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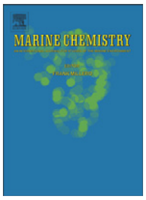

Applications of *in situ* pH measurements for inorganic carbon calculations

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ABSTRACT

This study examines the utility of combining pH measurements with other inorganic carbon parameters for autonomous mooring-based carbon cycle research. Determination of the full suite of inorganic carbon species in the oceans has previously been restricted to ship-based studies. Now with the availability of autonomous sensors for pH and the partial pressure of CO_2 (pCO_2), it is possible to characterize the inorganic carbon system on moorings and other unmanned platforms. The indicator-based pH instrument, SAMI-pH, was deployed with an autonomous equilibrator-infrared pCO_2 system in Monterey Bay, California USA from June to August 2007. The two-month time-series show a high degree of short-term variability, with pH and pCO_2 changing by as much as 0.32 pH units and 240 µatm, respectively, during upwelling periods. The pH and salinity-derived alkalinity (A_{Tsalin}) were used to calculate the other inorganic carbon parameters, including pCO_2, total dissolved inorganic carbon (DIC) and $CaCO_3$ saturation states. The calculated pCO_2 was within 2 µatm of the measured pCO_2 during the first day of the deployment and within 8 µatm over the first month. The DIC calculated from pH–A_{Tsalin} and pCO_2–A_{Tsalin} were within 5 µmol kg^{-1} of each other during the first month. However, DIC calculated from pH–pCO_2 differed by ~50 µmol kg^{-1} from the other estimates over the same period, reflecting the sensitivity of the pH–pCO_2 calculation to measurement error. The data continued to diverge during the final month and this difference was likely driven by extensive biofouling. Because of the relative insensitivity of CO_3^{2-} concentration to these errors, aragonite saturation calculated from the pH–pCO_2 pair was within 0.15 of the pH–A_{Tsalin} values over the entire deployment. These results show that *in situ* pH, when combined with other CO_2 parameters, can provide valuable insights into both data quality and inorganic carbon cycling.

1. Introduction

Our knowledge of the marine inorganic carbon system is primarily based upon studies conducted from ships. Consequently, except for a few ocean time-series stations (Bates, 2007; Dore et al., 2009; Santana-Casiano et al., 2007), we have sparse information on the temporal variability of inorganic carbon species in the major ocean basins and coastal margins. The inorganic carbon system poses additional measurement challenges because CO_2 exists in several different forms. Solving the equilibria, mass and proton balance equations that describe the marine inorganic carbon system results in two independent equations and four unknowns. Therefore, by measuring two inorganic carbon parameters, such as pH and total alkalinity (A_T), the remaining parameters can be calculated, i.e. partial pressure of CO_2 (pCO_2), dissolved inorganic carbon (DIC), bicarbonate, carbonate and $CaCO_3$ saturation states (Millero, 2007). Autonomous measurement systems could greatly improve the spatiotemporal coverage of inorganic carbon data but, of the four parameters measured on ships (pH, pCO_2, A_T, and DIC), only pCO_2 has been routinely measured autonomously (DeGrandpre et al., 1995; Friederich et al., 1995; Hood et al., 1999). Progress has been made on autonomous DIC and A_T technology (Sayles and Eck, 2009; Martz et al., 2006), but the complexity and performance requirements (<0.1% precision and accuracy) remain problematic. Autonomous potentiometric pH sensors have been available for many years and have been used in various marine studies (e.g. Mackey et al., 1989; Wootton et al., 2008). These sensors readily resolve pH changes in marine environments but their accuracy is not adequate for CO_2 system calculations (Dickson, 1993). However, results from another electrochemical method, the ISFET pH sensor, show promise (Martz et al., 2010) and progress has also been made measuring other inorganic carbon parameters (Byrne and Yao, 2008). Researchers have previously established that indicator-based pH methods provide the ~0.002 pH accuracy needed for inorganic carbon calculations (Byrne and Breland, 1989; Clayton and Byrne, 1993; Clayton et al., 1995). Autonomous instruments based on this technology

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have had high power requirements and could only be deployed for short intervals (Liu et al., 2006; Nakano et al., 2006). The Submersible Autonomous Moored Instrument for pH (SAMI-pH), developed over the past decade (Martz et al., 2003; Seidel et al., 2008), is a low-power indicator-based pH sensor that can be deployed for up to one year on moorings and other platforms (Emerson et al., 2011). Here we examine time-series from a SAMI-pH sensor, an autonomous equilibrator-infrared (eq-IR) CO_2 system (Friederich et al., 1995) and other sensors collected on a mooring in Monterey Bay, CA from June-August 2007.

2. Background

Previous work has shown that the four routinely measured CO_2 parameters, pH, pCO_2, DIC, and A_T are "internally consistent", that is, as stated above, all of the CO_2 species can be quantified by measurement of two of these parameters (Clayton et al., 1995; McElligott et al., 1998; Byrne et al., 1999; Wanninkhof et al., 1999; Millero, 2007; Ohline et al., 2007). This significant achievement was the culmination of a long and determined effort to improve CO_2 measurement technology and to further quantify and evaluate the CO_2 equilibrium (dissociation) constants (Dickson et al., 2007; Millero, 2007). Studies have found that the CO_2 dissociation constants of Mehrbach et al. (1973) refit by Dickson and Millero (1987) give the most accurate values when compared to measurements (Wanninkhof et al., 1999; Lee et al., 2000). Errors associated with different parameter pairs were also evaluated in these studies (e.g. Millero et al., 2006; Millero, 2007). The pH–DIC, pH–A_T, pCO_2–DIC and pCO_2–A_T combinations all produce computed values that are comparable to or better than the measurement accuracy and precision (Millero, 2007). The A_T-DIC pair predicts pCO_2 and pH with errors slightly larger than the measurements (Lee et al., 2000); whereas, the pH–pCO_2 pair leads to larger calculation errors (Millero, 2007).

