

**CARBONATE CHEMISTRY DYNAMICS ALONG THE U.S.
EASTERN CONTINENTAL SHELF**

by

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A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Oceanography

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ABSTRACT

The uptake of carbon dioxide (CO₂) from the atmosphere by seawater has caused ocean acidification globally. In addition to anthropogenic CO₂ uptake, the coastal ocean experiences enhanced acidification due to freshwater discharge, eutrophication, upwelling, etc. This coastal acidification affects the health of calcifying species and has a harmful impact on commercial fisheries and the marine ecosystem. It is critical to monitor coastal acidification and determine the spatial and temporal trends of related parameters. This dissertation focuses on the carbonate/bicarbonate buffering system, which is a chemical buffer system that regulates seawater pH. I analyze the carbonate chemistry dynamics and buffer capacities for the east coast using four shipboard datasets, satellite remote sensing data, and model outputs. Results suggest that total dissolved inorganic carbon and the aragonite saturation state along the U.S. eastern continental shelf have patterns that agree with predictions based on carbon dioxide equilibrium with the atmosphere. This indicates a solubility control mechanism that leads to low carbonate ion concentrations and aragonite saturation state in cold northern waters and the opposite in warm southern waters. In terms of short-term variability of aragonite state in the central Mid-Atlantic Bight, quantitative analyses show that physical advection and mixing processes are the dominant forces for a higher aragonite saturation state in slope waters while biological carbon removal and carbon dioxide degassing contribute to higher aragonite state in shelf waters. On decadal and longer time scales, dissolved inorganic carbon has increased while aragonite saturation state and pH have decreased

along the U.S. eastern continental shelf. However, dissolved inorganic carbon increase and aragonite saturation state decrease were dampened in the Mid-Atlantic Bight because of seawater temperature increase. The analyses of carbonate chemistry parameters in various spatial and temporal scales help us to better understand the processes that can alter carbonate chemistry in coastal waters. In addition, with specific regional-scale ocean models, the community can extend our ability of quantitative understanding carbonate chemistry dynamics and take necessary efforts to prevent the occurrence of low pH or undersaturation conditions in the future.

Chapter 1

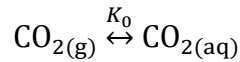
INTRODUCTION

The global carbon cycle encompasses the circulation and transformation of carbon between various systems, such as land, ocean, and atmosphere. As a major component of the Earth's climate system, the ocean plays an important role in the global carbon cycle through internal processes and interactions with the atmosphere and coastal margins. However, the quick, human release of carbon dioxide (CO₂) as a result of the burning of fossil fuels has dramatically increased the amount of CO₂ in the atmosphere and changed carbon cycling significantly since the start of the industrial revolution. Rising atmospheric CO₂ levels contribute to global warming as carbon emissions exceed the uptake rates by other reservoirs. Additionally, the increased amount of CO₂ in the atmosphere has increased the amount of CO₂ absorbed by the ocean through air-sea interactions, which leads to ocean acidification and affects the health of carbonate-bearing organisms (Orr et al., 2005; Doney et al., 2009).

Recent studies suggest that the coastal ocean is more sensitive to anthropogenic climate change than the open ocean (Melzner et al., 2013; Wallace et al., 2014; Turk et al., 2019). Upwelling, eutrophication, and river discharge influence coastal carbonate chemistry and contribute to coastal acidification (Feely et al., 2008; Cai et al., 2011; Vargas et al., 2016). The upwelling margins, such as the west coast of the United States, are affected by seasonal surface acidification primarily due to the intrusion of corrosive deep water (Feely et al., 2008, 2016). Identifying the sources and sinks of

CO₂ and flux rates in these domains will be essential to understanding coastal carbon cycling and acidification. In particular, 40-50% of global carbon export flux, i.e., the amount of carbon fixed in the upper ocean that is exported to the ocean interior (Falkowski et al., 1998), occur in coastal ocean (Muller-Karger et al., 2005; Dunne et al., 2007). However, as a major component of the global carbon cycle, the coastal ocean carbon budget is poorly constrained due to its complexity and limited spatial and temporal observations as well as model estimates (Regnier et al., 2013; Bauer et al., 2013).

The air-sea CO₂ flux is an important component in quantifying ocean carbon budget (Quéré et al., 2018). At the air-sea interface, the gaseous CO₂ (CO_{2(g)}) and aqueous CO₂ (CO_{2(aq)}) are related by the equilibrium:

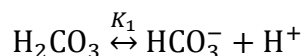


where K_0 is the Henry's Law constant and it is temperature, salinity, and pressure dependent (Weiss, 1974). CO_{2(g)} is usually denoted by $p\text{CO}_2$ or $f\text{CO}_2$, where p stands for partial and f stands for fugacity. Fugacity is the formal expression and it accounts for the non-ideal behavior of CO₂ gas. It can be converted into the commonly used $p\text{CO}_2$ using a temperature-dependent fugacity factor. Note that the differences between fugacity and partial pressure for CO₂ gas are usually very small (<1%) in coastal and open ocean. $p\text{CO}_2$ is very sensitive to temperature change. For example, $p\text{CO}_2$ would increase by roughly 12 μatm in a closed system when temperature increases by 1°C. Temperature change plays an important role in controlling seasonal $p\text{CO}_2$ variation in regions where the biological activity is weak (Takahashi et al., 2002).

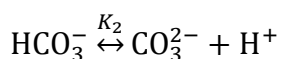
The carbonate chemistry is directly connected with CO₂ through reactions at the air-sea interface. CO_{2(aq)} immediately reacts with water to form carbonic acid:



The carbonic acid dissociates to form bicarbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻) by two reactions:



and



where K_1 and K_2 stand for the first and second dissociation constants of carbonic acid and are primarily controlled by temperature and salinity (e.g., Mehrbach et al., 1973; Dickson and Millero, 1987). These reactions control the distributions of carbonate chemistry parameters (see Chapter 4 for more details).

The carbonate equilibrium is an important buffer system regulating pH in oceanic and coastal waters. The total dissolved inorganic carbon (DIC) is one of the commonly measured carbonate chemistry parameters, which defined as the sum of dissolved carbonate species ($[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$). Another commonly measured carbonate chemistry parameter, the total alkalinity (TA), is defined as the excess base of a system (Dickson, 1992). The entire marine carbonate system can be determined with knowing any two of the four commonly measured carbonate chemistry parameters (DIC, TA, pH, $p\text{CO}_2$), along with temperature, salinity, and pressure.

My doctoral research focused on the carbonate chemistry dynamics along the U.S. eastern continental shelf, which is a typical passive continental margin that characterized with a broad and flat shelf. The Labrador Current and the Gulf Stream

are two major current systems in the North Atlantic that affect the dynamics of shelf waters. The Labrador Sea is an important region of deep water formation and atmospheric CO₂ uptake and sequestration (DeGrandpre et al., 2002). The cold Labrador Current originates in the West Greenland Coast and flows southward through the Gulf of Maine (GoME) to the New York Bight (Bailey and Hachey, 1951). The buoyancy-driven horizontal flow eventually transports the fresh and cold water onto the Mid-Atlantic Bight (MAB) shelf (Chapman and Beardsley, 1989). It meets with the warm Gulf Stream in the Grand Banks and influences regional temperature and salinity variabilities (Petrie and Drinkwater, 1993; Fratantoni and McCartney, 2009).

The Gulf Stream originates in the Gulf of Mexico. It flows northward parallel to the coast and separates from shelf water regions at Cape Hatteras which border the South Atlantic Bight (SAB). The Gulf Stream is beyond 600 m isobath in the SAB at a weakly deflected state but often penetrates the inner shelf at a strongly deflected state (Bane and Dewar, 1988). It strongly affects the shelf water dynamics along its propagation pathways in the SAB. The surface flow of the Gulf Stream transports water from the tropical Atlantic to the subtropical gyre and affects seawater alkalinity (Rodhe et al., 2002; Bates and Peters, 2007).

Another hydrographic feature along the U.S. eastern continental shelf is the development of a band of cold water below the seasonal thermocline due to stratification and shelf topography, referred to as the “cold pool”, in the middle and outer shelf of the MAB during summer (Houghton et al., 1982). The coldest water is commonly found in the New York Bight as a result of colder water advection from the east in the early spring and relative weak tidal mixing (Lentz, 2017). The advection of

cold pool water transports additional nutrients from the Georges Bank to the New York Bight and the southern MAB, while the nutrient concentrations decreases due to the enhancement of upward vertical flux, which in turn due to the enhanced warming of the cold pool (Hales et al., 2009; Lentz, 2017).

Three large-scale surveys, the first and second Gulf of Mexico and East Coast Carbon (GOMECC-1, -2) cruises and the first East Coast Ocean Acidification (ECO-A-1) cruise were conducted along the U.S. eastern continental shelf during the summer of 2007 (10 July – 4 August), 2012 (21 July – 13 August), and 2015 (19 June – 24 July). GOMECC-1 is the first dedicated cruise to provide a dataset of the carbonate chemistry parameters for the entire U.S. eastern continental shelf. The two GOMECC cruises cover the coastal regions starting in Galveston, TX and ending in Boston, MA (figure 1.1). The ECOA-1 cruise covers the Scotian Shelf, the GoME, the MAB, and the SAB (figure 1.1).

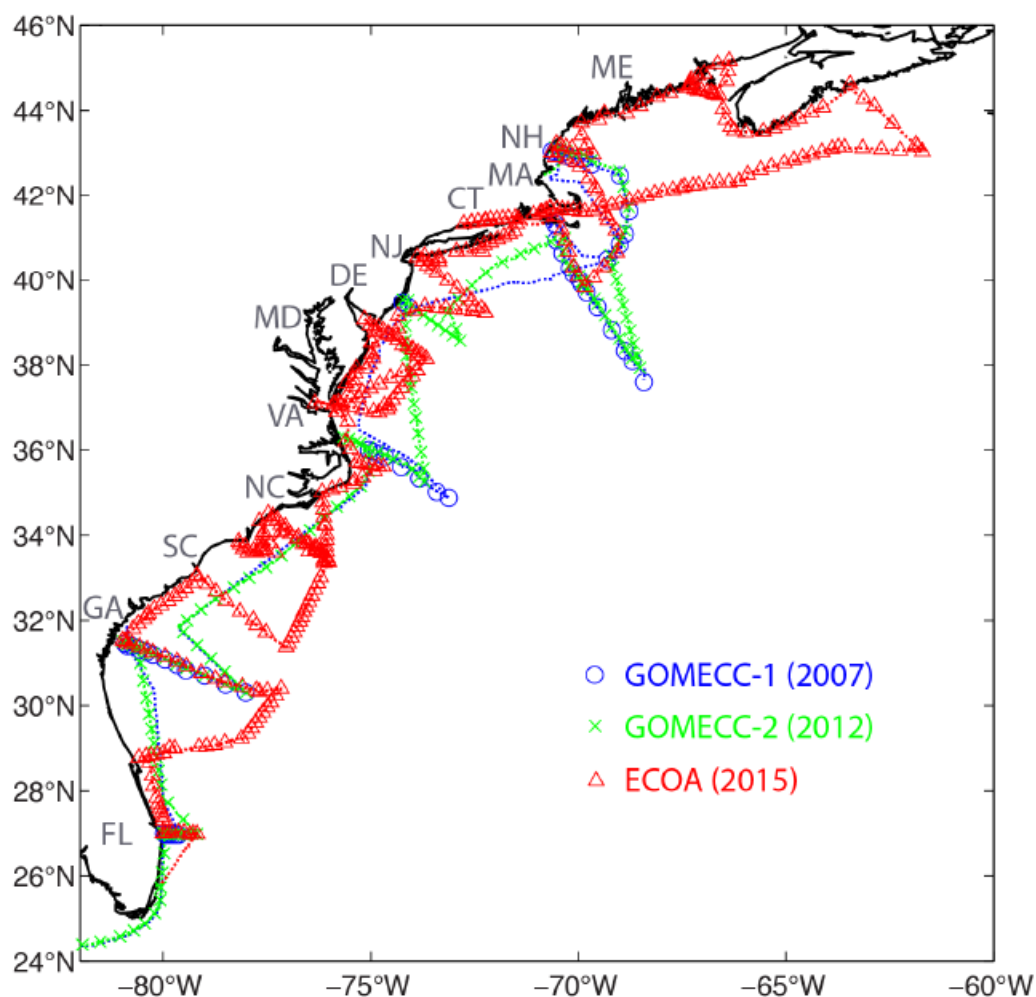


Figure 1.1 Map of the study area and cruise tracks (dashed lines) for the GOMECC-1 (blue), GOMECC-2 (green), and the ECOA-1 (red) cruises. The symbols represent the stations where CTD casts or discrete underway sampling were performed in the GOMECC-1, GOMECC-2, and ECOA-1 cruises, respectively.

Key carbonate parameters, such as DIC, TA, pH, and $f\text{CO}_2$, were measured during these cruises using state-of-the-art techniques (Wang et al., 2013; Wanninkhof et al., 2015). The overall internal consistency of the DIC-TA- $f\text{CO}_2$ measurements were examined to be excellent (Patsavas et al., 2015). Therefore, I am confident that the

measured carbonate parameters can faithfully represent the carbonate chemistry conditions at the time of water sample collection. The large-scale distributions of the carbonate chemistry parameters have been established using the GOMECC-1 and GOMECC-2 data (Wang et al., 2013; Wanninkhof et al., 2015). On top of this, my Ph.D. work focuses on temporal variations of the carbonate chemistry parameters and the comparison of the large-scale spatial distributions of carbonate chemistry parameters along the U.S. eastern continental shelf with those in other regions such as the U.S. west coast.

This dissertation attempts to study carbonate chemistry dynamics along the U.S. eastern continental shelf using shipboard measurements, satellite remote sensing data, and model outputs. The major chapters start with a short-term regional study in the central MAB. The control processes for the short-term variations of carbonate parameters in the central MAB is discussed in chapter 2. Chapter 3 focuses on understanding the decadal trends of carbonate parameters along the U.S. eastern continental shelf and the prediction of future change. The large-scale spatial distributions of carbonate parameters in the North America ocean margins and the control mechanisms are presented in chapter 4. Additionally, a study on the ocean carbonate system computation for anoxic waters using an updated CO2SYS program is presented in the appendix.

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Chapter 2

RAPID CHANGE OF ARAGONITE SATURATION STATE IN COASTAL WATERS OFFSHORE THE DELAWARE AND CHESAPEAKE BAYS¹

2.1 Abstract

The uptake of anthropogenic carbon dioxide (CO₂) from the atmosphere has resulted in a decrease in seawater aragonite saturation state (Ω_{arag}), which affects the health of carbonate-bearing organisms and the marine ecosystem. A rapid change in surface water Ω_{arag} , with an increase of up to 0.32, was observed in the central Mid-Atlantic Bight off the Delaware and Chesapeake Bays over a short period of 10 days in summer 2015. High frequency underway measurements for temperature, salinity, dissolved oxygen, oxygen to argon ratio (O₂/Ar), pH, $f\text{CO}_2$, and measurements based on discrete samples for pH, dissolved inorganic carbon (DIC) and total alkalinity (TA) are used to investigate how physical and biogeochemical processes contribute to the changes of Ω_{arag} . Quantitative analyses show that physical advection and mixing processes are the dominant forces for higher Ω_{arag} in slope waters while biological carbon removal and CO₂ degassing contribute to increased Ω_{arag} in shelf waters.

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2.2 Introduction

Use of fossil fuel has increased carbon dioxide (CO₂) uptake by the ocean and led to higher surface water CO₂ levels and acidification of seawater (Doney et al., 2009; Orr et al., 2005). Ocean acidification (OA) has received increasing attention due to its negative impact on calcifying organisms, and in broader terms, on marine ecosystems and biogeochemical processes (Feely et al., 2009; Ries et al., 2009). The saturation state of seawater with respect to carbonate mineral aragonite (Ω_{arag}) has often been used to track OA and has been widely used in coastal waters (Silverman et al., 2007; Yamamoto-Kawai et al., 2009; Friedrich et al., 2012; Wanninkhof et al., 2015). It has been recognized that Ω_{arag} affects the growth of some marine organisms that build calcium carbonate shells or skeletons. For example, coral calcification is very sensitive to small changes in seawater Ω_{arag} and the sustain growth of a normal skeleton might be terminated if seawater Ω_{arag} becomes too low (Cohen et al., 2009). Oyster larval production is correlated with Ω_{arag} (Kurihara et al., 2007; Watson et al., 2009; Barton et al., 2012), and mussel shell length is negatively affected by decreases in saturation state (Berge et al., 2006; Waldbusser et al., 2015). Therefore, it is important to monitor and understand the change in Ω_{arag} .

Analyses of Ω_{arag} , based on ocean carbonate system data collected over the past 40 years, suggest that the saturation state in the North Atlantic open-ocean surface water is decreasing at an average rate of 0.09% per year (Jiang et al., 2015). However, the difference of Ω_{arag} between two summertime ocean acidification studies along the U.S. east coast in 2007 and 2012 showed that variations in coastal surface water Ω_{arag} were 5-10 times larger than the 0.05-0.1 decreases expected from increasing anthropogenic CO₂ release into the atmosphere (Wang et al., 2013; Wanninkhof et al., 2015). Thus, in addition to documenting decadal trends, detailed studies of ocean

acidification in coastal regions are necessary to understand the role of local biogeochemical and physical processes in driving large Ω_{arag} variations.

Several studies reveal that Ω_{arag} can change rapidly in coastal areas. In the surface mixed layer, Ω_{arag} in coastal water displays much larger seasonal variations than in open-ocean waters (Cantoni et al., 2012; Jiang et al., 2015). Freshwater input and biological carbon uptake are two of the controlling factors over the seasonal variations of Ω_{arag} in coastal surface water (Yamamoto-Kawai et al., 2015). In addition, upwelling events along the continental shelf, which bring the low saturated or undersaturated bottom waters to the mixed layer, may dramatically decrease Ω_{arag} in surface water (Feely et al., 2008; Mathis et al., 2012). Coastal eutrophication (intense algal blooms in euphotic zone and followed by organic matter remineralization and oxygen consumption in bottom-waters and sediments) has also been identified as a major contributing factor to increased Ω_{arag} and pH in surface waters, while decreasing values in subsurface waters (Borges and Gypens, 2010; Cai et al., 2011). Although previous studies have shown various controlling mechanisms in different coastal areas accompanied by notable spatial and temporal variation of Ω_{arag} , there is a lack of short-term studies on the variability of OA in coastal waters in the Mid-Atlantic Bight (MAB).

Our study area, the central MAB, is an important habitat for marine organisms, such as the Atlantic blue crab (*Callinectes sapidus*), Atlantic surf clam (*Spisula solidissima*), and oyster (*Crassostrea virginica*) (Baker and Mann, 1994; Epifanio and Garvine, 2001; Munroe et al., 2013). Transport and mixing processes, as well as biological production and respiration, have been shown to affect temporal and spatial variability of marine carbonate properties in the MAB (Bates and Hansell, 1999;

DeGrandpre et al., 2002). Because of a limited number of comprehensive studies, the short-term variability of seawater Ω_{arag} in the MAB is not known. In this paper, we identify and quantify the short-term effects of changes in sea surface temperature (SST), sea surface salinity (SSS), percent saturation of dissolved oxygen (DO%), pH, and $f\text{CO}_2$ on Ω_{arag} in MAB surface water between two surveys within 10 days.

2.3 Methods

2.3.1 Sample collection and analysis

The study area in the central MAB was surveyed twice during the NOAA East Coast Ocean Acidification (ECO_A) cruise: 1-3 July 2015 (leg 1), and 9-11 July 2015 (leg 2). While ECO_A surveyed carbonate chemistry and net biological production in the entire U.S. east coast waters over a period of 34 days in summer 2015, the central MAB is the only area that was measured twice during the two legs. Underway samples for oxygen, $f\text{CO}_2$ and pH were taken from a scientific seawater supply line at a depth of ~5 meters along the cruise track (figure 2.1a). Discrete surface bottle samples for dissolved inorganic carbon (DIC), total alkalinity (TA), and pH were taken from the seawater supply line around every 3 hours. Samples from Niskin bottles in the CTD/Rosette system were taken to explore the depth distribution along transects in the MAB.

Underway dissolved oxygen was measured by an optode dissolved oxygen sensor (Aanderaa 4531) at a frequency of 30 s. The oxygen sensor was located at a flow-through cell in the chemistry laboratory. The resolution and accuracy of the raw dissolved oxygen data are better than 1 and 8 mM ($\approx 3\%$), respectively. The continuous

oxygen concentration data were calibrated with measurements of discrete bottle water samples using the Winkler titration method.

In situ continuous oxygen to argon ratio (O_2/Ar) was measured by an Equilibrator Inlet Mass Spectrometry (EIMS), with an instrument accuracy and precision of 0.3% and 0.2%, respectively (Cassar et al., 2009). Seawater was pumped from the underway system into a gas-permeable membrane contraction cartridge (MicroModule, Liqui-Cel Membrane) with a constant flow rate of 100 mL/min. Equilibrated gasses were diffused into a fused-silica capillary that connects to a quadrupole mass spectrometer (Pfeiffer vacuum) for measurements of ion current intensity and ratio at a frequency of once per second. Calibrations were conducted automatically every 3 h for 20 min by sampling the ambient air, which has a stable O_2/Ar ratio.

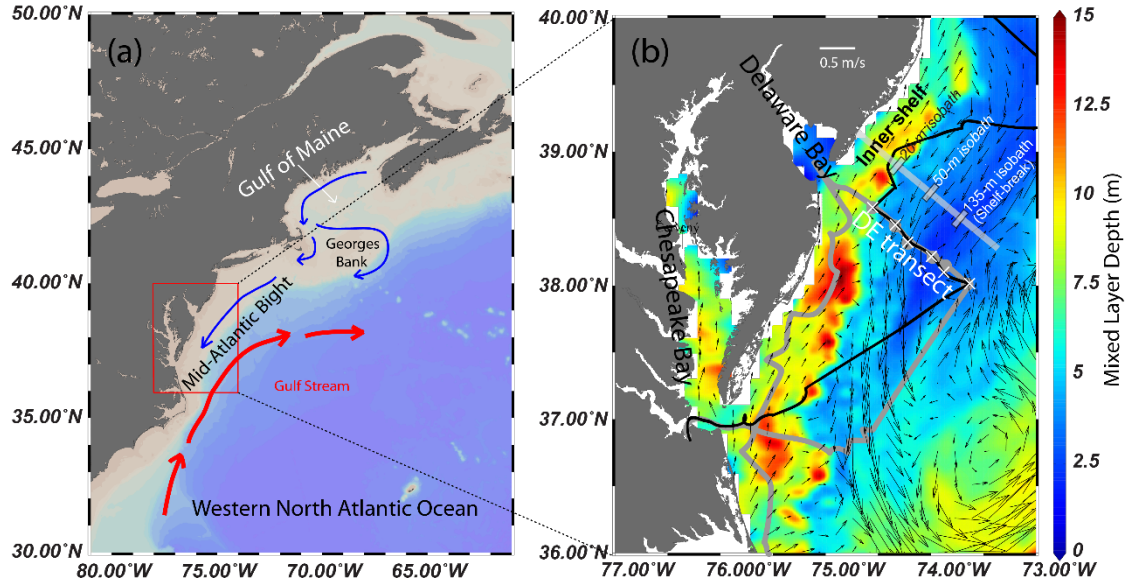


Figure 2.1: Map of the study region and locations of hydrographic stations. (a) Schematic drawing of the southward current from the Gulf of Maine (blue) and northward Gulf Stream (red) in the western North Atlantic Ocean (modified from Sutcliffe Jr. et al. (1976) and Ezer et al. (2013)). (b) Spatial variation of average current velocity and MLD between two legs in the central MAB using daily data generated from HYCOM. The arrows represent the direction and relative strength of surface current. The color scale indicates the average MLD (July 1-11, 2015). The black line is the leg 1 cruise track, and the gray line is the leg 2 cruise track. Discrete measurements of O_2 , pH, DIC, and TA are from the stations along the Delaware transect during leg 1 (white crosses) and leg 2 (gray dots). The study region is divided into inner, middle, outer shelf, and upper slope zones delineated by 20-, 50- and 135-m isobaths.

Seawater fCO_2 was measured by an autonomous underway fCO_2 system every 140 s following Pierrot et al. (2009). The CO_2 detector (Licor-6262) was located in the chemistry laboratory and was calibrated every 3 h with four CO_2 standards. The fugacity of CO_2 (μatm) in seawater at SST and 100% humidity is reported herein. The resolution and accuracy of seawater fCO_2 are 0.01 and 2 μatm , respectively. SST was measured by a remote temperature sensor, Sea-Bird Electronics (SBE) 38, which was

located at the bow intake before the seawater pump. The manufacturer-reported accuracy and precision for SST are 0.001 and 0.00038C, respectively. SSS was measured by a SBE 45, which was located in the chemistry laboratory near the CO₂ system, with reported accuracy and precision of 0.005 and 0.0002 practical salinity units.

Spectrophotometric pH_T (on the total proton concentration scale) measurements from discrete bottle samples were performed on board using an Agilent 8453 UV-visible spectroscopy system (Clayton and Byrne, 1993) and purified *m*-cresol purple dye obtained from R. Byrne's laboratory (Liu et al., 2011). Seawater in CTD-mounted Niskin bottles (10 L) was subsampled into narrow neck 125 mL borosilicate glass bottles. All samples were analyzed at 25°C within 2 h of collection. These pH values are reported on the total scale with a precision of 0.0005 based on our duplicate measurements. The estimated accuracy of spectrophotometric pH is better than 0.002 (Dickson et al., 2007; Liu et al., 2011).

The pH of underway seawater was also measured using a Honeywell Durafet[®] III pH electrode. The Durafet pH sensor was located in a flow-through cell, which has a volume of approximately 500 mL that was connected to the ship's underway water supply line. The frequency of this measurement was 30 s. The raw output of pH was presented on the NBS scale at temperatures in the flow-through cell without a calibration. Spectrophotometric pH_T analyses of discrete samples were used to calibrate the raw Durafet data following:

$$\text{Corrected pH}_T = \text{Measured pH}_T + \Delta\text{pH}, \quad (1)$$

where ΔpH is the difference between spectrophotometric pH (total scale) and the Durafet pH (NBS scale) at the temperature of seawater in the flow-through cell. This

correction is determined using an offset calculated from a linear regression of ΔpH and temperature ($r = 0.93$). Then this corrected pH_T was converted to pH_T at the in situ temperature using CO2SYS (van Heuven et al., 2011), with dissociation constants of carbonic acid, K_1 and K_2 , determined by Mehrbach et al. (1973) as refit by Dickson and Millero (1987). After the conversion from the NBS scale to total scale and the correction for temperature, underway pH at SST has an accuracy of better than 0.005.

The discrete profile and discrete surface underway DIC samples were analyzed on board using a coulometer (UIC Inc.) coupled with a DIC extractor inlet system following the methods described in Johnson et al. (1993). The system was calibrated with aliquots of pure CO_2 gas approximately twice per day with the change of coulometer cell solution. It was checked twice per day against certified reference material (CRM, provided by A. G. Dickson from Scripps Institution of Oceanography) and all values are adjusted to the cruise average of the CRMs. The overall accuracy and precision of DIC measurements are $2 \mu\text{mol kg}^{-1}$.

TA measurements were conducted on board using an automated titrator (AS-ALK2, Apollo SciTech) with a ROSSTM combination electrode 8102 (Thermo Fisher Scientific) at 22°C following Cai et al. (2010). Three pH buffers (pH = 4.01, 7.00, and 10.01) were used daily to calibrate the electrode. The concentration of hydrochloric acid was determined by titration of CRM. Briefly, hydrochloric acid was added to each 25 mL water sample to decrease its pH first to about 3.8 and then aliquots of hydrochloric acid were added stepwise until the titration reached a pH of less than 3.0. The titration end-point was then determined by a Gran titration method (Grasshoff et al., 1999). The TA measurement was repeated at least twice for each water bottle

sample to achieve a precision of better than $2 \mu\text{mol kg}^{-1}$. The overall accuracy of TA analysis is $2 \mu\text{mol kg}^{-1}$.

2.3.2 Estimation of mixed layer depths

To verify the mixed layer depth (MLD) produced by the HYbrid Coordinate Ocean Model (HYCOM), we calculated MLD using the conductivity, temperature, and depth (CTD) profiles from 12 stations for the two occupations of the Delaware transect. The MLD was computed based on a constant potential density difference criterion of 0.1 kg m^{-3} (Skylvingstad et al., 1999). The MLD calculated from these two different approaches agree fairly well (table 2.1, table 2.2). Note that the average MLD produced by HYCOM during July 1-11, 2015 was used in the calculation of $\Delta\text{DIC}_{\text{biol}}$ and $\Delta\text{DIC}_{\text{air-sea}}$.

Table 2.1: MLD calculated from CTD profiles with a constant potential density difference criterion.

Leg	Station	Latitude	Longitude	MLD_CTD (m)
1	62	38.56°N	74.57°W	7.1
2	86	38.59°N	74.57°W	6.1
1	63	38.45°N	74.35°W	8.6
2	84	38.45°N	74.34°W	4.5
1	64	38.32°N	74.23°W	8.1
2	83	38.32°N	74.24°W	4.5
1	65	38.22°N	74.00°W	6.6
2	81	38.22°N	73.98°W	4.0
1	66	38.08°N	73.88°W	5.0
2	80	38.15°N	73.87°W	4.0
1	67	38.00°N	73.66°W	8.1
2	78	38.01°N	73.66°W	8.1

Table 2.2: Comparison of MLD produced from two different approaches at the Delaware transect. *This column shows the average MLD from July 1-11, 2015, while the CTD profiles only provide MLD at July 2nd and July 11th, 2015.

Longitude	Mean_MLD_CTD (m)	Mean_MLD_HYCOM (m)*
74.57°W	6.6	7.0
74.35°W	6.6	4.2
74.24°W	6.3	4.2
73.99°W	5.3	2.2
73.88°W	4.5	2.8
73.66°W	8.1	3.7

2.3.3 Calculations of net community production (NCP)

In order to better understand biological perturbations on the carbonate system, we estimate surface water NCP, or the difference between gross primary production and community respiration, using the methods of Cassar et al. (2011). Owing to the similar physical characterizations of oxygen and argon, the ratio O_2/Ar can reflect the biological production that leads to oversaturation of O_2 with respect to air-water equilibrium (with temperature and air bubble influences removed). Biological oxygen supersaturation can be calculated as:

$$\Delta(O_2/Ar) = \frac{(O_2/Ar)_{water}}{(O_2/Ar)_{air}} - 1, \quad (2)$$

where $(O_2/Ar)_{water}$ and $(O_2/Ar)_{air}$ are O_2/Ar ratios in seawater and air, respectively.

