{kg}^{-1}$, whereas the accuracy is $2.0\,\mu\text{mol}\,\text{kg}^{-1}$, then we conclude that there is good agreement between the calculated and measured C_T values. Another way of assessing the degree of agreement is how close the RMSE is to the theoretical uncertainty: for example, a RMSE of 0.008 pH_T units (from C_T and A_T) demonstrates a good agreement between measured and calculated pH_T if the calculated uncertainty according to the Monte Carlo approach is 0.005.

3 Results and discussion

3.1 Comparison between two pCO_2 systems

The pCO_2 datasets obtained using the pCO_2-1 and pCO_2-2 systems are significantly correlated ($r = 0.956$, $p < 0.001$, df = 2679) (Fig. 1). We used a major axis model II

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

regression because both pCO$_2$ include some uncertainty (there are not one dependent and controlled variable and one independent variable). We used the MATLAB code from http://www.mbari.org/staff/etp3/regress.htm. The equation of the regression is pCO$_2$-1 = 0.89 ($\pm$2.06) + 0.99 ($\pm$ 0.01) × pCO$_2$-2. The comparison between both

5 sets of pCO$_2$ data revealed a mean residual of −2.0 µatm (pCO$_2$-1 minus pCO$_2$-2). The RMSE was 10.0 µatm.

Körtzinger et al. (2000) reported that even after correction of all differences between equilibrator temperature readings and following the time synchronization procedure, the remaining mean residual in their study was roughly 2 µatm for most of their cruise.

10 The study by Körtzinger et al. (2000) can be described as an ideal exercise with all instruments sharing a common seawater supply, positioned in the same laboratory and sharing common calibration gases. Considering that our cruise took place in coastal waters with strong gradients in temperature, salinity and pCO$_2$, with the instruments situated in different laboratories and using different sets of calibration gases, and known

15 water flow problems (Sect. 2.1.1), we conclude that an average difference of 2 µatm was reasonable.

The mean residual of pCO$_2$-1 compared with pCO$_2$ calculated from C_T and A_T was 3.0 µatm (n = 43), and of pCO$_2$-2 was 0.5 µatm (n = 156) (Table 1). Both of these mean residuals were well within the expected accuracy of pCO$_2$ calculated from C_T and A_T

20 measurements. The accuracies in C_T and A_T were ±2 µmol kg^{-1} and ±1.5 µmol kg^{-1}, respectively, and this translates into a propagated pCO$_2$ uncertainty of 4.1 µatm.

The residuals of the two pCO$_2$ datasets are presented in Fig. 2. A diurnal cycle was observed in the residuals after 8 days of the cruise, with the amplitude increasing over time and reaching a maximum difference between the two pCO$_2$ systems at

25 Julian date 177 (Figs. 2 and 3). The difference between pCO$_2$-1 and pCO$_2$-2 was in phase with the difference between pCO$_2$-1 and calculated pCO$_2$ values while the reverse was true for pCO$_2$-2. Temperature is a critical parameter for pCO$_2$ calculations. The two analytical pCO$_2$ systems were not in the same laboratory and therefore water spent different lengths of time and took different routes between the ship's seawater

intake and the two equilibrators, and therefore warmed differently. Temperature differences of 2 °C translate into pCO_2 differences of 32 µatm. This temperature effect was more important when the ship sailed through strong surface water temperature gradients. Rapid changes in seawater temperature up to 2–3 °C min^{-1} were observed on
Julian date 180. However, such rapid temperature changes at the seawater intake may not fully translate into pCO_2 changes in the equilibrator, as equilibrator pCO_2 is effectively integrated over equilibration time (around 8 min for CO_2 in both equilibrators). Small differences in the equilibration time between the two systems, i.e. how rapidly they respond to a change in seawater pCO_2, may account for some of the observed
differences between observations by pCO_2-1 and pCO_2-2. Moreover, no trend was observed between the difference in measured pCO_2-1 and pCO_2-2 vs. the difference between the temperature in equilibrator 1 and the sea surface temperature, whereas a positive relationship was observed for equilibrator 2 (Fig. 4).

The discrepancy between the two pCO_2 systems was negative at low light levels,
at night pCO_2-1 was smaller than pCO_2-2 and positive during daylight hours (pCO_2-1 larger than pCO_2-2) (Fig. 3). This pattern was consistent with respiration at night and photosynthesis during the day in the seawater supply to the pCO_2-2 equilibrator or in the equilibrator itself. The length of the seawater pipes to the equilibrator 2 was about twice as long as for equilibrator 1. Furthermore the equilibrator of pCO_2-2 was subject
to direct daylight, compared to the pCO_2-1 equilibrator which was shielded from light.

