The internal consistency of the North Sea carbonate system

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ABSTRACT

In 2002 (February) and 2005 (August), the full suite of carbonate system parameters (total alkalinity (A_T), dissolved inorganic carbon (DIC), pH, and partial pressure of CO_2 (pCO_2) were measured on two re-occupations of the entire North Sea basin, with three parameters (A_T, DIC, pCO_2) measured on four additional re-occupations, covering all four seasons, allowing an assessment of the internal consistency of the carbonate system. For most of the year, there is a similar level of internal consistency, with A_T being calculated to within ± 6 µmol kg^{-1} using DIC and pH, DIC to ± 6 µmol kg^{-1} using A_T and pH, pH to ± 0.008 using A_T and pCO_2, and pCO_2 to ± 8 µatm using DIC and pH, with the dissociation constants of Millero et al. (2006). In spring, however, we observe a significant decline in the ability to accurately calculate the carbonate system. Lower consistency is observed with an increasing fraction of Baltic Sea water, caused by the high contribution of organic alkalinity in this water mass, not accounted for in the carbonate system calculations. Attempts to improve the internal consistency by accounting for the unconventional salinity–borate relationships in freshwater and the Baltic Sea, and through application of the new North Atlantic salinity–boron relationship (Lee et al., 2010), resulted in no significant difference in the internal consistency.

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1. Introduction

Increasing atmospheric CO_2 has been partly mitigated by oceanic uptake, which currently accounts for 25–30% of the total CO_2 emissions (Canadell et al., 2007; Khatiwala et al., 2009; Le Quéré et al., 2015; Sabine et al., 2004). The uptake of CO_2 in surface waters causes a shift in the chemistry of seawater, notably increases in [H$^+$] and a decrease in [CO$_3^{2-}$] leading to the phenomenon known as ocean acidification (OA) (Caldeira and Wickett, 2003, 2005; Raven, 2005). Recent findings of Wootton et al. (2008), Provost et al. (2010), and Borges and Gypens (2010) indicate that ocean acidification is proceeding in coastal areas more rapidly than has been predicted. The associated changes related to OA have been shown to have a variety of effects on marine phytoplankton (Fabry et al., 2008). The coastal zone is responsible for a disproportionately large amount of primary production per surface area as compared to the open ocean (Wollast, 1998) and is responsible for a similarly large proportion of carbon export (Dunne et al., 2007). As such, understanding how these waters respond to acidification is vital

for accurately predicting the future consequences of continued CO_2 increase.

The North Sea has been identified as an effective continental shelf-pump of CO_2 (Thomas et al., 2004) and has thus undergone intensive study with respect to the CO_2 system. High temporally resolved datasets are necessary to understand the large, observed seasonal variability of the carbonate system in the North Sea (Bozec et al., 2006; Frankignoulle and Borges, 2001; Prowe et al., 2009). The use of voluntary observing ships (VOS) to collect underway pCO_2 data have been used extensively in the North Sea (Omar et al., 2010), complemented by measurements of one other of the measurable carbonate variables (total alkalinity (A_T), dissolved inorganic carbon (DIC), and pH). From at least two of the measured variables (a combination pair of A_T, DIC, pH, or pCO_2), the carbonate system can then be fully solved and quantified using thermodynamic relationships (Park, 1969), which can be integrated in computer programs, such as CO2SYS (Lewis and Wallace, 1998). These calculated parameters, however, are prone to errors, which have been well documented (Millero et al., 1993; Lee et al., 2000; Koeve and Oschlies, 2012; Hoppe et al., 2012). These errors are due to the accuracy of the two measured variables, and to the reliability of the first and second dissociation constants of carbonic acid (K_1, K_2). The assessment of the reliability of dissociations constants can be achieved with internal consistency studies.

The first internal consistency studies took place in the open ocean and focused on the reliability of the various sets of carbonic acid

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dissociation constants, which are used to calculate the distribution of inorganic carbon species. Acid dissociation constants describe the interaction between acids (HA), their dissociated proton (H+), and the conjugate base (A−), shown in Eq. (1).

$$K = \{H+\}\{A-\}/\{HA\}, \qquad (1)$$

where {} denote activities. The aforementioned determinations of K_1 and K_2 of carbonic acid were performed analytically on artificial seawater (ASW) (Goyet and Poisson, 1989; Hansson, 1973; Roy et al., 1993) and natural seawater (NSW) (Mehrbach et al., 1973) and the data were later refitted using improved computer-generated models (Dickson and Millero, 1987). These constants are technically *apparent* dissociation constants (denoted by K'), as they are based on concentrations (indicated by []), not activities, so that

$$K' = \{H^+\}[A^−]/[HA]. \qquad (2)$$

This approach also means that the K' values must be determined across the range of salinities, temperatures, and pressures at which they are to be applied and that the measurements take place in the same medium as the solution to which the K' value is to be applied. Assessments and comparisons of each set of constants have taken place in several locations, including the northwest European shelf (Ribas-Ribas et al., 2014), equatorial Pacific (Millero et al., 1993), and the North Atlantic (Lee et al., 1997), and spanning across several ocean basins (Millero et al., 1993,2002; Wanninkhof et al., 1999). At sea studies have been complemented by further work using laboratory set-ups (Lee et al., 1996; Lueker et al., 2000) and more recently investigations into inconsistencies in culture experiments (Hoppe et al., 2012; Koeve and Oschlies, 2012).The conclusions from these studies is that the first and second dissociation constants of carbonic acid (K'_1 and K'_2) calculated by Mehrbach et al. (1973) (refit by Dickson and Millero, 1987) are the most reliable when pCO_2 is being used in the calculations or is being calculated (Lee et al., 1996; Wanninkhof et al., 1999). These constants were the only ones determined in NSW and the difference in accuracy has been attributed to the lack of boric acid in the ASW (Mojica-Prieto and Millero, 2002). In solution, the majority of dissolved boron (BT = total boron) is present in two forms: boric acid and borate, following the equilibrium relationship below:

$$B(OH)_3 + H_2O \leftarrow K_B \rightarrow B(OH)_4{}^− + H^+ \qquad (3)$$

where $K_B = [B(OH)_4{}^−][H^+]/[B(OH)_3]$ (4)

In NSW boric acid interacts with $HCO_3^−$ and $CO_3^{2−}$ to lower the activities, and concentrations of $HCO_3^−$, and increase the activities and concentrations of $CO_3^{2−}$, thus lowering pK_1 and increasing pK_2. Calculations of pCO_2 depend directly on the ratio of K_2/K_1, thus errors in this ratio will be evident in a lack of internal consistency of pCO_2. In contrast, the lack of use of this ratio in calculations with pH, A_T, or DIC results in other dissociation constants being more appropriate, notably those of Roy et al., (1993) or Goyet and Poisson (1989) (Clayton et al., 1995; Lee et al., 1997). Despite this, in an attempt to homogenize the way carbon chemists carry out these calculations, it is now the recommended standard procedure to use the constants of Mehrbach et al. (1973), refit by Dickson and Millero (1987), on the Total pH scale (Dickson et al., 2007).

Beyond the scope of dissociation constants, additional errors have been associated with systematical differences in equipment (Körtzinger et al., 2000; Ribas-Ribas et al., 2014), high DIC/A_T ratios (>1.10) (Lee et al., 1996), the interference of fatty acids (Gripenberg, 1960), and contribution from organic acids and bases to A_T (Hernandez-Ayon et al., 2007; Koeve and Oschlies, 2012; Ulfsbo, et al., 2015). The latter errors are only thought to be a problem where dissolved organic carbon

(DOC) reaches particularly high concentrations (Koeve and Oschlies, 2012), thus this is not an issue for open ocean measurements, although presents a major problem for calculations in freshwaters (Abril et al., 2015). Similarly, the contributions of fatty acids and high DIC/A_T ratios in the open ocean are sufficiently low that internal consistency remains within the same order of magnitude as the measurement precision. In culture experiments, the differences between measured and calculated carbonate parameters have been much larger, and thus coastal areas where high primary production takes place could also be susceptible to large discrepancies in calculations of the carbonate system. Furthermore, in the original work of the recommended constants of Mehrbach et al. (1973), the constants were only determined to salinities above 26. The salinity range was extended in further work by Millero et al. (2006); however, the results have not yet been applied to further internal consistency studies. Coastal regions can also exhibit non-oceanic-like, chemical relationships with salinity, for example, the atypical borate–salinity relationship in the Baltic Sea (Kremling, 1972), which is not taken into account when performing carbonate system calculations and can lead to further error. Here we present the first internal consistency study performed in coastal waters with seasonal resolution over a range of salinities and biogeochemical regimes.

2. Methods

2.1. Hydrography

The hydrographic properties in the surface waters of the North Sea demonstrate the presence of 3 different water masses, acknowledged in the literature as North Atlantic water, Baltic water, and German Bight water, with the resulting composite water mass known as Central North Sea Water (Bozec et al., 2006; Kempe and Pegler, 1991; Salt et al., 2013). In the northern North Sea (nNS), North Atlantic water flows over the Shetland Shelf bringing characteristic warm and high saline waters into the North Sea. The inflowing water follows an anti-clockwise trajectory around the North Sea, with additional North Atlantic inflow occurring through the English Channel (Otto et al., 1990). In the southeast the Skagerrak water mass, a mixture of Central North Sea water and Baltic water, is easily identifiable through much lower salinities and temperatures than the central North Sea. The German Bight water comes from the coastal region bordering northwest continental Europe in the southeastern North Sea, where the riverine influence is greatest in the North Sea.

The North Sea can be divided into two biogeochemical regimes, within which behavior is determined by depth (Omar et al., 2010; Prowe et al., 2009; Thomas et al., 2005). The nNS (north of 56°N) is deeper than the south (50–400 m) and experiences more ocean-like behavior, e.g. higher salinity and seasonal stratification. The southern North Sea (sNS) is much shallower (<50 m) and remains well-mixed throughout the year. Both regions receive nutrient and organic carbon inputs from terrestrial sources, facilitating high primary production that leads to overall annual autotrophy in the nNS and near balanced trophic status in the sNS (Bozec et al., 2005; Schiettecatte et al., 2007).

