2015

Estimating daily primary production and nighttime respiration in estuaries by an in situ carbon method

Catherine M. Coupland
University of Rhode Island, ccoupland4@gmail.com

ESTIMATING DAILY PRIMARY PRODUCTION AND NIGHTTIME RESPIRATION IN ESTUARIES BY AN IN SITU CARBON METHOD

BY

CATHERINE M. COUPLAND

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

CATHERINE COUPLAND

APPROVED:

Thesis Committee:

Major Professor Candace A. Oviatt

Arthur J. Spivack

Arthur J. Gold

Michael E.Q. Pilson

Nasser H. Zawia
DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND

2015

ABSTRACT

A Dawn Dusk Dawn Carbon method was developed to estimate daily primary productivity and respiration in Narragansett Bay at 9 Narragansett Bay Fixed Site Monitoring Network stations. The method utilizes YSI temperature, salinity, and pH measurements and measured alkalinity values. The method was compared to a previously verified Dawn Dusk Dawn Oxygen method for Narragansett Bay developed by Smith (2011). The methods compared well with correlations coefficients between 0.69 – 0.96 for all four categories (surface production, surface respiration, bottom production, and bottom respiration) and both summers. In all categories, 2014 comparisons were more highly correlated than 2013.

Metabolic rate sensitivity to pH and alkalinity analyses, pH stability, and accuracy, were conducted to quantify error. The YSI pH sensors were stable over the dawn-dusk-dawn time period (i.e. 24 hours), with an average change between 15 minute readings of 0.01 units. Based on the manufacturers stated accuracy for the YSI sensor of 0.2 pH units, the surface metabolic rate estimates could be under or over estimated by -11 to 23% if the pH sensor was reading low or high by a systematic 0.2 unit offset. The bottom estimates could be over estimated by 8 to 11%, based on the same offset. The metabolic rate estimates are not significantly affected by a change in alkalinity, with ANOVA p values >0.9 for all categories and two stations. Four comparisons between a Satlantic SeaFET pH sensor and YSI pH sensors were conducted with four variable results due to

differing environmental deployment conditions, three of four comparisons indicated a linear trend between the two sensors.

The metabolic rates vary spatially throughout the Bay both summers 2013 and 2014. Average surface net primary production ranged from 0.11 – 0.38 gC m^{-3} day^{-1} in 2013 and 0.16 – 0.56 gC m^{-3} day^{-1} in 2014. The ranges of average surface respiration rates were nearly identical to the net surface production (within 0.01 gC m^{-3} day^{-1}) for both summers. The bottom production and respiration rates ranged from 0.03 - 0.32 gC m^{-3} day^{-1} and 0.00 to -0.31 gC m^{-3} $night^{-1}$, respectively, for 2013. The ranges of net primary production and respiration in 2014 were 0.01 – 0.56 gC m^{-3} day^{-1} and -0.01 to -0.56 gC m^{-3} $night^{-1}$, respectively. A north to south gradient in metabolic rates persists through the West Passage both summers, with the exception of North Prudence. North Prudence exhibits anomalously low metabolic rate estimates compared to surrounding sites. Previous studies around the North Prudence site have indicated a well mixed water column, with bottom water reaching the surface. This may be artificially lowering the estimates of surface production at the North Prudence site.

ACKNOWLEDGEMENTS

Above all, I would like to thank my advisor Dr. Candace Oviatt. She provided me the opportunity to explore oceanography many years ago, and it was then I knew my future path in life. It is only fitting that I would have the honor to work with her as my mentor. Over the last several years she has provided guidance, knowledge, patience and just the right amount of encouragement to keep me going and exploring in the world of oceanography. I can say with full confidence, I would not be the scientist, or person, that I am today without her help. As if this was not enough, she has became a true friend with whom I can discuss anything and everything, and always welcomes me warmly. I could not have asked for anything more from a graduate advisor. Thank you.

I would like to thank my other committee members, Arthur J Spivack, Arthur Gold, and Michael E.Q. Pilson. They have provided me with countless recommendations, knowledge, stimulating questions and kind words of encouragement throughout my years at GSO. Additionally, I thank Jason Grear who helped me tremendously in setting up the alkalinity equipment.

Heather Stoffel, I cannot thank you enough for all you have done for me over the last five years. You have taught me many skills, from working in the field to data management and analysis tools, patience, and most importantly you have always been there for me as a friend whenever I needed a shoulder to lean on.

Edwin Requintina and Laura Reed, thank you for keeping MERL going and always having open ears and a willingness to help, I couldn't not have done my

research with out you both. I was blessed to have an intern, Alyssa Rueb, for both summers as a graduate student. Thank you Alyssa, for being a hard working, smart, and comedic friend through thick and thin and helping me accomplish my research. I would also like to thank the buoy interns that assisted with data collection, Matt Bernardo and Jonathan Persia.

From my very first days as an intern myself, Leslie Smith has been there to guide me and show me the way. Her guidance, teaching, and maturity was invaluable to making me the person I am now. My research has consisted as an extension of her project, and without her, none of this would have been possible. Thank you for all you have done and continue to do.

I am appreciative for the funding that supported this research, provided by a grant from the NOAA Coastal Hypoxia Research Program.

Lastly, I will always appreciate the continuous support and encouragement from my family and friends, without which I would not have been able to pursue my goals. I would like to thank Chris Liberti. He has taught me to be a more confident, passionate, and understanding person. Chris has been with me for almost my entire journey in oceanography and his unwavering support, encouragement, and confidence in me has allowed me to accomplish my goals and maintain my sanity along the way. I will never be able to thank you enough.

PREFACE

The following thesis is presented in manuscript form and is being prepared for publication in Estuaries and Coasts.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Estimating daily primary productivity and nighttime respiration in estuarine waters using an in situ carbon method

Catherine M. Coupland[1]*, and Candace A. Oviatt[1]
[1] Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode
Island, 02882

Key Words: Narragansett Bay, primary productivity, metabolic rate, carbon dioxide, pH, alkalinity

Catherine Coupland: email: ccoupland4@gmail.com, phone 401- 595-0170 (*corresponding author)
C.A. Oviatt: email: coviatt@uri.edu, phone: 401-874-6661, fax: 401-874-6613

Publication status: in preparation for Estuaries and Coasts

ABSTRACT

A Dawn Dusk Dawn Carbon method was developed to estimate daily primary productivity and respiration in Narragansett Bay at 9 Narragansett Bay Fixed Site Monitoring Network stations. The method utilizes YSI temperature, salinity, and pH measurements and measured alkalinity values. The method was compared to a previously verified Dawn Dusk Dawn Oxygen method for Narragansett Bay developed by Smith (2011). The methods compared well with correlations coefficients between 0.69 – 0.96 for all four categories (surface production, surface respiration, bottom production, and bottom respiration) and both summers. In all categories, 2014 comparisons were more highly correlated than 2013.

Metabolic rate sensitivity to pH and alkalinity analyses, pH stability, and accuracy, were conducted to quantify error. The YSI pH sensors were stable over the dawn-dusk-dawn time period (i.e. 24 hours), with an average change between 15-minute readings of 0.01 units. Based on the manufacturers stated accuracy for the YSI sensor of 0.2 pH units, the surface metabolic rate estimates could be under or over estimated by -11 to 23% if the pH sensor was reading low or high by a systematic 0.2 unit offset. The bottom estimates could be over estimated by 8 to 11%, based on the same offset. The metabolic rate estimates are not significantly affected by a change in alkalinity, with ANOVA p values >0.9 for all categories and two stations. Four comparisons between a Satlantic SeaFET pH sensor and YSI pH sensors were conducted with four variable results due to

differing environmental deployment conditions, three of four comparisons indicated a linear trend between the two sensors.

The metabolic rates vary spatially throughout the Bay both summers 2013 and 2014. Average surface net primary production ranged from 0.11 – 0.38 gC m^{-3} day^{-1} in 2013 and 0.16 – 0.56 gC m^{-3} day^{-1} in 2014. The ranges of average surface respiration rates were nearly identical to the net surface production (within 0.01 gC m^{-3} day^{-1}) for both summers. The bottom production and respiration rates ranged from 0.03 - 0.32 gC m^{-3} day^{-1} and 0.00 to -0.31 gC m^{-3} $night^{-1}$, respectively, for 2013. The ranges of net primary production and respiration in 2014 were 0.01 – 0.56 gC m^{-3} day^{-1} and -0.01 to -0.56 gC m^{-3} $night^{-1}$, respectively. A north to south gradient in metabolic rates persists through the West Passage both summers, with the exception of North Prudence. North Prudence exhibits anomalously low metabolic rate estimates compared to surrounding sites. Previous studies around the North Prudence site have indicated a well-mixed water column, with bottom water reaching the surface. This may be artificially lowering the estimates of surface production at the North Prudence site.

INTRODUCTION

Coastal waters around the world have experienced high nutrient loading from urban centers and agricultural land for over a century (Diaz and Rosenberg 2008, Smith 2003). The negative impacts associated with high nutrient loading, eutrophication and particularly eutrophication induced hypoxia (Cloern 2001, Diaz 2001, Diaz and Rosenberg 2008, Gooday et al. 2009, Howarth et al. 2011, Kemp et al. 2005), were not recognized as marine water quality issues until 1969 when discussed in "Eutrophication: Causes, Consequences, Correctives" published by the U.S. National Academy of Sciences (Nixon 2009). Eutrophication can alter the characteristics and function of ecosystems (Boesch and Rabalais 1991, Elmgren 1989, Pearson and Rosenberg 1978, Rosenberg et al. 1990) including a shift from macro benthos primary production to pelagic phytoplankton as the dominant producers and reduced light penetration (Bonsdorff et al. 1997). The decomposition of excess phytoplankton can lead to hypoxia, which is known to be a stressor and lethal to many benthic and pelagic species (Diaz et al. 2004, Gray and Ying 2002, Pihl et al. 1991, Pihl et al. 1992).

Narragansett Bay is no exception to these issues. The Bay has experienced eutrophication and it's negative consequences for decades (Bergondo et al. 2005, Bonsdorff et al. 1997, Carpenter et al. 1998a, Codiga et al. 2009, Corrales and Maclean 1995, D'Avanzo et al. 1996, Deacutis 2008, Melrose et al. 2007, Nixon 1995). In response to concerns that hypoxia would continue to expand throughout Narragansett Bay, as well as a large fish kill in Greenwich Bay, the Rhode Island Department of Environmental Management has taken steps to

reduce nitrogen concentrations of point source (i.e. Wastewater Treatment Facility effluent) flowing into the Bay over the last decade. Point source nutrient reductions as well as implementation of more efficient fertilization techniques have become common practice in developed countries as awareness of marine eutrophication has expanded.

Estuaries are dynamic systems that do not always respond to nutrient reductions in the same way (Conley et al. 2009, Duarte et al. 2009, Kemp et al. 2009). The effects of climate change are evident in Narragansett Bay with an increase in water temperature by more than 1°C in the last 60 years (Smith et al. 2010). This increase in temperature has led to a reduction, and in many years, the elimination of the traditional winter-spring phytoplankton bloom in Narragansett Bay possibly due to increased grazing pressure (Oviatt et al. 2002, Smith et al. 2010). Nixon (2009) stressed a further reduction in nutrients to Narragansett Bay could reduce the winter-spring bloom to the point where minimal benthic-pelagic coupling occurred in the spring, reducing the regeneration of nutrients later in the season. This storage of nutrients in the benthos has traditionally been a source to producers later in the summer when the water column nutrients are depleted, and helps support the growth of secondary producers (Nixon et al. 2009). Given these complex relationships between the physical, chemical, and biological components of estuaries, understanding how primary production of Narragansett Bay responds to nitrogen reductions is critical to understanding the whole ecosystem, and to making informed decisions on the extent of nitrogen

reductions needed to reduce hypoxia without negatively effecting the growth of many commercial species.

The first response expected after nutrient reduction is a change in the production and respiration in a water body. Here we introduce a new carbon based method to estimate integrated daily metabolic rates. A method has been developed to estimate net daily primary productivity between dawn and dusk, and nighttime respiration rates between dusk and dawn. The technique utilizes *in situ* temperature, salinity and pH sensors throughout Narragansett Bay as well as measured alkalinity of water samples collected at the sensor sites.

The estimation of primary production and respiration in marine waters has been occurring for almost 100 years, with Gaarder and Gran (1927) performing the first oxygen 'light and dark bottle' incubations in the Oslo Fjord in 1916. This method has been employed by many researchers since then (Bender et al. 1987, Nixon and Oviatt 1972, Oviatt et al. 1981, Oviatt et al. 1986b, Smith 2011) and provided the first insight into how important phytoplankton and other marine primary producers are to an ecosystem. The oxygen light and dark bottle incubations are suitable in highly productive systems and can be used to estimate net and gross productivity as well as respiration.

While the oxygen light and dark bottle method works well for highly productive areas, where the productivity is very low, such as the open ocean, a change in oxygen during the incubation time is sometimes undetectable. As an alternative, a radioactive carbon (^{14}C) method was developed (Steeman Nielsen 1952) for use in the oligotrophic open ocean based on the uptake of ^{14}C to

quantify the phytoplankton primary production during incubation. The ^{14}C method can be used to detect smaller changes in primary productivity and has been used in hundreds of studies worldwide including estuarine studies (Kelly et al. 1985, Oviatt et al. 1986b, Oviatt 2008, Peterson 1980, Sampou and Oviatt 1991). In the ^{14}C method the water is filtered to remove large grazers prior to incubation. The resulting ^{14}C derived productivity measurement is an intermediate estimate between gross and net primary production (Bender et al. 1999, Ostrom et al. 2005). The oxygen light and dark bottle incubations and the ^{14}C incubations have several limitations, including eliminating the movement of plankton into and out of the mixed layer and grazing, and bottle effects including growth of bacteria on the bottle walls, silica from the glass bottles leaching into samples and provided a nutrient for diatoms, and lack of turbulence within the bottle thus relying fully on molecular diffusion for nutrients to reach cells (Marra 2009, Quay et al. 2010).

As an alternative to incubations, sampling open water over the dawn dusk dawn time period for consecutive days and measuring the oxygen concentration of the water with the Winkler titration method was employed to estimate primary productivity and respiration (Caffrey 2004, D'Avanzo et al. 1996, Nixon et al. 1976, Odum and Hoskin 1958, Oviatt et al. 1993, Oviatt et al. 1986a, Oviatt et al. 1986b, Sampou and Oviatt 1991, Vaudrey 2007). These studies were among the first to capture the effects of *in situ* processes on metabolic rates and would later become the framework for future *in situ* dawn dusk dawn studies (Middleton and Reeder 2003, Smith 2011). Oxygen respiration through grazing

and vertical mixing of cells throughout the water column were incorporated with the diel oxygen curve method and mesocosm experiments (Oviatt et al. 1986a, Oviatt et al. 1986b, Oviatt et al. 1987) removed the effects of advection on oxygen that are typically difficult to account for in open water *in situ* sampling regimes.

In addition to oxygen metabolic rates, chlorophyll *a* is often used to estimate net primary production in estuaries. Chlorophyll *a* fluorescence is measured either by extraction, *in situ* sensors, or satellite measurements and is often used as a proxy for biomass, although fluorescence of chlorophyll *a* per cell depends on size, species, and environmental conditions (Falkowski and Kiefer 1985). BZ_pI_o models were designed to estimate primary production using the relationship between chlorophyll *a* biomass (B), euphotic depth (Z_p) and irradiance (I_o), and the production estimated from ^{14}C incubations (Keller 1988). Once the relationship between the parameters is established, the productivity of the system can be estimated from chlorophyll *a* measurements and light intensity. BZ_pI_o models are often utilized in studies of eutrophic estuaries since these models perform best when the water column is light limited, where the euphotic depth is less than the overall depth (Brush and Brawley 2009, Brush 2002, Canion et al. 2013, Goebel et al. 2006, Smith 2011). This approach allows for water column integration to achieve a production in $gC\ m^{-2}day^{-1}$, but the relationships between the parameters are system specific and must be determined for each different ecosystem studied.

With rapidly changing technology, *in situ* sensors have become a frequent choice for measurement of physical, chemical, and biological parameters at high

temporal resolution. As part of the plan to reduce the flux of nitrogen into Narragansett Bay, the Rhode Island Department of Environmental Management collaborated with the University of Rhode Island's Graduate School of Oceanography (URI GSO), Narragansett Bay Commission (NBC) and the Narragansett Bay National Estuarine Research Reserve (NBNERR) to install a network of 13 buoys and land based sites that monitor *in situ* temperature, salinity, dissolved oxygen, pH and chlorophyll *a* at the surface and bottom of the water column. Four stations operate year round, while the other 9 operate May – October, all sites sample every 15 minutes. This dataset provides much improved temporal coverage compared to any of the previous sampling schemes.

Using these *in situ* data, Smith (2011) developed a Dawn Dusk Dawn Oxygen method (DDD-O_2) that calculated net primary production as the change between dawn and dusk *in situ* oxygen, and nighttime respiration as the change between dusk and the following dawn *in situ* oxygen. The DDD-O_2 method was verified using concurrent estimates of production from ^{14}C incubations, oxygen light and dark bottle incubations and a comparison with an *in situ* integrated 15-minute change in oxygen method (Smith 2011). The 15-minute method summed the change between each 15-minute oxygen reading between dawn and dusk for each day, and for dusk and the following dawn to estimate net production and respiration. A comparison between the DDD-O_2 method and a 15-minute integrated change in oxygen method indicated there was no statistical difference between the daily primary production estimated by either method, suggesting

that advection played a minor role in the metabolic rate estimates from the DDD-O_2 method (Smith 2011).

Oxygen in the mixed layer equilibrates with the atmosphere on daily time scales and thus a wind dependent air-sea gas exchange model for Narragansett Bay was used to correct for oxygen exchange in the DDD-O_2 method (Smith 2011). Since the parameters are measured *in situ*, grazing effects are implicit. The estimation of air–sea gas exchange by wind speed may not take into account the other forcings of gas transfer such as bubbles, energy dissipation, fetch, rain, or chemical enhancements (Wanninkhof et al. 2009). Additionally, the anemometers are not located at the standard 10 m height at either station. The gas exchange method accounts for this height discrepancy by using an equation from Vaudrey (2007) to standardize to a 10 m wind height. Smith (2011) quantified the effect of diffusion on metabolic rates by comparing the metabolic surface rates estimated with and without an air-sea gas exchange parameter. On average, the metabolic rates estimated with a diffusion parameter were 3.09% and 3.23% higher for Mt. View and Bullocks Reach (located 3 km northwest of Conimicut Point, in Providence River) than the metabolic rates estimated without an air-sea gas correction. There was no significant difference between the two sets of metabolic rates at the 5% level, on average.

Biomass is reported in units of carbon per volume, and thus a measurement of metabolic rates in oxygen must be converted to carbon using a photosynthetic quotient (PQ) and respiratory quotient (RQ). Smith et al. (2012)

derived a PQ for Narragansett Bay taking into account species composition, distribution and nutrient composition changes in recent years.

Anaerobic respiration has been observed in Narragansett Bay bottom waters for decades (Doering et al. 1987, Nowicki 1994, Sampou and Oviatt 1991, Seitzinger et al. 1980). More recently, focus on denitrification in estuaries has increased (Ehrlich 2014, Fulweiler et al. 2010, Fulweiler et al. 2007, Fulweiler et al. 2013, Herbert 1999). Denitrification utilizes nitrate (NO_3^-) as the terminal electron acceptor when oxygen is not present and is observed in hypoxic and anoxic waters. The DDD-O_2 oxygen method does not capture remineralization of organic matter to carbon dioxide through denitrification since the process has no effect on dissolved oxygen concentrations. If anaerobic respiration were a significant contributor to remineralization, the DDD-C method would include this fraction as part of the total respiration rate.

We compared the DDD-O_2 method to a Dawn Dusk Dawn Carbon (DDD-C) method. The advantages of the DDD-C method were the elimination of the need for an air-sea gas exchange coefficient to estimate diffusion, and the estimate of a PQ and RQ to convert units from oxygen to carbon. As with the oxygen method, the *in situ* sensors provide un-paralleled temporal coverage and suitable spatial coverage of Narragansett Bay. The comparison of the DDD-C method and the DDD-O_2 method enabled estimations of time and site specific PQ and RQ values for Narragansett Bay.

Several questions addressed in this manuscript include, are metabolic rate estimates from the DDD-C method comparable with the estimates from the DDD-

O_2 method? Can the DDD-C method be used to detect a change over time in metabolic rates in Narragansett Bay due to nitrogen reduction? Are the YSI pH sensors adequately precise and accurate for use in the DDD-C method? Is bi-weekly alkalinity sampling sufficient to capture variation in alkalinity within Narragansett Bay and what effect does a change in alkalinity have on estimates of metabolic rates? How do the calculated photosynthetic and respiratory quotients compare with the ones estimated by Smith (2012) for Narragansett Bay? Is advection altering our estimates of metabolic rates for Narragansett Bay?

METHODS

This study evaluated an *in situ* carbon method to estimate daily metabolic rates in Narragansett Bay, Rhode Island. Metabolic rates were determined by measurements of rates of dissolved carbon dioxides changes based on temperature, salinity, pH and alkalinity. A change in the carbon dioxide concentration in water was reflected in the pH of the water. Since carbon dioxide was removed from water during photosynthesis and released during respiration, changes in pH can be used to estimate changes in fixed carbon. The method estimated daily net productivity, or system apparent production, using the difference in carbon dioxide between dusk and dawn and system night respiration as the difference between dawn and the previous dusk, both estimates were converted to grams of carbon, to provide an integrated estimate of daily system metabolic rates per unit volume.

Two sets of measurements were gathered during this study to assess daily rates of carbon change: dawn and dusk data for temperature, salinity, and pH from nine of the Narragansett Bay Fixed Site Monitoring Network (NBFSMN) stations and bi-weekly sampling of alkalinity at the NBFSMN sites (Figure 1).

Monitoring site procedures

The NBFSMN sites were equipped with two Yellow Spring Incorporated (YSI) 6600 series data loggers, one at 1m below surface and the other 0.5m above the bottom. Each surface data logger recorded temperature, salinity, dissolved oxygen (DO), pH, Chlorophyll *a* fluorescence and depth every 15 minutes. The bottom data logger recorded temperature, salinity, dissolved oxygen (DO), pH, and depth every 15 minutes. GSO Dock site had only one data logger at 1 – 2 m below the surface depending on tide. The manufacturer published accuracy for the pH sensor was ± 0.2 units and the resolution was 0.01, however the sensors were calibrated and post calibrated in the lab and corrected for drift over the two-week deployment. The accuracy of the temperature sensors was ± 0.15°C with a resolution of 0.01°C. The accuracy of the specific conductivity sensors was ± 0.5% of reading + 0.001 mSiemens cm^{-1} and the resolution was 0.01 mSiemens cm^{-1}. Fifty mSiemens cm^{-1} is roughly equal to 32.8 ppt at 25°C (the instrument performs an internal calibration to calculate exact salinity).

Each station was serviced every two weeks by swapping the existing data logger with a newly calibrated data logger. Instruments were calibrated and maintained with quality control measures in the laboratory, field, and post deployment. The pH sensor was calibrated using two pH buffers, pH 7 and pH 10.

Salinity was calibrated using a specific conductivity solution of 50 µSiemens cm^{-1}. The sensors were post calibrated using the same solutions to quantify drift over the two-week period.

The data were reviewed, corrected, and documented before distribution in accordance to the NBFSMN QAPP (RIDEM 2014). Quality assurance measures include verification of calibrations and consistency among multiple instruments, corrections for sensor drift and biases due to biofouling, removal of outliers, and interpolation across selected intervals of missing data (RIDEM 2014). Calibrations and sensor drift corrections were verified through a three-point comparison: data from the retrieved sonde were compared to the newly calibrated sonde, as well as an independent profiling sonde, at the deployment depth. Outliers were removed based on exceeding two standard deviations or the 95th percentile, using monthly data for each station, in conjunction with inconsistencies in other parameters (RIDEM 2014). Any data removed for QA/QC reasons were documented in the metadata documentation accompanying the data products (Rhode Island Department of Environmental Management 2013, Rhode Island Department of Environmental Management 2014).

Alkalinity samples

Water samples were collected every two weeks at the same time as the instrument swap from the 9 stations in the study from July 2013 – September 2013 and June 2014 – September 2014. Water was collected using a Niskin bottle from 1 m below the surface and 0.5 m above the bottom (same depths as data loggers). A 250 ml dark Nalgene bottle was triple rinsed using site water and then

filled from the bottom using tubing and allowed to overflow by 1 volume. Samples were kept in a cooler on ice until returned to laboratory and kept in a refrigerator at 1.5°C for up to 24 hours until analysis.

In the laboratory, alkalinity was determined by potentiometric titration using a Metrohm Titrino Plus titrator (Model number 877). The pH electrode was calibrated daily using individual pH buffers 4, 7, and 10 in a jacketed beaker to maintain a constant temperature of 25°C. Weighed samples were titrated by adding 0.1ml of acid at a time to the sample to an end point of pH 2.9 in the jacketed beaker at 25°C. Certified Referenced Materials (CRMs) from the Dickson Laboratory at the Scripps Institution of Oceanography were titrated as a check. The average error of all of the CRMs titrations was ± 113 μmol kg^{-1} or approximately 5% of the reading. The acid used for titration was 0.1M HCl that had been standardized using TRIS to determine the exact concentration of the acid. The density is also calculated and used to calculate the total alkalinity. All alkalinity calculations and analysis performed using R 3.0.1 (R 2013) using the 'AT' function in the SeaCarb Package. The package was written by Andrew Dickson and uses the Non-linear least squared method described in Dickson et al. (2007).

Dawn dusk dawn metabolic rate estimation by a carbon method

From the 15 minutes buoy measurements, temperature, salinity, and pH, closest to the sunrise and sunset times are identified each day. The dissolved inorganic carbon (DIC) concentration at dawn and dusk were calculated using *in situ* temperature, salinity, pH, and measured alkalinity and the dissolved

carbonate system disassociation constant equations in Pilson (2013) and the carbon dioxide equation from Oviatt (1986b) (Table 1). The estimation of changes in fixed carbon were made (gC m^{-3} day^{-1} or gC m^{-3} $night^{-1}$), using the change in DIC converted to moles of carbon. See Appendix A for the method.

The rate that carbon dioxide equilibrates with the atmosphere is much slower than oxygen (Williams and Follows 2011), thus over the time period being sampled (dawn dusk dawn), the flux into or out of the mixed layer is negligible.

The timescales of air-sea equilibrium were estimated using the equations from Williams and Follows (2011). For a non –reactive gas (dissolved oxygen), the timescale to equilibrium is estimated by:

$$\tau = \frac{h}{K_g} \tag{1}$$

where τ is the time in seconds it takes to reach equilibrium, h is the depth of the mixed layer, and Kg is the gas transfer velocity as a function of wind speed.

For a reactive gas, such as carbon dioxide:

$$\tau = \frac{h}{K_g}\frac{DIC}{B[CO_2^*]} \tag{2}$$

where DIC is the concentration of all carbonate species (CO_2 aq, HCO_3^-, CO_3^{2-}), [CO_2*] is the concentration of CO_3^{2-}, and B is the Revelle buffer factor, defined as:

$$B = (\frac{\eth[CO_2^*]}{[CO_2^*]})/(\frac{\eth DIC}{DIC}) \tag{3}$$

The average DIC, $[CO_2^*]$, and B parameters were determined using all pH and alkalinity data used in the study and the CO2SYS.m function in Matlab v. R2013a

(MathWorks 2013). The mixed layer depth was determined throughout Narragansett Bay using temperature, conductivity, and depth (CTD) profiles. These profiles were collected twice monthly during the summers 2005 – 2013 at 30 stations throughout upper Narragansett Bay. Wind data for 2007 – 2014 were taken from the National Buoy Data Center, NOAA (http://www.ndbc.noaa.gov/) for the Quonset Point and Conimicut Point stations. A wind speed reading was taken every 6 minutes at each station and averaged over all summers to estimate an average summer wind speed on Narragansett Bay. An exchange coefficient of 10^{-5} m s^{-1} was estimated using an average wind speed of 4.56 m s^{-1} (Williams and Follows 2011). The time to equilibration for dissolved oxygen in Narragansett Bay using a mixed layer of 3.0 m and the exchange coefficient of 10^{-5} m s^{-1}, is approximately 3.5 days.