A multiple regression analysis was performed to estimate the relative importance of two factors (including temperature difference between the two equilibrators (ΔT_{eq}) and PAR) in determining the size of the pCO_2 differences ($\Delta pCO_2 = pCO_2$-1 $- pCO_2$-2). The analysis with ΔT_{eq} and PAR indicated that the correlation was statistically significant ($p < 0.0001$; $F = 587.6$) and that the two parameters together explained 38 % of the ΔpCO_2 variance. ΔT_{eq} and PAR were found to individually explain 17 % and 18 %, respectively, of the variance in ΔpCO_2. Thus we concluded that a combination of (a) biological activity in the seawater system or in equilibrator 2 and (b) major problems with water flow and temperature perturbations in pCO_2-2 (Sect. 2.1.1) partially ex-

plained the diurnal pattern in the pCO_2 differences between the two instruments. The first issue should be addressed in future studies by protection of seawater tubing and equilibrators from light and by regular cleaning of the seawater intake and equilibrators. In addition, the flow rate of the ship's seawater supply should be constant, while the water flow to equilibrators should be sufficient and kept constant by using a water flow controller. The temperature measurements inside the equilibrator should furthermore be accurate.

3.2 Intercomparison of measured and calculated variables

The results of the intercomparison between observed carbonate chemistry variables and those calculated from different pairs of measured variables are presented in Table 1. Statistical techniques were used to evaluate the agreement between the observed and the calculated values. The comparison between observed pH_T and pH_T calculated from observed C_T and A_T concentrations showed a mean residual of 0.001 pH_T units and a RMSE of 0.008 pH_T units (Table 1). This compared to the 0.004 pH_T units accuracy of the measurements. The linear correlation coefficient (r) between observed and calculated values was 0.952 (Table 1). pH_T calculated from C_T and A_T had an uncertainty of 0.005 pH_T units. The RMSE corresponded to twice the accuracy of the pH_T measurements, and a bit less than twice the uncertainty expected from the calculation, so we conclude that there was good agreement between calculated and measured pH_T.

The value of pH_T calculated from pCO_2-1 and A_T had a RMSE of 0.006 when compared to measured pH_T, and the same calculation with pCO_2-2 led to a RMSE of 0.013 (Table 1). The calculated values of pH_T using pCO_2-1 and A_T were therefore better (lower RMSE) than pH_T calculated from C_T and A_T, whereas the calculations using pCO_2-2 and A_T had a higher RMSE. Calculations of pH_T from the combination of pCO_2 with either C_T or A_T may be expected to yield more accurate estimates than calculations of pH_T from C_T and A_T (Table 1), because they do not require reliable estimates of the second dissociation constant of carbonic acid and are relatively in-

sensitive to uncertainties in C_T and A_T (Millero, 2007). However, this is not always the case, as shown here.

pCO_2 calculated from C_T and A_T compared to the pCO_2-1 and 2 observational datasets showed RMSE values of 6.3 µatm and 11.7 µatm, and mean residuals of 3.0 and 0.5 µatm (Table 1). This compares to an accuracy associated with direct measurement of pCO_2 of 4 µatm for pCO_2-1 and of 10 µatm for pCO_2-2. pCO_2 calculated from C_T and A_T is predicted to have an uncertainty of 2.3 µatm. We therefore conclude that our calculated dataset is in good agreement with the measured dataset. Hoppe et al. (2012) reported that, in experimental ocean acidification perturbation studies, pCO_2 values calculated from C_T and A_T were typically about 30 % lower than those calculated from C_T and pH_T or A_T and pH_T. Although calculated values were also lower than measured values (on average) in our study, our data showed a better agreement, perhaps because the highest observed pCO_2 was much lower than the pCO_2 range discussed by Hoppe et al. (2012) (highest pCO_2 here was 450 µatm, whereas in Hoppe's study the maximum was 2500 µatm).

pCO_2 and pH_T do not make a good pair for predicting other variables because they are not fully independent, i.e. the magnitude and variability of pCO_2 is primarily accounted for in pH_T (and vice versa) (Cullison Gray et al., 2011). This is verified here, where the mean residuals for A_T and C_T (observed minus calculated) are comparable to the calculated uncertainty, but both are one order of magnitude greater than the accuracy and precision of observations (Table 1).

C_T calculated from A_T and pCO_2 had RMSE values of $3.9\,\mu\mathrm{mol\,kg^{-1}}$ and $7.2\,\mu\mathrm{mol\,kg^{-1}}$ compared to the measurement datasets of systems pCO_2-1 and 2, and mean residuals of −1.7 and $-0.3\,\mu\mathrm{mol\,kg^{-1}}$ (Table 1). This compares to an accuracy associated with direct measurement of C_T of $2\,\mu\mathrm{mol\,kg^{-1}}$. A_T calculated from C_T and pCO_2-1 had MR values equal to $2.1\,\mu\mathrm{mol\,kg^{-1}}$ and a RMSE value of $4.6\,\mu\mathrm{mol\,kg^{-1}}$ and the calculated uncertainty is $3\,\mu\mathrm{mol\,kg^{-1}}$ (Table 1). This compares to an accuracy associated with direct measurement of A_T of $1.5\,\mu\mathrm{mol\,kg^{-1}}$.

