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INVESTIGATION OF NITROGEN CYCLING USING STABLE NITROGEN AND OXYGEN ISOTOPES IN NARRAGANSETT BAY, RI

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INVESTIGATION OF NITROGEN CYCLING USING STABLE NITROGEN AND OXYGEN ISOTOPES IN NARRAGANSETT BAY, RI

BY

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ABSTRACT

Estuaries regulate nitrogen (N) fluxes transported from land to the open ocean through uptake and denitrification. In Narragansett Bay, anthropogenic N loading has increased over the last century with evidence for eutrophication in some regions of Narragansett Bay. Increased concerns over eutrophication prompted upgrades at wastewater treatment facilities (WWTFs) to decrease the amount of nitrogen discharged. The upgrade to tertiary treatment – where bioavailable nitrogen is reduced and removed through denitrification – has occurred at multiple facilities throughout Narragansett Bay's watershed. Nitrogen remains limiting to primary production in the Bay proper which led to speculation that primary production throughout the system may result in large part from the high nutrient loads in the north. Tracing N sources is essential for attributing drivers of primary production and it has previously been done using stable isotopes. However, little information on the isotopic composition of the nutrient inputs is available and no data are available to assess the impact of upgrades to tertiary treatment on the isotopic composition of dissolved inorganic nitrogen or primary producers. The objective of this dissertation is to explore the spatial and temporal distribution of the stable isotopes of nitrogen in multiple forms, inorganic and organic, the impact of upgrades at the wastewater treatment facilities on nutrient fluxes and their isotopic compositions, and the role anthropogenic N plays in driving primary production within Narragansett Bay.

Samples were collected from 2007 through 2012, before and during upgrades to tertiary treatment. Samples from rivers and WWTFs were collected to characterize the potential impact of upgrades and anthropogenic source nitrate (NO_3^-) isotopic

variability. Surface water NO_3^- samples were collected from a north-south transect to trace the impact of the upgrades spatially. Finally, during the summers of 2011 and 2012, additional samples of subsurface nitrate, chlorophyll *a*, and macroalgae (2012 only) were collected to assess the relative importance of anthropogenic nitrogen to primary producers. All water samples were analyzed for nutrient concentrations (NO_3^-, PO_4^{3-}, NH_4^+) and stable nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) isotopic compositions of NO_3^-. Chlorophyll *a* content and the compound specific and bulk N isotopic composition of chlorophyll *a* and macroaglae, respectively, were measured.

Between 2009 and 2012, upgrades to tertiary treatment reduced nitrogen inputs to Narragansett Bay by 30 % but the impacts on regional concentrations were minimal. During that same time period, overall nitrate concentrations in surface water maintained a decreasing gradient downstream toward the ocean, and summer subsurface nitrate concentrations remain relatively static throughout the bay. Estimates of nitrogen availability relative to phosphate (N*) suggest that the bay switches from having excess N to exhibiting a deficit relative to what phytoplankton require at 41.7°N (the boundary between the Providence River Estuary and Narragansett Bay), regardless of N inputs upstream. On the other hand, a significant shift in the isotopic composition of the sources was observed. Tertiary treatment at one WWTF increased effluent nitrate $\delta^{15}N$ and $\delta^{18}O$ values by ~16 ‰ for both isotopes, and increased rivers by 4 ‰. North of 41.7°N (the Providence River Estuary) $\delta^{15}N$ values increased significantly by 2 ‰, but not south of this point (Narragansett Bay proper). The increase in $\delta^{15}N$ is attributed to the increased $\delta^{15}N$ from upgrades to tertiary treatment.

During the summers of 2011 and 2012, the subsurface $\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N$-chlorophyll *a* peaked mid-bay while macroalgal $\delta^{15}N$ decreased linearly throughout the bay. The differences between the $\delta^{15}N$ of macroalgae and chlorophyll *a* imply multiple sources of nitrogen supporting primary production. Phytoplankton are transported vertically and horizontally by tides/currents and mixing events. The exact position where they incorporate N is unknown, but they appear to be supported by subsurface nitrate. This runs counter to the idea that phytoplankton harvest nutrients upstream and are carried into the Bay by advection. Macroalgae are incorporating N at a fixed position, and may be supported by small, but consistent, benthic fluxes.

In conclusion, the river and WWTF data suggest that when seasonal means are significantly different from other sources, $\delta^{15}N\text{-}NO_3^-$ may be a useful tracer of inputs in the nutrient replete region of the Providence River Estuary. Beyond the Providence River Estuary, we find that anthropogenically-derived nitrate is mixed with offshore water and/or is recycled quite efficiently, overprinting any anthropogenic tracer signal. Primary producers rely on anthropogenic nutrients within the Providence River Estuary, but also derive nitrogen from vertical mixing and benthic nutrient dynamics within the bay proper. In the future, it is likely that anthropogenic N input reductions will continue to impact north of 41.7°N while mixing and recycling will dominate processes south of this point.

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While it's customary to start the acknowledgments with one's advisor, I will start at the beginning. Dr. Scott Nixon was the person who encouraged me to apply to GSO. When funding fell through, I got a call from Dr. Brian Heikes, asking if I would be willing to try something different. I accepted, and began a three year journey to my Master's degree with Brian as my advisor. I started my graduate career in CACS 210. Brian continues to be a pillar of support and guidance as I start my next chapter. I cannot thank him enough.

When Scott and I sat down to plan my Ph.D. work, we knew we'd need help, and found it in Dr. Rebecca Robinson who became my co-adviser. Becky displayed immense patience and support when she taught me about stable isotopes and methods. She challenged me to think outside the box, and reigned me in when I strayed too far. She and Scott made quite a team, encouraging both the geochemist and ecologist in me. They succeeded in making me a biogeochemist, and teaching me to see all possibilities and how to separate probable from improbable.

There are no words to adequately describe the immense gratitude I feel towards my co-advisors. Scott saw something in me I still haven't quite realized myself. Becky helped me pick up the pieces of my degree in May 2012 with guidance, tough love, and sweet treats. We eased into a relationship that I hope lasts for a long time. Her encouraging words, especially towards the end, continue to ring in my ears. I'm learning "don't panic" are the best words ever.

I must also acknowledge the unwavering support of my committee. I experienced set-backs and tragedy, yet they always believed I would succeed, even

when I didn't. Their ideas, insight, and brilliance have improved my dissertation and me. Dr. Candace Oviatt, Dr. Art Gold, Dr. Art Spivack, and Dr. Rick McKinney – I thank you from the bottom of my heart.

As we round our eighth year of marriage, I can't believe we're here. Through all those years you've been my loudest cheerleader. You signed on to a life with me knowing exactly who I am, and loved me more for it. You are Atlas – shouldering most of the burdens of our little world, even trying to shoulder the ones you can't. Maybe now you'll let me share the load. Michael, this degree is as much yours as it is mine – and I'm glad your name is on here, too. I hope to return the favor someday. *clink*

As always my parents continue to stand by my side and support me without fail or question. They instilled a sense of curiosity and love of the world in me. They fostered my curiosities with cameras, books, and an overdose of educational family vacations (but I am the go-to trivia person for military history). Their patience and dedication to my education (and learning challenges) set me on this journey. They willingly let me take my own path, learn how to teach myself, and make countless mistakes along the way. My lovely husband will have to share this degree with them; after all, they gave me my name and so much more.

Along the way, I've had the privilege to know and learn from some of the best people. The Nixon Lab, both past and present, has been immensely kind, supportive, and loving. Leanna, Lindsey, and Brita will always be my lab sisters, and I will forever be grateful to them for field and moral support, and undying friendship. The

Robinson Lab took me in and made me one of their own. I've learned much from all of you, thank you.

One companion has been in my life for 17 years – he's the little brother I never wanted and the best friend I needed. He's my pre-existing condition. For all these years, his quirky jokes, immense intelligence, and patient ear have made this journey tolerable and downright fun. As I'm finishing my Ph.D., he started – and ended – his in spectacular fashion. Nick, I wish you fair winds and following seas; Lord knows you deserve it.

I have been immeasurably blessed throughout my graduate career. No matter where I go from here, I know a large part of my heart will be firmly planted at GSO. To everyone I didn't mention – thank you. Last, but not least, I must thank my CACS 2nd floor friends: my final years at GSO were a pleasure because of you. And so, I end my graduate career in CACS 218, 8 doors down from where I started. I've come full circle, and it's because of the love, support, and dedication bestowed upon me from everyone I've met along this journey.

DEDICATION

"If ever there is tomorrow when we're not together... there is something you must always remember. You are braver than you believe, stronger than you seem, and smarter than you think. But the most important thing is, even if we're apart... I'll always be with you." ― A.A. Milne

Our parting conversations swirled around penguins, bars, and a task I will be working on the rest of my life. Under your guidance, love, and patience I became more confident. As much as you liked to live in my reflected glow, I grew stronger in yours. Not a day in my life will pass where I'm not reminded that I am who I am, and doing what I am, in part, because of your confidence and dedication to me. This wolf will be forever fearless because of you.

I dedicate this dissertation to my adviser, mentor, and friend Scott W. Nixon.

PREFACE

This thesis is prepared in manuscript format. Each manuscript is presented as a separate chapter, with chapter text subdivided in common scientific format. Tables and figures for each chapter follow the literature cited section. The first chapter, *Changes to nitrate isotopic composition ($\delta^{15}N$ and $\delta^{18}O$) of wastewater treatment effluent and rivers after upgrades to tertiary treatment in the Narragansett Bay, RI, watershed*, has been formatted for submission to the journal Environmental Science and Technology. The second chapter, *Changes to $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in Narragansett Bay after anthropogenic N input reductions*, will be submitted to the journal Biogeochemistry. Both the first and second chapters are co-authored by Rebecca Robinson, Lindsey Fields, and Scott Nixon. The third chapter, *Nitrate sources supporting Narragansett Bay phytoplankton and macroalgae using stable N isotopes*, will be submitted to the journal Estuaries and Coasts, and is co-authored by Rebecca Robinson, Anna DeLeon, Lindsey Fields, and Scott W. Nixon. The fourth chapter, *Dissertation Synthesis*, is a concise summary and synthesis of the work. It will not be submitted for peer review.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

PREFACE

Changes to nitrate isotopic composition ($\delta^{15}N$ and $\delta^{18}O$) of wastewater treatment effluent and rivers after upgrades to tertiary treatment in the Narragansett Bay, RI, watershed

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Abstract

Increasing anthropogenic nitrogen (N) in coastal waters led to policies which reduced N loads. Wastewater treatment facilities (WWTFs) are being upgraded to tertiary treatment – where bioavailable N is reduced and removed through denitrification within the treatment scheme. This upgrade has occurred at more than 12 facilities discharging into Narragansett Bay's watershed. Stable isotopes have previously been used as a tracer of nitrogen source; however, no studies have assessed changes to isotopes in nitrate inputs to Narragansett Bay after upgrades to tertiary treatment. To characterize the potential impact of these upgrades, and anthropogenic source nitrate (NO_3^-) isotopic variability at rivers and WWTFs, samples from rivers and WWTFs discharging to Narragansett Bay were collected in 2009 and 2012. Sampling occurred before, during, and after upgrades to tertiary treatment. Samples were analyzed for NO_3^- concentration, stable N ($\delta^{15}N$) and stable oxygen ($\delta^{18}O$) isotopic compositions of NO_3^-. WWTF $\delta^{15}N$ values range from -4 to +28 ‰, and $\delta^{18}O$ from -16 to +30 ‰ (2009 through 2013). Riverine $\delta^{15}N$ values range from +4 to +20 ‰ and $\delta^{18}O$ from -5 to +12 ‰ (2009 through 2013). The data were flux weighted using river flow or WWTF discharge rates and NO_3^- concentrations. Flux-weighted 2009-2010 annual average $\delta^{15}N$ for all rivers and WWTFs are +9 and +7 ‰, respectively, while 2012-2013 were +13 and +14 ‰. Flux-weighted average $\delta^{18}O$ for rivers and WWTFs are +1 and -2 ‰ for 2009-2010, and +5 and +7 ‰ for 2012-2013. On an annual basis, tertiary treatment at one WWTF increased effluent nitrate $\delta^{15}N$ and $\delta^{18}O$ values by ~16 ‰ for both isotopes (flux-weighted; $p<0.001$), and increased $\delta^{15}N$ and $\delta^{18}O$ of rivers by ~4 ‰ (flux-weighted; $p<0.01$). Overall, nitrogen inputs

decreased and the isotopic composition of nitrate increased to levels higher than those at the onset of tertiary treatment. Combined river and WWTF flux-weighted isotopic compositions from both sources show enriched isotopic values consistent with anthropogenic influence, and also show monthly variability. When seasonal means are significantly different from other sources, $\delta^{15}N\text{-}NO_3^-$ may be a useful tracer of inputs.

Introduction

Anthropogenic nitrogen (N) loads to coastal regions have increased over the last century (Nixon 1995; Boesch 2002), and are frequently cited as the primary cause of an excess production of organic matter, a process termed eutrophication (Nixon 1995). To reduce the negative effects of eutrophication, namely hypoxia, wastewater treatment facilities (WWTFs) have begun to include nitrogen removal practices in their treatment schemes (USEPA 2004; RIDEM 2005).

The wastewater treatment process consists of five steps: preliminary, primary, secondary, and tertiary treatment, followed by disinfection. Preliminary and primary treatments remove solids and grease/oil from water to be treated. Secondary treatment converts up to 90 % of the dissolved organic matter to inorganic N and then oxidizes ammonium (NH_4^+) to nitrate (NO_3^-), using microbial nitrifiers. The newest process, tertiary treatment, reduces NO_3^- through microbially-mediated denitrification to convert NO_3^- to the largely biologically unavailable N_2 gas. Finally, the wastewater is disinfected, often with chlorine, ultra-violet radiation, or ozone, and released. The entire process takes about 1 day (USEPA 2004). According to data collected in 2012

by the Narragansett Bay Commission (NBC), the company that owns two of the largest WWTF that discharge into Narragansett Bay, wastewater treatment inflow to one of their treatment facilities contains 61 % NH_4^+ and 1% NO_3^-, with the remainder organic N. During the full treatment process, including tertiary treatment, [NH_4^+] decreases by 98 % and [NO_3^-] increases by 3000 %. The final effluent composition is 77 % NO_3^-, 6 % NH_4^+, and 17 % organic N. Overall, total N decreased by 25 % (NBC 2012). Currently, NBC targets a monthly average N load of 607 μM (8.5 ppm) (NBC 2012). Here, we focus on the NO_3^- component of WWTF effluent.

Most WWTF and river inputs enter Narragansett Bay from the northern reaches through the Providence River and Mount Hope Bay and fluxes of DIN decrease downstream (Fig. 1-1). The major N inputs to Narragansett Bay (from runoff, rivers, groundwater, WWTFs, Rhode Island Sound, and atmospheric deposition) have been identified, and ~ 60% of total N input is anthropogenic in origin (Nixon et al. 1995; Nixon et al. 2008; Krumholz 2012). Rivers and wastewater treatment facilities comprise ~80% of the anthropogenic inputs, and rivers are the single largest contributor of N when upstream sewage discharge to the rivers is considered part of the river flow (Nixon et al. 1995; Nixon et al. 2008; Krumholz 2012). Tertiary treatment upgrades have taken place at more than 12 WWTFs in the Narragansett Bay watershed, including the three largest (Field's Point, Worcester, and Bucklin), with more planned in the near future (Fig. 1-2). Decreases in N sources to Narragansett Bay were observed for the period of 2006-2010, where wastewater treatment facility N contributions fell by approximately 20 % (Krumholz 2012).

The impact of a given nutrient source cannot be assessed with concentration and flux measurements alone and these measurements cannot distinguish among nutrient sources. Stable N isotopes (^{15}N:^{14}N, where $\delta^{15}N = [(R_{sample}/R_{standard}) - 1] \times 1000$ and $R = {}^{15}N/{}^{14}N$ in per mil notation, ‰) are often combined with concentration and flux measurements to aid in distinguishing sources (Jordan et al. 1997; Tucker et al. 1999; Costanzo et al. 2001; Cole et al. 2004; Savage 2005). The $\delta^{15}N$ of NO_3^- reflects the $\delta^{15}N$ of its source and any transformations to which it was subject. Published values of $\delta^{15}N$-NO_3^- in anthropogenic N from secondary sewage treatment plants, septic system leachate, and rivers range from 0 to +40 ‰ (average >10 ‰) while marine (near shore) water values range from +3 to +6 ‰ (average 5 ‰) (Table 1-1; Heaton 1986; Cole et al. 2004; Costanzo et al. 2001; Chaves 2004; Schlacher et al. 2005; DiMilla 2006). The published average $\delta^{15}N$ value of anthropogenic sources is > 10 ‰ (Heaton 1986), giving rise to a common assumption that the anthropogenic N end-member always bears an elevated $\delta^{15}N$ values relative to offshore (Heaton 1986; McClelland and Valiela 1998a; Costanzo et al. 2001; Savage 2005).

However, this assumption is not entirely supported by data. Two weaknesses in the assumption are: 1) particulate matter $\delta^{15}N$ values are often used to infer anthropogenic values; and 2) the $\delta^{15}N$ ranges from anthropogenic and offshore values overlap. In most studies, particulate matter from point sources (such as wastewater treatment effluent) or near discharge points are used. Particulate matter samples are made up of various organisms and materials which are captured on a filter, and therefore have an isotopic composition which reflects what is on the filter, but not necessarily reflecting the bioavailable N (Cifuentes et al. 1988; Battaglin et al. 1997;

DiMilla 2006). More importantly, published ranges of anthropogenic and offshore $\delta^{15}N$ overlap (WWTFs range from -3 to +40 ‰, while offshore values are near 5 ‰; Heaton 1986; Pardo et al. 1994; Dahnke et al. 2008; Deutsch et al. 2006, 2009; DiMilla 2006; Jordan et al. 1997), decreasing the certainty with which stable N isotopes can be used to uniquely identify anthropogenic discharges. Also, to our knowledge, no one has assessed how tertiary treatment will change the isotopic composition of WWTF discharges, further complicating the issue moving forward.

There is now less of a need to infer source $\delta^{15}N$ values from particulate matter since the N isotopic composition of nitrate is now relatively easy to measure since the introduction of the denitrifier method (Sigman et al., 2001). In addition, measurement of the oxygen isotope composition (^{18}O:^{16}O; $\delta^{18}O$, ‰) of NO_3^- is typically coupled to the $\delta^{15}N$ measurement (Casciotti et al., 2002). $\delta^{18}O$ values are useful to distinguish sources (freshwater versus seawater) and nutrient processing pathways (Wassenaar 1995; Mayer et al. 2002; Deutsch et al. 2005; Saccon et al. 2013). Variation in $\delta^{15}N$ and $\delta^{18}O$ values due to nitrification (secondary treatment) and denitrification (tertiary treatment) are described below.

Using representative $\delta^{15}N$ and $\delta^{18}O$ values of sources and considering fractionation processes, one can illustrate potential isotopic changes in a nitrate pool (Table 1-1; Fig. 1-3). Experimental work with laboratory cultures demonstrates that fractionation during consumption of nitrate through denitrification and assimilation leads to an increase in the $\delta^{15}N$ and the $\delta^{18}O$ values of nitrate in a 1:1 ratio across a range of measured isotope effects (+5 to +25 ‰) (Granger et al. 2004; Granger et al.

2008). Tertiary treatment uses denitrification, and therefore, is expected to increase the $\delta^{15}N$ and $\delta^{18}O$ values of the NO_3^- in final WWTF effluent.

In contrast, nitrification decreases the $\delta^{15}N$ and $\delta^{18}O$ values through the production of NO_3^- from NH_4^+, with $\delta^{15}N$ and $\delta^{18}O$ isotope effects of +15 to +30 ‰ and +17 to +30 ‰, respectively (Casciotti et al. 2010). During nitrification, the conversion of NO_2^- to NO_3^- is reversible, and has an inverse isotope effect, where the resulting NO_3^- is isotopically heavier than the NO_2^- (Casciotti 2009; Buchwald and Casciotti 2010). The inverse isotope effect imparts a signal when and where there is a significant accumulation of nitrite, as it does in WWTFs, or during warm months at the sediment-water interface in rivers. These two processes are expected to pull the $\delta^{15}N$ and $\delta^{18}O$ values of effluent and rivers away from the 1:1 line predicted for denitrification and have the potential to impart significant isotopic variability in anthropogenic NO_3^- inputs (Fig. 1-3).

We measured the N and O isotopic compositions of dissolved NO_3^- inputs from WWTFs (which discharge directly to the bay) and rivers monthly during 2009-2010 and 2012-2013 to assess the impact of anthropogenic N sources reductions on the nitrate isotopic contributions to Narragansett Bay. Our focus is to document temporal variability in the $\delta^{15}N$ and $\delta^{18}O$ values of nitrate, both with and without tertiary treatment at the WWTFs. These data will be used to test the assertion of an enriched anthropogenic isotopic signal using $\delta^{15}N$ and $\delta^{18}O$ of nitrate in WWTF and rivers discharging into Narragansett Bay and to evaluate the potential for using stable isotopes as a tracer of nitrogen source in this impacted system.

Methods

Narragansett Bay and Watershed

Narragansett Bay, including Mount Hope and Greenwich Bays and the Providence River Estuary, is 328 km^2 and has a mean depth of 8.3 m (Fig. 1-1) (Pilson 1985). River input is relatively low (around 100 m^3s^{-1}, or 7.56 $x10^6$ m^3d^{-1}) and most of the input occurs in the urbanized northern reaches (Fig. 1-1). Other freshwater sources, such as storm water and groundwater, are relatively small portions of the Narragansett Bay water budget, but are important to the budgets of the smaller bays and coves, like Greenwich Bay (Nixon et al. 1995; Spaulding 1987; Krumholz 2012).

The Blackstone, Pawtuxet, Ten Mile and Taunton Rivers are the largest rivers that discharge to the bay, in terms of flow, contributing a total of $5.79x10^6$ m^3 d^{-1} (2009-2010) and $3.08x10^6$ m^3 d^{-1} (Feb. – Sept. 2012) with peak flow in the spring and winter (Table 1-2). Within the watershed, twenty-nine WWTFs discharge to the bay and its tributaries. Three of the largest discharge directly to Narragansett Bay in the northern reaches (Field's Point, East Providence and Bucklin), and one discharges directly to Mount Hope Bay (Fall River) (Nixon et al. 2008; Krumholz 2012) (Fig. 1-1, Table 1-2).

Sample Collection

Water samples were collected from the riverine sources and wastewater treatment facilities, from March 2009 to January 2010 (referred to as 2009), and February 2012 to January 2013 (referred to as 2012). The Narragansett Bay Commission (NBC, in 2009-2010 and 2012-2013), the City of East Providence, through United Water, (2009-2010), and the City of Fall River, through Veolia Water

(2012-2013) cooperated in the sampling. The river samples were collected from the last gauged point or upstream of the last dam using a bucket lowered from a bridge into the rivers. Final, 24-hour composite effluent samples from the WWTF were collected by NBC, United Water or Veolia Water at the outflow pipe, filtered using glass fiber filters, and either acidified with hydrochloric acid to a pH 2 or frozen and stored at -20°C until analysis.

Laboratory Analysis

Samples were analyzed on a Lachat QuickChem 2000 flow injection autoanalyzer using EPA method 353.4 (Grasshoff 1976; US EPA 1997) for NO_{3+2}, and NO_2^- at the University of Rhode Island (URI) or at NBC and Veolia Water (through subcontractor Premier Laboratory), and have a minimum detection limit of 0.05 μM for NO_3^- and a precision of 0.02 μM. Selected samples were reanalyzed for NO_3^- concentrations by chemiluminescence using a Teledyne NOx analyzer (Braman and Hendrix 1989).

N and O isotope compositions were determined using the denitrifier method (Sigman et al. 2001, Casciotti et al. 2002) by gas chromatography-isotope ratio mass spectrometry. Stable isotope ratios are reported as the ratio of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ between the sample and a standard, and are expressed as $\delta^{15}N$ or $\delta^{18}O$ where $\delta = [(R_{sample}/R_{standard}) - 1] \times 1000$ and $R = {}^{15}N/{}^{14}N$ or $^{18}O/^{16}O$. Samples and working standards (IAEA N3, $\delta^{15}N = +4.7$ ‰, $\delta^{18}O = +25.6$ ‰; USGS 32, $\delta^{15}N = +180$ ‰, $\delta^{18}O = +25.7$ ‰; USGS 34, $\delta^{15}N = -1.8$ ‰, $\delta^{18}O = -27.9$ ‰) were analyzed in the same runs to normalize delta values to accepted standards (N_2 in air and VSMOW for

$\delta^{15}N$ and $\delta^{18}O$ respectively). Precision of the method is < 0.3 ‰ for $\delta^{15}N$ and < 0.5 ‰ for $\delta^{18}O$ based on the standard deviation of all standards measured during study.

Flux-Weighting Procedure

Isotopic measurements were flux-weighted with discharge flow measurements and NO_3^- concentrations from both freshwater sources to quantify the $\delta^{15}N$ and $\delta^{18}O$ of anthropogenic inputs to Narragansett Bay. To obtain annual average flow for rivers, we used Beale's unbiased estimator which compares the days we sampled to the average for the year and corrects for aliasing associated with individual events by assuming that the ratio of load to flow for the days when samples were taken is equal to the average annual ratio of load to flow. (Beale 1962; Fulweiler 2003) (Fig. 1-4). Next, we multiplied [NO_3^-] by the flow from either the WWTFs or rivers to obtain the flux of NO_3^-, then multiplied the flux by $\delta^{15}N$ and $\delta^{18}O$ values (units are flux-per mil). These results were then either summed by year for individual collection sites, or summed by month for all collection sites, and divided by the total flux for either year or month, respectively (flux-per mil / flux = per mil). The final result was a flux-weighted $\delta^{15}N$ and $\delta^{18}O$ value.

Results and Discussion

WWTF Process and Tertiary Treatment

Nitrate concentrations ranged from 9-584 μM for all WWTFs. Fall River (2012) had the lowest observed concentrations (Fig. 1-5). In both years Bucklin discharged the highest, or among the highest, concentrations (Fig. 1-5). Average nitrate concentrations decreased by about 130 μM between 2009 and 2012, however,

when an analysis of covariance (ANCOVA) was performed with season as the covariant (accounting for seasonal differences in nitrate concentration), the decrease in nitrate concentration was not significant (ANCOVA, $F(7,46) = 1.72$ $p = 0.2$). Nitrate flux between years decreased by about 40 %, however, when an ANCOVA was performed with season as the covariant, the decrease in flux was not significant (ANCOVA, $F(7,46) = 1.46$ $p = 0.2$) (Fig. 1-4).

For all treatment facilities, $\delta^{15}N\text{-}NO_3^-$ values ranged from -4 to +28‰ and $\delta^{18}O\text{-}NO_3^-$ values ranged from -16 to +30 ‰ (Fig. 1-5). Generally, Field's Point had the lowest $\delta^{15}N$ and $\delta^{18}O$ values in 2009, while Fall River had the lowest $\delta^{15}N$ values and Bucklin had the lowest $\delta^{18}O$ values in 2012. During 2012, Field's Point generally had the highest $\delta^{15}N$ and $\delta^{18}O$ values. No systematic pattern was evident in WWTF nutrient concentrations or isotopic compositions (Fig. 1-5).

Between 2009 and 2012, the flux-weighted average of all WWTF final effluent N and O isotopes increased by 7 ‰ (Table 1-3; flux-weighted, t-test, $p = 0.01$). We compared Field's Point pre-upgrade (2009) and post-upgrade (after Aug. 2012) to tertiary treatment and find, on average, WWTF effluent increased nitrate $\delta^{15}N$ and $\delta^{18}O$ by ~16 ‰ (Table 1-3; flux-weighted, t-test, $p < 0.005$) after upgrades. The 1:1 increase in $\delta^{15}N$:$\delta^{18}O$ is consistent with the fractionation during denitrification and tertiary treatment (Fig. 1-3; Granger et al. 2008).

The ratio of $\delta^{15}N$:$\delta^{18}O$ for all WWTF data was 1:1 for both 2009 and 2012 (Fig. 1-6a), which suggests that denitrification and/or assimilation are the dominant processes at WWTFs. In 2009 the only facility sampled to be using denitrification (tertiary treatment) was Bucklin. With the Bucklin removed from the 2009 data, the

$\delta^{15}N$:$\delta^{18}O$ remains 1:1 (though with a weaker, not significant correlation). In 2012, both Bucklin and Field's Point (after upgrades were complete) used tertiary treatment and the 1:1 ratio is consistent with this. The lack of change in the ratios between years suggests that denitrification occurs naturally in the treatment tanks, and tertiary treatment only stimulates the process further, enhancing the N reduction benefits.

