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pH Trends in Narragansett Bay using Narragansett Bay Fixed-Site Monitoring Network Data

Prepared by: Heather Stoffel and Joseph Langan
University of Rhode Island's Graduate School of Oceanography
for

State of Rhode Island Department of Environmental Management
Office of Water Resources
and
University of Rhode Island Coastal Institute

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Jason Grear (USEPA), Sue Kiernan (RI DEM), Nicole Rohr (URI CI), Candace Oviatt (URI GSO), Wilson Mendoza,
Q Kellogg (URI), and Conor Mc Manus (RIDEM)

Table of Contents

List of Tables

List of Figures

Executive Summary

Changes in pH, especially towards the more acidic scale, is of concern for marine resource managers given that acidic waters can reduce marine organisms' ability to access dissolved calcium carbonate. The short-term variability in pH in coastal systems is greater than the predicted decrease in pH in the open ocean over the next 100 years. One of the most significant drivers behind acidification in coastal and estuarine waters is nutrient and organic loadings. Nutrient input in coastal ecosystems have many sources, including watershed processes, sewage inputs, and metabolic remineralization. Eutrophication, excess phytoplankton production and biomass caused by excess nutrient loading, ultimately lowers pH through increased respiration rates from bloom-feeding organisms like bacteria on decomposing organic matter. This increased respiration oxidizes organic material, draws down localized oxygen levels, releases CO_2, and subsequently decreases pH.

Since Rhode Island waters have undergone extensive nutrient reductions in the past few years, examining pH trends is important to document for base line conditions. The Narragansett Bay Fixed Site Monitoring Network (NBFSMN) data is the most complete pH (NBS scale) dataset for this type of analysis. Trends were characterized for summer seasonal patterns along with year-round changes for surface and bottom conditions throughout the bay. The network data was also analyzed against state criteria for pH and exceedances based on recent research thresholds.

The results show pH varies seasonally, inter-annually and by station location. The lowest pH values occurred in the summer. The headwaters of the Bay receive an influx of freshwater and nutrients to the Bay, creating a down bay gradient in salinity, pH, and chlorophyll. The lower the salinity waters also have the lower the alkalinity causing a down bay gradient in pH. The Phillipsdale station generally has the largest range in pH, with a typical summer standard deviation of 0.45. Surface water in the West Passage tends to flow out to Rhode Island Sound during wet years, while ocean bottom water in the East Passage tends to flow toward the upper Bay (Kincaid, CHRP presentations). The GSO dock, in the lower West passage, has the lowest variability with a 0.10 standard deviation. The standard deviation varies from .45 at Phillipsdale (PD) to 0.1 at the GSO dock (GD). Since most of the bay's seasonal variability is much greater than the 0.1pH unit of change over 200 years in the open ocean, further analysis is needed to determine the forcing factors on changes of pH. The principal component analysis showed, the surface waters, chlorophyll and dissolved oxygen explain most of the data variation in surface waters. In the bottom water, dissolved oxygen explains most of the data variation during the summer season. Temperature affects the seasonal fluctuation in pH within Narragansett Bay. Although temperature affects the saturation state of CO2 and thus affects pH, biological activity is also a driving force behind the changes in pH at the Greenwich Bay station. The main seasonal drivers observed at Greenwich Bay show, in the winter months, to have a positive effect on pH from colder temperatures allowing for a higher saturation state for CO2 and the winter/spring bloom. In the summer is a negative effect pH from warmer temperatures, stratification limiting mixing to the bottom waters, and hypoxic events are known to occur at different magnitudes seasonally. The Upper Bay station at Conimicut Point shows the negative summer effect on pH. are more dramatic on changes in pH. The lower bay's productivity is driven more by the winter blooms vs summer bloom events compared to the upper bay. Therefore, the positive effects in the winter are more dramatic on changes in pH in the lower bay vs the summer negative changes.

The seasonal patterns in pH in Narragansett Bay are consistent with other New England estuaries. Determining the cause of the seasonal patterns can be difficult to determine because the relationships are non-linear in a coastal system. For example, changes in pH can be attributed to many factors including physical dynamics and biologic activities within the bay. In addition, ocean influx can possibly cause a system to be more dynamic (higher variability) without causing a long-term trend. (Cai,W. etal, 2001). The largest peaks are in the winter were observed with colder temperatures and the potential for winter spring blooms. The summer dips in pH were also documented when the bay observed warm stratified water column, reduced mixing, and hypoxic conditions found throughout the Upper Bay. However, these relationships are also potentially influenced by ocean influx that can reduce buffering and cause the system to be more dynamic. Based on the multi-linear regression analysis, the East Passage shows a slight downward trend in pH. Although it tested significant, this trend is not evident in the daily delta pH analysis. This maybe evident of the limitations of the sensitivity of the sensor or could be an area affected by ocean influx. Therefore, the East Passage maybe an area to focus on for carbonate chemistry analysis to determine if the offshore influence is affecting this area is significant.

All station data revealed that all monitored areas of Narragansett Bay are within Rhode Island's state water quality criteria for pH. However, based on recent literature of combine effects on different life stages of estuarine species found within Narragansett Bay, a low threshold of 6.5 is not protective enough of marine species (Wallace, 2014). A review of different pH thresholds may be needed to provide more adequate protection of marine life within Narragansett Bay with respect to eutrophication cumulative effects of hypoxia and low pH on all life stages as these studies results become available in the future. These stations will remain in place for the near future and pH levels will continue to be monitored. As more knowledge on the issue of ocean acidification in coastal estuarine waters becomes available, along with studies conducted within and around Narragansett Bay, water quality assessments relating to pH can be further examined.

The NBFSMN datasets are one of the most comprehensive resources for examining physical water quality, including pH, for Narragansett Bay. All the network data is available through the RIDEM OWR website: http://www.dem.ri.gov/programs/emergencyresponse/bart/stations.phpIf proper relationships can be established for the pH scales (NBS vs total scale), NBFSMN can serve as a link monitoring the carbonate system in the future and providing information needed to describe changes in the carbonate system over time within Narragansett Bay.

Other Effects of Coastal Eutrophication: A Time-Series Look at pH in Narragansett Bay

Introduction:

Changes in pH, especially towards the more acidic scale, is of concern for marine resource managers given that low pH waters can reduce marine organisms' ability to access dissolved calcium carbonate and have been shown to have other effects on marine life. This reduction in pH in the open ocean is often referred to as ocean acidification. Ocean acidification (OA) is caused by ocean absorption of atmospheric carbone dioxide, which in turn causes a decline pH and in carbonate ion concentrations. Carbonate ion concentration is often indexed as aragonite saturation state, which is the concentration of calcium and carbonate ions relative to the saturated equilibrium state (Dickson et al. 2007).

These forms of calcium carbonate are used by shell or skeleton forming organisms (Gazeau, et al, 2013). In coastal waters, this process is referred to as coastal acidification, given the differences in pH drivers in coastal oceans and estuaries. In the open ocean, pH levels are fairly stable. Therefore, the recent literature documents the present increase in CO_2 levels has decreased open ocean pH by about 0.1 units (Calderia and Wicket, 2003 and Baumann, et al, 2015). The documented decrease in pH in the open ocean is raising concern for the future of calcifying organisms, many of which are present in coastal habitats. This can negatively impact coastal and open ocean ecosystems and in turn commercial fisheries. For example, one model shows about a 13-50% reduction in the US Atlantic Sea Scallop biomass by the end of the century from ocean acidification (Rheuban et al, 2018). Grear, et al, (in Press) showed that levels of acidification already observed seasonally in estuaries of the northeastern US are enough to substantially increase risk to populations of quahogs (Grear, et al, in press). Shellfish and larval organisms are among the most susceptible to these long-term reductions in pH in the open ocean and during seasonal pH excursions in coastal ecosystems (Walbusser, et al, 2014). As the open ocean acidifies, the availability of carbonate ions (used in shell production) becomes limited (National Research Council, 2010). These changes reduce seawater buffering capacity, as does degradation of surplus organic matter in enriched estuaries, so the mixing of these too sources in the coastal zone can lead to nonlinear responses in carbonate chemistry (i.e., feedback effects that make systems less resistant to future enrichment effects or intrusion of low pH ocean water) (Cai, et al, 2011).

In contrast to ocean acidification, a coastal system pH can change > 0.1 NBS units on an hourly basis (Hofmann, et al, 2011). The short-term variability in pH in coastal systems is greater than the predicted decrease in pH in the open ocean over the next 100 years. The natural variability in pH in coastal systems is influenced by plankton metabolic rates, river discharge, upwelling, and human interactions.

One of the most significant drivers behind acidification in coastal and estuarine waters is nutrient loading. Nutrient input in coastal ecosystems have many sources, including watershed processes, sewage inputs, and metabolic remineralization. Eutrophication, excess phytoplankton production and biomass caused by excess nutrient loading, ultimately lowers pH through increased respiration rates from bloom-feeding organisms like bacteria on decomposing organic matter. Organic loading from watersheds causes similar effects on carbonate chemistry. This increased respiration oxidizes organic material (regardless of its origin), draws down localized oxygen levels, releases CO_2, and subsequently decreases pH. This process generally occurs in bottom waters where the organic matter sinks and oxidizes and where the resulting increase in dissolved inorganic carbon may be unavailable for uptake by light-limited plants and algae. Changes in the watershed over the past few decades, such as an increase in rainfall or nutrient loading from run off, together with metabolic processes and coastal ocean dynamics, can cause decadal changes of up to 0.5 units in coastal pH. Metabolic rates cause varying time scale fluctuations (e.g. diel to seasonal) in pH, with characteristic ranges of 0.3 pH units, and metabolically intense habitats exceeding this range on a daily basis. These changes are magnitudes higher than the changes observed in long-term pH of the open ocean (Duarte et al, 2013).

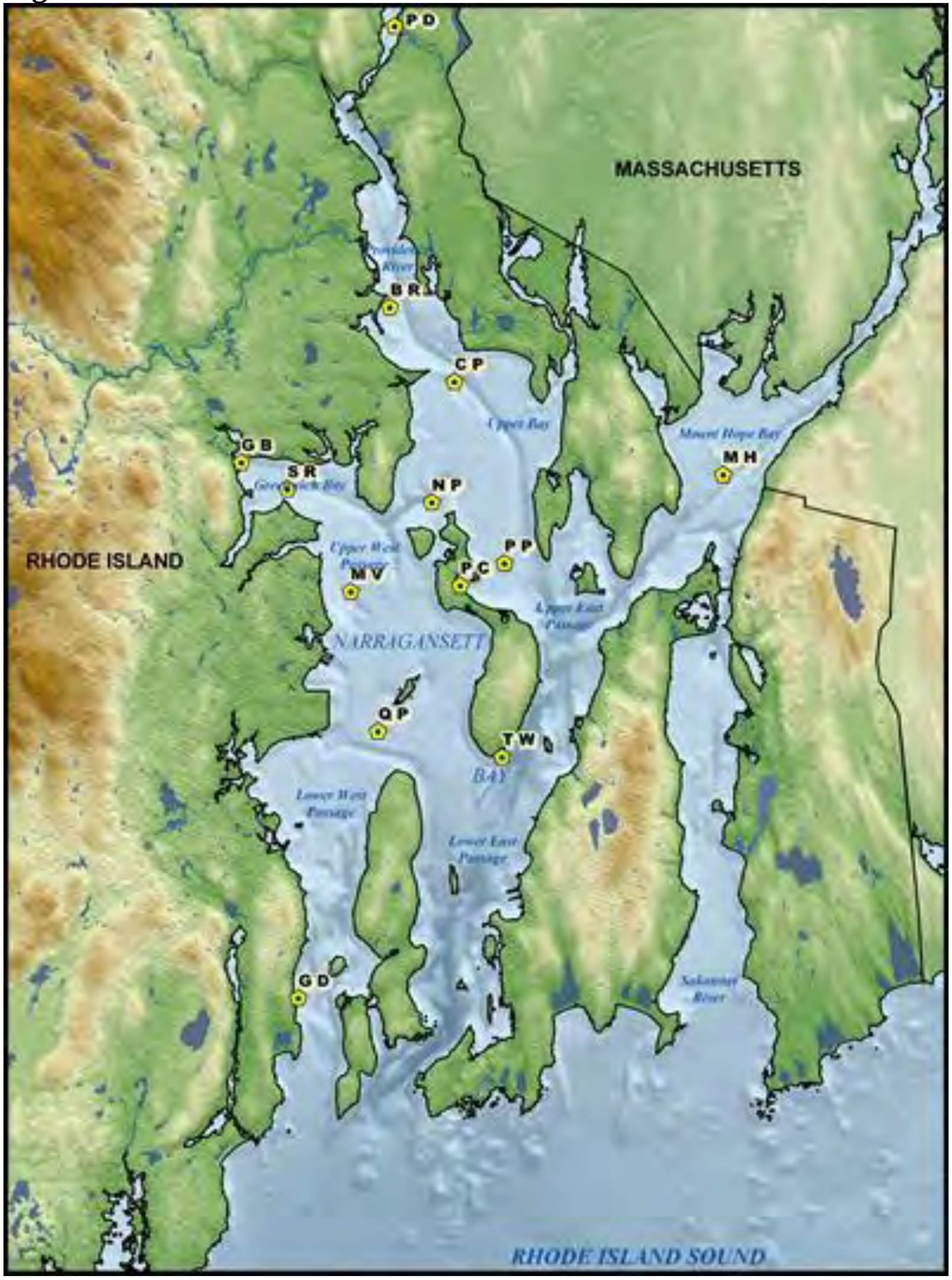
Managing such changes will not be simple. Coastal pH variability is greater than open-ocean pH variability, and human activities can sometimes lead to greater acidification in the coastal zone than in the open ocean, causing regionally or locally enhanced coastal acidification (Cai et al. 2011). The extent to which this increased variability emergences beyond the variability envelopes of recent evolutionary history will be a key question in predicting whether coastal biota will adapt. Furthermore, there are cumulative stressors on organisms with respect to eutrophication-driven coastal acidification. Not only is there a spectrum of anthropogenic perturbations of pH in coastal waters (Duarte et al. 2013), but there are also many overlapping jurisdictional authorities that regulate human activities in the coastal zone (Kelly RP et al. 2011). Nonetheless, discussions about how to manage the threat of OA to marine organisms have recently begun in many jurisdictions, and several US states have started to implement management strategies to combat the regional scale causes and effects of changing carbonate chemistry in the coastal zone. As local and regional OA governance emerges, successful management of the threat of coastal acidification requires understanding the dynamics and interactions of eutrophication, upwelling, and riverine runoff. This report provides a descriptive analysis of coastal acidification within Narragansett Bay over the past two decades using long-term monitoring of pH.

Sampling Collection Methods:

The carbonate chemistry of Narragansett Bay has become a recent research need, and adequate data is limited. For the purposes of this report, we examined the long-term record of pH (NBS scale) from one of the Bay's longest continuous water quality monitoring programs. Officially starting in 2005, several agencies, with RIDEM-OWR as the lead, established a network of fixed-site monitoring stations to assess water quality in Narragansett Bay. The network (Narragansett Bay Fixed-Site Monitoring Network) is now an essential component of Rhode Island's overall monitoring strategy for the Bay. The stations are located strategically along transect the length of Narragansett Bay and serve as sentinels of changing conditions. There is a greater concentration of sites in upper Narragansett Bay than lower purposefully, due to the greater presence of discharges from both wastewater treatment facilities and large tributary rivers (Figure 1). The DEM Office of Water Resources has taken a lead role in coordinating the multi-agency network effort known as the Narragansett Bay Fixed-Site Monitoring Network (NBFSMN).

Each station is equipped to provide high-resolution temporal water quality data. These stations measure near surface and near bottom temperature, salinity, oxygen, pH (NBS), chlorophyll and depth at 15-minute intervals where applicable. YSI 6-series sondes have been used during the time period of the analysis. Most sondes are equipped with wiper capabilities to limit fouling effects on the sensors. Each station in serviced on a two-week interval, where instruments are swapped for newly calibrated ones. Each sensor (C/T, pH, DO, depth, and CHL) is calibrated according to the NBFSMN Quality Assurance Project Plan (QAPP) (RIDEM, 2014). The pH sensors (flat glass and guarded) are calibrated using 7 & 10 NBS buffers on a two-week basis. As part of the QA/QC process, each sensor has a post deployment check in the calibration standards to validate the operations of each sensor. All QA/QC measures and flagged data are removed and documented in the metadata on an annual basis. The annual files are made available to the public through the lead agency website: **http://www.dem.ri.gov/programs/emergencyresponse/bart/stations.php.** The data files with the extension.corrected.xls were used in this analysis because these files contain QA/QCd values with minimize data gaps based on the programs QAPP approved criteria.

Figure 1. NBFSMN Station Locations



* PC-Potter's Cove not used in analysis since this station location is not representative of the Bay proper. This station is not operational in the winter due to freezing and located in a shallow cove.
Daily Average data was generated from these stations QA/QC'd corrected 15 min sampling interval record (Kellogg, 2018).

Each station is equipped to provide high-resolution temporal water quality data. These stations measure near surface and near bottom temperature, salinity, oxygen, pH (NBS), chlorophyll and depth at 15-minute intervals where applicable. The premise is to obtain a water column view of water quality conditions and processes throughout the Upper Bay. Buoy stations are deployed from May-October, concentrating on monitoring during the growing season of the summer months (June-September). Land-based stations operate year-round wherever possible. Some stations experience icing and are not operational during the winter (Table 1).

Table 1. Station and Sampling Characteristics of NBFSMN used in this analysis.

Group	**Station**	**Latitude N**	**Longitude W**	**Water Depth[b] (m)**	**Agency**	**Years Sites Operational**
Providence River and Upper Bay	Phillipsdale (PD)	41 50.505	71 22.332'		NBC	2004-present
	Bullock Reach (BR)	41 44.434'	71 22.480'	6	NBC	2001-present
	Conimicut Point (CP)	41 42.828'	71 20.628'	7	GSO/DEM	2003, 2005-present
	North Prudence (NP)	41 40.224'	71 21.283'	11	GSO/DEM	2001-present
West passage	Mt. View (MV)	41 38.304'	71 23.621'	7	GSO/DEM	2004-present
	Quonset Point (QP)	41 35.288'	71 22.839'	7	GSO/DEM	2005-present
	GSO Dock (GD)	41 29.535	71 25.137	2	GSO/DEM	1996-present
East passage	Poppasquash Point (PP)	41 38.907'	71 19.207'	8	GSO/DEM	2004-present
	T-Wharf (TW)	41 34.731'	71 19.287'	6	NBNERR	2003-present
Embay-ments	Greenwich Bay Marina (GB)	41 41.090'	71 26.762'	3	GSO/DEM	2003-present,
	Sally Rock (SR)	41 40.518	71 25.437	4	GSO/DEM	2008-present
	Mt. Hope Bay (MH)	41 40.808'	71 12.913'	5	GSO/DEM	2005-present

a. All 15-minute data available at http://www.dem.ri.gov/bart/stations.htm.

b. Depths relative to Mean Lower Low Water.

c. Each station has a shallow and a deep sensor; except for GSO Dock.

d. Year-round dock stations: Phillipsdale (not winter-area freezes over), GSO Dock, T-wharf, Greenwich Bay Marina. CP is used to represent a year-round surface record starting in 2008(see methods). 2004-2006 GB was a seasonal station. In 2003, no pH data was collected at GB.

