UMCES

UNIVERSITY OF MARYLAND CENTER for ENVIRONMENTAL SCIENCE

CHESAPEAKE BAY
WATER QUALITY MONITORING PROGRAM
ECOSYSTEM PROCESSES COMPONENT (EPC)

LEVEL ONE REPORT #33 (INTERPRETIVE)

A Program Supported by the Department of Natural Resources
State of Maryland

December 2016

Ref. No. [UMCES]CBL 2016-079

Maryland Department of Natural Resources

MARYLAND CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

ECOSYSTEMS PROCESSES COMPONENT (EPC)

LEVEL ONE REPORT No. 33 INTERPRETIVE REPORT

(July 1984 – December 2015)

Final Report

PREPARED FOR:

Maryland Department of Natural Resources
Tidewater Ecosystems Assessment
580 Taylor Avenue, D-2
Annapolis, MD 20401

December, 2016

J.M. Testa	Co-Principal Investigator
L.A. Harris	Co-Principal Investigator
W.R. Boynton	Co-Principal Investigator
C.L.S. Hodgkins	Senior Faculty Research Assistant
J.L. Humphrey	Senior Faculty Research Assistant
M.C. Day	Senior Faculty Research Assistant
D. Liang	Research Assistant Professor

University of Maryland Center for Environmental Science
Chesapeake Biological Laboratory (**CBL**)
PO Box 38, 146 Williams Street
Solomons, MD 20688

Technical Report Series No. TS-701-16 of the University of Maryland Center for Environmental Science.

Table of Contents

	Page No.
List of Figures	**ii**
List of Tables	**iv**
Executive Summary	**E-1**
Introduction and Objectives	**1-1**
Initial Investigation into the Next Phase of Water Quality Monitoring for Criteria Assessment in Maryland Coastal Waters	**2-1**
Community Metabolism in the Maryland Portion of the Chesapeake Bay, Coastal Waters, and Tributaries	**3-1**
Coupled Dissolved Oxygen and pH Variability and its Association with Ecosystem Metabolism	**4-1**

Table of Contents

List of Figures		Page No.
1-1	A simplified schematic diagram indicating degradation and restoration trajectories of an estuarine ecosystem.	1-4
2-1	Long term fixed stations and ConMon stations in POTMH, sampling frames for channel and shallow monitoring, and four channel and four shallow stations sampled from the frames.	2-4
2-2	Long term fixed stations and ConMon stations in CHOMH1 & CHOMH2, sampling frames for channel and shallow monitoring, three channel and three shallow stations sampled from the frames.	2-4
2-3	(a) Illustration of ROMS-RCA model grid (with 20 vertical sigma layers) with wet cells in red and (b) schematic diagram of the major state variables and transformation process in RCA, which is an abbreviation for Row-Column Aesop (Testa et al. 2014).	2-5
2-4	Scatter plots of observed bottom O2 at POTMH and CHOMH fixed stations, and the ROMS-RCA estimates within 0.025 decimal degrees, 2 meters in depth and 1 day.	2-6
2-5	Conceptual diagram of the five Chesapeake Bay tidal water designation use zones, with our interpretation of the 30-day DO criteria reported in Batiuk et al. (2009).	2-9
2-6	(a) Cumulative Frequency Diagram (CFD) based on model output in POTMH and (b) the corresponding residual CFD.	2-10
2-7	Residual Cumulative Frequency Diagram (CFD) in POTMH based on model output, and four sampling schemes: (1) Current denotes on four ConMon and four fixed stations (RET2.4, LE2.2, LE2.3 and CB5.3) (2) Channel includes three additional channel stations; (3) Shallow includes four additional shallow stations; (4) Both.	2-12
2-8	Residual Cumulative Frequency Diagram (CFD) in CHOMH1& CHOMH2 based on model output, and four sampling schemes: (1) Current denotes on three ConMon and three fixed stations (ET5.2, EE2.1 and CB4.2E) (2) Channel includes three additional channel stations; (3) Shallow includes four additional shallow stations; (4) Both. The Channel sampling CFD was over plotted by the Channel and Shallow sampling scheme.	2-13
2-9	Residual Cumulative Frequency Diagram (CFD) in POTMH based on the model output, existing efforts, and removal of each fixed station.	2-14
2-10	Residual Cumulative Frequency Diagram (CFD) in CHOMH1 & CHOMH2 based on the model output, existing efforts, and removal of each fixed station.	2-14
2-11	Residual Cumulative Frequency Diagram (CFD) in POTMH based on the model output, existing efforts, and removal of each ConMon station.	2-15
2-12	Residual Cumulative Frequency Diagram (CFD) in CHOMH1 &CHOMH2 based on the model output, existing efforts, and removal of each ConMon station.	2-16
3-1	Map of ConMon stations in Maryland used in development and analysis of ecosystem metabolism.	3-3
3-2	Typical diel dissolved oxygen time-series, showing periods of sunlight and dark (yellow and black bars along the x-axis), and where periods of net oxygen increases (green lines and circles) associated with net primary production and net oxygen decreases (red lines and circles) associated with net respiration occur.	3-4
3-3	Relationship between primary production and respiration across a multitude of ecosystems, where most systems tend to fall on the 1:1 line, where primary production equals reparation (from Testa et al. 2013). Also indicated are broad categories of “trophic state” that reflect the degree of eutrophication in the system. (MERL – Marine Ecosystems Research Laboratory at URI).	3-6

Table of Contents

List of Figures		Page No.
3-4	Relationship between primary production and respiration across all Maryland ConMon stations. Data clustered on the 1:1 line (not drawn) indicate measurements where primary production equals respiration. The fact that many data fall between rates of 0.5 to 1 g C m-2 y-1 indicate the potential for eutrophication at many times and places within Maryland waters (see Figure 3-3). These daily rates are scaled up to annual rates assuming constant daily metabolism and compared to trophic categories from Nixon (1995). While such simple upscaling is unrealistic give high daily variability, we lack estimates of metabolism for every month of the year to do an appropriate upscaling.	3-7
3-5	Time-series of gross primary production rates for two highly eutrophic sites (Sycamore Point in the Corsica River and Fort McHenry in the Patapsco River; top panels), an SAV-dominate site (Susquehanna Flats; bottom left panel), and a tidal freshwater, turbid site (Jug Bay in the upper Patuxent; bottom right panel).	3-9
3-6	Time-series of hourly respiration rates for two highly eutrophic sites (Sycamore Point in the Corsica River and Fort McHenry in the Patapsco River; top panels), an SAV-dominate site (Susquehanna Flats; bottom left panel), and a tidal freshwater, turbid site (Jug Bay in the upper Patuxent; bottom right panel).	3-10
3-7	Relationship of gross primary production rates for all days and all sites in the Maryland ConMon dataset and (top left) water temperature, (top right) salinity, (bottom left) pH, and (bottom right), chlorophyll-a.	3-12
3-8	Relationship of gross primary production rates and salinity for all days and all sites in the Maryland ConMon dataset, where the shading of the circles reflects the temperature for that day (see color bar to the right). Data are divided into temperature ranges below 10 deg C (top left), 10-20 deg C (top right), 20-25 deg C (bottom left), and > 25 deg C (bottom right).	3-13
3-9	Relationship of hourly respiration rates for all days and all sites in the Maryland ConMon dataset and (top left) water temperature, (top right) salinity, (bottom left) pH, and (bottom right), chlorophyll-a.	3-14
3-10	Map of shallow water tributaries where nutrient load estimates are available (left panel) and preliminary relationship of winter-spring total nitrogen load to summer (May to September) gross primary production averages across all data at all stations in a particular tributary (right panel).	3-16
4-1	Map of ConMon stations in Maryland used in the analysis of relationships between DO and pH.	4-3
4-2	Time-series of pH and DO, and the relationship between the two variables, at (top) Sycamore Point in the Corsica river estuary and (bottom) Jug Bay in the Patuxent Estuary.	4-10
4-3	Relationship between 15-minute changes in pH and DO at Sycamore Point in the Corsica River aggregated by month.	4-11
4-4	Mean 15-minute changes in DO (top panel) and pH (bottom panel) for all 110 ConMon stations, organized by month. Blue circles are individual months and stations, while the red line and black dashed lines are the monthly mean and median, respectively, across all stations. Note that fewer ConMon stations are active Nov-Mar.	4-12
4-5	Slope (top panel) and r2 (bottom panel) of correlations between 15-minute changes in DO and pH for all 110 ConMon stations, organized by month. Blue circles are individual months and stations, while the red line and black dashed lines are the monthly mean and median, respectively, across all stations. Note that fewer ConMon stations are active Nov-Mar.	4-13
4-6	Monthly slope of relationship between 15-minute changes in DO versus pH (color scale) versus salinity for all 110 ConMon stations.	4-14

Table of Contents

List of Figures		Page No.
4-7	Monthly averages for the slope of the relationship between 15-minute changes in DO versus pH (left panels), mean15-minute changes in DO (middle panels), and mean15-minute changes in pH (right panels) for a highly eutrophic (top panels, Sycamore Point in the Corsica River) and moderately eutrophic (bottom panels, Chesapeake Biological Laboratory in the Patuxent) ConMon station.	4-16
4-8	Monthly averages for the slope of the relationship between 15-minute changes in DO versus pH (left panels), mean15-minute changes in DO (middle panels), and mean15-minute changes in pH (right panels) for a freshwater (top panels, Jug Bay) and brackish water (bottom panels, Benedict) ConMon station within the same estuary (Patuxent River estuary).	4-17

List of Tables		Page No.
2-1	Definitions of queries for long term, new channel, ConMon, new shallow stations and the entire model grid.	2-7
2-2	Interpretations of the 30-day DO criteria and definition of habitats in POTMH and CHOMH1&2.	2-9
4-1	Summary statistics for DO and pH across 110 ConMon stations	4-4

Executive Summary 2016

The analytical work conducted by the Ecosystem Processes Component (EPC) of the Chesapeake Bay Water Quality Monitoring Program during FY 2016 encompassed four distinct efforts and these included the following:

1. Continuation and enhancement of the analysis of ConMon data from FY2014, but with a new emphasis on analyses to inform the development of the next-phase water-quality monitoring program in Maryland. In FY2016, we initialized an investigation into the most efficient and effective use of ConMon, continuous profiler deployments, and DATAFLOW in concert with the fixed station monitoring to quantify criteria failure in several Chesapeake Bay water-quality segments.

2. The development of an enhanced, flexible tool to compute estimates of gross primary production, respiration, and net ecosystem metabolism from oxygen, salinity, and temperature data at stations in the ConMon program. This tool builds on previous efforts to derive metabolic estimates from oxygen time-series and has resulted in an interactive tool to explore patterns of metabolism in space and time in Maryland waters, including long-term trends in metabolism at sites where the data allow.

3. An analysis of the ConMon data to quantify the nature and correspondence between DO and pH at all ConMon stations in the Maryland waters of Chesapeake Bay. This analysis included an examination of the relationships between DO and pH changes, as well as an assessment of the vulnerability of all ConMon sites to extreme high or low levels of pH, which can impact both habitat, the early life histories of important estuarine species, and biogeochemical cycling.

4. PI Testa of the EPC program continued his co-chairmanship of the Chesapeake Bay Program Integrated Trends Analysis Team, with PI Harris began her leadership of an ITAT-supported investigation into watershed-estuary interactions in the Potomac River.

In the following section key findings from the FY 2016 EPC work are summarized:

Analysis of Monitoring Program Design for Dissolved Oxygen Criteria Assessments:

- We utilized output from a dynamic biogeochemical model for Chesapeake Bay with ConMon and fixed station monitoring data to conduct an analysis of the suitability of different monitoring efforts to quantify oxygen criteria failure in the lower Potomac and Choptank Rivers.
- We considered three scenarios of increased monitoring effort: (1) more channel monitoring with the same frequency as the nearest long term station, (2) more shallow monitoring with high temporal resolution and (3) both. We also considered two scenarios of reduced monitoring effort by removing (4) each fixed or (5) ConMon station in turn from the each segment. Finally, we considered the unrealistic scenario of (6) monitoring covering all cells within each segment, which served as the "true" state of the ecosystem with which to compare to monitoring designs.

- Our approach of leveraging model and empirical data to assess monitoring design targeted water quality criteria that are specifically used to determine compliance with regulatory structures. Our proof of concept of this approach in two segments successfully demonstrated how results can lead to a variety of insights. For the 30-day criteria, it is clear that sampling design is sensitive to placement of deep water stations.

Community Metabolism in Maryland Tidal Waters:

- This effort included the development of a new tool to compute rates of gross primary production, respiration, and net ecosystem metabolism across 105 ConMon stations in the Maryland portion of Chesapeake Bay and its tributaries. We examined time-series of these metabolic rates across several stations and quantitatively related these rates to nutrient loading rates at a select group of stations. We also conducted an examination of spatial patterns in metabolic rates in relation to other environmental variables (temperature, pH, salinity).
- We completed a new script in Matlab software to automate computations of gross primary production, respiration, and net ecosystem metabolism from time-series of dissolved oxygen, temperature, and salinity data provided by ConMon monitoring systems. This code also aggregates other environmental variables from ConMon (pH, chlorophyll-a) and utilizes a separate wind speed data set to make the metabolic computations.
- We found clear relationships between metabolic rates and water temperature, salinity, and pH across all stations, but there were no clear temporal trends in metabolic rates for the vast majority of locations.
- We found that rates of metabolism were generally higher in high-nutrient systems, as well as in intermediate salinity stations where nutrients were high, but turbidity was relatively low.
- Future efforts will examine time-series of these rate data (especially at sentinel sites) to look for changes in trophic estimates over time that may be associated with changes in nutrient loading rates caused by management actions.

Relationships between DO and pH across ConMon stations:

- We quantified the nature and correspondence between DO and pH at 110 ConMon stations in the Maryland waters of Chesapeake Bay to examine seasonal patterns, temporal trends, and the vulnerability to extreme high or low pH values.
- There is a rich dataset for pH and dissolved oxygen in the Maryland ConMon database that allows for an analysis of the relationship between metabolism and pH changes.
- It appears that low-salinity regions show the largest changes in pH for a given change in oxygen, suggesting that reduced buffering capacity may make these sites more vulnerable to pH swings.
- Highly eutrophic stations reveal large swings in pH associated with CO_2 uptake and release, and pH tends to peak at these stations in spring months, where CO_2 uptake is high, but respiration-associated CO_2 production is low.
- Future analysis could consider spatial patterns in aragonite $CaCO_3$ saturation state because this metric could be computed from a full suite of carbonate system

parameters and would provide an index of habitat suitability for shell-forming organisms (e.g., oysters).

Synergistic Efforts:

- Jeremy Testa and Lora Harris co-chaired a session called "Ecological modelling and environmental management" at the International Society for Ecological Global Modelling Conference, Baltimore, MD.
- Jeremy Testa participated in and gave a presentation at the USEPA Chesapeake Bay Program STAC Workshop "Comparison of Shallow Water Models for Use in Supporting Chesapeake Bay Management Decision-making" at the Virginia Institute of Marine Sciences in April 2016.
- PI Testa of the EPC program continued his co-chairmanship of the Chesapeake Bay Program Integrated Trends Analysis Team.
- PI Testa participated in the STAC workshop "Conowingo Infill Influence on Chesapeake Water Quality" on January 13-14 2016 and made a presentation entitled "Sediment Nutrient Fluxes in the tidal Chesapeake Bay", which he co-authored with PI Boynton.
- PI Testa made a presentation to the USEPA Chesapeake Bay Program Modeling Workgroup on Jan 20, 2016 on aspects of modeling the Conowingo Reservoir and shallow waters of the Chesapeake Bay.
- PI Testa co-authored the draft report summarizing the USEPA Chesapeake Bay Program STAC workshop "Conowingo Infill Influence on Chesapeake Water Quality"
- PI Testa continued his collaboration with NOAA to make annual forecasts of the Chesapeake Bay hypoxic volume in June 2016, where he forecasted anoxic volumes for the early and late summer periods.
- PI Harris is team leader for a synthesis effort focused on the Potomac to support goals of the Integrated Trends Analysis Team.
- PI Harris continues to participate as a member of the Chesapeake Bay Program's Submerged Aquatic Vegetation Workgroup
- Dong Liang gave a presentation entitled "Leveraging a water quality model and monitoring data set to test sampling schemes that support evaluation of water quality criteria in the Chesapeake Bay" at the Chesapeake Modeling Symposium in Williamsburg, VA in June 2016. This presentation highlighted EPC work on the enhanced monitoring program.
- PI Boynton continued active service related to Bay issues on the MD-DC Nature Conservancy Board and on the Alliance for the Chesapeake Bay Board
- PI Boynton presented a talk concerning Bay ecology and restoration to the LEAD Maryland group, June, Solomons, MD
- PI Boynton continued service on the Bay Trust Fund Science Advisory Board
- Ms. Melissa Day attended the second PAXCON conference focused on developing a network of researchers, educators, and managers in the Patuxent watershed.

Chapter 1

Introduction and Objectives

J.M. Testa, L.A. Harris, W.R. Boynton, D. Liang, C.L.S. Hodgkins, J.L. Humphrey, and M.C. Day

1-1 BACKGROUND AND THE ECOSYSTEM PROCESSES COMPONENT (EPC) OF THE BIOMONITORING PROGRAM..... 1

1-2 NUTRIENT EFFECTS AND CONCEPTUAL MODEL OF WATER QUALITY PROCESSES IN CHESAPEAKE BAY SYSTEMS..... 3

1-3 GENERAL AND SPECIFIC OBJECTIVES OF THE EPC PROGRAM..... 5

1-4 REFERENCES..... 6

1-1 Background and the Ecosystem Processes Component (EPC) of the Biomonitoring Program

The first phase of the Chesapeake Bay Program was undertaken during a period of four years (1984 - 1987) and had as its goal the characterization of the existing state of the bay, including spatial and seasonal variation in water quality, living resources, and biogeochemical processes, which were keys to the identification of problem areas. During this phase of the program, the EPC measured sediment-water oxygen and nutrient exchange rates and determined the rates at which organic and inorganic particulate materials reached deep waters and bay sediments. Sediment-water exchanges and depositional processes are major features of estuarine nutrient cycles and play an important role in determining water quality and habitat conditions. The results of this EPC monitoring have been summarized in a series of interpretive reports (Boynton et al., annually from 1984 through 2011; and Bailey et al., 2008), and have been extremely useful in recent assessments of long-term changes in various regions of the Bay (e.g., Back River, mainstem Chesapeake Bay). The results of this characterization effort have confirmed the importance of deposition and sediment processes in determining water quality and habitat conditions. Furthermore, it is also now clear that these processes are responsive to changes in nutrient loading rates (Boynton and Kemp, 2008). Much of these data played a key role in formulating, calibrating and verifying Chesapeake Bay water quality models and these data are continuing to be used as the "gold standard" against which the sediment model is further tested and refined (e.g., Brady et al., 2013; Testa et al., 2013). We have also created a web-accessible and complete Chesapeake Bay sediment flux data base that is available to all interested parties (www.gonzo.cbl.umces.edu).

The second phase of the program effort, completed during 1988 through 1990, identified interrelationships and trends in key processes monitored during the initial phase of the program. The EPC was able to identify trends in sediment-water exchanges and deposition rates. Important factors regulating these processes have also been identified and related to water quality conditions

(Kemp and Boynton, 1992; Boynton et al., 1991; Cowan and Boynton, 1996; Boynton and Kemp, 2008).

In 1991 the program entered its third phase. During this phase the long-term 40% nutrient reduction strategy for the bay was re-evaluated. In this phase of the process, the monitoring program was used to assess the appropriateness of targeted nutrient load reductions as well as provide indications of water quality patterns that will result from such management actions. The preliminary re-evaluation report (Progress Report of the Bay-wide Nutrient Reduction Reevaluation, 1992) included the following conclusions: nonpoint sources of nutrients contributed approximately 77% of the nitrogen and 66% of the phosphorus entering the bay; agricultural sources were dominant followed by forest and urban sources; the "controllable" fraction of nutrient loads was about 47% for nitrogen and 70% for phosphorus; point source reductions were ahead of schedule and diffuse source reductions were close to projected reductions; further efforts were needed to reduce diffuse sources; significant reductions in phosphorus concentrations and slight increases in nitrogen concentrations have been observed in some areas of the bay; areas of low dissolved oxygen have been quantified and living resource water quality goals established; simulation model projections indicated significant reductions in low dissolved oxygen conditions associated with a 40% reduction of controllable nutrient loads. These results have recently been re-evaluated, modified and new goals established since 1991.

During the latter part of 1997, the Chesapeake Bay Program entered another phase of re-evaluation. Since the last evaluation, programs had collected and analyzed additional information, nutrient reduction strategies had been implemented and, in some areas, habitat improvements had been accomplished. The overall goal of the 1997 re-evaluation was the progress assessment of the program and the implementation of necessary modifications to the difficult process of restoring water quality, habitats and living resources in Chesapeake Bay. During this portion of the program, EPC was further modified to include 1) development of intensive spatial water quality mapping; 2) intensive examination of SAV habitat conditions in major regions of the Chesapeake Bay and development of a high frequency shallow water monitoring protocol (ConMon) that has been extensively implemented in many regions of the Bay and tributary rivers.

During the past several years (2008-2016) the EPC of the Biomonitoring Program has further evolved to focus on data analysis of water quality issues. Specifically, the EPC has accomplished the following: 1) rescued a rare, high quality, near-continuous and long-term water quality data set collected in the mesohaline portion of the Patuxent estuary from 1963-1969 and made this data set generally available; 2) examined multiple sites using dataflow results for a better understanding of the spatial features of water quality and factors, both local and remote, influencing these water quality distributions; 3) used ConMon data sets to assess DO criteria attainment and duration of low DO events in near-shore areas using a variety of computational approaches; 4) developed an algorithm for computing community-scale primary production and respiration using ConMon data for purposes of developing another metric of water quality and relating these fundamental ecosystem processes to important controlling factors such as nutrient loading rates, and 5) Combined numerical model simulations with fixed station, ConMon, and dataflow records to quantify different monitoring schemes in the Bay's numerous water quality segments. The specific goals of the FY2016 EPC Program are provided later in this chapter.

The Chesapeake Bay Water Quality Monitoring Program was initiated to provide guidelines for restoration, protection and future use of the mainstem estuary and its tributaries and to provide evaluations of implemented management actions directed towards alleviating some critical pollution problems. A description of the complete monitoring program, which has evolved substantially over time, is provided in the following documents: Magnien et al. (1987), Chesapeake Bay program web page: http://www.chesapeakebay.net/about/programs/monitoring

In addition to the EPC program portion, the monitoring program also has components that measure:

1. Freshwater, nutrient and other pollutant input rates at 9 river fall line locations.
2. Chemical, biological and physical properties of the water column at fixed locations in the mainstem Bay and tributary rivers.
3. High frequency (15 minute intervals) chemical, biological and physical properties of the water column at selected shallow water locations (ConMon Program) and high spatial resolution (Dataflow Program) surface water properties also at selected locations.
4. Benthic community characteristics (abundances, biomass and indices of health).
5. SAV distribution and density

1-2 Nutrient Effects and Conceptual Model of Water Quality Processes in Chesapeake Bay Systems

During the past three to four decades much has been learned about the effects of natural and anthropogenic nutrient inputs (e.g., nitrogen, phosphorus, silica) on such important estuarine features as phytoplankton production, algal biomass, seagrass abundance and distribution and oxygen conditions in deep waters (Nixon, 1981, 1988; Boynton et al., 1982; Kemp et al., 1983; D'Elia et al., 1983; Garber et al., 1989; Malone, 1992; Kemp and Boynton, 1992; Boynton and Kemp, 2008; Boynton et al., 2013). While our understanding is not complete, important pathways regulating these processes have been identified and related to water quality issues. Of particular importance here, it has been determined that 1) algal primary production and biomass levels in many estuaries (including Chesapeake Bay) are responsive to nutrient loading rates, 2) high rates of algal production and algal blooms are sustained through summer and fall periods by recycling of essential nutrients that enter the system during the high flow periods of the year, 3) the “nutrient memory” of estuarine systems is relatively short (one to several years for nitrogen and longer for phosphorus), 4) submerged aquatic vegetation (SAV) communities are responsive to water quality conditions, especially light availability, that is modulated both by water column turbidity regimes and epiphytic fouling on SAV leaf surfaces and 5) dissolved oxygen regimes are influenced both by the biology and physics of these systems and that near-shore and off-shore DO regimes exhibit important differences.

Nutrients and organic matter enter the bay from a variety of sources, including sewage treatment plant effluents, fluvial inputs, local non-point drainage and direct rainfall on bay waters. Dissolved nutrients are rapidly incorporated into particulate matter via biological, chemical and physical mechanisms. A portion of this newly produced organic matter sinks to the bottom, decomposes and thereby contributes to the development of hypoxic or anoxic conditions and loss of habitat for important infaunal, shellfish and demersal fish communities. Eutrophic (nutrient enriched) conditions favor the growth of a diverse assemblage of estuarine bacteria who play a major role in

consuming dissolved oxygen and the subsequent development of hypoxic and anoxic conditions. The regenerative and large short-term nutrient storage capacities of estuarine sediments ensure a large return flux of nutrients from sediments to the water column that can sustain continued high rates of phytoplanktonic growth and biomass accumulation. Continued growth and accumulation supports high rates of deposition of organics to deep waters, sustaining hypoxic and anoxic conditions typically associated with eutrophication of estuarine systems. To a considerable extent, it is the magnitude of these processes that determines water quality conditions in many zones of the bay. Ultimately, these processes are driven by inputs of organic matter and nutrients from both natural and anthropogenic sources. If water quality management programs are instituted and loadings of organic matter and nutrients decrease, changes in the magnitude of these processes are expected and will serve as a guide in determining the effectiveness of strategies aimed at improving bay water quality and habitat conditions. The schematic diagram in Figure 1-1 summarizes this conceptual eutrophication model where increased nitrogen (N) and phosphorus (P) loads result in a water quality degradation trajectory and reduced N and P loads lead to a restoration trajectory. There is ample empirical evidence for the importance of N and P load variation. For example, water quality and habitat conditions change dramatically between wet and dry years, with the former having degradation trajectory characteristics and the latter, restoration trajectory characteristics (Boynton and Kemp, 2000; Hagy et al., 2004; Kemp et al., 2005). However, the exact temporal sequence of restoration may range from simple and rapid reversals to complex and lengthy processes (Kemp and Goldman, 2008). Recent research efforts by members of this group have sought to better understand these feedbacks (Testa et al. 2014; Harris et al. 2015).