When ratios deviate from 1:1, a coupling of nitrification and denitrification would be supported. Nitrate created during nitrification (secondary treatment) is denitrified during tertiary treatment, which supplies organic matter/NH_4^+ for nitrification. Nitrification results in N with an isotopic composition equal to or less than the $\delta^{15}N$ of the source while the O isotopic composition is pulled towards the $\delta^{18}O$ of water. Denitrification and assimilation, on the other hand, cause an equal isotope effect for both $\delta^{15}N$ and $\delta^{18}O$ (Fig. 1-3; Granger et al. 2004, 2008; Casciotti et al. 2010). Within WWTFs undergoing only secondary treatment, nitrification would most likely be near-complete causing the resultant NO_3^- to bear N and O isotopic compositions close to the substrate NH_4^+ and H_2O, respectively. Speculatively, this NO_3^- can be further fractionated during denitrification or assimilation, increasing the $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-, and creating organic matter/NH_4^+ with a lower $\delta^{15}N$ than the $\delta^{15}N$-NO_3^- (Fig. 1-3). This lower $\delta^{15}N$-NH_4^+ can then fuel nitrification, adding lower $\delta^{15}N$-NO_3^- to the pool. During this time, the $\delta^{18}O$ will continue to resemble the $\delta^{18}O$-H_2O, which is a large and constant pool. The overall isotope effect will be that the $\delta^{15}N$ changes faster and to a larger degree than $\delta^{18}O$, keeping the $\delta^{15}N$:$\delta^{18}O$ ratio closer to 2:1, supporting the coupling of nitrification and denitrification.

However, even for 2009, when we expect nitrification to be the dominant control on the isotopic composition of WWTF nitrate, the $\delta^{15}N$ and $\delta^{18}O$ vary in a ratio of 1:1 (Fig. 1-6a). This implies that denitrification and/or assimilation may impact WWTF effluent isotopic signatures even prior to the implementation of tertiary treatment. Both denitrification and assimilation could occur prior to the formal addition of tertiary treatment, provided the conditions were right. Tertiary treatment, therefore, would enhance the denitrification process to reduce and remove more N than previously. In 2009, assimilation of the NO_3^- produced from nitrification must drive the isotope ratios by increasing $\delta^{15}N$ and $\delta^{18}O$ equally (Fig. 1-3 and 1-6a). In 2012, both assimilation and denitrification drove the isotope ratios (Fig. 1-3 and 1-6a).

Riverine nitrate concentrations ranged from 45-200 μM, which decrease from cooler to warmer months, and increased through the cooler months (Fig. 1-7). In 2009, the Taunton River had the lowest concentration, while, generally, the Blackstone River had the lowest concentrations in 2012. Nitrate flux decreased by 30 % between years and was statistically significant (ANCOVA, $F(7,52) = 5.74$, $p = 0.02$) (Fig. 1-4). Nitrate flux also significantly decreased between cooler months and warmer months (ANCOVA, $F(7,52) = 4.1$, $p = 0.01$) (Fig. 1-4).

Riverine isotopic compositions ranged from +4 to +20 ‰ and -5 to +12 ‰ for N and O, respectively (Fig. 1-7). The $\delta^{15}N$ values increased through the warm months and decrease through the cool months for both years, while the $\delta^{18}O$ values stayed roughly the same throughout both years (Fig. 1-7). The rivers, with the exception of Taunton, also showed an increase in $\delta^{15}N$ and $\delta^{18}O$ by ~ 4 ‰ (Table 1-3; flux-weighted, $p = 0.01$) while the Taunton River showed no change (Fig. 1-7). The

increase in $\delta^{15}N$ and $\delta^{18}O$ is likely due to the completion of the upgrades to tertiary treatment in WWTF that discharge to the rivers (Worcester, which is the largest facility to discharge to the rivers, and the second largest in the watershed, completed upgrades at the end of 2009; Fig. 1-2). The change is small relative to observed shift at Fields Point. Additionally, the river data (combined 2009 and 2012) showed a $\delta^{15}N$:$\delta^{18}O$ ratio of 1:1 (Fig. 1-6b-c). The shift in isotopic composition and steady ratio of 1:1 is likely for two reasons: (1) not all of the WWTF discharging rivers would have an increase in $\delta^{15}N$ (whether they have upgraded or not) or (2) the natural $\delta^{15}N$ signal is not expected to change. A change in a portion of the nitrate discharge is likely to be diluted as it mixes with the larger ambient nitrate field. The ratio of 1:1 is indicative of denitrification and assimilation controlling the isotopic composition of the rivers (Battaglin et al. 2001; Mayer et al. 2002; Granger et al. 2004, 2008). The processes underlying the shifts are discussed below in "Changes to $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-".

Changes to $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-

Nitrogen cycle processes, sources of N, and discharge from WWTFs and rivers can change seasonally. Wastewater treatment facilities are required to treat wastewater to the "maximum feasible extent", which includes the use of tertiary treatment when applicable and available (RIDEM 2005). The volume of flow to the WWTFs changes seasonally, which potential causes the residence time in the tank to vary as well (Fig. 1-4). A change in residence time could change the treatment process, creating seasonal trends in the N flux and $\delta^{15}N$ and $\delta^{18}O$. The seasonal changes in N flux from the discharge are noted (Fig. 1-4); however, no seasonal trends

are apparent in the isotopic time series data for any of the WWTFs discounting this as a potentially important process (Fig. 1-8).

Riverine $\delta^{15}N$ values displayed a temporally variable pattern with peaks in the late spring/early summer of both years (Fig. 1-7). Riverine discharge rates decrease from cooler to warmer months, and coincide with a decrease in NO_3^- concentration (Figs. 1-4 and 1-7). The increase in $\delta^{15}N$ and decrease in NO_3^- suggest that the rivers have undergone seasonally greater nitrate assimilation and/or denitrification compared with cooler months (Fig. 1-8). Assimilation is expected to drive the changes in concentration and N isotope ratios because the samples were collected in oxic water, where denitrification is unlikely to happen. The $\delta^{18}O$ isotopes should increase as well (Granger et al. 2004; Granger et al. 2008), but seasonal trends in $\delta^{18}O$ data showed no change or even a slight decrease from cooler months to warmer months, and maxima in the late spring (Figs. 1-7 and 1-8). The $\delta^{18}O$ data support the mixing of a new NO_3^- source during the warmer months or increases in nitrification (Bottcher et al. 1990; Brandes and Devol 1997; Aravena and Robertson 1998; Granger et al. 2004; Kendall et al. 2007; Granger et al. 2008). Addition of a new source of NO_3^- during only the warmer months is unlikely, except, maybe, a very large rain storm or discharge event from a treatment facility. On the other hand, an increase in nitrification rates should occur at higher temperatures and work to homogenize the O isotope signal.

Combined WWTF and Riverine Flux to Narragansett Bay

Narragansett Bay receives freshwater from both the WWTFs and rivers. The yearly pattern of N flux to the bay largely resembles the rivers, which is expected since the volume of WWTF discharge is an order of magnitude less than the river flow

(Fig. 1-4). However, the majority of the N within the rivers is sewage-derived, making the WWTFs which discharge into the Narragansett Bay watershed the largest N source (Krumholz 2012). The WWTF and riverine data were flux-weighted and combined to analyze the isotopic compositions of anthropogenic NO_3^- (Fig. 1-4).

A common assertion is that anthropogenic sources have high $\delta^{15}N$ values, and offshore or oceanic sources of nitrate have relatively low $\delta^{15}N$ (Heaton 1986; McClelland and Valiela 1998a; Costanzo et al. 2001; Savage 2005). On monthly timescales in 2009, at least for NO_3^-, this does not appear to be strictly true. The combined WWTF and river flux-weighted $\delta^{15}N$ values of freshwater sources varied from +5 to +10 ‰, (Fig. 1-4), which overlap with offshore N sources (~ +5 ‰) (DiMilla 2006; Sharp 2007, Kendall et al. 2007). However, the combined WWTF and river flux-weighted average for 2009 was +8.2 ‰ (Table 1-3), and is similar to the canonical anthropogenic $\delta^{15}N$ signal of values >8‰ (Heaton 1986; Kendall 1998; Mayer et al. 2002). In 2012, on monthly timescales, the combined anthropogenic flux-weighted data ranges from +10 to +15 ‰ (Fig. 1-4), with an average of +13.6 ‰ (Table 1-3). During the growing season 2012, the combined WWTF and river flux-weighted data averaged +13 ‰ (Fig. 1-4; Table 1-3). This implies that the addition of tertiary treatment improves the potential for using N isotopes as a source tracer to distinguish between offshore and anthropogenic sources.

The flux-weighted averages for both 2009 and 2012 are consistent with the view that anthropogenic N bears a high $\delta^{15}N$ value. However, the range of isotopes and yearly variations in freshwater discharge and N flux add challenges to using these data to trace anthropogenic inputs to Narragansett Bay. Mixing models which rely

solely on flux-weighted yearly averages for seasonal outputs could overestimate (in the winter, when isotopic compositions may be lower) or underestimate (in the summer, when isotopic compositions are higher) the relative importance of WWTFs and rivers. One strategy could be using a seasonal flux-weighted average which may improve the accuracy of the model because the seasonal average would incorporate both the discharge and N flux for that time of year. For these models to be successful, and for $\delta^{15}N$ to be a tracer of anthropogenic influence, all NO_3^- sources to a system must be isotopically distinct, and stable N isotope compositions must remain conserved. The increase in the flux-weighted average between years suggests the addition of tertiary treatment makes $\delta^{15}N$ a stronger tracer of nitrogen source, however, the conservation of the source $\delta^{15}N$ has yet to be rigorously tested in Narragansett Bay.

Conclusions

Our data showed a wide range in both $\delta^{15}N$ and $\delta^{18}O$ for riverine samples and WWTF final effluent discharging to the Providence River-Narragansett Bay system, consistent with work in other locations (Jordan et al. 1997; Mayer et al. 2002; Rock and Mayer 2004; Dahnke et al. 2008; Deutsch et al. 2009; Saccon et al 2013). The large range of $\delta^{15}N$ and $\delta^{18}O$ values is the result of the multiple processes occurring in WWTFS and rivers. Seasonal assimilation is also an important process in controlling river $[NO_3^-]$. An increase in $\delta^{15}N$ and $\delta^{18}O$ values of the nitrate inputs is associated with the overall decrease in nitrate flux resulting from the stimulation of denitrification as part of tertiary treatment in the facilities draining into the

Narragansett Bay watershed. Results from a single plant initiating tertiary treatment suggest that the impact on WWTF effluent $\delta^{15}N$ and $\delta^{18}O$ is quite large (16 ‰) (Table 1-3) and imply that WWTF upgrades are likely responsible for the $\delta^{15}N$ and $\delta^{18}O$ increases observed in the rivers as well. The flux-weighted averages suggest that overall anthropogenic N discharges contribute nitrate with high $\delta^{15}N$ values (~13 ‰; Table 1-3), but with significant seasonal variation. When seasonal means are significantly different from other sources, $\delta^{15}N\text{-}NO_3^-$ may be a useful tracer of inputs.

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Tables

Table 1-1. Major NO_3^- sources to rivers and estuaries and the ranges of their stable N and O isotopes. In reference column, numbers refer to individual references listed below.

Source	$\delta^{15}N$ (‰)	$\delta^{18}O$ (‰)	Reference
	Sources to Rivers		
Precipitation	-5 to +10	> +25	7, 9, 14, 15, 16
Soil Nitrate (from Nitrification)	-10 to +5	-10 to +15	9, 11
Synthetic Fertilizer Run-off	-2 to +2	-18 to +23	4, 9
Sewage; manure;	-1 to +40	-10 to +15	1, 8, 12, 17
Groundwater	-3 to +14	-15 to +2	1,4, 10, 13
	Sources to Estuaries		
Precipitation	-5 to +10	> +25	7, 9, 14, 15, 16
Rivers	-3 to +16	-1 to +7	3, 4, 15
Wastewater Treatment Facilities	-1 to +40	0 to +13	5, 6, 8
Groundwater	-3 to +14	0 to +2	1, 4, 13
Marine	+3 to +8	+3 to +4	2, 17

1: Aravena et al. 1993; 2: Chaves 2004; 3: Dahnke et al. 2008; 4: Deutsch et al. 2006; 5: Deutsch et al. 2009; 6: DiMilla 2006; 7: Hastings et al. 2003; 8: Jordan et al. 1997; 9: Kendall 1998; 10: Kendall et al. 2007; 11: Mayer et al. 2001; 12: Mayer et al. 2002; 13: McClelland & Valiela 1998b; 14: Paerl & Fogel 1994; 15: Pardo et al. 2004; 16: Russell et al. 1998; 17: Wankel et al. 2006

Table 1-2. River and Wastewater Treatment Facility yearly average flow data. Flow is in 10^3 m^3 d^{-1} for WWTFs and 10^6 m^3 d^{-1} for rivers. All 2012 River flow measurements include data from January to September. Data after that month are unavailable.

Name	**2009 Flow**	**2012 Flow**
Wastewater Treatment Facilities		
Bucklin	80.09	69.76
Field's Point	186.86	159.46
Fall River	N/A	70.47
East Providence	27.66	N/A
Total	294.61	299.72
Average	98.21	99.90
	Rivers	
Blackstone	2.55	1.54
Pawtuxet	1.13	0.65
Taunton	1.79	0.88
Ten Mile	0.32	
Total	5.79	3.08
Average	1.45	1.02

Table 1-3. Annual average flux-weighted $\delta^{15}N$ and $\delta^{18}O$ for nitrate discharging from WWTFs, rivers, and combined WWTF and river sources. Riverine flux was calculated using Beale's unbiased estimator (see text). Average flux-weighted $\delta^{15}N$ and $\delta^{18}O$ for nitrate discharging from Field's Point measured pre- and post-upgrades to tertiary treatment.

	2009		**2012**		**Difference**	
	$\delta^{15}N$ (‰)	**$\delta^{18}O$ (‰)**	**$\delta^{15}N$ (‰)**	**$\delta^{18}O$ (‰)**	**$\delta^{15}N$ (‰)**	**$\delta^{18}O$ (‰)**
WWTFs	+7.1	-2.1	+14.2	+6.8	7.1	8.9
Rivers	+9.1	+0.7	+13.4	+4.8	4.3	4.1
Combined	+8.2	-0.5	+13.6	+4.8	5.4	5.3

	Pre-upgrades		**Post-upgrades**		**Difference**	
	$\delta^{15}N$ (‰)	**$\delta^{18}O$ (‰)**	**$\delta^{15}N$ (‰)**	**$\delta^{18}O$ (‰)**	**$\delta^{15}N$ (‰)**	**$\delta^{18}O$ (‰)**
Field's Point	1.5	-4.5	18.5	11.9	17.0	16.4

Figures

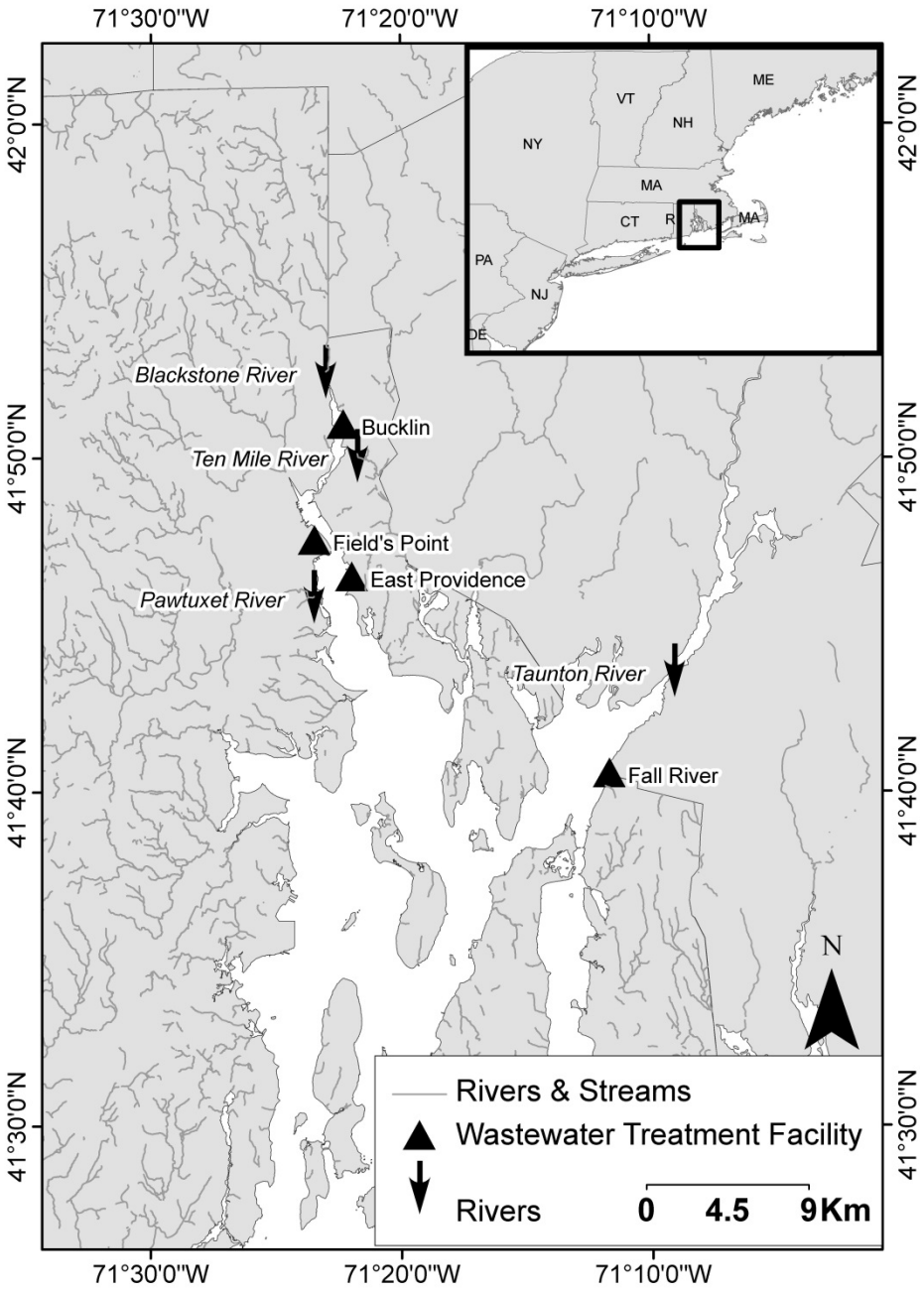

Figure 1-1. Narragansett Bay riverine and wastewater treatment facility (WWTF) collection map. Rivers are marked by arrows, and WWTFs are marked by triangles.

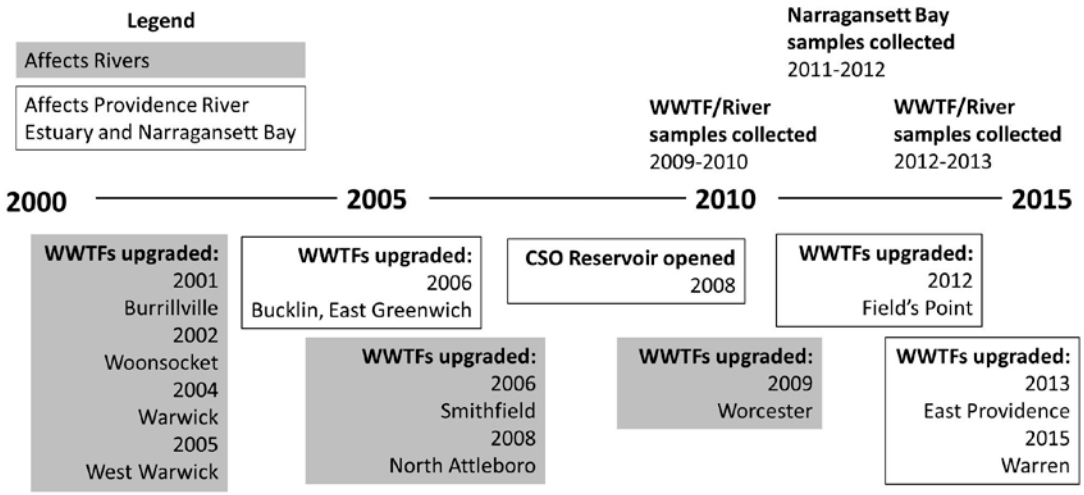

Figure 1-2. Timeline of upgrades to tertiary treatment by local wastewater treatment facilities (WWTFs). Dates of sample collections for this study are included above the time line (near 2010 and 2015). All WWTFs in shaded boxes discharge to rivers, while those in outlined boxes discharge to Narragansett Bay. The combined sewer overflow (CSO) reservoir (Providence, RI) discharges to Field's Point WWTF which discharges to Narragansett Bay.

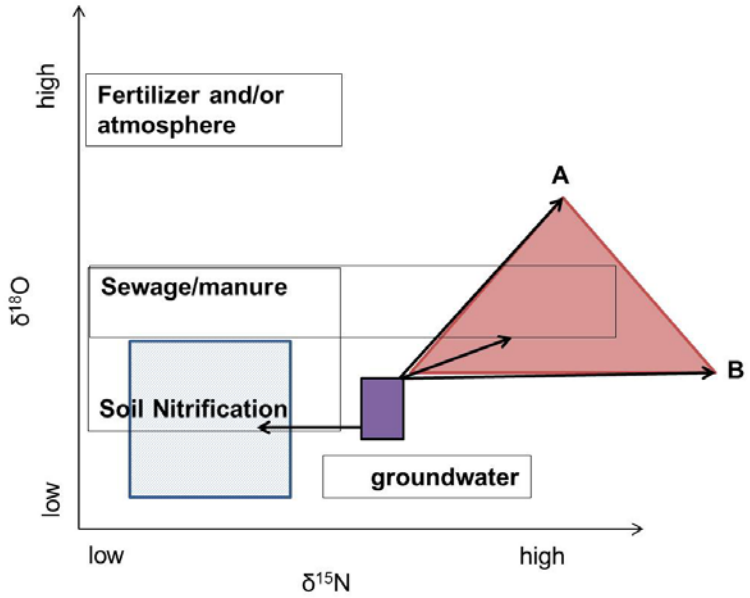

Figure 1-3. Model of how sources (boxes) and processes (arrows) affect the $\delta^{15}N$ and $\delta^{18}O$ of a parcel of water. Purple center box represents sample of water from an estuary. Boxes outlined in gray are potential sources (fertilizer and/or precipitation, sewage/manure, soil nitrate produced from nitrification, and groundwater) of water to the purple box. Line A represents the fraction which occurs during denitrification or assimilation. Line B represents fraction during nitrification. If the NO_3^- is denitrified or assimilated, we expect a fractionation of $\delta^{15}N$: $\delta^{18}O$ to be 1:1 (Granger et al. 2004; Granger et al. 2008). This would increase the isotopic composition of the purple box along line A. During nitrification, we expect the $\delta^{15}N$ to increase while the $\delta^{18}O$ remains mostly constant. This is because the pool of water, from which most of the oxygen in NO_3^- is derived, is much larger than the pool of N, and if nitrification goes to completion, the $\delta^{18}O$ of the NO_3^- will be the same as the water, following line B (Casciotti et al. 2002; Sigman et al. 2005). Therefore, we expect a slope that is not quite 1 and not quite 0, inside the orange triangle. If a large pool of NH_4^+ exists (such as those in wastewater treatment facilities (WWTFs)), it may be heavily fractionated during nitrification, leading to lower isotopic compositions than expected (blue box).

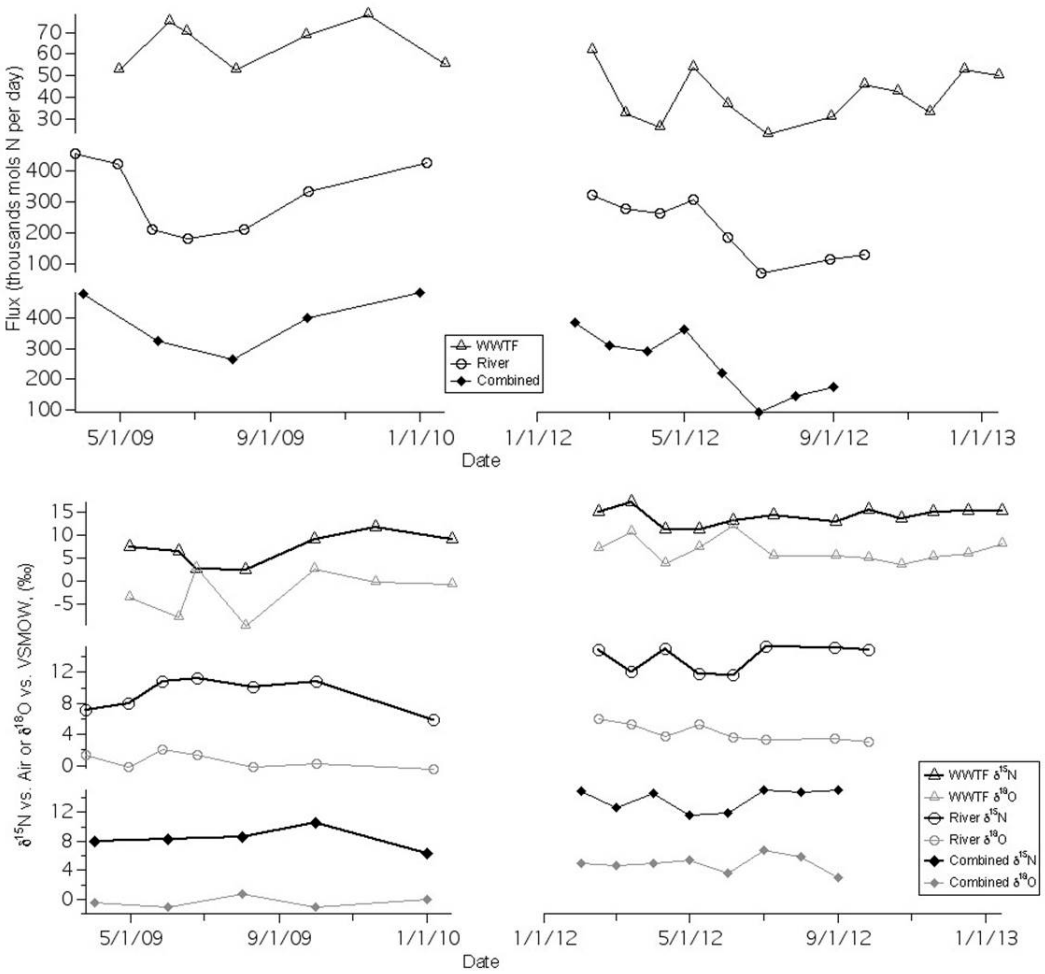

Figure 1-4. Flux and flux-weighted isotope values. Top Panel: Flux (thousands moles N per day) from all WWTFs (open triangles), all rivers (open circles), and all WWTFs and rivers combined (closed diamonds). Bottom Panel: Average flux-weighted $\delta^{15}N$-NO_3^- (black symbols) and $\delta^{18}O$-NO_3^- (gray symbols) for all WWTFs (triangles), all rivers (circles), and all WWTFs and rivers combined (diamonds) plotted against collection date (month/day/year).

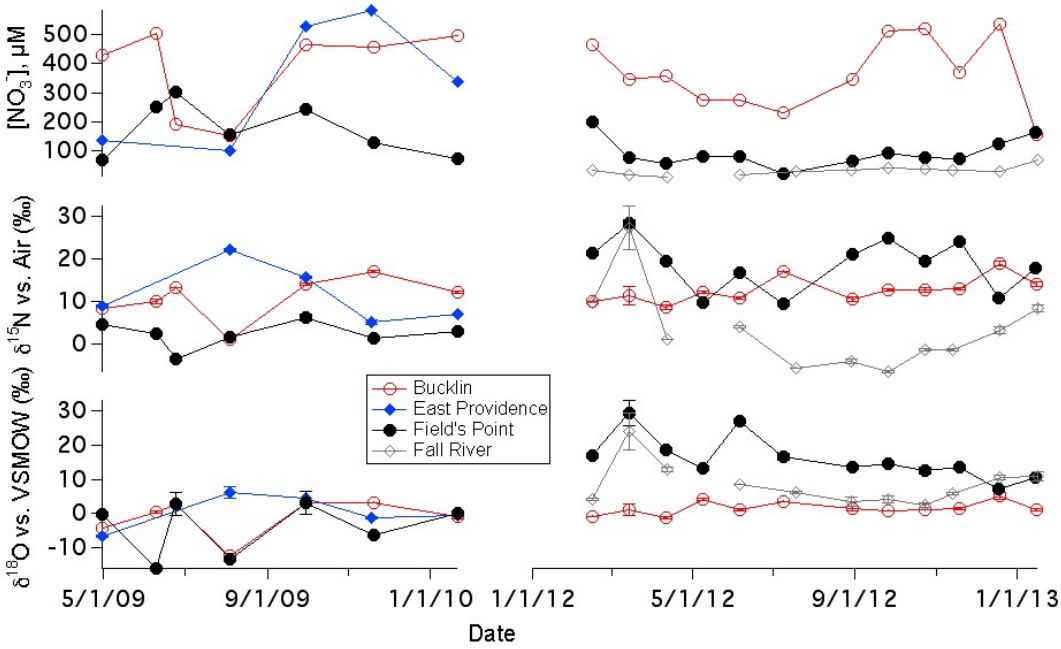

Figure 1-5. Wastewater effluent [NO_3^-] concentrations (top), $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ are plotted against collection day (month/day/year). Samples are from three major wastewater treatment facilities which discharge to Narragansett Bay and Mount Hope Bay sampled during two years. Bucklin (open circle), Field's Point (filled circle), and East Providence (filled diamond) were sampled in 2009-2010, while Bucklin, Field's Point, and Fall River (open diamond) were sampled in 2012-2013.