All stations' data have been through a QA/QC procedure and corrections applied to the data consistent with the NBFSMN Quality Assurance Project Plan (QAPP) (NBFSMN, 2014). The 15-min network data were averaged into daily average files accessed through a public access data portal (www.narrbay.org). The daily averaged and statistical data was used for all analyses presented herein.

For the purposes of the pH assessments, all 12 bay stations were analyzed on a summer seasonal basis (June-September) and three year-round stations were also examined for changes in pH levels. Dataset containing 75% or greater data were used in the analysis. The pH data presented in this paper is on the National Bureau of Standards (NBS) scale.

Methods for Analyses:

Seasonal Analysis:

Since stations were added to the network over the course of several years (2001-2008), each location was examined individually. Seasonal means, maximum, and minimum levels were calculated from June 1-September 30 for each year between 2001 and 2015, where data is available. In addition, since the pH data is not normally distributed, monthly mean, median, minimum, maximum, 5th and 95th percentiles were calculated at each station for the June 1st -September 30th summertime period. These analyses were used for descriptive analysis of pH at each station.

Annual Analysis:

Four stations were used in the long-term annual analysis based on each station's data record. Three stations were deployed year-round (GB, TW, GD) and a fourth was based on a combination of stations (CP). The three year-round stations are land-based deployments located at the western edge of Greenwich Bay at the mouth of Apponaug Cove (GB), South of Prudence Island facing the East Passage (TW), and in the southern West Passage near the Bay's mouth at the GSO dock (GD). These stations were added at different times over the course of the history of the network. GSO dock has the longest time series, dating back to mid-1995. For the purposes of this study, we started with 1996 since it was the first complete annual record. Greenwich Bay was a seasonal station prior to 2006. The T-Wharf surface and bottom record dates back to 2005 for the purposes of this analysis. A fourth station was added to have an Upper Bay representation; surface data is available at Conimicut Point (CP) to provide a year-round record since 2008. During the winter, using the near-by United States' Coast Guard buoy (#13), an instrument is deployed to from October through May at surface depth only (1m). Using this dataset and combining it with the surface data from the Conimicut Point (CP) seasonal buoy station, a year-round record is created for the surface water's in the Upper Bay. Year-round CP records were used in the annual analysis.

The annual statistics consist of time series analysis, anomaly analysis and principal component analysis. The time series plots were used to identify trends by station. For the anomaly analysis, monthly anomalies were plotted over time to analyze for trends in temperature, pH, DO, and chlorophyll. Monthly anomalies were calculated by subtracting the overall individual monthly mean from each monthly average for each of the parameters. Linear regressions were then plotted to determine a trend. Principle component analysis (PCA) and multi-linear regression analyses were used to explore differences in water parameters among sites and determine parameters that are influencing prospective trends in pH.

Principal Component Analysis and Multi-linear Regression Analysis:

The principal component analysis (PCA) and the multi-linear regressions were conducted as part of the seasonal and year-round analyses. Two multi-linear regressions were applied to each station using temperature, salinity, chlorophyll, as independent variables. One regression analysis used pH as a control variable and DO % as an added independent variable. The second regression analysis used DO% as the control variable and pH as an added independent variable. Year is also included as a variable to see if there is a time trend. Month and depth are incorporated into each model as control variables. Each station was analyzed based on an annual (Jan1-Dec 31) and/or seasonal (June1-Sept 30) data for all available years. Since most parameters are not normally distributed, temperature, salinity, and chlorophyll were log-transformed to reduce skewness. All variables (temp, salinity, chlorophyll, pH, and DO %) were then standardized by subtracting the mean and dividing by the standard deviation. A quadratic curve was applied to salinity function. Surface and bottom data were combined to produce water column averaged linear regressions. PCA was performed separately on surface and bottom measurements of temperature, salinity, DO %, pH, and chlorophyll (surface only) collected between June 1 and September 30 in order to compare study sites. As in the regression analyses, temperature, salinity, and chlorophyll were log-transformed to reduce skewness. Due to the varying scales of the measured water parameters, particularly after log-transformation, PCA was performed on the correlation matrices of the data.

State Criteria Exceedances:

The data will be examined for exceedances against state criteria thresholds using daily data. Rhode Island has state criteria for pH. The accepted range is 6.5-8.5 pH units. Exceedances have to exceed the criteria greater than 10% of the sample record. Daily pH data will be filtered for exceedances below or above the 6.5 and 8.5 thresholds. It will be noted if the excursions from these limits is greater than 10% of the sampling record for an individual year.

Since recent studies have shown that a low concentration of 6.5 may not be adequate in protecting organisms against acidification, two additional thresholds are analyzed for (7.4 and 7.7 pH units) based on recent research efforts. Recent studies by Wallace, Gobler, etc have shown that pH as low as 7.7-7.4 pH units have proven to limit available aragonite to shellfish and some larval finfish for normal development. These thresholds were chosen because the experiments conducted in these studies were on shellfish and larval finfish found in New England waters.

Data Limitations:

Total pH is a characteristic of seawater carbonate chemistry, which is a system of acid-base reactions involving carbon dioxide, carbonic acid, and carbonate and bicarbonate ions (Pimenta and Grear, 2018). When the equilibrium state is perturbed by an increase one of these components (e.g, carbon dioxide), dissociation reactions alter the concentration of hydrogen ions (i.e., pH) (Pimenta and Grear, 2018). Estimation of these states is used for computation of calcium carbonate availability, but typically requires data for at least two of the measurable carbonate system parameters (dissolved inorganic carbon, total alkalinity, total pH, and pCO2) (Pimenta and Grear, 2018). For Narragansett Bay, only one such parameter is typically available in monitoring data sets, including this one. A few shorter-term studies exist that, if analyzed further, may help to leverage the NBFSMN pH measurements for full carbonate system analysis (Grear, personal communication). However, these studies were not available during this analysis.

An additional limitation is presented via the pH scale used to measure estuarine pH. Total pH scale (pH_t) (total hydrogen scale) is the recommended scale for use in seawater because of the high sulfate concentration (Pimenta and Grear, 2018). The total scale measures both free hydrogen ion activity and hydrogen sulfate concentration. Whereas, the *YSI* brand probe style sensors, used in the NBFSMN, measures pH on the National Bureau of Standards scale.It is difficult to make a relationship between pH_t and pH_{NBS} because they measure differing chemical properties (Pimenta and Grear, 2018). Since we only have pH_{NBS}, we cannot calculate pH at equilibrium to define the carbonate cycle properly. We can only define the status of pH (pH on the National Bureau of Standards scale), not the total pH scale (which is what is recommended for describing pCO_2 changes on pH). Although it may be possible to convert the NBS data to the total scale, the data in their current form are best used for monitoring of qualitative patterns. Therefore, this paper is a general description of the status of pH in the Bay and any trends that can be described from the data analysis. At each station the parameters and processes that affect pH in the Rhode Island coastal waters of Narragansett Bay may differ, so each station was analyzed individually.

Results:

The results will be organized by analysis, seasonal and annual data. Since multi-linear regression analysis was conducted on both the seasonal and annual datasets and PCA was conducted only on the seasonal data, the results will be presented as seasonal and annual analysis results. The state criteria exceedances will be presented separately since the analysis was conducted on all available data for each station.

Seasonal Analysis:

The lowest pH values occurred in the summer. The headwaters of the Bay receive an influx of freshwater and nutrients to the Bay, creating a down bay gradient in salinity, pH, and chlorophyll. Each station's overall pH statistics are shown in Table 2. The Phillipsdale station generally has the largest range in pH, with a typical summer standard deviation of 0.45. Surface water in the West Passage tends to flow out to Rhode Island Sound during wet years, while ocean bottom water in the East Passage tends to flow toward the upper Bay (Kincaid, CHRP presentations). The GSO dock, in the lower West passage, has the lowest variability with a 0.10 standard deviation. The standard deviation varies from .45 at Phillipsdale (PD) to 0.1 at the GSO dock (GD). Since is most of the bay's seasonal variability is much greater than the 0.1pH unit of change in the open ocean, further analysis is needed to determine the forcing factors on changes of pH. phytoplankton biomass levels tend to have a north to south gradient in bloom concentrations and salinity in Narragansett Bay (Figure 2b) (Oviatt, 2002). pH range by station follows this same gradient (Figure 2a).

Table 2. Overall average statistics for all stations for surface water pH in Narragansett Bay (June 1-September 30).

Upper Bay & West Passage	PD	BR	CP	NP	MV	QP	GD
ave pH_{stdev}	**0.45**	**0.24**	**0.22**	**0.16**	**0.13**	**0.12**	**0.10**
ave pH_{mean}	**7.64**	**7.97**	**8.06**	**7.96**	**7.96**	**8.04**	**7.91**
ave pH min	**6.78**	**7.24**	**7.44**	**7.52**	**7.62**	**7.70**	**7.48**
ave pHmax	**9.17**	**8.88**	**8.79**	**8.66**	**8.56**	**8.42**	**8.35**
Greenwich Bay	GB	SR					
ave pH_{stdev}	**0.23**	**0.15**					
ave pH_{mean}	**7.77**	**7.95**					
ave pH min	**7.11**	**7.49**					
ave pHmax	**8.43**	**8.36**					
East Passage	PP	MH	TW				
ave pH_{stdev}	**0.16**	**0.16**	**0.13**				
ave pH_{mean}	**8.08**	**8.01**	**7.91**				
ave pH min	**7.68**	**7.51**	**7.41**				
ave pHmax	**8.66**	**8.48**	**8.39**				

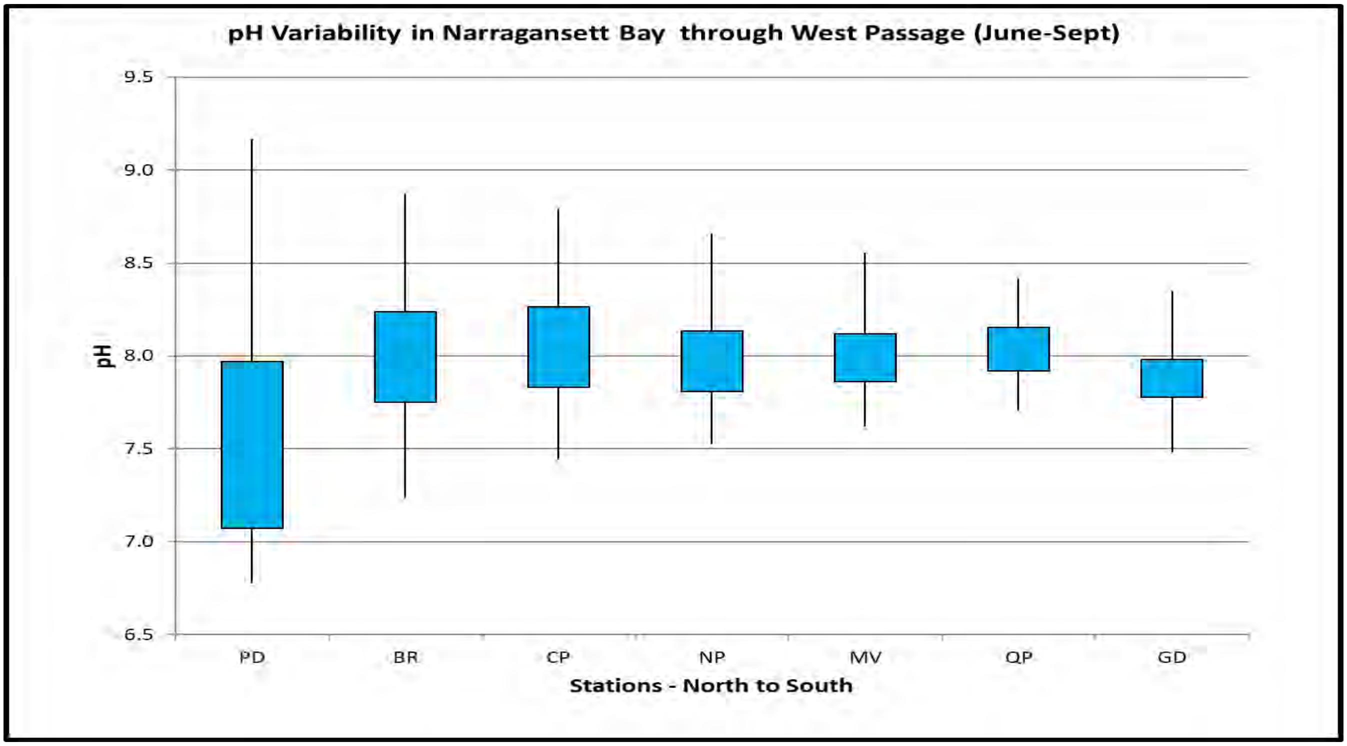
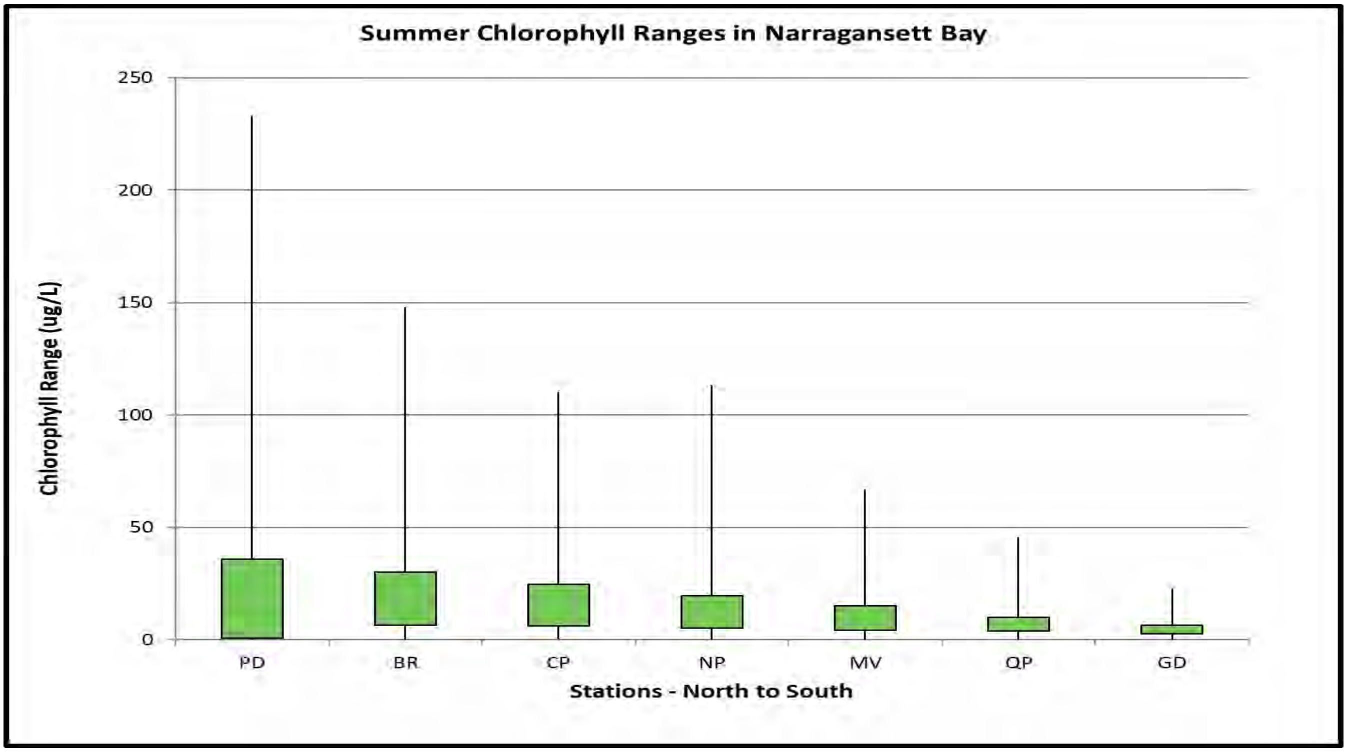


Figure 2a and 2b. Down bay gradient of surface pH and chlorophyll through the West Passage. Phillipsdale (PD) is located at the headwaters and has the highest variability. GSO Dock is located close to the mouth of the bay with the least variability. Box and whisker plots: box= average 1 stdev around mean, whiskers= average max, min based on all years of available data for the summer season (June 1-Sept 30)at each station.



pH varies seasonally, inter-annually and by station location. pH varies over the course of the seasonal record for each station with all stations within the Rhode Island state criteria for of 6.5-8.5 (Figures 3-5b). The Providence River stations, especially surface and bottom pH at Phillipsdale (overall average: 7.6 and 7.4, respectively), consistently have the lowest pH seasonal values (Figure 3). The seasonal surface values at Phillipsdale are within the same range as the seasonal bottom pH of the other Providence River and Upper Bay seasonal surface values. TWharf (TW) experiences the smallest variation in pH (Figure 4) inter-annually and vertically from surface to bottom.