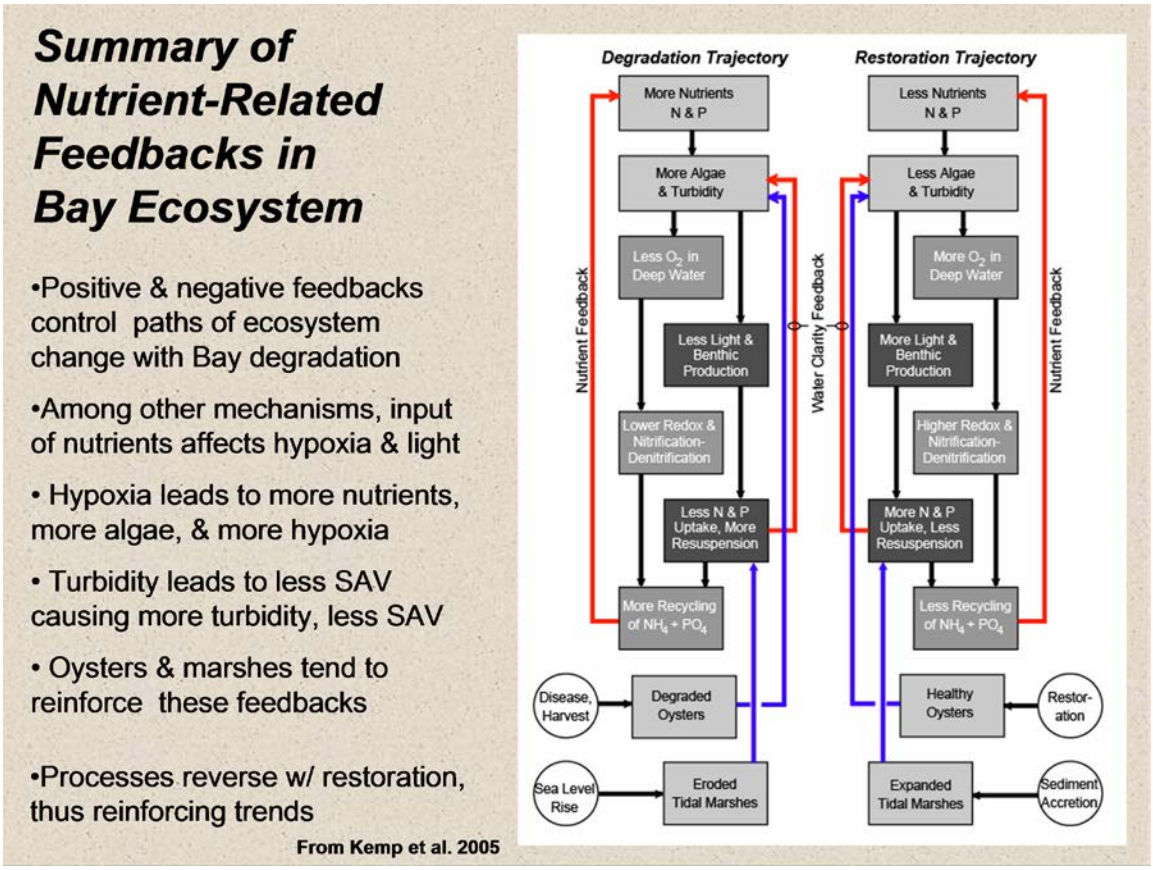

Figure 1-1. A simplified schematic diagram indicating degradation and restoration trajectories of an estuarine ecosystem. Figure was adapted from Kemp et al., 2005.

Within the context of this conceptual model, monitoring program data analysis has focused on SAV and other near-shore contemporary and historical habitat and water quality conditions to evaluate water quality criteria attainment. Recent EPC efforts have addressed management needs to understand the relative importance of local or regional drivers in controlling water quality and how quickly the biotic system may respond to changes in nutrient or sediment inputs from the watershed. Given the growing realization of the effects of climatic (i.e., "unmanageable") forces in driving variability in water quality and potentially masking trends associated with nutrient reduction efforts, we have focused on understanding the competing roles of climate and nutrient-driven biogeochemical processes in FY2016.

1-3 General and Specific Objectives of the EPC Program

The EPC has undergone multiple and significant program modification since its inception in 1984 but its overall objectives have remained consistent with those of other Monitoring Program Components. The specific objectives of the FY2016 EPC program were as follows:

1. Continued and enhanced the analysis of CONMON data from FY2014, but with a new emphasis on analyses to inform the development of the next-phase water-quality monitoring program in Maryland. In FY2016, we initialized an investigation into the most efficient and effective use of CONMON, continuous profiler deployments, and DATAFLOW in concert with the fixed station monitoring to quantify criteria failure in several Chesapeake Bay water-quality segments.
2. The development of an enhanced, flexible tool to compute estimates of gross primary production, respiration, and net ecosystem metabolism from oxygen, salinity and temperature data at stations in the CONMON program. This built on previous efforts to derive metabolic estimates from oxygen time-series and resulted in a tool to explore patterns of metabolism in space and time in Maryland waters, including long-term trends in metabolism at sites where the data allow.
3. Continued involvement in Bay Program workgroup exploring Bay program data for trends and explanation of trends in Bay water and habitat quality (ITAT). EPC Program PIs (JMT, LAH) continued their participation in STAC. This effort tied EPC activities to those of criteria assessment, trend analyses, land-estuarine linkages and other water quality issues investigated or reviewed by various Bay Program workgroups and formal committees.
4. Continue COORDINATION with other components of the Maryland Chesapeake Bay Water Quality Monitoring Program
5. Activities in the EPC program were coordinated with other components of the Maryland Chesapeake Bay Water Quality Monitoring Program. To be more explicit, during the FY2016 effort we used data from the River Input monitoring program, the Chesapeake Bay environmental modeling packages (estuary, watershed), NOAA buoy deployments (CBIBS), the long-term Biomonitoring program, ConMon program and Dataflow program. During the past several years we have become more skilled at efficiently obtaining and utilizing these diverse data sets.

1-4 References

Boynton et al., 1984 – 2015 EPC Interpretive Reports:

Boynton, W.R., W.M. Kemp, L. Lubbers, K.V. Wood and C.W. Keefe. 1984. Ecosystem Processes Component Level I Data Report No. 1. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 84-109.

Boynton, W.R., W.M. Kemp and J.M. Barnes. 1985. Ecosystem Processes Component Level I Data Report No. 2. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 85-121.

Boynton, W.R., W.M. Kemp, J.H. Garber and J.M. Barnes. 1986. Ecosystem Processes Component Level 1 Interpretive Report No. 3. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 86-56b.

Boynton, W.R., W.M. Kemp, J.H. Garber, J.M. Barnes, L.L. Robertson and J.L. Watts. 1987. Ecosystem Processes Component Level 1 Interpretive Report No. 4. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 88-06.

Boynton, W.R., W.M. Kemp, J.H. Garber, J.M. Barnes, L.L. Robertson and J.L. Watts. 1988. Ecosystem Processes Component Level 1 Interpretive Report No. 5. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 88-69.

Boynton, W.R., J.H. Garber, W.M. Kemp, J.M. Barnes, J.L. Watts, S. Stammerjohn and L.L. Matteson. 1989. Ecosystem Processes Component Level 1 Interpretive Report No. 6. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 89-080.

Boynton, W.R., J.H. Garber, W.M. Kemp, J.M. Barnes, L.L. Matteson, J.L. Watts, S. Stammerjohn and F.M. Rohland. 1990. Ecosystem Processes Component Level 1 Interpretive Report No. 7. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 90-062.

Boynton, W.R., W.M. Kemp, J.M. Barnes, L.L. Matteson, J.L. Watts, S. Stammerjohn, D.A. Jasinski and F.M. Rohland. 1991. Ecosystem Processes Component Level 1 Interpretive Report No. 8. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 91-110.

Boynton, W.R., W.M. Kemp, J.M. Barnes, L.L. Matteson, J.L. Watts, S. Stammerjohn, D.A. Jasinski and F.M. Rohland. 1992. Ecosystem Processes Component Level 1 Interpretive Report No. 9. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 92-042.

Boynton, W.R., W.M. Kemp, J.M. Barnes, L.L. Matteson, F.M. Rohland, D.A. Jasinski and H.L. Kimble. 1993. Ecosystem Processes Component Level 1 Interpretive Report No. 10. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 93-030a.

Boynton, W.R., W.M. Kemp, J.M. Barnes, L.L. Matteson, F.M. Rohland, D.A. Jasinski and H.L. Kimble. 1994. Ecosystem Processes Component Level 1 Interpretive Report No. 11. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 94-031a.

Boynton, W.R., W.M. Kemp, J.M. Barnes, L.L. Matteson, F.M. Rohland, L.L. Magdeburger and B.J. Weaver. 1995. Ecosystem Processes Component Level 1 Interpretive Report No 12. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 95-039.

Boynton, W.R., W.M. Kemp, J.M. Barnes, L.L. Matteson, F.M. Rohland, D.A. Jasinski, J.D. Hagy III, L.L. Magdeburger and B.J. Weaver. 1996. Ecosystem Processes Component Level 1 Interpretive Report No. 13. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCEES]CBL 96-040a.

Boynton, W.R., J.M. Barnes, F.M. Rohland, L.L. Matteson, L.L. Magdeburger, J.D. Hagy III, J.M. Frank, B.F. Sweeney, M.M. Weir and R.M. Stankelis. 1997. Ecosystem Processes Component Level 1 Interpretive Report No. 14. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCEES]CBL 97-009a.

Boynton, W.R., R.M. Stankelis, E.H. Burger, F.M. Rohland, J.D. Hagy III, J.M. Frank, L.L. Matteson and M.M. Weir. 1998. Ecosystem Processes Component Level 1 Interpretive Report No. 15. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCES]CBL 98-073a.

Boynton, W.R., R.M. Stankelis, J.D. Hagy III, F.M. Rohland, and J.M. Frank. 1999. Ecosystem Processes Component Level 1 Interpretive Report No. 16. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCES]CBL 99-0070a.

Boynton, W.R., R.M. Stankelis, J.D. Hagy, F.M. Rohland, and J.M. Frank. 2000. Ecosystem Processes Component Level 1 Interpretive Report No. 17. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCES]CBL 00-0174.

Boynton, W.R., R.M. Stankelis, F.M. Rohland, J.M. Frank and J.M. Lawrence. 2001. Ecosystem Processes Component Level 1 Interpretive Report No. 18. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCES]CBL 01-0088.

Boynton, W.R., R.M. Stankelis, F.M. Rohland, J.M. Frank, J.M. Lawrence and B.W. Bean. 2002. Ecosystem Processes Component Level 1 Interpretive Report No. 19. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCES]CBL 02-0125a.

Boynton, W.R. and F.M. Rohland (eds.); R.M. Stankelis, E.K. Machelor Bailey, P.W. Smail and M.A.C. Ceballos. 2003. Ecosystem Processes Component (EPC). Level 1 Interpretive Report No. 20. Chesapeake Biological Laboratory (CBL), Univ. of Maryland Center for Environmental Science, Solomons, MD 20688-0038. Ref. No. [UMCES]CBL 03-303. [UMCES Technical Series No. TS-419-03-CBL].

Boynton, W.R., R.M. Stankelis, P.W. Smail and E.K. Bailey. 2004. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 21. Jul. 1984 - Dec. 2003. Ref. No. [UMCES] CBL 04-086. [UMCES Technical Series No. TS-447-04-CBL].

Boynton, W.R., R.M. Stankelis, P.W. Smail, E.K. Bailey and H.L. Soulen. 2005. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 22. Jul. 1984 - Dec. 2004. Ref. No. [UMCES] CBL 05-067. [UMCES Technical Series No. TS-492-05-CBL].

Boynton, W.R., P.W. Smail, E.M. Bailey and S.M. Moesel. 2006. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 23. Jul. 1984 - Dec. 2005. Ref. No. [UMCES] CBL 06-108. [UMCES Technical Series No. TS-253-06-CBL].

Boynton, W.R., E.M. Bailey, S.M. Moesel, L.A. Moore, J.K. Rayburn, L.A. Wainger and K.V. Wood. 2007. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 24. Jul. 1984 - Dec. 2006. Ref. No. [UMCES] CBL 07-112. [UMCES Technical Series No. TS-536-07-CBL].

Bailey, E.M., M.A.C. Ceballos and W.R. Boynton. 2008. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 25. Jul. 1984 - Dec. 2007. Ref. No. [UMCES] CBL 08-080. [UMCES Technical Series No. TS-565-08-CBL].

Boynton, W.R., L.A. Wainger, E.M. Bailey and M.A.C Ceballos. 2009. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 26. Jul. 1984 - Dec. 2008. Ref. No. [UMCES] CBL 09-082. [UMCES Technical Series No. TS-583-09-CBL].

Boynton, W.R., L.A. Wainger, E.M. Bailey, A.F. Drohan and A.R. Bayard. 2010. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 26. Jul. 1984 - Dec. 2009. Ref. No. [UMCES] CBL 10-098. [UMCES Technical Series No. TS-606-10-CBL].

Boynton, W.R., L.A. Wainger, E.M. Bailey, A.R. Bayard, C.L. Sperling and M.A.C. Ceballos. 2011. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 28. Jul. 1984 – Dec. 2010. Ref. No. [UMCES] CBL 11-024. [UMCES Technical Series No. TS-620-11-CBL].

Boynton, W.R., L.A. Wainger, E.M. Bailey, A.R. Bayard, C.L.S.Hodgkins and M.A.C. Ceballos. 2012. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 29. Jul. 1984 – Dec. 2011. Ref. No. [UMCES] CBL 12-020. [UMCES Technical Series No. TS-637-12-CBL].

Boynton, W.R., L.A. Wainger, C.A. O'Leary, C.L.S. Hodgkins, A.R. Bayard and M.A.C. Ceballos. 2013. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 30. Jul. 1984 – Dec. 2012. Ref. No. [UMCES] CBL 2013-055. [UMCES Technical Series No. TS-655-13].

Boynton, W.R., J.M. Testa, C.L.S. Hodgkins, J.L. Humphrey and M.A.C. Ceballos. 2014. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 31. Jul. 1984 – Dec. 2013. Ref. No. [UMCES] CBL 2014-051. [UMCES Technical Series No. TS-645-14].

Testa, J.M., L.A. Harris, W.R. Boynton, C.L.S. Hodgkins, J.L. Humphrey and M.C. Day. 2015. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 32. Jul. 1984 – Dec. 2014. Ref. No. [UMCES] CBL 2015-043. [UMCES Technical Series No. TS-674-15].

Chapter 1 Text References:

Brady, D.C., J.M. Testa, D.M. Di Toro, W.R. Boynton, and W.M. Kemp. 2013. Sediment flux modeling: Calibration and application for coastal systems. Estuarine, Coastal and Shelf Science 117: 107-124.

Boynton, W.R., J.M. Testa, and W.M. Kemp. 2009. An Ecological Assessment of the Corsica River Estuary and Watershed Scientific Advice for Future Water Quality Management. Final Report to the Maryland Department of Natural Resources, Annapolis, MD, Ref. No. [UMCES]CBL 09-117.

Boynton, W. R., W. M. Kemp, and C. W. Keefe. 1982. A comparative analysis of nutrients and other factors influencing estuarine phytoplankton production, p. 69-90. In: V.S. Kennedy (ed.) Estuarine Comparisons. Academic Press, New York.

Boynton, W.R. and W.M. Kemp. 2000. Influence of river flow and nutrient loading on selected ecosystem processes: a synthesis of Chesapeake Bay data. pp. 269-298 *In:* J. Hobbie Ed. *A Blueprint for Estuarine Synthesis.* Beckman Center, University of California at Irvine, CA. [UMCES Contribution No. 3224-CBL].

Boynton, W.R. and Kemp, W.M. 2008. Estuaries, pp. 809-856. In: Capone, D.G., Bronk, D.A., Mulholland, M.R., and Carpenter, E.J. (Eds.), Nitrogen in the Marine Environment 2nd Edition. Elsevier Inc., Burlington, Massachusetts.

Boynton, W.R., C.L.S. Hodgkins, C.A. O'Leary, E.M. Bailey, A.R. Bayard and L.A. Wainger. 2014. Multi-decade Responses of a Tidal Creek System to Nutrient Load Restrictions: Mattawoman Creek, Maryland USA. 37(1): 111-127.

Cowan, J.L.W. and Boynton, W.R., 1996. Sediment-water oxygen and nutrient exchanges along the longitudinal axis of Chesapeake Bay: Seasonal patterns, controlling factors, and ecological significance. Estuaries 19(3): 562-580.

D'Elia, C.F., D.M. Nelson, and W.R. Boynton. 1983. Chesapeake Bay nutrient and plankton dynamics: III. The annual cycle of dissolved silicon. Geochim. Cosmochim. Acta 14:1945-1955.

Garber, J.H., W.R. Boynton, J.M. Barnes., L.L. Matteson., L.L. Robertson., A.D. Ward and J.L. Watts. 1989. Ecosystem Processes Component and Benthic Exchange and Sediment Transformations. Final Data Report. Maryland Department of the Environment. Maryland Chesapeake Bay Water Quality Monitoring Program. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No.[UMCEES]CBL 89-075.

Hagy, J. D., W. R. Boynton, C. W. Keefe and K. V. Wood. 2004. Hypoxia in Chesapeake Bay, 1950-2001: Long-term change in relation to nutrient loading and river flow. Estuaries 27(4): 634-658.

Harris, L.A., C.L.S. Hodgkins, M.C. Day, D. Austin, J.M. Testa, W. Boynton, L. Van Der Tak, and N.W. Chen. 2015. Optimizing recovery of eutrophic estuaries: Impact of destratification and re-aeration on nutrient and dissolved oxygen dynamics. Ecological Engineering. 75:470-483. DOI: 10.1016/j.ecoleng.2014.11.028

Kemp, W.M., W.R. Boynton, J.C. Stevenson, R.W. Twilley and J.C. Means. 1983. The decline of submerged vascular plants in Chesapeake Bay: summary of results concerning possible causes. Mar. Tech. Soc. J. 17(2):78-89.

Kemp, W.M. and W.R. Boynton. 1992. Benthic-Pelagic Interactions: Nutrient and Oxygen Dynamics. In: D.E. Smith, M. Leffler and G. Mackiernan [Eds.], Oxygen Dynamics in the Chesapeake Bay: A synthesis of Recent Research. Maryland Sea Grant Book, College Park, MD, p. 149-221.

Kemp, W. M., W. R. Boynton, J. E. Adolf, D. F. Boesch, W. C. Boicourt, G. Brush, J. C. Cornwell, T. R. Fisher, P. M. Glibert, J. D. Hagy, L. W. Harding, E. D. Houde, D. G. Kimmel, W. D. Miller, R. I. E. Newell, M. R. Roman, E. M. Smith, and J. C. Stevenson. 2005. Eutrophication of Chesapeake Bay: Historical trends and ecological interactions. Mar. Ecol. Prog. Ser. 303: 1-29.

Kemp, W. M. and E. B. Goldman. 2008. Thresholds in the recovery of eutrophic coastal ecosystems: a synthesis of research and implications for management. Maryland Sea Grant Publication Number UM-SG-TS-2008-01. 46 pp.

Magnien R.E., R.M. Summers, M.S. Haire, W.R. Boynton, D.C. Brownlee, A.F. Holland, F. Jacobs, W.M. Kemp, K.G. Sellner, G.D. Foster and D.A. Wright. 1987. Monitoring for management actions. First Biennial Report. The Maryland Office of Environmental Programs, Chesapeake Bay, Water Quality Monitoring Program, Baltimore, MD.

Malone, T.C. 1992. Effects of Water Column Processes on Dissolved Oxygen Nutrients, Phytoplankton and Zooplankton. In: D.E. Smith, M. Leffler and G. Mackiernan [Eds.], Oxygen Dynamics in the Chesapeake Bay: A synthesis of Recent Research. Maryland Sea Grant Book, College Park, MD, p. 149-221.

Nixon, S.W. 1981. Remineralization and nutrient cycling in coastal marine ecosystems, p. 111-138. In: B.J. Neilson and L.E. Cronin [Eds.], Estuaries and Nutrients. Humana Press, Clifton, NJ.

Nixon, S.W. 1988. Physical energy inputs and comparative ecology of lake and marine ecosystems. Limnol. Oceanogr. 33 (4, part 2), 1005-1025.

Progress Report of the Bay wide Nutrient Reduction Reevaluation, Chesapeake Bay Program. 1992. U.S. Environmental Protection Agency for the Chesapeake Bay Program [CSC.LR18.12/91].

Testa, J.M., D.C. Brady, D.M. Di Toro, W.R. Boynton, and W.M. Kemp. 2013. Sediment flux modeling: Nitrogen, phosphorus and silica cycles. Estuarine, Coastal and Shelf Science, 131:245-263.

Testa, J.M., Y. Li, Y.-J. Lee, M. Li, D.C. Brady, D.M. Di Toro, W.M. Kemp, and J.J. Fitzpatrick. 2014. Quantifying the effects of nutrient Loading on dissolved O_2 cycling and hypoxia in Chesapeake Bay using a coupled hydrodynamic-biogeochemical model. Journal of Marine Systems. doi:10.1016/j.jmarsys.2014.05.018.

Chapter 2

Initial Investigation into the Next Phase of Water Quality Monitoring for Criteria Assessment in Maryland Coastal Waters

D. Liang, J.M. Testa, L.A Harris, and W.R. Boynton

2-1 INTRODUCTION 1
2-2 METHODS 2
2-2.1 GENERAL DESIGN AND STUDY AREA DESCRIPTIONS 2
2-2.2 DATA MANIPULATIONS AND ANALYTICAL APPROACHES 7
2-3 RESULTS AND DISCUSSION 11
2-3.1 EFFECTS OF ADDITIONAL SAMPLING 11
2-3.2 EFFECTS OF REDUCED SAMPLING 13
2-3.3 FUTURE WORK 16
2-3.4 CONCLUSIONS AND IMPLICATIONS 17
2-A APPENDIX 17
2-A.1 SAMPLING FRAME DEFINITION 17
2-A.2 THREE DIMENSIONAL INTERPOLATION 18
2-4 REFERENCES 19

2-1 Introduction

The Maryland waters of Chesapeake Bay and its tributaries have a rich history of monitoring in support of the assessment of water-quality criteria. The monitoring program initiated in 1984 with fortnightly to monthly monitoring of hydrographic variables including dissolved oxygen, chlorophyll-a, and nutrients. Technological advances and a desire to better monitor shallow water habitats led to the initiation of the ConMon and Dataflow programs (to measure DO, temperature, salinity, pH, turbidity, and chlorophyll-a) near continuously over time (at fixed stations) and space (in surface water). In more recent years a limited number of deployments of vertical profiling devices have measured the same variables as ConMon with high temporal resolution. These efforts have yielded an enormous volume of data and insight into conditions within Chesapeake Bay, but the next-phase monitoring efforts must seek to reinvest these resources in new ways to support the identification and understanding of water-quality criteria failures in time and space, while also providing sufficient coverage to document improvements

and evidence of restoration.

The shallow-water monitoring program will soon reach the end of its first phase of implementation, and a new, more efficient, more focused, and more effective monitoring effort must be designed for future water quality criteria assessment. Although this next-phase program will use existing resources and technological investments made by EPA and DNR, its aim should be to identify the most efficient deployment of these resources that retains a meaningful assessment of criteria compliance in each of the 55 Maryland Bay water monitoring segments. The development of such a scheme is a multi-year effort, but here we describe an initial quantitative assessment of the balance between temporal and spatial observational coverage and effectiveness in identifying criteria compliance. In FY2016, we engaged in a quantitative assessment of potential new monitoring schemes that enable better understanding and planning for efficiency of the monitoring program. We combined simulations of water quality using a deterministic model, with empirical data and statistical evaluation of existing and plausible sampling schemes to evaluate cumulative frequency diagrams that test dissolved oxygen water quality. This work represents a proof of concept of this approach while also providing insights on the two tributary systems used as case studies in this first application.

The links to management goals in this case are of this work are direct: this analysis helps to determine whether future monitoring efforts can be optimized to efficiently deploy resources and effectively assess criteria.

2-2 Methods

2-2.1 General Design and Study Area Descriptions

Our general approach was to evaluate how a given sampling scheme in a monitoring segment, distributed in space and time would be able to accurately evaluate criteria compliance. At first glance, such an effort would seem impossible because it requires that we “accurately” know a true ecosystem state, when we know with certainty that we under-sample the ecosystem. Fortunately, the Chesapeake Bay management effort has a water-quality model that estimates dissolved oxygen concentrations at the time and space scales necessary to “accurately” assess criteria compliance. Therefore, we can sample the model output as if it were the true ecosystem, and measure how a given sampling of the model output reflects the true state of the ecosystem. For dissolved oxygen, we sampled the model output for a given tributary at the same time and space scales that we monitor it and compared the results to (1) quantify variability in oxygen in the “true” model case versus the simulated sampling and (2) evaluate criteria compliance in the two scenarios. We then used multiple simulations of different sampling schemes to identify uncertainties in representations of criteria compliance. Using this information, we can suggest for any tributary which sampling type (Dataflow, ConMon, etc.) and frequency would be necessary

to effectively know whether or not that system is in compliance. We emphasize here that the simulation output is a modeled representation of reality that we know has mismatches with the real condition of the estuary, however it provides a powerful tool for considering whether the sampling structure of the monitoring program can be re-designed to better meet criteria assessment at the high spatial and temporal resolutions considered for restoration.

We emphasize again that in practice, the "accurate" knowledge of the state of the ecosystem is not truly available. While this general understanding is intuitive to empiricists, there are also impacts on what statistical approaches are best used and a thorough consideration of these is critical to maximizing the utility of any new sampling schemes. Logistic constraints and small sample sizes within segments render the classical design based inference (Thompson 2012) of little use to estimate the state of the ecosystem. The complex interaction between biological and physical processes and sparse data also limit the application of model-assisted inference (Särdnal et al. 1992). Nevertheless, our perspective in this analysis was to seek an approach that could evaluate uncertainties associated with various sampling designs. To overcome these challenges, we utilized a water quality model that estimates dissolved oxygen (DO) concentration at the time and space scale necessary to accurately assess criteria failure. We then combined both empirical data, as well as virtual sampling of the model output to determine impacts of various sampling schemes.

We tested these analyses in two segments with contrasting observational histories and sources of nutrient inputs. We included a segment in mesohaline Potomac (POTMH) and two segments in mesohaline Choptank (CHOMH1 & CHOMH2). We developed a database that includes the locations of all monitoring types in each segment, the duration and frequency of their sampling, and the monitoring data available. We focused in this initial investigation on dissolved oxygen (DO) for criteria assessment and examined both long term fixed station monitoring and continuous monitoring (ConMon) in both segments (Figs. 2-1 & 2-2).

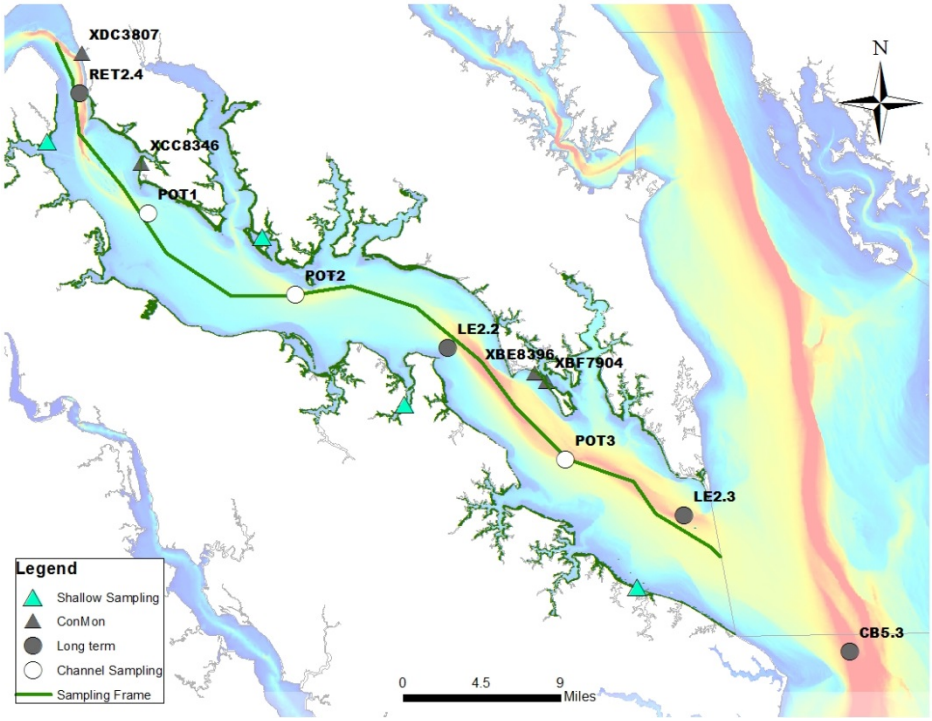

Figure 2-1. Long term fixed stations and ConMon stations in POTMH, sampling frames for channel and shallow monitoring, and four channel and four shallow stations sampled from the frames.