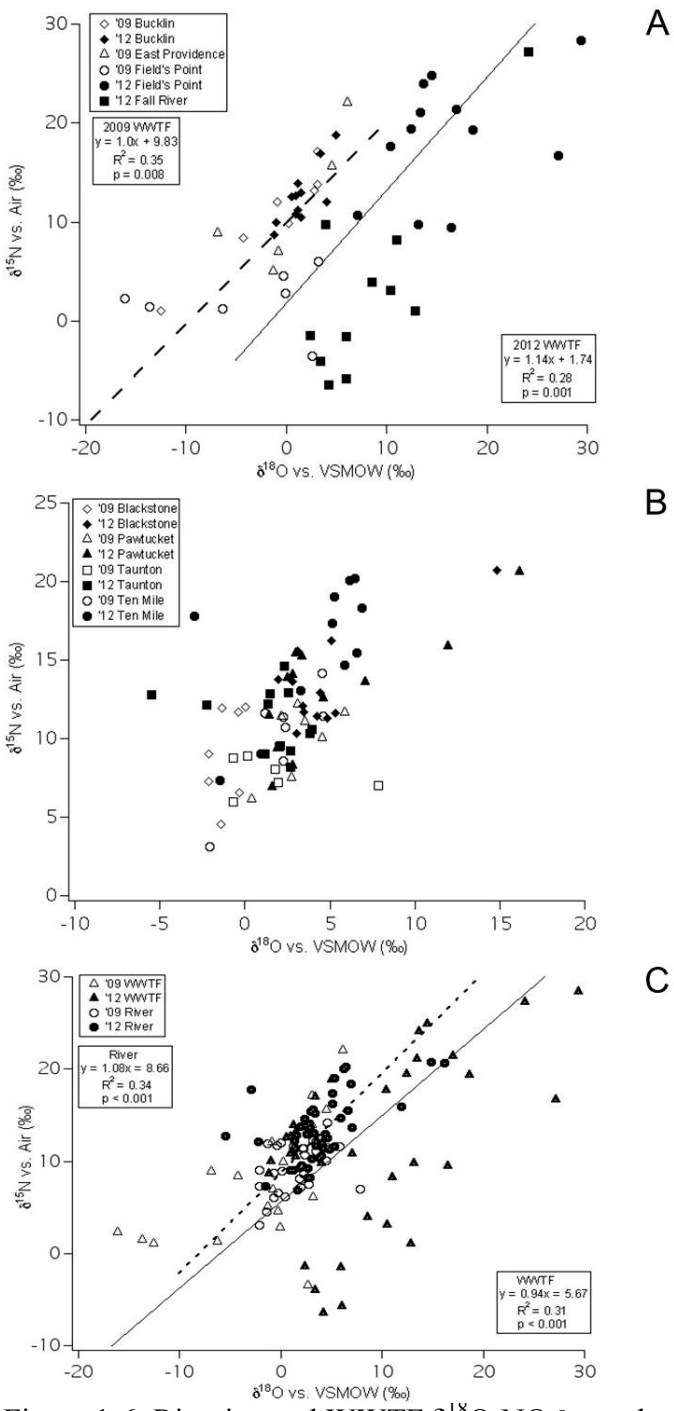

Figure 1-6. Riverine and WWTF $\delta^{18}O\text{-}NO_3^-$ are plotted against $\delta^{15}N\text{-}NO_3^-$. A: WWTF data plotted by treatment facility and year (2009: open symbols; 2012: closed symbols). Reduced major axis (model II) linear regressions were performed for each year (dashed line 2009, solid line 2012). B: Riverine data plotted by river name and year (2009: open symbols; 2012: filled symbols). C: Both riverine and WWTF data plotted for 2009 (open symbols) and 2012 (filled symbols). Reduced major axis (model II) linear regressions were performed on each N source (WWTF: solid line; Riverine: dotted line).

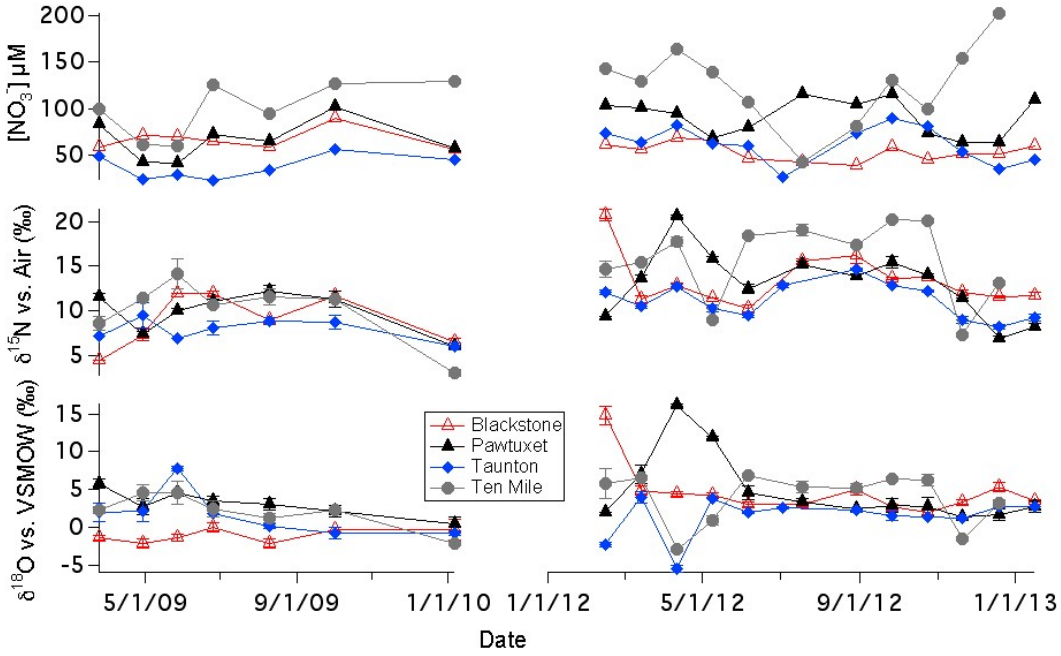

Figure 1-7. Riverine [NO_3^-] concentrations (top), $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- are plotted against collection day (month/day/year). River samples are from the major N sources to Narragansett Bay – the Blackstone (open triangle), Pawtuxet (filled triangle), Ten Mile (filled circle), and Taunton Rivers (filled diamond).

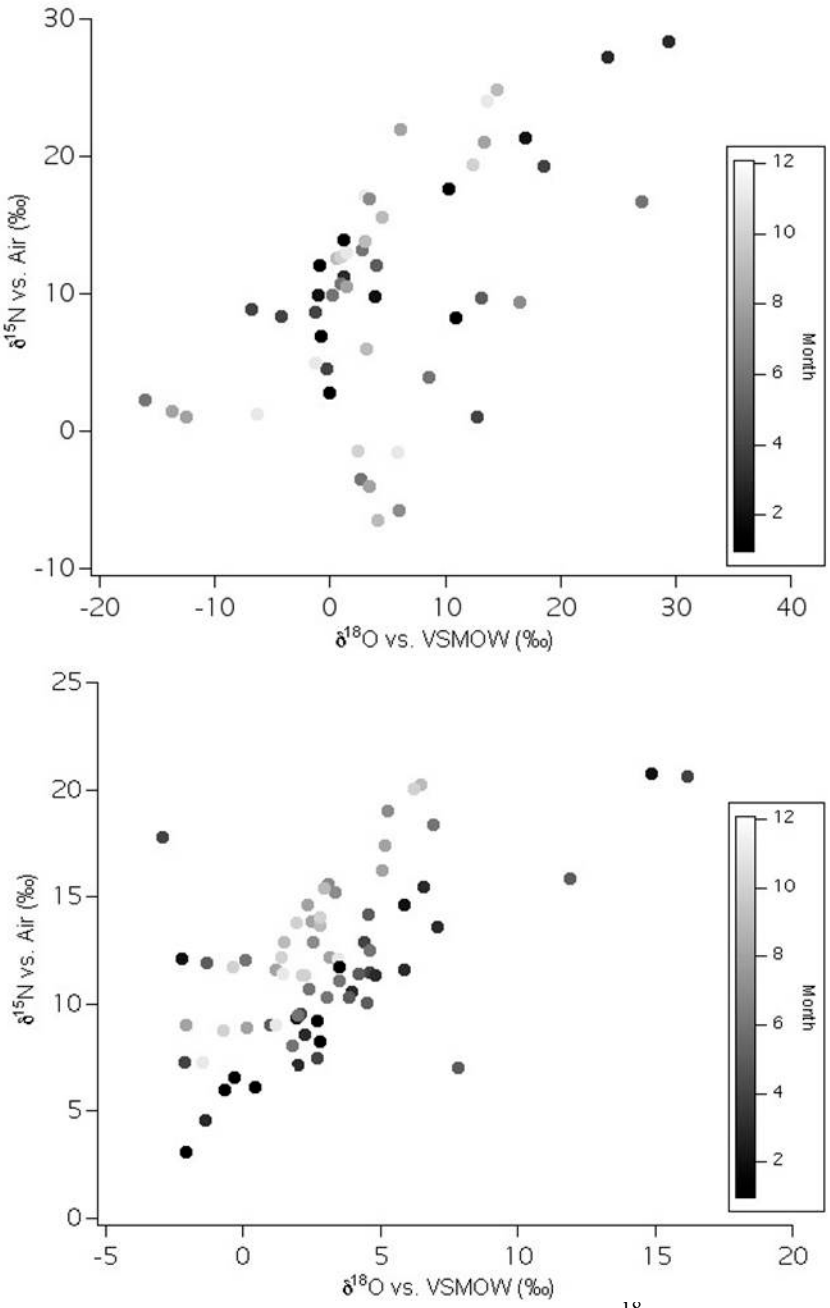

Figure 1-8. WWTF (top) and Riverine (bottom) $\delta^{18}O\text{-}NO_3^-$ are plotted against $\delta^{15}N\text{-}NO_3^-$ as a function of month of the year.

CHAPTER 2

PREFACE

Changes to standing stock concentrations and $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in Narragansett Bay after anthropogenic N input reductions

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Abstract

Estuaries regulate nitrogen (N) fluxes transported from land to the open ocean through uptake and denitrification. Anthropogenic N loading increased over the last century, prompting upgrades to wastewater treatment facilities to decrease the amount of nitrogen discharged. Upgrades occurred at multiple facilities discharging into Narragansett Bay's watershed and significant increases in the isotopic compositions of nitrogen and oxygen in nitrate were observed. Here, we use surface water samples collected before and after upgrades at one major facility (2007-2009 and 2011-2012) to evaluate how this isotopic signal is transmitted downstream. Samples were analyzed for nutrient (nitrogen, ammonium, and phosphate) concentrations as well as stable nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) isotopic compositions. Overall nitrate concentrations decrease toward the ocean, while $\delta^{15}N$ values of NO_3^- decrease to 41.7°N and then remain constant to the south, in Narragansett Bay proper. The $\delta^{18}O$ values do not show any significant gradient. Between 2007-2009 and 2011-2012, $\delta^{15}N$ values increased significantly, by ~2 ‰, in the Providence River Estuary (north of 41.7°N), but not in the rest of Narragansett Bay. The lack of change in $\delta^{15}N$ and $\delta^{18}O$ values in the Narragansett Bay suggests that mixing and recycling of nitrate overprints any anthropogenic isotopic signal inherited from upstream. N* calculations show that the bay switches from N-rich north of 41.7°N to N-deficient south of this latitude for both 2007-2009 and 2011-2012, implying that anthropogenic N input reductions have yet to change the N status of the Providence River Estuary and Narragansett Bay. Providence River Estuary remains N-rich, while Narragansett Bay proper remains N-poor.

Introduction

Estuaries regulate the material transported from land to the open ocean. In particular, estuaries ameliorate the impact of high riverine nutrient loads through biological consumption of nutrients, mixing, and denitrification, the bacterial reduction of nitrate in the absence of oxygen (Costanza et al. 1997; Herbert 1999). Anthropogenic nitrogen (N) loads to coastal regions increased over the last century, exploiting this essential function of estuaries (Nixon 1995; Boesch 2002), and are frequently cited as the primary cause of eutrophication (Nixon 1995), which leads to oxygen consumption, at times to life-threatening levels. Despite these observations, nitrogen often remains the limiting nutrient during the growing season in temperate estuaries and coastal regions because of rapid consumption of dissolved nitrogen species during photosynthesis and bacterial denitrification (Boynton et al 1982; Howarth 1988; Oviatt et al. 1995; Herbert 1999). Furthermore, it has been suggested that restricting nitrogen inputs to these systems may have consequences for consumers in the ecosystem, including societally and economically important species (Oczkowski et al. 2008; Nixon et al. 2009).

Anthropogenic N enters estuaries as dissolved inorganic nitrogen (DIN; ammonium, NH_4^+ and nitrate, NO_3^-) through agricultural runoff, rivers, urban runoff, and wastewater treatment effluent (Nixon et al. 1995; Herbert 1999; Nixon et al. 2008). In the water column, ammonium is readily consumed by phytoplankton and macroalgae or it is nitrified to nitrate (Culver-Rymsza 1988; York et al. 2007). In the anoxic sediments, it may be oxidized by nitrite during anaerobic ammonium oxidation (anammox) (Rich et al. 2008; Brin et al. *in prep*.). As a result of the rapid

transformations of NH_4^+ (Horrigan et al. 1990), NO_3^- is the most abundant form of DIN in the open waters of the Providence River Estuary and Narragansett Bay. Nitrate, in turn, is assimilated by phytoplankton and incorporated into organic matter or reduced to gaseous N_2O or N_2 through benthic denitrification. Benthic denitrification removes 20-30 % of NO_3^- loading to estuaries (Smith et al. 1985; Herbert 1999; Seitzinger et al. 2006; Fulweiler & Heiss 2014). Total DIN loadings to the bay are decreasing due to denitrification at wastewater treatment facilities (WWTFs), known as tertiary treatment (USEPA 2004; RIDEM 2005).

Narragansett Bay, including Mount Hope and Greenwich Bays, and the Providence River Estuary, is 328 km^2, has a mean depth of 8.3 m, a water residence time of about 28 days, and low freshwater input (around 100 m^3s^{-1}) compared to seawater (Fig. 2-1; Pilson 1985a). Water from the Providence River Estuary (~41.8°N to 41.7°N) enters Narragansett Bay proper (south of 41.7°N) primarily through the West Passage (Kincaid et al. 2008). Rhode Island Sound water enters Narragansett Bay primarily through the East Passage and mixes with Providence River Estuary water in the upper bay (Fig. 2-1; Kincaid et al. 2008).

The majority of anthropogenic nitrogen input to Narragansett Bay occurs in its northern reaches, primarily through rivers and WWTFs, including 10 facilities which discharge directly to the bay, and 19 which discharge to its tributaries. Rivers and WWTFs comprise ~80% of the anthropogenic inputs, and rivers are the single largest contributor of N when sewage discharge to the rivers is considered part of the river flow (Nixon et al. 1995; Nixon et al. 2008; Krumholz 2012). Other freshwater sources, such as storm water and groundwater, are relatively small portions of the

Narragansett Bay water budget, but are important to the budgets of the smaller bays and coves, like Greenwich Bay (Nixon et al. 1995; DiMilla 2006; Nowicki and Gold 2008; Spaulding 1987; Krumholz 2012). Starting in 2001, multiple WWTFs in the Narragansett Bay watershed upgraded to tertiary treatment, including the three largest, with more planned in the near future (Fig.2-2). Decreases in N input to Narragansett Bay were observed for the period of 2006-2010, where wastewater treatment facility N contributions fell approximately 20 % (Krumholz 2012). Field's Point, the largest WWTF in the watershed, added tertiary treatment in 2012 and N additions are expected to fall an additional 10 % by 2015 (Krumholz 2012; Narragansett Bay Commission 2013).

Stable N and oxygen (O) isotopes of NO_3^- are used to assess N cycling in the water column and, potentially, sources of N to estuaries, if the sources are isotopically distinct (Wassenaar 1995; Mayer et al. 2002; Deutsch et al. 2005; and Saccon et al. 2013). Isotopic fractionations are associated with all major N cycling processes. In addition, the relationship between N and O isotopic compositions of nitrate can further diagnose biological processing of nitrogen. Laboratory studies show that fractionation during consumption of nitrate, either by denitrification or nitrate assimilation, leads to an increase in the $\delta^{15}N$ and $\delta^{18}O$ values of nitrate in a 1:1 ratio across a range of measured isotope effects (Granger et al. 2004, 2008). Tertiary treatment uses denitrifying bacteria to remove nitrate, and an increase the N and O isotopic composition of NO_3^- is apparent in the effluent since its implementation (Schmidt et al. *in prep.*). Nitrification has the potential to impact both the N and O isotopic values

through the production of NO_3^- from NH_4^+ and the incorporation of O from water and oxygen during nitrification (Casciotti et al. 2010).

Large isotopic composition differences observed in WWTF nitrate effluent pre- and post-introduction of tertiary treatment (16 ‰ for both $\delta^{15}N$ and $\delta^{18}O$) appear to be significantly attenuated in rivers (4 ‰ for both $\delta^{15}N$ and $\delta^{18}O$) receiving treated effluent, likely as a result of dilution with the background nitrate pool (Schmidt et al. *in prep.*). Direct WWTF N flux is about 30 % of the riverine N flux, suggesting that its net impact on the estuary may be subtle but identifiable (Schmidt et al. *in prep.*). Here, we document the N and O isotopic distributions and examine whether the large differences in $\delta^{15}N\text{-}NO_3^-$ from inclusion of tertiary treatment at WWTF improves our ability to trace anthropogenic N within Narragansett Bay.

Methods

Sample Collection

Surface water samples were collected from 21 stations along a north-south transect in the Providence River Estuary and Narragansett Bay to Rhode Island Sound during 2007-2009, and 2011-2012 (Fig. 2-1). During 2007-2009, 9 stations were sampled. Samples were collected by deploying a bucket over the side of a boat, and transferred to opaque 1L high density polyethylene bottles and stored on ice (Krumholz 2012). Samples collected from 2007-2009 were part of the Nu-Shuttle cruises operated by the National Marine Fisheries Service in cooperation with the University of Rhode Island (URI) and the Rhode Island Department of Environmental Management (Melrose et al. 2007; Krumholz 2012). In 2011-2012, 12 surface stations

were sampled (Fig. 2-1). Samples were pumped through a hose plumbed to a 100 μm filter, where the hose and filter were flushed for 5 minutes with site water prior to collection (surface depth < 0.5 m). High density polyethylene bottles were tripled rinsed with site water prior to filling, and then stored on ice until returning to the laboratory. All samples were filtered using glass fiber filters (GFFs, pore size 0.7 μm), and the filtrate was frozen (-4°C in 2007-2009, and -20°C in 2011-2012) until further analysis.

During the 2011-2012 sampling excursions, salinity measurements were taken with a refractometer (precision of 1 ppt) calibrated using manufacturer methods before each sampling event. After the measurements were taken, the refractometer was calibrated using a 3 point calibration system. Salinities measured at the higher end of the spectrum were overestimated in the field by about 2 ppt. All salinity measurements were corrected with the new calibration curve using this equation: (measured salinity + 0.0066)/1.0537. Corrected salinities were used in this manuscript. We note that the highest measured salinities are still, on average, higher than what has been previously reported for the mouth of Narragansett Bay (www.narrabay.org; Shonting and Cook 1970). Given years of salinity data from Narragansett Bay showing maximum salinities of 33 ppt, we attribute our high values to measurement error. We are unsure of the cause and acknowledge that they may reflect additional analytical uncertainty associated with the refractometer.

Laboratory Analysis

The Marine Ecosystems Research Laboratory (MERL) at the University of Rhode Island (URI) analyzed the 2007-2009 samples for nitrate, ammonium, and

phosphorus (NO_3^-, NH_4^+, PO_4^{3-}) on either a Technicon or Astoria SFA autoanalyzer using colormetric methods of Strickland and Parsons (1968), Technicon (1972), Astoria-Pacific (2005), and Scott et al. (2005). Minimum detection limits for all parameters on the Technicon and Astoria were 0.2 μM and 0.1 μM, respectively. Intercalibrations between the two instruments were completed and detailed in Krumholz (2012). The Nixon laboratory (URI) analyzed the 2011-2012 samples on a Lachat QuickChem 2000 flow injection autoanalyzer using EPA methods 353.4 and 365.5 (Grasshoff 1976; USEPA 1997a; USEPA 1997b) for NO_{3+2}, NO_2^-, NH_4^+, and PO_4^{3-}which had a minimum detection limit of 0.05 μM.

Chlorophyll *a* concentrations were determined by passing 100 mL of sample water through glass fiber filters (pore size 0.7 μm) in triplicate. The filters were extracted in 10 mL of 90 % acetone (by volume) for 24 hours. Approximately 8 mL were transferred to a cuvette, wiped clean, and the chlorophyll *a* concentration read on a Turner A-10 fluorometer with a precision of 0.1 μg L^{-1}. Rhode Island EPSCoR supplied the instrument (http://web.uri.edu/rinsfepscor/).

N and O isotope compositions of the filtered water samples were determined using a denitrifier method that produces N_2O (Sigman et al. 2001, Casciotti et al. 2002) for analysis by gas chromatography isotope ratio mass spectrometry. Oxygen isotopes were measured for 2011-2012 only. Stable isotopes ratios were reported as the ratio of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ between the sample and a standard, and expressed as $\delta^{15}N$ or $\delta^{18}O$ where $\delta = [(R_{sample}/R_{standard}) - 1] \times 1000$ and $R = {}^{15}N/{}^{14}N$ or $^{18}O/^{16}O$. Samples and working standards (IAEA N3, $\delta^{15}N = +4.7$ ‰, $\delta^{18}O = +25.6$ ‰; USGS 32, $\delta^{15}N = +180$ ‰, $\delta^{18}O = +25.7$ ‰; USGS 34, $\delta^{15}N = -1.8$ ‰, $\delta^{18}O = -27.9$ ‰) were

analyzed in the same batch to normalize to accepted values (N_2 in air and VSMOW for $\delta^{15}N$ and $\delta^{18}O$ respectively, both with an isotopic composition of 0 ‰). Precision of the method was < 0.3 ‰ for $\delta^{15}N$ and < 0.5 ‰ for $\delta^{18}O$ based on the standard deviations of all standards measured.

Results

Pre-tertiary treatment upgrades (2007-2009)

Nitrate concentrations varied significantly throughout the sampling period, with a range from 5-35 μM. $[NO_3^-]$ was highest in the north and it decreased toward 41.7°N and leveled off in the lower bay. Surface $[NO_3^-]$ fell below detection limit south of 41.7ºN in the spring and summer, and 41.6ºN in the fall. Winter values were fairly homogenous south of 41.6° (Fig. 2-3). N* (deviation in DIN concentrations from expectations based on PO_4^{3-}; Gruber and Sarmiento 1997) showed a distinct change, where the Providence River Estuary (north of 41.7°N) was N-rich (positive N*) in the spring only while the Narragansett Bay proper (south of 41.7°N) consistently showed a N deficiency (negative N*) (Fig. 2-4).

The $\delta^{15}N$ values varied between 6 and 12 ‰, and generally decreased from 41.8°N to 41.7°N. South of this point, $\delta^{15}N$ values were nearly constant around 7.2 ± 1.5 ‰ (mean ± standard deviation), at least in part because they are limited to wintertime samples which showed little variability around a mean value of ~7 ‰ (Fig. 2-3). During fall and spring, values decreased to 41.7ºN, while summer values increased between the stations 1 and 2 (Fig. 2-1), and then decreased to 41.7ºN (Fig.

2-3). The range of source values was large (4-11 ‰), and the $\delta^{15}N\text{-}NO_3^-$ values at the station 1 were similar to if not bracketed by the source $\delta^{15}N$ values (Fig. 2-3).

During and post-tertiary treatment upgrades (2011-2012)

Nitrate concentrations in 2011-2012 spanned a larger range than in the 2007-2009 period, from below detection limit to 50μM, and showed a slightly weaker decrease downstream in the Providence River Estuary and Narragansett Bay such that there was NO_3^- above the detection limit during the fall (Fig. 2-5). The N* distributions were essentially the same as in 2007-2009, except the Providence River Estuary was N-rich for parts of the summer, fall and winter as well, while Narragansett Bay proper had a few instances of N-richness in the winter and fall (Fig. 2-4). $\delta^{15}N$ values in 2011-2012 showed a similar pattern to 2007-2009 with a decrease toward 41.7°N, and leveling off in the bay (7.5 ± 1.5 ‰; mean ± standard deviation) (Fig. 2-5). $\delta^{15}N$ values from the fall showed significant variability, 6-10‰, likely, at least in part, due to increase in sampling stations represented. Again, the winter data was relatively homogenous at 6.8 ± 0.6 ‰ (mean ± standard deviation) for the entire bay. Spring values decreased toward the south to 41.7°N, while summer values increased in the same region (Fig. 2-5). During 2011-2012, all $\delta^{15}N\text{-}NO_3^-$ values were lower than the source values, except for the summer, which increased between the source and station 1 (Fig. 2-5). The $\delta^{18}O$ values showed no trend with latitude or season (Fig. 2-5).

Discussion

Effects of upgrades on nitrate concentrations

Riverine and WWTF nitrate flux decreased by approximately 30 % between 2009 and 2012 due to upgrades to tertiary treatment (Schmidt et al. *in prep.*). This decrease has the potential to impact nitrate availability in both the Providence River Estuary and Narragansett Bay proper. For 2007-2009 and 2011-2012, nitrate concentrations at station 1 are significantly lower than the anthropogenic source input values (55-80 μM for the rivers, and 100-264 μM for WWTF effluent) (Figs. 2-3 and 2-5). The decrease in $[NO_3^-]$ between the anthropogenic sources and station 1 is due to assimilation and/or dilution when the point-source contributions are mixed with the lower nitrate waters of the Providence River Estuary and Narragansett Bay. Despite the large decrease in nitrate flux in rivers and WWTFs, average nitrate concentrations did not change between sample periods in either the Providence River Estuary or Narragansett Bay and if anything they are higher in 2012 (Figs. 2-3 and 2-5). This may reflect simple random variability associated with supply and demand dynamics or it could reflect a response or feedback of the system to the decreased supply. If overall nitrogen input reductions led to a decrease in production, lower rates of oxygen consumption at the seafloor and an associated reduction in denitrification would result. However no decrease in primary production has been documented (Smith 2011). Similarly, a reduction in oxygen consumption at the seafloor could also impact the flux of regenerated phosphate (Ingall and Jahnke 1994; Van Cappellen and Ingall 1994), which may lead to a decrease in N consumption in N replete regions of the system.

