



Mid-Atlantic Coastal Acidification Network Coastal and Ocean Acidification Monitoring Inventory Analysis

Report Prepared by Carly LaRoche¹, Kirstin Wakefield², and Janet J. Reimer³
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¹University of Virginia

²Mid-Atlantic Regional Association Coastal Ocean Observing System

³Mid-Atlantic Regional Council on the Ocean



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1.1 Abstract

Ocean acidification is causing long-term change in surface ocean pH globally, but the severity and effects of acidification vary widely at regional and local levels. Monitoring of seawater carbonate system parameters, pH, pCO₂, dissolved inorganic carbon, and total alkalinity, can provide crucial information regarding the local status of acidification. In this report, the locations and methods of carbonate system sampling and monitoring efforts conducted between 1984 and 2023 in the U.S. Mid-Atlantic were combined into a publicly available inventory (see MARCO Ocean Data Portal) and then analyzed in the context of regional monitoring priorities. This work was done in collaboration with the Mid-Atlantic Coastal Acidification Network (MACAN) to assess the spatiotemporal distribution of sampling efforts in the coastal waters of New York, New Jersey, Delaware, Maryland, and Virginia, as well as the eastern adjacent coastal and open ocean. We summarize sampling methodologies, data quality (GOA-ON), temporal frequency of sampling, and spatial

distribution of sites with respect to measurement depth, salinity, eutrophication, and ecosystems of interest. While the majority of sites in the inventory were sampled once via underway cruise, 3,340 sites across the Mid-Atlantic study region engaged in repeat monitoring efforts. High quality measurements were common in sampling efforts conducted between 2019 and 2023, but 60% of sites measured one carbonate system parameter at climate or weather quality while only 8% of sites measured two. Sampling was conducted across diverse estuarine and marine systems, but the inventory was lacking in sites that collect bottom and depth profile measurements, conduct biological co-monitoring, and collect high frequency, continuous data. Overall, gaps in the current distribution of seawater carbonate system sampling highlight areas of interest for future Mid-Atlantic monitoring that could be addressed through regional coordination efforts.

1.2 Introduction

Since the onset of the Industrial Revolution, the ocean has absorbed 30-40% of the carbon dioxide associated with anthropogenic emissions, resulting in ocean acidification: an increase in oceanic $p\text{CO}_2$ coinciding with a decrease in pH and calcium carbonate saturation state (Doney et al., 2009; Sabine et al., 2004). Along coastlines, localized environmental conditions like riverine freshwater inputs, eutrophication, upwelling, biogeochemical cycles, and seasonality, can further alter carbonate system patterns driving acidification (Cai et al., 2021; Feely et al., 2010; Wallace et al., 2014). This leads to significant variability in the magnitude and impact of acidification at the regional, coastal level (Gledhill et al., 2015; IPCC, 2021).

The Mid-Atlantic Region comprises five coastal states including New York, New Jersey, Delaware, Maryland, and Virginia, and is longitudinally bound by the extended continental shelf. The region is highly industrialized and populated, with over 34 million people residing in Mid-Atlantic coastal counties (NOEP, 2021). Several large, eutrophic estuaries are present in the region, including the Chesapeake Bay, the Delaware estuary, the Hudson estuary, and the Long Island Sound (Bricker et al., 2007). Summer upwelling and numerous freshwater inputs can act to further exacerbate acidification along the

Mid-Atlantic Coast (Glenn et al., 2004). In the U.S. Mid-Atlantic, the coastal waters of the northernmost states of the region are projected to cross sublethal acidification thresholds for bivalve larvae between 2071-2099 under RPC 8.5 CO₂ emissions (van Hooijdonk et al., 2014).

Monitoring coastal and ocean acidification (COA) at the regional level can help to resolve local spatiotemporal carbonate system variability while honing in on regionally important ecosystem, species, and socioeconomic impacts (Goldsmith et al., 2019; Saba et al., 2019). Organizations like the Mid-Atlantic Coastal Acidification Network (MACAN) serve as organizational bodies for regional efforts to monitor and address COA impacts. MACAN, which is co-coordinated by the Mid-Atlantic Regional Council on the Ocean (MARCO) and the Mid-Atlantic Regional Association Coastal Ocean Observing System (MARACOOS), serves as a facilitator for regional COA information sharing and response planning among an interdisciplinary network of scientists, policy-makers, resource managers, and industry partners. This report provides an analysis of current Mid-Atlantic carbonate system sampling and monitoring efforts based on the 2023 MACAN COA Inventory (LaRoche et al., 2023). The analysis and corresponding dataset are in support of MACAN's goals to aid in the development of a robust COA monitoring network driven by regional priorities.

Crucial to our understanding of the extent and impact of acidification is high quality acidification monitoring conducted at a sufficient spatiotemporal resolution (Newton et al., 2015). COA can be assessed by measuring four carbonate system parameters: pH, $p\text{CO}_2$, Dissolved Inorganic Carbon (DIC), and Total Alkalinity (TA) (Zeebe and Wolf-Gladrow, 2001). By measuring any two of these parameters in conjunction with salinity and temperature, the other two can be estimated, from empirical thermodynamic relationships, along with saturation state (Ω), which indicates whether conditions are favorable for calcium carbonate dissolution or precipitation (Lewis and Wallace, 1998). A variety of methods can be used to measure seawater inorganic carbon parameters, but commonly used tactics include discrete bottle sampling and continuous autonomous sensors (either stationary or on a moving platform like a glider or research vessel). To date, there are no viable remote sensing measurement approaches.

Previous publications, including the NOAA Ocean, Coastal, and Great Lakes Acidification Research Plan: 2020-2029, indicate several priorities for the Mid-Atlantic study region; there is a need for high quality carbonate system data in diverse ecosystems from estuaries to shelf environments, across a full depth profile, in conjunction with biological studies, and with consideration of other coastal acidification drivers like eutrophication and riverine inputs (Goldsmith et al., 2019; Kinkade et al., 2020; Saba et al., 2019). Higher spatial and temporal frequency of monitoring would also benefit efforts to resolve variability in regional models (Goldsmith et al., 2019; Kinkade et al., 2020). Additionally, anticipated COA effects to calcifying organisms highlight the need to improve regional understanding of COA impacts on local aquaculture and coastal communities (Ekstrom et al., 2015; Kinkade et al., 2020). In this report, the MACAN inventory data will be assessed in the context of the Mid-Atlantic regional monitoring priorities discussed above. We are, however, unable to assess direct completion of Mid-Atlantic objectives and action items with the inventory data alone.

1.3 Methods

1.3.1 General Methods and Study Area

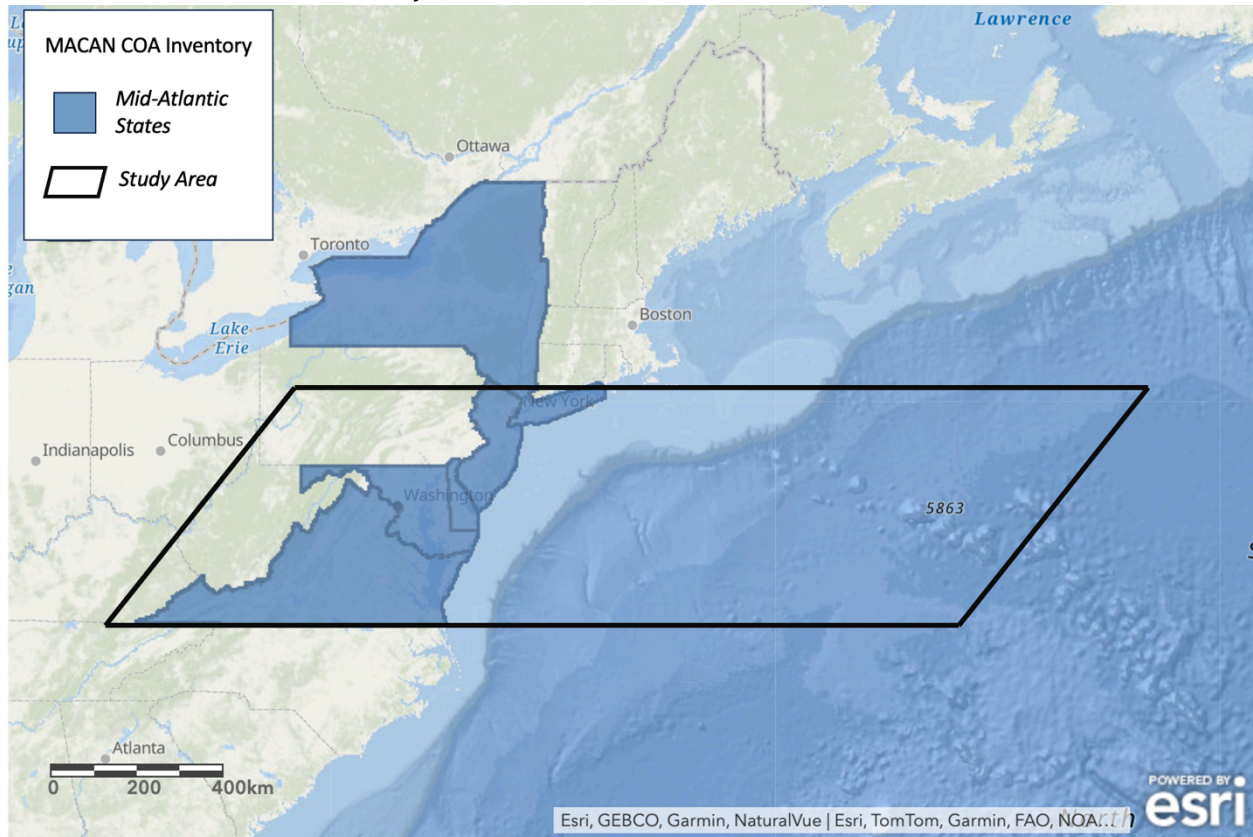


Figure 1: Map of study area, with the five Mid-Atlantic states, New York, New Jersey, Delaware, Maryland, and Virginia, highlighted in blue.