We estimated NCP (in $\text{mmol } O_2 \text{ m}^{-2} \text{ d}^{-1}$) using (Cassar et al., 2011):

$$NCP = k_{O_2} \cdot [O_2]_{sat} \cdot \Delta(O_2/Ar), \quad (3)$$

where $[O_2]_{sat}$ is the saturated concentration of oxygen in seawater that is calculated from temperature and salinity (Garcia and Gordon, 1992), and k_{O_2} is the gas exchange velocity calculated from the best-fit model for low and intermediate wind speed (Wanninkhof et al., 2009) using 10-day averaged wind speed (NOAA national data buoy center, www.ndbc.noaa.gov/) and normalizing height of measurement to 10 m above sea surface:

$$k = (3 + 0.1U + 0.064 U^2 + 0.011 U^3) \times \left(\frac{Sc}{Sc_0}\right)^n, \quad (4)$$

where U represents the average wind speed at 10-m height; the Schmidt numbers (Sc) is calculated at ambient temperatures and normalized to a Schmidt number Sc_0 at nominally 20°C (Jähne et al., 1987; Wanninkhof, 1992]; the exponent (n) equals -2/3 when $U \leq 4.2 \text{ m s}^{-1}$ or -1/2 when $U > 4.2 \text{ m s}^{-1}$ (Wanninkhof, 1992). Considering the O_2/Ar signal reflects the accumulated biological effect, NCP derived from O_2/Ar

represents the condition of a period prior to the start of measurement (Hamme et al., 2012). Thus, the 10-day average wind speed prior to measurements is used for gas transfer velocity and NCP calculations.

The error in NCP is estimated to be 1-2 mmol m⁻² d⁻¹ (Jonsson et al., 2013). The calculated NCP using equation (3) assumes a steady state, i.e., biological oxygen production balances gas exchange, and yields a constant NCP over the oxygen residence time in the mixed layer (Cassar et al., 2011; Hamme et al., 2012). For MLD less than 10 m, modeling results show that the use of equation (3) for O₂/Ar-NCP leads to an underestimation of ~5.6 mmol m⁻² d⁻¹ in NCP when the values vary between 0 and 10 mmol m⁻² d⁻¹ and an overestimation of ~0.1 mmol m⁻² d⁻¹ in NCP when the values vary between 10 and 25 mmol m⁻² d⁻¹ (Jonsson et al., 2013). However, the associated errors due to violations of assumptions are likely smaller than the modeling results of Jonsson et al. (2013) as water was strongly stratified with only small variations in the MLD.

2.3.4 Calculation of net air-sea CO₂ flux

Air-sea CO₂ flux affects carbon mass balance in the ocean (Takahashi et al., 2002; Olsen et al., 2003). We calculated air-sea CO₂ flux (F_{CO_2} , mmol CO₂ m⁻² d⁻¹) from underway fCO_2 :

$$F_{CO_2} = k_{CO_2} \times [CO_2]_s \times (fCO_{2\ sea} - fCO_{2\ air}), \quad (5)$$

where k_{CO_2} is the gas transfer velocity for CO₂ calculated from the Wanninkhof et al. (2009) model using the same 10-day averaged wind speed as calculating NCP in the previous section; $[CO_2]_s$ is the solubility of CO₂ estimated from temperature and salinity (Weiss, 1974); $fCO_{2\ sea}$ and $fCO_{2\ air}$ are fCO_2 in seawater and air, respectively.

The uncertainty in F_{CO_2} mainly comes from uncertainties in the wind speed and the coefficient between gas transfer velocity and wind speed (Wanninkhof et al., 2009). The uncertainty from wind speed has a relatively small effect in the MAB (DeGrandpre et al., 2002). The average atmosphere fCO_2 value along the Delaware transect has been used rather than the marine boundary layer values from Globalview reference to reduce the uncertainty in the calculated air-sea CO_2 flux.

2.3.5 Interpolating DIC and Ω_{arag} at 30-second interval

Ω_{arag} is defined as the ratio of the concentration product of calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}) to the stoichiometric solubility product of the aragonite mineral (K_{sp}), that is $\Omega_{arag} = [CO_3^{2-}][Ca^{2+}]/K_{sp}$. The concentration of carbonate ions can be calculated from any pairs of pH-DIC, pH-TA, and DIC-TA in CO2SYS (van Heuven et al., 2011). The concentration of calcium ions is determined from salinity using calcium/chlorinity ratio given in Riley and Tongudai (1967). K_{sp} varies with temperature and salinity and is determined from equations of Mucci (1983).

As discrete water sample data for pH, DIC, and TA are only available from a few hydrographic stations, and limited number of samples collected from the underway water supply line, to examine Ω_{arag} changes between the two legs in the context of available high spatial resolution physical and biogeochemical information, we generate high-resolution DIC and Ω_{arag} datasets using a combination of the calibrated underway pH and SSS-derived TA. We first developed a relationship between SSS and discrete TA measured by titration method. Then, surface water DIC and Ω_{arag} at a frequency of 30 seconds were calculated in CO2SYS (van Heuven et al., 2011) using the underway pH and calculated TA.

2.3.6 DIC mass balance in the surface mixed layer

Net biological production-respiration and air-sea CO₂ exchange both affect the sea surface mixed layer DIC mass balance, and thus the Ω_{arag} . Here we calculate ΔDIC_{biol} , which represents the change in DIC induced by biological activity (i.e., biological DIC utilization/production, in mmol m⁻³) from the O₂/Ar-based NCP (mmol O₂ m⁻² d⁻¹), mixed layer depth (MLD, m), the 10-day time interval between the two legs ($\Delta Date$, d), and the Redfield stoichiometric ratio of 138/106 for oxygen to carbon (Redfield et al., 1963):

$$\Delta DIC_{\text{biol}} = NCP \times \Delta Date / MLD / (138/106) \quad (6)$$

where NCP is calculated from the measurement of O₂/Ar during leg 2 representing the conditions over the residence time of O₂, which is approximately 10 days, prior to the measurement (Hamme et al., 2012). MLD is averaged over 10 days based on daily data generated by HYbrid Coordinate Ocean Model (HYCOM; <https://hycom.org/>). Note that the oxygen to carbon ratio can vary. For comparison, we also calculate ΔDIC_{biol} with an oxygen to carbon ratio of 170/117 for phytoplankton growth (figure 2.2) (Anderson, 1995; Hedges et al., 2002; Emerson et al., 2008).

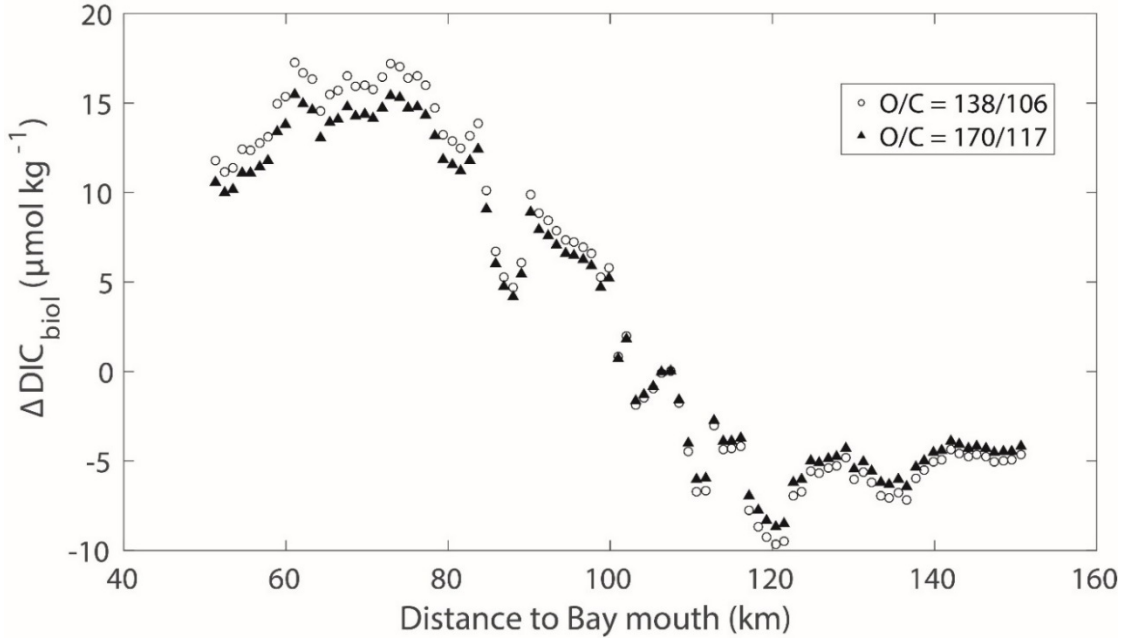


Figure 2.2: The comparison of calculated ΔDIC_{biol} with an oxygen to carbon ratio of 138/106 and 170/117, respectively, for phytoplankton growth. Note that the small variation in oxygen to carbon ratio has a minor effect on the analyses.

We calculate $\Delta DIC_{air-sea}$, which represents the DIC change caused by air-sea CO_2 flux over time in the surface mixed layer in the following manner:

$$\Delta DIC_{air-sea} = F_{CO_2} \times \Delta Date / MLD \quad (7)$$

where F_{CO_2} is calculated from leg 2 fCO_2 and MLD is averaged over 10 days based on daily data from the HYCOM model output.

The physically driven DIC change is calculated by balancing the total DIC change (ΔDIC) with the biologically driven DIC change (ΔDIC_{biol}), and air-sea CO_2 flux driven DIC change ($\Delta DIC_{air-sea}$):

$$\Delta DIC_{phys} = \Delta DIC - \Delta DIC_{biol} - \Delta DIC_{air-sea}. \quad (8)$$

2.3.7 Comparison of thermosalinograph and CTD salinity

A relationship between sea surface salinity (SSS) and discrete TA data measured by titration method was developed to estimate TA at high resolution. The SSS data measured by thermosalinograph (TSG) and CTD were compared to check the consistency before applying the empirical equation. The differences of SSS between TSG and CTD measurements are less than 0.04 at all station in the Delaware transect except at station 80, which has a difference of 0.08 (table 2.3). The average difference is 0.01, which equals to an average difference of 0.54 in TA estimation by using the empirical SSS-TA equation.

Table 2.3: Comparison of SSS measured by TSG and CTD.

Leg	Station	Latitude	Longitude	SSS_TSG	SSS_CTD	Difference
1	62	38.56°N	74.57°W	32.421	32.405	0.017
1	63	38.45°N	74.35°W	32.494	32.477	0.017
1	64	38.32°N	74.23°W	32.921	32.898	0.023
1	65	38.22°N	74.00°W	33.460	33.460	0.000
1	66	38.08°N	73.88°W	33.638	33.642	-0.005
1	67	38.00°N	73.66°W	34.296	34.312	-0.015
2	78	38.01°N	73.66°W	35.393	35.409	-0.015
2	80	38.15°N	73.87°W	33.994	33.914	0.080
2	81	38.22°N	73.98°W	33.474	33.513	-0.039
2	83	38.32°N	74.24°W	32.409	32.383	0.026
2	84	38.45°N	74.34°W	31.992	31.956	0.036
2	86	38.59°N	74.57°W	31.719	31.699	0.020

2.3.8 DIC normalization

To provide a first order comparison of the biogeochemical and physical (non-conservative mixing) influences across the shelf waters, we normalized DIC and TA to

a constant salinity to remove the DIC and TA variation across the shelf associated with the variation of salinity between two end-members. The essence of normalization is that the normalized conservative parameter (here nTA) should be nearly invariant with salinity. This is confirmed in our field data (figure 3.3). In this study, TA values were normalized to a value at salinity 33 with a nearshore end-member of 2103.7 ($TA^{S=end(1)}$) at salinity 31 and an offshore end-member of 2376.1 $\mu\text{mol kg}^{-1}$ ($TA^{S=end(2)}$) at salinity 36 (i.e., $nTA = 2212.0 \mu\text{mol kg}^{-1}$ at the reference salinity 33) following an approach similar to Friis et al. (2003):

$$\frac{nX - X^{S=meas}}{S^{ref} - S^{meas}} = \frac{X^{S=end(2)} - X^{S=end(1)}}{S^{end(2)} - S^{end(1)}}. \quad (9)$$

Therefore,

$$nX = \frac{X^{S=end(2)} - X^{S=end(1)}}{S^{end(2)} - S^{end(1)}} \times (S^{ref} - S^{meas}) + X^{S=meas}, \quad (10)$$

where nX and X^{meas} represent the normalized (at the reference salinity) and measured values (at any salinity) for a property (here TA and DIC). S^{meas} represents the measured in situ salinity. S^{ref} is the reference salinity. The average salinity of the discrete bottle samples, which equals to 33, is used as the reference salinity.

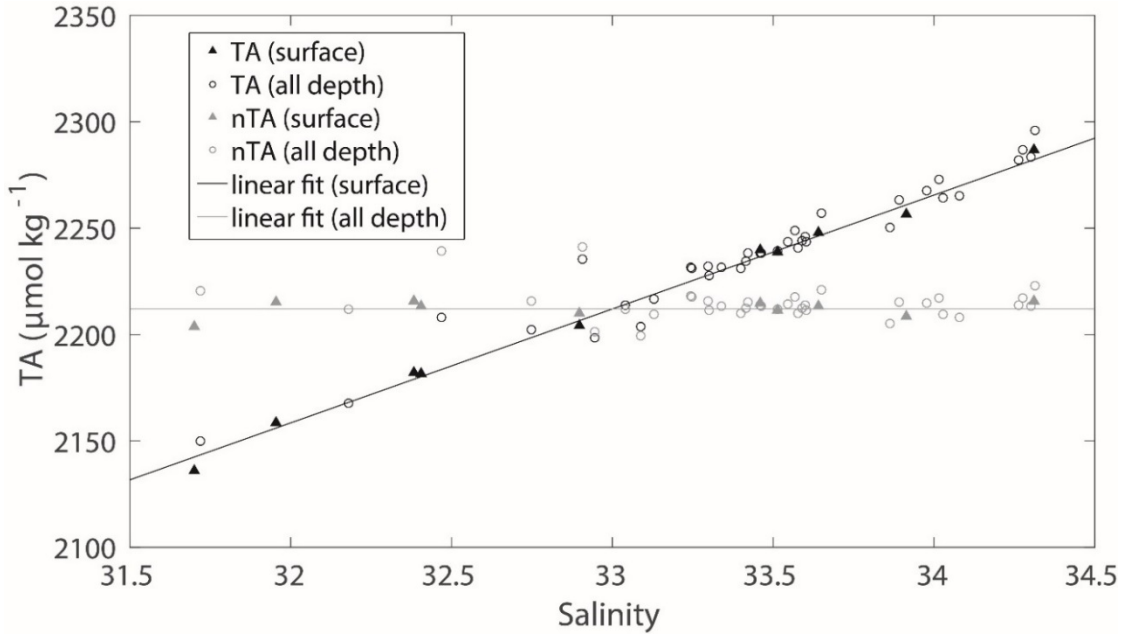


Figure 2.3: The salinity-TA relationship and normalization of TA to salinity 33. The $n\text{TA}$ is nearly invariant with salinity, indicating that this normalization approach is appropriate.

To examine the non-conservative behavior of DIC, we normalized DIC data in both leg 1 and leg 2 to the average salinity of the discrete seawater samples from the Delaware transect using the linear relationship between DIC and salinity in leg 1 following the established method presented in Equations 9 and 10. Specifically, DIC was normalized with two end-members of 1950.4 and 2067.4 $\mu\text{mol kg}^{-1}$ when salinities are 31 and 36, respectively.

2.4 Results

2.4.1 Hydrographic variability

The MAB includes the coastal area near the Chesapeake Bay and the Delaware Bay, two large estuaries on the U.S. east coast that interact with their adjacent shelf

area. In the middle shelf region, the MAB also receives a cold alongshore current that originates from the Labrador Sea and passes through the Gulf of Maine (figure 2.1; Fairbanks, 1982; Chapman and Beardsley, 1989; Mountain, 2003). Furthermore, the offshore region of the MAB is under the influence of the Gulf Stream, which affects the surface distribution of temperature and salinity along its route (figure 1b; Bumpus, 1973; Richardson, 1980; Pickart and Smethie, 1993).

The mean MLD and surface flow conditions in the MAB are generated by the HYCOM. During the study period in early July, the water column was strongly stratified with a surface mixed layer thickness of less than 10 meters, on the middle shelf, outer shelf, and upper slope (figure 2.1b). We verify the model-generated MLD from CTD profiles using a constant potential density difference criterion of 0.1 kg m^{-3} (Skylvingstad et al., 1999). These depths are consistent with the typical summer MLDs (~ 3.5 to 10 m) for MAB shelf waters (Signorini et al., 2013). They also agree with MLDs ranging from 5 to 15 m over the entire MAB shelf during spring and summer (Chen and He, 2015). Inner shelf water was well mixed and showed a northward surface flow (figure 2.1b). The middle and outer shelf regions were dominated by a strong southward surface flow (figure 2.1b). The upper slope region was delineated by 135 m isobath (shelf break) and extended eastward to the deeper ocean area. A strong northward surface flow was found on the upper slope.

During leg 1, SST in the coastal water near the Delaware Bay was almost constant at 23°C . Water became warmer further south, reaching up to 25°C near the Chesapeake Bay mouth (figure 2.4a). Cross-shelf salinity gradients were strong, due to freshwater discharge from the two large estuaries (figure 2.4b). A large change of SSS was observed at the Delaware transect, where the two legs overlapped (figure 2.4b).

SSS slightly decreased in the middle and outer shelf zones but increased up to 1.1 in the upper slope region (figure 2.4b).

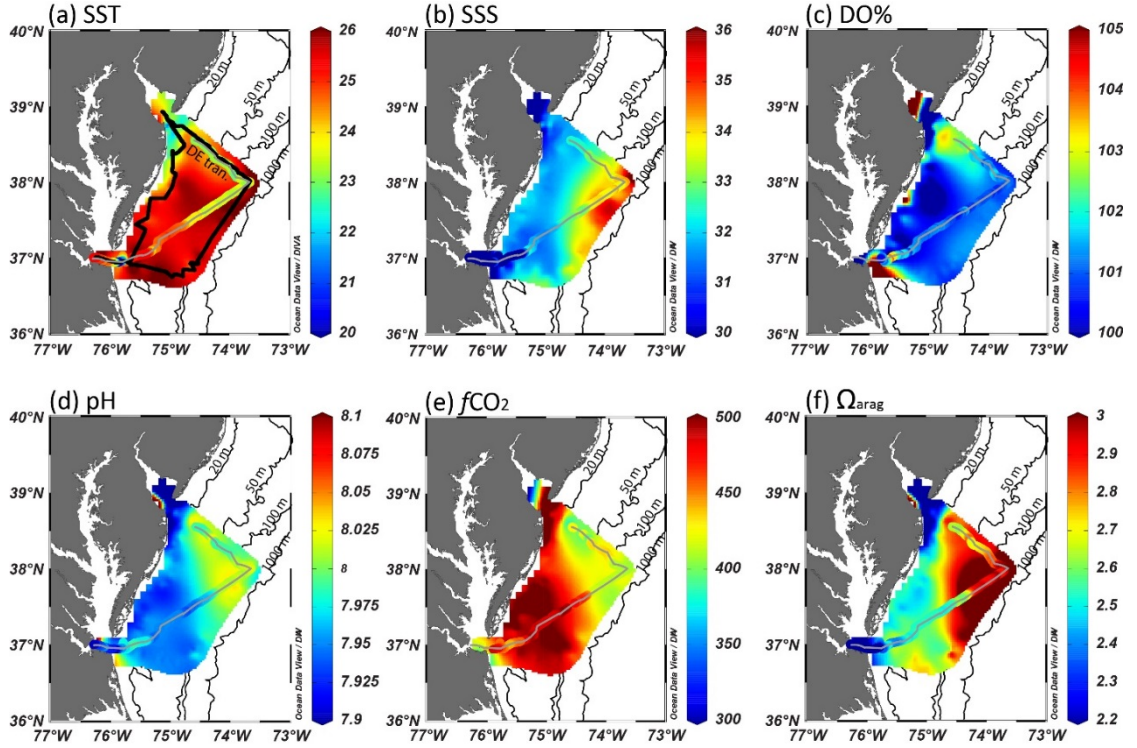


Figure 2.4: Distributions of physical and biogeochemical parameters in the central MAB. (a-f, from left to right) Distributions of SST, SSS, DO%, pH, $f\text{CO}_2$, pH, and Ω_{arag} for leg 1 (line) and leg 2 (interpolated as background using Ocean Data View with a Data-Interpolating Variational Analysis spatial gridding method) at MAB. Gray line indicates the cruise track of leg 1. The thick black line in panel (a) represents the cruise track of leg 2. The 20-, 50-, 100-, 1000-m isobaths are shown with black contour lines.

SST increased from leg 1 to leg 2 concurrently with an increase in ambient air temperature. In leg 2, SSS decreased in the middle and outer shelf region, due to dilution by freshwater from Delaware Bay as the coastal current shows a freshwater signature (Le Vine et al., 1998). The large increase in river discharge in the upper

Delaware River prior to, and during, the 10-day period of our study suggests that increased riverine input contributes to the decrease in salinity (figure 2.5). Another source of low salinity water to the middle shelf is the inflow of water from the north. Compared to leg 1, the warmer and more saline water in the upper slope region during leg 2 is a result of interaction with Gulf Stream water (Bane et al., 1988; Lee and Atkinson, 1983).

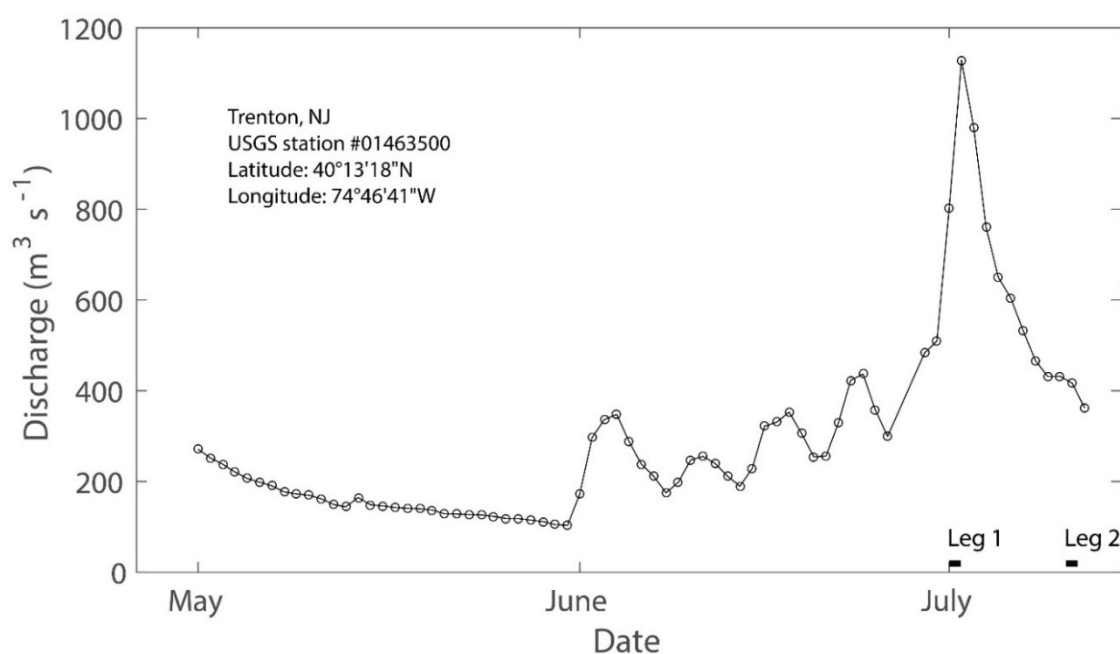


Figure 2.5: Daily Delaware River discharge rate at Trenton, New Jersey from May 1st to July 12th in 2015. The dates of leg 1 and leg 2 are marked as thick black lines.

2.4.2 DO%, pH, $f\text{CO}_2$, NCP, and FCO_2 distribution and variation

In leg 1, high DO% was observed on the inner shelf region near the Chesapeake Bay (figure 2.4c). Along the Delaware transect, DO% decreased from 103.4% on the middle shelf to 100.7% on the upper slope. Relatively low pH values

occurred on the inner shelf near the Delaware Bay and the inner and middle shelf region near the Chesapeake Bay (figure 2.4d). Higher pH values that ranged between 8.01 and 8.05 occurred on the middle shelf, outer shelf, and upper slope near the Delaware Bay (figure 2.4d). Coastal water $f\text{CO}_2$ ranged from 394 to 501 μatm , and was in general supersaturated with respect to atmospheric CO_2 . The pH variability closely reflected $f\text{CO}_2$, with pH decreasing as $f\text{CO}_2$ increased (figure 2.4d, 2.4e).

In leg 2 the overall DO%, pH, and $f\text{CO}_2$ offshore patterns were similar to leg 1 (figure 2.4). There were differences, however, in the measured values between the two legs. DO% increased on the inner shelf near the Chesapeake Bay from leg 1 to leg 2, but still decreased offshore (figure 2.4c). Note that the behavior of $\Delta(\text{O}_2/\text{Ar})$ (figure 2.6a) was similar to that of DO% in both legs, generally decreasing away from the mouth of Delaware Bay. There was a pH decrease on the inner shelf near the Chesapeake Bay from leg 1 to leg 2, with a concurrent $f\text{CO}_2$ increase (figure 2.4d, 2.4e).

Along the Delaware transect, NCP of leg 2 decreased from the middle shelf to the upper slope (15.9 to -3.6 $\text{mmol m}^{-2} \text{d}^{-1}$; figure 2.6b). NCP is positive on the middle shelf and negative on the upper slope. The transition from positive to negative NCP occurred on the outer shelf (figure 2.6b). Applying an overall uncertainty of 20% for NCP (Jonsson et al., 2013; Martin et al., 2013), the resulted uncertainty in $\Delta\text{DIC}_{\text{biol}}$ is 2.9 $\mu\text{mol kg}^{-1}$, corresponding to an uncertainty of 0.03 in $\Delta\Omega_{\text{arag}}$.

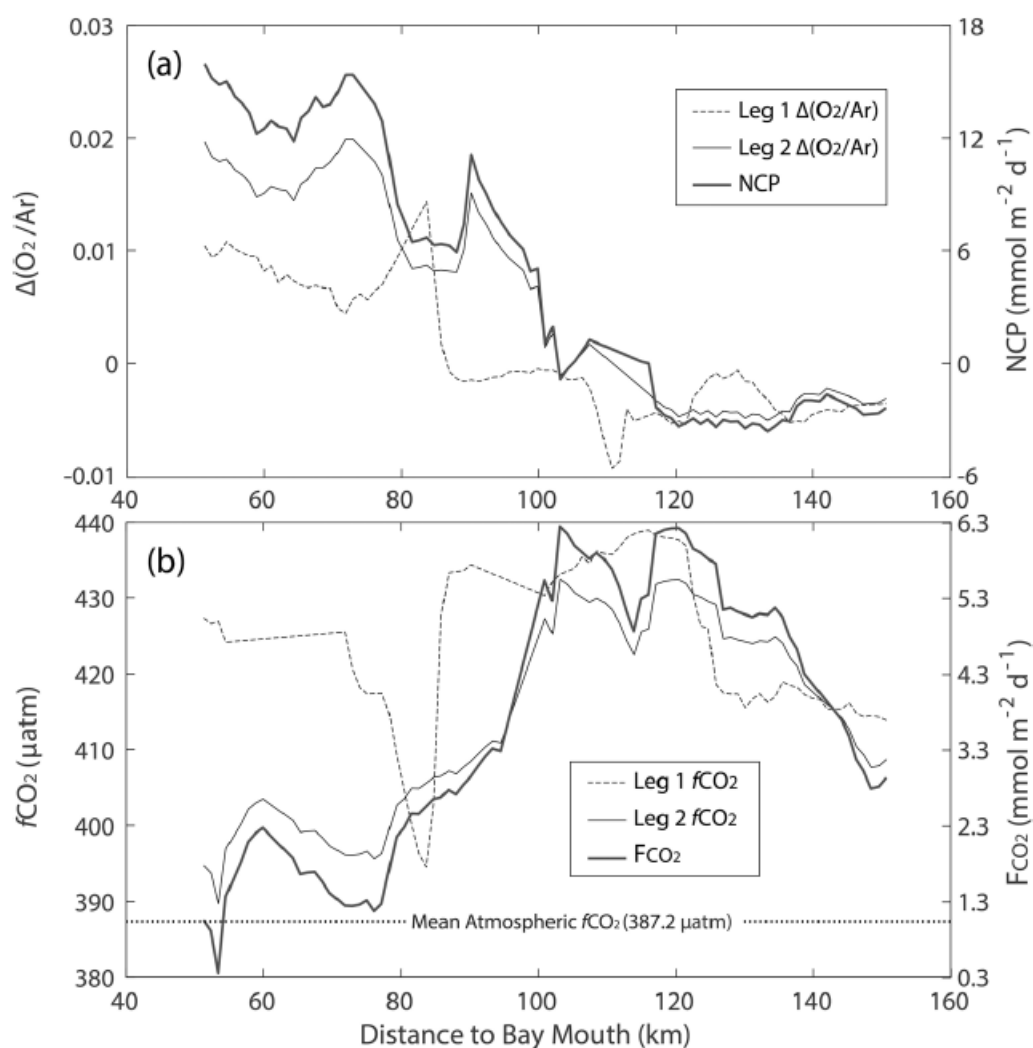


Figure 2.6: The variation of $\Delta(\text{O}_2/\text{Ar})$ and NCP with distance to the Delaware Bay mouth along the Delaware transect (a) and the variation of $f\text{CO}_2$ in two legs and the average F_{CO_2} with distance to the Delaware Bay mouth (b). The horizontal dashed line represents the mean in situ atmospheric $f\text{CO}_2$ during the study period.

F_{CO_2} of leg 2 ranged from 0.4 to 6.2 $\text{mmol m}^{-2} \text{d}^{-1}$, with the highest value found on the outer shelf where community respiration increased. The lowest F_{CO_2} value was on the middle shelf where net biological production increased (spike in O_2/Ar ; figure

2.6a). Using an uncertainty of 2 μatm for seawater $f\text{CO}_2$ (Pierrot et al., 2009) and an uncertainty of $\sim 15\%$ for gas transfer velocity as a result of parameterization difference, the uncertainty in F_{CO_2} is estimated to be $0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$, corresponding to uncertainties of $2.1 \text{ } \mu\text{mol kg}^{-1}$ in $\Delta\text{DIC}_{\text{air-sea}}$ and 0.02 in Ω_{arag} .

