Journal of Marine Systems 157 (2016) 52–64

Contents lists available at ScienceDirect

Journal of Marine Systems

journal homepage: www.elsevier.com/locate/jmarsys

The internal consistency of the North Sea carbonate system

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ARTICLE INFO

Article history:
Received 9 February 2015
Received in revised form 25 November 2015
Accepted 29 November 2015
Available online 15 December 2015

Keywords:
Carbon dioxide
North Sea
Internal consistency
Total alkalinity

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.

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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http://dx.doi.org/10.1016/j.jmarsys.2015.11.008
0924-7963/

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).

$$K = \{H+\}\{A-\}/\{HA\}, \tag{1}$$

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

$$K' = \{H^+\}[A^-]/[HA]. \tag{2}$$

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:

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

$$\text{where } K_B = \left[B(OH)_4{}^-\right]\left[H^+\right]/\left[B(OH)_3\right] \tag{4}$$

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.