Descriptive statistics and spatial analyses were conducted on 2023 COA inventories (LaRoche et al., 2023; Saba et al., 2019). Each unique sampling location counts as one site, with glider tracks being the exception; each glider deployment is assessed as one site due to the high volume of locations sampled during each glider deployment. While underway cruise data also exhibits high spatial frequency of sampling, data are assessed at the spatial frequency reported by source agencies to maintain metadata, such as collection date, unique to a single site.

For the purposes of this analysis, inventory data were clipped to assess sites within the coastal Mid-Atlantic region extending out to the U.S. Extended Continental Shelf (ECS) boundary (United States Department of State, 2023). The ArcGIS Pro tool Clip was used to exclude sites beyond the boundaries of Mid-Atlantic states and the ECS boundary (United

States Department of State, 2023). Regional priorities indicate a need for monitoring of carbonate system parameters across a range of salinities, including riverine freshwater endmembers, whose outflow can contribute to acidification in receiving waters. For this reason, riverine sites are included in the inventory analysis up to the Atlantic Seaboard Fall Line which is marked by the geologic boundary between the Piedmont and the Atlantic coastal plain. The Mid-Atlantic coastal states included in this analysis are New York, New Jersey, Delaware, Maryland, and Virginia (Figure 1). Although the northern edge of the study area exhibits some overlap with the coastal waters of adjacent states, we limit our discussion of state-specific coastal sampling to the five states served by MACAN. Coastal waters of adjacent northeast and southeast states are under the jurisdiction of the Northeast Coastal Acidification Network (NECAN) and the Southeast Ocean and Coastal Acidification Network (SOCAN). While beyond the scope of this report, further coordination and analysis of acidification monitoring efforts in boundary zones between Eastern U.S. Atlantic coastal regions is important for seamless integration of COA monitoring at the coast-wide and national level.

1.3.2 Data Quality categorization

In support of global ocean acidification observing goals, the Global Ocean Acidification Observing Network (GOA-ON) has defined two levels of carbonate system measurement quality: “Climate” and “Weather” (Newton et al., 2015). Climate quality data necessitates a relative standard uncertainty of 1% for carbonate ion concentrations and is suitable for observing long term trends in ocean carbon chemistry (Newton et al., 2015). This is achieved through a standard uncertainty of 0.003 for pH measurements, 2 $\mu\text{mol}/\text{kg}$ in TA and DIC measurements, and a relative standard uncertainty of 0.5% for $p\text{CO}_2$ measurements (Newton et al., 2015) (Table 1). Weather quality data, which is more appropriate for assessing spatial variability and short-term variation in carbonate system trends, requires a relative standard uncertainty of 10% for carbonate ion concentrations (Newton et al., 2015). Therefore, weather quality pH, TA, DIC, and $p\text{CO}_2$ measurements meet the following standards: 0.02 standard uncertainty for pH, 10 $\mu\text{mol}/\text{kg}$ standard uncertainty for TA and DIC, and 2.5% relative standard uncertainty for $p\text{CO}_2$. All data which have

uncertainty greater than the parameter-specific thresholds defined for weather quality are of undefined quality (Newton et al., 2015).

To evaluate the data quality of carbonate system sampling across the Mid-Atlantic, sites that reported sufficiently detailed methods were classified as climate quality, weather quality, and undefined quality. Sites that did not report sufficient methods to determine data quality are referred to as “unreported” data quality. Throughout this chapter, sample collection achieving climate or weather quality will be referred to as “high quality data”. Other factors influence the uncertainty of measured and calculated seawater carbonate system parameters and the overall quality of sites. In this work we employ a simplified treatment of data quality to enable large-scale characterization of data quality across many sites and collection types.

Table 1: Definitions of Climate, Weather, and Undefined Quality uncertainties for pH, pCO₂, TA, and DIC (After Newton et al., 2015)

Quality Category	pH standard uncertainty	pCO ₂ relative standard uncertainty	TA standard uncertainty	DIC standard uncertainty
Climate Quality	0.003	0.5%	2 μmol/kg	2 μmol/kg
Weather Quality	0.02	2.5%	10 μmol/kg	10 μmol/kg
Undefined Quality	>0.02	>2.5%	>10 μmol/kg	>10 μmol/kg

1.3.3 Spatial analysis of sites

Coastal Wetlands: Extent and type of coastal wetlands were produced by NOAA’s Office for Coastal Management and acquired for this analysis from the MARCO Mid-Atlantic Ocean Data Portal (NOAA Office for Coastal Management, 2023). The ESRI tool Summarize Nearby was used to quantify the number of sampling sites located within 0.5 kilometers of coastal wetlands.

Seagrass: Seagrass shapefiles produced by NOAA's Office for Coastal Management were intersected with the COA monitoring inventory data using ESRI's ArcGIS Pro in order to determine the number of carbonate system sampling and monitoring sites within seagrass beds (NOAA Office for Coastal Management, 2022). This analysis was repeated with high-quality sites and high-quality sites measuring two or more parameters. Results were evaluated at the Mid-Atlantic regional and state level.

Deep-sea Corals: A dataset modeling the distribution of deep-sea coral habitat for the order Alcyonacea was accessed through the MARCO Mid-Atlantic Ocean Data Portal for analysis (Kinlan et al., 2013). These data were produced for the Mid-Atlantic by the National Centers for Coastal Ocean Science in collaboration with scientists at the NOAA/NMFS Northeast Fisheries Science Center. Sites within predicted coral habitat were quantified with the ArcGIS Pro Intersect tool. Results were further filtered by collection depth, to determine the number of sites sampling within range of deep-sea coral habitat.

Shellfish Beds: Shapefiles of shellfish beds located in state waters were acquired from the NRDC. The NRDC collated shellfish bed data from numerous state agencies, and therefore the data do not necessarily have uniform methodology or sampling time periods. In this analysis, shellfish data were clipped to the Mid-Atlantic study area and so we include data from the following agencies: Delaware Division of Fish and Wildlife, New Jersey Department of Environmental Protection: Division of Fish and Wildlife, and Virginia Department of Environmental Quality. Similar shellfish shapefiles were not available for Maryland or New York, so they were excluded from the analysis. A buffer of one kilometer was produced around the shellfish beds to assess nearby sampling. Sites were then intersected with the buffered shellfish layer to determine the number of sampling or monitoring sites within one kilometer of a shellfish bed.

Estuary Eutrophication Score: Estuary eutrophication scores developed by Bricker and colleagues (2007) were used as a proxy for an estuary's potential to exhibit exacerbated coastal acidification due to eutrophic conditions. Scores were on a scale of 1-5, with 1 being Low Eutrophication and 5 being High Eutrophication (Bricker et al., 2007). The

number of carbonate system sampling or monitoring sites present within each eutrophication category was determined by using the Intersect tool in ArcGIS Pro. This analysis was repeated with high quality sites and high-quality sites measuring two or more parameters. Results were evaluated at the Mid-Atlantic regional and state level. Shapefiles were prepared by NRDC.

1.4 Results

1.4.1 Overview of carbonate system sampling in the Mid-Atlantic

There are 46,639 seawater carbonate system sampling sites within the Mid-Atlantic study area that operated anytime between 1984 and 2023 (Figure 2). The majority of sites in the inventory were active in the last ten years, with 31.2% of sites active between 2013-2018 and 38.3% of sites active between 2019-2023. The remaining 30.5% of sites were active before 2013. Underway shipboard measurements account for the majority of monitoring locations, with 92.8% of sites being sampled from research ships. Discrete and continuous sampling methods comprise 6.4% and <1% of all sampling sites, respectively. 43,299 sites were classified as one-time carbonate system sampling sites; few research cruises report repeat sampling efforts. The remaining 3,340 sites have engaged in repeat carbonate system sampling efforts.

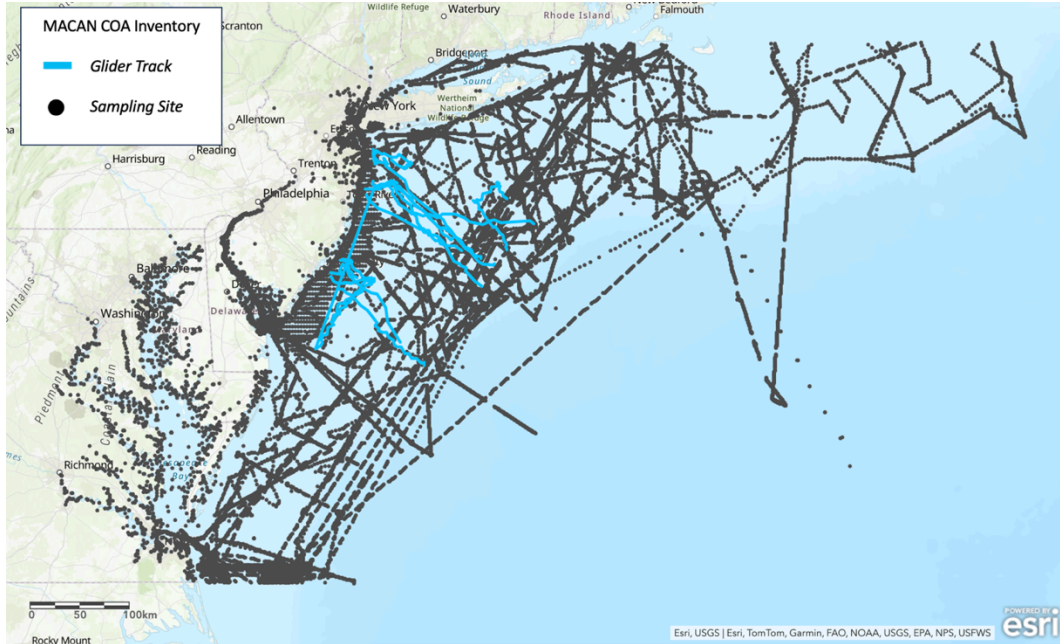


Figure 2: All seawater carbonate system sampling sites (black dots) and glider tracks (light blue lines) within the study area.