2.2. Measurements and comparisons

The data used in this study come from 6 separate re-occupations of the North Sea, which took place in August 2001, November 2001, February 2002, May 2002, August 2005, and August 2008. All four carbonate parameters were measured on two of these cruises; February 2002 and August 2005, with a precision of ±2–3 μmol A_T kg$^{−1}$ for A_T, ±1–2 μmol DIC kg$^{−1}$ for DIC, ±0.001 for pH, and ±1 μatm for pCO_2, respectively. The remaining cruises measured A_T, DIC, and pCO_2 with the same level of precision.

2.2.1. Carbonate system measurements

For all of the aforementioned cruises, A_T was measured by potentiometric titration to the second end-point (pK_2) of carbonic acid, using 0.1 M hydrochloric acid as the titrant. For the cruises taking place in August 2001, November 2001, February 2002, May 2002, and August 2005, the samples for A_T were filtered on GF/F shortly after sampling, prior to analysis. The resultant acid volumes and corresponding e.m.f values are fitted to a Gran titration plot using least squares (Gran, 1952). An uncertainty of ± 2–3 µmol A_T kg^{-1} was found as the combined precision for all cruises. Samples for DIC were not filtered in order to prevent gas exchange with the atmosphere. Any sediments or particles collected in the samples would likely settle to the bottom of the sample bottle before analysis and thus interference in the measurements should be minimal. All of the DIC data collected in the North Sea was analyzed by the coulometric method of Johnson et al. (1993), with an overall uncertainty of ± 1–2 µmol DIC kg^{-1} for all cruises. For quality control and calibration of both DIC and A_T, Certified Reference Material (CRM), of known DIC and A_T, acquired from Prof. Andrew Dickson (Scripps Institute of Oceanography, USA) were used.

In 2002 and 2005, discrete samples were taken from the CTD and analyzed for pH potentiometrically on the total hydrogen ion scale, calibrated using TRIS (2-amino-2-hydroxymethyl-1,3-propanediol) and AMP (2-aminopyridine) buffers prepared at a salinity of 35 according to Dickson (1993). The accuracy of this method is strongly dependent on the sensitivity of the pH meter and how accurately the two buffer solutions are made up. For the measurements used in this work, a precision of ± 0.001 pH units was attained. For all North Sea cruises, pCO_2 was measured continuously, underway, from surface waters, providing the greatest coverage of data. The instrument used continuous equilibration with a headspace and infrared detection with an accuracy of ± 1 µatm (Körtzinger et al., 1996). The calibration of pCO_2 measurements was carried out regularly (every 2–3 hours) using National Oceanic and Atmospheric Administration (NOAA, Global Monitoring Division, Carbon Cycle Greenhouse Gases Group) calibrated gas standards. For all cruises, a minimum of 3 calibration gasses were used, spanning a concentration range from 0 to 750 ppm.

The concentrations of silicate and phosphate are also required to account for their contribution to A_T, which can be of the order of up to 1 µmol A_T kg^{-1} in the North Sea. The inorganic nutrients nitrate (NO_3), ammonium (NH_4), dissolved silicate (H_4SiO_4), and phosphate (PO_4) were analyzed following the methods of Grasshof et al. (1983). Reference nutrient samples (RMNS Kanso, Japan) were analyzed in every run as a control, giving a precision of ± 0.2, 0.1, 0.2, and 0.01 for the four nutrients, respectively, for each cruise. The salinity and temperature values were recorded by CTD (conductivity–temperature–depth) and salinity values were calibrated post-cruise to salinity samples taken onboard.

2.3. Calculations

The internal consistency was assessed using the measured in-situ salinity, temperature, silicate, phosphate, and pressure values. The KSO_4 of Dickson (1990) is used and pH values are given throughout on the total hydrogen ion scale. Not all station positions were occupied and measured in all four seasonal cruises that are compared here. In order to overcome this, the percentage of data points considered internally consistent is often used and given in Tables 3 and 4, to allow direct comparison between the seasons without the loss of data. The calculations were performed using the CO2SYS program (Lewis and Wallace, 1998), adapted for MATLAB (van Heuven, 2011; http://cdiac.ornl.gov/ftp/co2sys/CO2SYS_calc_MATLAB_v1.1/). All calculated parameters as a function of two input parameters were explored, thus consisting of A_T (DIC, pH), A_T (DIC, pCO_2), A_T (pH, pCO_2), DIC (A_T, pH), DIC (A_T, pCO_2), DIC (pH, pCO_2), pH (DIC, A_T), pH (DIC, pCO_2), pH (A_T, pCO_2), pCO_2 (DIC, A_T), pCO_2 (DIC, pH), and pCO_2 (A_T, pH), for the following seven different sets of carbonic acid dissociation constants: Roy et al.

(1993)(R), Goyet and Poisson (1989)(GP), Hansson (1973), refit by Dickson and Millero (1987)(H), Mehrbach et al. (1973), refit by Dickson and Millero (1987)(M), Hansson (1973) and Mehrbach et al. (1973), refit by Dickson and Millero (1987)(HM), Mojica-Prieto and Millero (2002)(MM), and Millero et al. (2006)(ML). In the remaining text, for simplicity, the constants will be referred to by the abbreviations (R, GP, H, M, HM, MM, and ML). The parameterizations of these constants, along with the medium and salinity ranges for which they were determined, are shown in Table 1.

2.4. Assessment

The internal consistency of the carbonate system can be considered in a number of different ways. Here, we assess how accurate and precise it is by comparing measured parameters to calculated parameters. Comparing the measured and calculated values, an accurate but imprecise system would be indicated by an average difference (Δ) close to 0, but with a high level of variance, denoted by the standard deviation (σ). A precise but inaccurate system, however, is indicated by a small σ, but with a bias, indicated by an average Δ varying from 0. Thus, an inaccurate and imprecise system would have a high standard deviation and a large average Δ, while an accurate and precise system would show the inverse. The measured and calculated values of each parameter, for each set of apparent dissociation constants, was fitted to the form $Y = a.X + b$, by means of *total least squares* using Matlab 2012®, where X is the calculated value and Y is the observed value. By fitting the data using total least squares, we take into account the errors in both the x and y variables.

2.5. Error propagation

When calculating the carbonate parameters in CO2SYS, the uncertainties associated with the observations and calculations are carried through (propagated). Errors are introduced via the measurement techniques of the input parameters, the measurement techniques of the output parameters against which we compare our calculations, and the determinations of the K_1 and K_2 values of carbonic acid. The measurement errors carried through in the calculations depend on the input parameter combinations. These margins vary insignificantly over the range of conditions (e.g. temperature, salinity) observed in the North Sea. The error propagation for each calculated parameter, with all variations of input parameter, was calculated following Eq. (5).

$$(\varepsilon z)^2 = \{\delta z/\delta x\}^2 . (\varepsilon x)^2 + \{\delta z/\delta y\}^2 . (\varepsilon y)^2 \qquad (5)$$

The partial derivatives were determined seasonally, using average temperature and salinity values, and determined over the range of values observed. The determined errors for each set of input parameters for each season are given in brackets in the standard deviation section of Table 2a and 2b. The error calculation performed here does not take into account errors in the acid dissociation constants, as we later compare the performance of these constants. When the term "internally consistent" is used, it refers to whether the observed values and associated measurement errors fit within the limits of the calculated propagated error.

2.6. Total borate calculations

To independently calculate the total borate contribution from each water mass, the individual water mass fractions were first calculated, following Friis et al. (2003). To calculate the Elbe contribution, we used the salinity and A_T data from the stations closest to the German Bight (at latitudes >54.4°N and longitudes >8.0°E) to form a regression line with the Central North Sea end member. We then extrapolated this to a salinity of 0 to get a representative freshwater end member. This assumes that all the fresh water present comes from the same source,

Table 1
Table of parameterizations of the carbonic acid dissociation constants, with temperature and salinity range for each set, and the medium in which measurements were performed.

Constants	pK$_1$ and pK$_2$ parameterization:	Temperature range	Salinity range	Media
R	$\ln K_1 = 2.83655 - 2307.1266/T - 1.5529413.\ln(T) + (-0.20760841 - 4.0484/T).S^{0.5} + 0.08468345.S - 0.00654208.S^{1.5}$ $\ln K_2 = -9.226508 - 3351.6106/T - 0.2005743.\ln(T) + (-0.106901773 - 23.9722/T).S^{0.5} + 0.1130822.S - 0.00846934.S^{1.5}$	0–45	5–45	Artificial SW
GP	$pK_1 = 812.27/T + 3.356 - 0.00171.S.\ln(T) + 0.000091.S^2$ $pK_2 = 1450.87/T + 4.604 - 0.00385.S.\ln(T) + 0.000182.S^2$	−1 to 40	10–50	Artificial SW
H	$pK_1 = 851.4/T + 3.237 - 0.0106.S + 0.000105.S^2$ $pK_2 = -3885.4/T + 125.844 - 18.141.\ln(T) - 0.0192.S + 0.000132.S^2$	2–35	20–40	Artificial SW
M	$pK_1 = 3670.7/T - 62.008 + 9.7944.\ln(T) - 0.0118.S + 0.000116.S^2$ $pK_2 = 1394.7/T + 4.777 - 0.0184.S + 0.000118.S^2$	2–35	26–43	Natural SW
HM	$pK_1 = 845/T + 3.248 - 0.0098.S + 0.000087.S^2$ $pK_2 = 1377.3/T + 4.824 - 0.0185.S + 0.000122.S^2$	2–35	20–40	Artificial SW
MM	$pK_1 = -43.6977 - 0.0129037.S + 1.364e^{-4}.S^2 + 2885.378/T + 7.045159.\ln(T)$ $pK_2 = -452.0940 + 13.142162.S - 8.101e^{-4}.S^2 + 21263.61/T + 68.483143.\ln(T) + (-581.4428.S + 0.259601.S^2/T - 1.967035.S.\ln(T)$	0–45	5–42	Natural SW
ML	$pK_1 = -126.34048 + 6320.813/T + 19.568224.\ln(T) + 13.4038.S^{0.5} + 0.03206.S - 5.242e^{-5}.S^2 + (-530.659.S^{0.5} - 5.8210.S)/T + (-2.0664.S^{0.5}).\ln(T)$ $pK_2 = -90.18333 + 5143.692/T + 14.613358.\ln(T) + 21.3728.S^{0.5} + 0.1218.S - 3.688e^{-4}.S^2 + (-788.289.S^{0.5} - 19.189.S)/T + (-3.374.S^{0.5}).\ln(T)$	0–50	1–50	Natural SW

however, due to other rivers in the region having a similar catchment lithology, we assume that the chemical signal of the water will be similar. This resulted in a 0-salinity end member of 2616 μmol A$_T$ kg^{-1} in February 2002, and 1678 μmol A$_T$ kg^{-1} in August 2005. These values comparing well with recent seasonal A$_T$ data from the Elbe (Amann et al., 2012), which reports A$_T$ values of ~2500 μmol A$_T$ kg^{-1} in winter and ~1750 μmol A$_T$ kg^{-1} in summer at salinities <1, thus we assume our estimation is sufficient for the purpose of the calculation.