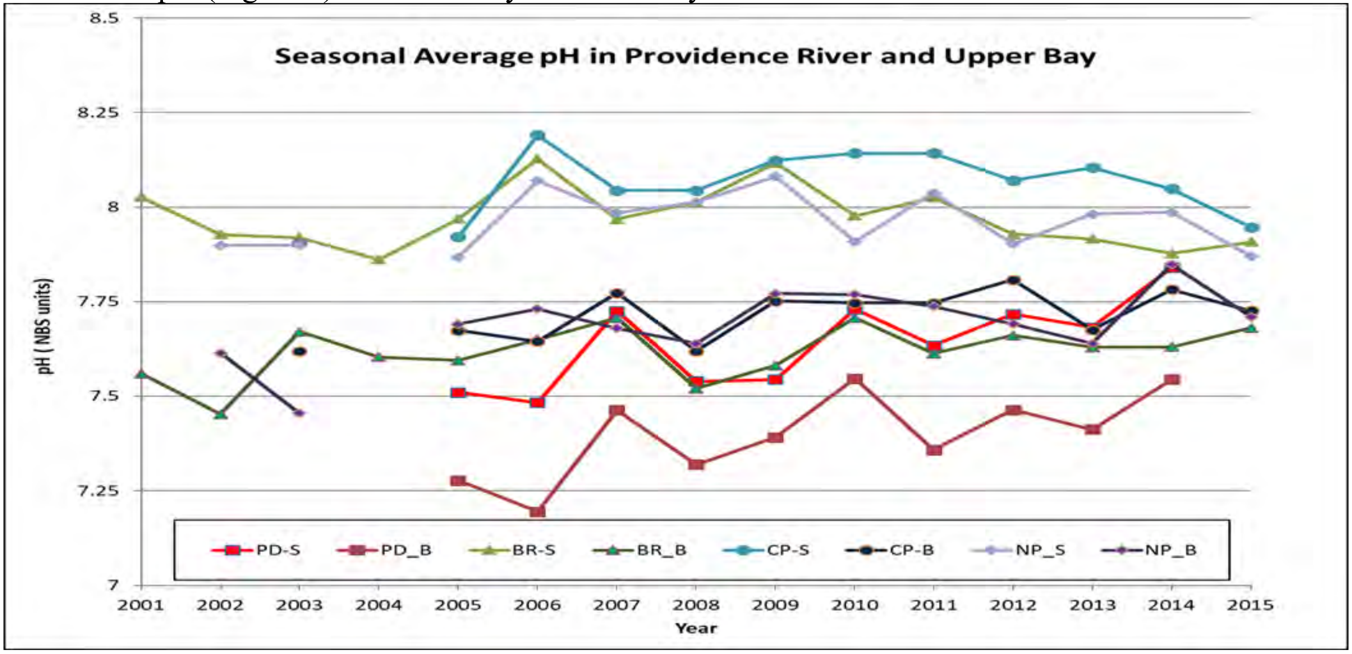


Figure 3. Upper Bay stations (Phillipsdale (PD), Bullock Reach (BR), Conimicut Point (CP), North Prudence (NP)) Surface (S) and Bottom (B). Average pH ranges from 7.20 (Phillipsdale furthest station upstream) to 8.19 (Conimicut Pt at the mouth of the Providence River during a highly productive summer, 2006)

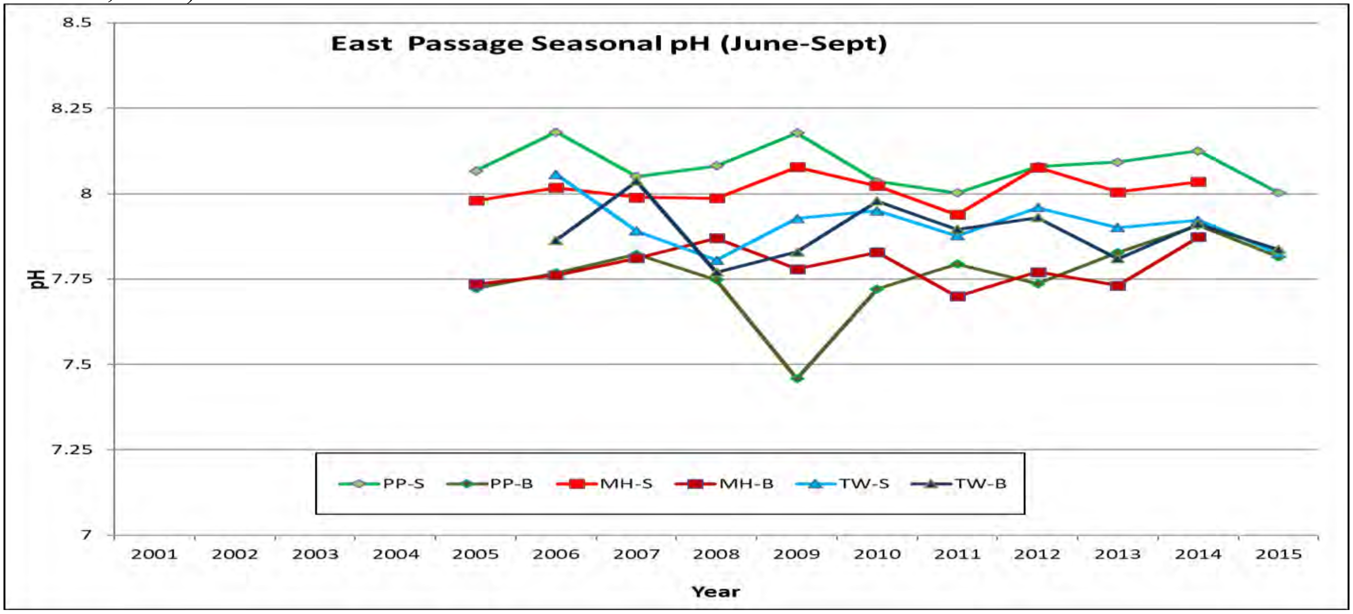


Figure 4. East Passage and Mt Hope Bay embayment (Poppasquash Point (PP), Mt. Hope Bay (MH), T-Wharf (TW). Average pH ranges from 7.45 (Poppasquash Bottom, 2009 unusually low pH season) to 8.18 (PP, northern most station for this grouping, during a highly productive summer, 2006).

Table 3. Overall Differences between Surface and Bottom pH (June 1- Sept 30, all available years of data by station)

Site	pH Surface	pH Bottom	Difference
PD	7.64	7.40	0.24
BR	7.97	7.62	0.35
CP	8.06	7.71	0.34
NP	7.96	7.68	0.28
PP	8.08	7.82	0.32
MV	7.96	7.74	0.22
QP	8.04	7.80	0.25
TW	7.91	7.89	0.03
GB	7.77	7.60	0.17
SR	7.949	7.60	0.34
MH	8.01	7.79	0.23
ALL STATIONS	7.94	7.70	0.25
BAY STATIONS	7.99	7.74	0.26

The overall pH for Narragansett Bay surface waters is 7.99. It is not unusual for an estuary to have a lower pH compared to the open ocean. The range of the pH in near equilibrium with the atmosphere found in the surface waters of the North Atlantic, which is 8.1 ±0.1 (Millero, 2007). The bottom waters of Narragansett Bay are less than the North Atlantic pH at 7.74 pHnbs. The differences in pH from surface to bottom range from .35 pH units in the Providence River to .02 pH units at TWharf (Table 3). Greenwich Bay stations also have lower seasonal pH values, especially in the bottom waters (over all seasonal average: 7.6 pH) (Figure 5a and 5b).

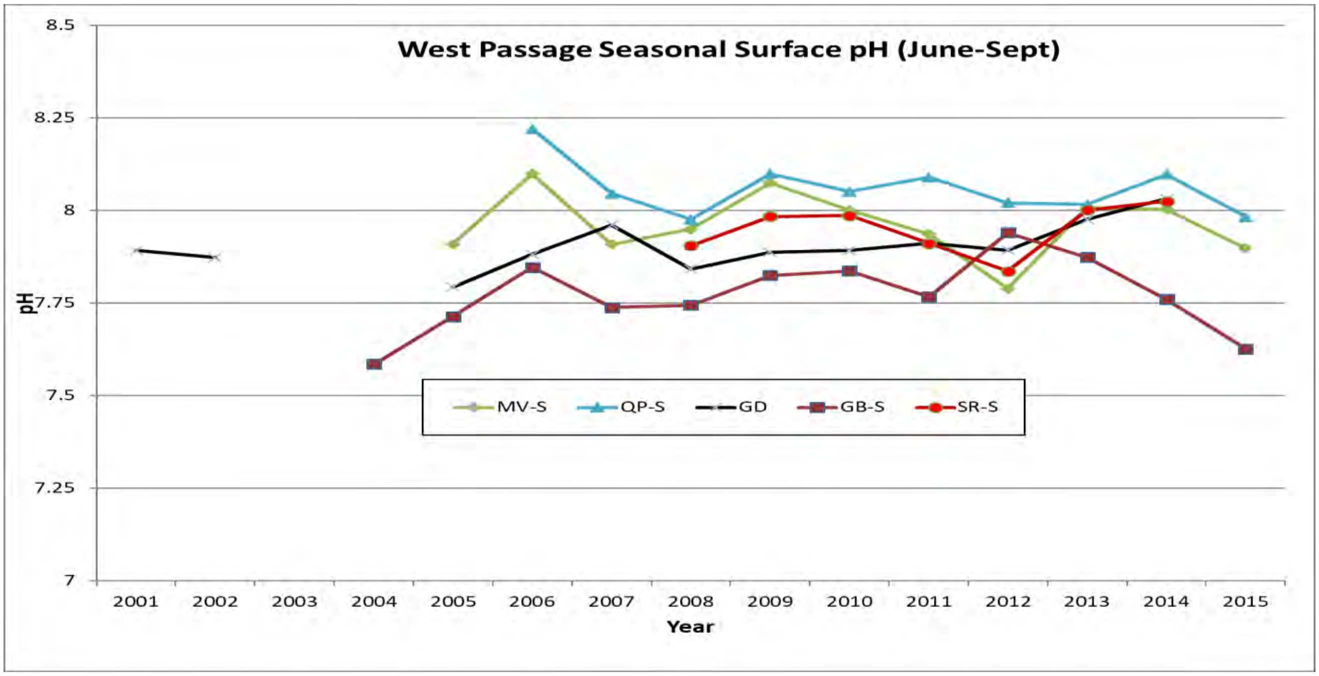


Figure 5a. West Passage and Greenwich Bay embayment (Greenwich Bay (GB), Sally Rock, (SR), Mount View (MV), Quonset Point (QP), GSO Dock (GD)). Average pH ranges from 7.58 (Greenwich Bay experiences the largest flux in pH and lowest salinities for this region of the bay) to 8.22 (Quonset Pt near mid-bay during a highly productive summer, 2006).

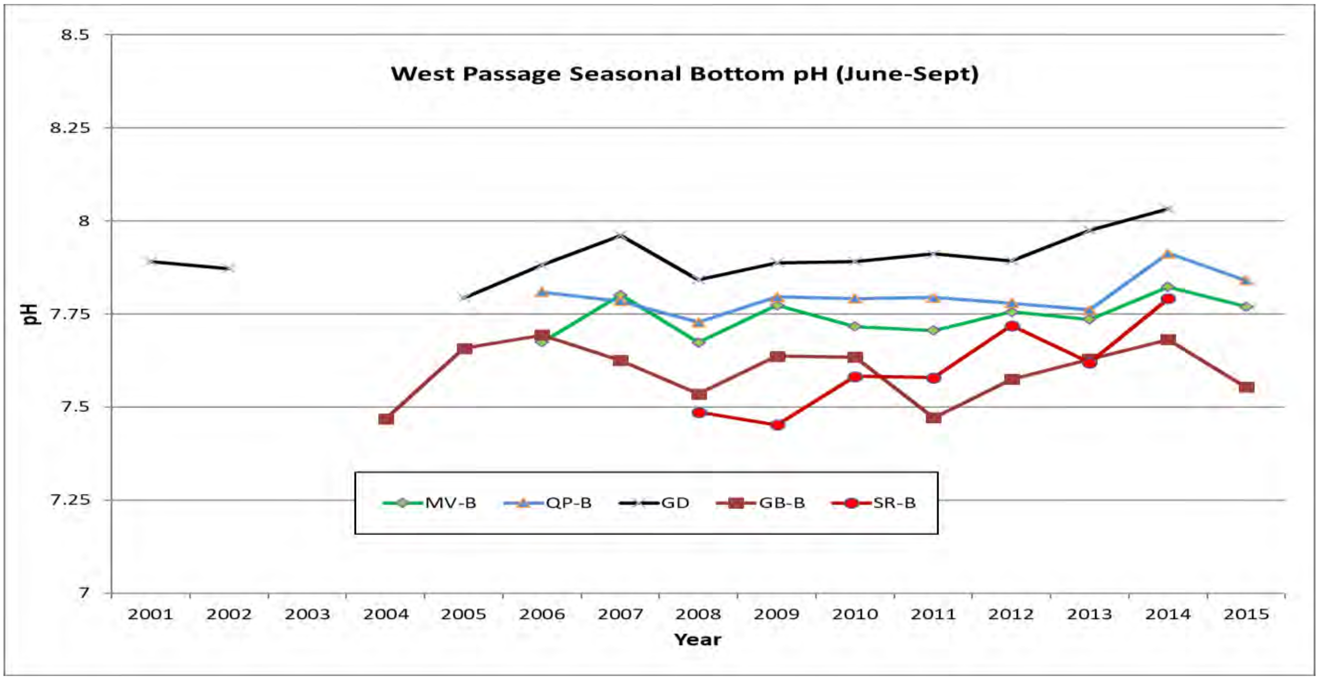


Figure 5b. Seasonal Average bottom pH levels within the West Passage. SR experiences the lowest pH (7.45 in 2009). The highest pH is at the mouth of the West Passage (GD).

Since pH is not normally distributed, results are also expressed using median, 5th percentile and 95th percentile results. Results were separated into surface and bottom results (Figure 6a and Figure 6b). Seasonally, monthly pH minimums in the surface waters (5th percentiles) are observed from July through September depending upon station, except for Phillipsdale (Figure 6a).

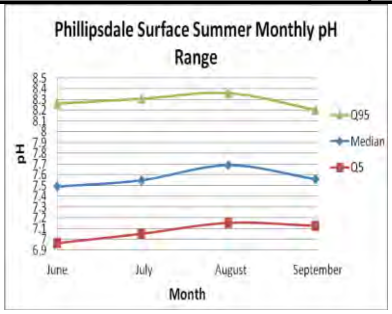
Phillipsdale experiences it seasonal minimums in June. However, when Phillipsdale is examined with all available data (March-December) as in Figure 6c, annual minimums occur during April when river flow is generally at its annual highest. The lower pH at the Phillipsdale station is caused by the amount of freshwater inputs because lower salinity waters have lower alkalinity.

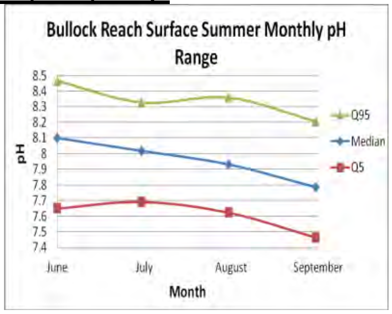
Surface maximums for the rest of the Bay (95th percentile) occurs during June for almost all stations, ranging from 8.46 pH nbs at Bullock Reach to 8.15pHnbs at GSO dock. Sally Rock shows a peak in 95th percentile in July (8.25 pHnbs). During June, temperatures are cooler allowing for more oxygen saturation and chlorophyll blooms are occurring with freshwater inputs delivering nutrients to the surface waters. Both factors have a positive effect on pH. In addition, the literature indicates that pH is increased during a phytoplankton bloom with carbon dioxide decline and decreased with poorly buffered freshwater inputs (Oczkowski, et.al, 2010). This is consistent with Wallace, et al. (2014), for surface waters, which suggests the pH minimums trail seasonal DO minimums into the late summer and early fall

This is not the case in the bottom waters of Narragansett Bay, where late summer degradation of organic matter from earlier blooms results in accumulation of inorganic carbon (and lower pH) before fall mixing gets under way (e.g., Gledhill et al, 2015). pH monthly minimums and the lowest monthly medians occur during July and August in the bottom waters on a bay-wide basis (Figure 6b). Median pH values are consistently lowest at Phillipsdale and Greenwich Bay from June-August (ranging from: 7.49 at PD in June to 7.54 at GB in July). Many areas of the bay experience monthly minimums (5th percentile) during September. The bottom waters in Narragansett Bay are prone to summer seasonal intermittent hypoxia. These events are most prevalent in July and August. PH seasonal minima in the bottom waters follow this same pattern.

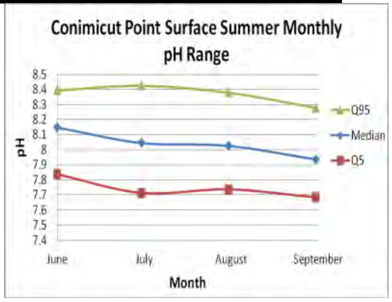
Figure 6a. **Summer Monthly Surface pH Quadrangles**. These stations are grouped by bay area. All available data from June 1-Sept 30 was used to produce all these plots. pH monthly minimums occur during July-Sept depending upon station, except for Phillipsdale.

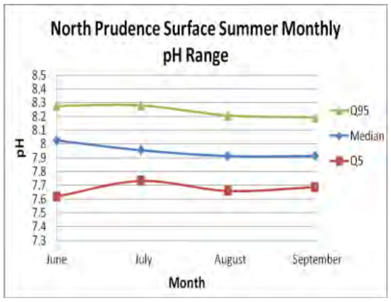
Providence River Stations (PD, BR, CP):



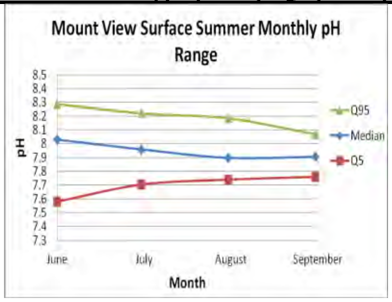


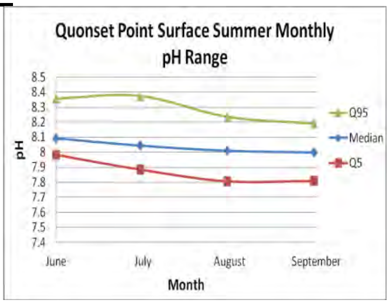
Upper Bay (CP and NP):

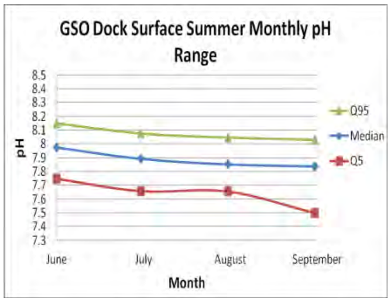




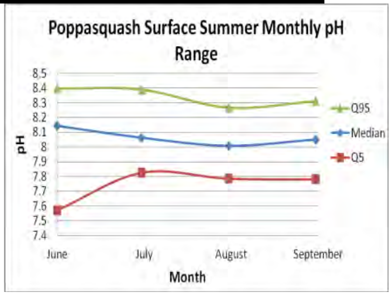
West Passage (MV, QP, GD):

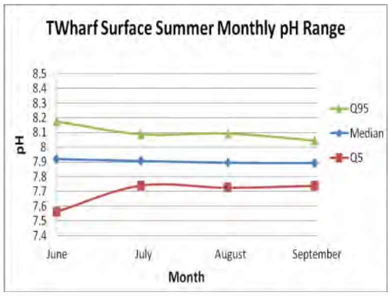




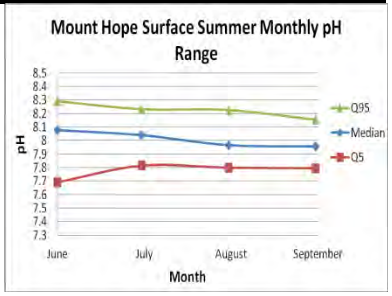


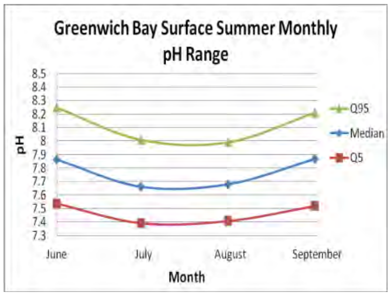
East Passage (PP, TW):





Embayments(MH, GB, SR):





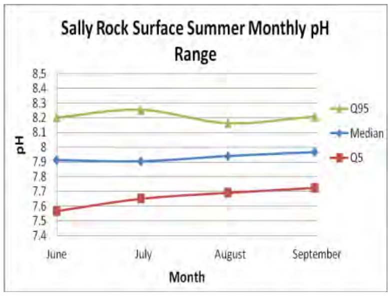
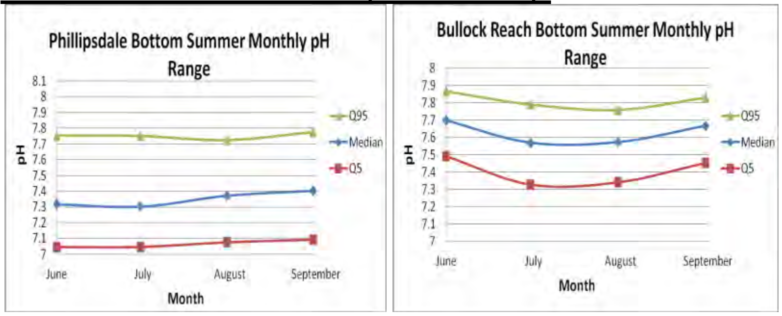
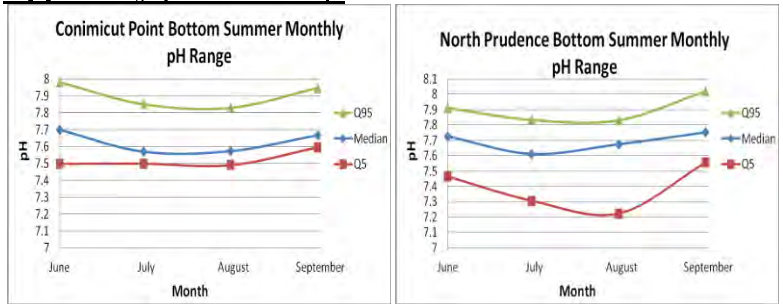


Figure 6b. **Monthly Bottom pH Quadrangles**. Minimum pH occurs during July and August.