Table 2: Summary of sites sampling pH, $p\text{CO}_2$, TA, and DIC in the Mid-Atlantic region. Information on participating sectors and number of sites reporting methods is included for each parameter.

Parameter	Number of Sites		Participating Sectors
	Total Sites	Sites Reporting Methods	Listed Most to Least
pH	19,507 + 13 glider tracks	2,785	State, Federal, Research/ Academic Institution, NGO, local gov
$p\text{CO}_2$	41,334	13,390	Research/ Academic Institution, Federal Agency
TA	6,705	6,705	Research/ Academic Institution, NGO, State Gov
DIC	2,357	2,357	Research/ Academic Institution, Federal Agency

Any	46,639	-	State Agency, Federal Agency, Research/Academic Institution, NGO, local government
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1.4.2 Data Quality

All sampling methodologies reported for $p\text{CO}_2$, DIC, and TA met either climate quality or weather quality criteria (Appendix 1). While nearly all sites measuring DIC and TA report methodologies, only 32.4% of sites measuring $p\text{CO}_2$ report methods. Of the 2,785 pH sampling sites for which methods were reported, 254 are of climate quality and 187 are of weather quality (Appendix 1). 10,933 sites, 23.4% of total sites, measure one carbonate system parameter to a high quality, while 5,801, or 12.4% of sites, measure two or more parameters at a high quality. The majority of sites measuring two or more carbonate system parameters at a high quality are single sampled sites; only 340 are repeat monitoring sites. Categorization of data quality was completed only for sites where methods were reported. Therefore, a large component of sites measuring pH and $p\text{CO}_2$ were not included in this analysis. Sites active before 2013 had the largest fraction of unreported methods/quality (Figure 3).

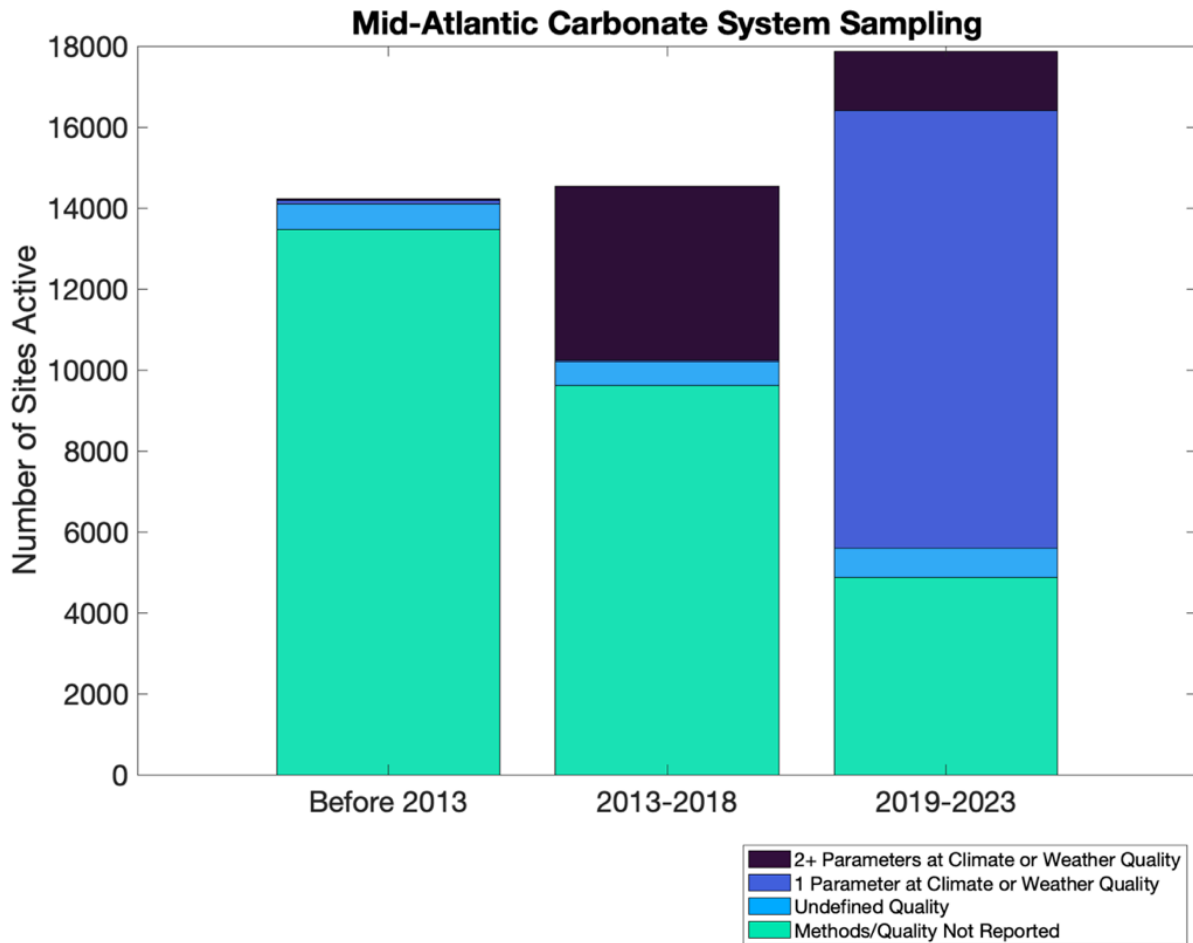


Figure 3: The number of seawater carbonate system sampling sites in the Mid-Atlantic study area active before 2013 (anytime between 1984-2013), between 2013-2018, and between 2019-2023. Different colors in each time period refer to different levels of data quality.

1.4.3 Summary of $p\text{CO}_2$, pH, TA, and DIC Sampling Efforts

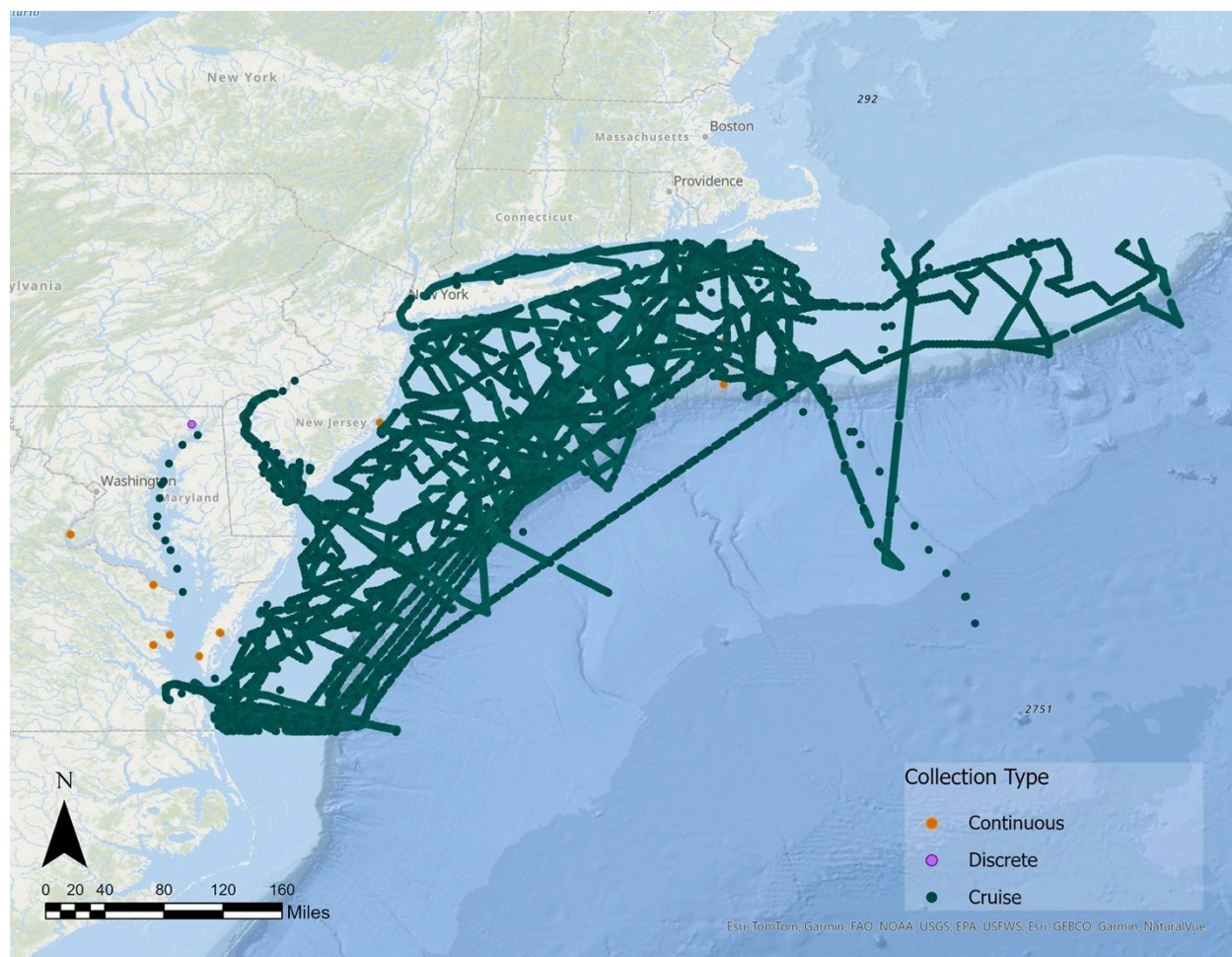


Figure 4: Map of Mid-Atlantic $p\text{CO}_2$ sampling sites, colored by collection method: continuous, discrete, or underway cruise.