The time to equilibration for carbon dioxide in Narragansett Bay was estimated using the same parameters above, and DIC = 1750 µmol kg^{-1}, [CO_2^*] = 14.93 µmol kg^{-1}, and a Revelle factor (B) = 13.8, on average. Carbon dioxide would equilibrate with the atmosphere in 29.5 days if no conditions changed, indicating that the diffusion between the dawn dusk dawn time periods is negligible and can be excluded from the model.

The DDD-C method was executed using MatLab v. R2013a (MathWorks 2013). There were 3 input files used in the method script:

1) 15-minute temperature, salinity and pH data for each of the 9 stations, from which the dawn and dusk readings were selected. Sites were run individually.

2) Sunrise and Sunset time data were downloaded from http://www.timeanddate.com/worldclock/astronomy.html?n=263 for Providence, Rhode Island. One file per year.
3) The alkalinity data were from samples measured every two weeks, surface and bottom. The measurement was applied to a week prior to sampling and a week after sampling.

Method comparison

The DDD-O_2 method for estimating metabolic rates by in situ changes in oxygen (taking into account air sea gas exchange) (Appendix B, C) has been has been compared to ^{14}C measurements of primary production, oxygen light and dark bottom estimates of net primary production and respiration rates, and a 15-minute integrated change in oxygen method (Smith 2011). The DDD-O_2 method (Appendix B) will be used to compare the metabolic rate estimates from the DDD-C method.

The metabolic rates calculated using the DDD-O_2 method were converted from $gO_2\ m^{-3}day^{-1}$ to $gC\ m^{-3}day^{-1}$ by a photosynthetic quotient (PQ) and respiratory quotient (RQ). The PQ and RQ were calculated using the average of each site for a given category (surface production, surface respiration, bottom production, bottom respiration) and year. The PQ is defined as the moles of oxygen produced per mole of carbon uptake.

$$PQ = \Delta \{O_2\} / \Delta \{DIC\} \quad (4)$$

The RQ is the opposite, the moles of oxygen consumed per mole of remineralized carbon.

$$RQ = \Delta \{DIC\} / \Delta \{O_2\} \quad (5)$$

The average PQ and RQ for all sites combine, differentiated by year and category, were used to convert the oxygen metabolic rates to carbon metabolic rates.

Alkalinity sample collection began late in summer 2013 (July 24th, 2013). The first sampling occurred on July 11th, however the methods changed between this first round and the July 24th sampling, thus the first set of data were discarded.

The metabolic rate dataset estimated from the DDD-C method presented here includes July 20th, 2013 – Sept 30th, 2013, and June 1st, 2014 – Sept 30th, 2014. The DDD-O_2 method metabolic rate estimates have been calculated for the same time periods.

A Reduced Major Axis regression and correlation test (Markovsky and Van Huffel 2007)was used to compare the metabolic rates estimated by the DDD-C and DDD-O_2 methods. The metabolic rate comparisons were separated into eight different datasets, surface productivity, surface respiration, bottom productivity, and bottom respiration for both 2013 and 2014 summers with all sites combine. The two methods have also been compared using a t test for each of the 4 comparison categories for each summer, as well as each site comparisons for both summers.

Error estimation – pH measurements

A pH stability analysis was conducted to ensure that the 15-minute pH readings from the buoy sensors were stable. The mean absolute differences between 15-minute readings were calculated for all sites and both summers.

The manufacturer stated accuracy of the pH sensor was 0.2 units. A sensitivity analysis was performed to quantify the impact on calculated metabolic rates of systematically changing the pH values by ± 0.2 units from the measured value. The analysis was performed on a subset of the main dataset using data from Conimicut Point, North Prudence, Mt. View, Quonset Point, and GSO dock from July 20th – September 30th, 2013. The percent change between the measured pH and the pH + 0.2 units, and the measured pH and the pH – 0.2 units has been calculated. For each of the 5 sites, a one-way Analysis of Variance (ANOVA) was performed to conclude if there was a difference between the metabolic rates estimated from the original pH, and the pH offset by either ± 0.2 units. For the ANOVA, the pH category (measured, plus 0.2 units, or minus 0.2units) was the grouping factor and the resulting metabolic rates were the dependent variable.

In order to validate the sensitivity the YSI pH sensors, a Satlantic SeaFET pH sensor with accuracy of 0.02 pH units and resolution of 0.001 pH units, when deployed in water between 0 – 50°C and a salinity of 20-38ppt, had been deployed for 4 days during late December 2014 in a 3 m diameter by 2.5 m deep round tank with a constant flow of water exchanging from the GSO pier. The two instruments were also deployed at the Greenwich Bay site for two weeks in April 2015, and at Conimicut Point for May 28th- June 12th, 2015 and June 16th – July 10th, 2015. Different individual YSI pH sensors were used for each deployment, since at any given time 17 different sensors are being used during the summer. There is a duplicate set to allow for a seamless swap of instruments, leading to at least 34 different pH sensors used throughout a summer. The comparison

between the two sensors will indicate whether there was an offset between the SeaFET and the YSI pH sensors.

Error estimation–alkalinity measurements

In order to determine whether bi-weekly alkalinity sampling provided sufficient resolution of the alkalinity in Narragansett Bay, an alkalinity frequency test was performed. From January 6th, 2015 – February 9th, 2015, alkalinity samples were collected every 3-4 days at the GSO dock. The range of alkalinity observed during this time period was comparable to typical values in Narragansett Bay. The alkalinity used in the sensitivity analysis ranged from 1798 to 2293 μmol kg^{-1}, with an average of 1987 μmol kg^{-1} for the twice-weekly alkalinity dataset. The bi-weekly dataset ranged from 1967 to 2096 μmol kg^{-1} with and average of 2026 μmol kg^{-1}. Three sets of metabolic rate estimates were calculated using buoy data from Conimicut Point and Quonset Point for July 1st, 2014 – August 9th, 2014 and alkalinity data with 3 different sampling frequencies: bi-weekly, weekly, and twice weekly. For the alkalinity sensitivity analysis, the percent change between all three (pairwise comparisons) estimates of metabolic rates was calculated. The normality of the data was testing using a Shapiro-Wilk test and both a one-way Analysis of Variance (ANOVA) and a Kruskal-Wallis test were conducted using R with alkalinity sampling frequency as the grouping factor and metabolic rates as the dependent variable.

Hydrodynamics at North Prudence

An Acoustic Doppler Current Profiler (ADCP) was deployed near the North Prudence buoy June 19th – Oct 10th, 2006 (Rogers 2008). Using the mean tidal

currents from this dataset, the impact of advection was examined by estimating if a water mass at one site could reach another site's sensors, taking into account magnitude and direction, in one tidal cycle. Due to the location of the ADCP, interactions between North Prudence and the three closest sites were considered (Conimicut Point, Poppasquash Point, Mt. View).

Alkalinity relationship with salinity in Narragansett Bay

A preliminary equation for total alkalinity calculated from salinity was investigated for summer 2013 and summer 2014. Future work includes a more detailed examination of the data and the mechanisms that drive change in alkalinity within the Bay.

Euphotic Depth

Light profiles were taken at every station at the same time as the sonde swap and alkalinity sample collection. Profiles were conducted using a Li-Cor light meter, with a hand held (model LI-250A), deck sensor (model LI-190R), and a spherical underwater sensor (model LI-193). Light was taken every meter at sites over 3.0 m deep, and every 0.5 m at sites with depths less than 3.0 m (Greenwich Bay, GSO Dock). Light readings were recorded both on the down cast and on the up cast, the light extinction and euphotic depth, defined as the depth at which 1% of the surface light reaches, was determined using the cast with the most consistent light (fewest passing clouds).

RESULTS

Method comparison

The DDD-C method estimates of metabolic rates were highly correlated to the estimates from the DDD-O_2 method (Smith 2011), with correlations ranging from 0.69 for 2013 bottom production, to 0.96 for 2014 bottom respiration (Table 2). For all four comparison categories, 2014 estimates of metabolic rates were more highly correlated than the 2013 estimates (Figures 2, 3). Greenwich Bay and Conimicut Point had the highest range of variability in their metabolic rates, and were the least correlated (Figure 4, Appendix D). Students t tests indicated that for all categories in 2013, the means of the metabolic rates from the DDD-C and the DDD-O_2 methods (oxygen converted to carbon) were significantly different from each other, whereas in 2014 only bottom respiration had significantly different means of metabolic rates between the two methods (Table 3).

Photosynthetic and respiratory quotient

The photosynthetic quotients calculated from the comparison of the two methods were within an acceptable range of values, 1.07 – 1.40. The average surface PQ for all sites for 2013 was 1.4 ± 0.23, the same as estimated by Smith et al. (2012), and the PQ was 1.22 ± 0.09 on average for all sites for 2014, the bottom PQs were 1.07 ± 0.33 and 1.29 ± 0.17 for 2013 and 2014 respectively (Table 4). The average 2013 surface RQ was smaller than the 2013 bottom RQ, (0.72 and 0.84, respectively), however the opposite was true in 2014, 0.79 and 0.72 for surface and bottom, respectively (Table 4), but all RQs were less than 1,

the value often used in estuarine studies (Caffrey 2004, Collins et al. 2013, Oviatt et al. 1986b).

pH stability, accuracy and sensitivity analyses

The pH sensors took a reading every 15 minutes and although only the dawn and dusk measurements are used for this method, the 15-minute readings were analyzed to determine if the pH sensor had high precision. The pH stability analysis indicated that the YSI pH sensor readings over the dawn dusk dawn time period were stable between 15-minute intervals. The mean absolute value difference between 15-minutes readings of the YSI pH sensors ranged between 0.01 – 0.02 pH units for the mean of all stations except Greenwich bay (Table 5). For both years, Greenwich Bay had higher variability between readings than the other sites with means ranging between 0.03 – 0.04 pH units, although the overall metabolic rates at the Greenwich Bay site were on average twice that of the other stations. Most importantly, the change in pH between 15-minute readings was in the direction consistent with productivity during the daytime and respiration during nighttime (pH increases during productivity and decreases during respiration), indicating that any change between dawn and dusk was likely a true change in pH and not an error in the sensor.

For each category (surface production, surface respiration, bottom production and bottom respiration) and each of the 5 sites used in the analysis, metabolic rates were estimated with the measured pH, and with systematic offsets of ± 0.2 pH units, to create three separate sets of metabolic rate estimates. The pH sensitivity analysis conducted on five sites of data showed that the

average percent change in calculated metabolic rates for all sites when the surface pH was increased by 0.2 pH units was 23% and 20% for production and respiration, respectively. The average percent change in metabolic rates when the surface pH was decreased by 0.2 pH units for all sites was a decrease in metabolic rates by 9% to 11% for production and respiration, respectively (Table 6). The bottom estimates of metabolic rates were increased by 10-11% on average for production and 8% for bottom respiration (Table 6). The timeline graphs of Conimicut Point for all four categories indicated that the higher magnitude metabolic rate estimates (more positive for production and more negative for respiration) were accentuated by the change in pH (Figure 5). The other 4 sites show a similar trend (Appendix D).

A one-way ANOVA for each category/site combination indicated that there was no significant difference in the means of metabolic rate estimates between the three datasets at the 5% level, on average. The only exception was Conimicut Point surface respiration, where the mean of the estimates from the pH – 0.2 dataset was significantly different from the estimates from the pH + 0.2 units dataset, however neither of the means from the offset pH datasets were significantly different from the estimates from the measured pH metabolic rates, determined using Tukey's Honest Significant Difference test (Table 7).

Production and respiration rates estimated with the DDD-C method were not constant throughout the Bay (Table 8). Conimicut point was the most variable and productive site out of the five sites used in the pH sensitivity analysis, thus the increase or decrease in pH at this site resulted in a greater

change in total fixed carbon rates at this site compared to the others. The mean summer daily surface productivity at Conimicut Point for 2013 is 0.33 gC $m^{-3}day^{-1}$, with a possible range based on ± 0.2 of 0.29 – 0.41 gC $m^{-3}day^{-1}$. In contrast, the mean summer daily surface productivity at North Prudence is 0.11 gC $m^{-3}day^{-1}$ with a possible range of 0.10 – 0.13 gC $m^{-3}day^{-1}$ (Table 9).

The YSI pH sensor accuracy was compared with a Satlantic SeaFET pH sensor with an accuracy of 0.02 units. The comparison between the SeaFET pH sensor and the YSI pH sensor during a 4-day tank deployment showed that there was a consistent offset of 0.03 pH units with YSI reading higher, when the pH ranged between 8.14 – 8.24 units (Figure 6a). The second SeaFET deployment occurred at the Greenwich Bay site from March 31st, 2015 – April 9th, 2015. There was not a linear offset between the two sensors and the range of pH measured by the YSI was 8.27 – 8.42 units, whereas the range measured by the SeaFET was 8.20 – 8.52 units (Figure 6b). The SeaFET was deployed along side a YSI sonde at Conimicut Point site from May 28th – June 12th, 2015, and again June 16th – July 10th. The first Conimicut Point deployment showed a predominant linear trend, with YSI pH sensor reading lower in most cases, with an offset of 0.05 on average (Figure 6c). The second Conimicut Point deployment data showed two distinct patterns. From the beginning of the deployment to 5 days, the YSI and SeaFET were reading the same values (Figure 6d, 7), however at that point a bloom occurred and the SeaFET sensor began to foul, introducing drift into the readings, resulting in a slow decline in overall pH by 0.3 units (Figure 7). The YSI sensors have a wiper that cleans the surface of each sensor every 15 minutes, reducing

fouling. The post-calibration of the YSI sensor indicated that over the 3-week deployment in June-July, the sensor had drifted 0.05 units.

Alkalinity sensitivity

To test the calculated metabolic rates sensitivity to alkalinity, three different alkalinity datasets were used. From the original dataset collected in January – February 2015, 3 values were chosen that were sampled two weeks apart each to comprise the biweekly alkalinity dataset. Alkalinity samples that were sampled a week apart (5 total) comprised the weekly dataset and the twice weekly alkalinity dataset contained all 9 values sampled during that time period. The increase in sampling frequency, and increased range of alkalinity values, had almost no effect on the resulting metabolic rates at either Conimicut Point or Quonset Point. For all 4 comparison categories, and 3 sets of metabolic rate estimates, the metabolic rates on average only changed by 2 – 8% (Table 10). For Conimicut Point and Quonset Point surface production, the timeline comparisons indicate that the estimates of metabolic rates based on each alkalinity dataset are very close (Figure 8, Appendix D). The metabolic rates estimated from the three sets of alkalinity were not all normal according to the Shapiro-Wilk test, but were not bimodal or skewed in one direction. Both the ANOVA and the Kruskal-Wallis tests indicated that the means of the three sets of metabolic rates, calculated from different alkalinity datasets were not significantly different from each other at the 5% level for each of the 4 categories, with all p values greater than 0.99 (Table 11).

Alkalinity and salinity relationship

Using an ordinary least squares regression, there was no relationship between measured alkalinity and salinity for the all combine data. However, when separated by year, there was a significant relationship ($p = 0.01$, at 5% level) between the two for 2013, but not for 2014 (Figure 9). The preliminary equation for 2013 was:

$y = 39.73x + 645.7$, $r^2 = 0.21$, $r = 0.46$

The equation for 2014:

$y = -11.11x + 2318.52$, $r^2 = 0.01$, $r = -0.09$

where x was salinity and y was measured alkalinity for both equations.

Spatial trends in metabolic rates

There was a north south gradient in metabolic rates from Conimicut Point to GSO Dock in 2013, ranging from 0.33 – 0.12 gC $m^{-3}day^{-1}$, with the exception of North Prudence. The average daily surface production at North Prudence in 2013 was the lowest of all stations with a daily average of 0.11 gC $m^{-3}day^{-1}$ (Table 8, Figure 10). In 2014, the trend was the same as in 2013 except GSO Dock had higher metabolic rates than Quonset Point. North Prudence and Quonset Point both had 0.16 gC $m^{-3}day^{-1}$ surface production and 0.16 gC $m^{-3}night^{-1}$ surface respiration and were the lowest of all the stations in 2014 (Table 8, Figure 10). The Greenwich Bay site had the largest system apparent production and nighttime respiration, and the highest variability, of all nine study sites for both summers. Conimicut Point was the next most productive, higher than Sally Rock, which is located within Greenwich Bay. Conimicut Point, Greenwich Bay, and

Sally Rock regularly have the highest number of hypoxic days of the nine sites (Table 12). For all sites, the metabolic rates were variable, and do not show blooms occurring throughout the summer.

The bottom respiration rates do not followed the same gradient trends, with both Conimicut Point and North Prudence exhibiting the second and third lowest bottom respiration rates for both summers. In contrast, Greenwich Bay has the highest metabolic rates for surface and bottom, both years. The bottom production and respiration at Greenwich Bay both years, is 3 – 5 times higher than any other site (Table 8, Appendix D). The oxygen converted to carbon metabolic rates showed the same trends as the carbon metabolic rates (Table 13, Figure 11).

Despite that net production and respiration rates were higher in 2014 than in 2013, the *in situ* chlorophyll *a* fluorescence sensors indicated a drop of 5 $\mu g\ l^{-1}$ in average chlorophyll *a* at Conimicut Point, and a reduction of 9.5 $\mu g\ l^{-1}$ at the North Prudence site. Average chlorophyll *a* concentrations varied by less than 1 $\mu g\ l^{-1}$ at the 3 lower bay stations in the West Passage between summer 2013 and 2014. The euphotic depth increased from summer 2013 to 2014 on average 38% at all sites except GSO Dock and Mt. Hope where it decreased by 1 and 2% respectively (Table 14). In summer 2013, the estimated euphotic depth at 5 of the sites was deeper than the average depth of the site, allowing for bottom production to occur. In summer 2014, all sites except North Prudence (the deepest site) had estimated euphotic depths greater than the average depth of the site.

Hydrodynamics at North Prudence

Acoustic Doppler Current Profile (ADCP) data from the North Prudence site (Rogers 2008) indicated that mean spring tide surface velocities are 0.5 m s^{-1} on average flowing to the northeast during a flood and to the southwest during ebb. Mean tides are 0.3 m s^{-1} on average flowing to the northeast and 0.2 m s^{-1} to the southwest (Figure 12). Based on the distance between each of the three surrounding stations (4.21 – 4.73 km), it is possible that water exchange is occurring between North Prudence, Poppasquash Point, and Mt. View during all tidal cycles. With direction of flow considered, it is not likely that water would exchange between Conimicut Point from North Prudence (Figure 12), since Conimicut Point is close to due north from North Prudence. An additional possibility for the anomalously low metabolic rates observed in the North Prudence surface waters may be mixing of lower productivity bottom water. In 2006, several cruises near the North Prudence site used a towable instrument that measured temperature, salinity, and current velocity and observed "chimneys" of uniformly mixed water from surface to bottom, surrounded by a stratified water column (Ullman , personal communication).

DISCUSSION

Method comparison

While the two models for oxygen and carbon production and respiration were highly correlated in both summers, it is interesting that in each category, they were more highly correlated in summer 2014 than summer 2013 (Table 2,

Figures 2,3). One possibility as to why this occurred is a difference in the water quality between the two summers. Summer 2013 was more hypoxic than average for Narragansett Bay, while 2014 was very below average for number of hypoxic days (Table 12), with the exception of Greenwich Bay and Sally Rock which exceeded or equaled the average number of hypoxic days. When the water is hypoxic, anaerobic respiration may be the primary remineralization process. In this case, the respiration would be reflected in the DDD-C method but not the DDD-O_2 method. However, for seven out of the nine sites, the oxygen converted to carbon respiration rates were higher in 2013 than the carbon respiration rates, although in most cases the difference was 0.01 $gCm^{-3}night^{-1}$ (Table 8, 13). There is not a large difference in the bottom respiration between the two methods that could be attributable to anaerobic respiration, and this is likely not the cause for higher correlations between the metabolic rate estimates in summer 2014.

One-way ANOVAs indicated that for 2013, the estimates of metabolic rates from the DDD-O_2 and DDD-C methods were significantly different at the 5% level from each other for all categories of surface production, surface respiration, bottom production and bottom respiration (Table 3). In 2014, only bottom respiration means were significantly different from each other. Interestingly, the bottom respiration had the highest correlation between the two methods out of any of the categories or summers. These differences are likely to be a result of the PQ and RQ used to convert the oxygen metabolic rates to carbon metabolic rates. In 2013, the average quotient for each of the 4 categories had a larger standard deviation than the average quotient calculated for each category in 2014 (Table

4). The average PQ and average RQ of all sites was used to convert all of the oxygen production and respiration rates to carbon metabolic rates. In 2013, the between site quotient variability was higher than in 2014, thus the average quotient was less representative of all of the sites in 2013 (Table 4), leading to a difference in metabolic rate means between the two methods for 2013, and not 2014.

The 2014 bottom respiration difference in means may also be an artifact of the respiratory quotient used. The RQ used to convert oxygen respiration rates to carbon respiration rates was 0.72 ± 0.24 with one outlier (Poppasquash Point) removed (Table 4). The average RQ without Poppasquash Point removed was 0.58, which led to an even greater difference between the means of the two methods when used to convert from oxygen to carbon. Conimicut Point and North Prudence both had low Bottom RQs for 2014, 0.51 and 0.53, respectively (Table 4). These were not removed from the dataset since they did not fall outside of two standard deviations from the averaged data, however, they are much lower than the other sites, and may have artificially lowered the average bottom RQ for 2014, leading to statistically different means between the two methods.

Although the means in 2013 and bottom respiration in 2014 were statistically different, they were not ecologically different (Table 3).

Photosynthetic and respiratory quotient

The photosynthetic quotient for 2013 surface production, 1.4 ± 0.23, was the same as the PQ derived for Narragansett Bay by Smith et al. (2012). For the

2014 surface production, the PQ was estimated to be 1.22 (Table 4), close to the PQ estimated for Narragansett Bay by Oviatt et al. (1986a, 1986b) of 1.24. The ammonia levels in the Bay were higher in 2014 than in 2013 (Oviatt Personal Communication), but not as high as the ammonia concentrations in the Bay during the 1980's mesocosm experiments (Oviatt et al. 1986a). Smith (2012) attributed the shift in PQ between the 1980's to the present to a shift in the dominant nitrogen species in the Bay. In the 1980's ammonia was the main source of nitrogen to phytoplankton in Narragansett Bay. However, after wastewater treatment facility upgrades, the primary source of nitrogen shifted to nitrate, which increases the PQ. A shift in PQ from 1.4 in summer 2013 to 1.22 in summer 2014 was more likely strictly a function of inter-annual variability of estimated metabolic rates over the course of two summers than a reflection of the change in nitrogen species concentrations present in the Bay. Several more years of data will allow for a more representative mean to be computed for a Bay wide estimate of a PQ. The respiratory quotients (RQ) estimated with the method comparison had a range of 0.72 – 0.84, and the PQs had a range of 1.07 – 1.4, indicating that production and respiration rates were roughly equal throughout the Bay (Table 3).

pH stability, accuracy and sensitivity analyses

A large concern of this study was whether the manufacturer stated accuracy of the YSI sensor (0.2 units) was acceptable for use in carbon metabolic rate method for Narragansett Bay. The pH stability analysis indicated that the YSI sensor was stable over the dawn dusk dawn period, it was not changing

erratically (Table 5) and was therefore acceptable for use in this method. The Greenwich Bay site had the highest average surface and bottom daily estimates of production and respiration rates for both summers (Table 8), two times greater than all sites except Conimicut Point. The larger variability between 15 minutes readings (Table 5) could be due to the high productivity and respiration occurring at the site, since the variation increased by roughly two fold.

In order to quantify how much effect a systematic offset of ± 0.2 pH units in the sensor would have on the estimates of metabolic rates, a pH sensitivity analysis was conducted. In all cases, increasing the pH by 0.2 units had a larger impact than decreasing the pH by 0.2 units (Table 6, Figure 5). This is due to the carbonate species buffering system, at a higher baseline pH more metabolism must occur to change the buffered pH by 0.2 units than would have to occur at lower pH values. The percent change varied by site, with surface values at all sites being more affected by varied pH than the bottom metabolic rate estimates. The sensitivity analysis showed that, at worst, the surface production estimates could be off by -10 – 23%, with all other estimates of metabolic rates affected by -11 – 11% (Table 6). At higher productivity sites such as Conimicut Point and Greenwich Bay this translates into a potential difference in metabolic rates of up to 0.08 gC $m^3 day^{-1}$ (Table 9).

Despite these relatively high percent changes between the metabolic rates estimated from the measured pH and the offset pH, the one-way ANOVAs computed for the pH sensitivity analysis indicated that for surface production, surface respiration, bottom production, and bottom respiration, for all sites, the

metabolic rates estimated with pH ± 0.2 units was not significantly different than the metabolic rates estimated from the measured pH, at the 5% level. Although the means are not significantly different from one another, a difference in surface production based on a possible error in the pH measurements should not be over looked. Surface respiration, bottom production and respiration are only marginally effected by an ± 0.2 unit offset in pH and detection of a decrease in metabolic rates should still be possible.

The Satlantic SeaFET pH sensor was employed specifically to answer the question of the YSI pH sensor accuracy. The four deployments had different environmental conditions and all four comparisons had different results. In a tank comparison, with high flow water, the relationship between the two sensors was linear (Figure 6a), whereas in Greenwich Bay, there was not a linear relationship present (Figure 6b). When the sensor was deployed at Conimicut Point during the summer, the first deployment showed a linear comparison, with the YSI reading 0.05 units lower than the SeaFET on average (Figure 6c). The two sensors reported the same pH values for the first part of the second deployment, but fouling caused the SeaFET sensor to drift over the rest of the deployment (Figure 6d, 7). The temperature and flow regimes were different for each of the four comparisons. The Greenwich Bay monitoring site is located on a dock on the inside of a boat slip at a marina, with the other side of the dock open to Greenwich Bay. Inner Greenwich Bay, where the monitoring site was located, had a tidal velocity on average of 0.046 m/s (Abdelrhman 2005, Balt et al. 2010), compared to an average of 0.5 m/s for the West Passage of Narragansett Bay

(Rogers 2008). When the sensors were deployed in higher flow waters (Conimicut Point and the head tank), the two sensors were linearly related, with small offsets of 0.03 and 0.05 units. In the last deployment at Conimicut Point, despite the downward trend in the SeaFET sensor, the pH readings mirrored the YSI pH readings throughout the whole deployment (Figure 7), indicating that the YSI is measuring the small changes in pH on hourly and daily time scales. Based on the YSI post calibration data, the sensor drifted by 0.05 units over the three week deployment. The summer averaged maximum daily change in pH at all sites ranges from 0.23 - 0.50 units (Table 15), well above the offsets observed in the pH sensor comparisons. Since the sensitivity analysis indicated that an offset of ± 0.2 units did not significantly change the metabolism estimates, the offsets observed would have minimal effect on the metabolic rate estimates; the YSI pH sensor is appropriate for use in estimating metabolic rates in Narragansett Bay. If nutrient reductions decrease metabolic rates in Narragansett Bay leading to a more oligotrophic system, the YSI sensors may no longer be suitable for use at the lower bay stations where production is already reduced compared to the upper bay stations since the true variance in pH may be within the error of the sensor.