2.4.3 TA, DIC, and Ω_{arag} distribution and variation

The measured TA and SSS from discrete bottle samples follow a linear relationship (figure 3.3):

$$\text{TA} = (54.49 \pm 1.39) \times \text{Salinity} + (414.19 \pm 45.76). \quad (11)$$

This linear fit has a root mean square error of $3 \text{ } \mu\text{mol kg}^{-1}$ ($n = 10$). The coefficient of determination r^2 of this fit is 0.99 and the residual values between observed and calculated TA range from -4 to $5 \text{ } \mu\text{mol kg}^{-1}$. The average difference between SSS measured by the thermosalinograph and CTD, which are applied to underway and discrete samples, respectively, is less than 0.1 salinity units (see Methods).

We assessed the uncertainties in the calculated high-resolution DIC and Ω_{arag} data. For leg 2, the average difference between the calculated DIC and the measured DIC is $2 \text{ } \mu\text{mol kg}^{-1}$ whereas the average difference is as large as $8 \text{ } \mu\text{mol kg}^{-1}$ in leg 1. The latter difference is not insignificant and we have not yet identified the source of error. For the purpose of this work, we adjust the Durafet pH to eliminate the average DIC differences between the calculated and measured DIC for leg 2. As a result, the final Ω_{arag} data calculated from underway measurements agree well with those that are calculated using spectrophotometric pH and titration TA data from discrete seawater sample measurements (figure 2.7).

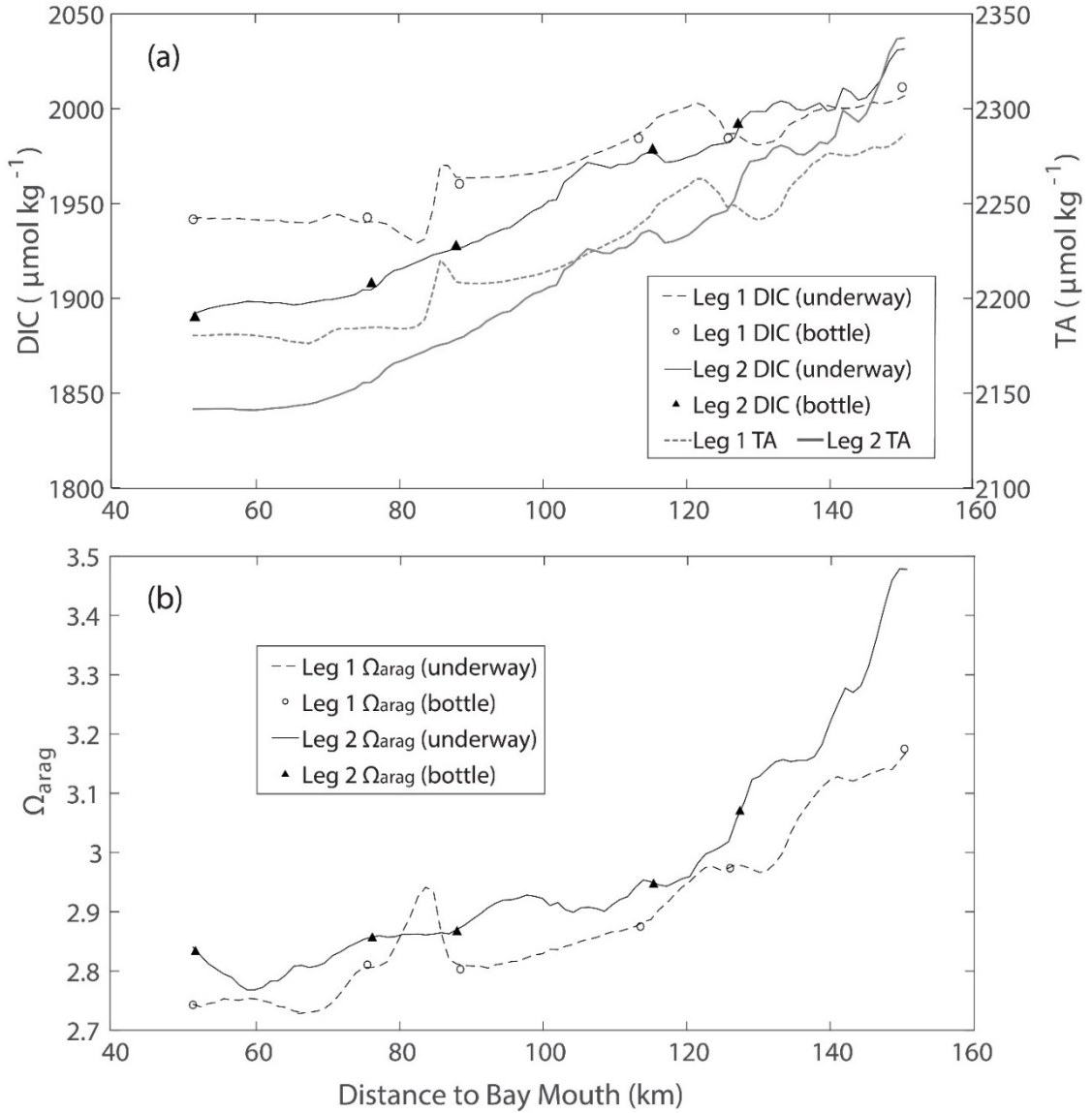


Figure 2.7: Distributions of DIC, TA, and Ω_{arag} along the Delaware transect. (a) Distributions of DIC and TA along the Delaware transect with the distance to the Delaware Bay Mouth and comparison of the calculated DIC using continuous underway data of TA and pH with the calculated DIC from discrete bottle sample data. The underway pH data were adjusted to eliminate a small difference between calculated and measured DIC. (b) Comparison of the calculated Ω_{arag} using underway data with the calculated Ω_{arag} from discrete bottle sample data.

In leg 1, Ω_{arag} gradients were strong across the shelf, as was surface salinity (figure 2.4f). Lower Ω_{arag} occurred on the inner shelf near the Chesapeake Bay than further offshore (increase from 2.2 to 3.2; figure 2.4f). The overall pattern of Ω_{arag} in leg 2 was similar to leg 1 (figure 2.4f), where Ω_{arag} increased from the middle shelf across to the upper slope, especially in the coastal waters near the Delaware Bay (figure 2.4f). The largest Ω_{arag} change between leg 1 and leg 2 occurred on the upper slope, with an increase of up to 0.32 (figure 2.4f).

Ω_{arag} varied according to the inorganic carbon chemistry data along the Delaware transect between two legs. On the middle shelf, the average DIC decreased $44 \mu\text{mol kg}^{-1}$ while TA decreased $30 \mu\text{mol kg}^{-1}$ (figure 2.7a). On the upper slope the DIC change was very small ($3 \mu\text{mol kg}^{-1}$ on average), however, the TA change was large with an average increase of $29 \mu\text{mol kg}^{-1}$ (figure 2.7a). However, the salinity normalized TA showed no increase while the salinity normalized DIC showed a decrease of $13 \mu\text{mol kg}^{-1}$ on average.

2.4.4 Assessment of the biological and physical influences

To provide a first-order assessment of the biogeochemical influence on the rapid change of Ω_{arag} over time, we plot the difference in Ω_{arag} and $f\text{CO}_2$ against $n\text{DIC}$ along the Delaware transect between the two legs ($\Delta\Omega_{\text{arag}}$, $\Delta f\text{CO}_2$, and $\Delta n\text{DIC}$, respectively; figure 2.8a, 2.8c). There are two distinct statistically significant linear correlations between both $\Delta\Omega_{\text{arag}}$ and $\Delta f\text{CO}_2$ to $\Delta n\text{DIC}$ concentrations on the middle shelf and the upper slope (figure 2.8a, 2.8c). We also note that $\Delta n\text{DIC}$ is expected to decrease if the NCP is negative; thus we examine $\Delta n\text{DIC}$ against the average DO% and NCP instead of the differences between the two legs (figure 2.8b, 2.8d). Increased DO%, NCP, and decreased $\Delta n\text{DIC}$ are observed on the middle shelf, whereas DO%

and NCP decrease on the upper slope with increased $\Delta n\text{DIC}$ (figure 2.8b, 2.8d). The region-specific regression relationships ($\Delta n\text{DIC}$ to $\Delta\Omega_{\text{arag}}$ and $\Delta f\text{CO}_2$) suggest two different water mass mixing schemes on top of the biological production signals ($\Delta n\text{DIC}$ to oxygen parameter relationships) influencing $\Delta\Omega_{\text{arag}}$.

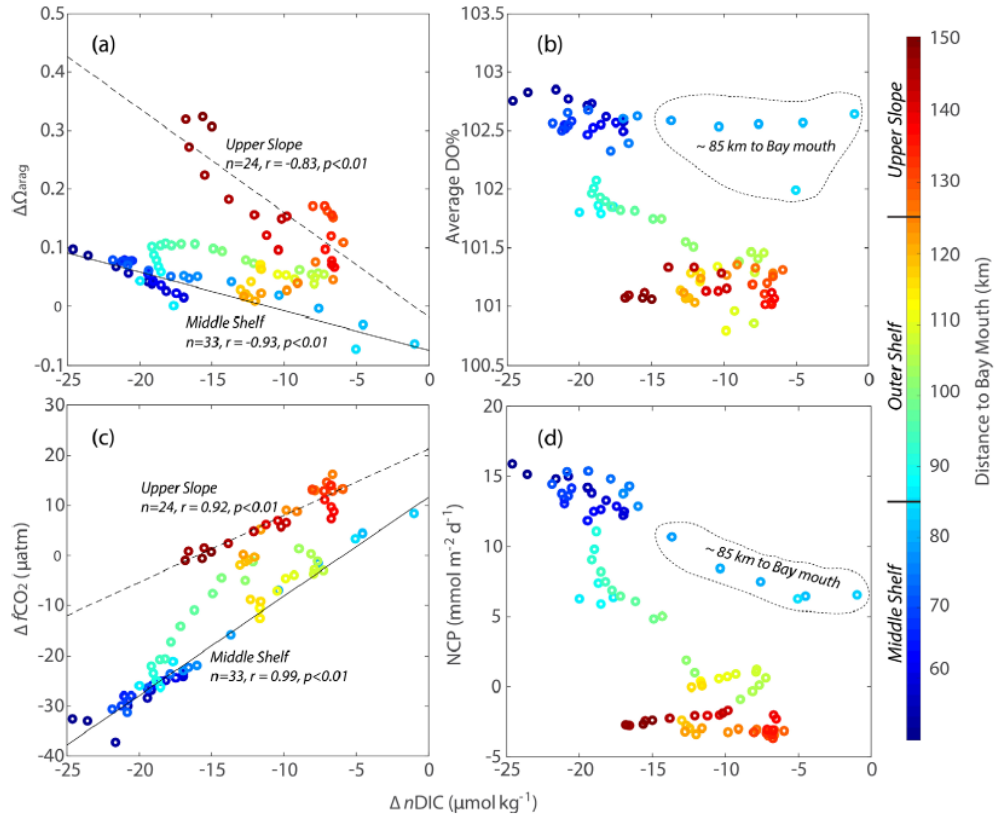


Figure 2.8: The relationship of (a) $\Delta\Omega_{\text{arag}}$, (b) average DO%, (c) $\Delta f\text{CO}_2$, and (d) NCP with $\Delta n\text{DIC}$ along the Delaware transect. The color bar shows the distance of each data point to the Delaware Bay mouth. Note that the yellow-greenish points are in between the middle shelf and the upper slope. Solid lines represent best-fit lines for the middle shelf where the surface seawater moved from north to south. Dashed lines represent best fit for the upper slope where the direction of net surface seawater movement is from south to north. Data points enclosed in the dashed regions are data from waters about 85 km from the bay mouth where the biological activity was increased with respect to surrounding waters during leg 1.

2.5 Discussion

2.5.1 General spatial distribution patterns

The summertime hydrographic setting in the MAB is consistent with previous studies through flux experiments and glider observations (Beardsley et al., 1985; Castelao et al., 2008). Local vertical stratification is strong with horizontal flows over the offshore region along isobaths (figure 2.1). In surface water, the alongshore variability of physical and chemical parameters are small, which is consistent with previous studies on the central MAB (DeGrandpre et al., 2002; Signorini et al., 2013). In contrast, large cross-shelf change is the dominant pattern in this region as a result of freshwater input from two large estuaries and the mixing with other water masses from adjacent regions that have different physical and chemical characteristics (Lentz, 2007; Mountain, 2003).

Surface TA is linearly correlated with salinity with a regression slope of 54.49, which is between the slopes for the Gulf of Maine and Gulf Stream waters (Cai et al., 2010). The tight relationship between TA and SSS along the Delaware transect suggests that mixing has a dominant control on the spatial distribution of TA, with other processes exerting less influence (Fry et al., 2015). The MAB has a lower annual mean DIC ($1968 \mu\text{mol kg}^{-1}$) compare to its adjacent regions, such as the South Atlantic Bight and Nantucket Shoals and Georges Bank (Signorini et al., 2013). Seasonal variability of DIC reveals that its concentration reaches a minimum ($\sim 1900 \mu\text{mol kg}^{-1}$) in summer, mainly as a result of biological uptake in spring and summer (Signorini et al., 2013). The average DIC concentration is $1960 \mu\text{mol kg}^{-1}$ along the Delaware transect in July, which is close to the annual mean DIC in the MAB but higher than the estimated summertime DIC. The average DIC concentration along the

Delaware transect is close to the average DIC concentration in the MAB if the inner shelf is included because of its low DIC.

2.5.2 Processes affecting Ω_{arag} change

There are two distinct features in the Ω_{arag} distribution: first, Ω_{arag} gradually increase offshore during both legs (figure 2.9a); second, Ω_{arag} is greater along the Delaware transect during leg 2 compared with leg 1, except in one small offshore patch about 85 km from the Delaware Bay mouth (figure 2.9a). Ω_{arag} in this patch is higher than its neighboring areas during both legs due to high biological production, as suggested by the DO% and O₂/Ar data. The difference in Ω_{arag} along the Delaware transect between the two legs ($\Delta\Omega_{arag}$) vary from -0.08 on the middle shelf to 0.32 on the upper slope (figure 2.9b).

To assess the contributions of thermodynamic, air-sea CO₂ flux, biological, and physical mixing to the change in Ω_{arag} from leg 1 to leg 2, we decompose $\Delta\Omega_{arag}$ into its major components:

$$\Delta\Omega = \Delta\Omega_{therm} + \Delta\Omega_{biol} + \Delta\Omega_{air-sea} + \Delta\Omega_{phys}, \quad (12)$$

where $\Delta\Omega_{therm}$ is the change in Ω_{arag} due to temperature- and salinity-dependent thermodynamics. $\Delta\Omega_{biol}$ is biologically driven Ω_{arag} change via photosynthesis and community respiration. $\Delta\Omega_{air-sea}$ is Ω_{arag} change due to air-sea CO₂ flux. Finally, $\Delta\Omega_{phys}$ is Ω_{arag} change caused by physical transport of different water masses and mixing. We note that equation 12 does not include a net calcification term. In this case, the strong linear relationship observed between TA and salinity (figure 2.3) over the entire water column suggests that there is no appreciable net calcification.

The terms in equation 12 use in situ SST, SSS, DIC, and TA data in leg 1 and ΔSST , ΔSSS , ΔDIC_{biol} , $\Delta DIC_{air-sea}$, and ΔDIC_{phys} is the change during the 10 days

between the two legs. Specifically, $\Delta\Omega_{therm}$ is calculated by subtracting Ω_{arag} computed using SST, SSS, DIC, and TA data from Ω_{arag} computed using SST+ Δ SST, SSS+ Δ SSS, DIC, and TA data. In other word, we assume constant DIC and TA values and only consider changes in SST and SSS between the two legs. The contribution of thermodynamic processes to the Ω_{arag} change is illustrated in figure 2.9. $\Delta\Omega_{biol}$, $\Delta\Omega_{air-sea}$, and $\Delta\Omega_{phys}$ are calculated from SST, SSS, DIC, and TA data, with ΔDIC_{biol} , $\Delta DIC_{air-sea}$, and ΔDIC_{phys} , that are calculated using equations 6-8, respectively. The contributions of biogeochemical and physical processes are illustrated in figure 2.10 and are discussed below.

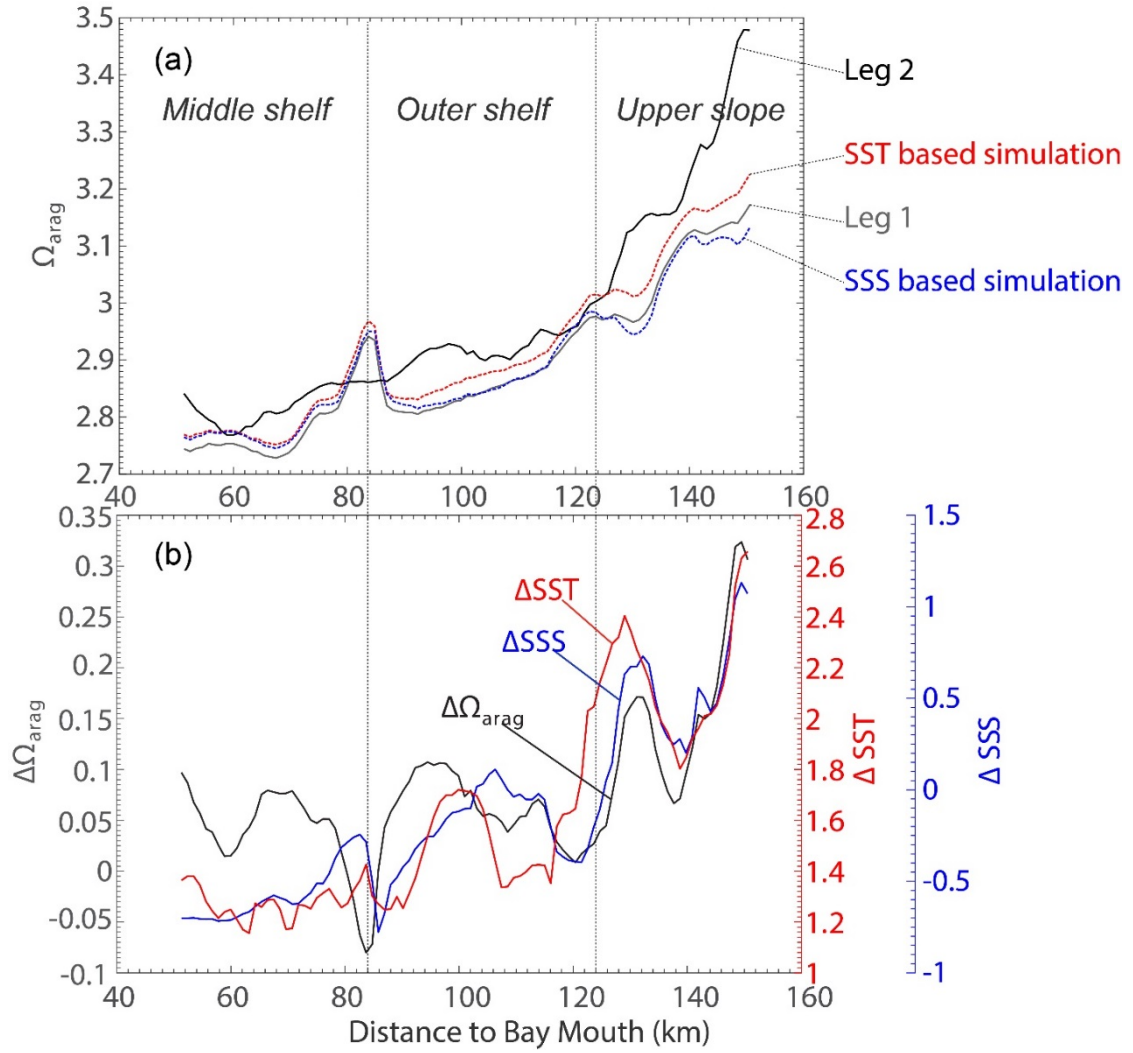


Figure 2.9: The spatial distribution of Ω_{arag} (a) along the Delaware transect during leg 1 (gray) and leg 2 (black) and changes in Ω_{arag} , SST, and SSS (b) between two legs along the Delaware transect. The red line represents modeled Ω_{arag} by applying SST in leg 2 to the rest parameters in leg 1. The blue line represents the modeled Ω_{arag} when using SSS of leg 2. Note that the increase in Ω_{arag} around 85 km offshore during leg 1 was caused by biological activity as indicated by high O_2/Ar data.

2.5.3 Thermodynamic influence on $\Delta\Omega_{\text{arag}}$

Carbonic acid equilibrium constants, which have an impact on calculated Ω_{arag} , are affected by the changes in temperature and salinity. Both the differences of SST and SSS between the two legs (ΔSST and ΔSSS) increase offshore (figure 2.9b). Water was warmer during leg 2 for the whole Delaware transect with ΔSST ranging from 1.2 to 2.7°C (figure 2.9b). SSS decreased on the middle shelf and outer shelf but increased on the upper slope between the two legs, with ΔSSS ranging between -0.8 and 1.1 (figure 2.9b). Warmer SST contribute to the increase in Ω_{arag} because the corresponding change of equilibrium condition results in an increase of carbonate ion concentration and decrease of aragonite stoichiometric solubility product (Feely et al., 2004; Orr et al., 2005). The SSS change may also affect Ω_{arag} through mixing with low-salinity river waters or saltier slope waters that are characterized with different TA:DIC ratios (Sabine et al., 2002; Wang et al., 2013).

However, even though ΔSST and ΔSSS are large, the resulting thermodynamic-only influences on Ω_{arag} are small (figure 2.9a). We further deconstruct $\Delta\Omega_{\text{therm}}$ into two terms, $\frac{\partial\Omega_{\text{arag}}}{\partial T}\Delta T$ and $\frac{\partial\Omega_{\text{arag}}}{\partial S}\Delta S$, to represent the contribution from temperature and salinity variations, respectively. In this study $\frac{\partial\Omega_{\text{arag}}}{\partial T}$ ranges from 0.018 to 0.020 and $\frac{\partial\Omega_{\text{arag}}}{\partial S}$ varies between -0.037 and -0.029, leading to maximum changes in Ω_{arag} of 0.05 and 0.04, respectively. To visualize the influences, we simulate $\Delta\Omega_{\text{arag}}$ from leg 1 by changing SST and SSS to fit the environmental conditions observed during leg 2. The increase in SST leads to an increase in Ω_{arag} ranging from 0.02 to 0.05. The changes of SSS lead to an average increase of Ω_{arag} by

0.02 on the middle shelf and an average decrease of Ω_{arag} by 0.02 on the upper slope, corresponding to ΔSSS of -0.6 and 0.5, respectively (figure 2.9). It is clear that SST and SSS changes can explain only a small part of the observed increase in Ω_{arag} during leg 2 and other causes must be identified.

2.5.4 Biological activity and air-sea CO₂ flux contributions to $\Delta\Omega_{\text{arag}}$

Biological activity plays an important role in controlling seawater DIC (Ishii et al., 1998; Gruber et al., 2002); thus biological activities can also play a key role in regulating Ω_{arag} . The shelf waters in the MAB are highly productive, but summertime high primary production is constrained to nearshore upwelling zones where the water depth is less than 30 m (Glenn et al., 2004; Filippino et al., 2011; Xu et al., 2011). The importance of biological activity on DIC change is denoted by the relationship between biological oxygen supersaturation-based NCP and $\Delta\text{DIC}_{\text{biol}}$ (equation 6).

High DO% and $\Delta(\text{O}_2/\text{Ar})$, which represent biological oxygen supersaturation (Craig and Hayward, 1987; Emerson et al., 2008), were observed on the middle shelf, corresponding to the high biological production and the resulted high DIC consumption as indicated by the more negative $\Delta n\text{DIC}$ (figure 2.8b, 2.8d). The average NCP based on $\Delta(\text{O}_2/\text{Ar})$ is estimated to be $41.4 \text{ g C m}^{-2} \text{ yr}^{-1}$ on the middle shelf of the Delaware transect, which agrees with the higher end of NCP estimates from DOC mass balance in the MAB of $11.7\text{-}59.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Vlahos et al., 2002). This biologically-induced DIC consumption results in an increase in Ω_{arag} ranging from 0.07 to 0.18 (figure 2.10).

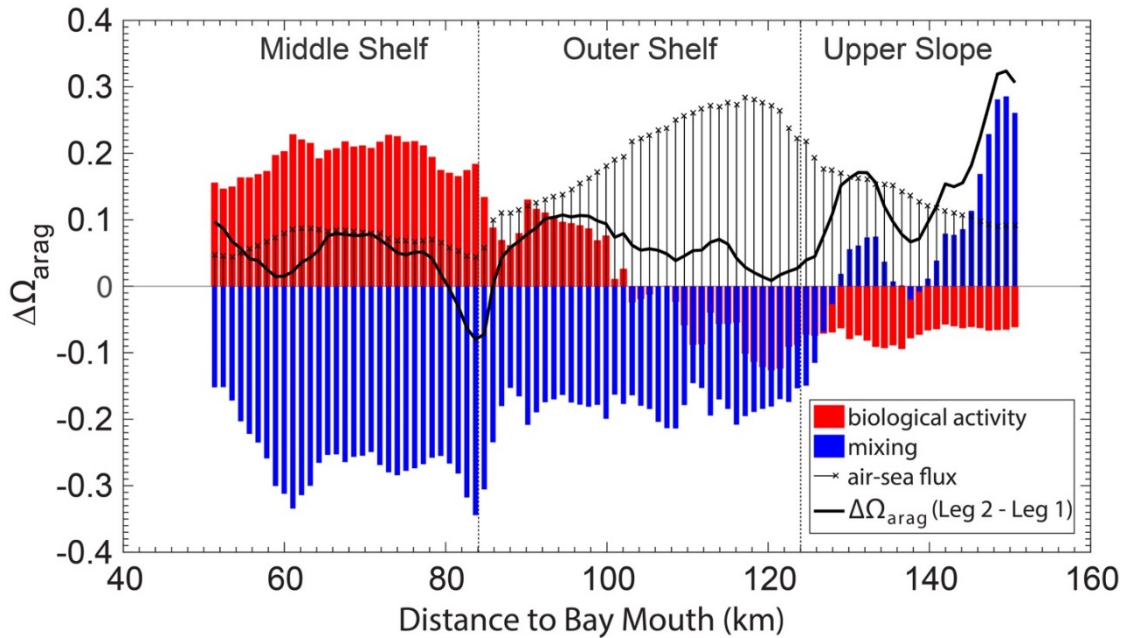


Figure 2.10: The contributions of biogeochemical and physical processes on the change of Ω_{arag} along the Delaware transect. The red bars are the impact on Ω_{arag} from biological activity, e.g. photosynthesis and community respiration. The blue bars are the impact on Ω_{arag} from the mixing of different water masses. The black stems with the crosses are the impact on Ω_{arag} from air-sea CO_2 flux. The solid black line represents the net change of Ω_{arag} between the two legs. Positive values mean biochemical and/or physical processes contribute to the increase of Ω_{arag} , and vice versa.

The transition from net autotrophy to net heterotrophy (i.e., the metabolic balance), as indicated by net oxygen production and consumption (or a switch from positive NCP to negative NCP), occurred on the outer shelf, corresponding to biologically-driven $\Delta\Omega_{\text{arag}}$ shifts from positive to negative values (figure 2.10). The decrease of NCP on the outer shelf and the upper slope waters is likely due to limited nutrient input and the intrusion of Gulf Stream waters that have low biomass in its surface water (Pelegrí and Csanady, 1991; Filippino et al., 2011). The entire MAB has

been identified as a net autotrophic region (Vlahos et al., 2002); however, the upper slope during the study period was a net heterotrophic region and featured an average DIC increase of $6.6 \mu\text{mol kg}^{-1}$ corresponding to a Ω_{arag} decrease of 0.07 (figure 2.10). Therefore, biological activity did not contribute to the elevated Ω_{arag} on the upper slope.

Biological activity (net primary production) also affects the overall inorganic carbon pool in the surface mixed layer, and thus $f\text{CO}_2$ and subsequent air-sea CO_2 flux. Changes to the total inorganic carbon pool influence carbonate acid equilibrium in the surface layer and therefore leads to a change in Ω_{arag} . The MAB has been identified as an annual sink for atmosphere CO_2 but the entire shelf is supersaturated with respect to atmospheric CO_2 in summer (DeGrandpre et al., 2002). Net CO_2 released from the ocean to the atmosphere in all regions is observed during our study period along the Delaware transect as well. The low new production and increase of SST contribute to the net CO_2 source in summertime (DeGrandpre et al., 2002; Signorini et al., 2013).

Net CO_2 release from the ocean to the atmosphere subsequently contribute to Ω_{arag} increases. The lowest CO_2 outgassing flux is found on the middle shelf, where NCP is highest (figure 2.6a) and the removal of CO_2 by photosynthesis was high, corresponding to high primary production that contributes to reducing the DIC concentration in the mixed layer (figure 2.10). However, the seawater is still supersaturated with respect to CO_2 , though the level has been drawn down compare to the outer shelf and the upper slope.

In contrast, the greatest CO_2 outgassing flux occurs on the outer shelf and contributes to an increase of 0.18 in Ω_{arag} due to the resulted decrease in DIC (figure

2.10). Note that the very shallow mixed layer depths during the study period causes the larger than usual impact of CO₂ outgassing on Ω_{arag} change. On the upper slope, the CO₂ degassing has a positive effect on Ω_{arag} and compensates in part for the biology-driven negative effect on Ω_{arag} (figure 2.10), leaving to the physical process as the major driver for the observed net increase in Ω_{arag} on the upper slope.

2.5.5 Physical mixing contribution to $\Delta\Omega_{\text{arag}}$

The existence of two distinct linear biological correlations on the middle and upper slope indicates that physical mixing also contributes to changes in Ω_{arag} (figure 2.8). $\Delta\Omega_{\text{arag}}$ covaries with ΔSST and ΔSSS on the upper slope (figure 2.9b), suggesting mixing with a warmer and saltier water mass in this region. Furthermore, $\Delta\text{DIC}_{\text{phys}}$ and ΔSSS show distinct distribution patterns in different regions, indicating different mixing patterns on the middle shelf, the outer shelf, and the upper slope (figure 2.11), except that the mixing patterns are similar on the middle shelf and the outer shelf with no statistical differences in terms of $\Delta\text{DIC}_{\text{phys}}$ - ΔSSS linear regression best-fit slopes. Therefore, combining with physical ocean model results and measured parameters in this study, we assume possible mixing patterns along the Delaware transect and then discuss how these mixing patterns affected the observed change in Ω_{arag} .