Nitrogen status (N*) in Providence River Estuary and Narragansett Bay

In order to evaluate the potential for the aforementioned denitrification and phosphate related feedbacks we employ the semi-conservative tracer, N* (N* = ($[NO_3^-]$ + $[NH_4^+]$) – 16$[PO_4^{3-}]$ + 2.9 (μM)). N* defines deviations in DIN concentrations from expectations based on PO_4^{3-}, assuming the Redfield ratio (Gruber and Sarmiento 1997; Sigman et al. 2005; Granger et al. 2011). This assumes that either N or P is the limiting nutrient to primary production in the estuary and identifies where N inputs or removals are occurring in a non-Redfieldian way, or by some other means than typical phytoplankton assimilation. Inputs from WWTF and rivers are biased heavily toward excess DIN because both terrestrial ecosystems and waste water treatment schemes remove PO_4^{3-} effectively (Vitousek and Howarth 1991; Smith et al. 1999; USEPA 2004). Inputs from offshore bear an N deficit due to the impact of benthic denitrification (where N is removed but not P) on the shelf (Sigman et al. 2005; Granger et al. 2011). The location of where excess inputs are diluted by waters bearing a deficit should shift if DIN load reductions are to have a significant impact primary production in the system (Fig. 2-3 and 2-5). For both years, the Bay generally becomes N deficient south of 41.7°N (Fig. 2-4). The N* calculation suggests that the effects of excess N from the Providence River Estuary is not reaching Narragansett Bay, and that the N reductions are not changing nitrogen status in either region. The Providence River Estuary (north of 41.7°N) continues to be N-rich, while Narragansett Bay (south of this point) is N-deficient. Both of the potential feedbacks described above would help to stabilize the nitrogen status of the system, one through a decrease in N removal via denitrification and the other through the addition of PO_4^{3-} to support

N drawdown by phytoplankton. If PO_4^{3-} is the key to drawing down NO_3^- in this system, then it follows that N reductions may have only a limited impact on remediating eutrophication

Effects of upgrades on isotope compositions

The N and O isotopes of nitrate provide us with a slightly different perspective of how DIN travels through the estuary. From the perspective of the large observed changes in the upstream input $\delta^{15}N$ value, one could predict an increase downstream to be observed as well. Changes between pre- and post-treatment upgrades are most likely felt in the Providence River Estuary because the majority of freshwater discharges there (Fig. 2-1; Pilson 1985a; Doering et al. 1990; Nixon et al. 2008; Kincaid et al. 2008). In the Providence River Estuary, between 2007-2009 and 2011-2012, $\delta^{15}N$ values increased significantly, by about 2 ‰ (Table 2-1; t-test, $p < 0.001$). Between 2007-2009 (avg. $\delta^{15}N\text{-}NO_3^- = 7.2 \pm 1.5$ ‰, n = 45; mean ± standard deviation) and 2011-2012 (avg. $\delta^{15}N\text{-}NO_3^- = 7.5 \pm 1.5$ ‰, n = 46) Narragansett Bay proper did not appear to show any change in $\delta^{15}N$.

The increase in $\delta^{15}N$ values in only the Providence River Estuary suggest that the tertiary treatment isotopic signal is lost in Narragansett Bay proper. Seasonally, this may be due to near complete uptake or denitrification of anthropogenically sourced DIN in the upper bay (Fig. 2-4). During the summer, N* calculations are near or below zero throughout the bay, indicating a deficiency in N, implying non-Redfieldian removal, such as from denitrification. Water column denitrification is highly probable during the summer in the Providence River Estuary due to very low $[O_2]$ at times (Prell et al. 2006). Sediment denitrification is probable throughout the

bay, and has been measured quite extensively (Fulweiler and Heiss 2014). However, N* calculations show that DIN is in excess in the Providence River Estuary and able to exchange with the Narragansett Bay proper only during the spring, fall and winter. This is consistent with previous work in the Providence River Estuary which suggests DIN fluxes out of the estuary into Narragansett Bay fueling primary production (Doering et al. 1990). The question then becomes, what is causing the isotopic signal to be overprinted and homogenized in the lower bay?

Mass Balance Mixing Models

While we assume N is exchanging between the Providence River Estuary and Narragansett Bay proper, based on our high NO_3^- concentrations remaining in the southern reaches of the Providence River Estuary and previous studies (Doering et al. 1990; Oviatt et al. 2002), oxygen isotopes within nitrate may help to confirm this. The oxygen within the nitrate molecule comes largely from the water in which the nitrate was created (5/6 from oxygen in the water molecule, 1/6 from dissolved O_2) (Casciotti et al. 2002; Sigman et al. 2005). Assuming that the oxygen isotopic composition of water is a good reflection of the conservative mixing of ocean and fresh water, then it should increase downbay from a fresh water endmember of ~-9.4‰ to an oceanic endmember of -1.3 ‰ (Knapp et al. 2008; Bowen 2013). The nitrate input from WWTF and rivers does not however, simply bear the low $\delta^{18}O$ value of the water in which the nitrate formed, (i.e. freshwater), but rather due to partial denitrification during tertiary treatment and some assimilation by phytoplankton, it bears a $\delta^{18}O$ value significantly greater than that predicted using a simple source model. The average $\delta^{18}O$ value of nitrate inputs to the system is 6 ‰ for the WWTFs and 2 ‰ for

the rivers (Fig. 2-7; Schmidt et al. *in prep.*). However, it still may be useful as a tracer.

One-to-one relationships between $\delta^{15}N$ and $\delta^{18}O$ values in a system suggest that the isotopic variability is driven by uptake or denitrification, the two processes described above as significantly enriching the $\delta^{18}O$ signal above that of the $\delta^{18}O$ of the water (Granger et al. 2004, 2008). Deviations from a one-to-one relationship between $\delta^{15}N$ and $\delta^{18}O$ value may reflect mixing with NO_3^- with a different balance of $\delta^{15}N$ or $\delta^{18}O$ values or *in-situ* nitrification of NH_4^+ to NO_3^- (Fig. 2-7; Casciotti et al. 2002; Sigman et al. 2005). Both of these processes are likely important in Narragansett Bay. Hypothetically, an increase of $\delta^{15}N$ relative to $\delta^{18}O$ may reflect the nitrification of an NH_4^+ source with a high $\delta^{15}N$ value relative to the background pool or the addition of oxygen with a $\delta^{18}O$ value less than the $\delta^{18}O$ value of the background NO_3-.

The increase of $\delta^{18}O$ relative to $\delta^{15}N$ observed in Narragansett Bay proper may result from mixing with Rhode Island Sound sourced nitrate or nitrification and oxygen exchange with ocean water at the expense of freshwater (Fig. 2-7). The recycling of nitrate through organic matter and NH_4^+ is likely a rapid and complete process in Narragansett Bay (Harrington et al. 1990; Berounsky 1990), resulting in a relatively constant $\delta^{15}N$ value but the $\delta^{18}O$ value will reflect that of the water, which should vary with salinity (Fig. 2-7). This effect is complicated by the elevated $\delta^{18}O$ values of the upstream NO_3^-. Nitrification will lower the overall $\delta^{18}O$ of nitrate, but the degree to which it is lowered depends upon the salinity of the water from which it gets its oxygen. Little change in the $\delta^{18}O$ of nitrate is observed along the Narragansett Bay transect. However, the subtle increase in $\delta^{18}O$ with no apparent change in $\delta^{15}N$ is

apparent when examining the relationship between $\delta^{15}N$ and $\delta^{18}O$ with respect to latitude (Fig. 2-7).

In an attempt to highlight processes that impact [NO_3^-] and N and O isotopes along the estuarine gradient, we used a simple mass balance mixing model (Fry 2002). The $\delta^{15}N$ value of a mixture is estimated assuming conservative mixing between endmembers of known nitrate concentrations, $\delta^{15}N\text{-}NO_3^-$ values and salinities (eqn 1) (Fry 2002):

$$\delta^{15}N_{mix} = [f(C_r\delta^{15}N_r) + (1\text{-}f)(C_s\delta^{15}N_s)]/C_{mix} \quad \text{eqn. 1}$$

where C_r and $\delta^{15}N_r$ are the flux-weighted river [NO_3^-] and isotopic composition, C_s and $\delta^{15}N_s$ are the oceanic [NO_3^-] and isotopic composition (average Rhode Island Sound samples collected Dec. 2005; C_s = 4.6 µM, $\delta^{15}N_s$ = 5.9 ‰, salinity = 35 ppt (Table 2-2)), and *f* is fractional contribution of river water, or salinity, based on salinity between the rivers (0) and the mouth of Narragansett Bay (35 ppt; *f* = (35-salinity)/35). C_{mix} is the weighted [NO_3^-] concentration between C_r and C_s ($C_{mix} = fC_r + (1\text{-}f)C_s$) (Fry 2002). C_r is 85 µM for the fall, and 76 µM for the winter while $\delta^{15}N_r$ is 14.9 ‰ for fall and winter (Table 2-2).

For the O isotope mass balance mixing model, equation 1 is adjusted slightly to account for fractionation during nitrification:

$$\delta^{18}O_{mix} = [f(C_r\delta^{18}O_r) + (1\text{-}f)(C_s\delta^{18}O_s)]/C_{mix} \quad \text{eqn. 1}$$

where $\delta^{18}O_r = \delta^{18}O\text{-}H_2O_r + 3$ ‰, $\delta^{18}O\text{-}H_2O_r$ = -9.4 ‰, and $\delta^{18}O_s = \delta^{18}O\text{-}H_2O_s + 3$ ‰ $\delta^{18}O\text{-}H_2O_s$ = -1.3 ‰ (Knapp et al. 2008; Bowen 2013). The concentration measurements remain the same.

While the mechanisms for fractionation of oxygen during nitrification are still being explored, ammonia-oxidizing bacteria show laboratory fractionation factors of +17 – +37 ‰ (Casciotti et al. 2010), and field measurements show an apparent fractionation (the measured difference between $\delta^{18}O\text{-}H_2O$ and $\delta^{18}O\text{-}NO_3^-$ in the field) of 3 ‰ (Brandes and Devol 1997). The fractionation between the $\delta^{18}O\text{-}H_2O$ and $\delta^{18}O\text{-}NO_3^-$ was not measured during this study; however, we employed the apparent fractionation factor of 3 ‰ (Brandes and Devol 1997) to account for the change in isotopic composition between $\delta^{18}O\text{-}H_2O$ and $\delta^{18}O\text{-}NO_3^-$. (Fig. 2-8).

The measurement error in the salinity estimates appears greater at higher salinities, which will shift measurements with higher salinities to slightly lower salinities (shift left on Fig. 2-8). This shift forces the higher salinity measurements to fall under the $\delta^{15}N$ mass balance mixing line, where before the values may have been to the right of the model (Fig. 2-8, solid and dotted lines, referred to as "mixing line"). For the $\delta^{18}O$ mixing, the higher salinity measurements will still be above the mixing line. For both cases, the shift to the left on Figure 8 may change the interpretation of the measurements against the model.

During the fall, measured NO_3^- concentrations and $\delta^{15}N$ values deviate significantly from the mixing line (Fig. 2-8). Nitrate concentration deviations range between 14 μM lower and 8 μM above the predicted mixing line, with most of the higher than expected values from the winter (Fig. 2-8). $\delta^{15}N$ values are, on average, 3.5 ‰ lower than the mixing line and winter $\delta^{15}N$ values are on average, 4 ‰ lower than predicted values (Fig. 2-8). The deviations from expectations imply that mixing

of two sources does not explain the data and that internal processing must be altering NO_3^- concentrations and the $\delta^{15}N$ of NO_3^- significantly.

The first difference to note between the previous mixing model and this one is that the $\delta^{18}O$ mixing line (solid line, Fig. 2-8) is a mirror image to the $\delta^{15}N$ mixing lines. In contrast to nitrogen isotopes, the freshwater source has a lower $\delta^{18}O$-H_2O than the oceanic source (Knapp et al. 2008; Bowen 2013). All of the measurements are on or above the mixing line, with a maximum offset of 13 ‰. For $\delta^{18}O$ values to be above the mixing line, processing of the nitrogen must be taking place, which may include uptake, denitrification and nitrification.

The decrease in $[NO_3^-]$ between the river source and station 1 (Providence River Estuary) means that NO_3^- is removed through benthic denitrification or uptake. This process is evident in both the N and O isotopic composition (Fig. 2-8). Benthic denitrification occurs within the sediments and little to no NO_3^- fluxes out of the sediments during denitrification (Granger et al. 2011). Therefore, benthic denitrification does not impart a significant isotopic change to the overlying water column. Denitrification in the water column is unlikely, even in the Providence River Estuary, during the fall and winter months when $[O_2]$ is well above the threshold for denitrification, so we will not consider it here. Any uptake of NO_3^- would increase the isotopic composition of the remaining NO_3^-. However, the measured isotopes are not elevated compared to mixing (Fig. 2-8). Therefore, other processing, such as coupled remineralization of ammonium and subsequent nitrification to NO_3^-, must control the measured $\delta^{15}N$-NO_3^-.

Nitrification may lower the $\delta^{15}N$ values of NO_3^- if NH_4^+ has a $\delta^{15}N$ value less than that of the endmembers selected or if nitrification is incomplete (Mariotti et al. 1981; Casciotti et al. 2003; Casciotti et al. 2010). No $\delta^{15}N\text{-}NH_4^+$ data for Narragansett Bay are available, however NH_4^+ concentrations in the bay proper are below detection (south of 41.7°N; data not shown), suggesting that nitrification is complete and the average $\delta^{15}N\text{-}NO_3^-$ values of NO_3^- produced through nitrification is likely to be approximately equal to the $\delta^{15}N$ value of the NH_4^+ source, recycled organic matter. In the Providence River Estuary, $[NH_4^+]$ range from 5-10μM and the production of nitrate with a low $\delta^{15}N$ value during nitrification is possible. Alternatively, partial consumption of either NH_4^+ or NO_3^-, both are in excess in the Providence River Estuary, in the surface and production of organic matter with low $\delta^{15}N$ values that is then recycled back into the NO_3^- pool may lower the $\delta^{15}N\text{-}NO_3^-$.

The raising and lowering of $\delta^{15}N\text{-}NO_3^-$ due to uptake and remineralization/nitrification is only partially cancelled because the isotope fractionation for uptake is 5-10 ‰ (Granger et al. 2004), while partial nitrification has a fractionation of 15-30 ‰ (Casciotti et al. 2010). This means the apparent cumulative effect of these processes would be to decrease the $\delta^{15}N\text{-}NO_3^-$. However, the $\delta^{18}O\text{-}NO_3^-$ would only show an increase due to uptake (Granger et al. 2004). The $\delta^{18}O\text{-}NO_3^-$ would be near the $\delta^{18}O$ mixing line if nitrification were the only process contributing to its $\delta^{18}O$ signature (Fig. 2-8). However, the measured data are above the mixing line, indicating an isotopic increase due to uptake that is not washed away during nitrification.

The combination of uptake and remineralization/nitrification continues downstream, and continues to decouple the N and O isotopic compositions (Figs. 2-7 and 2-8). This suggests that mixing with Rhode Island Sound nitrate becomes an important process affecting the N and O isotopic compositions of NO_3^-, as the mixing model would suggest, but that the internal processing has induced a lot of variability in the N and O isotope compositions throughout the system, variation that is amplified in the lower bay (Wankel et al. 2006).

Seasonal Changes to Isotopic Composition

This section analyzes the temporal changes to isotopic composition in a given year. During the spring and summer, primary production increases and nitrate uptake reaches its peak in Narragansett Bay (Fig. 2-6) (Pilson 1985b; Nixon et al. 2009). Several studies have suggested that new production in Narragansett Bay (south of 41.7°N) is supported by nitrogen carried downstream from the Providence River Estuary (north of 41.7°N) (Doering et al. 1990; Fulweiler and Nixon 2009; Nixon et al. 1995; Nixon et al. 2008; Oczkowski et al. 2008). This is difficult to test because, while there is surface NO_3^- within the Providence River Estuary, surface DIN concentrations are near zero in the Bay (Pilson 1985b; Nixon et al. 2009) (Figs. 2-3 and 2-5).

The N and O isotopic composition increases significantly between the fall/winter and spring/summer seasons during both 2007-2009 and 2011-2012 sampling intervals (Figs. 2-3 and 2-5; t-test, $p < 0.01$). Anthropogenic source values do not show any seasonal changes during each year. The increase in $\delta^{15}N$ and $\delta^{18}O$ values are associated with an increase in chlorophyll *a* concentration, implying greater

primary production in the warmer months than in the cooler months (Fig.2- 6). Therefore, we attribute the temporal increase in $\delta^{15}N$ and $\delta^{18}O$ values to fractionation of nitrate during uptake and assimilation in the spring/summer growing period. Uptake of nitrate fractionates O and N equally, such that it results in a coordinated increase in both $\delta^{15}N$ and $\delta^{18}O$, an effect that is clearly evident in the summer Providence River Estuary data (Fig. 2-7). Water-column denitrification also displays the same effect but it is not likely occurring in the oxygenated surface waters of Narragansett Bay or the Providence River Estuary.

Conclusion

The N* calculation and stable isotope measurements create a powerful tool for analyzing nitrogen status and processing within Narragansett Bay. While N* suggests that anthropogenic N does not reach the lower bay, we know from previous studies and oxygen isotope measurements of nitrate that the anthropogenic nitrate reaches the lower bay, but is transformed by nitrification and mixing with Rhode Island Sound water along the way. Nitrogen and oxygen isotope measurements combined with a salinity-weighted mixing model show that nitrification is the predominant surface nitrate isotope altering process in Narragansett Bay, and is responsible for a significant proportion of nitrate to the system.

Nutrient reductions started in 2001 and continue today (Fig. 2-2; Krumholz 2012). Anthropogenic nutrient reductions have caused a 20 % reduction in DIN flux from anthropogenic sources with a 17 % overall reduction in total nitrogen, annually (Krumholz 2012). However, no decreases in average chlorophyll concentration or

primary production rates have been noted in Narragansett Bay proper (south of 41.7 °N; Krumholz 2012; Smith 2011). This suggests the reductions that have occurred thus far are not affecting where the Bay is N-rich versus N-poor (Fig. 2-4). The observed nitrate isotope increases are consistent with these observations in that they are limited to the Providence River Estuary, where nutrients are replete year-round (Fig. 2-4). The very consistent location of the shift from N rich to N poor waters despite changes in anthropogenic nutrient inputs indicates that the distribution of nutrients in the Providence River Estuary (north of 41.7°N) and Narragansett Bay proper (south of 41.7°N) is controlled by anthropogenic inputs in the Providence River Estuary and recycling and mixing with Rhode Island Sound water in Narragansett Bay proper.

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Tables

Table 2-1. Comparison of 2007-2009 and 2011-2012 Providence River Estuary $\delta^{15}N$ and $\delta^{18}O$ data. N/A means that data not available. The difference between years is statistically significant ($p < 0.001$).

Year range	$\delta^{15}N \pm$ std. dev. (‰)	$\delta^{18}O \pm$ std. dev. (‰)	n
2007-2009	8.0 ± 1.3	N/A	36
2011-2012	9.7 ± 2.0	3.6 ± 2.0	24
Difference	1.7	N/A	

Table 2-2. $[NO_3^-]$ and N isotopic compositions from River and Rhode Island Sound (RIS) sources. River values are flux-weighted and from 2012-2013 sampling (Schmidt et al. *in prep.*). RIS data comes 2005 sampling (DiMilla 2006).

Source	$[NO_3^-]$ (μM)	$\delta^{15}N \pm$ std. dev. (‰)
River, fall	85	14.9
River, winter	76	14.9
RIS	4.6	5.9

Figures

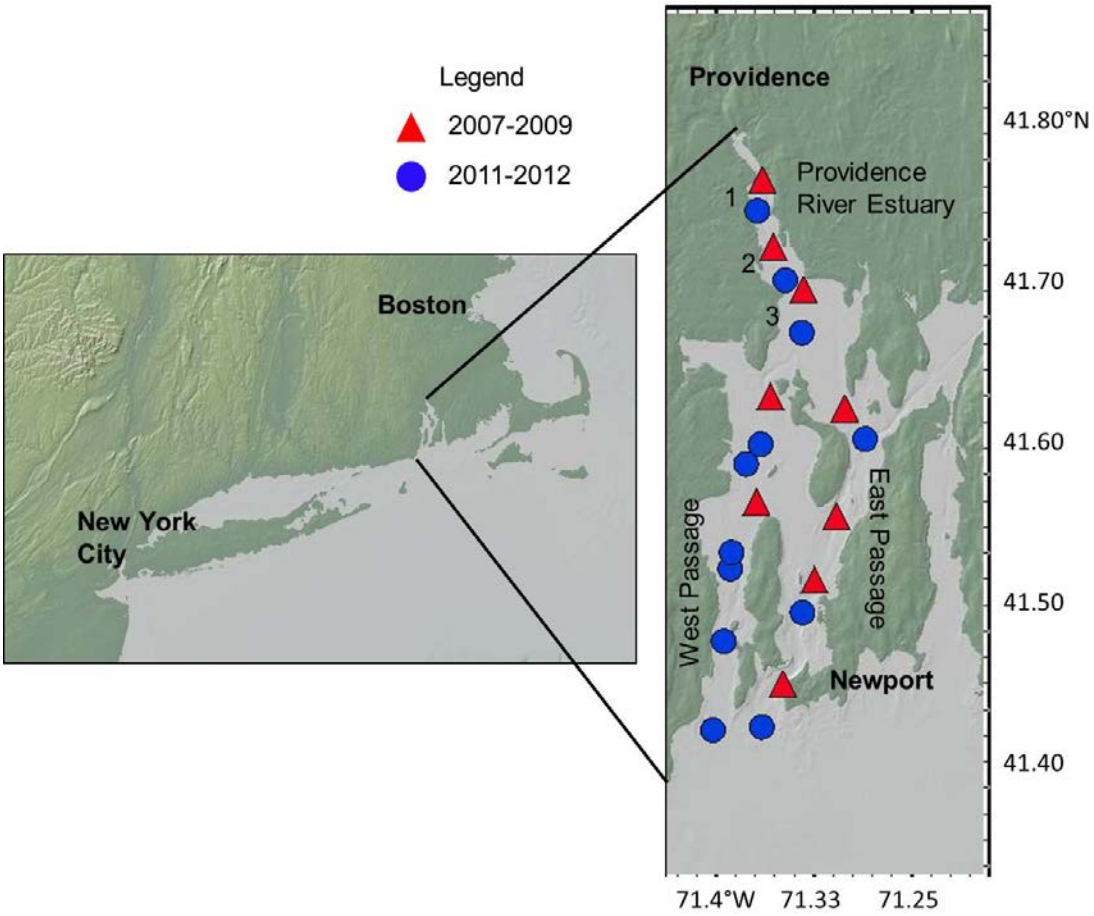

Figure 2-1. Narragansett Bay sample sites. Triangles are sites from 2007-2009 and circles are sites from 2011-2012. Numbers indicate sample stations referred to in the text for both the 2007-2009 and 2011-2012 samples.

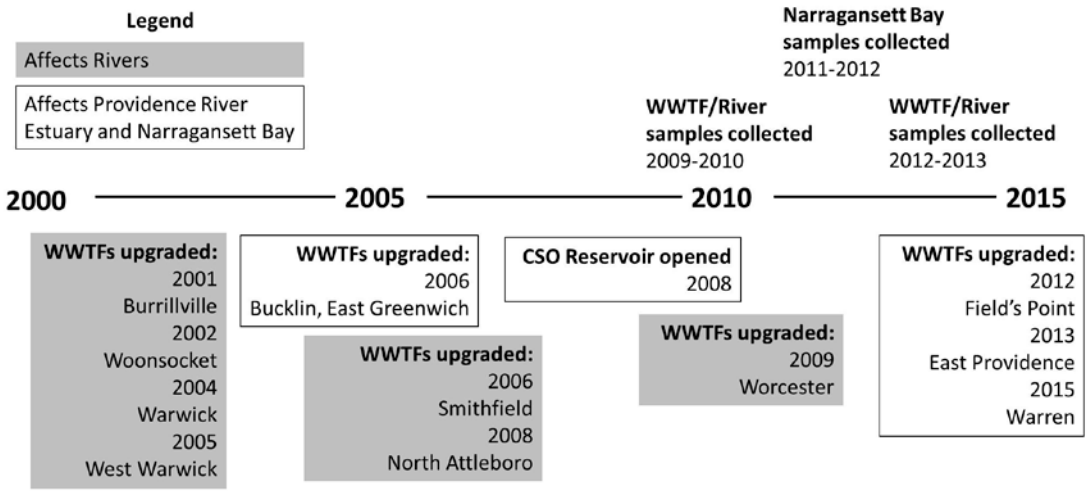

Figure 2-2. Timeline of upgrades to tertiary treatment by local wastewater treatment facilities (WWTFs). Dates of sample collections for this (Narragansett Bay) and a previous study (WWTF/River; Schmidt et al. *in prep.*) are included above the time line (near 2010 and 2015). All WWTFs in shaded boxes discharge to rivers, while those in outlined boxes discharge to Narragansett Bay. Combined sewer overflow (CSO) reservoir discharges to Field's Point WWTF which discharges to Narragansett Bay, therefore it is included as affecting the Providence River Estuary and Narragansett Bay.

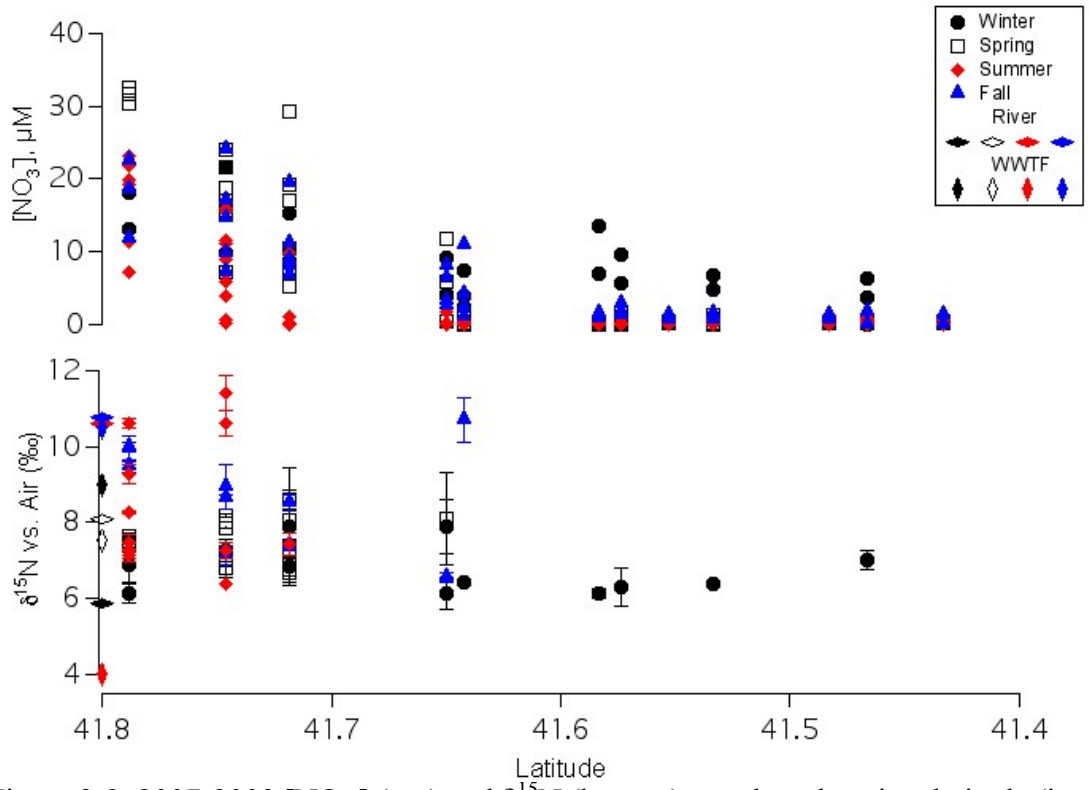

Figure 2-3. 2007-2009 [NO_3^-] (top) and $\delta^{15}N$ (bottom) are plotted against latitude (in decimal degrees). Samples are from all seasons: winter (circles), spring (squares), summer (diamonds), and fall (triangles). Plotted along the y-axis is flux-weighted $\delta^{15}N$ for rivers and WWTFs. Flux-weighted [NO_3^-] for rivers and WWTFs are not included on the top panel because they are off scale (55-80 µM and 154 – 264 µM, respectively) (Schmidt et al. *in prep.*).

