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- Large changes in surface water aragonite saturation state were observed off the Delaware and Chesapeake Bays over a short period of 10 days
- Biological carbon removal and CO₂ degassing largely affected the aragonite saturation state on the shelf
- Physical processes were the dominant forces for large aragonite saturation state changes in the slope water

Supporting Information:

Supporting Information S1

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Short-term variability of aragonite saturation state in the central Mid-Atlantic Bight

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Abstract The uptake of anthropogenic carbon dioxide (CO₂) from the atmosphere has resulted in a decrease in seawater aragonite saturation state (Ω_{araq}), which affects the health of carbonate-bearing organisms and the marine ecosystem. A substantial short-term variability of surface water $\Omega_{
m aracr}$ with an increase of up to 0.32, was observed in the central Mid-Atlantic Bight off the Delaware and the Chesapeake Bays over a short period of 10 days in summer 2015. High-frequency underway measurements for temperature, salinity, percentage saturation of dissolved oxygen, oxygen to argon ratio, pH, fCO₂, and measurements based on discrete samples for pH, dissolved inorganic carbon, and total alkalinity are used to investigate how physical and biogeochemical processes contribute to the changes of Ω_{araq} . Quantitative analyses show that physical advection and mixing processes are the dominant forces for higher $\Omega_{
m arag}$ in slope waters while biological carbon removal and CO₂ degassing contribute to increased Ω_{arag} in shelf waters.

1. 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 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 $\Omega_{
m arag}$ affects the growth of some marine organisms that build calcium carbonate shells or skeletons. For example, oyster larval production is correlated with Ω_{araq} [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 $\Omega_{
m araq}$, 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 shows that variations in coastal surface water $\Omega_{
m arag}$ are 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} exhibit substantial short-term variabilities 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 factors have been found to exert major control over the seasonal variations of Ω_{araq} 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, which leads to intense algal blooms in the euphotic



Figure 1. (a) Schematic drawing of the southward current from the Gulf of Maine (blue) and the northward Gulf Stream (red) in the western North Atlantic Ocean (modified from *Sutcliffe 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 arrow represents the direction and relative strength of the surface current. The color scale indicates the average MLD (1–11 July 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.

zone and followed by remineralization and oxygen consumption in bottom water, 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 the Mid-Atlantic Bight (MAB) coastal waters.

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 the 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 physical and biogeochemical processes on Ω_{arag} in the MAB surface water over 10 days between the two surveys.

2. Methods

2.1. Sample Collection and Analysis

The study area in the central MAB was surveyed twice during the NOAA East Coast Ocean Acidification (ECOA) cruise: 1–3 July 2015 (leg 1) and 9–11 July 2015 (leg 2). While ECOA 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 examined in both legs. Underway samples for oxygen, fCO_2 , and pH were taken from a scientific seawater supply line at a depth of ~5 m along the cruise track (Figure 1a). Discrete surface bottle samples for dissolved inorganic carbon (DIC), total alkalinity (TA), and pH were taken from the seawater supply line at a sampling interval of approximately 3 h. Full profile bottle samples were taken from Niskin bottles in the CTD/Rosette system along transects in the MAB.

Underway percentage saturation of dissolved oxygen (DO%) 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 μ M (\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.

Seawater fCO_2 was measured by an autonomous underway fCO_2 system every ~140 s following *Pierrot et al.* [2009]. The CO₂ detector (Licor-6262) was located in the chemistry laboratory and was calibrated every 3 h with four CO₂ standards. The fugacity of CO₂ (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 0.0003°C, 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 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:

corrected
$$pH_T =$$
 measured $pH_T + \Delta pH$, (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). The overall accuracy and precision of DIC measurements are 2 μ 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 subsample (25 mL) 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. 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 μ mol kg⁻¹. The overall accuracy of TA analysis is 2 μ mol kg⁻¹.