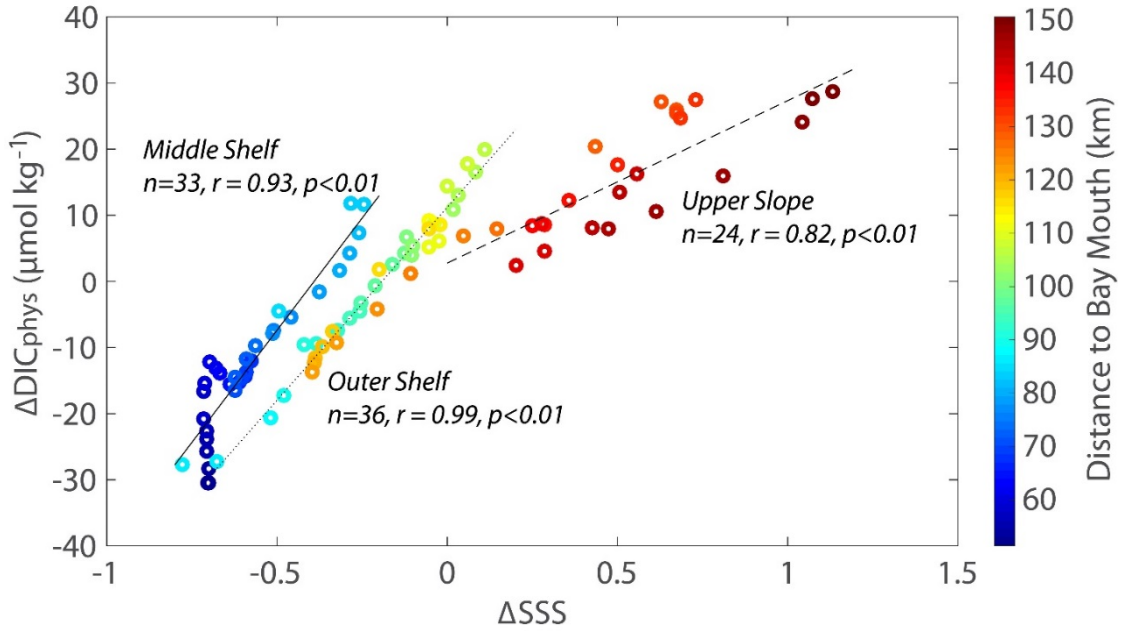


Figure 2.11: Relationship of ΔSSS and $\Delta\text{DIC}_{\text{phys}}$ along the Delaware transect. The color scale is the distance of each data point to the Delaware Bay mouth. The solid, dotted, and dashed lines represent linear regressions for the middle shelf, the outer shelf, and the upper slope, with best-fit slopes of 67.8 ± 4.8 , 58.4 ± 1.7 , and 24.6 ± 3.6 , respectively.

Upwelling, vertical mixing, and lateral transport and mixing are all possible physical processes on the middle shelf and the upper slope. Coastal upwelling has been identified as the primary factor that drives the rapid change of Ω_{arag} in the California Current System (Feely et al., 2008; Harris et al., 2013). However, Delaware transect is not located within a region where upwelling is typically observed since the nearshore upwelling boundary is at the shelf edge ~ 51 km away from the mouth of Delaware Bay (Voynova et al., 2013). As a result of strong surface heating and weak wind stress, the water column was strongly stratified in this region with a sharp

temperature and salinity gradient below the mixed layer. Therefore, it is not likely that upwelling plays a role in transport processes during the study period.

Lateral transport has previously been identified as the dominant physical process in the MAB (Biscaye et al., 1994). The southward surface current from the Gulf of Maine and northward Gulf Stream meanders are important water inflows into the MAB, and the freshwater flow only accounts for a minor part (~1%) of the total water inflow into this region (Beardsley and Boicourt, 1981). Argon supersaturation ($Ar\%$; calculated from $DO\%$ and $\Delta(O_2/Ar)$ following Kaiser et al. (2005)) decreases during the study period (figure 2.12), whereas vertical transport of colder waters would increase $Ar\%$ (Kaiser et al., 2005). The large decrease of $Ar\%$ in the upper slope water is due to advancement of the warm, saline Gulf Stream water (which contains less Ar) into the area along the Delaware transect, as indicated by the direction and strength of surface current (figure 2.1b).

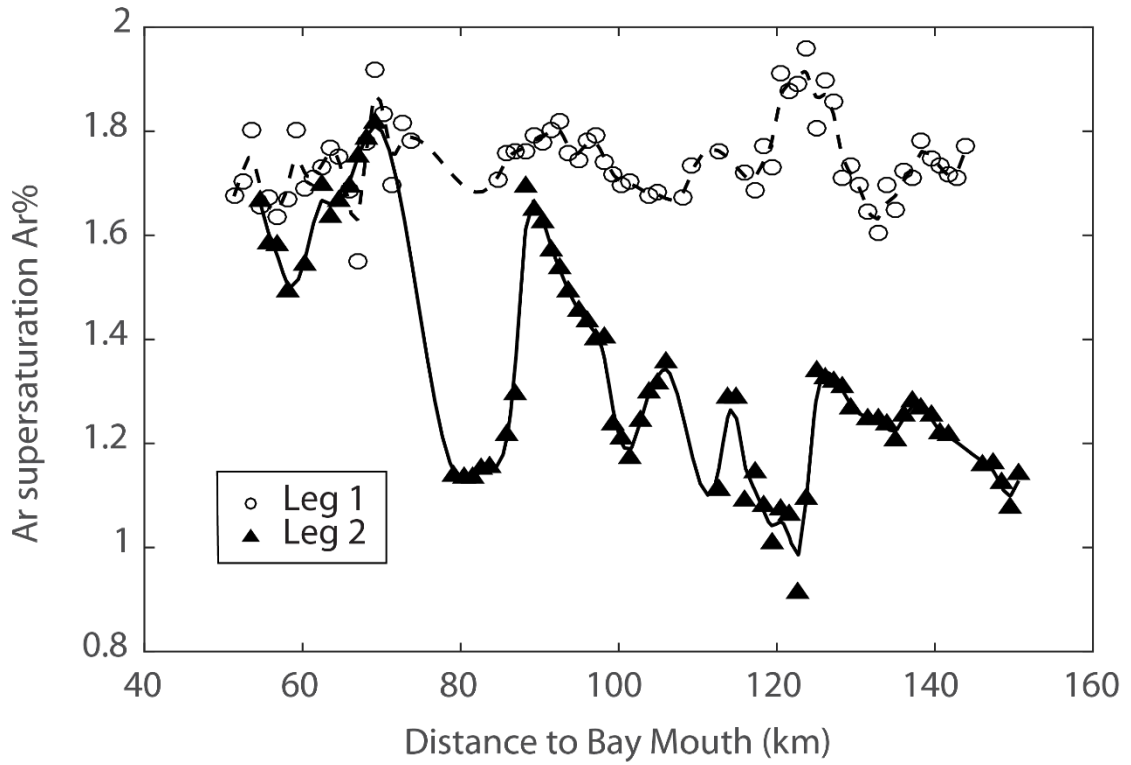


Figure 2.12: Ar supersaturation (Ar%) for the two legs along the Delaware transect. Open circles and polynomial curve fitted dashed line are Ar measurements from leg 1, triangles and polynomial curve fitted solid line are Ar measurements from leg 2.

In general, Ω_{arag} in the MAB is higher than values reported farther north in the Gulf of Maine but lower than Gulf Stream waters to the south during previous cruises (Wanninkhof et al., 2015; Jiang et al., 2015). That the change in Ω_{arag} is driven by physical mixing of different water masses is consistent with the direction and strength of surface current along the Delaware transect (figure 2.1b, figure 2.10). On the middle shelf, mixing with water that was transported by the southward surface current from the Gulf of Maine causes an average decrease of 0.26 in Ω_{arag} , thus canceling out

a large portion of the biological production and degassing-induced Ω_{arag} increase (figure 2.10).

The Gulf Stream was on the upper slope and contributed a maximum Ω_{arag} increase of 0.29 via transport and mixing with the northward surface current (figure 2.10). The average surface flow was toward the north with a velocity of ~ 25 cm/s during the study period. During a given period of 10 days, the lateral transport in the surface layer is capable of transporting warmer and saltier waters from ~ 220 km away from the south to the Delaware transect. On the upper slope, the northward flowing surface current has an important influence on the carbon chemistry. Ω_{arag} in the North Atlantic typically increases at lower latitudes (Jiang et al., 2015). $\Delta\Omega_{\text{arag}}$ due to water mass mixing (figure 2.10) agrees reasonably well with surface current patterns (figure 2.1a).

2.5.6 Towards future coastal acidification studies

Short-term signals due to biogeochemical and physical processes are important for interpreting observed Ω_{arag} changes and could mask the identification of decadal trends via occasional (once every few years) survey cruises. For example, under the complex influence of biogeochemical and physical processes in the central MAB, the Ω_{arag} along the Delaware transect during the ECOA cruise changes by 0.10 on the middle and outer shelf regions and up to 0.32 on the upper slope during leg 2 compared to the values in leg 1. Natural cycles over time, however, have not yet been identified in the MAB; therefore, results from sporadic cruises should be considered preliminary assessments of Ω_{arag} and acidification. Thus, careful sampling strategies and modeling are needed to identify decadal and longer-term trends.

Currently, large-scale OA surveys on the U.S. east coast are conducted every 3 to 5 years, while higher frequency regional OA surveys in the MAB are limited to shallow waters. In addition to large-scale synoptic surveys (e.g. the Gulf of Mexico and East Coast Carbon cruise (GOMECC) and ECOA), moorings at critical locations, satellite remote sensing, and coupled physical and biological modeling efforts will all aid in understanding coastal carbonate system dynamics (Hofmann et al., 2011; Salisbury et al., 2015). Furthermore, greater knowledge of regional physical conditions and its variability are necessary for a comprehensive view of the trends in coastal acidification.

2.6 Conclusions

The rapid change of Ω_{arag} in shelf waters near the Chesapeake Bay and the Delaware Bay is driven by a combination of physical mixing, gas transfer and biology. Mixing changes Ω_{arag} by up to 0.32 units. Biological DIC removal and CO_2 degassing to the atmosphere contribute a 0.23 and 0.25, respectively, to the change in Ω_{arag} . Our analyses show that biological activity is a major contributor to increased Ω_{arag} on the middle shelf, while surface lateral transport is the dominant factor that increased Ω_{arag} on the upper slope. In evaluations of long-term changes in ocean acidification, the possibility of a rapid change of Ω_{arag} as observed in this study needs to be considered.

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Chapter 3

DECADAL TRENDS OF CARBONATE CHEMISTRY VARIABLES ALONG THE NORTH AMERICAN EAST COAST²

3.1 Abstract

Coastal acidification affects calcifying species and threatens coastal ecosystems but is difficult to understand and predict future changes due to multiple interactions of the coast with the land, the open ocean, and the atmosphere. In this study, we used Surface Ocean CO₂ Atlas (SOCAT) fugacity of CO₂ ($f\text{CO}_2$) data product to develop algorithms to estimate coastal water $p\text{CO}_2$ using atmospheric CO₂, temperature, and salinity via a Bayesian-neural-network approach for the Mid-Atlantic Bight (MAB) and the South Atlantic Bight (SAB). Then we reconstructed DIC, pH, and calcium carbonate saturation state with respect to aragonite (Ω_{arag}) time series from 1982 to 2015 and predicted future DIC, pH, and Ω_{arag} variations up to the year 2100 under the Representative Concentration Pathway (RCP) 8.5 scenario. The reconstructed historical data suggest that the change in carbonate chemistry variables from 1982 to 2015 in the SAB is primarily driven by atmospheric CO₂ increase, while the change in the MAB is greatly altered by variations in temperature and salinity. On decadal and longer time scales, DIC will increase while pH and Ω_{arag} will decrease in both regions. However, DIC increase and Ω_{arag} decrease will be dampened in the MAB because of

² This chapter is based on a manuscript in preparation by Yuan-Yuan Xu, Wei-Jun Cai, Rik Wanninkhof, Joe Salisbury, Janet Reimer, and Baoshan Chen

increasing ocean temperatures. We found that the changes in the seasonal amplitudes of carbonate parameters in the SAB is mostly driven by atmospheric CO₂ increase and the decrease in buffer capacity. In the MAB, however, in addition to atmospheric CO₂ and the change in buffer capacity, the different patterns are driven by physical processes that bring in different water masses. In addition, we want to emphasize the importance of studying the change in seasonal amplitude as it has an influence on when undersaturation will come out.

3.2 Introduction

The carbonate system equilibrium is the major buffer mechanism in regulating seawater pH and calcium carbonate saturation state with respect to aragonite (Ω_{arag}), which is one of the two most abundant mineral forms of calcium carbonate and is the more soluble one. It is well known that the excess carbon dioxide (CO₂) in the atmosphere from human activities such as fossil fuel use has increased the amount of CO₂ absorbed by the ocean and has led to ocean acidification (Doney et al., 2009; Orr et al., 2005). In addition to anthropogenic climate change, upwelling, eutrophication, and river discharge affect carbonate chemistry in coastal waters and contribute to coastal acidification (Cai et al., 2011; Feely et al., 2008; Vargas et al., 2016; Wallace et al., 2014). Localized and regional acidification of coastal waters is not well understood due to its complexity and limited spatial and temporal observations or model estimates (Hofmann et al., 2011; Strong et al., 2014).

The North America east coast is a typical passive continental margin characterized by a broad shallow shelf. The cold Labrador Current and the warm Gulf Stream are two major current systems that affect the shelf water dynamics. The Labrador Current flows southward along the east coast of Nova Scotia and the Gulf of

Maine to the New York Bight (Bailey and Hachey, 1951). It eventually transports fresher and colder water into the Mid-Atlantic Bight (MAB) (Chapman and Beardsley, 1989). The Gulf Stream flows northward parallel to the coast and separates from shelf water in the Cape Hatteras and strongly affects the shelf water dynamics along its propagation pathway in the South Atlantic Bight (SAB) (Meinen and Luther, 2016).

Spatial and seasonal variabilities of seawater carbon dioxide partial pressure ($p\text{CO}_2$) have been studied in the MAB and the SAB (DeGrandpre et al., 2002; Jiang et al., 2008). In the MAB, $p\text{CO}_2$ increases with temperature nonlinearly and this process is not mitigated by new production because of stratification in spring and summer, which limits nutrient loading into the surface water (DeGrandpre et al., 2002). The seasonal cycle of CO_2 was found to follow the seasonal thermal cycle in the SAB (Jiang et al., 2008; Signorini et al., 2013). A recent study found that many continental shelves are increasing carbon sinks for atmospheric CO_2 as a result of a faster exchange of CO_2 with the ocean interior and increased biological production as the increase of anthropogenic nutrient inputs (Laruelle et al., 2018). However, long-term changes in DIC, pH, and Ω_{arag} in the MAB and the SAB were not studied yet due to the lack of long-term records.

Assessment of the long-term trend of carbonate chemistry seasonal cycle amplitude is important because it affects when calcifying species will be exposed to calcium carbonate undersaturation (Gruber et al., 2002; Kwiatkowschi and Orr, 2018; Sasse et al., 2015). It also affects the time of emergence for ocean acidification (OA)-related parameters, which suggests an estimated time when OA signal to emerge from natural variability (Salisbury and Jönsson, 2018; Turk et al., 2019). Studies on the changing seasonal cycle amplitudes of carbonate chemistry parameters are beginning

to emerge (Fassbender et al., 2018; Kwiatkowski and Orr, 2018; Landschützer et al., 2018). The interpolated global monthly sea surface $p\text{CO}_2$ has been provided (Landschützer et al., 2017). It was found that rising ocean temperatures and anthropogenic CO_2 concentration have altered the seasonal cycle amplitudes of carbonate chemistry parameters based on modeling work for the open ocean region at a global scale (Fassbender et al., 2018; Kwiatkowski and Orr, 2018; Landschützer et al., 2018). However, long-term interpolated monthly data is not available for coastal regions such as the MAB and the SAB.

To analyze long-term trends and the changes, we derived carbonate chemistry variables from other more easily available parameters to fill observation gaps. We firstly developed regional algorithms for sea surface $p\text{CO}_2$ from 1982 through 2015 using atmospheric CO_2 , temperature, and salinity via a Bayesian-neural-network-based interpolation approach (see Methods). Then we calculated other carbonate chemistry parameters such as DIC, pH, and Ω_{arag} for the MAB and the SAB using estimated $p\text{CO}_2$ and salinity-derived total alkalinity.

A recent study suggests that the ocean acidification signal in the most recent three decades in the Gulf of Maine is concealed as a result of rapid warming and salinity changes, which have a strong impact on the carbonate system (Salisbury and Jönsson, 2018). The long-term coastal temperature record shows that rapid warming and salinity change have also occurred in the MAB (Grotsky et al., 2017; Shearman and Lentz, 2009). Therefore, we also examined the influence of multi-decadal temperature and salinity change on the carbonate system in the MAB. Furthermore, we predicted $p\text{CO}_2$, DIC, pH, and Ω_{arag} for the MAB and the SAB under the Representative Concentration Pathway (RCP) 8.5 scenario for years up to 2100.

3.3 Data source and methods

3.3.1 Gridded in situ $p\text{CO}_2$ observations, atmospheric CO_2 , temperature, and salinity

Gridded seawater $p\text{CO}_2$ observations come from the global database Surface Ocean CO_2 Atlas (SOCAT, www.socat.info) version 5. The SOCAT database provides fugacity of carbon dioxide ($f\text{CO}_2$) data with a $1^\circ \times 1^\circ$ resolution in space and a monthly resolution in time from 1957 to 2017 for the global oceans and coastal seas. For consistency, we convert $f\text{CO}_2$ to $p\text{CO}_2$ and use $p\text{CO}_2$ through the paper from here. It synthesizes all publicly available surface ocean $f\text{CO}_2$ observations with a total of 21.5 million quality-controlled measurements. This quality-controlled product of surface ocean $f\text{CO}_2$ has an accuracy of better than 5 μatm (Bakker et al., 2016).

Monthly interpolated sea surface $p\text{CO}_2$ from 1982 through 2015 is estimated from monthly atmospheric CO_2 , temperature, and salinity. Atmospheric CO_2 data come from CarbonTracker, version CT2017 (<http://carbontracker.noaa.gov>) (Peters et al., 2007), which is a data assimilation system that is built by the National Oceanic and Atmospheric Administration's Earth System Research Laboratory (Peters et al., 2007). It provides CO_2 mole fractions with a temporal resolution of every 3-hour and spatial resolution of $1^\circ \times 1^\circ$ for the North American from 2000 to 2015. This CO_2 mole fraction has an accuracy of 0.1 parts per million (Peters et al., 2007). To extend the temporal coverage, we first calculate the average monthly difference between CarbonTracker data and the Mauna Loa CO_2 data (<https://www.esrl.noaa.gov/gmd/ccgg/trends/data.html>) for each grid box using data during the overlap period (2000-2015). Then we apply this difference to other years (1982-1999) when the CarbonTracker data are not available. The accuracy of the CO_2 measurements at the Mauna Loa Observatory is generally better than 0.2 ppm.

Sea surface temperature (SST) data were obtained from National Oceanic and Atmospheric Administration (NOAA) daily Optimum Interpolation SST (OISST, version 2) (Reynolds et al., 2007). OISST is a satellite-derived high resolution (0.25°×0.25°) dataset. Sea surface salinity (SSS) are obtained from the UK Met Office Hadley Center EN4 dataset (version 4.2.1, <https://www.metoffice.gov.uk/hadobs/en4/>). The EN4 dataset uses the World Ocean Database 2009 (WOD09) as its main data source (Good et al., 2013). Argo global data since 2000 and data from the Global Temperature and Salinity Profile Program since 1990 have been implanted into the EN4 dataset (Good et al., 2013). This EN4 dataset provides monthly-based 1°×1° gridded temperature and salinity data with uncertainty estimates. For our study region, the largest uncertainties are 1.3°C and 0.5 for temperature and salinity, respectively.

3.3.2 $p\text{CO}_2$ estimation and DIC, pH, and Ω_{arag} calculation

Using atmospheric $p\text{CO}_2$, SST, and SSS, monthly seawater $p\text{CO}_2$ at the equilibrium state ($p\text{CO}_{2\text{eq}}$) can be calculated for each 1°×1° grid box in the MAB and the SAB (figure 3.1). In this study, the equilibrium state refers to the condition that the seawater $p\text{CO}_2$ is in equilibrium with the atmospheric $p\text{CO}_2$ at 100% relative humidity, i.e., the net CO_2 exchange between atmosphere and the seawater is zero. $p\text{CO}_{2\text{eq}}$ is calculated using dry air CO_2 ($x\text{CO}_2$), temperature, and salinity:

$$p\text{CO}_{2\text{eq}} = x\text{CO}_2 \times (1 - p_w),$$

where p_w stands for water vapor pressure at the equilibrium temperature and salinity. It can be calculated from temperature and salinity according to Weiss and Price (1980):

$$p_w = \exp (24.4543 - 67.4509 \times (100/T) - 4.8489 \times \ln(T/100) - 0.000544 \times S),$$

where T is temperature on the Kelvin scale and S is salinity.

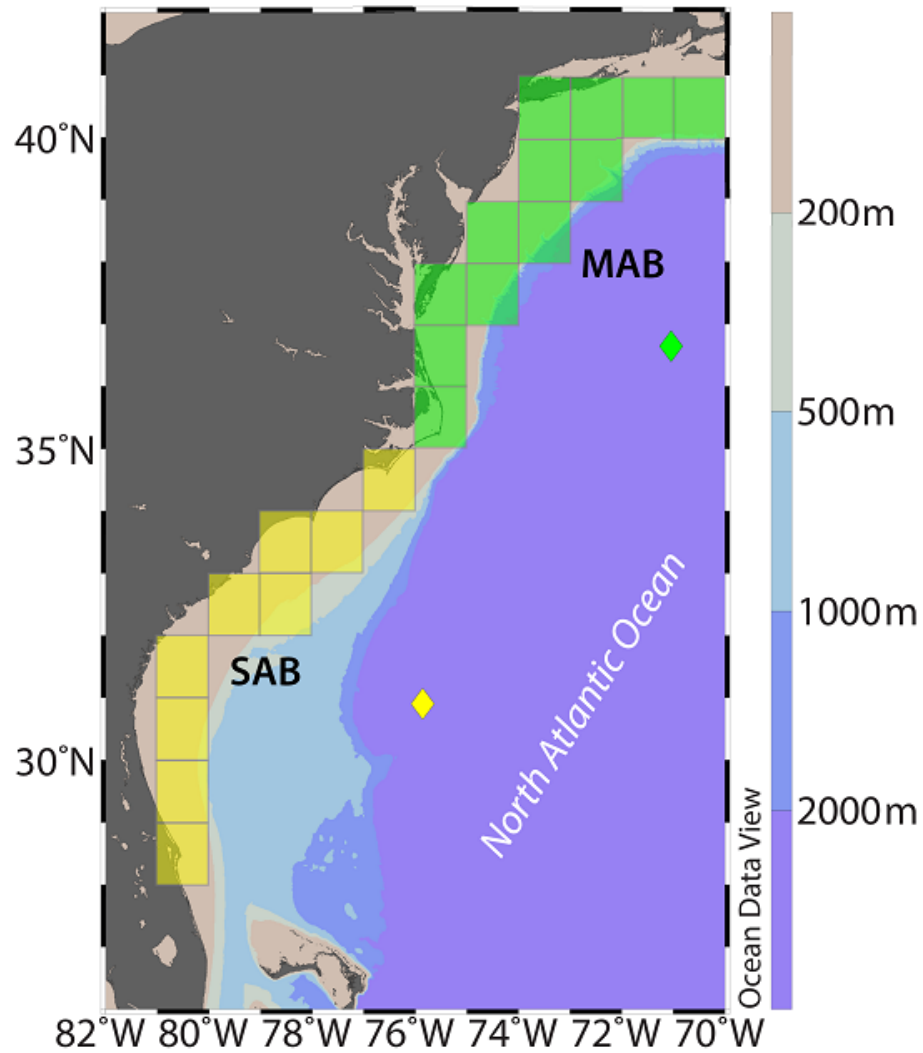


Figure 3.1: The map of MAB (left) and SAB (right) with grids (rectangle). The two diamond symbols represent the open ocean points. The color bar represents ocean bathymetry.

Then we estimate the difference between the observed seawater $p\text{CO}_2$ and $p\text{CO}_{2\text{eq}}$ using atmospheric CO_2 , SST, and SSS via a Bayesian-neural-network approach, which has been recently used by Bittig et al. (2018) to estimate open ocean CO_2 variables. The input parameters are latitude, longitude, SST, and SSS. The feedforward network is constructed by two hidden layers with tanh activation functions. The output parameter is the difference between the observed seawater $p\text{CO}_2$ and $p\text{CO}_{2\text{eq}}$. The SOCAT $p\text{CO}_2$ data, along with the corresponding $p\text{CO}_{2\text{eq}}$, latitude, longitude, SST, and SSS, have been used for training. Two separate training processes have been done for the MAB and the SAB with 939 and 355 numbers of observations, respectively.

Figures 3.2 and 3.3 show the comparison between the neural-network-based $p\text{CO}_2$ estimations and observations. Note that the gridded data at $1^\circ \times 1^\circ$ spatial resolution from the same region (i.e., the MAB or the SAB) have been averaged to represent the values for the MAB and the SAB. Thus the numbers of scatter points in figures 3.2 and 3.3 are smaller than the numbers of observations used for neural-network training. Statistically, the neural-network-based $p\text{CO}_2$ estimations agree well with observations with a R^2 of 0.83 for the MAB and a R^2 of 0.82 for the SAB. The root mean square errors are 18 and 22 μatm for the MAB and the SAB, respectively. We have improved $p\text{CO}_2$ estimations, especially for the MAB, compare to the work that has been done by Signorini et al. (2013). Compare to the MAB, the higher root mean square error in the SAB is primarily due to the poor fit of data in the grid box that locates in shelf regions near Georgia, where seawater $p\text{CO}_2$ is affected by estuaries that have high CO_2 inputs from rivers and intertidal saltmarshes (Jiang et al., 2008).

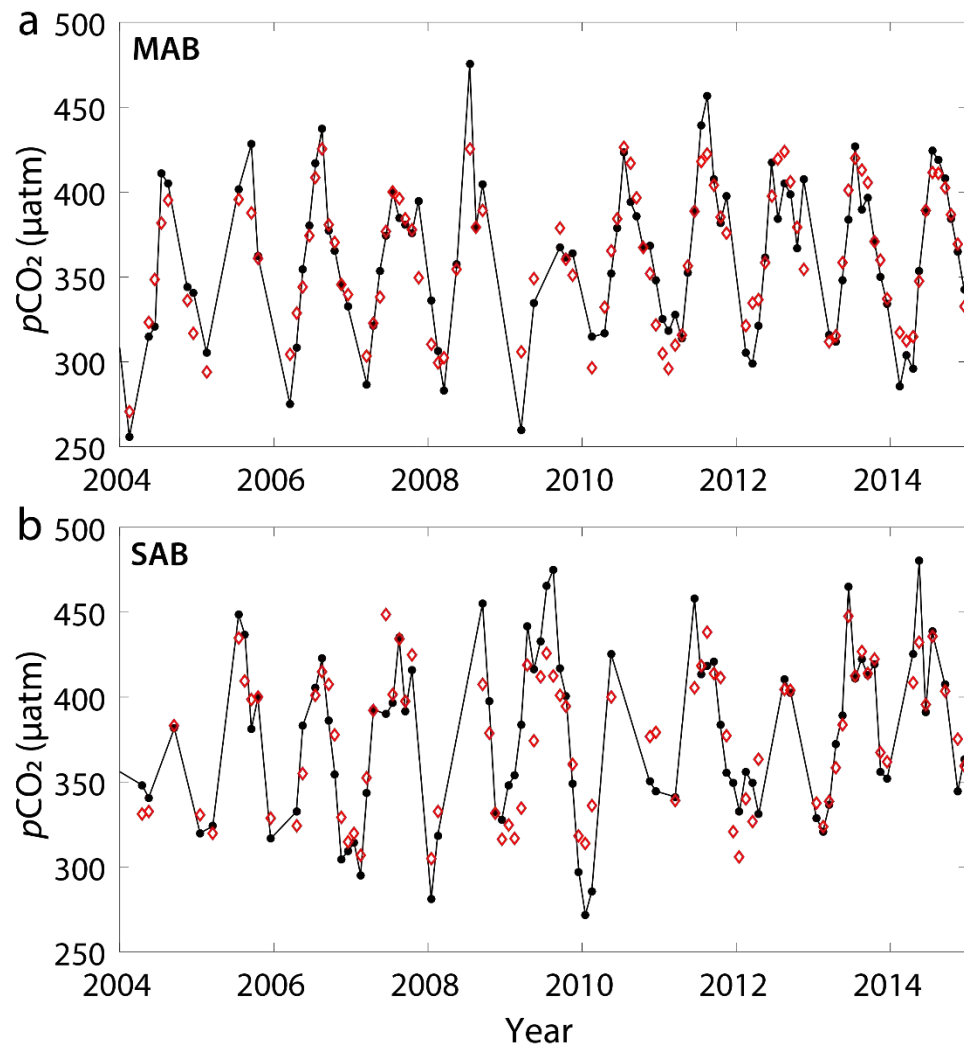


Figure 3.2: Time-series plots of $p\text{CO}_2$ estimations and observations for the MAB (upper column) and the SAB (lower column). The black dots with lines represent the observed $p\text{CO}_2$. The red diamond symbol represents our estimated $p\text{CO}_2$. Note that the data from 1994-2004 are not presented here because they are sparse.

