# Science Assessment of Chesapeake Bay Acidification: Toward a Research and Monitoring Strategy

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# Science Assessment of Chesapeake Bay Acidification: **Toward a Research and Monitoring Strategy**

## Smithsonian Environmental Research Center, Edgewater MD 11-13 March 2014

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#### **EXECUTIVE SUMMARY**

Scientists forecast that open ocean pH will continue to decline by 0.1 to 0.4 units, but such forecasts for estuaries and coastal oceans are far more challenging due to dramatic spatial and temporal variation in the processes that control pH. Chesapeake Bay is an intensively studied estuary that is well understood in terms of nutrient chemistry, hydrodynamics, ecology and fisheries, but poorly understood from the perspective of pH, the carbonate chemistry that largely controls pH, and the sensitivity of marine biota to pH change. This report is the outcome of a workshop focused on acidification in Chesapeake Bay, the goal of which was to assess the state of the relevant scientific knowledge. It is anticipated that this first step will be followed by engagement with the management community and stakeholder groups such as the aquaculture industry, culminating in the establishment of a Chesapeake Bay Acidification Network.

The carbonate chemistry of Chesapeake Bay and similar estuaries worldwide is highly sensitive to the chemistry of tributaries (rivers and streams), the terrestrial watersheds that feed into tributaries, and therefore human activities on land. Land use in Chesapeake Bay varies from agriculture to urban development across small distances and is constantly changing, creating complex spatial and temporal patterns that are certain to influence Bay acidification. Overlaid on spatial and temporal variation in climate, ocean pH, and Bay sediments, it is clear that an estuarine acidification observing network in Chesapeake Bay requires a high density of spatial and temporal observations. Fortunately, the infrastructure developed over several decades to monitor the chemical and biological health of Chesapeake Bay can be leveraged to address this newly emerging biogeochemical perturbation, a phenomenon that shares mechanistic links with nutrient eutrophication. The most efficient strategy for capturing key sources of spatial and temporal variation is to add acidification observing platforms across the full suite of existing Bay water quality observation assets, including shore-, vessel-, and buoy-based sampling stations. This goal will require cooperation among county, state and federal agencies and academic institutions, another area where the Chesapeake Bay already has extensive experience.

Scientists working in Chesapeake Bay have begun to work on estuarine acidification, providing a framework for the design of an observing network. For example, total alkalinity in major tributaries such as the Susquehanna and Potomac has been rising in recent decades, perhaps due to human activities; it appears that upper portions of the Bay are likely sources of  $CO_2$  while lower portions are  $CO_2$  sinks; and it is clear that tidal wetlands are point sources of  $CO_2$ -enriched water and perhaps alkalinity to the Bay. Finally, academic institutions have been developing and testing the sensor technology required to build a highly resolved acidification observation network.

The information gaps to be filled by a Chesapeake Bay Acidification Network are large, requiring a process for setting priorities. The workshop identified four goals that will advance our capacity to forecast Bay acidification: (i) determine Bay-wide patterns of pH, pCO<sub>2</sub>, dissolved inorganic carbon, total alkalinity and CO<sub>2</sub> fluxes at the air-water interface, with sufficient resolution to capture temporal (daily, seasonal, annual) and spatial (sub-watershed) variation, (ii) understand the biogeochemical and physical controls on pH-relevant chemical fluxes across the key interfaces of land:estuary, ocean:estuary, and sediment:water column, (iii) link the carbonate system to biological processes in the water column such as photosynthesis and respiration, and (iv) determine the sensitivity of Bay biota to natural variation in Bay carbonate chemistry and acidification-driven changes thereof.

The workshop posed several questions to guide the planning of a Chesapeake Bay Acidification Network (CBAN): Is elevated atmospheric  $CO_2$  an important driver of Bay pH? How important are the fluxes that cross ecological subsystem boundaries to estuarine pH? Does CBAN need to capture short-term (e.g. weather-scale) and long-term (e.g. climate-scale) variation in order to forecast acidification trends? How can existing Bay observing networks and expertise be leveraged to address acidification? Which

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combinations of carbonate system parameters will yield the most robust data for an estuarine system? What are the specific biological impacts of acidification should CBAN be designed to detect, and how do these impacts influence socioeconomic conditions in the Chesapeake Bay region?

#### INTRODUCTION

Chesapeake Bay is arguably the most intensively studied estuary in the world. Indeed, much of our understanding of basic estuarine chemistry, hydrodynamics, ecology, and fisheries can be attributed to research carried out in this ecosystem. Chesapeake Bay continues to be studied extensively across many dimensions, yet little attention has been paid to carbonate chemistry dynamics and drivers, information that is critical as we seek to make projections about how the Bay ecosystem, and other estuaries, will be affected by elevated atmospheric carbon dioxide  $(CO_2)$  in coming decades. Despite this dearth of information, Chesapeake Bay is an excellent model system for understanding complex coastal acidification processes. The combined scientific and environmental monitoring activities and infrastructure overseen by state and federal agencies, as well as academic institutions, and non-governmental organizations, provide a vast number of observing platforms and opportunities (shorebased, vessel-based, and buoy-based) with the potential for advancing carbonate chemistry measurements. Given the sheer number of researchers who currently focus their efforts on various aspects of Chesapeake Bay and its watershed, the prospects for developing acidification-based collaborations are expansive and promising.

The combustion of fossil fuels during the past 200 years has resulted in a significant increase in atmospheric CO<sub>2</sub> from approximately pre-industrial levels of 280 parts per million by volume (ppmv) to the current global average of ~400 (IPCC AR5 2013). Projections of fossil fuel use suggest atmospheric concentrations are likely to rise significantly (doubling or more) in the next 100 years and that we are experiencing CO<sub>2</sub> input to the atmosphere that is unprecedented (Hönisch et al., 2012). Since 1800, surface ocean pH has decreased ~0.1 units, and further reductions of 0.1 to 0.4 units are anticipated due to rising CO<sub>2</sub> (Doney et al., 2009; Caldeira & Wickett, 2003, 2005; Orr et al., 2005). There is widespread concern that these changes will produce irreversible ecological regime shifts in marine habitats, such as massive reductions in coral reef habitats and inhibition of other calcifying biota.

However, current predictions regarding the effects of elevated atmospheric  $CO_2$  are driven almost exclusively by the open ocean assumption of an air-water equilibrium, regardless of geographic or oceanographic setting. Such assumptions do not hold in coastal marine habitats, which are influenced significantly by terrestrial and near-shore phenomena, including significant biological perturbation to the water's carbonate chemistry. To explore the complex nature of acidification processes and mechanisms, carbonate chemistry dynamics, and potential environmental and ecological impacts, the Integrated Ocean Observing System (IOOS) funded the Alliance for Coastal Technologies (ACT) to organize a workshop focused on acidification in Chesapeake Bay.

A workshop was convened on March 11-13, 2014 to explore the current scientific knowledge and critical information gaps related to carbonate chemistry dynamics, processes, and mechanisms that ultimately determine the pH environment of Chesapeake Bay. In particular, the workshop focused on how elevated atmospheric  $CO_2$  may affect coastal marine and estuarine waters, with a specific focus on Chesapeake Bay, recognizing that the air:sea interface is but one of several important biogeochemical boundaries that affect carbon dynamics in this and many other estuaries and coastal marine ecosystems. Ultimately, the goal of the workshop was to evaluate the state of the science as it relates to coastal ocean acidification and to begin amassing information on current monitoring assets, data sources, and data gaps as they relate to measuring and monitoring carbonate chemistry, with an eye toward designing a Chesapeake Bay

Acidification Network (CBAN), modeled on efforts such as the California Current and Northeast Coastal Acidification Networks (CCAN and NECAN, respectively) elsewhere in the country.