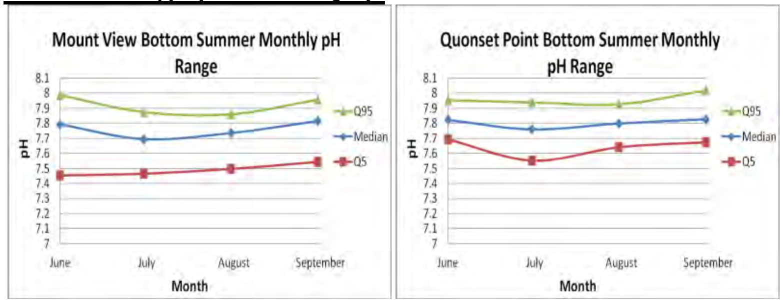
Providence River Stations (PD and BR):



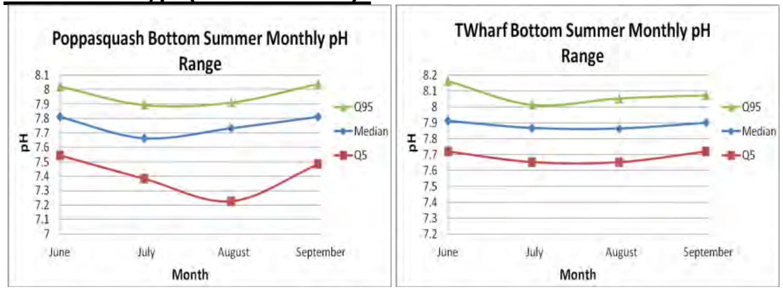
Upper Bay (CP and NP):



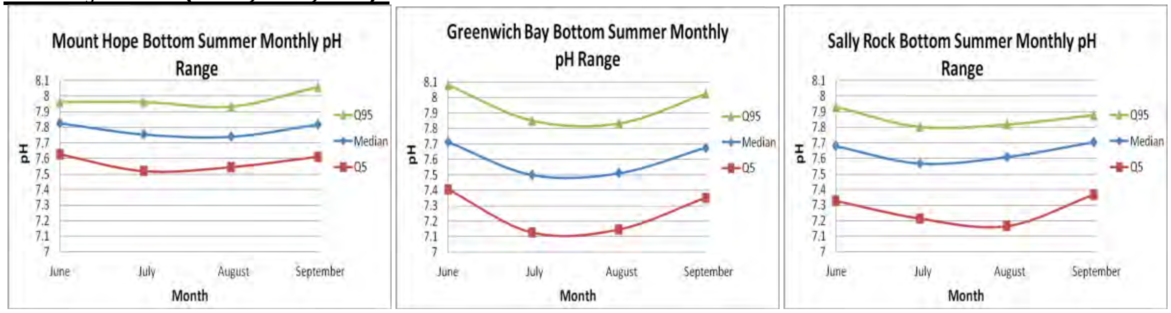
West Passage (MVand QP):



East Passage (PPand TW):



Embayments(MH, GB, SR):



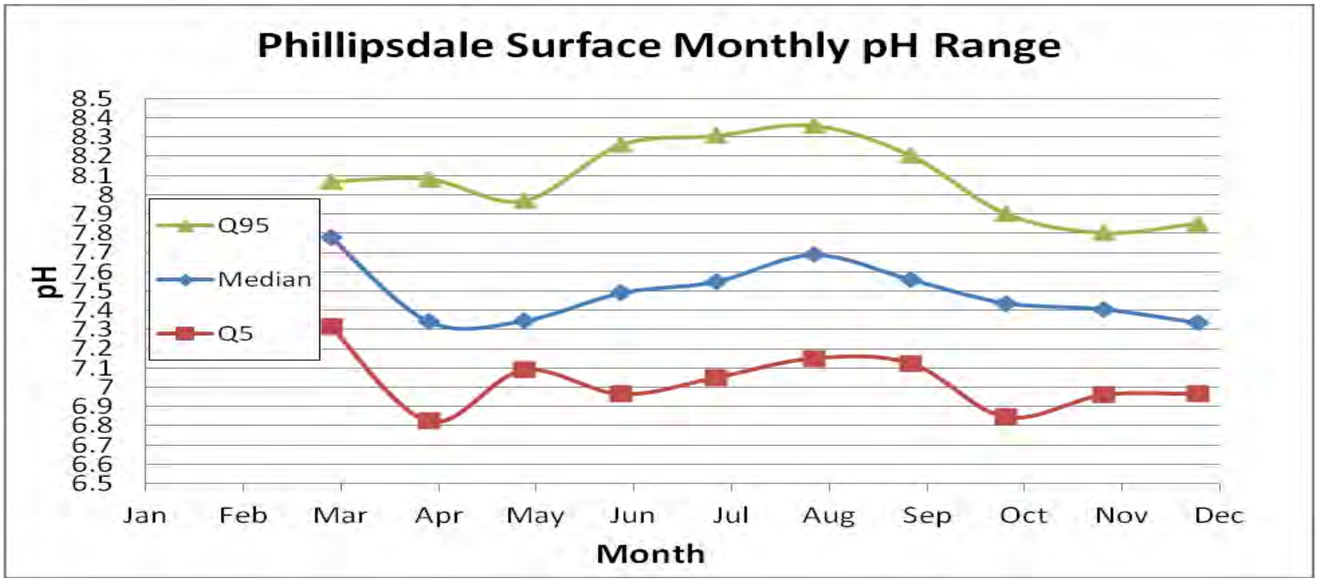


Figure 6c. Phillipsdale Monthly Ranges in pH at Surface.

To examine how pH relates to other parameters, plots of seasonal averages surface pH readings were plotted against salinity and chlorophyll. The premise is to give a first glance look at how the pH from stations fall out against different parameters to give an idea if certain parameters have a relationship with pH

pH was plotted against salinity as shown in Figure 7. Phillipsdale had much lower salinities and lower pH seasonal averages than all the other stations (these stations are circled in red). This is likely because this is the northern most station with a strong influence from river inputs. On several occasions throughout the stations record, salinity has been zero during storm events. This is considered a brackish area. Greenwich Bay, circled in black in Figure 7, shows lower pH at similar salinities this suggests possible biological activity influencing pH.

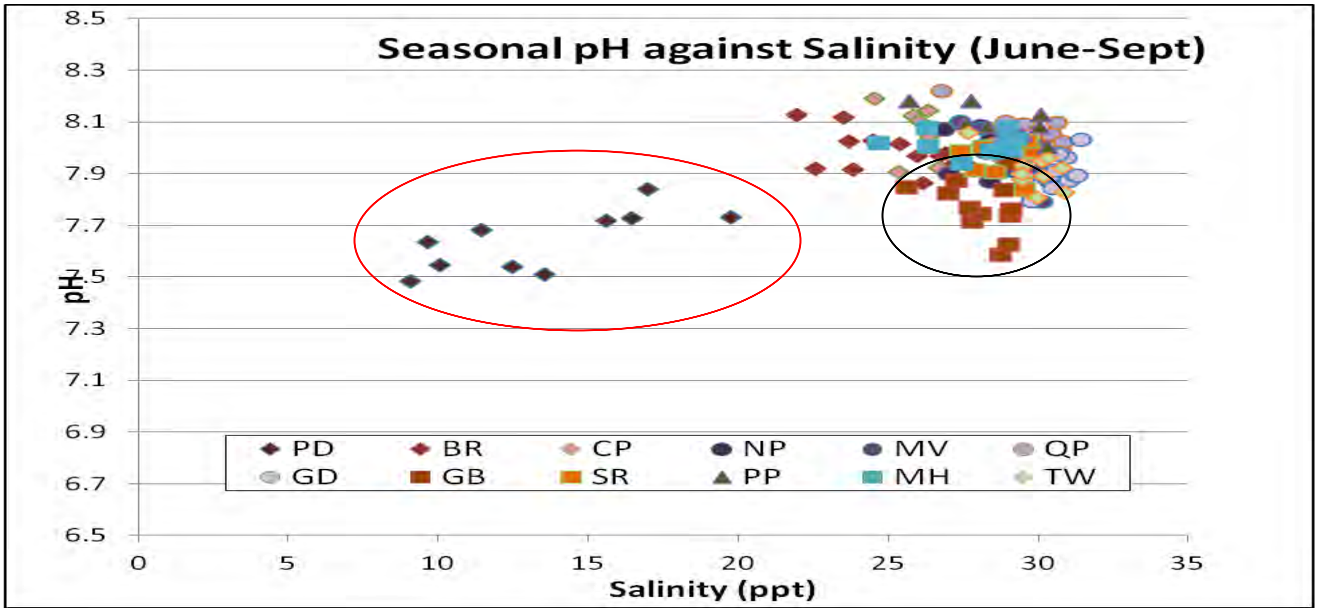


Figure 7. Seasonal mean pH vs salinity by station. Phillipsdale (circled in red) is the only station that shows a realationship with salinity. Greenwich Bay (circled in black) shows lower pH than the other grouped bay stations at similar salinities.

To examine biological activity on pH, pH was plotted against chlorophyll (figure 8). Phillipsdale was not included in this plot since the salinity range is less than the other station by about 5ppt. Most stations pH values range between 7.75-8.25 pH NBS units. Greenwich Bay shows the lowest pH values (about 7.6 pH NBS units) with the highest chlorophyll levels (over 20 ug/L on average). The overall seasonal average chlorophyll being over 20 ug/L suggests this area is eutrophic. Bullock Reach also has a high overall season average for chlorophyll at 19 ug/L. Greenwich Bay has lower pH values because it is a shallow embayment where oxygen levels decline to hypoxic conditions during respiration period in the overnight hours. To identify the relationships between pH and other parameters, a principal component analysis was conducted on the daily average data by station for the summer season from June through September.

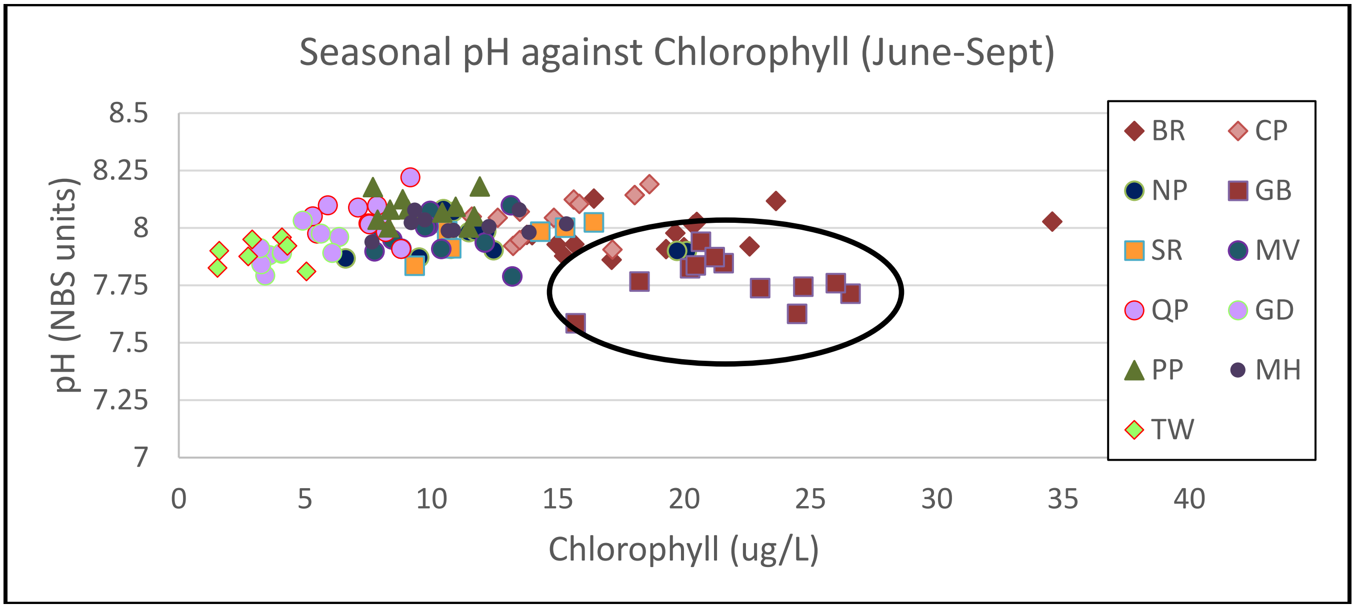


Figure 8. Seasonal average pH versus total chlorophyll by station for the Providence River to GSO dock. Phillipsdale is not included in this plot. Greenwich Bay data circled in black.

A PCA was applied to all data from June 1-September 30 to understand the drivers of variation among sampling sites and gain insight into correlation among water parameters. The data was divided by depth, surface and bottom station data. At the surface, each of the water parameters account for a similar amount of the data variance (Figure 9). However, the loadings for the first two principal components indicate that pH, DO %, and chlorophyll explain the most variation in descending order. The results also suggest that there are two groups of correlated variables: 1) DO % and pH, and 2) chlorophyll, salinity, and temperature. At the bottom, temperature explains much more of the data variance than pH, DO, and salinity individually (Figure 10). This latter group of parameters appear to be strongly correlated in contrast to the surface, where salinity is most correlated with temperature. At both depths, there is only minor variation in principal components scores among sites.

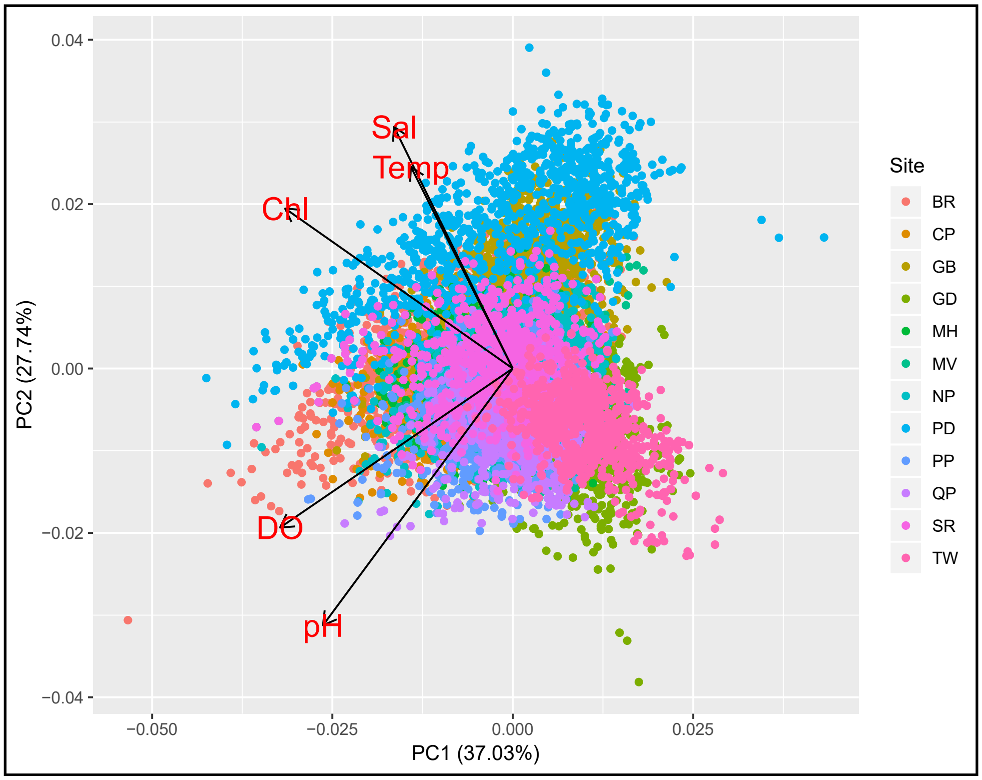


Figure 9. Surface Principal Component Analysis Biplot. Surface data for all stations, June-Sept. The first two principal components explained 64.8% of the variation in the data.

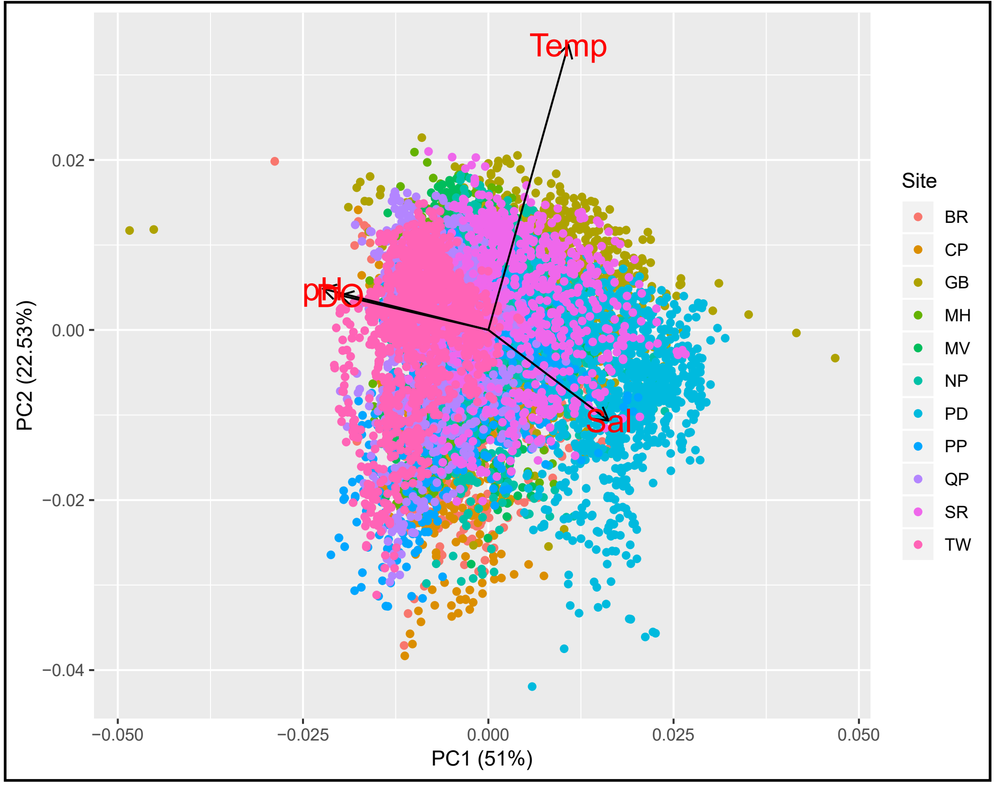


Figure 10. Bottom Principal Component Analysis Biplot. Bottom data for all stations, June-Sept. The first two principal components explained 73.5% of the variation in the data.