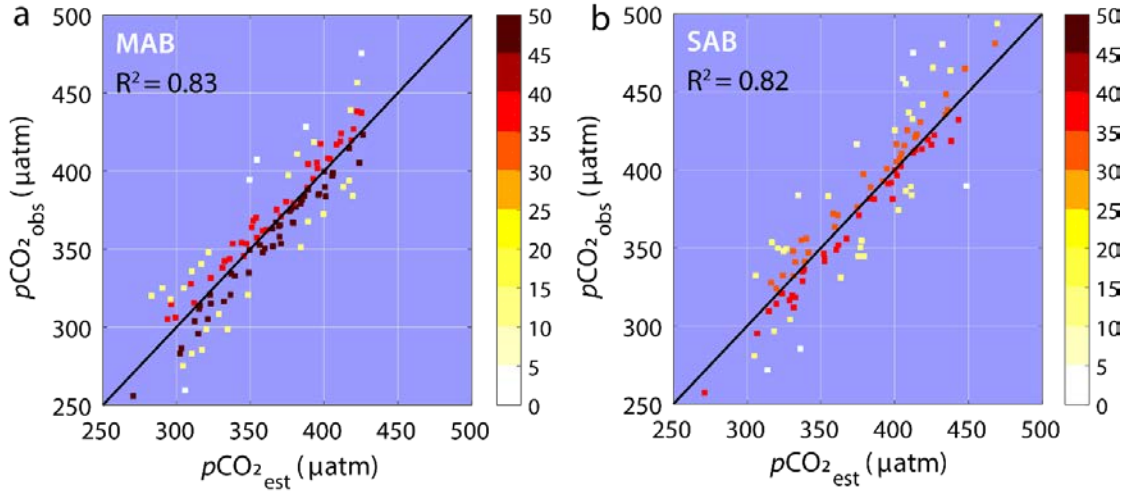


Figure 3.3: Scatter-plots of $p\text{CO}_2$ estimations versus observations for the MAB (left column) and the SAB (right column). The black 1:1 line represents where estimation equals the observation. The color bar represents the histogram frequency of the differences between the estimations and observations. Darker colors indicate higher frequencies and light colors indicate lower frequencies. The R^2 values of the fitted regression lines for estimations and observations are shown on each panel.

DIC, pH, and Ω_{arag} are then calculated from $p\text{CO}_2$ and salinity-derived TA using CO2SYS (Van Heuven et al., 2009) with the first and second dissociation constants of carbonic acid in seawater (K_1 and K_2) from Lueker et al. (2000). TA is derived from salinity using their linear relationships from Cai et al. (2011). Note that separate salinity-TA relationships have been applied for the MAB and the SAB. The errors in $p\text{CO}_2$ estimation lead to errors in DIC, pH, and Ω_{arag} estimations. Figure 3.4 shows the comparison between the neural-network-based DIC, pH, and Ω_{arag} estimations and observations. The neural-network-based DIC, pH, and Ω_{arag} estimations agree well with observations with R^2 values of 0.96 (DIC), 0.83 (pH), and 0.94 (Ω_{arag}) for the MAB and R^2 values of 0.77 (DIC), 0.84 (pH), and 0.92 (Ω_{arag}) for

the SAB. For DIC estimation, the errors are $9 \mu\text{mol kg}^{-1}$ and $12 \mu\text{mol kg}^{-1}$ for the MAB and the SAB, respectively. For pH estimation, the errors are 0.020 and 0.021 for the MAB and the SAB, respectively. For Ω_{arag} estimation, the errors are 0.09 and 0.12 for the MAB and the SAB, respectively.

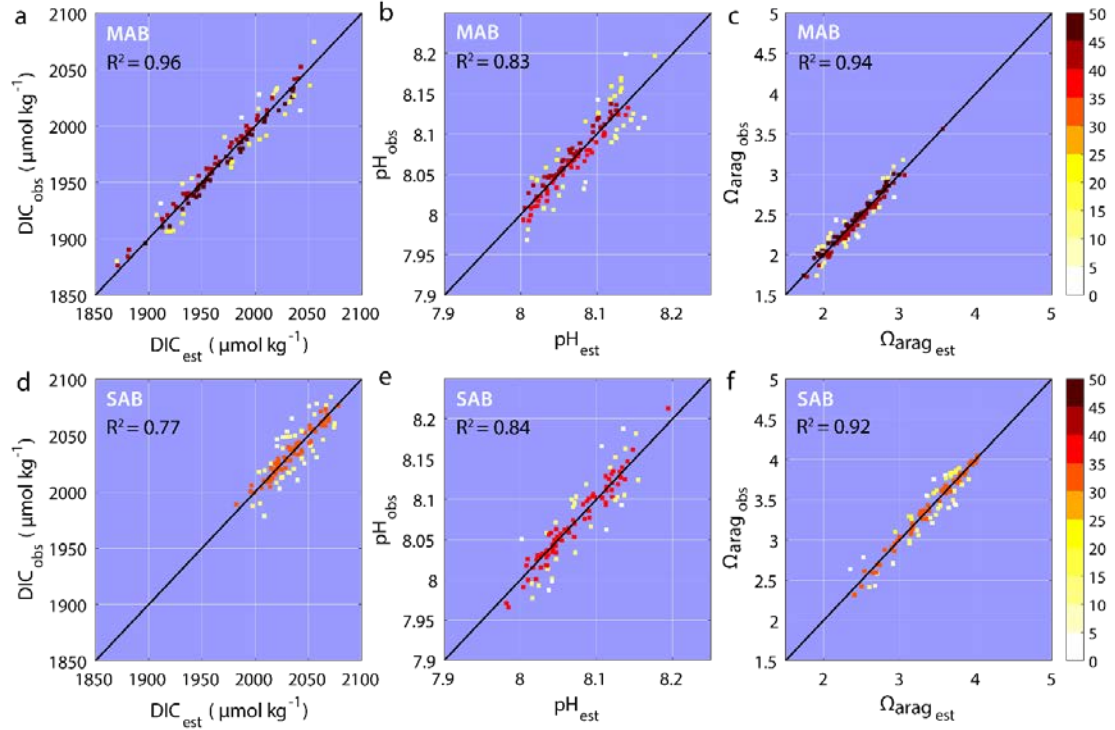


Figure 3.4: Scatter-plots of DIC, pH, and Ω_{arag} estimations versus observations for the MAB (upper column) and the SAB (lower column). The black 1:1 line represents where estimation equals observation. The color bar represents the histogram frequency of the differences between the estimations and observations. Darker colors indicate higher frequencies and light colors indicate lower frequencies. The R^2 values of the fitted regression lines for estimations and observations are shown on each panel.

3.3.3 Prediction of $p\text{CO}_2$, DIC, pH, and Ω_{arag}

We apply the networks for estimating $p\text{CO}_2$ in the MAB and the SAB to future atmospheric CO_2 , SST, and SSS data to predict carbonate chemistry variables towards the end of this century. Monthly atmospheric CO_2 data, starting from 2006, are extracted from Meteorological Research Institute-Earth System Model Version 1 (MRI-ESM1, Yukimoto et al., 2011). Monthly temperature and salinity data, starting from 2006, are extracted from the Max-Planck-Institute Earth System Model (MPI-ESM) output with a climate change experiment for the RCP8.5 scenario (Giorgetta et al., 2013). We compare the MPI-ESM model SSS data with SOCAT salinity data and EN4 salinity data and find discrepancies among these data sets. Figure 3.5 shows the comparison of these three data sets. EN4 salinity data agree well with SOCAT salinity data with an average difference of 0.13 for both the MAB and the SAB. However, MPI-ESM salinity data are much higher than SOCAT salinity data for the MAB and the SAB with average differences of 2.67 and 0.82, respectively. Therefore, we adjust MPI-ESM salinity data for the MAB and the SAB by subtracting the average differences (2.45 for the MAB and 0.78 for the SAB) between MPI-ESM salinity and EN4 salinity during the overlap period (2006-2015).

In the prediction, we assume that the air-sea $p\text{CO}_2$ disequilibrium in the next few decades will follow the same pattern as expressed by the neural-network algorithms that have been developed based on historical data mostly from the past two decades. This assumption is likely wrong over a long period (e.g., one century), but a first approximation based on the fact the neural-network that is developed using data from the 2000s works well for estimating $p\text{CO}_2$ for 2010s (the root mean square errors are 27 and 24 μatm for the MAB and the SAB, respectively) proves that our neural network approach contains prognostic value to predict future carbonate chemistry

variables for the MAB and the SAB. Thus, the prediction under the same air-sea disequilibrium pattern will still provide us some clues about the changes in the seasonal amplitudes of carbonate chemistry parameters in the near future.

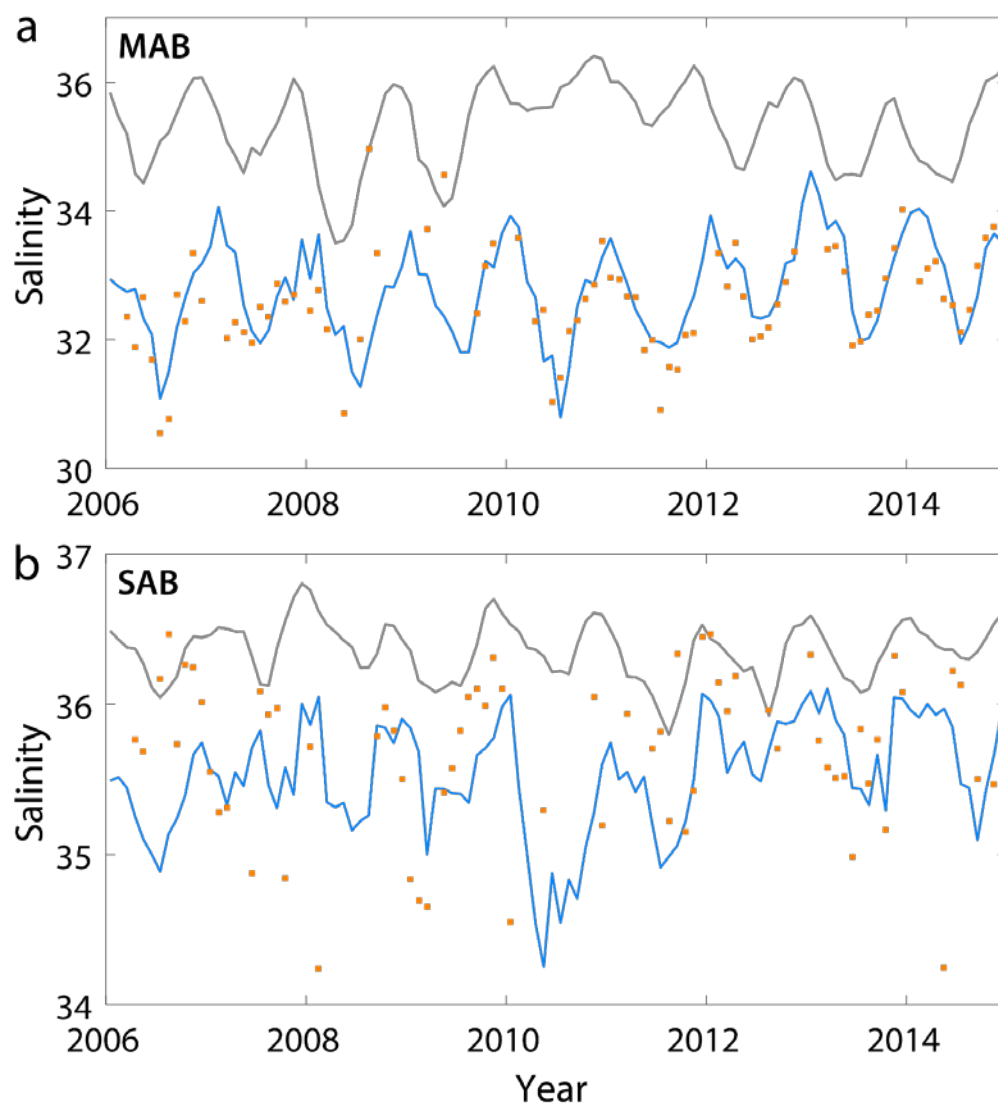


Figure 3.5: Time-series plots of SOCAT salinity (orange dots), EN4 salinity (blue line), and MPI-ESM_LR salinity (gray line) for the MAB (upper column) and the SAB (lower column).

We also compare the carbonate chemistry variables in the MAB and the SAB with the values in the open ocean. We choose two grid points in the north Atlantic Ocean at the latitudinal ranges of the MAB and the SAB for comparison. The open ocean $p\text{CO}_2$, DIC, and pH are obtained directly from MPI-ESM model output while Ω_{arag} is calculated from DIC and TA using CO2SYS (Van Heuven et al., 2009). Coastal data are also available from MPI-ESM model output. However, we prefer to use our neural-network algorithms because of salinity discrepancy in the MAB and the SAB, which has a strong influence on carbonate chemistry variables such as DIC and Ω_{arag} .

3.4 Results and Discussion

3.4.1 Historical $p\text{CO}_2$, DIC, pH, and Ω_{arag} variations in the MAB and the SAB

We reconstructed monthly carbonate chemistry variables in the MAB and the SAB from 1982 to 2015. Seawater $p\text{CO}_2$ increased in both the MAB and the SAB as the increase of atmospheric CO_2 (figure 3.6a, 3.6b). The rate of $p\text{CO}_2$ increase in the MAB ($1.83 \pm 0.19 \mu\text{atm per year}$) was higher than that of the SAB ($1.44 \pm 0.14 \mu\text{atm per year}$). In the MAB, there was no trend in DIC from 1982 to 2005, but it was increasing from 2005 to 2015 at a rate of $3.23 \pm 1.47 \mu\text{mol kg}^{-1} \text{ per year}$ (figure 3.6c). This DIC increase in the MAB was primarily driven by the large increase in salinity as the latitudinal position of the Gulf Stream north wall was displayed strongly northward and the retreat of the Labrador Current (Grotsky et al., 2017). For the SAB, coastal ocean DIC increased at a rate of $1.24 \pm 0.09 \mu\text{mol kg}^{-1} \text{ per year}$ during 1982-2015 (figure 3.6d). The overall DIC increase was faster in the SAB than in the MAB ($1.00 \pm 0.22 \mu\text{mol kg}^{-1} \text{ per year}$) during 1982-2015.

Corresponding to DIC variations, the rate Ω_{arag} decreases in the SAB (0.0103 ± 0.0010 per year, figure 3.6h) was faster than that of the MAB (0.0063 ± 0.0015 per year, figure 3.6g). In the MAB, as the DIC increase during 2005-2015 was primarily driven by the transportation of water from the southern regions which had higher Ω_{arag} , Ω_{arag} in the MAB increased slightly during this period instead of decreasing due to anthropogenic CO_2 uptake (figure 3.6g). For pH, the decrease rate in the SAB (0.0014 ± 0.0002 per year, figure 3.6f) was slower than that of the MAB (0.0020 ± 0.0002 per year, figure 3.6e) due to the thermodynamic influence on pH through changing carbonic acid equilibrium constants, which exceeded the influence on pH caused by the slower increase in DIC.

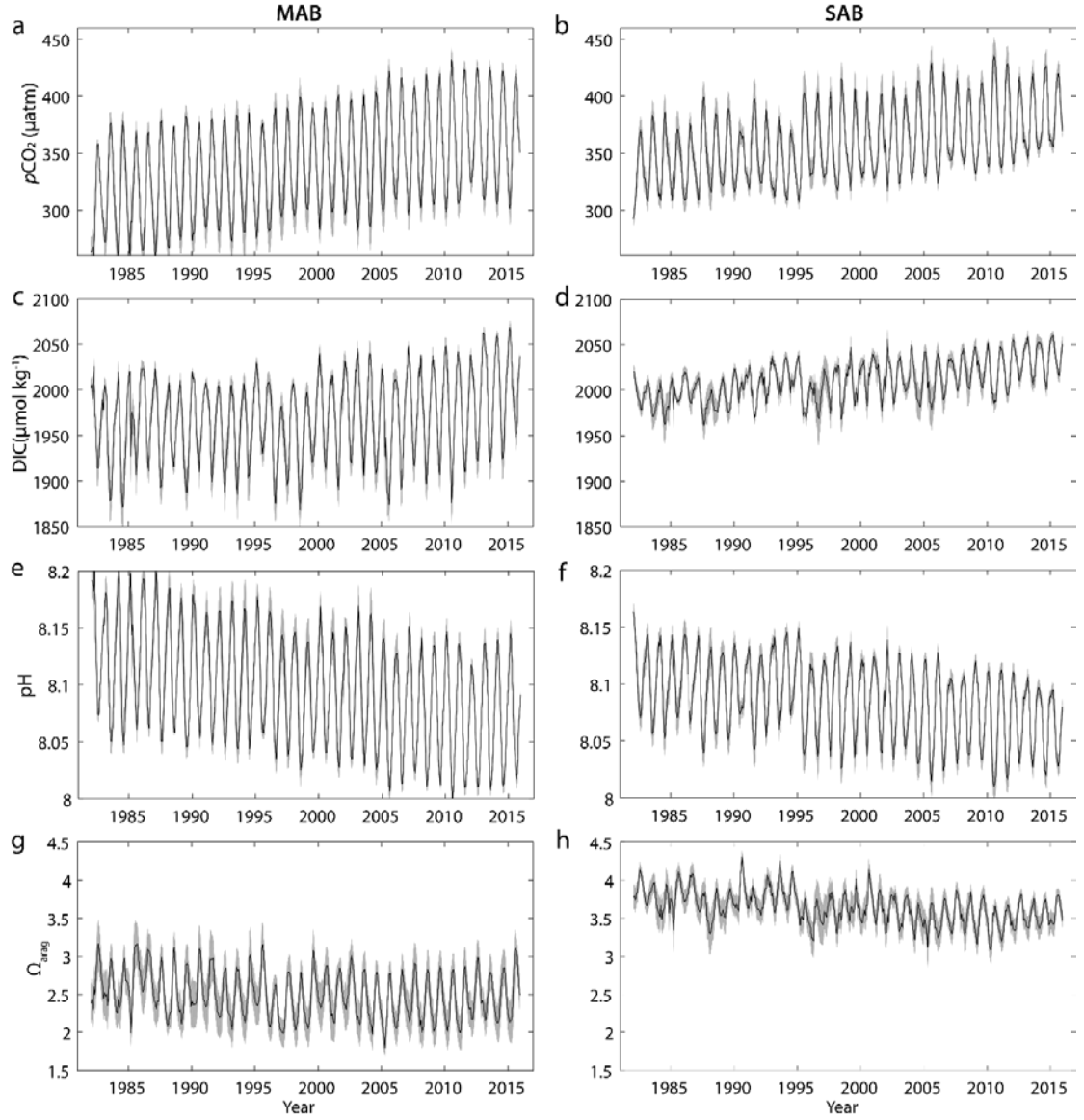


Figure 3.6: $p\text{CO}_2$, DIC, pH, and Ω_{arag} reconstruction for the MAB (left column) and the SAB (right column). The black line with gray shade represents monthly data and uncertainties (1σ) for the MAB and the SAB.

3.4.2 $p\text{CO}_2$, DIC, pH, and Ω_{arag} prediction under climate change

Under the RCP8.5 scenario, seawater $p\text{CO}_2$ will increase as the increase of atmospheric CO_2 in both the MAB and the SAB (figure 3.7a, 3.7b). The increase of $p\text{CO}_2$ in the MAB will be slightly higher than that of the SAB (figure 3.7a, 3.7b). DIC will increase linearly at rates of 1.61 ± 0.03 and $2.10 \pm 0.02 \mu\text{mol kg}^{-1}$ per year, respectively, in the MAB and the SAB (figure 3.7c, 3.7d). The rate of DIC increase in the MAB will be slower than that of the SAB (figure 3.7c, 3.7d). This is largely due to the predicted SST increase in the MAB. The North American east coast from Cape Hatteras to the Scotian Shelf is predicted to experience enhanced warming under climate change because of the retreat of the Labrador Current and the northerly shift of the Gulf Stream (Saba et al., 2016; Thomas et al., 2017). This increase in SST raises seawater $p\text{CO}_2$ and thus reduces air-sea $p\text{CO}_2$ differences during spring, fall, and winter when seawater $p\text{CO}_2$ is lower than atmospheric $p\text{CO}_2$. So annual air-sea CO_2 influx will become smaller and MAB would turn to a weaker CO_2 sink. As a result, DIC in the MAB will increase slower than that in the SAB. By 2100, DIC will increase 73 and 165 $\mu\text{mol kg}^{-1}$, respectively, in the MAB and the SAB compare to the values in 2015.

Following the increase in DIC, Ω_{arag} will decrease at a rate of 0.0127 ± 0.0004 per year in the MAB (figure 3.7e). Ω_{arag} in the SAB will decrease at a faster rate of 0.0157 ± 0.0002 per year (figure 3.7f). Note that temperature also influences Ω_{arag} by changing the first and second carbonic acid dissociation constants. The thermodynamic influence on dissociation constants accounts for part of the slower Ω_{arag} decrease in the MAB because Ω_{arag} would increase with temperature when DIC and TA are constant, while the solubility control which affects $p\text{CO}_2$ and thus air-sea CO_2 flux has a much larger influence on Ω_{arag} change. By 2100, Ω_{arag} will decrease by

1.04 and 1.36 in the MAB and the SAB, respectively, compared to the values in 2015. Especially, Ω_{arag} in the MAB will reach undersaturation as early as 2078 due to the uptake of anthropogenic CO_2 and the large seasonal amplitude, which was earlier than that of the SAB and the South Pacific (110°W, 40°S, Kwiatkowski and Orr, 2018). While, as temperature keeps increasing, the thermodynamic influence on pH through changing carbonic acid equilibrium constants would result in a faster decrease in pH and this effect exceeds the influence on pH caused by the slower increase in DIC. As a result, the rates of pH decrease in the MAB (figure 3.7g) is predicted to be larger than that of the SAB (figure 3.7h). In consequence, pH will decrease by 0.37 and 0.32 in the MAB and the SAB, respectively, by 2100 compared to the values in 2015.

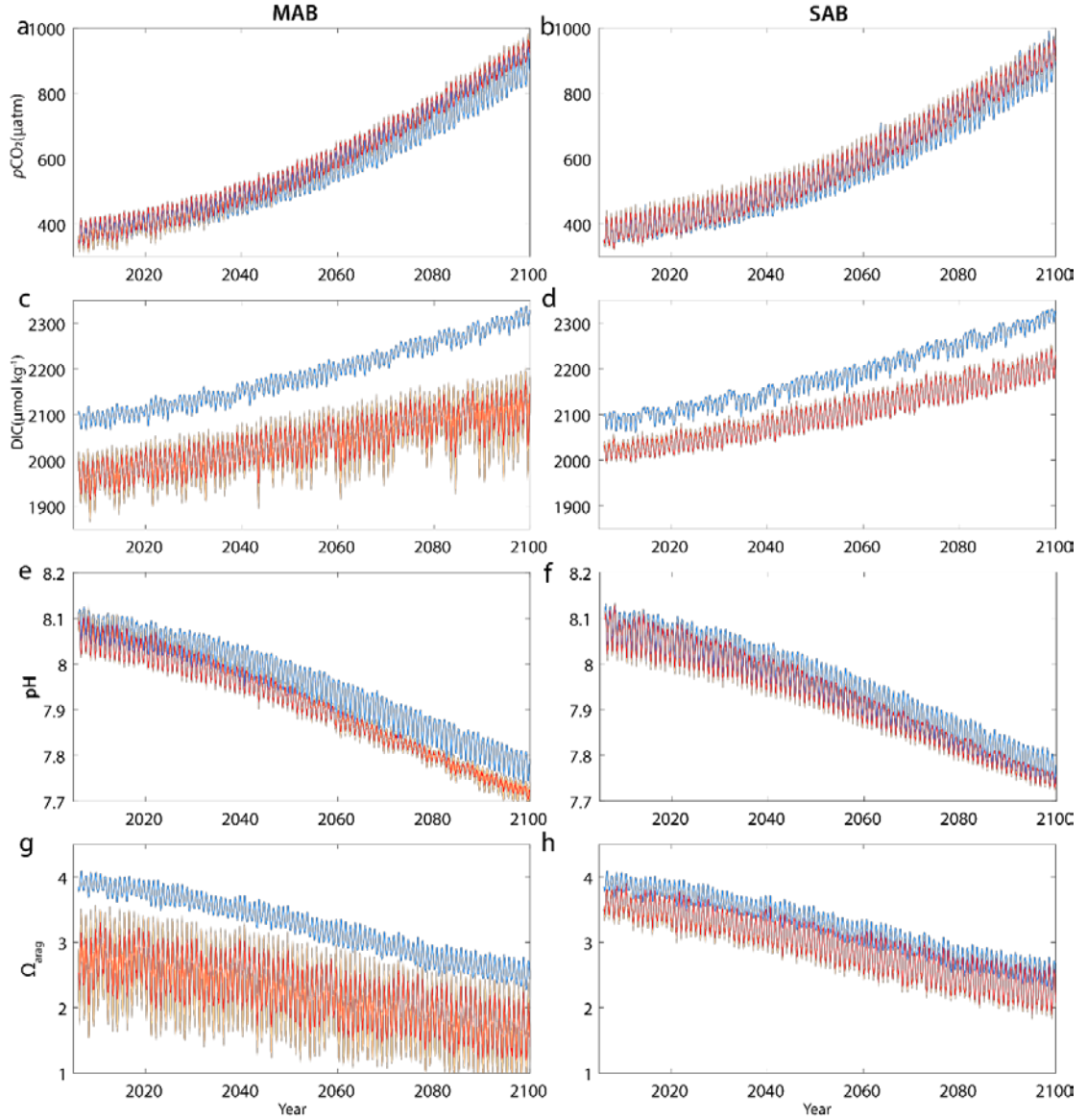


Figure 3.7: The projected (2006–2100, under the RCP8.5 scenario) $p\text{CO}_2$, DIC, pH, and Ω_{arag} with increasing atmospheric CO_2 for the MAB (left column) and the SAB (right column). The red line with shade represents monthly data and uncertainties (1σ) for the MAB and the SAB. The blue line represents open ocean data (see location in figure 3.1).

In addition to the changes in annual mean values, it can be seen from figure 3.7 that the seasonal amplitude of DIC $p\text{CO}_2$, pH and Ω_{arag} will also change during 2006-2100. To further assess the change in seasonal amplitudes of $p\text{CO}_2$, DIC, pH, and Ω_{arag} , we calculate seasonal amplitudes from monthly data for each year by subtracting the minimum values in each year from the maximum values in each year. Note that a significant periodicity of $p\text{CO}_2$, DIC, pH, and Ω_{arag} at about 4 years per cycle is presented in the MAB and the SAB according to the frequency analysis of detrended and normalized annual anomalies during 2006-2100 via the multi-taper method (Ghil et al., 2002; Thomson, 1982). This significant periodicity is impacted, to a large degree, by the North Atlantic Oscillation (NAO), which exerts a strong influence on temperature variations in the North Atlantic region (Czaja and Frankignoul, 2002; Visbeck et al., 2001).

Most of the seasonal amplitudes in the coastal oceans are significantly different from those in the open ocean (figure 3.8). In the MAB, the average seasonal amplitudes of DIC and Ω_{arag} are higher than those in the open ocean by 160% and 175%, respectively. The differences between the average seasonal amplitudes of DIC and Ω_{arag} in the SAB and those in the open ocean of the same latitudinal range are smaller compared to the differences between the MAB and the open ocean (figure 3.8). But the average seasonal amplitudes of DIC and Ω_{arag} are still higher than those in the open ocean of the same latitudinal range by 52% and 67%, respectively. Although the annual mean Ω_{arag} will be still higher than 1 by 2100, the larger seasonal amplitude of Ω_{arag} in coastal regions will lead to earlier exposure of undersaturation for carbonate-bearing organisms. Moreover, Ω_{arag} in the MAB and the SAB becomes

lowest in the early spring of each year at the time of recruitment, which makes it worse for the survival of carbonate-bearing organisms.

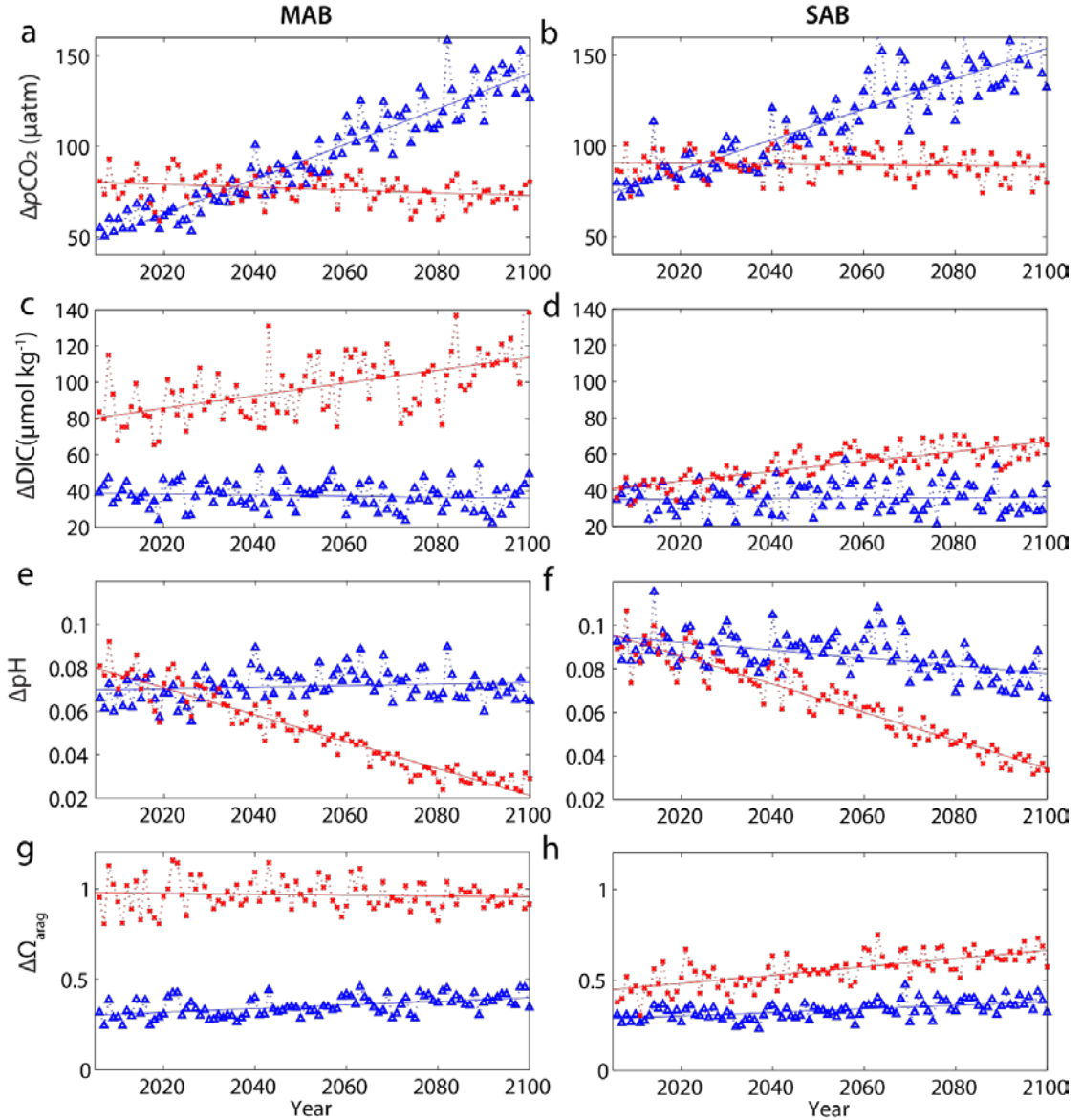


Figure 3.8: Seasonal amplitudes of carbonate chemistry variables for the MAB (left column) and the SAB (right column). The red cross symbols represent data from the MAB and the SAB. The blue triangles represent open ocean data.