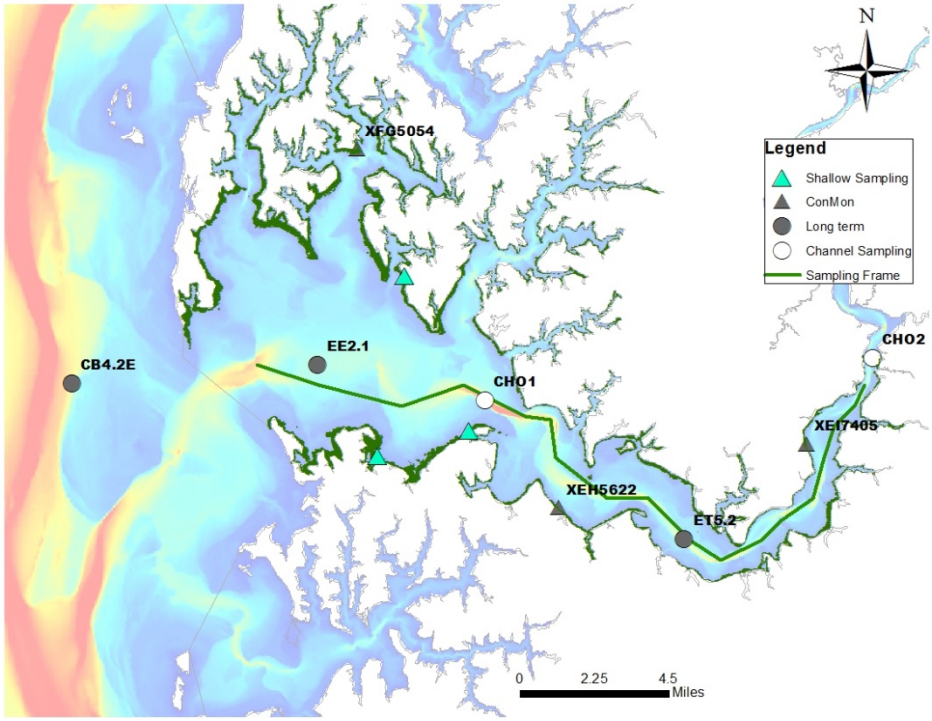

Figure 2-2. Long term fixed stations and ConMon stations in CHOMH1 & CHOMH2, sampling frames for channel and shallow monitoring, three channel and three shallow stations sampled from the frames.

We utilized a coupling of the Regional Ocean Modeling Systems (ROMS) to the biogeochemical model (RCA). The ROMS-RCA model (Testa et al. 2014) estimates water column DO every four hours over the 80 × 120 grid covering the entire Chesapeake Bay and major tributaries (Fig. 2-3). Skill assessment of the ROMS-RCA model suggests that the model outputs are unbiased (Fig. 2-4). The uncertainties in the model estimates are likely to increase the variance of our analyses, but not likely to produce bias in the assessment results. We can therefore sample the model output and measure how a given scheme reflects the true state of criteria compliance.

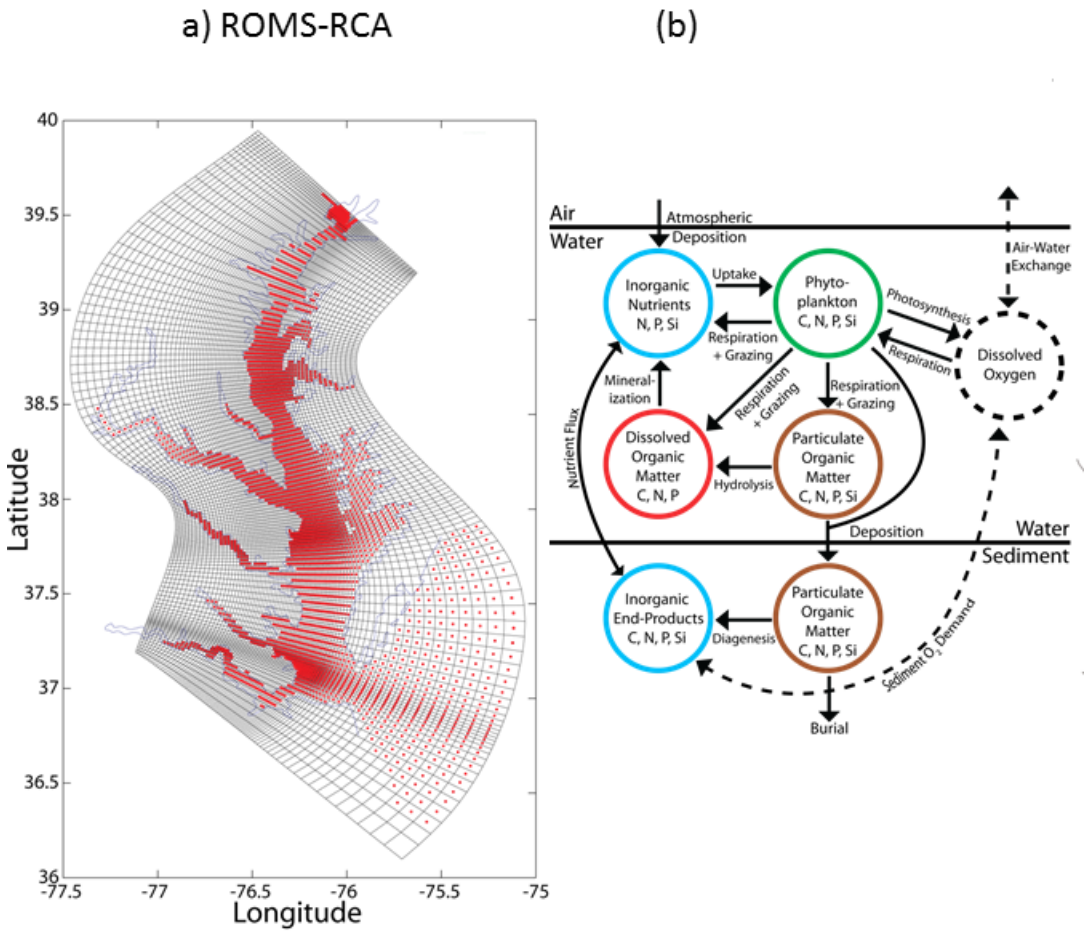

Figure 2-3. (a) Illustration of ROMS-RCA model grid (with 20 vertical sigma layers) with wet cells in red and (b) schematic diagram of the major state variables and transformation process in RCA, which is an abbreviation for Row-Column Aesop (Testa et al. 2014).

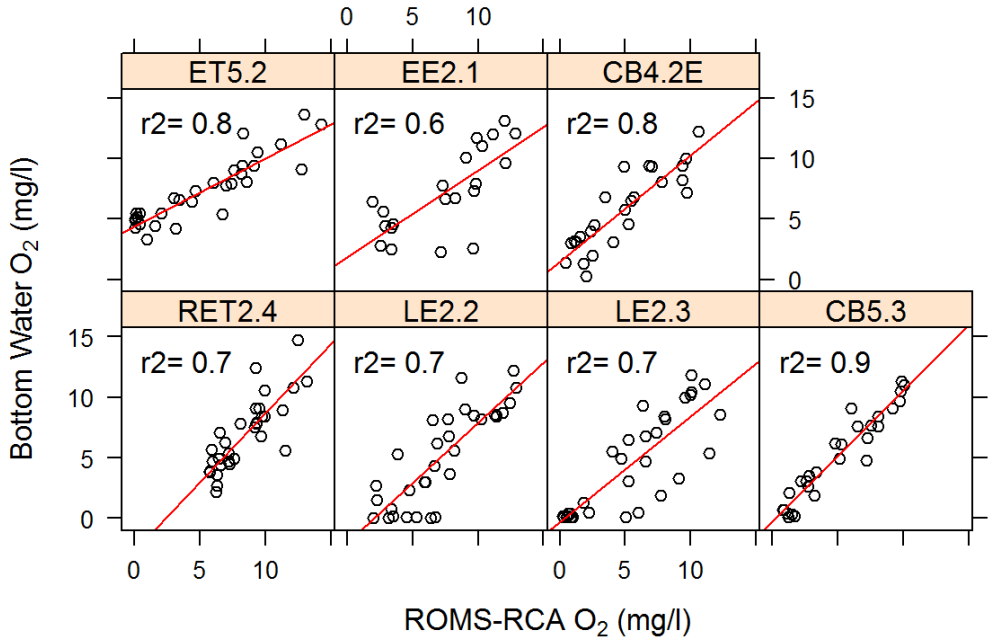

Figure 2-4. Scatter plots of observed bottom O_2 at POTMH and CHOMH fixed stations, and the ROMS-RCA estimates within 0.025 decimal degrees, 2 meters in depth and 1 day.

We utilized a stratified and spatially balanced design (Stevens and Olsen 2004) to sample each segment. We considered two strata (1) deep channel and (2) shallow water. The sampling frames of both strata were developed based on the bathymetry of the segment in this initial investigation. Details of the frame development can be found in the appendix. The sample sizes were determined based on the existing long term fixed, mainstem, and shallow monitoring efforts. Specifically, we considered three additional channel and four shallow stations in POTMH, and two additional channel and three shallow stations in CHOMH1 & CHOMH2 (Figures 2-1 & 2-2). As described below, we also considered reduced sampling scenarios. The stations were sampled with equal probability while maintaining spatial balance. Such design is known to achieve efficiency in sampling water quality (Stevens and Olsen 2004). The sampling was implemented using the *spsurvey* package in R (Kincaid et al. 2011).

We used the cells developed by the Bay Interpolator team (*Vol3DInterp*) to represent each segment (Bahner 2006). Each cell is defined by a 1 km by 1 km area and 1 meter depth, and therefore contains a 0.001 km^3 volume of water. Overall there are 5,732 cells in POTMH and 2,012 cells in CHOMH1 & CHOMH2. We estimated DO concentration at each cell in order to assess the habitat-specific compliance as described below.

2-2.2 Data Manipulations and Analytical Approaches

Once we identified the existing and potential fixed and shallow monitoring stations through the design described above, we implemented the sampling at those stations from the model output following seven scenarios. The existing fixed and shallow sampling represented the baseline. Even though the long term monitoring was conducted approximately every two weeks, resulting in a total of 32 cruises when ROMS-RCA simulation was conducted (2004-2005). Since then, the cruise schedule has been changed to fortnightly frequency during the summer and monthly frequency during other seasons. To accurately represent the current fixed station monitoring effort, we used the long term sampling schedule after the change (2010-2011). Specifically, we extracted the Julian days of the baseline cruises to form the days in 2004 and 2005. There are a total of 25 cruises implemented as the baseline long term station sampling.

We considered seven scenarios in total:

Current

1. Both fixed channel and shallow water monitoring as currently sampled (see Figures 2-7 and 2-8, see figure caption for number of stations)

Additional Monitoring Effort (see Figures 2-7 and 2-8)

2. Channel sampling: more channel monitoring stations with the same frequency as the nearest long term station (see figure caption for number of stations)
3. Shallow sampling: more shallow monitoring stations with high temporal resolution (see figure caption for number of stations)
4. Both: more channel and more shallow monitoring stations

"True" state of the ecosystem

5. Model data to represent the 'best case' unrealistic scenario of monitoring all cells within each segment (see Figures 2-7 and 2-12)

Reduced monitoring effort

6. Removing each fixed channel monitoring station one at a time from each segment
7. Removing each ConMon station one at a time from the segment.

Table 2-1. Definitions of queries for long term, new channel, ConMon, new shallow stations and the entire model grid.

Station	Space (Decimal Deg)	Depth (Meter)	Time (Decimal Day)
Long Term	0.025	2	1
New Channel	Nearest	All	1
ConMon	Nearest	1	All
New Shallow	Nearest	1	All
Model Grid	0.1	1	All

Each sampling scenario was implemented as a query of the model output stored in *ncdf* files. Table 2-1 summarizes the definition of the multi-dimensional query by types of stations. The queries were implemented using the *ncdf4* package in R (Pierce et al. 2012). A query returns null when there is no model output within the specified spatial-temporal neighborhood. For example, there are a total of 2,721 queries corresponding to long term monitoring data at the existing stations between 2004 and 2005. Among these queries, 2,158 returned DO estimates from the model output; the remaining 563 measurements lacked model output within 2 meters of the sampling depth at the stations. Similarly over 2,012 and 5,792 queries that represent "true" state in CHOMH1 & CHOMH2 and POTMH, 1,667 and 5,399 returned model output within the specified neighborhood. The cells without model output were mainly in the deep channel of the segment where the nearest model output extended beyond the depth neighborhood. Due to the highly stratified nature of both segments, we evaluated compliance using only cells with model output in the following analyses.

We specified Cumulative Frequency Diagram (CFD) parameters to assess 30-day criteria (Batiuk et al. 2009). The query results were organized into cruises. Temporal averaging was conducted for queries corresponding to shallow monitoring and the entire model. Specifically, the high temporal resolution results were averaged by the duration of each bay wide cruise. We then applied three dimensional interpolation (*Vol3DInterp*) to estimate the DO concentration at each cell. The default parameters were used in *Vol3DInterp* interpolation. Details are reported in the appendix. An enclosing polygon specific to each segment was used to avoid using data across the tributaries (Jensen et al. 2006).

Cell specific interpolation results were compared with seasonal and habitat specific criteria to assess compliance of DO during that cruise (Batiuk et al. 2009). The criteria accounted for four bay habitats: shallow water, open water, deep water, and deep channel. Season specific stressful DO conditions were characterized for the specific habitat and living resources (Fig. 2-5). Table 2-2 lists our interpretation of the 30-day criteria and definitions of each habitat.

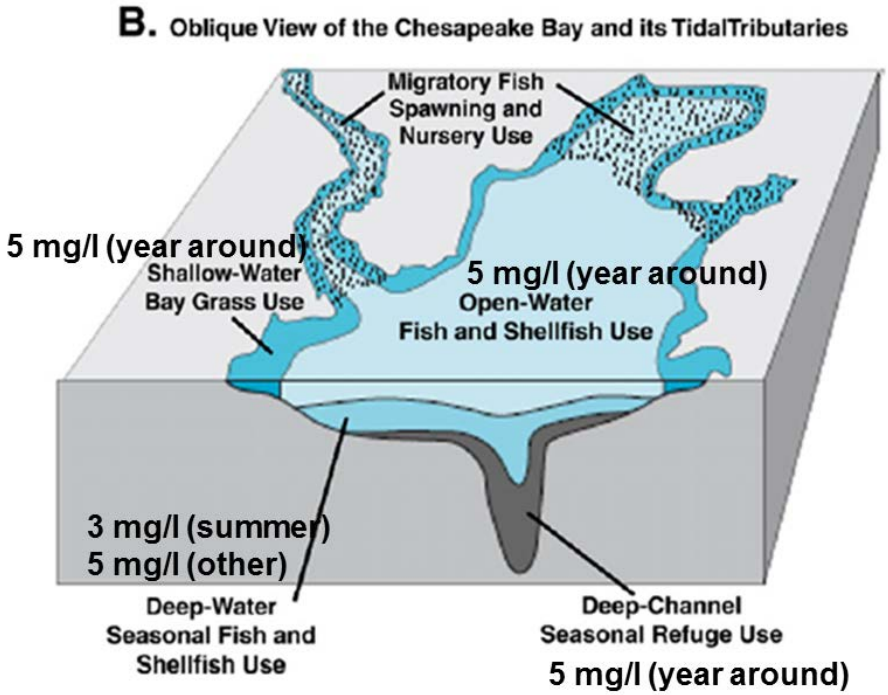

Figure 2-5. Conceptual diagram of the five Chesapeake Bay tidal water designation use zones, with our interpretation of the 30-day DO criteria reported in Batiuk et al. (2009).

Table 2-2. Interpretations of the 30-day DO criteria and definition of habitats in POTMH and CHOMH1 & CHOMH2.

Habitat	Depth Description	Assessment Period	30-day Mean Criteria (mg/L)
Open-Water fish and Shellfish Use	Cells less than or equal to 2 m in cells deeper than 2 m	Year-Round	>=5
Deep-Water fish and Shellfish use	All cells between 2 and 8 meters	June 1 to September 30	>=3
		October 1 to May 31	>=5
Deep-Channel Seasonal Refuge Use	All cells deeper or equal to than 8 m	Year-Round	>=5
Shallow-Water Bay Grass Use	Entire cell depth is 2 meters or less	Year-Round	>=5

We calculated the proportion of volume out of compliance for each cruise. During several cruises, fewer stations were sampled, which led to lower coverage of the interpolation of that segment, especially in deep channels. Therefore, we used the proportion of compliance only when over half of the volume of water was interpolated within that portion of the segment; otherwise the proportion from that cruise was removed from the CFD calculation. Instances when this resulted in ties in the proportions out of compliance, e.g. during winter months when failure was rare, the maximum proportion of time was used to define CFD to be conservative. The reference of CFD was based on 10% allowable space and time exceedance (Chesapeake Bay Program 2003, Secor et al. 2006). To facilitate visualization, we calculated the difference between the actual attainment curves and the reference curves, which was termed residual CFD in this report. At a given spatial scale, a positive residual CFD would indicate non-allowable exceedance while a negative residual CFD would indicate allowable exceedance (Fig. 2-6).

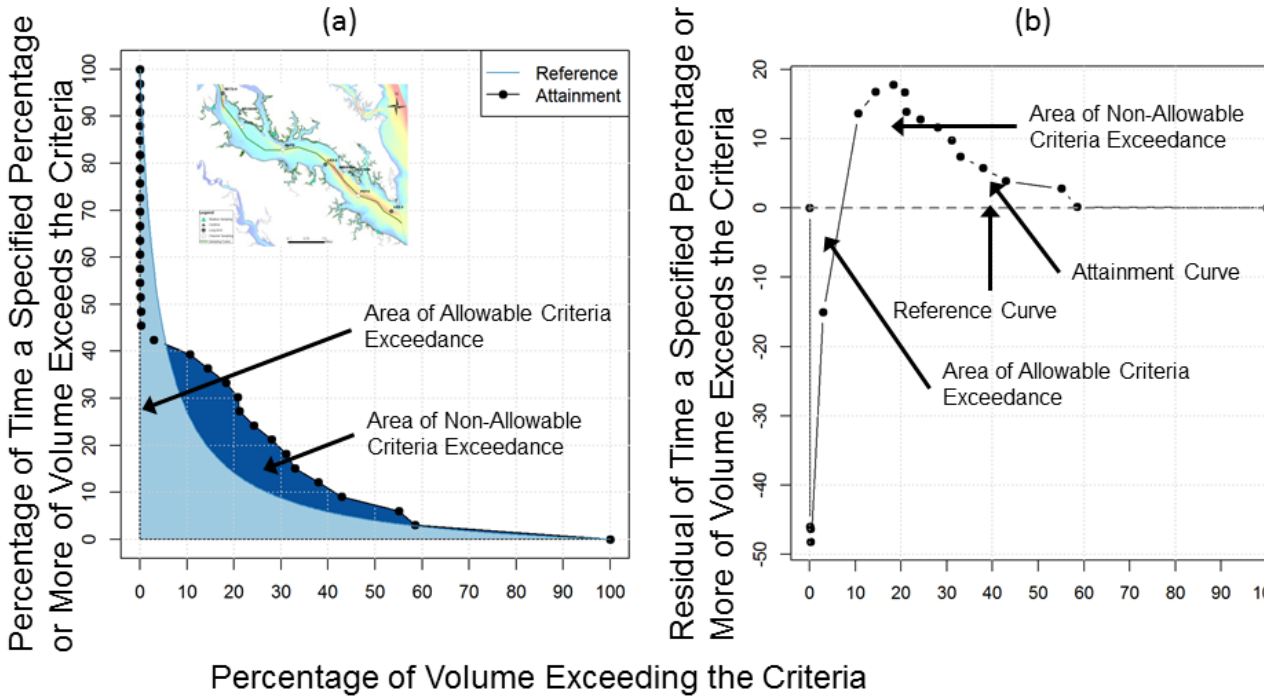

Figure 2-6. (a) Cumulative Frequency Diagram (CFD) based on model output in POTMH and (b) the corresponding residual CFD.

2-3 Results and Discussion

2-3.1 Effects of Additional Sampling

Sampling effects vary with spatial scales, defined as the proportion of volume exceeding criteria (Figs. 2-7 & 2-8). Proportion exceedance is estimated using interpolated data at the few stations within each segment. Given the spatial balanced nature of the existing four stations, low proportion (<0.2) of exceedance would indicate criteria exceedance at a specific station, interpolated to its adjacent volume of water; Larger proportions, e.g. above 0.6, would suggest exceedance occurring at multiple stations and indicate criteria failure global to the entire segment during that cruise. The sampling scheme has differential and scale-specific impacts on assessing criteria failure. At a local scale (less than 0.2 proportion exceedance) and global scale (greater than 0.6 proportion exceedance), additional sampling efforts did not change the CFDs. For the Potomac mesohaline segment (POTMH), sampling effects are more obvious at the middle scale (between 0.2 and 0.6 proportion exceedance, Fig. 2-7). These sampling effects are seen as the greatest discrepancy between the modeled CFD exceedances (representing the hypothetical 'true' oxygen criteria exceedance, yellow line in figure) and all of the tested sampling regimes exceedances (both the current monitoring scheme and the proposed enhanced sampling schemes). Based on the modeled CFD indicating the highest exceedance, the interpretation is that all of the sampling regimes will miss problem dissolved oxygen areas in the segment. The sampling scheme that includes additional channel stations above the current monitoring (pink line in the figure) offered the most improvement for the measurement of exceedance (i.e. reduced the discrepancy between the modeled 'true' exceedance and the measured exceedance between 0.5 and 0.6 proportion exceedance. This matches our expectations that lower dissolved oxygen conditions will more often occur in deeper waters where water column stratification is more likely. Among the sampling schemes tested, the greatest differences are seen between the current monitoring efforts results (blue line in figure) and the expected impact of adding more shallow water monitoring (green line in figure); however, the results suggested that adding more shallow water monitoring led to less accurate assessment than the current monitoring scheme. This also reinforces the interpretation that the lowest dissolved oxygen conditions in this segment are found in the deeper portions.

The sampling effects on DO criteria exceedance in the Choptank mesohaline segments (CHOMH1 & CHOMH2) are similar to the Potomac mesohaline in that the modeled results indicate the highest exceedance among the sampling schemes tested, so problem DO areas are being missed by all of the sampling schemes tested (Fig. 2-8). However, unlike in the Potomac mesohaline segment, in the Choptank mesohaline segments the sampling results suggest more failure than the modeled 'true' exceedances at a more global scale (greater than 0.7 proportion exceedance), i.e. sampling is over-estimating the amount of DO failure in this segment. A

sampling regime with additional channel stations (pink line in figure) again reduced the discrepancy between modeled 'true' and measured exceedance at the middle scale (Fig. 2-8). We expect that a similar analysis with a 7-day criteria would indicate that adding more shallow water monitoring would lead to more accurate assessment, especially in the shallow portion of the segment.

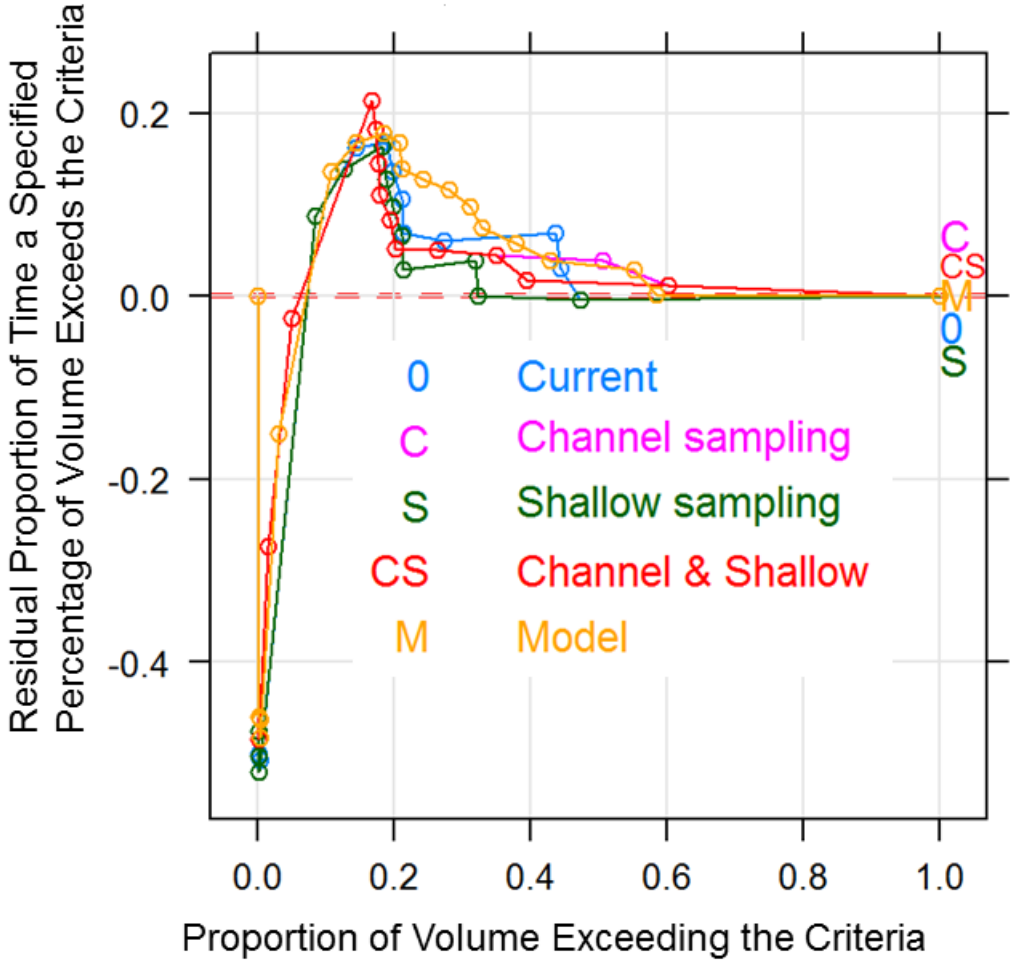

Figure 2-7. Residual Cumulative Frequency Diagram (CFD) in POTMH based on model output, and four sampling schemes: (1) Current denotes on four ConMon and four fixed stations (RET2.4, LE2.2, LE2.3 and CB5.3) (2) Channel includes three additional channel stations; (3) Shallow includes four additional shallow stations; (4) Both.