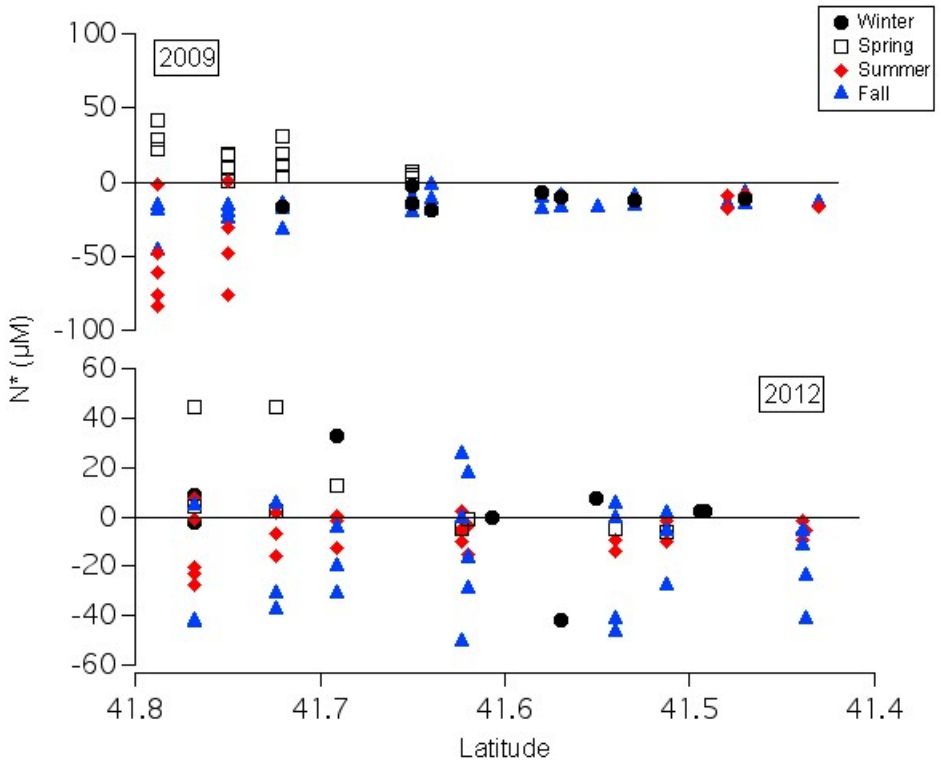

Figure 2-4. N* versus latitude for 2007-2009 (top panel), and 2011-2012 (bottom panel). Winter values are filled circles, spring values, open squares, summer, filled diamonds, and fall, filled triangles. The solid black line marks the dividing line between N-rich (above zero) and N-deficient (below zero).

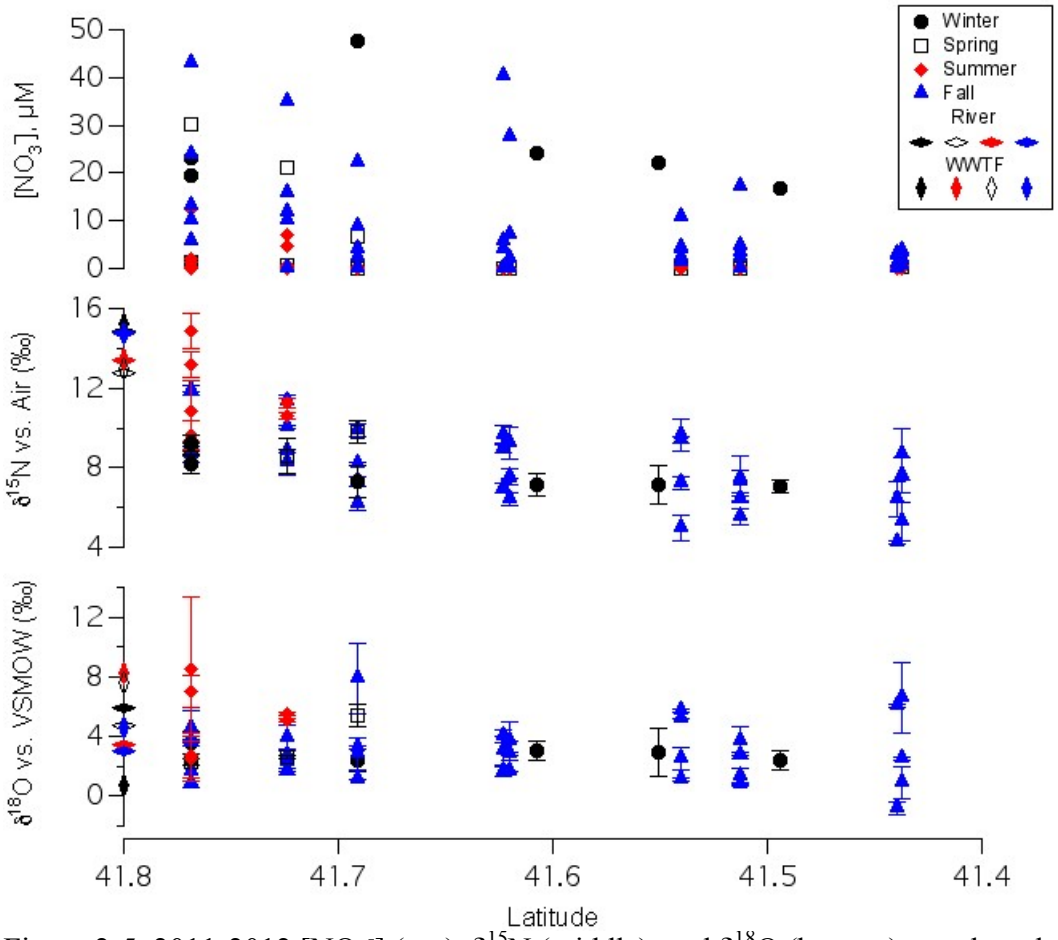

Figure 2-5. 2011-2012 [NO_3^-] (top), $\delta^{15}N$ (middle), and $\delta^{18}O$ (bottom) are plotted against latitude (in decimal degrees). Samples are from all seasons: winter (black dots), spring (open squares), summer (red diamonds), and fall (blue triangles). Plotted along the y-axis is flux-weighted $\delta^{15}N$, and $\delta^{18}O$ for rivers and WWTFs. Flux-weighted [NO_3^-] for rivers and WWTFs are not included on the top panel because they are off scale (60-85 µM and 100 – 181 µM, respectively) (Schmidt et al. *in prep.*).

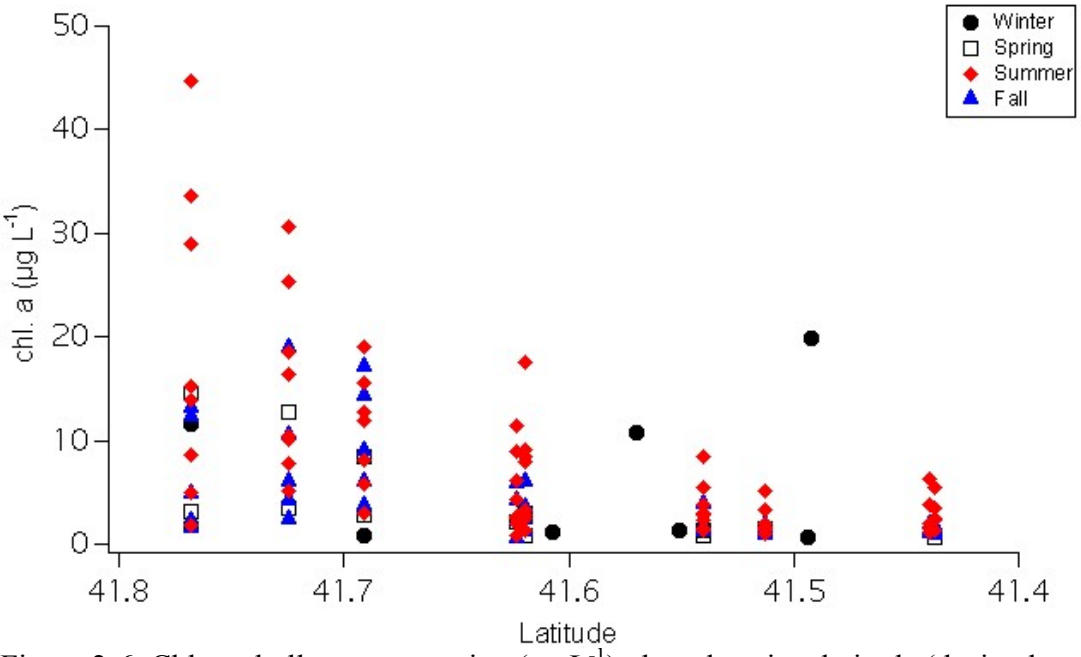

Figure 2-6. Chlorophyll a concentration (µg L^{-1}) plotted against latitude (decimal degrees) for all seasons during 2011-2012. Winter is circles, spring is squares, summer is diamonds, and fall is triangles.

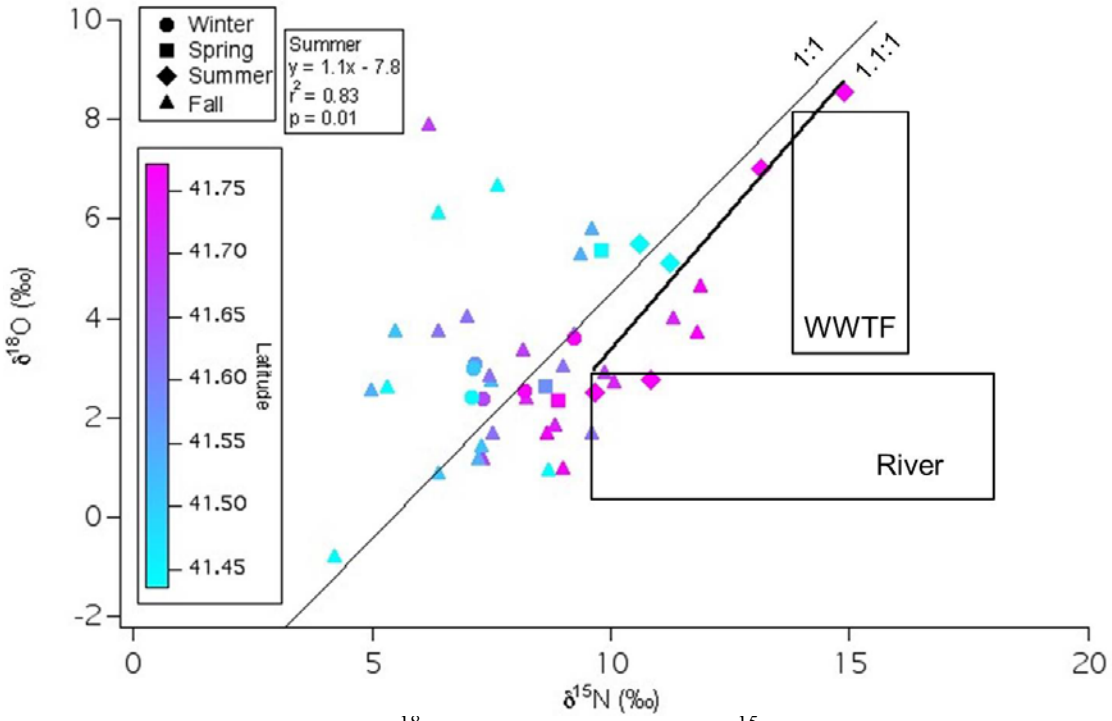

Figure 2-7. Narragansett Bay $\delta^{18}O\text{-}NO_3^-$ plotted against $\delta^{15}N\text{-}NO_3^-$ for all seasons. Winter is circles, spring squares, summer diamonds, and fall triangles. $\delta^{15}N$ vs $\delta^{18}O$ plotted as a function of latitude. Darker colors are higher latitudes (Providence River Estuary and upper bay), lighter color lower latitudes (mid to lower bay). The thin black line is a 1:1 line, while the thick black line is the linear regression for the summer values. The boxes represent flux-weighted $\delta^{15}N$ and $\delta^{18}O$ plus/minus standard deviation of WWTFs and river sources.

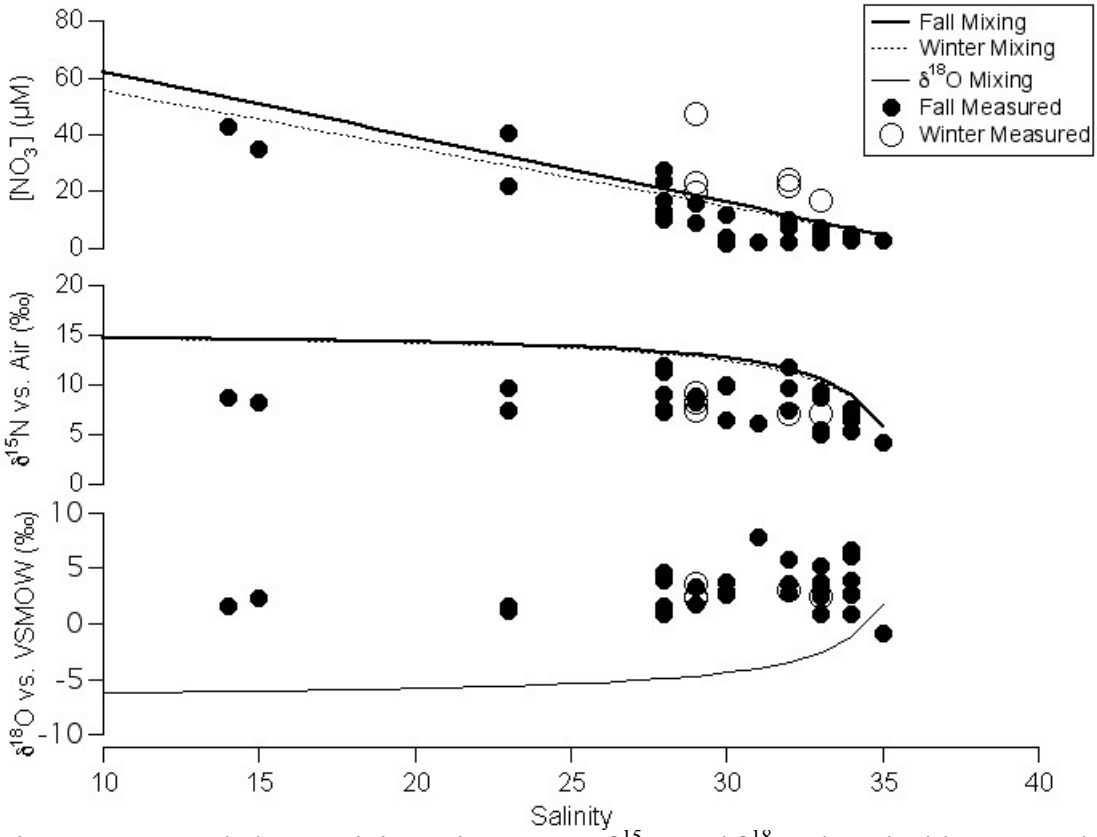

Figure 2-8. Mass balance mixing using $[NO_3^-]$, $\delta^{15}N$, and $\delta^{18}O$ plotted with measured data against salinity. Nitrate concentration and $\delta^{15}N$ mixing are from the flux-weighted river and oceanic endmembers. $\delta^{18}O$ sources are from the $\delta^{18}O$-H_2O from river and oceanic endmembers and are adjusted by 3 ‰ due to apparent fractionation during nitrification. Fall mixing is the thick solid line, winter mixing is the dotted line, and $\delta^{18}O$ mixing is the thin solid line. Fall measured data are the closed circles while the winter measured data are the open circles. Some winter measured data are hidden behind fall data.

CHAPTER 3

PREFACE

Nitrate sources supporting Narragansett Bay phytoplankton and macroalgae using stable N isotopes

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Abstract

Narragansett Bay has experienced anthropogenic nitrogen loading for the last 200 years, with evidence for eutrophication in some regions of the estuary-bay system. The large nutrient load is concentrated in the northern urban estuary, but it has been speculated that primary production throughout the system may result in large part from these loads. We measured the isotopic composition ($\delta^{15}N$) of surface and subsurface nitrate, chlorophyll *a*, and macroalgae from summer 2011 and 2012 to evaluate N sources to primary producers. The N isotopic compositions of surface and subsurface nitrate, and chlorophyll *a* ranged from 5-35 ‰, increased through the lower bay by 30 ‰, and then decreased by 30 ‰ at the mouth of the bay. Macroalgal $\delta^{15}N$ ranged from 7-15 ‰ and tended to decrease toward the ocean. The differences between the macroalgae and chlorophyll *a* imply multiple sources of nitrogen supporting primary production and/or a significant difference in how the nutrient isotope signal is incorporated by macroalgae and phytoplanton. Macroalgae are assimilating N from a fixed position, and may be utlizing small, but consistent, benthic fluxes of dissolved inorganic nitrogen (DIN). Phytoplankton, like the nutrients they use, are, on the other hand, transported vertically and horizontally by tides/currents and mixing events. Phytoplankton appear to be using nitrate from the local subsurface waters where they were collected. Macroalgae metabolism integrates nutrients over approximately one week, while phytoplankton which integrate nutrients over 2-3 days. These results suggest that primary production is supported by multiple sources of N, from the anthropogenic inputs in the north, Rhode Island Sound in the south, and benthic-pelagic coupling in the bay proper.

Introduction

Human development on North American coasts led to significant increases in nitrogen (N) input to coastal systems. Estuaries reduce the impact of high riverine nutrient loads through photosynthetic consumption of nutrients, mixing, and denitrification (Costanza et al. 1997; Herbert 1999). The Providence River Estuary and Narragansett Bay received high inputs of anthropogenic N since the late 1800s (Nixon et al. 2008). Nitrogen budgets suggest that 60 % of nitrogen discharging into this system is anthropogenic in origin (Nixon 1995; Nixon et al. 2008).

Approximately 80 % of anthropogenic inputs to Narragansett Bay are from rivers and WWTFs in the northern reaches (Nixon et al. 1995; Nixon et al. 2008; Krumholz 2012). This creates a nutrient gradient in the bay, where more nutrients and chlorophyll *a* are found in the north and decrease down bay (Oviatt et al. 2002; Schmidt et al. *in prep.(a)*). Nitrogen reductions at local WWTFs aim to reduce instances of hypoxia in the Providence River Estuary and upper Bay (Fig. 3-1). However, reducing anthropogenic N inputs may have downstream impacts because of nitrogen's role as the limiting nutrient, potentially reducing primary and secondary production in the lower bay (Oviatt et al. 2002; Nixon et al. 2009).

Combined stable N isotopes of nitrate and nutrient concentration measurements represent a potential way to distinguish local nutrient sources to primary producers in estuarine settings (Wassenaar 1995; Wankel et al. 2009 Deutsch et al. 2005; and Saccon et al. 2013). This approach assumes that the isotopic composition of N sources would be reflected in organisms relying on those nutrients. In attempting to distinguish the ultimate sources to organisms, i.e. anthropogenic

versus open ocean, it has been posited that anthropogenic sources would bear higher nitrogen isotope values, reflecting waste water inputs (Heaton 1986; McKinney et al. 2001; Cole et al. 2004; York et al. 2007; Oczkowski et al. 2008; Rainmonet et al. 2013). The approach was employed in Narragansett Bay and the N isotopic composition of clams (used as a proxy for phytoplankton, their primary food source) and macroalgae differed with respect to distance from anthropogenic sources (Oczkowski et al. 2008). The clams showed no isotopic change while the macroalgae isotopic composition decreased with distance from high $^{15}N/^{14}N$ isotope value endmember source. The clam results suggested that the phytoplankton on which they feed use a single source of N and it was speculated that this source is anthropogenic in origin from new production in the Providence River Estuary and Upper Narragansett Bay, which is transported downbay through subtidal circulation. The clam results are consistent with conclusions drawn by York et al. (2007) in a study conducted in the Child's River-Waquoit Bay, MA. York et al. (2007) measured the N isotopic composition directly in chlorophyll *a* (chl *a*), ammonium (NH_4^+), and nitrate (NO_3^-). They found a steep decline in the NH_4^+ and NO_3^- isotopes coupled with a steady chl *a* isotopic composition along a salinity gradient, suggesting the phytoplankton took up NH_4^+ in excess in the headwaters, where NH_4^+ is replete, and used it for photosynthesis down the estuary.

The problem with this line of reasoning is that the residence time of water in Narragansett Bay is about 28 days (Pilson 1985) and the lifetime of a typical phytoplankton is 2-3 days (Riper et al. 1979). It is unlikely that phytoplankton from the upper bay are being deposited very far down the estuary, which is 40 km long, in

2-3 days. Moreover, documentation of the nitrogen isotopic composition of nitrate does not support the interpretation of the macroalgae results. Variations in the nitrogen isotopic composition of nitrate from the Providence River Estuary to Narragansett Bay do not resemble a conservative mixing trend (Schmidt et al. *in prep.(a)*).

In a first step toward reconciling the above results, we sought to evaluate local sources of dissolved nitrogen to phytoplankton and macroalgae by making coordinated measurements of nitrate, and chlorophyll *a*, and macroalgae N isotope values across the system. We analyzed stable N isotopes of nitrate, chlorophyll *a,* and macroalgae alongside nitrate and chlorophyll *a* concentrations in order to examine whether multiple sources of nitrogen are supporting primary production in the Bay and to identify those sources if possible.

Methods

Narragansett Bay and Watershed

Narragansett Bay, including Mount Hope and Greenwich Bays and the Providence River Estuary, is 328 km^2, has a mean depth of 8.3 m, and a residence time of about 28 days (Fig. 3-1) (Pilson 1985). Freshwater input is relatively low (around 100 m^3s^{-1}) and most of the input occurs in the urbanized northern reaches, primarily through four rivers and ten wastewater treatment facilities discharging directly to the Bay. Other freshwater sources, such as storm water and groundwater, are relatively small portions of the Narragansett Bay water budget, but are important to the budgets of the smaller bays and coves (Nixon et al. 1995; DiMilla 2006; Nowicki and Gold

2008). Water from the Providence River Estuary (41.8°N to 41.7°N) enters Narragansett Bay proper (south of 41.7°N) and is carried to the south primarily through the West Passage while Rhode Island Sound water enters Narragansett Bay primarily through the East Passage and mixes with Providence River Estuary water in the upper bay (Fig. 3-1, Kincaid et al. 2008).

Sample Collection

Water samples were collected from 9 stations along a north-south transect in the Providence River Estuary and Narragansett Bay to Rhode Island Sound during the summers of 2011 and 2012 (Table 3-1; Fig. 3-1). Samples were pumped through a hose, where the hose was flushed for 5 minutes with site water prior to collection. Surface samples were collected from approximately one half meter below the surface and sub-surface water samples were collected from one meter off the bottom of Narragansett Bay (depths ranging from 3-30 m; Table 3-1). High density polyethylene bottles were tripled rinsed with site water prior to filling, and then stored on ice until returning to the lab. The water passed through a 178 and 100 μm filters to remove detritus and grazers. The 100 μm filter was chosen as an attempt to exclude most zooplankton while retaining as much phytoplankton as possible (Rau et al. 1990; Rolff 2000; Harmelin-Vivien 2008). Then, in the lab, the water was passed through pre-combusted filters (GF/F, pore size 0.7 μm). Filters were collected for analysis of chlorophyll *a* concentration and isotopic composition. The remaining filtrate was collected and reserved for nutrient and isotopic analysis.

Macroalgae samples were collected from 24 sites in July 2012 from rocks just below the water surface at low tide by kayak. All conspicuous species were sampled,

and at least 3 individuals per species were collected (Fig. 3-1). Samples were rinsed with DI water, and epiphytic algae and organisms were removed. Macroalgae were visually sorted by species to the best of our abilities, and multiple individuals of the same species were dried together at 65°C for at least 24 hours and then ground to a fine powder using a Wiley Mill and mortar and pestle. Subsamples were weighed in tin capsules for isotopic analysis. Individuals were frozen for identification. When multiple individuals were identified in a single sample, we removed the sample from statistical analysis so that the isotopic compositions reported for each sample are from a single species.

Concentration Analysis

Nutrient samples were analyzed on a Lachat QuickChem 2000 flow injection autoanalyzer using EPA method 353.4 (Grasshoff 1976; USEPA 1997) for nitrates and nitrite (NO_{3+2}, and NO_2^-, respectively) concentrations which has a minimum detection limit of 0.05 μM for NO_3^-, and a precision of 0.02 μM for NO_3^-.

Chlorophyll *a* concentrations were determined by passing 100 mL of site water through glass fiber filters (pore size 0.7 μm) in triplicate. The filters were extracted in 10 mL of 90 % acetone (by volume) four 24 hours. Approximately 8 mL was transferred to a cuvette, wiped clean, and the chlorophyll *a* concentration read on a Turner A-10 fluorometer with a precision of 0.1 μg/L. Rhode Island Experimental Program to Stimulate Competitive Research (EPSCoR) supplied the instrument (http://web.uri.edu/rinsfepscor/).

Isotopic Analysis

All stable isotopes ratios are reported as the ratio of $^{15}N/^{14}N$ between the sample and a standard, and are expressed as $\delta^{15}N$ where $\delta = [(R_{sample}/R_{standard}) - 1] \times 1000$ and $R = {}^{15}N/{}^{14}N$. Samples and working standards were analyzed together to normalize delta values to ultimate standards (N_2 in air, with an isotopic composition of 0 ‰)

Nitrate N isotope compositions in nitrate and chlorophyll *a* (preparation method below) were determined using the denitrifier method (Sigman et al. 2001, Casciotti et al. 2002) by gas chromatography isotope ratio mass spectrometry (Thermo Delta V). Precision of the method is < 0.3 ‰ for $\delta^{15}N$. Macroalgal samples were analyzed on a Isoprime 100 mass spectrometer interfaced with a Micro Vario Elemental Analyzer. Precision was <0.3 ‰.

***Nitrogen Bound in Chlorophyll* a**

The amount of water collected from each station varied depending upon biomass present in order to provide enough chlorophyll for replicate measurements (approximately 1-2 L in the Providence River Estuary, 3-5 L in the upper bay, and 10-30 L in the lower bay). Chlorophyll $\delta^{15}N$ was determined following Higgins et al. (2009) which is a modification of the method described in Sachs et al. (1999). In short, chlorophyll pigments were extracted at least 24 hours using 2:1 dichloromethane:methanol (DCM:MeOH). The extracts were filtered through a gravity-fed silica (Si) column, dried under nitrogen and brought up in a small amount of DCM for further analysis. High-pressure liquid chromatography (HPLC) with a normal-phase Si chromatography column was used to separate the pigments in each

sample at Rhode Island's Institutional Development Award (IDeA) Network of Biomedical Research Excellence (INBRE) facility (http://www.uri.edu/inbre/index.shtml). Samples were eluted on a gradient from 100 % hexane to 75:25 % MeOH:ethyl acetate and fractions containing all chlorophyll compounds were collected. The fractions were dried and stored at -80°C, and later, the nitrogen in the dried pigment fractions was oxidized to nitrate (NO_3^-) using re-crystallized persulfate solution (0.11 M). NO_3^- concentrations were then analyzed by chemiluminescence using a Teledyne NOx analyzer (Braman and Hendrix 1989). Then, isotopic analysis of the N in NO_3^- was completed using the denitrifier method.

The total background N (blank) comes from the solvents used, HPLC, and persulfate oxidation. A full explanation for the choice of solvents, HPLC columns, and oxidation techniques are available in Higgins et al. (2009). Briefly, all solvents, HPLC columns, and persulfate added < 3 nmol N to the samples or approximately 2 % of our target N collection. The final N yields after purification and final oxidation were measured. Sixteen samples had yields higher than 80 %. Samples with lower yields are not discussed in the manuscript as any partial collection or conversion to nitrate may impart an isotopic fractionation.

Results

Nitrate concentrations ranged from 0-13 μM in surface waters, and rapidly decreased from the Providence River Estuary (PRE) (north of 41.7°N) to the Bay proper (south of 41.7°N), where concentrations fell below detection limits (Fig. 3-2). In the subsurface water, nitrate concentrations ranged from 1-6 μM and they remain

relatively static with a high value at the mouth of the bay (Fig. 3-2). At station 1 in August 2011 and 2012, [NO_3^-] was greater in the surface waters than in the subsurface (Figs. 3-1 and 3-2). Nitrate N isotopic compositions ranged from 10-15 ‰ in surface waters with the highest values (>12‰) occurring at stations 1 and 2 (Figs. 3-1 and 3-2). South of 41.7°N, surface nitrate concentrations were too low for isotope measurements (Fig. 3-2). In subsurface waters, isotopic compositions ranged from 5-35 ‰, with a distinct maximum mid-bay (41.55°N) (Fig. 3-2). Surface and subsurface nitrate isotopes did not vary systematically with their respective nitrate concentrations (Fig. 3-3).

Chlorophyll *a* concentrations ranged from 1-17 μg L^{-1}, with a distinct peak around 41.75ºN in the PRE (Fig. 3-4). Nitrogen isotopic composition of N bound within chlorophyll *a* (δ^{15}N-chl) also ranged from 5-35 ‰, and like subsurface nitrate, showed a peak mid-bay (Fig. 3-4). Chl *a* isotopes increased as surface nitrate concentrations decreased (Fig. 3-3).