The larger errors from the pH-pCO_2 pair are commonly attributed to the strong covariance between pH and pCO_2 (Dickson and Riley, 1978) but can be more clearly understood by examining the relationship between DIC, pCO_2 and pH. The DIC is

$$\mathrm{DIC} = [\mathrm{CO_2(aq)}] + [\mathrm{H_2CO_3}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] \tag{1}$$

At the average seawater pH (8.0), approximately 90% of the inorganic carbon is present as HCO_3^-. Simplifying Eq. (1) to $\mathrm{DIC} \approx [\mathrm{HCO_3^-}]$ and using the inorganic carbon equilibrium and mass balance expressions, it can be seen that H^+ and pCO_2 are directly proportional to each other for a given DIC, temperature and salinity:

$$\mathrm{DIC} \approx \frac{K_1 K_0 pCO_2}{[H^+]} \tag{2}$$

where K_0 and K_1 represent the temperature and salinity dependent CO_2 solubility and first dissociation constant for carbonic acid, respectively. Propagating typical random measurement uncertainties in Eq. (2) of ± 2 μatm and ± 0.002 pH units, which are equivalent to ~± 1% relative standard deviation (RSD), produces a random DIC error of ± 20–30 μmol kg^{-1}, with similar results for A_T (Dickson and Riley, 1978). Small systematic errors in either pH or pCO_2 will also yield large errors in DIC and A_T when using the pH–pCO_2 pair. Another way of looking at Eq. (2) is that because H^+ and pCO_2 are not conservative properties they must exactly track together with temperature, pressure or salinity, or erroneous changes in DIC will be predicted. Other parameters such as CO_3^{2-}, which is used to calculate $CaCO_3$ saturation states, are less sensitive to errors in the pH–pCO_2 calculation because CO_3^{2-} is only a small portion of the total CO_2 of seawater. A ~1% error in CO_3^{2-} only equals ~2 μmol kg^{-1}. Similar arguments can be made for the calculation of DIC from A_T and pH, but the propagated uncertainty is closer to 0.1%. Of course, A_T cannot at present be measured autonomously; however, one of the special properties of seawater A_T is its quasi-conservative nature, which sets it apart from the other CO_2 parameters. In some studies, pH has been used with A_T calculated from known relationships with salinity (Clayton et al., 1995) and the calculated DIC has been used to quality control DIC data (Byrne et al., 1999). Consequently, if A_T–salinity (or salinity-temperature) relationships are known (e.g. Lee et al., 2006), A_T may be another parameter that can be used for mooring-based CO_2 system calculations.

While obviously much is already known about the strengths and weaknesses of CO_2 inorganic system calculations, mooring-based pH and pCO_2 time-series are a unique form of data that have never been analyzed in this way. With three inorganic carbon parameters, pH, pCO_2 and salinity-derived A_T (A_{Tsalin}), calculated and measured values can be compared. This redundancy makes possible an *in situ* assessment of measurement accuracy and long-term stability for all of the inorganic carbon species. Specifically here, we focus on comparisons of the measured and calculated pCO_2, calculated DIC and calculated $CaCO_3$ saturation states. We also examine the time-series range of variability and relationship between pH and other measured parameters for this upwelling-influenced coastal region.

3. Methods

3.1. Field site

As part of an ongoing monitoring program run by the Monterey Bay Aquarium Research Institute (MBARI) in Moss Landing, CA, USA, a suite of physical and biogeochemical sensors were deployed in Monterey Bay on the MBARI M0 buoy. The buoy is located ~8 km offshore on the 70 m isobath (36.83° N, 121.90° W) (Fig. 1). The location is in an upwelling shadow that receives advected water from the Point Año Nuevo upwelling center to the northwest. Point Año Nuevo experiences frequent upwelling events in the spring and summer (Skogsberg, 1936; Skogsberg and Phelps, 1946).

The deployment took place from June 21 to August 28, 2007. M0 is equipped with meteorological and ocean sensors that measure wind speed and direction, air and water temperature, salinity, nitrate, air and sea surface pCO_2, and other parameters. A SAMI-pH (Seidel et al., 2008) was added to the M0 buoy for this deployment. The nitrate, salinity, and pH sensors were all located between 0.75 and 1.5 m depths, the approximate depth of the intake tube for the pCO_2 equilibrator. The pH sensor was separated from the pCO_2 intake tube

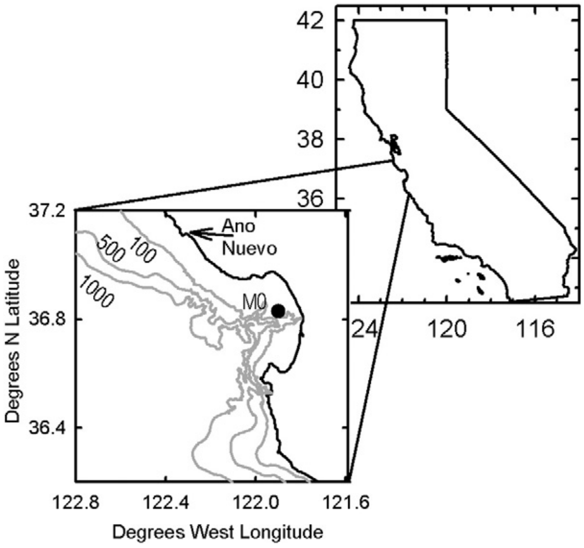

Fig. 1. Deployment location of the MBARI M0 mooring in Monterey Bay, California, USA.