The workshop was held at an opportune time because the Maryland General Assembly was considering a bill to create a task force to evaluate the effects of acidification in Chesapeake Bay and other state waters. House Bill 118 was passed by both chambers of the Maryland Legislature in April and approved by the Governor in May 2014. The proposed task force will be composed of members from state agencies, representatives from the aquaculture industry and waterman's associations, and the National Aquarium and University of Maryland Center for Environmental Science, with staff support from the Maryland Department of Natural Resources (MD DNR). Maryland follows Maine as the second state on the east coast to pursue legislation aimed at understanding the effects of acidification on the natural resources of coastal ocean ecosystems.

#### BACKGROUND

At the federal level, the Federal Ocean Acidification Research and Monitoring (FOARAM) Act of 2009 (P.L. 111-11) is currently the single most important law focused on ocean acidification in the United States. FOARAM is aimed at supporting research and monitoring of acidification in the waters of the U.S. and seeks to evaluate the possible effects on the nation's fisheries and natural resources. In addition to authorizing federal funding across multiple federal agencies, FOARAM established the National Oceanographic and Atmospheric Administration's Ocean Acidification Program. In March 2014, a Strategic Plan for Federal Research and Monitoring of Ocean Acidification, prepared by the Interagency Working Group on Ocean Acidification, was released. Among many recommendations, the strategic plan suggests the following:

"A successful strategy for ocean acidification research requires special attention to integrated efforts, regionally, nationally, and internationally. Effective management of marine resources in response to ocean acidification will require researchers viewing their contributions in a broader perspective, but there is also clearly a need for research on issues such as vulnerable and economically important species to be conducted at regional scales."

"For shallow water coastal and estuarine environments and areas inaccessible by openocean ships, a similar sampling strategy, as outlined for the open-ocean carbon measurements, is recommended, but at much higher temporal and spatial resolution than for the open ocean. These activities will be integrated with ongoing ship-based surveys in coastal areas, but at higher frequencies as required (hourly for time-series measurements). Federal agencies should encourage state and regional entities, including the tribal nations, to add ocean acidification monitoring to the existing coastal and estuarine water quality monitoring programs. This monitoring may also lead to development of acidification source budgets for these waters which are heavily influenced by land-based activities (Feely et al., 2012)."

Such recommendations are consistent with the collaborative local and regional approaches to research and monitoring that are necessary for understanding acidification in Chesapeake Bay.

Abrupt and extensive oyster spat production failures in shellfish hatcheries of the Pacific Northwest in 2005-2009, believed linked to acidification of coastal waters, prompted Washington State to convene a blue ribbon panel of experts to investigate the phenomenon. The panel explored causes and trends of acidification in Washington state waters, including processes at local and regional levels, and made recommendations for how the state should respond to the observed conditions (Feely et al., 2012). The panel identified several local and regional scale processes that exacerbate acidification, including: 1) Seasonal upwelling of high CO<sub>2</sub>/low pH and nutrient-rich water from the deep ocean, a process that is now enriched by anthropogenic carbon that was put into the atmosphere approximately a half century ago; 2) Nutrient and carbon runoff at the land:sea interface, which can strongly affect biological productivity, producing hypoxic conditions locally; and 3) Local upwind sources of CO<sub>2</sub>, and oxides of nitrogen and sulfur, all of which can function as acids to reduce surface pH in coastal waters. Depth was identified as an especially important characteristic of estuaries with respect to local acidifying processes.

With the exception of upwelling. Chesapeake Bay is subject to all of the same acidifying processes that occur in west coast estuaries. Because Chesapeake Bay is a shallow estuary with high nutrient loading and extensive muddy sediments, it supports rich biological productivity (photosynthesis and benthic respiration) that strongly influences pCO<sub>2</sub>/pH patterns and dynamics. Land use patterns, including shoreline and watershed habitat and development, affect Chesapeake Bay's water quality (e.g., freshwater riverine input, point and non-point sources). Although a lot of focus has been placed on nutrient loading in the Bay, especially as it relates to eutrophication, far less attention has been paid to those parameters that directly affect carbonate chemistry, such as the flux of total CO<sub>2</sub> (TCO<sub>2</sub> also referred to in this document as dissolved inorganic carbon, DIC) and total alkalinity across the land:water interface, and CO<sub>2</sub> flux across the atmosphere and bay water interface. Further, the effects of intertidal and subtidal habitats, such as salt marshes and seagrasses, on local carbonate chemistry have not been investigated. Lastly, the exchange of  $TCO_2$  of the bay with the offshore ocean water is not known either.

The complex and dynamic nature of Chesapeake Bay is known to cause a high degree of spatial and temporal variability in salinity, temperature, dissolved oxygen, turbidity and other measures of water quality, which in turn shape the distribution of aquatic species in the Bay. In contrast, we know very little about the spatial and temporal variation in carbonate chemistry parameters such as pCO<sub>2</sub> and pH. Understanding how local-scale carbonate chemistry affects the distribution of species and ecosystem services will inform better practices for managing natural resources (e.g., natural habitats and fisheries), aquaculture inside and outside of hatcheries, and restoration of foundational species that build habitat such as oysters, other shellfish, and seagrasses. Much of this local variation is driven by biological and biogeochemical processes such as photosynthetic drawdown of CO<sub>2</sub>, benthic respiration by microbes and macrofauna, tidal export of  $TCO_2$  and total alkalinity from saltmarshes. A holistic understanding of the biological and physical process operating at local and regional scales on carbonate chemistry can inform where to site hatcheries, ovster hatcheries, and other management decisions.

Given the heterogeneous nature of Chesapeake Bay, an observing network that focuses on carbonate chemistry will require highly resolved spatial density and temporal observations from shore-, vessel-, and buoy-based sampling stations. Optimizing these measurements to provide accurate and reliable information for the least effort is a key challenge that will require strong interdisciplinary collaborations and leveraging of existing observing and research programs and assets. We advocate incorporating observing efforts across the many biogeochemical features of Chesapeake Bay, with special focus on the fluxes across environmental compartments (Fig. 1) to elucidate carbon chemistry dynamics. Additionally, research should focus on the localized effects these fluxes and chemical dynamics have on surrounding biota in order to understand current and future impacts.

#### **WORKSHOP OVERVIEW**

We sought to engage a range of experts from both the regional and national stage. Participants (see below) included experts in carbon chemistry, biogeochemistry, and hydrodynamic modeling of Chesapeake Bay, many from academic and research institutions. We also received input from experts engaged in a variety of coastal and Chesapeake Bay observing systems, as well as scientific contributors from various related state, regional and federal efforts. Representatives of the U.S. Integrated Ocean Observing Program (IOOS) and NOAA's Ocean Acidification Program attended as did representatives of NGOs. The sections on *Steering Committee* and *Participants* provide the complete list of workshop attendees. Importantly, the workshop participants provided a broad range of experience and information on various aspects of coastal ocean acidification, including ongoing efforts to investigate and monitor carbon chemistry in other coastal regions such as the Pacific Northwest and New England Coasts.

The workshop consisted of several short presentations to put a focus on what is known about carbonate chemistry in coastal ecosystems and Chesapeake Bay in particular, and a series of discussions that were guided by a set of charge questions. Presentations summarized research, environmental monitoring and modeling efforts, as well as contemporary and historical water quality measures that inform our current state of knowledge with regard to carbonate chemistry dynamics and acidification in Chesapeake Bay.

#### CHARGE QUESTIONS

A series of charge questions was posed to help stimulate and guide discussion in the workshop.