The long-term trends of the seasonal amplitudes in the coastal oceans also display some different patterns compare to those in the open ocean (figure 3.8). In terms of the long-term trend from 2006 to 2100, the seasonal amplitude of $p\text{CO}_2$ will increase in the open ocean of both the MAB and the SAB latitudinal ranges at rates of 0.97 ± 0.03 and 0.84 ± 0.05 μatm per year, respectively (figure 3.8a, 3.8b), due to anthropogenic CO_2 uptake from the atmosphere (Kwiatowski and Orr, 2018). However, the seasonal amplitude of $p\text{CO}_2$ in the MAB is predicted to decrease slightly at a rate of 0.08 ± 0.03 μatm per year from 2006 to 2100 (figure 3.8a), which is primarily caused by the increase in buffer capacity that is due to the intrusion of seawater with higher buffer capacity from the southern region. On the other hand, there is no significant trend in the seasonal amplitude of $p\text{CO}_2$ in the SAB (figure 3.8b), which can be attributed to thermodynamic effect because of the increase in the seasonal amplitude of SST.

There is no significant trend in the DIC seasonal amplitude in the open ocean from 2006 to 2100 (figure 3.8c, 3.8d). However, the seasonal amplitudes of DIC are predicted to increase in both the MAB and the SAB at rates of 0.35 ± 0.05 and 0.27 ± 0.02 $\mu\text{mol kg}^{-1}$ per year (figure 3.8c, 3.8d). As for pH, the seasonal amplitude will increase slightly at a rate of 0.00018 ± 0.00003 per year in the open ocean of the SAB latitudinal range while there is no significant trend in the open ocean of the MAB latitudinal range (figure 3.8e, 3.8f). For the coastal ocean, the pH seasonal amplitude is predicted to decrease in both the MAB and the SAB at rates of 0.00062 ± 0.00002 and 0.00065 ± 0.00002 per year (figure 3.8e, 3.8f). In terms of Ω_{arag} , the seasonal amplitude will increase in the open ocean (figure 3.8g, 3.8h). Ω_{arag} seasonal amplitude will increase in the SAB at a faster rate (0.0023 ± 0.0002) than that of the ocean open

while no significant trend is predicted for the MAB (figure 3.8g, 3.8h). The increase in the seasonal amplitude of Ω_{arag} indicates a lower Ω_{arag} in the early spring when Ω_{arag} becomes lowest in a year. This will accelerate the emergence of undersaturation and threaten the survival of marine carbonate-bearing organisms.

3.5 Conclusions

Contrary to open ocean acidification, coastal acidification is difficult to investigate due to its complexity and the lack of observations and model results. In this study, we address the coastal acidification problem via the Bayesian-neural-network approach to reconstruct and predict carbonate chemistry variables for the past and future decades. We found that seawater $p\text{CO}_2$, DIC, pH, and Ω_{arag} variations in the SAB are primarily controlled by the increase in atmospheric CO_2 and the change in buffer capacity, while in the MAB the atmospheric CO_2 influence is modified significantly by temperature and salinity variations, which is driven by physical processes that bring in different water masses. Our neural-network algorithms for estimating the carbonate chemistry variables in the coastal ocean can be added to more complex ocean circulation models to further investigate carbon chemistry variability in a changing world.

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Chapter 4

SURFACE WATER CARBONATE CHEMISTRY ALONG NORTH AMERICA EAST COAST³

4.1 Abstract

The increase of anthropogenic carbon dioxide gas (CO_2) in the atmosphere has acidified the ocean and affected the health of marine organisms and oceanic ecosystems. While spatial patterns of carbonate chemistry properties, and the underlying mechanisms controlling their variability, have been a focus of recent studies in the global ocean, such large-scale syntheses are lacking for highly dynamic coastal oceans. This limits our ability to build a mechanistic understanding and to better predict ocean acidification in coastal domains. Here, we show that total dissolved inorganic carbon (DIC) and calcium carbonate mineral saturation states of aragonite (Ω_{arag}) along the North America east coast have patterns that agree with predictions based on CO_2 equilibrium with the atmosphere. This suggests a solubility control mechanism that leads to low carbonate ion (CO_3^{2-}) concentrations and Ω_{arag} in cold northern waters and the opposite in warm southern waters. We further illustrate

³ This chapter is based on a manuscript entitled “Controls on Surface Water Carbon Chemistry along North American Ocean Margins” in preparation by Wei-Jun Cai, Yuan-Yuan Xu, Richard A. Feely, Rik Wanninkhof, Bror Jönsson, Simone R. Alin, Leticia Barbero, Jessica Cross, Kumiko Azetsu-Scott, Andrea Fassbender, Brendan R. Carter, Li-Qing Jiang, Pierre Pepin, Baoshan Chen, Najid Hussain, Janet Reimer, Liang Xue, Joe E. Salisbury, Martin Hernandez-Ayon, Chris Langdon, Qian Li, Adrienne J. Sutton, Chen-Tung A. Chen, and Dwight Gledhill

that strongly buffered chemical species, such as bicarbonate (HCO_3^-) and CO_3^{2-} , are less sensitive to rising anthropogenic DIC concentrations, while weakly buffered minor species, H^+ and CO_2 , are most sensitive to short-term local processes affecting the acid-base equilibrium, which are often decoupled from the longer time-scale air-sea CO_2 gas exchange.

4.2 Introduction

The uptake of anthropogenic CO_2 from the atmosphere has acidified the ocean as indicated by increases in sea surface partial pressures of CO_2 ($p\text{CO}_2$) and acidity (or $[\text{H}^+]$) as well as decreases in pH, carbonate ion concentration ($[\text{CO}_3^{2-}]$), and calcium carbonate (CaCO_3) mineral saturation state (Caldeira et al., 2003; Orr et al., 2005; Brewer et al., 2009; Bates et al., 2012; Takahashi et al., 2014). The latter is roughly the ratio of $[\text{CO}_3^{2-}]$ to its saturated value below which a certain mineral phase may dissolve (in this paper we use only the saturation state of aragonite, Ω_{arag} , a mineral form the skeletons of corals and other marine organisms are comprised of, which has a saturation state just 1.5 times lower than that of calcite). More than a decade of ocean acidification research has now provided comprehensive observations of spatial and temporal distributions and fundamental understanding of global ocean carbonate chemistry and biogeochemistry (Takahashi et al., 2014; Jiang et al., 2015), and has begun to reveal how ocean chemistry (e.g. pH and Ω_{arag}) and marine organisms are responding to anthropogenic CO_2 uptake (Waldbusser et al., 2015; McNeil et al., 2016; Albright et al., 2018; Kwiatkowski and Orr., 2018; Landschützer et al., 2018; Perez et al., 2018). In the coastal ocean, ocean acidification research has focused on the examination of how anthropogenic CO_2 induced acidification is attenuated or enhanced by biological production (removing CO_2) in surface waters and subsequent

respiration (adding CO₂) in subsurface waters, resulting from human-induced coastal eutrophication (Feely et al., 2010; Cai et al., 2011; Sunda et al., 2012; Wallace et al., 2014; Hagens et al., 2015; Feely et al., 2018). However, despite many recent efforts, we still know little about the large-scale patterns of carbonate chemistry and the mechanisms controlling its variability in coastal waters, largely due to limited observations and the added complication of dynamic and large magnitude local processes.

Surface water distributions of $p\text{CO}_2$, pH, total alkalinity (TA), DIC and Ω_{arag} in ocean margins are strongly influenced to various degrees by river inputs, coastal circulations, vertical mixing, local seasonal temperature variation, balance of biological production and respiration (DeGrandpre et al., 2002; Feely et al., 2008; Jiang et al., 2008; Signorini et al., 2013; Wang et al., 2013; Huang et al., 2015; Wanninkhof et al., 2015; Turi et al., 2016; Feely et al., 2018). Rivers usually bring more acidified waters with a high DIC/TA ratio and thus may weaken the capacity of coastal seas to withstand ocean acidification (Salisbury et al., 2009; Joesoef et al., 2017; Moore-Maley et al., 2018). However, anthropogenically enriched riverine nutrients may lead to elevated biological CO₂ removal and alkalification in surface waters whereas CO₂ accumulation and acidification may occur in bottom waters where biogenic material is ultimately respired (Borges et al., 2010; Cai et al., 2011). Coastal upwelling can bring low pH and low Ω_{arag} waters to shallow nearshore regions and stress coastal biological systems (Feely et al., 2011). Importantly, coastal currents may bring waters from warm (or cold) locations to cold (or warm) locations, resulting in chemical speciation changes due to temperature driven acid-base equilibrium shifts and air-sea gas exchange. When an isolated water mass cools down, its acid-base

equilibrium will shift to reduce CO_2 and H^+ concentrations (that is reduce $p\text{CO}_2$ and increase pH), but this does not affect $[\text{CO}_3^{2-}]$ by much. As a result, cooling may shift a water mass from being a potential source of CO_2 to the atmosphere in warm, subtropical waters to a potential sink for CO_2 in cold, mid-latitude and subarctic waters (e.g., Völker et al., 2002), partially compensating the acid-base equilibrium $p\text{CO}_2$ reduction and pH increase. Additionally, cooling leads to an increase in the CO_2 solubility constant, which allows more CO_2 uptake, reducing pH and greatly reducing $[\text{CO}_3^{2-}]$ (e.g., $\text{CO}_2 + \text{CO}_3^{2-} \rightarrow 2\text{HCO}_3^-$). The net result of chemical speciation and solubility changes during cooling leads to an increase in $[\text{CO}_2]$ and DIC, a very small increase in pH, and a large decrease in $[\text{CO}_3^{2-}]$. However, since acid-base equilibrium is nearly instantaneous while CO_2 gas exchange is accomplished over a time scale of one to a few months (where coastal ocean physical transport occurs on a similar time scale of weeks to months), one would expect to see incomplete gas exchange and intermediate levels of air-sea disequilibrium. On timescales of days to a few weeks, biological productivity can also decouple surface water properties and their equilibrium with the atmosphere (Turi et al., 2016).

A comparative study of marine carbonate chemistry across physically and biologically dissimilar ocean margins will enhance our understanding of the mechanisms controlling CO_2 parameter distributions, variability, and responses to global and regional ocean warming and acidification. Here we report results from concerted large-scale, regional studies of marine carbonate chemistry in major North American ocean margins and reveal the fundamental global and local controls on carbonate properties by both anthropogenic CO_2 invasion and coastal ocean processes.

4.3 Methods

4.3.1 Description of the field program

A map of the North America east coast with major currents is illustrated in figure 4.1. Starting in 2007, under the auspices of NOAA's Climate Program Office and, since its inception in 2010, Ocean Acidification Program (OAP), in collaboration with academic partners and international collaborators, have conducted multiple surveys of the North American east coast. Two large-scale surveys, the Gulf of Mexico and East Coast Carbon (GOMECC) 1 and 2, have been conducted along the east coast in the summer of 2007 (GOMECC-1) and 2012 (GOMECC-2) using state-of-art techniques to study distributions of carbonate parameters (Wang et al., 2013; Wanninkhof et al., 2015). The most recent quality-controlled survey data used in this chapter are the East Coast Ocean Acidification (ECO-A). Results from these cruises are presented along the coastal lines on a map of the North American continent and the associated ocean margins while previous cruises in the same regions are also presented at the same latitude parallel to the coast.

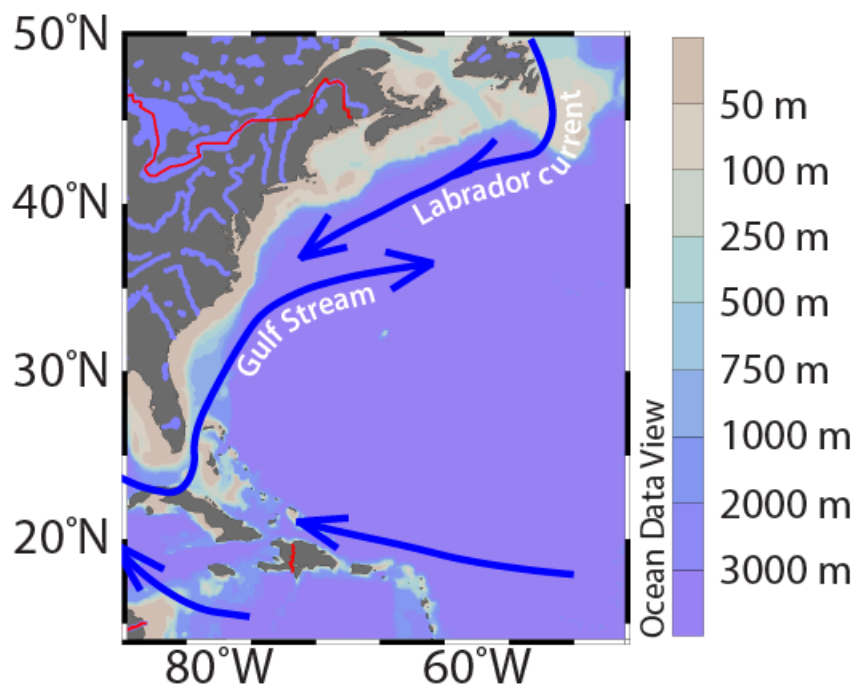


Figure 4.1: Map of the North American ocean margins. The thick blue lines with arrows are the major currents. The color bar represents water depth.

In this work, all DIC samples were measured at sea by coulometric titration using a modified Single-Operator Multi-Metabolic Analyzer (SOMMA) system and TA was measured by acidimetric titration using the open cell method (Jiang et al., 2015; Wanninkhof et al., 2015). Both DIC and TA measurements were calibrated daily using Certified Reference Materials (CRM) from Dr. Andrew Dickson's laboratory at Scripps Institution of Oceanography. The overall uncertainty of each of these two measurements is $2 \mu\text{mol kg}^{-1}$. DO was measured by a Winkler titration technique.

4.3.2 Calculated pH, $p\text{CO}_2$, and Ω_{arag}

In this study, for the purpose of examining spatial distributions, pH, $p\text{CO}_2$, and Ω_{arag} are calculated from DIC and TA using the CO2SYS program (Richaud et al., 2016), with carbonic acid dissociation constants of Dickson and Millero (1987). We use the DIC-TA pair because both parameters were measured at high quality during all cruises. Good internal consistency among multiple parameters was observed and potential issues were identified in an earlier study (Patsavas et al., 2015). pH is expressed on the total proton concentration scale. Ω_{arag} is defined as the concentration product of dissolved calcium and carbonate ions divided by the aragonite mineral solubility product. The values at equilibrium are calculated assuming that seawater $p\text{CO}_2$ is in equilibrium with atmospheric $p\text{CO}_2$. In this case, the input pair to CO2SYS is $p\text{CO}_2$ and TA. The atmospheric CO_2 data, as a dry air mole fraction, was extracted from the NOAA Marine Boundary Layer Reference product. The uncertainty of these annual CO_2 data is 0.12 $\mu\text{mol/mol}$.

4.3.3 Definitions of buffer factors (γ , β , ω , and Revelle factor)

Buffer factors (γ , β , ω , and Revelle factor) are calculated using the following equations (Frankignoulle, 1994; Egleston et al., 2010; Álvarez et al., 2014):

$$\begin{aligned}\gamma_{\text{DIC}(\text{CO}_2)} &= \left(\frac{\partial \ln[\text{CO}_2]}{\partial \text{DIC}} \right)^{-1} = \left(\frac{\Delta[\text{CO}_2]}{[\text{CO}_2]} / \Delta \text{DIC} \right)^{-1} = \text{DIC} - \frac{T_{\text{Ac}}^2}{S}; \\ \beta_{\text{DIC}(\text{H})} &= \left(\frac{\partial \ln[\text{H}^+]}{\partial \text{DIC}} \right)^{-1} = \left(\frac{\Delta[\text{H}^+]}{[\text{H}^+]} / \Delta \text{DIC} \right)^{-1} = \frac{\text{DIC} \times S - T_{\text{Ac}}^2}{T_{\text{Ac}}}; \\ \omega_{\text{DIC}(\text{CO}_3^{2-})} &= \left(\frac{\partial \ln[\text{CO}_3^{2-}]}{\partial \text{DIC}} \right)^{-1} = \left(\frac{\Delta[\text{CO}_3^{2-}]}{[\text{CO}_3^{2-}]} / \Delta \text{DIC} \right)^{-1} = \left(\frac{\partial \ln \Omega}{\partial \text{DIC}} \right)^{-1} = \left(\frac{\Delta \Omega}{\Omega} / \Delta \text{DIC} \right)^{-1} \\ &= \text{DIC} - \frac{T_{\text{Ac}} \times (2[\text{CO}_2] + [\text{HCO}_3^-])}{P}\end{aligned}$$

With $S = [HCO_3^-] + 4[CO_3^{2-}] + \frac{[H^+] \times [B(OH)_4^-]}{K_B + [H^+]} + [H^+] + [OH^-]$ and

$$P = [HCO_3^-] - \frac{[H^+] \times [B(OH)_4^-]}{K_B + [H^+]} - [H^+] - [OH^-]$$

As well as

$$TA_c = [HCO_3^-] + 2[CO_3^{2-}] \text{ and}$$

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

$$\text{Revelle factor (RF)} = \frac{\partial \ln[CO_2]}{\partial \ln DIC} = \frac{\Delta[CO_2]}{[CO_2]} / \frac{\Delta DIC}{DIC} = DIC/\gamma.$$

4.3.4 CO₂ system sensitivity

The sensitivity of the CO₂ system to temperature change and DIC increase has been examined using two approaches. One is the inverse of the buffer factors. The other is based on the calculation using CO2SYS. How various species respond to temperature increase in a closed system (no exchange of CO₂ with the air) and in an open system (with air-sea exchange) is presented in figure 4.2 and table 4.1. It is shown that for the same fractional DIC increase, [CO₂] and [H⁺] have greater changes than those of [CO₃²⁻] and [HCO₃⁻] (figure 4.2, table 4.1).

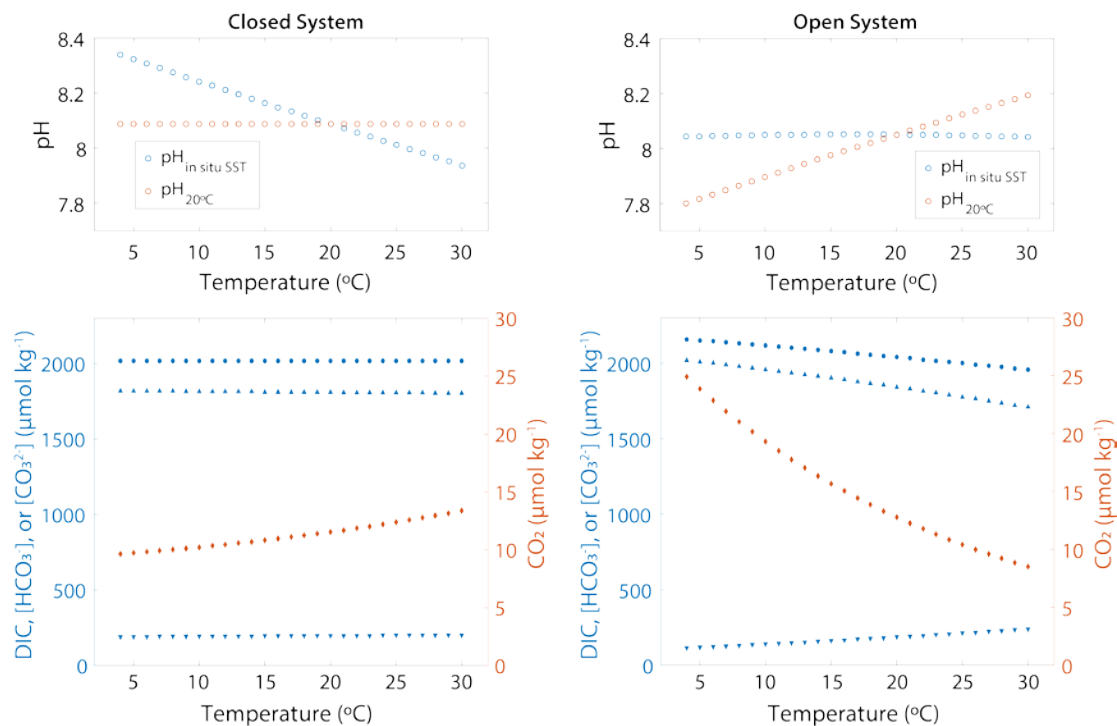


Figure 4.2: Temperature dependence of CO₂ system species concentrations. Left column: Closed system (constant DIC = 2020 μmol kg⁻¹ and TA = 2300 μmol kg⁻¹). Right column: Open system at constant pCO₂ (= 395 μatm) and TA (= 2300 μmol kg⁻¹).

Table 4.1: Sensitivity of CO₂ system parameters to temperature change in a closed system (a & b: no exchange with the atmosphere) and an open system (c & d: exchange the atmosphere). b is similar to a but with a DIC reduction of 50 $\mu\text{mol kg}^{-1}$ simulating biological removal of CO₂. d is similar to c but with a disequilibrium of 45 μatm below the atmosphere simulating biological removal of CO₂. Note that $[\text{CO}_2] = p\text{CO}_2 \times K_0$ and $[\text{CO}_3^{2-}] = (K_1/K_2)^{-1} \times [\text{HCO}_3^-]^2 / [\text{CO}_2] \approx \text{DIC}^2 / p\text{CO}_2 \times (K_0)^{-1} (K_1/K_2)^{-1}$. Since both K_0 and (K_1/K_2) will increase with temperature decrease, a decrease in temperature from 35 to 15 will increase $[\text{CO}_2]$ and decrease $[\text{CO}_3^{2-}]$ in a system open to the atmosphere (see part c & d).

a. Closed system at $S = 35$, $\text{TA} = 2300 \mu\text{mol kg}^{-1}$ and $\text{DIC} = 2000 \mu\text{mol kg}^{-1}$.

SST	[CO ₂]	pCO ₂	pH _T	[HCO ₃ ⁻]	[CO ₃ ²⁻]	DIC	Ω _{arag}
30.0	12.13	483.4	7.972	1772.9	214.9	2000.0	3.50
25.0	11.24	397.3	8.045	1775.2	213.5	2000.0	3.39
20.0	10.48	324.5	8.120	1777.8	211.7	2000.0	3.29
15.0	9.83	263.3	8.197	1780.6	209.6	2000.0	3.21
change	-2.30	-220.1	0.225	7.67	-5.36	0.00	-0.29
% change	-19.0	-45.5	2.822	0.43	-2.5	0.0	-3.7

b. Closed system at $S = 35$, $\text{TA} = 2300 \mu\text{mol kg}^{-1}$ and $\text{DIC} = 1950 \mu\text{mol kg}^{-1}$.

SST	[CO ₂]	pCO ₂	pH _T	[HCO ₃ ⁻]	[CO ₃ ²⁻]	DIC	Ω _{arag}	ΔpH(ΔDIC)
30.0	10.30	410.6	8.03	1717.3	237.4	1965.0	3.87	0.057
25.0	9.54	337.0	8.10	1719.4	236.1	1965.0	3.75	0.058
20.0	8.88	275.0	8.18	1721.8	234.3	1965.0	3.64	0.058
15.0	8.32	222.9	8.26	1724.5	232.2	1965.0	3.55	0.058
change	-1.99	-187.7	0.23	7.2	-5.20	0.00	-0.31	0.001
% change	-19.3	-45.7	2.86	0.42	-2.2	0.0	-4.1	1.754

c. Open system at $S = 35$, $\text{TA} = 2300 \mu\text{mol kg}^{-1}$ and $p\text{CO}_2 = 395 \mu\text{atm}$.

SST	[CO ₂]	pCO ₂	pH _T	[HCO ₃ ⁻]	[CO ₃ ²⁻]	DIC	Ω _{arag}
30.0	9.91	395.0	8.042	1703.69	242.9	1956.5	3.95
25.0	11.18	395.0	8.047	1773.34	214.3	1998.8	3.40
20.0	12.76	395.0	8.050	1840.42	186.4	2039.6	2.90
15.0	14.74	395.0	8.050	1904.14	159.7	2078.6	2.45
change	4.83	0.00	0.008	200.45	-83.14	122.14	-1.51
% change	48.7	0.0	0.099	11.8	-34.2	6.2	-38.2

d. Open system at $S = 35$, $TA = 2300 \mu\text{mol kg}^{-1}$ and $p\text{CO}_2 = 350 \mu\text{atm}$.

SST	[CO ₂]	$p\text{CO}_2$	pH _T	[HCO ₃ ⁻]	[CO ₃ ²⁻]	DIC	Ω_{arag}	$\Delta\text{pH}(\Delta p\text{CO}_2)$
30.0	8.78	350	8.084	1660.33	260.34	1929.46	4.24	0.041
25.0	9.91	350	8.090	1732.44	230.82	1973.17	3.66	0.042
20.0	11.30	350	8.093	1802.41	201.77	2015.49	3.14	0.043
15.0	13.06	350	8.095	1869.39	173.76	2056.21	2.66	0.045
change	4.28	0	0.011	209.05	-86.58	126.76	-1.58	0.003
% change	48.7	0	0.136	12.6	-33.3	6.6	-37.2	7.317

When the system is under the condition of constant DIC and TA (so-called closed system), [CO₂] increases (from 12.1 to 16.8 $\mu\text{mol kg}^{-1}$) and pH (at in situ temperature) decreased (from 8.263 to 7.846) as temperature increases from 15 to 30 °C. While [CO₃²⁻] also increases (from 162.5 to 173.8 $\mu\text{mol kg}^{-1}$), the relative change is small. On a relative scale, [HCO₃⁻] decreases little with increasing temperature. When the system is in equilibrium with the atmosphere (the so-called open system at constant $p\text{CO}_2$ and TA), DIC, [HCO₃⁻] and [CO₂] would decrease while [CO₃²⁻] would increase with increasing temperature. Here the temperature effect has two components: (1) via CO₂ solubility $K_0 = [\text{CO}_{2\text{aq}}]/p\text{CO}_2$ and (2) via the dissociation constants of carbonic acid (K_1 and K_2). Here we have K_1 for $\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$, K_2 for $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$, and $K = K_1/K_2$ for the combined reaction: H_2CO_3 (or $\text{CO}_{2\text{aq}} + \text{H}_2\text{O}$) + $\text{CO}_3^{2-} = 2\text{HCO}_3^-$. Thus, $K_1/K_2 = [\text{HCO}_3^-]^2/([\text{H}_2\text{CO}_3] \times [\text{CO}_3^{2-}])$ or $[\text{CO}_3^{2-}] = (K_1/K_2)^{-1} \times [\text{HCO}_3^-]^2/[\text{H}_2\text{CO}_3] \approx (K_1/K_2)^{-1} \times \text{DIC}^2/[\text{H}_2\text{CO}_3]$.

By convention, [CO_{2aq}] and [H₂CO₃] are not differentiated and are combined as one in [CO₂]. Both K_1 and K_2 would increase with temperature (more dissociation). But since K_2 increases more than K_1 , the combined constant decreases and the

combined reaction moves to the left (figure 4.3), thus leading to increases in CO_2 and $[\text{CO}_3^{2-}]$. Thus, in a closed system, $[\text{CO}_2]$ and $p\text{CO}_2$ will increase and pH will decrease with temperature increase. In an open system, the initial increase in temperature would lead to higher CO_2 and possibly CO_2 degassing. Also, the decrease in K_0 with increasing temperature is much more sensitive than the combined K_2 and K_1 effect (figure 4.3), thus allowing less $[\text{CO}_2]$ in water for the same $p\text{CO}_2$ and lower $[\text{HCO}_3^-]$ and DIC. But CO_2 degassing would lead to higher $[\text{CO}_3^{2-}]$.

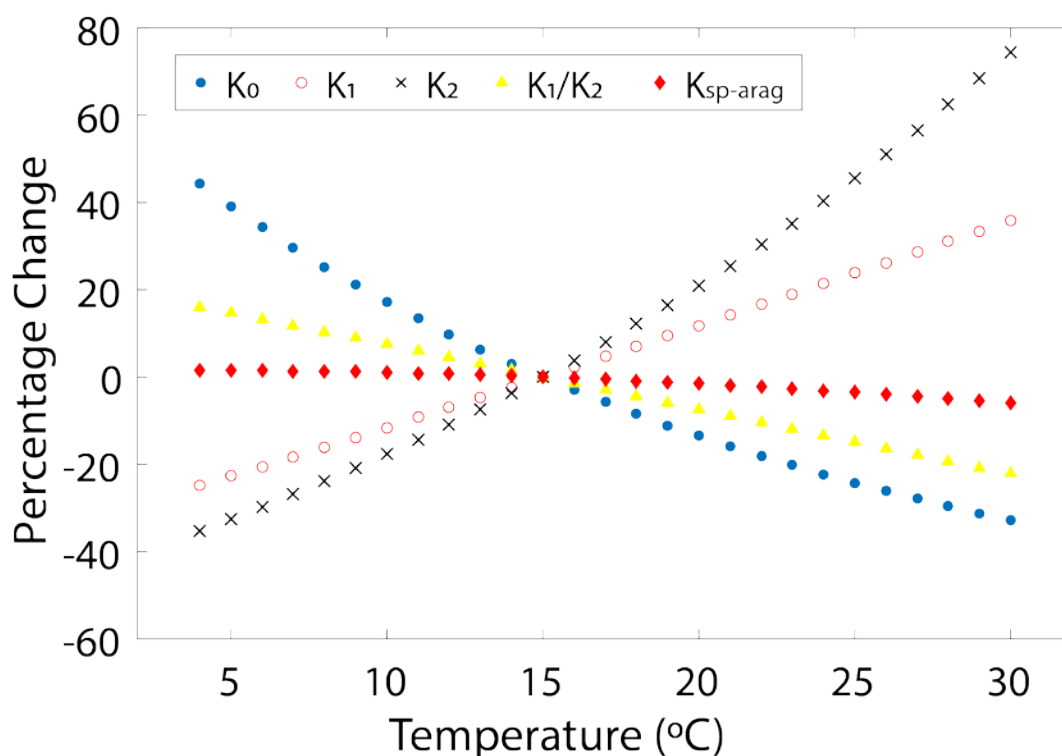


Figure 4.3: Temperature dependence of the thermodynamic constants of the marine CO_2 system relative to those at 15°C . In this paper, K_0 is from Weiss (1973), and K_1 and K_2 are from Dickson and Millero (1987). The aragonite mineral carbonate saturation constant $K_{sp-arag}$ is from Mucci (1983). See Methods for explanation.

