9-30-2019

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Estuarine, Coastal and Shelf Science 225 (2019) 106189

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

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

Scientific considerations for acidification monitoring in the U.S. Mid-Atlantic Region

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A B S T R A C T

Coastal and ocean acidification has the potential to cause significant environmental and societal impacts. Monitoring carbonate chemistry parameters over spatial and temporal scales is challenging, especially with limited resources. A lack of monitoring data can lead to a limited understanding of real-world conditions. Without such data, robust experimental and model design is challenging, and the identification and understanding of episodic acidification events is nearly impossible. We present considerations for resource managers, academia, and industry professionals who are currently developing acidification monitoring programs in the Mid-Atlantic region. We highlight the following considerations for deliberation: 1) leverage existing infrastructure to include multiple carbonate chemistry parameters as well as other water quality measurements, 2) direct monitoring efforts in subsurface waters rather than limiting monitoring to surface waters, 3) identify the best available sensor technology for long-term, in-situ monitoring, 4) monitor across a salinity gradient to account for the complexity of estuarine, coastal, and ocean environments, and identify potential areas of enhanced vulnerability, 5) increase sampling frequency to capture variability, 6) consider other drivers (e.g., freshwater discharge, nutrients, physiochemical parameters) that may affect acidification, and 7) conduct or continue monitoring in specific ecological and general regions that may have enhanced vulnerability. Through the incorporation of these considerations, individual monitoring programs can more efficiently and effectively leverage resources and build partnerships for a more comprehensive data collection in the region. While these considerations focus on the Mid-Atlantic region), similar strategies can be used to leverage resources in other locations.

1. Monitoring for coastal acidification in the mid-atlantic

1.1. Introduction

The Mid-Atlantic Coastal Acidification Network (MACAN), co-coordinated by the Mid-Atlantic Regional Council on the Ocean (MARCO) and the Mid-Atlantic Regional Association Coastal Ocean Observing System (MARACOOS), was established to fulfill regional priorities and serve as a platform to address coastal and ocean acidification in the Mid-Atlantic region. MACAN[1] coordinates workshops and webinars to share information that helps to increase the understanding of the processes associated with estuarine, coastal, and ocean acidification. In addition, MACAN seeks to guide research to predict consequences for marine resources and devise local adaptation strategies to enable communities and industries to better prepare and respond to acidification issues in the Mid-Atlantic region. To achieve these goals, the Mid-Atlantic region has created a coordinated and comprehensive network of resource managers, academic researchers, and other stakeholders who work together to answer important research questions for the region. More comprehensive acidification monitoring will advance understanding of variability and long-term changes to carbonate systems and will help inform research on biological impacts and potential

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[1] http://midacan.org/.

https://doi.org/10.1016/j.ecss.2019.04.023
Received 15 October 2018; Received in revised form 7 April 2019; Accepted 14 April 2019
Available online 27 April 2019

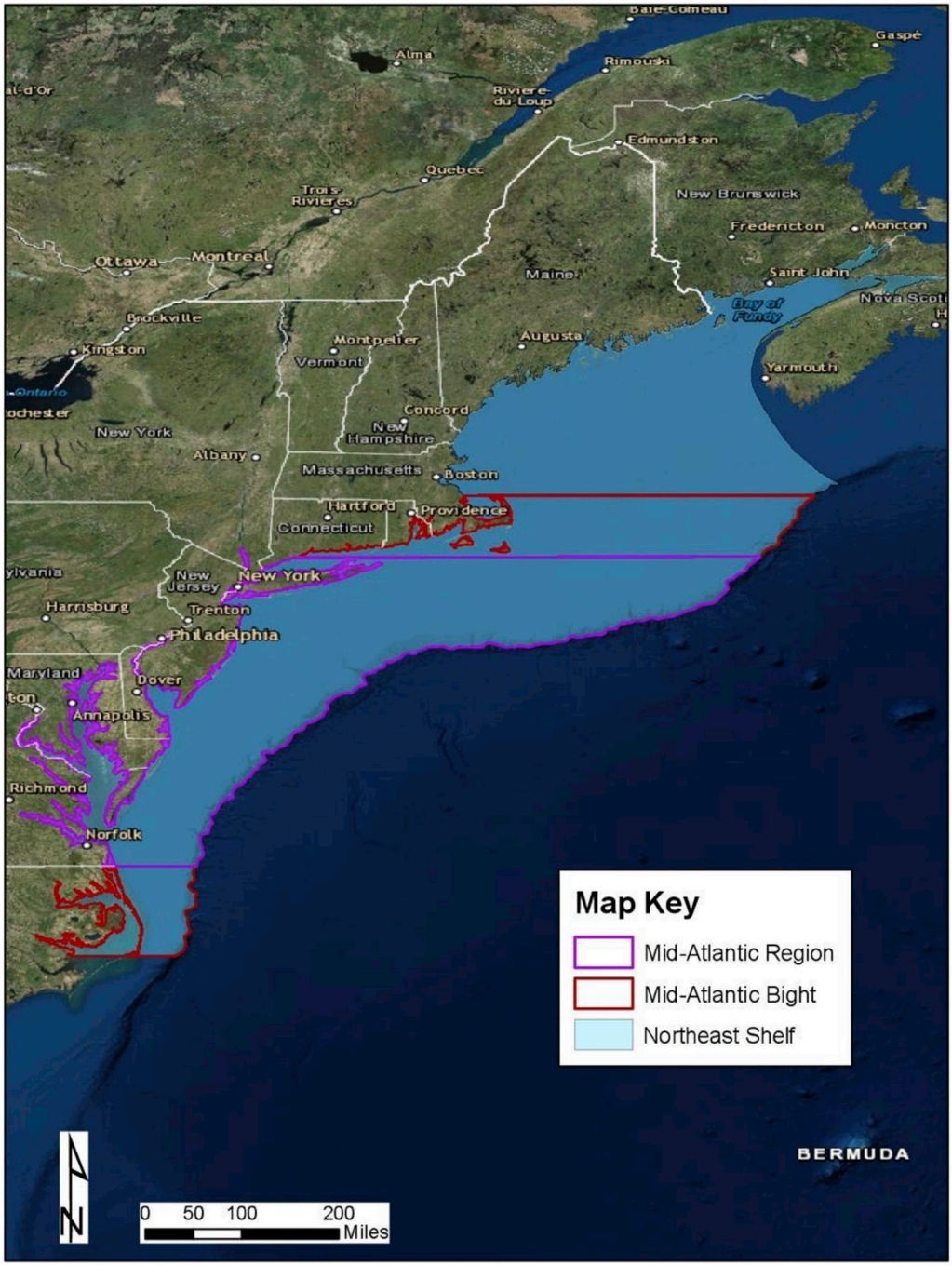

Fig. 1. The Northeast Shelf of the United States (denoted in light blue) reaches from Cape Sable to Cape Hatteras. The Mid-Atlantic Bight (outlined in red), which sits within the Northeast Shelf, stretches from Georges Bank to Cape Hatteras. The Mid-Atlantic Region (outlined in purple), as defined by MACAN, sits within the Mid-Atlantic Bight, and covers New York through Virginia.

ecosystem responses (National Academies of Sciences, Engineering, and Medicine, 2017). Leveraging existing monitoring to incorporate carbonate chemistry measurements will be important to build and enhance predictive models and anticipate future conditions that can inform adaptive strategies to support species vulnerable to acidification. Comprehensive data collection will require a mosaic of research institutions working collaboratively. Therefore, we have compiled a review of current monitoring, available technology, existing infrastructure, and areas of ecological and economic importance to guide development of collaborative monitoring efforts in the Mid-Atlantic.

1.2. Significance of acidification in the Mid-Atlantic Region

The Mid-Atlantic region extends from the south of Long Island, New York to Virginia, and is bordered by the U.S. Northeast Shelf (NES) (Fig. 1), an area defined from Cape Sable, Nova Scotia to Cape Hatteras, North Carolina. The coastal and ocean ecosystems of the Mid-Atlantic not only support human recreation and commerce, but also protect coastlines from storms, coastal flooding, and erosion (National Research Council, 2010). Furthermore, the northern portion of the Mid-Atlantic region experiences lower pH and buffering capacity (Wang et al., 2013; Wanninkhof et al., 2015) resulting in a sensitive region that supports ecologically and economically important species and habitats.

The coastal Mid-Atlantic region is defined by a broad continental shelf that extends several hundred kilometers offshore. The NES has multiple shelf-break canyons and is bounded offshore by the shelf-break front and inshore by five major estuarine systems. The NES undergoes one of the most extreme seasonal changes in ocean temperature compared to other coastal environments (Houghton et al., 1982; Biscaye et al., 1994; Schofield et al., 2008), and these seasonal temperature fluctuations are associated with variable ecological processes (Friedland et al., 2015).

In late spring and early summer, a strong thermocline develops at a depth of about 20 m across the entire shelf, isolating a continuous mid-shelf "cold pool" of water that extends throughout the Mid-Atlantic Bight (MAB) from Georges Bank to Cape Hatteras (Houghton et al., 1982). An area described as having cold (< 10 °C) and relatively low salinity (< 34 psμ) waters (Chen et al., 2018), the cold pool has been linked to the distribution and recruitment of commercial and recreational fin and shellfish species (Goldberg and Walker, 1990, Steves et al., 2000; Sullivan et al. 2000, 2005; Weinberg, 2005). Upwelling occurs annually each summer, driven by southwest winds associated with the Bermuda High (Glenn and Schofield, 2003; Glenn et al., 2004), and Ekman forcing of cold subsurface water to the surface layers (Glenn et al., 2004). Off the coast of the Mid-Atlantic seaboard, upwelled water that initially occurs uniformly along the coast is concentrated into an alongshore line of recurrent upwelling eddies that are associated with the underlying topography (Song et al., 2001) and co-located with regions of enhanced primary productivity and historically intense fishing activity (Church et al., 1984; Wood et al., 1996). Localized coastal upwelling can bring deeper waters with high concentrations of carbon dioxide (CO_2) and low pH to the surface and thus exacerbate coastal acidification conditions (Feely et al., 2008) similar to what is observed along the Pacific Northwest coast (Barton et al., 2015; Feely et al., 2016).