The borate alkalinity (BAlk) was then calculated for the water mass end members from total boron concentrations. The total boron concentrations (BT) were calculated from (a) the equations of Barth (1998) Eqs. (6) and(7) for the Elbe (German Bight) salinity–boron relationship, (b) Gripenberg (1960) Eq. (8) for the Baltic salinity–boron ratio, (c) Uppström, (1974) for the North Atlantic ratio and also the revised North Atlantic ratio of Lee et al. (2010). At a salinity of 35, the two seasonal linear relationships of Barth (1998), for summer (September 1994) and winter (February 1995), yield an approximate difference of 6 μmol kg^{-1} in the calculated [B(OH)$_4^-$]. As such, for our calculations, Eq. (6) was used for the calculations of August 2005 (summer), and Eq. (7) for the calculation of February 2002 (winter). The water mass fractions were then multiplied by the theoretical BAlk contribution and summed to obtain the actual BAlk of the sample. All of the following Eqs. (6–9) are given for total borate concentration (BT) in mol kg^{-1} seawater.

$$BT = (0.000127/10.811).S + 1.66e^{-5} (\text{for September 1994}) \quad (6)$$

$$BT = (0.000136/10.811).S + 1.57e^{-5} (\text{for February 1995}) \quad (7)$$

The Baltic Sea has demonstrated a number of chemical relationships varying from standard ocean behavior. The chlorinity–boron relationship has been documented by Gripenberg, (1960), Dyrssen and Uppstrom (1974), and Kremling (1967), who all noted a positive anomaly in the boron/chlorinity ratio. There is little variation in their findings, with the ratio varying from 0.22 (Kremling, 1967) to 0.244 (Gripenberg, 1960). Here, we use the following equation from the data presented by Gripenberg (1960):

$$BT = (0.000244/10.811).(S/1.80655) \quad (8)$$

For the North Atlantic fraction, the traditional seawater relationship of Uppström (1974) was used:

$$BT = (0.000232/10.811).(S/1.80655) \quad (9)$$

Furthermore, Lee et al. (2010) recently found boron–salinity relationships significantly different to those reported by Uppström (1974), which were based on measurements solely from the Pacific Ocean. Here, we also apply this new boron–salinity equation Eq. (10), to test whether this improves our internal consistency in the North Sea.

$$BT = (0.0001336/10.811).S \quad (10)$$

3. Results and discussion

3.1. A seasonal comparison

The sampling program of the North Sea is shown in Fig. 1, with the different distinct, biogeochemical regions labeled. The two seasons in which data were collected of all four measurable carbonate parameters were winter (February) and summer (August). These two data sets allow us to compare the internal consistency in two very different conditions, in terms of values of the carbonate variables, and water temperature. As the North Sea is a temperate coastal sea, it is characterized by high primary production during summer and very low, or no, production in winter. The seasonal cycle is fully assessed in the works of Bozec et al. (2006) and Thomas et al. (2009), thus here the discussion is kept brief. The average DIC in February 2002 was 64 μmol DIC kg^{-1} higher than that in August. The average A$_T$ changed by just 2 μmol A$_T$ kg^{-1}; however, the various contributions of chemical species to A$_T$ showed larger variability. The changes in A$_T$ contributions in the North Sea from February to August are shown in Figs. 2a and b, respectively. For average conditions in the North Sea, the HCO$_3^-$ and CO$_3^{2-}$ species were by far the greatest contributors to A$_T$ supplying ~2212 μmol A$_T$ kg^{-1}, followed by borate (~68 μmol A$_T$ kg^{-1}), hydroxide (~3 μmol A$_T$ kg^{-1}), phosphate (~0.07 μmol A$_T$ kg^{-1}), and silicate (~0.04 μmol A$_T$ kg^{-1}). The largest changes between the summer and winter situation were in carbonate alkalinity (HCO$_3^-$ + 2*CO$_3^{2-}$), which was significantly lower in August, when photosynthesis was ongoing. The contribution of silicate and phosphate were also much smaller then, due to lower concentrations resulting from uptake by phytoplankton. The borate contribution remains the second largest contributor to A$_T$ for both seasons but was slightly higher in August. Isolating the various contributors to this change, we find that the increases in temperature, salinity, and pH from February to August all affect an individual increase of ~3 μmol kg^{-1} in B(OH)$_4^-$ (total increase ~9 μmol kg^{-1}).

The change in average pCO$_2$, from February 2002 to August 2005, was just 8 μatm; however, this is not representative of the entire

Table 2

Calculated statistics for all calculated values of parameters compared to the measured values during February 2002 (a) and for August 2005 (b). Both datasets were tested using the dissociation constants of Roy et al. (1993) (R), Goyet and Poisson (1989) (GP), Hansson (1973), refit by Dickson and Millero (1987) (H), Mehrbach et al. (1973), refit by Dickson and Millero (1987) (M), Hansson (1973) and Mehrbach et al. (1973), refit by Dickson and Millero (1987) (HM), Mojica-Prieto and Millero (2002) (MM), and Millero et al. (2006) (ML).