Alkalinity sensitivity

One assumption of the study was that bi-weekly alkalinity sampling would be sufficient to capture the variability of the alkalinity in Narragansett Bay. An alkalinity sensitivity analysis revealed that the variance in alkalinity throughout the bay has little effect on the metabolic rate estimates. Despite the much higher

range captured in the twice-weekly alkalinity sampling, the three sets of metabolic rate estimates only varied by 2 – 8 % on average over the 40 day test period (Figure 8). The p values for the ANOVA on both sites were higher than 0.99 for all four categories (Table 11) at the 95% confidence level. This indicates that while total alkalinity is necessary for calculating total carbon dioxide, the total alkalinity value does not significantly change the estimates of metabolic rates; pH is the main driver of change for the metabolic rate estimates. We conclude that measuring alkalinity every two weeks is adequate for in situ estimation of carbon apparent production and night respiration.

Alkalinity and salinity relationship

Given the lack of alkalinity effect on metabolic rate estimates, a preliminary investigation into deriving an equation to calculate total alkalinity from salinity was undertaken for Narragansett Bay. In order to make this a valuable equation, much more work will have to be put towards analyzing the alkalinity trends and fluxes, taking into account the influence from different species of nutrients, freshwater mixing, and average river flows between years. Our preliminary investigation shows that there is a significant relationship ($p = 0.01$, at 5% level) between alkalinity and salinity in 2013 when river flow was high (Figure 9a). However, in 2014, a particularly dry year, there was no relationship between alkalinity and salinity in Narragansett Bay (Figure 9b).

Spatial trends in metabolic rates

Metabolic rates varied at the different stations around the Bay (Table 8, Figure 10). Greenwich Bay has the highest metabolic rates for surface and

bottom, both summer 2013 and 2014 (Table 8, Figure 10). The site is relatively shallow, 3 m on average, allowing light to reach the bottom and increasing bottom production. A wastewater treatment facility is located in Greenwich Cove that enters Greenwich Bay 2 km south of the monitoring site. This facility upgraded to tertiary treatment in 2006 but still provides a supply of nutrients to the western end of Greenwich Bay, leading to high productivity rates. The next most productive site was Conimicut Point, at the mouth of the Providence River Estuary, which receives nutrients from numerous wastewater treatment plants. The nutrient gradient persists down the length of the West Passage (Krumholz 2012, Oviatt personal communication) and one might expect the productivity gradient to follow suit. There was a gradient in metabolic rates from the head of the bay to the mouth, through the West Passage, with the exception of anomalously low rates at North Prudence, discussed in detail later (Figure 10).

The bottom production rates are slightly higher than the bottom respiration rates at Quonset Point, Poppasquash Point, Mt Hope, and Greenwich Bay in 2013. Given the low light levels in the bottom 0.5 m layer of water at most stations, it is unclear why the net production rates are equal to or larger than the bottom respiration rates. Respiration rates would be expected to be higher, as organic matter is being deposited to the bottom layer from the surface mixed layer. The higher bottom production rates may be caused by lower carbon dioxide concentration water mixing down to the bottom layer in the case of shallower sites (i.e. Greenwich Bay and Mt. Hope). Poppasquash Point and Quonset Point both receive saltier ocean water with lower carbon dioxide

concentrations in the bottom layer during flooding tides, possibly increasing production estimates and lowering respiration rate estimates. The same trends were evident in the oxygen metabolic rates (Figure 11).

The surface metabolic rates were highest at Greenwich Bay, Conimicut Point, and Sally Rock, the three sites with the highest average number of hypoxic days (Table 12), indicating that metabolic rates are a driver of hypoxia. The system apparent production and night respiration were higher at many sites in 2014 than in 2013 (Table 8), possibly due to the increased light penetration at most sites (Table 14). Although metabolic rates were higher, the hypoxia was drastically lower in summer 2014, than summer 2013 (Table 12). Codiga et al. (2009) showed a strong relationship between June rainfall and hypoxia within Narragansett Bay. June 2013 experienced >25 cm of rainfall to the Narragansett Bay watershed, compared to <6 cm in June 2014, indicating that meteorological variability is a stronger driver on the severity of hypoxia within Narragansett Bay than production rates.

Hydrodynamics at North Prudence

To investigate the anomalously low metabolic rates at North Prudence, acoustic Doppler current profiler (ADCP) data from Rogers (2008) was examined (Figure 12). Based solely on distance, water from North Prudence could exchange with water from Conimicut Point, Poppasquash Point, and Mt. View stations during an average tidal cycle. When current direction is taken into account, it is not likely that water would move between North Prudence to Conimicut Point, but it is likely that water would move towards Mt. View since it is southwest of

North Prudence. Additionally, Kincaid (personal communication) has observed, with current tilt meters, water flowing up the East Passage, wrapping around the tip of Patience Island and flowing past the North Prudence site. Given this, advection was likely moving water between Poppasquash Point, North Prudence and Mt. View. However, the metabolic rates at all three sites mentioned prior, were higher than at the North Prudence site, advection of these waters to North Prudence would not result in anomalously low metabolic rates. The North Prudence site was located on the east slope into a deep channel, caused by a geographic constriction (Figure 1). During 3 separate cruises in summer 2006, sections of well mixed water, thought to be the product of eddies, were observed on the slope of the channel (Ullman , personal communication)These eddies were likely responsible for mixing low productivity bottom water up to the surface at the North Prudence site. Water column profiles were taken during each sonde swap and alkalinity collection. The analysis of all profiles taken during the study time period at North Prudence indicated that the site was more stratified in summer 2013 than summer 2014. The average difference between surface and bottom temperature and salinity for 2013 was 1.41°C and 1.98 psu, respectively, and 0.90°C and 0.56 psu for 2014 temperature and salinity difference. For both summers, the profiles at North Prudence had a smooth gradient of both temperature and salinity from surface to bottom; there was not a strong pycnocline evident in any profiles. This further indicates that bottom water was likely mixed up towards the surface and reduced estimates of surface net primary production.

CONCLUSION

The DDD-C method was reliable for estimating metabolic rates in Narragansett Bay. Each method of metabolism estimation has advantages and disadvantages, as said best by Oviatt et al. (1986b),

"Every measure of primary production has its own complexities".

The *in situ* carbon method approach presented here has high temporal resolution, captures the effects of biological vertical mixing and grazing, accounts for anaerobic respiration and eliminates a need for an air-sea gas exchange coefficient. However, it is not without limitations. As with the DDD-O_2 method, the DDD-C method does not account for advection, an advantage of incubation studies, and it does suffer from a possible error introduced by the pH sensors. This method may be particularly useful in estuaries where metabolic rates are high, estuaries where air-sea gas exchange is elevated, and possibly estuaries with high anaerobic respiration rates.

Nonetheless, the development of this method provides another option for estimating metabolic rates, and when used in conjunction with the DDD-O_2 method, can be used to estimate photosynthetic and respiratory quotients for a system.

References

Abdelrhman M.A. 2005. Simplified modeling of flushing and residence times in 42 embayments in New England, USA, with special attention to Greenwich Bay, Rhode Island. *Estuarine, Coastal and Shelf Science*. 62. 339-351

Balt C, Kincaid C, Ullman D (2010) The Role of Environmental Forcing in Controlling Water Retention Gyres in Subsystems of Narragansett Bay. Dissertation or Thesis, University of Rhode Island

Bender M., Orchardo J., Dickson M., Barber R., Lindley S. 1999. In vitro O 2 fluxes compared with 14 C production and other rate terms during the JGOFS Equatorial Pacific experiment. *Deep Sea Research Part I: Oceanographic Research Papers*. 46. 637-654

Bender M., Grande K., Johnson K., Marra J., Williams P., Sieburth J., Pilson M., Langdon C., Hitchcock G., Orchardo J. 1987. A comparison of four methods for determining planktonic community production. *Limnology and Oceanography*. 32. 1085-1098

Bergondo D.L., Kester D.R., Stoffel H.E., Woods W.L. 2005. Time-series observations during the low sub-surface oxygen events in Narragansett Bay during summer 2001. *Marine Chemistry*. 97. 90-103

Boesch D.F., Rabalais N.N. 1991. Effects of hypoxia on continental shelf benthos: comparisons between the New York Bight and the Northern Gulf of Mexico. *Geological Society, London, Special Publications*. 58. 27-34

Bonsdorff E., Blomqvist E., Mattila J., Norkko A. 1997. Coastal eutrophication: causes, consequences and perspectives in the archipelago areas of the northern Baltic Sea. *Estuarine, Coastal and Shelf Science*. 44. 63-72

Brush M.J., Brawley J.W. 2009. Adapting the light· biomass (BZI) models of phytoplankton primary production to shallow marine ecosystems. *Journal of Marine Systems*. 75. 227-235

Brush MJ (2002) Development of a numerical model for shallow marine ecosystems with application to Greenwich Bay, Rhode Island. Dissertation or Thesis, University of Rhode Island

Caffrey J.M. 2004. Factors controlling net ecosystem metabolism in US estuaries. *Estuaries*. 27. 90-101

Canion A., MacIntyre H.L., Phipps S. 2013. Short-term to seasonal variability in factors driving primary productivity in a shallow estuary: Implications for modeling production. *Estuarine, Coastal and Shelf Science*. 131. 224-234

Carpenter S.R., Caraco N.F., Correll D.L., Howarth R.W., Sharpley A.N., Smith V.H. 1998a. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications*. 8. 559-568

Cloern J.E. 2001. Our evolving conceptual model of the coastal eutrophication problem. *Marine Ecology Progress Series*. 210. 223-253

Codiga D.L., Stoffel H.E., Deacutis C.F., Kiernan S., Oviatt C.A. 2009. Narragansett Bay hypoxic event characteristics based on fixed-site monitoring network time series: intermittency, geographic distribution, spatial synchronicity, and interannual variability. *Estuaries and Coasts*. 32. 621-641

Collins J.R., Raymond P.A., Bohlen W.F., Howard-Strobel M.M. 2013. Estimates of new and total productivity in central Long Island Sound from in situ measurements of nitrate and dissolved oxygen. *Estuaries and Coasts*. 36. 74-97

Conley D.J., Paerl H.W., Howarth R.W., Boesch D.F., Seitzinger S.P., Havens K.E., Lancelot C., Likens G.E. 2009. Controlling eutrophication: nitrogen and phosphorus. *Science*. 323. 1014-1015

Corrales R.A., Maclean J.L. 1995. Impacts of harmful algae on seafarming in the Asia-Pacific areas. *Journal of Applied Phycology*. 7. 151-162

D'Avanzo C., Kremer J., Wainright S. 1996. Ecosystem production and respiration in response to eutrophication in shallow temperate estuaries. *Marine Ecology Progress Series*. 141. 263-274

Deacutis CF (2008) Evidence of ecological impacts from excess nutrients in upper Narragansett Bay. In: Science for Ecosystem-based Management. Springer, pp 349-381

Diaz R.J., Solan M., Valente R.M. 2004. A review of approaches for classifying benthic habitats and evaluating habitat quality. *Journal of Environmental Management*. 73. 165-181

Diaz R.J. 2001. Overview of hypoxia around the world. *Journal of Environmental Quality*. 30. 275-281

Diaz R.J., Rosenberg R. 2008. Spreading dead zones and consequences for marine ecosystems. *Science (New York, N.Y.)*. 321. 926-929

Doering P., Kelly J., Oviatt C., Sowers T. 1987. Effect of the hard clam Mercenaria mercenaria on benthic fluxes of inorganic nutrients and gases. *Marine Biology*. 94. 377-383

Duarte C.M., Conley D.J., Carstensen J., Sánchez-Camacho M. 2009. Return to Neverland: shifting baselines affect eutrophication restoration targets. *Estuaries and Coasts*. 32. 29-36

Ehrlich A, L (2014) Elucidating the molecular response of microbial nitrogen fixation in estuarine sediments to hypoxia. Dissertation or Thesis, University of Rhode Island

Elmgren R. 1989. Man's impact on the ecosystem of the Baltic Sea: energy flows today and at the turn of the century. *Ambio*. 326-332

Falkowski P., Kiefer D.A. 1985. Chlorophyll a fluorescence in phytoplankton: relationship to photosynthesis and biomass. *Journal of Plankton Research*. 7. 715-731

Fulweiler R.W., Nixon S.W., Buckley B.A. 2010. Spatial and temporal variability of benthic oxygen demand and nutrient regeneration in an anthropogenically impacted New England estuary. *Estuaries and Coasts*. 33. 1377-1390

Fulweiler R., Brown S., Nixon S., Jenkins B. 2013. Evidence and a conceptual model for the co-occurrence of nitrogen fixation and denitrification in heterotrophic marine sediments. *Marine Ecology Progress Series*. 482.

Fulweiler R., Nixon S., Buckley B., Granger S. 2007. Reversal of the net dinitrogen gas flux in coastal marine sediments. *Nature*. 448. 180-182

Gaarder T., Gran H.H. 1927. Investigations of the production of plankton in the Oslo Fjord. *Conseil permanent international pour l'exploration de la mer*. 42. 1-48

Goebel N.L., Kremer J.N., Edwards C.A. 2006. Primary production in Long Island sound. *Estuaries and Coasts*. 29. 232-245

Gooday A., Jorissen F., Levin L., Middelburg J., Naqvi S., Rabalais N., Scranton M., Zhang J. 2009. Historical records of coastal eutrophication-induced hypoxia. *Biogeosciences*. 6. 1707-1745

Gray J.S., Ying Y. 2002. Effects of hypoxia and organic enrichment on the coastal marine environment. *Marine Ecology Progress Series*. 238. 249-279

Herbert R. 1999. Nitrogen cycling in coastal marine ecosystems. *FEMS Microbiology Reviews*. 23. 563-590

Howarth R., Chan F., Conley D.J., Garnier J., Doney S.C., Marino R., Billen G. 2011. Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. *Frontiers in Ecology and the Environment*. 9. 18-26

Keller A.A. 1988. Estimating phytoplankton productivity from light availability and biomass in the MERL mesocosms and Narragansett Bay. *Marine Ecology Progress Series*. 45. 159-168

Kelly J.R., Berounsky V.M., Nixon S.W., Oviatt C.A. 1985. Benthic-pelagic coupling and nutrient cycling across an experimental eutrophication gradient. *Marine Ecology Progress Series*. 26. 207-219

Kemp W., Testa J., Conley D., Gilbert D., Hagy J. 2009. Temporal responses of coastal hypoxia to nutrient loading and physical controls. *Biogeosciences*. 6. 2985-3008

Kemp W., Boynton W., Adolf J., Boesch D., Boicourt W., Brush G., Cornwell J., Fisher T., Glibert P., Hagy J. 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. *Marine Ecology Progress Series*. 303. 1-29

Kincaid,C. 2015. Current Flow in Upper Narragansett Bay. Personal Communication

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

Krumholz,J. .2012Changes in nutrient standing stock in a temperate estuary with decreased nitrogen and phosphorus loading. *University of Rhode Island*

Markovsky I., Van Huffel S. 2007. Overview of total least-squares methods. *Signal Processing*. 87. 2283-2302

Marra J. 2009. Net and gross productivity: weighing in with 14C. *Aquatic Microbial Ecology*. 56. 123-131

MathWorks .2013MatLab

Melrose D.C., Oviatt C.A., Berman M.S. 2007. Hypoxic events in Narragansett Bay, Rhode Island, during the summer of 2001. *Estuaries and Coasts*. 30. 47-53

Middleton R.J., Reeder B.C. 2003. Dissolved oxygen fluctuations in organically and inorganically fertilized walleye (Stizostedion vitreum) hatchery ponds. *Aquaculture*. 219. 337-345

Nixon S.W. 2009. Eutrophication and the macroscope. *Hydrobiologia*. 629. 5-19

Nixon S.W., Fulweiler R.W., Buckley B.A., Granger S.L., Nowicki B.L., Henry K.M. 2009. The impact of changing climate on phenology, productivity, and benthic–pelagic coupling in Narragansett Bay. *Estuarine, Coastal and Shelf Science*. 82. 1-18

Nixon S.W. 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia*. 41. 199-219

Nixon S.W., Oviatt C.A., Garber J., Lee V. 1976. Diel metabolism and nutrient dynamics in a salt marsh embayment. *Ecology*. 740-750

Nixon S.W., Oviatt C.A. 1972. Preliminary measurements of midsummer metabolism in beds of eelgrass, Zostera marina. *Ecology*. 150-153

Nowicki B.L. 1994. The effect of temperature, oxygen, salinity, and nutrient enrichment on estuarine denitrification rates measured with a modified nitrogen gas flux technique. *Estuarine, Coastal and Shelf Science*. 38. 137-156

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

Ostrom N.E., Carrick H.J., Twiss M.R., Piwinski L. 2005. Evaluation of primary production in Lake Erie by multiple proxies. *Oecologia*. 144. 115-124

Oviatt C., Keller A., Reed L. 2002. Annual primary production in Narragansett Bay with no bay-wide winter–spring phytoplankton bloom. *Estuarine, Coastal and Shelf Science*. 54. 1013-1026

Oviatt C., Doering P., Nowicki B., Zoppini A. 1993. Net system production in coastal waters as a function of eutrophication, seasonality and benthic macrofaunal abundance. *Estuaries*. 16. 247-254

Oviatt C., Buckley B., Nixon S. 1981. Annual phytoplankton metabolism in Narragansett Bay calculated from survey field measurements and microcosm observations. *Estuaries*. 4. 167-175

Oviatt,C.A. 2015. Nutrients in Narragansett Bay. Personal Communication

Oviatt CA (2008) Impacts of nutrients on Narragansett Bay productivity: A gradient approach. In: Science for Ecosystem-based Management. Springer, pp 523-543

Oviatt C.A., Quinn J.G., Maughan J., Ellis J.T., Sullivan B.K., Gearing J.N., Gearing P.J., Hunt C.D., Sampou P.A., Latimer J.S. 1987. Fate and effects of sewage sludge in the coastal marine environment: A mesocosm experiment. *Marine Ecology Progress Series*. 41. 187-203

Oviatt C.A., Keller A.A., Sampou P.A., Beatty L.L. 1986a. Patterns of productivity during eutrophication: a mesocosm experiment. *Marine Ecology Progress Series*. 28. 69-80

Oviatt C.A., Rudnick D.T., Keller A.A., Sampou P.A., Almquist G.T. 1986b. A comparison of system (O 2 and CO 2) and C-14 measurements of metabolism in estuarine mesocosms. *Marine Ecology Progress Series*. 28. 57-67

Pearson T., Rosenberg R. 1978. Macrobenthic succession in relation to organic enrichment and pollution of the marine environment. *Oceanography and Marine Biology: an Annual Review*. 16. 229-311

Peterson B.J. 1980. Aquatic primary productivity and the 14C-CO2 method: A history of the productivity problem. *Annual Review of Ecology and Systematics*. 359-385

Pihl L., Baden S., Diaz R. 1991. Effects of periodic hypoxia on distribution of demersal fish and crustaceans. *Marine Biology*. 108. 349-360

Pihl L., Baden S.P., Diaz R.J., Schaffner L.C. 1992. Hypoxia-induced structural changes in the diet of bottom-feeding fish and Crustacea. *Marine Biology*. 112. 349-361

Pilson ME (2013) An Introduction to the Chemistry of the Sea. Cambridge University Press

Quay P., Peacock C., Björkman K., Karl D. 2010. Measuring primary production rates in the ocean: Enigmatic results between incubation and non-incubation methods at Station ALOHA. *Global Biogeochemical Cycles*. 24.

R .2013R

Rhode Island Department of Environmental Management (2014) Narragansett Bay Fixed-Site Monitoring Network (NBFSMN) 2014 Datasets. In: . www.dem.ri.gov/bart 2014

Rhode Island Department of Environmental Management (2013) Narragansett Bay Fixed-Site Monitoring Network (NBFSMN) 2013 Datasets. In: . www.dem.ri.gov/bart 2013

Rogers JM (2008) Circulation and transport in upper Narragansett Bay. Dissertation or Thesis, University of Rhode Island

Rosenberg R., Elmgren R., Fleischer S., Jonsson P., Persson G., Dahlin H. 1990. Marine eutrophication case studies in Sweden. *Ambio*. 102-108

Sampou P., Oviatt C. 1991. A carbon budget for a eutrophic marine ecosystem and the role of sulfur metabolism in sedimentary carbon, oxygen and energy dynamics. *Journal of Marine Research*. 49. 825-844

Seitzinger S., Nixon S., Pilson M.E., Burke S. 1980. Denitrification and N_2O production in near-shore marine sediments. *Geochimica et Cosmochimica Acta*. 44. 1853-1860

Smith L.M., Silver C.M., Oviatt C.A. 2012. Quantifying variation in water column photosynthetic quotient with changing field conditions in Narragansett Bay, RI, USA. *Journal of Plankton Research*.

Smith,L.M. .2011A Comparison of In Situ and Incubation metabolism estimation methods: Narragansett Bay, RI, USA. *University of Rhode Island*

Smith L.M., Whitehouse S., Oviatt C.A. 2010. Impacts of climate change on Narragansett Bay. *Northeastern Naturalist*. 17. 77-90

Smith V.H. 2003. Eutrophication of freshwater and coastal marine ecosystems a global problem. *Environmental Science and Pollution Research*. 10. 126-139

Steeman Nielsen E. 1952. The use of radioactive carbon (14C) for measuring organic production in the sea. *Conseil Permanent International pour l'Exploration de la Mer*. 18. 117-140

Stoffel,H. 2015. Annual totals of Hypoxic days at the Narragansett Bay Fixed Site Monitoring Network sites 2001-1014. Personal Communication

Ullman,D.S. 2007. Hydrography of West Passage and Warwick Neck, Narragansett Bay.

Vaudrey J.M. 2007. Estimating total ecosystem metabolism (TEM) from the oxygen rate of change: A comparison of two Connecticut estuaries.

Wanninkhof R., Asher W.E., Ho D.T., Sweeney C., McGillis W.R. 2009. Advances in quantifying air-sea gas exchange and environmental forcing. *Marine Science*. 1.

Williams RG, Follows MJ (2011) Ocean Dynamics and the Carbon Cycle: Principles and Mechanisms. Cambridge University Press

TABLES

Table 1. Equations 1- 9 from Pilson (2013) and equations 10-11 from Oviatt et al (1986) used to calculate total carbon dioxide in method. TAlk = Total Alkalinity, TCO_2 = Total Carbon Dioxide

Number	Variable	Equation
1	T	Temperature in K, t°C + 273.15
2	S	Salinity in ‰
3	pK_1^*	$pK_1^* = 17.788 - 0.073104T - 0.0051087S + 1.1463 \times 10^{-4}T^2$
4	pK_2^*	$pK_2^* = 20.919 - 0.064209T - 0.011887S + 8.7313 \times 10^{-5}T^2$
5	K_B^*	$K_B^* = \exp((-8966.90 - 2890.53S^{0.5} - 77.942S + 1.728S^{1.5} - 0.0996S^2)/T + (148.0248 + 137.1942S^{0.5} + 1.62142S) + (-24.4344 - 25.085S^{0.5} - 0.2474S) \ln T + (0.053105S^{0.5})T)$
6	K_1^*	$K_1^* = 10^{-(pK_1)}$
7	K_2^*	$K_2^* = 10^{-(pK_2)}$
8	f_H	$f_H = 0.739 + 0.0307S + 0.0000794S^2 + 0.00006443T - 0.000117ST$
9	K_W^*	$K_W^* = \exp(148.9802 - 13847.26/T - 23.6521 \ln(T) + (-5.977 + 118.67/T + 1.0495 \ln(T)) S^{0.5} - 0.01615S) \times f_H \times 10^{-14}$
10	a_H	$a_H = 10^{-(pH)}$
11	TCO_2	$TCO_2 = [TAlk - \frac{K_W^*}{a_H} - \frac{K_B^* \times S \times 1.243X10^{-5}}{a_H + K_B^*}] * [\frac{a_H^2}{K_1^*(a_H + 2K_2^*)} + \frac{a_H + K_2^*}{a_H + 2K_2^*}]$

Table 2. The Dawn Dusk Dawn Oxygen method was compared with the Dawn Dusk Dawn Carbon method using a Reduced Major Axis regression and correlation test for all categories and summers. 2014 had higher correlations in all cases than 2013. The bottom respiration discrepancy may be due to higher rates of anaerobic respiration occurring in the much more hypoxic summer of 2013 than in 2014.

	2013 Correlations	**2014 Correlations**
Surface Production	0.8	0.86
Surface Respiration	0.76	0.87
Bottom Production	0.69	0.94
Bottom Respiration	0.77	0.96

Table 3. The average metabolic rate for each category for both summers is listed ($gCm^{-3}day^{-1}$ or $night^{-1}$). The p values are from t tests comparing the DDD Oxygen method metabolic rates to the DDD Carbon method metabolic rates. All categories for 2013 are significantly different from each other, where as in 2014, only bottom respiration is significantly different. Despite being significantly different, these differences would not lead to a difference in classification of the water body as eutrophic or oligotrophic.

	Category	O_2 converted to C Average	Carbon Average	p value
2013	Surface Production	0.25	0.22	6.88E-05
	Surface Respiration	-0.26	-0.23	4.13E-05
	Bottom Production	0.13	0.10	1.95E-02
	Bottom Respiration	-0.11	-0.09	1.93E-02
2014	Surface Production	0.27	0.26	3.16E-01
	Surface Respiration	-0.27	-0.26	6.00E-01
	Bottom Production	0.13	0.13	7.91E-02
	Bottom Respiration	-0.12	-0.13	3.69E-03

Table 4. The photosynthetic and respiratory quotients for all stations and summers. The fields with asterisks were not included in the averages because they were over 2 standard deviations of the mean of the rest of the data points in that category. The averages for each year and category were used to convert gO_2 $m^{-3}day^{-1}$ to $gCm^{-3}day^{-1}$.

Photosynthetic Quotient	**Surface PQ**		**Bottom PQ**	
Site	**2013**	**2014**	**2013**	**2014**
Conimicut Point	1.25	1.31	0.57	1.3
North Prudence	1.77	1.28	1.3	1.49
Mt. View	1.11	1.12	1.06	1.3
Quonset Point	1.6	1.26	0.97	1.1
GSO	1.31	1.09		
Mt. Hope	1.2	1.2	0.85	1.47
Poppasquash Point	1.61	1.18	0.87	-40.45*
Greenwich Bay	1.23	1.32	1.34	1.08
Sally Rock	1.56	0.51*	1.59	0.35*
Average	**1.4**	**1.22**	**1.07**	**1.29**
Standard Deviation	**0.23**	**0.09**	**0.33**	**0.17**

Respiratory Quotient	**Surface RQ**		**Bottom RQ**	
Site	**2013**	**2014**	**2013**	**2014**
Conimicut Point	0.81	0.77	2.19*	0.51
North Prudence	0.7	0.74	1.05	0.53
Mt. View	0.87	0.85	0.8	0.77
Quonset Point	0.66	0.74	0.85	0.83
GSO	0.72	0.87		
Mt. Hope	0.88	0.8	1.08	0.68
Poppasquash Point	0.69	0.84	0.84	0.18*
Greenwich Bay	0.72	0.72	0.75	0.92
Sally Rock	0.63	0.8	0.49	0.83
Average	**0.74**	**0.79**	**0.84**	**0.72**
Standard Deviation	**0.09**	**0.05**	**0.20**	**0.16**

Table 5. The mean and median absolute value change between 15-minute pH readings with the YSI sensors is below. Data were from June 1– Sept 30 of both 2013 and 2014. All stations except Greenwich Bay had similar mean surface pH changes between 0.007 and 0.024 units, with bottom changes for all stations between 0.008 and 0.017 units. Greenwich bay had about twice the variability of the other stations on average with bottom stability between 15-minute pH readings higher than surface reading stability.