$p\text{CO}_2$ is the most commonly measured carbonate system parameter at sites in the Mid-Atlantic, with 41,334 sites measuring $p\text{CO}_2$ in the inventory, representing 88.6% of all monitoring sites (Figure 4). The vast majority of $p\text{CO}_2$ measurements are collected by ship underway sampling. Only 14 sites collect $p\text{CO}_2$ data via continuous or discrete methods at a stationary site. $p\text{CO}_2$ sampling is most frequently carried out by academic and research institutions, as well as federal agencies.

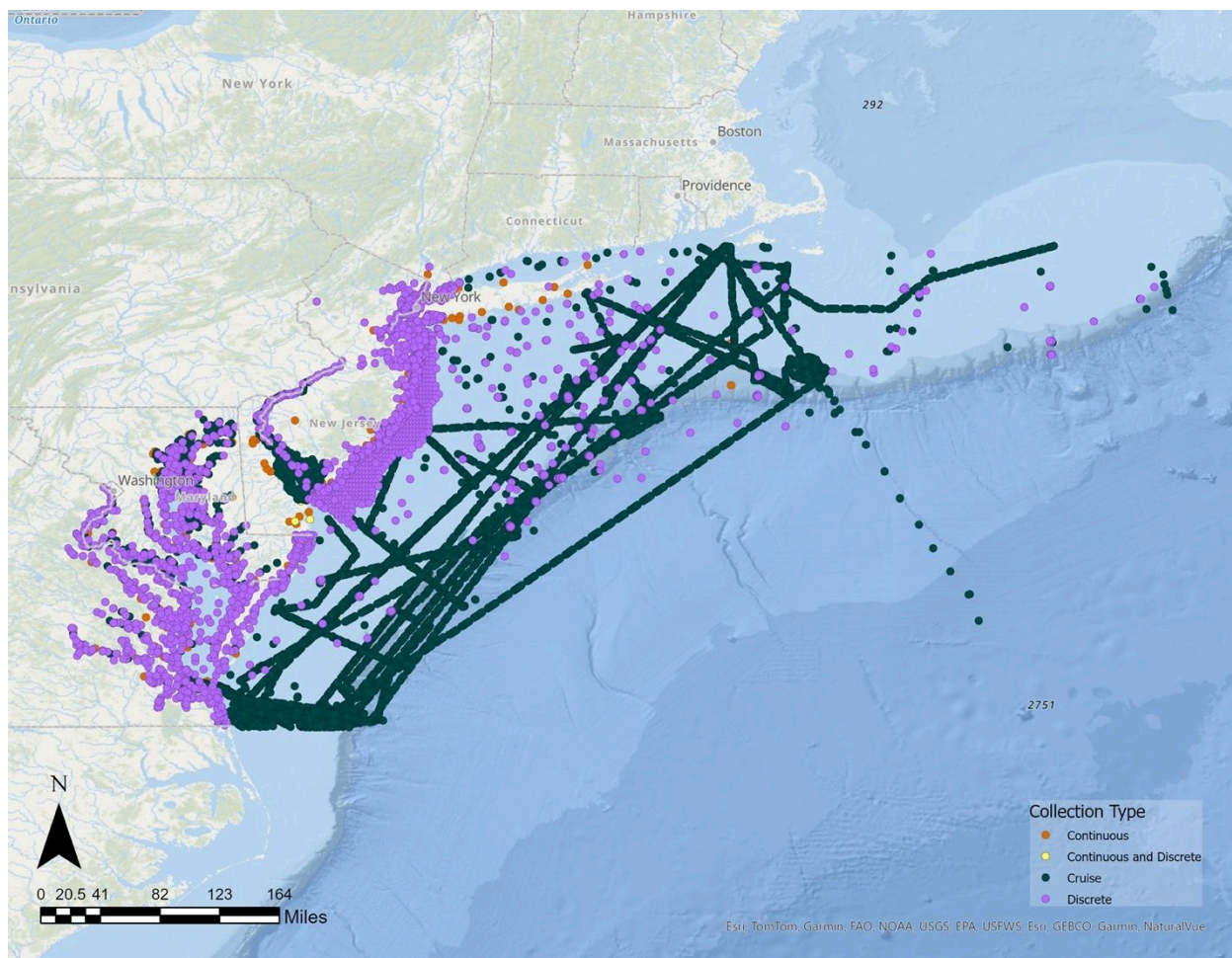


Figure 5: Map of Mid-Atlantic pH sampling sites, colored by collection method: continuous, continuous and discrete, discrete, or cruise.

pH was measured at 19,507 sites and across 13 glider deployments. Together, cruise sampling and discrete sampling account for nearly all pH monitoring sites, comprising 80% and 18% of sites sampling pH, respectively (Figure 5). When compared to other carbonate system parameters, pH has the greatest variability in methodology with 15 unique methods represented in the inventory. Among discrete sites that detail methodology, handheld probes are the most common sensors in use with employment at nearly 2,000 sites. A variety of handheld probes are used to measure pH in the Mid-Atlantic, including YSI Water Quality Meters, Oakton Handheld Meters with pH Probes, Eureka Manta2 Water Probes, and more (Figure 7). Spectrophotometry was used at 426 discrete sites. Less than 2% of all pH monitoring sites used continuous methods to measure pH (Figure 6). YSI EXO

multiparameter sondes were the most common sensor reported in the inventory for continuous monitoring of pH. Other continuous sensors in use across the region include the Honeywell Durafet III, the Sunburst SAMI-pH, and the Seabird SeaFET™. Of the methods discussed, the Sunburst SAMI-pH continuous sensor and spectrophotometry discrete sampling were the only ones that produced climate quality data. Weather quality data can be obtained with potentiometry, the Honeywell Durafet III, and the Oakton handheld pH probe. Many sectors participate in pH monitoring, with state and federal agencies accounting for the majority of sampling. Other sectors participating in pH monitoring include academic or research institutions, NGOs, and local governments. It is important to note that pH monitoring is often conducted for the purpose of understanding water quality, rather than ocean acidification dynamics.

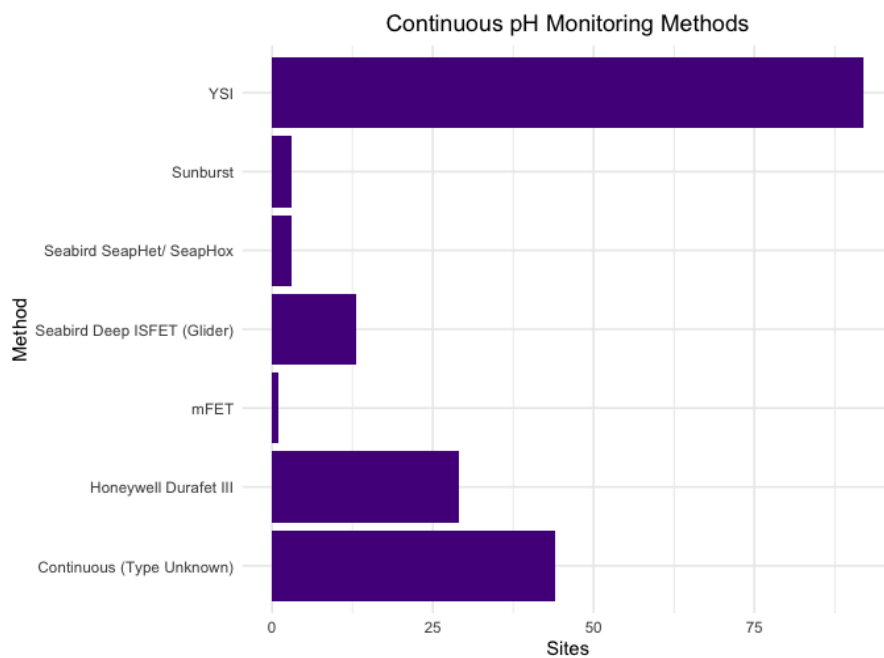


Figure 6: Continuous methods used at pH sampling sites across the Mid-Atlantic inventory.