As the most densely populated and urbanized region of the United States, the developed coastal land in the Mid-Atlantic drains nutrients and other materials into several major estuarine systems, potentially exacerbating ocean acidification (Cai et al., 2011; Miller et al., 2009; Waldbusser et al., 2010; Wallace et al., 2014). While open ocean acidification is caused by the diffusion of atmospheric CO_2 into surface waters, decreased pH in estuarine and coastal waters can be due to a variety of additional local drivers, such as stormwater runoff. Eutrophication from excess nutrient and carbon inputs can result in hypoxic conditions and enhanced respiration, exacerbating the acidification of estuarine and coastal waters (Baumann et al., 2014; Borges and Gypens, 2010; Wallace et al., 2014). Freshwater (e.g. rivers, streams) is naturally low in alkalinity compared to brackish and saline waters, but their corresponding chemistry can depend on the geomorphological nature of their headwaters. Tidally driven land-sea interactions, such as CO_2 and total alkalinity outwelling from coastal wetlands, can play important roles at ecological scales (Wang et al., 2016). Extreme precipitation events and overall annual precipitation amounts are projected to increase for the Mid-Atlantic region, bringing increased amounts of less alkaline freshwater and more runoff into the ocean (USGCRP, 2017). With the Atlantic coast, similar to the Gulf Coast, facing above-average risks for sea level rise and storm surges, there is a potential for cascading impacts associated with rising water temperatures, ocean acidification, and heavier precipitation that threaten vulnerable aquatic species and the communities that rely on them (USGCRP, 2018). In the Eastern U.S., alkalinity in streams and rivers is on the rise and the increased chemical weathering may alter the coastal carbon cycle, impact water quality, and increase bicarbonate concentrations in freshwater systems (Kaushal et al., 2013).

The ecological consequences of ocean acidification are expected to have economic and societal impacts (Poe et al., 2014). However, there is uncertainty regarding the ecological and biogeochemical impacts of coastal acidification, and concentrated efforts to examine these potential impacts are underway (e.g., Saba et al., 2019). Several single-species acidification studies have been conducted to determine responses (i.e., survival, hatching success, larval development and growth, metabolic rates, immune response, organ development, acid-base regulation, and sense of smell) on Mid-Atlantic organisms including crustaceans, mollusks, finfish, submerged aquatic vegetation, and some phytoplankton (reviewed in Saba et al., 2019). Although negative responses to acidification are reported in several studies, overall responses are highly variable both within and among species. Historical studies (Fisher, 1977) suggest potential evolutionary tolerances of estuarine species compared to open ocean organisms due to the dynamic temperature and salinity fluctuations in estuarine habitats; however, recent experiments indicate marine organisms may have the potential for adaptation to pH fluctuations (Stillman and Paganini, 2015). Responses are also variable with the addition of stressors other than acidification (i.e., temperature, low dissolved oxygen (DO)) and scaling lab-based experiments to ecosystem-level impacts is challenging (Gobler and Baumann, 2016). This suggests that there is some potential for tolerance and/or acclimation of some individuals or species to acidification. These early findings highlight the need to conduct further research to address not only potential for acclimation and adaptation, but also to design more realistic experiments that better represent the natural variability of the environment.

There is a recognized need to monitor acidification along with other environmental stressors, as they frequently occur together and may exacerbate organismal responses. While an organism may be able to compensate or acclimate to one stressor (such as warmer temperatures), multiple stressors may result in non-linear and/or additive responses that are difficult to predict. The potential impact of multiple stressors is especially relevant in the currently warming NES (Forsyth et al., 2015; Wu et al., 2012; Zhang and Gawarkiewicz, 2015; Saba et al., 2015) as well as in the Mid-Atlantic estuaries that experience periodic hypoxic and low pH events due to eutrophication (Bever et al., 2013; Hagy et al., 2004; Irby et al., 2018).

1.3. Importance of monitoring

Aragonite, a mineral consisting of a more soluble form of calcium carbonate, is an essential component for shell-forming organisms such as clams, mussels, and oysters and for the skeletal structures of coral. Symbolized by $\underline{\Omega}_{Arag}$ (omega), aragonite saturation is a measure of the mineral calcium carbonate to form or to dissolve in seawater. Calcifying organisms require Ω_{Arag} in excess of 1.0 to optimally produce shells or skeletons as levels below 1.0 are considered corrosive, and skeletons and shells may be subject to dissolution (Hofmann et al., 2010). At present, there is no widely accepted method for the direct measurement of carbonate concentration [CO_3^{2-}]. Thus, most measurements consist of at least two of the four carbonate chemistry parameters: partial pressure of carbon dioxide in the water (pCO_2), pH, total dissolved inorganic carbon (DIC), and total alkalinity (TA). In the open ocean, measuring any two of the four carbonate chemistry parameters, in addition to salinity, temperature, and pressure (or depth), can be used to calculate the remaining parameters (Millero, 2007; USEPA, 2018). In coastal systems, inclusion of more than one parameter is necessary to calculate carbonate chemistry, particularly to account for pH variability, to adequately assess ecosystem functions, and to better interpret organismal response. Some researchers find that measuring three or four parameters are useful due to certain constants being less reliable and the availability of certified standard reference materials may be less suitable for low salinity samples from coastal and estuarine environments (USEPA, 2018). However, some members of the scientific community find that over-parameterization can result in issues of its own (Baranyi et al., 1996). While the Mid-Atlantic hosts many existing monitoring sites at which a suite of water quality parameters are measured, most sites only have a single carbonate chemistry parameter, which limits the use of these data to fully constrain the carbonate system. More comprehensive monitoring will:

1. Increase understanding of the current state of carbonate chemistry in the region by incorporating transect and continuous monitoring, allowing short-term and long-term changes to be identified over time.
2. Allow the identification of habitats that are susceptible to periods of low aragonite saturation state (Ω_{Arag}) and/or high spatiotemporal carbonate system variability to better understand the impacts of acidification on economically and ecologically valuable species.
3. Improve understanding of multi-stressor effects on the process of acidification by targeting acidification monitoring where other stressor monitoring occurs or incorporating additional monitoring to capture other known stressors (e.g., regions of excess nutrients, low DO).
4. Provide a model warning system that would assist scientists studying ecological processes, water quality managers and conservationists monitoring impacts, and commercial operators implementing adaptive strategies.
5. Inform and improve ecosystem models, specifically the development of coastal forecast models with the capability to predict the variability and trajectory of low pH and carbonate concentrations.
6. Advance our scientific understanding of the dynamics and controls on the carbonate system in the Mid-Atlantic region to inform management practices.

1.4. Existing monitoring of carbonate parameters

During the development of MACAN, one of our first priorities was to create a map depicting past, current, and ongoing acidification monitoring efforts in the Mid-Atlantic that would guide the development of the regional monitoring recommendations outlined here. We gathered information from the participating academic institutions, federal and state agencies, and commercial shellfish industry to develop the current interactive monitoring map that will be continually updated through MACAN efforts (Fig. 2[2]). In Fig. 2 map series, there are 4 collection types: (1) continuous monitoring, often by autonomous sensors at moored stations, (2) ongoing fixed stations which have regular field sampling conducted by an individual(s), (3) former fixed stations, and (4) cruise data that is collected by a survey vessel as part of a research cruise. From this map, we are able to better visualize current monitoring efforts and identify potential data gaps.

Estuaries and Bays: To the best of our knowledge, sampling pH, and other water quality parameters, in Mid-Atlantic estuaries/bays began in 1984 by the Chesapeake Bay Program (CBP). However, studies that expanded sampling beyond pH (e.g. temperature, total alkalinity, oxygen, and salinity) date back from 1969 to 1971 per the AESOP cruises (NODC, 2010). Most estuarine sampling relevant to acidification monitoring to date is focused on general water quality (e.g. DO, temperature, salinity, pH and turbidity), which includes probe or spectrophotometric measurements of pH along with temperature, salinity, and DO, but typically no other measurements of the carbonate chemistry (e.g. pCO_2, TA, DIC) (Figs. 2c and 3). Water quality measurements are collected by multiple approaches, the most common being monthly or semi-monthly sampling at set stations in tributaries and throughout the Mid-Atlantic bays/estuaries (e.g. Barnegat Bay, Delaware Inland Bays, Chesapeake Bay, and Delaware Bay).

Continuous monitoring stations (i.e., moorings with autonomous sensors) provide higher temporal resolution sampling but have been used less frequently. The Chesapeake Bay Interpretive Buoy System[3] (CBIBS) is a NOAA program of 10 buoys that capture water quality, meteorological, and oceanographic data. Current collaborators with CBIBS includes the University of Delaware, whom contributed a SeapHOx sensor on the bottom mooring at Gooses Reef to capture hourly measurements of temperature, salinity, pH, and DO beginning in the summer of 2016. In addition, the Virginia Institute of Marine Science (VIMS) deployed a SeapHOx sensor on the York River Spit buoy in November 2016. The First Landing CBIBS site, which is near the mouth of the Chesapeake Bay, has now been co-located with a buoy called the First Landing OA that is outfitted with a moored NOAA/Pacific Marine Environmental Laboratory (PMEL) MAPCO2 system (pCO_2 and pH) sensor to capture real-time, surface measurements.[4]

Another promising development is the integration of pH and pCO_2 sensors inside commercial shellfish hatcheries in selected locations around the southern portion of the Chesapeake Bay, yielding partnerships between industry and the academic community that can help us understand how commercially important species (e.g. oysters and clams) in the region are faring against increasingly acidic conditions. In New Jersey, the Barnegat Bay Partnership (BBP) installed United States Environmental Protection Agency (U.S. EPA)-funded high precision pH and pCO_2 monitoring equipment to leverage existing continuous water quality measurements.[5] Like BBP, Long Island Sound also received funding to acquire high-frequency and high-precision instrumentation to monitor acidification and these observations are on-going. Estuarine research cruises with water chemistry sampling remain limited, and even fewer are focused specifically on acidification; however, these efforts have allowed an assessment of the high spatial resolution in carbonate chemistry in the region's estuaries, specifically in the Chesapeake and Delaware Bays (e.g., Brodeur et al., 2019; Joesoef et al., 2015, 2017). A recent study using data from Chesapeake Bay cruises that occurred in 2013–2015 reported severe acidification and increased carbonate dissolution associated with eutrophication and low DO (Cai et al., 2017).