2.2. 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, O_2/Ar reflects 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

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

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

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

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

where $[O_2]_{sat}$ is the saturated concentration of oxygen in seawater that is calculated from temperature and salinity [*Garcia and Gordon*, 1992]; 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:

$$k = (3 + 0.1U + 0.064 \ U^{2} + 0.011 \ U^{3}) \times \left(\frac{Sc}{Sc_{0}}\right)^{n},$$
(4)

where U represents the normalized wind speed; the Schmidt number (Sc) is calculated at ambient temperatures and normalized to a Schmidt number (Sc₀) at nominally 20°C [*Jähne et al.*, 1987; *Wanninkhof*, 1992]; the exponent (n) equals -2/3 when $U \le 4.2$ m s⁻¹ or -1/2 when U > 4.2 m s⁻¹ [*Wanninkhof*, 1992]. Considering the O₂/Ar signal reflects the accumulated biological effect, NCP derived from O₂/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 analytical 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 oxygen residence time in the mixed layer [*Cassar et al.*, 2011; *Hamme et al.*, 2012]. For mixed layer depth (MLD) that is 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 during this study 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. 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 fCO₂:

$$F_{CO_2} = k_{CO_2} \times [CO_2]_s \times (fCO_2 \text{ sea} - fCO_2 \text{ air}),$$
(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 for NCP calculation in the previous section; $[CO_2]_s$ is the solubility of CO₂ estimated from temperature and salinity [*Weiss*, 1974]; *f*CO₂ sea and *f*CO₂ air are *f*CO₂ 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 *f*CO₂ 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 CO₂ flux.

2.4. Interpolating DIC and $\Omega_{\rm arag}$ at 30 s Interval

 Ω_{arag} is defined as the ratio of the concentration product of calcium ions (Ca²⁺) and carbonate ions (CO₃²⁻) 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 ion 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 ion 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 only a small number of discrete water samples for pH_T, DIC, and TA measurements are available from hydrographic stations and 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} data sets using a combination of the calibrated underway pH and SSSderived TA. We first develop a relationship between SSS and discrete TA measured using titration method. Then, surface water DIC and Ω_{arag} at a frequency of 30 s are calculated in CO2SYS [*van Heuven et al.*, 2011] using the underway pH and the calculated TA.

2.5. 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 Δ DIC_{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 (Δ Date, d), and the Redfield stoichiometric ratio of 138/106 for oxygen to carbon [*Redfield et al.*, 1963]:

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

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 Δ DIC_{biol} with an oxygen to carbon ratio of 170/117 for phytoplankton growth (supporting information Figure S1) [*Anderson*, 1995; *Hedges et al.*, 2002; *Emerson et al.*, 2008].

We calculate $\Delta DIC_{air-sea}$, which represents the DIC change caused by air-sea CO₂ flux over time in the surface mixed layer in the following manner:

$$\Delta DIC_{air-sea} = F_{CO_2} \times \Delta Date/MLD, \tag{7}$$

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 (Δ DIC) with the biologically driven DIC change (Δ DIC_{biol}), and air-sea CO₂ flux driven DIC change (Δ DIC_{air-sea}):

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

2.6. DIC Normalization

To provide a first-order comparison of the biogeochemical and physical (nonconservative mixing) influences across the shelf waters, we normalize DIC and TA to a constant salinity to remove the DIC and TA variations across the shelf associated with the variation of salinity between two end-members. The essence of normalization is that the normalized conservative parameter (here *n*TA) should be nearly invariant with salinity. This is confirmed with our field data (supporting information Figure S2). In this study, TA values are normalized to a value at salinity 33 with a nearshore end-member of 2103.7 (TA^S = end (1)</sup>) at salinity 31 and an offshore end-member of 2376.1 μ mol kg⁻¹ (TA^S = end (2)</sup>) at salinity 36 (i.e., *n*TA = 2212.0 μ mol kg⁻¹ at the reference salinity 33) following an approach similar to *Friis et al.* [2003]:

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

Therefore,

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

To examine the nonconservative behavior of DIC, we normalize 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 is normalized with two end-members of 1950.4 and 2067.4 μ mol kg⁻¹ when salinities are 31 and 36, respectively.

3. Results

3.1. 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 receives a cold alongshore current that originates from the Labrador Sea and passes through the Gulf of Maine [*Fairbanks*, 1982; *Chapman and Beardsley*, 1989; *Mountain*, 2003] (Figure 1a). Meanwhile, 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 [*Bumpus*, 1973; *Richardson*, 1980; *Pickart and Smethie*, 1993] (Figure 1a).

