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**VERIFICATION OF PH FLUCTUATIONS IN
NARRAGANSETT BAY**

BY

CATHLEEN TURNER

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
IN
OCEANOGRAPHY**

UNIVERSITY OF RHODE ISLAND

2015

MASTER OF SCIENCE IN OCEANOGRAPHY THESIS
OF
CATHLEEN TURNER

APPROVED:

Thesis Committee:

Major Professor Arthur Spivack

Steven D'Hondt

Brad Seibel

Nasser H. Zawia
DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
2015

ABSTRACT

In order to understand potential changes in pH driven by increasing atmospheric carbon dioxide, we first need to understand what controls pH and its variability in estuaries today. We measured total alkalinity, dissolved inorganic carbon, pH, temperature and salinity of samples taken hourly for 24 hours once a month at three sites in Narragansett Bay (2/2010 to 4/2011) to understand the controls on daily and seasonal pH variation: GSO, Greenwich Bay (GB), and Potter Cove (PC). We also measured in situ pH (pHe) and temperature every five minutes at the same sites and during the same time periods. Our calculations of pH (pHc) from total alkalinity, dissolved inorganic carbon, salinity and temperature measurements indicate daily pH variation of 0.10 to 0.62. The largest pHc range for GSO was on April 1st 2010, which had range of pHc of 8.36 to 7.94. The pHe range on the same day was from 8.19 to 8.01. The largest pHc range for PC was on March 8th 2011, which had range of pHc of 8.68 to 8.16. The pHe range on the same day was from 9.02 to 8.46. The largest pHc range for GB was on May 13th 2010, which had range of pHc of 8.04 to 7.42. The pHe range on the same day was from 7.91 to 7.52. We propagate errors in our calculations and use a conservative mixing model to determine if this variation in pH is valid or an artifact of error. The variations in pH are real and are not an artifact because the observed daily range in pH is greater than the pH range due to total error. We compared pH determined from dissolved inorganic carbon and total alkalinity measurements to pH determined from a conservative mixing model. The comparisons show that daily pH variation is not completely explained by the mixing of waters with different salinity, alkalinity, and dissolved inorganic carbon. Short-

term pH change that cannot be explained by the model and have carbon dioxide and dissolved oxygen deviation from equilibrium are driven by biological activity, primarily photosynthesis and respiration. The fractional departure of dissolved carbon dioxide ($([\text{CO}_2^*] - [\text{CO}_2^*]_{\text{sat}})/[\text{CO}_2^*]$, $\text{CO}_2^* = \text{dissolved and hydrated CO}_2$) and dissolved oxygen ($([\text{O}_2] - [\text{O}_2]_{\text{sat}})/[\text{O}_2]$) are anti-correlated, but not clearly linked to chlorophyll concentration. The mixing efficiency of the estuary provides a physical explanation as to why pH below equilibrium concentrations of CO_2 co-varies with low dissolved oxygen concentrations.

ACKNOWLEDGMENTS

This work was supported in part by the University of Rhode Island Sea Grant. A University of Rhode Island fellowship and teaching assistantship supported me in the first year and a half of my graduate education and writing.

My deepest gratitude goes to those who have supported me with their resources and time. I thank Professor Arthur Spivack, my major professor, for his encouragement, expertise, and guidance in this research project. I am indebted to Professor Steven D'Hondt for his guidance and for granting me access to his data. Their insight helped me reach meaningful conclusions.

I express my sincerest gratitude to Dennis Graham and Leah Lewis for collecting and analyzing the samples. I am extremely fortunate to have used data of very high quality for my thesis. I thank Dr. Kenneth Raposa and Dr. Daisy Durant for helping Dennis and Leah collect the data at Potters Cove.

I warmly thank Professor Michael Q. E. Pilson, Professor John T. Merrill, Dr. Robert Pockalny, and Dr. David Ullman for helpful discussions and for helping me interpret external data. I thank my committee member Professor Brad Seibel for teaching me how to read scientific publications.

I thank my fellow graduate students (Justine Sauvage, Emily Walsh, Mary Dzaugis, Yiya Huang) and Dr. John Kirkpatrick for providing much helpful discussion and support. Last but not least, I thank my family and friends for their love, encouragement, and moral support- Da Wei and Cristhel Santillian.

PREFACE

This thesis is written in manuscript format. I intend to submit this work to submit to the scientific journal Springer known as Estuaries and Coasts. The thesis is being prepared for publication.

The following authors are involved in the publication of the manuscript:

Cathleen L. Turner¹, Arthur J. Spivack¹, Steven D'Hondt¹, Kenneth B. Raposa²,
Daisy Durant²

¹ Graduate School of Oceanography, University of Rhode Island, Narragansett,
RI 02882, USA

² Narragansett Bay National Estuarine Research Reserve, PO Box 151-
Prudence Island, RI 02872, USA

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“Verifying pH Change in Narragansett Bay, a Temperate Estuary”

by

Cathleen L. Turner¹, Arthur J. Spivack¹, Steven D'Hondt¹, Kenneth B.

Raposa², Daisy Durant²

Is in preparation for submission to Estuaries and Coasts

Beginning of the Manuscript

¹ Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA

² Narragansett Bay National Estuarine Research Reserve, PO Box 151-Prudence Island, RI 02872, USA

INTRODUCTION

When gas phase carbon dioxide (CO_2) dissolves in seawater and is hydrated, it forms carbonic acid and readily dissociates into bicarbonate and hydrogen ion, decreasing the pH of seawater. If anthropogenic CO_2 emissions continues to increase at a rate of 1% per year, the average pH of the surface ocean is predicted to fall 0.3 to 0.4 pH units by 2100 (Haugen and Drange 1996; Brewer 1997). This drop in pH is equivalent to a 100 to 150% increase in the concentration of H^+ ions. The effects of elevated H^+ ions in seawater are physiological (e.g., Seibel et al 2012), behavioral (e.g., Kim et al 2013), and can affect a community's composition (e.g., Landes et al 2013). The decrease in pH can inhibit the ability of marine calcifiers to calcify (Barton 2012; Fabry et al 2008; Andersson 2012; Hoffman et al 2010) and can affect the growth and survival of economically important larvae found in estuaries, such as the hard clam (Talmage and Gobler 2010; Waldbusser et al 2010). In order to understand potential estuarine changes in pH driven by increasing atmospheric carbon dioxide (global change to CO_2), we first need to understand what controls pH and its variability in estuaries today on short and long-term timescales.

Estuarine pH can change rapidly if (i) there is a rapid change in salinity (S), total alkalinity (TA), and dissolved inorganic carbon (DIC) (Zeebe and Wolf-Gladrow 2011). Total alkalinity and DIC are in turn influenced by the balance of respiration and photosynthesis (e.g., Hinga 2002). Estuarine salinity and alkalinity vary in space and time on both short and long term-timescales (e.g., Magnuson 1997). We use can use a simple conservative mixing model for DIC, TA and salt to explain pH variance as result of these related variables.

The objective of this work is to determine the validity and cause of observed short-term (24-hour) pH changes in Narragansett Bay. We compare the potential 24-hour pH range that might result from maximum total error, i.e. worst-case scenario, to the 24-hour pH range calculated from DIC and TA. We also compare pH calculated from TA and DIC measurements to pH measured in situ using an electrode. To determine what drives pH change in Narragansett Bay, we compare pH determined from DIC and TA observations to the outputs of a simple conservative mixing model for data collected over the course of more than one year. Lastly, we infer pH change as a result biological activity from non-conservative DIC, TA, and DO.

Conceptual Background

The fundamental assumption in a conservative mixing model is that there is chemical continuity when river and ocean water are mixed. Since the carbonate system inhibits the degassing or evasion of CO₂ compared to a non-reactive gas, such as dissolved oxygen (DO) (Williams and Follows 2011), a conservative mixing model approach can be applied to determine the cause of pH change in an estuary (Cai et al. 1998, Boyle et al. 1974). Consider a quantity of river water with a known mass (M_r), salinity, S_r , and alkalinity, TA_r mixed with a quantity of ocean water with a known mass (M_o), salinity, S_o , and alkalinity, TA_o :

$$M = M_r + M_o \quad (1)$$

$$M_r = f_r M \quad (2)$$

$$M_o = f_o M \quad (3)$$

where f_r and f_o are the proportions of freshwater and seawater respectively.

