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Biogeosciences
Discussions

Interactive comment on “On CO_2 pertubation experiments: over-determination of carbonate chemistry reveals inconsistencies” *by* C. J. M. Hoppe et al.

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Final author comment on BGD manuscript Hoppe et al. 2010

1 Introduction

We thank all authors for their constructive comments on our manuscript dealing with discrepancies in over-determined seawater carbonate systems. We have, however, the feeling that the intention of this study was not fully understood by the referees. We are, by no means, questioning the work done by marine chemists on the thermo-

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dynamic consistency of the marine carbonate system. Nonetheless, for yet unknown reasons, similar inconsistencies of high magnitude arise in the few over-determined datasets available from CO_2 perturbation experiments conducted by different teams of marine biologists. As different combinations of input parameters for the calculation of the carbonate system result in different pCO_2 values, we were seeking to identify this phenomenon and raise the awareness for it. Our practical suggestion to involve pH as an input parameter is based on the finding that direct $[CO_2]$ measurements by means of membrane inlet mass spectroscopy (MIMS) as well as the CO_2 concentration of the equilibration gases compare very well with the pCO_2 values calculated from either TA and pH or DIC and pH.

We would very much appreciate if marine chemists found a way to explain the differences in internal consistency of the carbonate system between their studies and those of several members of the Ocean Acidification community. The comments of the referees as well as from the open discussion contributions, however, do not provide an explanation for the phenomenon we described (see detailed responses below).

2 Answer to Tyrell et al.

In their comment, Tyrell et al. suggest the contribution of DOM to TA to be causing the discrepancies. We generally agree that there are problems arising from the use of TA as an input parameter, as DOM may contribute to TA in the titration but is not accounted for in the calculations. We therefore conducted another experiment in artificial seawater (ASW; Grasshoff et al., 1999), containing no DOM . The measurements of pCO_2-manipulated ASW yield the very same relationship as found for the nutrient-enriched North Sea seawater (Table 1, Fig. 1) and in the dataset from the oligotrophic Red Sea (Schneider and Erez, 2006). We therefore conclude that the contribution of DOM to TA cannot be causing the discrepancies described.

3 Answer to Dr. Zhai

Dr. Zhai questions whether we used the appropriate dissociation constants of carbonic acid. As we discussed already in the manuscript (and as Prof. Dickson pointed out in his comment), the differences in pCO_2 values arising from the use of the available constant pairs are comparably small and do not change the observed pattern of discrepancies. We choose the constant pair yielding the smallest discrepancies. In a revised version of the manuscript we could, however, use the Mehrbach constants (Mehrbach et al. 1973, refit by Dickson and Millero 1987) if desired.

4 Answer to Prof. Dickson

The invited referee Prof. Dickson questions the reliability of our results as they do not compare well with previous work done by marine chemists (e.g. Luecker et al., 2000; Millero et al., 2002). Although we do not know the reasons for these differences (and we did not state otherwise), the described phenomenon is nonetheless apparent in other labs working with state-of-the-art methodology applied in Ocean Acidification research laboratories. As mentioned in the manuscript, it has been hypothesised that differences in measuring protocols may play a considerable role with regard to the magnitude of the discrepancies at high pCO_2 (McElligott et al., 1998). Although we cannot achieve the low analytical uncertainties in carbonate chemistry parameters as published by authors such as Prof. Dickson, we nonetheless followed commonly suggested procedures (Dickson, 2010), e.g. corrected for inaccuracies by using appropriate CRMs and determined the pH spectrophotometrically. In the following we will respond to the specific points of criticism raised by Prof. Dickson:

(a) He criticises that the measurement temperatures with respective standard deviations are not stated clearly for all measurements. The $[CO_2]$ as well as the potentiometric pH measurements were conducted at 15±0.2^{o}C. The spectrophotometric pH measurements were conducted at 25±0.1^{o}C and calculated for 15^{o}C using CO2sys (Lewis and Wallace 1998). We will state this more clearly in the revised version.

(b) Prof. Dickson criticises that our samples were not poisoned with $HgCl_2$ prior to storage and analysis. As all samples (also [CO_2] and pH; this will be stated in the revised version) were at least 0.6 μm filtered, stored at 2^{o}C and measured within one week, it is highly improbable that biological activity would have changed the carbonate system of the samples to a considerable extent. Also, this could not explain the systematically re-occurring discrepancies. We would also like to draw the referees' attention to the study of Schneider and Erez (2006), in which the same phenomenon appears for $HgCl_2$-poisoned seawater samples.