Continental shelf waters: With the exception of nearshore sampling by the New Jersey Department of Environmental Protection (NJDEP) and three Ocean Observing Initiative[6] (OOI) moorings located east of the northern New Jersey coast, the majority of acidification sampling in shelf waters of the Mid-Atlantic is conducted via cruises with underway pCO_2 systems and discrete samples, primarily sponsored by NOAA. This provides sporadic high spatial resolution sampling (about every four years on average) to examine long-term trends (i.e., decadal), but does not provide the temporal resolution needed to understand daily, seasonal, and interannual variability. Sampling for water chemistry parameters in the surface waters of the U.S. NES has been conducted since 1973 with occasional measurements of carbonate chemistry (for example the 1993–1996 DOE Ocean Margin Program,2007[7] and2012[8] NOAA Ocean Acidification Program (NOAA OAP) funded the Gulf of Mexico East Coast Carbon Cruise [GOMECC] and later the East Coast Ocean Acidification Cruises [ECOA] in 2015 and 2018). The ECOA2015[9] cruise was dedicated to acidification measurements and another similar cruise occurred in the summer of 2018 (ECOA, 2018) as NOAA remains committed to continuing this cruise every four years under NOAA OAP funding. Additionally, the New York State Department of Environmental Conservation (NY DEC) has committed to monitoring carbonate chemistry seasonally for ten years (2018–2028) per the creation of the NY Ocean Acidification Task Force[10]. NY DEC in partnership with Stony Brook University scientists will be conducting seasonal cruises monitoring surface pCO_2 and pH continuously. Surface samples will be supplemented by periodically taking discrete samples for laboratory analysis of TA and DIC. In addition, TA, DIC, and pH

[2] http://portal.midatlanticocean.org/ocean-stories/every-map-tells-a-story/.
[3] https://buoybay.noaa.gov/.
[4] https://www.pmel.noaa.gov/co2/story/First+Landing+OA.
[5] https://www.barnegatbaypartnership.org/wp-content/uploads/2018/03/BBP_Annual-Report-Feb2018_forWeb-Final.pdf.
[6] http://oceanobservatories.org/about/.
[7] http://www.aoml.noaa.gov/ocd/gcc/GOMECC1/CruiseReportfinal.pdf.
[8] http://www.aoml.noaa.gov/ocd/gcc/GOMECC2/Cruise_Report_June2014.pdf.
[9] http://www.aoml.noaa.gov/ocd/gcc/ECOA1/.
[10] https://www.dec.ny.gov/press/114477.html.

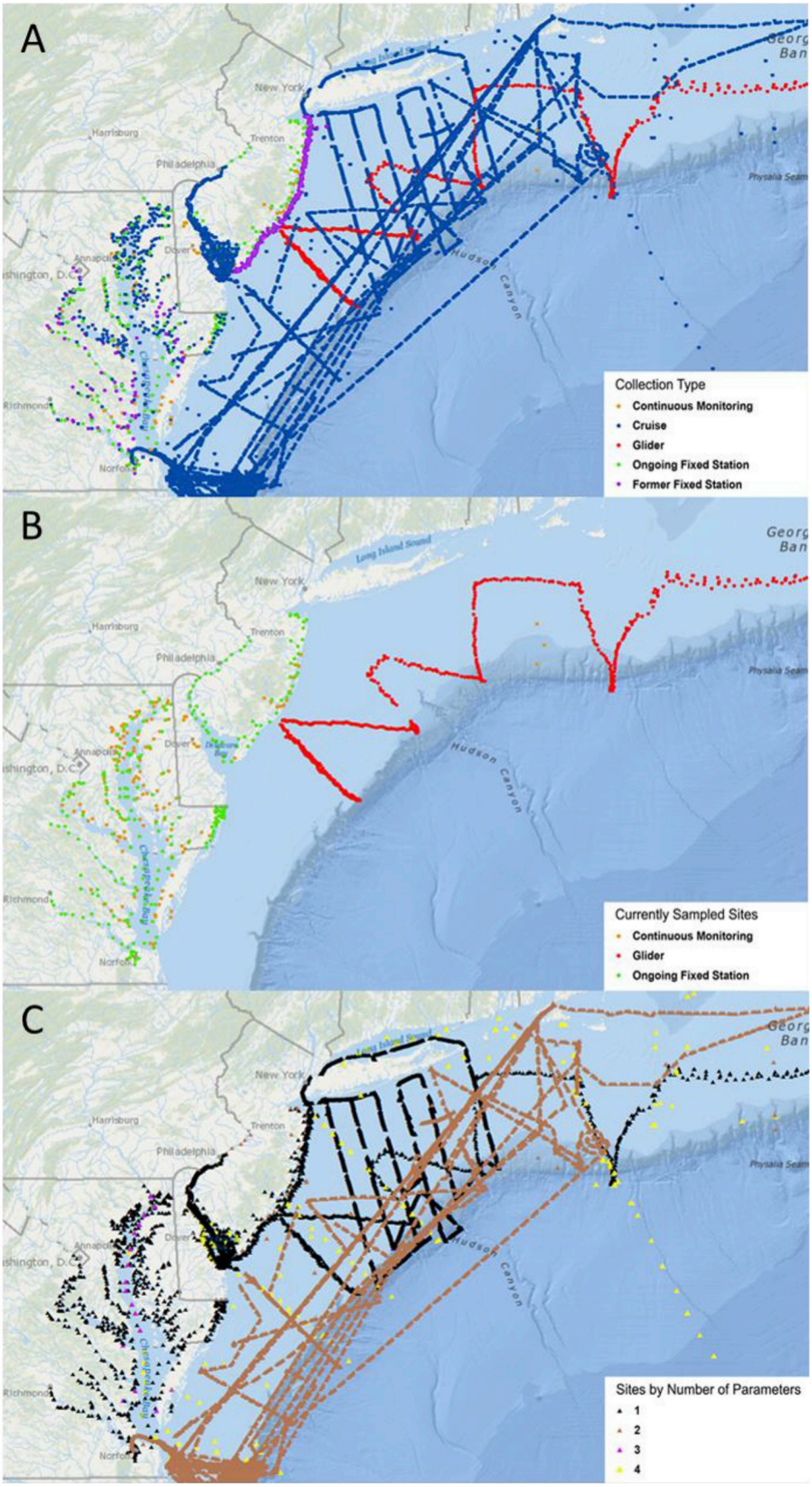

Fig. 2. Carbonate chemistry monitoring in the Mid-Atlantic region.A) all sampling; B)current sampling; C) sites by number of carbonate chemistry parameters

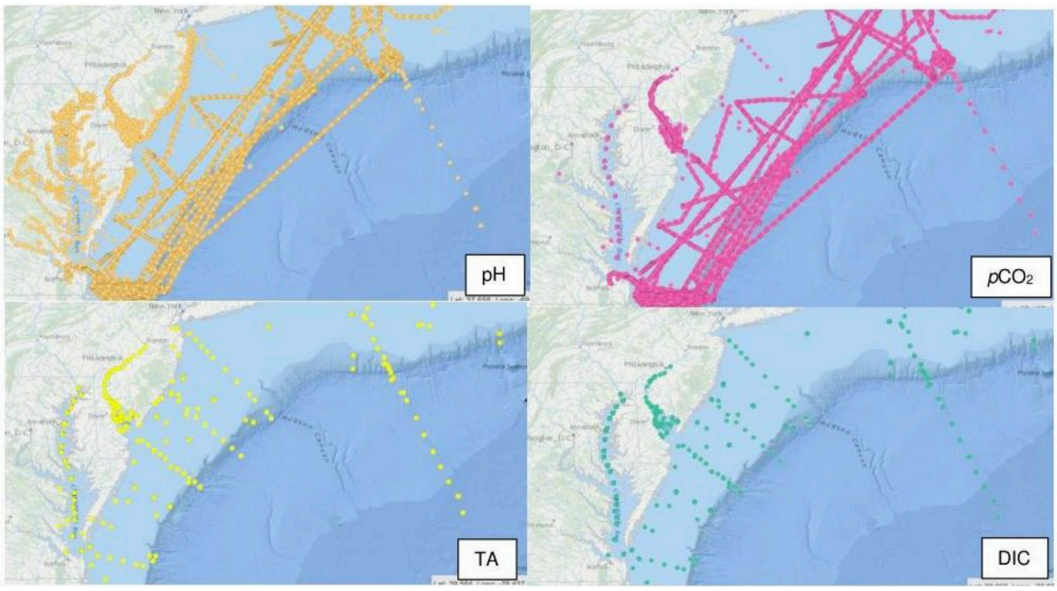

Fig. 3. Sampling locations specific for individual carbonate chemistry parameters.pH is the most commonly measured parameter (top left) compared to $pCO^{2,}$ TA, and DIC.

samples will be collected from periodic CTD (Conductivity, Temperature, Depth) casts along transects in the New York Bight (roughly from Montauk to Hudson Canyon).

1.5. Current state of acidification in the mid-Atlantic

A majority of investigations on carbonate chemistry in the Mid-Atlantic shelf waters published thus far are focused on surface waters. The most commonly measured carbonate system parameter along the U.S. NES is pCO_2. Surveys of the NES depict large natural seasonal and spatial variability and possible decadal changes of surface carbonate chemistry (Boehme et al., 1998; Wang et al., 2013, 2017; Wanninkhof et al., 2015; Xu et al., 2017). Regional algorithms based on satellite data (Signorini et al., 2013) and calculated surface pCO_2 (Boehme et al., 1998) on the Mid-Atlantic shelf depict strong seasonal variability with the lowest values during the winter-spring transition and highest values during the summer-fall transition. Furthermore, high short-term (> 10 days) and interannual variability in Ω_{Arag} occurred in the central MAB, and the drivers of this variability differ spatially (Xu et al., 2017). Ω_{Arag} can directly impact calcifying organisms as aragonite is a form of calcium carbonate essential to shell formation. The dominant driver of short-term Ω_{Arag} variability in shelf waters is thought to be biological activity (i.e., respiration and photosynthesis), while physical advection and mixing processes may exert a more dominant influence on Ω_{Arag} variability in slope waters (Xu et al., 2017). In addition, Ω_{Arag} is highly dependent on source water whereby Ω_{Arag} is higher in regions of greater influence from well buffered Gulf Stream water (southern portion of the east coast) and lower in the northern regions with higher influences of the weaker buffered southward coastal currents fed by Labrador Sea slope water (Wanninkhof et al., 2015) and the Gulf of Maine (Wang et al., 2013). Thus, processes impacting the relative proportions or rate of supply of these different source waters likely drives large-scale variability in carbonate chemistry on the NES, and especially in the Mid-Atlantic region where there is high interchange between these source waters. The stability of the Gulf Stream coupled with multi- and decadal oscillations may result in large-scale variability, but this is a current knowledge gap. Additionally, the weakly buffered northern region of the NES is expected to have greater susceptibility to ocean acidification (Wang et al., 2013; Wanninkhof et al., 2015). There is evidence of acidification occurring on the NES as shown by surface water pCO_2 that is currently increasing at rates of 1.93 ± 1.59 µatm yr^{-1} (Wang et al., 2017), similar to the rate of increase observed in the surface waters of the open ocean (Bates et al., 2014; Kitidis et al., 2016). However, the pCO_2 trend in the NES has been directly related to warming in this region (0.1–0.3 °C $decade^{-1}$) (Wu et al., 2012), and, interestingly, cannot be correlated directly to CO_2 invasion, or ocean acidification (Wang et al., 2017). This temperature-pCO_2 correlation, however, is both temporally and spatially variable in Mid-Atlantic shelf waters (Boehme et al., 1998; Wang et al., 2017), spurring research focused on providing a better understanding of these processes and the drivers of increased surface pCO_2 in shelf waters.