	2013			
Site	Surface Mean	Surface Median	Bottom Mean	Bottom Median
Conimicut Point	0.024	0.01	0.013	0.01
North Prudence	0.018	0.01	0.012	0.01
Mt. View	0.013	0.01	0.014	0.01
Quonset Point	0.009	0.01	0.008	0.01
GSO	0.015	0.01		
Mt Hope	0.015	0.01	0.012	0.01
Poppasquash	0.012	0.01	0.008	0.01
Greenwich Bay	0.033	0.02	0.038	0.02
Sally Rock	0.012	0.01	0.013	0.01

	2014			
Site	Surface Mean	Surface Median	Bottom Mean	Bottom Median
Conimicut Point	0.018	0.01	0.013	0.01
North Prudence	0.015	0.01	0.015	0.01
Mt. View	0.010	0.01	0.011	0.01
Quonset Point	0.008	0.00	0.009	0.01
GSO	0.011	0.01		
Mt Hope	0.011	0.01	0.015	0.01
Poppasquash	0.007	0.00	0.012	0.01
Greenwich Bay	0.032	0.02	0.042	0.03
Sally Rock	0.009	0.01	0.017	0.01

Table 6. The percent change between the original metabolic rate estimates, and the estimates from increasing or decreasing the pH by 0.2 units. On average, if the pH is increased by 0.2 units in the surface waters, the metabolic rate estimate will increase by 23% and 21% for production and respiration, respectively. If the surface pH is decreased by 0.2 units, the metabolic rate estimates will decrease by 9-11% for production and respiration. The bottom metabolic rate estimates increase by 8-11% regardless of whether the pH is increased or decreased.

		Surface Production		Surface Respiration		Bottom Production		Bottom Respiration	
		Plus 0.2	Minus 0.2	Plus 0.2	Minus 0.2	Plus 0.2	Minus 0.2	Plus 0.2	Minus 0.2
Conimicut Point	Mean	22	-12	24	-11	4	13	4	12
	Median	24	-12	25	-14	0	11	0	-14
North Prudence	Mean	21	-7	20	-7	7	12	8	9
	Median	20	-6	20	-8	8	11	8	-8
Mt. View	Mean	23	-7	21	-7	15	5	15	5
	Median	23	-8	22	-7	17	0	14	-7
Quonset Point	Mean	22	-9	23	-9	16	1	16	5
	Median	23	-9	24	-10	16	0	15	-10
GSO	Mean	25	-12	10	-23				
	Median	24	-13	22	-13				
Average for all sites		**23**	**-9**	**21**	**-11**	**10**	**8**	**11**	**8**

Table 7. Carbon metabolic rates were estimated with the measured pH, increased pH by 0.2 units and decreased pH by 0.2 units. The results for each category were compared using a one-way ANOVA and indicated that only Conimicut Point surface respiration was significantly different. A Tukey's HSD test indicated that there was only significant difference between the metabolic rates estimated from the increased and decreased pH sets, there was no difference between the metabolic rates from the measured pH and either of the increased or decreased pH metabolic rates datasets.

Category	Conimicut Point p value	North Prudence p value	Mt. View p value	Quonset Point p value	GSO p value
Surface Production	0.126	0.721	0.374	0.412	0.418
Surface Respiration	0.033	0.706	0.114	0.123	0.328
Bottom Production	0.941	0.992	0.867	0.865	
Bottom Respiration	0.926	0.995	0.834	0.878	

Table 8. Average daily carbon metabolic rates for each summer and site (gC m^{-3} d^{-1} or n^{-1}). In 2014, bottom production and respiration were both statistically higher than in 2013, surface values were not significant.

	2013 Summer Metabolic Rates July 20th - Sept 30th			
Site	Surface Production	Surface Respiration	Bottom Production	Bottom Respiration
Conimicut Point	0.33	-0.34	0.07	-0.07
North Prudence	0.11	-0.15	0.04	-0.04
Mt. View	0.21	-0.23	0.11	-0.11
Quonset Point	0.14	-0.14	0.09	-0.08
GSO	0.12	-0.11		
Mt Hope	0.26	-0.28	0.03	0.00
Poppasquash	0.19	-0.21	0.09	-0.08
Greenwich Bay	0.38	-0.39	0.32	-0.31
Sally Rock	0.27	-0.24	0.10	-0.09
Average	**0.22**	**-0.23**	**0.10**	**-0.10**

	2014 Summer Metabolic Rates June 1st - Sept 30th			
Site	Surface Production	Surface Respiration	Bottom Production	Bottom Respiration
Conimicut Point	0.32	-0.32	0.01	-0.01
North Prudence	0.16	-0.16	0.05	-0.04
Mt. View	0.23	-0.24	0.10	-0.10
Quonset Point	0.16	-0.16	0.06	-0.05
GSO	0.20	-0.21		
Mt Hope	0.24	-0.23	0.06	-0.06
Poppasquash	0.23	-0.23	0.00	-0.01
Greenwich Bay	0.56	-0.55	0.56	-0.56
Sally Rock	0.23	-0.24	0.16	-0.17
Average	**0.26**	**-0.26**	**0.13**	**-0.13**

Table 9. Mean and possible metabolic rates ($gCm^{-3}day^{-1}$ or $gCm^{-3}night^{-1}$) if the YSI pH sensor is off by 0.2 units in either direction. Surface values for Conimicut Point, the most productive site of these five, could be off by 0.08 $gCm^{-3}day^{-1}$ if the YSI pH sensor is reading 0.2 pH units high of the true pH. Bottom values are not highly affected.

Site	Surface Production	Surface Respiration	Bottom Production	Bottom Respiration
Conimicut Point Mean	0.33	-0.33	0.07	-0.08
Possible Range	0.29 to 0.41	-0.30 to -0.41	No Change	-0.09
North Prudence Mean	0.11	-0.14	0.04	-0.06
Possible Range	0.10 to 0.13	-0.13 to -0.17	0.05	No Change
Mt. View Mean	0.21	-0.23	0.11	-0.1
Possible Range	0.19 to 0.25	-0.21 to -0.28	0.12 to 0.13	-0.11 to -0.12
Quonset Point Mean	0.14	-0.15	0.09	-0.06
Possible Range	0.13 to 0.17	-0.14 to -0.19	0.09 to 0.10	-0.07
GSO Dock Mean	0.12	-0.13		
Possible Range	0.11 to 0.15	-0.1 to -0.15		

Table 10. Average percent change in metabolic rate estimates when the sampling frequency for alkalinity was changed from bi-weekly (BW) to weekly (W) and twice weekly (TW). A change in alkalinity sampling frequency only resulted in changes in metabolic rates of 1-8% on average.

Sampling Frequency Comparison	biweekly to weekly	biweekly to twice weekly	weekly to twice weekly	biweekly to weekly	biweekly to twice weekly	weekly to twice weekly
	Surface Production			Surface Respiration		
Conimicut Point	1	5	5	2	5	5
Quonset Point	2	5	4	2	4	4
	Bottom Production			Bottom Respiration		
Conimicut Point	2	4	6	3	6	7
Quonset Point	2	7	8	2	4	4

Table 11. The one-way ANOVA tested whether the means of the metabolic rates estimated using 3 different alkalinity datasets were significantly different from one another. In all cases, the change in alkalinity values did not impact metabolic rates significantly.

	Conimicut Point p Value	Quonset Point p Value
Surface Production	0.993	0.998
Surface Respiration	0.991	0.993
Bottom Production	0.999	0.998
Bottom Respiration	1	0.994

Table 12. 2014 had significantly lower number of hypoxic days at all stations than in 2013, when compared to the 2001 – 2012 average (Stoffel 2015) * Not all stations began in 2001, all but Sally Rock were operational by 2005 (Sally Rock: 2008)

Station	2013	2014	2001-2012 Average*
Conimicut Point	43.1	3.4	23.4
North Prudence	21.2	2.1	14.2
Mt. View	21.7	0.3	13.9
Quonset Point	4.4	3	3.8
GSO Dock	0	0	0.1
Mt. Hope	34.4	5.3	10.3
Poppasquash Point	21	3	13.2
Greenwich Bay	47.5	25.1	51.7
Sally Rock	41.5	20.1	41.4

Table 13. Average daily oxygen method metabolic rates for each summer and site (gC m^{-3} d^{-1} or n^{-1}). Data were converted to carbon using the average PQ or RQ for each category and summer. North Prudence was anomalously low compared to surround sites, as seen in the carbon metabolic rates as well. The bottom production rates, particularly in 2013 when euphotic depth was shallower, may be reflecting oxygen mixed into the bottom layer, in addition to algal production of oxygen in the bottom, increasing overall rates of bottom production.

2013 Summer Oxygen to Carbon metabolic rates
July 20th - Sept 30th

Site	Surface Production	Surface Respiration	Bottom Production	Bottom Respiration
Conimicut Point	0.36	-0.36	0.05	-0.02
North Prudence	0.14	-0.14	0.07	-0.05
Mt. View	0.22	-0.24	0.13	-0.12
Quonset Point	0.19	-0.20	0.13	-0.09
GSO	0.14	-0.16		
Mt Hope	0.27	-0.25	0.03	-0.03
Poppasquash	0.24	-0.24	0.06	-0.05
Greenwich Bay	0.38	-0.43	0.42	-0.35
Sally Rock	0.32	-0.32	0.13	-0.10
Average	**0.25**	**-0.26**	**0.13**	**-0.10**

2014 Summer Oxygen to Carbon Metabolic rates
June 1st - Sept 30th

Site	Surface Production	Surface Respiration	Bottom Production	Bottom Respiration
Conimicut Point	0.35	-0.33	0.01	-0.02
North Prudence	0.17	-0.17	0.06	-0.05
Mt. View	0.22	-0.22	0.12	-0.10
Quonset Point	0.17	-0.17	0.05	-0.05
GSO	0.19	-0.19		
Mt Hope	0.23	-0.23	0.08	-0.06
Poppasquash	0.23	-0.22	0.02	-0.03
Greenwich Bay	0.61	-0.61	0.52	-0.44
Sally Rock	0.23	-0.24	0.17	-0.15
Average	**0.27**	**-0.27**	**0.13**	**-0.11**

Table 14. The average euphotic depth (Zeu, defined as depth to 1% light level) at each site for summers 2013 and 2014 show large differences in water clarity between the two summers. Six light profiles on average were taken each summer between June through September. Average euphotic depths increased at all sites except two between summer 2013 and 2014, despite production and respiration rates at most sites being higher in 2014. Five profiles were taken at Greenwich Bay in summer 2014, with large variability in the profiles. Three of the sampling days a euphotic depth of 4.3 -6.3 m, while the other two days had euphotic depths of 17.7 and 18.5 m. The five days from summer 2013 had a range of 2.9 – 6.5 m for euphotic depths.

Site	2013 Zeu (m)	2014 Zeu (m)	Ave. Depth (m)	Percent Change
Conimicut Point	6.2	9.7	9.4	56
North Prudence	7.5	8.7	11.5	15
Mt. View	7.3	8.4	7.5	14
Quonset Point	8.1	9.2	7.8	14
GSO Dock	7.0	6.9	2.8	-2
Greenwich Bay	4.9	10.4	2.9	111
Sally Rock	5.6	6.4	4.5	16
Mt. Hope	6.3	6.3	4.9	-1
Poppasquash Point	7.5	10.2	8.3	36

Table 15. Summer 2013 pH data (15 minute data) were used to determine the maximum change in pH occurring each day, and averaged over the whole summer. The minimum and maximum did not always coincide with the dawn and dusk reading. The more productive sites, Greenwich Bay and Conimicut point, have the highest daily change in pH. All surface values are larger than the 0.03 unit offset from the head tank comparison between the SeaFET and YSI sensor and 0.05 unit offset in the May-June Conimicut Point deployment of the two sensors.

Site	Average Surface pH Maximum 24-hour change	Average Bottom pH Maximum 24-hour change
Conimicut Point	0.42	0.25
North Prudence	0.30	0.18
Mt. View	0.26	0.22
Quonset Point	0.31	0.25
GSO Dock	0.23	N/A
Greenwich Bay	0.50	0.50
Sally Rock	0.23	0.25
Poppasquash Point	0.24	0.19
Mt. Hope	0.31	0.25

FIGURES

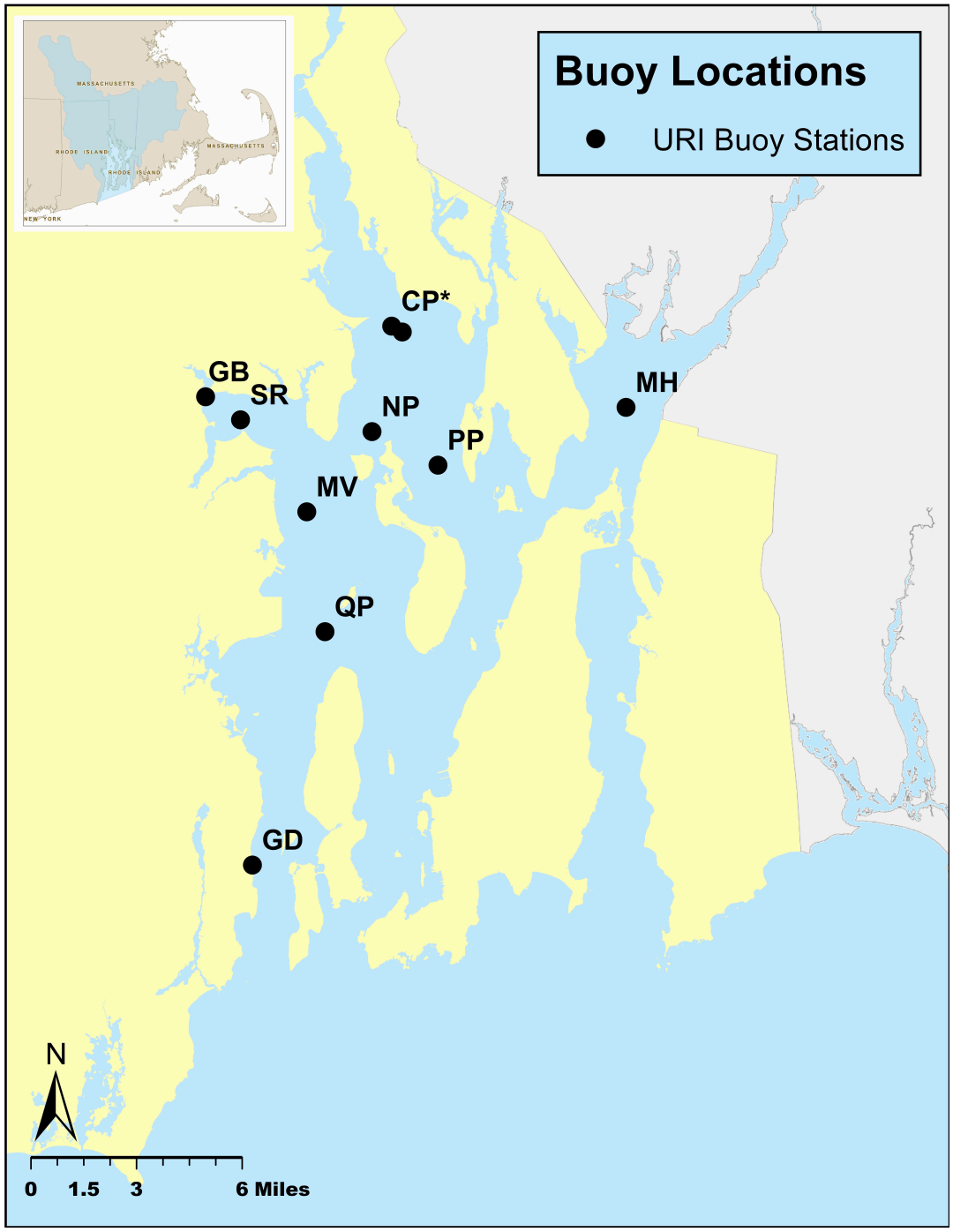


Figure 1. The Narragansett Bay Fixed Site Monitoring Network sites operated by University of Rhode Island's Graduate School of Oceanography and used for this study. Conimicut Point has a summer location and a winter location on the map.

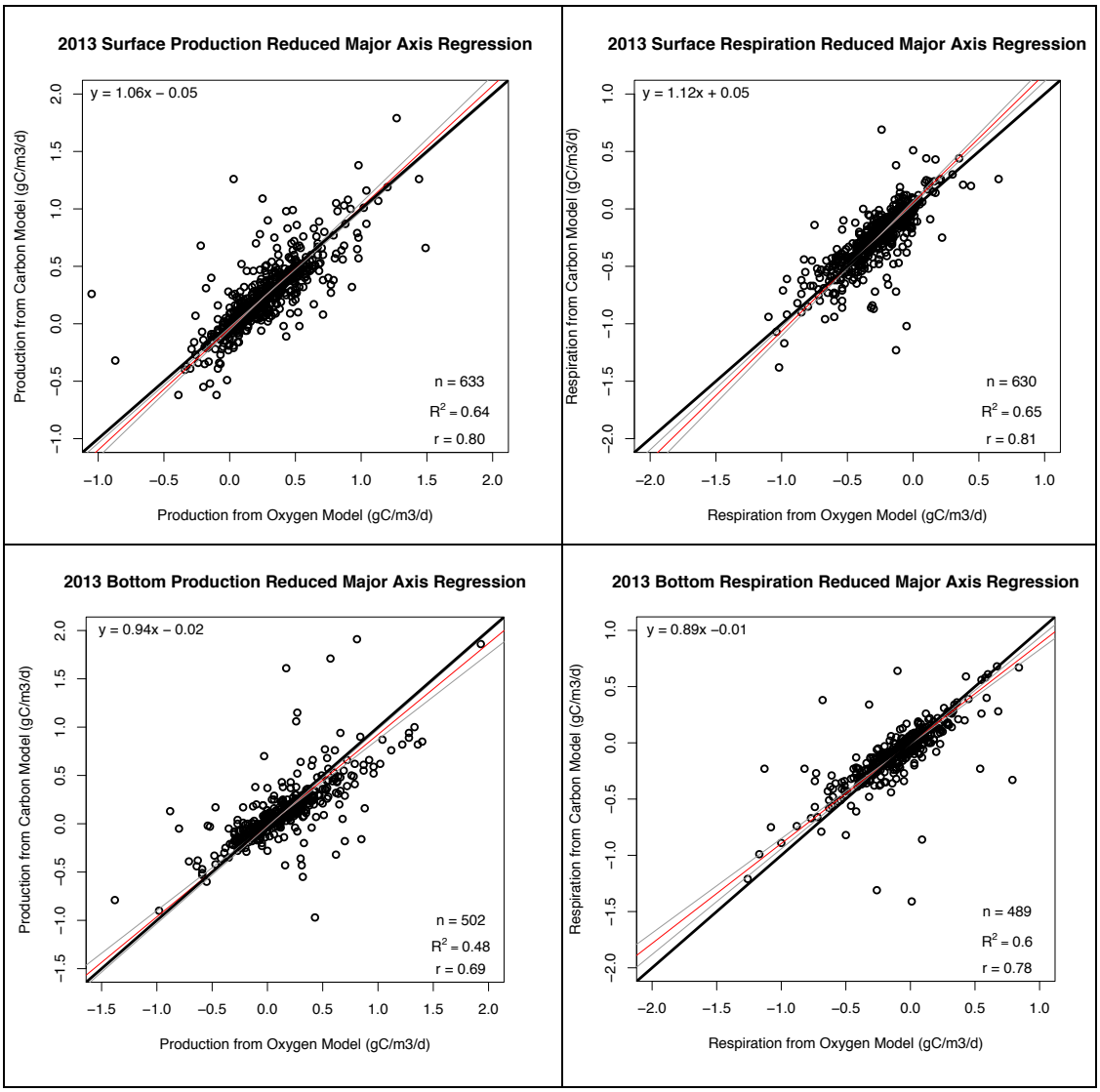


Figure 2. The two methods compared well in 2013. The black line is the 1 to 1 line, and the red and gray lines are the regression and 95% confidence intervals respectively. Correlations ranged from 0.69 for bottom production to 0.81 for surface respiration. Metabolic rate estimates from the oxygen method have been concerted to carbon using the average PQ and RQ from the comparison of the two methods for each year and category.

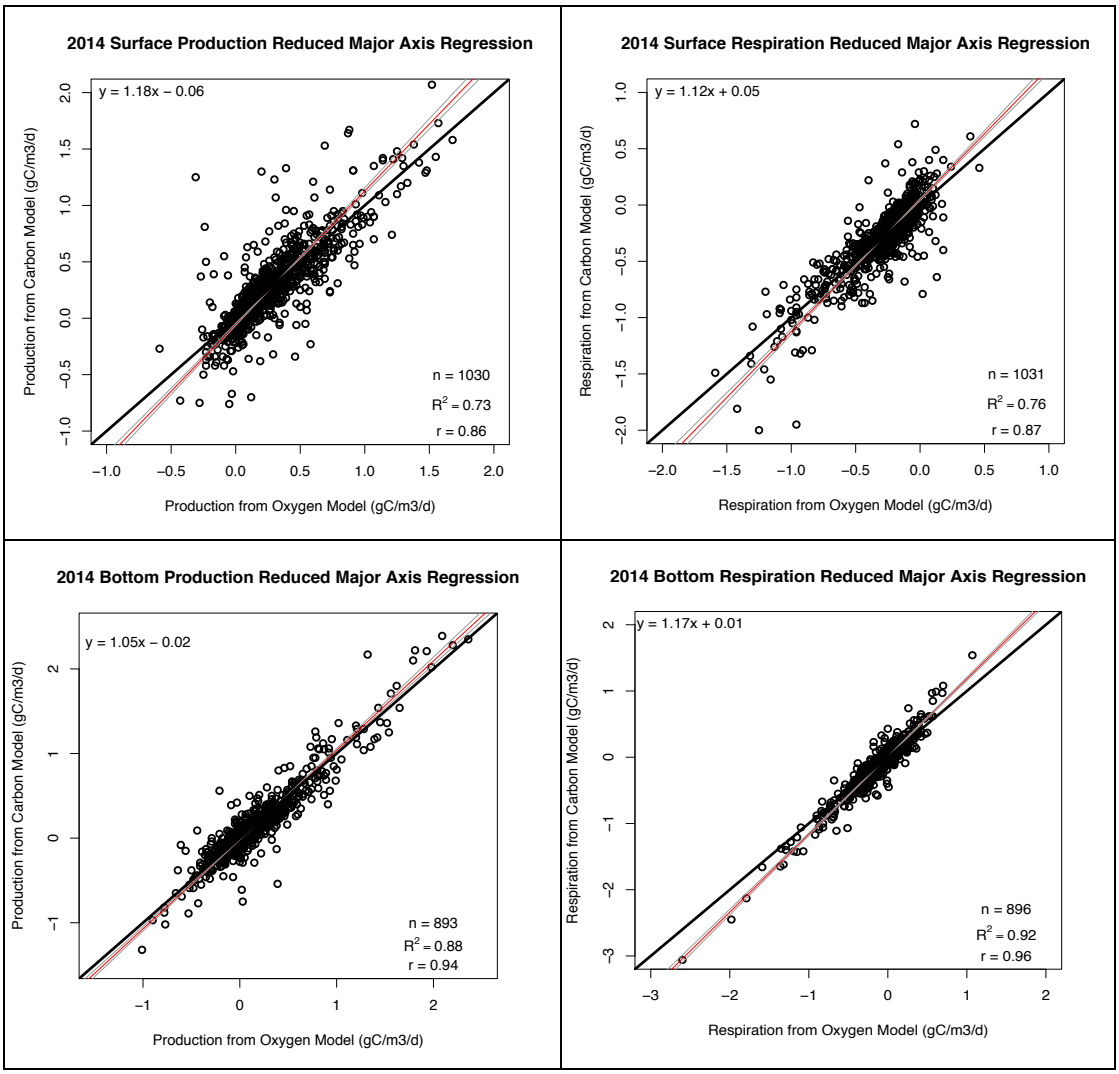


Figure 3. The two methods for estimating metabolic rates were compared for summer 2014. The black line is the 1 to 1 line, and the red and gray lines are the regression and 95% confidence intervals respectively. Metabolic rate estimates from the oxygen method have been concerted to carbon using the average PQ and RQ from the comparison of the two methods for each year and category.
The correlations for 2014 were much higher than in 2013. In summer 2014, the bottom respiration had the highest correlation between the two Dawn Dusk Dawn methods. The carbon method captures anaerobic respiration through the change in carbon dioxide, where as the oxygen method could not detect this respiration. This difference may be responsible for the large discrepancy in correlations for bottom respiration between the two years.

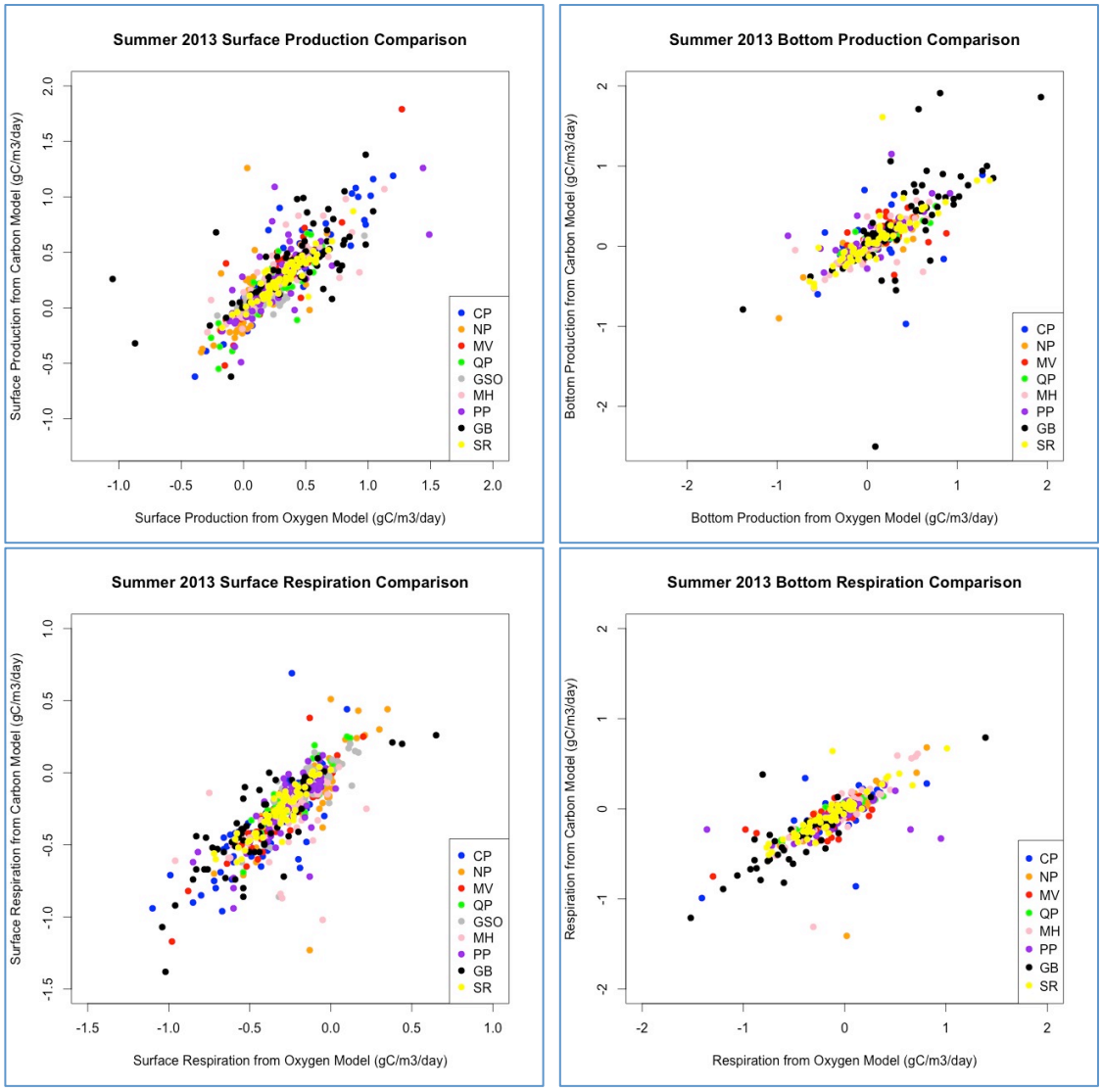


Figure 4. Metabolic rate estimates from the oxygen method have been converted to carbon using the average PQ and RQ from the comparison of the two methods for each year and category. Summer 2013 had more variability between the two methods, with Greenwich Bay exhibiting the most variability. The Greenwich Bay site has the highest production and respiration of the nine study sites, followed by Conimicut Point. The black points represent the Greenwich Bay site in these plots and the blue points are Conimicut Point.