Then if we know f_r and f_o :

$$TA = f_r TA_r + f_o TA_o \quad (4)$$

$$DIC = f_r DIC_r + f_o DIC_o \quad (5)$$

$$S = f_r S_r + f_o S_o \quad (6)$$

The TA, DIC, and S depend on the relative contributions of the river (TA_r , DIC_r , S_r) and the ocean (TA_o , DIC_o , S_o). Since in the conservative mixing case we assume no DIC, TA, and S are lost or gained during the mixing process, the pH change from what it was initially (pH_r or pH_o) is said to be conservative (*conservative pH change*). Conservative pH change is simply a consequence of a two-end-member dilution process. After all parameters (TA, DIC, S, temperature) are determined, the final pH of the mixture, can be calculated. Although TA and DIC and the proportions of the water sources, f_r and f_o , can change over time due to events such as spring snow melt (yearly), floods (days to hours), or even the ebb and flow of a tide (hours to minutes), pH equilibrium is rapidly established. Hence, the rate of pH change in this simplified, two-end-member estuarine system is governed by the rate at which the chemical, biological and physical environment changes, be it on the scale of minutes to months.

Estuaries experience spatial and temporal variability in salinity (and consequently alkalinity) and temperature; it is necessary to have long-term and frequent measurements in many locations to acquire a basic understanding of an

estuarine environment. Many organizations have established long-term monitoring sites (for example, the National Estuarine Research Reserve System) in estuaries and estuarine habitats where high frequency pH measurements are made. Accurate interpretation of these measurements requires accurate determination of whether short and long-term variation of pH electrode data is real or an artifact.

It is technically challenging to get reproducible pH measurements. The conventional method of measuring pH in situ with an electrode requires frequent calibration and depends on salinity and temperature (Provoost et al. 2010). Absolute error of pH electrode measurements can be caused by salinity change (a 10-unit salinity change can cause pH error of ± 0.03 , Easley and Byrne 2012), random user error (e.g., Duarte et al. 2013), or dramatic pH change when the electrode has been calibrated with one point (e.g., ± 3 , Waters 2012); the absolute error can exceed the real hourly pH change that can be attributed due to real environmental processes, even for large changes due to floods or phytoplankton blooms.

Short-term pH change can be verified by more than one approach. The first approach is analytical: determine pH using an independent method. Once any two of DIC, pH, or TA of a seawater sample have been determined, the concentrations of all dissolved inorganic carbon species or pH can be calculated. The pH, calculated from DIC and TA, can be compared to the pH measured with an electrode.

The second approach is to evaluate whether the observed pH changes are well explained by physical and biological processes. This approach requires understanding how changes in the environment lead to a change in pH. Salinity, temperature, TA, and DIC are often used to study how changes in an estuarine environment affect the

carbon dioxide system (e.g. Jung et al. 2008, Wang and Cai 2004; Cai et al. 2000). However, TA and DIC are not always conservatively mixed in an estuary. Benthic respiration, in the form of sulfate reduction or nitrification, generates DIC and TA (Jiang et al. 2008; Krumins et al, 2013) and consumes dissolved oxygen (Abril 2001; Cai et al. 2011). Photosynthesis consumes DIC and produces dissolved oxygen. It does not affect TA in an environment predominately buffered by the carbonate system within a pH range of 7 to 9 (Morel and Hering 1993). If the pH change at a site cannot be attributed to conservative mixing and the concentration of dissolved oxygen is above or below a concentration if it were at equilibrium with the atmosphere, the pH change can be attributed to biological activity.

METHODS AND MATERIALS

Study Sites

Narragansett Bay (Figure 1) is a partially to well-mixed estuary that receives water from the Rhode Island Sound (RIS) and a variety of small rivers; its circulation is dominantly driven by wind and tidal forcing (Kincaid et al. 2002). The bay is rectangular with an area of 328 km² (Pilson 1985) and has a drainage basin of approximately 4,700 km² (Ries 1990). It has a north-south decreasing salinity gradient. The northern portion of the estuary is shallow, with a mean depth that ranges from 7.6 to 8.3 meters (Pilson 1985). The depth increases considerably at the mouth (~37 m). The salinity range of waters that enter the Bay from RIS is typically 31 to 33.5 g kg⁻¹ (Pilson 1985). The main freshwater discharges into the upper bay are the Blackstone and Pawtucket Rivers, as well as the Taunton River via Mount Hope Bay (Spaulding

and Swanson 2008). The Taunton, Blackstone, and Pawtuxet Rivers contribute 75% of the freshwater to the bay; the rest is from minor tributaries (Ries 1990). Groundwater is not thought to be a significant source of freshwater to the bay (Pilson 1985, Ries 1990).

The Rhode Island Department of Environmental Management (RIDEM) and Narragansett Bay National Estuarine Research Reserve (NBNERR) are the authorities that monitor and report the environmental conditions of Narragansett Bay. Our three study sites are representative of the middle and lower portions of Narragansett Bay and are monitored by the RIDEM and NBNERR: (1) Greenwich Bay (GB), a semi-enclosed inlet of the sea diluted with freshwater, (2) Potter Cove (PC), a sea cove diluted with freshwater that sits on the East Passage, and (3) the Graduate School of Oceanography (GSO), the southernmost site located in West Passage. Data collection at GB and GSO are managed by RIDEM. PC data collection is managed by NBNERR.

The GB site (41.68° N, -71.44° W) is the shallowest site in our study (~ 1.6 meters) and receives direct freshwater input from the Pawtucket River and other minor rivers. Greenwich Bay is surrounded by an urban land-use area, receives impaired waters from the East Greenwich sewage treatment plant, and experiences periods of low dissolved oxygen concentration (Granger et al. 2000). The land surrounding Potter Cove is not urban. The site (41.64° N, -71.34° W) is thought to be representative of an estuary environment impaired by water that flows from the north (Durant and Raposa 2010). The site has a depth of 2 to 4 meters. GSO is located on the west side of West Passage (41.49° N, -71.42° W). Its depth is ~ 3 meters (Fox and Stoffel 2013).

Sampling and in situ measurements

We collected samples for TA, DIC, and salinity with an automated sampler (Teledyne ISCO 6712 Portable Sampler) hourly for a 24 hour period, once a month from February 2010 to April 2011.

We measured in situ pH (pH_e), with an ISCO 701 temperature and pH combination/glass electrode module every five minutes during the same 24-hour sampling period. We calibrated the pH electrode with TRIS buffer for the first and second 24-hour sampling periods at all sites; we calibrated the electrodes for subsequent sampling days calibrated with certified NBS buffers.

The auto-sampler dispensed each sample into a 350 mL ISCO soda-glass container with a polytetrafluoroethylene (PTFE) lined lid. In order to stop respiration and photosynthesis, the containers were pre-loaded with 1 mL of saturated mercuric chloride to poison the sample and to obtain a 0.02% concentration of mercuric chloride in a 350 mL sample (SOP Dickson 2007). Each container contained a floating lid, to leave no headspace once a sample was added. Only samples with no headspace (e.g., samples in which the lid worked properly) are considered in this study.

Several hours after a sampling period, subsamples were transported from the soda-glass containers into separate containers for TA and DIC measurements. For TA measurements, a 40-mL portion of each sample was dispensed into a borosilicate glass vial (USP #1685). A rubber septa sealed the vial without headspace. For DIC measurements, a 60-mL portion of each sample was stored in a low-density polyethylene (LDPE) bottle with a high-density polyethylene lid (HDPE) (Fisher

Scientific) without headspace. The samples were stored in the dark for analysis within a month to three months of their collection.

We obtained additional dissolved oxygen (DO) and pH electrode data from the RIDEM and NBNERR (GSO and GB - RIDEM data: NBFSMN 2010 and NBFSMN 2011; PC data- cdmo.baruch.sc.edu : 2010 and 2011). We refer to pH electrode data measured by RIDEM and NBNERR as pH external electrode, or pH_{EE}. A YSI 6600EDS was used to measure pH, DO, salinity, temperature, and chlorophyll at GB. YSI 6600 EDS and YSI 6920 were used to measure pH, DO, salinity, temperature, and chlorophyll at GSO. At PC, NBNERR measures the same parameters (using a YSI 6600 EDS or V2) except chlorophyll. All parameters are measured in-situ, at the same location as our monitoring sites every fifteen minutes. RIDEM and NBNERR calibrate their pH electrodes with YSI pH buffers solutions that are also NBS-certified reference materials. While the raw data is not available online, the quality control and assurance procedure for RIDEM data can be found online (<http://www.dem.ri.gov/pubs/qapp/nbfsmn.pdf>). Gaps in the data set reflect periods when there was sensor failure. Drift (sensor offset that propagates over subsequent measurements over time) is corrected using calibrations from the beginning, middle, and end of the deployment period.