Even though subsurface waters are sampled during large cruise efforts every 3–4 years (i.e., GOMECC, ECOA), there is far less published information available on carbonate chemistry below the surface on the U.S. NES. However, DIC is significantly higher while Ω_{Arag} is significantly lower in most bottom water compared to surface water on the shelf (Wang et al., 2013). The ECOA 2015 cruise also revealed the existence of a large spatial area of low pH and Ω_{Arag}in bottom waters of the MAB and these conditions correlate well to the strength of the cold pool (Cai and Wanninkhof, unpublished; Fig. 4). This is likely due to a combination of enhanced seasonal stratification, biological activity, and the inflow of Labrador Sea slope water into the cold pool. This likely impacts pelagic and benthic organisms (finfish, groundfish, lobster, shellfish) on the shelf and will create episodic low pH events throughout the water column consistent with upwelling regions that have high variability in pH (reviewed in Hofmann et al., 2011; Yu et al., 2011) where deep, corrosive (low pH) water is upwelled to the surface, similar to what is observed on the West Coast (Feely et al. 2008, 2010, 2016). Additionally, intermittent events such as hurricanes and coastal storms that generate excess rainfall, increase sedimentation, and nutrient runoff exert short-term yet dramatic impacts (e.g. decreased pH and TA and increased DIC) due to terrestrial water inputs (Johnson et al., 2013).

Despite having significantly more sources of data compared to the coastal shelf waters, Mid-Atlantic estuarine systems have limited information on carbonate chemistry trends. One study consisting of 15 years (2002–2016) of high-frequency temperature, DO, and pH data collected from the U.S. National Estuarine Research Reserves System[11] (NERRS) (Baumann and Smith, 2017), including three Mid-Atlantic

[11] https://oceanservice.noaa.gov/ecosystems/nerrs/.

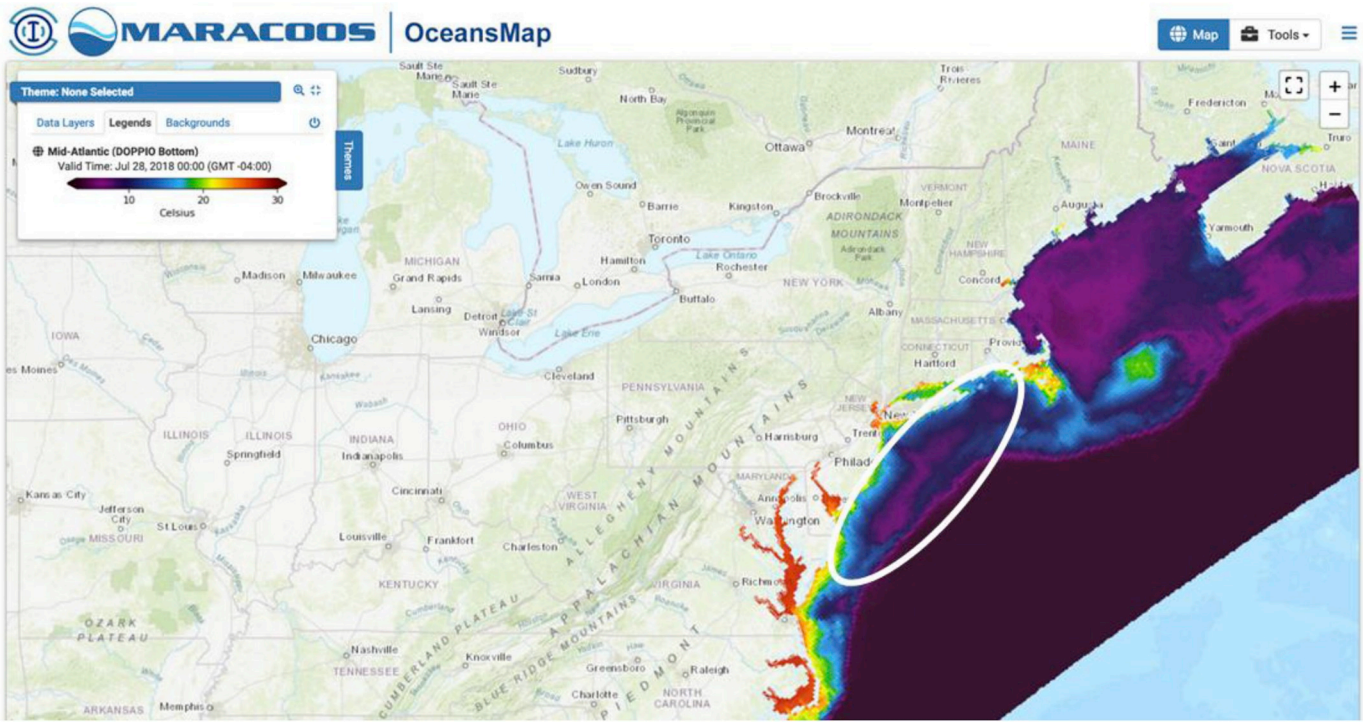

Fig. 4. This figure provides an example of the temperature difference (°C) and approximate geographic location of the cold pool in the Mid-Atlantic region from the MARACOOS OceansMap using a numerical simulation with the Regional Ocean Modeling System (ROMS)(Chen et al., 2018).

NERRS sites – Jacques Cousteau (NJ), Delaware (DE), and Chesapeake Bay (VA) – exhibited high daily, seasonal, interannual, and decadal variability in pH and was tightly correlated to temperature and biological activity (Baumann and Smith, 2017). Additionally, episodic low pH events occur in the Chesapeake Bay, and these are associated with other biological processes and stressors (i.e., eutrophication, hypoxia) that trigger biogeochemical changes leading to low pH at mid-depths (Cai et al., 2017). Similar trends have been documented in shelf waters in other regions where nutrient-rich rivers discharge (Cai et al., 2011), so we can hypothesize that these trends might also be occurring in other Mid-Atlantic estuaries.

Due to the stochasticity, high diel and seasonal variability, precipitation in wet versus dry years, and the episodic nature of these systems, as well as high spatial variability, it is more difficult to tease out the gradual long-term trends. However, an analysis of a 23-year water quality monitoring dataset of the CBP[12] revealed that pH has significantly decreased in polyhaline waters (salinities > 18), but not in lower salinity regions of Chesapeake Bay (Waldbusser et al., 2011). This was linked to eutrophication-induced productivity increases in the lower salinity region that was then transported and respired in polyhaline waters (Waldbusser et al., 2011).

2. Technology[13] and temporal considerations

2.1. Available technology and limitations

There is a need for sensors on depth-profiling equipment to allow for high spatial and temporal resolution sampling. So far, *in situ* monitoring for pCO_2 and pH are the most widely used sensors while DIC and TA analysis involving traditional bottle sampling techniques are more limited, both spatially and temporally (Wang et al., 2015). The measurement of pH, via spectrophotometric or potentiometric determination (Dickson et al., 2007), appears very simple but has always been a challenge for the ocean science community (Dickson, 1993; Dickson et al., 2007). In addition, researchers must also consider the appropriate scale in which pH measurements are collected depending on instrumentation and environment. For purposes of coastal and ocean acidification, pH_T (total hydrogen scale) is recommended for seawater (Bresnehan et al., 2014; Marion et al., 2011; USEPA, 2018). The widely used spectrophotometric pH may also be capable of delivering high-quality measurements for in-situ, ruggedized equipment. This low-cost pH technique is considered ideal for long-term deployments as it needs minimal reagent and does not require calibration with exception for pH indicator solution for laboratory characterization prior to deployment.

Early autonomous monitoring efforts have been limited mainly to surface waters, and water column profiles were only possible via manual sampling from a ship. However, improvements to pH sensor technology (i.e., ISFET, DuraFET, Deep-Sea DuraFET) (Bergveld, 2003; Bresnehan et al., 2014; Gonski et al., 2018; Johnson et al., 2016; Martz et al., 2010; Seidel et al., 2008) have demonstrated that these sensors can respond rapidly to changes in pH and can be quite stable despite large gradients in pressure, temperature, and water chemistry conditions in which the sensors operate. Automated DIC and TA sensor technology is rapidly developing (Liu et al., 2013; Sayles and Eck, 2009; Wang et al., 2015); but, autonomous measures of pH and pCO_2 (i.e. Sunburst Sensors) remain most common as they are currently more developed and field robust. There are miniaturized sensor systems that may provide unique benefits due to low power needs and simple design with minimal drift; however, these sensors that are capable of capturing pH and pCO_2 require more investigation (Clarke et al., 2015).

Currently, profiling floats and buoys have successfully used optical instrumentation (Alverson and Baker, 2006; Argo Science Team, 1998; Boss et al., 2008; Fiedler et al., 2013; Son et al., 2006) with long periods of endurance in the ocean and accommodating depths of thousands of meters. The commercial availability of gliders and autonomous platforms make the development of smaller, sophisticated devices to measure carbonate chemistry profiles across spatial and temporal scales

[12] https://www.chesapeakebay.net/.

[13] The authors of this paper, MACAN, and affiliated organizations do not necessarily endorse any specific technology mentioned herein. Any mention of specific technology and/or models is for informational purposes only.

attractive for in-situ, long-term monitoring. For instance, Woods Hole Oceanographic Institution is advancing their current high-resolution sensors for DIC, pCO_2, and pH for Autonomous Underwater Vehicles (AUV), Remotely Operated Vehicles (ROV), and other CTD platforms. In the Mid-Atlantic, there is a recent project funded by the National Science Foundation to integrate a pH sensor into a Slocum glider, and this new sensor platform is currently being tested by Rutgers University in coastal waters (Saba, unpublished). Partnerships among academia, industry, non-governmental organizations (NGOs) or other entities can leverage interests and may also offset cost related roadblocks when exploring high-resolution technology for long-term monitoring. Collaborative opportunities such as York Spit buoy, located at the mouth of the York River, demonstrate intelligent leveraging and partnership between NOAA and VIMS. The York Spit buoy monitors pH with SeapHOx sensors located just below the surface but could be further enhanced by an additional pCO_2 sensor.