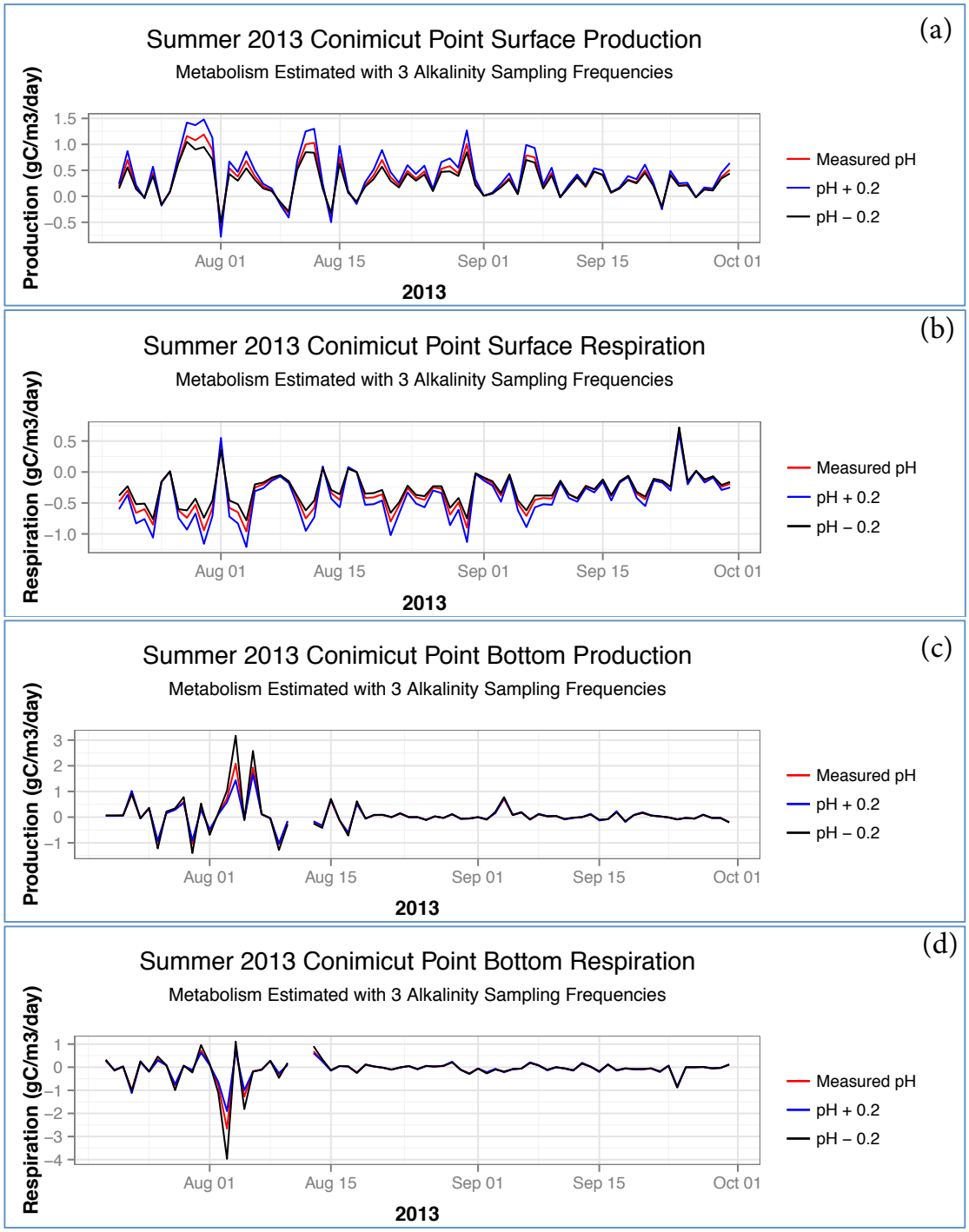
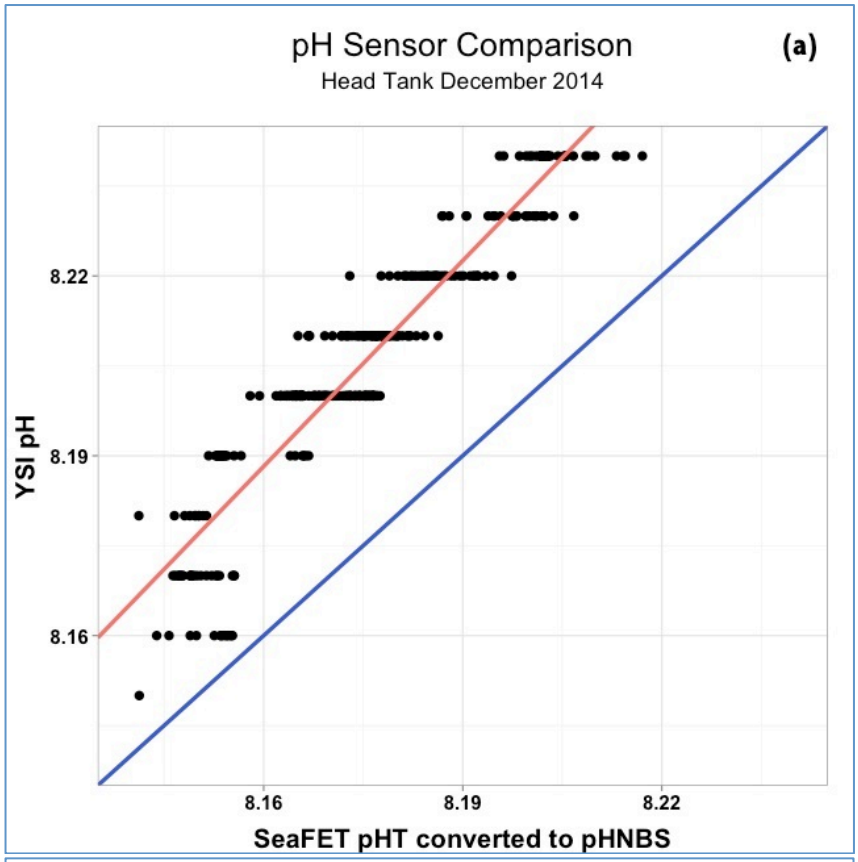
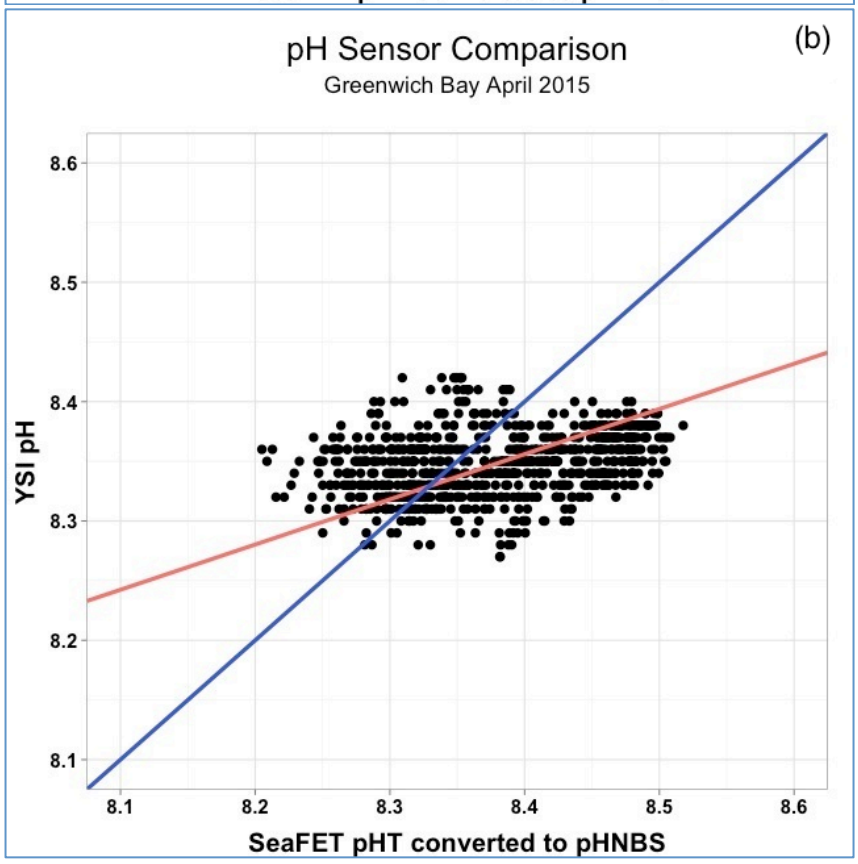


Figure 5. The pH sensitivity analysis indicated that as the variability of the metabolic rate estimates increase or decrease away from zero, the effect of a change in pH is exaggerated. In the second half of the summer, the bottom production and respiration were minimally affected by a change in pH. The breaks in the data in the bottom plots are due to missing pH data for those days.


pH Sensor Comparison
(a)
Head Tank December 2014
YSI pH
8.22
8.19
8.16
8.16
8.19
8.22
SeaFET pHT converted to pHNBS


pH Sensor Comparison
(b)
Greenwich Bay April 2015
YSI pH
8.6
8.5
8.4
8.3
8.2
8.1
8.1
8.2
8.3
8.4
8.5
8.6
SeaFET pHT converted to pHNBS

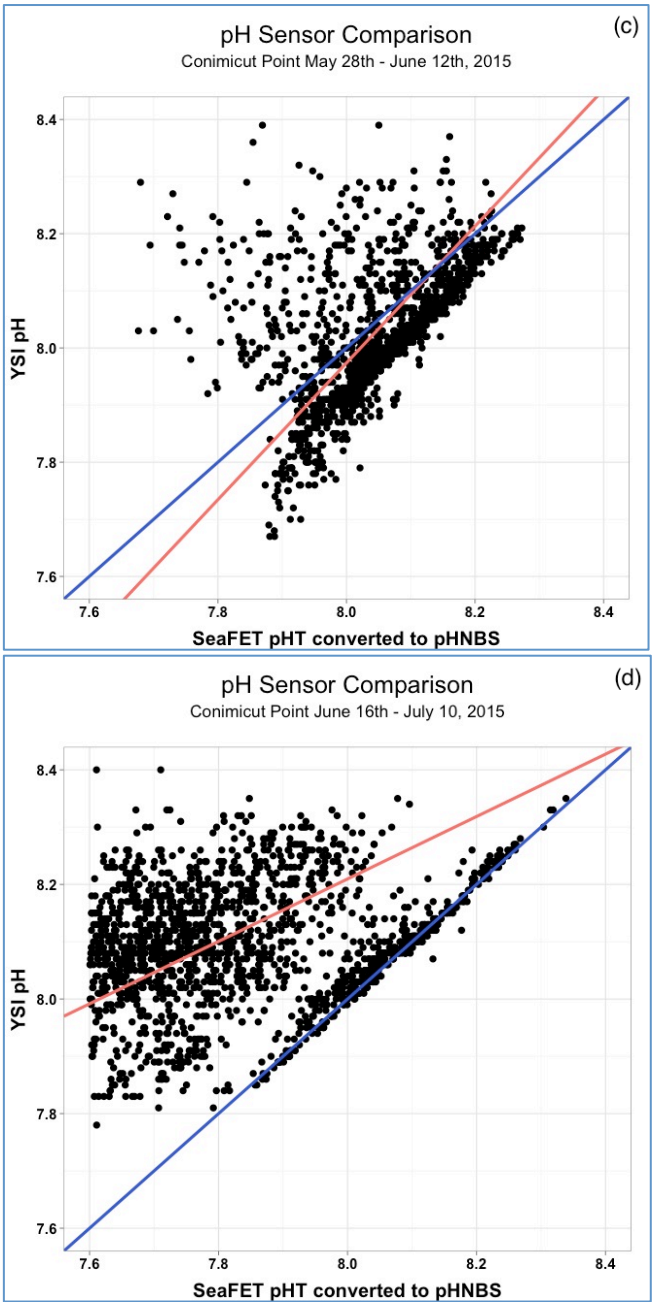


Figure 6. Four side-by-side deployments of a SeaFET pH sensor and YSI sensors occurred between December 2014 and July 2015. The blue line is a 1 to 1 line and the red line is the Reduced Major Axis regression line. In a) the comparison took place in a constantly flowing tank and the relationship was linear with an offset of 0.03 pH units. In b) the deployment occurred in Greenwich Bay, a very low flow environment, and no relationship existed between the two sensors. In c) and d) the deployments occurred at Conimicut Point site and a linear relationship was dominant in (c), and was present at the beginning of deployment (d), the points following the one to one line, however after 5 days, fouling caused drift in the SeaFET sensor, and the comparison deteriorated.

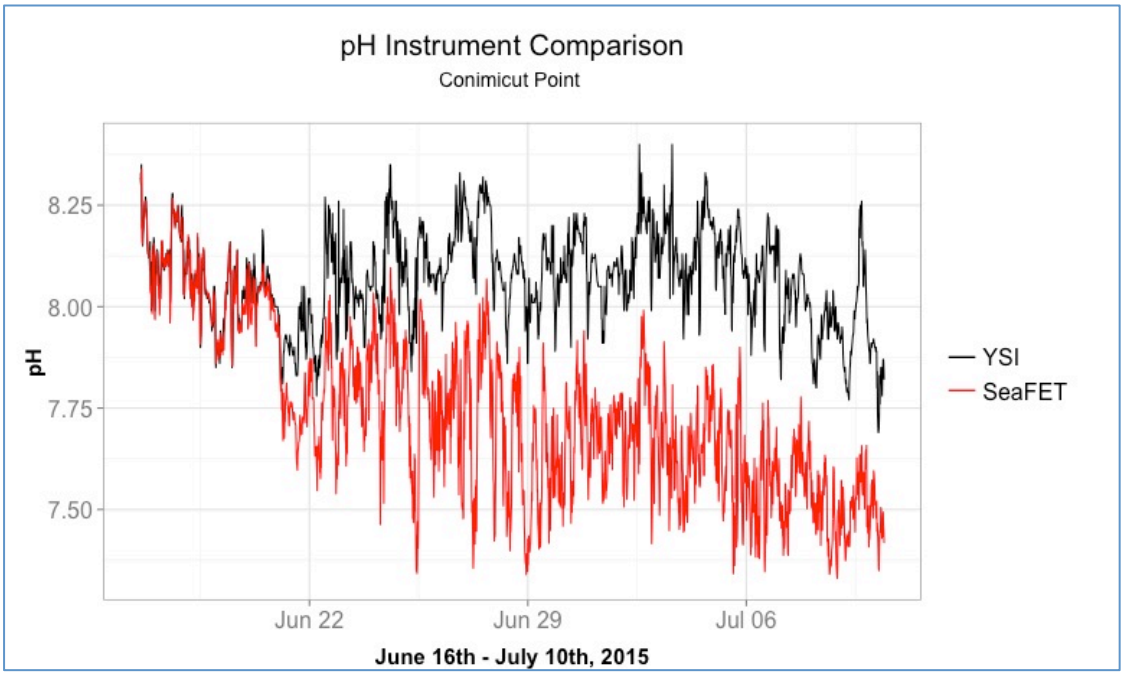


Figure 7. The second deployment at Conimicut Point started with very high agreement between the two sensors, however on June 21st, a bloom started and fouling occurred on the SeaFET sensor, leading to drift over the rest of the deployment. The trends are similar between the two sensors, but there is an offset present for the majority of the deployment. Post calibration data for the YSI sensor indicated that the sensor drifted 0.05 units over the three week deployment.

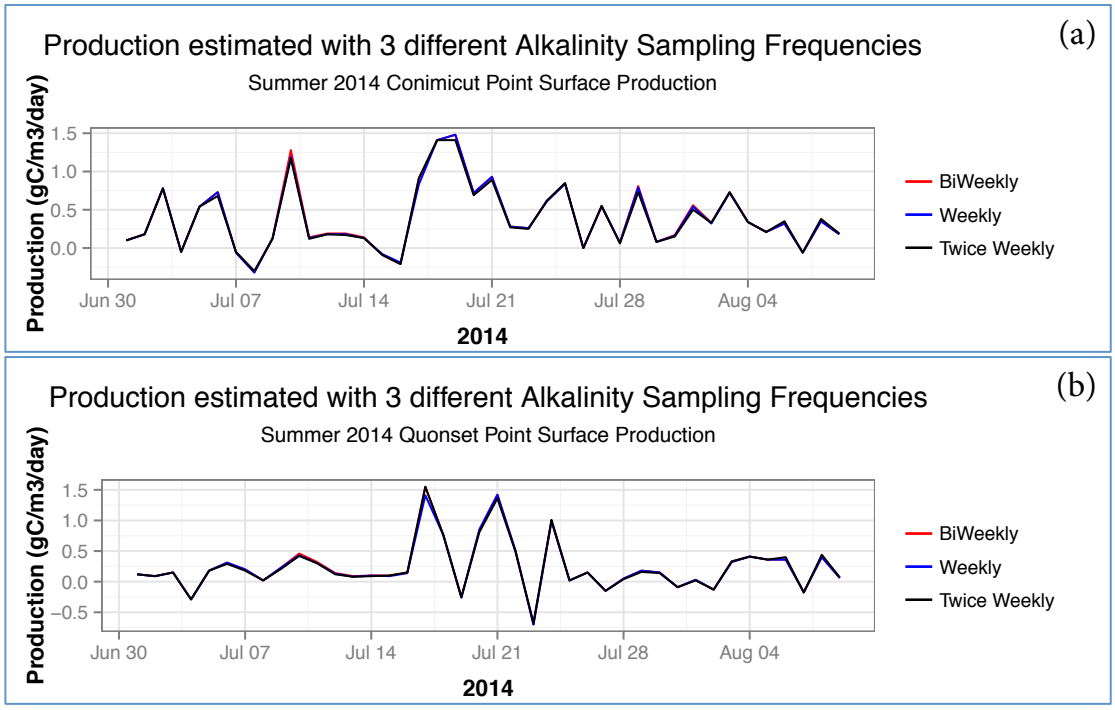


Figure 8. In order to quantify the effect of alkalinity measurements on metabolic rates, alkalinity was measured every 3-4 days and separated into three datasets. The twice-weekly dataset had a greater range of total alkalinity than either the weekly or biweekly datasets. Metabolic rates were estimated using buoy data from summer 2014 and the three different alkalinity datasets. Even though the range of alkalinity was greater during the twice-weekly sampling scheme, it had little effect on the metabolic rate estimates for either site, with an average percent change between the metabolic rate estimates of 1 – 8%.

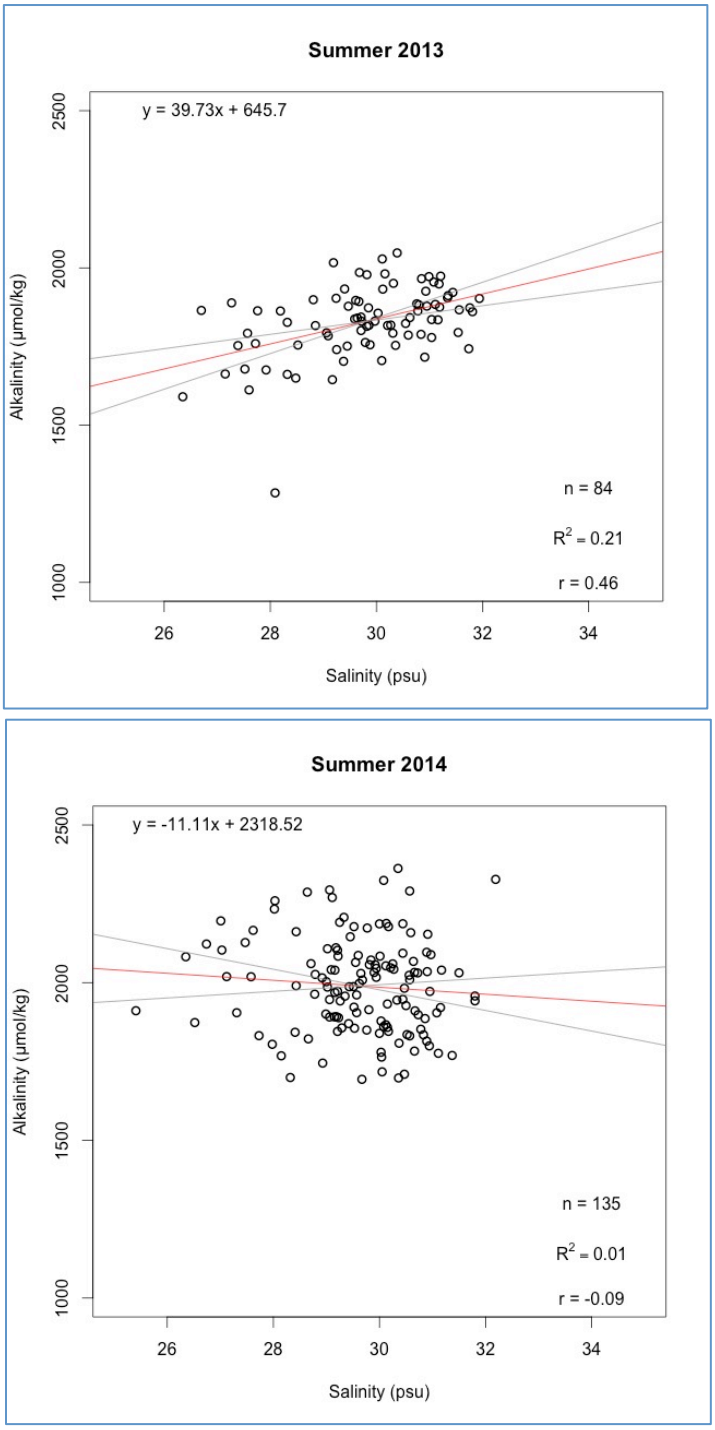


Figure 9. A preliminary investigation into a relationship between salinity and alkalinity in Narragansett Bay showed that there is a moderate relationship between the two for 2013, a very wet year with high river flow, but no relationship for 2014, which was drier than average, indicating that this relationship may be heavily flow dependent.

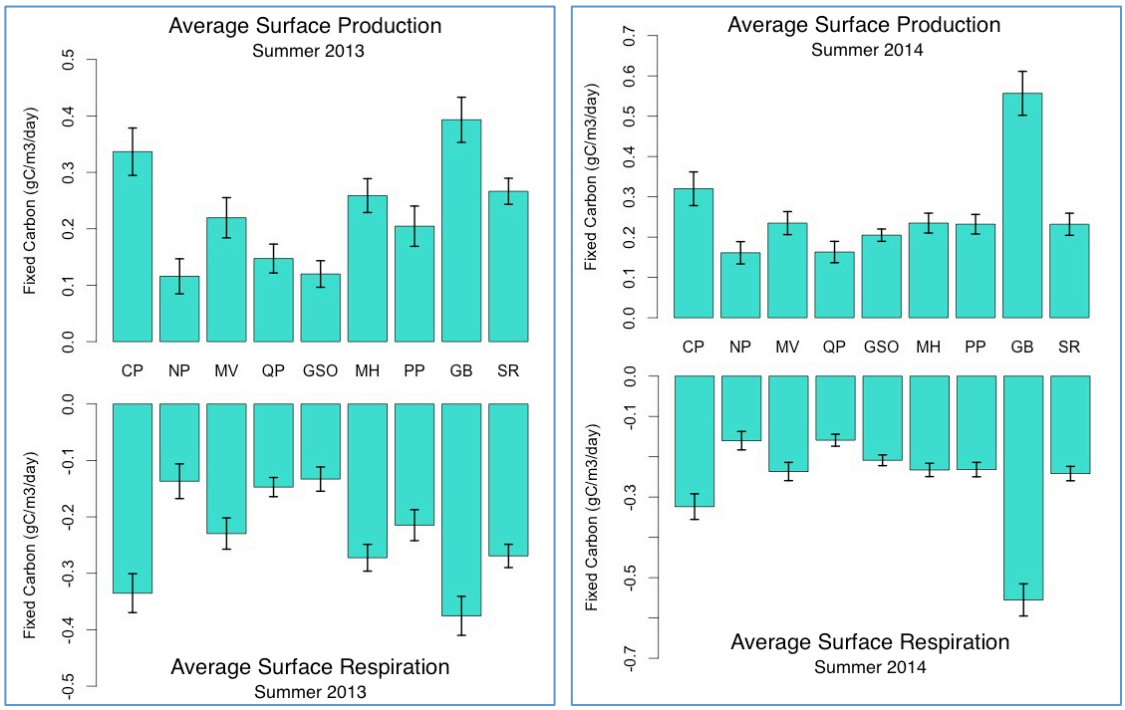


Figure 10. The surface carbon metabolic rate spatial patterns changed between the two summers. A gradient down the West Passage from Conimicut Point (CP) to GSO Dock is persistent both years with North Prudence exhibiting suppressed metabolic rates compared to the surrounding sites both years. Overall, metabolic rates were higher in 2014 for all categories, but the difference between surface means were not significant at the 95% confidence level. Note: scales are different between
years.