Chemical Analyses

We measured TA using an open-cell titration with a semi-automatic titration system (Metrohm 809 Titrando) fitted with syringe pumps and a high-precision pH meter (Metrohm pH Electrode Model 6.0234.100). The samples were titrated to 210

mV, which is approximately a pH of 4. TA was determined using the slope and intercept values of the Gran titration curve (Edmond, 1970). We measured DIC by extraction and infrared (IR) measurement of purged CO₂ using an Automated Infra Red Inorganic Carbon Analyzer (AIRICA) system. The AIRICA system acidifies and strips the CO₂ out of a known volume of seawater ranging from 500 µL up to 2000 µL and integrates the infrared absorbance from CO₂. The AIRICA system consists of 4 main components: a syringe module, a sample stripping manifold, a LICOR LI-7000 non-dispersive CO₂ infrared analyzer and a personal computer. Although the peak area is measured three times per sample, only the mean of the last two measurements is used, to avoid any carryover effect between samples. The peak area of the sample compared to that of the standard is used to determine the sample's DIC concentration. We determined salinity from chlorinity by semi-automatic titration (Metrohm 794 Basic Titrino 100) fitted with a silver titrode electrode (Metrohm Model 6.0433.110). We measured chlorinity by silver nitrate titration following IODP Technical Note 15 Protocol using a 1 M silver nitrate solution (Gieskes et al. 1991). We used certified Dickson standards as references (CRM 94, 100, and 102) for all DIC, TA, and salinity measurements of all samples except for samples taken during two 24-hour sampling periods: GB on 3/25/2011 and PC on 4/14/2011. For these two sampling periods, we used IAPSO P139 reference standards as references. We calibrated the IAPSO standard using CRM 102 reference material.

Quality Control and Assurance

From August 2010 to May 2011, we took replicates of the samples for the first measurement in each 24-hour period to determine the uncertainty associated with sampling. We used a solution with a known mass of dissolved borax as an internal consistency test for the TA measurements. We measured the TA of the borax solution at the beginning, middle, and end of each subsampling set of TA measurements.

Error Analysis

We determined the uncertainty for TA from analysis of the standard deviation of sample replicates and borax solutions. Pooled standard deviations were first calculated and propagated to determine the relative uncertainty due to analysis, handling, and storage (Dickson 2007). We determined the analytical uncertainty for DIC by taking the difference between the two peak area measurements of each sample from a set of (i) 10 randomly chosen 24 hour sampling set and (ii) 10 randomly selected Dickson standard measurements for CRM 94, 100, and 102. We then propagated the uncertainty determined from the peak area with the uncertainty determined from the sample replicates to obtain the relative uncertainty due to analysis, handling, and storage. We determined the uncertainty of the salinity measurements from the standard deviation of the titration volume of silver nitrate used to determine the chlorinity (and subsequently salinity) of the standards.

We calculated the maximum error range for the calculated pH of each sample (pH_{rer}) to compare the variability of the calculated parameters due to error to the daily range of the parameter. The motivation of this calculation is to determine the

sensitivity of the calculated parameters to errors in salinity, DIC, TA, and temperature measurements. The errors can be correlated or not correlated. If the errors of DIC and TA measurements are not correlated, the total error propagation in calculated pH_c is $\pm .0062$ if the accuracy of DIC and TA is assumed to be $\pm 2 \mu\text{mol kg}^{-1}$ and $\pm 4 \mu\text{mol kg}^{-1}$ (Zeebe and Wolf-Gladrow 2011). In this study, we calculate the worst-case scenario, as if the errors of DIC, TA, salinity, and temperature were correlated.

Parameter calculation

We calculated pH and associated parameters (Revelle factor, $B = ((\Delta[\text{CO}_2] / [\text{CO}_2]) / (\Delta[\text{DIC}] / [\text{DIC}]))$, (pCO_2), and the degree of saturation of calcite and aragonite Ω_c and Ω_a , respectively, Appendix B) using the program CO2SYS (Lewis and Wallace, 1998). We used carbonate dissociation constants from Cai and Wang (1998). These dissociation constants are appropriate for the salinity ranges in this study (17.89 to 31.71 g kg^{-1}) and allow us to determine a pH value from the DIC and TA on the NBS pH scale. RIDEM and NBNERR calibrate their pH electrodes using NBS buffers. The values of K_{sp} for calcite and aragonite are from Mucci (1983).

Conservative Mixing Model

The mixing model assumes that salinity, TA, and DIC are conservatively mixed. A substance is conservatively mixed when the plot of its value against salinity is linear (e.g., Boyle et al. 1974, Liss 1978, Cai et al. 2010). Non-conservative behavior is characterized by a non-linear relationship of the constituent with salinity (Boyle et al. 1974). When a property is conservatively mixed, the temporal variability

of its end members' compositions is not important, as long as the average is constant over the flush time of the estuary (Loder and Reichard 1982, Sharp et al. 1982). TA is thought to be mixed conservatively in Narragansett Bay (Magnuson 1997; Boucher 1991).

For this modeling exercise, we assumed all freshwater inputs to be from rivers and runoff, since groundwater inputs to Narragansett Bay are smaller than riverine inputs (Ries 1990). We calculated pH based on the proportion of freshwater and seawater. pH calculated from TA and S is temperature-dependent. The model requires the temperature of the river (t_r) and ocean (t_o) end members, or a final temperature (t_f). We determined the final temperature of the mixture by assuming adiabatic mixing. In addition to the conservative mixing of TA, DIC, and salinity we considered a scenario at which: (1) t_r and t_o are the same temperature, (2) t_r and t_o are different temperatures using the following equation:

$$t_f = (f_r c_{pr} t_r + f_o c_{po} t_o) / (f_r t_r + f_o t_o) \quad (7)$$

That is, the TA, DIC, and salinity depend on the relative contributions of the river end-member (TA_r , DIC_r , S_r) and the ocean end-member (TA_o , DIC_o , S_o). After all parameters (TA_f , DIC_f , S_f , t_f) were determined, pH was calculated. The result is a pH mixing line that shows pH at different proportions of freshwater and seawater. The pH from the conservative mixture was then compared to i) the pH of our samples if DIC were to be in equilibrium with the atmosphere and ii) pH calculated from DIC and TA measurements.

To quantify pH change that is non-conservative with respect to DIC and not due to biological activity, we calculated pH if it were in equilibrium with the atmosphere and compared it to pH determined from conservative mixing. We determined pH at equilibrium with the atmosphere (pHeq) from the partial pressure of atmospheric CO₂ and water properties (salinity, TA, temperature). The pH of the conservative mixing line is not equal to pHeq because the mixing model assumes that DIC is not lost or gained due to gas exchange. Therefore, pHeq at 25°C should be greater than the pH of the conservative mixing line at 25°C. Conversely, pHeq at 5°C should be lower than the 5°C pH mixing line. Other factors that can contribute to the difference between pHeq and the pH of the mixing line are (i) temporal variation in the end-members being mixed, such as events with significantly lower river alkalinity (e.g., runoff from acid sulfate soils, Cornfield 2000) and (ii) processes that generate alkalinity within the estuary (e.g., removal of sulfate from the water column by sulfate reduction coupled to pyrite precipitation, Gallagher et al. 2012, Krumins et al. 2012).

RESULTS

Monthly data in Narragansett Bay

TA and salinity are strongly correlated at all sites (Figure 2a). DIC and salinity are less strongly correlated (Figure 2b), indicating that DIC is non-conservative. TA and DIC are most strongly correlated at GSO and less so at GB (Figure 2c). At all sites, the days with the minimum values of salinity, TA, and DIC coincided with days

with the largest ranges. Our March and April 2010 data from GB and GSO exhibit the lowest salinity, DIC, and TA for those sites (Figure 3 a, b, c, d). These minima at GSO and GB coincided with heavy and persistent rains that led to record-breaking levels of peak river discharge and water levels at many long-term U.S.G.S stream gages (Zarriello et al. 2013). The largest salinity, DIC, and TA ranges in our PC data occurred on March 8, 2011, shortly after a precipitation event. Peak DIC occurred during the summer at all sites, a period of warmer temperature (Figure 3 d).

Maximum and minimum pHe and pHc was observed at all sites during winter 2011 and summer 2010, respectively (Figure 4). The largest 24-hour pHe range for GSO and PC occurred in 2011, while GB had the largest 24-hour pHe in July 2010. For GSO and GB, the largest 24-hour range in salinity, TA, and DIC did not coincide with the largest 24-hour range of pHc and pHe. GSO had the largest 24-hour range in salinity (9.3 gkg^{-1}), TA ($580.0 \text{ } \mu\text{molkg}^{-1}$), DIC ($555.4 \text{ } \mu\text{molkg}^{-1}$) on April 1st 2010, but the pHc maxima (8.78) and largest 24-hour pHe range (.42) took place on March 16th 2011. GB had the largest 24-hour range in salinity (8.8 gkg^{-1}), TA ($675.8 \text{ } \mu\text{molkg}^{-1}$), DIC ($566.6 \text{ } \mu\text{molkg}^{-1}$) on March 18th 2010, but the largest 24-hour range in pHc (.62) took place on May 13th 2010. At GSO and GB, the pHc range from the days with the largest ranges in DIC, TA, and salinity (0.18 and 0.25, respectively) was much less than the days with the largest ranges in pHc. At PC, the days of maximum pHc range and TA, salinity, and DIC coincided.