4.3.5 Data availability

Discrete bottle data from all National Oceanic and Atmospheric Administration (NOAA) ocean acidification regional research cruises are available at NOAA's National Centers for Environmental Information:

<https://www.nodc.noaa.gov/ocads/data/0083633.xml> (GOMECC-1);

<https://www.nodc.noaa.gov/oads/data/0117971.xml> (GOMECC-2);

<https://www.nodc.noaa.gov/oads/data/0159428.xml> (ECOIA).

Atmospheric CO₂ data are available at <https://www.esrl.noaa.gov/gmd/ccgg/mbl/>.

4.4 Results and discussion

4.4.1 Carbonate chemistry property distributions

The North American east coast is characterized by broad, shallow shelves influenced on the landside by river and wetland inputs and on the seaside by alongshore currents, most notably the northbound Gulf Stream and the southbound Labrador and Scotian Current (figure 4.1, Atkinson et al., 1983; Wiseman et al., 1997; Richaud et al., 2016). Here, summertime sea surface temperature (SST) (figure 4.4a) and salinity (SSS) (figure 4.4b) decrease from southwest to northeast as a result of climatic zonation of the source waters (that is warm, high salinity source waters are derived from the tropical regions and cold, low salinity source waters from the Arctic and subarctic regions), ocean circulation, and local modifications by rivers (Atkinson et al., 1983; Richaud et al., 2016). The TA follows that of salinity with the highest TA in the south, a sharp south-to-north decrease along the east coast (Wanninkhof et al., 2015; Feely et al., 2018), excluding some nearshore modifications by major rivers (Cai et al., 2010; figure 4.4c). In contrast to the sharp meridional decline in TA, DIC concentrations along the Atlantic coast exhibit less of a decrease moving south to

north, and even show some high values in the northern regions. Thus, the DIC/TA ratio exhibits a large south-to-north gradient, with the lowest values in the south, and it is significantly correlated with SST ($r = -0.89$, $n = 548$, $p < 0.01$) (figure 4.4f). Note while the south region has high DIC values, its DIC/TA ratio is the lowest along the entire North American east coast. Along North American east coast and during summertime, dissolved O₂ percentage (DO%, figure 4.4g) is generally close to the atmospheric saturation with a few very high values in the Gulf of Maine, reflecting a high biological production there (Townsend et al., 2015).

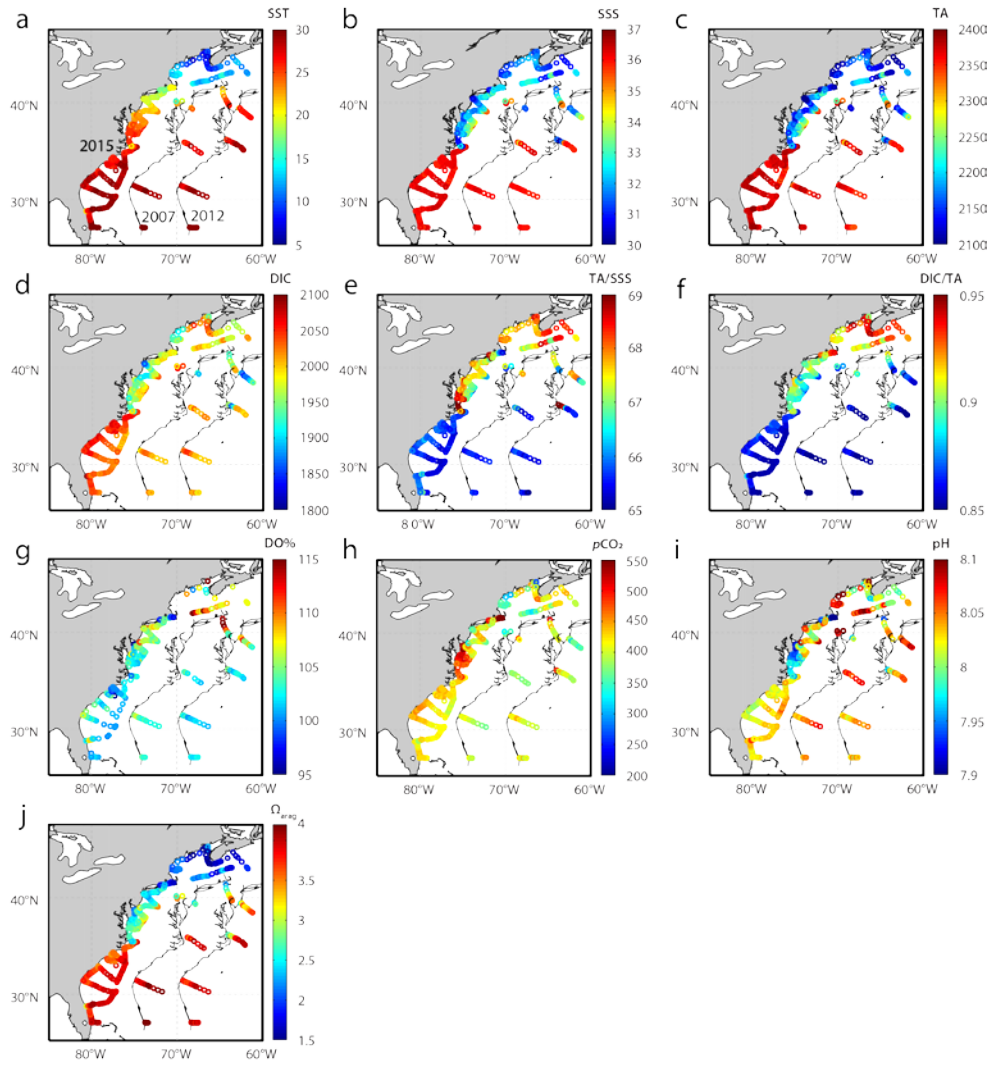


Figure 4.4: Distributions of physical and biogeochemical parameters important to understand the marine carbonate system in surface seawater along the North American ocean margins. (a) Sea surface temperature (SST), (b) sea surface salinity (SSS), (c) total alkalinity (TA), (d) total dissolved inorganic carbon (DIC), (e) TA/SSS, (f) DIC/TA, (g) dissolved oxygen (DO%), (h) partial pressure of CO_2 ($p\text{CO}_2$), (i) pH (in total proton concentration scale; Dickson, 1993), and (j) aragonite mineral saturation state (Ω_{arag}). See Methods for methodology of determinations of these parameters. To conserve space, only the 2015–2017 data are presented on the exact geographic locations in a North American ocean margins map while earlier data are plotted with an offset on the map with the purpose to show that the general patterns presented here repeat in various cruises at somewhat different times.

Table 4.2: Statistical correlations (r values) between various parameters. Note red color indicates p value larger than 0.05 or not statistically significant.

a. Correlations with SST.

	number of observations	SST & TA	SST & DIC	SST & $p\text{CO}_2$	SST & pH	SST & Ω_{arag}	SST & DIC/TA
Atlantic Coast	548	0.60	0.05	0.36	-0.25	0.89	-0.89

b. Correlations with SSS.

	number of observations	SSS & TA	SSS & DIC	SSS & $p\text{CO}_2$	SSS & pH	SSS & Omega	SSS & DIC/TA
Atlantic Coast	548	0.99	0.79	-0.12	0.29	0.84	-0.81

c. Correlations with DO%.

	number of observations	DO & TA	DO & DIC	DO & $p\text{CO}_2$	DO & pH	DO & Ω_{arag}	DO & SST	DO & SSS	DO & DIC/TA
Atlantic Coast	411	0.21	0.04	-0.30	0.34	0.26	0.18	0.26	-0.31

d. Correlations with DIC/TA.

	number of observations	DIC/TA & $p\text{CO}_2$	DIC/TA & pH	DIC/TA & Ω_{arag}
Atlantic Coast	548	0.06	-0.19	-1.00

Interestingly, the large-scale spatial distribution of Ω_{arag} , an important metric for ocean acidification stress on organisms, bears little resemblance to those of $p\text{CO}_2$ and pH along any of the margins (figure 4.4h). Rather, the Ω_{arag} distribution is similar to SST ($r = 0.89$, $n = 548$, $p < 0.01$) and TA ($r = 0.84$, $n = 548$, $p < 0.01$) and most closely aligned inversely to the DIC/TA ratio ($r = -1.00$, $n = 548$, $p < 0.01$) along the east coast (see table 4.2 for other margins). There is also a strong south-to-north decreasing gradient as reported before (Wang et al., 2013; Wanninkhof et al., 2015). The highest Ω_{arag} appears in the south which is consistent with highest SST and TA and lowest DIC/TA ratio there.

Sea surface $p\text{CO}_2$ and pH (in total proton concentration scale; Dickson, 1993) however show complex spatial patterns and no significant correlation with SST, DO%, or DIC/TA (table 4.2), reflecting the influence of multiple processes on their distributions along the east coast (figure 4.4h, 4.4i). In the mid-latitude regions, low $p\text{CO}_2$ and high pH appear in areas of high DO% suggesting biological CO_2 removal there (e.g. in the Gulf of Maine; Townsend et al., 2015). Low $p\text{CO}_2$ and high pH also appear together in the central MAB near the Chesapeake Bay and the Delaware Bay reflecting net respiration.

4.4.2 Global patterns versus local variability

To explore the first-order controlling mechanisms on large-scale distribution patterns of carbonate chemistry parameters, we first examine how well DIC, $p\text{CO}_2$, pH and Ω_{arag} distributions can be predicted from equilibrium with atmospheric CO_2 by calculating these parameters from SST, SSS, and TA under the assumption of a rapid sea surface CO_2 equilibration with the atmosphere (figure 4.5). Over a large latitudinal span involving multiple water masses along the North American east coast, DIC and

Ω_{arag} generally follow the solubility-based predictions (figure 4.5a, 4.5b). This atmospheric CO_2 solubility control mechanism would dictate a high DIC and low Ω_{arag} in cold northern waters where CO_2 solubility is high and a low DIC and high Ω_{arag} in warm southern waters where CO_2 solubility is low if ocean salinity and TA are the same (see Methods and figure 4.2c, 4.2d). This is a known principle in global open ocean basins, but it has not been reported before in coastal oceans (Broecker and Peng, 1982; Carter et al., 2014; Takahashi et al., 2014; Jiang et al., 2015). Therefore, even though there is a small DIC decrease northward following the decrease in salinity, the DIC decrease is much smaller than the TA decrease due to CO_2 uptake from the atmosphere in cold northern waters. The fact that the DIC/TA ratio is lowest in the south and highest in the northern coastal waters reflects just this temperature regulated solubility effect.

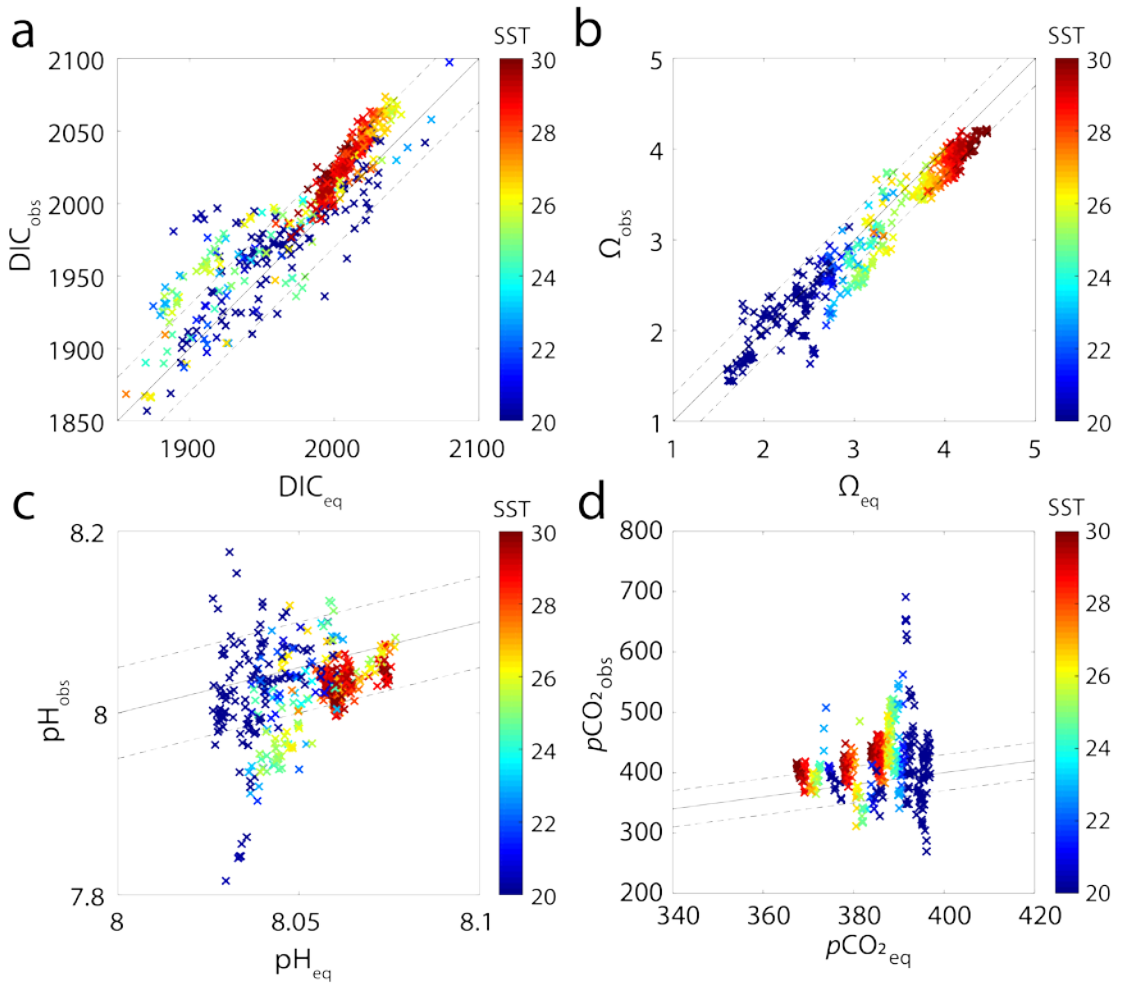


Figure 4.5: Observations vs. calculated values at equilibrium with atmospheric CO_2 along North American east coast. Data from all three surveys (GOMECC-1, -2, and ECOA) have been used in this plot. DIC_{obs} , Ω_{obs} , pH_{obs} , and $p\text{CO}_{2\text{obs}}$ stand for the measured DIC and properties calculated from measured DIC and TA. DIC_{eq} , Ω_{eq} , pH_{eq} , and $p\text{CO}_{2\text{eq}}$ represent values calculated under the conditions of seawater equilibrium with atmospheric $p\text{CO}_2$ at the time of field programs (see Methods). pH_{obs} and pH_{eq} are on the total proton concentration scale. The dashed lines around the 1:1 line are ± 0.05 for pH and $\pm 30 \mu\text{atm}$ for $p\text{CO}_2$.

When it comes to pH, only a weak solubility control can still be seen along the North American east coast (figure 4.5c). Finally, along all the margins, $p\text{CO}_2$ values do not usually reflect the atmospheric values and thus must be strongly driven by local physical (upwelling, mixing, and SST at the time of observation) and biological processes rather than CO_2 exchange with the atmosphere. The range of variation is much larger in the MAB with high values reflecting local biological activities (figure 4.4h, figure 4.5d).

4.4.3 Sensitivity of carbonate chemistry to perturbations

A fundamental question to ask then is why local physical and biological modifications are least apparent for DIC and Ω_{arag} , but most apparent for pH and $p\text{CO}_2$. We argue that this is determined by both the different sensitivities of carbonate system species to DIC and temperature alterations and the response times to air-sea gas exchange. Firstly, chemical equilibrium among acid-base species and the associated thermodynamic constants leads to larger relative changes in $[\text{CO}_2]$ and $[\text{H}^+]$ than in $[\text{CO}_3^{2-}]$ and $[\text{HCO}_3^-]$ when DIC or temperature is altered in seawater in both closed and open systems (figure 4.2, figure 4.3, figure 4.6, table 4.1). The sensitivity of $p\text{CO}_2$ to temperature change in an isolated water (no exchange with the atmosphere) is even greater (twice) than that of $[\text{CO}_2]$ since the solubility constant increases while $p\text{CO}_2$ decreases with declining temperature (figure 4.6, table 4.1).

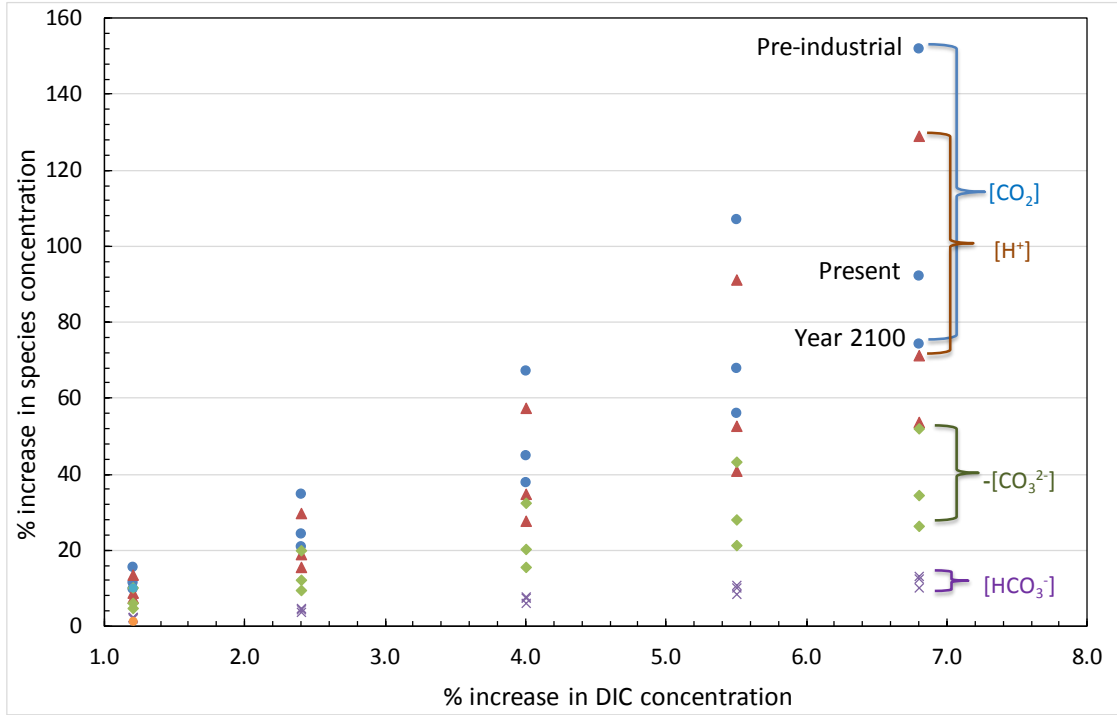


Figure 4.6: Sensitivity of marine CO₂ system components to increasing DIC. Percentage increase in concentrations of inorganic carbon species versus the percentage increase in DIC. Three DIC concentrations correspond to the pre-industrial (on the top for each species, as labeled and illustrated for the highest DIC increase example), the present (in the middle for each species), and end of the 21st century (in the bottom for each species). On top of each of the three scenarios, we allow DIC to increase from 1.2% to 6.8% along the x-axis (each increment is about 25 μmol kg⁻¹).

The sensitivities of different species toward DIC change may be expressed by the inverse of a set of buffer factors defined as (Egleston et al., 2010):

$$\gamma_{DIC(CO_2)}^{-1} = \frac{\Delta[CO_2]}{[CO_2]} / \Delta DIC,$$

$$\beta_{DIC(H^+)}^{-1} = \frac{\Delta[H^+]}{[H^+]} / \Delta DIC = -2.3\Delta pH / \Delta DIC,$$

and

$$\omega_{DIC(CO_3^{2-})}^{-1} = \frac{\Delta[CO_3^{2-}]}{[CO_3^{2-}]} / \Delta DIC = \frac{\Delta \Omega}{\Omega} / \Delta DIC.$$

Here $\gamma_{DIC(CO_2)}^{-1}$, the sensitivity of CO_2 to DIC change is directly linked to the Revelle factor (RF), defined as

$$RF = \frac{\Delta[CO_2]}{[CO_2]} / \frac{\Delta DIC}{DIC} = DIC \times \gamma_{CO_2}^{-1},$$

which is often used by marine chemists. In other words, each buffer factor (or the inverse of the sensitivity) represents the ability of a species to resist change when DIC is altered (see the mathematically more rigorous definitions in Methods). Note as both $[CO_2]$ and $[H^+]$ would increase but $[CO_3^{2-}]$ would decrease when DIC increases, a negative sign is added before ω for discussion.

Along North American east coast, we observe $-\omega = 0.17\text{--}0.39$ for CO_3^{2-} , which is greater than $\beta = 0.15\text{--}0.28$ for H^+ and $\gamma = 0.13\text{--}0.23$ for CO_2 (figure 4.7). By default, the buffer factor for DIC (roughly also for HCO_3^-) against DIC change would be 1. The clear differences between these buffer factors, though previously not emphasized, indicate that HCO_3^- and CO_3^{2-} are better buffered against (or less sensitive to) DIC increases than CO_2 and H^+ , as is measured by the size of their respective buffer factor (figure 4.7, 4.8, 4.9). Currently the southern east coast waters still have the buffering capacity to cope with atmospheric CO_2 increase while those of the northern east coast are at the point of depletion of their buffering capacity or simply to say $[CO_3^{2-}]$ is low in weakly buffered waters, supporting and expanding conclusions made by two previous studies (Feely et al., 2008; Sunda et al., 2012).

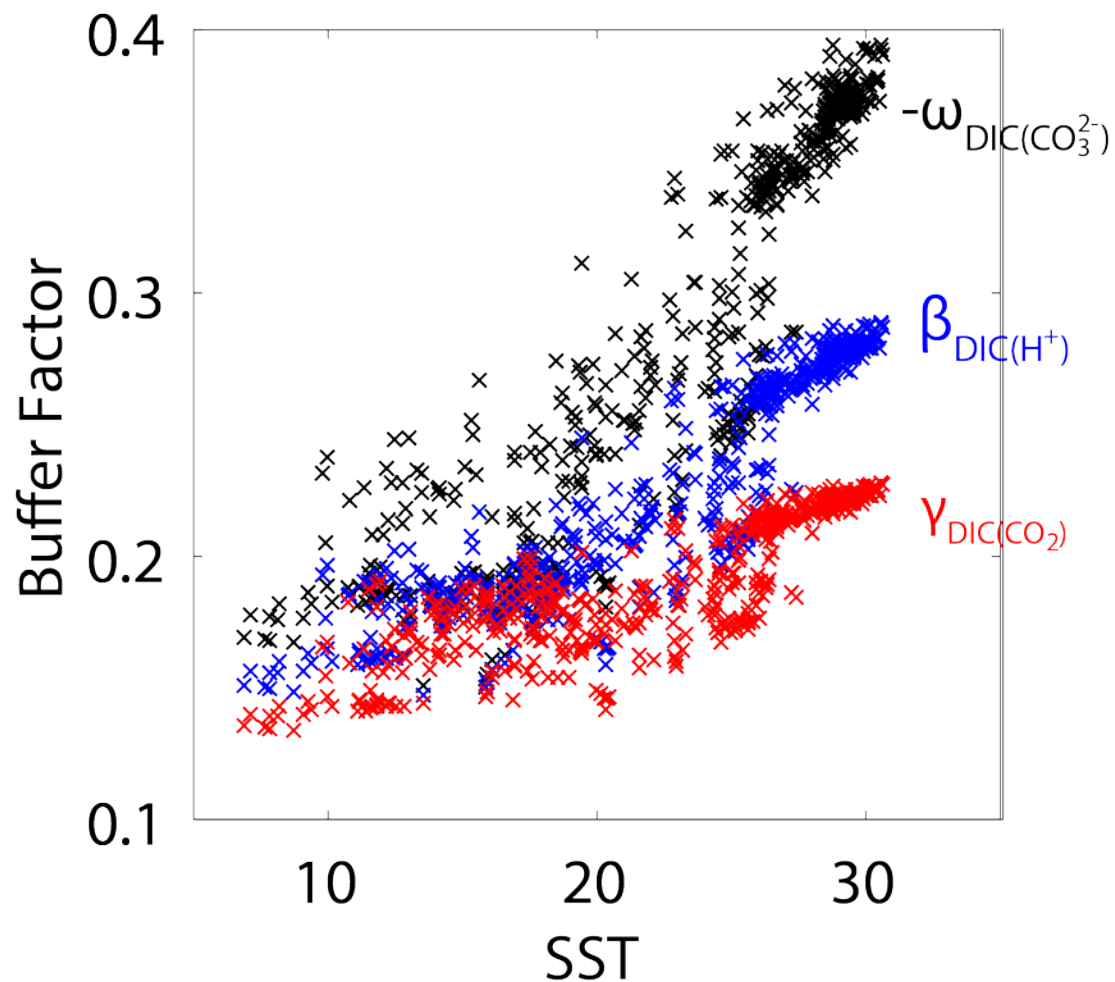


Figure 4.7: Variations of buffer factors with temperature in the North American ocean margins. These buffer factors reflect the sensitivity of water chemistry to changes in DIC at constant TA. Larger buffer factor values indicate greater buffer capacity and lower sensitivity to changes in DIC. Their mathematical definitions are precisely given in Methods but an easy to understand version is presented in the main text.

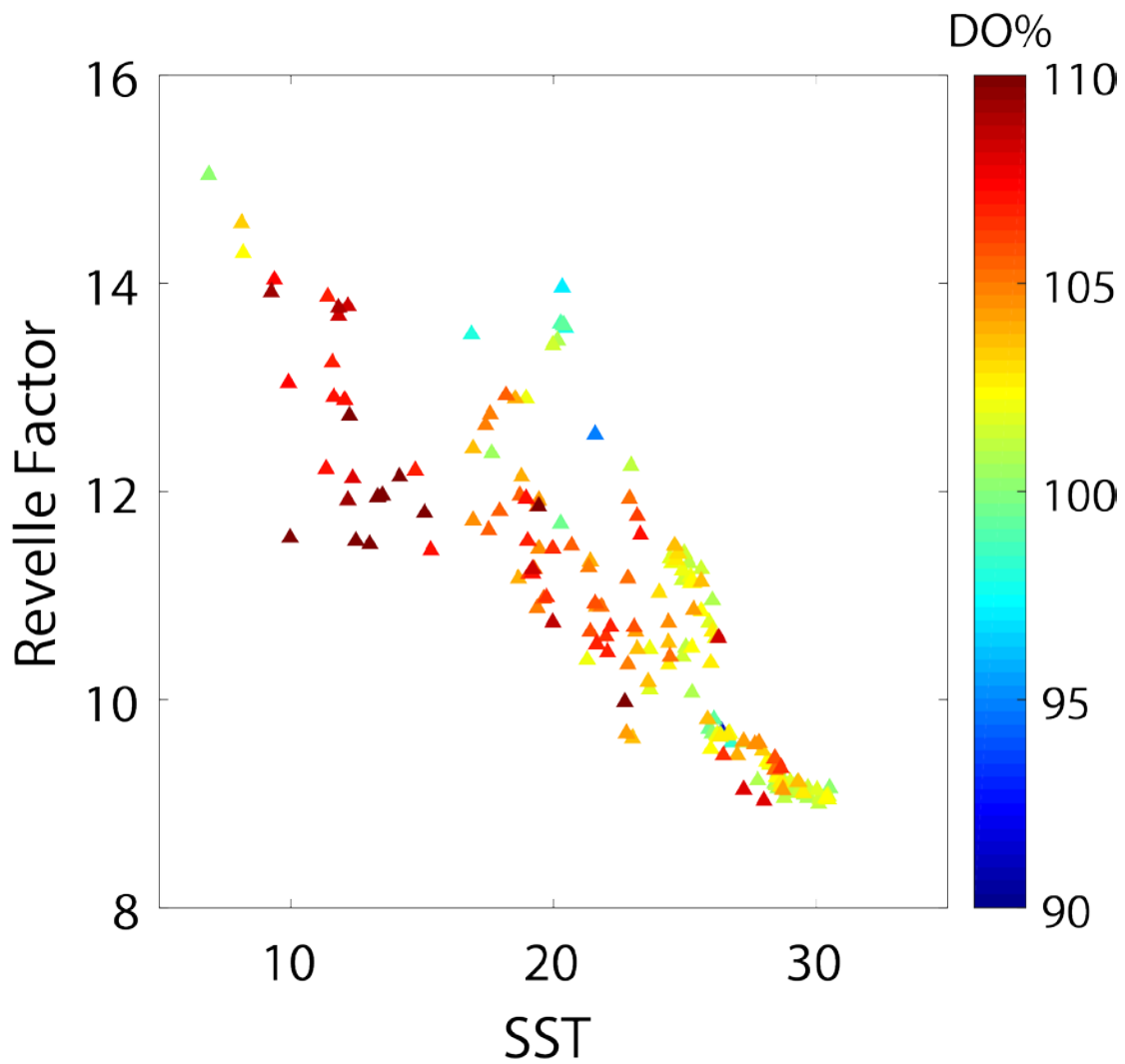


Figure 4.8: Revelle Factor vs. SST along the North American east coast, with color code to show the corresponding DO%. As $RF = DIC/\gamma$, lower RF means stronger buffering capacity.