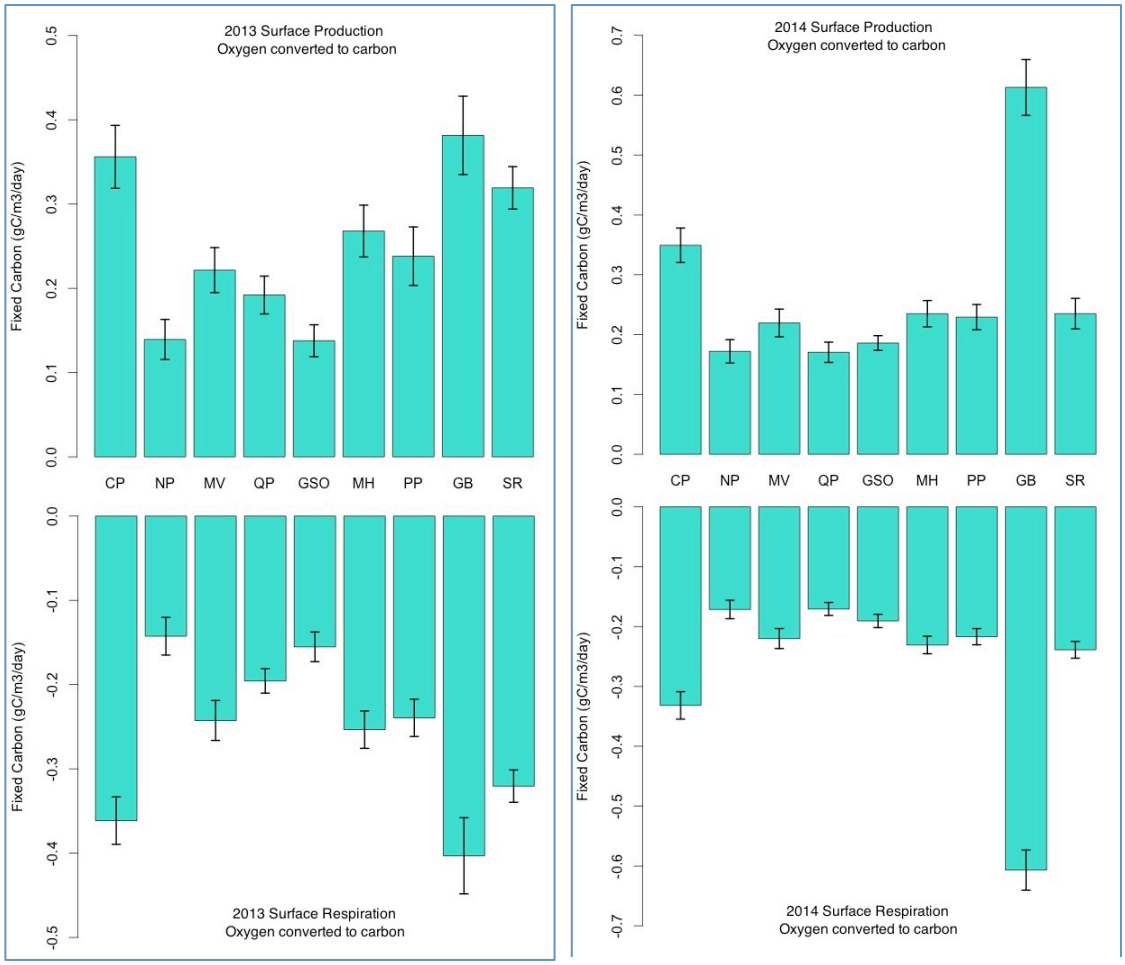


Figure 11. Oxygen metabolic rates converted to carbon units using the average PQ and RQ for each category and summer. The oxygen metabolic rates follow the same pattern as the carbon metabolic rates, with high production and respiration at Greenwich Bay and low metabolic rates at North Prudence. Note: scales are different between years.

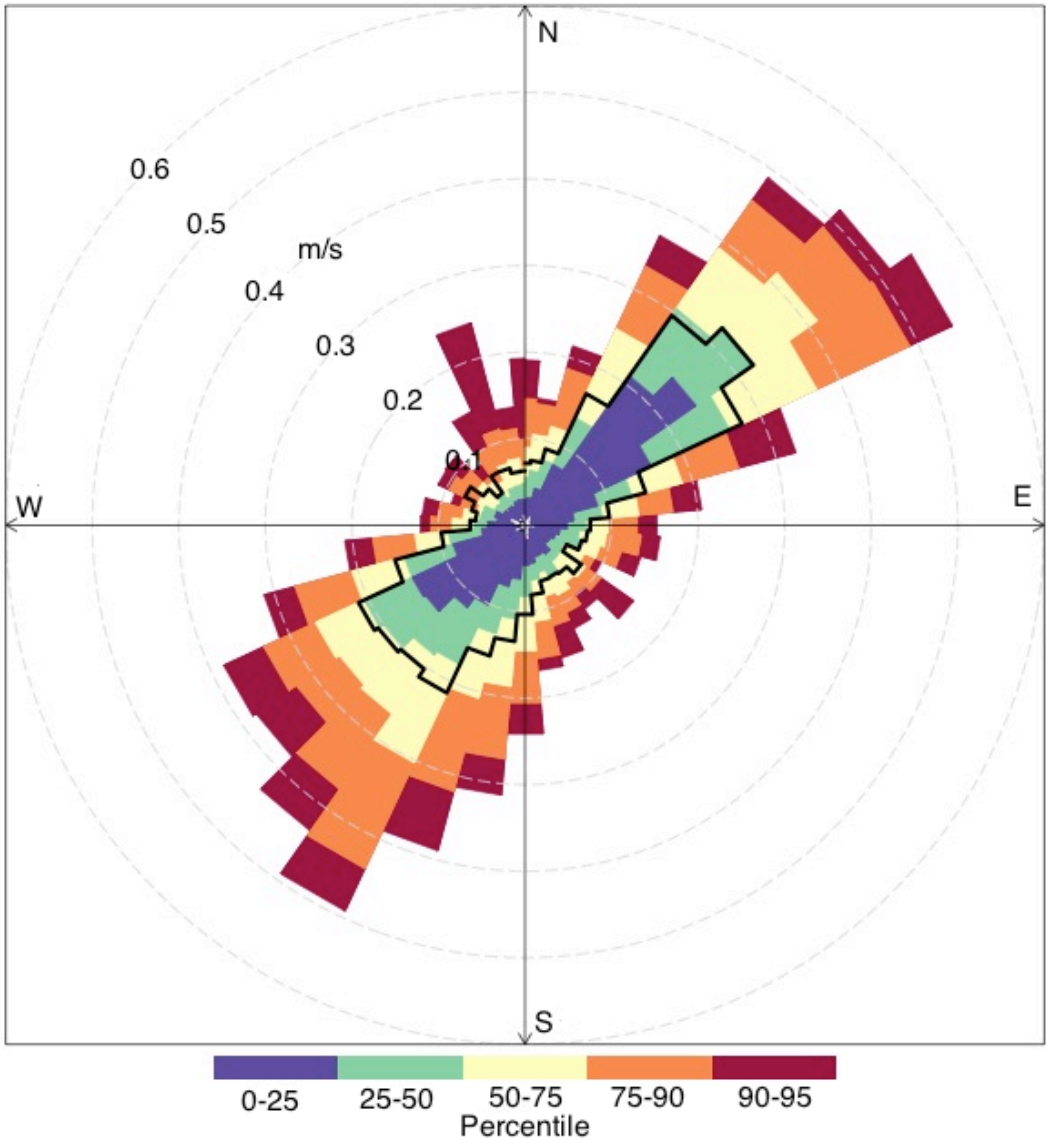


Figure 12. Average Warwick Neck current velocities from June 19th – Oct 10th, 2006. The average velocity is noted with the black line on the figure. The primary tidal current directions are northeast and southwest, with an average velocity of 0.25 m/s and an average spring tide velocity of 0.5 m/s.

APPENDICES

Appendix A. Dawn to Dusk Carbon Method

The following MATLAB code was used to estimate metabolic rates for each site and year. The equations utilized are listed in Table 1. Code was written by Leslie Smith and updated by Catherine Coupland in 2014.

```
%% Dawn to Dusk TCO2 Calculations
%This file calculates the change between dusk to dawn and dawn to
dusk in
%TCO2  TA values are from Summer 2013 Buoy TA titrations
%The values for dawn to dusk and dusk to dawn are also calculated
here
% Boric Acid equation updated by CMC 07/24/2014

% Clear all variables and close all open matlab figures
clear all
close all
clc
fprintf('** Loading Data... **\n\n')

%%   ENTER IN SOME INFORMATION

% Load the Data
Buoy = 'QP_BuoyO215min_2014.txt';
Cruise = 'AlkJuly_Test.txt';
Sun = 'SunTimes_14_AlkT.txt';

AvgDepth = 10.75;  % Average Depth for that station that summer
OffBot = 0.5;    % Distance of the bottom sensor off the bottom

%%   ASSIGNING VARIABLES

% Read the file and store the data into 'D':
% THE NUMBER IN THIS COMMAND CORRESPONDS TO THE NUMBER OF ROWS OF
COLUMN
% HEADERS IN THE RAW DATA - MAY NEED TO ADJUST!!!
BuoyData = importdata(Buoy, '\t', 1);
CruiseData = importdata(Cruise, '\t',1);
SunData = importdata(Sun, '\t',1);

% Assign variables from the columns in the datafile:
% Remember that you count text columns and data columns separate

% Buoy Data
BuoyDate = BuoyData.data(:,1);          % Date
Time = BuoyData.data(:,2);              % Time
STemp = BuoyData.data(:,4);             % Surf Temperature
```

```
SSal = BuoyData.data(:,5);              % Surf Salinity
SpH = BuoyData.data(:,6);               % Surf pH
BTemp = BuoyData.data(:,8);             % Bot Temperature
BSal = BuoyData.data(:,9);              % Bot Salinity
BpH = BuoyData.data(:,10);              % Bot pH
Depth = BuoyData.data(:,11) + OffBot;   % Depth Bot sensor + dist off
bot

% Cruise Data
JulStart = CruiseData.data(:,1);        % Julian Start Date for
Cruise
JulEnd = CruiseData.data(:,2);          % Julian End Date for Cruise
Zeu = CruiseData.data(:,3);             % Euphotic Depth
Surf_TA = CruiseData.data(:,4);         % Surface Alk
Bot_TA = CruiseData.data(:,5);          % Bottom Alk

% Sun Rise/Set Times
SunDate = SunData.data(:,1);            % Date
SunRise = SunData.data(:,2);            % Sun Rise Time
SunSet = SunData.data(:,3);             % Sun Set Time


%% Step 1: Pull out the Dawn and Dusk Measurements Based on Sun
Rise/Set

for Date_idx = 1:length(SunDate);
    temp_SunRise = SunRise(Date_idx);
    temp_SunSet = SunSet(Date_idx);
    temp_SunDate = SunDate(Date_idx);
   for Min_idx = find((BuoyDate == temp_SunDate));
       temp_Time = Time(Min_idx);
       temp_BuoyDate = BuoyDate(Min_idx);
       temp_STemp = STemp(Min_idx);
       temp_SSal = SSal(Min_idx);
       temp_SpH = SpH(Min_idx);
       temp_BTemp = BTemp(Min_idx);
       temp_BSal = BSal(Min_idx);
       temp_BpH = BpH(Min_idx);
       temp_Depth = Depth(Min_idx);
       for rise_idx = find ((temp_Time <= (temp_SunRise + 0.12)) &
(temp_Time > ...
            (temp_SunRise - 0.13)));
            RiseTime = temp_Time(rise_idx);
            RiseSTemp = temp_STemp(rise_idx);
            RiseSSal = temp_SSal(rise_idx);
            RiseSpH = temp_SpH(rise_idx);
            RiseBTemp = temp_BTemp(rise_idx);
            RiseBSal = temp_BSal(rise_idx);
            RiseBpH = temp_BpH(rise_idx);
            if temp_Depth(rise_idx) == Inf,
                RiseDepth = AvgDepth + OffBot;
            else
                RiseDepth = temp_Depth(rise_idx);
            end
       end
   end
```

```
   % Compile all the values just calculated into one column
   % Each loop adds a row to each column
   RiseALL_Time(Date_idx,1) = RiseTime;
   RiseALL_STemp(Date_idx,1) = RiseSTemp;
   RiseALL_SSal(Date_idx,1) = RiseSSal;
   RiseALL_SpH(Date_idx,1) = RiseSpH;
   RiseALL_BTemp(Date_idx,1) = RiseBTemp;
   RiseALL_BSal(Date_idx,1) = RiseBSal;
   RiseALL_BpH(Date_idx,1) = RiseBpH;
   RiseALL_Depth(Date_idx,1) = RiseDepth;

    for set_idx = find ((temp_Time <= (temp_SunSet + 0.12)) &
(temp_Time > ...
            (temp_SunSet - 0.13)));
            SetTime = temp_Time(set_idx);
            SetSTemp = temp_STemp(set_idx);
            SetSSal = temp_SSal(set_idx);
            SetSpH = temp_SpH(set_idx);
            SetBTemp = temp_BTemp(set_idx);
            SetBSal = temp_BSal(set_idx);
            SetBpH = temp_BpH(set_idx);
            if temp_Depth(set_idx) == Inf,
                SetDepth = AvgDepth + OffBot;
            else
                SetDepth = temp_Depth(set_idx);
            end

    end
   SetALL_Time(Date_idx,1) = SetTime;
   SetALL_STemp(Date_idx,1) = SetSTemp;
   SetALL_SSal(Date_idx,1) = SetSSal;
   SetALL_SpH(Date_idx,1) = SetSpH;
   SetALL_BTemp(Date_idx,1) = SetBTemp;
   SetALL_BSal(Date_idx,1) = SetBSal;
   SetALL_BpH(Date_idx,1) = SetBpH;
   SetALL_Depth(Date_idx,1) = SetDepth;
end

%% LET THE CALCUATIONS BEGIN!!!!!!!

%%%%%Surface Dawn Calculation%%%%%%
% Set Variables
RiseS_T = RiseALL_STemp;
RiseS_S = RiseALL_SSal;
RiseS_pH = RiseALL_SpH;
RiseS_K = RiseALL_STemp + 273.15;        % Temperature in Kelvin
% Set Constants
RiseS_pK1 = 17.788 - 0.073104.*RiseS_K - 0.0051087.*RiseS_S +
1.1463.*10.^(-4)...
    .*RiseS_K.^2;
RiseS_pK2 = 20.919 - 0.064209.*RiseS_K - 0.011887.*RiseS_S +
8.7313.*10.^(-5)...
    .*RiseS_K.^2;
RiseS_lnKb = (-8966.90 - 2890.53.*RiseS_S.^(0.5) - 77.942.*RiseS_S +
1.728.*RiseS_S.^(1.5) ...
    - 0.0996.*RiseS_S.^2)./RiseS_K + (148.0248 +
```

```
137.1942.*RiseS_S.^(0.5) + 1.62142.*RiseS_S) + ...
    (-24.4344 - 25.085.*RiseS_S.^(0.5) -
0.2474.*RiseS_S).*log(RiseS_K) + (0.053105.*RiseS_S.^(0.5)).*RiseS_K;

%Sub Equations
RiseS_aH = 10.^(-RiseS_pH);
RiseS_K1 = 10.^(-RiseS_pK1);
RiseS_K2 = 10.^(-RiseS_pK2);
RiseS_Kb = exp(RiseS_lnKb);
%RiseS_TA = 54.86.*RiseS_S + 400;
    % for Katie's data we have measurements of TA.
RiseS_fH = 0.739 + 0.0307.*RiseS_S + 0.0000794.*RiseS_S.^2 +
0.00006443.*RiseS_K...
    - 0.000117.*RiseS_S.*RiseS_K;
RiseS_Kw = exp(148.9802 - 13847.26./RiseS_K - 23.6521.*log(RiseS_K)
...
    + (-5.977 + 118.67./RiseS_K +
1.0495.*log(RiseS_K)).*RiseS_S.^(0.5) ...
    - 0.016155).*RiseS_fH.*10.^(-14);

% Load Total Alkalinity Measurements
Rise_S_TCO2_ALL = [];
for cruise_idx = [1:length(Zeu)],
    temp_JulStart = JulStart(cruise_idx);
    temp_JulEnd = JulEnd(cruise_idx);
    temp_Surf_TA = Surf_TA(cruise_idx);
    matchingdays = find((SunDate >= temp_JulStart) & (SunDate <=
temp_JulEnd));
    if sum(matchingdays) >= 1
        for Julian_idx = find((SunDate >= temp_JulStart) & (SunDate
<= temp_JulEnd));
            temp_RiseS_Kw = RiseS_Kw(Julian_idx);
            temp_RiseS_aH = RiseS_aH(Julian_idx);
            temp_RiseS_Kb = RiseS_Kb(Julian_idx);
            temp_RiseS_S = RiseS_S(Julian_idx);
            temp_RiseS_K1 = RiseS_K1(Julian_idx);
            temp_RiseS_K2 = RiseS_K2(Julian_idx);
            for t_idx = [1:length(temp_RiseS_Kw)];
                % Mother of all equations
            temp_RiseS_TCO2 = ((temp_Surf_TA -
(temp_RiseS_Kw./temp_RiseS_aH) -
temp_RiseS_Kb.*temp_RiseS_S.*1.243...
        .*10.^(-5)./(temp_RiseS_aH +
temp_RiseS_Kb)).*(temp_RiseS_aH.^2./(temp_RiseS_K1.*(temp_RiseS_aH
...
        + 2.*temp_RiseS_K2)) + (temp_RiseS_aH +
temp_RiseS_K2)./(temp_RiseS_aH + 2.*temp_RiseS_K2)).*(12./10.^3));

    %The conversion at the end converts TCO2 from umol/L to g m-2 -->
    % 1 mole/10^6 umol, 1 mol C/1 mol CO2, 12g C/ 1 mol C, 10^3L/m^3
                eval(['RiseS_TCO2', num2str(cruise_idx),' =
temp_RiseS_TCO2;']);
            end
        end
    Rise_S_TCO2_ALL = [Rise_S_TCO2_ALL; eval(['RiseS_TCO2',
num2str(cruise_idx)])];
    end
end
```

```
%%%%% Surface Dusk Calculation%%%%%
% Set Variables
SetS_T = SetALL_STemp;
SetS_S = SetALL_SSal;
SetS_pH = SetALL_SpH;
SetS_K = SetS_T + 273.15;       % Temperature in Kelvin

% Set Constants
SetS_pK1 = 17.788 - 0.073104.*SetS_K - 0.0051087.*SetS_S + 1.1463.*10
...
    .^(-4).*SetS_K.^2;
SetS_pK2 = 20.919 - 0.064209.*SetS_K - 0.011887.*SetS_S + 8.7313.*10
...
    .^(-5).*SetS_K.^2;
SetS_lnKb = (-8966.90 - 2890.53.*SetS_S.^(0.5) - 77.942.*SetS_S +
1.728.*SetS_S.^(1.5) ...
    - 0.0996.*SetS_S.^2)./SetS_K + (148.0248 +
137.1942.*SetS_S.^(0.5) + 1.62142.*SetS_S) + ...
    (-24.4344 - 25.085.*SetS_S.^(0.5) - 0.2474.*SetS_S).*log(SetS_K)
+ (0.053105.*SetS_S.^(0.5)).*SetS_K;

%Sub Equations
SetS_aH = 10.^(-SetS_pH);
SetS_K1 = 10.^(-SetS_pK1);
SetS_K2 = 10.^(-SetS_pK2);
SetS_Kb = exp(SetS_lnKb);
%SetS_TA = 54.86.*SetS_S + 400;
SetS_fH = 0.739 + 0.0307.*SetS_S + 0.0000794.*SetS_S.^2 + 0.00006443
...
    .*SetS_K - 0.000117.*SetS_S.*SetS_K;
SetS_Kw = exp(148.9802 - 13847.26./SetS_K - 23.6521.*log(SetS_K) ...
    + (-5.977 + 118.67./SetS_K +
1.0495.*log(SetS_K)).*SetS_S.^(0.5)...
    - 0.016155).*SetS_fH.*10.^(-14);

% Load Total Alkalinity Measurements
Set_S_TCO2_ALL = [];
for cruise_idx = [1:length(Zeu)],
    temp_JulStart = JulStart(cruise_idx);
    temp_JulEnd = JulEnd(cruise_idx);
    temp_Surf_TA = Surf_TA(cruise_idx);
    matchingdays = find((SunDate >= temp_JulStart) & (SunDate <=
temp_JulEnd));
    if sum(matchingdays) >= 1
    for Julian_idx = find((SunDate >= temp_JulStart) & (SunDate <=
temp_JulEnd));
        temp_SetS_Kw = SetS_Kw(Julian_idx);
        temp_SetS_aH = SetS_aH(Julian_idx);
        temp_SetS_Kb = SetS_Kb(Julian_idx);
        temp_SetS_S = SetS_S(Julian_idx);
        temp_SetS_K1 = SetS_K1(Julian_idx);
        temp_SetS_K2 = SetS_K2(Julian_idx);
        for t_idx = [1:length(temp_SetS_Kw)];
            % Mother of all equations
           temp_SetS_TCO2 = ((temp_Surf_TA -
temp_SetS_Kw./temp_SetS_aH - temp_SetS_Kb.*temp_SetS_S.*1.243...
```

```
    .*10.^(-5)./(temp_SetS_aH +
temp_SetS_Kb)).*(temp_SetS_aH.^2./(temp_SetS_K1.*(temp_SetS_aH ...
    + 2.*temp_SetS_K2)) + (temp_SetS_aH +
temp_SetS_K2)./(temp_SetS_aH + 2.*temp_SetS_K2)).*(12./10.^3));
%The conversion at the end converts TCO2 from umol/L to g m-2 -->
% 1 mole/10^6 umol, 1 mol C/1 mol CO2, 12g C/ 1 mol C, 10^3L/m^3
              eval(['SetS_TCO2', num2str(cruise_idx),' =
temp_SetS_TCO2;']);
            end
         end
    Set_S_TCO2_ALL = [Set_S_TCO2_ALL; eval(['SetS_TCO2',
num2str(cruise_idx)])];
    end
end


%%%%% Bottom Dawn Calculation%%%%%
% Set Variables
RiseB_T = RiseALL_BTemp;
RiseB_S = RiseALL_BSal;
RiseB_pH = RiseALL_BpH;
RiseB_K = RiseB_T + 273.15;     % Temperature in Kelvin

% Set Constants
RiseB_pK1 = 17.788 - 0.073104.*RiseB_K - 0.0051087.*RiseB_S + 1.1463
...
    .*10.^(-4).*RiseB_K.^2;
RiseB_pK2 = 20.919 - 0.064209.*RiseB_K - 0.011887.*RiseB_S + 8.7313
...
    .*10.^(-5).*RiseB_K.^2;
RiseB_lnKb = (-8966.90 - 2890.53.*RiseB_S.^(0.5) - 77.942.*RiseB_S +
1.728.*RiseB_S.^(1.5) ...
    - 0.0996.*RiseB_S.^2)./RiseB_K + (148.0248 +
137.1942.*RiseB_S.^(0.5) + 1.62142.*RiseB_S) + ...
    (-24.4344 - 25.085.*RiseB_S.^(0.5) -
0.2474.*RiseB_S).*log(RiseB_K) + (0.053105.*RiseB_S.^(0.5)).*RiseB_K;

%Sub Equations
RiseB_aH = 10.^(-RiseB_pH);
RiseB_K1 = 10.^(-RiseB_pK1);
RiseB_K2 = 10.^(-RiseB_pK2);
RiseB_Kb = exp(RiseB_lnKb);
%RiseB_TA = 54.86.*RiseB_S + 400;
RiseB_fH = 0.739 + 0.0307.*RiseB_S + 0.0000794.*RiseB_S.^2 +
0.00006443 ...
    .*RiseB_K - 0.000117.*RiseB_S.*RiseB_K;
RiseB_Kw = exp(148.9802 - 13847.26./RiseB_K - 23.6521.*log(RiseB_K)
...
    + (-5.977 + 118.67./RiseB_K +
1.0495.*log(RiseB_K)).*RiseB_S.^(0.5)...
    - 0.016155).*RiseB_fH.*10.^(-14);
% Load Total Alkalinity Measurements
Rise_B_TCO2_ALL = [];
for cruise_idx = [1:length(Zeu)],
    temp_JulStart = JulStart(cruise_idx);
    temp_JulEnd = JulEnd(cruise_idx);
    temp_Bot_TA = Bot_TA(cruise_idx);
```

```
    matchingdays = find((SunDate >= temp_JulStart) & (SunDate <=
temp_JulEnd));
    if sum(matchingdays) >= 1
    for Julian_idx = find((SunDate >= temp_JulStart) & (SunDate <=
temp_JulEnd));
        temp_RiseB_Kw = RiseB_Kw(Julian_idx);
        temp_RiseB_aH = RiseB_aH(Julian_idx);
        temp_RiseB_Kb = RiseB_Kb(Julian_idx);
        temp_RiseB_S = RiseB_S(Julian_idx);
        temp_RiseB_K1 = RiseB_K1(Julian_idx);
        temp_RiseB_K2 = RiseB_K2(Julian_idx);
        for t_idx = [1:length(temp_RiseB_Kw)];
            % Mother of all equations
           temp_RiseB_TCO2 = ((temp_Bot_TA -
temp_RiseB_Kw./temp_RiseB_aH - temp_RiseB_Kb.*temp_RiseB_S.*1.243...
    .*10.^(-5)./(temp_RiseB_aH +
temp_RiseB_Kb)).*(temp_RiseB_aH.^2./(temp_RiseB_K1.*(temp_RiseB_aH
...
    + 2.*temp_RiseB_K2)) + (temp_RiseB_aH +
temp_RiseB_K2)./(temp_RiseB_aH + 2.*temp_RiseB_K2)).*(12./10.^3));
%The conversion at the end converts TCO2 from umol/L to g m-2 -->
% 1 mole/10^6 umol, 1 mol C/1 mol CO2, 12g C/ 1 mol C, 10^3L/m^3
              eval(['RiseB_TCO2', num2str(cruise_idx),' =
temp_RiseB_TCO2;']);
          end
     end
    Rise_B_TCO2_ALL = [Rise_B_TCO2_ALL; eval(['RiseB_TCO2',
num2str(cruise_idx)])];
    end
end


%%%%% Bottom Dusk Calculation%%%%%
% Set Variables
SetB_T = SetALL_BTemp;
SetB_S = SetALL_BSal;
SetB_pH = SetALL_BpH;
SetB_K = SetB_T + 273.15;       % Temperature in Kelvin

% Set Constants
SetB_pK1 = 17.788 - 0.073104.*SetB_K - 0.0051087.*SetB_S + 1.1463 ...
    .*10.^(-4).*SetB_K.^2;
SetB_pK2 = 20.919 - 0.064209.*SetB_K - 0.011887.*SetB_S + 8.7313 ...
    .*10.^(-5).*SetB_K.^2;
SetB_lnKb = (-8966.90 - 2890.53.*SetB_S.^(0.5) - 77.942.*SetB_S +
1.728.*SetB_S.^(1.5) ...
    - 0.0996.*SetB_S.^2)./SetB_K + (148.0248 +
137.1942.*SetB_S.^(0.5) + 1.62142.*SetB_S) + ...
    (-24.4344 - 25.085.*SetB_S.^(0.5) - 0.2474.*SetB_S).*log(SetB_K)
+ (0.053105.*SetB_S.^(0.5)).*SetB_K;

%Sub Equations
SetB_aH = 10.^(-SetB_pH);
SetB_Kb = exp(SetB_lnKb);
SetB_K1 = 10.^(-SetB_pK1);
SetB_K2 = 10.^(-SetB_pK2);
%SetB_TA = 54.86.*SetB_S + 400;
```

```
SetB_fH = 0.739 + 0.0307.*SetB_S + 0.0000794.*SetB_S.^2 + 0.00006443
...
    .*SetB_K - 0.000117.*SetB_S.*SetB_K;
SetB_Kw = exp(148.9802 - 13847.26./SetB_K - 23.6521.*log(SetB_K) ...
    + (-5.977 + 118.67./SetB_K + 1.0495.*log(SetB_K)).*SetB_S.^(0.5)
...
    - 0.016155).*SetB_fH.*10.^(-14);

% Load Total Alkalinity Measurements
Set_B_TCO2_ALL = [];
for cruise_idx = [1:length(Zeu)],
    temp_JulStart = JulStart(cruise_idx);
    temp_JulEnd = JulEnd(cruise_idx);
    temp_Bot_TA = Bot_TA(cruise_idx);
    matchingdays = find((SunDate >= temp_JulStart) & (SunDate <=
temp_JulEnd));
    if sum(matchingdays) >= 1
    for Julian_idx = find((SunDate >= temp_JulStart) & (SunDate <=
temp_JulEnd));
        temp_SetB_Kw = SetB_Kw(Julian_idx);
        temp_SetB_aH = SetB_aH(Julian_idx);
        temp_SetB_Kb = SetB_Kb(Julian_idx);
        temp_SetB_S = SetB_S(Julian_idx);
        temp_SetB_K1 = SetB_K1(Julian_idx);
        temp_SetB_K2 = SetB_K2(Julian_idx);
        for t_idx = [1:length(temp_SetB_Kw)];
            % Mother of all equations
           temp_SetB_TCO2 = ((temp_Bot_TA -
temp_SetB_Kw./temp_SetB_aH - temp_SetB_Kb.*temp_SetB_S.*1.243...
    .*10.^(-5)./(temp_SetB_aH +
temp_SetB_Kb)).*(temp_SetB_aH.^2./(temp_SetB_K1.*(temp_SetB_aH ...
    + 2.*temp_SetB_K2)) + (temp_SetB_aH +
temp_SetB_K2)./(temp_SetB_aH + 2.*temp_SetB_K2)).*(12./10.^3));
%The conversion at the end converts TCO2 from umol/L to g m-2 -->
% 1 mole/10^6 umol, 1 mol C/1 mol CO2, 12g C/ 1 mol C, 10^3L/m^3
              eval(['SetB_TCO2', num2str(cruise_idx),' =
temp_SetB_TCO2;']);
        end
    end
    Set_B_TCO2_ALL = [Set_B_TCO2_ALL; eval(['SetB_TCO2',
num2str(cruise_idx)])];
    end
end


%% Calculate Production from the TCO2 change from Dawn to Dusk
% This calculation takes the TCO2 concentration at dawn and subtracts
it
% from the TCO2 concentration at dusk at each sensor.

% Subract TCO2 concen at dawn from dusk
DawnToDusk_Surf = -1.*(Set_S_TCO2_ALL(1:(length(SunDate)-1)) -
Rise_S_TCO2_ALL(1:(length(SunDate)-1)));

    % Values are multiplied by -1 because changes in the water
    % column are inverse to organic matter production, i.e. a
    % dec in TCO2 in the water column means an increase in
```

```
    % organic matter

DawnToDusk_Bot = -1.*(Set_B_TCO2_ALL(1:(length(SunDate)-1)) -
Rise_B_TCO2_ALL(1:(length(SunDate)-1)));



%% Calculate Respiration from the TCO2 change from Dusk to Dawn
% This calculation takes the TCO2 concentration at dusk and subtracts
it
% from dawn the next day for each sensor.

% Do some Dusk to next day Dawn Subtraction for the Surface
DuskToDawnS = -1.*(Rise_S_TCO2_ALL(2:(length(SunDate))) -
Set_S_TCO2_ALL(1:(length(SunDate)-1)));


% Do same Dusk to next day Dawn Subtraction for the Bottom
DuskToDawnB = -1.*(Rise_B_TCO2_ALL(2:(length(SunDate))) -
Set_B_TCO2_ALL(1:(length(SunDate)-1)));


Output = [DawnToDusk_Surf, DawnToDusk_Bot, DuskToDawnS, DuskToDawnB];
```