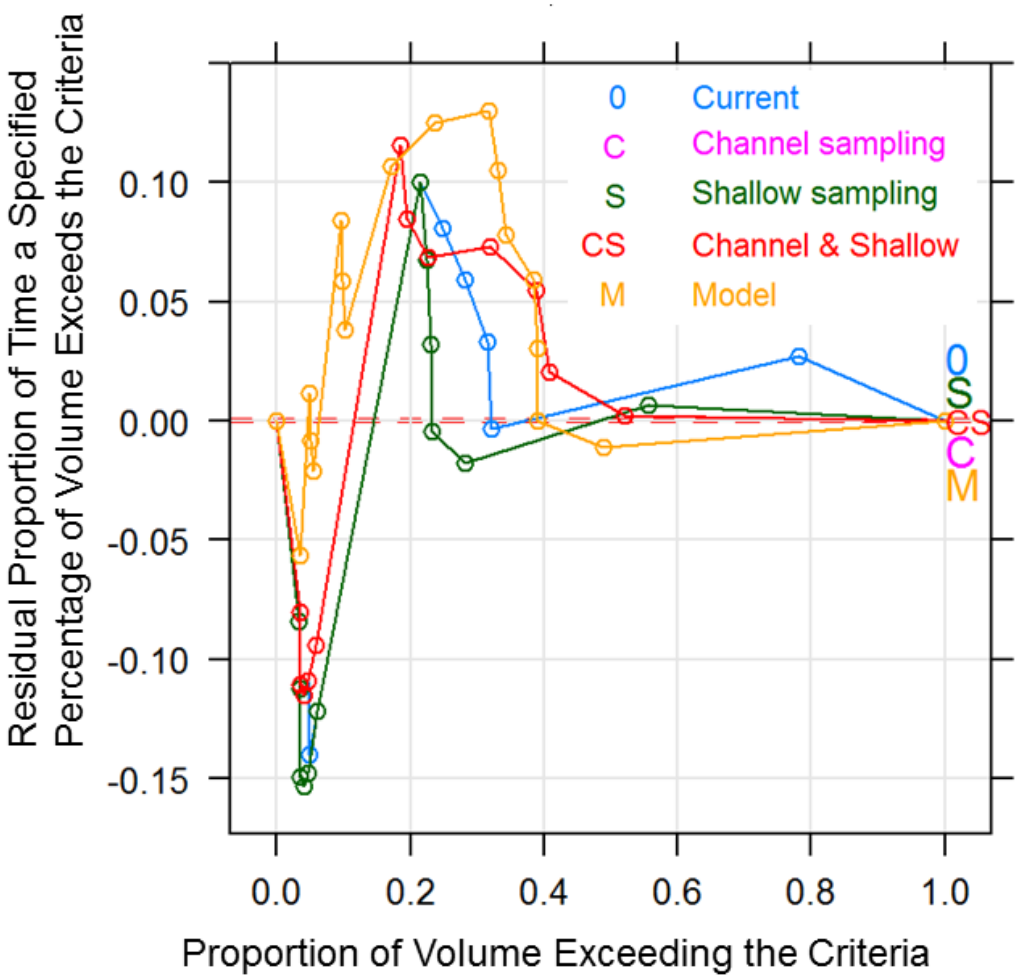

Figure 2-8. Residual Cumulative Frequency Diagram (CFD) in CHOMH1& CHOMH2 based on model output, and four sampling schemes: (1) Current denotes on three ConMon and three fixed stations (ET5.2, EE2.1 and CB4.2E) (2) Channel includes three additional channel stations; (3) Shallow includes four additional shallow stations; (4) Both. The Channel sampling CFD was over plotted by the Channel and Shallow sampling scheme.

2-3.2 Effects of Reduced Sampling

The effects of reducing fixed stations vary spatially (Figs. 2-9 & 2-10). In POTMH, removal of lower estuary stations (LE2.2 and LE2.3) moved the CFD closer to the reference curve (residual = 0, red line in figures), which indicates an under-estimating of the criteria failure. Removing each of these stations resulted in exceedance curves that are lower than the measured by all of the current monitoring stations together (panel "All stations" in Figure 2-9), indicating the importance of these two stations to measurement of DO criteria for this segment. Removal of stations RET2.4 and CB5.3 has much less obvious effects on the measurement of the exceedance for the segment. The same contrasts can be observed in CHOMH1 & CHOMH2 (Fig. 2-10). The CFD without ET5.2 suggested incorrectly, that no exceedance while both modeled and 'All

stations' results indicate that exceedances to occur; this indicates that the ET5.2 station is important to the determination of DO criteria for this segment. Removal of EE2.1 has the opposite effects, suggesting more exceedance than indicated by the modeled 'true' exceedance, suggesting that this station adds to the error in the estimates of DO criteria assessment for this segment.

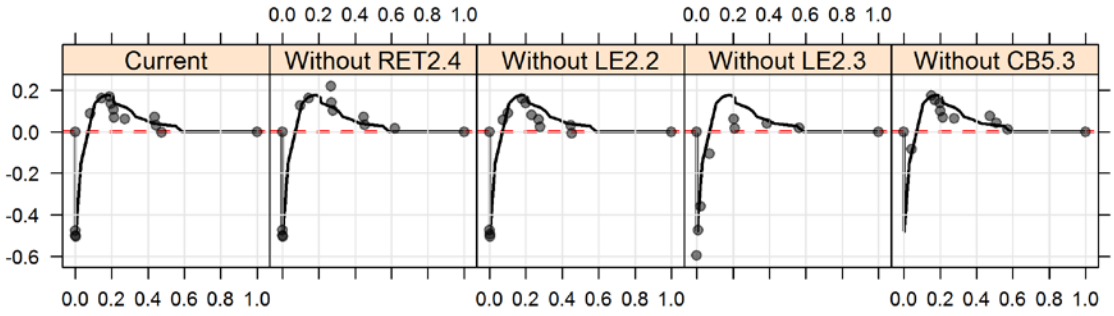

Figure 2-9. Residual Cumulative Frequency Diagram (CFD) in POTMH based on the model output, existing efforts, and removal of each fixed station.

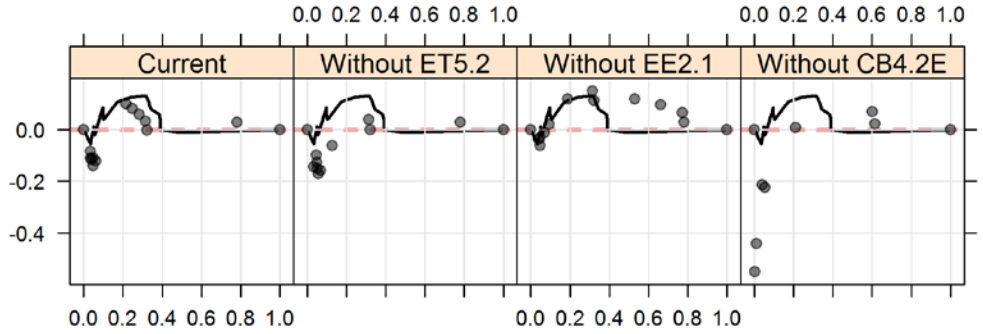

Figure 2-10. Residual Cumulative Frequency Diagram (CFD) in CHOMH1 & CHOMH2 based on the model output, existing efforts, and removal of each fixed station.

The effects of reducing ConMon stations do not vary in space and are more subtle than those of removing fixed stations (Figs. 2-11 & 2-12). The CFDs without each ConMon station are not different from those with the station. Although in POTMH, removal of ConMon stations (XCC8346, XDC3807) makes the CFDs larger at more global spatial scale.

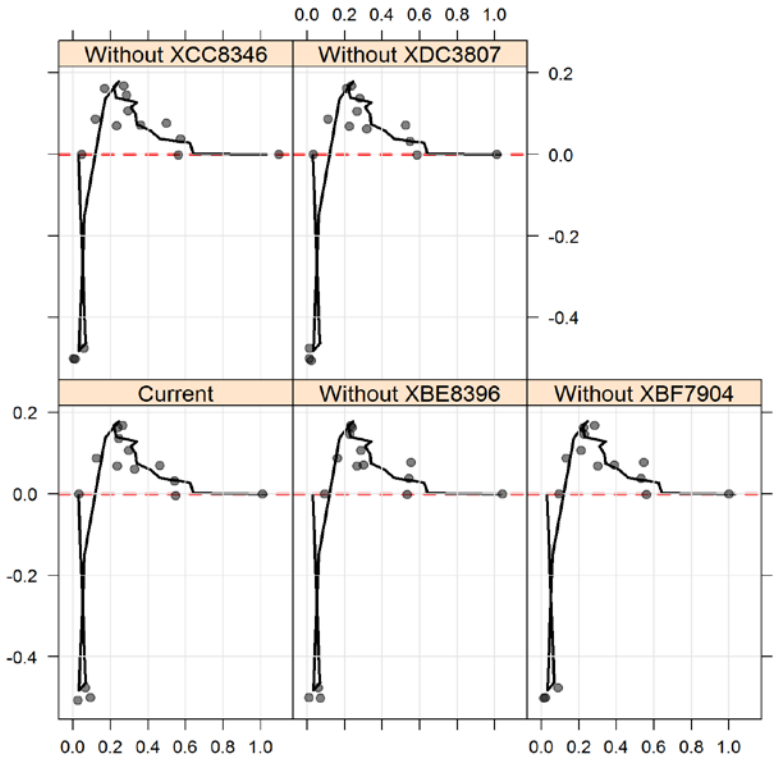

Figure 2-11. Residual Cumulative Frequency Diagram (CFD) in POTMH based on the model output, existing efforts, and removal of each ConMon station.

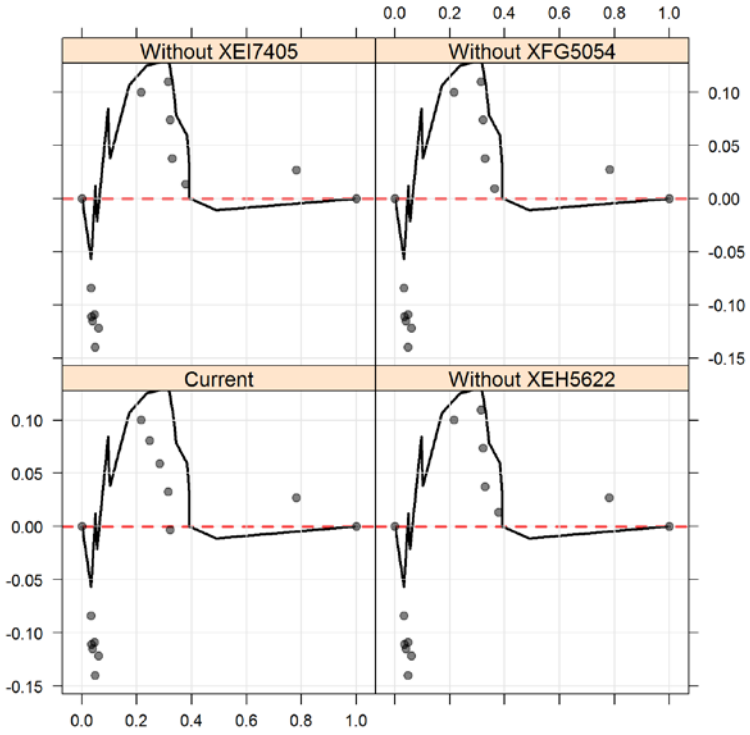

Figure 2-12. Residual Cumulative Frequency Diagram (CFD) in CHOMH1 &CHOMH2 based on the model output, existing efforts, and removal of each ConMon station.

The analyses suggest that current sampling scheme can either under-estimate criteria failure (misses problem area) as in POTMH (Fig. 2-7) or over-estimate criteria failure (biased sampling) as in CHOMH1 & CHOMH2 (Fig. 2-8). The existing channel sampling in POTMH misses the exceedance captured by the model, indicating that more sampling is needed. The sampling scheme in CHOMH1 & CHOMH2 on the other hand is biased toward low oxygen areas in deep channels. The Choptank is a wide and shallow system, more channel efforts would be needed to reduce the biased sampling.

2-3.3 Future Work

Our analyses shared the same objectives as prior studies of water quality monitoring, but we utilized recent analytical developments in criteria assessment (Batiuk et al. 2009 and Secor et al. 2006). Specifically, we applied the CFD that incorporates the spatial and temporal variability of stressful DO conditions. In addition, we applied habitat specific criteria for the protection of a variety of living resources in Chesapeake Bay. We also utilized spatial sampling methods (Stevens and Olsen 2004) to incorporate any autocorrelation in the DO distribution to improve sampling efficacy.

Our analyses could be improved in the following aspects. (1) We only assessed 30-day criteria over the habitats. The shallow habitat is known to exhibit higher spatiotemporal variability, which would be better assessed using the 7-day or instantaneous criteria. We can use the high frequency outputs from the ConMon stations to better assess the criteria in the shallow water. We also need to incorporate the highly complex shorelines in the shallow by using higher model output resolution. (2) The CFD allows quantification of the differences between the attainment curves of various sampling schemes, but it lacks the ability to assess the statistical significance of the differences. We experimented with Monte Carlo simulation approaches to test the significance of differences, but the Monte Carlo method is computationally intensive. We could instead exploit the link between CFD and the classical Kolmogorov-Smirnov test to develop an inferential tool. Bootstrapping methods may be utilized to account for the temporal auto-correlation, especially when assessing the 7-day or instantaneous criteria. (3) As currently implemented, the sampling frames were based on bathymetry only. In practice, a variety of logistical and financial constraints need to be considered in developing a frame. (4) We could apply the similar analyses to a larger set of the segments in the Chesapeake Bay.

2-3.4 Conclusions and Implications

Our approach of leveraging model and empirical data to assess monitoring design targeted water quality criteria that are specifically used to determine compliance with regulatory structures. Our proof of concept of this approach in two segments successfully demonstrated how results can lead to a variety of insights. For the 30-day criteria, it is clear that sampling design is sensitive to placement of deep water stations. We are eager to consider how additional criteria may provide added information in the selection of shallow water and more frequent temporal sampling in the enhanced monitoring program.

2-A Appendix

2-A.1 Sampling Frame Definition

The shallow sampling frame was developed using the bathymetry data. All raster cells within 2.0 meter in depth in each segment were extracted. The cells within 5,000 meters in Euclidean distance to the existing ConMon stations (Figs. 2-3 & 2-4) were excluded. There are 40,364 potential locations in POTMH and 18,826 locations in CHOMH1 & CHOMH2. The frame for channel sampling was developed by creating 1,000 points along the deep channel of each segment, and removing points within 2,500 meters of the existing long term fixed stations (Figs. 2-3 & 2-4). There are 853 potential locations in POTMH and 758 locations in CHOMH1 & CHOMH2.

2-A.2 Three Dimensional Interpolation

The interpolation involves (1) linear interpolation at each station and cruise down the water column; (2) layer specific inverse distance weighting (IDW). The layers were defined in half meter increment. Within each layer, at most eight observations within 25,000 meters to the interpolation cell were extracted. The IDW weight was defined using the squared distance. The interpolator returns missing value when there is not enough (less than three observations) within 25,000 meters at the same depth layer. An enclosing polygon shape file was used to restrict neighbor search to only estuaries connected to the target cell, thus no interpolation over the land was allowed. The interpolator was implemented using R statistical computing language.

2-4 References

Bahner, L., 2006. Vol3D – Chesapeake Bay and Tidal Tributary Interpolator. NOAA Chesapeake Bay Office.After Vol3DInterp

Batiuk, R.A., Breitburg, D.L., Diaz, R.J., Cronin, T.M., Secor, D.H. and Thursby, G., 2009. Derivation of habitat-specific dissolved oxygen criteria for Chesapeake Bay and its tidal tributaries. *Journal of Experimental Marine Biology and Ecology, 381*, pp.S204-S215.

Chesapeake Bay Program (2003). *Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll a for the Chesapeake Bay and Its Tidal Tributaries.* Annapolis MD.

Kincaid, T.M., Olsen, A.R., Stevens, D., Platt, C., White, D. and Remington, R., 2011. *spsurvey: Spatial survey design and analysis*. CRAN R package version 3.1. (Accessed 05/26/2016)

Jensen, O.P., Christman, M.C. and Miller, T.J., 2006. Landscape-based geostatistics: a case study of the distribution of blue crab in Chesapeake Bay. *Environmetrics*, *17*(6), pp.605-621.

Pierce, D., 2012. *ncdf4: Interface to Unidata netCDF (version 4 or earlier) format data files*. CRAN R package version 1.15. (Accessed 05/26/2016), *URL http://CRAN. R-project. org/package= ncdf4*.

Särdnal, C.E., Swensson, B. and Wretman, J.H., 1992. *Model assisted survey sampling*. Springer New York.

Secor, D. H., M. C. Christman, F. Curriero, D. Jasinski, E. Perry, S. Preston, K. Reckhow and M. Trice (2006). *The Cumulative Frequency Diagram Method for Determining Water Quality Attainment. Report of the Chesapeake Bay Program STAC Panel to Review of Chesapeake Bay Program Analytical Tools*. Chesapeake Research Consortium. Edgewater MD.

Stevens Jr, D.L. and Olsen, A.R., 2004. Spatially balanced sampling of natural resources. *Journal of the American Statistical Association*, *99*(465), pp.262-278.

Testa, J.M., Li, Y., Lee, Y.J., Li, M., Brady, D.C., Di Toro, D.M., Kemp, W.M. and Fitzpatrick, J.J., 2014. Quantifying the effects of nutrient loading on dissolved O_2 cycling and hypoxia in Chesapeake Bay using a coupled hydrodynamic–biogeochemical model. *Journal of Marine Systems*, *139*, pp.139-158.

Thompson, Steven K. 2012. *Sampling, 3rd Edition*. Wiley, Hoboken New Jersey.

Chapter 3

Community Metabolism in the Maryland Portion of Chesapeake Bay, Coastal Waters, and Tributaries.

J.M. Testa, J.L. Humphrey, C.L.S. Hodgkins, L.A. Harris, and W.R. Boynton

3-1 INTRODUCTION 1

3-2 METHODS AND DATA SOURCES 2

3-2.1 COMPUTING COMMUNITY PRODUCTION AND RESPIRATION FROM O_2 TIME-SERIES 2

3-2.2 DESCRIPTION AND OPERATION OF METABOLISM MATLAB CODE 3

3-2.3 DATA SOURCES AND LOCATION 5

3-3 RESULTS AND DISCUSSION 6

3-3.1 PATTERNS OF GROSS PRIMARY PRODUCTION AND RESPIRATION 6

3-4 CONCLUSIONS AND IMPLICATIONS 17

3-5 REFERENCES 18

3-1 Introduction

Community production and respiration have repeatedly been shown to be responsive to nutrient enrichment in lakes (e.g., Vollenweider 1976) and many estuaries and coastal waters (e.g., Boynton et al 1982; Testa et al. 2013). In the case of many Chesapeake Bay areas, nutrient enrichment is cited as one of the reasons for listing waterways as being impaired and in need of restoration. In many instances measurements of such fundamental features of ecosystem function as production and respiration are too expensive or simply too difficult to undertake. However, Maryland DNR (MD-DNR) established multiple water quality monitors (ConMon Program) making measurements of water quality variables that can be used to make these estimates. In this chapter we report on the methods and results of community production and respiration computations for the entirety of the ConMon database in the Maryland portion of the Chesapeake Bay and coastal waters.

System metabolism (i.e., community production and respiration; basically the production and utilization of organic matter) has gained broad application in estuarine areas. Perhaps the best single example of this was reported by Caffrey (2004) where high frequency DO, temperature, and salinity data from 42 sites located within 22 National Estuarine Research Reserves between 1995 and 2000 were assembled. She computed the same metabolism estimates described here and reported the following: 1) highest production and respiration rates occurred in the SE USA during summer periods; 2) temperature and nutrient concentrations were the most important

factors explaining variation in rates within sites; 3) freshwater sites were more heterotrophic than more saline sites; 4) nutrient loading rates explained a large fraction of the variance among sites and; 5) metabolic rates from small, shallow, near-shore sites were generally much larger than in adjacent, but larger, deeper off-shore sites.

The fact that nutrient loading rates and concentrations were strong predictors of metabolic rates is especially relevant to efforts being made in Chesapeake Bay and associated tributaries. Additionally, Danish investigators have been using this technique in a variety of shallow Danish systems and they have started to use four different approaches for estimating the metabolic parameters of interest (Gazeau et al. 2005), including the open water DO approach. Their evaluations suggest that all techniques produce similar estimates with regard to magnitude of production or respiration. A convergence of estimates, using different techniques, suggests a robust set of variables and that is consistent with the needs of a monitoring program.

This effort represents a continuing activity by the Ecosystem Processes Component (EPC) of the Maryland Biomonitoring Program. This activity is consistent with the process-based approaches we have recommended for many years and this effort is another such example. We have developed a new program for computing metabolism in Matlab that allows for rapid computation of metabolic rates and compiles and saves other YSI data (temperature, salinity, pH, chlorophyll-a) to use in analysis of metabolic rates. Because the ConMon system at each sampling site is in place for about 200 days per year (potentially every day from April through October) a large number of rate measurements (~200) of system production (related to nutrient conditions) and system respiration (related to hypoxia) can be made and examined. Such a large number of observations at a large number of sites is likely unprecedented in estuarine monitoring programs.

The specific objectives of this effort include the following: 1) a summary of mean rates of community P and R across 105 ConMon stations; 2) quantitatively relating these rates to nutrient loading rates at a select group of stations; and 3) an examination of spatial patterns in metabolic rates and the implications of these patterns.

3-2 Methods and Data Sources

3-2.1 Computing Community Production and Respiration from O_2 Time-Series

The basic concept and method for computing community production and respiration was developed by Odum and Hoskin (1958) and, with numerous modifications, has been applied to estimate these rate processes in streams, rivers, lakes, estuaries, and the open ocean. The technique is based on following the oxygen concentration in a body of water for a 24 hour period. During hours of daylight, oxygen concentration increases in the water due to the release of O_2 as a by-product of photosynthesis. During hours of darkness, O_2 concentration declines due

to O_2 consumption by both primary producers and all other heterotrophs. The rate processes (gross primary production, GPP; nighttime respiration, Rn) are estimated by computing the rate of change in O_2 concentrations during day and night periods. This rate of change is then corrected for O_2 diffusion across the air-water interface and the result is an estimate of GPP and Rn. ConMon data are exactly the type of data needed for these computations in that all the needed variables are measured (dissolved oxygen, temperature, and salinity), the measurement frequency is high (15 minute intervals) and the measurement period is for 9 or more months per year. It is very rare when a rate process can be estimated with such temporal intensity.

3-2.2 Description and Operation of Metabolism Matlab Code

Based on earlier work by Burger and Hagy (1998) for calculating community metabolism from near-continuous monitoring data, we developed a Matlab program to compute GPP, Rn, and Net Daytime Production (NDP, net O_2 production during daylight hours). We computed metabolic rates based on ConMon data for 105 stations (Fig. 3-1) in the Maryland portion of Chesapeake Bay.

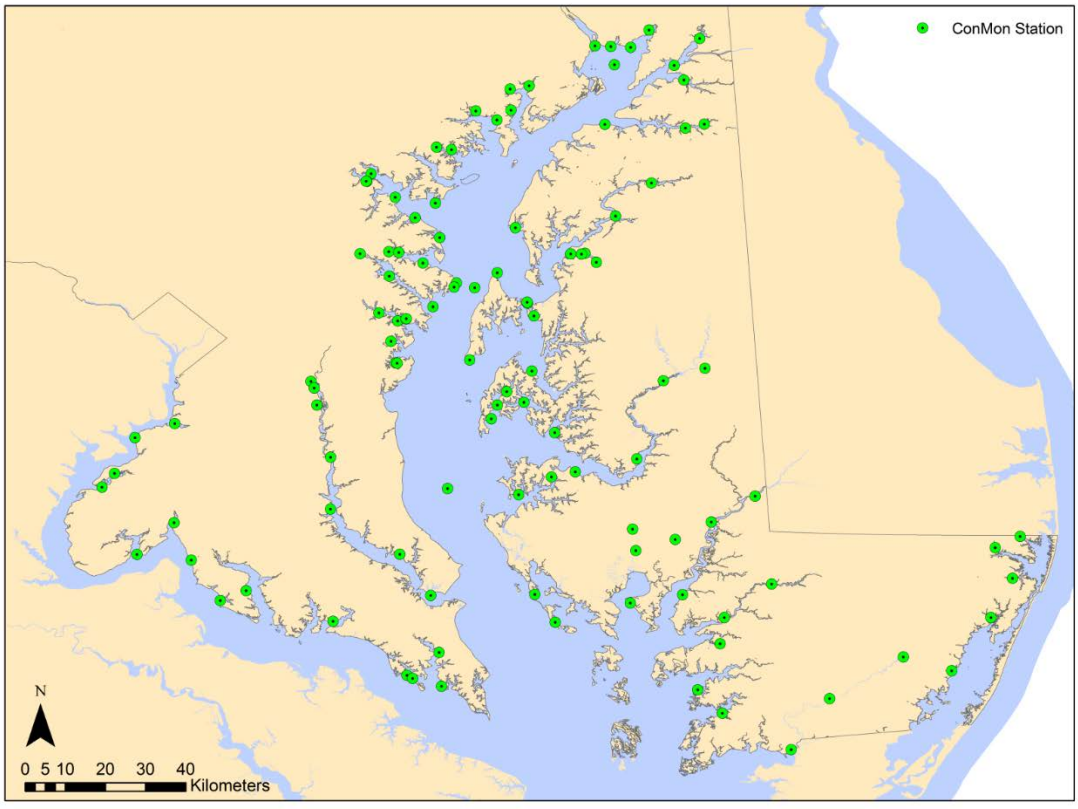

Figure 3-1. Map of ConMon stations in Maryland used in development and analysis of ecosystem metabolism.

Briefly, sunrise and sunset times for each date are calculated based on the latitude and longitude of the station and used to compute a "Metabolic Day", which begins at sunrise on the current day and continues to the observation immediately before sunrise on the following day (Fig. 3-2). The change in DO, time, air/sea exchange, and oxygen flux is then calculated between each consecutive observation and sums of these changes are calculated for each metabolic day for the periods between sunrise and sunset, and also between sunset and the next sunrise. From these sums, four primary metabolic variables are calculated:

Rn = Nighttime (sunset to following sunrise) summed rates of DO flux corrected for air/water diffusion.

rnhourly = Rn divided by the number of nighttime hours

NDP = The sum (both positive and negative) of oxygen flux (corrected for air-water diffusion) for the sunrise to sunset period in a given day.

GPP = NDP + (rnhourly*hours of daylight)

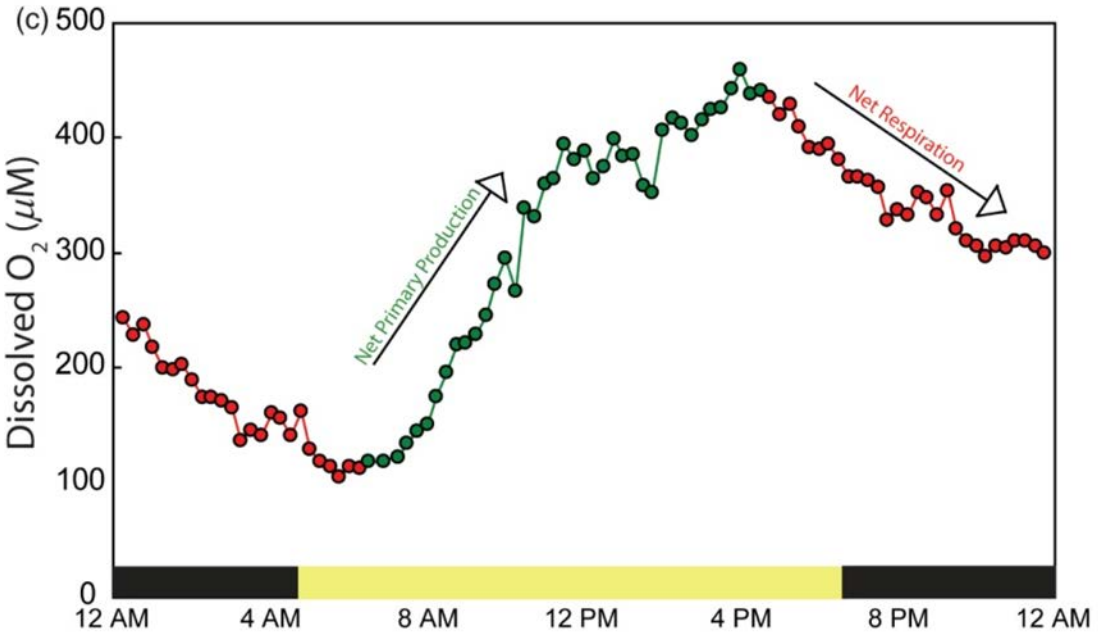

Figure 3-2. Typical diel dissolved oxygen time-series, showing periods of sunlight and dark (yellow and black bars along the x-axis), and where periods of net oxygen increases (green lines and circles) associated with net primary production and net oxygen decreases (red lines and circles) associated with net respiration occur.