			R	GP	H	M	HM	MM	ML
A_T	Regress (slope)	DIC,pH	0.999	1.000	0.998	1.001	0.999	0.999	1.001
		DIC, pCO_2	0.997	0.997	0.995	1.000	0.997	0.998	0.999
		pH, pCO_2	1.022	1.035	1.042	1.013	1.031	1.009	1.027
	R^2	DIC, pH	0.93 (<0.01)	0.93 (<0.01)	0.93 (<0.01)	0.93 (<0.01)	0.93 (<0.01)	0.93 (<0.01)	0.93 (<0.01)
	(p-value)	DIC, pCO_2	0.92 (<0.01)	0.92 (<0.01)	0.93 (<0.01)	0.93 (<0.01)	0.92 (<0.01)	0.92 (<0.01)	0.93 (<0.01)
		pH, pCO_2	0.03 (0.19)	0.03 (0.20)	0.06 (0.18)	0.06 (0.05)	0.04 (0.13)	0.05 (0.07)	0.06 (0.05)
	Average ΔA_T (σ)	DIC, pH (± 2)	3 (8)	1(8)	4 (7)	−2 (7)	2 (8)	3 (8)	2 (7)
	($\mu mol\ kg^{-1}$)	DIC, pCO_2 (± 2)	8 (9)	8 (9)	12 (9)	1 (8)	8 (9)	6 (8)	6 (8)
		pH, pCO_2 (± 43)	−50 (63)	−79 (62)	−93 (62)	−32 (60)	−70 (61)	−23 (61)	48 (60)
DIC	Regress (slope)	TA, pH	1.001	1.000	1.002	0.999	1.001	1.002	0.999
		TA, pCO_2	1.003	1.003	1.005	1.000	1.003	1.002	1.001
		pH, pCO_2	1.024	1.036	1.045	1.013	1.033	1.011	1.027
	R^2	TA, pH	0.89 (<0.01)	0.90 (<0.01)	0.90 (<0.01)	0.90 (<0.01)	0.90 (<0.01)	0.90 (<0.01)	0.90 (<0.01)
	(p-value)	TA, pCO_2	0.88 (<0.01)	0.88 (<0.01)	0.90 (<0.01)	0.90 (<0.01)	0.89 (<0.01)	0.89 (<0.01)	0.90 (<0.01)
		pH, pCO_2	0.06 (0.07)	0.06 (0.07)	0.06 (0.07)	0.07 (0.05)	0.06 (0.06)	0.07 (0.04)	0.07 (0.04)
	Average ΔDIC (σ)	TA, pH (± 8)	−3 (7)	−1 (7)	−4 (7)	2 (7)	−2 (7)	−3 (7)	−2(7)
	($\mu mol\ kg^{-1}$)	TA, pCO_2 (± 7)	−7 (8)	−7 (8)	−11 (7)	−1 (7)	−7 (8)	−5 (7)	6 (7)
		pH, pCO_2 (± 42)	−50 (59)	−76 (58)	−92 (57)	−29 (55)	−68 (57)	−25 (56)	44 (55)
pH	Regress (slope)	DIC, A_T	1.001	1.000	1.001	0.999	1.000	1.001	1.000
		A_T, pCO_2	0.999	0.998	0.998	0.999	0.998	1.000	0.999
		DIC, pCO_2	0.999	0.998	0.998	0.998	0.999	0.999	0.999
	R^2	DIC, A_T	0.23 (<0.01)	0.23 (<0.01)	0.25 (<0.01)	0.24 (<0.01)	0.24 (<0.01)	0.25 (<0.01)	0.25 (<0.01)
	(p-value)	A_T, pCO_2	0.53 (<0.01)	0.53 (<0.01)	0.53 (<0.01)	0.57 (<0.01)	0.55 (<0.01)	0.56 (<0.01)	0.56 (<0.01)
		DIC, pCO_2	0.49 (<0.01)	0.49 (<0.01)	0.49 (<0.01)	0.53 (<0.01)	0.51 (<0.01)	0.52 (<0.01)	0.53 (<0.01)
	Average ΔpH (σ)	DIC, A_T (± 0.008)	−0.006 (0.017)	0.001 (0.017)	−0.008 (0.017)	0.004 (0.017)	−0.004 (0.017)	−0.007 (0.017)	0.004 (0.017)
		A_T, pCO_2 (± 0.001)	0.009 (0.011)	0.014 (0.011)	0.016 (0.011)	0.006 (0.010)	0.012 (0.011)	−0.004 (0.011)	0.011 (0.011)
		DIC, pCO_2 (± 0.001)	0.010 (0.012)	0.015 (0.012)	0.018 (0.012)	0.006 (0.011)	0.014 (0.011)	0.005 (0.011)	0.011 (0.011)
pCO_2	Regress (slope)	DIC, A_T	0.959	0.959	0.936	0.994	0.957	0.969	0.980
		DIC,pH	0.975	0.963	0.956	0.985	0.967	0.987	0.973
		A_T, pH	0.976	0.963	0.957	0.985	0.967	0.989	0.972
	R^2	DIC, A_T	0.14 (<0.01)	0.14 (<0.01)	0.14 (<0.01)	0.17 (<0.01)	0.16 (<0.01)	0.17 (<0.01)	0.18 (<0.01)
	(p-value)	DIC, pH	0.52 (<0.01)	0.52 (<0.01)	0.53 (<0.01)	0.57 (<0.01)	0.54 (<0.01)	0.56 (<0.01)	0.56 (<0.01)
		A_T, pH	0.52 (<0.01)	0.52 (<0.01)	0.53 (<0.01)	0.56 (<0.01)	0.54 (<0.01)	0.55 (<0.01)	0.56 (<0.01)
	Average ΔpCO_2	DIC, A_T (± 8)	15 (18)	15 (18)	24 (17)	2 (17)	16 (17)	11 (17)	7 (17)
	(σ) (μatm)	DIC, pH (± 4)	9 (10)	14 (11)	17 (11)	5 (10)	12 (10)	5 (10)	10 (10)
		A_T, pH (± 3)	9 (11)	14 (11)	16 (11)	6 (10)	12 (11)	4 (10)	10 (10)
A_T	Regress	DIC, pH	0.992	0.994	0.996	0.997	0.995	0.995	0.998
		DIC, pCO_2	0.994	0.994	0.995	1.001	0.996	0.999	1.000
		pH, pCO_2	0.977	0.991	0.999	0.962	0.988	0.960	0.976
	R^2	DIC, pH	0.96 (<0.01)	0.96 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)
	(p-value)	DIC, pCO_2	0.94 (<0.01)	0.94 (<0.01)	0.94 (<0.01)	0.94 (<0.01)	0.94 (<0.01)	0.94 (<0.01)	0.94 (<0.01)
		pH, pCO_2	0.18 (<0.01)	0.19 (<0.01)	0.19 (<0.01)	0.22 (<0.01)	0.22 (<0.01)	0.20 (<0.01)	0.21 (<0.01)
	Average ΔA_T (σ)	DIC, pH (± 2)	18 (7)	14 (7)	10 (6)	7 (6)	11 (6)	12 (6)	5 (6)
	($\mu mol\ kg^{-1}$)	DIC, pCO_2 (± 3)	14 (9)	13 (9)	11 (9)	1 (9)	9 (9)	3 (9)	0 (9)
		pH, pCO_2 (± 55)	53 (52)	19 (51)	1 (51)	86 (52)	28 (51)	96 (52)	55 (51)
DIC	Regress	A_T, pH	1.008	1.006	1.004	1.003	1.005	1.005	1.002
		A_T, pCO_2	1.006	1.005	1.004	0.999	1.004	1.001	1.000
		pH, pCO_2	0.984	0.997	1.004	0.964	0.992	0.963	0.977
	R^2	A_T, pH	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)
	(p-value)	A_T, pCO_2	0.95 (<0.01)	0.95 (<0.01)	0.96 (<0.01)	0.96 (<0.01)	0.95 (<0.01)	0.96 (<0.01)	0.96 (<0.01)
		pH, pCO_2	0.17 (<0.01)	0.18 (<0.01)	0.18 (<0.01)	0.21 (<0.01)	0.21 (<0.01)	0.19 (<0.01)	0.19 (<0.01)
	Average ΔA_T (σ)	A_T, pH (± 3)	−16 (6)	−13 (6)	−9 (6)	−6 (6)	−10 (6)	−11 (6)	−4 (6)
	($\mu mol\ kg^{-1}$)	A_T, pCO_2 (± 3)	−12 (7)	−11 (7)	−9 (7)	1 (7)	−8 (7)	−3 (7)	0 (7)
		pH, pCO_2 (± 36)	33 (48)	5 (47)	−8 (47)	76 (48)	16 (47)	78 (48)	47 (47)
pH	Regress	DIC, A_T	1.004	1.003	1.002	1.002	1.002	1.003	1.001
		A_T, pCO_2	1.001	1.000	1.000	1.002	1.001	1.002	1.001
		DIC, pCO_2	1.001	1.000	1.000	1.002	1.000	1.002	1.001
	R^2	DIC, A_T	0.92 (<0.01)	0.92 (<0.01)	0.92 (<0.01)	0.92 (<0.01)	0.92 (<0.01)	0.92 (<0.01)	0.92 (<0.01)
	(p-value)	A_T, pCO_2	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)
		DIC, pCO_2	0.95 (<0.01)	0.95 (<0.01)	0.95 (<0.01)	0.95 (<0.01)	0.95 (<0.01)	0.95 (<0.01)	0.95 (<0.01)
	Average ΔpH (σ)	DIC, A_T (± 0.007)	−0.031 (0.012)	−0.024 (0.012)	−0.018 (0.012)	−0.012 (0.012)	−0.020 (0.012)	−0.021 (0.012)	−0.009 (0.012)
		A_T, pCO_2 (± 0.001)	0.009 (0.009)	−0.003 (0.008)	0.000 (0.008)	−0.014 (0.008)	−0.005 (0.008)	−0.015 (0.008)	−0.009 (0.008)
		DIC, pCO_2 (± 0.001)	−0.006 (0.009)	−0.001 (0.009)	0.002 (0.009)	−0.014 (0.009)	−0.003 (0.009)	−0.015 (0.009)	−0.009 (0.009)
pCO_2	Regress	DIC, A_T	0.939	0.942	0.952	1.004	0.959	0.984	1.000
		DIC, pH	1.014	1.000	0.994	1.035	1.006	1.036	1.021
		A_T, pH	1.022	1.006	0.998	1.038	1.011	1.041	1.023
	R^2	DIC, A_T	0.89 (<0.01)	0.89 (<0.01)	0.89 (<0.01)	0.89 (<0.01)	0.89 (<0.01)	0.89 (<0.01)	0.89 (<0.01)
	(p-value)	DIC, pH	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)	0.96 (<0.01)
		A_T, pH	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)	0.97 (<0.01)
	Average ΔpCO_2 (σ)	DIC, A_T (± 6)	22 (15)	22 (14)	17 (14)	−2 (13)	15 (14)	5 (13)	0 (13)
	(μatm)	DIC, pH (± 4)	−5 (8)	−1 (8)	2 (8)	−12 (8)	−2 (8)	−13 (8)	−8 (8)
		A_T, pH (± 3)	−8 (8)	−3 (8)	0 (8)	−13 (8)	−4 (8)	−14 (8)	−8 (8)

North Sea, as the pCO$_2$ range was two times larger in August (287–455 µatm) compared to February (315–396 µatm). The range reflected the two biogeochemical regimes within the North Sea: the stratified nNS, where stratification enables prolonged phytoplankton growth causing a large drawdown of CO$_2$, shows very low pCO$_2$ values in August, whereas in the sNS, very low pCO$_2$ values are observed only in spring, and a combination of remineralization and higher temperatures lead to much higher pCO$_2$ in August (Bozec et al., 2005; Schiettecatte et al., 2007; Thomas et al., 2004, 2005). In February, the water column is well-mixed throughout, and biological activity is lower thus leading to a more homogenous surface distribution of pCO$_2$.

The results from all internal consistency calculations using the 4 carbonate parameters, with various dissociation constants, in the February 2002 and August 2005 data sets, are shown in Tables 2a and b, respectively. A regression slope of >1 indicates that the measured value is larger than the calculated values. A regression slope of 1.000 is achieved with several combinations in both seasons. Overall, in February, when the three parameters involved are DIC, A$_T$, and pCO$_2$, (e.g. DIC (A$_T$,pCO$_2$), A$_T$ (DIC,pCO$_2$), or pCO$_2$(DIC,A$_T$)), we find that the constants of M are the most suitable, whereas when DIC, A$_T$, and pH are involved, the constants of GP outperform the others. The largest deviations are consistently observed when the input parameters are pH and pCO$_2$, with MM producing the most accurate and precise reproduction of measurements. We also observe that the observed standard deviations of

differences are largely comparable with the propagation error, with the exception of pH, in which we observe notably larger discrepancies than can be accounted for from the propagation error. In August, the constants of ML are the best choice when the parameter combination is A$_T$, DIC, and pCO$_2$ and, additionally, when A$_T$, DIC, and pH are all involved. However, for calculations using both pH and pCO$_2$, the constants of GP and H are the most accurate.