Comparison of Measurement Error to Observations

The total relative errors for TA, DIC, and salinity at 1 standard deviation are 1.8%, 1.4%, and 1.2% respectively (Table 1). The calculated error range for pH_c, determined from the combined error of TA, DIC, and salinity measurements is less than the observed daily range (Figure 5). The offsets between pH_c, pH_e and pH_{EE} shown in Figures 6, 7, and 8 are not due to error in TA, DIC, salinity, and in-situ temperature measurements, because the calculated error contribution is small (<.05, Figure 5). Additionally, Huang and Cai (2012) found that TA and DIC samples can be stored with minimal error if they are in borosilicate glass (for TA) and high density polyethylene (HDPE) bottles (DIC); samples can be stored in the dark for a period of at least 3 months. For explanations as to what could contribute to the error of the pH measurements, consult Appendix C. Technical Notes and Details.

Comparison of pH_c to pH Electrode Measurement

At all sites, pH_c, pH_{EE} and pH_e rise or fall similarly over a 24-hour sampling period (Figures 6, 7, and 8). That is, variations are similar while absolute values are parallel but offset. For most observations, the offset between pH_c and pH_e or pH_{EE} falls between -.5 and .5 (Figure 9). For GB, the offset between pH_c to pH_e and pH_{EE} is not constant over time of the study (Figure 6). pH_c agrees well or is larger than pH_{EE} at PC except for sample numbers 200 to 222 (which corresponded to March 9th 2011) (Figure 7). For that day, pH_c steadily rose while pH_{EE} remained at pH ~9 during the same period. There is agreement between pH_c and pH_e at GSO, except for offsets

from sample numbers 0 to 50 and 283 to 300 (Figure 8). Between pH_c and pH_{EE} at GSO, the offset is not constant from 2010 to 2011.

Determination of Conservative Mixing Model End-members

The salinity, alkalinity, and DIC of the end-members are of key importance for determining the output of the model. Differences in the TA, salinity, and DIC end-members cause a shift in the calculated parameters. Below we summarize the salinity, DIC, TA, and temperature values used for the river and ocean end-members. We obtained all values from external data resources. We used 2010 Nu-Shuttle transect data (environmental monitoring data obtained from the circular transect of the bay) to estimate temperature and salinity of water entering the bay (http://www.narrbay.org/d_projects/nushuttle.htm); data from 2011 was not available. The water entering the bay was generally cold (5°C). USGS data indicate that the temperature of the river end-members varies by season. Two isothermal lines are used to represent winter (5°C) and peak summer temperature (25°C). Here we briefly summarize our data sources. For the methodology used to determine the river and ocean end-member, refer to Appendix C. Technical Notes and Details.

We determined river end-member composition from United States Geological Survey (USGS) and the National Water Information Systems data (NWIS) using data from the major rivers and minor tributaries (Blackstone, Pawtucket, Taunton and Branch Rivers) from 1990 to 2010.

- TA: A weighted TA determined from TA measurements made by the USGS and NWIS)- **$360\ \mu\text{mol kg}^{-1}$**

- DIC: Determined using TA if assumed to have a pH of 7- **442 $\mu\text{mol kg}^{-1}$**
- Salinity: Determined from measurements made by the USGS and NWIS- **0 g kg^{-1}**

The ocean end-members were determined from a transect of Woods Hole data from the Gulf of Mexico East Coast Carbon Program (<http://www.aoml.noaa.gov/oce/gcc/GOMECC/>).

- TA: TA average of seawater with the same salinity range entering the bay (31–33.5 Pilson 1985, 2010 Nu-Shuttle transect data)- **2168 $\mu\text{mol kg}^{-1}$**
- DIC: DIC average of seawater with the same salinity range entering the bay (31–33.5 Pilson 1985, 2010 Nu-Shuttle transect data)- **2033.44 $\mu\text{mol kg}^{-1}$**
- S: Salinity average of seawater with the same salinity range entering the bay (31–33.5 Pilson 1985, Nu-Shuttle data) - **32.5 g kg^{-1}**

Northwest Pacific coast estuaries are acidified by upwelled water because Pacific deep water is enriched in DIC (Feely et al. 2008). While deep water of the North Atlantic is less enriched than deep Pacific water (Cai et al. 2010; Key et al. 2004), upwelled water in the North Atlantic can affect the pH of an estuary because it is higher in DIC and TA than surface water (Key et al. 2004). In 2009, a hydrographic survey and moored observations found anomalously warm and saline water in RIS at a depth of 30-50 m; this anomaly is thought to have been brought to the RIS during the interaction of deep Mid-Atlantic Bight (MAB) water with a Gulf Stream warm core ring (Ullman et al. 2014). The anomalous water appeared and then mixed with the RIS during the fall and early winter. No study has investigated the effect of deep MAB

water on the carbonate chemistry of Narragansett Bay; however, we use the temperature and salinity values to estimate the effect of this anomalous water on the pH. We used an additional ocean end-member, labeled “Anomaly” to model the effects of the upwelling of mid-Atlantic bight (MAB) water. The water is warm (15°C) and has high salinity (35 gkg⁻¹). We determined TA and DIC for this anomalous water using the same method that we used to determine the ocean end-member.

Comparing Model Results to pH Calculated from DIC and TA

Figure 10 shows how pH can vary due to the mixing of river and ocean end-members with two different modeling assumptions for the conservation of DIC:

1) DIC is conserved. pH_{mix} is the pH from the mixture of river and ocean end-members. The pH_{mix} lines in Figure 10 show how pH_{mix} increases due to increasing salinity, as shown by f_o approaching 1, and decreasing temperature. The pH_{mix} at 5°C is higher than pH_{mix} at 25 °C.

2) DIC is not conserved. A state of equilibrium is when the DIC flux is equal to zero; there is no dissolution of CO₂ into the estuarine water, nor does it evade out of it. We calculated pH_{equil} , the pH at this equilibrium state, from the concentration of atmospheric CO₂ and the in-situ TA, salinity, and temperature measurements. pH_{equil} shows the final pH a measurement if its DIC were to equilibrate with the atmosphere.

Since the carbonate system inhibits the degassing or evasion of CO₂ compared to a non-reactive gas, the pH of a river and ocean water mixture, pH_{mix} , may not necessarily be at equilibrium and equal pH_{equil} . However, pH_{equil} and pH_m increase linearly with increasing salinity (Figure 10). While pH_{equil} varies due to temperature

and possibly seasonal variations in alkalinity, its range is clearly less than of pH_c (Figure 11), which was determined from in-situ TA, DIC, temperature, and salinity.

The zone of stability, a segment where pH doesn't sharply decrease with salinity is between 0.5 and 1 f_o because high salinity is accompanied by high alkalinity. The pH_c of GSO are grouped together at the upper pH range; the outliers are connected to the great flood of 2010 (Figure 11). PC has a larger pH range than GSO and has points of the same temperature that exceed pH_{mix}. GB has a larger pH_c range than PC and GSO. At all sites the variation of pH_c exceeds that of pH_{mix} and pH_{equil}.

DISCUSSION

Explanation for pH Electrode Differences

The specific electrodes used to make the pH measurements may contribute to the offsets of pH_c, pH_e, and pH_{EE}. Individual electrodes identified with unique ID numbers used to measure pH_{EE} at PC tend to have a positive offset (pH_c>pH_{EE}), a negative offset (pH_c<pH_{EE}), or an offset centered at 0 (pH_c~pH_{EE}). The time from calibration did not appear to have an influence on the magnitude of the offsets. In this simple case, since the offsets are constant within the sample period one may simply apply a correction factor to an electrode with a previously mentioned defect.

What Controls Short-Term pH Change in an Estuary?

Temperature varied seasonally (0.8 to 26.4 °C), but not significantly over individual 24-hour periods, which is generally within a range of 5°C (Figure 4 and

Figure 15). Points of the same color are samples that were usually collected on the same day; these pH values have a large range. Within a narrow range of fraction ocean water mixed, f_o , there is significant short term pH change. This span of pH values for a constant value of f_o indicate that the pH range within a day (as shown as a temperature bracket for example, 15 to 20 °C) is not solely explained by daily variations of salinity, TA, and temperature. We can sort which of the variables (temperature, TA, DIC) is the most important influence on these short term pH fluctuations.

Temperature is not a significant control of pH_{equil} because nearly all of the samples in Figure 10 fall within the pH_{equil} range of 7.9 to 8.1. Since pH_{equil} is a function of alkalinity and DIC at equilibrium, the narrow span of pH_{equil} can also be attributed to changes in alkalinity. A span of pH_{equil} at one f_o value can be due to seasonal variability in the ocean and river end-members, or non-conservative sinks and/or sources of alkalinity. However, this range is considerably smaller than the ranges of pH_c shown in Figure 11.