Air-water diffusion of oxygen is considered in these computations and the diffusion correction is based on the difference between observed DO percent saturation and 100% saturation multiplied by a time-varying diffusion coefficient. For these computations, we used a reaeration coefficient

(k, m h^{-1}), which was empirically derived by Marino & Howarth (1993) and is a function of wind speed at 10 m. The relationship does not work for wind speeds > 10 m s^{-1}, so any observations above that threshold are removed. The relationship is for wind at 10 m, so an empirically derived conversion is applied (Kremer et al. 2003). We used wind-data from the long-term station at Thomas Point Light. We compared metabolic rates computed with these time-varying aeration coefficients to those using a constant diffusion coefficient of 0.5 g O_2 m^{-2} hr^{-1}, which has been done in several prior investigations (e.g., Caffrey, 2004). We did not find substantial differences in the magnitude of the rates computed with either approach, and considering that the effect of wind-induced aeration varies substantially across space with differences in fetch related to the size of an estuary and position relative to a given wind direction, we opted for the constant exchange coefficient.

One of the primary assumptions of this method is that temporal changes in DO measured by the continuous monitors are due solely to metabolism (i.e., oxygen production from photosynthesis and oxygen loss from respiration) occurring at the station and not due to advection of water masses with different oxygen conditions moving past the instrument. Because the Chesapeake Bay is a tidal system, this may not always be the case. Depending on the hydrodynamics of a given station, this assumption may be more or less realistic and may also be variable from date to date. One way of censoring dates where DO is affected by advection is to preview the data graphically prior to metabolism calculations and determine if there is a relationship between salinity and DO. Large changes in salinity suggest moving water masses and therefore, advection. These dates could then be flagged and reviewed before metabolism variables are calculated, potentially excluding some measurements that do not align with assumptions of applying the metabolic computation. In this effort, we did not exclude such data, given the enormous number of data and the desire to apply a consistent approach across stations.

We converted oxygen-based measures of metabolism to carbon based measures by assuming a photosynthetic quotient (PQ) and respiration quotient (RQ) of 1 (mol C metabolized to mol O_2 metabolized) and using the respective molar weights of oxygen and carbon to convert from grams to moles. Although PQ values larger than 1 have been used (~1.2 to 1.4) to convert rates of gross primary production from oxygen to carbon, we chose 1 because our GPP estimates were derived from estimates of net daytime oxygen production (GPP-R).

3-2.3 Data Sources and Location

Continuous monitoring data from 2001 to 2014 for all stations (Fig. 3-1) were obtained from the MD-DNR Tidewater Ecosystems Assessment division (B. Cole) in electronic (.txt) file format. Because of the near-continuous characteristic of these measurements, a data set with no error and complete days was developed using an R (www.R-project.org) program. Data with failing or invalid codes (as detailed in the MDDNR SWMP QAPP: Michael et al., 2013), missing data, and

duplicates were isolated. These rows in their entirety were removed to provide a complete and error free dataset.

3-3 Results and Discussion

3-3.1 Patterns of Gross Primary Production and Respiration

Measurements made across a wide variety of ecosystems have indicated that gross primary production and respiration tend to be balanced over time (Fig. 3-3). This balance reflects how new carbon produced by primary production is ultimately respired at proportional rates. Ecosystems that tend to be exceptions to this rule include blackwater rivers (where low light availability but high carbon content lead to net heterotrophy) and starting algal cultures (where primary production during the exponential growth phase temporarily exceeds respiration; Fig. 3-3).

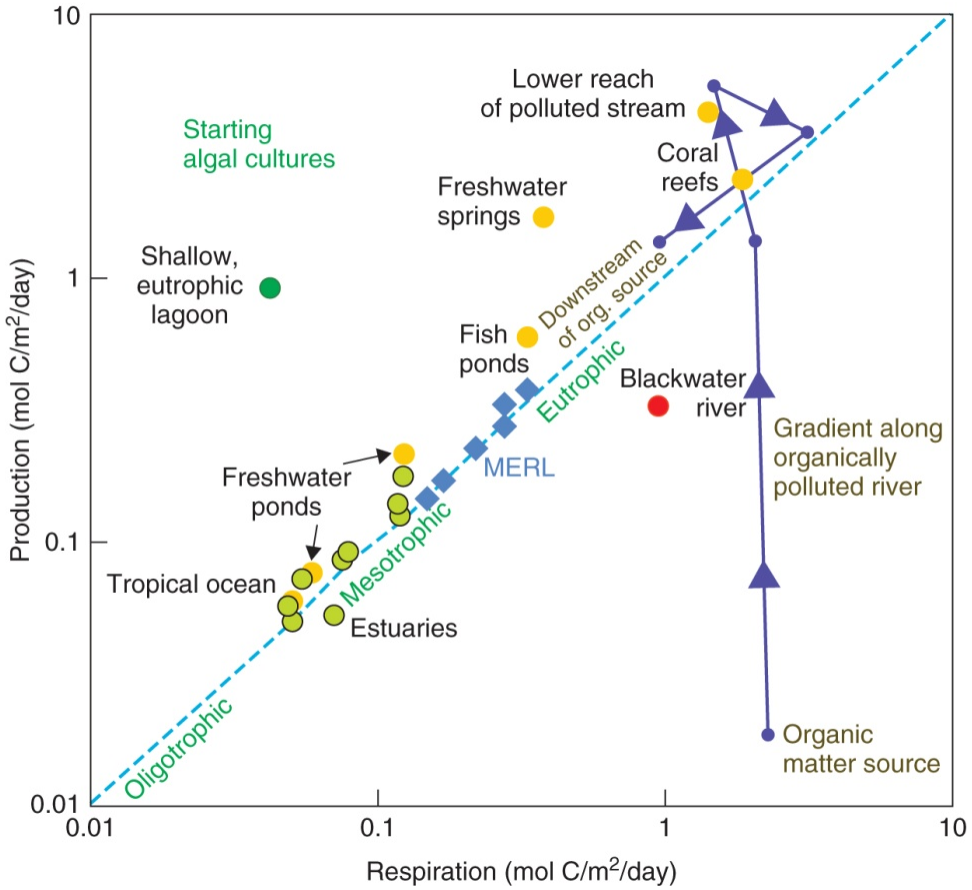

Figure 3-3. Relationship between primary production and respiration across a multitude of ecosystems, where most systems tend to fall on the 1:1 line, where primary production equals reparation (from Testa et al. 2013). Also indicated are broad categories of "trophic state" that reflect the degree of eutrophication in the system. (MERL – Marine Ecosystems Research Laboratory at URI).

Interestingly, upon plotting all daily gross primary production and respiration measurements from the Maryland ConMon stations, this tendency for metabolic balance is maintained, where GPP and respiration fall along the 1:1 line (Fig. 3-4). In comparing the scales of Figure 3-3 and 3-4, it is clear that many of the observations within the Maryland ConMon stations are high relative to other ecosystems, categorizing many stations as either "mesotrophic" or "eutrophic". The substantial amount of scatter around the 1:1 line in Figure 3-4 underscores the fact that GPP and respiration can be temporarily out of balance, leading to significant heterotrophy and/or autotrophy.

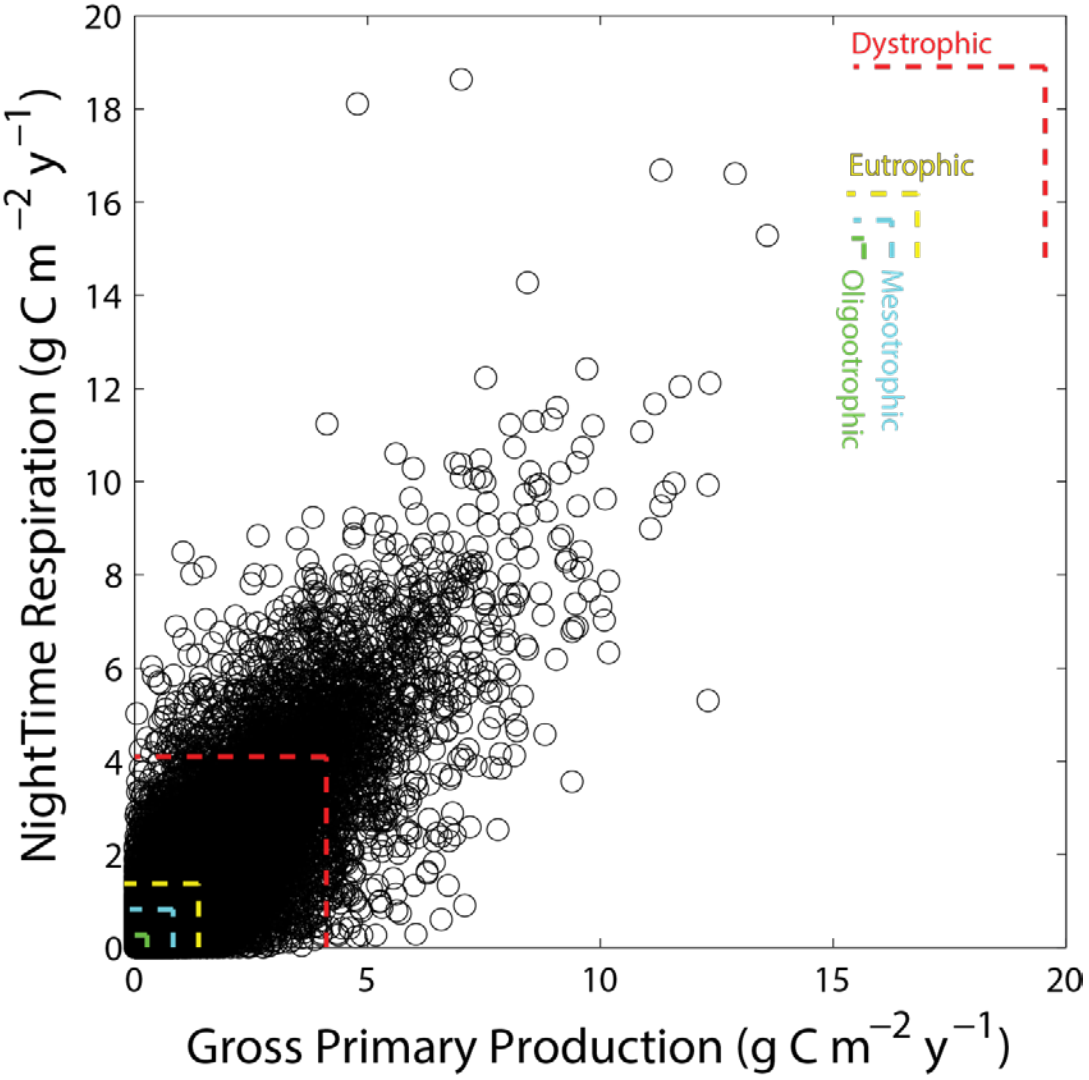

Figure 3-4. Relationship between primary production and respiration across all Maryland ConMon stations. Data clustered on the 1:1 line (not drawn) indicate measurements where primary production equals respiration. The fact that many data fall between rates of 0.5 to 1 g C m^{-2} y^{-1} indicate the potential for eutrophication at many times and places within Maryland waters (see Figure 3-3). These daily rates are scaled up to annual rates assuming constant daily metabolism and compared to trophic categories from Nixon (1995). While such simple upscaling is unrealistic give high daily variability, we lack estimates of metabolism for every month of the year to do an appropriate upscaling.

Temporal variation in GPP and respiration appears to follow an annual cycle where rates peak in warm months for the majority of the stations examined (Figs. 3-5 & 3-6). We would expect annual peaks in GPP to correspond to peak light availability during summer, while respiration would follow the annual temperature cycle, which includes late summer peaks (Testa et al. 2013). The offset of peak GPP in early summer and peak respiration in later summer tends to lead to early summer (or even spring) peaks in net ecosystem production (GPP-R; Smith and Kemp 1995). Despite similar seasonal variations, there were substantial differences in the magnitude of GPP and R across ConMon stations. Figures 3-5 and 3-6 illustrate that rates of GPP and respiration can be 3-4 times as high in highly eutrophic, phytoplankton-dominated systems (Corsica River, Patapsco River) as compared to SAV-dominated systems or the turbid, low GPP systems that characterize the tidal fresh reaches of many Bay tributaries (e.g., Jug Bay in the upper Patuxent River). Total nitrogen (TN) concentrations measured near all of these sites range within 1.0-2.0 mg/L (2005-2014 data), which are generally quite high. Because these metabolic rates are not only a function of nutrient availability, but also light availability and local physical conditions (e.g., water residence time), it is difficult to separate out differences between stations without a more comprehensive analysis of water characteristics (e.g., TSS, water clarity, etc).

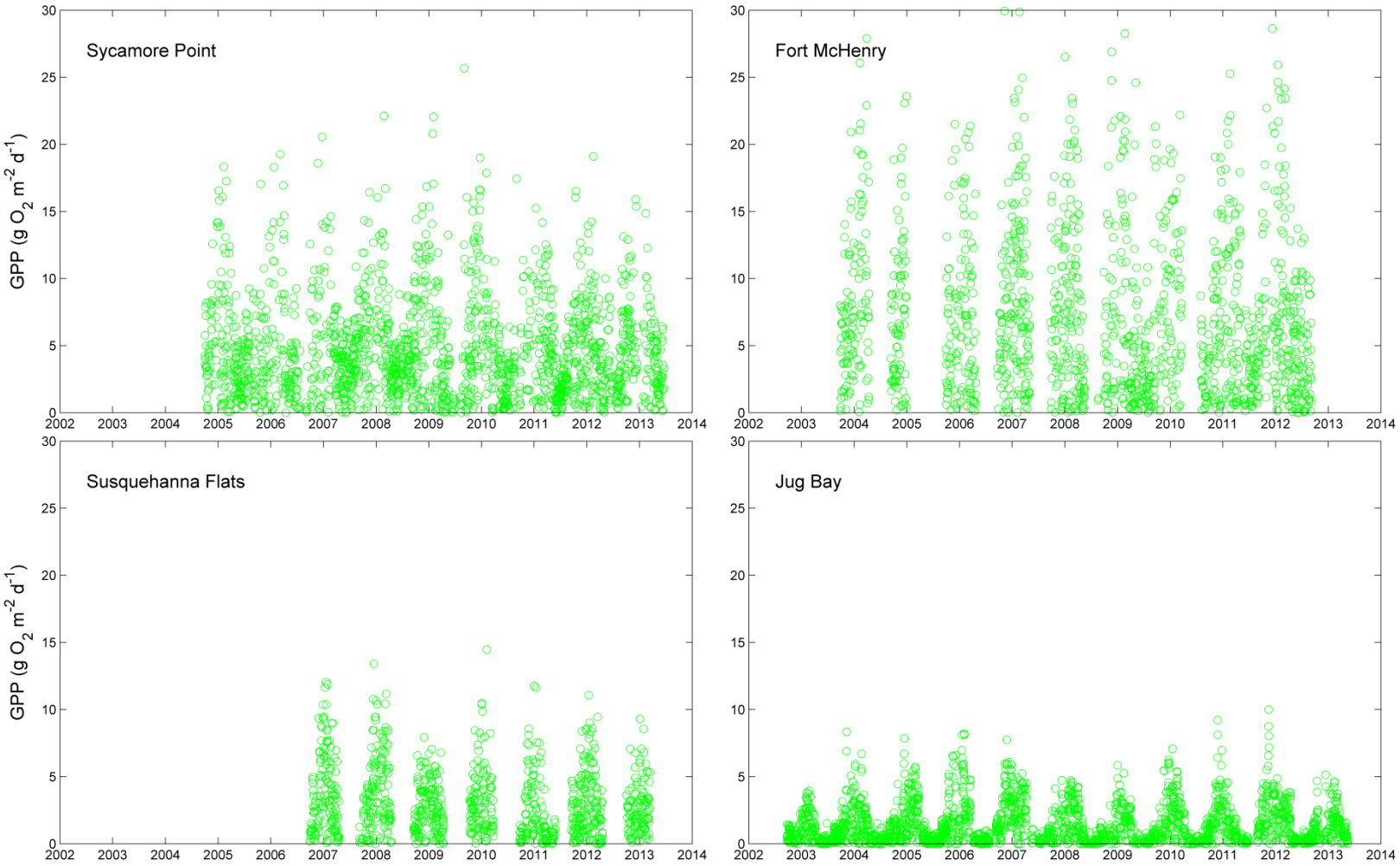

Figure 3-5. Time-series of gross primary production rates for two highly eutrophic sites (Sycamore Point in the Corsica River and Fort McHenry in the Patapsco River; top panels), an SAV-dominate site (Susquehanna Flats; bottom left panel), and a tidal freshwater, turbid site (Jug Bay in the upper Patuxent; bottom right panel).

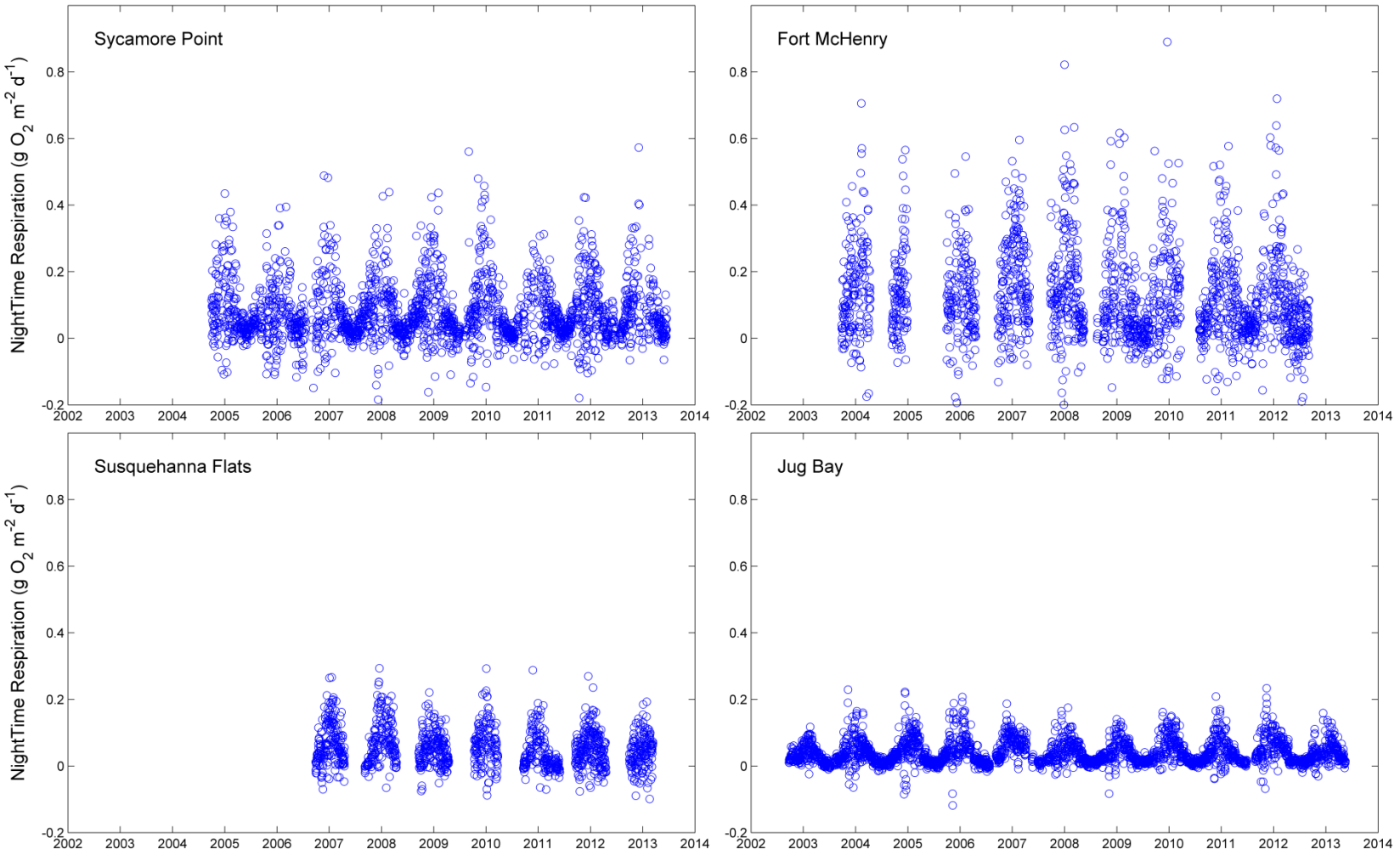

Figure 3-6. Time-series of hourly respiration rates for two highly eutrophic sites (Sycamore Point in the Corsica River and Fort McHenry in the Patapsco River; top panels), an SAV-dominate site (Susquehanna Flats; bottom left panel), and a tidal freshwater, turbid site (Jug Bay in the upper Patuxent; bottom right panel).

An exploratory analysis of the relationship between metabolic rates and local water conditions is possible with contemporaneous ConMon data, and is revealing of some explanatory factors. While these comparisons also reveal a dominant influence of temperature on metabolic rates, the cross-system comparisons describe a peak in both GPP and respiration at moderate salinities (5-10 salinity units; Figs. 3-7 & 3-9). Given that high turbidity and flushing rates are expected in low salinity waters, while higher salinity waters (e.g., Maryland Coastal Bays) are poor in nutrients, we might expect peak GPP (and associated respiration) to occur in these moderate salinity waters of an estuary like the Chesapeake Bay. In fact, the collection of comparably high GPP rates that occurred in very-low salinity waters (Fig. 3-8) were restricted to the warmest temperature periods, which reflects high GPP rates during these seasons, where turbidity is at seasonal minima and river flows (and associated flushing) are low. Similar patterns were found for these variables related to water temperature, which further emphasizes the relationship between GPP and respiration (Fig. 3-9). pH was generally higher at elevated rates of GPP and respiration, which reflects the fact that CO_2 was removed from the water during these periods of high photosynthetic activity.

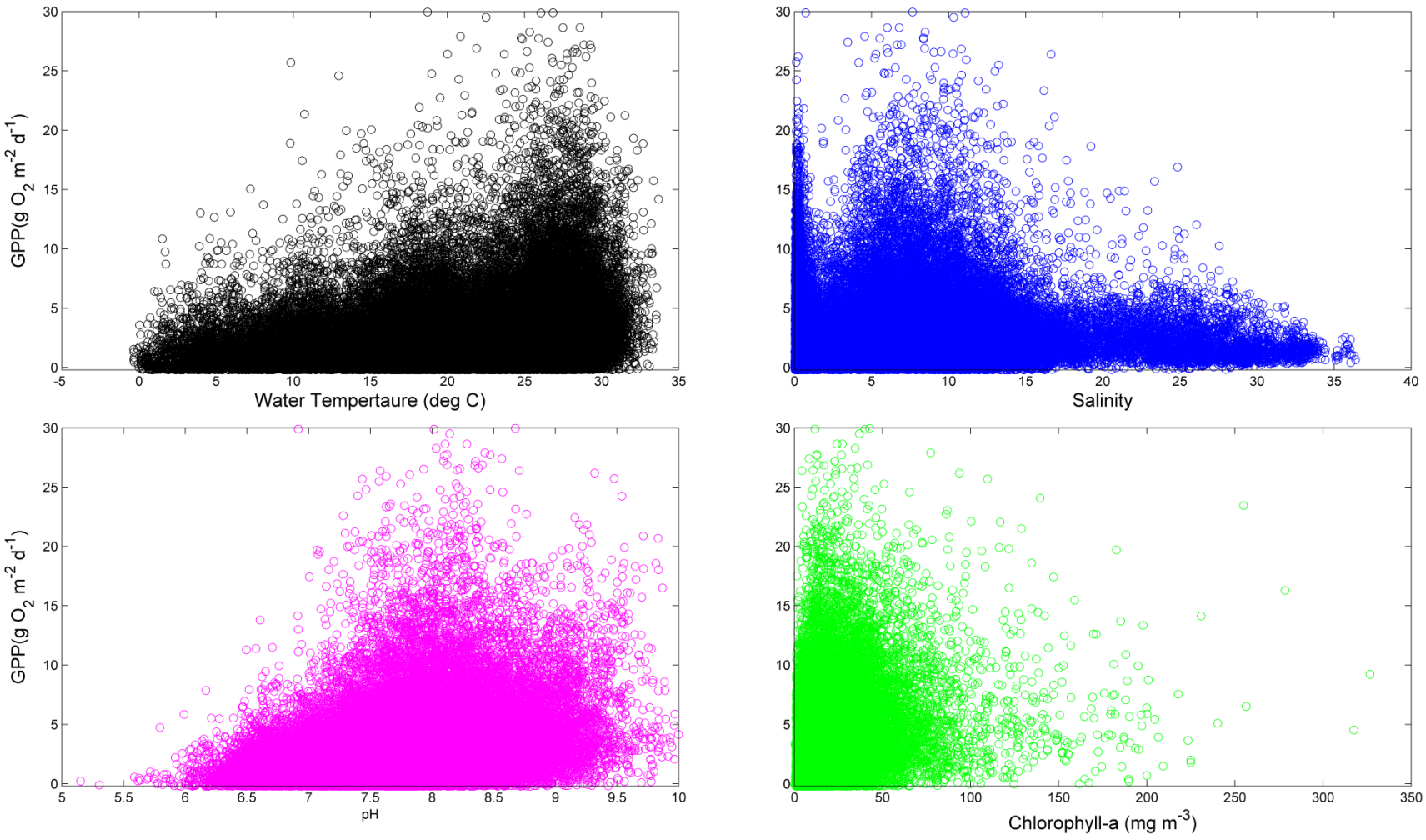

Figure 3-7. Relationship of gross primary production rates for all days and all sites in the Maryland ConMon dataset and (top left) water temperature, (top right) salinity, (bottom left) pH, and (bottom right), chlorophyll-a.