#### Charge Question A - What is currently known about acidification of Chesapeake Bay?

When compared with open oceans and growing data sets in coastal settings such as Puget Sound and the Gulf of Maine, very little attention has been given to Chesapeake Bay. Nevertheless, retrospective analyses of pH data from the Chesapeake Bay Program's historical data set (1984-2008) indicate significant spatial variation with respect to changes in pH, including across salinity zones in the mainstem of the Bay's tributaries. Rates of pH change apparently far exceed those directly attributable to atmospheric CO<sub>2</sub> rise (Waldbusser et al., 2011). These historical pH data are dominated by daytime measurements, when photosynthesis can raise pH through the fixation of CO<sub>2</sub>, so must be interpreted with some degree of caution. Partial pressure measurements of  $CO_2$  in the Rhode River, a mesohaline reach of Chesapeake Bay, taken once a minute over more than two years (2012-2014, Miller unpublished data) reveal strong diurnal swings in pCO<sub>2</sub>/pH. CO<sub>2</sub> concentrations decline during the day due to photosynthetic activity (increasing pH), and rebound at night from benthic respiration (decreasing pH, Miller unpublished data). These diurnal patterns vary strongly across seasons because of temperature effects on biological activity. For example, the acidifying effects of respiration diminish substantially during the cold winter months. In the Rhode River, pCO<sub>2</sub>/pH also shows strong spatial variability, much of which can be traced to tidal saltmarshes that deliver water high in pCO<sub>2</sub> and total alkalinity on falling tides.

Recent carbonate chemistry measurements from the Delaware Bay and main stem of Chesapeake Bay (Cai unpublished data, Salisbury unpublished data) suggest that the upper portions of these bays are likely sources of  $CO_2$  (net heterotrophic) and the lower portions are  $CO_2$  sinks (net autotrophic). These results are especially interesting considering recent reviews that suggest that estuaries are believed generally to be strong sources of  $CO_2$  (Cai, 2011; Borges & Abril, 2011).

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The importance of fluvial processes are apparent when making comparisons across hydrogeomorphic regions of the Chesapeake Bay watershed, and these must be considered in order to understand the chemical nature of the Bay. Upward trends in total alkalinity in many east coast rivers, including the Susquehanna, Potomac, and Patuxent Rivers, are apparent in recent decades, perhaps due to human activities that accelerated carbonate rock weathering through acid deposition, mining, and other land use changes activities (Raymond & Cole, 2009; Kaushal et al., 2013). Given the importance of these tributaries as sources of freshwater to Chesapeake Bay, changes to total alkalinity likely have important effects on local and regional carbonate buffering capacity.

It is clear that carbonate chemistry varies spatially and temporally in Chesapeake Bay, but the full extent of that variation is not known because the carbonate system has not been widely measured in this context.

#### Charge Question B – How do biological and biogeochemical processes affect acidification in the Bay?

There is strong evidence that Chesapeake Bay is influenced significantly by both biological and biogeochemical processes. The importance of photosynthetic CO<sub>2</sub> drawdown is well recognized in coastal ecosystems, and is a phenomenon frequently witnessed during phytoplankton blooms that result in  $CO_2$ reduction and pH elevation. Widespread hypoxia and anoxia are often telltale signs of extreme benthic respiration but benthic respiration also plays an important role in diurnal and seasonal fluctuations in water column pCO<sub>2</sub>/pH. Because of the Bay's relative shallow water depth, organic carbon that rains out of the water column is typically decomposed via aerobic and anaerobic processes, generating extensive release of CO<sub>2</sub> back into the water column. In heterotrophic estuary reaches, high pCO<sub>2</sub> is associated with escape of CO<sub>2</sub> to the atmosphere however, such CO<sub>2</sub> flux between the air and water remains to be quantified over much of Chesapeake Bay and many other coastal ecosystems.

Unlike oceanic systems, where sediments are typically aerobic and low in organic materials (Schlesinger & Bernhardt, 2013; Cai & Reimers, 1995), tidal marsh soils and Bay sediments are hot spots of sulfate reduction, a biogeochemical process that generates both CO<sub>2</sub> and net alkalinity (Giblin, 1988; Cai & Wang, 1998; Cai, 2011). Sulfate reduction may play an important role in carbonate chemistry dynamics across much of Chesapeake Bay, but this process has yet to be quantitatively characterized.

Tidal saltmarshes are important transition zones between upland terrestrial ecosystems and many temperate coastal bays and estuaries. Depending on a marsh's particular soil type, the cation exchange capacity may make them important sites of cation exchange (e.g.,  $H^+$  displacing  $K^+$ ), generating net alkalinity (Megonigal unpublished data). Furthermore, saltmarsh plants transfer significant amounts of carbon to soils through root respiration and productivity. Root respiration releases CO<sub>2</sub> directly to the rhizosphere where plant roots, soil solids, and porewater meet. Root productivity supports soil microbes that break down organic material to CO<sub>2</sub>, with sulfate reduction being one of the dominant microbial respiration pathways as discussed above. A portion of the CO<sub>2</sub> produced in soils is exported to adjacent tidal creeks. Thus, tidal salt marshes are believed to be an important source of  $CO_2$  in coastal waters. The extent of CO<sub>2</sub> input, and concomitant changes to pH and other aspects of carbonate chemistry has yet to be quantified in Chesapeake Bay or other Mid-Atlantic coastal ecosystems where tidal saltmarshes are frequently dominant transitional habitats.

Nutrient runoff and eutrophication are important drivers of water quality in Chesapeake Bay (Jordan & Weller 1996), and are also expected to influence the Chesapeake's carbonate chemistry. For example, eutrophication-driven phytoplankton blooms draw down CO<sub>2</sub> from the water column, much of which is released in benthic sediments once the bloom ends and dead biomass is subjected to microbial decomposition. Though eutrophication by itself is unlikely to explain spatial and temporal patterns in the Bay carbonate system, understanding the relationships between nutrient runoff and carbonate chemistry will be important.

There are many biological and biogeochemical influences on carbonate chemistry in Chesapeake Bay, and these appear to be diverse and widespread. The significant investments made over many decades on issues such as nutrient discharges into the bay will be very useful for building a robust program on acidification. However, most of the key processes and pathways that relate directly to coastal ocean acidification have received little attention to date.

Charge Question C – Given the complexities of coastal ocean acidification, what scientific questions and information are most urgent for understanding and predicting future changes in Chesapeake Bay? Unlike in the open ocean where the surface waters closely track atmospheric gas concentrations, coastal ecosystems and estuaries are strongly influenced by physical, chemical, and biological processes that affect their chemistry in complicated and significant ways. Shallow waters, variable buffering capacity, and the influence of biological activities such as photosynthesis and respiration (both aerobic and anaerobic) drive local pH, pCO<sub>2</sub>, and TCO<sub>2</sub>, and even TA, at regional and local scales. Although many of these activities are indeed fueled by widespread eutrophication, carbonate dynamics are not directly explained strictly by increased nutrients in coastal systems. Rather, coastal carbonate dynamics are driven by a variety of processes and phenomena. For example, in estuaries fluxes of carbon across system boundaries such as air:water, land:estuary, ocean:estuary, and sediment:water can affect pCO<sub>2</sub> and pH in estuarine waters (Fig. 1).



**Figure 1.** Simplified Conceptual Model. Key ecosystem components and the interfaces between them that regulate carbonate chemistry in estuarine and coastal landscapes. Arrows represent potential linkages across which  $CO_2$  and/or  $TCO_2$  can move (e.g., air:water, land:estuary, ocean:estuary, sediment:water). Arrow size does not connote extent of flux. Observing systems and efforts should focus explicitly on measuring flux rates across these subsystems and be designed to detect how these fluxes are changing through time.