So far in this paper we have checked the consistency of the carbonate system and assessed the quality of the carbonate system measurements. On the whole, the sizes of the offset between measured and calculated values agreed well with expectations based on theoretical calculation and accuracies. The four independent datasets of carbonate chemistry variables are deemed to be of high-quality and therefore suitable to be used as a basis for evaluations of the impacts of OA on ocean biogeochemistry, the estimation of the air–sea fluxes of CO_2, calculation of carbon budgets and the estimation of anthropogenic CO_2 concentrations in different water masses.

Next, we examine possible reasons for discrepancies between measurements and calculated values and make "good practice" recommendations where possible or applicable:

1. The duration of seawater transit in the ship's underway system from the seawater intake to the point of sample collection or measurement (1 to 3 min) varied between the carbonate chemistry measurements. It is important to recognise the period of time it takes for the seawater to arrive in the equilibrator of a pCO_2 instrument. This will allow correction for the difference between the intake temperature and the equilibrator temperature. The omission of a time correction results in unrealistic spikes in the difference between seawater temperature and the temperature inside the equilibrator. This will also reduce the variability in pCO_2 via the temperature correction. However, the average pCO_2 value is still likely to be correct. In addition, both the underway seawater system and the equilibrators tend to smooth out short-lived signals in temperature and pCO_2. This would affect the measurement reliability by smoothing strong gradients. These effects are particularly important in regions with rapid changes in carbonate chemistry and sea water temperature, for example in shelf sea regions with freshwater outflow and in regions with sea ice melt.

2. To obtain high quality pCO_2 datasets we recommend that special care be taken with the operation of the equilibrator systems, including (a) careful control of the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

seawater supply and the water flow through the equilibrator; (b) accurate temperature readings and (c) prevention of plankton and microbial growth in the equilibrator by complete shielding from light.

3. Differences between the recorded sampling time and the actual sampling time also need to be taken into account. C_T and A_T are discrete measurements, while pCO_2 and pH_T are continuous measurements. In addition to the transit times between the intake and the instrument, pCO_2 is an integrated measurement over the timescale of equilibration (around 8 min) and pH_T is an integrated measurement over the timescale of filling the sample chamber (ca. 60 s). When comparing carbonate chemistry datasets, corrections should be made for the non-synchronous timing of sample collection for the different variables.

4. It is recommended to characterise the extinction coefficients of each batch of pH-indicator-dye on the instrument used for ship-board pH analysis, rather than use published values (Clayton and Byrne, 1993; Zhang and Byrne, 1996; Hopkins et al., 2000; Mosley et al., 2004; Gabriel et al., 2005; Liu et al., 2011). This is particularly important where the indicator has not been purified (Yao et al., 2007) and where the detection system has a wider optical bandwidth than that used in the literature to characterize the indicator (the optimal bandwidth is 15–20 nm; Rérolle et al., 2013). The discrepancy between pH_T values calculated with our coefficients and values calculated with coefficients from Zhang and Byrne (1996) was about 0.02 pH_T units (Rérolle et al., 2013). We estimated that about 0.005 pH_T units of the observed discrepancy was due to impurities in the indicator and about 0.015 was due to the wider bandpass detection window in our ship-board pH system.

5. When comparing a pair of variables, it is important to examine the residuals as a function of time as well as constructing a scatterplot of one variable against the other. For example, from examination of Fig. 1 alone we would not have identified the diurnal variation between the two pCO_2 systems (Fig. 2).

◄	►
◄	►
Back	Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3.3 Borate constants

The calculations of the carbonate chemistry variables were undertaken for a second time using another borate constant (Lee et al., 2010) for all combinations of pairs. We then compared the results obtained against those using the original borate constant, from Uppström (1974). Only data obtained using pCO_2-1 and not pCO_2-2 were used in the comparison. We also omitted the pair pH_T – pCO_2 from consideration because they were not a good pair for calculation. Statistically significant differences (ANOVA, p values < 0.001) were seen for pCO_2 and pH_T calculated from C_T and A_T using the different borate constants. There were also significant differences between C_T values calculated from A_T and pH_T using the different constants, and A_T calculated from both C_T and pH_T and C_T and pCO_2. There were, however, no statistically significant differences when calculating pH_T from pCO_2-1 and either C_T or A_T, or pCO_2 calculated from pH_T and either C_T or A_T (Fig. 5 and Table 2). The residuals were on the whole smaller when using the borate constant from Uppström (1974) compared with Lee et al. (2010) (Fig. 5). The mean residuals were up to 3.5 µatm, 0.002 pH_T units, 1.9 µmol kg^{-1} and 2.3 µmol kg^{-1} for pCO_2, pH_T, C_T and A_T, respectively when comparing results obtained using the constants from Lee et al. (2010) minus the results obtained using the constants from Uppström (1974). These discrepancies are not significant in an ocean acidification context, but they are substantial in terms of air–sea flux calculations in coastal waters.