Sulfate reduction and denitrification, which generate alkalinity, are active in Narragansett Bay sediment (Elderfield et al. 1981, Gains and Pilson 1972, Sampu and Oviatt 1991, Berousky and Nixon 1983). However, reoxidation of reduced S, and Fe decreases alkalinity. If these sedimentary processes (sulfate reduction, and oxidation of reduced species) are in balance; the net impact on alkalinity is zero (Kling et al. 1991). These non-conservative influences might conceivably affect pH seasonally, but they cannot drive pH variation in the water column on hourly time-scales.

Non-conservative alkalinity (TA generation or reduction) does not affect pH in the short term as evidenced by the narrow range of pH_{equil} (Figure 10). The range in 24-hour pH change does not appear to be driven by changes in TA because pH_{equil} follows the curvature of the pH mixing line (Figure 10) and if non-conservative alkalinity processes occur on a short-time scale, pH_{equil} would have a large range at given temperature and f_o .

Figure 12 shows the daily difference between the 24-hour DIC range and the 24-hour TA range of a site. Positive values indicate DIC had a higher daily range than TA, and vice versa. DIC generally has a higher daily range than TA. Since we have already explained why temperature and TA are not the principal cause of observed pH changes within a 24-hour period, the only variable that remains to drive pHc variation is DIC.

Net Heterotrophy and Autotrophy Explained by Excess and Deficit DO and CO₂

The departure of dissolved O₂ or CO₂ from equilibrium can be driven by biology. The fractional departure from equilibrium for DO and CO₂ from Williams and Follows (2011) are:

$$dO_2 = ([O_2] - [O_2]_{\text{sat}}) / [O_2] \quad (8)$$

$$dCO_2^* = ([CO_2^*] - [CO_2^*]_{\text{sat}}) / [CO_2^*] \quad (9)$$

where CO_2^* is dissolved and hydrated CO₂. The fractional departure from equilibrium of carbon dioxide is positive when there is excess CO₂. As a result, the pH

measured is below the pH of the water if it were at equilibrium with the atmosphere (Figure 13). Atmospheric gas exchange can erode the biological imprint. While in our data, the correlation between excess CO_2^* and DO is not as strong as its relationship to pH below or above equilibrium (Figure 14), the general trends of the fractional departure of CO_2^* and DO are anti-correlated (Figures 15).

pH disequilibrium due to excess or deficit carbon dioxide and the fractional disequilibrium of DO are correlated (Figures 16 , 17). The fractional disequilibrium of DO ('biological' signal left as DO) is less than the fractional disequilibrium of CO_2 because, excess DO is more efficiently eroded by gas exchange than excess CO_2 due to the buffering of the carbonate system.

Interestingly, the fractional disequilibrium of carbon dioxide does not clearly correlate with chlorophyll at GSO or GB (Figure 18). The deficit of carbon dioxide during the 2010 flood at Narragansett Bay (March/April 2010) was less than that of April and May 2011 (last 50 samples), a time when highly nutrient-enriched flood runoff contributed to the highest April concentration of phytoplankton in 12 years (Dawicki 2010). An important factor to consider when comparing these two periods is that the water residence time of the estuary was probably much shorter during April 2010 than April 2011 because of the extreme flooding. One episode when high chlorophyll concentrations correlated with a large CO_2^* deficit was during the winter-spring bloom of 2011 (the last 50 sample numbers). This finding highlights two important points: (1) pH change due to photosynthesis doesn't necessarily occur instantaneously because time must pass for the 'biological signal' to accumulate, and (2) mixing and gas exchange can erode a biological pH perturbation.

The Role of Mixing Efficiency on Short-term pH change

While biological processes influence pH, physical processes such as water residence time and gas exchange influence the extent to which the biological ‘signal’ will accumulate. The efficiency at which gas exchange erodes a deficit or excess is determined by the gas exchange timescale (Williams and Follows 2011). By comparing the exchange timescale to the timescales of other estuarine processes, such as the length of a tidal cycle or water residence time, we can further our understanding of hourly and seasonal pH variations.

The timescale to equilibrium for a non-reactive gas such as DO is

$$T=h/K_g, \quad (10)$$

where T is the equilibration timescale of DO (days), h is the water depth of the site (m), and K_g (ms^{-1}) is the coefficient of gas exchange which is a function of windspeed and water turbulence. In contrast, the timescale for CO_2 equilibrium is

$$T_c = (h \text{ DIC})/(K_g B [\text{CO}_2^*]), \quad (11)$$

where B is the Revelle Buffer Factor. In this work we refer to T and T_c as the mixing efficiency of DO and CO_2 respectively.

While wind speed is typically the principal parameter used to estimate the gas-exchange coefficient (e.g., Roques 1985, Raymond and Cole 2001, Ho et al. 2014, Wanninkhof (1992)), turbulence due to tidal currents in estuaries when wind speed is

below 5 ms^{-1} can be more important than the wind in controlling gas exchange coefficients (Borges et al. 2004, Raymond and Cole 2001). The coefficient of gas exchange due to wind and flow is

$$K_g = K_{g,\text{wind}} + K_{g,\text{flow}} \quad (12)$$

(Borges et al. 2004). While Roques (1985) mentioned the impact that currents may have on gas exchange of DO in Narragansett Bay, he parameterized the gas-exchange coefficient of DO only in terms of wind speed. However, tidal currents in Narragansett Bay may not be important because currents are small. At Quonset Point, in Narragansett Bay's West Passage, the average current velocity is 0.26 ms^{-1} (NOAA ports 5/20/2014) and the tidal range is 1.2 m. This current velocity and tidal range are smaller (Table 2) than in the Scheldt Estuary where Borges et al. (2004) argued that turbulence due to currents is important. Based on Borges et al.'s (2004) equation at a velocity of $.26 \text{ ms}^{-1}$, the contribution to the gas-exchange coefficient due currents is 5.0 cmh^{-1} , and translates to equilibration timescales for CO_2 and DO of ~ 70 and 5 days, respectively. Thus, for the purposes of determining time to equilibration for monthly values at all sites in this study, we only consider the wind-speed dependence of the gas-exchange coefficient.

We use the parameterization given by Wanninkhof (1992) for K_g because it contains a formulation for both DO and CO_2 based on the wind speed and physical properties of the water. We used hourly mean wind speeds from Quonset Point and

matched them with each sample (National Oceanic and Atmospheric Administration (2013)).

We calculate the water residence time to compare it to the gas exchange mixing efficiency (h/Kg) of the bay. We estimate the monthly average freshwater discharge (Q_m) by adding the monthly average discharge within the period of the study of Blackstone, Pawtuxet, and Taunton rivers obtained from the USGS hydrology database. The monthly average residence time was determined using Q_m and the relation by Pilson (1985), who derived a relation between the residence time and freshwater input using the following empirical relation:

$$T=41.8e^{-.00435FW} \quad (13)$$

where T is the flushing time in days of the Bay and FW is the freshwater input in m^3 per s. The shortest residence times were during the Great Flood of 2010 (March 2010-9.2 days; April 2010-16.7 days). The residence time of Narragansett Bay in this study period is 30 with a standard deviation of 9 days.

DO equilibrates much more quickly than CO_2 (Figure 19). On average, the equilibrium timescales of DO and CO_2 are 9 and 155 days, respectively (the standard deviation is 7 and 155 days). If the wind speed is less than 5 ms^{-1} , the time scale to equilibrium of CO_2 due to tidal and non-tidal currents is at least 70 days (much greater than the residence time of the bay). Hence, the equilibrium timescale of CO_2 generally exceeded the flushing time of the bay, with the exception of GB from April 2010 to October 2010.

Interestingly, the highest disequilibrium values of $d\text{CO}_2^*/\text{CO}_2^*$ and DIC in this study are found at GB. This anomaly may be due to two separate reasons: (1) GB is an exceptionally productive site with strong biological pH variation despite the mixing efficiency due to wind, or 2) the mixing efficiency of GB is overestimated. At all sites, excess $d\text{CO}_2^*/\text{CO}_2^*$ occurs during the summer. Deficit $d\text{CO}_2^*/\text{CO}_2^*$ and DIC start by October. This transition coincides with seasonal overturning of the thermocline in the Rhode Island Sound (Shonting and Cook 1970).

CONCLUSION

Our calculations of pH from TA and DIC measurements validate the relatively large magnitudes of 24-hour and seasonal pH changes recorded by electrodes in Narragansett Bay. The largest pHc range for GSO was on April 1st 2010, which had range of pHc of 8.36 to 7.94. The pHe range on the same day was from 8.19 to 8.01. The largest pHc range for PC was on March 8th 2011, which had range of pHc of 8.68 to 8.16. The pHe range on the same day was from 9.02 to 8.46. The largest pHc range for GB was on May 13th 2010, which had range of pHc of 8.04 to 7.42. The pHe range on the same day was from 7.91 to 7.52. Offsets between pH measured by electrodes and pH calculated from TA and DIC are nearly constant over individual days but vary on longer time-scales. The causes of these offsets are not entirely clear.