A greater understanding of the relative importance of carbon fluxes ( $pCO_2$ ,  $TCO_2$ ) across ecosystem boundaries will be vital for modeling coastal carbonate chemistry and for forecasting how rising CO<sub>2</sub> may influence acidification of the Bay directly and, perhaps more importantly, indirectly through biological and biogeochemical processes. The flux of CO<sub>2</sub> across the air:sea interface is well understood in open ocean surface waters, and when combined with rates of atmospheric CO<sub>2</sub> concentration increase, is the basis on which acidification predictions are formulated. Although the atmosphere is pushing increasingly harder on all surfaces and ecosystems of the globe, it is not yet clear how increased atmospheric  $pCO_2$ will propagate through the ecological subsystems of the Chesapeake Bay and other coastal ecosystems. Measurements that enable such fluxes to be quantified will be vital for generating predictive models about

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the extent of acidification through time, and that inform the design of biological experiments and observation networks.

In addition to fluxes in carbon, inputs of total alkalinity to estuaries and coastal waters from rivers, tidal saltmarshes, and other fringing habitats at the land:water interface can have important impacts on the buffering capacity of receiving waters. In some cases, possibly even ameliorating effects of added rising  $CO_2$  on pH.

Estuaries, by definition, lie between sources of freshwater and the ocean. As such, estuaries and other coastal waters are strongly influenced by these two carbonate chemistry end-members. The relative influence of each will have important impacts on the carbonate chemistry of these systems. On the western margins of continents in the Northern hemisphere, deep water upwelling brings low pH water to the surface. On the Pacific coast of the US, upwelling is connected to the observed low pH and lower than expected aragonite saturation states in coastal surface waters (Feely et al., 2012). When combined with rising atmospheric CO<sub>2</sub> concentrations and other physical, biological, and biogeochemical processes encountered in near shore/estuarine waters, adverse pH and associated carbonate chemistry conditions can be detrimental to commercial shellfish culturing inside and outside of hatcheries. Indeed, this is now occurring with some frequency on the Pacific coast (Feely et al., 2012). Although deep water upwelling is not an issue in Chesapeake Bay, the physical, biological, and biogeochemical processes that are present result in strong fluctuations of the carbonate system at various time scales (e.g., diurnal, tidal, seasonal) in Chesapeake Bay.

Characterizing the temporal and spatial patterns of the carbonate system in Chesapeake Bay will yield insights on the range of carbonate chemistry conditions that contemporary biota can tolerate. Insights on the effects of changing carbonate chemistry at ecologically relevant scales (e.g., local and regional) will be relevant to a variety of commercial and recreational fisheries. In some instances, as with oysters, the local carbonate chemistry may be an important consideration when determining the locations of habitat restoration. By extension, conditions may affect the success of ovsters and other shellfish that are reared in the natural environment. Given the close ties between shellfish hatcheries and their immediate natural environments (i.e., the quality of the natural water supplies to hatcheries) the possibility of changes in water quality should be contemplated.

Other expected changes such as sea level rise, increasing water temperature, changes in salinity distributions, and changes to current patterns/volumes of rainfall in Chesapeake Bay and its watershed will also need to be taken into consideration.

The following information will be critical for understanding acidification processes in Chesapeake Bay:

- 1. Determine the Bay-wide patterns of pH,  $pCO_2$ , dissolved inorganic carbon (DIC =  $TCO_2$ ), TA and CO<sub>2</sub> fluxes at the air:water interface. Measurements should capture daily and seasonal variation.
- 2. Understand the biogeochemical and physical controls on carbonate system fluxes across the key interfaces of land:estuary, ocean:estuary, soil/sediment:water (see Fig. 1).
- 3. Link CO<sub>2</sub>/DIC fluxes to photosynthesis, respiration and the metabolic balance of these in order to understand which biological processes are forcing the carbonate system.
- 4. With respect to acidification, put Chesapeake Bay in the larger context of estuaries of the world as a net  $CO_2$  source, sink, or both.

#### Charge Question D – What are the current sources of data and scientific information that could help characterize acidification dynamics in Chesapeake Bay?

Although there is a rich history of environmental research in Chesapeake Bay, relatively little attention has been paid specifically to the carbonate system. Despite the lack of coordinated and systematic study of carbonate chemistry of the Bay, there is an extensive biogeochemical literature describing processes and mechanisms that will be critical for understanding the nature of coastal ocean acidification in this system. For example, there are studies of sulfate reduction in the Bay and Bay tributaries, estuarine primary productivity, and the distributions of phytoplankton biomass, seagrass beds, and tidal marshes, all of which can provide insights on the potential drivers of carbonate dynamics in the Bay. An extensive review of the biogeochemical, ecosystem ecology and ecosystem metabolism in Chesapeake Bay is a necessary initial step toward understanding the processes that influence acidification in this system.

Given the widespread and ongoing research and monitoring taking place in Chesapeake Bay, there are extensive opportunities for adding observations and measurements aimed at characterizing the dynamics and mechanistic drivers of Bay carbonate chemistry and coastal acidification. Additional observations and research efforts could leverage Chesapeake Bay's existing infrastructure and monitoring programs (e.g., existing water quality stations, water quality and oceanographic cruises), thereby rapidly increasing our knowledge about coastal acidification at regional and local scales. These extensive technological assets, observing opportunities (buoys, cruises, shore-based), and research facilities and programs make Chesapeake Bay an especially attractive system in which to advance the study of coastal acidification. As the nation's largest estuary. Chesapeake Bay is an extremely important ecosystem that contains and sustains a remarkable diversity of natural, commercial, and recreational resources.

Below is a sampling of some of the programs and institutions that actively conduct environmental monitoring in and around Chesapeake Bay, typically through coordinated observing networks. These and other active research and observing programs in the region provide a rich opportunity for partnership and collaboration.

At the federal level, NOAA provides the most comprehensive network of oceanographic observations in the US. NOAA does research and collects extensive ocean acidification measurements across much of the US via the Ocean Acidification Program and associated regional laboratories, such as the Pacific Marine Environmental Laboratory (PMEL) and the Atlantic Oceanographic and Meteorological Laboratory (AOML). NOAA also founded and leads the Global Ocean Acidification Observing Network (GOA-ON), whose charge is to: 1) Improve our understanding of global ocean acidification (OA) conditions, 2) Improve our understanding of ecosystem response to OA, and 3) Acquire and exchange the data and knowledge necessary to optimize modeling for OA and its impacts. NOAA's ocean acidification observations are collected via a combination of mooring-based instruments, float and pier-based instruments, and coordinated oceanographic cruises. NOAA maintains a series of data portals for ocean acidification that are web-based and available to the public.

U.S. IOOS is an operational system and a network of government, industry, academia, NGO and other partners responsible for regional observations, data management, modeling and analysis, education and outreach, and research and development. The overarching purpose of IOOS is to address regional and national needs for ocean data and information. IOOS is comprised of eleven Regional Associations (RAs), which guide development of, and stakeholder input to, regional observing activities. The RAs serve the nation's coastal communities, including the Great Lakes, the Caribbean and the Pacific Islands and territories. "Today the U.S. IOOS has a mandate to lead the integration of ocean, coastal, and Great Lakes observing capabilities, in collaboration with Federal and non-Federal partners, to maximize access to data and generation of information products, inform decision making, and promote economic, environmental, and social benefits to our nation and the world IOOS" (www.ioos.noaa.gov). In the United States, IOOS is organized into a collection of smaller coastal and ocean observing systems that collect data at regional scales.