Appendix B. Dawn Dusk Dawn Oxygen method

The following MATLAB code estimates metabolic rates in $gO_2m^{-3}day^{-1}$ or $night^{-1}$. The code was written by Leslie Smith in 2010 (Smith 2011). For each day at sunrise and sunset, the buoy data closest to sunrise and sunset times are pulled out and used to calculate the change in oxygen between dawn and dusk and dusk and the following dawn.

```
%% Dawn to Dusk Calculation Model
% Written in September 2010 by LS
% Edited in August 2013 so that the outputs are day time and night
time
% rates at surface and bottom sensors (and mid when available), i.e.
no
% integration with depth --> All code about depth has been removed.


%% Clear all variables and close all open matlab figures
clear all
close all
clc
fprintf('** Loading Data... **\n\n')
%%   ENTER IN SOME INFORMATION

% Load the Data
Buoy = 'GB_BuoyO215min_2013.txt';
Sun = 'SunTimes_13_Sept.txt';
Wind = 'K_2013_M.txt';

% If there is a Mid Depth make sure to "un" comment out the following
% lines: 48, 77, 85, 97, 106, 114, 199, 206, 217, 225, 231

PQ = 1.4;       % From Smith, et al. 2012
RQ = 1;         % RQ of 1


%%   ASSIGNING VARIABLES

% Read the file and store the data into 'D':
% THE NUMBER IN THIS COMMAND CORRESPONDS TO THE NUMBER OF ROWS OF
COLUMN
% HEADERS IN THE RAW DATA - MAY NEED TO ADJUST!!!
BuoyData = importdata(Buoy, '\t', 1);
SunData = importdata(Sun, '\t',1);
```

```
WindData = importdata(Wind, '\t',1);

% Assign variables from the columns in the datafile:
% Remember that you count text columns and data columns separate

% Buoy Data
BuoyDate = BuoyData.data(:,1);          % Date
Time = BuoyData.data(:,2);              % Time
SO2 = BuoyData.data(:,3);               % Surf O2 (mgO2 L-1)
STemp = BuoyData.data(:,4);             % Surf Temp
SSal = BuoyData.data(:,5);              % Surf Salinity
BO2 = BuoyData.data(:,7);               % Bot O2 (mgO2 L-1)
% MO2 = BuoyData.data(:,12);            % Mid O2 (mgO2 L-1)

% Sun Rise/Set Times
SunDate = SunData.data(:,1);            % Date
SunRise = SunData.data(:,2);            % Sun Rise Time
SunSet = SunData.data(:,3);             % Sun Set Time

% Wind Data
Date = WindData.data(1:122,1);          % Date
K_DawnToDusk = WindData.data(1:122,2);      % K Dawn to Dusk Coeff
    % Day = 6am to 6pm
K_DuskToDawn = WindData.data(1:122,3);      % K Dusk to Dawn Coeff
    % Note in the calc of this K, the night K is averaged with the
    % following morning K
    % Night = 6pm to Midnight; Morning = midnight to 6am

%% Step 1: Pull out the Dawn and Dusk Measurements Based on Sun
Rise/Set

for Date_idx = 1:length(SunDate);
    temp_SunRise = SunRise(Date_idx);
    temp_SunSet = SunSet(Date_idx);
    temp_SunDate = SunDate(Date_idx);
   for Min_idx = find((BuoyDate == temp_SunDate));
       temp_Time = Time(Min_idx);
       temp_BuoyDate = BuoyDate(Min_idx);
       temp_SO2 = SO2(Min_idx);
       temp_STemp = STemp(Min_idx);
       temp_SSal = SSal(Min_idx);
       temp_BO2 = BO2(Min_idx);
       % temp_MO2 = MO2(Min_idx);
       for rise_idx = find ((temp_Time <= (temp_SunRise + 0.12)) &
(temp_Time > ...
            (temp_SunRise - 0.13)));
            RiseTime = temp_Time(rise_idx);
            RiseSO2 = temp_SO2(rise_idx);
            RiseT = temp_STemp(rise_idx);
            RiseS = temp_SSal(rise_idx);
            RiseBO2 = temp_BO2(rise_idx);
            % RiseMO2 = temp_MO2(rise_idx);
       end
   end


   % Compile all the values just calculated into one column
```

```
   % Each loop adds a row to each column
   RiseALL_Time(Date_idx,1) = RiseTime;
   RiseALL_SO2(Date_idx,1) = RiseSO2;
   RiseALL_T(Date_idx,1) = RiseT;
   RiseALL_S(Date_idx,1) = RiseS;
   RiseALL_BO2(Date_idx,1) = RiseBO2;
   % RiseALL_MO2(Date_idx,1) = RiseMO2;

    for set_idx = find ((temp_Time <= (temp_SunSet + 0.12)) &
(temp_Time > ...
            (temp_SunSet - 0.13)));
            SetTime = temp_Time(set_idx);
            SetSO2 = temp_SO2(set_idx);
            SetT = temp_STemp(set_idx);
            SetS = temp_SSal(set_idx);
            SetBO2 = temp_BO2(set_idx);
            % SetMO2 = temp_MO2(set_idx);

    end
   SetALL_Time(Date_idx,1) = SetTime;
   SetALL_SO2(Date_idx,1) = SetSO2;
   SetALL_T(Date_idx,1) = SetT;
   SetALL_S(Date_idx,1) = SetS;
   SetALL_BO2(Date_idx,1) = SetBO2;
   % SetALL_MO2(Date_idx,1) = SetMO2;
end

%% Calculate Percent Oxygen Saturation
% This section was copied from the 'O2 Saturation' model that I wrote
in
% May 2010

% Load the Coefficients

A0 = 5.80871;
A1 = 3.20291;
A2 = 4.17887;
A3 = 5.10006;
A4 = -9.86643*10^(-2);
A5 = 3.80369;

B0 = -7.01577*10^(-3);
B1 = -7.70028*10^(-3);
B2 = -1.13864*10^(-2);
B3 = -9.51519*10^(-3);

C0 = -2.75915*10^(-7);

% Convert Temperature

Rise_Ts = log((298.15 - RiseALL_T)./(273.15 + RiseALL_T));
Set_Ts = log((298.15 - SetALL_T)./(273.15 + SetALL_T));

% Super Massive Equation

Rise_lnO2 = A0 + A1.*Rise_Ts + A2.*Rise_Ts.^2 + A3.*Rise_Ts.^3 + ...
```

```
    A4*Rise_Ts.^4 + A5.*Rise_Ts.^5 + RiseALL_S.*(B0 + B1.*Rise_Ts +
...
    B2.*Rise_Ts.^2 + B3.*Rise_Ts.^3) + C0.*RiseALL_S.^2;
Rise_O2Sat = exp(Rise_lnO2);

Set_lnO2 = A0 + A1.*Set_Ts + A2.*Set_Ts.^2 + A3.*Set_Ts.^3 + ...
    A4*Set_Ts.^4 + A5.*Set_Ts.^5 + SetALL_S.*(B0 + B1.*Set_Ts + ...
    B2.*Set_Ts.^2 + B3.*Set_Ts.^3) + C0.*SetALL_S.^2;
Set_O2Sat = exp(Set_lnO2);

% Calculate the Density of the water parcel
P = ones(length(RiseALL_T),1);       % Already takes into account 1
atm
                                     % & the surf sonde is 1m below
the surf
%Run the function

Rise_dens = sw_dens(RiseALL_S,RiseALL_T,P);
Set_dens = sw_dens(SetALL_S,SetALL_T,P);

% Convert the units
% The initial units are in umol/kg and we want to convert them to
mgO2L-1

Rise_O2mgL = Rise_O2Sat*32.*Rise_dens.*10.^3./(10.^6.*10.^3);
Set_O2mgL = Set_O2Sat*32.*Set_dens.*10.^3./(10.^6.*10.^3);

%% Calc Air-Sea Gas exchange coefficients
% Air-Sea Gas exchange correction taken from Vaudrey Dissertation
% These are claculated for full data set --> June 1 through Sept 1
SDRise = 0.209.*(Rise_O2mgL - RiseALL_SO2)./(Rise_O2mgL);
SDSet = 0.209.*(Set_O2mgL - SetALL_SO2)./(Set_O2mgL);

SDAvg_DawnToDusk = mean([SDRise(1:122),SDSet(1:122)], 2);
    % Saturation Deficit, units atm
    % The "2" averages by row instead of column
    % SDAvg2 = (SDRise + SDSet)./2;
       % Used the above equ to double chech that the average was
correct
       % (9/15/10)

D_DawnToDusk = K_DawnToDusk.*SDAvg_DawnToDusk;
    % D is the flux of O2 across the surf of the water
    % K is calculated in a wind program windavg_NightDay
        % and is an average of QP and CP NOAA stations

SDAvg_DuskToDawn = mean([SDRise(2:123),SDSet(1:122)],2);
    % Average Dusk from the Dawn the next morning

D_DuskToDawn = K_DuskToDawn.*SDAvg_DuskToDawn;

%% Calculate Production from the oxygen change from Dawn to Dusk
% This calculation takes the oxygen concentration at dawn and
subtracts it
% from the oxygen concentration at dusk.  Surface data are corrected
for
```

```
% air sea gas exchange.

% Subract O2 concen at dawn from dusk
DawnToDusk_RawS = SetALL_SO2(1:122) - RiseALL_SO2(1:122);
DawnToDusk_B = SetALL_BO2(1:122) - RiseALL_BO2(1:122);
% DawnToDusk_M = SetALL_MO2(1:92) - RiseALL_MO2(1:92);
    % By doing it as (1:92) it only runs for June 1 - Aug 31

% Subract out Air-Sea Gas Exhange for the surface
DawnToDusk_S = DawnToDusk_RawS - D_DawnToDusk;

% We want to leave output in gO2 m-3 d-1, the conversion below has
been
% deactivated
% DaySurface = DawnToDusk_S./PQ.*(12/32);
% DayBottom = DawnToDusk_B./PQ.*(12/32);
% DayMid = DawnToDusk_M./PQ.*(12/32);

%% Calculate Respiration from the oxygen change from Dusk to Dawn
% This calculation takes the oxygen concentration at dusk and
subtracts it
% from dawn the next day.  Surface data are corrected for
% air sea gas exchange.

% Do some Dusk to next day Dawn Subtraction for the Surface
DuskToDawn_RawS = RiseALL_SO2(2:123) - SetALL_SO2(1:122);
DuskToDawn_B = RiseALL_BO2(2:123) - SetALL_BO2(1:122);
% DuskToDawn_M = RiseALL_MO2(2:93) - SetALL_MO2(1:92);
    % Rise 2:93 runs June 2 to Sept 1, Set 1:92 runs June 1 to Aug 31

% Air-Sea Gas exchange correct the data
DuskToDawn_S = DuskToDawn_RawS - D_DuskToDawn;

% We want to leave output in gO2 m-3 d-1, the conversion below has
been
% deactivated
% NightSurface = DuskToDawn_S.*RQ.*(12/32);
% NightBottom = DuskToDawn_B.*RQ.*(12/32);
% NightMid = DuskToDawn_M.*RQ.*(12/32);


Output = [DawnToDusk_S,DawnToDusk_B,DuskToDawn_S,DuskToDawn_B];
% Units are in g02 m-3 day-1

% Output_Mid =
[DawnToDusk_S,DawnToDusk_B,DawnToDusk_M,DuskToDawn_S,DuskToDawn_B,Dus
kToDawn_M];
```

Appendix C. Air-sea gas exchange coefficient method

The following MATLAB code estimates a 12 hour day time and nighttime air-sea gas exchange coefficient using wind data from two NOAA National Buoy Data. The two gas exchange coefficients are averaged together to provide one gas exchange coefficient for all sites for day time, and another for night time. The code was written by Leslie Smith and utilizes an equation developed by Vaudrey (2007) and a coefficient for Narragansett Bay derived by Kremer (2003b).

```
% This file reads in a text file containing wind information.  The
text
% file has information for the first 7 columns:  YYYY MM DD hh mm  WD
WSPD
% Be sure to update the values in the first block of this code before
you
% run it.  Also it is a good idea to delete the excel file that was
already
% made if you re-run the code.
% This file does the following:
%   - Reads in data
%   - Gets rid of bad data
%   - Plots the data that was read in
%   - Filters the data based a moving average filter
%   - Stores the data in an excel spreadsheet
%   - Stores another excel spreadsheet with air/sea gas exchange
calcs

% Clear all variables and close all open matlab figures
clear all
close all
clc

% SET THESE VALUES BEFORE RUNNING THE
CODE:%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% (1)Create start/stop dates for plotting
StartM = 07;            % Start Month
StartD = 20;            % Start Day
EndM = 10;              % End Month
EndD = 01;              % End Day
% (2) The name of the file that you are reading from, with.txt
extension:
filename = 'CPTR1_2013_edits.txt';
% (3) Enter the number of hours you want to filter:
%Hours2Filt = 24;
```

```
% (4) Enter the name of the file you want to export to Excel%
%xlfile = 'QPWind06_24hr';           % Wind information file
%xlfile2 = 'QPWind06_DailyAvg';      % Daily windspeed avg + K

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%
% SET AIR/SEA GAS EXCHANGE VARIABLES HERE:
height = 20.73;                 % Station height (m) %%%Must
Change!!!!

D = importdata(filename);

% Read the file and store the data into 'D':
% THE NUMBER IN THIS COMMAND CORRESPONDS TO THE NUMBER OF ROWS OF
COLUMN
% HEADERS IN THE RAW DATA - MAY NEED TO ADJUST!!!
% D = importdata(filename, ' ', 2); (8/22/13 - previously had this
code in
% here.  Looks like was to remove header rows.  But for some reason
with my
% input file with one header row (even when I changed the value to 1)
it
% got messed up.  Looks like it loads things alright as I have it in
line
% 40.

% Assign variables from the columns in the datfile:
YYYY = D.data(:,1);                      % Year
MM = D.data(:,2);                        % Month
DD = D.data(:,3);                        % Day
hh = D.data(:,4);                        % Hour
mm = D.data(:,5);                        % Minute
ss = zeros(size(mm));                    % Seconds - need seconds for
matlabs datenum command
WD = D.data(:,6);                        % Wind direction
WSPD = D.data(:,7);                      % Wind Speed
TIME = datenum([YYYY,MM,DD,hh,mm,ss]);  % Make a time in Matlab's
datenum format

% Make a giant data matrix: 1st column = time, 2nd column = Wind Dir,
3rd
% column = Windspeed
datamatrix = [TIME,WD,WSPD];

% Find indices with bad Wind Direction (WD) and windspeed data:
% Bad_indices = find(((datamatrix(:,2) > 998)) | (datamatrix(:,3) >
98));

% Find indices with ONLY bad Wind Speed data  this will make
incorrect
% North South vectors in the first sheet exported:
Bad_indices = find((datamatrix(:,3) > 98));

% Erase rows with bad data:
datamatrix(Bad_indices,:) = [];
```

```
% Chop out parts of the datamatrix for periods of time we want:
StartD = datenum(YYYY(1), StartM, StartD);
StopD = datenum(YYYY(1), EndM, EndD);
fprintf(['Start Date: ',datestr(StartD),'\n'])   % show start date on
screen
fprintf(['End Date: ',datestr(StopD),'\n'])    % show end date
% Find indices within our time window:
time_indices = find(((datamatrix(:,1) >= StartD)) & (datamatrix(:,1)
<= StopD));
% Create new matrix 'datamatrix2' with our time window
datamatrix2 = datamatrix(time_indices,:);


% Calculate average value of raw windspeed for a 24 hr period by
looping
% through each day and calculating the average value of that day:

% Create a variable to store the avg 24 hr windspeed:
AvgDailyWind = [];

% Create a new vector 'datamatrix3' from damatrix2 that is in the
form:
% [YYYY, MM, DD, HH, MM, SS, Windspeed]
datamatrix3 = datevec(datamatrix2(:,1));
datamatrix3 = cat(2,datamatrix3,datamatrix2(:,3));

% Calculate the number of months that span the period of data we are
% analyzing:
NumMonths = max(datamatrix3(:,2)) - min(datamatrix3(:,2));

% Create a starting variable to store data from the night before for
% day/night averages
NightData = [];

% Loop through the number of months:
for count = [0:NumMonths],
   % Pull out the section of data that corresponds to everything in
this
   % particular month
   current_month = count + min(datamatrix3(:,2));
   temp_month_data_indices = find(datamatrix3(:,2) == current_month);
   temp_month_data = datamatrix3(temp_month_data_indices,:);
   % Find the number of days in the month we are analyzing:
   NumDays = max(temp_month_data(:,3)) - min(temp_month_data(:,3));
   for count2 = [0:NumDays],
      % CALCULATE AVG VALUES FOR A 24 HR PERIOD
      % Pull out the section of data that corresponds to everything
in this
      % particular day
      current_day = count2 + min(temp_month_data(:,3));
      temp_day_indices = find(temp_month_data(:,3) == current_day);
      % Check to see if there is an occasion of very bad data and
there are
      % no good points for that day:
      if isempty(temp_day_indices),
          fprintf(['Ignoring horrible section of data!!!: month =
',...
```

```
            num2str(current_month), ' day = ',
num2str(current_day), '\n'])
        continue
    end
    temp_day_data = temp_month_data(temp_day_indices,:);

    % Calculate the average windspeed for this day:
    AvgWind = sum(temp_day_data(:,7))/length(temp_day_data);
    DayStamp = temp_day_data(1,[1:3]);
    NumDataPoints = length(temp_day_indices);
    % Calculate the U10 velocity:
    Uten = AvgWind*(1/(0.097*log(height/10) + 1));
    % Calculate the oxygen exchange coeff.
    K = 0.55*exp(0.15*Uten);
    %Kremer et al 2003 says coefficient here is 0.55
    EntireDayAvg = [DayStamp,AvgWind,K,NumDataPoints];

    % CALCULATE VALUES FOR THE MORNING MIDNIGHT-6AM PERIOD
    MorningData_indices = find(temp_day_data(:,4) < 6);
    % Check to see if there is an occasion of very bad data and
there are
    % no good points for that day:
    if isempty(MorningData_indices),
        MorningData = [];
        MorningAvg = [NaN,NaN,NaN];
    else
        MorningData = temp_day_data(MorningData_indices,:);
        AvgWindMorning = sum(MorningData(:,7))/length(MorningData);
        NumPointsMorning = length(MorningData_indices);
        UtenMorning = AvgWindMorning*(1/(0.097*log(height/10) +
1));
        KMorning = 0.55*exp(0.15*UtenMorning);
        MorningAvg = [AvgWindMorning,KMorning,NumPointsMorning];
    end


    % CALCULATE VALUES FOR THE DAYTIME (6AM-6PM) PERIOD
    % Pull out the section of data that corresponds to daytime
    DayData_indices = find(temp_day_data(:,4) >= 6 &
temp_day_data(:,4) < 18);
    % Check to see if there is an occasion of very bad data and
there are
    % no good points for that day:
    if isempty(DayData_indices),
        DayData = [];
        DayAvg = [NaN,NaN,NaN];
    else
        DayData = temp_day_data(DayData_indices,:);
        AvgWindDay = sum(DayData(:,7))/length(DayData);
        NumPointsDay = length(DayData_indices);
        UtenDay = AvgWindDay*(1/(0.097*log(height/10) + 1));
        KDay = 0.55*exp(0.15*UtenDay);
        DayAvg = [AvgWindDay,KDay,NumPointsDay];
    end


    % CALCULATE VALUES FOR EVENING 6PM-MIDNIGHT PERIOD
```

```
      NightData_indices = find(temp_day_data(:,4) >= 18);
      % Check to see if there is an occasion of very bad data and
there are
      % no good points for that day:
      if isempty(NightData_indices),
          NightData = [];
          NightAvg = [NaN,NaN,NaN];
      else
          NightData = temp_day_data(NightData_indices,:);
          AvgWindNight = sum(NightData(:,7))/length(NightData);
          NumPointsNight = length(NightData_indices);
          UtenNight = AvgWindNight*(1/(0.097*log(height/10) + 1));
          KNight = 0.55*exp(0.15*UtenNight);
          NightAvg = [AvgWindNight,KNight,NumPointsNight];
      end

    % Add this newest calculation to the entire dataset:
      NextRow2Add = [EntireDayAvg,MorningAvg,DayAvg,NightAvg];
      AvgDailyWind = cat(1,AvgDailyWind,NextRow2Add);

   end % end days loop

end % end months loop


% Export the second sheet:
xldatacells2 = num2cell(AvgDailyWind);
colheader2 = {'Year','Month','Day','Avg Windspeed - 24',...
    'K - 24','# Data Pts - 24','Avg Windspeed - Morning',...
    'K - Morning','# Data Pts - Morning','Avg Windspeed - Day',...
    'K - Day','# Data Pts - Day','Avg Windspeed - Night',...
    'K - Night','# Data Pts - Night',};
xloutput2 = [colheader2; xldatacells2];
% xlswrite(xlfile2, xloutput2)
% 8/22/13 - Even though cannot export to Excel from Mac Matlab, the
above
% variables do provide an output matrix can use.
```

Appendix D. Supporting Figures

Appendix D supplies additional figures for categories not explicitly discussed in the text but are relevant to the method testing. The sections are as follows:

D.1 – 2014 Method Comparison by site.

D.2 – Impact of increasing or decreasing pH on metabolic rates for North Prudence, Mt. View, Quonset Point, and GSO Dock, 2013.

D.3 - Impact of alkalinity variation on metabolic rates for Conimicut Point and Quonset Point surface respiration, bottom production, and bottom respiration.

D.4 – Spatial Trends in bottom metabolic rate estimates

D.1 – 2014 Method Comparison by Site

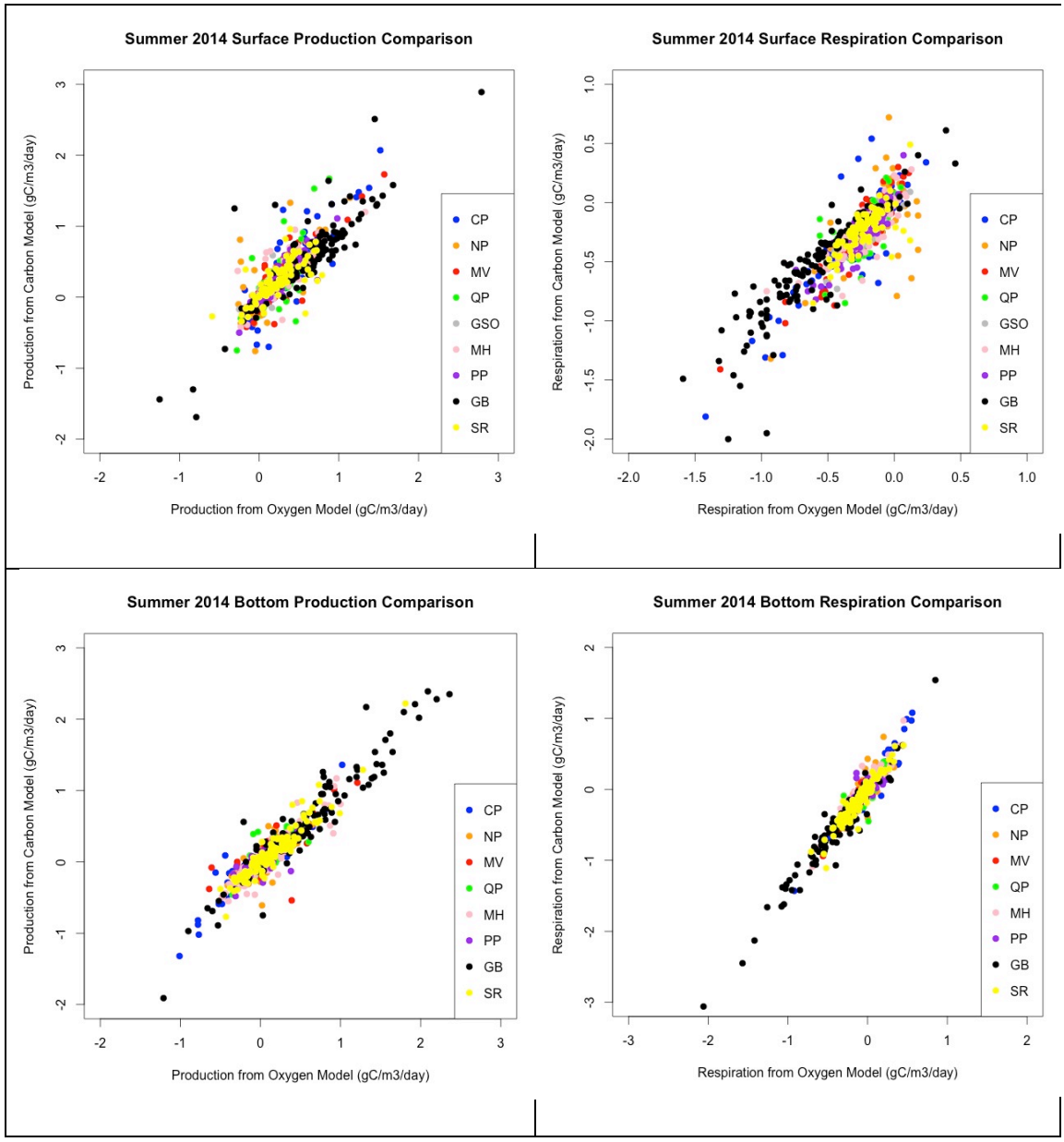


Figure D. 1-1 The bottom metabolic rate estimates were very strong in 2014 with little variance, compared to 2013. The surface comparisons were stronger in 2014 than in 2013, but not to the same degree as the bottom comparisons. Greenwich Bay and Conimicut Point are still the most variable sites in 2014.