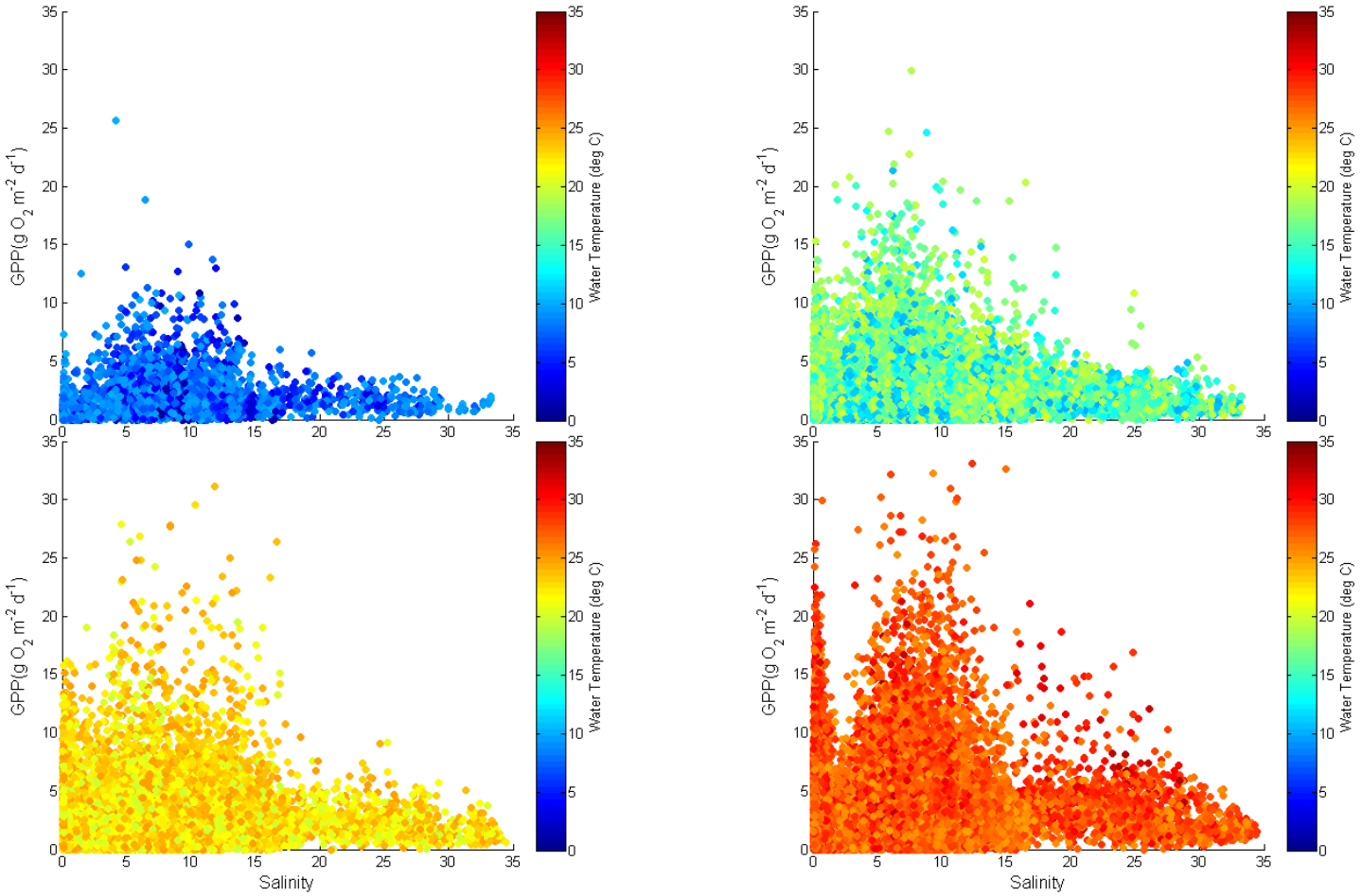

Figure 3-8. Relationship of gross primary production rates and salinity for all days and all sites in the Maryland ConMon dataset, where the shading of the circles reflects the temperature for that day (see color bar to the right). Data are divided into temperature ranges below 10 deg C (top left), 10-20 deg C (top right), 20-25 deg C (bottom left), and > 25 deg C (bottom right).

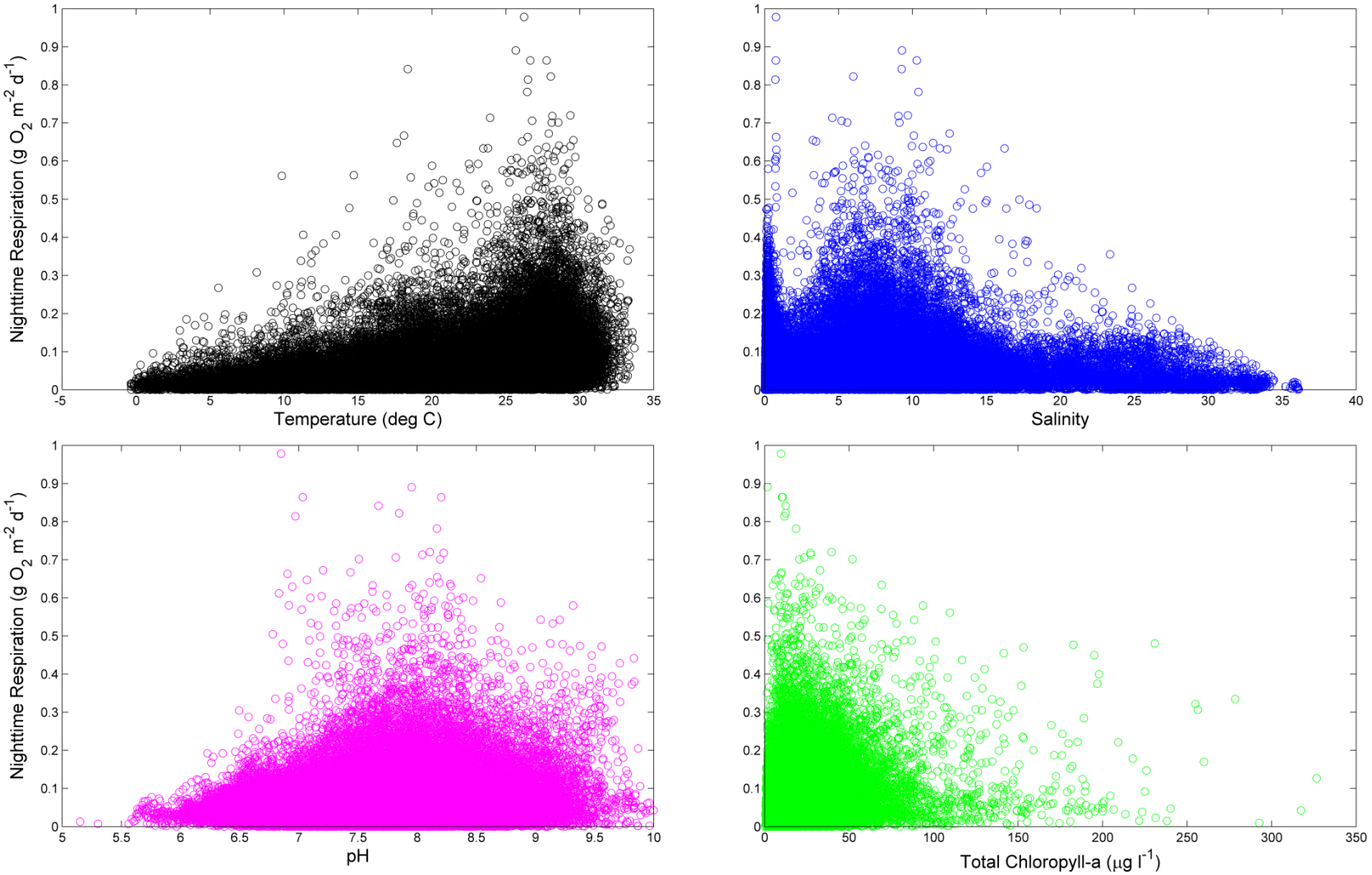

Figure 3-9. Relationship of hourly respiration rates for all days and all sites in the Maryland ConMon dataset and (top left) water temperature, (top right) salinity, (bottom left) pH, and (bottom right), chlorophyll-a.

We sought to associate the magnitude of GPP and respiration with local nutrient loading from the watershed and thus we revisited the 19 shallow-water stations where we previously built models to predict chlorophyll-a (Testa et al. 2015). For these tributaries, we computed the April to October mean GPP and respiration for all ConMon stations within a particular tributary, and regressed these mean metabolic rates to the January to May total nitrogen (TN) and total phosphorus (TP) loads from the Chesapeake Bay Watershed Model. We found these regressions for all variables to indicate relatively weak correlations (Fig. 3-10), but we show the relationship between GPP and TN load for further inspection. The lack of a clear relationship between these variables, although we would expect GPP and TN load to be positively correlated, likely reflects the confounding effects of flushing rate and differing primary producers (e.g., SAV) in altering load-metabolism relationships. Upon related GPP to a composite metric that includes variability in nutrient availability in addition to tributary depth and residence time (Testa et al. 2015), the relationship improves (Fig. 3-10), highlighting the importance of flushing in controlling metabolism in these tributaries. Mattawoman and Piscataway Creek do not follow the general pattern of elevated GPP with increasing flushing, which may be associated with the fact that the effects of flushing will be muted in systems dominated by rooted vascular plants (SAV), as is the case in these two tributaries.

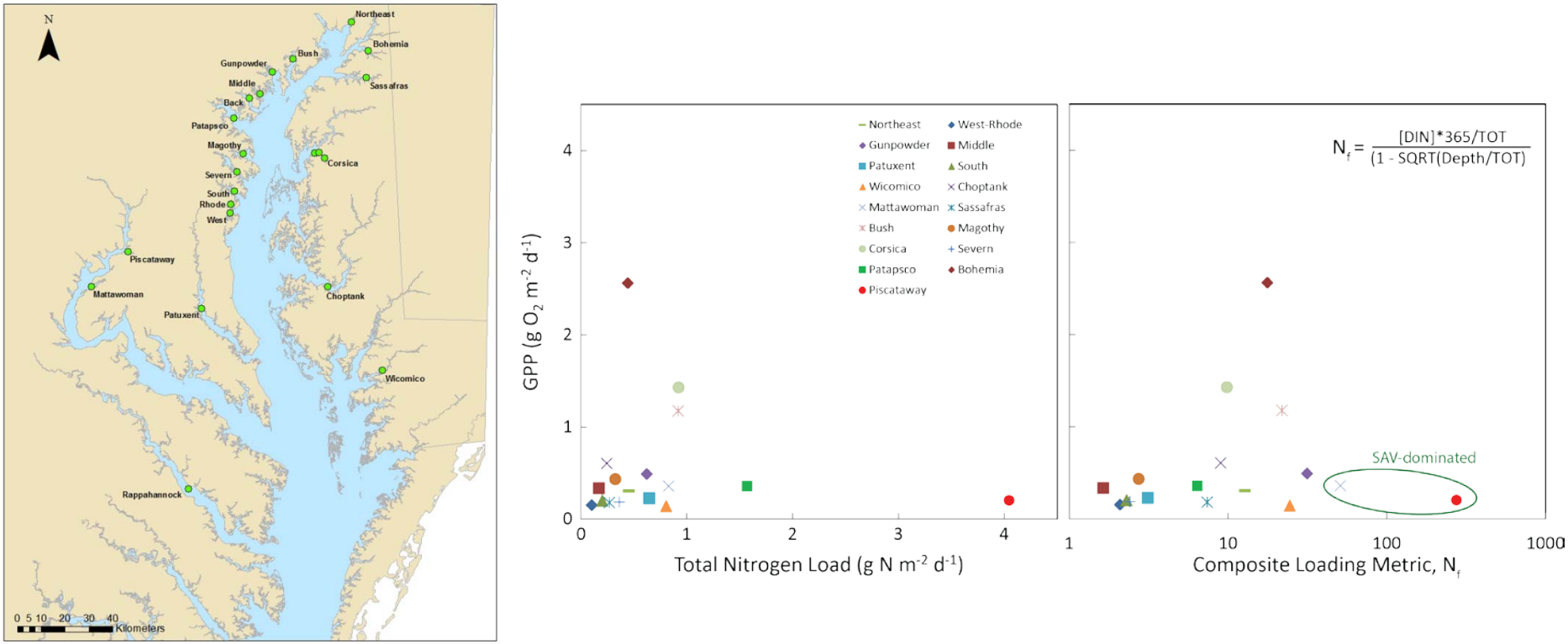

Figure 3-10. Map of shallow water tributaries where nutrient load estimates are available (left panel). Preliminary relationship of winter-spring total nitrogen load to summer (May to September) gross primary production averages across all data at all stations in a particular tributary (center panel). Panel on the far right is the summer GPP estimates related to a composite loading metric that accounts for flushing time (TOT), as in Testa et al. (2015).

The effort to compute metabolic rates for multiple years across 105 stations has already led to numerous insights into the spatial and temporal patterns of primary production and respiration in Maryland tidal waters. There are many additional efforts left to be completed to fully integrate these rates within the other monitoring efforts in Chesapeake Bay. First, the quantification of total suspended solids (TSS), light availability (Secchi depth), and nutrient concentrations for all of the ConMon stations would allow for a more mechanistic understanding of the differences between metabolic rates across space. We have begun the process of relating these metabolic indices to local estimates of nutrient loading and physical conditions (flushing rate), but there is an opportunity to expand this effort to the other tributaries, as well as to associate BMP activities that have been performed on land to changes in metabolic rates over time at sentinel stations (e.g., Back River). Finally, there is room for a more comprehensive analysis of trends over time at select stations, focusing on changes in metabolic rates that may be associated with management actions and climatic changes. These efforts would be similar to prior efforts to examine oxygen criteria failure frequency over time (Boynton et al. 2014). Changes in climate may have substantial effects on metabolic rates and oxygen depletion, where elevated temperatures may increase respiration and lead to more frequent low-DO excursions, while elevated freshwater inputs may reduce primary production through increased flushing and turbidity or increase primary production via elevated nutrient inputs. Efforts to identify an approach for estimating annual rates (ConMon permits, at most, 200 days per year of sampling), would also yield values that could be more readily placed in a comparative analysis with other estuarine systems.

3-4 Conclusions and Implications

During this contract period we completed the following tasks:

- Derived estimates of ecosystem primary production and respiration as useful indicators of trophic state using ConMon datasets containing high frequency measurements of dissolved oxygen, temperature, and salinity.
- Developed an analysis of derived metabolic rates for 105 ConMon stations and these rates indicate clear relationships between metabolic rates and water temperature, salinity, and pH.
- A Matlab package is now available to process ConMon data directly from a text file or website and generate estimates of metabolic rates and trophic status.
- Developing a scheme to ‘annualize’ the metabolic rates for a more realistic comparison with published numeric criteria for establishing “trophic state”, or extent of eutrophication and associate these rates with nutrient availability.

- Examining time-series of these rate data (especially at sentinel sites) to look for changes in trophic estimates over time that may be associated with changes in nutrient loading rates caused by management actions.

3-5 References

Boynton, W. R., W. M. Kemp, and C. W. Keefe. 1982. A comparative analysis of nutrients and other factors influencing estuarine phytoplankton production, in Estuarine Comparisons, edited by V. S. Kennedy, pp. 69-90, Academic Press, New York.

Boynton, W.R., J.M. Testa, C.L.S. Hodgkins, J.L. Humphrey and M.A.C. Ceballos. 2014. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 31. Jul. 1984 – Dec. 2013. Ref. No. [UMCES] CBL 2014-051. [UMCES Technical Series No. TS-645-14].

Burger, N. H. and J. D. Hagy. 1998. Patuxent River high frequency monitoring, p. 153-183. In: W. R. Boynton and F. M. Rohland (eds.).Ecosystem Processes Component Interpretive Report No. 15. Ref. No. [UMCES]CBL 98-073a. Solomons, MD.

Caffrey, J. M. 2004. Factors controlling net ecosystem metabolism in U.S. estuaries., Estuaries, 27, 90-101.

Gazeau, F., A. V. Borges, C. Barrón, C. M. Duarte, N. Iversen, J. J. Middelburg, B. Delille, M. D. Pizay, M. Frankignoulle, and J. P. Gattuso. 2005. Net ecosystem metabolism in a micro-tidal estuary (Randers Fjord, Denmark): evaluation of methods, Marine Ecology Progress Series, 301, 23-41.

Kremer, J. N., A. Reischauer, and C. D'Avanzo. 2003. Estuary-specific variation in the air-water gas exchange coefficient for oxygen, Estuaries, 26, 829-836.

Marino, R., and R. W. Howarth. 1993. Atmospheric oxygen exchange in the Hudson River: dome measurements and comparison with other natural waters, Estuaries, 16, 433-445.

Michael, B., T. Parham, M. Trice, B. Smith, D. Domotor, and B. Cole. 2013. Quality Assurance Project Plan for the Maryland Department of Natural Resources Chesapeake Bay Shallow Water Quality Monitoring Program for the period July 1, 2013 – June 30, 2014. http://mddnr.chesapeakebay.net/eyesonthebay/documents/SWM_QAPP_2013_2014_FINAL.pdf

Odum, H. T., and C. M. Hoskin. 1958. Comparative studies of the metabolism of marine waters, Publications of the Institute of Marine Science-University of Texas, 5, 16-46.

Smith, E. M., and W. M. Kemp. 1995. Seasonal and regional variations in plankton community production and respiration for Chesapeake Bay, Marine Ecology Progress Series, 116, 217-231.

Testa, J.M., W.M. Kemp, C.S. Hopkinson, and S.V. Smith. 2013. Ecosystem Metabolism. In: Day, J.W., Crump, B.C., Kemp, W.M., and Yáñez-Arancibia,A. (Eds.), Estuarine Ecology, Volume 2, Chapter 15. John Wiley & Sons, Inc., Hoboken, NJ.

Testa, J.M., L.A. Harris, W.R. Boynton, C.L.S. Hodgkins, J.L. Humphrey and M.C. Day. 2015. Ecosystem Processes Component (EPC). Maryland Chesapeake Bay Water Quality Monitoring Program, Level 1 report No. 32. Jul. 1984 – Dec. 2014. Ref. No. [UMCES] CBL 2015-043. [UMCES Technical Series No. TS-674-15].

Vollenweider, R. A. 1976. Advances in defining critical loading levels for phosphorus in lake eutrophication, Memorie dell'Istituto Italiano di Idrobiologia, 33, 53-83.

Chapter 4

Coupled Dissolved Oxygen and pH Variability and its Association with Ecosystem Metabolism

J.M. Testa, C.L.S. Hodgkins, and J.L. Humphrey

4-1 INTRODUCTION 1
4-2 METHODS 2
4-2.1 STUDY AREA DESCRIPTIONS 3
4-2.2 DATA MANIPULATIONS AND ANALYTICAL APPROACHES 9
4-3 RESULTS AND DISCUSSION 9
4-3.1 TEMPORAL CORRELATIONS BETWEEN DO AND PH 9
4-3.2 SPATIAL PATTERNS OF DO AND PH 14
4-3.3 FREQUENCY OF EXTREME PH LEVELS 18
4-3.4 CONCLUSIONS AND IMPLICATIONS 18
4-4 REFERENCES 19

4-1 Introduction

Of the many challenges to the restoration of coastal ecosystems, ocean acidification has only recently emerged as a topic of interest in estuaries and coastal zones. This is in part due to the complexity of processes that influence carbonate chemistry across multiple temporal and spatial scales in these dynamic habitats (Salisbury et al. 2008, Feely et al. 2010, Borges and Gypens 2010, Waldbusser et al. 2011, Cai et al. 2011, Hofmann et al. 2011, Arias et al. 2011, Barton et al. 2012). It is, however, clear that in many systems eutrophication (and the consequent enhanced production-respiration) coupled with increasing atmospheric CO_2 results in additive acidification effects on carbonate chemistry as noted for diverse regions including, the Chesapeake Bay (Waldbusser et al. 2011), the Gulf of Mexico (Cai et al. 2011), and the California Current (Gruber et al. 2012). Because eutrophication tends to be associated with elevated respiration in deep waters, it can generate both suppressed pH and elevated hypoxia, which interact to generate elevated stress on marine organisms (Miller et al. 2016).

While much of the attention related to hypoxia has focused on seasonal, deep water habitats, the majority of attention on pH declines associated with elevated atmospheric CO_2 has focused on

the open ocean. Surprisingly, far less attention has focused on high-frequency and large fluctuations in both dissolved oxygen (hereafter DO) and pH in productive, shallow water habitats, including those in Chesapeake Bay and its tributaries. Much of the shallow habitat within Chesapeake Bay is within tributaries, where nutrient inputs and nutrient concentrations are relatively high and rates of primary production and respiration are correspondingly large. High rates of photosynthesis in these habitats leads to high-rates of CO_2 uptake and increases in pH, while high respiration rates during the night generate CO_2 and cause pH declines. Corresponding daytime increases and nighttime declines in DO accompany these pH changes, often in lockstep. Despite recent efforts to understand the co-variability in DO and pH changes – and the implications of these changes on the acidification potential of Chesapeake Bay waters – a comprehensive analysis of coupled DO-pH dynamics has yet to be achieved. Because quantification of these variations is key to understanding how these shallow environments will fare in the face of nutrient load reductions, tools and data sets that consider the shallows are increasingly useful for coastal water management.

The goal of this chapter is to (1) quantify the nature and correspondence between DO and pH at 110 ConMon stations in the Maryland waters of Chesapeake Bay, (2) examine relationships between DO and dissolved inorganic carbon and what this implies for phytoplankton contributions to DO and pH changes, and (3) assess the vulnerability of all 110 ConMon sites to extreme high or low levels of pH, which can impact both habitat, the early life histories of important estuarine species, and biogeochemical cycling.

4-2 Methods

The continuous monitoring (ConMon) program in Maryland shallow waters provides detailed time series of water quality information that can be applied to water quality assessments at many tributary and mainstem Bay sites in Maryland. These data offer some of the best information for understanding hourly to interannual dynamics of DO and other conditions (e.g., water clarity, temperature, salinity, pH, and chlorophyll-a) relevant to sustaining aquatic organisms. Here and in the past, the Ecosystem Processes Component (EPC) has examined ConMon data to develop indicators of estuarine condition or health and relate these metrics to variables (e.g., chlorophyll-a, temperature, etc.) that represent processes that control criteria compliance due to both manageable factors (e.g., nutrient loading) and climate-related, unmanageable factors (e.g., temperature, tidal mixing).

4-2.1 Study Area Descriptions

We included 110 ConMon stations in our analysis, spanning at 15-year period that includes enormous gradients of salinity, temperature, and DO conditions. Continuous monitoring data from 2001 to 2014 for all stations (Fig. 4-1, Table 4-1) were obtained from the Maryland Department of Natural Resources Tidewater Ecosystems Assessment division (B. Cole) in electronic (.txt) file format. Because of the near-continuous characteristic of these measurements, a data set with no error and complete days was developed using an R (www.R-project.org) program. Data with failing or invalid codes (as detailed in the MDDNR SWMP QAPP: Michael et al., 2013), missing data, and duplicates were isolated. These rows in their entirety were removed to provide a complete and error free dataset. The date was then expanded into separate month, day, and year columns for future analysis. This standardization was essential for our model averaging exercise and z-scores so that equal samples were available for all days used in the analyses. A full description of these stations is provided in Table 4-1.

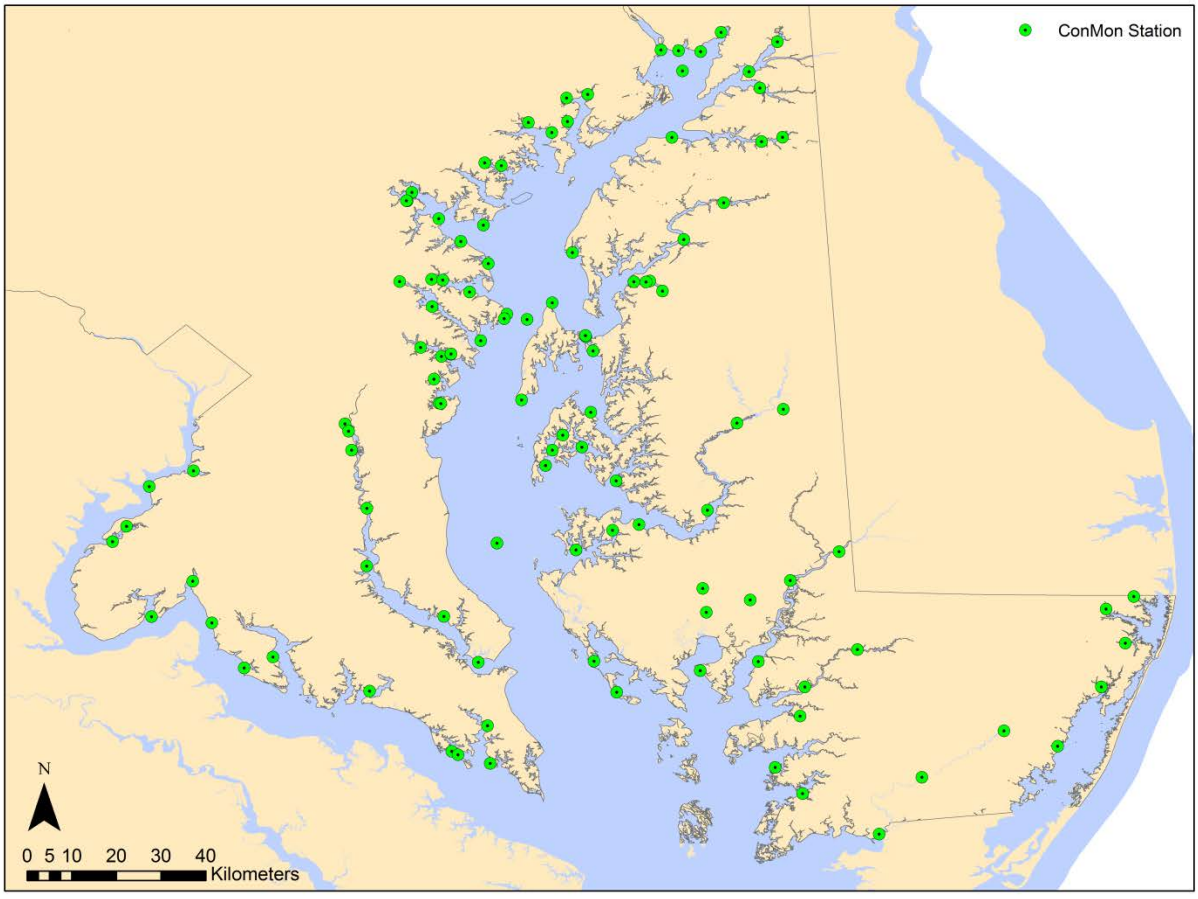

Figure 4-1. Map of ConMon stations in Maryland used in the analysis of relationships between DO and pH.