The Mid-Atlantic Regional Association Coastal Ocean Observing System (MARACOOS) - the IOOS RA in the Mid-Atlantic - coordinates oceanographic observation in the Chesapeake Bay region and surrounding coastal waters. In cooperation with NOAA's Chesapeake Bay Office (NCBO), IOOS/MARACOOS supports operation and enhancement of the Chesapeake Bay Interpretive Buoy System (CBIBS). CBIBS is a collection of "smart buoys" that collect real-time data, including water quality and weather data. CBIBS consists of several buoys (~11) that are positioned across the Bay. These data are collected in real time and made available to the public via the MARACOOS and IOOS webbased data portals. At present, some CBIBS buoys measure pH, but none are measuring pCO<sub>2</sub>. NCBO provides extensive remote sensing through NOOA's CoastWatch program to collect oceanographic satellite data on water quality (chlorophyll, sediments, water temperature). Together, IOOS, MARACOOS and NCBO maintain a broad variety of environmental observing programs that will no doubt be central to any proposed Chesapeake Bay Acidification Network.

In response to Executive Order No. 13508 (Chesapeake Bay Protection and Restoration, 2009), the Environmental Protection Agency (EPA) developed total daily maximum loads (TMDLs) for the Chesapeake Bay and its estuaries. In conjunction with USGS, and other partners, EPA has observing assets throughout the Chesapeake Bay watershed to monitor water quality, with a strong focus on nutrient and sediments loads. Understanding watershed inputs to the Bay will be an important component to understanding spatial variability of acidification in Chesapeake Bay and the complex nature of interacting environmental stressors that are in play here.

The National Estuarine Research Reserve System is comprised of 28 reserves nationwide and maintains two reserves in Chesapeake Bay (VA and MD). NERRS carries out coordinated monitoring and research across its national network in support of scientifically based assessment of coastal management at local, regional, and national scales. In addition to providing an extensive set of standardized real time environmental measurements (available to the public on the web), NERRS serves as a model network system and as a possible partner for CBAN.

At the state level, the Maryland Department of Natural Resources (MD DNR) "Eyes on the Bay" Program is designed to monitor various environmental parameters, primarily chemical and biological, to assess the health of Chesapeake Bay, and to track the effectiveness of environmental management actions. The Eyes on the Bay program consists of approximately 31 continuous monitoring stations in Chesapeake and coastal bays, as well as over 70 monthly (or more frequent) monitoring stations (22 in the Bay's mainstem and 45 in tidal tributaries). Core DNR monitoring consists of continuous monitoring stations and fixed monthly monitoring stations. A typical continuous monitoring station collects data on dissolved oxygen, salinity, water temperature, pH, turbidity, chlorophyll concentration, and water depth. Monthly parameters measured are dissolved oxygen, Secchi depth, salinity, water temperature, and pH. This program partners with a wide range of federal, state, county, non-profit and for-profit organizations. Eyes on the Bay data are publically accessible on the web.

There are also a variety of university-based, federal, and state laboratories located throughout the Chesapeake Bay region. The Virginia Institute of Marine Sciences operates the Virginia Estuary and Coastal Observing System (VECOS). The Smithsonian Environmental Research Center (SERC) is measuring pCO<sub>2</sub> at one minute intervals at three locations in the Maryland portion of Chesapeake Bay, two of which are in the Rhode River (Miller et al.) and one at the UMCES Chesapeake Biological Laboratory (CBL) (Tamburri et al.) research pier at the mouth of the Patuxent River. Water samples are collected weekly to twice weekly for total alkalinity titration in order to calculate pH, TCO<sub>2</sub>, and

associated carbonate system measures. Underway pCO<sub>2</sub>/TA measurements are also occasionally performed using the same instrument mounted on a boat. The University of Delaware (Cai et al.) is conducting oceanographic cruises in both the Delaware and Chesapeake estuaries to make carbonate chemistry measurements. Miller and Cai are two investigators known to be monitoring carbonate chemistry dynamics in nearshore and mainstem of Chesapeake Bay, but there are no doubt other investigators, laboratories, and programs that focus on carbon chemistry or biogeochemistry that can participate in CBAN.

From the non-profit sector, the Sustainable Fisheries Partnership has been collaborating with investigators at Virginia Tech University (Kuhn et al.) and the University of New Hampshire (Salisbury et al.) to track water quality and carbonate chemistry in oyster hatcheries in Chesapeake Bay. These efforts are aimed at understanding baseline water conditions under which they are operating, and to enable these hatcheries to detect changes that may affect the health and yield of their oyster spat production.

The above are some examples of current activities aimed at understanding carbonate chemistry and acidification in Chesapeake Bay. There are many additional research projects directed at understanding the impacts of elevated CO<sub>2</sub> on species that live in Chesapeake Bay (e.g. Breitburg of SERC, combined effects of diurnal DO and pH cycling on oysters and fish; Lane/Miller of CBL, effects of elevated CO<sub>2</sub> on juvenile blue crab growth, calcification, physiology; and Megonigal/Neale/Miller of SERC, tidal outwelling of DIC and TA). A concerted effort should be made to identify the regional base of expertise in carbonate chemistry, biogeochemistry, acidification research, and environmental monitoring in and around Chesapeake Bay in order to assess that community's capacity to measure and understand short term and long terms changes in the Bay's carbonate chemistry system. Additionally, a list of experts, potential collaborators and partners, and monitoring programs that are already focused on coastal acidification questions, but in other regions, should be compiled.

#### Charge Question E – What information gaps and data requirements must be considered in the design of a Chesapeake Bay Acidification Network?

- 1. How important is elevated atmospheric  $CO_2$  to  $pCO_2/pH$  of the water? Because many coastal ecosystems experience frequent shifts in pCO<sub>2</sub>/pH that are not the direct effect of a physical exchange of CO<sub>2</sub> across the air:sea interface (e.g., biological activity such as photosynthesis and benthic respiration, export of  $TCO_2$  from land to water via riverine input and tidal exchange), a fuller characterization of carbon flux among environmental compartments is required. Thus, understanding how a changing atmosphere will affect water chemistry requires a better understanding of the processes and mechanisms at work in Chesapeake Bay, many of which are local in nature. Furthermore, it is important to understand the influence of the open ocean acidification signal that is accumulated in offshore ocean water, and then mixed into the Bay.
- 2. How important are the fluxes that cross ecological subsystem boundaries (e.g., land:estuary, sediment:water, ocean: estuary) to carbonate chemistry cycling and fluctuations? Compared to the open ocean, the carbonate chemistry of Chesapeake Bay is far more influenced by chemical constituents that originate on land, bay sediments, intertidal wetlands, and other boundaries of the Bay water column (Fig 1). The global trend of increasing atmospheric CO<sub>2</sub> that drives open ocean acidification will interact with long-term trends in riverine alkalinity export, pCO<sub>2</sub> export from tidal wetlands, and the effects of eutrophication in estuarine sediments, and many other interactions. Management decisions that consider estuarine acidification will need to consider the relative importance of the different drivers of carbonate system change.