A multi-linear regression was applied to each station using surface and bottom data combined to address which parameters influence pH the most. Table 4 shows the individual station results grouped by bay region. Since the data is not normally distributed, the coefficients are all standardized; the covariate with the largest coefficient (effect) will generally have the largest correlation. However, because these covariates are correlated with each other, the coefficients will not represent the exact effect of the covariates on pH, DO%, nor the exact correlation. DO% multi-linear regression results can be found in Appendix A. The values represented in these two tables are estimates. Based on the results in Table 4, the largest effect on pH at Phillipsdale is salinity followed by chlorophyll. This can be graphically described in Figure 9 when pH is plotted against salinity. pH at Providence River and Upper Bay stations (BR, CP, and NP) is affected primarily by dissolved oxygen, chlorophyll, and salinity respectively. pH at the upper and mid-West Passage stations (MV and QP) are affected by salinity followed by dissolved oxygen. The pH at lower west passage station (GD) is most strongly affected by temperature. Dissolved oxygen mainly effects pH at the East Passage stations (PP and TW). The changes in pH in the embayments are primarily driven by biological activity. Mt. Hope Bay pH behaves similarly to the Upper Bay stations with chlorophyll being the variable with the highest effect on pH. The same process driving the changes in dissolved oxygen are also behind the variability in pH in Greenwich Bay (photosynthesis and respiration). Sally Rock and Greenwich Bay have standard coefficients >0.3. This is because Greenwich Bay is a eutrophic shallow embayment and the oxygen is driven by primary production. Year is listed as a variable in the multi-linear regression results to show any relative change in pH over the course of the sampling record. Poppasquash is the only station that shows a negative correlation over time (PP standardized coefficient for year: -0.0552, p-value: <.001). However, it is difficult to determine effects on pH from reduced buffering and the effects of higher production/respiration in lower salinity areas.

Since this change is quite small at Poppasquash Pt, and within the error of the instrument itself, another trend analysis approach was used. Based on Baumann, et al. (2017), the daily change (difference between daily max and min) in pH (ΔpH) was examined by first finding the daily range of pH (max minus min on a daily basis). The seasonal average (June-September) of daily ΔpH was calculated and then the dataset was normalized t Poppasquash Pt to observe if the daily range in pH is increasing at Poppasquash Pt. The seasonal averages were normalized using the overall average of ΔpH for the whole 12-year record (figure 11). There is no evidence of the Δ pH increasing over time. This station is showing a downward trend in pH that is somewhat consistent with changes in daily DO %, except for 2016 (figure 12). This is consistent with the multi-linear regression analysis that showed DO% to have the largest correlation with changes in pH. The delta pH anomalies are also somewhat consistent with the wet/dry year analysis, except for 2017 (figure 13). The east passage maybe a prospective area to examine for the potential of coastal acidification.

Table 4. Summer Multi-Linear Regression Analysis by Station. The stations are grouped by bay regions. Highlighted variables appear to have the largest effect on pH. These are standardized coefficients since the log of the salinity had to be taken twice to normalize the data.

Providence River: Site	PD		BR			
Variable	Coefficient	p-value	Coefficient	p-value	Coefficient	p-value
DO%	0.4761	<.001	0.4416	<.001		
Temp	-0.2565	<.001	-0.1681	<.001		
Salinity	2.6096	<.001	0.2215	<.001		
Salinity^2	-0.6105	<.001	-0.0349	0.08		
Chl	0.4845	<.001	0.1065	<.001		
Year	0.0183	0.005	0.0039	0.119		
Upper Bay:						
Site	CP		NP			
DO%	0.1673	<.001	0.3384	<.001		
Temp	-0.1876	<.001	0.0589	0.031		
Salinity	0.2341	<.001	0.4464	<.001		
Salinity^2	-0.0707	0.029	-0.0452	0.081		
Chl	0.4083	<.001	0.1571	<.001		
Year	0.0377	<.001	0.0347	<.001		
West Passage:						
Site	MV		QP		GD	
DO%	0.2202	<.001	0.2734	<.001	0.1767	<.001
Temp	0.1958	<.001	0.1399	<.001	0.396	<.001
Salinity	0.4811	<.001	0.3465	<.001	0.1588	<.001
Salinity^2	0.2096	<.001	0.2205	<.001	0.0524	<.001
Chl	0.1457	<.001	0.043	0.09	0.189	<.001
Year	0.0146	0.002	0.016	<.001	0.0558	<.001
East Passage:						
Site	PP		TW			
DO%	0.3228	<.001	0.2814	<.001		
Temp	0.0603	0.08	-0.0259	0.311		
Salinity	-0.1315	<.001	-0.0309	0.043		
Salinity^2	0.0846	<.001	-0.0081	0.451		
Chl	0.1078	<.001	0.0835	<.001		
Year	-0.0552	<.001	0.0297	<.001		
Embayments:						
Site	MH		GB		SR	
DO%	0.1828	<.001	0.3401	<.001	0.3281	<.001
Temp	0.016	0.474	0.1151	<.001	-0.0007	0.979
Salinity	0.1186	<.001	0.1496	<.001	-0.0773	0.044
Salinity^2	-0.0966	<.001	0.0534	<.001	-0.0399	0.084
Chl	0.2294	<.001	0.0579	0.021	0.2872	<.001
Year	0.0199	<.001	0.0156	<.001	0.0345	<.001

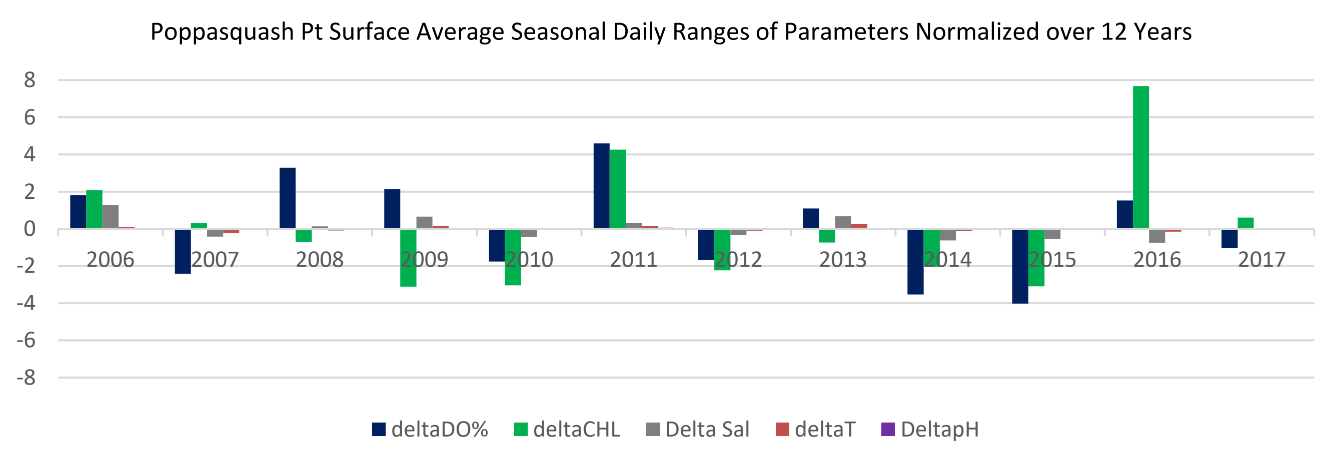


Figure 11. Poppasquash Pt surface seasonal anomalies in delta temp, sal, DO%, and pH.

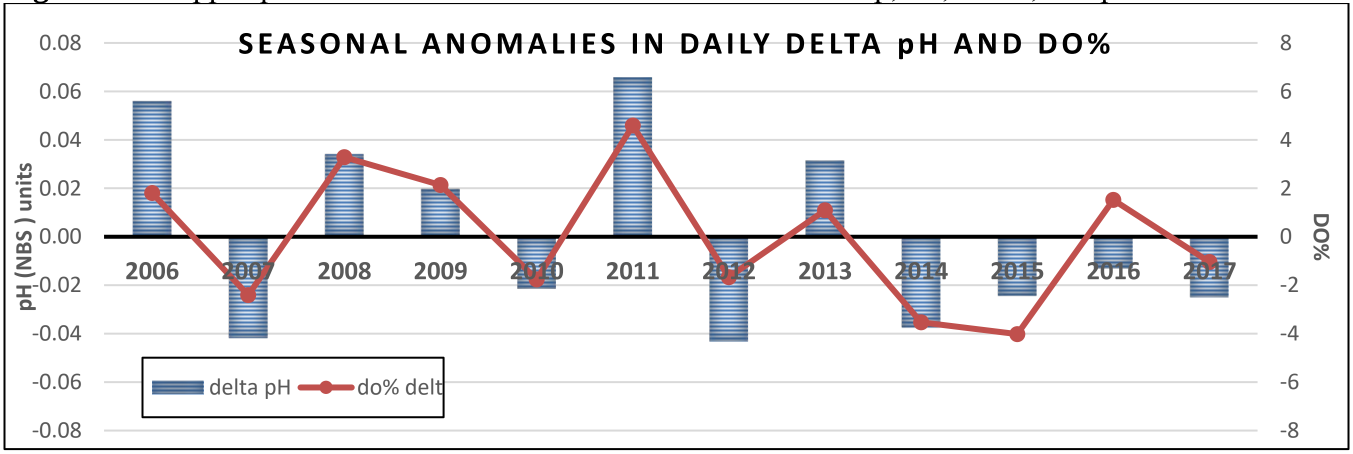


Figure 12. Normalized seasonal delta pH and delta DO % since the multi-linear regressions suggests DO% influences the changes in pH the most.

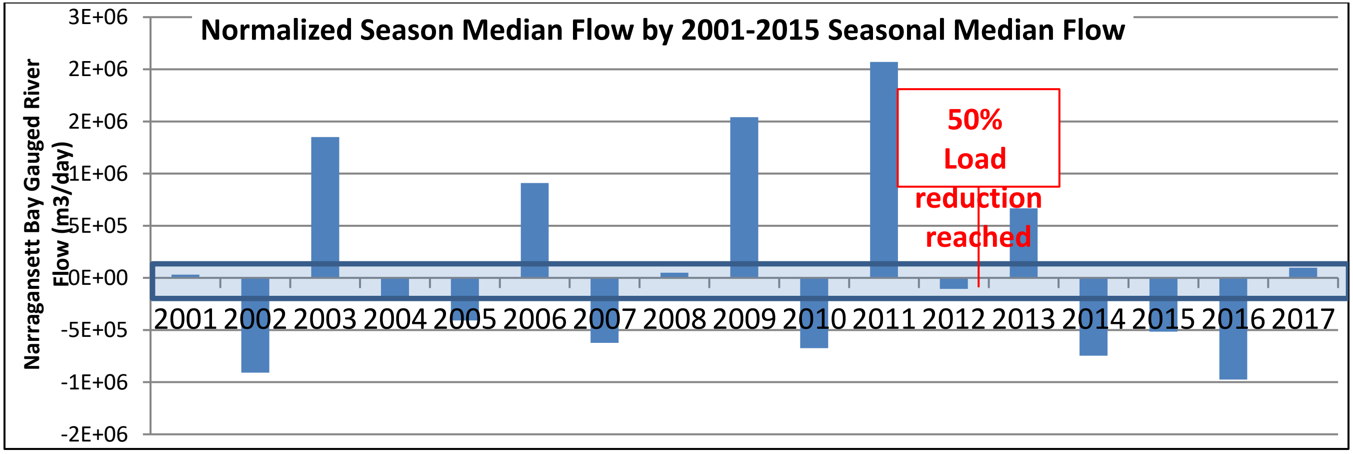


Figure 13. Median seasonal flow based on major gauged river flow data (Kellogg, 2018). The blue box indicates the difference in median river flow from the 15-year median to the overall river flow median. For this study to compare the 15-year period, the area in blue represents the normal range seasonal river flow for the time period in relation to the overall median flow.

Annual Analysis:

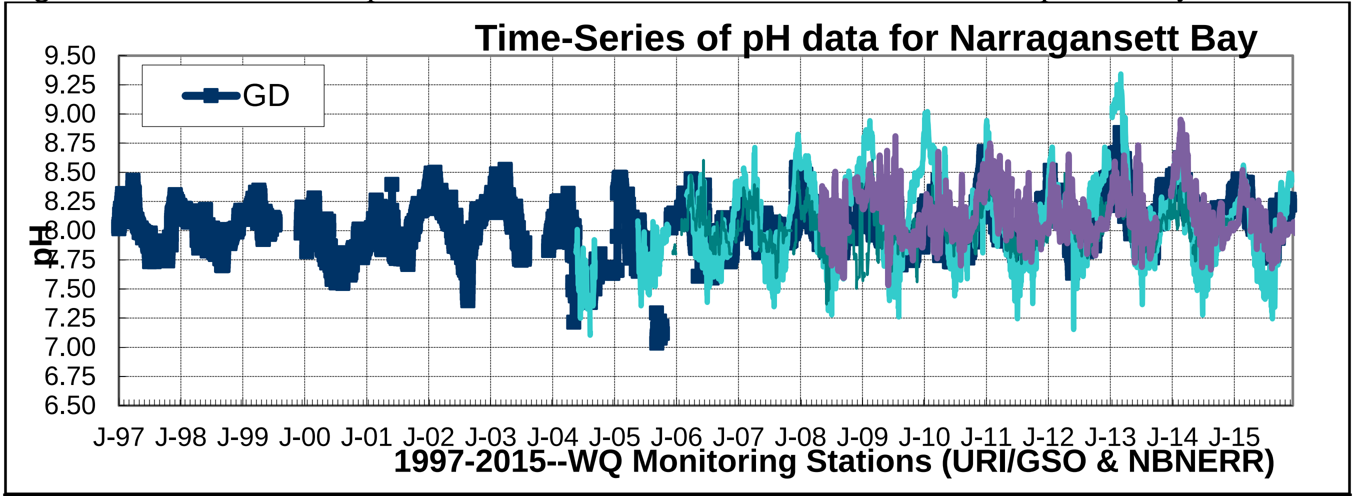
A graph with the daily pH values depicts the seasonal trends in pH (Figure 14). pH within the lower bay (TW & GD) had a smaller overall range than the Upper Bay and embayments (CP &GB) (1.3 pH units at GD, 1.2 at TW, 1.4 at CP and 2.2 at GB). The down-Bay GSO dock station generally has the least seasonal variability. One exception occurred during a major flood event in October 2005. It is also possible to have erroneous data that could not be detected or removed by the QA/QC process. The GSO dock shows a slight increase in pH over time. Peak pH occurs during the winter/spring of each year at the GSO dock (Figure 14a). This area is also subject to winter/spring blooms depending upon environmental factors, such as temperature <3.5°C (Oviatt, 2002). The peaks in pH in recent year have been consistent with observed winter spring blooms.

The winter/spring bloom in Narragansett Bay has occurred sporadically over recent decades. Documented winter/spring blooms occurred in 2008, 2010, 2011, and 2013 at all sites (Figure 14b). Continuous chlorophyll data began to be collected in 2004. Prior to 2004, chlorophyll measurements were collected by grab samples and are not represented here. These blooms have been observed at all stations to varying degrees of intensity. The Upper Bay station (CP) and Greenwich Bay (GB) are plotted on the secondary vertical axis with a maximum chlorophyll measurement of 258 ug/L at GB and 141ug/L at CP during the 2011 winter bloom event. The less intense blooms occur in the lower bay with peaks of 23 ug/L at GSO Dock (GD) in 2011 and 23 ug/L at TWharf (TW) in 2012.

Over an annual cycle, levels of pH NBS and DO were strongly coupled and highly dynamic within Narragansett Bay, particularly within surface waters where peak levels in Greenwich Bay of pH NBS (9.34) and peak DO (159%) occurred in winter coincide with the winter-spring bloom. Minimal values of pH values of 7.10 and 24% for dissolved oxygen, occurred during the summer respiration peak at Greenwich Bay (Figure 14c). The other year-round stations within Narragansett Bay have similar temporal patterns that were observed for DO, although the range in values was smaller for surface waters by 14 DO% less at CP to 58 DO% at TW when compared to DO% range at Greenwich Bay.

The largest dips in pH occur during the summer. These dips that are observed annually correspond with hypoxic events that occur in the areas of Greenwich Bay and Upper Narragansett Bay. Figure 15 shows the average annual cycles by month of temperature, salinity, pH, DO% and total chlorophyll at all winter surface stations (GB, CP, TW, GD). Greenwich Bay reports the lowest winter temperatures (-0.23 °C) during January and February and the highest temperatures (27° C) during July and August. The lowest salinities occur in Spring at all stations, generally, April is the annual monthly minimum. Conimicut Pt has the largest annual range (5.8 ppt) in salinity with minimums occurring in April (18.6 ppt). The low minimums in April are influenced by a large flood event that occurred in 2010. Dissolved oxygen peaks in the late winter (Feb-Mar) and annual minimums are reached during late summer (August-September). The largest variability is in the Upper Bay and Greenwich Bay during the summer (June-September) with a range 57-68 percent saturation during the summer months. Surface conditions at CP, TW, and GD all show seasonal pH minimums in September. This annual cycle is consistent with other studies that suggest coastal acidification is an annual feature of eutrophic estuaries across the Northeast US that co-occurs with seasonally low oxygen (Wallace, et.al., 2014). Greenwich Bay surface waters have seasonal pH minimums in July (S-7.35 pH nbs) and the largest variability in the summer months (0.6 pH units). The winter and spring in the lower bay are the most productive times of year, TW and GD showing monthly peaks in chlorophyll from Feb -June with monthly averages from 10-14 ug/L. The Upper Bay has eutrophic maximums for much of the year. The peak in the chlorophyll at CP in April corresponds with on large event during April 2011, where the chlorophyll max was at 141 ug/L The peak in the chlorophyll at CP in April corresponds with on large event during April 2011, where the chlorophyll max was at 141 ug/L. The fall is the least productive time with average chlorophyll levels at less than 6 ug/L. Greenwich Bay is eutrophic most of the year with month chlorophyll averages over 20 ug/L for 8 months a year.

Figure 14a. Time series of pH for land-based station. These three stations are operational year-round.