Table 4-1. Summary statistics for DO and pH across 110 ConMon stations

Name	Stream Code	Three Letter	Tributary	Station Depth	Salinity	DO min	DO max	pH min	pH max	DO vs pH slope	DO vs pH R Square	hour pH > 9.5	% pH >9.5
Snow Hill	POK0316	SNO	Pocomoke River	3.3	0.06	2.08	9.42	5.09	7.12	0.09	0.07	0	0
Williston Lake	XFI9597	WLK	Williston Lake	1.2	0.08	1.88	32.01	5.44	9.74	0.16	0.58	25	<1
Susquehanna Flats	XKH0375	FLT	Chesapeake Bay	0.4	0.13	1.5	20.21	6.85	10.17	0.09	0.26	3623	13
Havre de Grace	XKH2949	SUS	Susquehanna River	3.5	0.14	4.76	13.95	6.95	9.33	0.27	0.77	0	0
Piscataway	XFB2184	PIS	Potomac River	1.2	0.14	0	19.18	6.17	9.89	0.19	0.68	37	<1
Stump Point	XKH2870	STU	Chesapeake Bay	1.4	0.15	3.98	14.64	6.95	9.16	0.26	0.66	0	0
Fenwick	XFB0231	FEN	Potomac River	0.8	0.15	2.43	22.19	6.34	10.04	0.14	0.48	432	2
Pocomoke City	POK0187	POC	Pocomoke River	5.7	0.16	2.27	9.27	5.5	7.54	0.09	0.04	0	0
Mataponi	MTI0015	MTI	Patuxent River	0.6	0.16	0	16.31	4.8	9.03	0.08	0.38	0	0
Charlestown	XKI5022	NOR	Northeast River	1.8	0.18	3.79	15.77	6.32	9.8	0.20	0.64	101	<1
Jug Bay	PXT0455	JUG	Patuxent River	1.3	0.18	0.58	15.71	6.31	9.1	0.11	0.55	0	0
Carpenters Point	XKH2797	CAR	Northeast River	0.8	0.20	3.34	16.49	7.16	9.89	0.14	0.44	43	<1
Iron Pot Landing	WXT0013	IPL	Patuxent River	1.6	0.21	1.36	14.47	6.19	9.37	0.08	0.39	0	0
Mattawoman	XEA3687	MAT	Potomac River	1.5	0.29	0	19.91	5.53	9.88	0.15	0.41	112	<1
Indian Head	XEB5404	IND	Matawoman Creek	1.4	0.30	2.02	12.59	5.94	9	0.29	0.62	0	0
Budds Landing	XJI2396	BUD	Sassafras River	2	0.43	0.19	23.17	5.76	10.27	0.11	0.51	1829	6
Otter Point Creek	XJG7035	OPC	Bush River	0.5	0.43	0.13	20.61	6	10.82	0.18	0.50	1953	3
Georgetown Yacht Basin	XJI1871	GYB	Sassafras River	1.8	0.48	3.18	15.06	6.76	9.54	0.27	0.70	1	<1
Deep Landing	CHE0348	DEE	Chester River	1.7	0.67	2.73	14.09	6.19	9.42	0.21	0.64	0	0
Sharptown	XEJ2464	SPT	Nanticoke River	1.9	0.75	3.41	11.99	6.06	8.42	0.15	0.55	0	0
Mariners Point Park	XJF4289	MPP	Gunpowder River	1.5	0.75	3.55	13.24	6.31	8.99	0.26	0.54	0	0
Church Point	XJG7461	BCP	Bush River	1.5	0.81	1.84	19.27	6.22	9.99	0.13	0.54	314	2
Upper Ferry	WIW0144	UPF	Wicomico River	1.8	0.93	2.51	14.52	6.09	9.05	0.18	0.59	0	0
Aberdeen	XJG2718	GUN	Gunpowder River	1.2	1.03	3.04	14.34	5.81	9.51	0.39	0.52	0	0
Lauderick Creek	XJG4337	LAU	Bush River	1.3	1.25	2.68	17.17	5.98	9.55	0.22	0.59	3	<1
Betterton	XJH2362	BET	Sassafras River	1.8	1.46	4.36	14.8	6.75	9.25	0.28	0.80	0	0

Table 4-1. Continued Summary statistics for DO and pH across 110 ConMon stations

Name	Stream Code	Three Letter	Tributary	Station Depth	Salinity	DO min	DO max	pH min	pH max	DO vs pH slope	DO vs pH R Square	hour pH > 9.5	% pH >9.5
Long Point	XJI8369	BOH	Bohemia River	1.5	1.55	3.64	14.17	6.5	9.41	0.15	0.46	0	0
Locust Point Marina	XKI3890	LOC	Elk River	1.5	1.57	3.92	17.15	5.82	9.59	0.27	0.77	12	<1
High Banks	CHO0417	HBK	Choptank River	2	1.63	2.84	12.27	5.93	8.16	0.14	0.65	0	0
Decoursey Bridge	TRQ0146	TRQ	Transquaking River	0	2.00	1.63	13.27	6.33	17.2	0.17	0.27	1	<1
Kings Landing	PXT0311	KNG	Patuxent River	1.8	2.03	2.64	13.45	6.36	8.71	0.10	0.68	0	0
Hollywood Beach	XKI0256	HOL	Elk River	1.8	2.08	5.53	11.63	6.85	8.96	0.34	0.74	0	0
Cutter Marina	MDR0038	MDR	Middle River	2	2.15	3.05	112.4	6.14	8.99	0.01	0.03	0	0
Strawberry Point	FRG0002	STP	Middle River	1.8	2.16	1.25	14.32	5.42	9.31	0.18	0.44	0	0
Vienna	XDJ8905	VNA	Nanticoke River	2.7	2.93	4.07	11.53	5.97	8.37	0.14	0.65	0	0
Drawbridge	CCM0069	CCM	Chicamicomico River	2.5	4.48	0.1	13.98	5.76	9.22	0.08	0.40	0	0
Rolphs Wharf	XIH0077	ROL	Chester River	3	4.62	0.37	15.84	6.2	8.84	0.16	0.64	0	0
Bestpitch	TRQ0088	BST	Transquaking River	2.7	4.75	0.13	10.74	6.35	8.13	0.10	0.61	0	0
Fort Howard	XIF1735	HOW	Chesapeake Bay	0.6	4.78	1.6	17.54	7.07	9.69	0.16	0.83	8	<1
Blossom Point	XDB4544	BLO	Potomac River	0.5	4.85	2.24	21.41	6.81	9.34	0.19	0.79	0	0
Port Tobacco	XDB8884	PRT	Potomac River	1.3	5.40	1.05	16.4	5.89	9.32	0.14	0.66	0	0
Down's Park	XHF6841	DWN	Chesapeake Bay	0.9	6.15	0.3	24.15	6.95	9.63	0.14	0.83	17	<1
Fort Armistead	XIE2581	ARM	Patapsco River	1.5	6.22	0	21.05	6.8	9.67	0.13	0.82	10	<1
Fort Smallwood	XHF9808	SMA	Patapsco River	0.6	6.36	0	19.95	6.9	9.8	0.13	0.61	36	<1
Sycamore Point	XHH3851	COR	Corsica River	1.8	6.76	0	21.73	6.19	10.17	0.11	0.69	2141	3.5
Popes Creek	XDC3807	POP	Potomac River	1.8	6.84	1.44	14.43	6.83	9.02	0.12	0.71	0	0
Shelltown	POK0009	SHL	Pocomoke River	1.7	6.97	1.62	12.61	5.75	8.6	0.12	0.44	0	0
Masonville Cove - Bottom	XIE4741	MSB	Patapsco River	2	7.01	0.06	23.47	6.57	9.84	0.11	0.75	1	<1
Gratitude Marina	XHG8442	THX	Chesapeake Bay	2	7.21	0.96	20.48	6.4	9.5	0.16	0.79	0	0
Whitehurst	CTT0001	WHI	Magothy River	2.9	7.26	0.67	20.53	6.91	9.48	0.14	0.70	0	0
Ben Oaks	SEV0116	BEN	Severn River	2.3	7.46	0	180.8	6.35	9.85	ND	ND	ND	ND
Jamaica Point	XEI7405	JAM	Choptank River	1.8	7.60	2.23	17.69	6.64	9.33	0.18	0.80	0	0
Benedict	XED0694	BCT	Patuxent River	1.7	7.61	0.2	15.74	6.42	9.02	0.10	0.62	0	0

Table 4-1. Continued Summary statistics for DO and pH across 110 ConMon stations

Name	Stream Code	Three Letter	Tributary	Station Depth	Salinity	DO min	DO max	pH min	pH max	DO vs pH slope	DO vs pH R Square	hour pH > 9.5	% pH >9.5
Beards Creek	XGE7059	BDS	South River	1.5	7.82	0.13	16.97	6.77	9.28	0.14	0.84	0	0
Emory Creek	XHH5046	EMO	Corsica River	1.9	7.95	0	17.6	6.77	9.81	0.18	0.88	71	1
Annapolis CBIBS	XGF7832	NAP	Chesapeake Bay	5.49	8.02	2.11	19.01	6.55	9.14	0.11	0.66	0	0
Masonville Cove	XIE4741	MSV	Patapsco River	2	8.04	0.01	18.42	6.69	9.53	0.11	0.72	36	<1
Swan Point	XCC8346	SWN	Potomac River	0.8	8.08	0.65	20.61	6.85	9.11	0.13	0.83	0	0
Baltimore Harbor	XIE5748	MCH	Patapsco River	3	8.13	0.1	20.96	6.64	9.79	0.12	0.77	41	<1
Possum Point - Surface	XHH4931	PPT	Corsica River	2.4	8.20	0.37	18.1	6.88	9.6	0.14	0.84	7	<1
Masonville Cove Pier	XIE4742	MSC	Patapsco River	2	8.24	0.44	19.12	6.99	10.14	0.14	0.84	161	<1
Love Point	XHG2318	LUV	Chesapeake Bay	0.6	8.29	1.01	20.46	6.96	9.45	0.14	0.75	0	0
Sandy Point - East Beach	XHF0561	SPE	Chesapeake Bay	2	8.33	1.37	15.47	0	9.36	0.18	0.78	0	0
Harness Creek Upstream	ZDM0002	HCU	South River	1.3	8.40	0	21.11	6.87	9.56	0.14	0.78	2	<1
Possum Point - Bottom	XHH4931	PPB	Corsica River	2.4	8.52	0.05	16.91	6.67	9.63	0.14	0.81	13	<1
Cedar Point	XGE5984	CED	South River	2	8.59	2	15.11	7.2	9.14	0.12	0.69	0	0
Harness Creek Downstream	ZDM0001	HCD	South River	1.8	8.67	0.11	17.73	6.83	9.58	0.13	0.81	4	<1
Whitehaven	XCJ6023	WHV	Wicomico River	1.8	8.70	1.18	10.62	3.74	8.33	0.14	0.68	0	0
Shady Side	XGE0284	WSR	West River	1.6	8.74	0.22	17.03	6.64	9.09	0.13	0.82	0	0
The Sill Bottom	XHH4916	SIB	Corsica River	4.2	8.75	0	16.25	6.82	9.91	0.15	0.75	13	<1
The Sill Surface	XHH4916	SIL	Corsica River	4.2	8.77	2.52	17.72	6.95	9.6	0.17	0.86	5	<1
SERC	XGE3275	RHO	Rhode River	2.2	8.78	0.16	17.72	6.93	9.2	0.13	0.79	0	0
Sandy Point - South Beach	XHF0460	SPS	Chesapeake Bay	1.8	8.84	1.65	16.46	6.84	9.28	0.15	0.67	0	0
Sherwood Forest	XHE1973	SHW	Severn River	3.2	9.07	0.1	14.74	6.91	9.09	0.13	0.70	0	0
Wicomico Beach	XCC9680	WIB	Potomac River	0.5	9.10	1.87	19.11	6.64	9.44	0.14	0.78	0	0
Stonington	XHF3719	MAG	Magothy River	1.9	9.26	0.28	19.26	0	9.25	0.14	0.75	0	0
Cattail Creek	CTT0014	CAT	Magothy River	0	9.29	0	15.49	6.41	8.57	0.08	0.48	0	0
Chesapeake Yacht Club	XGE0320	CYC	West River	2	9.34	0.34	17.15	6.78	9.72	0.11	0.72	146	<1
Tyaskin	XCI9167	TYA	Nanticoke River	0.9	10.16	4.51	17.84	6.91	9.01	0.18	0.57	0	0
Kent Point	XGF0681	KNT	Eastern Bay	0.5	10.32	1.99	17.41	7.13	8.92	0.12	0.55	0	0

Table 4-1. Continued Summary statistics for DO and pH across 110 ConMon stations

Name	Stream Code	Three Letter	Tributary	Station Depth	Salinity	DO min	DO max	pH min	pH max	DO vs pH slope	DO vs pH R Square	hour pH > 9.5	% pH >9.5
Little Monie Creek	LMN0028	LMN	Wicomico River	0.8	10.66	1.04	12.12	5.54	8.11	0.09	0.48	0	0
Kent Narrows Outside	XGG8458	KNO	Chester River	0.8	10.75	1.88	14.85	6.96	9.2	0.13	0.55	0	0
Hambleton Point	XFG9164	HAM	Eastern Bay	0.8	11.00	1.83	19.06	7.28	9.19	0.12	0.74	0	0
Garys Creek	XEG4991	GAR	Little Choptank River	1.5	11.01	0.45	12.95	6.84	8.84	0.14	0.78	0	0
Horn Point Lab	XEH5622	HPL	Choptank River	1.8	11.03	0.7	15.02	7.09	9.19	0.13	0.64	0	0
Fishing Bay	XCH8097	FSB	Fishing Bay	1.8	11.05	1.1	12.89	6.77	8.71	0.17	0.66	0	0
Breton Bay (Pawpaw Point)	XCD5599	BBY	Potomac River	1	11.05	0.01	18.14	6.48	9.63	0.12	0.71	40	<1
Kent Narrows Inside	XGG8359	KNI	Chester River	0.6	11.05	1.42	17.82	6.99	9.36	0.11	0.62	0	0
Pin Oak	XDE4587	PIN	Patuxent River	1.2	11.05	0.16	16.33	7.05	9.34	0.14	0.75	0	0
Chesapeake Biological Lab	XCF9029	CBL	Patuxent River	2.4	11.14	0.7	17.03	5.91	9.25	0.12	0.74	0	0
Gooses - Bottom	XEF3551	GOB	Chesapeake Bay	12	11.28	4.66	20.05	3.04	9.79	ND	ND	ND	ND
Mulberry Point	XFG5054	MUL	Choptank River	1.3	11.38	2.61	13.74	7.17	9.04	0.13	0.75	0	0
CBEC	XGG6667	CBE	Eastern Bay	1.8	11.42	0.9	14.59	6.95	9.08	0.14	0.71	0	0
Sage Point	XBF6843	SAG	Potomac River	1.2	12.08	0.48	14.83	7.12	9.2	0.12	0.70	0	0
Piney Point	XBE8396	PNY	Potomac River	1.4	12.19	0.02	18.23	6.89	9.65	0.13	0.73	6	<1
Casson Point	XEG2646	LIL	Little Choptank River	1.5	12.41	3.4	15.32	7.13	8.95	0.13	0.56	0	0
Harris Creek Upstream	XFG6431	HAU	Harris Creek	3.8	12.51	4.4	13	7.36	9.29	ND	ND	0	0
St Georges Creek	XBF7904	SGC	Potomac River	1.8	12.65	0.26	16.12	6.99	9.45	0.11	0.67	0	0
Harris Creek Profiler/profiler surf	XFG4618	PRO	Harris Creek	2.5	13.03	2.03	12.97	7.49	8.63	ND	ND	ND	ND
House Point	XCG9168	HPT	Honga River	0.6	14.13	3.87	12.76	7.05	8.86	0.10	0.51	0	0
St. Mary's College	XCF1440	SMC	St. Mary's River	4.3	14.47	0	15.14	6.7	9.3	0.11	0.70	0	0
Muddy Hook Cove	XCG5495	HON	Honga River	0.9	14.50	2.6	15.52	6.96	9.11	0.07	0.43	0	0
Harris Creek Downstream	XFG2810	HAD	Harris Creek	3	14.56	4.47	12.94	7.49	8.58	ND	ND	0	0
Manokin	XBI6387	MAN	Manokin River	1.5	15.13	3.38	15.27	6.91	8.82	0.22	0.69	0	0
Big Annemessex	XBJ3220	BAN	Big Annemessex River	1.2	15.35	3.05	11.55	7.18	8.74	0.11	0.57	0	0
Pocomoke Sound	XAJ5327	SOU	Pocomoke River	3.8	15.51	6.14	8.76	7.77	8.11	ND	ND	0	0

Table 4-1. Continued Summary statistics for DO and pH across 110 ConMon stations

Name	Stream Code	Three Letter	Tributary	Station Depth	Salinity	DO min	DO max	pH min	pH max	DO vs pH slope	DO vs pH R Square	hours pH > 9.5	% pH > 9.5
Gooses - Surface	XEF3551	GOO	Chesapeake Bay	12	17.05	0	13.02	7.05	8.78	0.12	0.72	1	<1
Profiler Bottom	XHF0488	PRB	Chesapeake Bay	16	17.69	0.01	7.37	7.17	8.09	-0.10	0.01	0	0
Bishopville Prong	XDM4486	BSH	Coastal Bays	0.8	19.06	0	31.1	5.71	9.8	0.08	0.74	2	<1
Newport Creek	NPC0012	NPC	Coastal Bays	1	19.30	0.08	15.77	5.92	8.81	0.08	0.52	0	0
Greys Creek	XDN6921	GYK	Coastal Bays	0.9	20.41	0.11	31.06	5.87	9.4	0.05	0.33	0	0
Turville Creek	TUV0021	TUV	Coastal Bays	0.8	22.13	0.02	17.85	6.13	9.17	0.09	0.76	0	0
Public Landing	XBM8828	PUB	Coastal Bays	0.6	28.35	0.62	16.58	6.94	8.75	0.07	0.45	0	0

4-2.2 Data Manipulations and Analytical Approaches

At each station we extracted all observations of pH and DO available for that site and computed the changes in each constituent over the 15-minute interval, yielding a rate of change for either DO or pH. We then examined the corresponding change in time between these samples, and when this time exceeded 15 minutes (due to a break in the sensor deployment or missing data), we removed that time from the rate-of-change time-series. We then built regressions between these 15-minute rate-of-changes between DO versus pH for (1) the entire dataset and (2) for the data from each calendar month of the year. These latter regressions were used to evaluate seasonal changes in the strength of the correlation between DO and pH, as well as to compute the slope of the correlation for each month. An evaluation of the slopes allows us to compute a quantitative change in pH relative to DO, which reveals the extent to which pH varies for a given change in DO (i.e., metabolic change) and the associated implications for buffering capacity and metabolic effects on pH variability across seasons and stations.

We also generated a dataset that includes basic statistics on pH, DO, and salinity at each station, which includes the mean, maximum, and minimum DO, pH and salinity at each station over the entire time-series. This dataset helps us interpret changes in the slope between DO and pH (via salinity-associated changes in buffering capacity), as well as the potential for extreme pH at each station, which impact habitat, as well as the cycling of nitrogen and phosphorus (Seitzinger et al. 1991, Gao et al. 2014). In addition, we quantified the number of measurements of pH that exceeded 9.5 at each station, which has been identified as a threshold above which sediment phosphorus releases are enhanced (Seitzinger et al. 1991). We calculated both the amount of time that pH exceeded 9.5, as well as which seasons when these pH extremes occurred.

4-3 Results and Discussion

4-3.1 Temporal Correlations Between DO and pH

We found that DO and pH (and 15-minute changes in these variables) were generally well-correlated across ConMon stations in the Maryland portion of Chesapeake Bay (Table 4-1, Figs. 4-2 & 4-3). A more detailed view of a subset of stations reveals that seasonal and diel variability in DO and pH contrasts among stations, where some stations include diel cycling hypoxia and pH variation that exceeds 1 pH unit/day, while other, less productive stations, fluctuate less (Fig. 4-2). These two descriptive observations emphasize two important points: (1) that DO and pH variation is largely driven by local metabolism at these stations, and (2) that metabolic controls on pH may dominate other sources of variation in shallow Chesapeake environments.

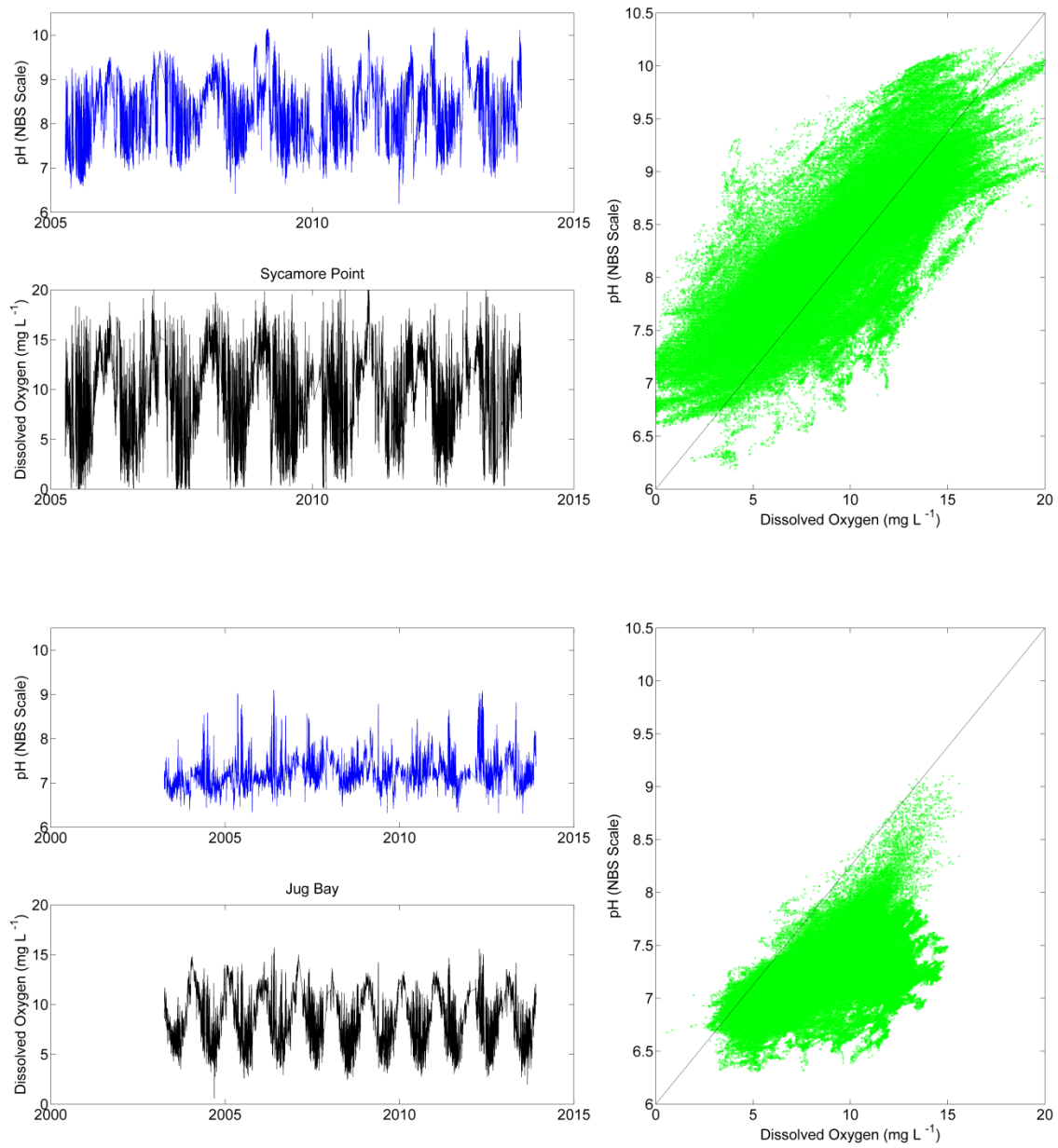

Figure 4-2. Time-series of pH and DO, and the relationship between the two variables, at (top) Sycamore Point in the Corsica river estuary and (bottom) Jug Bay in the Patuxent Estuary.

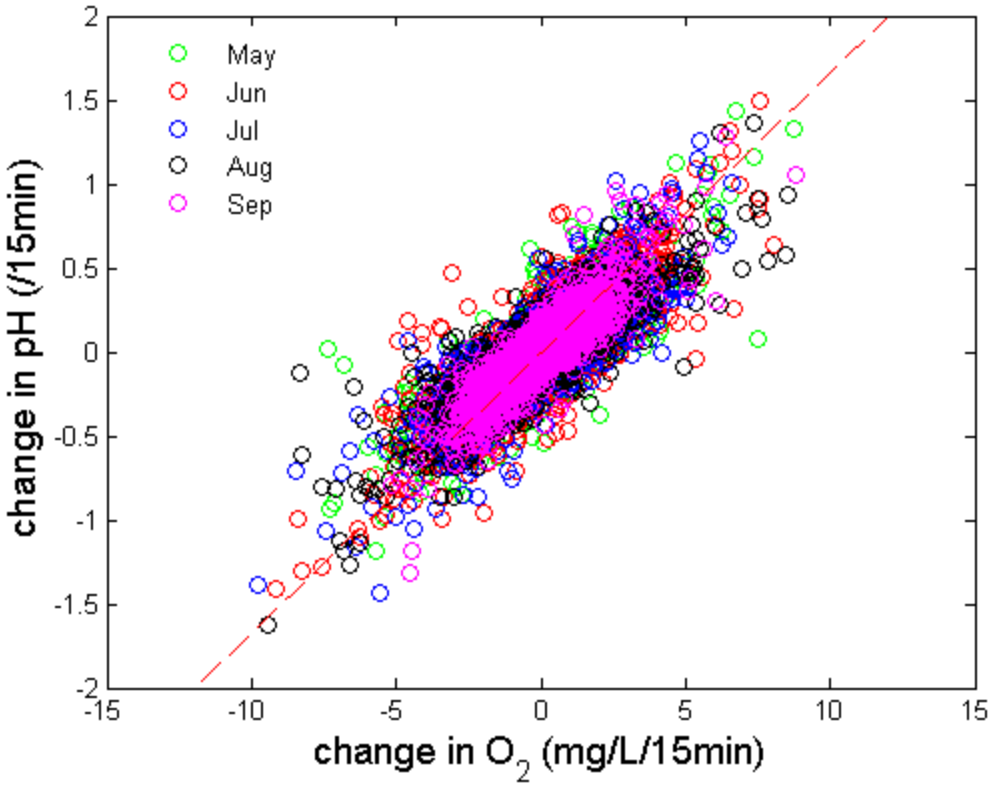

Figure 4-3. Relationship between 15-minute changes in pH and DO at Sycamore Point in the Corsica River aggregated by month.

The 15-minute changes in DO and pH both appear to be higher during warm summer months (median ~0.04 pH units 15-min^{-1}, 0.2 mg O_2 l^{-1} 15-min^{-1}) than cooler months (Fig. 4-4). These central tendencies exist despite high variation among stations, where July DO changes range from near zero to 1 mg O_2 l^{-1} and July pH changes range from zero to ~0.08 pH units (Fig. 4-4). These seasonal patterns are consistent with the fact that metabolic rates tend to be higher during warmer months (Cowan and Boynton 1996, Harding et al. 2002), driving more rapid rates of DO and CO_2 production and consumption. Interestingly, the slope of the relationship between DO and pH, despite much variation, appears to peak during spring months, which indicates more relative change in pH relative to O_2 (Fig. 4-5). This might result from the fact that salinity tends to be lower during these months (when freshwater input is high), which would lead to lower buffering capacity and thus larger pH changes for a given production or consumption of CO_2. We might limit such speculation given that the r^2 values of the correlation between 15-minute changes in DO versus pH are most variable during these spring months, while these r^2 values tend to be highest during warmer months, when the metabolic signal dominates changes in DO and pH (Fig. 4-5).