Though there is a need for accurate and precise autonomous in-situ measurements in the Mid-Atlantic Region, the same can be said for sensors for long-term deployment. Present monitoring needs require continued precision and accuracy to appropriately characterize coastal conditions by limiting equipment known to experience bio-fouling issues and to accurately capture salinity shifts. Bio-fouling can present challenges in less than a week in some systems, particularly eutrophic, however, there are some anti-fouling technologies (i.e. paints, chlorination, wipers/scrapers) that have been investigated to enhance confidence in sensor measurements over long deployments (Delauney et al., 2010). Self-calibrating systems are rare and at times require field observations for calibration. Sensor accuracy is not only essential but dependent on quality control technique and that varies by user (Bresnahan et al., 2014; McLaughlin et al., 2017). Sensors used in coastal systems need to be robust at a range of conditions, particularly pH which is a salinity- and temperature-dependent measurement, and compatible with sensor instrumentation measuring other carbonate chemistry parameters. Prior to deployment, sensors should be rigorously calibrated and adequately developed to withstand pressure and the range of diverse marine environments (Bresnahan et al., 2014) in addition to long conditioning periods to minimize drift (Clarke et al., 2015).

3. Building collaborative monitoring efforts

3.1. General concepts to consider

Monitoring in the Mid-Atlantic, like other regions of the United States, is limited by the resources available. These regional monitoring considerations emphasize leveraging existing monitoring and structures. Continuous monitoring sites for region-wide monitoring are favorable over intermittent fixed sampling sites for the purpose of improved temporal resolution in the estuaries and nearshore, which will help us understand short-term signals in acidification. Shelf cruises will need to be continued to gain spatial resolution for the determination of long-term patterns. Though MACAN focuses on the use of monitoring to develop a region-wide understanding of changes in acidification, it is worth noting that for interests in smaller geographic areas there is a trade-off between temporal and spatial resolution. Entities seeking to site shellfish operations or describe habitat or ecosystem dynamics may be more interested in spatial resolution than a program seeking to separate the oceanic and watershed footprints, which might be interested in a high frequency observation signal.

While the combination of monitoring pCO_2 and pH are not the most effective for understanding the full impacts of acidification, they are the easiest to monitor with the best sensors currently available for *in situ* measurements. High resolution, in-situ measurements are important for capturing biogeochemical variability in dynamic coastal systems to better understand natural variability amidst anthropogenic influences. Ideally, in order to characterize Ω_{Arag}, it is important to measure DIC or TA with pH or pCO_2. There is value in measuring pH and pCO_2 with a less convenient parameter, TA or DIC, to more accurately characterize the carbonate chemistry. Thus, there is certainly a tradeoff in which variables to measure.

In developing a monitoring strategy, it is important to monitor different habitats across different salinity gradients as well as major sources of inputs, such as rivers, wetlands, and upstream of source waters to understand the spectrum of impacts to the region. It is possible to determine a relationship between salinity and TA in portions of the Chesapeake Bay and the shelf of New Jersey as was previously determined for the Atlantic along the East Coast of the U.S. (Cai et al., 2010a,b; Wang et al., 2013), but this requires numerous measurements to calibrate whether the relationship is non-linear, seasonally variable, and/or dependent upon the strength of land-sea interactions. Thus, it is important to collect data to establish this relationship, if possible, as well as data to be included in mechanistic models, including predictive models. A future goal for the Mid-Atlantic could be to coordinate an inter-laboratory carbonate chemistry calibration across the region, similar to and/or building on the Chesapeake Bay Coordinated Split Sample Program that currently exists within the Chesapeake Bay mainstem and tributaries across participating state, federal and academic monitoring agencies[14] and building from examples provided by Pimenta and Grear (USEPA, 2018). This may also help in creating a path for other laboratories to begin to conduct analytical chemistry, which will be relevant as more NGOs and citizen scientist groups become active in collecting data for acidification monitoring and the demand for data analysis increases. These monitoring considerations may also guide potential short-term pilot studies in the region to further optimize site selection and lead to larger investments in continuous monitoring.[15]

3.2. General gaps

Need for high sampling frequency: With the exception of a few fixed autonomous stations, the sampling frequency throughout much of the region is too low to adequately capture short-term episodic events that could have immediate impacts to industries and managed ecosystems. For instance, the acidification-focused shelf cruises that have occurred in the Mid-Atlantic region occur only once every four years. The Mid-Atlantic is a dynamic region in which acidity can be highly variable due to pollution (i.e. river discharge/runoff or atmospheric deposition), currents, biological activity (photosynthesis and respiration), sediment-water interactions, wetland inputs, etc., which can occur at varying timescales (such as diurnal and tidal). These processes must all be considered when designing and implementing a regional monitoring system. Though seasonal sampling can offer further understanding of chemical changes resulting from seasonal weather and ocean current conditions, monthly or higher frequency observations may better capture variability in temperature, primary production and respiration providing much needed baseline Ω_{Arag} data (Balch and Fabry, 2008). At a minimum, for any long-term trend to be detectable requires a fine enough resolution to cover short-term variability, such as seasonal or shorter time scale, so that long-term trends can emerge from the short-term variability (Keller et al., 2014).

Need for measurements of multiple carbonate chemistry parameters: Few current monitoring efforts such as the Global Ocean Acidification Observing Network (i.e. GOA-ON[16]) combine frequent monitoring with an adequate number of carbonate system parameters for monitoring the

[14] https://www.chesapeakebay.net/what/programs/chesapeake_bay_quality_assurance_program/quality_assurance_split_sample_and_blind_audit_programs.

[15] For more precise guidelines to developing monitoring methods, protocols and programs see Dickson et al., (2007), McLaughlin et al., 2017, Riebesell et al., (2010), and USEPA 2018.

[16] http://goa-on.org/.

status of acidification. Even in cases where high-frequency observations are being recorded, often only one acidification parameter such as pH is measured, which does not allow full characterization of acidification (including Ω_{Arag}) (Fig. 2c).

Need for high-resolution depth-profiling measurements: Most current sampling is done in surface waters, but subsurface waters are typically more acidic due to the biological remineralization of sinking particulate organic surface material. While surface water mapping of pH can be valuable, episodes of low surface pH are typically driven by mixing events where low pH water either upwells to the surface from below the thermocline or flows onto the shelf via rivers and bays, warranting the need for vertical profiling. The benthic environment is an important habitat for benthic calcifiers and other economically important species in the region such as lobsters and scallops. This lack of benthic monitoring is true particularly on the shelf. A likely area of impact in the benthic environment is the shelf cold pool, particularly off the coast of New Jersey, where Ω_{Arag} is naturally lower than at the surface. The OOI's Pioneer array[17] located southeast of Long Island, NY, is the only continuous monitoring system capturing measurements at bottom depth on the shelf. The OOI Pioneer Array is only supplemented by seasonal CTD casts in the New York Bight and the ECOA cruises. The ECOA 2018 cruise measured full water column profiles. Being able to monitor carbonate chemistry parameters throughout the water column is critical in order to track the movement of acidified water, understand the variability of acidification, and predict how mixing events and circulation will impact acidification across the shelf. While ships can provide detailed water column profile data, their costly operation limits both temporal and spatial coverage. Moorings can collect high-resolution temporal data but cannot resolve spatial variability and still require ships for maintenance and calibration visits. Therefore, there is a critical need to develop and deploy new, cost-effective technologies that can routinely provide high-resolution data on regional scales in our coastal ocean as well as coordinate disparate monitoring efforts.

Need for biological response monitoring: While not the focus of this paper, we would be remiss not to mention the importance of monitoring biological response indicators (i.e., plankton). For instance, changes in the surface plankton community due to high pCO_2 and low pH could alter the transport of carbon to bottom waters (Moy et al., 2009), which could result in a source of uncertainty relative to other measured characteristics of water chemistry (Grear et al., 2017). Long-term understanding of changes to ocean biogeochemical cycling will require an understanding of the effects of ongoing changes on plankton ecology and other aquatic organisms.

4. Monitoring other drivers

While the measurement and monitoring of carbonate chemistry parameters provides the metrics to directly assess acidification, such studies should be placed within the context of other drivers that may cause water chemistry changes when conducted within estuarine and coastal environments. The influence of environmental phenomena such as rainfall, runoff, temperature, salinity, deoxygenation, circulation patterns, and wind direction and intensity (as they relate to storm surge, upwelling, downwelling, and blow-out tidal conditions) in coastal environments can have rapid and profound effects on acidification events (Abril and Borges, 2004; Cai et al., 2017; Gobler et al., 2014; Johnson et al., 2013; Salisbury et al., 2008; Waldbusser and Salisbury, 2014). Other stressors such as pollutants (namely excess nutrients that result in eutrophication), algal blooms (both benign and harmful species), and hypoxia may also interact with the acidification of local inshore and nearshore waters. Temperature fluctuations alone may greatly affect the ability of water to absorb and retain CO_2 (Crovetto, 1991; Diamond and Akinfiev, 2003), and thus may greatly influence seasonal and interannual variability in acidification trends. By co-locating monitoring for carbonate chemistry parameters with other stressor monitoring, experimental studies and empirical models will be better able to mimic real-world dynamics that can help to enable better prediction of acidification events as well as species and ecosystem impacts.

Several programs are currently monitoring a variety of water quality and other parameters for inshore and nearshore waters within the Mid-Atlantic region. In some cases, augmenting or upgrading established hardware with additional sensors would maximize the return on investment. Leveraging existing water quality monitoring assets by collocating carbonate measures with existing stations would also avoid the need to permit and build new infrastructure and capitalize on historical datasets. Furthermore, observers of DO in coastal waters are already familiar with the highly dynamic nature of processes driving production and respiration and the sampling challenge it creates, and have thus thought about these considerations in setting up their stations and sampling programs.

While continuous abiotic water-quality monitoring stations are outnumbered by stations intermittently sampled via cruises or remote sensing, several agencies conduct such measurements within coastal and estuarine waters of the Mid-Atlantic. The United States Geological Survey (USGS), the NERRS, the NJDEP, Maryland Department of Natural Resources, Delaware Department of Natural Resources and Environmental Control, Virginia Department of Environmental Quality, the U. S. EPA National Estuary Program[18] (NEP), and a number of educational and research institutions (Stockton University, Monmouth University, Chesapeake Research Consortium, etc.) operate water-monitoring equipment at fixed stations within areas of importance. In order to assemble a robust acidification-monitoring network, it may be efficient to expand the capabilities of partners' stations by augmenting their current equipment. Existing water quality stations that are already observing temperature, specific conductivity, DO, chlorophyll-a, and pH could be leveraged for acidification monitoring by deploying a pCO_2 sensor and some bottle sampling for quality assurance checks and calibration of the sensors. These networks may also provide opportunities for developing and testing new sensors.

While not as robust as multi-parameter water-monitoring stations, the USGS operates a network of stream flow sensors that inventory stream and river flow-rates as well as measure nutrients, alkalinity, and pH within the targeted study area. Because these systems transport materials/chemical species that influence the chemistry of coastal waters, inclusion of these data in conjunction with meteorological data is needed to understand event-based (e.g. rain events, drought) influences within the system. Meteorological data available via the NOAA National Weather Service, USGS, NERRS, US Forest Service, various universities, and private stations (i.e., WeatherFlow, Weather Underground, commercial airfields, etc.) can track atmospheric temperature, precipitation, Phased-Array Radar, and wind-forced phenomena (storm surge, upwelling, blow-out tidal conditions). Augmentation of select sites to capture atmospheric deposition of pollutants and nutrients (particularly nitrogen and sulfur species) (Gao, 2002; Gao et al., 2007) is recommended to understand the interplay between direct atmospheric deposition vs. terrigenous deposition via riverine input and surface runoff (Da et al., 2018; St-Laurent et al., 2017).