In February and August, the variability in the standard deviations between the dissociation constants (e.g. comparing $\sigma \Delta A_{T,R}$ with $\sigma \Delta A_{T,ML}$) were relatively minor compared to the differences obtained with various input parameter combinations (e.g. comparing $\sigma \Delta A_{T,(pH,pCO2)}$ with $\sigma \Delta A_{T,(DIC,pH)}$ etc.). As such, beyond assessing the parameter combinations with the largest degree of noise, the standard deviations are not further discussed in this section. The results for both February and August are consistent, showing that the best regression coefficients for A$_T$ were attained with the inputs (DIC, pCO$_2$), for DIC it was (A$_T$, pCO$_2$), and for pCO$_2$ it was (DIC, A$_T$). For A$_T$ and DIC, this is in line with smaller error propagations, as similarly found by Dickson and Riley (1974); however, the much improved result for calculating pCO$_2$ using (DIC,A$_T$) is indicative of the improvements in measurement accuracy obtained with these parameters with the use of CRMs. When calculating pH, a regression coefficient of 1.000 was attained with all combination parameters. Similarly, consistency was found in the parameter input combinations resulting in the greatest precision, with
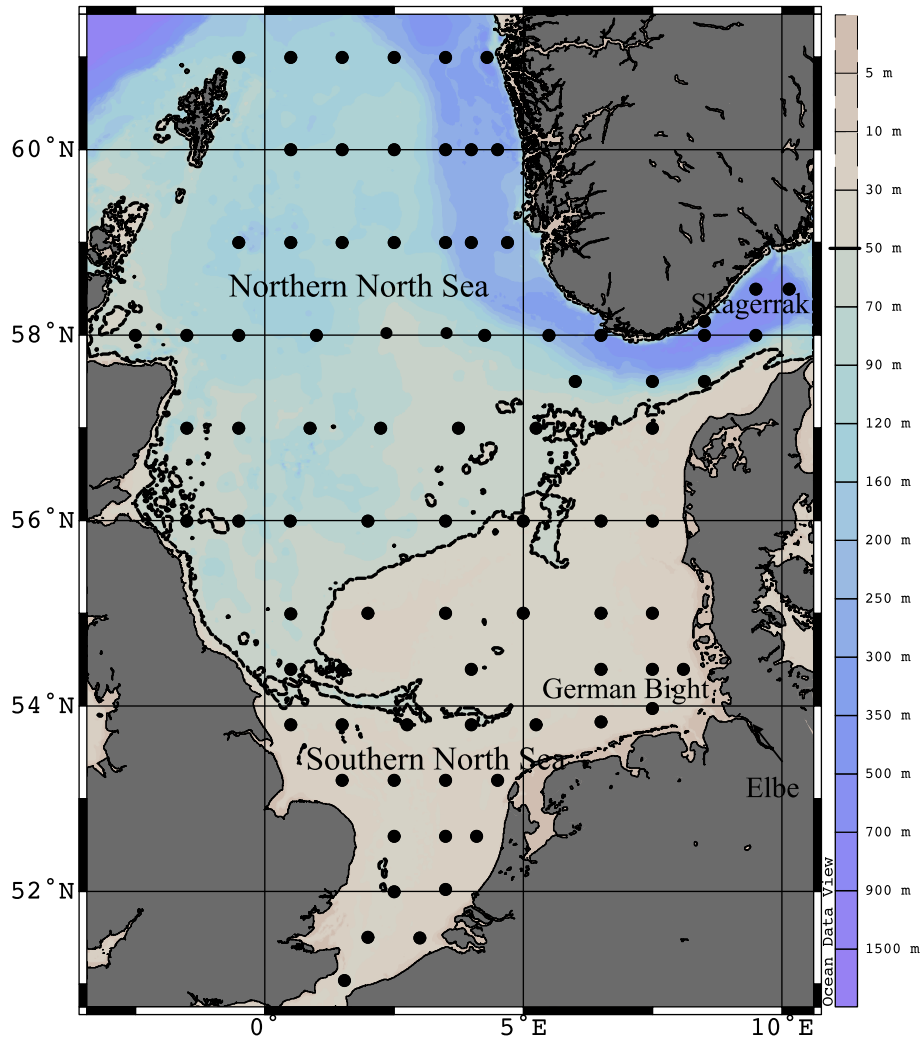
Fig. 1. Map of the North Sea region, with the stations sampled marked in black. The 50 m depth contour is marked, which separates the southern North Sea from the northern North Sea.

A_T being best represented by (DIC, pH), DIC by (A_T, pH), pH by (A_T, pCO$_2$), and pCO$_2$ by (DIC, pH). The combination pair resulting in the lowest residuals varied between the two seasons, possibly indicating a bias in some of the measurements. The prevalence of better results being obtained when using pH as an input parameter indicate that these measurements are reliable; however, the difference in the resulting residuals from e.g. DIC (A_T, pH) and DIC (A_T, pCO$_2$) are still directly comparable.

The results from February show a slight overall decrease in precision, represented by a higher standard deviation, compared to that obtained in August; however, the average differences show a similar level of accuracy for DIC and pCO$_2$ and a mildly lower bias in February for A_T

and pH. The standard deviations of the differences between the calculated and measured parameters (Δ) for February 2002 and August 2005 (shown in brackets, respectively) are approximately double to those found in the open ocean by Lee et al. (1997), of ±3 μmol A_T kg^{-1} in A_T (±7, 6 μmol kg^{-1}), ±3 μmol DIC kg^{-1} in DIC (±7, 6 μmol kg^{-1}), and ±1.3% in pCO$_2$ (±10, 8 μatm; ±3%, 2%).

3.1.1. The effects of salinity on dissociation constants

Different salinity and temperature parameterizations used in the determination of pK$_1$ and pK$_2$ (Table 1) are largely responsible for the deviations in the calculations between dissociation constants. Plotting the difference in ΔA_T between results from different dissociation
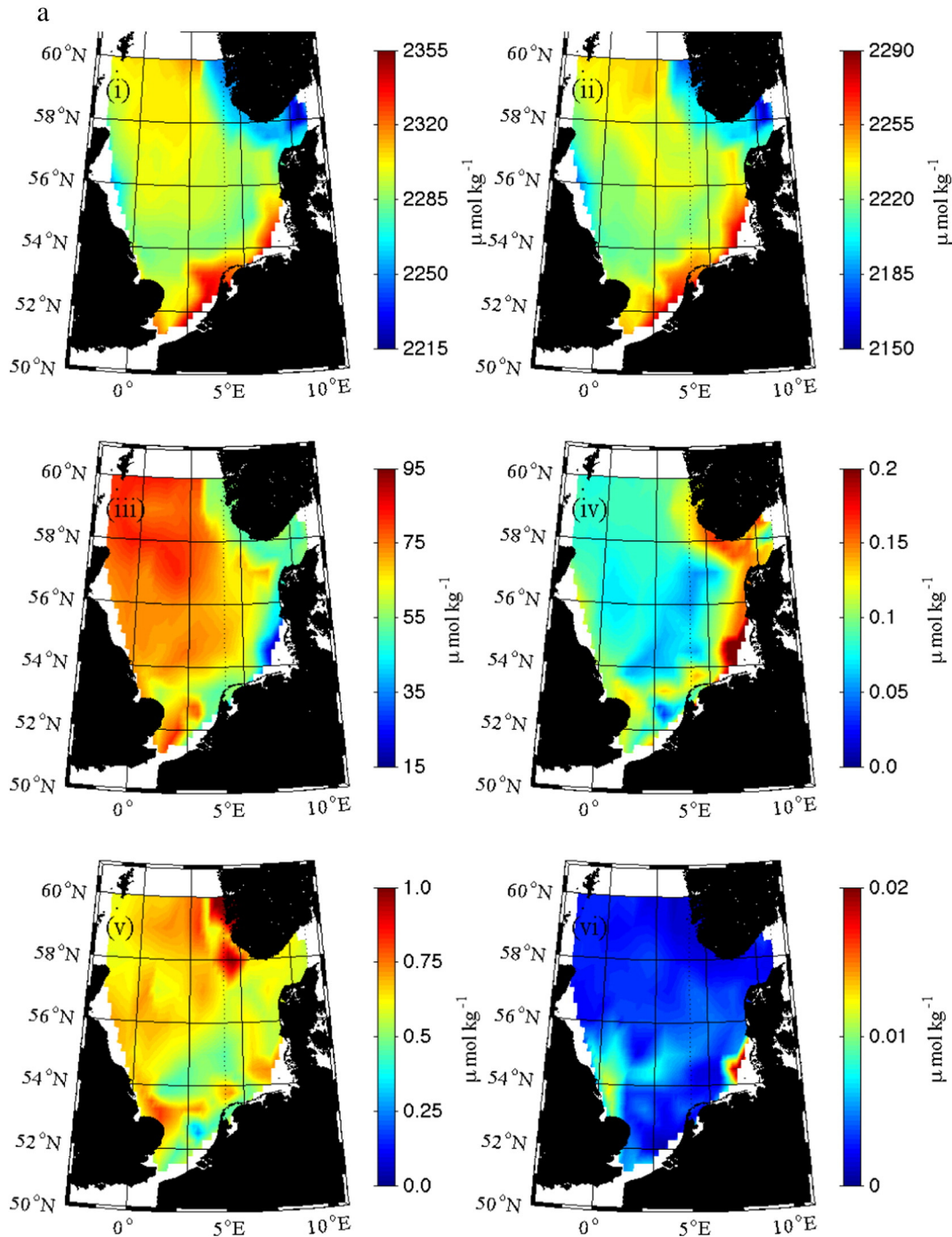
Fig. 2. The distribution of total alkalinity in the North Sea and respective contributions to total alkalinity by (i) carbonate species, (ii) borate, (iii) silicate, (iv) phosphate, and (v) ammonia in February 2002 (panel a) and in August 2005 (panel b).