- 3. How must CBAN be designed in order to best capture Bay's short term "Weather" variability and long term "Climate" acidification trends? Understanding how "coastal acidification" may change with changing atmospheric pCO<sub>2</sub> requires characterizing both short-term variation (tidal, diurnal, seasonal cycling and dynamics) and long-term trends (directional shifts across years to decades). Detecting long term trends requires that data of adequate accuracy and precision be collected over a long enough period to indicate directional shifts. Such observations are being carried out in open ocean settings on a global scale (e.g., GOA-ON). However, because Chesapeake Bay experiences much greater short term temporal fluctuations and spatial variability in water quality (including its carbonate chemistry) than the open ocean, observations must be far more dense to capture and resolve local and regional phenomena.
- 4. How can existing observing networks (e.g., Eyes on the Bay, MARACOOS) be leveraged and/or complemented to yield data that addresses acidification in Chesapeake Bay? The spatial and temporal coverage of such existing observation can be leveraged by adding new instrumentation to existing water quality stations and vessel-based sampling cruises. Instrumentation is available to reliably measure carbonate chemistry parameters such as pCO<sub>2</sub>, TCO<sub>2</sub>, total alkalinity, (although see discussion of pH measurement in estuaries below). These would be economical add-ons that take advantage of existing infrastructure (e.g., shore-based stations and possibly buoys) and expensive vessel time.
- 5. What investigators/experts and research programs are active in Chesapeake Bay, either working directly on carbonate chemistry/acidification or related areas? This information will be important for gauging the current capacity and expertise to address acidification. Understanding who is working on aspects of this issue will be helpful for building collaborations/partnerships and shoring up deficiencies, perhaps through collaborations with experts outside the region.
- 6. Which combinations of carbonate parameters will yield the most reliable data? Total alkalinity, pH, pCO<sub>2</sub>, and TCO<sub>2</sub> each can be useful, depending on the goal or question, but each has its own challenges, especially in estuarine settings. For example, though pH would seem to be an obvious measurement to make, the measurement is compromised by several characteristics of estuarine system such as heavy biofouling and rapidly changing salinity and ionic strength in both time and space. Chesapeake Bay presents serious challenges for autonomous deployments of pH probes, both for glass bulb and solid state versions. Furthermore, pH probes and dye-based spectrophotometric pH methods have been designed for use in either fresh water or marine water of >20ppt (Dickson, pers. comm.; Yao & Byrne, 2001; Zhang & Byrne, 1996); however, Mosely et al. (2004) demonstrate spectrophotometric pH measurements across an estuarine gradient. From this perspective, pH may not yet be a fully reliable parameter to measure in estuarine settings. Total alkalinity titration of filtered discrete water samples is traditionally used to determine the carbonate buffering capacity of water; however, in some coastal waters organic acids such as humic substances may contribute organic components (non-carbonate alkalinity) to total alkalinity. Work by Cai et al. (1998) concluded that protonation and deprotonation of humic substances occurs rapidly in initial stages of fresh and salt water mixing, such that these organic compounds may not be contributing appreciably to total alkalinity in middle to high salinity bay waters. Partial pressure of  $CO_2$  (**pCO**<sub>2</sub>) is measured accurately via active air:water equilibration in combination with an infrared gas analyzer (IRGA). Although historically this measurement has required a very expensive instrument, modern electronics and IRGAs make this a much more accessible parameter for measurement.  $pCO_2$  has the advantage of being a real time measurement, and one in which the sensor is not in direct contact with the water. Total dissolved inorganic carbon (denoted as  $TCO_2$ ) can also be assessed from discrete water samples that are filtered and sealed to prevent gas exchange with the atmosphere.

7. What are the biological impacts of rising pCO2 and acidification in estuarine systems? To date there are relatively few *in-situ* experimental data related to biological responses to acidification in Chesapeake Bay. Arnold et al. (2012) observed that submerged aquatic plants (Saint Mary's and Severn Rivers, MD) exposed to elevated CO<sub>2</sub> grow substantially faster than under ambient conditions. However, these sea grasses showed significant reductions in concentrations of many carbon-based secondary compounds (e.g., phenolics) that serve as chemical armaments against herbivory and disease. Laboratory experiments by Miller et al. (2009) conducted in mesohaline conditions (18ppt) typical of Chesapeake Bay show that larvae of the native oyster (Crassostrea *virginica*) experience strong reductions in growth and calcification under elevated  $CO_2$  but that the non-native congener species Crassostrea ariakensis showed no such reductions, suggesting species-specific effects may be important in coastal systems. Studies by Ries et al. (2009) suggest that calcification by blue crabs (Callinectes sapidus) and other crustaceans increases at high CO<sub>2</sub> levels. Breitburg and collaborators have been using a flow-through lab-based experimental platform to investigate the combined effects of acidification and dissolved oxygen for species found in Chesapeake Bay. Although, individual species response studies are common in acidification research, few have investigated species assemblage/community level responses in estuarine settings.

#### RECOMMENDATIONS

- 1. The Chesapeake Bay Acidification Network (CBAN) should seek to understand both chemical and biological effects of acidification dynamics, and aim to understand how long term trends in atmospheric CO<sub>2</sub> concentration will affect the Bay's ecosystems.
- 2. Given the widespread ongoing research and monitoring taking place in Chesapeake Bay currently, the opportunities for adding observations and measurements aimed at characterizing the carbonate system dynamics and the underlying mechanistic drivers of carbonate chemistry as it relates to coastal acidification are extensive. Such efforts could leverage the Bay's existing infrastructure and monitoring programs (e.g., existing water quality stations, water quality and oceanographic cruises), thereby rapidly increasing our knowledge about coastal acidification at regional and local scales. MD-DNR's "Eves on the Bay Program" is a good example of an observing network that could be supplemented to begin collecting carbonate chemistry data.
- 3. Amass descriptions of Chesapeake Bay's water quality research programs, monitoring networks and infrastructure that can be leveraged for carbon chemistry observations. This should include measurement and observation platforms such as buoys, piers, land-based water quality stations, ship and boat cruise locations and frequency. The goal is to identify the most promising opportunities to collect new high quality data.
- 4. A list of investigators and laboratories from the Chesapeake Bay region with expertise in carbon chemistry analyses (e.g., pCO<sub>2</sub>, Total CO<sub>2</sub>, Total Alkalinity, and pH) should be collected to assess the region's current capacity to make high quality carbon measurements, to determine the need to develop local and regional expertise, and to promote collaborations with investigators from other regions.
- 5. Research efforts should be focused on understanding and quantifying the flux of inorganic carbon across the ecological subsystems of the Bay watershed that affect acidity in the Bay (e.g., land:bay, ocean:bay, sediment:bay). Cross-boundary fluxes will have strong effects on water chemistry at local, ecologically relevant scales.