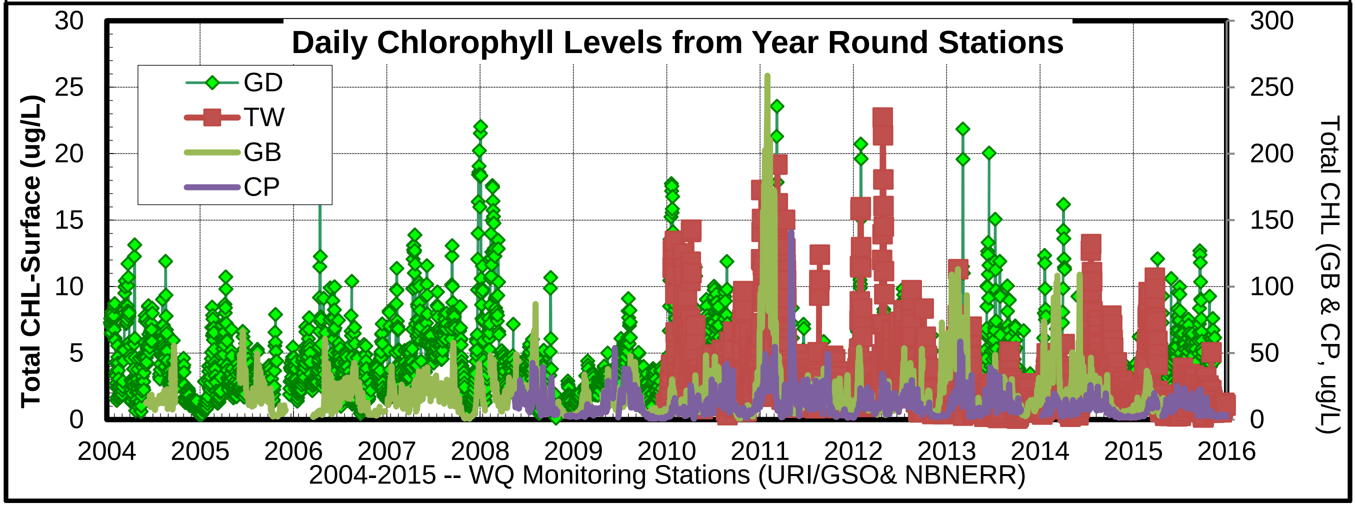


Figure 14b. Chlorophyll daily averages from year round surface stations. GB and CP on secondary vertical axis because chlorophyll levels are magnitude higher.

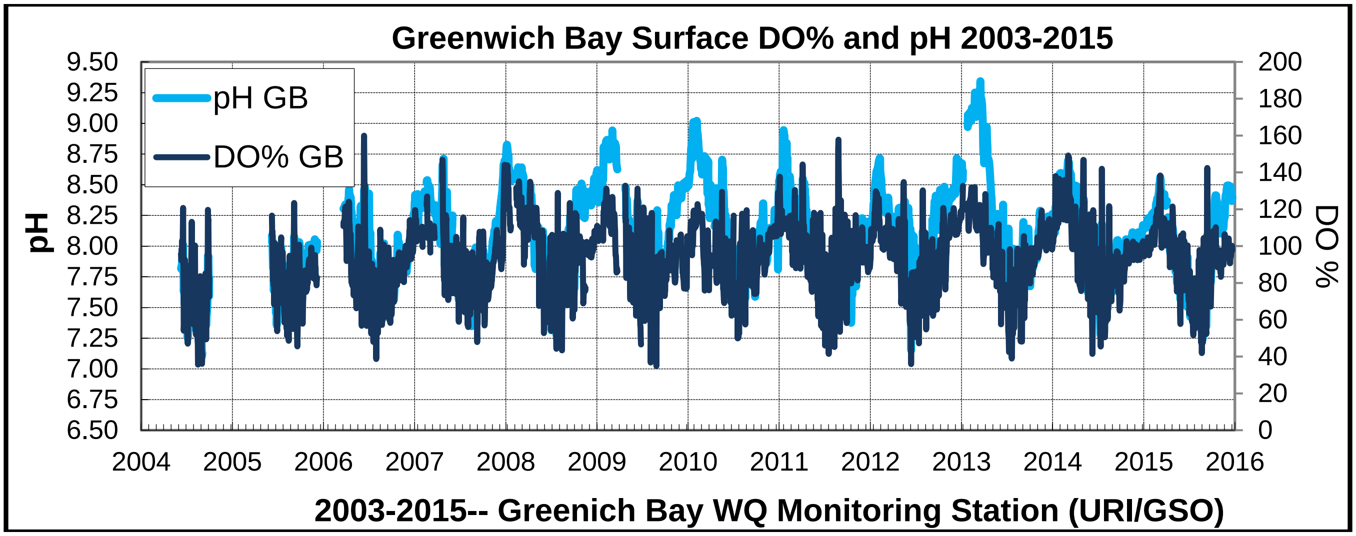


Figure 14c. Greenwich Bay surface DO% and pH daily time series.

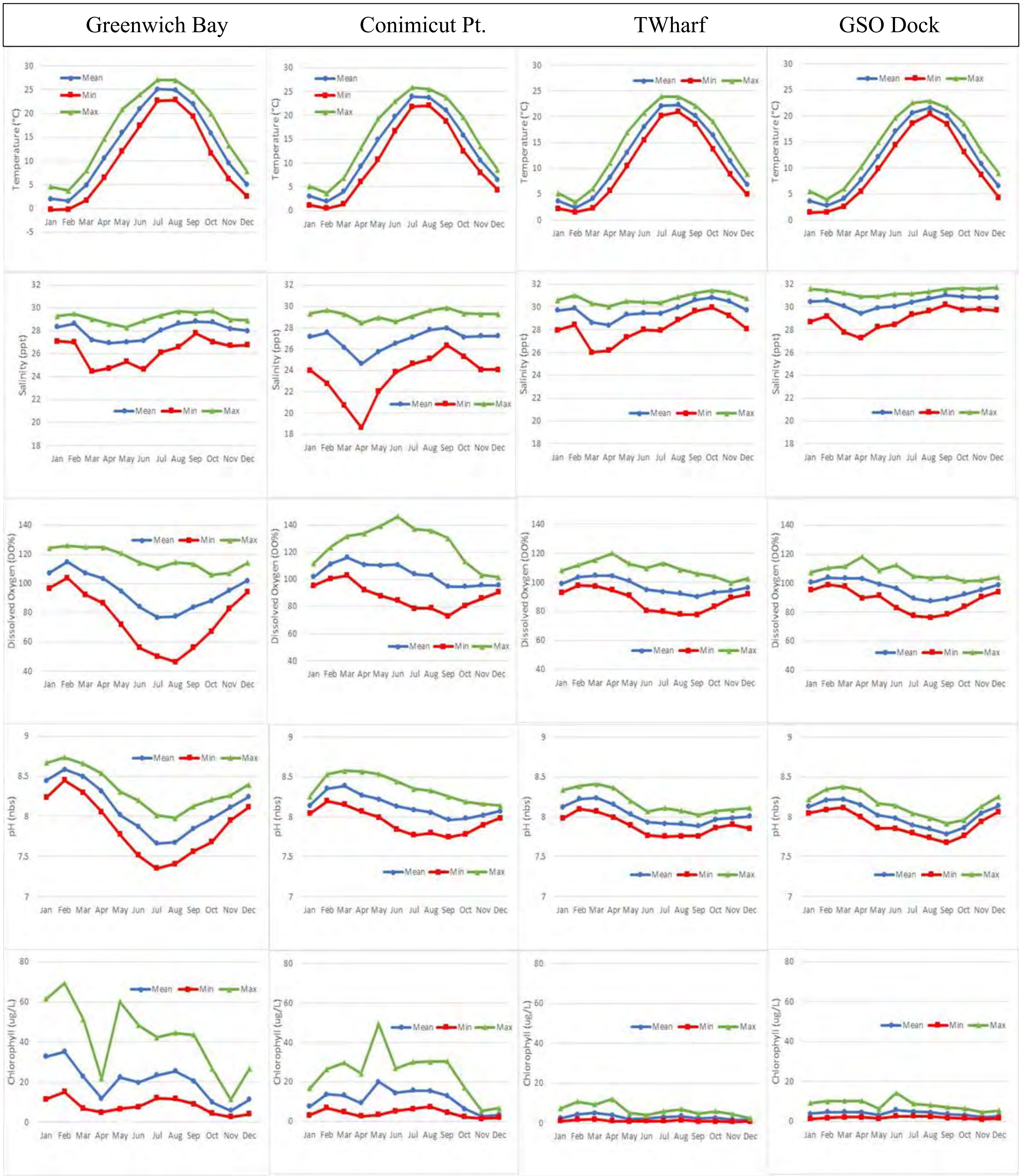


Figure 15 Overall monthly statistics for temperature, salinity, DO%, pH and total chlorophyll for all year round surface stations (GB, CP,TW, and GD). Monthly averages based on each stations available data (GB: 2006-2015, CP: 2008-2015, TW: 2006-2015, GD:1996-2015).

Each station was examined for monthly anomalies to examine trends over time in the annual data. To calculate the monthly anomalies for each parameter, the individual monthly means were calculated and then normalized using the overall monthly means (Jan-Dec) for each station based on the entire dataset for each station. All stations results showed 2012 as an anomalous warm year by about 3 degrees (Figures 16-19). This is consistent with region-wide findings (Baumann and Smith 2018). Although each station shows an increase in temperature, changes in other parameters varied.

GSO dock has the longest record and does not show a significant increase in pH over the data record (1997-2017) (Figure 16). Temperature has slightly increased at the GSO dock since 1997. Dissolved oxygen has decreased consistent with temperature increase. The pH has been increasing since 2011. Chlorophyll has also increased slightly. The driver behind the chlorophyll increase is consistent with an increase in the number of winters with a winter-spring bloom at this location in recent years.

The mid-east passage TWharf (TW) has a slight increase in temperature since 2006 (Figure 17). Dissolved oxygen has decreased more rapidly than temperature has increased. The variablity in pH anomalies has decreased over the course of the record. This is consistent with Baumann and Smith (2018). Baumann and Smith examined annual anomalies derived from averaging monthly anomalies for each parameter. Their research showed that temperature increased slightly, dissolved oxygen decreased by over 5%, and pH showed a slight increase. On an annual basis, temperature was decoupling with DO % and pH.

The shorter Conimicut Point dataset to 2008 showed no trends in any parameters. The year 2011 was anomolous in total chlorophyll at this station. January and Febuary were about 18 ug/L above the monthly averages (Figure 18). All stations report positive anomolies during this time period suggesting this was a bay wide event. It coinsides with an increase in pH, suggesting changes in metabolism as the main force behind the changes in pH during 2011.

Greenwich Bay has a sporadic data record and long-term trends are difficult to determine. From 2003-2006, data was recorded seasonally. Starting in 2007 the data record became year-round. An anomolous high month in total chlorophyll occurred during the winter of 2011 (Jan-Mar) (Figure 19). This event drove the monthly average chlorophyll 90 ug/Lof the month average for January and Febuary of 2011(Figure 19). The month following the bloom was anamolously low in pH by 0.37 pH units. During the winter of 2013, another lesser bloom occurred that is consistent with increases in pH during the same time period. These anamolies indicate chlorophyll as the main driver during these time periods.

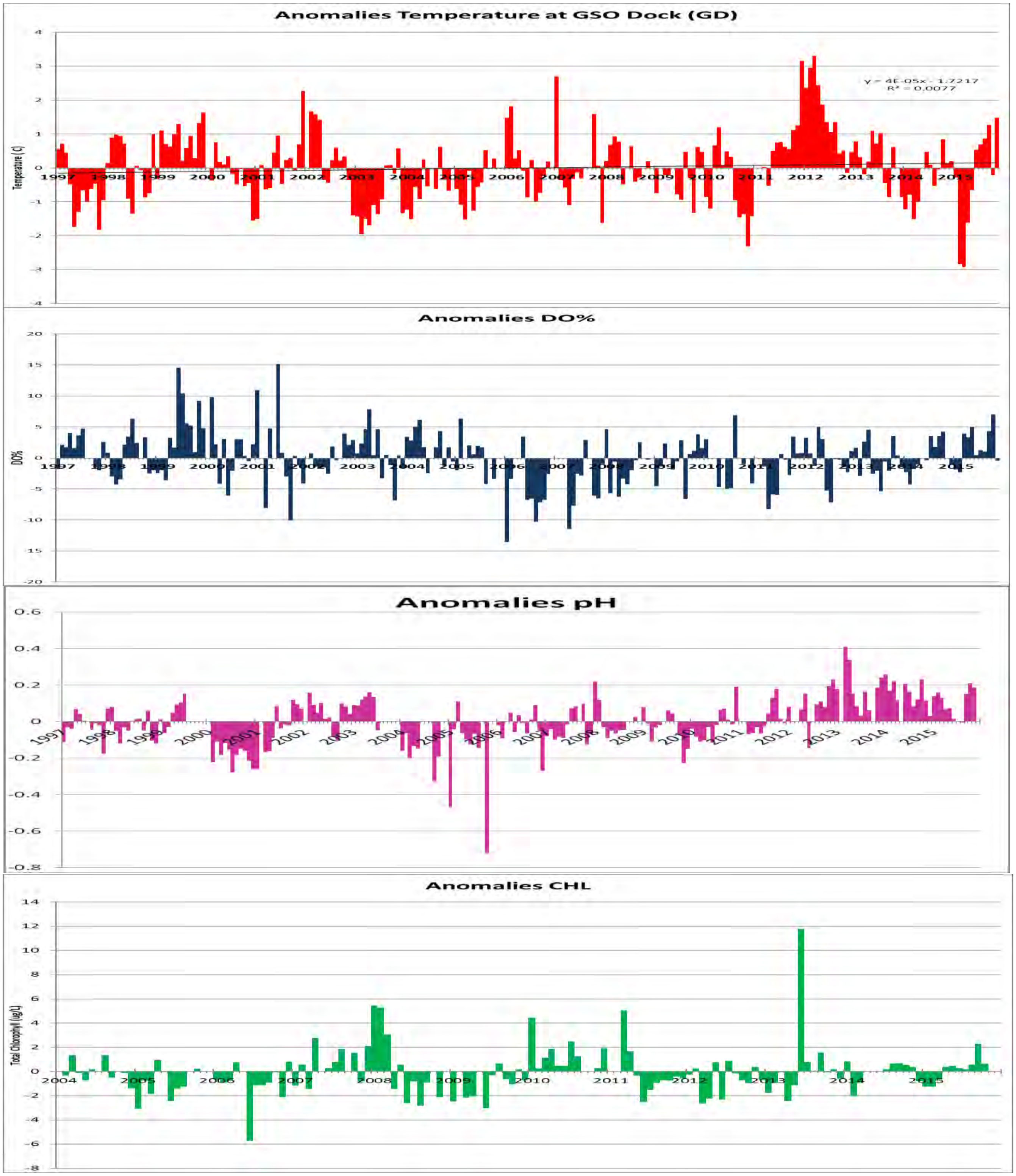


Figure16. Monthly anomalies by parameter at the GSO dock. Temperature has slightly increased at the GSO dock since 1997. Dissolved oxygen has decreased consistent with temperature increase. PH has been increasing since 2011. Chlorophyll has also increased slightly.

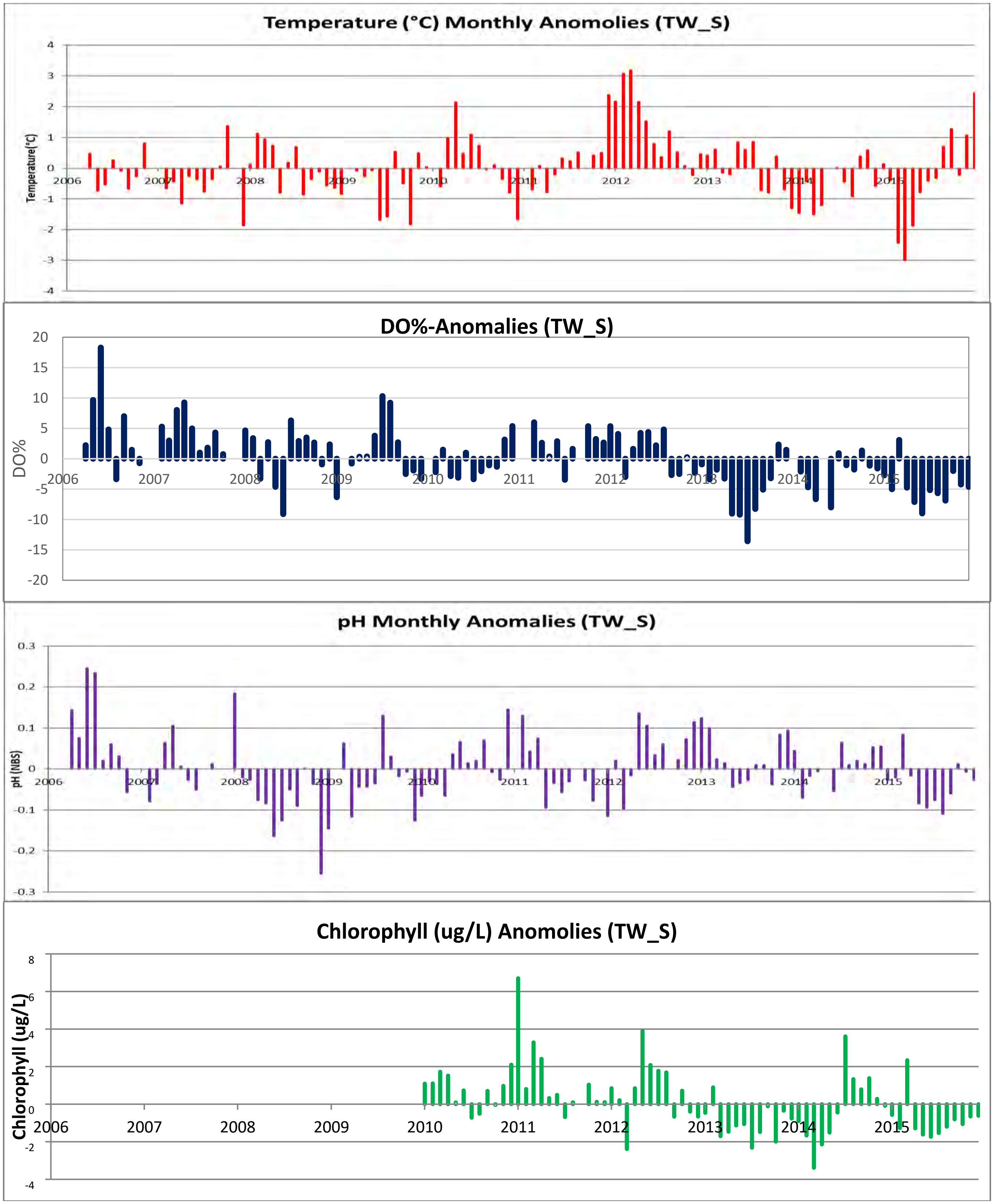
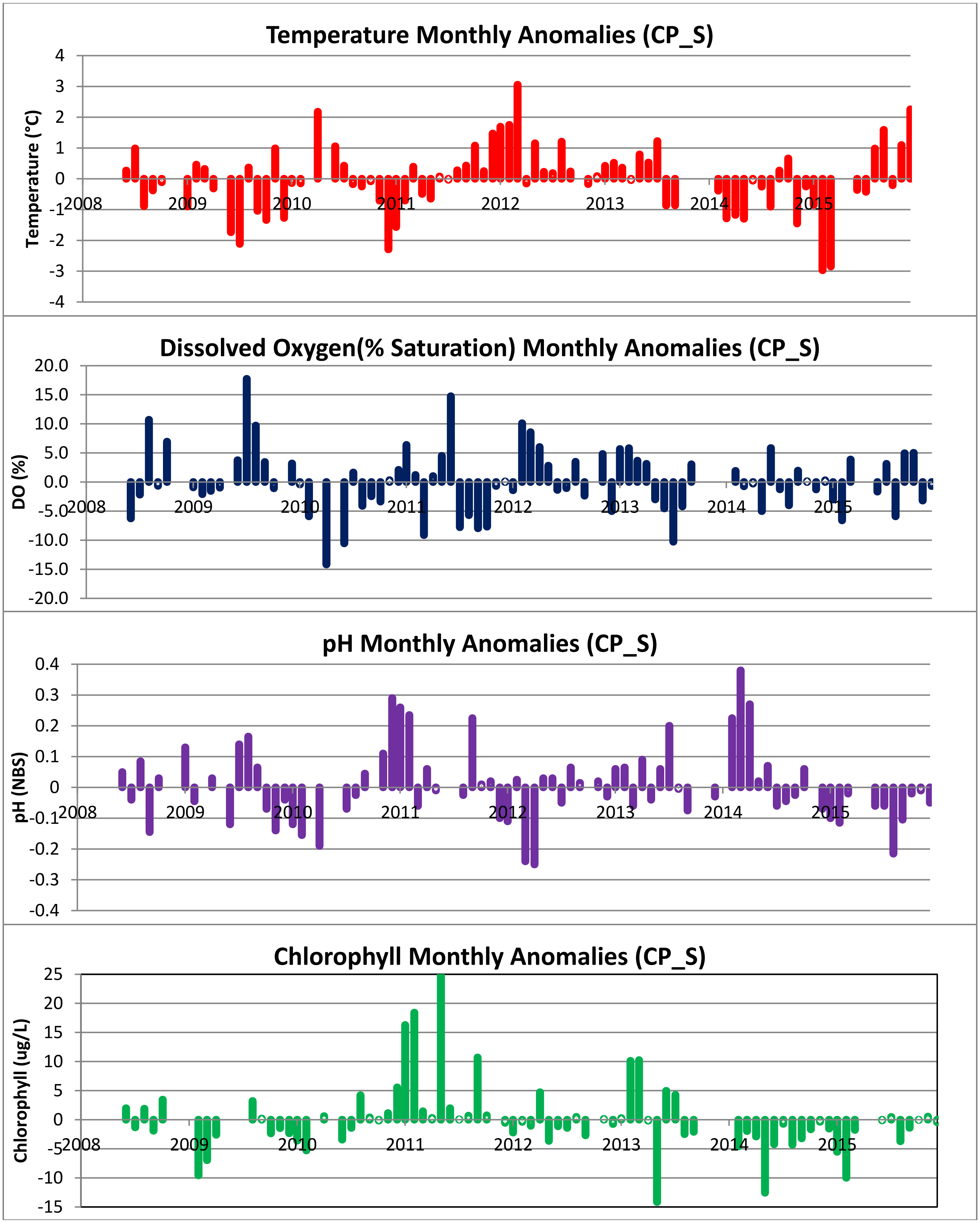