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 m, on the middle shelf, the outer shelf, and the upper slope (Figure 1b). We verify the model-generated MLDs with the calculated MLDs from CTD profiles using a constant potential density difference criterion of 0.1 kg m⁻³ [*Skyllingstad et al.*, 1999] (supporting information Text S1 and supporting information Tables S1 and S2). These depths are in the range of the typical summer MLDs (~3.5–10 m) for the 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 derived from a regional-scale ocean model [*Chen and He*, 2015]. Inner shelf water was well mixed and showed a northward surface flow (Figure 1b). The middle and outer shelf regions were dominated by a strong southward surface flow (Figure 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 2a). Cross-shelf salinity gradients were strong because of freshwater discharge from the two large estuaries (Figure 2b). A large change of SSS was observed at the Delaware transect, where the two legs overlapped (Figure 2b). SSS slightly decreased in the middle and outer shelf zones but increased up to 1.1 on the upper slope (Figure 2b).

SST increased from leg 1 to leg 2 concurrently with an increase in ambient air temperature. However, SSS decreased from leg 1 and leg 2 in the middle and outer shelf regions. 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 (supporting information Figure S3). 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 on the upper slope during leg 2 is a result of interaction with Gulf Stream water [*Bane et al.*, 1988; *Lee and Atkinson*, 1983].

3.2. DO%, pH, fCO₂, NCP, and F_{CO2} Distribution and Variation

In leg 1, high DO% was observed on the inner shelf near the Chesapeake Bay (Figure 2c). Along the Delaware transect, DO% decreased from 103.4% on the middle shelf to 100.7% on the upper slope. Relatively low pH values were detected on the inner shelf near the Delaware Bay and the inner shelf and middle shelf regions near the Chesapeake Bay (Figure 2d). Higher pH values that ranged between 8.01 and 8.05 were found in the middle shelf, outer shelf, and upper slope waters near the Delaware Bay (Figure 2d). Coastal water fCO_2 ranged from 394 to 501 µatm and was in general supersaturated with respect to atmospheric



Figure 2. (a–f) (left to right) Distributions of SST, SSS, DO%, pH, fCO₂, pH, and Ω_{arag} for leg 1 (line) and leg 2 (interpolated as the 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 Figure 2a represents the cruise track of leg 2. The 20, 50, 100, 1000 m isobaths are shown with black contour lines.

 CO_2 . The pH inversely varied with fCO_2 as pH decreased when fCO_2 increased and vice versa (Figures 2d and 2e).

The overall offshore DO%, pH, and fCO_2 distribution patterns in leg 2 were similar to those in leg 1 (Figure 2). 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 2c). Note that the behavior of $\Delta(O_2/Ar)$ (Figure 3a) was similar to that of DO% in both legs, generally decreasing away from the Delaware Bay mouth. There was a pH decrease on the inner shelf near the Chesapeake Bay from leg 1 to leg 2, with a concurrent fCO_2 increase (Figures 2d and 2e).

Along the Delaware transect, NCP of leg 2 decreased from the middle shelf to the upper slope (15.9 to -3.6 mmol m⁻² d⁻¹; Figure 3b). It was positive on the middle shelf but negative on the upper slope. The transition from positive to negative NCP occurred on the outer shelf (Figure 3b). Applying an overall uncertainty of 20% for NCP [*Jonsson et al.*, 2013; *Martin et al.*, 2013], the resulted uncertainty in Δ DIC_{biol} is 2.9 µmol kg⁻¹, corresponding to an uncertainty of 0.03 in $\Delta\Omega_{arag}$.

 F_{CO_2} of leg 2 ranged from 0.4 to 6.2 mmol m⁻² d⁻¹, with the highest value found on the outer shelf where community respiration increased. The lowest F_{CO_2} value was found on the middle shelf where net biological production increased (spike in O₂/Ar; Figure 3a). Using an uncertainty of 2 µatm for seawater *f*CO₂ [*Pierrot et al.*, 2009] and an uncertainty of ~15% for gas transfer velocity as a result of parameterization difference, the uncertainty in F_{CO_2} is estimated to be 0.6 mmol m⁻² d⁻¹, corresponding to uncertainties of 2.1 µmol kg⁻¹ in Δ DIC_{air-sea} and 0.02 in Ω_{arag} .