5. Leveraging of existing monitoring infrastructure

Though there are at present four measurable carbonate chemistry parameters (pCO_2, TA, DIC, pH), a more feasible and reliable monitoring approach would be to measure at least two parameters in areas of importance. So far, the current monitoring maps demonstrate that

[17] http://oceanobservatories.org/array/coastal-pioneer/.

[18] https://www.epa.gov/nep.

the vast majority of estuarine and near coastal waters of the Mid-Atlantic have sites where only one parameter is measured, typically continuous or fixed measurements of pH along with other water quality measurements (Fig. 2). In general, DIC and TA are the most infrequently sampled parameters and have a limited geographic focus.

An efficient way to leverage the ongoing sampling in the Mid-Atlantic is to either measure an additional parameter at an existing monitoring site or to leverage other environmental variables that are measured simultaneously. The technology for pH and pCO_2 sensors is highly developed and many instruments are commercially available, whereas DIC and TA autonomous monitoring sensors are still in the development stage. One approach to efficiently add DIC or TA might be to access its likely variability at given locations. For example, as discussed above, salinity and TA correlate fairly well. To avoid oversampling, examining salinity records may give good insight as to how often TA could be sampled.

In some coastal waters, pH has been measured over many decades, and provide valuable long-term datasets. These pH data are useful for the study of short-term variability (e.g., tidal and seasonal), but they are not well calibrated to detect an ocean acidification signal, which is long-term and occurs in small changes (0.001–0.003 pH units/yr). These probe measurements can resolve 0.1 pH unit changes but not as fine as the 0.001 pH needed. Though there are studies (e.g. AESOP cruises in NOAA archive) that occurred in the Chesapeake Bay as early as 1969 (NODC, 2010), the CBP has more than 30 years of pH data starting in 1984 from 49 stations in the Chesapeake Bay mainstem that has been taken once each month during the cooler months and twice each month in the warmer months.[19] The pH, along with DO, temperature, and salinity measurements provide meaningful information concerning the physical, chemical, and biological dynamics of a system. In the absence of a second measured carbonate chemistry parameter, the development of regionally specific relationships between TA and salinity (e.g. Cai et al., 1998; Cai et al., 2010; Shadwick et al., 2010; Wang et al., 2013) allow a second carbonate parameter to be estimated with moderate confidence. This derived alkalinity, along with water quality pH measurements, can be used to expand/compute datasets to consider the full CO_2 system. A strategy moving forward for these long-term dataset sites may be to deploy high accuracy pH/pCO_2 sensors at key selected locations for long-term monitoring, and adding new DIC/TA sensors when they become available. For lower accuracy pH/pCO_2 measurements, regular inter-calibrations should be performed, and they should be used appropriately to detect and study signals (e.g., tidal, episodic, diurnal, seasonal, etc.).

Empirical multivariate relationships have been applied to compute pH (and other CO_2 system parameters) in individual coastal regions of the western U.S. based on hydrographic data such as temperature, salinity, pressure, oxygen, and nitrate (e.g. Alin et al., 2012; Juranek et al., 2009). These approaches yield reliable estimates of the CO_2 system in part due to the stoichiometric relationships governing biologically driven changes to the CO_2 system, and in part due to dependence of the thermodynamic drivers of the CO_2 system on temperature, pressure and salinity (Zeebe and Wolf-Gladrow, 2001). While these approaches will not yield carbonate system data of the same quality as obtained through the direct measurement of two parameters, they may provide insight to changes at many existing locations and allow priorities for new observations to be developed. Furthermore, although those methods are promising, there are some challenges applying them on the east coast, including the impact of physical processes on alkalinity in the region.

6. Optimizing monitoring in areas of importance

Because of the scale of acidification, the instrument costs, and the ever-increasing competition for limited resources, implementing a comprehensive long-term monitoring program becomes challenging. One way to address this challenge is to focus monitoring efforts in areas most vulnerable to changing water chemistry (e.g. areas with a potential abundance of acidification drivers) and/or to prioritize monitoring in areas with a known presence of sensitive or ecologically/commercially important species. Key areas of importance along the U.S. Mid-Atlantic include the cold pool (Fig. 4), estuary systems (including oyster aquaculture and restoration sites), and deep-sea coral habitat (Fig. 5). These areas are highlighted below as well as possible programs that could be leveraged to increase monitoring in these areas.

6.1. Cold pool

The cold pool is the designation given to remnant winter water in the MAB centered between the 40 and 70 m isobaths (Bigelow, 1933; Lentz, 2017) (Fig. 4). The cold pool is formed when vernal warming of the surface water sets up the seasonal thermocline that isolates the cold bottom water from surface waters and plays an important role in the distribution of MAB demersal biota (Colvocoresses and Musick, 1984). The presence of colder water during the summer provides a refuge for potentially vulnerable boreal species such as ocean quahogs and sea scallops as well as for surf clams (Cooley et al., 2015; Hare et al., 2016).

While significant efforts have been expended to determine the physiochemistry of the cold pool (e.g. temperature, DO, nutrients, etc.) (Biscaye et al., 1994; Falkowski et al., 1983; Houghton et al., 1982), few studies have focused on measuring the carbonate chemistry and analyzing how that chemistry might change with increasing atmospheric CO_2 and water temperatures (Wang et al., 2013; Cai and Wanninkhof unpublished). Unlike the aged deep water in the Atlantic and Pacific, the annual formation of cold pool water may mean its carbonate chemistry would reflect near real-time increases in atmospheric CO_2 and pCO_2 in its source water, the Labrador Current, which has a low buffering capacity due to ice melt and runoff from source areas. Still, expected changes in the pCO_2 of the cold pool due to increases in atmospheric CO_2 can be confounded by any concurrent increases in temperature and other physical factors not related to the atmosphere.

Furthermore, from 1982 to 2014, bottom waters of the U.S. NES experienced an average increase in temperature of 0.2 °C/decade (Kavanaugh et al., 2017). An increased in water temperature alone will increase pCO_2, decrease pH, and increase Ω_{Arag} in the cold pool. To understand how future changes in atmospheric CO_2, water temperature, and other source water factors will affect the cold pool's carbonate chemistry, it is paramount that monitoring be conducted to determine present conditions, their variability, and drivers of change. A vigorous water quality monitoring program using Slocum gliders is already established by Rutgers University and supported by MARACOOS (Schofield et al., 2010) and the NJDEP. While the pH glider effort is currently underway with sensors currently reaching 200 m depth (Grace Saba, pers. comm.), continued efforts should be made to take advantage of this established program by outfitting additional gliders (which can host sensors at 100 m, 200 m, and 1000 m depths) with sensors for measuring pH and pCO_2 as well as DIC/alkalinity (when they become available).

There are existing buoys operated by the National Data Buoy Center and U.S. Army Corp of Engineers that range between 20 and 200 km offshore where additional sensors, such as NOAA's PMEL CO_2 system and bottom moored pH sensors, could be incorporated to capture these signals. The OOI Pioneer Array[20] off the shelf south of New England, near Martha's Vineyard, provides climate quality measurements of

[19] https://www.chesapeakebay.net/what/downloads/cbp_water_quality_database_1984_present.

[20] https://oceanobservatories.org/.

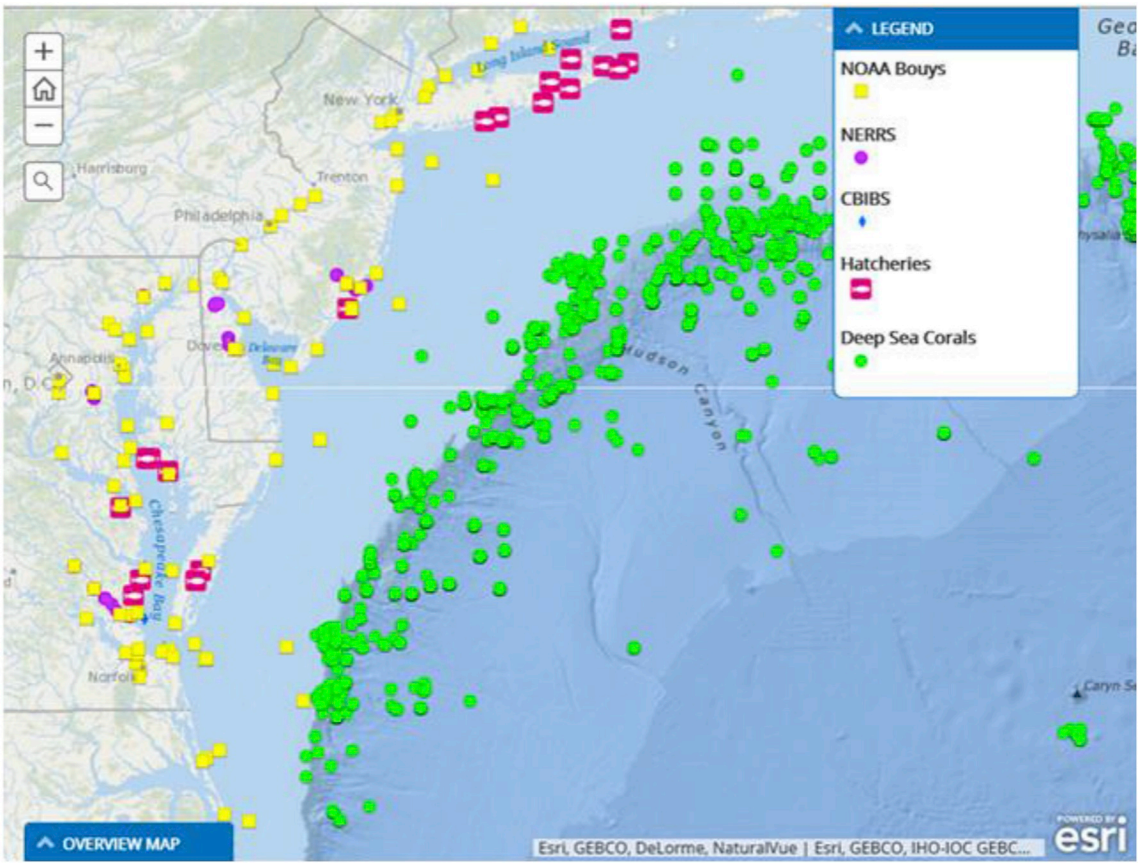

Fig. 5. Mid-Atlantic map depicting some of the recommended and priority coastal and ocean acidification monitoring areas.

pCO_2 and pH via sensors and bottle measurements of DIC, TA, and pH are collected regularly for quality control. Additionally, to better understand how coastal upwelling of cold pool water nearshore affects carbonate chemistry dynamics in estuaries, a prime location for monitoring is in Little Egg Inlet off of Long Beach Island, NJ. An existing underwater structure from previous monitoring at the former Rutgers University Long-Term Ecosystem Observatory at 15 m (LEO-15[21]) could be leveraged for monitoring carbonate chemistry parameters. The LEO-15 has 2 nodes available for monitoring in 15 m of water at 8.1 km and 9.6 km offshore from the Rutgers Marine Field Station. Monitoring at this site would also help tease apart effects of physical signals in the estuary versus ocean.