4 Conclusions

Our results show that it is possible to obtain good consistency between measurements of different variables of the carbonate system, even outside the somewhat artificial conditions of an intercomparison exercise. However, our retrospective intercomparison revealed several source of discrepancies, leading to the following recommendation for best practice: (a) undertake characterization of the pH-indicator-dye in order to obtain

correct extinction coefficients for the dye and analytical system in the temperature and salinity range used; (b) take account of the transit time of seawater from the intake to the equilibrator, when comparing $p\text{CO}_2$ with other simultaneous measurements; (c) examine residuals as a function of time in order to detect temporal biases in mea-
surements; (d) prevent microbial growth in the equilibrator for $p\text{CO}_2$ measurements by complete shielding from light.

We obtained smaller residuals using Uppström (1974) rather than Lee et al's (2010) borate constant. As found in other studies, the variables pH_T and $p\text{CO}_2$ are far from an ideal pair for calculation of C_T or A_T, emphasizing the desirability of developing a C_T or A_T sensor for autonomous high resolution measurements.

References

Bakker, D. C. E., Nielsdóttir, M. C., Morris, P. J., Venables, H. J., and Watson, A. J.: The island mass effect and biological carbon uptake for the subantarctic Crozet Archipelago, Deep-Sea Res Pt. II, 54, 2174–2190, doi:10.1016/j.dsr2.2007.06.009, 2007.

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

Cullison Gray, S. E., DeGrandpre, M. D., Moore, T. S., Martz, T. R., Friederich, G. E., and Johnson, K. S.: Applications of in situ pH measurements for inorganic carbon calculations, Mar. Chem., 125, 82–90, 2011.

Dickson, A. G.: An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data, Deep-Sea Res., 28, 609–623, 1981.

Intercomparison of carbonate chemistry measurements

M. Ribas-Ribas et al.

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Dickson, A. G.: Standard potential of the reaction AgCl(s) + 1/2H$_2$(g) = Ag(s) + HCl(aq) and the standard acidifty constant of the bisulfate ion in synthetic seawater from 273.15 K to 318.15 K, J. Chem. Thermodyn., 22, 113–127, doi:10.1016/0021-9614(90)90074-z, 1990.

Dickson, A. G.: Interactive comment on "On CO$_2$ pertubation experiments: over-determination of carbonate chemistry reveals inconsistencies" by Hoppe, C. J. M., Langer, G., Rokitta, S. D., Wolf-Gladrow, D. A. and Rost, B., Biogeosciences Discuss., 7, C1286-C1293, 2010.

Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, Deep-Sea Res., 34, 1733–1743, doi:10.1016/0198-0149(87)90021-5, 1987.

Gabriel, M., Forja, J., Rubio, J., and Gómez-Parra, A.: Temperature and salinity dependence of molar absorptivities of thymol blue: Application to the spectrophotometric determination of pH in estuarine waters, Cienc. Mar., 31, 309–318, 2005.

Hardman-Mountford, N. J., Moore, G., Bakker, D. C., Watson, A. J., Schuster, U., Moore, G., Bakker, D. C. E., Watson, A. J., Schuster, U., Barciela, R., Hines, A., Moncoiffe, G., Brown, J., Dye, S., Blackford, J., Somerfield, P. J., Holt, J., Hydes, D. J., and Aiken, J.: An operational monitoring system to provide indicators of CO$_2$-related variables in the ocean, ICES J. Mar. Sci., 65, 1498–1503, 2008.

Hopkins, A. E., Sell, K. S., Soli, A. L., and Byrne, R. H.: In-situ spectrophotometric pH measurements: the effect of pressure on thymol blue protonation and absorbance characteristics, Mar. Chem., 71, 103–109, 2000.

Hoppe, C. J. M., Langer, G., Rokitta, S. D., Wolf-Gladrow, D. A., and Rost, B.: Implications of observed inconsistencies in carbonate chemistry measurements for ocean acidification studies, Biogeosciences, 9, 2401–2405, doi:10.5194/bg-9-2401-2012, 2012.

Johnson, K. M., Sieburth, J. M., Williams, P. J. L., and Brandstrom, L.: Coulometric total carbon-dioxide analysis for marine studies – automation and calibration, Mar. Chem., 21, 117–133, 1987.

Johnson, K. M., Körtzinger, A., Mintrop, L., Duinker, J. C., and Wallace, D. W. R.: Coulometric total carbon dioxide analysis for marine studies: measurement and internal consistency of underway TCO$_2$ concentrations, Mar. Chem., 67, 123–144, doi:10.1016/s0304-4203(99)00055-9, 1999.

Juranek, L., Feely, R., Peterson, W., Alin, S., Hales, B., Lee, K., Sabine, C. L., and Peterson, J.: A novel method for determination of aragonite saturation state on the continental shelf of

central Oregon using multi-parameter relationships with hydrographic data, Geophys. Res. Lett., 36, L24601, doi:10.1029/2009GL040778, 2009.

Kirkwood, D.: Simultaneous Determination of Selected Nutrients in Sea Water, International Council for the Exploration of the Sea (ICES) CM, 100, 29, 1989.