Using a conservative mixing model, we have shown that pH variation at the three studied sites is mainly due to differences in DIC driven by photosynthesis and respiration, rather than simply changes in TA and DIC from mixing of different proportions of ocean and river water. Excess carbon dioxide correlates with deficit dissolved oxygen and vice-versa, indicating that DIC varies seasonally due to

respiration and photosynthesis. However, the relation between excess and deficit carbon dioxide is not clearly linked to chlorophyll concentration. The relationship of DO to DIC is complicated by the differences in gas exchange rates of O_2 and CO_2 . Analysis of the gas exchange mixing efficiency of the estuary provides a physical explanation as to why pH values below equilibrium CO_2 covary with low DO concentrations.

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Tables and Figures

TABLES

Table 1. Summary of error (analytical and storage) for all parameters measured in situ or in the lab.

Parameter	Method	Uncertainty	Source
pH	Isco 701 pH/Temperature Module (electrode)	± 0.1 pH units from 0 to 11.9 pH and ± 0.2 pH units from 12.0 to 14.0 pH	manufacturer
Temperature		$\pm 1^\circ\text{C}$.	
TA	Open-cell titration using IOPCC protocol with Dickson Standards CRM 94, 100, 102 IAPSO P139 for May and March 2011 at PC and GB	% relative error (1 s.t.d.)= 1.8%	sample replicates borax control
DIC	AIR-DIC ¹ with Dickson Standards CRM 94, 100, 102	% relative error (1 s.t.d.)= 1.4%	sample replicates
Salinity	Silver nitrate titration	% relative error (1 std)=1.2%	sample replicates

Table 2. Tidal and non-tidal currents. Tidal Currents was from NOAA ports, non-tidal currents summarized from various sources by Hicks (1959) compared to the tidal amplitude and water current in Borges et al. 2004.

Tidal Current	.257	ms^{-1}	
Tidal Amplitude	4.0	m	
Non-tidal Currents	River Runoff	Depth of Non-tidal motion	Surface Non-tidal Currents
	m^3s^{-1}	m	cms^{-1}
Providence River	9.4	2.7	11.3
West Passage	2.5	3.4	4.1
	2.5	9.1	12.3
East Passage	4.5	4.6	2.6
	4.4	8.2	2.6
	2.7	1.8	5.7
	11.6	20.1	19.0
Mt. Hope Bay	6.2	1.8	1.5
Sakonnet R.	1.7	8.2	3.6
Average tidal amplitude, water current at three stations in the Scheldt Estuary			
Location	Mean Water Level	Tidal Amplitude	Water Current
	m	m	ms^{-1}
Vlissingen	14.7	4.9	.603
Hansweert	8.6	4.8	.537
Antwerpen	10.8	5.5	.733

FIGURES

Figure 1. Sampling sites at Narragansett Bay, Rhode Island.

Figure 2. Linear relationships of A) alkalinity (TA) to salinity, B) total dissolved inorganic carbon (DIC) to salinity, and C) TA to DIC from February 2010 through April 2011 at all three sites.

Figure 3. A) Salinity measurements during the study period (2/10-4/11). B) Total dissolved inorganic carbon (DIC) measurements during the study period. C) Alkalinity measured (TA) during the study period. D) Temperature measured in situ during the study period.

Figure 4. Top: pH measured in situ by electrodes during the study period (pHe). Bottom: pH determined from alkalinity, total dissolved inorganic carbon, salinity, and in situ temperature measurements (pHc).

Figure 5. Range of relative error (rer) of pHc calculated from chemical measurements (shown filled) compared to the observed daily range in pHc (shown empty).

Figure 6.A) pH calculated from chemical measurements (pH_c) compared to pH measured by our electrodes (pH_e) at Greenwich Bay, over sample number. B) calculated pH (pH_c) compared to pH measured by RIDEM's electrodes (pH_{EE}) at Greenwich Bay, over sample number.

Figure 7. A) pH calculated from chemical measurements (pH_c) compared to pH measured by our electrodes (pH_e) at Potter Cove, over sample number. B) calculated pH (pH_c) compared to pH measured by NBNERR's electrodes (pH_{EE}) at Potter Cove, over sample number.

Figure 8. A) calculated pH (pHc) compared to our pH measured by our electrodes (pHe) at GSO over sample number. B) calculated pH (pHc) compared to pH measured by RIDEM's electrodes (pH_{EE}) at GSO over sample number.

Figure 9. A) The pH measurements from the electrodes (with pH_{EE} measured by the external electrodes and pH_e measured by our electrodes) compared to calculated pH (pH_c), with calculated pH in the X axis. B) The pH measurements from the electrodes compared to calculated pH (pH_c) over time.

Figure 10. A) pH_{mix} compared to pH_{eq} (pH if DIC was at equilibrium with the atmosphere) at Greenwich Bay . B) pH_{mix} compared to pH_{eq} at Potter Cove, C) pH_{mix} compared to pH_{eq} at GSO.

Figure 11. pH(TA,DIC) denotes pH calculated, also referred as pH_{c} . A) pH_{mix} compared to pH_{c} at Greenwich Bay. B) pH_{mix} compared to pH_{c} at Potter Cove. C) pH_{mix} compared to pH_{c} at GSO.

Figure 12. Magnitude of daily DIC range relative to daily TA range.

Figure 13. The fractional departure from equilibrium of carbon dioxide ($d\text{CO}_2^*/\text{CO}_2^*$) and its relationship to pH (the difference between pH calculated from TA and DIC and pH when DIC is at equilibrium to the atmosphere ($\text{pH m} - \text{pH eq}$)).

Figure 14. The fractional departure from equilibrium of carbon dioxide ($d\text{CO}_2^*/\text{CO}_2^*$) and its relationship to the fractional departure from equilibrium of dissolved oxygen ($d\text{O}_2/\text{O}_2$).

Figure 15. The fractional departure from equilibrium of carbon dioxide ($d\text{CO}_2^*/\text{CO}_2^*$) and the fractional departure from equilibrium of dissolved oxygen ($d\text{O}_2/\text{O}_2$) compared to sample number at A) Greenwich Bay, B) Potter Cove, and C) GSO. Missing intervals of $d\text{O}_2/\text{O}_2$ are due to a lack of dissolved oxygen data available during that period.

Figure 16. The departure of pH from equilibrium and the fractional departure from equilibrium of dissolved oxygen (dO_2/O_2) compared to sample number at A) Greenwich Bay, B) Potter Cove, and C) GSO.

Figure 17. The departure of pH from equilibrium and the fractional departure from equilibrium of dissolved oxygen (dO_2/O_2) in bottom water compared to sample number at Greenwich Bay.

Figure 18. The fractional disequilibrium of carbon dioxide ($d\text{CO}_2^*/\text{CO}_2^*$) compared to Chlorophyll concentration determined by fluorescence ($\mu\text{g/L}$).

Figure 19. The timescales of carbon dioxide equilibration and dissolved oxygen equilibration compared to the flushing time of the bay. The flushing time of the bay was calculated from river discharge and a relation of freshwater input to flushing time (Pilson 1984).

Appendix B. Additional Results

Method and Results Summary

We evaluated Revelle factor ($B = ((\Delta[\text{CO}_2] / [\text{CO}_2]) / (\Delta[\text{DIC}] / [\text{DIC}]))$), partial pressure of carbon dioxide ($p\text{CO}_2$), and the degree of saturation of calcite and aragonite (Ω_c and Ω_a , respectively) using the program CO2SYS (Lewis and Wallace, 1998). Carbonate dissociation constants are from Cai and Wang (1998). The dissociation constants are appropriate for the salinity ranges in this study (17.89 to 31.71 gkg^{-1}) and allow us to determine a pH value from the DIC and TA on the NBS pH scale. RIDEM and NBNERR calibrate their pH electrodes using NBS buffers. The values of K_{sp} for calcite and aragonite are from Mucci (1983). For the Revelle factor ($B = ((\Delta[\text{CO}_2] / [\text{CO}_2]) / (\Delta[\text{DIC}] / [\text{DIC}]))$), partial pressure of carbon dioxide ($p\text{CO}_2$), and the degree of saturation of calcite and aragonite (Ω_c and Ω_a , respectively). The degree of saturation is determined by the following relation:

$$\Omega_c = [\text{Ca}^{2+}][\text{CO}_3^{2-}] / K_{sp_c}$$

$$\Omega_a = [\text{Ca}^{2+}][\text{CO}_3^{2-}] / K_{sp_a}$$

The solubility constants for calcite (K_{sp} calcite) and aragonite (K_{sp} aragonite) can be found in Mucci (1983).