- 6. The Long-term goal should be to successfully quantify and attribute carbonate chemistry dynamics to particular drivers such as elevated atmospheric CO<sub>2</sub>, changes in river discharge to the Bay, changes in the pH of ocean water mixing into the Bay, or water column processes such as photosynthesis and respiration.
- 7. Shore-based  $pCO_2$  measurements indicate strong influences of diurnal and tidal cycling, as well as strong seasonal variation. Temporal and spatial variability can be orders of magnitude higher than in the open ocean. Seasonal and interannual dynamics need to be placed in a long-term context through observation with the goal of understanding how such patterns may be trending through time.
- 8. Sources of total alkalinity, a measure of a water body's ability to resist change in pH with changing  $CO_2$  concentrations, need identification and quantification. Alkalinity-generating biogeochemical processes such as sulfate reduction are widespread in Chesapeake Bay and hydrologically coupled tidal saltmarshes. It is likely that tidal wetland soil processes control outwelling of alkalinity and pCO<sub>2</sub> from marshes to adjacent estuaries, and tidal marsh outwelling is important at local and regional scales.
- 9. Efforts should be made to determine the need and feasibility of "weather-" versus "climate-" quality measurements (as defined in the Blue Ribbon Panel report) for characterizing and quantifying carbonate chemistry/acidification in Chesapeake Bay over time and space.
- 10. Caution should be exercised when considering making direct measurements of pH in many reaches of Chesapeake Bay that fall within the oligonaline to lower polyhaline salinity zones (0-20 psu). First, pH probes have been designed specifically for use in fresh water or marine water of salinity  $\geq 20$  psu. Likewise, spectrophotometric/dye pH methods are similarly constrained. At present, the accuracy of pH measurement in waters of 1-20 psu is not well characterized. Second, changing ionic strength (correlated with changing salinity) may adversely affect pH measurements due to differences from calibration solution ionic strength. Third, the physical and chemical influences of biofouling may adversely affect field deployed pH probes, resulting in drift or poor operation. Continued efforts to develop reliable pH measurements should be sought.
- 11. Although there are some technical obstacles in measuring pH in estuarine settings, pH is an important parameter in the carbonate system and continued refinement of pH technology is much needed. Given the uncertainty surrounding pH measurement in the Bay (past and present), any program on estuarine acidification should also measure pCO<sub>2</sub>, TCO<sub>2</sub>, and total alkalinity, all of which are readily available for determining carbonate chemistry. However, the extent and effect of non-carbonate alkalinity on carbonate chemistry calculations should be formally determined. Direct real-time measurements of pCO<sub>2</sub> are taking place in Chesapeake Bay and should be expanded, as measurement of this parameter may avoid a common over-estimation error associated with calculating pCO<sub>2</sub> from pH and alkalinity (Abril et al., 2014).
- 12. Instrumentation, both shore-based and vessel-based, needs to be considered. Opportunities to colocate carbonate chemistry measuring devices with existing water quality stations and cruise opportunities should be explored.
- 13. Current Chesapeake Bay biogeochemical models do not include information on carbonate chemistry; however, as inorganic carbon budgets begin to emerge, these parameters should be added to existing models, especially those being used to understand dissolved oxygen dynamics.

#### REFERENCES

- Abril, G., Bouillon S., Darchambeau, F., Teodoru, C.R., Marwick, T.R., Tamooh, F.,...Borges, A.V. (2014). Technical Note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters. Biogeosciences Discussions, 11, 11701-11725. doi:10.5194/bgd-11-11701-2014
- Arnold, T., Mealey, C., Leahey, H., Miller, A.W., Hall-Spencer, J.M., Milazzo, M., & Maers, K. (2012), Ocean acidification and the loss of phenolic substances in marine plants. PLoS ONE, 7(4), e35107. doi:10.1371/journal.pone.0035107
- Borges, A., & Abril, G. (2011). 5.04-Carbon Dioxide and Methane Dynamics in Estuaries. Treatise on Estuarine and Coastal Science, Volume 5: Biogeochemistry. doi:10.1016/B978-0-12-374711-2.00504-0
- Cai, W.J. (2011). Estuarine and coastal ocean carbon paradox: CO2 sinks or sites of terrestrial carbon incineration? Annual Review of Marine Science, 3, 123-145.
- Cai, W.J. & Reimers, C.E. (1995). Benthic oxygen flux, bottom water oxygen concentration and core top organic carbon content in the deep northeast Pacific Ocean. Deep-Sea Research, 42, 1681-1699.
- Cai, W.J. & Wang, Y. (1998). The chemistry, fluxes and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. Limnology and Oceanography, 43, 657-668.
- Caldeira, K & Wickett, M.E. (2003). Anthropogenic carbon and ocean pH. Nature, 425, 365.
- Caldeira, K. & Wickett, M.E. (2005). Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean, Journal of Geophysical Research - Oceans, 110(C9), C09504. doi:10.1029/2004JC002671
- Doney, S.C., Fabry, V.J., Feely, R.A, & Kleypas, J.A. (2009). Ocean acidification: The other CO<sub>2</sub> problem. Annual Review of Marine Science, 1, 169-192. doi:10.1146/annurev.marine.010908.163834
- Executive Order No. 135083 (2009). Chesapeake Bay Protection and Restoration. Part 6, Protest Chesapeake Bay as the Climate Changes, 3 CFR 13508.
- Feely, R.A., Klinger, T., Newton, J.A., & Chadsey, M. (2012). Scientific summary of ocean acidification in Washington State marine waters. NOAA OAR Special Report.
- Giblin, A. E. (1988). Pyrite formation in marshes during early diagenesis. *Geomicrobiology Journal*, 6, 77-97. doi:10.1080/01490458809377827
- Global Ocean Acidification Observing Network. GOA-ON 2014. www.goa-on.org/
- Hönisch, B., Ridgwell, A., Schmidt, D.N., Thomas, E., Gibbs, S.J., Sluijs A., Zeebe, R., Williams, B. (2012). The geological record of ocean acidification, Science 335, 1058-1063. doi: 10.1126/science.1208277

- Interagency Working Group on Ocean Acidification (IWGOA) 2014. Strategic Plan for Federal Research and Monitoring of Ocean Acidification www.whitehouse.gov/sites/default/files/microsites/ostp/ NSTC/iwg-oa strategic plan march 2014.pdf
- Intergovernmental Panel on Climate Change (IPCC). 2013. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 1535.
- Jordan, T.E. & Weller, D.E. (1996). Human contributions to terrestrial nitrogen flux. Bioscience 46, 655-664. doi: 10.2307/1312895
- Kaushal, S.S., Likens, G.E., Utz, R.M., Pace, M.L., Grese, M., & Yepsen, M. (2013). Increased river alkalinization in the Eastern US. Environmental science & technology, 47(18), 10302-10311. doi: 10.1021/es401046s
- Mid-Atlantic Regional Association for Coastal Ocean Observing System. MARACOOS 2014. http://maracoos.org/mission
- Miller, A.W., Revnolds, A.C., Sobrino, C., & Riedel, G.F. (2009). Shellfish face uncertain future in high CO<sub>2</sub> world: Influence of acidification on oyster larvae calcification and growth in estuaries. PLoS ONE 4(5), e5661. doi:10.1371/journal.pone.0005661
- Mosley, L. M., Husheer, S. L., & Hunter, K. A. (2004). Spectrophotometric pH measurement in estuaries using thymol blue and *m*-cresol purple. Marine chemistry, 91(1), 175-186.
- Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Yool, A. (2005). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature, 437(7059):681-686.
- Raymond, P. A., and Cole, J. J. (2003). Increase in the export of alkalinity from North America's largest river. Science, 301(5629), 88-91.
- Ries, J.B., Cohen, A.L. & McCorkle, D.C. (2009). Marine calcifiers exhibit mixed responses to CO2induced ocean acidification. Geology, 37, 1131-1134.
- Schlesinger, W.H. & Bernhardt, E.S. (2013). Biogeochemistry: An analysis of global change. San Diego, CA: Academic Press.
- Waldbusser, G. G., Voigt, E. P., Bergschneider, H., Green, M. A., & Newell, R. I. (2011). Biocalcification in the eastern oyster (Crassostrea virginica) in relation to long-term trends in Chesapeake Bay pH. Estuaries and Coasts, 34(2), 221-231.
- Washington State Blue Ribbon Panel Report (2012). Ocean Acidification: From Knowledge to Actions, Washington State's Strategic Response. 12-01-015.
- Yao, W., & Byrne, R. H. (2001). Spectrophotometric determination of freshwater pH using bromocresol purple and phenol red. *Environmental science & technology*, 35(6), 1197-1201.

Zhang, H., & Byrne, R. H. (1996). Spectrophotometric pH measurements of surface seawater at in-situ conditions: absorbance and protonation behavior of thymol blue. Marine Chemistry, 52(1), 17-25.