Kitidis, V., Hardman-Mountford, N. J., Litt, E., Brown, I., Cummings, D., Hartman, S., Hydes, D., Fishwick, J. R., Harris, C., Martínez-Vicente, V., Woodward, E., Malcolm, S., and Smyth, T. J.: Seasonal dynamics of the carbonate system in the Western English Channel, Cont. Shelf Res., 42, 30–40, doi:10.1016/j.csr.2012.04.012, 2012.

Körtzinger, A., Mintrop, L., Wallace, D. W. R., Johnson, K. M., Neill, C., Tilbrook, B., Towler, P., Inoue, H. Y., Ishii, M., Shaffer, G., Saavedra, R. F. T., Ohtaki, E., Yamashita, E., Poisson, A., Brunet, C., Schauer, B., Goyet, C., and Eischeid, G.: The international at-sea intercomparison of f CO$_2$ systems during the R/V *Meteor* Cruise 36/1 in the North Atlantic Ocean, Mar. Chem., 72, 171–192, 2000.

Lamb, M. F., Sabine, C. L., Feely, R. A., Wanninkhof, R., Key, R. M., Johnson, G.C., Millero, F.J., Lee, K., Peng, T. H., Kozyr, A., Bullister, J. L., Greeley, D., Byrne, R. H., Chipman, D. W., Dickson, A. G., Goyet, C., Guenther, P. R., Ishii, M., Johnson, K. M., Keeling, C. D., Ono, T., Shitashima, K., Tilbrook, B., Takahashi, T., Wallace, D. W. R., Watanabe, Y. M., Winn, C., and Wong, C. S.: Consistency and synthesis of Pacific Ocean CO$_2$ survey data, Deep-Sea Res Pt. II, 49, 21–58, doi:10.1016/S0967-0645(01)00093-5, 2001.

Lee, K., Kim, T. W., Byrne, R. H., Millero, F. J., Feely, R. A., and Liu, Y. M.: The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans, Geochim. Cosmochim. Ac., 74, 1801–1811, doi:10.1016/j.gca.2009.12.027, 2010.

Lewis, E. and Wallace, D. W. R.: Program Developed for CO$_2$ System Calculations, ORNL/CDIAC-105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US, Department of Energy, Oak Ridge, Tennessee, 1998.

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

Lueker, T. J., Dickson, A. G., and Keeling, C. D.: Ocean p CO$_2$ calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2: validation based on laboratory measurements of CO$_2$ in gas and seawater at equilibrium, Mar. Chem., 70, 105–119, 2000.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Mehrbach, C., Culberso, C. H., Hawley, J. E., and Pytkowic, R. M.: Measurement of apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, Limnol. Oceanogr., 18, 897–907, 1973.

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

Millero, F. J., Pierrot, D., Lee, K., Wanninkhof, R., Feely, R., Sabine, C. L., Key, R. M., and Takahashi, T.: Dissociation constants for carbonic acid determined from field measurements, Deep-Sea Res. Pt. I, 49, 1705–1723, 2002.

Mosley, L. M., Husheer, S. L., and Hunter, K. A.: Spectrophotometric pH measurement in estuaries using thymol blue and m-cresol purple, Mar. Chem., 91, 175–186, 2004.

Rérolle, V. M. C., Floquet, C. F. A., Mowlem, M. C., Bellerby, R., Connelly, D. P., and Achterberg, E. P.: Seawater-pH measurements for ocean-acidification observations, Trends Anal. Chem., 40, 146–157, doi:10.1016/j.trac.2012.07.016, 2012.

Rérolle, V., Floquet, C. F., Harris, A. J., Mowlem, M. C., Bellerby, R. R., and Achterberg, E. P.: Development of a colorimetric microfluidic pH sensor for autonomous seawater measurements, Anal. Chim. Acta, 786, 124–131, 2013.

Rérolle, V. M. C., Ribas-Ribas, M., Kitidis, V., Brown, I., Bakker, D. C. E., Lee, G. A., Shi, T., Mowlem, M. C., and Achterberg, E. P.: Controls on pH in surface waters of northwestern European shelf seas, Biogeosciences Discuss., 11, 943–974, doi:10.5194/bgd-11-943-2014, 2014.

Schuster, U. and Watson, A. J.: A variable and decreasing sink for atmospheric CO_2 in the North Atlantic, J. Geophys. Res.-Oceans, 112, C11006, doi:10.1029/2006JC003941, 2007.

Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W., and Sutherland, S. C.: Seasonal variation of CO_2 and nutrients in the high-latitutde surface oceans – a comparative study, Global Biogeochem. Cy., 7, 843–878, doi:10.1029/93GB02263, 1993.

Uppström, L. R.: The boron/chlorinity ratio of deep-sea water from the Pacific Ocean, Deep-Sea Res Pt. I, 21, 161–162, 1974.

Van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., and Wallace, D. W. R.: CO2SYS v 1.1, MATLAB Program Developed for CO_2 System Calculations, ORNL/CDIAC-105b, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US DoE, Oak Ridge, TN, 2011.