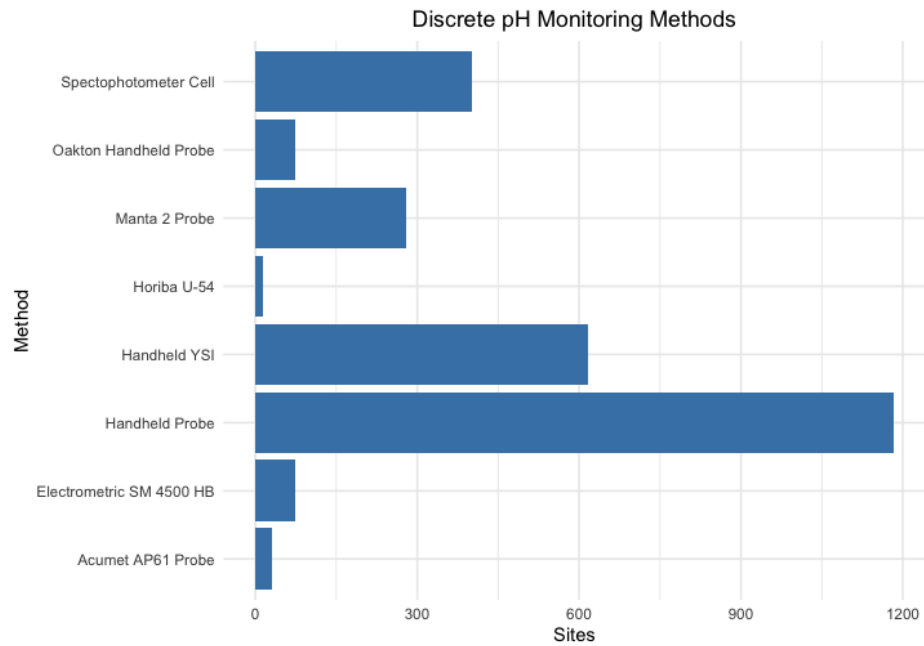


Figure 7: Discrete methods used across pH sampling sites in the Mid-Atlantic inventory.

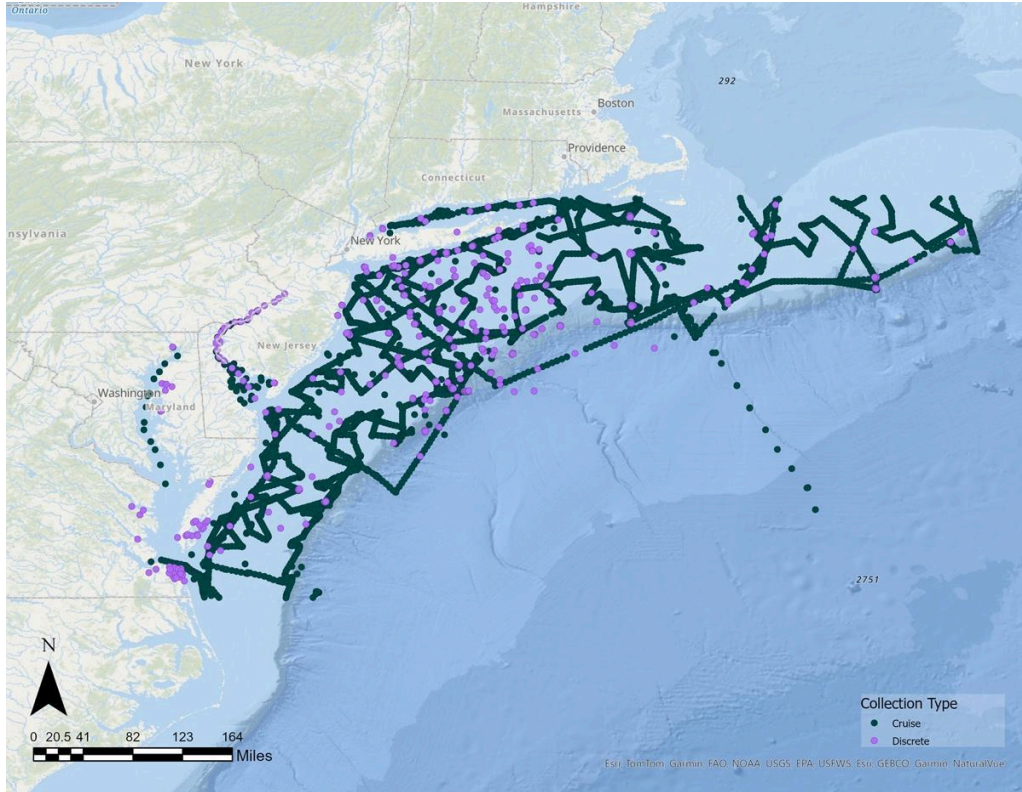


Figure 8: Map of Mid-Atlantic TA sampling sites, colored by collection method: discrete or underway cruise.

Total Alkalinity (TA) is measured at 6,705 sites in the Mid-Atlantic, with over 90% of sites collecting TA samples via underway cruise (Figure 8). At the remaining 589 sites, TA is collected and measured with discrete methods. Academic or research institutions are most likely to measure TA, but some sampling has been done by NGOs or State Government organizations.

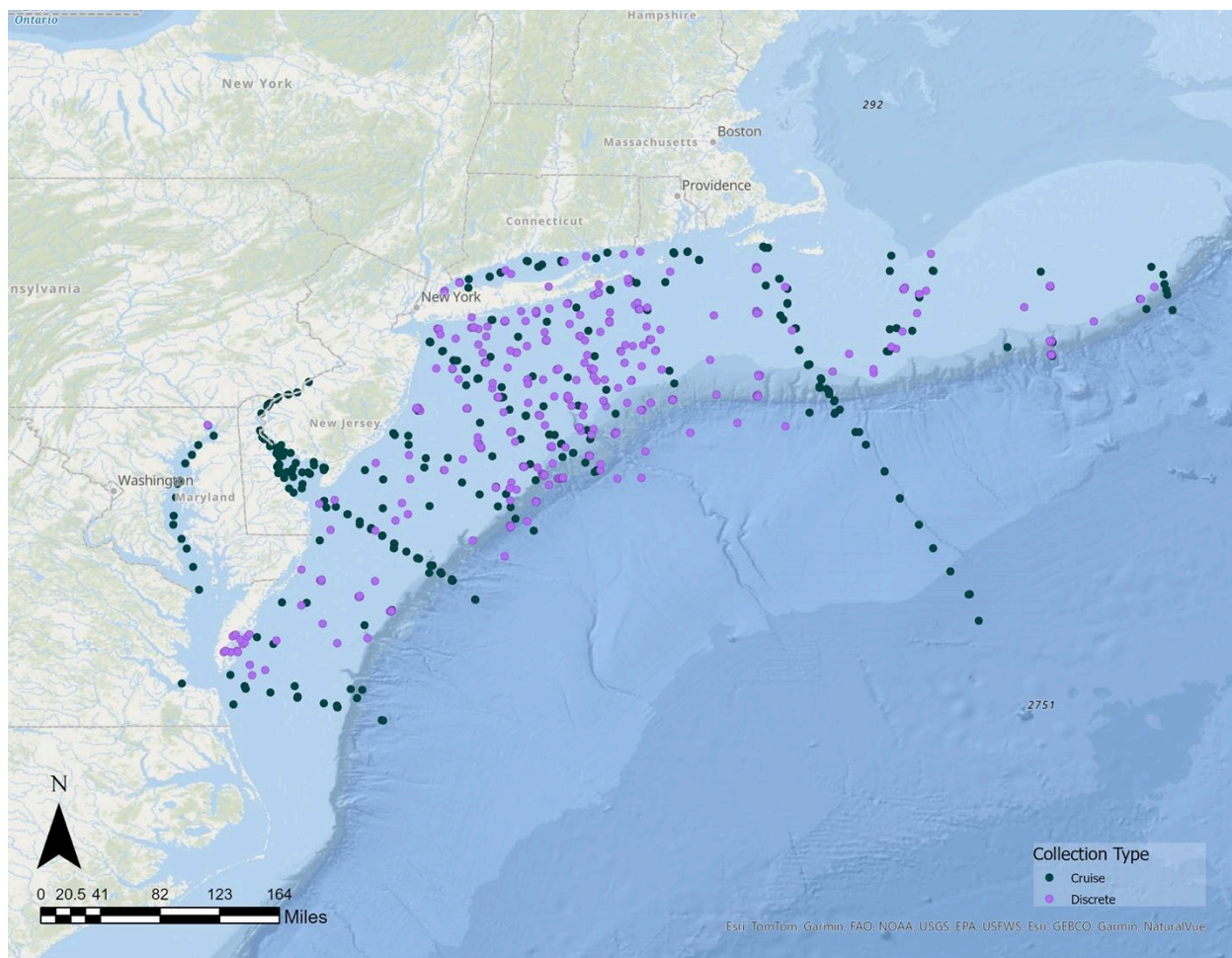


Figure 9: Map of Mid-Atlantic DIC sampling sites, colored by collection method: discrete, or cruise.

DIC is measured at the fewest number of sites in the Mid-Atlantic, with a total of 2,357 locations (Figure 9). Much like the other carbonate system parameters, the majority of DIC sampling occurred during a cruise. Discrete sampling methods make up the remaining 19% of sites where DIC was collected. Sectors that participate in DIC monitoring include academic and research institutions and federal agencies.

1.4.4. Spatial Distribution of COA Monitoring

1.4.4a Offshore vs. Coastal sampling

The majority of pH measurements were offshore, beyond Coastal Zone Management Act Boundary (CZMA), which is defined as three nautical miles from shore. 32% of sites in the study area were located nearshore within the CZMA Boundary. When

considering the spatial distribution of high-quality sites, the discrepancy between the number of offshore and coastal sites grows. Only 14% of sites that measure at least two climate or weather quality parameters are located within the coastal zone. The majority of coastal monitoring sites collected data via underway cruise sampling. In addition to cruises, there are 362 continuous monitoring sites and a little over 2,500 discrete monitoring sites.

Table 3: Distribution of carbonate system sampling between coastal and offshore sites across the entire inventory time period, from 2013-2023, and from 2019-2023.