Finally, macroalgae δ^{15}N values ranged from 7-15 ‰ and declined downstream in the bay (Fig. 3-5). The range of isotope values decreased farther south, with the narrowest range at the mouth of the bay. Within the Providence River Estuary (north of 41.7ºN), the range of δ^{15}N values was quite wide. Brown algae (Phaeophyta) had significantly lower isotope values than red (Rhodophyta) or green algae (Chlorophyta) (Table 3-2; ANOVA, $F(2,71) = 6.81$, $p < 0.005$). Additionally, the West Passage δ^{15}N values of macroalgae were significantly enriched compared to the East Passage (ANOVA, $F(1,82) = 8.38$, $p = 0.005$).

Discussion

Surface and Bottom Water NO_3^- and Chlorophyll a*-bound N*

During the summer, the surface water NO_3^- falls below detection limits just south of 41.7°N, while it remains at measureable concentrations in the subsurface, consistent with photosynthetic uptake of nutrients and replenishment below from remineralization and/or advection. In the Providence River Estuary (north of 41.7°N), the surface and bottom δ^{15}N-NO_3^- and δ^{15}N-chl values ranged from 5 - 35 ‰ (Fig. 3-6). The large range of δ^{15}N values may reflect uptake of multiple N sources (ammonium and nitrate) or partial denitrification of nitrate

Phytoplankton tend to take up NH_4^+ preferentially over NO_3^- (Culver-Rymsza 1988; York et al. 2007), and therefore the δ^{15}N-chl could be representative of the isotopic composition of NH_4^+. Within the Providence River Estuary, [NH_4^+] ranged from 0-16 μM, and was less than 2 μM south of 41.7°N. Therefore, if NH_4^+ has any impact it would be in the Providence River Estuary. The availability of NH_4^+ here may account for the weak correlation between subsurface δ^{15}N-NO_3^- and δ^{15}N-chl (slope = 0.63, r^2 = 0.66; p = 0.001; Fig. 3-7). When the subsurface NO_3^- and chlorophyll *a* samples north of 41.7°N are removed, the regression for the lower bay improves with a slope of 0.85 (r^2 = 0.85; p = 0.007) (not shown in Fig. 3-7). Moreover, surface δ^{15}N-NO_3^- (only present in Providence River Estuary) and δ^{15}N-chl do not show any systematic relationship (Fig. 3-7). It appears that in the N replete regions of the bay, like the Providence River Estuary (north of 41.7°N), phytoplankton derive their N from NH_4^+, first, and then surface and bottom NO_3^-.

Additional variability in the subsurface $\delta^{15}N\text{-}NO_3^-$ could come from low oxygen concentrations at depth and the resulting denitrification. Denitrification is the bacterial reduction of nitrate in the absence of oxygen to serve as a terminal electron acceptor. It is thought to occur under $[O_2] < 5\text{-}10\mu M$. Low oxygen events occur frequently in the summertime subsurface of the Providence River Estuary (Prell and Deacutis 2006). This process would lower the subsurface $[NO_3^-]$ and raise the $\delta^{15}N\text{-}NO_3^-$ value, as denitrification is a fractionating process with a large isotope effect that causes an increase in $\delta^{15}N$ values with the progressive consumption of the nitrate pool (Granger et al. 2008). This process is not likely to be important outside of the Providence River Estuary because oxygen concentrations do not fall below the threshold for denitrification in the open waters of Narragansett Bay (Melrose et al. 2007).

The coordinated changes in the $\delta^{15}N$-chl and subsurface $\delta^{15}N\text{-}NO_3^-$ values suggest that these two pools are related (Figs. 3-6 and 3-7). Given the depletion of NH_4^+ and surface nitrate in Narragansett Bay, it stands to reason that the dominant source of N to the phytoplankton is the subsurface pool and that the $\delta^{15}N$-chl would track the $\delta^{15}N\text{-}NO_3^-$ (Figs. 3-6 and 3-7). The extreme enrichments, as high as 30-35‰ in the mid-bay, on the other hand, are harder to explain. Since denitrification in this region of the bay is restricted to the sediment and sedimentary denitrification driven isotopic enrichment is rarely felt by the water column because exchange of sedimentary nitrate with the overlying water column is near zero, denitrification is not going to explain the high values (Granger et al. 2011). That leaves nitrate assimilation as the primary cause of the enrichment in both the substrate (surface NO_3^-) and

product (chlorophyll *a*) pools (Granger et al. 2004). Freshwater delivery in 2012 was lower than previous years supporting the idea that subsurface nitrate was an accessible source of nutrients to the phytoplankton.

There should be a predictable relationship in the $\delta^{15}N$ values of the chlorophyll *a* and nitrate pools. We used simple steady-state and closed-system estimates of the relationships between nitrate and the phytoplankton N to describe the observed patterns (Mariotti et al. 1981). A steady-state system is one where nutrients are constantly replenished while in a closed-system there is no replenishment of nutrients. Estuaries fall in between these models, where the semi-stratified surface may serve to restrict replenishment during bloom events, but the system is nowhere near closed either. A mixing event would bring nutrients towards the surface, where they would be used rapidly in the summer growing season. The equations governing these systems are as follows.

In a steady-state model, the reactant (or the nutrients, i.e. nitrate) behaves like equation 1, while in a closed system, the reactant behaves like equation 2:

$$\delta^{15}N_{react} = \delta^{15}N_{initial} + \varepsilon\,(1-f) \qquad \text{eqn. 1}$$

$$\delta^{15}N_{react} = \delta^{15}N_{initial} - \varepsilon \ln(f) \qquad \text{eqn. 2}$$

$\delta^{15}N_{initial}$ is the isotopic composition of the single nitrate source, while f is the fraction of the $[NO_3^-]$ remaining, and $\delta^{15}N_{react}$ corresponds to the isotopic composition of the source as $[NO_3^-]$ decreases with consumption. The fractionation factor associated with assimilation, ε, is reported to average around 5 ‰ (Granger et al. 2004).

The products ($\delta^{15}N_{prod}$) are governed by a different set of equations (eqns. 3 and 4). The products are phytoplankton and macroalgae where:

$$\delta^{15}N_{prod} = (\delta^{15}N_{initial} - \varepsilon f) - 5\ ‰ \quad \text{eqn. 3}$$

$$\delta^{15}N_{prod} = (\delta^{15}N_{initial} - \varepsilon \ln(f)) - 5\ ‰ \quad \text{eqn. 4}$$

The fractionation factor (ε, 5 ‰) remains the same as before. We also subtracted an additional 5 ‰ from the equations. This is to account for the isotopic composition differences between phytoplankton whole cell and N-bound within chlorophyll *a* (Sachs et al. 1999; Pantoja et al. 2002; Higgins et al. 2009).

For our calculations, we assumed a single source of NO_3^-. This is justified by our focus on samples from south of 41.7°N, far enough away from anthropogenic sources for their isotopic compositions to a have minimal impact on the nitrate pool in the bay (Schmidt et al. *in prep.(a and b)*). We assigned the source of nitrate as having a concentration of 6 μM, and a $\delta^{15}N$ value of 8 ‰. This is essentially what appears at the mouth of Narragansett Bay and equal to the composition of surbsurface water collected at station 8 (Fig. 3-1).

The steady state system for both the products and reactants produces a linear increase in the isotopic composition as the fraction of nitrate remaining decreases. In the closed system, both the products and reactants produce an exponential increase in the isotopic composition as the fraction of remaining nitrate decreases. In our models, the reactants will be isotopically enriched comparative to the products (Fig. 3-9).

We expect our data to fall within the area bounded by the product lines – that is, we expect our products to look like a hybrid between the steady-state and closed system (Fig. 3-9). For the most part, the $\delta^{15}N$-chl data do look like the hybrid model with some clear exceptions (Fig. 3-9). Two of the values ($\delta^{15}N$ = 33 ‰) corresponds to the increase noted in the subsurface $\delta^{15}N$-NO_3^- and $\delta^{15}N$-chl, and there are three

points with $\delta^{15}N$ values significantly higher than predicted by estimates. These deviations may reflect additional sources of nitrate to the system, either associated with benthic fluxes or unaccounted for anthropogenic inputs. The conformity of much of the $\delta^{15}N$-chl data to the closed system approximation implies that primary producers are consuming nitrate quickly and nearly completely when pulses of nitrate reach the surface (Fig. 3-9).

Subsurface nitrate does not show the near-complete drawdown or the pattern of isotopic enrichments predicted. Instead, the nitrate concentrations tend to be significantly higher, in the 2 μM range, than the near zero values that are observed in the surface and expected for such high enrichments of the product pool (Figs. 3-2 and 3-3). The subsurface $\delta^{15}N$-NO_3^- values tend to be lower than predicted, by as much as 9 ‰ for the mid-bay maximum. This maximum estimate comes from the assumption that the $\delta^{15}N$-chl value reflects the product value – 5‰. Assuming ε = 5 ‰, the mid-bay $\delta^{15}N$-chl value of 33 ‰ would require a nitrate source with a $\delta^{15}N$- NO_3^- of 43 ‰. The measured value is 35 ‰. These observations suggest mixing of the partially consumed nitrate pool (it cannot be completely consumed or else the isotopic signature would be removed as well) with a replenished subsurface nitrate pool, likely due at least in part to tidal flow from Rhode Island Sound. An additional source of nitrate from rapid recycling and nitrification of isotopically enriched organic N back into the nitrate pool would also help work to maintain the high $\delta^{15}N$ values in subsurface nitrate.

Macroalgae

This portion of our study parallels the 2006 study by Oczkowski et al. (2008), allowing for a direct comparison across years. Both studies noted a 3 ‰ decrease in $\delta^{15}N$ from the head of Narragansett Bay to the mouth, though the steepness of the decline in $\delta^{15}N$ is less than the previous study due to more variation in the isotope values (Oczkowski et al. 2008; Fig. 3-5). The 2012 mean $\delta^{15}N$ values are significantly higher, by 1 ‰, than in 2006 (t-test, $p < 0.001$). The increase between 2006 and the current study is potentially due to the increase in $\delta^{15}N\text{-}NO_3^-$ from upgrades to tertiary treatment by local wastewater treatment facilities. An associated increase in $\delta^{15}N\text{-}NO_3^-$ occurred in the Providence River Estuary post upgrades supporting this interpretation (Schmidt et al. *in prep.(a)*). However, south of 41.7°N, no evidence for a change in the nutrient isotopes is available (Schmidt et al. *in prep.(a)*). If the change was only occurring upstream, then one would predict a steepening of the downstream gradient, rather than a decrease. The differences between the East and West Passage noted in our study are very similar to those in the 2006 study, and have been attributed to the circulation patterns in the Bay (Oczkowski et al. 2008). Water from Rhode Island Sound enters Narragansett Bay through the East Passage, and mixes with anthropogenic water from the Providence River Estuary and flows out the West Passage (Kincaid et al. 2008). However, no evidence for a change in $\delta^{15}N\text{-}NO_3^-$ between passages is available. This suggests that macroalgal $\delta^{15}N$ may not be a straightforward reflection of the nutrient field.

In 2012, Chlorophyta and Rhodophyta were significantly enriched compared to Phaeophyta (Table 3-2). The causes for the differences between phyla may be related

to metabolism. Rainmonet et al. (2013) noted that annual species (like *Ulva* spp., a member of Chlorophyta) may have experienced faster uptake and tissue turnover, while perennial species (like *Fucus* spp., a Phaeophyte) may experience slower metabolic responses. The difference in rate of DIN uptake and turnover will be evident in the N isotope composition, and impact the fractionation between the source DIN and δ^{15}N-macroalgae (Rainmonet et al. 2013). Annual macroalgae passively take up nutrients, especially in nutrient-replete regions, and have small fractionation factors, while perennial actively take up nutrients, and integrate longer temporal changes in DIN (Rainmonet et al. 2013). In the Providence River Estuary, *Ulva* δ^{15}N ranged from 8-15 ‰ (avg. 11 ‰) and the lone *Fucus* spp. collected had a $\delta^{15}N = 10$ ‰. Surface and subsurface $\delta^{15}N\text{-}NO_3^-$ in the same region ranged from 8-20 ‰. While both species δ^{15}N were similar to the $\delta^{15}N\text{-}NO_3^-$, and showed evidence of the N source within their isotope composition, the *Ulva* spp. was enriched compared to *Fucus* spp, which could be the result of metabolic differences. Therefore, any differences between phyla may be due to metabolic differences within the individual species.

The δ^{15}N-macroalgae values are in the range summer surface and subsurface $\delta^{15}N\text{-}NO_3^-$, and δ^{15}N-chl values in the Providence River Estuary (Fig. 3-6). The δ^{15}N-macroalgae values compare best with surface $\delta^{15}N\text{-}NO_3^-$, and when compared, have a slope of 1, with an $r^2 = 0.7$ (Fig. 3-8). A weak correlation exists with subsurface NO_3^-, but it is not statistically significant ($p = 0.39$).

The δ^{15}N values of subsurface NO_3^- compare relatively well to the δ^{15}N-macroalgae values for the entire system, with the exception of samples collected near 41.5°N (Fig. 3-8). Without the samples near 41.5°N, a regression between subsurface

$\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N$-macroalge has a slope of 0.26, but it is not significant ($r^2 = 0.34$; $p = 0.08$). Even though not statistically significant, the agreement between subsurface $\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N$-macroalge suggests that subsurface N, at least in part, supports macroalgal growth in the summer. The large difference between $\delta^{15}N\text{-}NO_3^-$ and macroalgae at 41.5°N likely reflects a local, transient increase in the nitrate pool, potentially related to uptake by primary producers discussed above. This signal appears in the $\delta^{15}N$-chl measured at the same site. Since macroalgae are longer lived than phytoplankton, and their $\delta^{15}N$ values reflect the integrated signal from a period of days (Costanzo et al. 2001; Fertig et al. 2009), they are not likely to reflect instantaneous conditions the way phytoplankton and nitrate are (Riper et al. 1979). The fact that it is apparent at all implies that it was a relatively long lived or high amplitude event during the summer of 2012, or perhaps a persistent feature in the bay nutrient dynamics.

As with the $\delta^{15}N$ values of chlorophyll *a* and nitrate, we expect a predictable relationship between the $\delta^{15}N$ values of macroalgae and nitrate. Using the same hybrid model as above, we expect the $\delta^{15}N$-macroalgae values to fall in the area between the steady-state and closed system models (Fig. 3-9). The macroalgae data do fit with the model expectations, like much of the $\delta^{15}N$-chl data (Fig. 3-9). As with the $\delta^{15}N$-chl, the conformity of the $\delta^{15}N$-macroalgae suggests that both primary producers quickly and nearly completely take up nitrate quickly when pulses reach the surface (Fig. 3-9).

Conclusion

Two groups of primary producers, phytoplankton (as chlorophyll *a*), and macroalgae displayed different N isotope patterns down bay. Variability in the N isotopes of chlorophyll matched those of the subsurface nitrate, with a peak near 41.5°N (Figs. 3-6 and 3-7). The macroalgae N isotopes decreased linearly with a difference of ~3 ‰ between the head and mouth of Narragansett Bay, consistent with previous observations (Fig. 3-5; Oczkowski et al. 2008). The different patterns of $\delta^{15}N$ along the latitudinal gradient stem from the increase to about 33-35 ‰ in the $\delta^{15}N$-chl and subsurface $\delta^{15}N$-NO_3^- while the $\delta^{15}N$-macroalgae remain static, or slightly decrease in the same region (Figs. 3-5 and 3-6). The isotopic differences could be from a number of factors, such as different nutrient sources, partial nutrient consumption, or turn-over time. However, sampling was limited to one summer, and therefore this aspect of primary production in Narragansett Bay warrants further study.

In conclusion, nitrate, chlorophyll *a*, and macroalgae mostly adhere to a predictable pattern driven by nutrient pulses and rapid uptake in the summer (Fig. 3-9). Turn-over times differ between the two primary producers and may affect their measured isotopic composition. Additionally, the upgrades to wastewater treatment facilities have been documented in $\delta^{15}N$ values of macroalgae, and while the upgrades are probably evident in the phytoplankton, this has not been documented. This suggests that multiple sources of nitrogen are supporting primary producers including anthropogenic inputs, Rhode Island Sound water, and recycling/remineralization in Narragansett Bay.

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Tables

Table 3-1. Subsurface sample depths at all stations. Latitude is in decimal degrees.

Latitude	Area of Bay[a]	Depth (m)
41.76	PRE	3.5
41.72	PRE	9.5[b]
41.69	Upper	6.3
41.62	West	8.7
41.62	East	14.0
41.54	West	10.0
41.51	East	29.0
41.43	West	31.0
41.43	East	26.0

[a]The Bay is divided into areas significant to the study (Fig. 3-1): PRE: Providence River Estuary; Upper: Upper Bay, not distinctly in either passage or PRE; West: West Passage; East: East Passage.
[b]The location of this sample is on the edge of the 14 m deep shipping channel

Table 3-2. ANOVA comparisons between macroalgal phyla.

Level	$\delta^{15}N$ Mean (‰)	n		
Phylum				
Chlorophyta	11.0	38	A	
Rhodophyta	10.9	26	A	
Phaeophyta	9.2	10		B

Values with the same letter are not significantly different ($p > 0.05$)

Figures

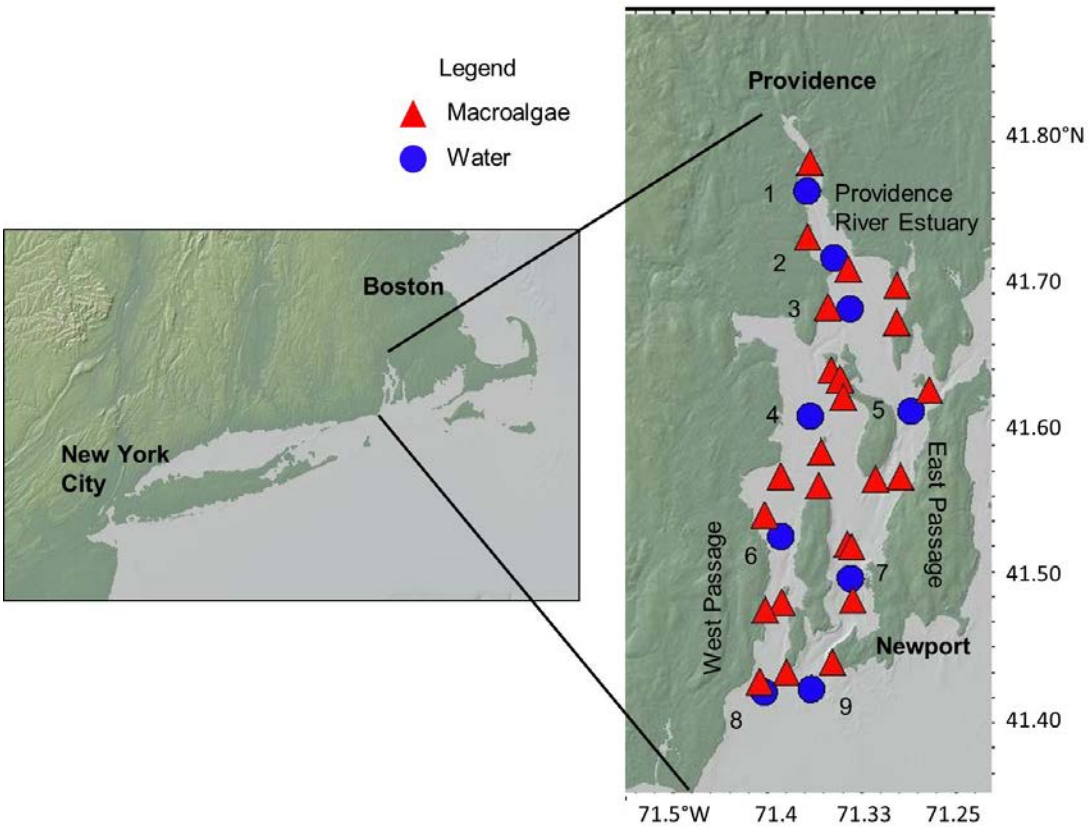

Figure 3-1. Narragansett Bay with sample sites depicted. Red triangles are macroalgae sample sites while blue circles are where DIN, and chlorophyll *a* samples were taken. Numbers indicate sample stations referred to in the text for DIN and chlorophyll *a* samples.

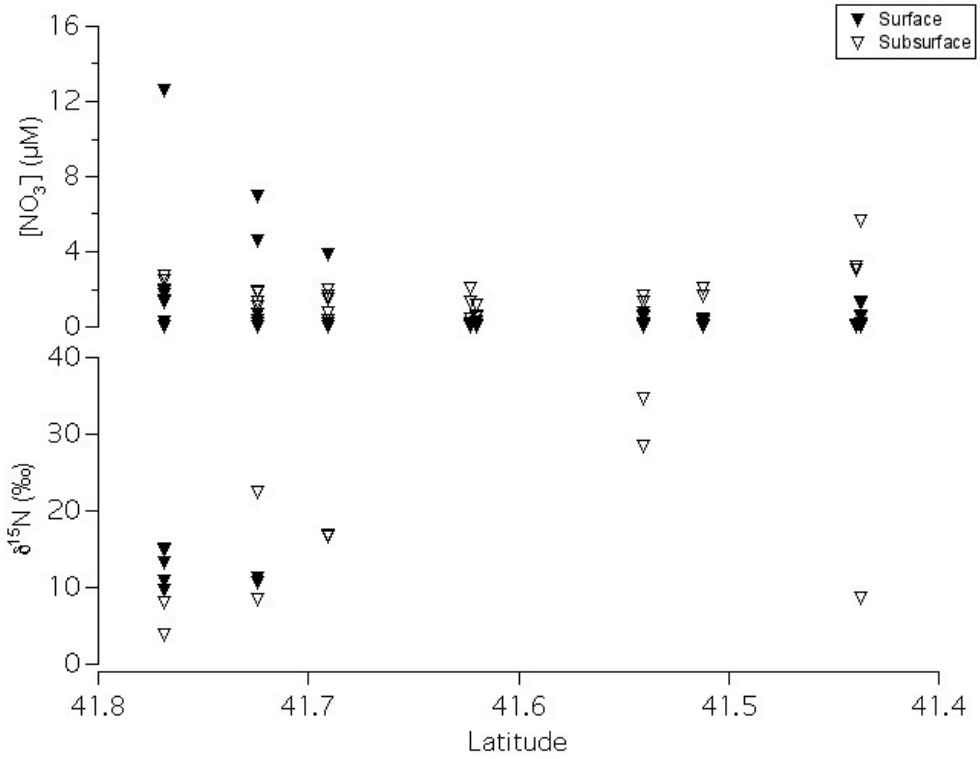

Figure 3-2. Surface (closed upside-down triangles) and subsurface water (open upside-down triangles) [NO_3^-] (top) and $\delta^{15}N$ (bottom) plotted against latitude (in decimal degrees).

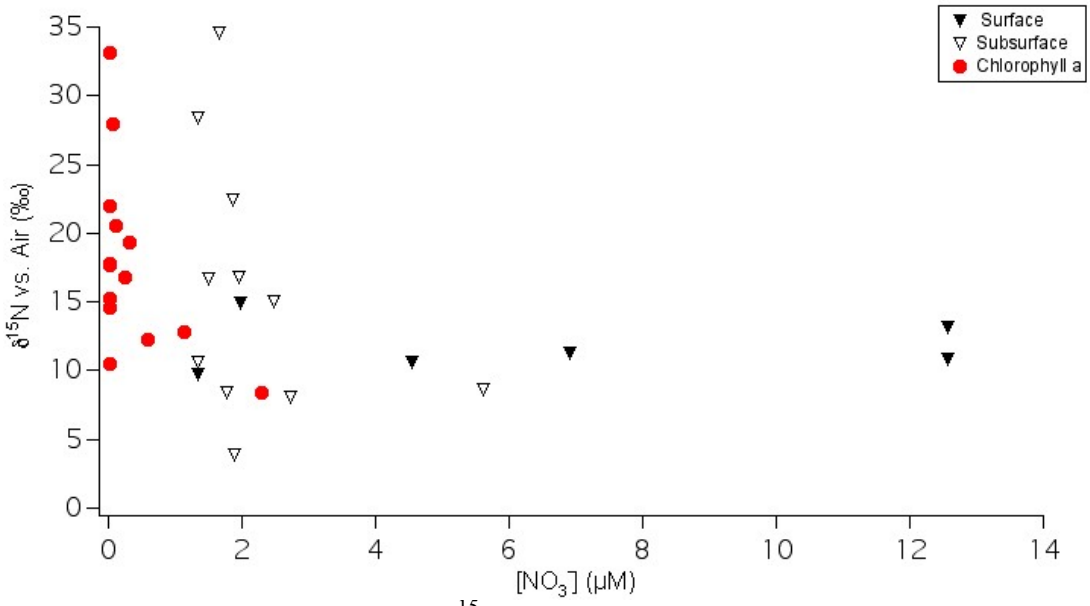

Figure 3-3. $[NO_3^-]$ plotted against $\delta^{15}N\text{-}NO_3^-$ for surface (closed upside down triangles) and subsurface (open upside down triangles) and $\delta^{15}N$-chl (red circles).

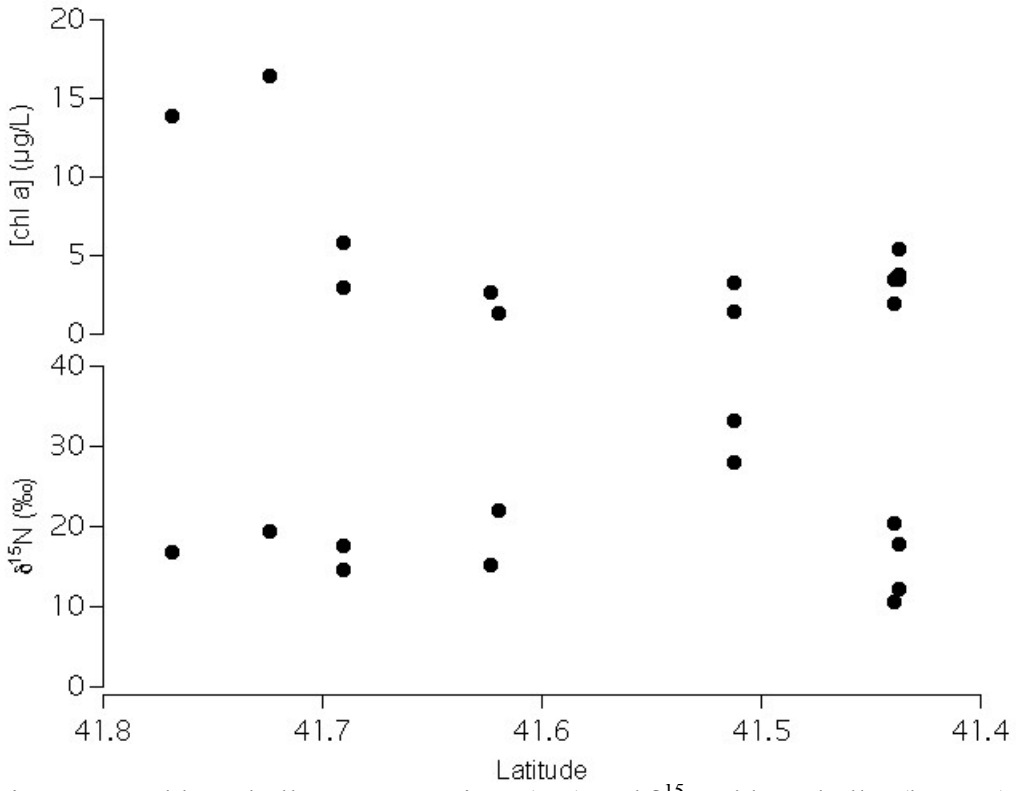

Figure 3-4. Chlorophyll *a* concentrations (top) and δ^{15}N-chlorophyll *a* (bottom) plotted against latitude (decimal degrees).