The seasonal variation of the Revelle Factor, Ω_c , and Ω_a appears to behave oppositely to what is expected due to temperature (lowest values in the winter, highest in the summer) (Figures 11-13, see below). $p\text{CO}_2$ (determined from TA, DIC, salinity and in-situ temperature) peaks during the late spring to summer at all sites (Figure 14, see below).

Only at GB did the largest daily range in Ω_c and Ω_a coincide with the largest daily range in salinity. It is clear that for Narragansett Bay, the factors that control pH_c, the Revelle Factor, and Ω_c and Ω_a are more complex than dilution of TA and DIC by precipitation or freshwater discharge.

Additional Figures

Figure App B 1. Sampling sites at Narragansett Bay, Rhode Island.

Figure App B 2. The linear relationship of alkalinity (TA) and salinity at all three sites.

Figure App B 3. The linear relationship of total dissolved inorganic carbon (DIC) and salinity at all three sites.

Figure App B 4. The linear relationship of total dissolved inorganic carbon (DIC) and alkalinity (TA) at all three sites.

Figure App B 5. Salinity measurements during the study period.

Figure App B 6. Total dissolved inorganic carbon (DIC) measurements during the study period.

Figure App B 7. Alkalinity measured (TA) during the study period.

Figure App B 8. Temperature measured in situ during the study period.

Figure App B 9. pH electrode (pHe) measured in situ during the study period.

Figure App B 10. pH determined from alkalinity, total dissolved inorganic carbon, salinity, and in situ temperature measurements, referred as pH c.

Figure App B 11. The Revelle Factor determined from alkalinity, total dissolved inorganic carbon, salinity, and in situ temperature measurements.

Figure App B 12. The degree of saturation of calcite (Ω_c) determined from alkalinity, total dissolved inorganic carbon, salinity, and in situ temperature measurements.

Figure App B 13. The degree of saturation of aragonite (Ω_A) determined from alkalinity, total dissolved inorganic carbon, salinity, and in situ temperature measurements.

Figure App B 14. pCO₂ determined from alkalinity, total dissolved inorganic carbon, salinity, and in situ temperature measurements.

Figure App B 15. Range of relative error (rer) in salinity measurements (shown as filled shapes) compared to the observed daily range.

Figure App B 16. Range of relative error (rer) in total dissolved inorganic carbon (DIC) measurements (shown as filled shapes) compared to the observed daily range.

Figure App B 17. Range of relative error (rer) of alkalinity (TA) measurements (shown as filled shapes) compared to the observed daily range.

Figure App B 18. Range of relative error (rer) of the partial pressure of carbon dioxide (pCO₂) determined from calculations (shown as filled shapes) compared to the observed daily range.

Figure App B 19. Range of relative error (rer) of pH determined from calculations (shown as filled shapes) compared to the observed daily range (empty shapes).

Figure App B 20. Range of relative error (rer) of the Revelle Factor determined from calculations (shown as filled shapes) compared to the observed daily range (empty shapes).

Figure App B 21. Range of relative error (rer) of the degree of saturation of calcite (Ω_C) determined from calculations (shown as filled shapes) compared to the observed daily range (empty shapes).

Figure App B 22. Range of relative error (rer) of the degree of saturation of calcite (Ω_A) determined from calculations (shown as filled shapes) compared to the observed daily range (empty shapes).

Figure App B 23. pH calculated compared (pH c) to pH our electrode (pH e) at Greenwich Bay, over sample number.

Figure App B 24. pH calculated (pH c) compared to RIDEM pH electrode (pH EE) at Greenwich Bay, over sample number.

Figure App B 25. pH calculated (pH c) compared to pH our electrode (pH e) at Potters Cove, over sample number.

Figure App B 26. pH calculated (pH c) compared to NBNERR's pH electrode (pH EE) at Potters Cove, over sample number.

Figure App B 27. pH calculated (pH c) compared to our pH electrode (pH e) at GSO over sample number.

Figure App B 28. pH calculated (pH c) compared to RIDEM's pH electrode (pH EE) at GSO over sample number.

Figure App B 29. The pH measurements from the electrodes (pH EE is the external electrode and pH e is this study's electrode) compared to calculated pH (pH c), with pH calculated in the X axis.

Figure App B 30. The pH measurements from the electrodes (pH EE is the external electrode and pH e is this study's electrode) compared to calculated pH (pHc) over time.

Figure App B 31. Model of pH under conservative mixing conditions.

Figure App B 32. Model of pH under conservative mixing conditions at GB, with DIC at equilibrium with the atmosphere.

Figure App B 33. Model of pH under conservative mixing conditions at PC, with DIC at equilibrium with the atmosphere.

Figure App B 34. Model of pH under conservative mixing conditions at PC, with DIC at equilibrium with the atmosphere.

Figure App B 35. Model pH mixing compared to field observations at Greenwich Bay.

Figure App B 36. Model pH mixing lines compared to field observations at Potters Cove.

Figure App B 37. Model pH mixing lines compared to field observations at GSO.

Figure App B 38: Modeled pCO₂ mixing lines under conservative mixing.

Figure App B 39. Modeled pCO₂ mixing lines compared to Greenwich Bay data determined from in situ temperature, salinity, DIC, and TA.

Figure App B 40. Modeled pCO₂ mixing lines compared to Potters Cove pCO₂ data determined from in situ temperature, salinity, DIC, and TA.

Figure App B 41. Modeled pCO₂ mixing lines compared to GSO pCO₂ data determined from in situ temperature, salinity, DIC, and TA.

Figure App B 42. Modeled degree of saturation of calcite (Ω_C) mixing lines.

Figure App B 43. Modeled degree of saturation of calcite (Ω_C) mixing lines compared to Greenwich Bay Ω_C data determined from in situ temperature, salinity, DIC, and TA.

Figure App B 44. Modeled degree of saturation of calcite (Ω_C) mixing lines compared to Potters Cove Ω_C data determined from in situ temperature, salinity, DIC, and TA.

Figure App B 45. Modeled degree of saturation of calcite (Ω_C) mixing lines compared to GSO Ω_C data determined from in situ temperature, salinity, DIC, and TA.

Figure App B 46. Modeled degree of saturation of aragonite (Ω_A) mixing lines.

Figure App B 47. Modeled degree of saturation of aragonite (Ω_A) mixing lines compared to Greenwich Bay Ω_A data determined from in situ temperature, salinity, DIC, and TA.

Figure App B 48. Modeled degree of saturation of aragonite (Ω_A) mixing lines compared to Potters Cove Ω_A data determined from in situ temperature, salinity, DIC, and TA.

Figure App B 49. Modeled degree of saturation of aragonite (Ω_A) mixing lines compared to GSO Ω_A data determined from in situ temperature, salinity, DIC, and TA.

Figure App B 50. The difference between total dissolved inorganic carbon measured (DIC_m) and total dissolved inorganic carbon at equilibrium with the atmosphere (DIC_{eq}).

Figure App B 51. DIC and DO over sample number at Greenwich Bay.

Figure App B 52. DIC and DO over sample number at Potters Cove.

Figure App B 53. DIC and DO over sample number at GSO.

Figure App B 54. The fractional departure from equilibrium of carbon dioxide ($d\text{CO}_2^*/\text{CO}_2^*$) and the relationship to pH (the difference between pH calculated from TA and DIC and pH when DIC is at equilibrium to the atmosphere ($\text{pH m} - \text{pH eq}$)).

Figure App B 55. The fractional departure from equilibrium of carbon dioxide ($d\text{CO}_2^*/\text{CO}_2^*$) and the relationship to the fractional departure from equilibrium of dissolved oxygen ($d\text{O}_2/\text{O}_2$).

Figure App B 56. The fractional departure from equilibrium of carbon dioxide (dCO_2^*/CO_2^*) and the relationship to the fractional departure from equilibrium of dissolved oxygen (dO_2^*/O_2) compared to sample number. Top left Greenwich Bay, top right is Potters Cove, bottom left is GSO.

Figure App B 57. The departure of pH from equilibrium and the relationship to the fractional departure from equilibrium of dissolved oxygen (dO_2/O_2) compared to sample number. Top left Greenwich Bay, top right is Potters Cove, bottom left is GSO.

Figure App B 58. The departure of pH from equilibrium and the relationship to the fractional departure from equilibrium of dissolved oxygen (dO_2/O_2) compared to sample number. This site is Greenwich Bay and the fractional departure of disequilibrium of oxygen of bottom water.

Additional Tables

Table 1. Contribution of nitrogen alkalinity (N-ALK~ NH₄) at Greenwich Bay Marina, summer of 2010.
Nutrient measurements were made by Save the Bay.