Sampling time period	Offshore	Total Coastal	New York	New Jersey	Delaware	Maryland	Virginia
All sites (1984-2023)	31,684	14,955	1,736	4,352	5,844	1,512	1,494
Sites Active 2013-2023	18,613	13,792	1,712	4,036	5,830	1,168	1,046
Sites Active 2019-2023	14,712	3,153	1,406	492	24	331	900

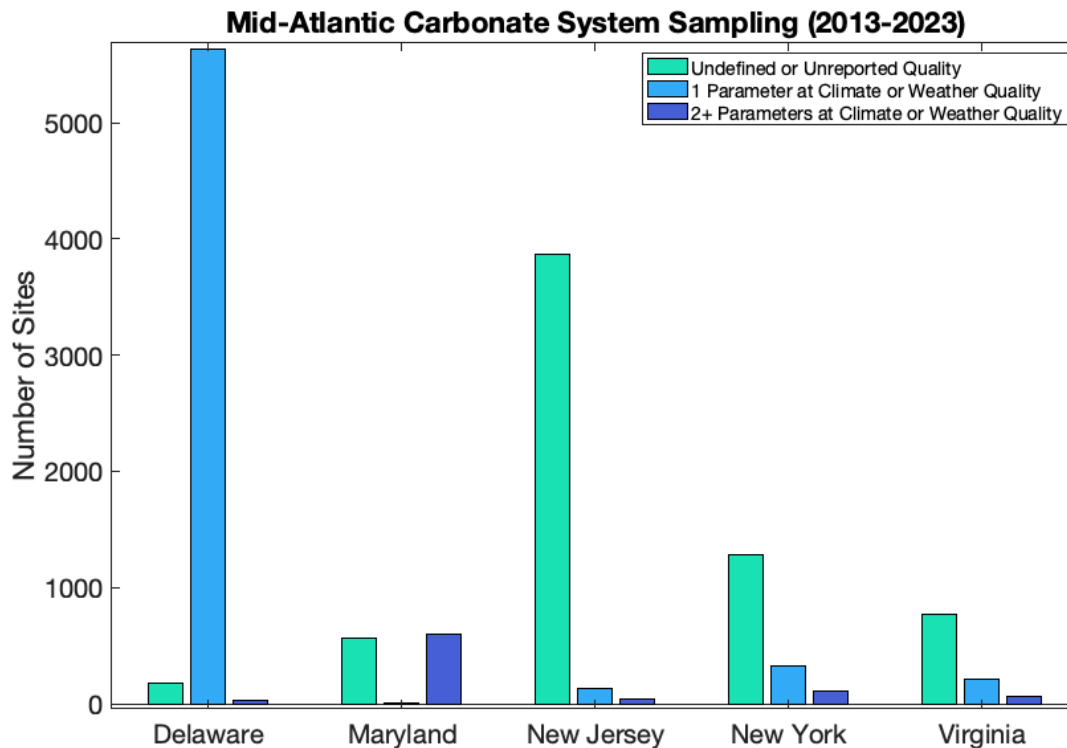


Figure 10: Number of sites in each Mid-Atlantic state active between 2013-2023. Colors correspond to three levels of data quality: undefined or unreported, one parameter measured to climate or weather quality, or two or more parameters at climate or weather quality.

1.4.4b Collection Depth

For the 17,358 sites that report collection depth, the majority of carbonate system sampling occurred at surface level. When considering collection depth patterns of each carbonate system parameter individually, surface sampling alone is most common for all parameters except for DIC, for which 89% of sites collect samples in profile (n = 533). Proportionally, TA and $p\text{CO}_2$ were infrequently collected in profile, with over 90% of samples for both parameters collected at the surface. Through a combination of profiling glider deployments and bottom-moored sensors, pH sampling occurs across the greatest variety of collection depths. In addition to the profiling glider deployments, 1,537 pH sampling sites collect samples at multiple depths.

Table 4: Number of sites collecting samples at various depths, including bottom, surface, profile, and surface and bottom, for each carbonate system parameter.

Carbonate System Parameter	Collection Depth				
	Bottom Only	Surface Only	Profile	Surface and Bottom	Number of sites reporting collection depth
pH	34	1,560	676 + 13 glider tracks	861	3,144
pCO ₂	0	13,352	37	3	13,392
TA	0	4,375	476	0	4,851
DIC	0	57	476	0	533
Any	34	15,657	806	861	17,358

1.4.4c Estuarine Sampling

Estuaries and coastal bays in the Mid-Atlantic encompass a diverse array of coastal habitats, including salt marshes, seagrass meadows, and oyster reefs. These productive ecosystems support high biodiversity (Basset et al., 2013; Sharpe et al., 2009). Commercial fisheries in the Mid-Atlantic rely on estuaries, with 83-97% of total catch by value attributed to estuarine landings (Lellis-Dibble et al., 2008). Several estuarine species of economic importance, including Eastern Oysters, are expected to be negatively impacted by projected end-of-century OA conditions in the Mid-Atlantic (Waldbusser et al., 2011).

Estuaries exhibit naturally variable carbonate chemistry due to acidic freshwater inputs, steep spatial gradients in physical parameters, and varied influence from biological processes (Feely et al., 2010; Salisbury et al., 2008). Eutrophication, driven by excessive nutrient loading from anthropogenic sources, can amplify acidification through biogeochemical pathways (Cai et al., 2011; Wallace et al., 2014). The presence of vulnerable species and reliant economies and communities necessitates an understanding of the

variability and drivers of acidification in Mid-Atlantic coastal ecosystems (Ekstrom et al., 2015). Here, we assess the spatial distribution of carbonate system sampling across salinity gradients, levels of eutrophication, and proximity to coastal ecosystems of interest.

1.4.4d Salinity Gradient: Chesapeake Bay

Estuaries exhibit physical and chemical gradients that impart influence on pH, DIC, TA, and $p\text{CO}_2$. Carbonate system sampling across a gradient of mean surface salinity was assessed in the Chesapeake Bay estuary. Salinity in the Chesapeake Bay and surrounding tributaries ranges from freshwater (< 0.5 ppt) to polyhaline (18-30 ppt). In the Chesapeake Bay, carbonate system sampling is conducted across a full range of salinities, with the most sites occurring at low salinities (0-1 ppt) and mid-salinities (10-15 ppt). The middle to upper Chesapeake Bay is predominantly characterized by mesohaline (5-18 ppt) conditions. With 1,314 sites, the majority of carbonate system sampling is occurring within the mesohaline areas of the Chesapeake Bay. While carbonate system sampling is active across a wide range of salinities, most sampling efforts are of undefined or unreported quality. Sites that sample at least one parameter to climate or weather quality are present across all salinity categories, with clusters of increased sampling at mid-salinities (10-15 ppt) and high salinities (24-25 ppt).

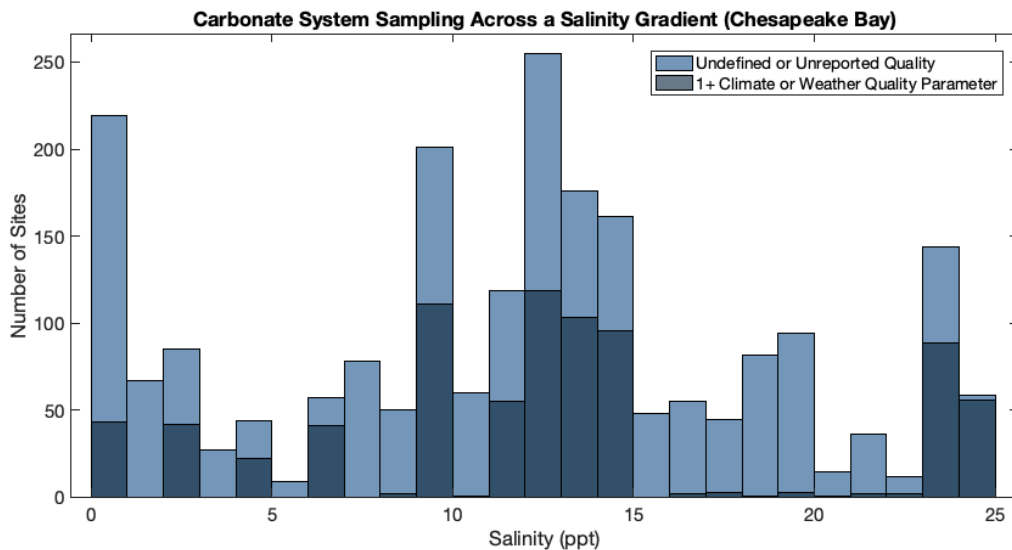


Figure 11: Chesapeake Bay seawater carbonate system sampling across a salinity gradient. Colors represent quality level of measurements.