D.2 - Impact of increasing or decreasing pH on metabolic rates for North Prudence, Mt. View, Quonset Point, and GSO Dock, 2013

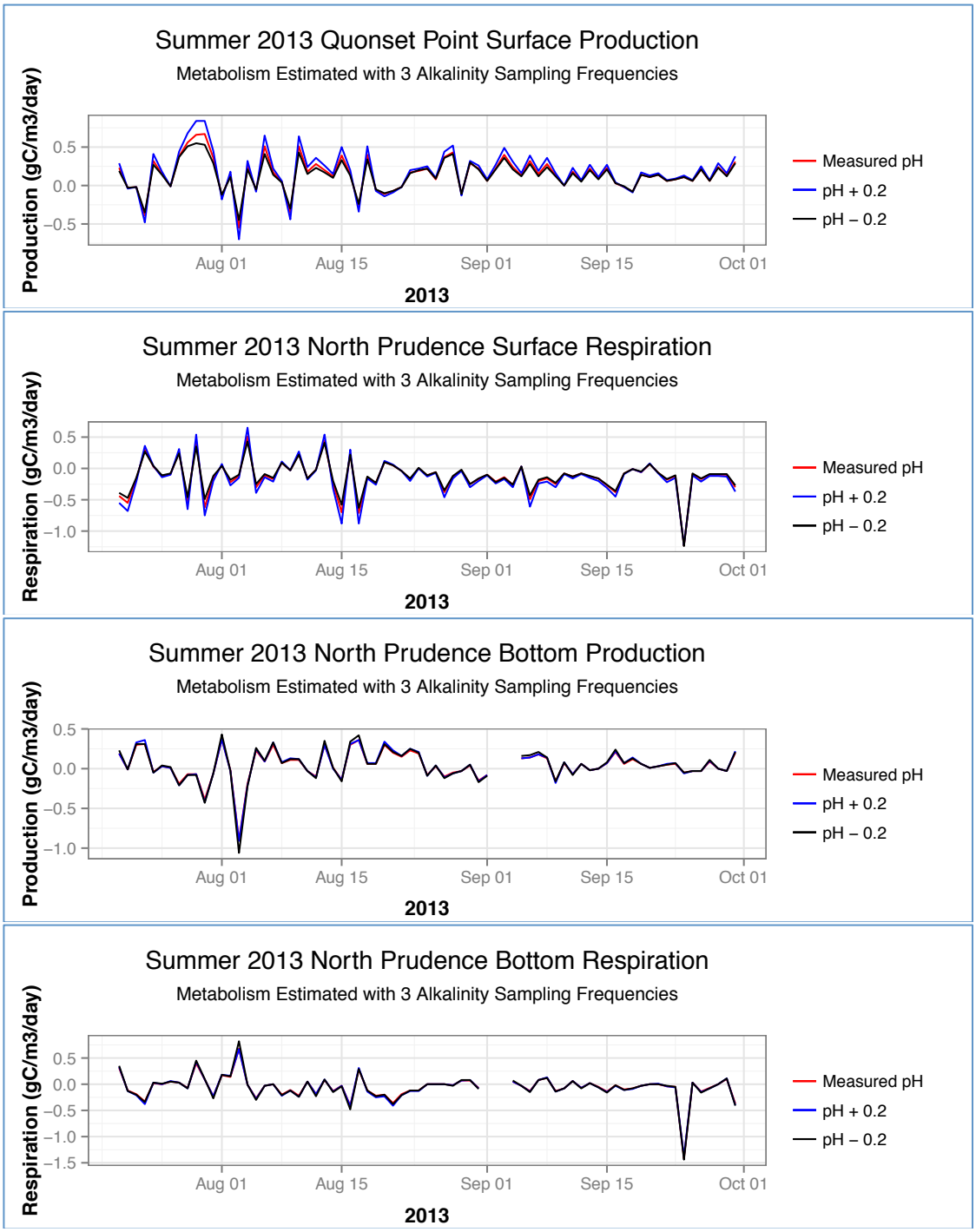


Figure D.2-1 Surface Production at North Prudence is visually the most impacted by a change in the pH, whereas the bottom production and respiration are not effected greatly due to a change in pH. The percent change due to pH is constant across all sites, but the metabolic rate estimates vary.

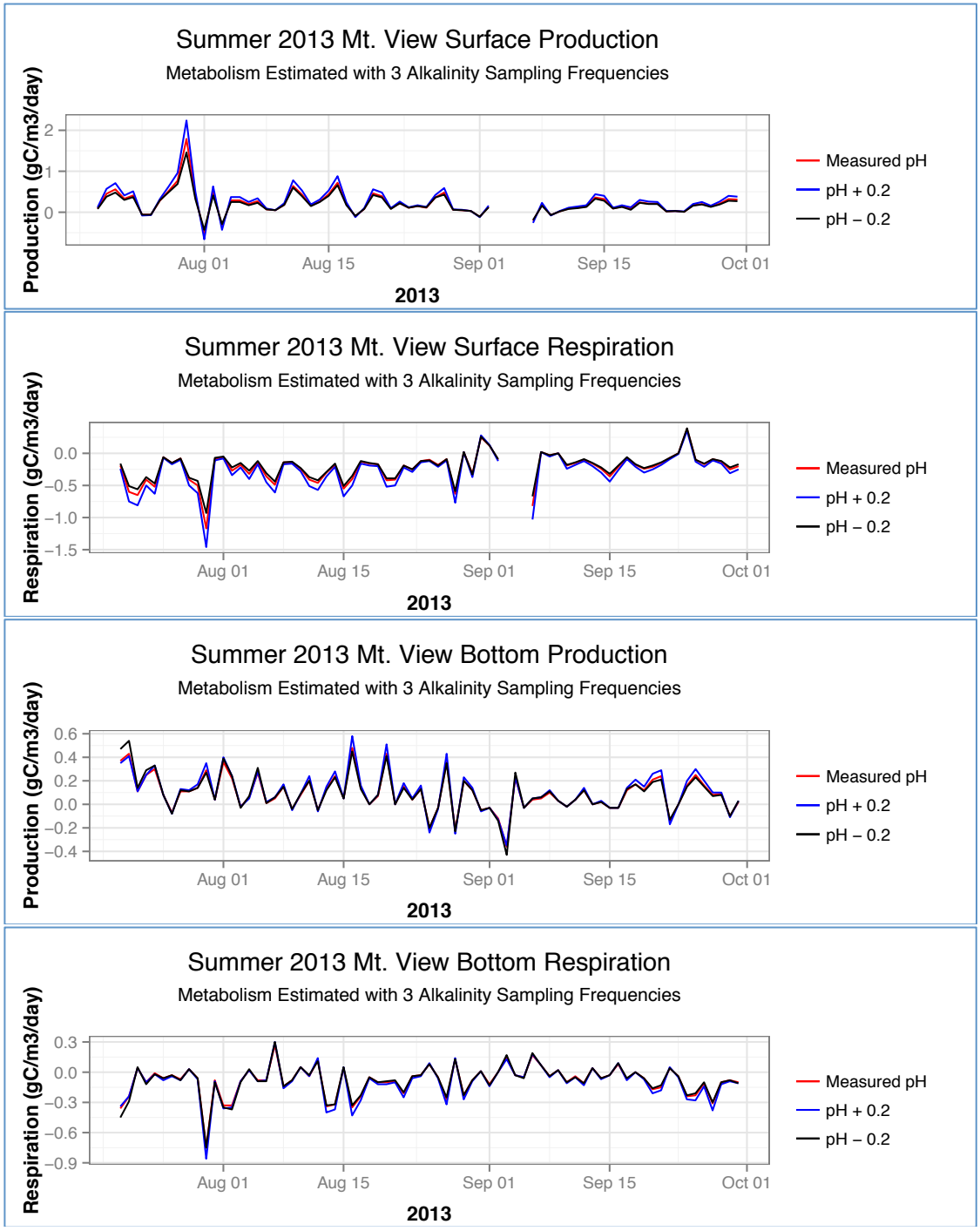


Figure D.2-2 Mt. View has higher metabolic rates than North Prudence, and the impact on the metabolic rates was greater for Mt. View, though the percent change is the same. Surface estimates are more impacted than bottom estimates from an error in pH.

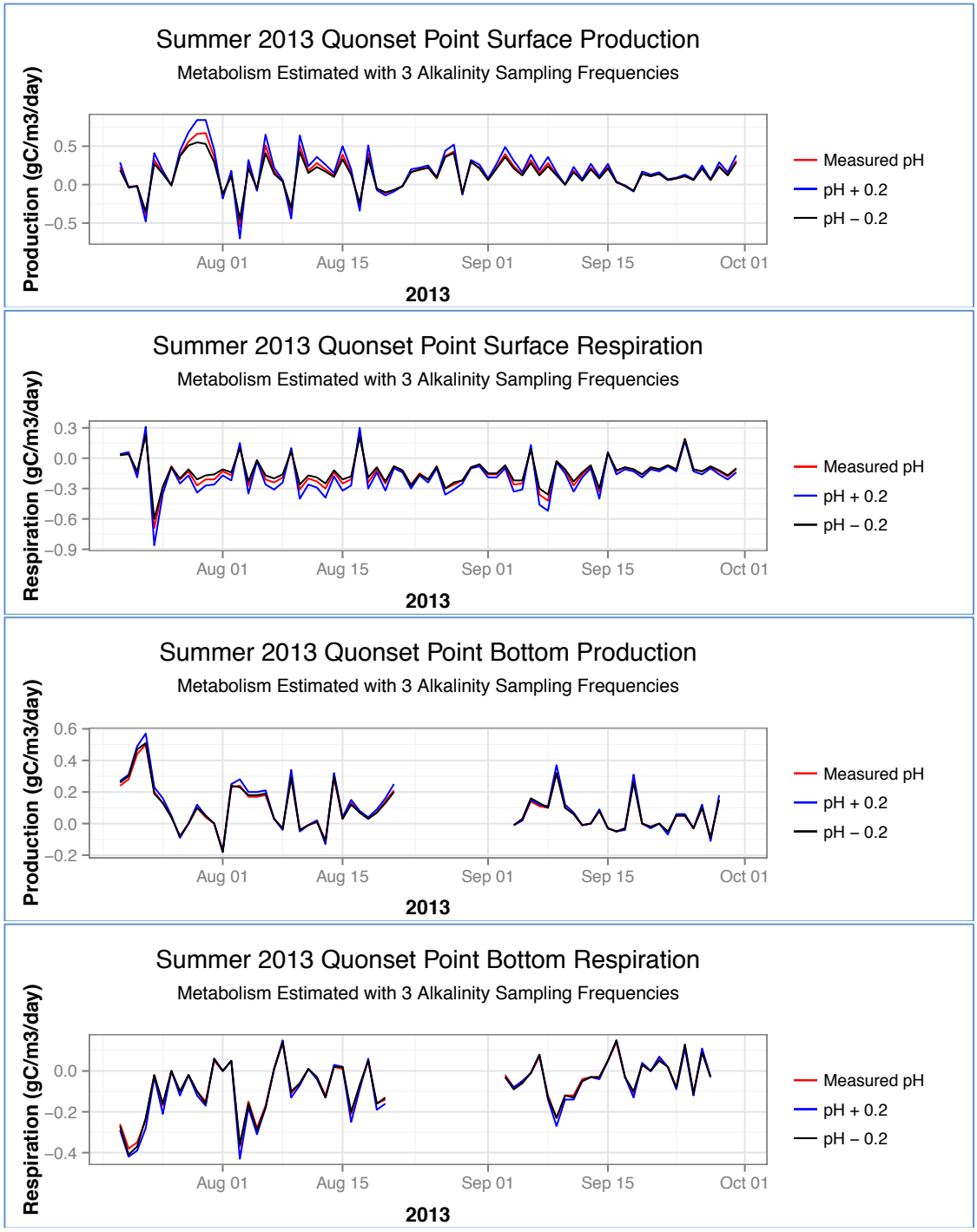


Figure D.2-3 The surface production estimates are exaggerated on the positive side, but not the negative side, whereas the surface respiration estimates follow the opposite pattern. Again, bottom production and respiration values are not affected as much as the surface values.

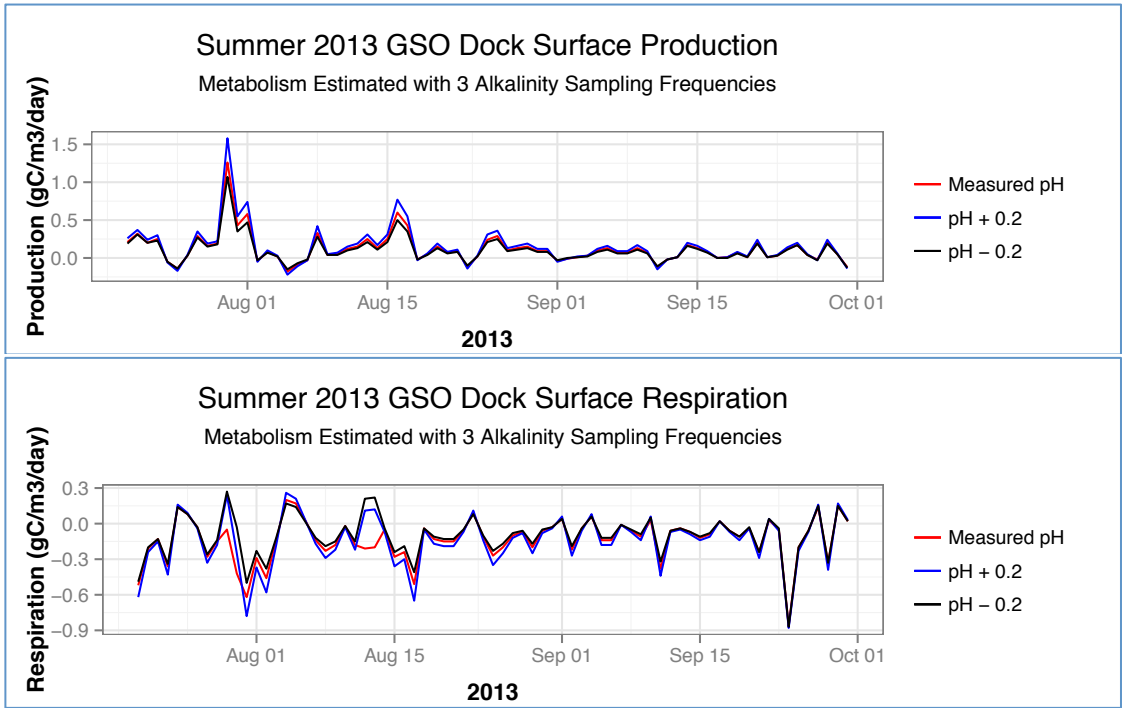


Figure D.2-4 GSO Dock estimates are effected by a change in pH earlier in the summer when the variance in metabolic rates were higher. Interestingly, when the pH was decreased the metabolic rate estimates increased in some cases.

D.3 - Impact of alkalinity variation on metabolic rates for Conimicut Point and Quonset Point surface respiration, bottom production, and bottom respiration.

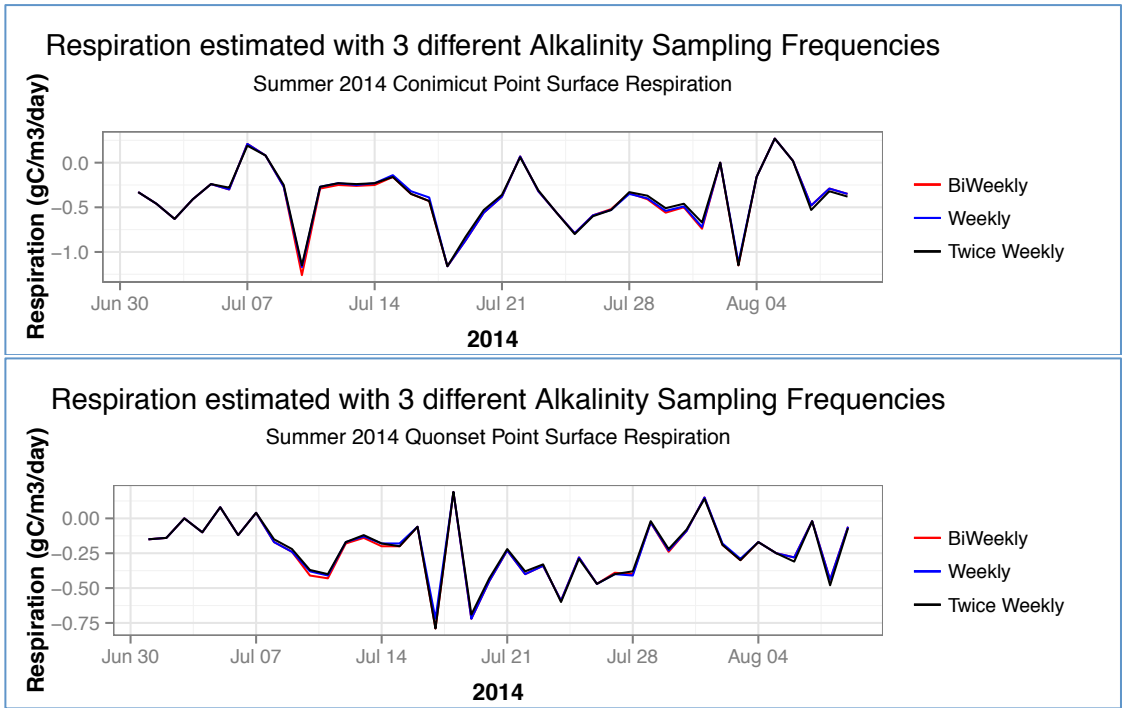


Figure D.3-1 Increasing the range of alkalinity values and the sampling frequency has little to no effect on the surface respiration rate estimates.

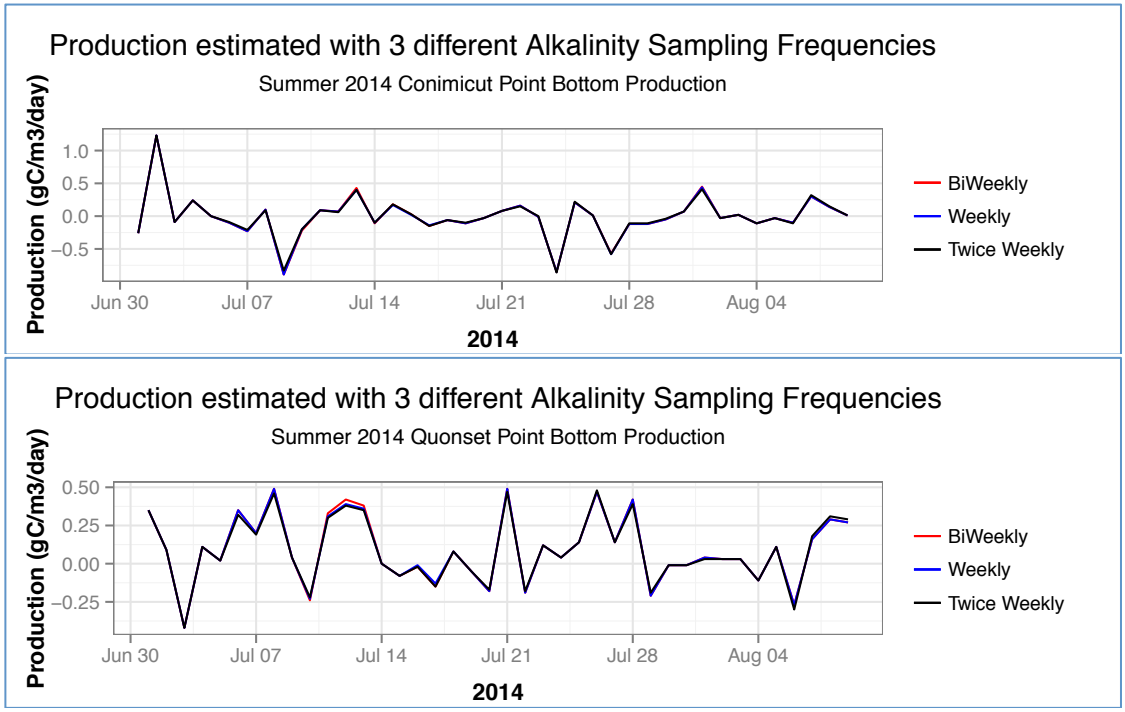


Figure D.3-2 The alkalinity values did not alter the bottom net production estimates significantly.

D.4 Spatial trends of bottom metabolic rates

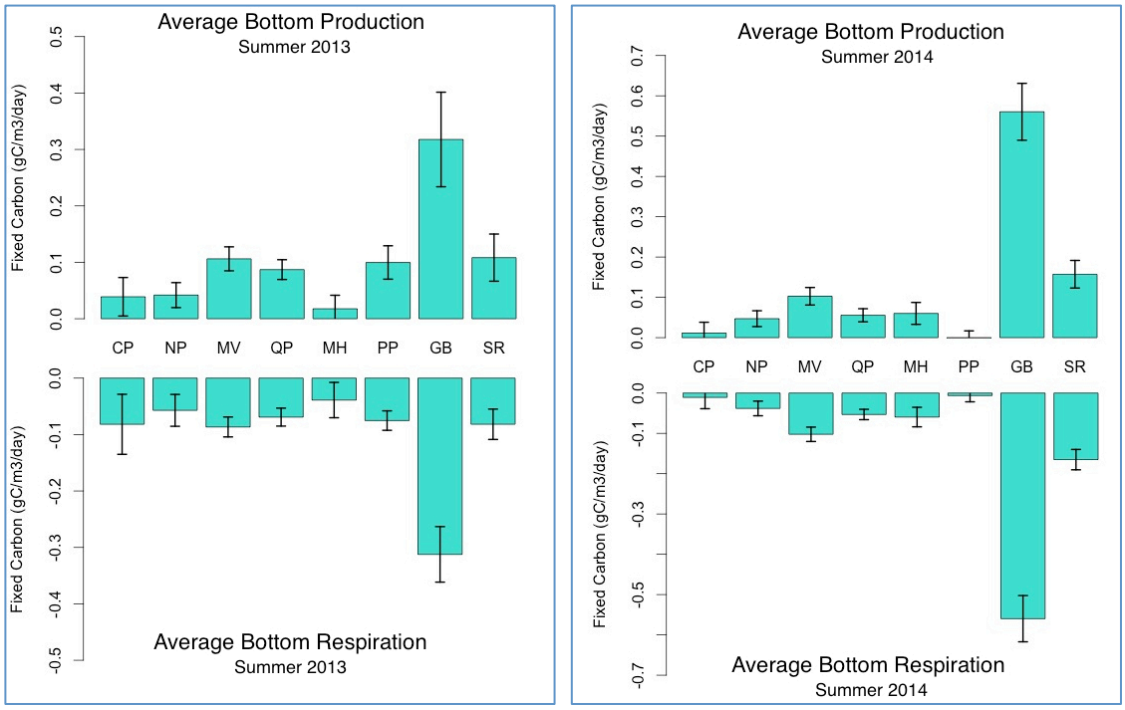


Figure D.4 -1 Both summers, Greenwich Bay has the highest production and respiration in the bottom waters. This site is the shallowest site, allowing light to reach the bottom at times. In 2014, water clarity was increased compared to 2013, and metabolic rates were increased for most stations. Note, the scales on the y-axis are different between years.

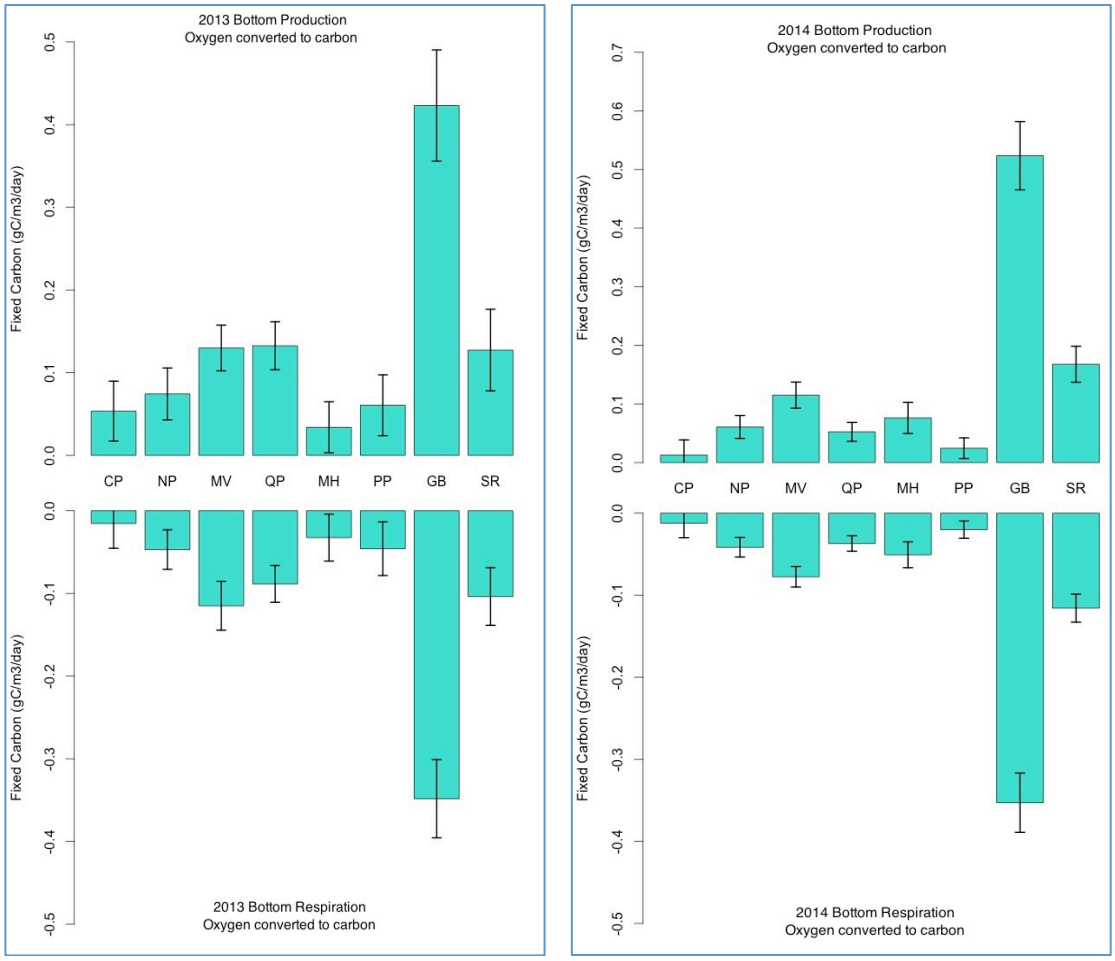


Figure D.4-2 The metabolic rates from the oxygen method were converted to carbon using respective PQ and RQs for the category and summer. The spatial trends are the same in the oxygen method as they are in the carbon method.