Date/ Time	Measured in this Study	Save the Bay Measurements		TA Contribution
	TA	NH ₄	NO ₂ +NO ₃	NH ₄
	umol/kg	ug/L	ug/L	%
May 2010	1860.8	90	40	2.6E-01
June 2010	1839.6	80	20	2.4E-01
July 2010	1911.0	240	30	6.8E-01
August 2010	1973.0	90	10	2.5E-01
September 2010	1944.9	160	20	4.5E-01
October 2010	1971.5	140	80	3.9E-01

Table 2. Percent Contribution to Alkalinity (%) determined from 5 year average data of total dissolved inorganic nitrogen and silica. Data Source: Tank-98 data managed by C. Oviatt URI-GSO:

Parameter	AVG (%)	STD	N	STD ERR	ME
Carbonate Alkalinity (CA)-from our study	96.5	1.9E-02	1.6E+02	1.5E-03	3.0E-03
Non-Carbonate Alkalinity (NC : Si-ALK+ P-ALK+ N-ALK)	3.7	2.0E-02	1.6E+02	1.6E-03	3.2E-03

Table 3. The average difference between calculated parameters with and without non-carbonate alkalinity contributors. Data Source: Tank-98 data managed by C. Oviatt URI-GSO:

$\Delta X = X_{\text{calculated with CA}} - X_{\text{calc with CA + NC}}$	AVG	STD	N	STD ERR	ME (95% CI)
$\Delta p\text{CO}_2$ (uatm)	-1.5E+00	1.0E+00	156	8.3E-02	1.6E-01
ΔpH	1.5E-03	1.1E-03	156	8.4E-05	1.7E-04
$\Delta \text{Revlle Factor}$	-4.9E-03	1.1E-02	156	8.5E-04	1.7E-03
$\Delta \Omega_{\text{C}}$	1.4E-02	9.4E-03	156	7.5E-04	1.5E-03
$\Delta \Omega_{\text{A}}$	8.9E-03	6.1E-03	156	4.9E-04	9.6E-04

Appendix C. Technical Notes and Details

Methodology Used to Determine the River and Ocean End-members

The river end-member TA obtained from our linear fit of all of TA-S data ($y = 58.821x + 301.55$, $R^2 = 0.9398$) is similar to TA determined from USGS and National Water Information Systems (NWIS) TA and river discharge data (TA_c). The intercept is lower than the alkalinity determined from the USGS data, perhaps because the alkalinity of the floodwater from the March and April 2010 may have been lower than average. However, we have no river TA from this period to test this hypothesis. The USGS determines TA by Gran titration, using an endpoint of pH 4.5 (Rounds 2012), a value close to the endpoint titration used in this study (pH ~ 4). TA_c is the averaged TA weighted by river discharge (Cai et al. 2010 Supplementary Materials) for data of the major rivers and minor tributaries (Blackstone, Pawtucket, Taunton and Branch Rivers) from 1990 to up to 2010, since no TA measurements were made by the USGS during our study period. While rivers in the Eastern U.S. have become increasingly alkaline (Kaushal et al. 2013), alkalization of the Branch River has been statistically insignificant (Kaushal et al. 2013 Supporting Information). Blackstone River alkalinity is increasing at a rate of $\sim 0.16 \text{ mgL}^{-1}\text{yr}^{-1}$. Since the most recent data is from 2001, the TA of the river end-member may be underestimated (by $\sim 30 \text{ } \mu\text{molkg}^{-1}$); The salinity of the measurements are reported by the USGS as conductivity; all values below the detection limit. DIC is not measured by the USGS. We determined the DIC end member from TA_c and the average pH obtained from the USGS of rivers mentioned earlier.

The end-members determined in this study are similar to those found by Segarra (2002) for TA and DIC of the Blackstone, Runnins, and Palmer Rivers. While Boucher (1991) attributed high pH to high alkalinity resulting from fertilizer runoff at the Taunton River, Segarra (2002) found nitrate to be a minor component of alkalinity (less than 10%). The contribution of alkalinity due to nutrients determined from T-98 and Save the Bay (environmental monitoring organization) measurements confirm the minor role of non-carbonate alkalinity contribution to pH and other calculated parameters (Table 1, 2, and 3 in Appendix B). Alkalinity and DIC was measured by Segarra following the Dickson et al. (2007) standard procedure.

Despite extensive literature search, we found no published studies of TA and DIC of the Rhode Island Sound (RIS). Estimates of TA and DIC for RIS are needed to estimate the ocean end-member for the conservative mixing model. We used data from the Gulf of Mexico East Coast Carbon Program to estimate TA and DIC of water entering Narragansett Bay. From the GEOMECC data we used data from the Woods Hole Transect (a transect of the Mid Atlantic Bight that began at Woods Hole) for our calculations. We determined the ocean end-member from the average of TA and DIC data for the salinity range of the water that enters the bay ($31 - 33.5 \text{ gkg}^{-1}$). Alkalinity samples for the GEOMECC study were collected and analyzed following the Dickson et al. (2007) standard procedure and used Dickson Certified Reference Material to standardize the titrant (Cai et al. 2010). Their procedure was similar to the procedure that we used for this study, except their samples were not poisoned with mercuric chloride.

What contributes to error?

The offsets between pH_C, pH_E and pH_{EE} are probably not due to error in TA, DIC, salinity, and in-situ temperature measurements, because the calculated error contribution is too small (<.05, Figure 19). Additionally, Huang and Cai (2012) found that TA and DIC samples can be stored with minimal error if they are in borosilicate glass (for TA) and high density polyethylene (HDPE) bottles (DIC); samples can be stored in the dark for a period of at least 3 months. Thus, the differences between these independent pH estimates is likely due to errors associated with the electrodes. Various factors can contribute to electrode errors, such as a dramatic changes in pH or salinity, the type of buffer used to calibrate the electrode, or the protocol used to handle or correct the data.

In this study, rapid changes in temperature or salinity do not appear to have significantly affected offsets between the electrodes. Calculated instance on April 2010 GSO and GB experienced a dramatic change in salinity in the course of 24 hours but the offset between pH_C and the pH measured by electrodes was not different from other days (Figure 9 in Figures).

The electrodes used to measure pH_{EE} are all calibrated with the same YSI-NBS certified buffers. For some days, pH_{EE} was corrected because of the quality of the buffer (RIDEM notes). The pH_{EE} values used in this study were corrected according to the quality control and quality assurance methods established by RIDEM (GB and GSO) and NBNERR (PC). Because we do not have access to the raw data, we estimate how well calculated pH matches the ‘corrected’ pH determined by RIDEM and NBNERR. No samples from our measurement period for GSO coincided

with pH values that were corrected by RIDEM (sample notes found in RIDEM data file). Only the November 2010 24 hour sampling set of GB fell on the same period when pH_{EE} values were corrected. pH_c was higher than pH_{EE} , but the offset does not appear less than or greater than the offset from other days. pH_e was corrected for March, April, and May 2010 at GSO, but the offset does not appear to be different than the offset observed on other days. No quality control quality control code was listed for pH_{EE} at PC during this study's sampling days. In short, the method used to correct pH does not appear to cause distinct offsets. Consequently, the difference between pH_c , pH_e , and pH_{EE} is not due to the correction methods.

Non-carbonate alkalinity (NC-TA) is a minor component of TA in Narragansett Bay (less than 4%) and does not contribute to the offset between the pH_c , pH_e , and pH_{EE} values (Table 3 in Appendix B). To estimate the contribution of non-carbonate alkalinity to our calculations, we used the bi-weekly average of 5 year nutrient data from (SiO_4 , NO_3 , NO_2 , NH_4 , and PO_4) MERL T-98 (data collection and analysis is managed by C. Oviatt and field measurements during the summer of 2010 at GB made by Save the Bay).

pH_e was calibrated with TRIS buffer for the first 50 to 100 samples at all sites; For subsequent sampling intervals, the electrodes were calibrated with certified NBS buffers. The pH calculated using seawater scale is .159 less than pH calculated using the NBS scale (Lewis and Wallace, 1998). While the pH meter did not have different calibration points (pH=7,10) when using different buffers, the offset at the beginning of the sample sequence at all sites is at a similar range (~0.2), and may partly be due to this calculation difference. The offset between pH_c and pH_e is negative ($pH_c < pH_e$)

for the last 50 to 100 measurements, but it cannot be explained by using an NBS buffer. pH_{EE} is not offset like pH_e for the last measurements and is less clear; it is either less than (GSO, GB) or equal to (PC) pH_c .

The specific electrode used to make the pH measurements may contribute to the offset. The same electrodes identified with unique ID numbers used to measure pH_{EE} at PC tend to have a positive offset ($pH_c > pH_{EE}$), a negative offset ($pH_c < pH_{EE}$), or an offset centered at 0 ($pH_c \sim pH_{EE}$) (electrode ID numbers and sonde dates from Daisy Durant, personal communication). The time from calibration did not appear to have an influence on the span of the offset. In this simple case, since the offsets are constant within the sample period one may simply apply a correction factor to an electrode with a previously mentioned defect.

Appendix C References

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