6.2. Estuarine systems

A vulnerability and adaptation assessment of U.S. shellfisheries to ocean acidification found that the most socially vulnerable communities (e.g., human communities either highly sensitivity to and/or with low adaptive capacity to ocean acidification) are spread along the U.S. East Coast and Gulf of Mexico (Ekstrom et al., 2015). This analysis also found that a number of socially vulnerable communities are located near water bodies that are exposed to a high rate of acidification or at least one local amplifier, indicating that these places could be highly vulnerable to acidification. Local amplification of acidification can result from inflows of low alkalinity freshwater, intrusion of low pH water from upwelling, and microbial degradation of excess nutrients. An assessment of estuarine condition in the U.S. found that, of the estuaries assessed, the Mid-Atlantic coast is the most impacted by eutrophication (Bricker et al., 2008). Most U.S. East Coast rivers are low in alkalinity, and upwelling occurs all along the Mid Atlantic coast during the summertime. To understand the effect of each one of these drivers, monitoring in the bays and estuaries of the Mid-Atlantic can provide information to better understand the chemistry for a full suite of systems and conditions.

Along the U.S. Mid-Atlantic coast, estuarine systems include fisheries highly vulnerable to acidification, a gradient of drivers, and existing or legacy monitoring of both water quality and ecosystem structure (i.e. CBP, EPA NEP sites, NERRS). As an example, one system that fits these parameters is the Barnegat Bay-Little Egg Harbor-Great Bay estuarine complex located in central New Jersey. Shellfish production was once vitally important to the economy of this region (Ford, 1997), and significant efforts are underway to restore the shellfishing industry here (Fig. 5). This estuarine complex encompasses a broad range of anthropogenic impacts and local acidification amplifiers. Barnegat Bay is a highly eutrophic system while Great Bay is regarded as one of the least disturbed estuaries in the densely populated urban corridor of the Northeastern United States (Fertig et al., 2014; Kennish and O'Donnell, 2002). The condition of Little Egg Harbor estuary lies between those two extremes. The inlets for Barnegat Bay and the mouth of Great Bay are common locations for summertime upwelling, suggesting these systems also have the potential to be impacted by deep ocean nutrients and acidified water during the warmest and most productive time of the year (Glenn et al., 2004; Warsh, 1987). These systems all receive inflow from low pH and low alkalinity rivers and streams, however these systems benefit from existing water quality monitoring resources due to the presence of two Federal estuary programs, the Barnegat Bay Partnership and the Jacques Cousteau National Estuarine Research Reserve. Other systems that have monitoring resources in place, yet could be vulnerable to changing acidification, include the Chesapeake and Delaware Bays.

[21] https://marine.rutgers.edu/nurp/facilities.html.

In general, the long-term water quality monitoring of the CBP[22] is an important long-term dataset, which can help provide important data for model hindcasting and to understand pH changes over time. Existing monitoring at NERRS and NEP sites are similarly important for their historical insight and potential for expansion into monitoring additional acidification parameters. Adding sensors to CBIBS buoys (Fig. 5) in the Chesapeake Bay to measure more than pH will be another efficient way to leverage existing monitoring, such as NOAA has recently done with the First Landing buoy.[23] In addition to enhancing existing infrastructure and entities already operating at these buoys, another benefit of these sites is that they currently monitor several other water quality parameters (e.g. pH, DO, temperature, nutrients, etc.), facilitating an understanding of the interaction and impacts of multi-stressors in these locations. Two buoys in the CBIBS network to prioritize are Gooses Reef, at the mouth of the Little Choptank River, and the York River Spit buoy which both currently include a SeapHOx operated by the University of Delaware and VIMS respectively (Fig. 5). The SeapHOx measures pH and these sites could be leveraged by adding a sensor for pCO_2. Furthermore, leveraging monitoring taking place at the NERRS, NEP, and USGS monitoring sites, many of which already use sensors to monitor pH and would only require an additional sensor for pCO_2, could fill monitoring gaps while also taking advantage of existing infrastructure and resources.

The U.S. EPA's National Coastal Conditions Assessment[24] which will next take place in 2020, will pilot a coastal acidification monitoring study at a subset of sites which will add spatial resolution to our understanding of acidification in the region and provide an opportunity to better understand multi-stressors. This program, which is administered nationally under EPA's National Aquatic Resource Surveys[25] program, rotates ecosystem specific surveys every five years. Leveraging this existing monitoring program provides another opportunity to make efficient use of existing programs and resources.

Oyster aquaculture and restoration: Two important subset areas of focus in estuarine systems include oyster aquaculture and restoration sites (Fig. 5). One of the fastest growing global food sectors is the aquaculture industry (Clements and Chopin, 2017), and the Mid-Atlantic is primed for aquaculture growth. However, the biological implications of acidification may be problematic for aquaculture and could result in a potential production loss (Clements and Chopin, 2017). Given the highly variable nature of Mid-Atlantic coastal/estuarine waters and the need from industry for data to be very local in order to be useful, the monitoring of aquaculture sites within the Mid-Atlantic should be done sub-regionally (Clements and Chopin, 2017) to determine ranges of “normal” water quality parameters. Monitoring upstream and downstream of oyster hatcheries would provide an opportunity to understand both upstream drivers (such as rain events) and downstream drivers (such as upwelling). This will require partnerships between the aquaculture industry and the scientific community to implement adequate monitoring, such as those successfully established on the West Coast (Barton et al., 2015). One such Mid-Atlantic example exists within the coastal and estuarine waters of Virginia when hatchery difficulties experienced in 2010 and 2011 prompted five shellfish hatcheries to partner with academic researchers at Virginia Tech, the VIMS, and the University of New Hampshire to correlate water quality trends with spawning failures and successes.[26]

Oyster reef restoration activities to improve nutrient removal and ecological benefits have also been growing. Representing millions of dollars of ecological and economic investment by governmental entities and environmental groups, shellfish restoration sites in the Mid-Atlantic typically include water quality monitoring. For instance, Chesapeake Bay efforts significantly ramped up in 2010 starting with the Harris Creek[27] tributary of the Choptank River. This large-scale oyster restoration project and sanctuary supports water quality monitoring for basic parameters such as pH, DO, temperature and salinity (NOAA, 2017) until at least 2021.[28] Future potential sites for monitoring restored oyster reefs include Breton Bay and St. Mary's River in Maryland, along with Virginia tributaries of the Potomac River.[29] These reefs could also be considered for acidification monitoring in order to opportunistically make use of existing structures, monitoring efforts, and stakeholder interest in the future health of each reef.

Certainly, in both aquaculture site monitoring and within restoration project areas, there will be an interest in collecting other important drivers of shellfish variability. This document is focused on ocean and coastal acidification, and thus emphasizes the need for monitoring for those drivers in these key areas due to their potential vulnerability, but we also acknowledge that resources will need to be leveraged for competing considerations.

6.3. Deep-sea coral habitat

Deep-sea corals in the northeastern U.S. belong to three major groups: the Hexacorals (or Zoantharia), the Ceriantipatharians, and the Octocorals (or Alcyonaria). Deep-sea corals provide important marine habitat that contributes to marine biodiversity. Their slow growth and reproduction rates make them vulnerable to ecosystem disturbance. In response to this vulnerability, NOAA Fisheries and the Mid-Atlantic Fishery Management Council created the Frank R. Lautenberg Deep-Sea Coral Protection Area[30] which encompasses some of the coral habitats shown in Fig. 5.

This deep-sea coral protection zone encompasses more than 38,000 square miles along the edge and slope of the MAB where bottom trawling is prohibited. The area also includes 15 discrete zones of protection that are mainly associated with submarine canyons that exhibit a high presence of corals.

Like the cold pool, little is known about the carbonate chemistry associated with deep-sea coral habitat or how changes in that chemistry might affect the corals and vice versa. Monitoring is needed to better inform experiments and models that are developed to provide insight into acidification effects on these corals. Currently there is no regular carbonate chemistry monitoring of any deep-sea coral sites in the Mid-Atlantic canyons. Canyons could be monitored between 350 m and 600 m depth, where corals primarily exist and could be tracked for signs of acidification impacts. As with the cold pool, Slocum gliders seem well suited for monitoring the carbonate chemistry of these areas, although the greater depths (~1200 m) present a challenge for sensor packages. AUVs and ROVs are platforms that could be used for short surveys during some of the cruises to map the water column in high resolution, particularly as there are more sensors available for these vehicle operations.

7. Developing partnerships to fill data gaps

Partnerships and collaborations with local groups can provide resources, expertise, knowledge, and manpower for these monitoring

[22] http://data.chesapeakebay.net/WaterQuality.
[23] https://buoybay.noaa.gov/locations/first-landing.
[24] https://www.epa.gov/national-aquatic-resource-surveys/ncca.
[25] https://www.epa.gov/national-aquatic-resource-surveys.
[26] Kuhn, D., Erskine, A.J. 2017. Perspectives from the Commercial Shellfish Industry. https://youtu.be/zxmWm7U18qY.
[27] http://dnr.maryland.gov/fisheries/pages/oysters/harris-creek.aspx.
[28] https://chesapeakebay.noaa.gov/habitats-hot-topics/2016-oyster-reef-monitoring-report-released.
[29] http://dnr.maryland.gov/fisheries/Documents/Oyster_Sanctuaries_of_the_Cheapeake_Bay_and_Its_Tidal_Tributaries_September_2010.pdf.
[30] http://www.mafmc.org/newsfeed/2016/noaa-fisheries-announces-final-rule-on-mid-atlantic-councils-frank-r-lautenberg-deep-sea-coral-protection-area.

efforts. A few entities, such as federal and state government agencies and academic institutions, heavily contribute to existing efforts to monitor and study coastal acidification in the United States. Other entities and stakeholders, including industry, environmental NGOs, and citizen science volunteers also assist with acidification monitoring in local areas. There is a need for continued funding sources to initiate and/or maintain monitoring efforts for long-term studies (e.g. at least 3–5 years) as well as to build these partnerships.