b
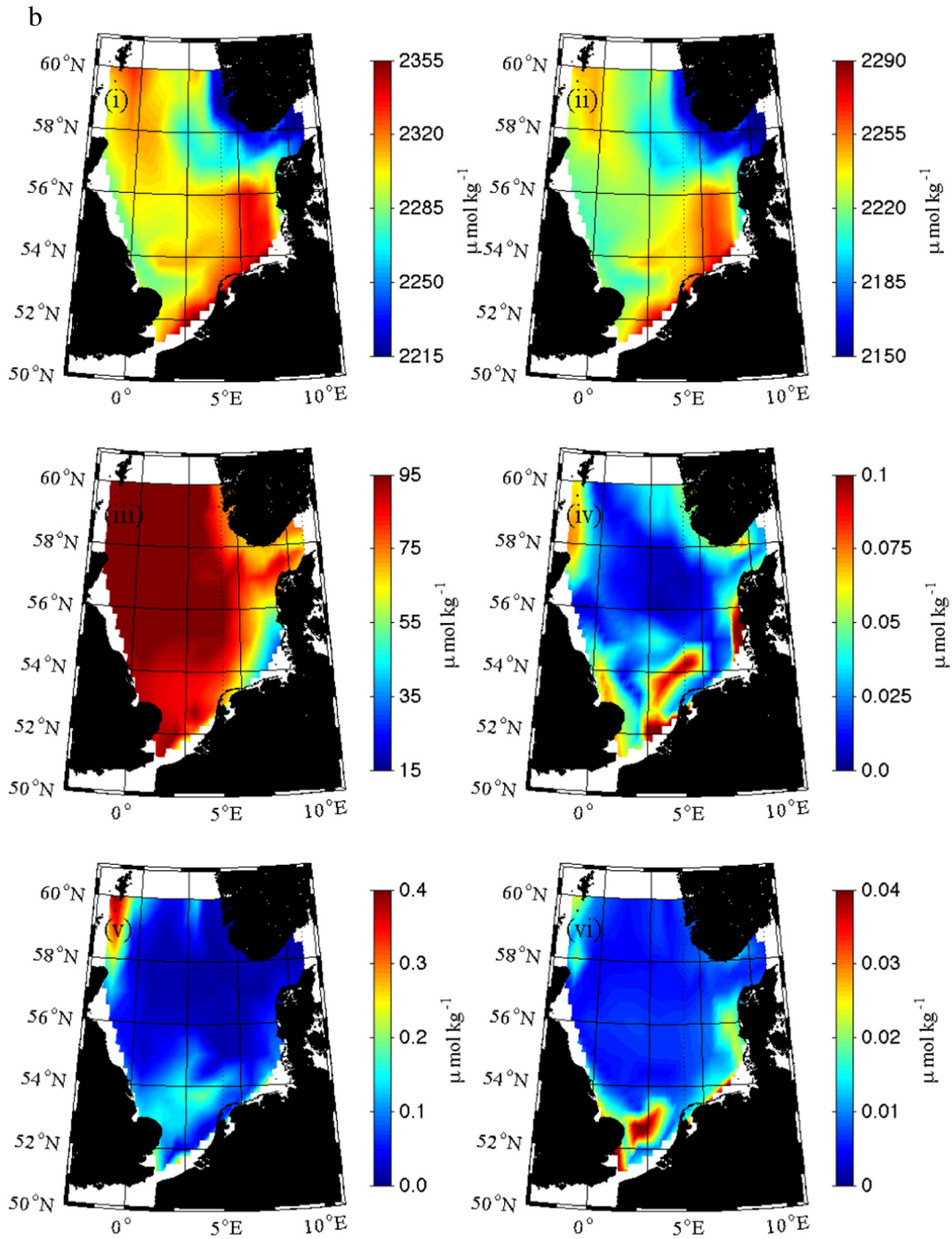
Fig. 2 (*continued*).

constants (e.g. the differences between the residuals using the constants of R and the residuals using the constants of M: $\Delta A_T^R - \Delta A_T^M$; or ΔDIC, ΔpH, and ΔpCO_2) shows an exponential-like increase, or decrease, around a salinity of ~34.5 (Fig. 3), indicating that at higher salinities, the choice of dissociation constants becomes more significant. We compared the differences in residuals of all dissociation constants to those of M and found the same relationship to that shown in Fig. 3 for the constants of R, GP, H, and HM. The differences in ΔA_T between M and MM showed a gradual linear increase with salinity, with a slope of 0.3 ($R^2 = 0.9$, p-value < 0.01), indicating that across the range of 5 salinity units, there is an increase of 1.5 μmol A_T kg^{-1} difference in ΔA_T. The residuals resulting from the use of constants ML showed no discernible difference to those of M over the salinity range investigated. At lower

salinities, the ratio of K_1/K_2 is larger (Mosley et al., 2010; Zeebe and Wolf-Gladrow, 2001) leading to relatively greater HCO_3^- concentrations compared to CO_2 and CO_3^{2-}. This ratio is used directly in the calculation of pH and A_T from DIC and pCO_2. Due to the different parameterizations of K_1 and K_2 for the different constants, the difference in this ratio between constants may become larger or smaller at lower salinities. This will lead to larger or smaller differences between the measured and calculated parameters. As such, at lower salinities, one would expect, overall, lower variation between the calculations from the different dissociation constants, as is observed here.

To investigate the performance of the six dissociation constants across a range of different salinities, the North Sea data from August ('05) and February ('02) were split into two groups; low salinity waters,
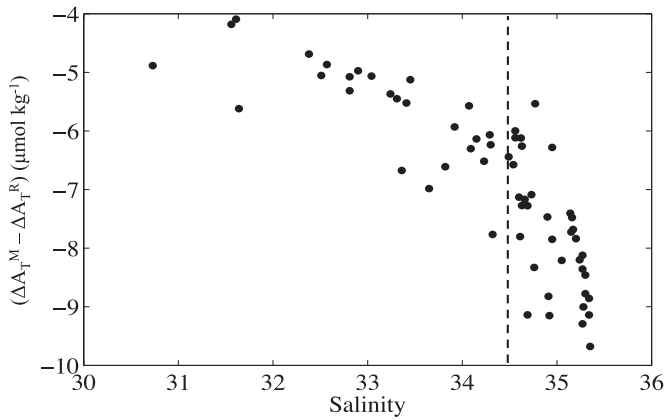
Fig. 3. The difference in ΔA_T (µmol A_T kg^{-1}) across the measured salinity range. The ΔA_T^R and ΔA_T^M are calculated using (DIC, pCO$_2$) as input parameters.

with salinities less than 34.5, and high salinity waters, with salinities greater than or equal to 34.5. The 1 standard deviation (σ) of ΔA_T, ΔDIC, ΔpH, and ΔpCO$_2$ is larger, for all parameters and in both seasons, for low salinity waters compared to high salinity waters. In February, in high salinity waters, the standard deviation of ΔA_T is 2 µmol A_T kg^{-1} lower than that of the total dataset; ΔDIC is 1 µmol DIC kg^{-1} lower, ΔpH is 0.002 lower and ΔpCO$_2$ is 2 µatm lower. In the less saline waters, there is an increase in the standard deviation of ΔA_T, ΔDIC, ΔpH, and ΔpCO$_2$ by 2 µmol A_T kg^{-1}, 1 µmol DIC kg^{-1}, 0.003, and 2 µatm,

respectively. The same pattern is observed in August; however the differences are marginally smaller.

Furthermore, in February, there is a clear dichotomy between the different dissociation constants in low and high salinity waters (Fig. 4). As previously mentioned, in winter, when DIC, A_T, and pH are involved in calculations (that is to say, the calculation of pH (DIC, A_T) or DIC (A_T, pH) or A_T (DIC, pH)), the constants of GP produce the least deviation between measured and calculated parameters. However, we find that in high salinity (S > 34.5) waters, the constants of M become more appropriate and in the lower salinity waters (S < 34.5), the constants of R outperform the others. Despite these changes, the constants of MM and ML show little variation in performance between the two salinity environments. For August, there was no difference between the most suitable constants for the entire dataset compared to the different salinity regimes regarding measurements with DIC, A_T, and pH, with the constants of GP still most closely representing the measurements. With regard to measurements of pH, pCO$_2$, and DIC, however, in the lower salinity waters, the constants of H outperformed those of GP. Similarly to February, the constants of MM and ML also perform well and show the best consistency across the entire salinity range, with the constants of ML generally displaying a greater level of accuracy. The salinity range does not change between the two seasons; however, in February 2002, a 3.5-fold higher Elbe river discharge was recorded compared to August 2005 (GKSS, 2012, http://coast.gkss.de/staff/kappenberg/elbe/abfluss/elbe.abfluss). A larger proportion of freshwater in the North Sea could explain why a greater difference is observed between the two salinity environments during this time.

From this application of the various dissociation constants of carbonic acid, we show that the range of salinity directly affects the robustness
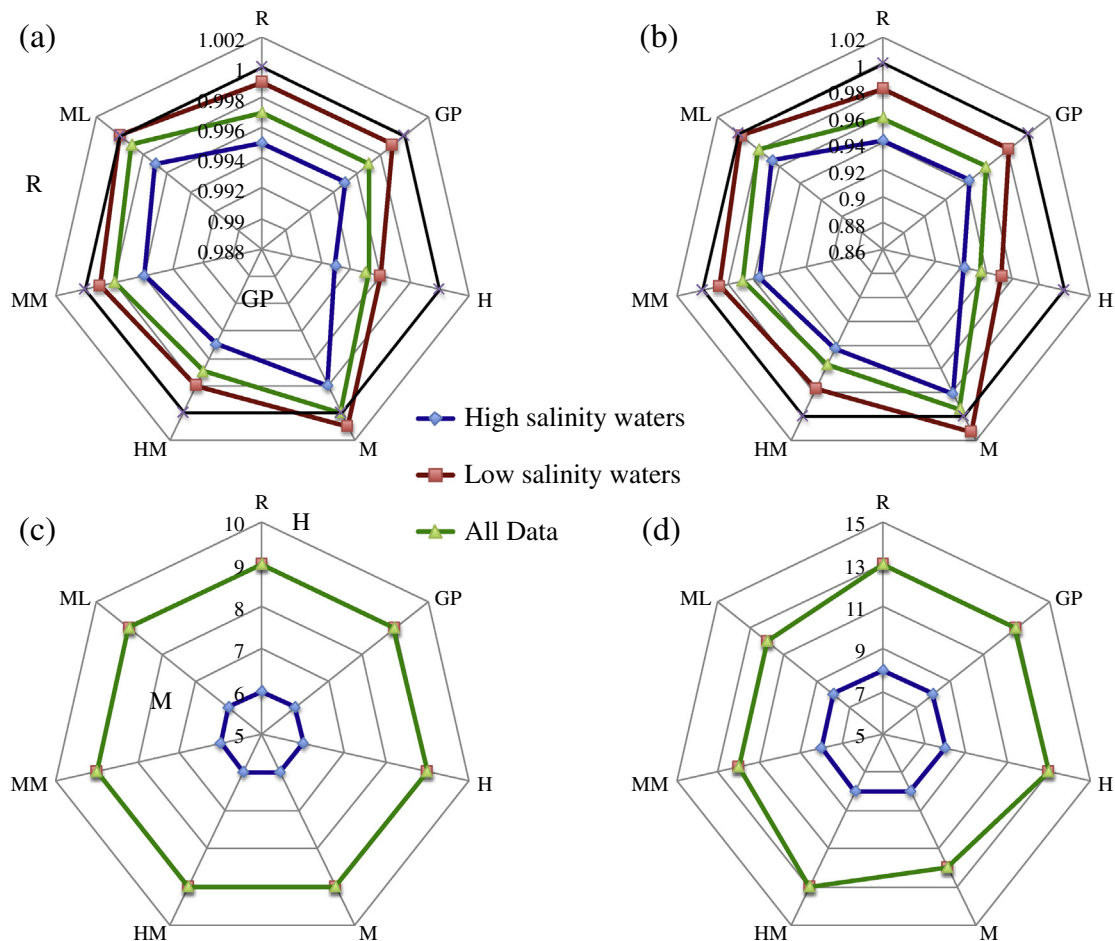
Fig. 4. Radar plot showing (a) the regression coefficients for A_T (DIC, pCO$_2$) and (b) pCO$_2$ (DIC, A_T) in different salinity environments, and their respective standard deviation (c, d) of the fit.