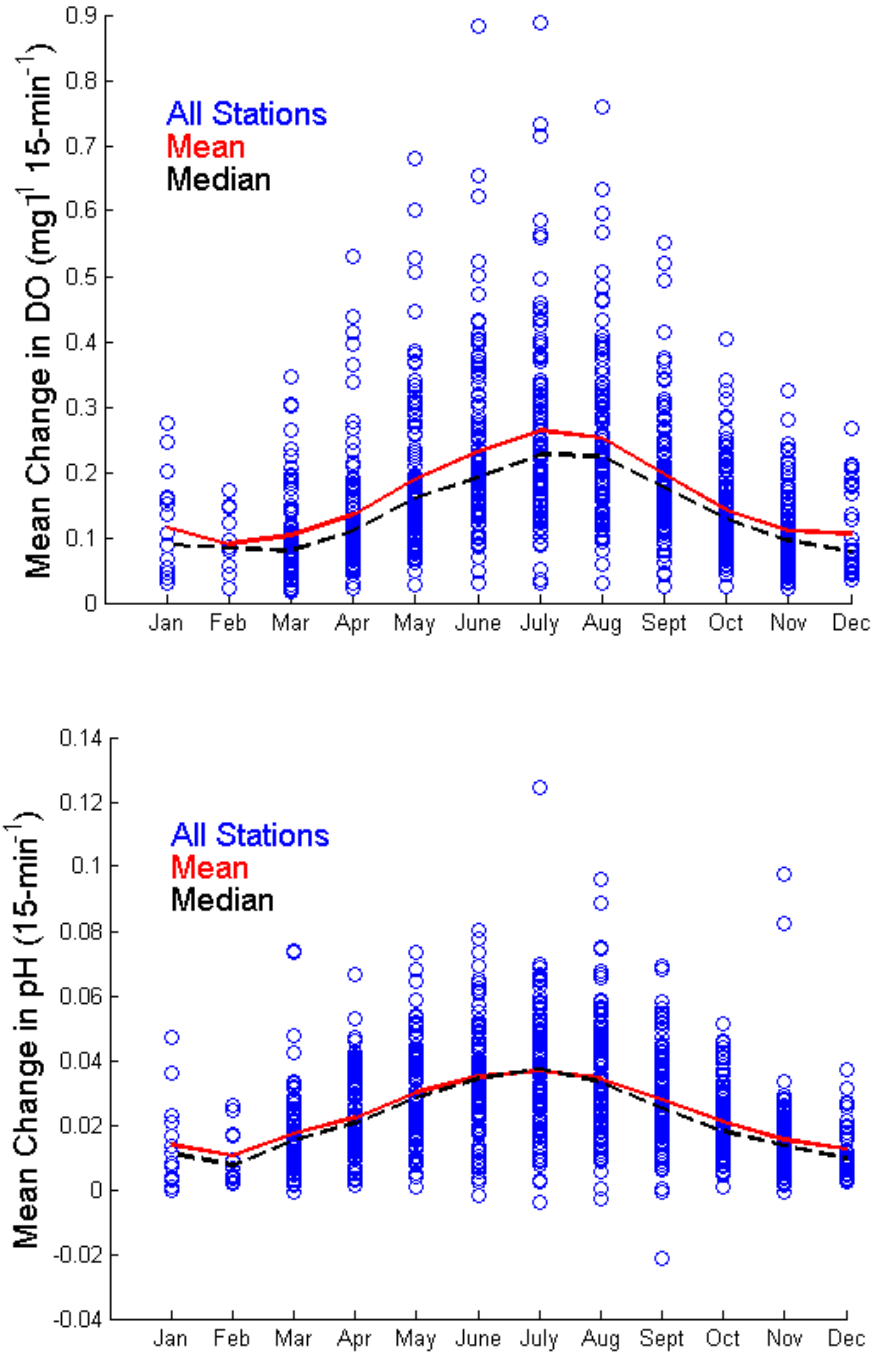

Figure 4-4. Mean 15-minute changes in DO (top panel) and pH (bottom panel) for all 110 ConMon stations, organized by month. Blue circles are individual months and stations, while the red line and black dashed lines are the monthly mean and median, respectively, across all stations. Note that fewer ConMon stations are active Nov-Mar.

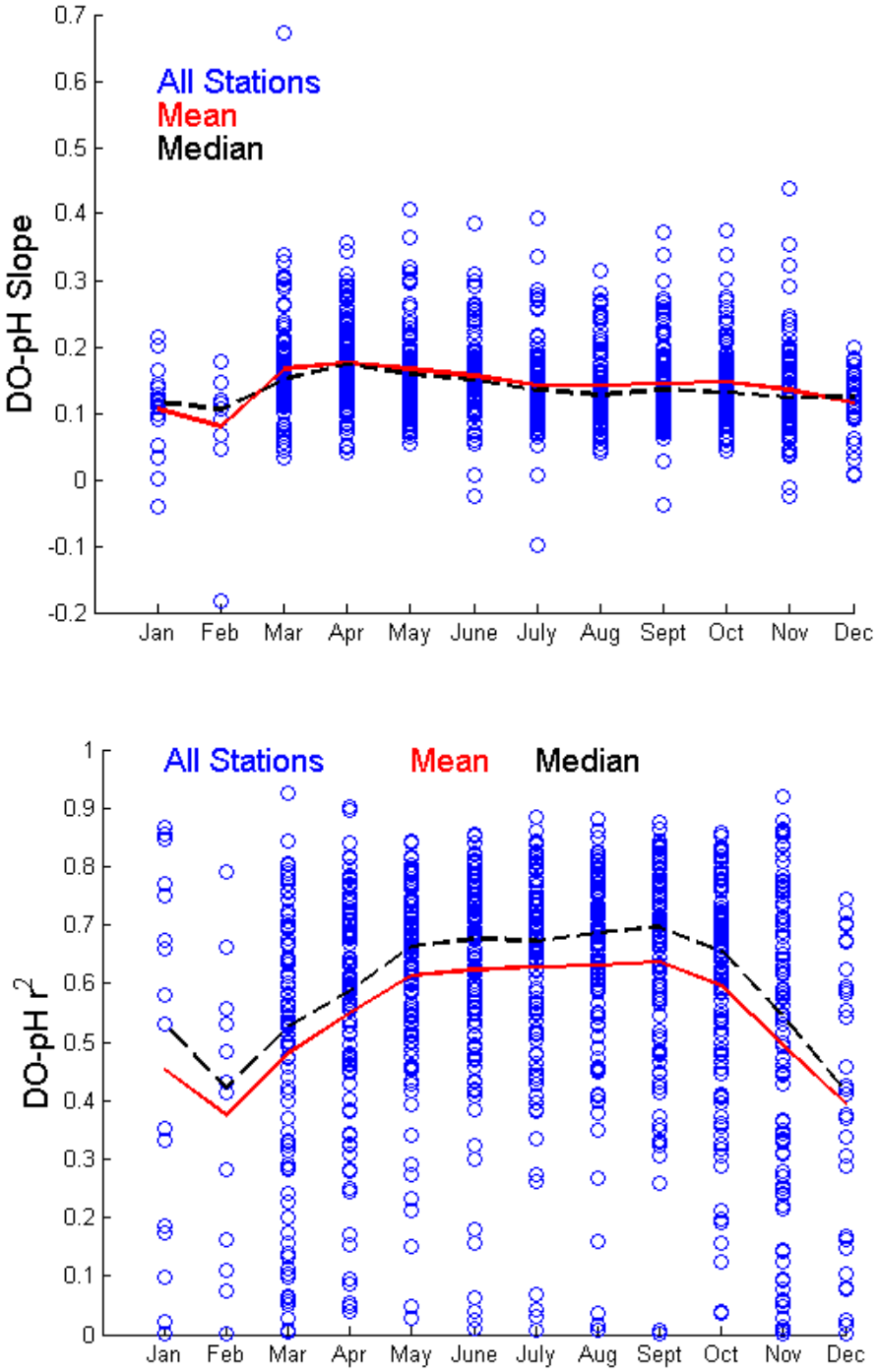

Figure 4-5. Slope (top panel) and r^2 (bottom panel) of correlations between 15-minute changes in DO and pH for all 110 ConMon stations, organized by month. Blue circles are individual months and stations, while the red line and black dashed lines are the monthly mean and median, respectively, across all stations. Note that fewer ConMon stations are active Nov-Mar.

4-3.2 Spatial Patterns of DO and pH

It is clear that there are strong spatial patterns in the nature of the DO-pH relationship that have implications for the sensitivity of different Chesapeake regions to long-term acidification and extremes in pH. When the slopes of the DO-pH relationship are plotted against salinity across all 110 stations, it is clear that the slopes are generally > 0.2 at freshwater sites (< 1 salinity unit), while slopes are lower at moderate to high-salinity sites (including the coastal Bays; Fig. 4-6). This broad pattern that emerges from such a large dataset suggests that pH in the lower salinity sites, which tend to be more poorly buffered relative to seawater, is more sensitive to changes in metabolic production and consumption of CO_2. The interpretation relies on a set of assumptions; (1) pH is primarily recording changes in CO_2 and other sources of acidity (organic acids, sulfide, etc.) and (2) that salinity-induced effects on CO_2 and O_2 solubility are not biasing the potential air-water exchanges effects of these two variables. To address these assumptions, we computed changes in dissolved inorganic carbon (DIC) concentrations from ConMon pH and total alkalinity (TAlk) from an empirical equation (Waldbusser et al. 2013, W.-J. Cai, unpublished) using the CO2SYS software. The resulting relationships between 15-minute changes in DO and DIC are tightly correlated, suggesting these artifacts are not substantial.

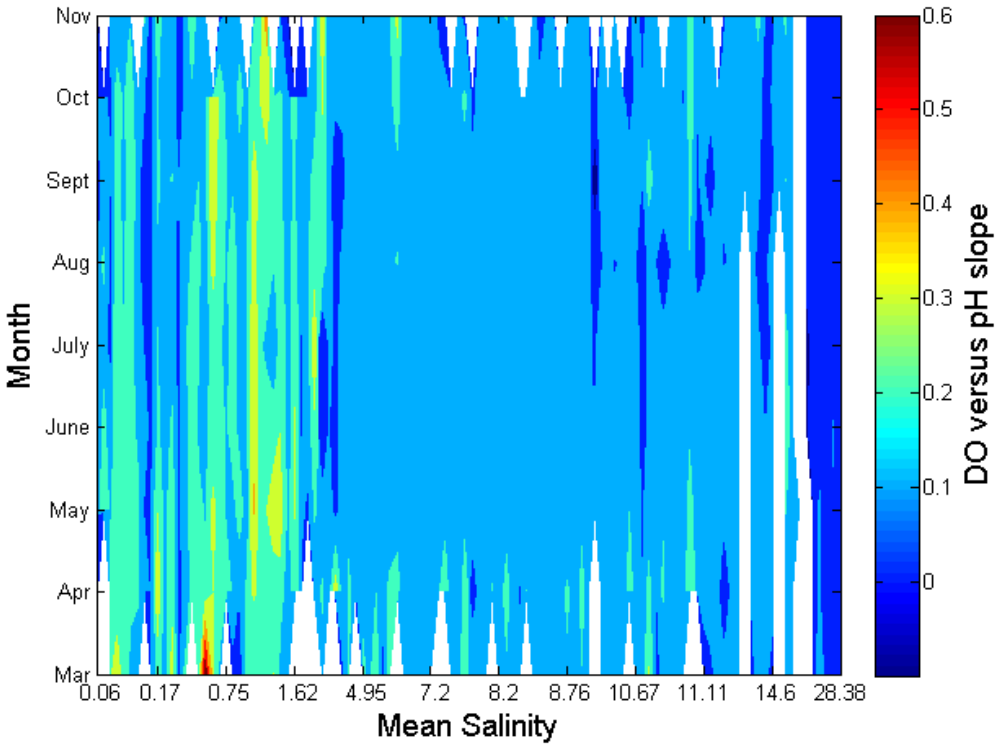

Figure 4-6. Monthly slope of relationship between 15-minute changes in DO versus pH (color scale) versus salinity for all 110 ConMon stations.

We also observed spatial patterns in the nature of DO and pH changes associated with eutrophication. Mean monthly 15-minute changes in DO approach 0.6 mg l^{-1} in July at the eutrophic Sycamore Point site in the Corsica River, while at the same time of year, DO changes are only 0.2 mg l^{-1} at the less-enriched CBL (Chesapeake Biological Laboratory) Pier (Fig. 4-7). Similar differences exist for peak 15-minute pH changes, but the overall slope of the DO-pH relationship is similar across these two sites (Fig. 4-7). Another example of spatial differences can be found in the Patuxent River estuary, where the tidal freshwater, highly turbid site at Jug Bay had smaller 15-minute DO and pH changes than the more saline site at Benedict where more light was available for primary production, indicating that metabolic intensity can overwhelm the higher buffering capacity of the higher salinity Benedict site (Fig. 4-8).

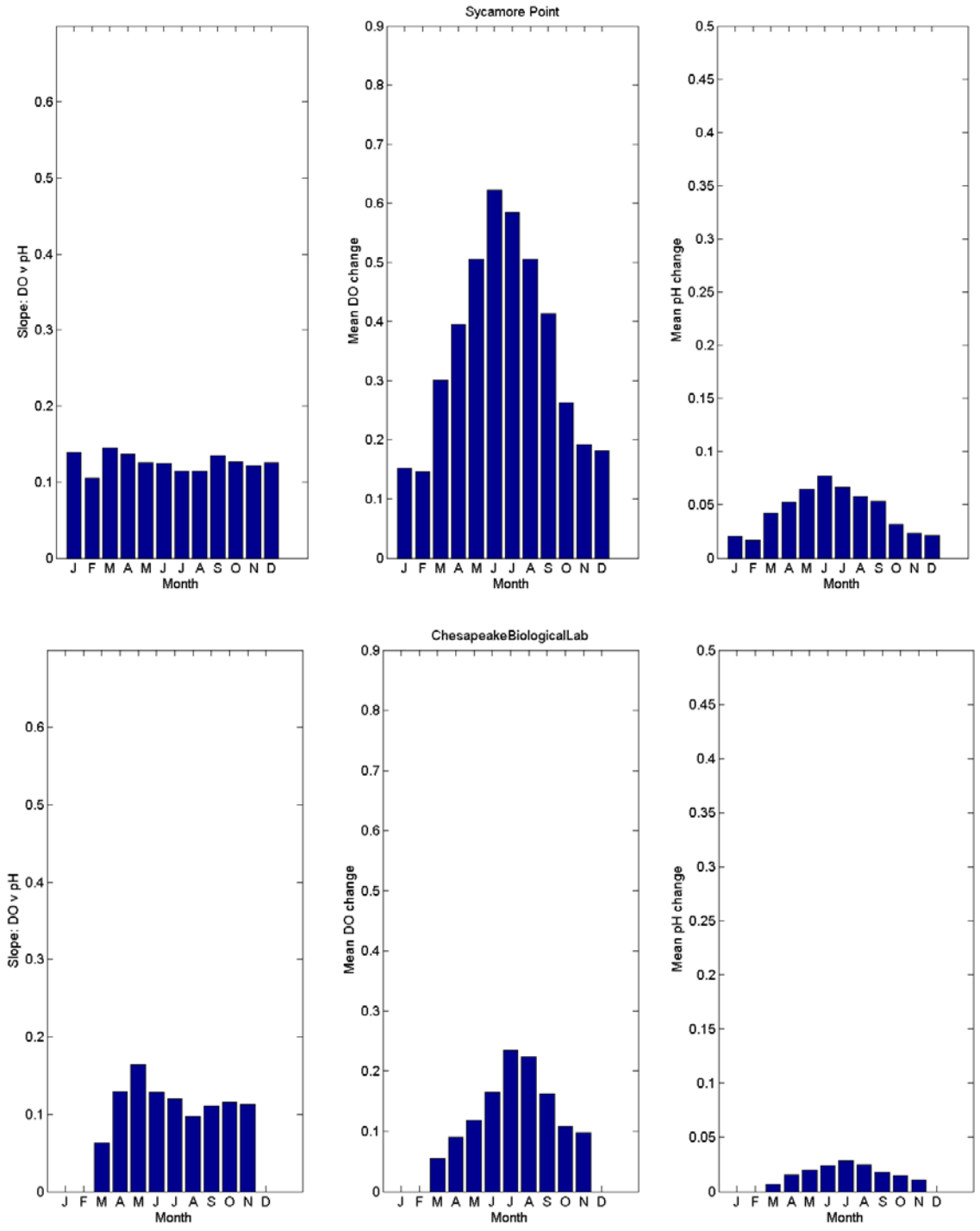

Figure 4-7. Monthly averages for the slope of the relationship between 15-minute changes in DO versus pH (left panels), mean15-minute changes in DO (middle panels), and mean15-minute changes in pH (right panels) for a highly eutrophic (top panels, Sycamore Point in the Corsica River) and moderately eutrophic (bottom panels, Chesapeake Biological Laboratory in the Patuxent) ConMon station.

.

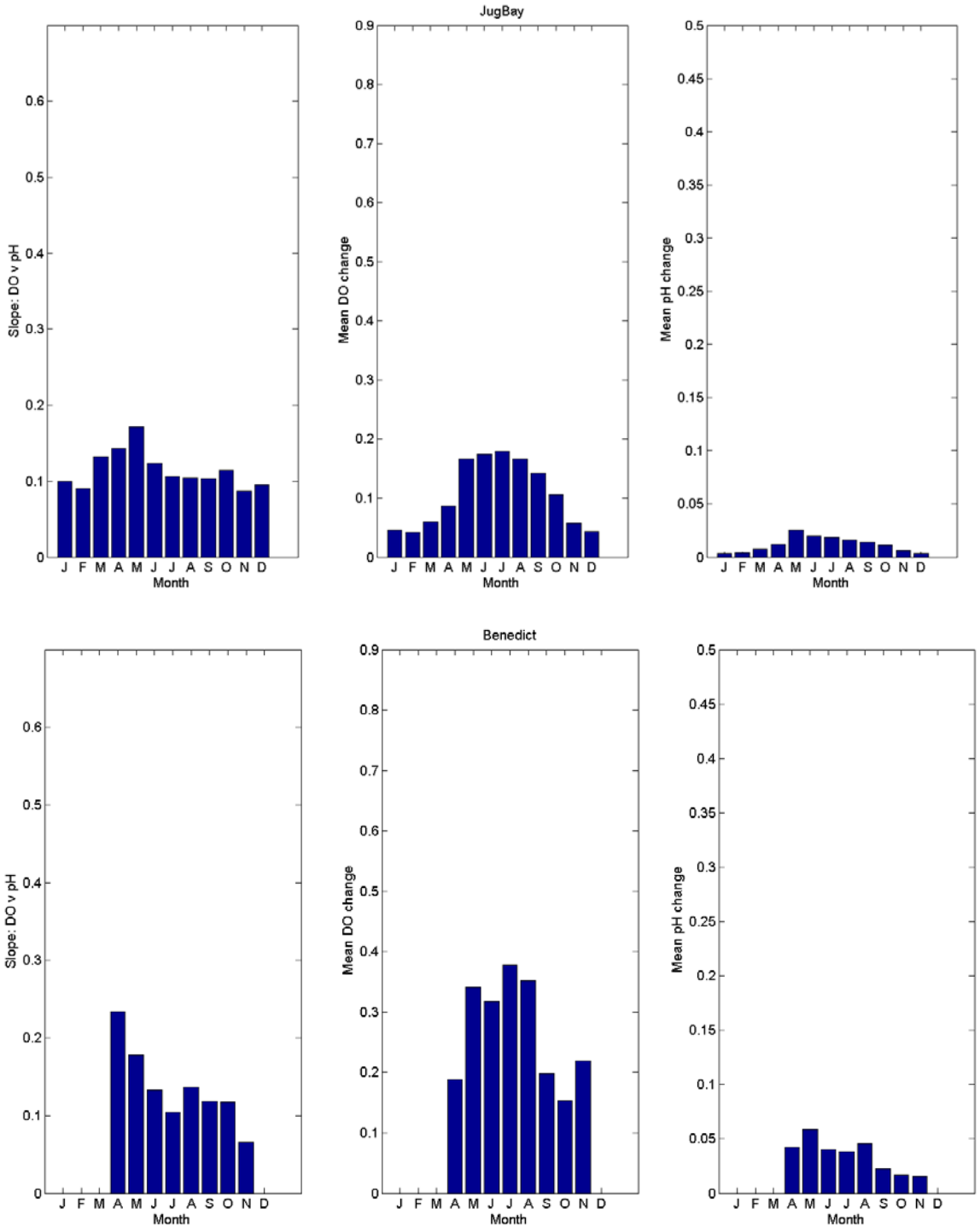

Figure 4-8. Monthly averages for the slope of the relationship between 15-minute changes in DO versus pH (left panels), mean15-minute changes in DO (middle panels), and mean15-minute changes in pH (right panels) for a freshwater (top panels, Jug Bay) and brackish water (bottom panels, Benedict) ConMon station within the same estuary (Patuxent River estuary).

4-3.3 Frequency of Extreme pH Levels

Our assessment of the tendency for pH extremes across the 110 ConMon stations reveals that such extremes (above 9.5) are restricted to a relatively small subset of stations and tend to occur in cooler months (Table 3.1). Only 36 of 110 ConMon stations included one or more observations of pH above 9.5 (33%), and of these 33%, only 17 stations (15% of total) had high pH excursions for over 24 hours of the total record. Six stations had relatively regular pH extremes, including Sycamore Point (Corsica River), Susquehanna Flats (upper Chesapeake Bay mainstem), Budds Landing (Sassafras River), Otter Point Creek (Bush River), Fenwick (Potomac River), and Church Point (Bush River). Aside from Sycamore Point, which is a uniquely eutrophic station, the mean salinity at all of these stations is less than 1, emphasizing the sensitivity of freshwater environments to pH extremes. Twelve of the 36 stations where pH exceeded 9.5 exhibited some of these pH excursions during cool months (between October and March), and for 7 of those stations, greater than 80% of the high pH values occurred in cool months. Such high-pH values in cool months likely occur under conditions of exceptionally high primary production (which consumes CO_2 and elevates pH) with relatively lower respiration, given the low temperature (Smith and Kemp 1995, Testa and Kemp 2008). Indeed, the stations where high winter pH occurred included three stations in the eutrophic Corsica River estuary (Possum Point, Emory Creek, Sycamore Point), but the other stations were more distributed and tended to include higher salinity conditions where spring primary production is relatively high, such as Goose's Reef (mesohaline mainstem Chesapeake Bay), Chesapeake Yacht Club (West River), Masonville Cove Pier (Patapsco River), and Lauderick Creek (Bush River). Winter pH extremes likely have less of an impact on sediment-phosphorus fluxes, given that dissolved sediment P pools are smaller during this period, but at the other 24 stations where pH extremes occurred during summer, sediment-phosphorus fluxes could have been temporarily enhanced. Because many of the stations included in this analysis were not deployed during some winter months, our ability to capture all pH events at the ConMon sites is limited. In the six stations where pH extremes were most frequent, there were no long-term trends in the frequency of high or low pH extremes.

4-3.4 Conclusions and Implications

- There is a rich dataset for pH and dissolved oxygen in the Maryland ConMon database that allows for an analysis of the relationship between metabolism and pH changes
- It appears that low-salinity regions show the largest changes in pH for a given change in oxygen, suggesting that reduced buffering capacity may make these sites more vulnerable to pH swings
- Highly eutrophic stations reveal large swings in pH associated with CO_2 uptake and release, and pH tends to peak at these stations in spring months, where CO_2 uptake is high, but respiration-associated CO_2 production is low

- Future analysis could consider spatial patterns in aragonite saturation state because this metric could be computed from a full suite of carbonate system parameters and would provide an index of habitat suitability for shell-forming organisms (e.g., oysters)

4-4 References

Arias, A. H., Piccolo, M. C., Spetter, C. V., Freije, R. H., and Marcovecchio, J. E. 2011. Lessons from multi-decadal oceanographic monitoring at an estuarine ecosystem in Argentina. International Journal of Environmental Research, 6, 219-234.

Barton, A., Hales, B., Waldbusser, G. G., Langdon, C., and Feely, R. A. 2012. The Pacific oyster, Crassostrea gigas, shows negative correlation to naturally elevated carbon dioxide levels: Implications for near-term ocean acidification effects. Limnology and Oceanography 57: 698-710.

Borges, A., and Gypens, N. 2010. Carbonate chemistry in the coastal zone responds more strongly to eutrophication than to ocean acidification. Limnology and Oceanography 55: 246-353.

Cai, W., X. Hu, W. Huang, M.C. Murrell, J.C. Lehrter, S.E. Lohrenz, W. Chou, W. Zhai, J.T. Hollibaugh, Y.Wang, P.Zhao, X. Guo, K. Gundersen, M. Dai, and G. Gong. 2011. Acidification of subsurface coastal waters enhanced by eutrophication. Nature Geoscience 4: 766-770.

Feely, R. A., Alin, S. R., Newton, J., Sabine, C. L., Warner, M., Devol, A., and Maloy, C. 2010. The combined effects of ocean acidification, mixing, and respiration on pH and carbonate saturation in an urbanized estuary. Estuarine, Coastal and Shelf Science, 88: 442-449.

Gao, Y., J. C. Cornwell, D. K. Stoecker, and M. S. Owens. 2014. Influence of cyanobacteria blooms on sediment biogeochemistry and nutrient fluxes, Limnology and Oceanography, 59(3), 959-971.

Gruber, N., C. Hauri, X. Lachkar, D. Loher, T.L. Frolicher, and G.K. Plattner. 2012. Rapid progreSsion of ocean acidification in the California Current System. Science 337: 220-223.

Hofmann, G. E., Smith, J. E., Johnson, K. S., Send, U., Levin, L. A., Micheli, F., and Martz, T.R. 2011. High-frequency dynamics of ocean pH: a multi-ecosystem comparison. PloS one, 6(12), e28983.

Michael, B., T. Parham, M. Trice, B. Smith, D. Domotor, and B. Cole. 2013. Quality Assurance Project Plan for the Maryland Department of Natural Resources Chesapeake Bay Shallow Water Quality Monitoring Program for the period July 1, 2013 – June 30, 2014. http://mddnr.chesapeakebay.net/eyesonthebay/documents/SWM_QAPP_2013_2014_FINAL.pdf

Miller, S.H., D.L. Breitburg, R.B. Burrell, and A.G. Keppel. 2016. Acidification increases sensitivity to hypoxia in important forage fishes, Marine Ecology Progress Series, 549, 1-8.

R Core Team. 2015. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria (http://www.R-project.org/).

Salisbury J., M. Green, C. Hunt, and J. Campbell. 2008. Coastal acidification by rivers: A threat to shellfish? Eos, Transactions American Geophysical Union 89: 513.

Seitzinger, S.P. 1991. The effect of pH on the release of phosphorus from Potomac Estuary sediments: implications for blue-green algal blooms, Estuarine, Coastal and Shelf Science, 33, 409-418.

Smith, E.M. and W.M. Kemp. 1995. Seasonal and regional variations in plankton community production and respiration for Chesapeake Bay. Marine Ecology Progress Series 116: 217-231.

Testa, J.M. and W.M. Kemp. 2008. Variability of biogeochemical processes and physical transport in a partially stratified estuary: a box model approach. Marine Ecology Progress Series 356: 63-79.

The MathWorks, Inc. 2014. MATLAB The Language of Technical Computing 2014a. Natick, Massachusetts.

USEPA (U.S. Environmental Protection Agency). 2010. Chesapeake Bay Phase 5.3 Community Watershed Model EPA 903S10002 - CBP/TRS-303-10 U.S. Environmental Protection Agency, Chesapeake Bay Program Office, Annapolis MD. December 2010.

Waldbusser, G.G., E.P. Voigt, H. Bergschneider, et al. 2011. Biocalcification in the eastern oyster (Crassostrea virginica) in relation to long-term trends in Chesapeake Bay pH. Estuaries and Coasts 34: 221-231.

Waldbusser, G.G., E.N. Powell, and R. Mann. 2013. Ecosystem effects of shell aggregations and cycling in coastal waters: An example of Chesapeake Bay oyster reefs. Ecology 94: 895-903.