Figure 3. (a) The variation of $\Delta(O_2/Ar)$ and NCP with distance to the Delaware Bay mouth along the Delaware transect. (b) The variation of fCO_2 and the average F_{CO_2} with distance to the Delaware Bay mouth. The horizontal dashed line represents the mean in situ atmospheric fCO_2 during the study period.

3.3. TA, DIC, and Ω_{arag} Distribution and Variation

The measured TA and SSS from discrete bottle samples follow a linear relationship (supporting information Figure S2):

$$TA = (54.49 \pm 1.39) \times salinity + (414.19 \pm 45.76)$$
(11)

This linear fit has a root-mean-square error of 3 μ 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 μ 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 (supporting information Text S2 and supporting information Table S3).

We make comparisons to assess the uncertainties in the calculated high-resolution DIC and Ω_{arag} data. The average difference between the calculated DIC and the measured DIC is 2 µmol kg⁻¹ for leg 2 whereas the average difference is as large as 8 µmol kg⁻¹ for leg 1. The latter 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 difference between the calculated and measured DIC for leg 1. 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 from discrete seawater sample measurements (Figure 4).

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



Figure 4. (a) Distribution of DIC and TA along the Delaware transect with 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.

 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 µmol kg⁻¹ while TA decreased 30 µmol kg⁻¹ (Figure 4a). On the upper slope the DIC change was very small (3 µmol kg⁻¹ on average), however, the TA change was large with an average increase of 29 µmol kg⁻¹ (Figure 4a). However, the salinity-normalized TA showed no increase while the salinity-normalized DIC showed a decrease of 13 µmol kg⁻¹ on average.

3.4. Assessment of the Biological and Physical Influences

To provide a first-order assessment of the biogeochemical influence on the short-term variability of Ω_{arag} , we plot the difference in Ω_{arag} and fCO_2 against difference in *n*DIC along the Delaware transect between the two legs ($\Delta\Omega_{arag}$, ΔfCO_2 , and Δn DIC, respectively; Figures 5a and 5c). There are two distinct statistically significant linear correlations between both $\Delta\Omega_{arag}$ and ΔfCO_2 to Δn DIC on the middle shelf and the upper slope. We also note that biological activity has an accumulate influence on the change in DIC; thus we examine Δn DIC against the average DO% and NCP instead of the differences between the two legs (Figures 5b and 5d). High DO%, NCP, and more negative Δn DIC are observed on the middle shelf, whereas low DO% and NCP values are found on the upper slope with small Δn DIC (Figures 5b and 5d). The region-specific regression relationships (Δn DIC to $\Delta\Omega_{arag}$ and ΔfCO_2) suggest two different water mass mixing schemes on top of the biological production signals influence $\Delta\Omega_{arag}$.

4. Discussion

4.1. 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



Figure 5. The relationship of (a) $\Delta\Omega_{aragr}$ (b) average DO%, (c) ΔfCO_2 , and (d) NCP with Δn 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 data located 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 lines 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.

strong with horizontal flows over the offshore region along isobaths (Figure 1). In surface water, the alongshore variabilities 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 [*Mountain*, 2003; *Lentz*, 2008].

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 influences [*Fry et al.*, 2015]. The MAB has a lower annual mean DIC (1968 μ mol kg⁻¹) compare to its adjacent regions, such as the South Atlantic Bight, Nantucket Shoals, and Georges Bank [*Signorini et al.*, 2013]. Seasonal variability of DIC reveals that its concentration reaches a minimum (~1900 μ mol kg⁻¹) in summer, mainly as a result of biological uptake in spring-summer [*Signorini et al.*, 2013]. The average DIC concentration is 1960 μ mol kg⁻¹ along the Delaware transect, which is close to the annual mean DIC in the MAB but higher than the estimated summertime DIC because the inner shelf, which has a relative low DIC concentration, is not included in the Delaware transect in this study.