of carbonate system calculations with different constants. Specifically, the constants R, H, GP, and HM show much larger errors in mediums with a larger freshwater constituent compared to those of MM and ML. The larger range of salinities for which these latter constants were determined is likely to contribute to more accurate determinations of K_1 and K_2, thus also leading to more accurate K_1/K_2 ratios. Based on these results, for datasets that cover a large range of salinities, for consistency, one can achieve the best overall results using the constants of ML in carbonate system calculations. Despite this, and bearing in mind that the current recommended dissociation constants for carbonate system measurements are those of M, all further calculations and comparisons are performed using this set of constants.

3.1.2. The role of borate alkalinity

The ratio of K_1/K_2 varies between different parameterizations of carbonic acid dissociation constants, partly depending on whether the constants were determined in artificial seawater (ASW) or natural seawater (NSW). In NSW, interactions between borate and carbonate cause an increase in K_1 and a decrease in K_2 (Mojica-Prieto and Millero, 2002), which does not occur in ASW due to the lack of boric acid. As such, we suggest that finding the constants of R, GP, and H to perform comparably with those of M in less saline waters may be indicative of the lower borate concentrations in freshwater and thus the errors in pK_2, arising from the lack of boric acid in their ASW medium, are minimized. Fig. 2a and b clearly show that borate is the second largest non-carbon contributor to A_T, constituting on average ~4% (Zeebe and Wolf-Gladrow, 2001), thus deviations from the true borate concentration can potentially cause substantial errors in calculations involving A_T. Additionally, the K_B of the boric acid system is very close to ocean pH, thus any miscalculation of $[H^+]$ can also lead to significant errors in the calculation of $[B(OH)_3]$ and $[B(OH)_4^-]$.

Borate has a long residence time in the oceans leading to a conservative relationship with salinity, thus in carbonate system calculations, the total boron contribution is calculated using the linear relationship to chlorinity as found by Uppström (1974), and the borate then calculated using a thermodynamically derived K_B. The data used by Uppström (1974) are based on data obtained from the Pacific Ocean. However, recent findings suggest that this relationship is not consistent in all the world's oceans (Lee et al., 2010). Lee et al. (2010) recently found that this relationship is not as ubiquitous in the oceans as originally thought and has made adjustments which, on provisional tests, led to an increase in the internal consistency of carbonate system calculations in the North Atlantic. The Uppström (1974) borate–salinity relationship was substituted in CO2SYS for the new Lee et al. (2010) relationship, to see if this improved the internal consistency. The new calculations led to a maximum difference in borate alkalinity of 4 μmol A_T kg^{-1}, during both seasons. Despite this change, the influence on internal consistency was almost imperceptible and resulted in no significant improvement.

In the North Sea, the Baltic input through the Skagerrak and the Elbe input in the German Bight have also revealed non-conventional salinity–borate relationships (Barth, 1998; Kremling, 1972). To evaluate the potential error introduced into calculations of the carbonate system in the North Sea by unaccounted-for borate, the borate concentrations in the Elbe- and Baltic-influenced areas of the North Sea were calculated using the water mass fractions and borate–salinity equations from the literature (see Section 2.5). This "pre-calculated" borate contribution to alkalinity (BAlk$_{pre}$) was then implemented into CO2SYS, replacing the normal salinity–borate calculation (Uppström, 1974). For comparative purposes, BAlk was also calculated using the traditional Uppström (1974) equation but using various $[H^+]$ determinations, including that from direct pH measurements, using DIC and A_T as input parameters and using A_T and pCO$_2$ as input parameters (DIC/pCO$_2$ produce the same results as A_T/pCO$_2$, hence have not been included). The BAlk$_{pre}$ calculations showed little change from the BAlk concentrations, the difference showing a normal distribution with 0 as the mean of the absolute

values and σ of 3 μmol kg^{-1}. The equations of Barth (1998) are very similar to the oceanic relationships, thus no significant difference was observed in the German Bight between the two calculations. The greatest difference occurs in the Skagerrak where the Uppström (1974) ratio underestimates the BAlk compared to the equation derived from Gripenberg's data. The differences in calculation resulted in a maximum difference in BAlk of 8 μmol kg^{-1} in August 2005. Despite these differences, using the new calculated BAlk$_{pre}$ values in CO2SYS did not improve the internal consistency; on the contrary, the changes caused greater deviations between the measured and calculated parameters, reducing the number of internally consistent stations for all input combinations. Thus we conclude that the non-conservative salinity–borate relationships in the North Sea are not limiting factors for the internal consistency.

When the $[H^+]$ from pH measurements is used to calculate BAlk directly, and this value is implemented into the thermodynamic calculations, the overall internal consistency is again unimproved. On the other hand, when the BAlk calculated using $[H^+]$ from (DIC, A_T) is implemented, the internal consistency improves notably if DIC or A_T are being calculated, for both seasons. The number of internally consistent (IC) stations in February and August, for A_T(DIC,pH) and DIC(A_T,pH), increased by 11% (7 stations) and 36% (29 stations). The internal consistency of A_T(DIC,pCO$_2$) increased by 8% and 19% for February and August, respectively, and DIC (A_T,pCO$_2$) increased by 6% and 16% stations, respectively. It should be noted that the $[H^+]$ calculated from (DIC, A_T) is only used to calculated the BAlk, whereas the $[H^+]$ used in the other CO2SYS calculations is calculated from the stated input parameters. As such, we can conclude that it is the effect of miscalculation of $[H^+]$ on the BAlk concentration that contributes significantly to a lack of internal consistency for (A_T, pCO$_2$) and (DIC, pCO$_2$). This can be illustrated by Fig. 5(a), where the change in ΔA_T between the measured and calculated values are plotted against the change in $[H^+]$ between that calculated from (DIC, A_T) and (DIC, pCO$_2$). When the $[H^+]$ from (DIC, A_T) is used to calculate BAlk the ΔA_T values are shifted toward the x-axis (0), indicative of the improvement in internal consistency. The reason for such a bias is unknown and may be caused by an undetected bias in one of the measured parameters.

3.2. Seasonal comparison (A_T, DIC, and pCO$_2$)

3.2.1. Seasonal internal consistency

The results from the internal consistency study from all 6 data sets, using just three carbonate parameters (A_T, DIC, and pCO$_2$), show a clear dominance of the constants of M and ML outperforming the others. Both of these sets of constants show comparable results. The results of the seasonal calculations with the use of M constants are given in Table 3. The statistics indicate that the internal consistency of the North Sea follows a seasonal pattern, with May – the most biologically productive time period – producing less consistent results and the rest of the year displaying a good level of consistency. These findings are in agreement with those of Koeve and Oschlies (2012), who similarly noted significant inconsistencies in the carbonate system in waters of high biological activity.

Additionally, the largest fraction of Baltic water found in the Skagerrak is present in May (17%). Further analysis shows that during this season, there is a significant (p = 0.008, R^2 = 0.55), positive correlation between the Baltic fraction and the deviation between calculated and measured parameters (Fig. 5(b)). Despite this, in May, the internal consistency could also not be improved by changing the BAlk calculation as done above (see Section 3.1.2). However, Gripenberg (1960) concluded, from back titrations of alkalinity, that while borate did not directly affect the accuracy of the A_T titrations, the interactions between boric acid and organic material could lead to underestimated alkalinity values. Recent work by Ulfsbo et al. (2015) similarly find that in the Baltic, dissolved organic matter can contribute up to 30 μmol A_T kg^{-1} to alkalinity, thus rendering the A_T equation in CO2SYS invalid. It thus seems
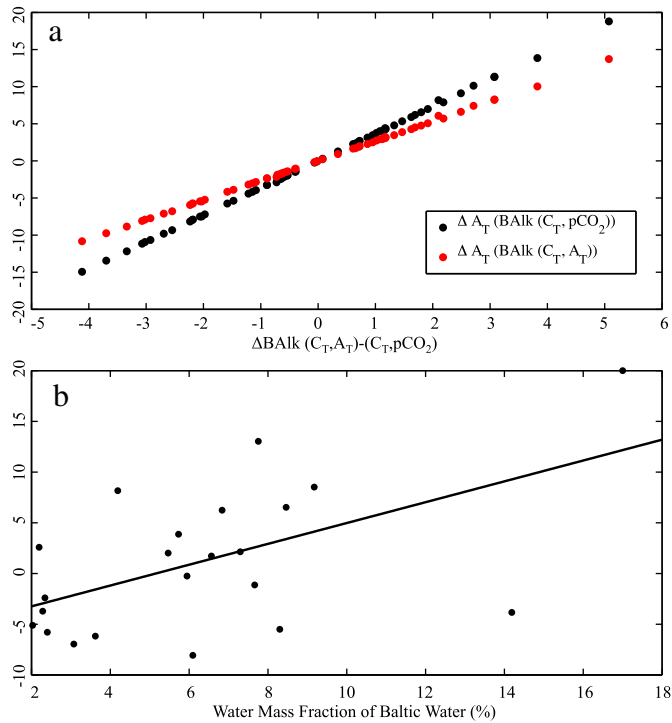
Fig. 5. (a) The change in ΔA_T caused by the difference in BAlk calculated using the $[H^+]$ from (DIC, A_T) (red) and (DIC, pCO_2) (black). (b) Regression of ΔDIC with the calculated water mass fraction of Baltic water, selectively displaying those with a fraction of 2% or higher.

likely that the lack of internal consistency observed in Baltic-influenced waters in May stems from additional organic material in the water at this time of year, with possibly further errors introduced from the interaction of this organic material with boric acid.