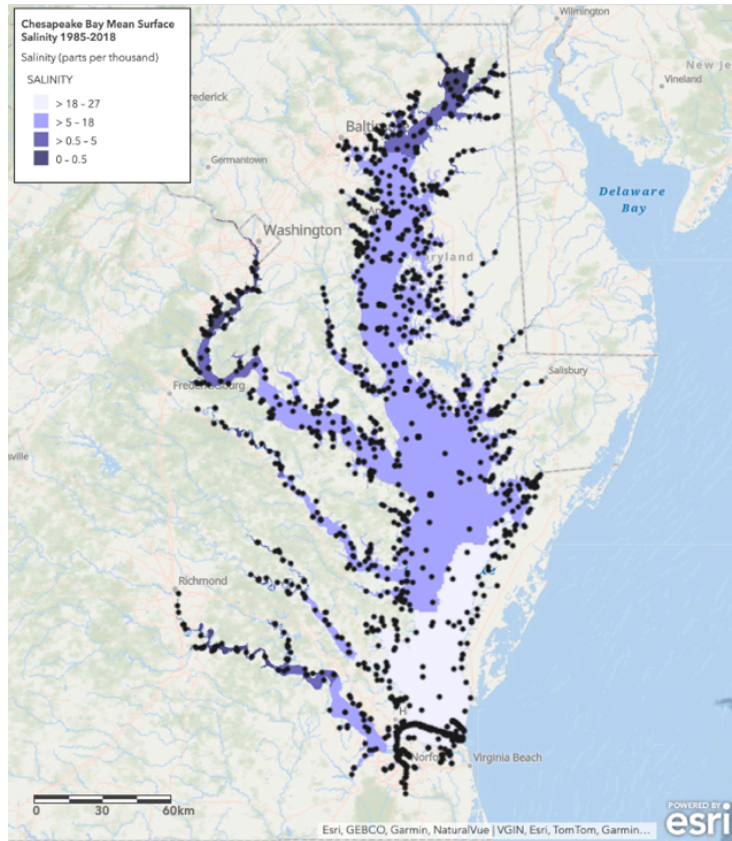


Figure 12: Chesapeake Bay seawater carbonate system sampling across a salinity gradient. Salinity ranges include freshwater (0-0.5 ppt), oligohaline (0.5-5 ppt), mesohaline (5-18 ppt), to polyhaline (18-30 ppt).

1.4.4e Eutrophication

Prominent Mid-Atlantic estuaries and coastal bays exhibit moderate to high levels of eutrophication, with the highest regional eutrophication scores seen in the Long Island Sound, the coastal bays of southern New Jersey, and the Chesapeake Bay (Bricker et al., 2007). Approximately half of the 2,588 sites in highly eutrophic estuaries measure one or more carbonate system parameters at climate or weather quality. Moderately high eutrophication areas, seen in the Chesapeake Bay and the south shore of Long Island, contain 450 sampling sites, ~98% of which had undefined or unknown quality. Regions of

high and moderately-high eutrophication displayed similar densities of sampling sites, with an average of 2.2 and 1.7 sites per square kilometer, respectively.

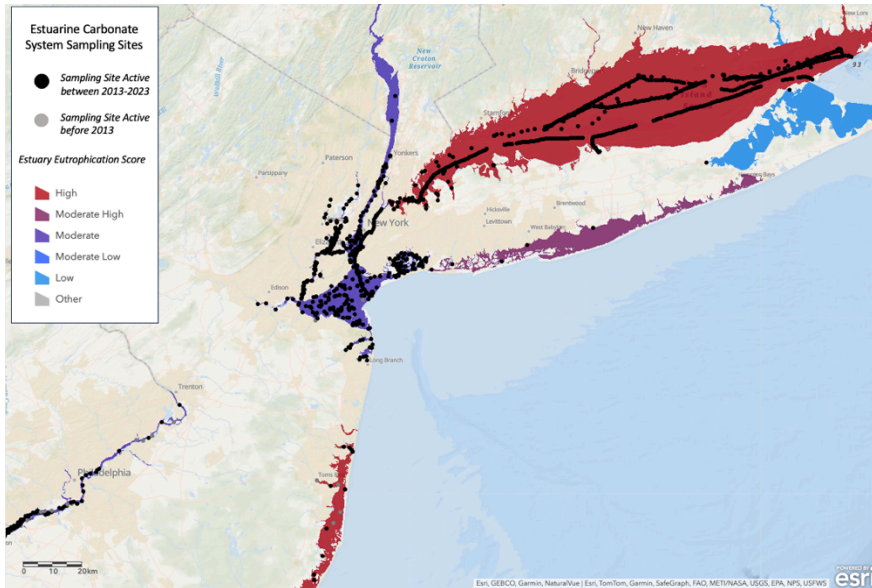


Figure 13: Carbonate system sampling sites located within estuaries or coastal bays, taking a closer look at the northern Mid-Atlantic region. Sites active anytime between 2013-2023 in black and sites active prior to 2013 in gray.

Despite accounting for 80% of the estuarine area in the Mid-Atlantic, moderate-high to highly eutrophic regions have a lower density of carbonate system measurements than estuaries with lower eutrophication scores (Figure 13; Figure 14). Moderately eutrophic areas, including the Delaware Bay, Raritan Bay, and New York Bay, have over 10,000 unique sampling sites with a mean sampling density of 28 sites per square kilometer. The majority of the sampling sites in the moderately eutrophic region were collected by underway cruise and are not repeat sampling efforts. Despite high sampling density among moderately eutrophic sites, fewer than 100 sites measure carbonate system parameters to a high quality. This discrepancy likely reflects the large proportion of historic cruise sampling that did not report methods, yielding inconclusive quality levels.

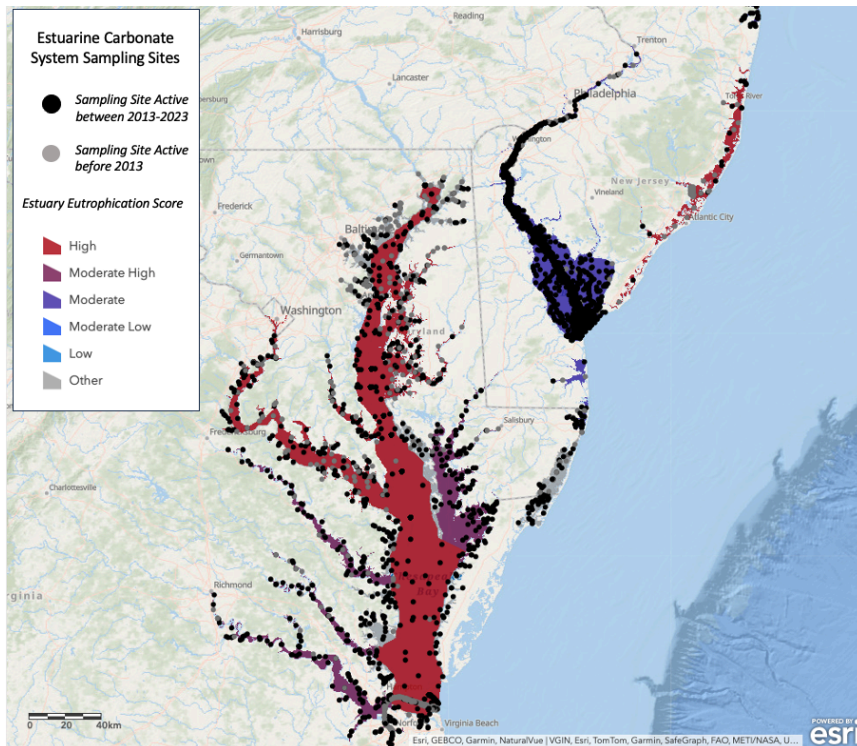


Figure 14: Carbonate system sampling sites located within estuaries or coastal bays, taking a closer look at the southern Mid-Atlantic states. Sites active anytime between 2013-2023 in black and sites active prior to 2013 in gray.

Table 5: Number of carbonate system sampling sites located in Mid-Atlantic estuaries exhibiting high, moderate high, and moderate eutrophication scores. Density of sampling and number of high quality sites are reported.

Eutrophication Score	Area (km ²)	Total Number of Monitoring Sites	Mean Density (Sites per km ²)	Sites measuring 1 parameter at Climate or Weather Quality	Sites measuring 2+ parameters at Climate or Weather Quality
High	1,182	2,588	2.2	629	726
Moderate High	269	450	1.7	3	5
Moderate	363	10,010	28	49	48

1.4.4f Proximity to Marine and Estuarine Intertidal Habitats

Biological processes exert influence on estuarine and marine carbon cycles, leading to variable effects on the extent of acidification (Johnson et al., 2013). Estuaries host biological hotspots like salt marshes and seagrass meadows that have opposing effects on carbonate chemistry. Salt marshes, which are prevalent across Mid-Atlantic estuaries, are exporters of DIC and can exacerbate acidification in nearby coastal waters (Baumann et al., 2015; Wang et al., 2016). Alternatively, seagrass meadows have been shown to increase pH locally, lessening the effects of acidification (Hendriks et al., 2014; Ricart et al., 2021). In other ecosystems, biological effects on carbonate chemistry can differ based on the specific biological processes at work. For example, aerobic and anaerobic respiration, primary production, and nitrification, all produce or consume DIC and TA in variable quantities.

In the coastal zone, 9,014 carbonate system sampling sites are located within 0.5 km of estuarine intertidal habitats and 297 sites located within 0.5 km of marine intertidal habitats. Of estuarine intertidal sites, 65% are adjacent to emergent marsh sites and ~1% are located near aquatic beds, comprising seagrass and macroalgal habitats. Using a different data source estimating Mid-Atlantic seagrass area, there are 63 sites located within seagrass meadows. Regionally, emergent marsh area greatly exceeds the area of submerged aquatic vegetation. The remaining estuarine intertidal sites were located near a variety of coastal habitats, including unconsolidated shore (comprising mudflats, sandy bottoms, etc.), coastal forests, scrub-shrub, and rocky shore. There are 2,144 carbonate system sampling sites located within 1 km of shellfish survey sites, 133 of which are measuring two or more parameters at a high quality.