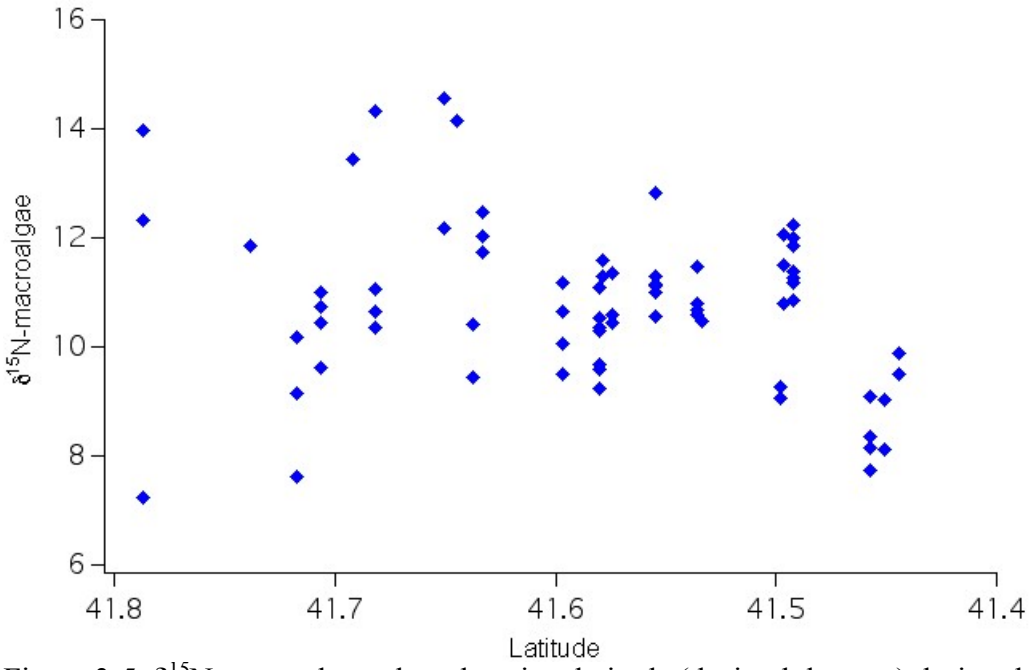

Figure 3-5. δ^{15}N-macroalgae plotted against latitude (decimal degrees) during the summer 2012. The linear regression for the data is included.

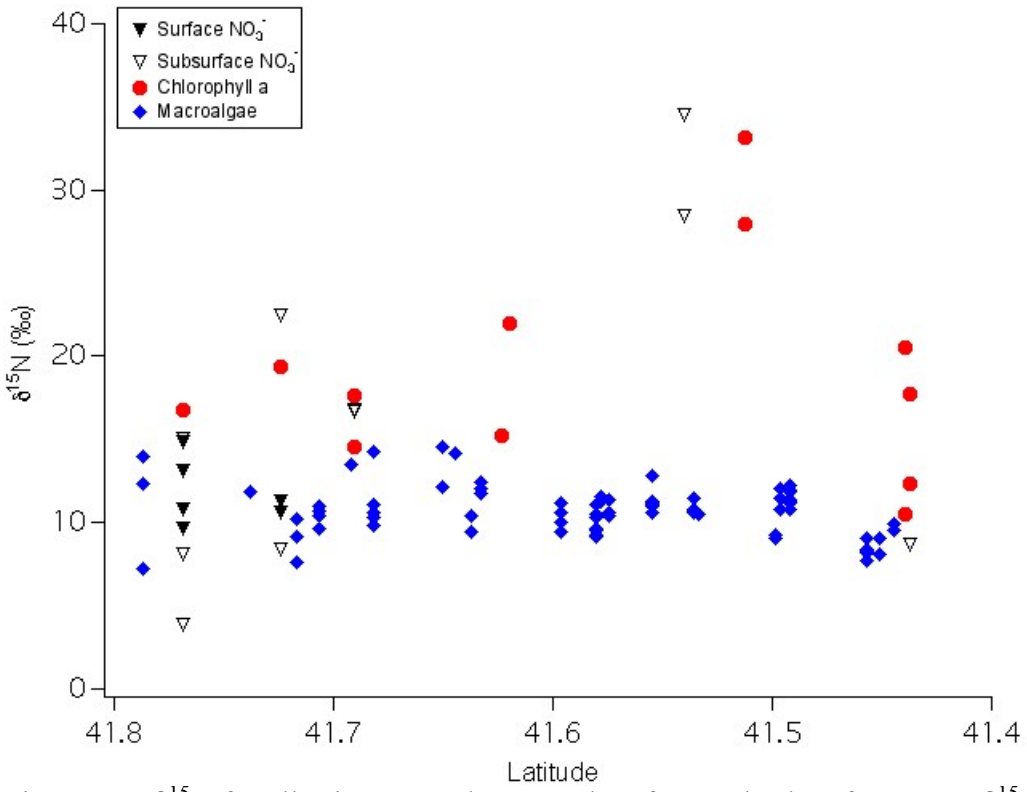

Figure 3-6. $\delta^{15}N$ for all primary producers and surface and subsurface water $\delta^{15}N$-NO_3^- versus latitude.

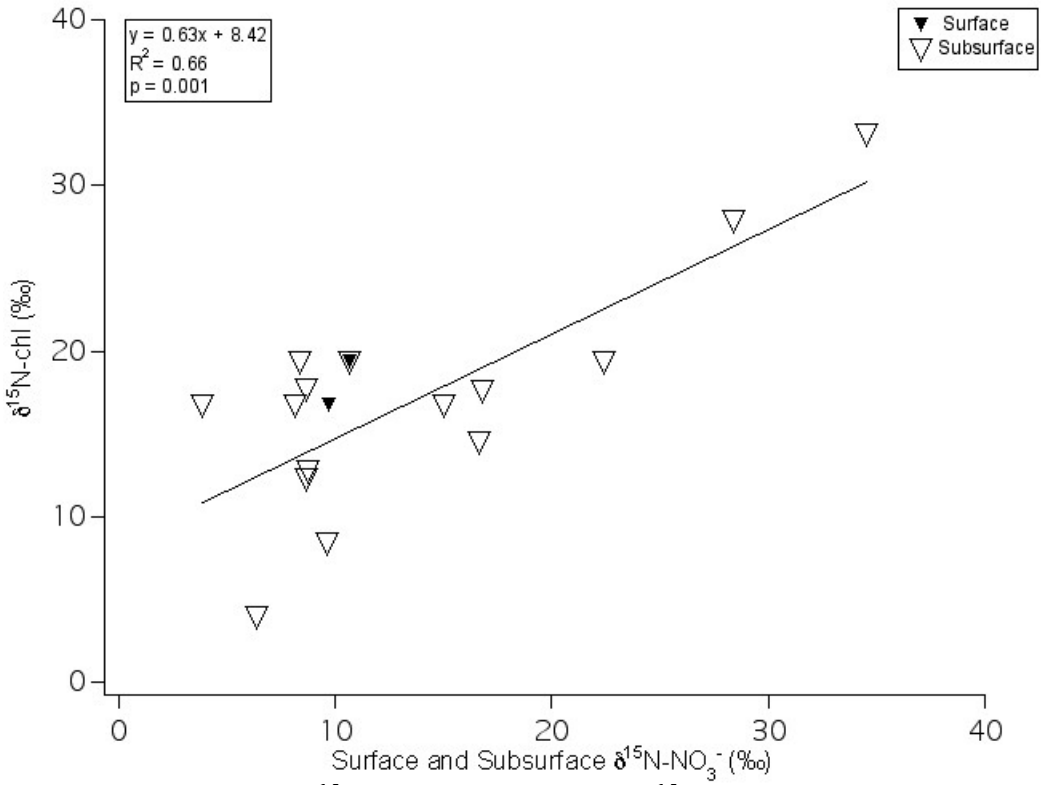

Figure 3-7. Subsurface $\delta^{15}N\text{-}NO_3^-$ plotted against $\delta^{15}N$-chl. Solid line is the linear regression.

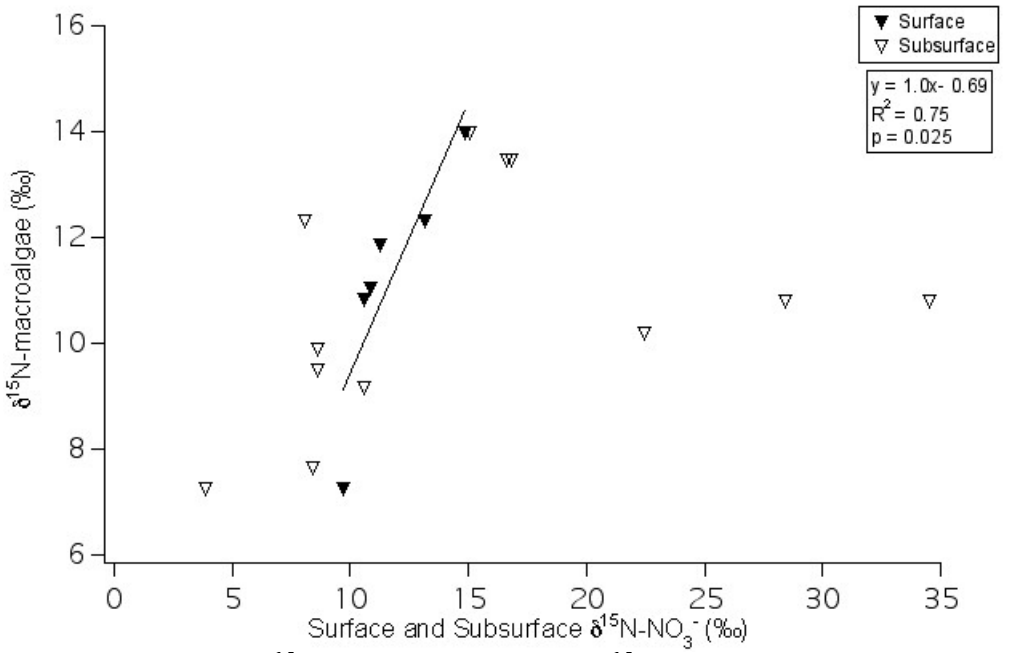

Figure 3-8. Surface $\delta^{15}N\text{-}NO_3^-$ plotted against $\delta^{15}N$-macroalgae in the Providence River Estuary (north of 41.7°N). Solid line is the linear regression.

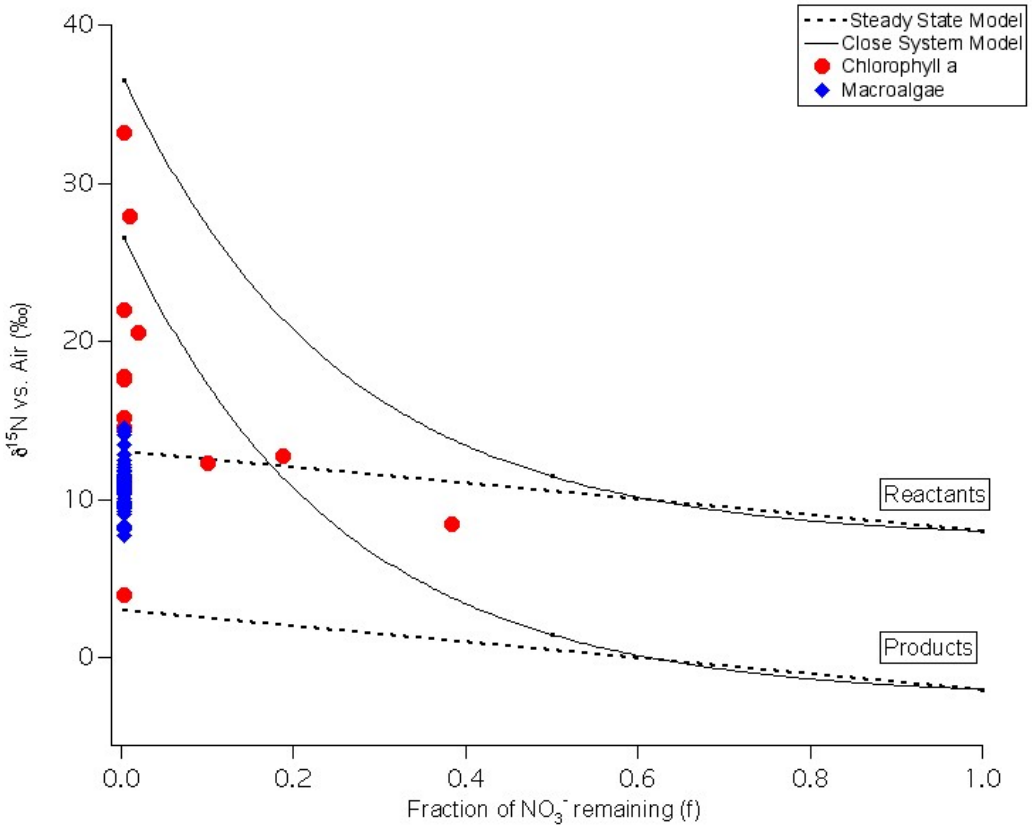

Figure 3-9. Steady-state and closed-system hybrid model. The steady-state (solid line) and close system (dashed line) are plotted against fraction of nitrate remaining (f). The top curve and line model the behavior of the reactants, while the bottom curve and line model the products and account for the isotopic fractionation between phytoplankton whole cell and the N bound within chlorophyll *a*). Measured δ^{15}N-chl (filled circles) and δ^{15}N-macroalgae filled diamonds) are also plotted.

CHAPTER 4

PREFACE

Dissertation Synthesis

Courtney E. Schmidt

Not submitted for peer review

Synthesis

The vital and permanent connection between land and ocean is what makes estuaries the "first responder" of anthropogenic impact on coastal ecosystems. Estuaries are often most sensitive to nitrogen (N) enrichment as it is the growth-limiting nutrient in these systems. However, N is not delivered uniformly to an estuary and can vary according to nearby land use and seasonal changes, such as rainfall. As a consequence of human population growth, fertilizer production, and greater socio-economic status world-wide, anthropogenic nutrient inputs increased over the last two centuries (Rabalais et al. 1996; Caraco and Cole 1999; Nixon et al. 2008) and are considered the primary cause of eutrophication – an excess of organic input associated with nutrient-stimulated primary production (Nixon 1995). Recently, concerns over the negative effects of eutrophication (such as low water-column oxygen concentrations) led to upgrades at wastewater treatment facilities as a way to reduce anthropogenic N loads (RIDEM 2005; Greening and Janicki 2006; Cloern et al. 2007). But, the downstream effects of these reductions are only starting to be understood (Nixon 2009; Duarte et al. 2009).

In this dissertation, I investigated nitrogen cycling within Narragansett Bay using nitrogen (N) and oxygen (O) stable isotopes (the ratio of $^{15}N/^{14}N$ or $^{18}O/^{16}O$, in per mil (‰) notation). I measured nutrient (nitrate, ammonium, and phosphorus) concentrations and stable isotopic compositions of N and O of nitrate entering the system from wastewater treatment facilities and rivers and moving through surface and subsurface waters of Narragansett Bay. I also measured chlorophyll *a* content and the compound specific and bulk N isotopic composition of chlorophyll *a* and

macroalgae (seaweed), respectively. I used the isotope data to explore the impact of upgrades at the wastewater treatment facilities on nutrient fluxes and their isotopic compositions, the ability to trace anthropogenic N from a dissolved inorganic nutrient form through primary production and, more generally, the role that anthropogenic N plays in driving primary production within Narragansett Bay.

Upgrades to wastewater treatment facilities resulted in an approximately 30 % decrease in nitrate fluxes to Narragansett Bay between 2009 and 2012 (Krumholz 2012; Schmidt, this study). However, my data suggest that the current flux reductions have not changed where N shifts from abundant to deficient in the Providence River Estuary and Narragansett Bay proper. N*, which estimates nitrogen (ammonium and nitrate) excess or deficiency relative to phosphate via Redfield expectations (16:1 N:P) (Gruber and Sarmiento 1997), suggests that the Bay becomes N-deficient at about 41.7°N before and during upgrades (between 2007 and 2012). The latitude of 41.7°N marks the boundary from the Providence River Estuary, which is replete with nutrients year-round, to Narragansett Bay proper, where nutrient depletion is achieved rapidly in the late spring and maintained through early fall. While N* measures the status of nutrients in a system, it does not address the complexities of nutrient removal or the time scales at which nutrients are removed. The stationary nature of this transition suggests that the estuary's nitrogen cycle has not yet responded to the reductions (which are still ongoing) or that the response maintains the current balance in nitrogen status along the nutrient gradient.

Significant changes to the isotope compositions of nitrate sources were observed. Sampling that bracketed upgrades to a single wastewater treatment facility

(Field's Point) documented an N and O isotopic value increase of ~16 ‰ in the effluent nitrate. The rivers showed isotopic increases of 4 ‰ for N and O. The proportional increases in both N and O isotopes are consistent with the effects of denitrification, the N reduction process added during upgrades to wastewater treatment facilities (Granger et al. 2008). The isotopic impact of these changes in upstream facilities is apparent within the Providence River Estuary, where $\delta^{15}N$ values increased by ~2 ‰. No isotopic changes attributable to the upgrades were observed in Narragansett Bay proper, likely because of intense mixing with Rhode Island Sound water and N recycling.

Two groups of primary producers, phytoplankton (as chlorophyll *a*) and macroalgae displayed different N isotope patterns down bay. Variability in the N isotopes of chlorophyll tracked that of the subsurface nitrate, with a peak near 41.5°N. The macroalgae N isotopes decreased linearly with a difference of 3 ‰ between the head and mouth of Narragansett Bay, consistent with previous results (Oczkowski et al. 2008). This suggests the nutrient sources to these two groups are different, possibly because of their position in the water column. Macroalgae are incorporating N at a fixed position, and may be supported, at least in part, by small, but consistent, benthic fluxes. Phytoplankton, on the other hand, are transported vertically and horizontally by tides/currents and mixing events. The exact position where they incorporate N is unknown, but they appear to be supported by local, subsurface nitrate.

Smayda and Borkman (2008) concluded after 30 years of sampling between the head of the Providence River Estuary and West Passage that the bay has multiple zones: the Providence River Estuary "Enrichment Zone" where nutrients are replete all

year long (north of 41.7°N), the Upper bay basin "Depuration Zone" (~41.69°N), and the "N-limited Zone" beginning at the upper West Passage (~ 41.65°N). The results of this dissertation fit well with this zonation. Dissolved inorganic nitrogen became deficient at 41.7°N between 2007 and 2012, which occurred before and during major reductions to sewage inputs. The chlorophyll *a* and subsurface nitrate isotopic compositions suggest that small vertical injections of nutrients, either new or recycled, support primary production in the N-limited zone.

With limited present information and prediction capabilities, environmental monitoring is critical to address the individual challenges of a specific estuary. Classically, eutrophication has been monitored by nutrient concentrations, fluxes, and measures of primary production, which all suggest a fairly monotonic decrease downstream. More recently, stable nitrogen isotopes, chlorophyll *a* concentrations, light, wind, and dissolved oxygen metrics have demonstrated the spatial and temporal complexities of nutrient uptake and recycling (Costanzo et al. 2001; Cole et al. 2004; Scavia and Bricker 2006; Wilkerson et al. 2006; Chen et al. 2008; Nixon 2009; Schmidt, this study). In the case of Narragansett Bay, circulation, dilution and recycling appear to be key factors in determining the strength of anthropogenic nitrogen influence as far as the isotopes are concerned. In the Providence River Estuary, stable N and O isotopes are good indicators of source input, but rapid nitrogen removal in the estuary and recycling within the Bay makes continuous tracing of anthropogenic sources with N and O isotopes difficult, if not impossible. Therefore, stable N and O isotopes may be a useful tracer of nitrate in systems where

sources are isotopically distinct and recycling is not a dominant process; however because nitrate is so often a limiting nutrient, such situations are likely rare.

In conclusion, this dissertation highlights the complexities of tracing anthropogenic inputs in highly dynamic systems. I was not able to continually trace the anthropogenic N inputs from their sources to Rhode Island Sound. However, I was able to demonstrate that intense mixing and recycling occurs in the Bay and brings nutrients to the euphotic zone, supporting primary production. In short, while stable isotopes were not helpful to trace ultimate sources of nutrients (anthropogenic or oceanic), they were helpful to trace proximal sources of nutrients (recycling, and pulses of nutrient input through vertical mixing). Narragansett Bay is evolving because of the reductions to anthropogenic inputs. With continued monitoring, we will be able to learn from our efforts at point-source reduction and assess the balance between nutrient inputs, recycling and mixing in Narragansett Bay.

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APPENDIX: DATA

Table A-1. Wastewater treatment facility (WWTF) data.

Date	ID	$[NO_3^-]$ µM	$[NH_4^+]$ µM	Flow (thousands m^3/day)	Flow (millions m^3/day)	$\delta^{15}N\text{-}NO_3^-$ (‰)	st.dev	$\delta^{18}O\text{-}NO_3^-$ (‰)	st.dev
4/30/2009	Bucklin	429.68	1.58	84.41	0.08441	8.34		-4.25	
6/10/2009	Bucklin	504.38	96.07	68.76	0.06876	9.89	0.66	0.22	0.19
6/24/2009	Bucklin	190.97	219.42	68.76	0.06876	13.19	0.03	2.75	0.62
8/4/2009	Bucklin	153.00	481.93	73.89	0.07389	0.99	0.06	-12.54	0.11
9/30/2009	Bucklin	466.13	9.72	57.46	0.05746	13.83	0.36	3.06	0.11
11/20/2009	Bucklin	458.38	100.80	112.01	0.11201	17.07	0.22	3.05	0.08
1/22/2010	Bucklin	497.25	48.25	75.56	0.07556	12.03	0.39	-0.88	0.82
4/30/2009	East Providence	135.62	530.05	34.14	0.03414	8.82	0.22	-6.85	0.48
8/4/2009	East Providence	100.90	186.66	24.30	0.02430	21.98	0.27	6.08	1.63
9/30/2009	East Providence	527.63	150.47	20.71	0.02071	15.52	0.40	4.49	0.00
11/18/2009	East Providence	584.25	28.76	27.25	0.02725	5.00	0.48	-1.28	0.21
1/22/2010	Providence	338.62	122.33	29.90	0.02990	6.89		-0.77	
4/30/2009	Field's Point	67.96	760.32	177.99	0.17799	4.52	0.47	-0.32	0.73
6/10/2009	Field's Point	249.02	631.98	152.27	0.15227	2.28	0.20	-16.11	0.10
6/24/2009	Field's Point	303.84	361.00	152.27	0.15227	-3.51	0.33	2.62	3.39
8/4/2009	Field's Point	156.70	484.86	162.81	0.16281	1.41		-13.67	
9/30/2009	Field's Point	241.07	373.92	131.96	0.13196	6.00	0.78	3.21	3.52
11/20/2009	Field's Point	127.89	711.03	210.17	0.21017	1.25		-6.32	

Date	ID	$[NO_3^-]$ µM	$[NH_4^+]$ µM	Flow (thousands m^3/day)	Flow (millions m^3/day)	$\delta^{15}N\text{-}NO_3^-$ (‰)	st.dev	$\delta^{18}O\text{-}NO_3^-$ (‰)	st.dev
1/22/2010	Field's Point	70.55	747.44	256.12	0.25612	2.76	0.40	-0.10	0.07
2/15/2012	Bucklin	465.51	7.14	68.74	0.06874	9.91	0.06	-1.04	0.02
3/14/2012	Bucklin	346.04	8.64	61.21	0.06121	11.20	2.04	1.16	1.70
4/11/2012	Bucklin	357.09	24.57	54.21	0.05421	8.66	0.49	-1.25	0.45
5/9/2012	Bucklin	274.23	23.36	125.15	0.12515	12.03	0.29	4.07	0.48
6/6/2012	Bucklin	274.20	129.30	73.93	0.07393	10.76	0.37	0.93	0.21
7/9/2012	Bucklin	232.43	48.00	78.81	0.07881	16.90	0.01	3.41	0.01
8/30/2012	Bucklin	347.40	13.70	54.43	0.05443	10.47	0.43	1.42	0.70
9/26/2012	Bucklin	511.00	7.50	57.92	0.05792	12.54	0.27	0.55	0.10
10/24/2012	Bucklin	519.40	11.93	60.53	0.06053	12.64	0.49	0.95	0.00
11/19/2012	Bucklin	368.30	12.43	59.24	0.05924	13.00	0.14	1.44	0.46
12/19/2012	Bucklin	538.30	10.57	59.73	0.05973	18.75	0.46	4.99	1.00
1/16/2013	Bucklin	157.01	85.71	83.17	0.08317	13.89	0.57	1.19	0.44
2/15/2012	Fall River	33.57	1285.71	57.16	0.05716	9.75	0.01	3.96	0.21
3/14/2012	Fall River	17.14	1142.86	48.45	0.04845	27.24	5.14	24.12	5.38
4/12/2012	Fall River	8.60	1357.14	48.07	0.04807	1.01	0.11	12.81	0.55
5/9/2012	Fall River		928.57	185.86	0.18586				
6/6/2012	Fall River	17.90	1142.86	59.05	0.05905	3.92	0.20	8.58	0.03
7/18/2012	Fall River	30.00	928.57	48.07	0.04807	-5.80	0.12	6.02	0.46
8/29/2012	Fall River	32.86	1142.89	61.70	0.06170	-4.07	0.49	3.36	1.23
9/26/2012	Fall River	39.29	1214.30	54.13	0.05413	-6.51	0.38	4.18	0.89
10/24/2012	Fall River	35.00	1070.43	45.80	0.04580	-1.46	0.21	2.39	0.78
11/14/2012	Fall River	33.60	735.70	69.65	0.06965	-1.57	0.34	5.93	0.23
12/19/2012	Fall River	28.60	892.90	53.00	0.05300	3.09	0.68	10.44	0.65
1/17/2013	Fall River	66.40	707.10	114.70	0.11470	8.23	0.80	10.96	1.46

Date	ID	$[NO_3^-]$ µM	$[NH_4^+]$ µM	Flow (thousands m^3/day)	Flow (millions m^3/day)	$\delta^{15}N\text{-}NO_3^-$ (‰)	st.dev	$\delta^{18}O\text{-}NO_3^-$ (‰)	st.dev
2/15/2012	Field's Point	200.64	433.57	140.17	0.14017	21.37	0.16	16.97	0.03
3/14/2012	Field's Point	77.79	631.43	135.44	0.13544	28.36	0.89	29.35	3.82
4/11/2012	Field's Point	54.43	543.57	120.79	0.12079	19.27	0.27	18.60	0.54
5/9/2012	Field's Point	80.21	312.14	242.30	0.24230	9.71	0.06	13.13	0.10
6/6/2012	Field's Point	80.20	477.86	193.70	0.19370	16.68	0.23	27.11	0.30
7/9/2012	Field's Point	18.93	423.57	184.05	0.18405	9.41	0.49	16.47	0.85
8/30/2012	Field's Point	65.50	127.14	153.01	0.15301	21.03	0.14	13.41	0.19
9/26/2012	Field's Point	90.30	235.00	155.66	0.15566	24.82	0.13	14.50	0.09
10/24/2012	Field's Point	77.10	131.43	126.51	0.12651	19.41	0.41	12.43	1.16
11/19/2012	Field's Point	73.00	301.43	128.33	0.12833	24.00	0.01	13.66	0.56
12/18/2012	Field's Point	125.40	382.14	153.91	0.15391	10.72	0.42	7.07	0.20
1/15/2013	Field's Point	164.71	138.57	179.66	0.17966	17.66	0.50	10.35	0.02

Table A-2. Riverine data.