Weiss, R. F. and Price, B. A.: Nitrous-oxide solubility in water and seawater, Mar. Chem., 8, 347–359, doi:10.1016/0304-4203(80)90024-9, 1980.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Yao, W., Liu, X., and Byrne, R. H.: Impurities in indicators used for spectrophotometric seawater pH measurements: assessment and remedies, Mar. Chem., 107, 167–172, 2007.

Zhang, H. N. and Byrne, R. H.: Spectrophotometric pH measurements of surface seawater at in-situ conditions: absorbance and protonation behavior of thymol blue, Mar. Chem., 52, 17–25, 1996.

Intercomparison of carbonate chemistry measurements

M. Ribas-Ribas et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

BGD

11, 2793–2822, 2014

Intercomparison of carbonate chemistry measurements

M. Ribas-Ribas et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Results of comparisons between direct measurements and values calculated (using the software CO2SYS) from measurements of other variables. r is Pearson's correlation coefficient, df is degrees of freedom, RMSE is root mean square error and MR is mean of the Residuals. The measurement accuracy is from Sect. 2.1.

Measured variable	Input variables for calculation	Comparison statistics				Benchmarks	
		r	df	RMSE*	MR*	Calculated Uncertainty*	Measurement accuracy*
pCO_2-1 (μatm)	C_T and pH_T	0.984	31	5.2	3.2	3.5	
	A_T and pH_T	0.990	27	5.5	1.9	3.9	4.0
	C_T and A_T	0.987	43	6.3	3.0	4.1	
pCO_2-2 (μatm)	C_T and pH_T	0.949	97	11.2	3.9	3.5	
	A_T and pH_T	0.947	93	11.3	3.9	3.9	10.0
	C_T and A_T	0.937	156	11.7	0.5	4.1	
pH_T	C_T and A_T	0.952	218	0.008	0.001	0.005	
	A_T and pCO_2-1	0.991	27	0.006	0.002	0.003	
	A_T and pCO_2-2	0.951	93	0.013	0.004	0.011	0.004
	C_T and pCO_2-1	0.984	31	0.006	0.004	0.004	
	C_T and pCO_2-2	0.943	97	0.014	0.004	0.013	
A_T (μmol kg^{-1})	C_T and pH_T	0.996	218	4.4	−0.2	3.1	
	C_T and pCO_2-1	0.997	43	4.6	2.1	3.0	
	C_T and pCO_2-2	0.991	156	8.6	0.4	7.0	1.5
	pH_T and pCO_2-1	0.802	27	36.3	−12.8	35.5	
	pH_T and pCO_2-2	0.596	93	75.6	−23.1	72.8	
C_T (μmol kg^{-1})	A_T and pH_T	0.994	218	4.0	0.2	2.4	
	A_T and pCO_2-1	0.997	43	3.9	−1.7	2.5	
	A_T and pCO_2-2	0.989	156	7.2	−0.3	5.8	2.0
	pH_T and pCO_2-1	0.680	31	32.2	−18.8	31.9	
	pH_T and pCO_2-2	0.528	97	69.8	−21.9	63.4	

* These columns have the units corresponding with the variables on the first column.

Table 2. Directly measured pH_T, partial pressure of CO_2 (pCO_2-1), dissolved inorganic carbon (C_T) and total alkalinity (A_T) are compared to values calculated from measurements of other variables using different borate constants. RMSE is root mean square error and MR is mean of the residuals. The two different borate constants are from Lee et al. (2010) and Uppström (1974).

Measured variable	Borate constant: Calculated variable from	Lee RMSE[*]	MR[*]	Uppström RMSE[*]	MR[*]
pCO_2-1 (µatm)	C_T and pH_T	5.3	3.2	5.2	3.2
	A_T and pH_T	5.4	1.4	5.5	1.9
	C_T and A_T	10.1	8.0	6.3	3.0
pH_T	C_T and A_T	0.012	−0.005	0.008	0.001
	A_T and pCO_2-1	0.006	0.002	0.006	0.002
	C_T and pCO_2-1	0.006	0.004	0.006	0.004
A_T (µmol kg^{-1})	C_T and pH_T	6.6	2.9	4.4	−0.2
	C_T and pCO_2-1	7.3	5.3	4.6	2.1
C_T (µmol kg^{-1})	A_T and pH_T	6.1	−2.7	4.0	0.2
	A_T and pCO_2-1	6.1	−4.4	3.9	−1.7