The federal government, through its ocean, coastal and science agencies, is a significant partner currently addressing acidification monitoring. The NOAA OAP funds many scientific studies and monitoring efforts[31] (e.g. the Integrated Ocean Observing System[32]), and is heavily involved with the exchange of information on acidification among stakeholders[33] and governmental agencies[34] in part through MACAN. The National Science Foundation also funds and facilitates acidification data collection through the Ocean Observatories Initiative. Federal programs closer to shore, such as the NERRS, survey water quality and are well-positioned for acidification monitoring and the NOAA-maintained CBIBS can be outfitted with acidification sensors to augment its data collecting abilities. Other monitoring activities, such as discrete water sampling, are also conducted by government scientists and agencies when continuous monitoring is not available or practical. For instance, the EPA has routine coastal monitoring of their ocean disposal sites and this monitoring program has leveraged intra-agency opportunities to sample for water quality and coastal acidification and may have flexibility for future partnerships on this platform.

State governments also play a significant role in tracking water quality and often provide much needed infrastructure for research. The Chesapeake Bay is one of the most heavily studied water bodies in the U.S. in part due to monitoring programs that are heavily funded through Maryland and Virginia state efforts. Few states in the region have allocated funds for acidification monitoring specifically; however, both Maryland (completed[35]) and New York (on-going) have established Ocean Acidification Task Forces that, in part, seek to identify priorities to study and monitor ocean acidification and its impacts. Many states have monitored pH as part of their water quality measurements, and an investment in additional carbonate chemistry parameters would help to understand how/if acidification is changing and provide insights on how those changes could impact species, ecosystems, human communities and economies. Government-academic partnerships are commonly utilized in monitoring including at buoys and cruises, and should be continued and expanded as a mechanism for leveraging limited resources.

Universities, private research institutions, and even some high schools provide much of the manpower for extensive study of water quality and chemistry for research purposes. At least ten academic and private research institutions support much of this research activity in the region via research cruises, remote surveys, and studies of important marine habitats such as corals, oyster reefs, and estuaries. The Chesapeake Biological Laboratory at the University of Maryland Center for Environmental Science is one example of a site continuously collecting pCO_2 measurements near Solomons, Maryland that also is supported by many other continuous water and atmospheric measurements.[36] Researchers from academic institutions also conduct many discrete sampling studies. The Billion Oyster Project[37] in New York City collects and manages water quality data from high schools, middle schools and citizen scientists in the area who use oyster restoration kits.[38] These institutions conducting monitoring provide additional opportunities for partnerships with other entities or industries as well as offer examples for similar partnerships to be built.

Multi-year marine industry involvement in acidification monitoring has so far been limited to the shellfish hatcheries in Virginia. There are at least 33 shellfish hatcheries and nurseries in the Mid-Atlantic region (Zemeckis, 2019), and some which do not currently monitor the carbonate chemistry have expressed interest in monitoring their intake waters for any signs of acidification. Fishing groups have participated intermittently in some acidification workshops and meetings, but not yet in sustained monitoring efforts. Thus, there are opportunities to build new industry partnerships for monitoring in both hatcheries and with fishing groups.

Environmental NGOs in the region interested in monitoring acidification generally engage in oyster reef restoration efforts in specific locations. These groups educate local community members, restaurants, fishermen, and officials on the benefits of wild oyster beds to improve water quality, fish habitat, and natural coastal protections which have follow-on economic and recreational benefits. As some of these projects to reseed hundreds of acres of nearshore benthic areas with oyster larvae near completion, these NGOs and their state government partners look to closely monitor the health and water quality at these sites to ensure a self-sustaining reef can persist. The largest projects can be found in the Chesapeake Bay (10 Billion Oysters, 2018; NOAA CBO, 2017) and Hudson-Raritan Bay (USACE, 2017) areas, although none of these sites monitor at least two of the four carbonate chemistry parameters yet.

Citizen volunteers can also play a role in water quality data collection. New York state has a volunteer reef diver program through its Department of Environmental Conservation whereby divers can record the environmental conditions and animals they observe for the Department during dives.[39] The New York Harbor SEALs also monitor the Hudson River Estuary for water quality.[40] In Maryland, the Magothy River Association, an NGO, provides dive volunteers for water quality monitoring and oyster reef restoration activities.[41] In Virginia, researchers at VIMS coordinate a citizen science program to monitor oysters called CSI Oyster. With coordination and basic science kits, these volunteers might be able to augment or help verify data from acidification monitoring sites. For more information on how to start a monitoring effort, including for citizen science, see *Guidelines for Measuring Changes in Seawater pH and Associated Carbonate Chemistry in Coastal Environments of the Eastern United States* (USEPA, 2018). An important note, however, with citizen science programs is the need to ensure the data collected is quality assured and controlled; thus, partnering with experts in monitoring, such as those in the Ocean Acidification Information Exchange[42] can help with developing programs that collect data that is useful and consistent across citizen science efforts.

8. Developing a repository for monitoring data

Monitoring data in the Mid-Atlantic is currently hosted on a variety of platforms from university data portals, to state agency data portals, to various agency and academic website clearinghouses. As of now, there is no one repository that exists to compile all regional acidification monitoring data. Therefore, there is a need to designate a centralized location where detailed acidification data can be collected and

[31] https://oceanacidification.noaa.gov/CurrentProjects.aspx.
[32] https://ioos.noaa.gov/.
[33] https://www.oainfoexchange.org/index.html.
[34] https://oceanacidification.noaa.gov/_iwgoa/Home.aspx.
[35] http://dnr.maryland.gov/waters/bay/Documents/MDOATF/OA_Report_010915.pdf.
[36] http://cblmonitoring.umces.edu/.
[37] https://billionoysterproject.org/get-involved/schools/.
[38] http://billionoyster.wpengine.com/restoration-station/.
[39] https://www.dec.ny.gov/outdoor/9211.html.
[40] http://harborseals.org/.
[41] http://www.magothyriver.org/projects/oyster-program/volunteer-diver-program/.
[42] https://www.oainfoexchange.org/index.html.

regularly updated to answer research questions and inform stakeholders. Before discussing potential options for fulfilling this role, however, there are important caveats. A regional repository should ingest data from the original source to ensure that the data incorporated into a central database is quality-controlled. Also, one centralized entity, possibly MACAN, should coordinate the development of protocols across monitoring locations, with input from knowledgeable monitoring entities.

MARACOOS's OceansMap[43] is likely the most well suited in the region for integrating data. The OceansMap site presents near real-time data from ocean observing platforms deployed in the Mid-Atlantic region, including those from autonomous gliders, CBP continuous monitoring buoys, NERRS stations, satellites measuring sea surface temperature and ocean color, HF radars measuring ocean currents, as well as model forecasts (e.g. bottom oxygen forecasts for the Chesapeake Bay). There is also an effort underway primarily through VIMS to expand existing forecasts for the Chesapeake Bay to include ocean acidification metrics. Additionally, OceansMap is currently in the process of integrating data from the PMEL First Landing OA buoy deployed in April 2018 which monitors pCO_2 and pH. At the national scale, these primary datasets from MARACOOS could be shared with the Ocean Acidification Data Stewardship and the IOOS Pacific Region Ocean Acidification[44] data explorer. It may also be useful to have other monitoring or data integration sites reference the data on the MARACOOS portal, such as the regional NERRS Centralized Data Management Office website[45] and the Mid-Atlantic Ocean Data Portal[46] since this information will likely be useful for efforts undertaken by these other regional entities. This recommended approach of using one portal as the central hub of acidification data will provide additional opportunities to analyze data and answer research and stakeholder questions across a variety of scales and interests. Additionally, the MACAN website includes a regularly updated repository for regional oceanic and coastal publications.[47]

9. Summary of recommendations

In summary, we have outlined the key components for comprehensive and collaborative acidification monitoring in the Mid-Atlantic region. These recommendations are not ranked or listed in order of importance as all should be considered to develop a fully-fledged OA monitoring program and no single recommendation should take precedent. There is a need to 1) leverage existing infrastructure to include multiple carbonate chemistry parameters as well as other water quality parameters, 2) direct monitoring efforts in subsurface and bottom waters rather than limiting monitoring to surface waters, 3) identify the best available sensor technology for long-term, in-situ monitoring, 4) monitor across a salinity gradient to account for the complexity of estuary, coastal and ocean environments and further identify potential areas of enhanced vulnerability, 5) increase sampling frequency to capture variability, 6) include other drivers (e.g., freshwater discharge, nutrients, physiochemical parameters, etc.) that may affect acidification, and 7) conduct or continue monitoring in specific ecological regions that may have enhanced vulnerability (e.g., the cold pool, estuarine systems, and cold-water coral habitat). In order to build this robust monitoring network in the region, various entities, universities, organizations, industries, etc. will need to develop effective partnerships that leverage individual resources and expertise. Finally, there is a need to consolidate disparate monitoring efforts into one centralized portal for the data to be useful to many researchers and interested practitioners.

As monitoring programs are developed, incorporation of these considerations will help leverage resources and produce robust, relevant data. The data produced from these efforts will help us understand how acidification is occurring in the estuaries, coastal, and open ocean environments during episodic and long-term changes in acidification, and ultimately how acidification may impact ecologically and economically important habitats and species in the region. While we have focused these scientific considerations for building acidification monitoring on the Mid-Atlantic U.S., many of the general concepts we have outlined can be adapted for other U.S. regions and around the world with similar ecological features.

[43] http://oceansmap.maracoos.org/.
[44] http://www.ipacoa.org/.
[45] http://cdmo.baruch.sc.edu/.
[46] http://portal.midatlanticocean.org/visualize.
[47] http://midacan.org/reference-library.

Acknowledgements

The views expressed in this document are those of the author and do not necessarily represent the official views or policies of the U.S. EPA, MARCO, MARACOOS, NOAA, the Ocean Conservancy. The authors would like to thank the following individuals for providing additional insight to this monitoring strategy: A.J. Erskine, Bevans Oyster Company; Laura McKay, Virginia Department of Environmental Quality Coastal Zone Management Program. Thank you to Nick Meade, Virginia Department of Environmental Quality Coastal Zone Management Program, and John Bognar, Rutgers University, for their assistance in developing the series of MACAN monitoring maps on the Mid-Atlantic Ocean Data Portal for use in developing this document. The authors would also like to thank the following people for reviewing a draft version of this document: Marjorie Friedrichs, Jason Grear, Roman Jesien, Whitman Miller, Erica Ombres, Mike Osterling, Julie Reichert, Jeremy Testa, Aleck Wang, and Marianne Walch.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecss.2019.04.023.

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