(c) Prof. Dickson requests a clear statement on the overall uncertainties. The partial pressure of CO_2 can be calculated from any pair of measured carbonate system parameters and temperature, salinity, and pressure. In response to Prof. Dicksons and Dr. Wanninkhofs comments we estimated the overall uncertainties of pCO_2 for the measured pairs (pH; TA), (pH; DIC), and (DIC; TA). The overall uncertainties depend on the uncertainties of the measured quantities and the uncertainties of the equilibrium constants of the carbonate system. We used the following uncertainties: $u_{\mathrm{DIC}} = 7$ μmol kg^{-1}, $u_{\mathrm{TA}} = 5$ μmol kg^{-1}, $u_{\mathrm{K_0}} = 5.3 \cdot 10^{-4}$ mol kg^{-1} atm^{-1} (based on an uncertainty of 0.003 for pK_0, Millero, 1995); $u_{\mathrm{K_1}} = 4.0 \cdot 10^{-8}$ mol kg^{-1} (based on an uncertainty of 0.008 for pK_1, Millero, 1995); $u_{\mathrm{K_2}} = 4.5 \cdot 10^{-11}$ mol kg^{-1} (based on an uncertainty of 0.013 for pK_2, Millero, 1995); $u_{\mathrm{K_B}} = 3.6 \cdot 10^{-11}$ mol kg^{-1} (based on an uncertainty of 0.0042 for pK_B, Millero, 1995); $u_{\mathrm{K_W}} = 1.0 \cdot 10^{-15}$ mol^2 kg^{-2} (based on an uncertainty of 0.01 for pK_W, Millero, 1995) and $u_{\mathrm{B_T}} = 0.12$ μmol kg^{-1} (based on an uncertainty of 0.01 for salinity). The overall uncertainty is calculated from the combination of variances as follows

$$u^2_{\mathrm{pCO_2}} = \sum_{i=1}^{N}\left(\frac{\partial p\mathrm{CO_2}}{\partial x_i}\right)^2 u^2_{x_i} + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{\partial p\mathrm{CO_2}}{\partial x_i}\frac{\partial p\mathrm{CO_2}}{\partial x_j}u^2_{x_i,x_j} \tag{1}$$

where x_i are the independent variables DIC, TA, pH, $\mathrm{K_0}$, $\mathrm{K_1}$, $\mathrm{K_2}$, K_B, $\mathrm{K_W}$, $\mathrm{B_T}$ and u_{x_i} are the corresponding uncertainties. No estimates exist for the covariances of the uncertainties, $u^2_{x_i,x_j}$; small values of covariances in the uncertainties can be expected for those pairs (x_i, x_j) that are based on independent measurements. We have neglected all terms including $u^2_{x_i,x_j}$.

For the measured pairs (pH; TA), (pH; DIC), and (DIC; TA), the functions $\mathrm{pCO_2}$ $(x1,\ x_2,\ldots,\ x_N)$ were derived from formulas given in Zeebe and Wolf-Gladrow (2001, Appendix B). For (pH; TA) and (pH; DIC) they read

$$\mathrm{pCO_2}\left(\mathrm{pH},\mathrm{TA},\mathrm{K_0},\mathrm{K_1},\mathrm{K_2},\mathrm{K_B},\mathrm{K_W},\mathrm{B_T}\right) = \frac{\mathrm{TA} - \dfrac{\mathrm{K^*_B B_T}}{\mathrm{K^*_B} + [\mathrm{H^+}]} - \dfrac{\mathrm{K^*_W}}{[\mathrm{H^+}]} + [\mathrm{H^+}]}{K_0\left(\dfrac{\mathrm{K^*_1}}{[\mathrm{H^+}]} + 2\dfrac{\mathrm{K^*_1K^*_2}}{[\mathrm{H^+}]^2}\right)} \tag{2}$$

$$\mathrm{pCO_2}\left(\mathrm{pH},\mathrm{DIC},\mathrm{K_0},\mathrm{K_1},\mathrm{K_2}\right) = \frac{\mathrm{DIC}}{K_0\left(1 + \dfrac{\mathrm{K^*_1}}{[\mathrm{H^+}]} + \dfrac{\mathrm{K^*_1K^*_2}}{[\mathrm{H^+}]^2}\right)} \tag{3}$$