[*] These columns have the units corresponding with the variables on the first column.
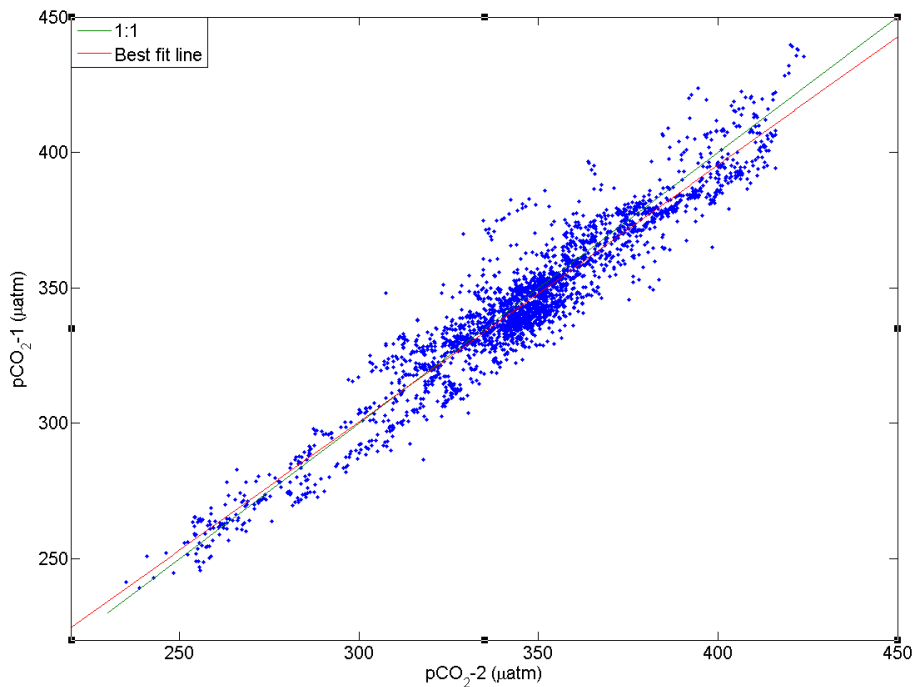
Fig. 1. Relationship between two independently measured pCO_2 datasets. The line of perfect agreement (1 : 1 line, in green) and the best fit line (in red) are also shown.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
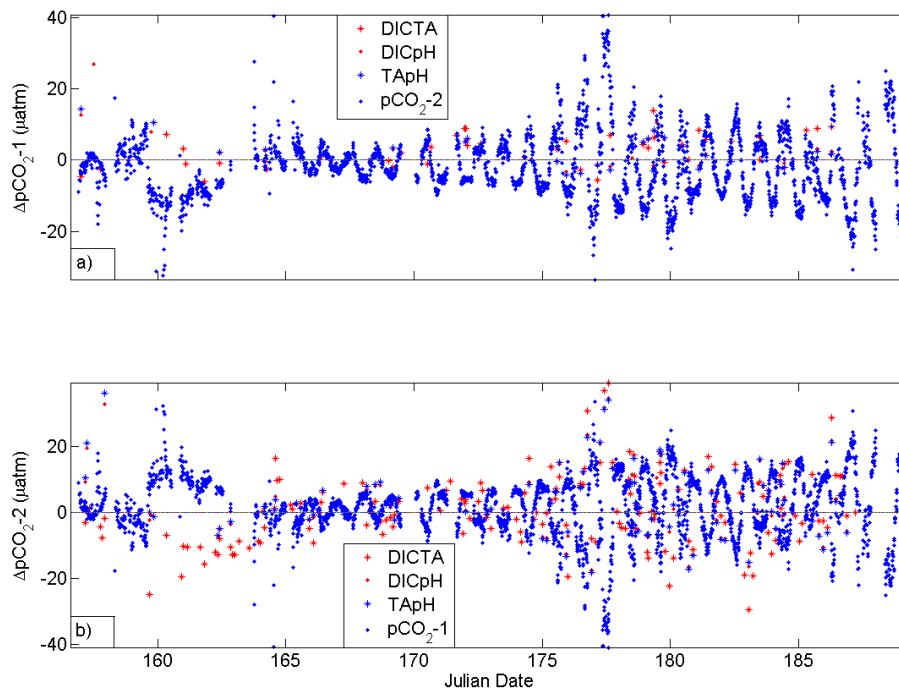
Fig. 2. $p\text{CO}_2$ residuals, here defined as $p\text{CO}_2$-1 **(a)** and $p\text{CO}_2$-2 **(b)** and another a measured or calculated $p\text{CO}_2$ value. Shown are measured $p\text{CO}_2$ (1 in **a** and 2 in **b**) minus $p\text{CO}_2$ calculated from: C_T and A_T (red plus symbols); C_T and pH_T (red dots); A_T and pH_T (blue plus symbols); and the other measured $p\text{CO}_2$ (2 in **a** and 1 in **b**, blue dots).