Salinity-normalized TA is constant as the variation with salinity is removed [*Friis et al.*, 2003]. The salinitynormalized DIC for leg 2 is lower than the concentration in leg 1 by up to 25 μ mol kg⁻¹. Given the strong stratification during our study period, vertical mixing is weak and we attribute the drawdown of *n*DIC and the resulted increase in Ω_{arag} to biological uptake, CO₂ degassing from water to the atmosphere, and lateral



Figure 6. (a) The spatial distribution of Ω_{arag} along the Delaware transect during leg 1 (gray) and leg 2 (black). 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 higher biological activity than its adjacent areas. (b) Changes in Ω_{arag} , SST, and SSS between two legs along the Delaware transect.

mixing with other water masses that have lower DIC [*Mathis et al.*, 2011; *Polsenaere and Abril*, 2012; *Wang et al.*, 2013]. Upwelling of water with high DIC into the mixed layer is not included because it raises DIC [*Feely et al.*, 2008], which is in contrast to the observed decrease in DIC.

The Delaware transect is characterized by Ω_{arag} values around 2.9, which falls between summertime Ω_{arag} in the South Atlantic Bight (~3.5) and the Gulf of Maine (~2) in shelf waters [*Jiang et al.*, 2010; *Wang et al.*, 2013; *Wanninkhof et al.*, 2015]. During leg 1, Ω_{arag} values are lower than those in leg 2 for all stations (Figure 4). The processes that control DIC and Ω_{arag} changes are further discussed below.

4.2. Processes Affecting Ω_{arag} Change

There are two distinct features in the Ω_{arag} distribution: first, Ω_{arag} gradually increases offshore during both legs (Figure 6a); 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 6a). Ω_{arag} in this patch is higher than its neighboring areas during leg 1 due to high biological production (Figure 6a), as suggested by $\Delta(O_2/Ar)$ data (Figure 3). The difference in Ω_{arag} along the Delaware transect between the two legs ($\Delta\Omega_{arag}$) varies from -0.08 on the middle shelf to 0.32 on the upper slope (Figure 6b).

To assess the contributions of thermodynamic, air-sea CO_2 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:

$$\Delta \Omega = \Delta \Omega_{\text{therm}} + \Delta \Omega_{\text{biol}} + \Delta \Omega_{\text{air-sea}} + \Delta \Omega_{\text{phys}}, \tag{12}$$

where $\Delta\Omega_{\rm therm}$ is the change in $\Omega_{\rm arag}$ due to temperature-dependent and salinity-dependent thermodynamics. $\Delta\Omega_{\rm biol}$ is biologically driven $\Omega_{\rm arag}$ change via photosynthesis and community respiration. $\Delta\Omega_{\rm air-sea}$ is $\Omega_{\rm arag}$ change due to air-sea CO₂ flux. Finally, $\Delta\Omega_{\rm phys}$ is $\Omega_{\rm arag}$ 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 (supporting information Figure S2) over the entire water column suggests that there is no appreciable net calcification.



Figure 7. The contributions of biogeochemical and physical processes on the change of $\Omega_{\rm arag}$ along the Delaware transect. The red bars are the impacts on $\Omega_{\rm arag}$ from biological activity, e.g. photosynthesis and community respiration. The blue bars are the impacts on $\Omega_{\rm arag}$ from the mixing of different water masses. The black stems with the crosses are the impacts on $\Omega_{\rm arag}$ from air-sea CO₂ flux. The solid black line represents the net change of $\Omega_{\rm arag}$ between the two legs. Positive values mean biochemical and/or physical processes contributions to the increase of $\Omega_{\rm arag}$ and vice versa.

The terms in equation (12) are calculated using in situ SST, SSS, DIC, and TA data in leg 1 and the differences of SST and SSS over 10 days between the two legs (Δ SST and Δ SSS) along with ΔDIC_{biol} , $\Delta DIC_{air-sea}$, and ΔDIC_{phys} . 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 words, 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 6.

 $\Delta\Omega_{\text{biol}}$, $\Delta\Omega_{\text{air-sea}}$, and $\Delta\Omega_{\text{phys}}$ are calculated from SST, SSS, DIC, and TA data, with $\Delta\text{DIC}_{\text{biol}}$, $\Delta\text{DIC}_{\text{air-sea}}$, and $\Delta\text{DIC}_{\text{phys}}$ that are calculated using equations (6)–(8), respectively. The contributions of biogeochemical and physical processes are illustrated in Figure 7 and are discussed below.