For the measured pair (DIC; TA) $\mathrm{pCO_2}$ is a function of DIC, TA, $\mathrm{K_0}$, $\mathrm{K_1}$, $\mathrm{K_2}$, K_B, $\mathrm{K_W}$, and $\mathrm{B_T}$. It cannot, however, be expressed in closed form (calculation of $\mathrm{pCO_2}$ includes an algebraic equation of fifth order in $[\mathrm{H^+}]$). The partial derivatives of $\mathrm{pCO_2}$ with respect to the various variables were calculated numerically. We calculated the overall uncertainties for a low (149 μatm) and a high (722 μatm) partial pressure of $\mathrm{CO_2}$ at (pH, DIC, TA) = (8.417, 1945 μmol kg^{-1}, 2385 μmol kg^{-1}) and (pH, DIC, TA) = (7.848, 2256 μmol kg^{-1}, 2385 μmol kg^{-1}), respectively. As an example, Figure 2 shows the contribution of uncertainty variances in various parameters to the overall uncertainty for a pCO_2 of 722 μatm calculated from DIC and TA. As shown in table 2, the calculated overall uncertainties of the performed measurements fall well within the range of the errors assumed in the manuscript and therefore do not provide an explanation for the phenomenon described.

(d) Prof. Dickson furthermore criticises that it is not clear what replications were done. In principle, each pCO_2 level was manipulated in triplicates. For each of these, the spectrophotometric pH determinations and TA measurements were done in technical duplicates, DIC measurements were performed in technical triplicates, while the values of the potentiometric pH measurements are based on a single measurement. The ”standard deviation of technical replicates” of potentiometric measurements (i.e. repeatability) was calculated for $n = 30$ measurements of a single sample. In case of the $[CO_2]$ measurements by means of MIMS, triplicate measurements were performed. The ”average precisio” was estimated from $n = 15$ MIMS calibrations (reproducibility). We will state this more clearly in the revised version.

(e) Prof. Dickson claims we have drawn the conclusion that ”it is the lower calculated pCO_2 that is necessarily the wrong one” and he questions how justified this assertion may be. We did not draw such a conclusion. Our goal was simply to raise awareness to the fact that different pairs of measured input parameters yield different calculated pCO_2 values. In order to achieve comparability of different datasets, it is essential that the Ocean Acidification community decides to use one particular pair of input parameters (as long as the phenomenon described is not resolved). Based on coherence of measured pCO_2 by infrared gas sensors and by means of MIMS with calculated pCO_2 values based on pH, we suggested the use of the latter as an input parameter. This suggestion is merely one of plausibility and does not touch the question of what is right or wrong.

Besides the overall uncertainty of the methodology, in the following we provide further information on the calibration methods applied to the different measurements. In case of the TA measurements, the pH-electrode was calibrated with certified NIST-buffers. TA estimates from Gran titration (linear curve fit; f_1/volume; $r^2 = 0.9999$; Gran 1952) were corrected for daily offsets between $\text{CRM}_{\text{measured}}$ and $\text{CRM}_{\text{defined}}$ (on average -13 μmol kg^{-1}). An internal North Sea seawater standard was additionally measured, the corrected TA value was always 2445±5 μmol kg^{-1} (repeatability; $n = 10$). In case of the DIC measurements, the analyser was calibrated with NaHCO_3 solutions with concentrations ranging from 1800 to 2300 μmol DIC kg^{-1}. CRMs were used for corrections of errors in instrument performance (baseline drift etc.). On average, the CRMs were measured with an offset of 3±5 μmol kg^{-1} from the assigned value (reproducibility; $n = 20$). The instrument performance of the spectrophotometer used for the pH_{total} measurements (Cary 4000, Varian) was validated complying with the US Pharmacopeia requirements. Corrections for pH shifts due to the addition of dye were performed (Dickson et al., 2007). Furthermore, the average values of CRM measurements (Tris buffer, obtained from Prof. Dickson) at the beginning and the end of one measuring run were used to correct the sample values. On average, the CRMs were measured with an offset of 0.003±0.003 from the assigned value (repeatability; $n = 7$).