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#### WORKSHOP AGENDA

Alliance for Coastal Technologies Workshop

Science Assessment of Chesapeake Bay Acidification: Towards a Research and Monitoring Strategy

#### 11 March 2014 Smithsonian Environmental Research Center, Edgewater MD

8:00 a.m.	Coffee and continental breakfast			
Overview and background				
8:30 a.m. – 8:45 a.m.	Welcome (NOAA IOOS), Workshop Outline and Objectives, Participant Introductions (Tamburri ACT)			
8:45 a.m. – 9:00 a.m.	Opening Remarks NOAA Ocean Acidification Program (Jewett and Gledhill NOAA)			
9:00 a.m. – 9:30 a.m.	Presentation: Lessons learned from related coastal monitoring efforts (Newton UW/NANOOS)			
9:30 a.m. – 10:00 a.m.	Presentation: State of the Science, ocean acidification observing technologies (Gledhill, NOAA)			
10:00 a.m. – 10:15 a.m.	Break			
Charge Question A - What is cu 10:15 a.m. – 10:25 a.m 10:25 a.m. – 10:35 a.m. 10:35 a.m. – 10:45 a.m. 10:45 a.m. – 12:00 p.m.	<ul> <li>rrently known about acidification of Chesapeake Bay?</li> <li>Presentation: Historic Data on Chesapeake Bay (Waldbusser OSU)</li> <li>Presentation: Coastal Monitoring (Miller SERC)</li> <li>Presentation: Bay Main Stem Measurements (Cai UDE)</li> <li>Group Discussion</li> <li>1. Are coastal ecosystems ever at an air:sea equilibrium?</li> <li>2. What is known about carbonate chemistry, and its variability, in the Bay?</li> <li>3. How do biological and physical processes influence carbonate chemistry in the Bay?</li> <li>4. What is known about benthic processes influences on Bay carbonate chemistry?</li> <li>5. What is known about impacts of riverine input to the carbonate chemistry of the Bay?</li> </ul>			
12:00 p.m. – 1:00 p.m.	Lunch			
Charge Question B – How do bu 1:00 p.m. – 1:15 p.m. 1:15 p.m. – 2:45 p.m.	<ul> <li><i>iological and biogeochemical processes affect acidification in the Bay?</i></li> <li>Presentation: Land:Sea Interactions (Megonigal SERC)</li> <li>Group Discussion</li> <li>1. How do land:sea interactions (such as runoff from fringing habitats) affect carbon budget of the Bay?</li> <li>2. What biological and biogeochemical processes are driving carbonate chemistry of the Bay?</li> <li>3. Is there significant "Blue Carbon" sequestration in the Bay?</li> </ul>			
2:45 p.m. – 3:00 p.m.	Break			
3:00 p.m. – 3:30 p.m.	Visit SERC dock $pCO_2$ installation			

3:00 p.m. – 5:00 p.m.	Visit Global Change Research Wetland
5:30 p.m. – 7:00 p.m.	Reception at new Mathias Laboratory Building, SERC

#### 12 March 2014 Smithsonian Environmental Research Center, Edgewater MD

8:30 a.m. – 9:00 a.m.	Coffee and continental breakfast		
9:00 a.m. – 9:30 a.m.	Review of day one and goals of day two (Miller SERC and Tamburri ACT)		
Charge Question $C$ – Given t information is most urgent fo	he complexities of coastal ocean acidification, what scientific questions and r understanding and predicting future changes in Chesapeake Bay?		
9:30 a.m. – 10:45 a.m.	Group Discussion		
	1. Will sea level rise influence land:sea interactions in a way that affects carbon cycling?		
	2. How might changing precipitation patterns affect riverine input and carbonate chemistry dynamics?		
	3. What will be the effects of multiple stressors (pH/CO <sub>2</sub> , DO, Temp, eutrophication) on the ecology of the Bay?		
10:45 a.m. – 11:00 a.m.	Break		
Charge Question $D$ – What a characterize acidification dy	re the current sources of data and scientific information that could help namics in Chesaneake Bay?		
11.00  a m = 11.10  a m	Presentation: Existing Monitoring/Observations in the Bay		
11.00 a.m. 11.10 a.m.	(Wilson MARACOOS)		
11:10 a.m. – 11:20 a.m.	Presentation: Eves on the Bay (Michael MD DNR)		
11:20 a.m. – 11:30 a.m. VT)	Presentation: VA Shellfish Hatchery Monitoring (Kuhn,		
11:30 a.m. – 12:30 p.m.	Group Discussion		
r.	1. What are the existing water quality monitoring programs around the Bay and where do they operate?		
	<ol> <li>What academic sampling efforts (cruise data, shore-based monitoring) are in operation?</li> </ol>		
12:30 p.m. – 1:30 p.m.	Lunch		

Charge Question E – What are the information gaps and data requirements must be considered if contemplating a Chesapeake Bay Acidification Network? 1:30 p.m. – 2:15 p.m. Group Discussion

1:30 p.m. – 2:15 p.m.	Group Discussion		
	1.	What chemical measurements are required?	
	2.	What are the spatial and temporal resolution and quality	
		requirements for monitoring data?	
	3.	Can existing efforts be augmented/leveraged in an expanded Bay acidification observing network?	
	4.	How should existing and new data be managed, analyzed and	
		disseminated to be of greatest value?	
2:15 p.m. – 2:30 p.m.	Break		

2:30 p.m. – 3:00 p.m. Tamburri ACT)

Conclusions, recommendations and next steps (Miller SERC and

3:00 p.m.

Adjourn

#### 13 March 2014 Chesapeake Bay Laboratory, Solomons MD

9:30 a.m. - 12:00 p.m.

Visit the ACT pCO2 and pH instrument test platform and pH Sensor Verification deployments off CBL Research Pier

#### Acidification of Chesapeake Bay

The combustion of fossil fuels during the past 200+ years has resulted in a significant increase in atmospheric CO<sub>2</sub> from approximately 280 pre-industrially to the current ~400 parts per million by volume (ppmv). Projections of fossil fuel use suggest that atmospheric concentrations may rise as high as 800 or 1000 ppmv in the next 100 years. Since 1800, surface ocean pH has declined  $\sim 0.1$  units, and further reductions of 0.1 to 0.4 units are anticipated due to rising CO<sub>2</sub>. There is widespread concern that these changes will lead to irreversible ecological regime shifts in marine habitats, such as massive reductions in coral reef habitats and the inhibition of other calcifying biota.

However, current predictions regarding the effects of elevated atmospheric CO<sub>2</sub> are driven almost exclusively by the open ocean assumption of an air: water equilibrium, regardless of geographic/oceanographic setting. Such assumptions clearly do not hold in coastal marine habitats, which are influenced substantially by terrestrial and near-shore phenomena, including significant biological perturbation to the water's carbonate chemistry and biogeochemical coupling of land and sea. Relying on the prevailing air:sea equilibrium assumption of open ocean acidification will surely result in unsound ecological predictions in coastal habitats.



To address effects of acidification processes in nearshore ecosystems, we will hold a workshop in Annapolis, MD (March 11-13, 2014). The workshop is designed to assess the science required for understanding coastal acidification in Chesapeake Bay. Chesapeake Bay is the largest and arguably one of the most productive and complex estuaries in North America. Advancing our abilities to measure and understand carbonate chemistry dynamics/acidification in Chesapeake Bay will enable us to make better predictions of ecological/environmental changes here and in other similar coastal ecosystems. A prime goal of the workshop will be to amass information on current monitoring assets, data sources, and data gaps as they relate to measuring and monitoring carbonate chemistry, with an eye toward designing a Chesapeake Bay Monitoring Network (CBAN).



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