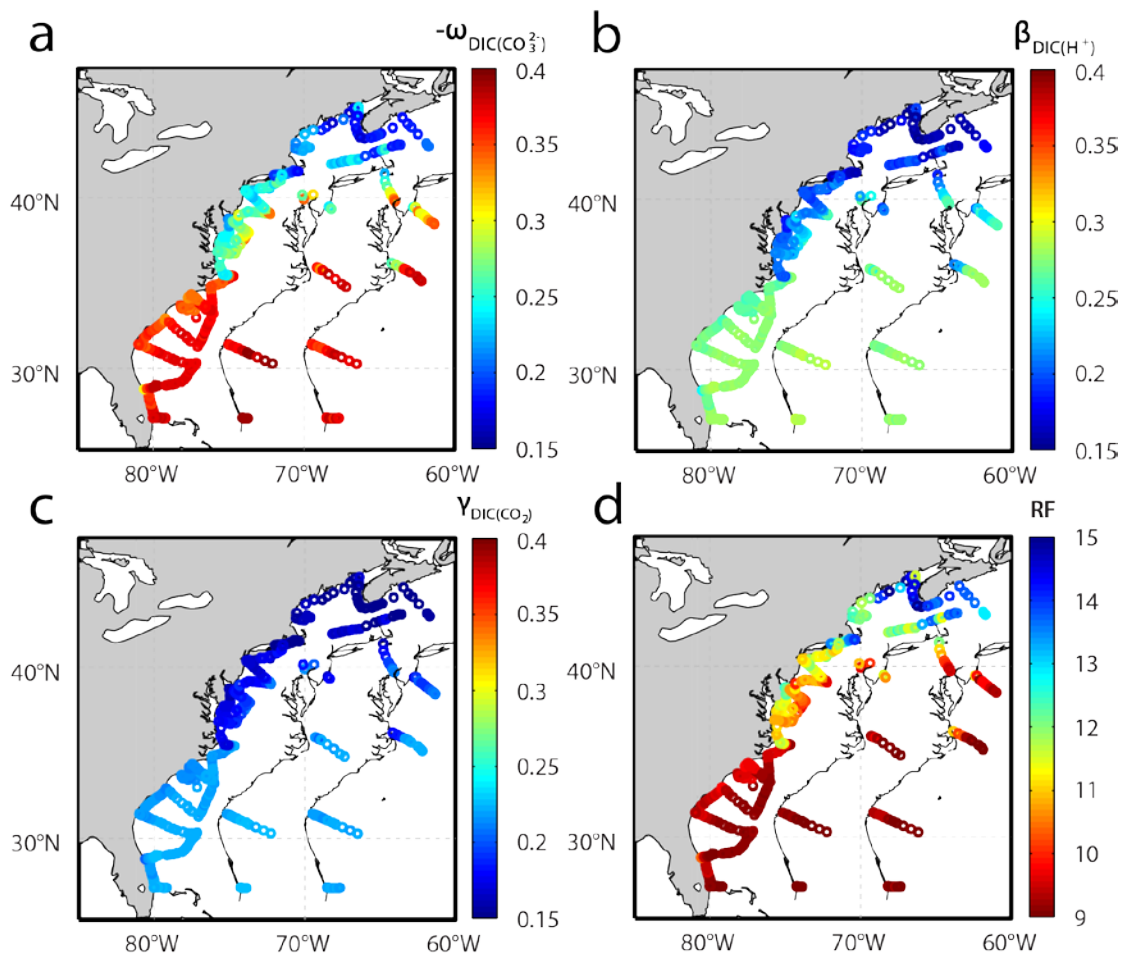


Figure 4.9: Distributions of buffer factors in North American ocean margins. Here the buffer factors γ , β , and $-\omega$ represent the ability of $[\text{CO}_2]$, $[\text{H}^+]$, and $[\text{CO}_3^{2-}]$, respectively, to resist a change in DIC. The Revelle Factor (RF) is related to γ as $\text{RF} = \text{DIC}/\gamma$. See Methods for definitions and calculation equations.

While acid-base equilibrium is essentially instantaneous, air-sea gas exchange would compensate $p\text{CO}_2$ and pH changes following the equilibrium law. However, as gas exchange takes one to a few months to complete and thus only applies to the processes at that time scale (that is coastal current transports water from warm/cold locations elsewhere), it cannot quickly compensate for changes in $p\text{CO}_2$ and pH caused by the impacts of short-term local physical processes (upwelling, river-ocean or vertical mixing and rapid temperature changes) and biological activities (removal or adding CO_2) (Carter et al. 2014).

4.5 Conclusions

Our study illustrates that, in non-upwelling regions, DIC and Ω_{arag} values are largely controlled by CO_2 solubility where the large-scale latitudinal temperature differences across regions plays a much larger role than local physical and biological forcings. In contrast, $p\text{CO}_2$ and pH strongly reflect short-term, local modifications by ocean physical and biological processes. Our data from upwelling dominated regions, however, suggest that the large-scale solubility mechanism is disturbed much more easily along ocean margins than in the open ocean as dynamic coastal conditions further accentuate the contrasts between longer time scale air-sea equilibrium and modifications by short-term, local physical and biological processes.

A similar argument to the one above on spatial variations in coastal oceans has recently been made for the contrasting seasonal responses of Ω_{arag} , pH and $p\text{CO}_2$ to DIC increase in the global open ocean via model exercises under increasing atmospheric CO_2 in the 21st century. Our work shows that such future open ocean acidification scenarios have already been observed clearly in the ocean margins where fossil fuel-induced CO_2 and respiration produced CO_2 (in upwelled waters) meet,

which likely foreshadows future changes in ocean acidification indicators in the global ocean. As organisms respond to pH and carbonate saturation state differently (both during development and calcification), these recent findings, including ours, emphasize the importance of examining multiple aspects of organismal and ecosystem responses to ocean acidification with respect to $p\text{CO}_2$, pH, Ω_{arag} , and DIC changes under warmer and higher CO_2 future ocean conditions.

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Chapter 5

CONCLUDING REMARKS AND FUTURE DIRECTIONS

In this dissertation, I present the temporal and spatial and distributions of surface carbonate chemistry parameters along the U.S. eastern continental shelf. Here I highlight the major results and conclusions from this dissertation. Surface carbonate chemistry parameters change rapidly in the central Mid-Atlantic Bight off the Delaware and Chesapeake Bays. In slope waters, these short-term variations of carbonate chemistry parameters are primarily driven by physical advection and mixing processes. For shelf waters, biological carbon removal and CO₂ degassing are the dominate processes that account for the short-term variations of carbonate chemistry parameters. Due to the rapid variations of carbonate chemistry parameters in this region, careful sampling strategies and long-term observations are necessary to determine the trends of carbonate chemistry parameters under climate change for the MAB. At the decadal scale, historical observations since 1982 suggest that the changes of carbonate chemistry parameters in the SAB are majorly driven by atmospheric CO₂ increase. For the MAB, in addition to atmospheric CO₂ increase, the variations in temperature and salinity, which are driven by changes in ocean circulation, contribute to the changes of carbonate chemistry parameters. Under the RCP8.5 scenario, the Bayesian-neural-network based prediction up to 2100 indicates that DIC increase and Ω_{arag} decrease will be dampened in the MAB due to seawater temperature increase. Surface mixed layer undersaturation is predicted to occur in the MAB from 2078 due to anthropogenic CO₂ uptake and the large seasonal amplitude of

Ω_{arag} . The seasonal amplitude of Ω_{arag} is predicted to increase in the SAB under the RCP8.5 scenario. This indicates that the SAB will suffer from low Ω_{arag} earlier and longer compared to the prediction from annual variations. The analyses of large-scale spatial distributions of carbonate chemistry parameters along the U.S. eastern continental shelf show that DIC and Ω_{arag} distributions have patterns that agree with predictions based on air-sea CO_2 equilibrium. This indicates an underlying solubility control mechanism that results in low carbonate ion concentrations and Ω_{arag} in cold northern waters and the opposite in warm southern waters. However, pH and $p\text{CO}_2$ distributions have different patterns that do not agree with predictions based on air-sea CO_2 equilibrium. The reason is that H^+ and CO_2 are weakly buffered minor chemical species and they are most sensitive to short-term local processes that affecting the acid-base equilibrium, which are often decoupled from long-term air-sea CO_2 equilibrium.

There are certainly some limitations in the studies that are included in this dissertation. In the study of decadal trends of carbonate chemistry parameters along the North American east coast, it is assumed that the air-sea $p\text{CO}_2$ disequilibrium over the next few decades will keep the same patterns. Although a first approximation according to historical data suggests that the Bayesian-neural-network based approach contains prognostic value to predict near-future carbonate chemistry parameters for the MAB and the SAB, it is likely that the air-sea $p\text{CO}_2$ disequilibrium will not strictly follow the same pattern over the next few decades. The temporal and spatial coverage of high-quality measurements of carbonate chemistry parameters in the past has limited our ability to make a better prediction. While, I believe that this situation will change in the future with more and more data available, especially from moorings and

gliders that provide a continuous measurement. For example, three Ocean Observing Initiative (OOI) moorings have been established in the MAB to collect high-resolution carbonate chemistry data (Goldsmith et al., 2019). For large-scale spatial variability along the U.S. eastern continental shelf, we still rely heavily on ship observations that are conducted every three to five years. The study of temporal distributions of surface water carbonate chemistry parameters along the U.S. eastern continental shelf is based on three summer large-scale surveys that have been conducted in 2007, 2012, and 2015. Note that only summer cruises are available for the purpose of studying the large-scale spatial distribution. All analyses, results, and conclusions for the large-scale spatial distributions of carbonate chemistry parameters are based on observations in summer. We have little knowledge of the large-scale spatial distributions of carbonate chemistry parameters in other seasons. The distributions may be completely different in other seasons due to processes such as the vertical mixing, which is a very weak factor that affects the surface water carbonate chemistry in summer due to the strong stratification in most regions. Studying carbonate chemistry in other seasons are necessary but not available so far due to the high-cost ship operation and severe sea conditions. However, marine carbonate-bearing organisms have to survive all year around. Our results suggest that Ω_{arag} in the MAB and the SAB becomes lowest in the early spring of each year at the time of recruitment of most marine carbonate-bearing organisms. Therefore, it will be valuable to have acidification surveys in the early spring to assess the vulnerability of coastal carbonate-bearing organisms to the changes in carbonate chemistry parameters. I look forward to large-scale acidification surveys in Spring, Fall, or Winter to be conducted in the next few years.

The work in this dissertation focuses on the temporal and spatial distributions of carbonate chemistry parameters in the surface mixed layer. However, temporal and spatial distributions of carbonate chemistry parameters in the sub-surface layer are also important because they affect the benthic marine community (Uthicke et al., 2013; Brodie et al., 2014). These can be studied with observations from the past three large-scale acidification surveys along the U.S. eastern continental shelf. The GOMECC-1, -2, and ECOA-1 cruises have surveyed four overlapping hydrographic station transects: the Massachusetts transect that borders the MAB and the Gulf of Maine, the North Carolina transect near Cape Hatteras which borders the SAB, the Georgia transect that extends from Savannah to the open ocean, and the East Florida transect that locates near West Palm Beach. Cross-shelf distributions of carbonate chemistry parameters have been studied by Wang et al. (2013) using GOMECC-1 data. Wanninkhof et al. (2015) have compared observations from GOMECC-1 and GOMECC-2 cruises. With data from ECOA-1, the changes of carbonate chemistry parameters at the four overlapping transects from 2007 to 2015 can be determined. To study the long-term trends of carbonate chemistry parameters for the subsurface layer, the current challenge is the lack of long-term observations. One possible approach is establishing empirical relationships to estimate the carbonate chemistry parameters from more readily available hydrographic data such as temperature, salinity, and dissolved oxygen concentration, which allow us to reconstruct carbonate chemistry parameters when and where direct observations are not available. For example, Alin et al. (2012) have developed empirical models using oxygen, temperature, salinity, and sigma theta as proxy variables to estimate carbonate chemistry parameters in the southern California Current System. Similar work can be accomplished using GOMECC-1,

GOMECC-2, and ECOA data in the future to study the long-term trends of carbonate chemistry parameters along the U.S. eastern continental shelf.

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Appendix A

OCEAN CARBONATE SYSTEM COMPUTATION FOR ANOXIC WATERS USING AN UPDATED CO2SYS PROGRAM⁴

Abstract

In anoxic/hypoxic waters, the presence of hydrogen sulfide (H₂S) and ammonia (NH₃) influences results of the computation of parameters in the ocean carbonate system. To evaluate their influences, H₂S and NH₃ contributions to total alkalinity are added to CO2SYS, which is a most often used publicly available software package that calculates oceanic carbonate parameters. We discuss how these two metabolites affect the carbonate parameters and compare the differences in total alkalinity, dissolved inorganic carbon, pH, $f\text{CO}_2$, and aragonite saturation state between the CO2SYS packages with and without considering the acid-base systems of H₂S and NH₃. The results show that, without considering these two acid-base systems, even low to moderate concentrations (e.g., 2-20 $\mu\text{mol kg}^{-1}$) of these metabolites cause errors in the calculated carbonate parameters larger than the accuracies of the best measurements, and thus it is important to include contributions from these metabolites. The outputs from this updated version of CO2SYS agree well with outputs from

⁴ Xu, Y.-Y., Pierrot, D., Cai, W.-J., 2017. Ocean carbonate system computation for anoxic waters using an updated CO2SYS program. *Mar. Chem.* 195, 90–93. doi: 10.1016/j.marchem.2017.07.002

AquaEnv, which is the only other computation program for the ocean carbonate system that includes the acid-base systems of H₂S and NH₃. Users are encouraged to use the updated version of CO2SYS to calculate carbonate parameters in anoxic/hypoxic waters.

1 Introduction

Total alkalinity (TA) of seawater has been explicitly defined as the amount of hydrogen ions equivalent to the excess of proton acceptors over proton donors in one kilogram of seawater where the zero level of protons is defined by a logarithmic acid dissociation constant that is equal to 4.5 at 25°C and zero ionic strength (Dickson, 1981). That is to say, in the acid-base systems of a seawater sample, acids are proton donors when their logarithmic dissociation constants are equal to or less than 4.5 while bases formed from weak acids are proton acceptors when their logarithmic dissociation constants are larger than 4.5 (Wolf-Gladrow et al., 2007). Over common ranges of temperature, salinity, and pressure for water samples, the logarithmic acid dissociation constants of hydrogen sulfide (H₂S) and ammonium ion (NH₄⁺) are larger than 4.5; thus, hydrosulfide ion (HS⁻) and ammonia (NH₃) are proton acceptors and contributes to TA.

In addition to carbonic acid species, other acid or base species found in seawater include boric acid (H₃BO₃), phosphoric acid (H₃PO₄), silicate acid (H₄SiO₄), H₂S, NH₃, hydrogen sulfate (HSO₄⁻), and hydrofluoric acid (HF), and their dissociation products. Thus, TA can be expressed by the following equation (Dickson, 1981):

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] \\ & + [\text{SiO(OH)}_3^-] + [\text{HS}^-] + [\text{NH}_3] + \cdots \\ & - [\text{H}^+]_{\text{F}} - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - \cdots \end{aligned} \quad (1)$$

where $[H^+]_F$ is the free proton concentration, and the ellipses represent additional unidentified or neglected acid or base species. As one of the most often measured parameters of the ocean carbonate system, TA is typically determined by a hydrochloric acid titration of seawater. Since 1996, following the development of certified reference materials for TA, it has been possible to attain an accuracy of better than $2 \mu\text{mol kg}^{-1}$ (Dickson et al., 2003).

CO2SYS is the first publicly available software package that has been widely used in the calculation of parameters in the ocean carbonate system (Lewis and Wallace, 1998). Currently, the most popular Excel[®] version is available from Pierrot et al. (2006) and the MATLAB[®] version is available from van Heuven et al. (2009). There are around 10 other similar software packages for carbonate system parameter calculation and comparison of these 10 packages demonstrates that they essentially generate the same results (Orr et al., 2015). Nevertheless, CO2SYS has been the most cited software package based on a recent assessment of the literature and this trend is expected to continue. Only one among the 10 packages, AquaEnv (written in R programming language), can perform calculations in anoxic waters (Hofmann et al., 2010).

With input of two parameters among TA, DIC, pH and $f\text{CO}_2$ (or $p\text{CO}_2$); temperature, salinity, and pressure; and total concentrations of the minor acid or base species, CO2SYS uses the necessary stoichiometric/apparent constants to calculate and return a detailed state of the carbonate parameters. Note the influence of H_2S and NH_3 is essentially the same on $p\text{CO}_2$ and $f\text{CO}_2$, and thus $p\text{CO}_2$ is not discussed here. The acid-base systems taken into account in previous versions of CO2SYS are water, carbonic acid, boric acid, phosphoric acid, silicic acid, hydrogen sulfate, and

hydrofluoric acid. Here, we incorporate the H_2S and NH_3 acid systems into the CO2SYS program and assess the uncertainties if these two acid-base systems are not considered.

H_2S and NH_3 are present in anoxic/hypoxic waters and contribute to TA. H_2S , or its ionic species HS^- , is generally found in anoxic waters such as the deep waters of the Black Sea (Luther et al., 1991), the Framvaren Fjord (Millero 1991a), and the anoxic waters in the Chesapeake Bay formed during the summer months (Luther et al., 1988; Millero, 1991b). It is also present in hypoxic waters such as in the Baltic Sea (Hietanen et al., 2012). NH_3 , or its dominant ionic species NH_4^+ , is present in oxic, hypoxic, and anoxic waters and its concentration generally increases with water column depth.

It is necessary to incorporate these two metabolites, especially H_2S , into CO2SYS as the expansion of anoxic/hypoxic waters. The global oceanic oxygen content has declined during the past 50 years and more intense deoxygenation conditions may occur in the future because of global warming; and these trends are expected to continue (Keeling et al., 2010; Falkowski et al., 2011; Schmidtke et al., 2017). As a result, oxygen minimum zones are expected to expand and the size and severity of hypoxic zones will increase (Keeling et al., 2010), which in turn lead to the expansion of H_2S -containing waters that are toxic to many marine organisms (Gilly et al., 2013; Schunck et al., 2013).

To provide a tool for the community to assess the potential role of H_2S and NH_3 on the calculation of parameters in ocean carbonate system using CO2SYS, we have added these two acid-base systems to this popular package. H_2S and NH_4^+ acids dissociation constants, as a function of salinity and temperature, are from Yao and

Millero (1995) and Clegg and Whitfield (1995), respectively, and the pressure effect on these constants is from Millero (1995). We evaluate H₂S and NH₃ contributions to alkalinity and discuss their importance in the calculation of parameters in ocean carbonate system such as pH and DIC.

2 Methods

2.1 pH-TA equation

When DIC-TA or $f\text{CO}_2$ (or $p\text{CO}_2$)-TA is the input pair in CO2SYS, pH is solved from the pH-TA equation with Newton's method (Lewis and Wallace, 1998). In all previous versions, the pH-TA equation includes TA and its major contributors (but not H₂S and NH₃) that can be calculated from the total acid concentrations, acid dissociation constants, and pH (Pierrot et al., 2006; van Heuven et al., 2009):

$$[\text{TA}] - ([\text{C-Alk}] + [\text{B-Alk}] + [\text{P-Alk}] + [\text{Si-Alk}] + [\text{OH}^-] - [\text{H}^+]_{\text{F}} - [\text{HSO}_4^-] - [\text{HF}]) = 0 \quad (2)$$

where C-Alk is the alkalinity contributed by carbonic acid, B-Alk is the alkalinity contributed by boric acid, P-Alk is the alkalinity contributed by phosphoric acid, and Si-Alk is the alkalinity contributed by silicic acid. To assess the influences of H₂S and NH₃ on the calculated carbonate parameters, the alkalinities contributed by these two acid-base systems (H₂S-Alk and NH₃-Alk) are added to the pH-TA equation.

2.2 Acid-base reaction of H₂S

H₂S dissociates into HS⁻ and then S²⁻ with $pK_{\text{H}_2\text{S}} = 6.6$ and $pK_{\text{HS}^-} = 14$ (at 25°C when salinity = 35). S²⁻ is not included in the alkalinity equation because its

concentration is negligible as indicated by the very high pK_{HS^-} . The dominant equilibrium in seawater is



Here, the first acid dissociation constant of H_2S (K_{H_2S}) is defined as follows:

$$K_{H_2S} = [H^+][HS^-]/[H_2S] \quad (4)$$

where K_{H_2S} can be calculated using the formulation of Yao and Millero (1995) that is originally from Millero et al. (1988). With the total H_2S concentration given by $[TH_2S] = [H_2S] + [HS^-]$, H_2S -Alk can be calculated by

$$H_2S\text{-Alk} = [TH_2S] \times \frac{K_{H_2S}}{K_{H_2S} + [H^+]} \quad (5)$$

2.3 Acid-base reaction of ammonia

In natural water, NH_4^+ and NH_3 are at equilibrium:



Here, the acid dissociation constant of the ammonium ion ($K_{NH_4^+}$) is defined as follows:

$$K_{NH_4^+} = [H^+][NH_3]/[NH_4^+] \quad (7)$$

and $pK_{NH_4^+}$ is calculated using temperature (-2 to 40°C) and salinity (0 to 40) from the equation and associated coefficients given in Clegg and Whitfield (1995). The value of $pK_{NH_4^+}$ is 9.2 at 25°C when salinity is 35. With the total ammonia given by $[TNH_3] = [NH_4^+] + [NH_3]$, NH_3 -Alk is calculated by

$$NH_3\text{-Alk} = [TNH_3] \times \frac{K_{NH_4^+}}{K_{NH_4^+} + [H^+]}. \quad (8)$$

2.4 H₂S and NH₄⁺ data

We use the data reported in Zhang and Millero (1993) and Yao and Millero (1995), which represent moderate and extreme ranges of TH₂S and TNH₃ concentrations, respectively, to evaluate their contributions to seawater alkalinity. Zhang and Millero (1993) reported that TH₂S concentrations increase rapidly below the oxic-anoxic interface in the Cariaco Trench and reach a maximum value of 57 $\mu\text{mol kg}^{-1}$ in the eastern basin at a depth of 1300 m. TNH₃ concentrations range from 0 to 20 $\mu\text{mol kg}^{-1}$ in the eastern basin of the Cariaco Trench (Zhang and Millero, 1993). High concentrations of TH₂S and TNH₃ (up to 5711 $\mu\text{mol kg}^{-1}$ and 1617 $\mu\text{mol kg}^{-1}$, respectively) are found in the permanently super-anoxic Framvaren Fjord in southern Norway (Yao and Millero, 1995). The distribution of TH₂S shows the same pattern as the distributions of TA and DIC, indicating its source to be from sulfate reduction which produces both HCO₃⁻ and HS⁻ (Yao and Millero, 1995).

3 Results and Discussion

3.1 The influence of H₂S and NH₃ on the calculation of TA

The calculated TA from other carbonate parameters is directly affected by [HS⁻] and [NH₃] according to Equation 1. The difference between TA calculated with and without the influence from these two terms (ΔTA) equals to the sum of H₂S-Alk and NH₃-Alk:

$$\Delta\text{TA} = \text{TA}_{\text{without}} - \text{TA}_{\text{with}} = -(\text{H}_2\text{S-Alk} + \text{NH}_3\text{-Alk}) \quad (9)$$

In the Cariaco Trench, H₂S-Alk increases with depth and the maximum value in this region is 54 $\mu\text{mol kg}^{-1}$ (Table A.1). NH₃-Alk has a maximum value of only 0.5 $\mu\text{mol kg}^{-1}$. In the Framvaren Fjord, H₂S-Alk reaches a maximum concentration of

3766 $\mu\text{mol kg}^{-1}$ (Table A.1). $\text{NH}_3\text{-Alk}$ has a maximum value of 3 $\mu\text{mol kg}^{-1}$, although it exceeds the uncertainty of the TA measurement.

Table A.1: Profiles of $\text{H}_2\text{S-Alk}$ and $\text{NH}_3\text{-Alk}$ in the Cariaco Trench and the Framvaren Fjord. Values for H_2S , NH_3 , $\text{H}_2\text{S-Alk}$, $\text{NH}_3\text{-Alk}$ are in units of $\mu\text{mol kg}^{-1}$.

<i>Cariaco Trench</i>					<i>Framvaren Fjord</i>				
Depth (m)	TH_2S	$\text{H}_2\text{S-Alk}$	TNH_3	$\text{NH}_3\text{-Alk}$	Depth (m)	TH_2S	$\text{H}_2\text{S-Alk}$	TNH_3	$\text{NH}_3\text{-Alk}$
320	0	0	0	0	25	0	0	0	0
340	4	4	4	0.1	30	517	368	143	0
360	8	7	3	0.1	40	1113	774	150	0
400	19	18	8	0.2	60	1735	1141	402	1
450	25	24	9	0.2	80	2810	1891	701	1
600	38	36	13	0.3	90	3844	2562	1120	2
800	46	43	15	0.4	100	4449	2954	1259	2
1100	52	49	17	0.4	140	5011	3340	1601	3
1300	57	54	20	0.5	170	5711	3766	1617	3

The contribution to TA from NH_3 is relatively much smaller than the contribution from H_2S , though TH_2S and TNH_3 concentrations can be in the same order of magnitude in anoxic waters. This is first because the pK_a value of the $\text{NH}_3\text{-NH}_4^+$ system ($\text{pK}_a \approx 9.2$) is one order of a magnitude higher than the typical seawater pH. Thus, in seawater, the concentration of the alkalinity contributing species (NH_3) is rather small even if TNH_3 is high. In contrast, the pK_a of the $\text{H}_2\text{S-HS}^-$ system is about 6.6 and thus the concentration of the alkalinity contributing species (HS^-) is relatively high. Considering that the current accuracy of TA measurement is 2 $\mu\text{mol kg}^{-1}$ (Dickson et al., 2003), the contribution from NH_3 could be ignored when TNH_3 is

lower than 1000 $\mu\text{mol kg}^{-1}$, as is usually the case in seawater. In contrast, the acid-base system of H_2S needs to be considered when TH_2S is larger than 2 $\mu\text{mol kg}^{-1}$. Note that these are approximate values for evaluation; the exact concentrations depend on pH.

4.2 The influence of H_2S and NH_3 on the calculated DIC, pH, $f\text{CO}_2$, and Ω_{arag}

The calculated DIC, pH, $f\text{CO}_2$ (or $p\text{CO}_2$) are thus affected by the acid-base systems of H_2S and NH_3 when TA is one of the input parameters to CO2SYS. We define ΔDIC as the differences in the calculated DIC with and without the influence of H_2S and NH_3 . It can be expressed by the following equation when pH and TA are input parameters:

$$\Delta\text{DIC} = \Delta\text{DIC}_{\text{without}} - \Delta\text{DIC}_{\text{with}} = (\text{H}_2\text{S-Alk} + \text{NH}_3\text{-Alk}) \times \frac{[\text{H}^+]^2 + K_1 \times [\text{H}^+] + K_1 \times K_2}{K_1 \times [\text{H}^+] + 2 \times K_1 \times K_2} \quad (10)$$

Therefore, DIC is overestimated without considering the acid-base systems of H_2S and NH_3 by up to 51.4 $\mu\text{mol kg}^{-1}$ in the Cariaco Trench and up to 4087 $\mu\text{mol kg}^{-1}$ in the Framvaren Fjord. Furthermore, the influence on DIC is larger than on TA when $[\text{H}^+]^2$ is larger than $K_1 \times K_2$ (i.e., water pH is lower than $(\text{p}K_1 + \text{p}K_2)/2$, which is 7.40 at $S=35$ and $t=25^\circ\text{C}$ according to Millero et al., 2006).

When DIC-TA or $f\text{CO}_2$ (or $p\text{CO}_2$)-TA are the input pairs, pH and Ω_{arag} are overestimated without considering the H_2S and NH_3 . Ω_{arag} is also overestimated when pH-TA is the input pair. In both basins, the difference in the calculated pH from the input pair of DIC-TA exceeds the current accuracy of pH measurements (< 0.005 , Dickson et al., 2007) from the first sample below the oxic/anoxic interface. In particular, the calculated Ω_{arag} without H_2S and NH_3 reaches an unacceptable value of 34 in the Framvaren Fjord when using the input pair of DIC-TA.

The calculated $f\text{CO}_2$ is underestimated when the input pair is DIC-TA. But it is overestimated when the input pair is pH-TA. In CO2SYS, $f\text{CO}_2$ is calculated from the input pair of DIC-pH according to the following equation:

$$f\text{CO}_2 = \text{DIC} \times \frac{[\text{H}^+]^2}{([\text{H}^+]^2 + K_1 \times [\text{H}^+] + K_1 \times K_2) / K_0} \quad (11)$$

where K_0 is the solubility coefficient of CO_2 in seawater. When DIC and TA are used as input parameters, the calculation without H_2S and NH_3 leads to an overestimation of pH, which further leads to an underestimation of $f\text{CO}_2$. However, when pH and TA are the input parameters, the calculation without H_2S and NH_3 results in an overestimation of DIC, which further leads to an overestimation of $f\text{CO}_2$ according to Equation 11. In addition, when using data from the same seawater sample, the errors in the calculated $f\text{CO}_2$ with an input pair of pH-TA are smaller than the errors with an input pair of DIC-TA. However, even with the input pair of pH-TA, the errors exceed field measurement uncertainty ($2 \mu\text{atm}$ for surface seawater, Pierrot et al., 2009) in the Cariano Trench where TH_2S is higher than $14 \mu\text{mol kg}^{-1}$ (compare to a concentration of $4 \mu\text{mol kg}^{-1}$ when the input pair is DIC-TA).

4.3 Comparison with the carbonate parameters calculated using AquaEnv

To check the agreement of packages, we compare the outputs from this updated version of CO2SYS with the outputs from AquaEnv (Hofmann et al., 2010), which also includes the acid-base systems of H_2S and NH_3 . These two packages use different equations for the dissociation constant of NH_4^+ . In AquaEnv, the dissociation constant of NH_4^+ in mol kg^{-1} -solution on the free proton pH scale is calculated with the equations from Millero (1995) corrected by Lewis and Wallace (1998). The two packages are also different in that the dissociation constants in the subroutines of the

two packages are on different pH scales, although users have the option to select the input and output pH scales. In CO2SYS, all dissociation constants are converted to the seawater scale except the dissociation constants of sulfuric acid and hydrofluoric acid that are on free scale (Lewis and Wallace, 1998). In the subroutines of AquaEnv, dissociation constants are on free scale. Despite these differences, the agreement between the two packages is excellent. The differences in the calculated H₂S-Alk (or NH₃-Alk) are less than 0.4 $\mu\text{mol kg}^{-1}$ anywhere in the column in the Cariaco Trench. In the Framvaren Fjord, even with very high TH₂S and TNH₃ concentrations (>1000 $\mu\text{mol kg}^{-1}$) in the anoxic waters, the two packages still agree well with differences in the calculated H₂S-Alk (or NH₃-Alk) smaller than 2.0 $\mu\text{mol kg}^{-1}$ in all depths.

5 Conclusions

The acid-base systems of H₂S and NH₃ are added to CO2SYS to evaluate their influences on other calculated carbonate parameters. The outputs from the updated CO2SYS agree well with those from AquaEnv. The updated Excel version of CO2SYS characterizing H₂S and NH₃ is available online at <http://cdiac.ornl.gov/ftp/oceans/co2sys/>. It is recommended for the study of the carbonate system in waters where H₂S and NH₃ are present, especially in anoxic waters where TH₂S is higher than 2 $\mu\text{mol kg}^{-1}$ and/or TNH₃ is higher than 1000 $\mu\text{mol kg}^{-1}$.

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