Prof. Dickson points out that the differences between potentiometric pH_{NBS} and spectrophotometric pH_{total} measurements vary more than theoretically expected. We agree on this, however, the variation is due to uncertainties and errors associated with the potentiometric rather than with the spectrophotometric measurements. As also discussed in our manuscript, measurements of seawater pH with a NBS calibrated electrode are generally not recommended (e.g. Dickson, 2010). With these measurements we were, however, trying to realistically mimic measuring practise in the fast growing field of Ocean Acidification research. Our intention was simply to point out that the inconsistencies described are not caused by lower quality potentiometric pH measurements.

In his referee comment, Prof. Dickson does an examplary calculation how to match the pCO_2 values calculated from the three input pairs. The errors required to meet his calculation are considerably larger than the uncertainties in our measurements. Furthermore, it is highly improbable that such a systematic phenomenon could be occurring several times and in different laboratories. Furthermore, there is no reason why the pH should be systematically measured 0.03 units too high (e.g. by outgassing of CO_2) while at the same time DIC would also be measured 15 μmol kg^{-1} too high (e.g. by ingassing of CO_2). Although the criticism regarding the description of our methods is justified, we would like to emphasise that the measurement errors discussed above result in random errors in calculated pCO_2 and therefore cannot serve as an explanation for the systematic phenomenon described in our manuscript.

Furthermore, Prof. Dickson questions the data quality of Schneider and Erez (2006). As already pointed out in the introduction, we do not negate that the discrepancies could be caused by low data quality. This is, in our opinion, no adequate reason to ignore the implications this might have for the OA community. As shown in Fig. 3, other datasets exist showing the same phenomenon. In addition to the North Sea seawater and artificial seawater used in our study, the phenomenon can be observed in water from the Baltic and the Red Sea (Thomsen et al. 2010 and Schneider and Erez 2006, respectively). Although not strictly over-determined, the dataset of Iglesias-Rodriguez et al. (2008, as reported in the EPOCA data base) gives another hint that this phenomenon is also present in other laboratories. If one assumes equilibration of the aerated seawater with the gas mixtures used (280-750 ppmv), the offset of the pCO_2 values calculated from TA and DIC to the target pCO_2 reveals the very same relationship as observed in our data (Fig. 3).

Prof. Dickson stated we should have tested our method on a sample of reference material. As the uncertainties of our methods are relatively high and the discrepancies at ambient pCO_2 are rather low, the measurement of a single sample at one pCO_2 cannot provide more insight into a phenomenon that is dependent on pCO_2 itself. Prof. Dick-

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son also recommends validating our methods and verifying our results in collaboration with another laboratory. We agree that it is, as always, desirable to conduct follow-up studies directly comparing the results from different laboratories, maybe revealing the reasons for the discrepancies described. We are nonetheless convinced that this and previous datasets provide sufficient information to raise the awareness for this problem and should therefore be published.

5 Answer to Dr. Wanninkhof

The second invited referee, Dr. Wanninkhof, criticises our experimental approach. In his comment, he has often referred to Prof. Dickson. In the following we will respond to the specific points not answered above.

1. Dr. Wanninkhof criticises the use of CRMs as the only mean of calibration. We disagree, as we have not based our calibrations based on CRMs only. See our detailed response regarding calibration procedures.
2. The referee criticises the use of calculation programs such as CO2sys for manipulated seawater. Besides the fact that this program is commonly used for CO_2 perturbation experiments, calculations were double-checked using independent matlab scripts (Zeebe and Wolf-Gladrow, 2001). Other calculation methods than those described by Dickson (2010) are, to our knowledge, not available.
3. Dr. Wanninkhof also questions the reliability of $[CO_2]$ measured by MIMS. As mentioned above, the measurements of $[CO_2]$ by means of MIMS are not particularly important for the conclusions we draw in our manuscript. Even taking into account potential sources of calibration errors (e.g. weighing, temperature differences, etc.), the $[CO_2]$ values calculated from the MIMS measurements are sufficient to favour the pCO_2 values calculated from pH with either TA or DIC.

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As shown in Figure 1 of the submitted manuscript, the carbonate system was proven to be equilibrated with the gas mixture used for aeration and the [CO_2] values measured by means of MIMS fall (at least for two of the three samples) into the range of the pCO_2 stated by the gas supplier.

4. The reviewer criticises that temperature values are not listed in figures and tables. We fully agree and will change this in the revised manuscript (see above for further details).

5. He also reminds us of the fact that outgassing of CO_2 can be an issue at high pCO_2 levels. We are fully aware of this fact and, in our opinion, sufficiently prevented this to occur (e.g. by storing all samples in air-tight bottles, opening the DIC vials less than a minute prior to measurements). Furthermore, as shown for Prof. Dicksons example calculation, outgassing cannot explain the phenomenon described (not only pH but also DIC would have to increase to get matching results; e.g. outgassing from pH samples and ingassing to DIC samples would have to be assumed).

Dr. Wanninkhof states that our results regarding the pairs of input parameters are not surprising, as the correlation of pH and pCO_2 is not too sensitive to variations in TA and DIC. We totally agree with this, but as our data does not claim otherwise, we are not sure which point he wants to make here.

He furthermore points out that non-carbonate contribution to TA should be determined in order to allow a more correct calculation of carbonate alkalinity. This is an important point also raised in the comment by Tyrrell et al. We tested this possibility with a ASW dataset, but unfortunately it does not provide an explanation for the phenomenon described (see above).

Dr. Wanninkhof proposes that the constant ratio pCO_2(TA;DIC)/pCO_2(TA;pH) could be caused by a constant bias in measurement of one of the parameters (likely TA or DIC) or the dissociation constant used. We disagree, as the very same pattern of discrepancies is apparent after both TA and DIC manipulation. We would like to draw the reviewer's attention to the corresponding paragraph in the manuscript (p. 11). Regarding the possible effect of the dissociation constant used, we checked this with all available dissociation constants. As discussed by Millero et al. (2002, 2006) and in the background information in Prof. Dicksons review, this issue is not resolved yet. We are nonetheless grateful for stressing this point.

Dr. Wanninkhof states that ”TA and DIC are good parameters to estimate CO_3^{2-} ... (at low pCO_2)”. We agree that this is true, given the current uncertainties in the determination of TA, DIC and pH and the equilibrium constants. This might change in the future, however, if we were able to decrease, for example, the uncertainties in pH determination. We wonder what Dr. Wanninkhof would recommend for high pCO_2 scenarios.

Dr. Wanninkhof poses the question why we do not recommend measuring pCO_2 as the key parameter. Even though direct pCO_2 measurements would be desirable, this method is unfortunately not yet used to a large extend in our scientific community.

Conclusion

All over-determined datasets we found in the context of OA research (and thus including high pCO_2 values) show the same phenomenon. A systematic offset (all pCO_2 calculated from TA and DIC are lower than those calculated from pH with either TA or DIC) appears in at least four datasets from different laboratories. Even though we cannot provide an explanation for the discrepancies, we hope that our contribution will raise the awareness for this somewhat hidden but apparently widespread phenomenon.

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Table 1. Measured and calculated carbonate chemistry parameters of manipulated artificial seawater (as described by Grasshoff et al., 1999) at 15^{o}C. Dissociation constants of Roy et al. (1993) were used for calculations.

measured parameters			calculated pCO_2		
TA (μmol kg^{-1})	DIC (μmol kg^{-1})	pH_{total}	(TA;DIC) (μatm)	(TA;pH) (μatm)	(DIC;pH) (μatm)
1961	1860	7.60	710	1105	1074
2172	2119	7.49	1181	1598	1570
2173	2087	7.60	922	1217	1197
2172	2122	7.47	1213	1648	1618
2389	2199	7.88	541	665	655
2391	2199	7.88	534	663	652
2390	2184	7.88	496	662	648
2612	2192	8.20	220	299	289
2605	2204	8.20	237	306	297
2597	2206	8.19	245	308	301

Table 2. Overall uncertainty of pCO_2 for DIC and TA as input parameters as calculated from contributions of various parameters. The overall uncertainty of pCO_2 is 53 μatm; it is mainly due to uncertainties in DIC, K_2, and K_1.

input pair	pCO_2 (μatm)	overall uncertainty (μatm)	main contributors
DIC; pH	149	10	pH; K_1
	722	45	pH; K_1
TA; pH	149	11	pH; K_1
	722	47	pH; K_1
TA; DIC	149	10	K2; K_1
	722	53	DIC; K_2; K_1

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Figure 1. Comparison of discrepancies in calculated pCO_2 as found for artificial seawater (ASW) and North Sea seawater (NSW).

Figure 2. Calculation of a pCO_2 of 722 μatm from DIC and TA: contributions of uncertainties in various parameters (closed circles) to the overall uncertainty (open circle). The plot shows the variances. The overall uncertainty of pCO_2 is 53 μatm; it is mainly due to uncertainties in DIC, K_2, and K_1.

Figure 3. Comparison of discrepancies between pCO_2 calculated from TA and pH and pCO_2 calculated from TA and DIC (or, in case of Iglesias-Rodriguez et al. 2008, target pCO_2) as found in different datasets.

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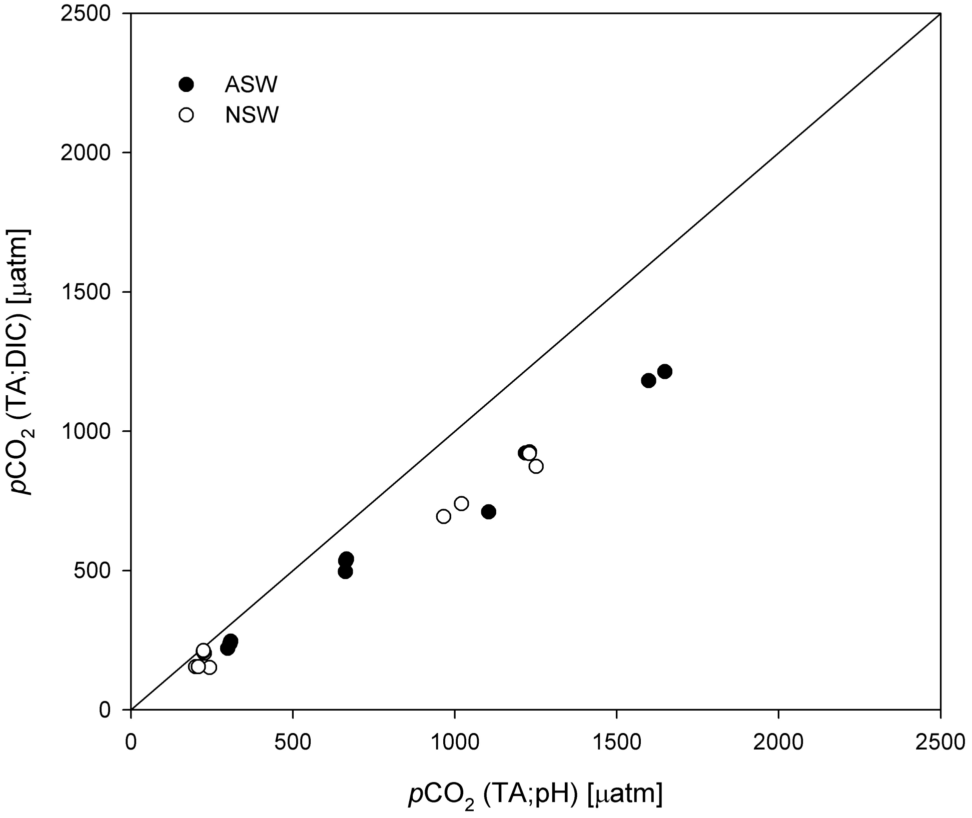
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$p\mathrm{CO_2}$ (TA;DIC) [µatm]
$p\mathrm{CO_2}$ (TA;pH) [µatm]

Fig. 1.