Figure17. Anomalies by parameter at the TWharf Surface. Temperature has slightly increased at the TWharf since 2006. Dissolved oxygen has decreased consistent with temperature increase. This is consistent with Baumann, H. and Smith E. findings 2018. Chlorophyll data missing pior to 2010 for this analysis.


Temperature Monthly Anomalies (CP_S)

Dissolved Oxygen(% Saturation) Monthly Anomalies (CP_S)

pH Monthly Anomalies (CP_S)

Chlorophyll Monthly Anomalies (CP_S)

Figure18. Anomalies by parameter at the Conimicut Point Surface. Temperature was anamolous in 2012 at all stations by about 3 degrees. A winter chlorophyll bloom in 2011 driving pH up with DO.

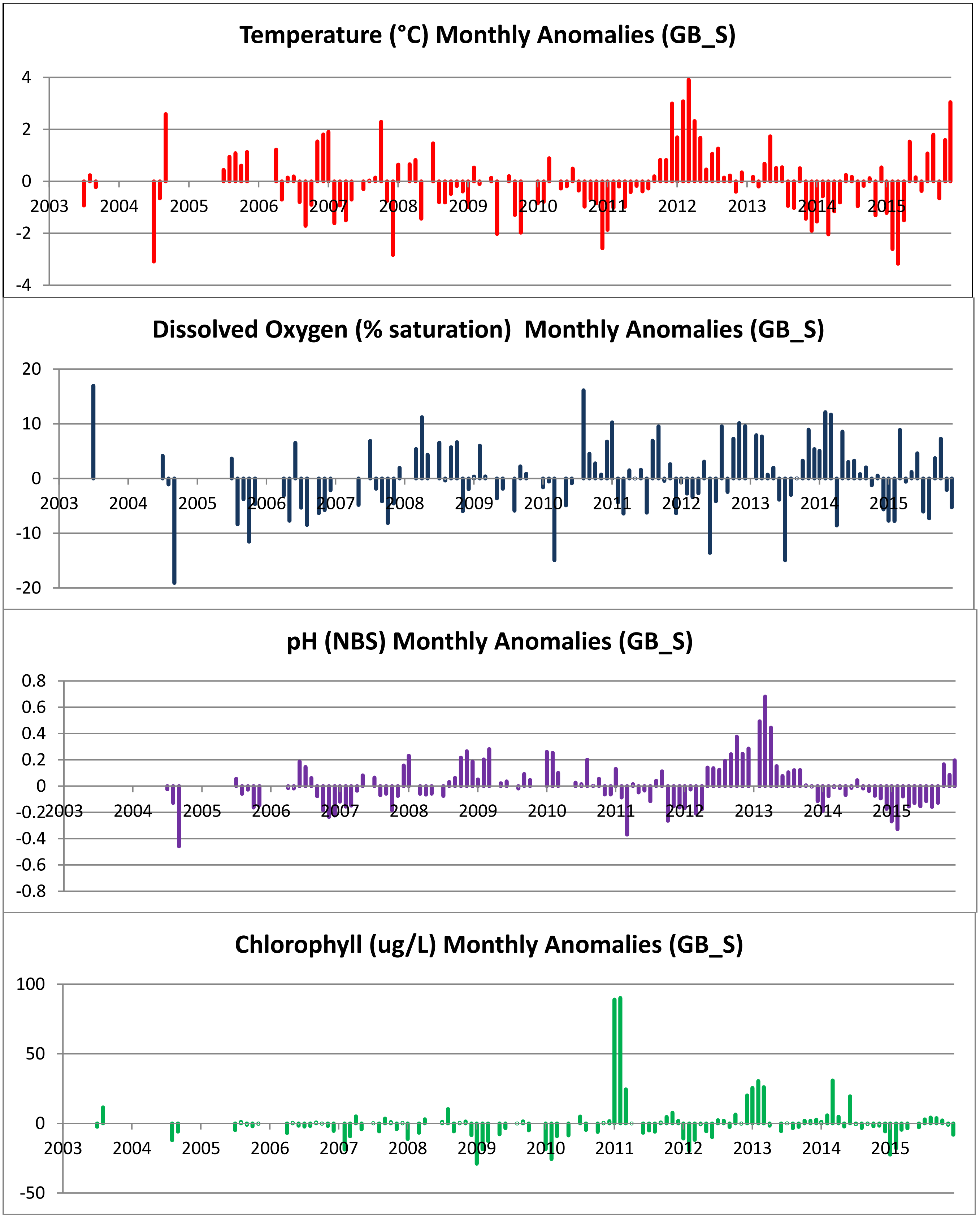


Figure19. Anomalies by parameter at the Greenwich Bay Surface. Temperature was anamolous in 2012 at all stations by about 3 degrees. A large winter chlorophyll bloom in 2011.

Multiple linear regression (MLR) was conducted on the GSO dock, TWharf , and Greenwich Bay using pH as the dependent variable (Table 5). The stations with two depths (surface and bottom) were separated to examine any significant difference based on depth. Changes in pH at GSO dock are influenced primarily by changes in temperature (coefficient .4653). Dissolved oxygen was the next largest factor with a coefficient value of 0.2128. This is expected since pH has a seasonal pattern similar to temperature and dissolved oxygen. TWharf has two depths near surface and bottom. These stations show similar results with dissolved oxygen and temperature being the leading factors in influencing changes in pH (surface: DO% coefficient =0.2926; bottom: DO% coefficient =0.3217 and Temp coefficient =0.3075). Since they have similar results, it indicated that the surface and bottom pH are responding in the same way. Here, as surface pH increases and decreases, so does bottom pH. Greenwich Bay surface and bottom show the same pattern. However, changes in surface pH are strongly correlated with dissolved oxygen and the salinity factors (DO% coefficient =0.229, salinity combined coefficient values of 0.293 and -0.08). Greenwich Bay bottom is more strongly influenced by dissolved oxygen (DO% coefficient = 0.342).

Table 5. Year-Round Multi-Linear Regression Analysis by Station. The stations are listed based on longest dataset. Conimicut Pt and Upper Bay winter station information is not included in this analysis. Highlighted variables appear to have the largest effect on pH.

GSO Dock:

Site	GD	
Variable	Coefficient	p-value
DO%	0.2128	<0.001
Temp	0.4653	<0.001
Salinity	0.0064	0.5639
Salinity^2	0.0096	0.001
Chl	0.1419	<0.001
Year	0.0868	<0.001

TWharf:

Site	TW-S		TW-B	
Variable	Coefficient	p-value	Coefficient	p-value
DO%	0.2926	<0.001	0.3217	<0.001
Temp	0.1270	<0.001	0.3075	<0.001
Salinity	-0.0170	0.069	-0.0393	0.049
Salinity^2	-0.0130	0.01	0.0104	0.289
Chl	0.1453	<0.001	0.0633	<0.001
Year	0.0583	<0.001	-0.0179	<0.001

Greenwich Bay:

Site	GB-S		GB-B	
Variable	Coefficient	p-value	Coefficient	p-value
DO%	0.2290	<0.001	0.3420	<0.001
Temp	0.1075	<0.001	0.1789	<0.001
Salinity	0.2930	<0.001	0.1805	<0.001
Salinity^2	-0.0807	<0.001	0.0625	0.003
Chl	0.0335	0.111	-0.0796	<0.001
Year	0.0249	<0.001	0.0143	<0.001

All of the year round surface stations showed a slightly positive increase in pH. GSO dock and TWharf surface are showing the largest significant increases with a coefficient of 0.0868 and 0.583, respectively. Greenwich Bay surface is only showing a slight increase of 0.0249. Greenwich Bay bottom also only shows a slight significant increase of 0.0143. TWharf bottom is showing a slight significant decrease of -0.0179. Further analysis of this area maybe needed to determine if there is a decoupling of dissolved oxygen and pH at this station or if there is influence from offshore waters coming into the bay as Poppasquash Point also shows a slight decrease.

State Criteria Exceedances:

The Rhode Island state criteria for pH is 6.5-8.5 pH units. Exceedances are defined when greater than 10% of the sample record is outside this range. Both thresholds were examined for exceedances.

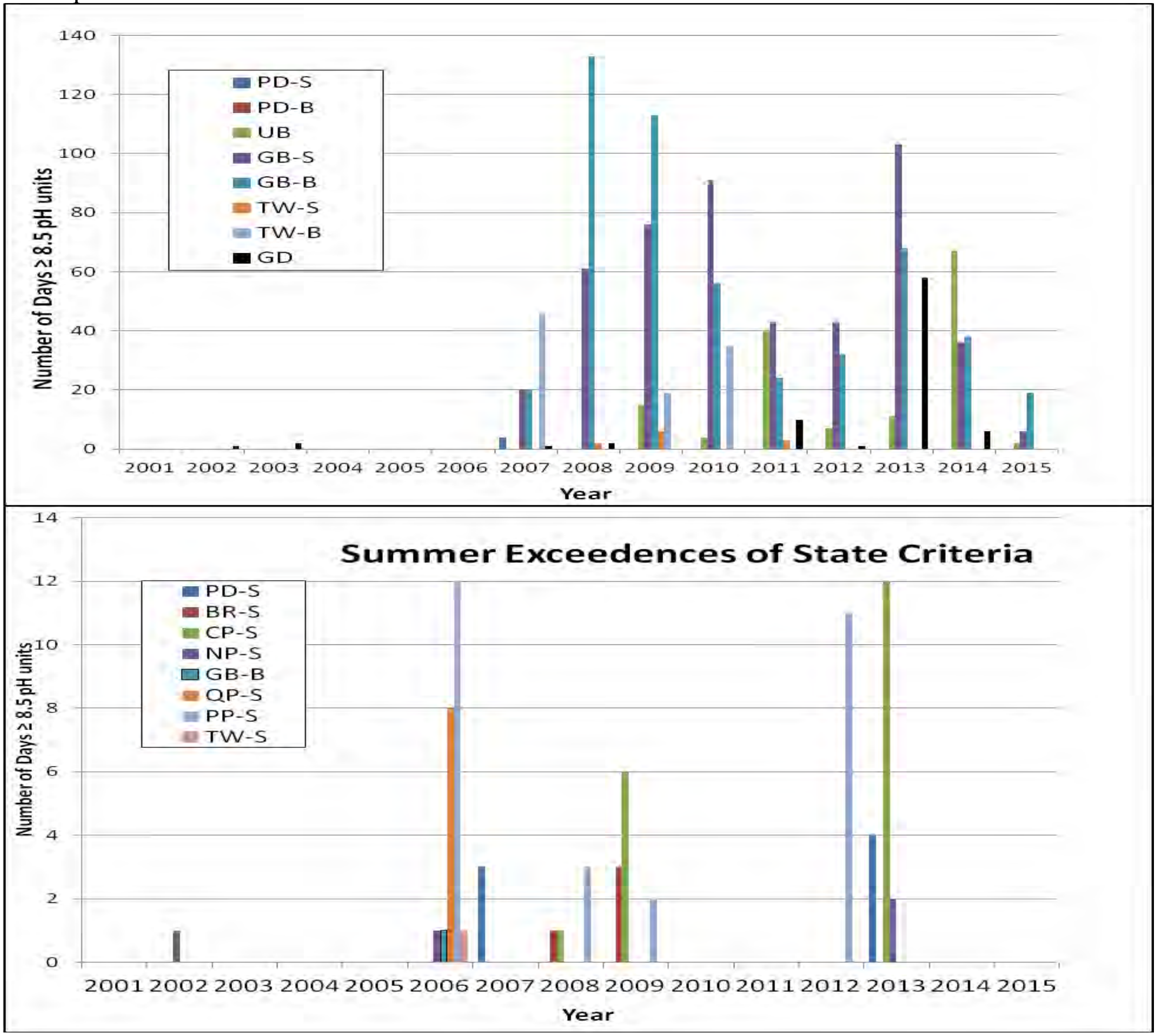
The exceedances of the 6.5 threshold can be found in Table 6. These exceedances have only occurred when during storm events when salinity was at or close to 0 ppt. These exceedances are not greater than 10 % of the sample record; therefore, every station is in compliance with the present state criteria for the 6.5 pH threshold.

Table 6. Exceedances of 6.5 criteria based on daily averages. PH has a highercorrelated with salinity than with chlorophyll.The Greenwich Bay exccedence occurred during hurricane Irene.

Station	Date	pH	Salinity	DO mg/L	ChL
PD-S	01/21/07	6.49	4.02	16.64	2.14
PD-S	01/22/07	6.26	5.20	14.25	1.07
PD-S	01/24/07	5.90	1.17	13.28	0.94
PD-S	01/25/07	5.77	0.11	12.48	1
GB-B	8/8/2011	5.91			
GB-B	8/9/2011	6.07			

There are exceedances on the alkaline side of the criteria scale (8.5). The exceedances are divided into winter and summer stations (Figures 20a and 20b). The winter exceedances correspond with winter spring bloom events at these stations. The summer exceedances all occurred during wet summers with higher production rates compared to dry summers. Based on the 8.5 threshold, Greenwich Bay surface and bottom stations are the only stations consistently over the criteria by greater than 10% of the sample record. The overall percent of time the surface and bottom have spent in exceedance of the 8.5 threshold at Greenwich Bay is 14.6% and 13.6%, respectively. The data does suggest that changes pH at Greenwich Bay are influenced by metabolism based on the PCA and multi-linear regression analysis results showing a tight correlation between pH and dissolved oxygen. However, since the general rule of thumb is that for every mole of nitrate uptake by phytoplankton, a mole of alkalinity is produced. This the increase in pH during a bloom is not purely the result of CO2 uptake (Goldman, J.C. and P.G. Brewer 1980; Wolf-Gradrow, D.A., et al 2007). There is an indication of eutrophic conditions at this station, which have been well documented by RIDEM (RIDEM, 2003; RIDEM 2005; RIDEM 2008; RIDEM 2018).

Figure 20a and 20b. Exceedences of high end (8.5) of state criteria (6.5-8.5 pH). Figure 20a represents stations with exceedences from year round stations, including the whole record fromPhillipsdale. Figure 20b represents the stations with exceedences from summer seasonal stations.



Based on Wallace et al, the lower threshold of 6.5 may be too low to adequately provide protection for life in Narragansett Bay. There are several sources that have looked at negative effects of ocean acidication on organisms in Northeast showing these thresholds to me much higher than 6.5 (Gledhill, et al, 2015; Kroeker, et al, 2010). Coastal acidification can be linked to eutrophication. Low pH can be an observed effect of eutrophication induced low oxygen. To examine this closer, a threshold of 7.4 is applied to all stations for all available daily data. These exceedances all occurred during the growing season (May-October) with the exception of Phillipsdale which had exceedances year-round, largely based on freshwater inflow events to this area. Phillipsdale is located in the headwaters of the bay.

Since recent studies have shown that a low concentration of 6.5 may not be adequate in protecting organisms against acidification, two additional thresholds are analyzed for (7.4 and 7.7 pH units). Figures 21a and 21b show the exceedances at the 7.4 threshold. Figure 21a is dominated by exceedance at the Phillipsdale station, an area which has large salinity ranges. Extremely wet years, such as 2006, have the largest number of days (164 days) less than the 7.4 threshold. 2008 and 2009 show the largest number of exceedences bay wide. To examine this further, Phillipsdale was removed from the plot (figure 21b). In this graph, the Upper Bay (BR and CP) and Greenwich Bay (SR) show the largest exceedences, except for Poppasquash Pt during 2009 (48 days). 2008 an 2009 were average and above average flow years, respectively. The wet weather events that occurred late in the summer of 2008 and 2009 caused more severe hypoxia in the Upper Bay (NBEP, 2017). 2009 was an anamalous year with respect to weather, winds, and hypoxia. Having wet weather in late summer, made hypoxia more intense compared to other years with similar river flow totals (NBEP, 2017). Severe hypoxia can decrease pH because during decreases in dissolved oxygen metabolic CO_2, in the form of carbonic acid, is released resulting in a shift in the carbonate system toward lower pH (Baumann, et al, 2015).