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
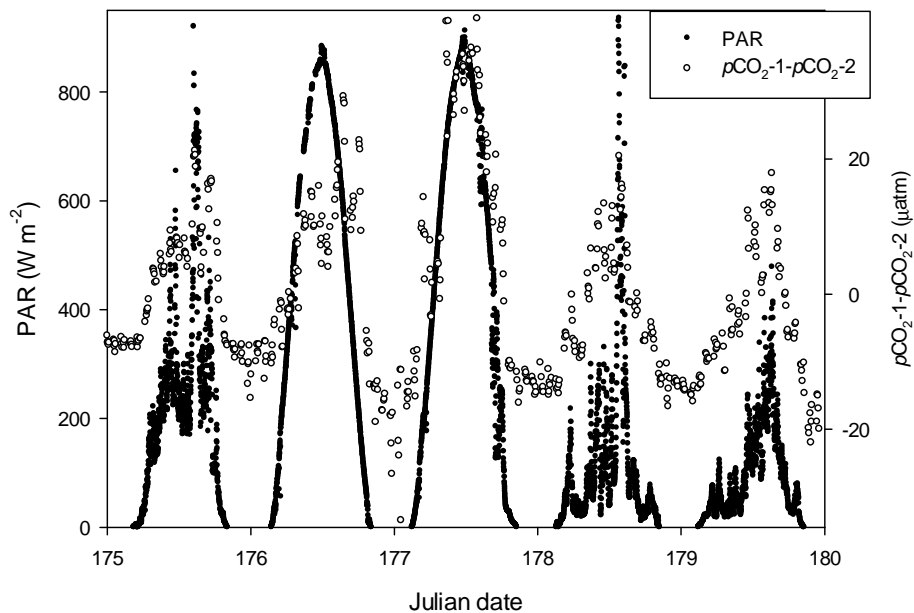
Fig. 3. Comparison over five days between the pCO_2 difference between instruments 1 and 2 (µatm; white circles) and the phototosynthetically active radiance (PAR (W m^{-2}), in black circles).
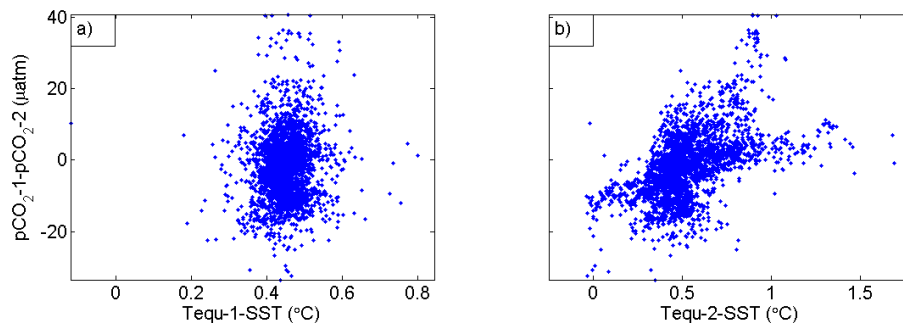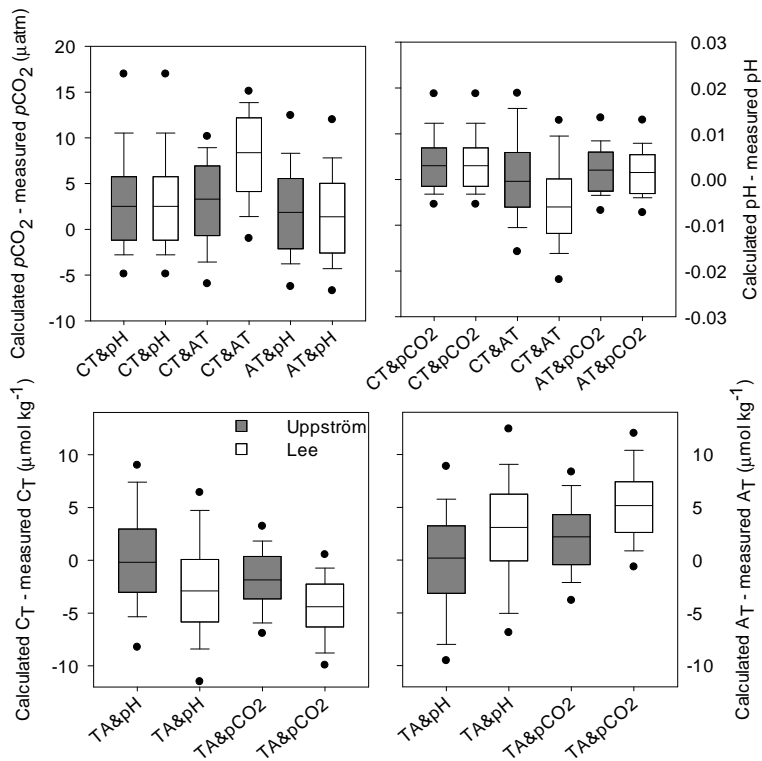
Fig. 4. Difference between the two pCO$_2$ datasets and **(a)** the difference between the temperature inside equilibrator 1 and sea surface temperature, and **(b)** the difference between the temperature inside equilibrator 2 and sea surface temperature.

Fig. 5. Box-and-whisker plots of the residuals between calculated variables and measured variables from different pairs of measured variables (denoted on the x axis) for the two sets of borate constants. Grey plots denotes the constants by Uppström (1974), and white are Lee et al. (2010). Only results for pCO_2-1 are shown. The boxes show the median and the 5th and 95th percentiles. Table 2 presents the RMSE and MR.

Title Page

Abstract   Introduction

Conclusions   References

Tables   Figures

|◄   ►|

◄   ►

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion