**Biogeosciences
Discussions**

Potential impact of DOC accumulation on fCO$_2$ and carbonate ion computations in ocean acidification experiments

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Abstract

The internal consistency of measurements and computations of components of the CO_2-system, namely total alkalinity (A_T), total dissolved carbon dioxide (C_T), CO_2 fugacity ($f CO_2$), and pH, has been confirmed repeatedly in open ocean studies when the
5   CO_2 system had been over determined. Differences between measured and computed properties, such as $\Delta f CO_2$ (=$f CO_2$(measured) − $f CO_2$(computed from A_T and C_T))/$f CO_2$(measured)× 100), there are usually below 5%. Recently, Hoppe et al. (2010) provided evidence of significantly larger $\Delta f CO_2$ in experimental setups. These observations are currently not well understood. Here we discuss a case from a series of
10   phytoplankton culture experiments with $\Delta f CO_2$ of up to about 25%. $\Delta f CO_2$ varied systematically during the course of these experiments and showed a clear correlation with the accumulation of dissolved organic carbon (DOC).

Culture and mesocosm experiments are often carried out under very high initial nutrient concentrations, yielding high biomass concentrations that in turn often lead to a
15   substantial build-up of DOC. DOC can reach concentrations much higher than typically observed in the open ocean. To the extent that DOC includes organic acids and bases, it will contribute to the alkalinity of the seawater contained in the experimental device. Our analysis suggests that whenever substantial amounts of DOC are produced during the experiment, standard computer programs used to compute CO_2 fugacity can
20   underestimate true $f CO_2$ significantly when the computation is based on A_T and C_T. Alternative explanations for large $\Delta f CO_2$, e.g. uncertainties of pKs, are explored as well, but are found to be of minor importance. Unless the effect of DOC-alkalinity is accounted for, this might lead to significant errors in the interpretation of the system under consideration to the experimentally applied CO_2 perturbation, which could mis-
25   guide the development of parameterisations used in simulations with global carbon cycle models in future CO_2-scenarios.

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1 Introduction

One of the largest anthropogenic perturbations of the marine environment is caused by the invasion of anthropogenic CO_2 into the ocean (Sabine et al., 2004). CO_2 entering the ocean changes the seawater carbonate equilibrium, decreases pH and the concentration of carbonate ions ($[CO_3^{2-}]$) and increases the ocean fCO_2 (Bates, 2001; Keeling et al., 2004; Byrne et al., 2010). Changes of seawater chemistry are expected to impact individual species, as well as on the community and ecosystem level (Raven et al., 2005). The potential for marine organisms, communities and ecosystems to adapt to these changes is not well understood, making the ocean acidification issue a high priority field of research (Doney et al., 2009). An obvious approach to such studies are experimental manipulations in which individual species or even whole ecosystems are studied under high fCO_2 conditions expected for the future (Orr et al., 2005), as well as low fCO_2 conditions known to predominate during the preindustrial era (Barnola et al., 1987).

Characterizing the seawater carbon dioxide system and its individual components, in the ocean as well as in experimental setups, requires to perform high quality measurements of at least two out of the four measurable properties of the carbon dioxide system, namely total alkalinity (A_T), total dissolved carbon dioxide (C_T), CO_2 fugacity (fCO_2), and pH. Instrumentation and protocols have significantly developed through the recent two decades allowing for very precise measurements of the marine CO_2 system (DOE, 1994; Dickson et al., 2007; Dickson, 2010). The internal consistency of these measurements and computations of components of the CO_2-system has been studied repeatedly when the CO_2 system had been over determined, i.e. where more than two types of measurements where available (McElligott et al., 1998; Wanninkhof et al., 1999; Lee et al., 2000; Millero et al., 2002, 2006). For the recommended choice of thermodynamic constants, the degree of inconsistency (computation error), expressed as $\Delta X = (X_{meas} - X_{calc})/X_{meas} \times 100$, of high quality measurements is usually well below 5% for fCO_2 (Lee et al., 2000).

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Recently, Hoppe et al. (2010) in a discussion paper gave evidence for much higher and systematic differences of measured and computed pCO_2 from experimental manipulations of North Sea water prepared for studies of ocean acidification on plankton. These authors measured pCO_2 as well as computed it from the following pairs of other measured variables, $A_T + C_T$, $A_T +$ pH, and $C_T +$ pH. The largest deviations from measured pCO_2 where obtained when computing pCO_2 from A_T and C_T, with respective ΔpCO_2 values of 25 % (± 0.3; geometric mean $\pm$ variance; $N = 12$, computed from data from Table 1 of Hoppe et al., 2010). Smaller deviations where found when calculating pCO_2 from C_T and pH ($\Delta X = 6.0 \pm 0.3\%$; $N = 11$) or A_T and pH ($4.6 \pm 0.4\%$; $N = 11$). ΔpCO_2 was independent of the method of seawater manipulation (bubbling, acid/base addition) and the magnitude of pCO_2. In a commentary to the Hoppe et al. paper, Tyrrell (2010) proposed that a possible explanation of the high ΔpCO_2 values might be related to an unrecognized contribution of dissolved organic matter (DOM), or more explicitly organic acids/bases, to measured A_T and the inability of implementations of the standard seawater chemical model (i.e. available software tools) used for carbon system calculations to correctly account for this effect when computing pCO_2. Such software imply established models of seawater chemistry, in particular concerning the involved chemical species and related thermodynamic constants. Though weak organic acids and bases are formally part of this concept, e.g. in the definition of alkalinity (Dickson, 1981; see also Sect. 3.2), their quantitative contribution to alkalinity is usually assumed to be of minor importance, and their composition (and hence their dominant pK values) are not well known. Hence these substances are not explicitly included in the algorithms applied in any of the respective software tools in use.

Based on recently published experimental work (Kim and Lee, 2009) we here explore the role of DOC accumulation during culture and mesocosm experiments on the computation of fCO_2 and the carbonate ion concentration, and how a neglect of DOC impacts on sea water alkalinity can affect the interpretation of ocean acidification experiments.

2 Experiments and analytical methods

In order to demonstrate the effect of freshly produced DOC on carbonate system computations we make use of data from a series of phytoplankton culture experiments published recently and described in detail by Kim and Lee (2009). In short, strains
5 of three phytoplankton species (Prorocentrum minimum, Skeletonema costatum, and Chaetoceros curvisetus) were collected from Jangmok Bay, Korea (34.6° N, 128.5° E) and incubated at 20 °C in filtered and autoclaved seawater augmented with nutrients (initial concentrations of 70 µmol/L nitrate, 5 µmol/L phosphate, and 50 µmol/L silicate). In order to extend the growth period and duration of the experiment a low photon flux
10 density (10 µmol photons m^{-2} s^{-1}; 12:12 light/dark cycle) yielding low specific growth rates was chosen. Phytoplankton cultures were periodically bubbled with air containing 5% CO_2 in order to maintain the solution pH in the range 7.8–8.2, within which spectrophotometric pH measurement applied in this study is optimal (Clayton and Byrne, 1993). Prior to each sampling the culture solution was mechanically mixed, minimizing
15 the possibility of sampling bias due to solution inhomogeneity.

For dissolved organic carbon (DOC) analysis, seawater samples were filtered through a pre-combusted filter (nominal pore size 0.7 µm; Whatman GF/F), filtrates were collected in precombusted glass vials (Corning 430052), acidified with 10% H_3PO_4 solution and purged (10 min) with ultrapure N_2 gas in order to remove inor-
20 ganic carbon. Sub-samples (triplicates) were injected into the combustion tube of a Shimadzu TOC-VCPH total organic carbon analyzer (Shimadzu Scientific Instruments, Kyoto, Japan) containing a platinum catalyst at 650° C, for oxidation of DOC to CO_2. CO_2-detection was with a non-dispersive infrared detector. The total alkalinity (A_T) and total inorganic carbon (C_T) values were determined using potentiometric
25 acid titration and coulometric titration in a VINDTA system (Marianda, Kiel, Germany). The measurement precisions were ± 1.5 µmol/kg for A_T and ± 2 µmol/kg for C_T (for details see Kim and Lee, 2009). Measurements of seawater pH were made to a precision of ± 0.001 at 25 °C using a double-wavelength spectrophotometric procedure and

m-cresol purple indicator, following Clayton and Byrne (1993). Nitrate was measured following a manual procedure (Hansen and Koroleff, 1999). All A_T and nutrient measurements were performed on seawater samples filtered (nominal pore size 0.7 µm; Whatman GF/F) under a slight vacuum pressure (<17 kPa) to remove all phytoplankton cells. Measurements of C_T and pH were performed on unfiltered seawater samples to avoid CO_2 gain or loss during the filtration process (see supplementary data in Kim and Lee, 2009).

No direct measurements of $f CO_2$ are available from this experiment. $f CO_2$ (and $[CO_3^{2-}]$, the carbonate ion concentration) are computed independently from the following pairs of measurements: C_T + pH, A_T + pH, and A_T + C_T. For all computations we apply the Matlab-version of CO2SYS (Lewis and Wallace, 1998; van Heuven et al., 2009; http://cdiac.ornl.gov/oceans/co2rprt.html), using carbonic acid dissociation constants of Mehrbach et al. (1973), as refitted by Dickson and Millero (1987), and other ancillary thermodynamic constants (Millero, 1995). In the absence of measured $f CO_2$ values, we compute e.g. $\Delta f CO_2 (A_T + C_T) = (f CO_{2(reference)} - f CO_{2(At+Ct)})/f CO_{2(reference)} \times 100$, using $f CO_{2(Ct+pH)}$ as the reference, $f CO_{2(reference)}$. This choice of the $f CO_{2(reference)}$ is a priori derived from our working hypothesis that the significant $\Delta f CO_2$, which we report is due to the alkalinity effect from DOM (organic acids/bases) accumulating during the experiments. Organic acids/bases are not known to affect the analytical methods applied to measure pH and C_T in our study. A posteori the choice of the reference is justified by the thought experiment and related model simulations presented in Sect. 3.2. We compute $\Delta [CO_3^{2-}] = ([CO_3^{2-}]_{(reference)} - [CO_3^{2-}]_{(At+Ct)})/[CO_3^{2-}]_{(reference)} \times 100$, accordingly.

3   Results

3.1   Jangmok Bay phytoplankton cultures

During the incubation, the NO_3 concentration in all three cultures (*P. minimum*, *S. costatum* and *C. curvisetus*) dropped below the detection limit ($0.2\,\mu mol\,L^{-1}$) approximately
5 2 weeks after the incubation commenced (Fig. 1a). DOC increased during this period and continued to increase after NO_3 became (and remained) depleted (Fig. 1b), as did measured A_T (Kim and Lee, 2009). ΔDOC, the amount of accumulated DOC, was as high as $50\,\mu mol\,L^{-1}$ at the end of the experiments. Due to the intentional periodical bubbling with CO_2-enriched air (see methods section), C_T concentrations
10 increased over the course of the experiment (not shown), rather than decreased as observed regularly in micro- or mesocosm experiments where the pH is allowed to drift freely (e.g. Goldman, 1999; Riebesell et al., 2007). During the experiment both $\Delta f CO_2$ and $\Delta[CO_3^{2-}]$ increased with time (Fig. 2), reaching values as high as 23% and -24% for ΔfCO_2 and $\Delta[CO_3^{2-}]$, respectively. Initial values of ΔfCO_2 ($\Delta[CO_3^{2-}]$) were
15 2 to 6% (-2 to -5%), which is similar to ranges of ΔX values observed during open ocean consistency studies (Lee et al., 2000). There is a clear relationship of ΔfCO_2 and $\Delta[CO_3^{2-}]$ with the concentration of DOC accumulating during the experiment (ΔDOC, Fig. 3), not surprising in view of the tight relationship between ΔDOC and ($A_{T(measured)}$-$A_{T(Ct+pH)}$), observed by Kim and Lee (2009). The difference between measured A_T and
20 A_T computed from pH and C_T increased in tight correlation with nitrate consumption with final values of about $20\,\mu mol\,kg^{-1}$ (S. costatum and C. curvisetus cultures) and $42\,\mu mol\,kg^{-1}$ (P. minimum culture), slopes of A_T(measured) $- A_T(C_T+pH)$ and ΔDOC ranged between 0.82 and 1.21 (Kim and Lee, 2009).

3.2   A model experiment

25 In this section we quantitatively explore the potential role of organic acids/bases for CO_2-system computations by means of a thought experiment and numerical

simulations. We consider a water sample with a total alkalinity of $2400\,\mu mol\,kg^{-1}$, a known total DOC-alkalinity of $50\,\mu mol\,kg^{-1}$, $S = 35$, $T = 25°C$, total-PO_4 and total-$Si(OH)_4 = 0\,\mu mol\,kg^{-1}$ of which subsamples have been manipulated by bubbling to provide a range of $f CO_2$ between 100 and $3000\,\mu atm$. The high-end range of $f CO_2$
5 is relevant in low oxygen waters, which had equilibrated with the atmosphere under current conditions (Brewer and Peltzer, 2009).

Furthermore, we have coded a modified version of the CO2SYS-program, which accounts for the contribution of organic acids/bases to total alkalinity when computing missing variables of the CO_2-system from known pairs of input variables. Here we
10 simplify and assume that the dissociation of organic acids/bases can be described by a single dissociation constant and choose a pK value of 4.2. Using our virtual input data of A_T, total DOC-A_T, S, T, total phosphate, total silicate and the given range of $f CO_2$, we compute C_T and pH for all $f CO_2$ subsamples. In order to check the consistency of our A_T, $f CO_2$, C_T and pH data we compute $f CO_2$ from all possible pairs
15 of input variables using the CO2SYS-DOC code version and compare the diagnosed $f CO_2$ values against the $f CO_2$ values imposed in the thought experiment. We find that the imposed $f CO_2$, $f CO_2(A_T+C_T)$, $f CO_2(C_T+pH)$, and $f CO_2(A_T+pH)$ all agree with each other within 10^{-5} %. Note that in this section $\Delta f CO_2$ is always computed using the imposed $f CO_2$ (which, in real experiments, would be the measured $f CO_2$) as the
20 reference.

In the following we will treat our virtual dataset like an over-determined CO_2-system dataset having all four possible measurements, i.e. C_T, A_T, $f CO_2$ and pH. Since this is a thought experiment, we will treat these data as being perfect measurements, i.e. not associated with any random error. Importantly, we now return to the
25 standard procedure and do all computations with the standard version of CO2SYS. Computing again $f CO_2$ from all three possible input pairs and computing $\Delta f CO_2$ against $f CO_2(measured)$ (Fig. 4a), we find that $f CO_2(C_T+pH)$ is in perfect agreement with $f CO_2(measured)$, $\Delta f CO_2(A_T+pH)$ is small, negative, and constant, while $\Delta f CO_2(A_T+C_T)$ is much larger and variable over the range of explored $f CO_2$. For

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the given value of DOC-A_T $\Delta f CO_2(A_T+pH)$ is about −2.2%, and $\Delta f CO_2(A_T+C_T)$ is about 15% at low $f CO_2$. Moreover, $\Delta f CO_2(A_T+C_T)$ increases about linearly up to 1000 µatm and shows an approximately constant value of about 28% between 2000 and 3000 µatm, before it decreases again at even higher $f CO_2$ (not shown). For the conditions assumed here, the maximum of 28.6% is observed at about 2700 µatm.

The observed behaviour is easily understood when considering the equations used to compute $f CO_2$, or more specificly the CO_2 concentration, $[CO_2{}^*]$ (Eqs. 1–4; e.g. Dickson, 2007).

$$C_T + pH: \qquad [CO_2{}^*] = \frac{C_T [H^+]^2}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \qquad (1)$$

$$A_T + pH: \qquad [CO_2{}^*] = \frac{A_C [H^+]^2}{K_1([H^+] + 2K_2)} \qquad (2)$$

$$A_T + C_T: \qquad [CO_2{}^*] = \frac{[H^+][HCO_3^-]}{K_1} \qquad (3)$$

$$\text{with} \qquad [HCO_3^-] = \frac{C_T K_1 [H^+]}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \qquad (3a)$$

$$\text{all}: \qquad f CO_2 = \frac{[CO_2{}^*]}{K_0} \qquad (4)$$

where $[H^+]$ is the hydrogen ion concentration, K_0 is the solubility coefficient of CO_2 in seawater, K_1 and K_2 are the first and second dissociation constants of carbonic acid and A_C is the carbonate alkalinity (Eq. 6). $[CO_2{}^*]$ is the sum of aqueous carbon dioxide and true carbonic acid. We follow the notation of Dickson et al. (2007).

Obviously (Eq. 1), when C_T and pH are used as input variables, the computation of $[CO_2{}^*]$ is not affected by any uncertainty related to the DOC-alkalinity, and hence,

given the assumption of high quality pH and C_T measurements $fCO_2(C_T+pH)$ equals the measured fCO_2. When the computation of fCO_2 is based on the pair of A_T and pH (Eq. 2), all uncertainty resides in the estimate of A_C, the carbonate alkalinity (Eq. 6), while [H+] is from a measured variable (pH). The carbonate alkalinity is computed as the difference between measured A_T and the sum of all minor components of seawater alkalinity, in particular borate alkalinity, P-, Si-, S-, and F-alkalinity, $[OH^-]$, $[H^+_{free}]$, and eventually the DOC-alkalinity, indicated by eclipses in Eqs. 5 and 6. Hence, in our model calculations, the absolute error of A_C is equivalent to the value of the effective DOC-alkalinity if this term cannot be quantified in the computation due to a lack (or ignorance) of respective data and pK values. The relative error, i.e. $\Delta fCO_2(A_T+pH)$, scales with ΔA_C which, in our idealised example is to the first order equivalent to (2400-50-2400)/(2400-50) × 100 = −2.1%.

$$A_T = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)^-\right] + \left[OH^-\right] + \left[HPO_4^{2-}\right] \tag{5}$$
$$+ 2\left[PO_4^{3-}\right] + \left[SiO(OH)_3^-\right] + \left[NH_3\right] + \left[HS^-\right] + \ldots$$
$$- \left[H^+\right]_F - \left[HSO_4^-\right] - \left[HF\right] - \left[H_3PO_4\right] - \ldots$$

$$
\begin{aligned}
A_C &= \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] \\
&= A_T - \left(
\begin{array}{l}
\left[B(OH)^-\right] + \left[OH^-\right] + \left[HPO_4^{2-}\right] \\
+ 2\left[PO_4^{3-}\right] + \left[SiO(OH)_3^-\right] + \left[NH_3\right] + \left[HS^-\right] + \ldots \\
- \left[H^+\right]_F - \left[HSO_4^-\right] - \left[HF\right] - \left[H_3PO_4\right] - \ldots
\end{array}
\right)
\end{aligned}
\tag{6}
$$

Computing $[CO_2^*]$ from A_T and C_T (Eq. 3) requires to first estimate the hydrogen ion concentration, $[H^+]$. The principle technique to achieve this, as applied in carbon cycle models and software tools like CO2SYS, involves iterative approaches such as

the Newton-Raphson method (Lewis and Wallace, 1998; Orr et al., 1999; Follows et al., 2006). Terms given in the large bracket of Eq. (7) are computed for an initial guess of the pH, and for given thermodynamic constants (depending on T, S, and pressure), silicate, phosphate concentrations and total borat, fluorid, and sulfate. The latter total concentrations are usually computed from relationships with salinity. The residual is analysed to derive a new estimate of the pH, from which in turn the various alkalinity components (large bracket) are recomputed. This process is repeated until the residual is sufficiently small and a consistent pH is derived.

$$\text{Residual} = A_T - \left(\begin{array}{c} [\text{HCO}_3^-] + 2\left[\text{CO}_3^{2-}\right] + [B(\text{OH})^-] + [\text{OH}^-] + \left[\text{HPO}_4^{2-}\right] \\ + 2\left[\text{PO}_4^{3-}\right] + [\text{SiO(OH)}_3^-] + [\text{NH}_3] + [\text{HS}^-] + ... \\ - [H^+]_F - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - ... \end{array} \right) \quad (7)$$

Software tools and carbon cycle models may differ on the treatment of the individual components of the bracketed term of Eq. (7). For example, [HS-] and [NH$_3$] are often omitted since concentrations are usually neglectable under oxic conditions and at seawater pH. Additional proton acceptors or donors, like organic acids and basis, are formally part of the alkalinity definition and indicated as eclipses in lines 2 and 3 of Eqs. (5–7), respectively. However, they usually have no representation in the software codes. Given that, in our thought experiment, the measurement of A_T contains a significant amount of organic acids, while the equations coded in the standard version of CO2SYS do not include these alkalinity components, a wrong pH will be derived. For the example of our thought experiment, computational errors (relative anomalies), $\Delta[H^+]$ and $\Delta[\text{HCO}_3^-]$, are shown in Fig. 4b. It is obvious that $\Delta f\text{CO}_2(A_T+C_T)$ scales very much with $\Delta[H^+]$ while the contribution from $\Delta[\text{HCO}_3^-]$ is less important. In fact, when inserting Eq. (3a) into (3) we get an equation identical in form to equation 1, however, with the obvious difference that for the pair C_T+pH the pH is measured while for the pair A_T+C_T it is computed through the described iterative procedure.

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For a fixed $f\mathrm{CO}_2$ value (400 µatm) we explore a range of total DOC-A_T values between 0 and 50 µmol kg^{-1}, leaving everything else unchanged. An almost linear and positive correlation can be found between $\Delta f\mathrm{CO}_2(A_\mathrm{T}+C_\mathrm{T})$ and DOC-A_T (Fig. 5a), and a negative correlation of $\Delta f\mathrm{CO}_2(A_\mathrm{T}+\mathrm{pH})$ with DOC-A_T. Both relationships are very similar to those observed in the culture experiments between ΔfCO$_2$ and the accumulated DOC (Fig. 5b). In particular, the computation error $\Delta f\mathrm{CO}_2(A_\mathrm{T}+\mathrm{pH})$ associated with even quite high DOC-A_T appears to be moderate compared with the $\Delta f\mathrm{CO}_2(A_\mathrm{T}+C_\mathrm{T})$. For consistency, we also checked whether uncertainties in thermodynamic constants contribute to the observed magnitude of $\Delta f\mathrm{CO}_2(A_\mathrm{T}+C_\mathrm{T})$. Applying several other published sets of thermodynamic constants, which may alternatively be chosen in CO2SYS, we find only a minor contribution of this choice to ΔfCO$_2$ (not shown). The effects of DOC-alkalinity presented also depend on the choice of the pK value of the organic acid/base system, with lower effects if the pK value is close to the mean pH of seawater (Fig. 6).

4 Discussion

Data from a larger number of experimental ocean acidification studies have recently been archived in the Pangaea database (Nisumaa et al., 2010). This EPOCA/EUR-OCEANS data compilation also provides an overview of the dominantly used measurement protocols in recent ocean acidification experiments. About 90% (49%) of the papers from which data have been archived by Nisumaa and co-workers (see their Fig. 5) used A_T (C_T) as one of the measured variables of the carbonate system, that is, close to 50% of the studies computed $f\mathrm{CO}_2$, carbonate ions or other variables of the CO$_2$-system from the pair of A_T and C_T. Only 17% of the studies measured $p\mathrm{CO}_2$ directly and there is only a small number of experiments (about 5%) during which the carbon dioxide system had been over determined (Nisumaa et al., 2010). Also DOC measurements have been carried out in only a small subset of these experiments. It is hence very difficult to access the wider significance of our observations from the publicly available data.

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Phytoplankton culture experiments described in detail by Camiro-Vargas et al. (2005) and Hernández-Ayon et al. (2007) provide an example which is even more extreme than the data presented here. These authors grew cultures of Rhodomonas sp. in high nutrient (initial concentrations: $NO_3 = 1200\,\mu mol/L$, $PO_4 = 60\,\mu mol/L$) batch cul-
5   tures. Using data of measured A_T, C_T, and pH from Hernández-Ayon et al. (2007) (we assume a mean salinity of 35), we compute $\Delta f CO_2$ values between about 30% at the beginning of the experiment and up to 90% about a week later. This huge $\Delta f CO_2$ is in agreement with a large observed difference between measured and computed A_T (up to $800\,\mu mol\,kg^{-1}$). Hernández-Ayon et al. (2007) suggest that the difference between
10   measured and computed A_T, is indicative of a large accumulation of DOM from phyto-plankton growth stimulated by high initial concentrations of nitrate and phosphate. By the end of the experiment nitrate was depleted (Camiro-Vargas et al., 2005) and DOC had increased to $>3000\,\mu mol/L$ (Hernández-Ayón, personal communication, 2010).

This points to an essential difference between open ocean datasets, which are char-
15   acterized by a high degree of consistency between measured and computed $f CO_2$ (e.g. Lee et al., 2000) and typical experimental approaches often used in ocean acid-ification research. Experimental studies have often applied nutrient additions much higher than found in typical open-ocean seasonal nutrient variations. This conse-quently yields large phytoplankton blooms in experimental systems, and, in line with
20   the closed-system nature of the experiments a marked production and temporal accu-mulation of fresh DOM (e.g. Norrman et al., 1995; Meon and Kirchman, 2001; Wetz and Wheeler, 2003; Wohlers et al., 2009). We compiled literature data describing net DOC accumulation observed in batch or mesocosm experiments. Given a consider-able degree of variability, which most likely is related to dominant species, specific
25   growth conditions, and pre-incubation history, a general relationship between initial ni-trate available and drawn down and net DOC accumulation is evident (Fig. 7). Seasonal variations in surface waters of the open ocean are usually small, with about 3–6 µmol/kg in subtropical waters near Bermuda (Hansell and Carlson, 2001) and 20–30 µmol/kg in some high latitudes systems (e.g. Carlson et al., 1998). Most of the oceanic DOM is

refractory. Importantly, experimental DOC accumulation is usually larger than the highest seasonal DOC variations observed in the ocean and up to two orders of magnitude larger than those reported from subtropical surface waters.

The fraction of freshly produced and accumulating DOM, which is in the form of organic acids or bases, and which may act as proton acceptors during alkalinity titration, is not known. Combining the experimental evidence of organic proton acceptors (i.e. ΔA_T; Hernandéz-Ayón et al., 2007; Muller and Bleie, 2008; Kim and Lee, 2009) with the widespread observation of large amounts of DOM accumulating in phytoplankton culture and bloom experiments (Fig. 7), however, we suggest that significant differences between measured $f\mathrm{CO_2}$ and $f\mathrm{CO_2}$ computed from A_T and C_T is not a singularity of our datasets, but likely as widespread as the DOM accumulation in such experiments itself.

Because concentrations of DOC are also often elevated in coastal waters, compared with the open ocean (at times >200 µmol/kg; e.g. Cauwet, 2002 for a review), coastal waters may occasionally be prone to the $\mathrm{CO_2}$-computational issue shown here. This is due to additional sources, like river inflow, and also to larger autochthonous DOM production supported by higher nutrient levels and more intense plankton blooms. We are not aware of any published studies of $\mathrm{CO_2}$-system over-determinations from coastal waters, that analyse the magnitude of $\Delta f\mathrm{CO_2}$. One study compared measure A_T and A_T computed from pH and C_T in California Bay showing that measured and computed alkalinity may differ by 50 to 200 µmol/kg (Hernández-Ayón et al., 2007). Extrapolating our simulations shown in Fig. 5a to such high DOC-alkalinities yields $\Delta f\mathrm{CO_2}(A_\mathrm{T}+C_\mathrm{T})$ of up to 50% and $\Delta f\mathrm{CO_2}(A_\mathrm{T}+\mathrm{pH})$ of up to −10%. So far no comprising analysis of ΔA_T and DOC is available for coastal waters. However, from the ΔA_T observed in California Bay waters by Hernández-Ayón et al. (2007), the elevated DOM concentrations found in coastal waters and the elevated magnitude of phytoplankton blooms in coastal waters, partly by phytoplankton species known to release significant amounts of DOM (e.g. Cadée and Hegeman, 2002), we speculate that $\Delta f\mathrm{CO_2}$ in coastal waters may, at times be significantly larger than in open ocean waters, and perhaps similar to what we

observed in our experimental datasets. From the strong seasonal variability of DOM concentrations in coastal waters (Williams, 1995; Suratman et al., 2009; Sintes et al., 2010) one can further speculate that $\Delta f\mathrm{CO_2}$ may show considerable seasonlity as well. Further studies are needed.

⁵ Global biogeochemical models are our major tools to extrapolate from small, experimental scales to the global ocean and into the future. It is via the use of such models that we may be able to extrapolate the experimentally observed sensitivities of, for example, calcium carbonate and organic matter production (e.g. Zondervan et al., 2001; Riebesell et al., 2008; Rost et al., 2008) or $\mathrm{N_2}$-fixation rates (e.g. Barcelos e Ramos et

¹⁰ al., 2007) to seawater $f\mathrm{CO_2}$ levels onto the global scale. Only global biogeochemical models will allow for a proper calculation of the net effect on e.g. atmospheric $\mathrm{CO_2}$ of the various proposed biogeochemical responses and feedbacks to global warming, de-oxygenation and ocean acidification. Early model experiments aiming for first order quantifications of global impacts of ocean-acidification induced biogenic feedbacks on

¹⁵ the carbon cycle, based their parameterizations, e.g. of IC:OC ratios, on relatively small sets of experimental evidence (e.g. Heinze, 2004; Gehlen et al., 2007; Hofmann and Schellnhuber, 2009) yielding already a factor-of-four range in the simulated strength of the global $\mathrm{CO_2}$-calcification feedback (Ridgwell et al., 2009). It is generally acknowledged that part of the difficulty of deriving robust parameterisations for biogeochemical

²⁰ impacts of ocean acidification arises form the fact that different species, strains and experimental conditions can lead to different responses for identical changes in the carbonate chemistry. Parameterizations of $\mathrm{CaCO_3}$ production applied in global models have used either $f\mathrm{CO_2}$, $[\mathrm{CO_3^{2-}}]$, or the saturation state (Ω) as master variables (i.e. as x-axes) when putting together results from different experiments. The accu-

²⁵ racy of these master variables of carbon dioxide chemistry has been taken for granted and not recognized as a significant source of uncertainty in the development of such parameterizations.

The majority of ocean acidification experiments studying the response of phytoplankton or whole pelagic ecosystems have reported A_T as one of two measured variables

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of the carbon dioxide system, and about 50% of the reports compiled by Nisumaa et al. (2010) used the pair of A_T and C_T to compute other components of the CO_2 system. Given the results of our study, that the computation of master variables of the CO_2 system if based on A_T and C_T is uncertain due to the usually not quantified contribution of DOM to A_T, it is unclear how the available information from recent ocean acidification experiments can be safely used to develop such functional relationships. It is well possible that the response to ocean acidification found in some studies is overestimated when calculating $f CO_2$ from A_T and C_T as suggested already by Hoppe et al. (2010), however, when results from a variety of studies with unknown reliability of $f CO_2$ ([CO_3^{2-}], omega) values and its time course are compiled together to derive some mean or general functional relationship, this relationship might simply be wrong and unconstrained.

5 Conclusions and recommendations for ocean acidification experiments

In a series of phytoplankton culture experiments the $f CO_2$ and the carbonate ion concentration, [CO_3^{2-}], computed from A_T and C_T differed significantly from that computed from C_T and pH. Maximum differences of up to about 25% relative to the reference values are observed, and even higher values of up to 90% are estimated from literature data. $\Delta f CO_2$ is not constant in these experiments, but increases over time and particularly after nitrate is depleted. An approximately linear relationship of $\Delta f CO_2$ (and Δ[CO_3^{2-}]) with the accumulation of freshly produced DOC is found. The correlation of $\Delta f CO_2$ with DOC accumulation points to the potential role of organic proton acceptors during alkalinity titration as a cause for elevated $\Delta f CO_2$ observed in this study and elsewhere (Hernández-Ayón et al., 2007; Hoppe et al., 2010). Software tools regularly used to compute missing variables of the CO_2-system, like the CO2SYS (Lewis and Wallace, 1998), which we used in our study, usually do not account for organic proton acceptors. We set up a code version which includes a simplistic model of organic acids (pK = 4.2) and performed numerical simulations which provided dependencies

of $\Delta f\mathrm{CO}_2(A_\mathrm{T}+C_\mathrm{T})$ and $\Delta f\mathrm{CO}_2(A_\mathrm{T}+\mathrm{pH})$ very much in agreement with the culture experiments.

Computing $f\mathrm{CO}_2$ from A_T and C_T instead of measuring it was a standard procedure in many ocean acidification experiments conducted so far (Nisumaa et al., 2010). We propose that computed $f\mathrm{CO}_2$ from these experiments published in the literature is uncertain. The same argument applies when computing carbonate ion concentrations ($[\mathrm{CO}_3^{2-}]$), saturation states (Ω), or pH from these experiments. Moreover, there is no easy way to quantify the strength of $\Delta f\mathrm{CO}_2$ ($\Delta p\mathrm{CO}_2$, $\Delta[\mathrm{CO}_3^{2-}]$) for the individual experiments since over determination of the carbon-dioxide system has been very rare in these experiments and DOM release has been measured only in a few studies. Amount, composition, and timing of DOM production and accumulation are all known to be variable. Culture and microcosm experiments for example have shown that a large increase in DOM is often associated with nutrient depletion (e.g. Berman and Holm-Hansen, 1974; Wetz and Wheeler, 2003), which might indicate that results from nutrient replete ocean acidification culture experiments are less affected and $\Delta f\mathrm{CO}_2$ is small here. However, other studies found species-specific response with high DOM release also under nutrient replete conditions in some species and low release in others (e.g. Biddanda and Benner, 1997). Most importantly, some studies have suggested that DOC production and fate vary itself with $p\mathrm{CO}_2$ (Engel et al., 2004), complicating the issue further.

In the recently published guide for the best practice for ocean acidification research and data reporting (Riebesell et al., 2010) the available measurement techniques for studies of the carbon dioxide system in seawater in ocean acidification experiments have been discussed and evaluated in detail. While for natural seawater the measurement of A_T and C_T is recommended (Dickson et al., 2007; Dickson, 2010), our analysis emphasizes that in phytoplankton culture and bloom experiments the carbon dioxide may be better characterized by (spectrophotometrical) pH and appropriate (e.g. coulometric) C_T measurements (Dickson, 2010; Hoppe et al., 2010). From this the suggestion is drawn that whenever possible experimentalists should over determine the CO_2

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system, adding appropriate pH or $f\mathrm{CO_2}$ measurements to high quality A_T and C_T measurements. This will also help to better understand the extent of the DOM-alkalinity issue in general and with respect to already published experimental work, hopefully clarifying whether these results can still be used when deriving parameterizations for

5   global simulations.

We base our concern on a relatively small number of experiments for which we have direct evidence for significant, large, and temporally variable $f\mathrm{CO_2}$ computation errors. Clearly there is a need for more such experimental studies, which should combine over determination of the carbon dioxide system (i.e. high quality measurements of

10 pH, C_T, A_T, $f\mathrm{CO_2}$) and detailed determination of dissolved organic matter (e.g. Muller and Bleie, 2008), before the case can be settled. Given that amount and composition of DOM production and accumulation is highly variable, differs by species (phytoplankton group), growth rates, and experimental conditions (e.g. Nagata, 2000 for an overview), we expect a high variability of $\Delta f\mathrm{CO_2}$.

15 We conclude that, difficulties in developing model parameterization do not only arise from variations in the observed functional responses (of e.g. the IC:OC ratio, PIC production, POC production, etc.; i.e. values on the y-axes) but most likely also from uncertainties of the relevant values on the x-axes, i.e. the independent variables, often $f\mathrm{CO_2}$, ($p\mathrm{CO_2}$), pH, or $[\mathrm{CO_3^{2-}}]$ to which parameterizations refer.

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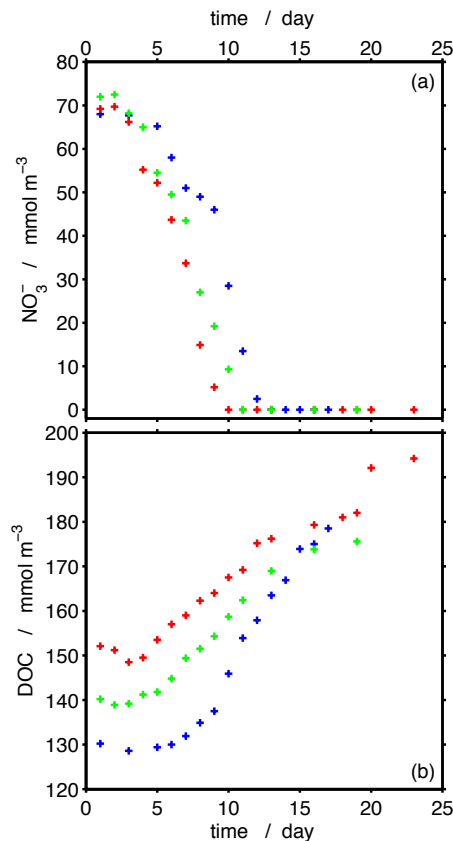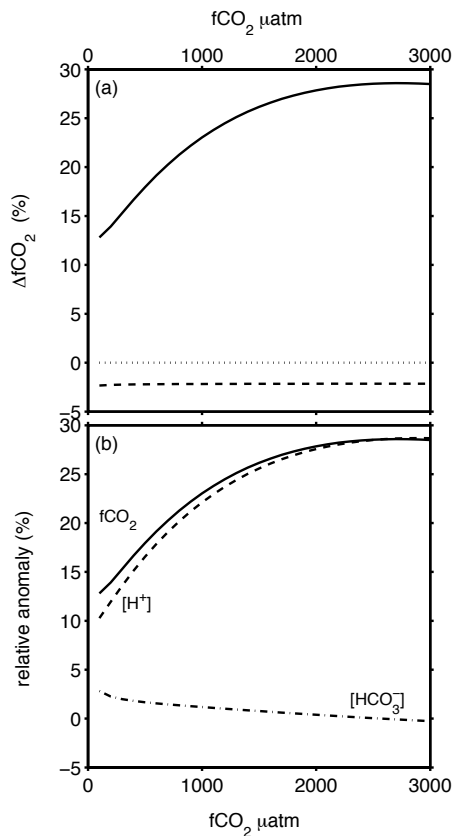
Fig. 1. Time course development of nitrate (mmol m^{-3}; **(a)**) and DOC (mmol m^{-3}; **(b)**) concentrations during three phytoplankton culture experiments. Blue: Prorocentrum minimum (Dinoflagellate), red: Skeletonema costatum (Diatom), green: Chaetoceros curvisetus (Diatom).
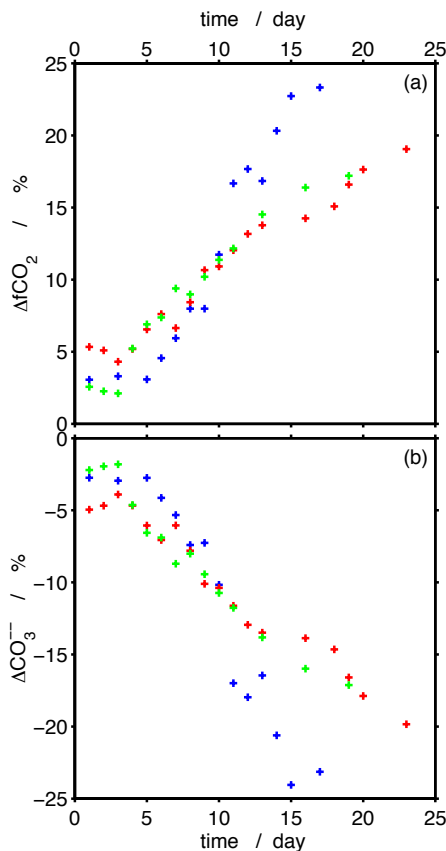
Fig. 2. Time course of $\Delta f\mathrm{CO}_2$ **(a)** and $\Delta[\mathrm{CO}_3^{2-}]$ **(b)** during phytoplankton culture experiments. Colour code as in Fig. 1. $\Delta f\mathrm{CO}_2$ and $\Delta[\mathrm{CO}_3^{2-}]$ are computed as follows: $\Delta f\mathrm{CO}_2 = (f\mathrm{CO}_{2(\mathrm{Ct+pH})} - f\mathrm{CO}_{2(\mathrm{At+Ct})})/f\mathrm{CO}_{2(\mathrm{Ct+pH})}$; $\Delta[\mathrm{CO}_3^{2-}] = ([\mathrm{CO}_3^{2-}]_{(\mathrm{Ct+pH})} - [\mathrm{CO}_3^{2-}]_{(\mathrm{At+Ct})})/[\mathrm{CO}_3^{2-}]_{(\mathrm{Ct+pH})}$.
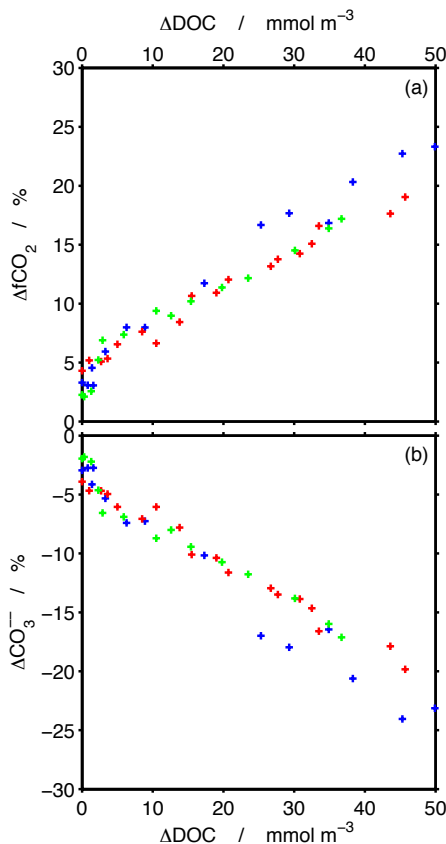
Fig. 3. (a) Relationship between DOC accumulated during the experiment (ΔDOC) and **(a)** $\Delta f CO_2$ and **(b)** $\Delta[CO_3^{2-}]$. Colour code as in Fig. 1, $\Delta f CO_2$ and $\Delta[CO_3^{2-}]$ computed as explained in Fig. 2.

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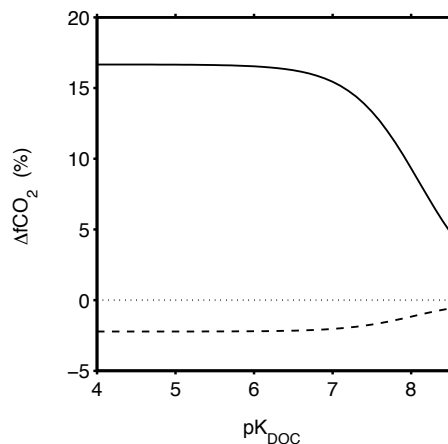Full Screen / Esc

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Interactive Discussion

Fig. 4. Numerical simulations assuming a DOC-alkalinity of $50\,\mu\text{mol kg}^{-1}$(for details see Sect. 3.2). **(a)** $\Delta f\text{CO}_2(A_\text{T}+C_\text{T})$ (solid line), $\Delta f\text{CO}_2(A_\text{T}+\text{pH})$ (dashed line), and $\Delta f\text{CO}_2(C_\text{T}+\text{pH})$ (dotted lines). **(b)** relative anomalies (%) of $f\text{CO}_2$, $[H^+]$, $[\text{HCO}_3^-]$.
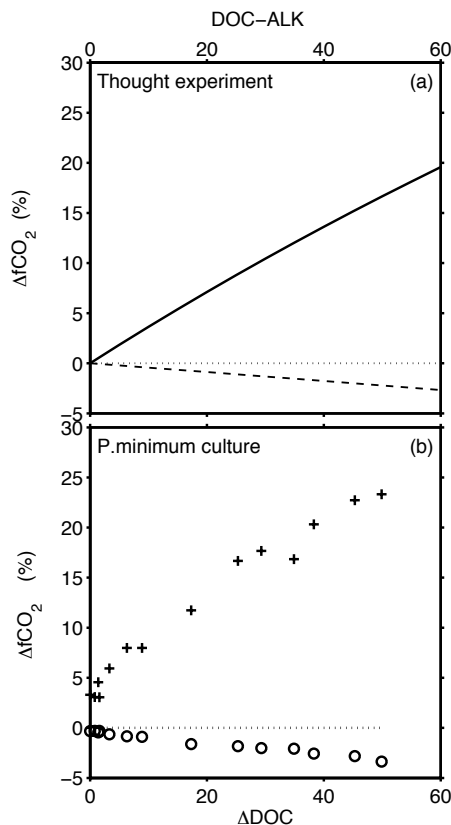
Fig. 5. $\Delta f CO_2(A_T + C_T)$ (solid line, +), $\Delta f CO_2(A_T + pH)$ (dashed line, o), and $\Delta f CO_2(C_T + pH)$ (dotted lines) from **(a)** a thought experiment and numerical simulations (for details see Sect. 3.2) and **(b)** the P. minimum culture. X-axes is either the DOC-alkalinity (μmol kg^{-1}) assumed in the numerical simulations **(a)** or **(b)** the measured DOC accumulation over the experiment (μmol L^{-1}).

Fig. 6. $\Delta f CO_2(A_T + C_T)$ (solid line, +), $\Delta f CO_2(A_T + pH)$ (dashed line, o), and $\Delta f CO_2(C_T + pH)$ (dotted lines) as a function of the choice of the pK of the organic acid/base system. We assume a total DOC-alkalinity of $50\,\mu mol\,kg^{-1}$, a true $f CO_2$ of $400\,\mu atm$, and standard conditions as explained in the text (Sect. 3.2).
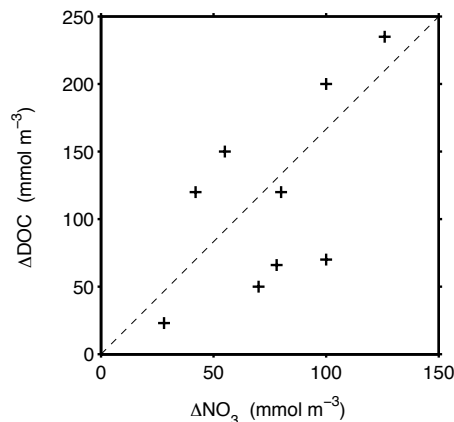
Fig. 7. DOC accumulation observed as a function of net drawdown of nitrate in phytoplankton culture and mesocosm experiments. Data where taken from the following references: Norrman et al., 1995; Meon and Kirchman, 2001; Wetz and Wheeler, 2003; Kragh and Søndergaard, 2004; Søndergaard et al., 2000; Aluwihare and Repeta, 1999; Myklestad et al., 1989; Kim and Lee (2009); this study; Engel et al., 2004; Schulz et al., 2008; Wohlers et al. (2009); Biddanda and Benner, 1997.