The North Sea receives a high input of allochthonous dissolved organic matter, for which analysis of colored dissolved organic matter (CDOM) indicates that it contains a high proportion of terrigenous sources (Stedmon et al., 2010). Thus may contain terrestrial "titratable" compounds, which are also not accounted for in our calculations. It has been suggested that fatty acids and humic substances may contribute to measured A_T, and in the Baltic Sea, there is a higher than average concentration of both. The contribution of fatty acids to A_T has been fairly extensively examined by Osterroht (1993) and maximum contributions of <1 µmol A_T kg^{-1} to alkalinity were found, which is insufficient to cause the inconsistencies observed here. In contrast, more recently, the presence of humic substances has been shown to contribute to large excess A_T in the Baltic Sea (Ulfsbo et al., 2015). The contribution of organic matter to A_T has been observed elsewhere, as well. Muller

and Bleie (2008), using the technique of Hernandez-Ayon et al. (2007) on fjord surface waters, compared the A_T estimation of DIC to the measured value and found that organic alkalinity can contribute from 2 to 22 µmol A_T kg^{-1} in regions of high organic matter. These errors are sufficiently large to account for the noted decrease in internal consistency observed in the North Sea in May, compared to other seasons.

As the North Sea consists of two different biogeochemical regimes, the nNS and the sNS, we investigated whether these two environments contributed toward a difference in the internal consistency of the carbonate system. The North Sea was subsequently divided along the 56°N latitude and the internal consistency re-examined in both areas, applying just the constants of M (Table 4). In May, there is a significant increase in the standard deviation of ΔDIC and ΔpCO_2 in the nNS compared to the sNS; however, ΔA_T shows no difference. As previously mentioned, there is greater freshwater influence in the sNS. However, the difference observed between the nNS and sNS is larger than the difference previously mentioned between oceanic and estuarine waters. In the nNS, larger blooms of phytoplankton are maintained for long periods due to seasonal, thermal stratification, which is in contrast to the sNS where rapid remineralization takes place in the permanently well-mixed water column. Errors have previously been associated with intense biological activity (Hoppe et al., 2012; Kim and Lee, 2009). Thus, we are inclined to suggest that this may have a similar effect here. However, it is interesting that the errors in ΔA_T are not affected on a north-south latitudinal gradient, like ΔpCO_2 and ΔDIC.

The different regimes in the nNS and sNS also influence the dominant phytoplankton species present in each location. Calcifying organisms and the presence of coccolithophores are well documented in the nNS, where the development of coccolithophore blooms is controlled by the North Atlantic influence and the stratification of the water column (Burkill et al., 2002; Houghton, 1991). The presence of coccolithophores in waters sampled for DIC could conceivably lead to a degree of CaCO$_3$ dissolution during the DIC titration. This would introduce a degree of noise to the DIC values in the NNS, and possibly account for some of the larger errors observed in this region. Furthermore, Fraga and Alvarez-Salgado (2005) quantified the change in A_T during photosynthesis and found that the differences are caused predominantly by CaCO$_3$ formation. Calcification influences the A_T/DIC (X) ratio of the waters as it removes one mole of DIC per 2 moles of A_T (Wolf-Gladrow et al., 2007). Lee et al. (1996, 1997) found that high X ratios (>1.10) can impact the sensitivity of pK$_2$, thus affecting the consistency between

Table 3
Derived linear regressions, using total least squares, and standard deviations of differences between measured and calculated parameters (A_T, DIC, and pCO_2) with the percentage of internally consistent stations for all six cruises. The calculations were performed using the acid dissociation constants of Mehrbach et al. (1973), refit by Dickson and Millero (1987).

Input combination		Aug '01	Nov '01	Feb '02	May '02	Aug '05	Aug '08
A_T (DIC,pCO_2)	Regress	0.999	1.001	1.000	0.993	1.001	1.000
	Std	29	8	8	27	9	9
	IC (%)	15.5	47.7	43.5	9.4	34.9	50.2
DIC (A_T,pCO_2)	Regress	1.000	0.999	1.000	1.007	1.000	1.000
	Std	24	7	7	23	7	8
	IC (%)	17	48	44	9	39	52
pCO_2 (DIC,A_T)	Regress	0.976	1.004	0.994	0.906	1.004	0.998
	Std	41	15	17	41	13	15
	IC (%)	26	50	40	20	49	57

Table 4
Calculated internal consistency statistics for all data sets divided into northern North Sea stations (nNS) (latitude $>56°N$) and southern North Sea stations (sNS) (latitude $<56°N$).

| Area	Input combination		Aug '01	Nov '01	Feb '02	May '02	Aug '05	Aug '08
nNS (lat>56°N)	A_T (DIC, pCO_2)	Regress	1.00	1.00	1.00	0.99	1.00	1.00
		Std	27	8	8	27	9	9
		IC (%)	16.0	52.8	44.7	7.4	34.8	48.1
	DIC (A_T, pCO_2)	Regress	1.00	1.00	1.00	1.01	1.00	1.00
		Std	22	7	6	27	7	9
		IC (%)	16.0	52.8	44.7	7.4	28.3	44.4
	pCO_2 (DIC, A_T)	Regress	1.01	1.01	0.99	0.87	1.01	1.00
		Std	30	13	14	48	13	17
		IC (%)	32	55	40	15	46	54
	No. stations		25	53	38	54	46	54
sNS (lat≤56°N)	A_T (DIC, pCO_2)	Regress	1.00	1.00	1.00	0.99	1.00	1.00
		Std	29	8	8	27	9	9
		IC (%)	20.6	41.7	38.5	10.3	44.1	56.8
	DIC (A_T, pCO_2)	Regress	1.00	1.00	1.00	1.00	1.00	1.00
		Std	24	8	8	12	7	7
		IC (%)	17.6	41.7	38.5	10.3	44.1	56.8
	pCO_2 (DIC, A_T)	Regress	0.96	1.00	1.00	0.97	1.00	1.00
		Std	46	17	19	19	14	15
		IC (%)	23.5	47.2	38.5	25.6	52.9	59.5
	No. stations		34	36	26	39	34	37
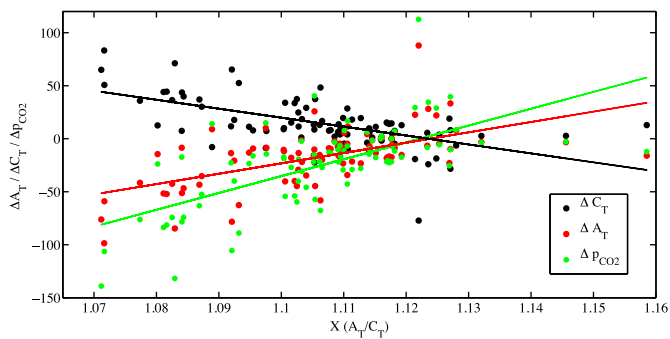
Fig. 6. The change in ΔDIC and ΔA_T (both in µmol kg^{-1}) and ΔpCO_2 (in µatm) observed with a varying ratio of A_T/DIC (X) during May 2002.

measured and calculated carbonate parameters. The range of X (A_T/DIC) found in the North Sea varies from 1.06 to 1.16 throughout the year, with the smallest range (1.06–1.09) occurring in February and the largest range (1.07–1.16) found in May. During May, X also shows a positive linear correlation with ΔDIC, ΔA_T, and ΔpCO_2 with R^2 values of 0.6, 0.6, and 0.7, respectively (Fig. 6). The size of the error introduced by varying X can be up to 5 µmol A_T kg^{-1}, as found by Lee et al. (1996), which would contribute a large proportion of the errors we observe in the North Sea.

4. Conclusions

On a basin-wide scale in the North Sea, we find that the carbonic acid dissociation constants of Mehrbach et al. (1973, refit by Dickson and Millero, 1987), and the constants of Millero et al., (2006) provide the best internal consistency. In the case of the former constants, this is in agreement with previous findings (Lee et al., 1996; Wanninkhof et al., 1999). In regions of lower than average ocean salinity, there is markedly less deviation between the internal consistency of the different constants and the constants of ML outperform those of M. At high salinities, these two sets of constants are comparable in performance, thus over datasets with a wide variety of salinities, we recommend the use of ML constants for more consistent results.

In the North Sea in general, we find that the internal consistency of the carbonate system is much less than that found in the open ocean, by approximately 2-fold, which is unsurprising considering the additional input of terrestrial compounds in coastal areas, and generally higher productivity. Application of the new borate–salinity relationship noted by Lee et al. (2010), and further accounting for the non-conventional salinity–borate relationships in the water masses contributing to the North Sea, did not result in any improvement in the internal consistency. The internal consistency is relatively constant throughout the year, with the exception of May, where there is a marked decrease in our ability to accurately calculate the carbonate system. Waters in which the Baltic Sea constituent is larger than 2% show lower internal consistency in May driven by the presence of excess organic alkalinity unaccounted for in carbonate system calculations. In the entire North Sea, there is a significant correlation between the internal consistency and X (A_T/DIC), similar to that found in previous studies. Higher X values in the nNS compared to the sNS are likely to contribute to the larger errors observed in this area through the increased sensitivity on pK$_2$.

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