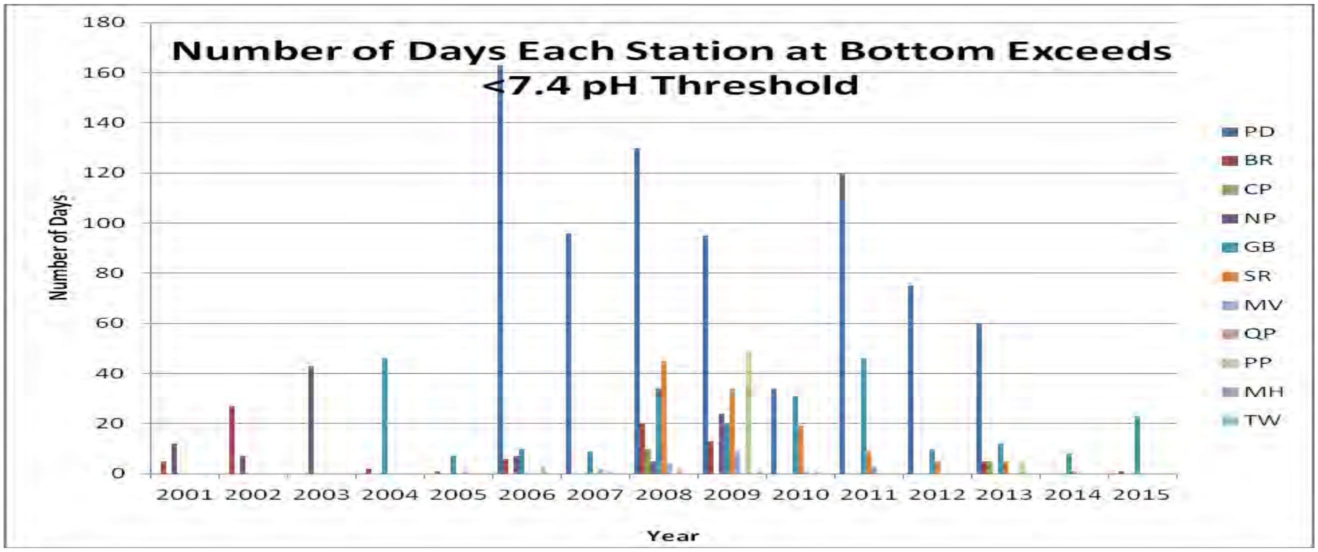
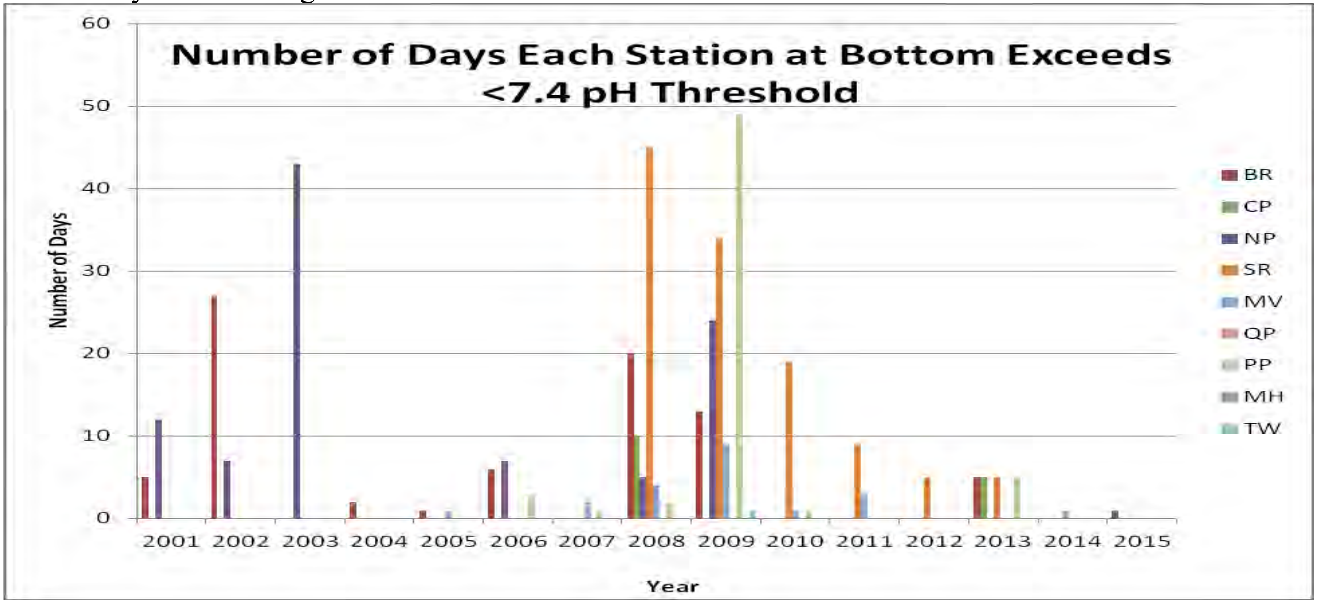


Figure 21a and 21b. Exceedances of 7.4 low pH threshold (Wallace, et al, 2014). Phillipsdale (PD) shows exceedence throughout seasons. This is further evidence that the PD station is influenced by salinity changes. Greenwich Bay shows exceedence annually on surface and bottom suggesting highly influenced by primary production. In Figure 15b, the data suggests wet and pre-nitrogen removal treatment years have higher instances of exceedences.



The 7.7 threshold was examined in the surface and bottom waters (Figures 22a and 22b). Again, with large fluctuations in metabolism and salinity Phillipsdale surface waters has the largest number of exceedances at over 200 days annually. Large freshwater inputs from Hurricane Irene during August 2011 drove salinity levels to zero at Phillipsdale which contributed to the low pH levels at this station. Phillipsdale and Greenwich Bay are shallow eutrophic systems with over all pH (7.64 and 7.7, respectively). Phillipsdale experiences lower salinities, hence lower pH values. Phillipsdale, being located at the headwaters of the bay, has a reduced buffering because of the freshwater inputs causing the carbonate chemistry, including pH, to be more easily altered by the metabolic activity of an enriched estuary. In the bottom water (figure 22b), Phillipsdale has more exceedance because of the combination of low salinities and low oxygen conditions and thus higher CO2 conditions this station experiences annually. Areas in the Upper Bay prone to intermittent hypoxia during the summer have over 50 days less than 7.7 pH units (PD, BR, SR, CP, NP and MV). Poppasquash Pt only had exceedances over 50 days during 2009 and 2013, wet summer seasons.

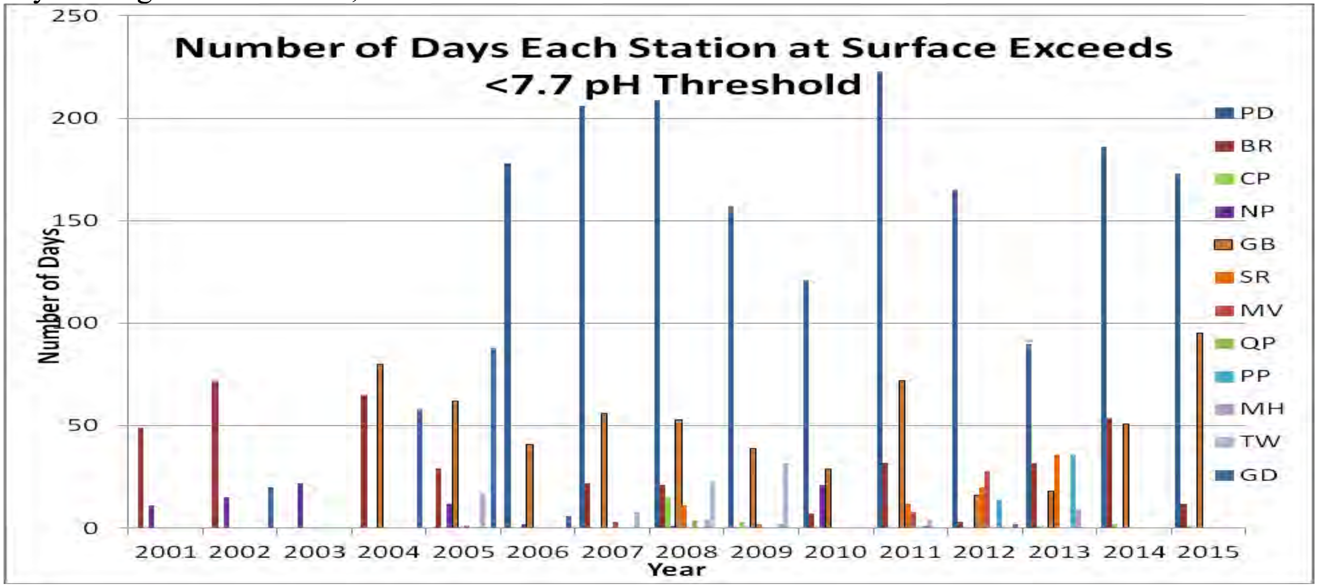
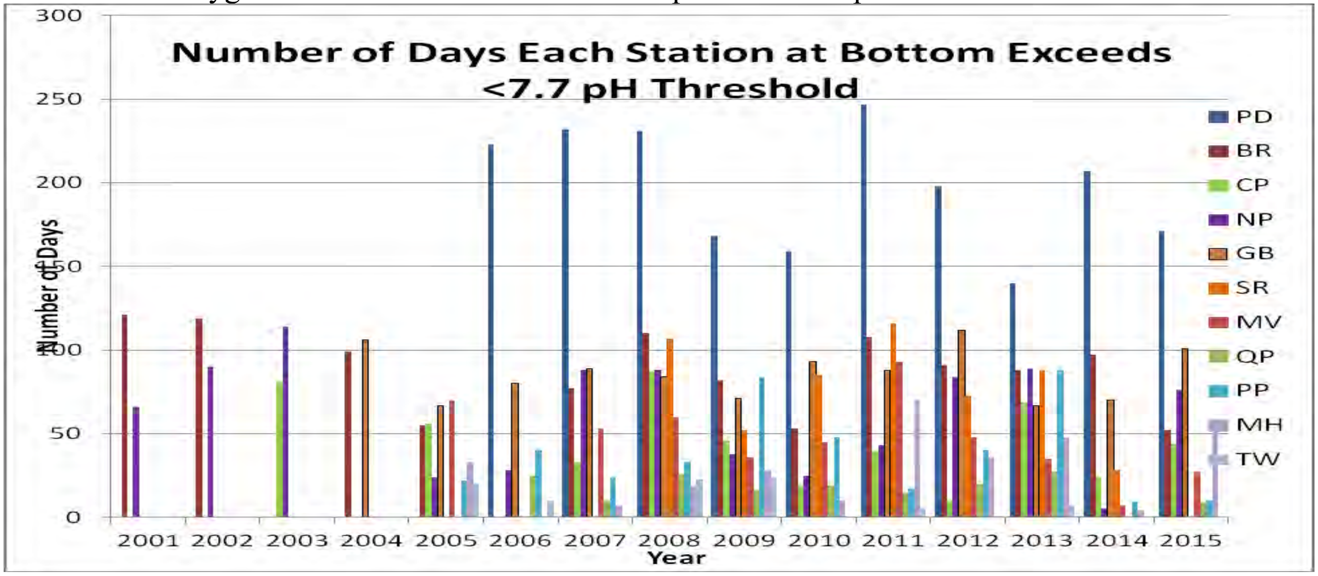


Figure 22a and 22b. Exceedances of 7.7 low pH threshold (Wallace, et al, 2014). Phillipsdale (PD) shows exceedence throughout seasons. At this threshold the same stations that our labelled as impaired for dissolved oxygen also have annual occurance of pH below 7.7 pbs in the bottom waters.



Discussion:

Coastal acidification generally exhibits higher variability than the open ocean, resulting in short-term episodic events primarily limited to summer months in Narragansett Bay. The summer seasonal average surface pH levels range from 7.6 in the headwaters to 7.91 in the lower bay, with peaks in the Upper Bay of 8.08 pH (nbs) units. The peaks in the summer correspond with primary production in this area. These conditions are like other New England eutrophic estuaries, such as Waquoit Bay (Baumann and Smith, 2017). Seasonal minimums in the surface waters are consistent with previous work (Wallace, et al, 2014). In addition, this analysis shows fluctuation in pH are strongly coupled with changes DO. Metabolic processes are the dominant drivers in the pH variability found in Narragansett Bay. This has been documented in previous studies to be a characteristic feature of nearshore habitats (Baumann, et al, 2015; Hoffman,et al, 2011, Oczkowski, et al, 2016; Wallace, et al, 2014; Waldbusser, C.G., and J.E. Salisbury, 2014).

Recent work has highlighted that co-occurring low pH and low DO levels can have a compound negative effect on marine organisms (Gobler and Baumann 2016; Gobler, et al, 2014). For example, while early-stage juvenile clams are generally not affected under hypoxic conditions, their growth rates were depressed by acidification and hypoxia (Gobler and Baumann 2016). Acidification has been shown to inhibit the performance of many calcifying invertebrates, as well as, some vertebrates, including fish. (Gobbler, 2014). Many of the bivalve studies have focused on sensitivity of larval stage, which is concerning because their abundance overlaps with extremes in pH and because these larval impairments are sufficient to cause significant risk at the population level (Grear et al. in Press). In addition, Burnett's study suggests the co-occurrence of hypoxia and acidification, due to increased pCO_2, may have contributed to the decline in oyster populations where dissolved oxygen concentrations are known to be low (Burnett, 1997). Based on Codiga et al, Narragansett Bay experiences intermittent inter-annual variable hypoxic condition throughout the Upper Bay and Wallace, et al has documented pCO_2>1000 uatm during the summer months. Many of the bivalve studies have focused on sensitivity of larval stage, which is concerning because their abundance overlaps with extremes in pH and because these larval impairments are sufficient to cause significant risk at the population level (Grear et al. in Press). Aragonite saturation states (Omega) during these events were as low as 1.3, only slightly above the saturation threshold and possibly below recommended thresholds for healthy shellfish. According to the buoy data, pH is often even lower than 7.8 and may thus be corrosive for shellfish and other calcifiers (i.e., Omega < 1.0). Measurements of additional parameters of the carbonate system would be necessary for definitive Omega estimates for the buoy sites (Greer, personal communication).

Upper Narragansett Bay bottom waters experience such conditions (<7.7 pH units and 4.8 mg/L) on a bay wide average of 62.3% of the time during June-Sept, ranging 11.2% to 80.3% throughout the Upper Bay and its embayments (Table 7). This suggests that Narragansett Bay's aquatic life regularly experiences acidified and hypoxic conditions throughout the summer's primary growing period. Future work will be needed to examine sensitive species against multiple stressors in these identified high-risk areas (such as Greenwich Bay and Providence River). Some research on this is presently being conducted by EPA's Jason Grear.

Coastal managerial criteria based strictly on oxygen levels, but not pH, may not adequately protect marine life in some ecosystems. Gobler and Baumann suggest future environmental regulations developed to protect estuarine organisms in regions prone to hypoxia should consider the concurrent effects of acidification on these animals, particularly as climate change accelerates the intensity of acidification in coastal zones.

Table 7. Percent of time each bottom station is experiencing low pH and low dissolved oxygen (DO) conditions relative to the 7.4 pH units and 7.7 pH units and 2.9 mg/L and 4.8 mg/L DO thresholds.

Station		**% Readings <7.4pH and <2.9 mg/L**	**% Readings <7.7pH and <2.9 mg/L**	**% Readings <7.7pH and <4.8mg/L**
PD		31.1%	14.6%	43.1%
BR		69%	21.5%	74.1%
CP		100%	17.7%	80.3%
NP		68.4%	15.4%	57.6%
GB		48%	23.8%	69.9%
SR		43%	29.3%	75.4%
MV		60%	13.7%	47.7%
QP		0%	7.2%	76.6%
PP		22.9%	17.8%	74.9%
MH		0%	14.7%	75.2%
TW		0%	0.0%	11.2%

Conclusions:

Although there are limitations with the NBFSMN data to fully describing the carbonate system in Narragansett Bay, the data does provide recent trends in pH throughout the bay. The seasonal patterns in pH in Narragansett Bay are consistent with other New England estuaries. Changes in pH can be attributed physical and biological variability within the bay and the response of that activity to nutrient reductions. The largest peaks are in the winter which correspond with winter spring blooms. The summer dips in pH correspond with hypoxic conditions found throughout the Upper Bay. Based on the multi-linear regression analysis, the East Passage shows a slight downward trend in pH. Although it tested significant, this trend is not evident in the daily delta pH analysis. This maybe evident of the limitations of the sensitivity of the sensor. Therefore, the East Passage maybe an area to focus on for carbonate chemistry analysis to determine if any offshore influence is affecting this area.

All annual stations showed 2012 as an anomalous warm year, this is consistent with regional findings (Baumann, 2018). Temperature is negatively correlated with pH. This is demonstrated in the lower-than-average pH levels and above average temperatures during 2012. Temperature affects the seasonal fluctuation in pH. Biological activity and physical parameters are among the driving forces behind the changes in pH at the Greenwich Bay station. The winter/spring bloom occurs during cold winter months and hypoxia events occur during the warmer summer months. The drivers in the winter months have a positive effect on pH f and in the summer is a negative effect. The Upper Bay station at Conimicut Point shows a similar effect on pH from biological activity (chlorophyll changes). The lower bay's productivity is driven more by the winter blooms vs summer bloom events compared to the upper bay. The annual stations reveal the return of the recent winter/spring bloom and its possible positive effect on pH at the GSO dock station. This is inconsistent with the lower bay station in the East Passage. TWharf is the only station, again in the East Passage, to show a downward trend over time. This change is smaller than the seasonal change at Poppasquash Pt. This is well within the error of the sensors. There is also a downward trend in DO% that is inconsistent with the changes in the other parameters. This area does not normally document large chlorophyll blooms, exceptions of 2011and 2013 winter/spring blooms. These changes in external influences from both the ocean and the watershed makes attribution of drivers difficult because they all affect pH in differing ways. Examining daily fluctuations in pH, as done with Poppasquash Pt, may be a better way to analyze long term trends. This area may need more investigation to determine the actual cause of the rates of changes in temperature, pH and DO%.

All station data revealed that all monitored areas of Narragansett Bay are within Rhode Island's state water quality criteria for pH. These stations will remain in place for the near future and pH levels will continue to be monitored. As more knowledge on the issue of ocean acidification in coastal estuarine waters becomes available, along with studies conducted within and around Narragansett Bay, water quality assessments relating to pH can be further examined.

Based on recent literature of combine effects on different life stages of estuarine species found within Narragansett Bay, a low threshold of 6.5 is not protective enough of marine species (Wallace, 2014). A review of different pH thresholds may be needed to provide more adequate protection of marine life within Narragansett Bay with respect to eutrophication cumulative effects of hypoxia and low pH on all life stages as these studies results become available in the future.

The NBFSMN datasets are one of the most comprehensive resources for examining physical water quality, including pH, for Narragansett Bay. All the network data is available through the RIDEM OWR website: http://www.dem.ri.gov/bart/stations.htm. If proper relationships can be established for the pH scales (NBS and pH_t), NBFSMN can serve as a link monitoring the carbonate system in the future and providing information needed to describe changes in the carbonate system over time within Narragansett Bay.

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