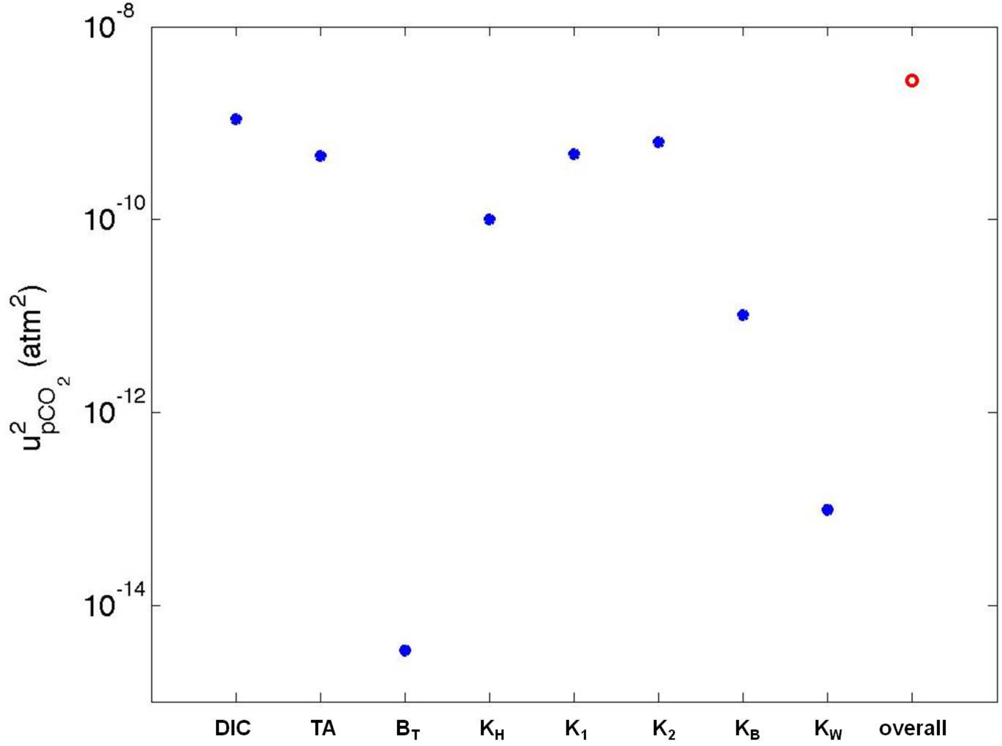

Fig. 2.

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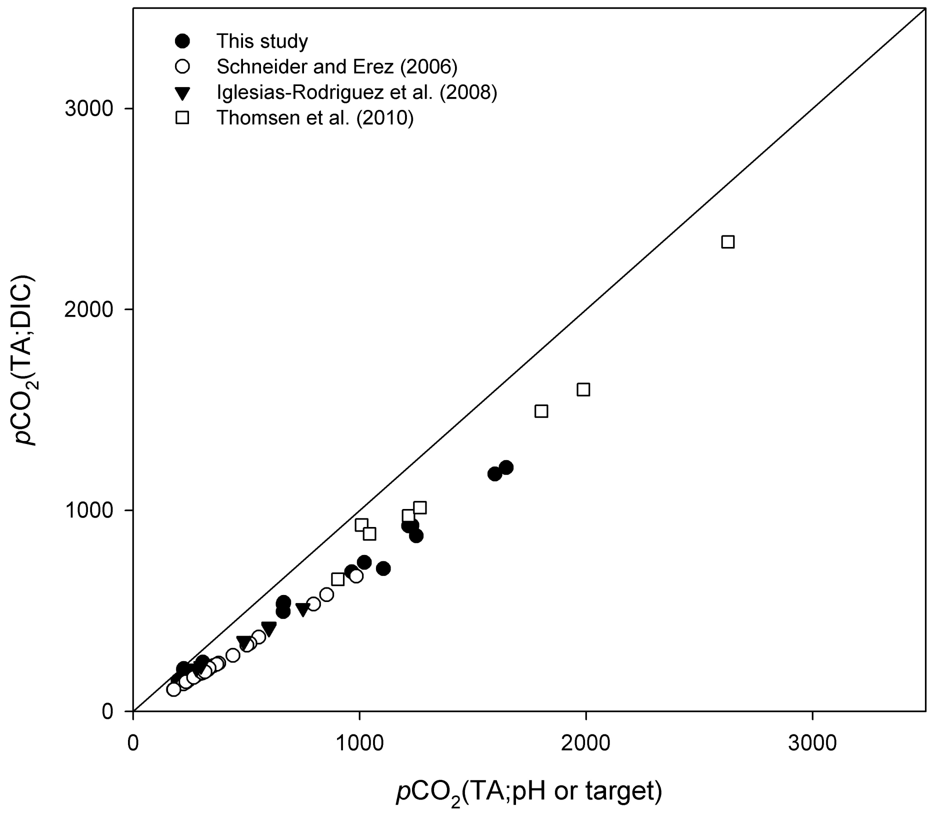
● This study
○ Schneider and Erez (2006)
▼ Iglesias-Rodriguez et al. (2008)
□ Thomsen et al. (2010)
pCO$_2$(TA;DIC)
0
1000
2000
3000
pCO$_2$(TA;pH or target)
0
1000
2000
3000

Fig. 3.