1.4.4g Spatial Distribution of Deep Sea Corals

While sparsely studied, deep-sea corals are an important marine resource in the Mid-Atlantic that are prevalent in submarine canyons just beyond the continental shelf break (Packer et al., 2007; Shank et al., 2020). Deep-sea corals provide essential habitat to

fish and other invertebrates. Their slow growth rates make these organisms particularly vulnerable to any changes in environmental conditions, including ocean acidification (Turley et al., 2007). Under current ocean acidification rates in the North Atlantic, the depth of the aragonite saturation horizon is expected to rise in the water column, such that deep-sea corals will be exposed to water that is undersaturated with respect to aragonite by 2050 (Perez et al., 2018). While there is still limited information about how Mid-Atlantic deep-sea corals may respond to acidification, some evidence suggests that they could experience decreases in net calcification or, in extreme cases, dissolution of existing coral structure. In a study off the coast of California, living deep-sea corals were found to be robust to acidification effects when experiencing aragonite undersaturation (Hennige, et al., 2020). However, dead coral skeletons, which typically form the underlying foundation of living coral structures, became more porous under acidified conditions (Hennige, et al., 2020). Crumbling dead coral structures endangered structural integrity at the ecosystem scale (Hennige, et al., 2020).

Here, we assess distribution of carbonate system sampling efforts that coincide with modeled deep-sea coral habitat for the Mid-Atlantic shelf (Kinlan et al., 2013). In total, there were 6,219 sites where seawater carbonate chemistry sampling occurred within the spatial footprint of the deep-sea coral habitat. Of those, the majority were surface samples, with only 99 sites collecting samples in profile. In this case, surface samples do not adequately represent the conditions experienced in the habitat of interest, as the deep-sea corals are found on the seafloor, at depths between 700 and 1850 meters.

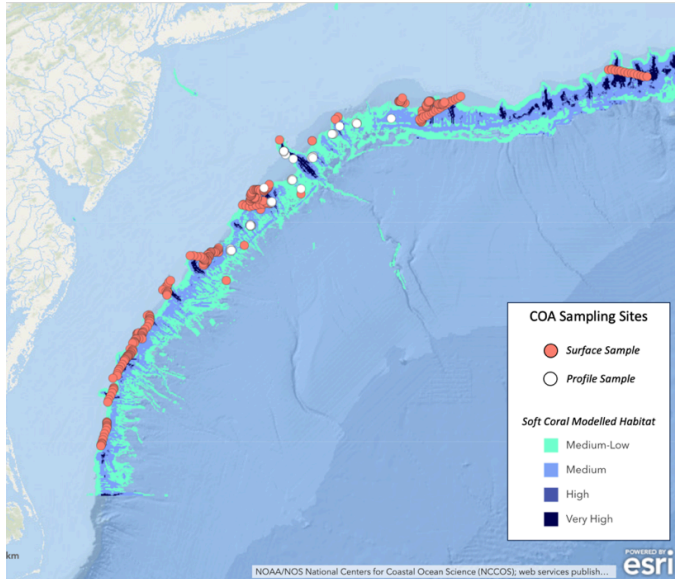


Figure 15: COA sampling sites measuring 2+ carbonate system parameters at a high quality that overlap with modeled deep-sea coral habitat. White circles represent samples that were collected in profile.

1.5 Summary

The current state of Mid-Atlantic seawater carbonate system monitoring are summarized with respect to a subset of Mid-Atlantic acidification research priorities as discussed in regional studies and the NOAA Ocean, Coastal, and Great Lakes Acidification Research Plan: 2020-2029 (Goldsmith et al., 2019; Kinkade et al., 2020; Saba et al., 2019). Below, we highlight data quality, spatial distribution of sampling across diverse ecosystems, and sampling with respect to known drivers of coastal acidification.

Data Quality of Carbonate System Sampling

A key priority identified for the region is for carbonate system data to be of a quality befitting the intended use of the data (Kinkade et al., 2020). Climate and weather quality data are appropriate for assessing long-term COA changes and short-term or spatial COA patterns, respectively (Newton et al., 2015). In Mid-Atlantic carbonate system sampling efforts between 2019 and 2023, 60% of sites measured one carbonate system parameter at climate or weather quality, while 8% of sites measured two parameters to a high quality. While there is a large proportion of sites reporting high quality data, increasing the number of seawater carbonate system parameters being measured to two or more would allow for

complete characterization of the carbonate system. The majority of sites measuring two or more carbonate system parameters at a high quality were sampled only once, while only 340 sites in the MACAN inventory are repeat monitoring sites. Many sites in the MACAN inventory, especially those active prior to 2013, do not have sufficient metadata to assess methods or data quality. Explicit reporting of data quality, methodology, and QA/QC for past, present, and future COA monitoring sites will allow for improved opportunities for data sharing and comparison across the Mid-Atlantic region.

Sampling Across Diverse Ecosystems

COA monitoring across a diverse array of ecosystems and depths can resolve spatial heterogeneity in regional carbonate system conditions, and is therefore a Mid-Atlantic monitoring priority (Goldsmith et al., 2019; Kinkade et al., 2020; Saba et al., 2019). According to analysis of the MACAN inventory, Mid-Atlantic carbonate system sampling sites are located across varied ecosystems from estuaries to the continental shelf, with high quality sites located in proximity to seagrass meadows, emergent wetlands, deep-sea coral habitat, and shellfish beds. Bottom and profiled depth measurements are infrequent, representing only 10% of reported measurement depths. In particular, the coastal zone has few high-quality, bottom measurements. Benthic and profiling samples were most likely to be collected during cruises, offshore, and at sites that did not engage in repeat monitoring. Additionally, few high frequency, continuous measurements are being collected in benthic sites. In the coastal zone, there are a total of 34 continuous pH sensors of undefined quality moored at depth. Offshore glider deployments in recent years have substantially increased the amount of high frequency carbonate system measurements occurring across a range of depths.

Sampling with Respect to Coastal Acidification Drivers

Another regional priority is to assess acidification with respect to drivers of coastal acidification, including eutrophication and freshwater inputs (Goldsmith et al., 2019; Kinkade et al., 2020; Saba et al., 2019). In sections 1.4.4c and 1.4.4d, we discuss the number of sites in the MACAN inventory located in eutrophic estuaries and across a salinity

gradient in the Chesapeake Bay, respectively. Despite accounting for 80% of the estuarine area in the Mid-Atlantic, moderate-high to highly eutrophic regions have a lower density of carbonate system measurements than estuaries with lower eutrophication scores. In the Chesapeake Bay, carbonate system sampling is well distributed across low-to-high salinities.

1.6 Appendix 1: Data Quality

Table 1: pH methods reported in the Mid-Atlantic with associated accuracy, precision, and quality category.

pH Measurement Method	Accuracy	Precision	Quality
YSI EX02	± 0.1 pH units within $\pm 10^{\circ}\text{C}$ of calibration temp; ± 0.2 pH units for entire temp range	± 0.01 pH units	Undefined
Sunburst SAMI-pH	± 0.003 pH units	± 0.001 pH units	Climate
Seabird Seaphox V2	± 0.05 pH units (factory calibration)	± 0.004 pH units	Undefined
Honeywell Durafet [®] -based pH Sensor	± 0.01 - 0.03 pH units	± 0.005 pH units	Weather
Spectrophotometric pH (m-Cresol Purple dye)	± 0.01 pH units	± 0.0004 units	Weather
Oakton handheld pH probe	± 0.01 pH units	± 0.01	Weather
Manta 2 probe	± 0.1 pH units within 10°C of calibration; ± 0.2 otherwise	± 0.01	Undefined
Horiba U-54	± 0.1 pH units	± 0.05 pH	Undefined
YSI handheld	± 0.2 pH units	± 0.01	Undefined
Potentiometry	± 0.02 pH units	No Data	Weather

Table 2: TA methods reported in the Mid-Atlantic with associated accuracy, precision, and quality category.

TA Measurement Method	Accuracy	Precision	Quality
<u>Apollo-Scitech</u>	0.1% or better		Climate
<u>Contros HydroFIA TA</u>	$\pm 5 \mu\text{mol kg}^{-1}$	$\pm 2 \mu\text{mol kg}^{-1}$	Weather
<u>Metrohm 765</u>	$\pm 0.2\%$		Weather

Table 4: $p\text{CO}_2$ methods reported in the Mid-Atlantic with associated accuracy, precision, and quality category.

$p\text{CO}_2$ Measurement Method	Accuracy	Quality
<u>LI-7000</u> Infrared Analyzer	Accuracy: 1%.	Weather
<u>LI-6262</u> Infrared Analyzer	$\pm 1 \text{ ppm}$ at 350 ppm (<3 ppm maximum). $\pm 2 \text{ ppm}$ at 1000 ppm (<6 ppm maximum).	Climate
Pro Oceanus Pro CV	$\pm 0.5\%$	Climate

1.7 Appendix 2: Supplemental Data Tables

Table 1: Total number of sampling sites and high-quality sampling sites located within or nearby ecosystems of interest.

Ecosystem Type	Total Number of Sampling Sites	Number of High-Quality Sampling Sites measuring 2+ parameters	
Seagrass	63	0	
Deep-Sea Soft Corals	6,219	600	
Estuarine Intertidal	Emergent Marsh	5,814	-

(sites within 0.5 km)	Unconsolidated Shore	2,717	-
	Aquatic Bed (Macroalgal or submerged aquatic veg)	85	-
	Other (scrub-shrub, rocky shore, etc.)	398	-
Marine Intertidal (sites within 0.5 km)	Unconsolidated Shore	279	-
	Rocky Shore	18	-
Within 1km of Shellfish Survey Site		2,144	133

Table 2: Number of sampling sites in the Chesapeake Bay located across four salinity classes.

Salinity Range	Number of Sampling Sites (Chesapeake Bay)
Polyhaline (18-30 ppt)	433
Mesohaline (5-18 ppt)	1,314
Oligohaline (0.5-5 ppt)	293
Freshwater (< 0.5)	149

1.8 References

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