4.2.1. Thermodynamic Influence on $\Delta \Omega_{arag}$

Carbonic acid equilibrium constants, which have an impact on calculated Ω_{arag} , are affected by temperature and salinity. Both Δ SST and Δ SSS increase offshore (Figure 6b). Water is warmer during leg 2 for the whole Delaware transect with Δ SST ranging from 1.2 to 2.7 (Figure 6b). SSS decreases on the middle shelf and outer shelf but increases on the upper slope between the two legs, with Δ SSS ranging between -0.8 and 1.1 (Figure 6b). Warmer SST contributes to the increase in Ω_{arag} because the corresponding change of equilibrium condition results in an increase of carbonate ion concentration and a decrease of aragonite stoichiometric solubility product [*Feely et al.*, 2004; *Orr et al.*, 2005]. The SSS change also affects Ω_{arag} through mixing with low-salinity river waters or saltier slope waters that are characterized by different TA/DIC ratios [*Sabine et al.*, 2002; *Wang et al.*, 2013].

However, even though Δ SST and Δ SSS are large, the resulted thermodynamic-only influences on Ω_{arag} are small (Figure 6a). We further deconstruct $\Delta\Omega_{therm}$ into two terms, $\frac{\partial\Omega_{arag}}{\partial T} \Delta T$ and $\frac{\partial\Omega_{arag}}{\partial S} \Delta S$, to represent the contribution from temperature and salinity variations, respectively. In this study $\frac{\partial\Omega_{arag}}{\partial T}$ ranges from 0.018 to 0.020 and $\frac{\partial\Omega_{arag}}{\partial S}$ 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 $\Delta\Omega_{arag}$ by changing SST and SSS. 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 Δ SSS of -0.6 and 0.5, respectively (Figure 6). It is clear that SST and SSS changes can explain only a small part of the observed increase in Ω_{arag} between two legs and other causes must be identified.

4.2.2. Biological Activity and Air-Sea CO $_2$ 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]; thereby it also plays a key role in regulating Ω_{arag} . The shelf waters in the MAB are highly productive but the 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 Δ DIC_{biol} (equation (6)).

High DO% and $\Delta(O_2/Ar)$, which represent biological oxygen supersaturation [*Craig and Hayward*, 1987; *Emerson et al.*, 2008], are observed on the middle shelf, corresponding to the high biological production and high DIC consumption as indicated by the more negative Δn DIC (Figures 5b and 5d). The average NCP based on $\Delta(O_2/Ar)$ is estimated to be 41.4 g C m⁻² 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 11.7–59.9 g C m⁻² yr⁻¹

[*Vlahos et al.*, 2002]. This biologically induced DIC consumption results in increases in Ω_{arag} ranging from 0.07 to 0.18 (Figure 7).

The transition from net autotrophy to net heterotrophy, as indicated by net oxygen production and consumption (or a switch from positive NCP to negative NCP), occurs on the outer shelf, corresponding to biologically driven $\Delta\Omega_{arag}$ shifts from positive to negative values (Figure 7). The decrease of NCP on the outer shelf and the upper slope waters is due to limited nutrient input and the intrusion of Gulf Stream water that has 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 is a net heterotrophic region and features an average DIC increase of 6.6 µmol kg⁻¹ corresponding to a Ω_{arag} decrease of 0.07 (Figure 7). Therefore, biological activity did not contribute to the elevated Ω_{arag} on the upper slope.

Biological activity (net photosynthesis) also affects the overall inorganic carbon pool in the surface mixed layer, and thus fCO_2 and subsequent air-sea CO_2 flux. Changes of the total inorganic carbon pool influence carbonate acid equilibrium in the surface layer and therefore lead to changes in Ω_{arag} . The MAB has been found 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 the increase of SST contribute to making this region as a net CO_2 source in summer [*DeGrandpre et al.*, 2002; *Signorini et al.*, 2013].

Net CO₂ release from the ocean to the atmosphere subsequently contributes to Ω_{arag} increase. The lowest CO₂ outgassing flux is found on the middle shelf, where NCP is highest (Figure 3a) and the removal of CO₂ by photosynthesis is high, corresponding to high primary production that contributes to reducing the DIC concentration in the mixed layer (Figure 7). However, the seawater is still supersaturated with respect to CO₂, though the level has been drawn down compare to the outer shelf and the upper slope.

In contrast, the greatest CO₂ outgassing flux occurs on the outer shelf and contributes to an increase of 0.18 in Ω_{arag} due to reducing DIC (Figure 7). Note that the very shallow mixed layer depths during the study period cause 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 7), leaving to the physical process as the major driver for the observed net increase in Ω_{arag} in this region.

4.2.3. Physical Mixing Contribution to $\Delta \Omega_{arag}$

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 5). $\Delta\Omega_{arag}$ covaries with Δ SST and Δ SSS on the upper slope (Figure 6b), suggesting that the mixing with a warmer and saltier water mass occurs in this region. Furthermore, Δ DIC_{phys} and Δ SSS show distinct distribution patterns in different regions, indicating different mixing patterns on the middle shelf, the outer shelf, and the upper slope (Figure 8), except that the mixing patterns are similar on the middle shelf and the outer shelf with no statistical differences in terms of Δ DIC_{phys}- Δ SSS linear regression best fit slopes. We assume possible mixing patterns along the Delaware transect according to physical ocean model outputs and measured parameters and then discuss how these mixing patterns affect the observed change in Ω_{arag} .

Upwelling, vertical mixing, and lateral mixing are all possible physical water mass movement patterns on the middle shelf and the upper slope. Coastal upwelling has been identified as the primary factor that drives the short-term variability of Ω_{arag} in the California Current System [*Feely et al.*, 2008; *Harris et al.*, 2013]. However, the 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 Delaware Bay mouth [*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 sharp temperature and salinity gradients below the mixed layer. Therefore, it is not likely that upwelling plays a role in driving the change of Ω_{arag} 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 (\sim 1%) of the total water inflows into this region [*Beardsley and Boicourt*, 1981]. Argon supersaturation (Ar%; calculated



Figure 8. Relationship of Δ SSS and Δ DlC_{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.

from DO% and Δ (O₂/Ar) following *Kaiser et al.* [2005]) decreases during the study period (Figure 9), 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 the advancement of the warm and 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 1b).

In general, Ω_{arag} in the MAB is higher than values reported further north in the Gulf of Maine but lower than the Gulf Stream waters to the south during previous cruises [Wanninkhof et al., 2015; Jiang et al., 2015]. The change in Ω_{arag} that is driven by physical mixing of different water masses is consistent with the direction and strength of surface current along the Delaware transect (Figures 1b and 7). On the middle shelf, mixing with water that is transported by the southward surface current from the Gulf of Maine causes an average decrease of 0.26 in Ω_{arag} , thus cancelling out a large portion of the biological-induced and degassinginduced Ω_{arag} increase (Figure 7).

The Gulf Stream passes the upper slope and causes a maximum Ω_{arag} increase of 0.29 via the mixing with local waters (Figure 7). The average surface flow is moving towards 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. This transporting of water masses has an important influence on the carbon chemistry as Ω_{arag} in the North Atlantic varies with latitude [*Jiang et al.*, 2015]. As a result, the changes of Ω_{arag} driven by water mass mixing (Figure



Figure 9. Ar supersaturation (Ar%) for the two legs along the Delaware transect. Open circles represent Ar measurements from leg 1. Triangles are Ar measurements from leg 2.

7) agree reasonably with surface current patterns (Figure 1a).

4.3. Toward Future Coastal Acidification Studies

Short-term signals due to biogeochemical and physical processes are important for interpreting the 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 shelf and the 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 3–5 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 their variabilities are necessary for a comprehensive view of the trends in coastal acidification.

5. Conclusions

The short-term variability of Ω_{arag} in shelf waters near the Delaware Bay and the Chesapeake Bay is driven by a combination of physical mixing, gas transfer and biological activity. Mixing changes Ω_{arag} by up to 0.30 units. Biological DIC removal and CO₂ degassing to the atmosphere contribute 0.23 and 0.25, respectively, to the change in Ω_{arag} . Our analyses show that biological activity is a major contributor to the increased Ω_{arag} on the middle shelf, while surface lateral transport is the dominant factor that increases Ω_{arag} on the upper slope. In evaluations of long-term changes in ocean acidification, the possibility of a substantial short-term variability of Ω_{arag} as observed in this study needs to be considered.

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