Date	ID	$[NO_3^-]$ µM	$[NH_4^+]$ µM	Flow (millions m^3/day)	$\delta^{15}N$-NO_3^- (‰)	st.dev	$\delta^{18}O$-NO_3^- (‰)	st.dev
3/25/2009	Blackstone	59.16	37.49	3.47	4.55	0.01	-1.38	0.37
4/29/2009	Blackstone	71.05	3.97	3.62	7.29	0.67	-2.13	0.66
5/27/2009	Blackstone	70.50	4.51	1.58	11.95	0.05	-1.34	0.40
6/25/2009	Blackstone	65.12	4.55	1.46	12.02	0.31	0.06	0.67
8/10/2009	Blackstone	58.35	2.71	1.86	9.05	0.23	-2.10	0.64
10/2/2009	Blackstone	90.01	3.68	1.62	11.70		-0.36	
1/7/2010	Blackstone	56.07	9.29	3.19	6.54	0.36	-0.33	1.33
3/25/2009	Pawtuxet	83.90	13.34	1.19	11.60	0.33	5.86	0.64
4/29/2009	Pawtuxet	42.51	13.14	1.79	7.49	0.20	2.72	1.08
5/27/2009	Pawtuxet	41.24	7.42	0.96	10.02	0.31	4.52	0.02
6/25/2009	Pawtuxet	73.10	8.05	0.55	11.07	0.22	3.50	0.67
8/10/2009	Pawtuxet	64.75	4.12	0.85	12.17	0.68	3.13	0.80
10/2/2009	Pawtuxet	102.32	2.88	0.63	11.37	0.92	2.12	0.81
1/7/2010	Pawtuxet	57.97	21.73	1.60	6.11	0.13	0.43	0.92
3/25/2009	Taunton	48.62	4.73	2.30	7.18	0.03	1.98	1.15
4/29/2009	Taunton	24.77	2.16	2.40	9.54	1.45	2.07	1.44
5/27/2009	Taunton	29.74	6.16	1.44	7.01	0.04	7.84	0.24
6/25/2009	Taunton	23.00	2.78	0.87	8.05	0.78	1.81	0.40
8/10/2009	Taunton	34.06	4.72	0.98	8.88	0.38	0.14	0.33
10/2/2009	Taunton	56.76	2.19	1.64	8.76	0.82	-0.71	0.72
1/7/2010	Taunton	45.90	5.34	2.19	6.00	0.38	-0.69	0.28
3/25/2009	Ten Mile	99.52	0.64	0.37	8.58	0.76	2.26	0.42
4/29/2009	Ten Mile	61.21	1.93	0.49	11.46	0.17	4.61	1.04
5/27/2009	Ten Mile	60.40	3.91	0.27	14.16	1.66	4.57	1.46

Date	ID	$[NO_3^-]$ µM	$[NH_4^+]$ µM	Flow (millions m^3/day)	$\delta^{15}N$-NO_3^- (‰)	st.dev	$\delta^{18}O$-NO_3^- (‰)	st.dev
6/25/2009	Ten Mile	125.42	4.75	0.19	10.71	0.26	2.37	1.07
8/10/2009	Ten Mile	94.45	8.59	0.16	11.61	0.85	1.20	0.54
10/2/2009	Ten Mile	126.39	6.28	0.22	11.34		2.24	
1/7/2010	Ten Mile	129.96	7.34	0.41	3.09	0.39	-2.07	0.03
2/15/2012	Blackstone	61.07	2.80	1.97	20.74	0.62	14.85	1.19
3/14/2012	Blackstone	56.00	1.17	1.93	11.33	0.39	4.83	0.63
4/11/2012	Blackstone	68.71	0.50	1.72	12.89	0.28	4.43	0.31
5/9/2012	Blackstone	66.60	4.61	1.88	11.42	0.00	4.23	0.31
6/6/2012	Blackstone	46.40	1.12	1.37	10.30	0.40	3.05	0.31
7/18/2012	Blackstone	43.00	6.48	0.51	15.61	0.29	3.12	0.31
8/29/2012	Blackstone	38.71	1.97	0.85	16.25	0.95	5.08	0.82
9/26/2012	Blackstone	58.43	1.64	0.67	13.64	0.18	2.82	0.37
10/24/2012	Blackstone	45.29	2.11	0.00	13.79	0.05	1.96	0.23
11/20/2012	Blackstone	51.90		0.00	12.11	0.27	3.43	0.23
12/19/2012	Blackstone	51.90		0.00	11.62	0.16	5.35	0.67
1/16/2013	Blackstone	60.22			11.70	0.39	3.49	0.15
2/15/2012	Pawtuxet	103.57	15.14	0.78	9.35	0.06	1.93	0.06
3/14/2012	Pawtuxet	100.71	7.79	0.67	13.60	0.44	7.07	1.26
4/11/2012	Pawtuxet	94.29	13.71	0.58	20.61	0.16	16.17	0.15
5/9/2012	Pawtuxet	69.10	6.43	0.88	15.87	0.27	11.92	0.21
6/6/2012	Pawtuxet	79.60	14.32	0.67	12.52	0.47	4.62	0.91
7/18/2012	Pawtuxet	116.40	1.71	0.31	15.19	0.42	3.36	0.41
8/29/2012	Pawtuxet	104.23	1.99	0.30	13.85	0.26	2.48	0.22
9/26/2012	Pawtuxet	116.43	5.42	0.36	15.38	0.62	2.97	0.97
10/24/2012	Pawtuxet	73.57	4.83	0.00	14.04	0.19	2.79	1.23

Date	ID	$[NO_3^-]$ µM	$[NH_4^+]$ µM	Flow (millions m^3/day)	$\delta^{15}N$-NO_3^- (‰)	st.dev	$\delta^{18}O$-NO_3^- (‰)	st.dev
11/20/2012	Pawtuxet	64.00		0.00	11.41	0.06	1.45	0.06
12/19/2012	Pawtuxet	64.00		0.00	6.89	0.21	1.62	0.71
1/16/2013	Pawtuxet	109.81			8.23	0.40	2.82	0.75
2/15/2012	Taunton	73.57	4.65	1.21	12.13	0.27	-2.23	0.26
3/14/2012	Taunton	63.30		1.15	10.56	0.25	3.97	0.72
4/11/2012	Taunton	82.86	0.50	0.78	12.77	0.32	-5.51	0.43
5/9/2012	Taunton	62.10	8.93	1.32	10.33	0.40	3.83	0.01
6/6/2012	Taunton	59.60	4.89	0.77	9.46	0.29	2.01	0.09
7/3/2012	Taunton	27.00	4.29	0.30	12.89	0.28	2.55	0.14
8/29/2012	Taunton	73.20	6.59	0.50	14.61	0.12	2.33	0.35
9/26/2012	Taunton	90.00	2.72	0.36	12.87	0.04	1.51	0.68
10/24/2012	Taunton	80.71	2.69	0.00	12.18	0.13	1.39	0.06
11/20/2012	Taunton	54.40		0.00	9.00	0.38	1.19	0.12
12/19/2012	Taunton	34.90		0.00	8.20	0.32	2.70	0.15
1/16/2013	Taunton	45.04			9.22	0.41	2.69	0.03
2/15/2012	Ten Mile	143.57	0.50	0.22	14.65	0.87	5.87	2.00
3/14/2012	Ten Mile	129.80		0.22	15.46	0.08	6.59	0.03
4/11/2012	Ten Mile	163.57	0.50	0.16	17.80	0.52	-2.95	0.08
5/9/2012	Ten Mile	139.60	6.01	0.28	9.01	0.22	0.97	0.68
6/6/2012	Ten Mile	106.80	10.46	0.19	18.34	0.16	6.90	0.05
7/18/2012	Ten Mile	43.40	4.29	0.10	19.00	0.61	5.28	0.78
8/29/2012	Ten Mile	81.43	23.07	0.14	17.37	0.23	5.15	0.66
9/26/2012	Ten Mile	130.36	0.58	0.12	20.20	0.12	6.45	0.14
10/24/2012	Ten Mile	100.00	1.74	0.00	20.06	0.10	6.20	0.78
11/20/2012	Ten Mile	154.60		0.00	7.31	0.02	-1.48	0.33

Date	ID	$[NO_3^-]$ µM	$[NH_4^+]$ µM	Flow (millions m^3/day)	$\delta^{15}N$-NO_3^- (‰)	st.dev	$\delta^{18}O$-NO_3^- (‰)	st.dev
12/19/2012	Ten Mile	202.50		0.00	13.07	0.27	3.27	0.42

Table A-3. Data from Nu-Shuttle cruises (2007-2009). These data were collected as part of the NOAA Bay Window Study.

Date	Station	Latitude	$[NO_3+NO_2]$ µM	$[NH_4]$ µM	$[PO_4]$ µM	$\delta^{15}N$-NO_3^- (‰)	st. dev	Salinity (ppt)
6/22/2007	11	41.75	11.65	0.24	0.89	6.37	0.01	26.93
6/22/2007	12	41.788	19.88	4.24	1.82	7.48	0.22	25.68
8/9/2007	2	41.48	1.41	5.24	1.18			
8/9/2007	4	41.47	0.86	2.22	0.86			
8/9/2007	11	41.75	16.01	3.35	6.16	7.27	0.23	
8/9/2007	12	41.788	21.94	23.97	8.26	8.28	0.05	
9/10/2007	4	41.47	1.84	1.09	0.88			
9/10/2007	5	41.53	1.28	1.16	0.96			
9/10/2007	6	41.57	1.29	1.58	0.98			
9/10/2007	8	41.64	1.01	1.12	1.09			
9/10/2007	9	41.72	8.92	6.03	2.29			
9/10/2007	11	41.75	14.55	13.26	3.53	8.64	0.10	
9/10/2007	12	41.788	22.53	28.11	4.6	9.97	0.11	
9/10/2007	14	41.65	2.73	1.2	1.42			
9/10/2007	16	41.58	0.94	1.88	1.08			
9/20/2007	6	41.57	2.89	0.16	1			30.46
9/20/2007	8	41.64	10.98	-0.06	1	10.70	0.57	28.54
9/20/2007	9	41.72	7.99	0.28	1.66			27.99
9/20/2007	11	41.75	9.92	2.95	2.32	8.93	0.60	26.97
9/20/2007	12	41.788	18.61	19.06	3.61	9.94	0.33	27.14
9/20/2007	14	41.65	6.38	0.58	1.3	6.57	0.11	29.43
10/16/2007	1	41.55	1.29	5.72	1.76			30.69
10/16/2007	2	41.48	1.25	3.93	1.47			31.07
10/16/2007	3	41.43	1.39	1.88	1.32			
10/16/2007	4	41.47	1.66	2.08	1.4			

Date	Station	Latitude	$[NO_3+NO_2]$ µM	$[NH_4]$ µM	$[PO_4]$ µM	$\delta^{15}N$-NO_3^- (‰)	st. dev	Salinity (ppt)
10/16/2007	5	41.53	1.53	2.94	1.53			31.36
10/16/2007	6	41.57	1.64	5.79	1.74			31.23
10/16/2007	8	41.64	2.31	7.42	2.07			30.09
10/16/2007	9	41.72	6.76	19.86	3.89			28.82
10/16/2007	11	41.75	23.96	21.82	4.1	7.13	0.25	28.20
10/16/2007	12	41.788	11.84	24.1	5.37	9.47	0.16	27.67
10/16/2007	14	41.65	3.35	14.96	2.62			30.20
10/16/2007	16	41.58	1.53	6.97	1.9			30.56
12/13/2007	4	41.47	6.26	2.17	1.41	7.00	0.27	
12/13/2007	5	41.53	6.74	3.02	1.6	6.40	0.07	
12/13/2007	6	41.57	9.56	3.5	1.63	6.32	0.52	
12/13/2007	8	41.64	4.00	4.37	1.9	6.41	0.01	
12/13/2007	9	41.72	10.67	7.9	2.37	6.84	0.00	
12/13/2007	14	41.65	9.08	4.13	1.92	6.15	0.43	
12/13/2007	16	41.58	13.62	2.9	1.66	6.14	0.11	
3/18/2008	9	41.72	16.97	9.55	1.12	6.87	0.45	
3/18/2008	11	41.75	15.43	14.52	1.4	7.84	0.02	
3/18/2008	12	41.788	31.75	34.32	1.74	7.39	0.09	
3/18/2008	14	41.65	11.71	6.16	0.98	8.12	1.22	
4/15/2008	9	41.72	19.25	6.38	0.61	7.29	0.22	24.92
4/15/2008	11	41.75	17.12	12.79	0.92	7.04	0.19	24.24
4/15/2008	12	41.788	32.56	10.92	1.48	7.64	0.03	24.37
4/15/2008	14	41.65	5.99	0.83	0.19			27.88
5/8/2008	9	41.72	5.17	1.85	0.41	6.69	0.09	
5/8/2008	11	41.75	7.28	8.63	1.14	8.19	0.05	
5/8/2008	12	41.788	30.36	38.04	2.69	7.47	0.24	

Date	Station	Latitude	$[NO_3+NO_2]$ µM	$[NH_4]$ µM	$[PO_4]$ µM	$\delta^{15}N\text{-}NO_3^-$ (‰)	st. dev	Salinity (ppt)
6/26/2008	12	41.788	19.31	5.09	4.73	7.13	0.18	
7/29/2008	11	41.75	8.95	0.29	2.68	11.43	0.44	
7/29/2008	12	41.788	11.29	23.41	7.11	7.28	0.23	
8/29/2008	2	41.48	0.26	3.18	1.52			
8/29/2008	3	41.43	0.24	2.05	1.34			
8/29/2008	11	41.75	11.05	5.48	4.24	10.60	0.33	
8/29/2008	12	41.788	11.36	14.87	5.62	9.28	0.27	
2/17/2009	14	41.65	4.16	1.4	0.71	7.90	0.73	
3/19/2009	9	41.72	10.45	2.22	0.28	8.62	0.25	21.05
4/16/2009	9	41.72	29.33	3.17	0.28	8.07	0.49	
4/16/2009	11	41.75	18.88	3.76	0.41	6.80	0.26	
4/16/2009	14	41.65	1.78	0.23	0.14			26.48

Table A-4. 2011-2012 surface water data. Salinity was corrected between collection and analysis (see chapter 2).

Date	Stn	Latitude	Salinity (ppt)	Corrected Salinity (ppt)	Temp (°C)	[chl a] (µg/L)	$[NO_3^-]$ (µM)	$[NH_4^+]$ (µM)	$[PO_4^{3-}]$ (µM)	$\delta^{15}N$-NO_3^-	stdev	$\delta^{18}O$-NO_3^-	stdev	$\delta^{15}N$-PM	stdev	$\delta^{15}N$-chla	stdev	N*
5/25/2011	1	41.768336	12	11	19.7	3.18	30.17	19.31	0.50	8.90	0.35	2.33	0.20					44.38
5/25/2011	2	41.724222	15	14	19.2	3.53	21.19	20.14	0.00	8.63	0.89	2.62	0.12					44.23
5/25/2011	3	41.690747	25	24	18.5	2.87	6.57	2.96	0.00	9.81	0.58	5.37	0.76					12.43
5/25/2011	4	41.619800	30	28	16.1	0.9	0.07	0.39	nd									
5/25/2011	6	41.540378	31	29	15.5	0.89	nd	0.22	nd									
5/25/2011	8	41.437311	30	28	15.8	0.64	0.22	0.42	nd									
7/5/2011	1	41.768336	23	22	24.3	15.29	1.97	2.46	0.00	14.87	0.85	8.54	4.88					7.33
7/5/2011	2	41.724222	26	25	25.9	7.71	0.18	0.43	nd									
7/5/2011	3	41.690747	28	27	25.6	5.86	3.80	2.15	0.53									0.37
7/5/2011	4	41.619800	33	31	24.5	3.39	0.09	0.15	nd									
7/5/2011	5	41.623092	32	30	21.5	2.02	0.08	0.01	0.51									-5.17
7/5/2011	6	41.540378	32	30	21.3	1.55	0.12	nd	nd									
7/5/2011	7	41.512458	33	31	20.1	1.03	0.09	nd	0.29									-1.65
7/5/2011	8	41.437311	33	31	18.7	1.38	0.06	0.33	nd									
7/5/2011	9	41.439353	34	32	18.2	1.57	0.11	0.15	0.29									-1.48
8/2/2011	1	41.768336	25	24	25.5	1.87	nd	0.78	1.66									-22.9
8/2/2011	2	41.724222	29	28	24.8	5.19	nd	0.17	1.17									-15.7
8/2/2011	3	41.690747	28	27	25.4	8.12	0.03	0.15	0.99									-12.8
8/2/2011	4	41.619800	30	28	25.3	2.78	0.11	0.01	1.16									-15.5
8/2/2011	5	41.623092	29	28	24.0	0.89	0.10	0.21	0.84									-10.2
8/2/2011	6	41.540378	30	28	24.8	3.85	0.47	0.28	1.11									-14.1
8/2/2011	7	41.512458	31	29	24.8	1.32	0.30	0.56	0.87									-10.2
8/2/2011			32	30		1.65	0.56	1.14	1.21									-14.8
8/23/2011	1	41.768336	21	20	24.7	4.92	12.56	14.90	3.63	10.82	1.51	2.75	1.47					-27.7

Date	Stn	Latitude	Salinity (ppt)	Corrected Salinity (ppt)	Temp (°C)	[chl a] (µg/L)	$[NO_3^-]$ (µM)	$[NH_4^+]$ (µM)	$[PO_4^{3-}]$ (µM)	$\delta^{15}N\text{-}NO_3^-$	stdev	$\delta^{18}O\text{-}NO_3^-$	stdev	$\delta^{15}N\text{-}PM$	stdev	$\delta^{15}N\text{-}chla$	stdev	N*
8/23/2011	2	41.724222	20	19	24.9	18.53	6.91	1.26	0.61	11.25	0.22	5.10	0.14					1.31
8/23/2011	3	41.690747	23	22	25.3	12.75	0.19	0.16	nd									
8/23/2011	4	41.619800	30	28	24.7	7.87	nd	0.34	nd									
8/23/2011	5	41.623092	35	33	24.9	8.92	nd	0.86	0.08									2.48
8/23/2011	6	41.540378	31	29	23.2	5.52	nd	0.28	nd									
8/23/2011	7	41.512458	36	34	22.9	2.05	0.23	0.54	0.62									-6.25
8/23/2011	8	41.437311	32	30	22.5	2.32	1.27	0.45	nd									
8/23/2011	9	41.439353	32	30	21.5	1.24	0.12	0.05	0.76									-9.09
9/28/2011	1	41.768336	20	19	22.9	12.28	5.81	0.19	nd									
9/28/2011	2	41.724222	20	19	23.0	18.94	nd	nd	nd									
9/28/2011	3	41.690747	24	23	22.5	17.00	nd	nd	nd									
9/28/2011	4	41.619800	30	28	21.2	5.98	nd	nd	nd									
9/28/2011	5	41.623092	30	28	20.7	2.15	0.02	0.14	0.26									-1.1
9/28/2011	6	41.540378	31	29	20.2	1.50	1.22	3.41	0.18									4.65
9/28/2011	7	41.512458	32	30	19.0	1.52	0.09	0.44	0.58									-5.85
9/28/2011	8	41.437311	34	32	19.5	0.83	0.71	1.09	nd									
9/28/2011	9	41.439353	35	33	19.9	0.93	0.04	0.07	0.57									-6.11
11/22/2011	1	41.768336	15	14	10.4	2.08	42.81	6.50	3.00	8.65	0.39	1.63	0.39	10.65	1.31			4.21
11/22/2011	2	41.724222	16	15	10.8	5.94	34.96	3.81	2.29	8.23	0.62	2.33	0.83	9.86	0.28			5.03
11/22/2011	3	41.690747	24	23	10.1	14.16	22.08	3.85	2.10	7.34	0.23	1.13	0.05	10.40	0.77			-4.77
11/22/2011	4	41.619800	30	28	10.8	2.37	27.64	4.93	1.14	7.54	0.41	1.62	0.04	13.22	1.86			17.23
11/22/2011	5	41.623092	24	23	10.3	0.54	40.4	6.96	1.59	9.61	0.46	1.65	0.33	16.41	7.31			24.82
11/22/2011	6	41.540378	30	28	10.9	1.17	10.61	3.95	1.16	7.22	0.31	1.12	0.09	15.14	0.27			-1.1
11/22/2011	7	41.512458	30	28	11.8	1.22	17.16	3.87	1.45	7.28	0.59	1.37	0.50	13.49				0.73
1/6/2012	3	41.690747	31	29	5.0	0.87	47.56	5.21	1.43	7.34	0.81	2.37	0.72	13.3		16.54	0.58	32.79

Date	Stn	Latitude	Salinity (ppt)	Corrected Salinity (ppt)	Temp (°C)	[chl a] (µg/L)	$[NO_3^-]$ (µM)	$[NH_4^+]$ (µM)	$[PO_4^{3-}]$ (µM)	$\delta^{15}N\text{-}NO_3^-$	stdev	$\delta^{18}O\text{-}NO_3^-$	stdev	$\delta^{15}N\text{-}PM$	stdev	$\delta^{15}N\text{-}chla$	stdev	N*
1/6/2012	4	41.60717	34	32	5.4	1.18	24.12	1.74	1.80	7.16	0.58	3.08	0.69	14.3	7.9			-0.04
1/6/2012	6	41.55063	34	32	6.5	1.35	22.23	0.72	1.13	7.11	0.98	2.99	1.63	13.9		19.43	0.05	7.77
1/6/2012	8	41.49408	35	33	6.8	0.72	16.87	0.96	1.15	7.08	0.30	2.42	0.60	20.9				2.33
1/10/2012	1	41.768336				1.79	23.22	6.96	2.20	8.19	0.47	2.53	1.27	16.2	0.1	14.99	0.44	-2.12
2/3/2012		41.492147	34	32	4.8	19.95	0.21	0.59	0.10					10.96		19.02	0.67	2.1
2/6/2012	1	41.768336			4.4	11.53	19.56	7.36	1.31	9.22	0.38	3.59	0.77	11.13		22.11	0.75	8.86
2/6/2012		41.57	27	26	3.8	10.68	nd	0.33	2.80					15.27		26.76	0.56	-41.6
4/29/2012	1	41.768336	31	29	13.4	14.62	1.27	0.67	0.02					13.92				4.52
4/29/2012	2	41.724222	31	29	13.0	12.81	0.63	0.39	0.11					11.31				2.16
4/29/2012	3	41.690747	31	29	12.9	8.44	nd	0.06	nd					11.28				
4/29/2012	4	41.619800	34	32	12.5	2.99	nd	0.20	0.24					10.01	3.89			-0.74
4/29/2012	5	41.623092	34	32	11.7	2.19	0.07	0.20	0.51					8.46	3.82	11.37	0.20	-4.99
4/29/2012	6	41.540378	34	32	11.9	1.28	nd	0.15	0.49					10.81	3.96	12.08		-4.79
4/29/2012	7	41.512458	36	34	10.6	1.45	0.05	0.51	0.60					7.59	2.49	10.12		-6.14
6/6/2012	1	41.768336	26	25	18.2	8.68	1.33	12.44	2.33	9.67	0.76	2.52	1.47	10.75		9.67	0.49	-20.6
6/6/2012	2	41.724222	28	27	17.9	10.41	4.54	2.98	1.09	10.61	0.17	5.49	0.15	14.24				-7.02
6/6/2012	3	41.690747	30	28	17.3	11.95	nd	0.38	0.31					13.47				-1.68
6/6/2012	4	41.619800	31	29	16.4	9.12	nd	0.21	0.40					11.20	2.93	7.42	0.31	-3.29
6/6/2012	5	41.623092	33	31	16.7	4.24	nd	0.47	0.60					22.67	0.27			-6.23
6/6/2012	6	41.540378	34	32	16.5	2.98	0.02	0.69	0.80					18.35	1.05			-9.19
6/6/2012	7	41.512458	32	30	16.5	3.23	0.06	0.58	0.61					26.62	0.90	27.92		-6.22
6/6/2012	8	41.437311	34	32	16.4	2.46	nd	0.20	0.54					30.10	2.28	27.63		-5.54
6/6/2012	9	41.439353	35	33	15.9	1.91	0.12	0.80	0.62					27.60	5.91	20.50	0.52	-6.1
6/20/2012	1	41.768336	22	21	22.2	33.55	nd	0.31	0.27					10.89	0.57	18.04		-1.11
6/20/2012	2	41.724222	25	24	22.9	10.10	nd	0.14	0.15					9.75	0.25	11.24	0.30	0.64
6/20/2012	3	41.690747	29	28	22.8	2.94	nd	0.30	0.46					7.54	0.71	14.57	0.17	-4.16

Date	Stn	Latitude	Salinity (ppt)	Corrected Salinity (ppt)	Temp (°C)	[chl a] (µg/L)	$[NO_3^-]$ (µM)	$[NH_4^+]$ (µM)	$[PO_4^{3-}]$ (µM)	$\delta^{15}N\text{-}NO_3^-$	stdev	$\delta^{18}O\text{-}NO_3^-$	stdev	$\delta^{15}N\text{-}PM$	stdev	$\delta^{15}N\text{-}chla$	stdev	N*
6/20/2012	4	41.619800	30	28	20.1	1.36	nd	0.61	0.41					19.27	1.88	22.02	0.20	-3.05
6/20/2012	5	41.623092	30	28	20.1	2.64	nd	0.41	0.21					21.95	0.65	15.21		-0.05
6/20/2012	6	41.540378	31	29	19.1	1.30	nd	0.62	0.88					18.02	2.19			-10.6
6/20/2012	7	41.512458	31	29	19.3	1.44	nd	0.38	0.49							33.17		-4.56
7/3/2012	1	41.768336	27	26	24.3	13.87	0.24	0.21	0.61					10.09	13.70	16.77	0.16	-6.41
7/3/2012	2	41.724222	25	24	24.1	16.43	0.31	0.29	0.47					25.11	1.86	19.34	0.18	-4.02
7/3/2012	3	41.690747	29	28	23.7	5.81	nd	0.35	0.96					24.98	0.41	17.63	0.48	-12.1
7/3/2012	4	41.619800	30	28	23.5	2.49	nd	nd	0.87					28.43	7.88			-11.0
7/3/2012	5	41.623092	30	28	23.0	2.46	nd	0.20	0.35					23.85	0.20	14.85		-2.5
7/3/2012	6	41.540378	30	28	22.8	2.29	0.12	0.84	1.91					22.41	2.50			-26.7
7/3/2012	7	41.512458	31	29	22.1	1.62	nd	0.13	0.70					18.30	3.06	5.53		-8.17
7/3/2012	8	41.437311	34	32	22.1		nd	0.34	0.69					23.33	4.51			-7.8
7/3/2012	9	41.439353	34	32	22.1	3.76	0.07	nd	0.56					22.72	0.93			-5.99
8/8/2012	1	41.768336	25	24	26.1	44.73	0.25	0.24	3.74									-56.5
8/8/2012	2	41.724222	29	28	26.6	30.69	0.36	0.37	2.34									-33.8
8/8/2012	3	41.690747	30	28	25.7	18.96	nd	0.39	4.17									-63.4
8/8/2012	4	41.619800	31	29	24.9	8.39	nd	0.37	1.16									-15.3
8/8/2012	5	41.623092	30	28	24.9	11.43	nd	0.35	2.47							7.83		-36.3
8/8/2012	6	41.540378	32	30	24.3	8.47	0.72	1.04	1.09									-12.8
8/8/2012	7	41.512458	30	28	23.9	5.17	nd	0.11	3.35									-50.6
8/8/2012	8	41.437311	31	29	22.7	5.41	0.17	0.14	0.58							17.76	1.56	-6.07
8/8/2012	9	41.439353	31	29	22.6	6.23	nd	nd	2.50									-37.1
8/20/2012	1	41.768336	25	24	25.6	29.00	12.56	1.72	7.56	13.15	0.63	7.02	1.09					
8/20/2012	2	41.724222	25	24	25.4	25.39	0.69	0.38	5.55									-84.8
8/20/2012	3	41.690747	28	27	24.9	15.64	nd	0.28	5.22							32.58		-80.3
8/20/2012	4	41.619800	31	29	23.7	17.63	nd	0.94	3.06									-45.1

Date	Stn	Latitude	Salinity (ppt)	Corrected Salinity (ppt)	Temp (°C)	[chl a] (µg/L)	$[NO_3^-]$ (µM)	$[NH_4^+]$ (µM)	$[PO_4^{3-}]$ (µM)	$\delta^{15}N\text{-}NO_3^-$	stdev	$\delta^{18}O\text{-}NO_3^-$	stdev	$\delta^{15}N\text{-}PM$	stdev	$\delta^{15}N\text{-}chla$	stdev	N*
8/20/2012	5	41.623092	30	28	24.3	6.19	0.18	1.08	2.94									-42.9
8/20/2012	6	41.540378	31	29	23.0	2.89	0.54	1.89	1.88							17.11	0.54	-24.8
8/20/2012	7	41.512458	31	29	23.1	2.00	nd	0.30	4.28							11.14	0.33	-65.3
8/20/2012	8	41.437311	34	32	22.2	3.51	0.60	1.29	3.49							12.29	0.49	-51.1
8/20/2012	9	41.439353	34	32	22.6		nd	0.11	1.82							10.53	0.24	-26.1
9/24/2012	1	41.768336	34	32	19.8	13.03	10.12	10.13	4.11	11.80	0.00	3.66	0.09	6.68	0.08			-42.6
9/24/2012	2	41.724222	30	28	19.4	10.48	10.18	7.40	3.67	11.29	0.31	3.95	0.86	7.51	0.53			-38.2
9/24/2012	3	41.690747	32	30	19.5	8.95	4.05	2.35	1.86	9.85	0.31	2.86	1.03	10.23	0.50			-20.5
9/24/2012	4	41.619800	32	30	19.4	2.34	1.93	2.63	1.54	6.39	0.34	3.71	0.05	8.05	0.05			-17.2
9/24/2012	6	41.540378	34	32	19.4	1.72	2.30	2.75	3.42	9.61	0.84	5.76	0.07	7.67	0.20	8.41		-46.8
9/24/2012	7	41.512458	35	33	19.2	1.48	2.23	2.76	0.45	5.49	0.44	3.70	0.93	8.39	1.94			0.69
9/24/2012	8	41.437311	35	33	19.1	1.18	2.06	3.20	2.03	8.71	1.30	0.90	1.03	5.70	0.77	17.6		-24.3
9/24/2012	9	41.439353	35	33	19.0	1.20	1.13	0.88	1.05					7.76	0.87	12.79		-11.9
10/17/2012	1	41.768336	30	28	15.5	4.76	23.88	16.01	5.36	11.88	0.23	4.60	1.13	5.80	0.53			-43.0
10/17/2012	2	41.724222	32	30	15.1	4.11	11.74	6.88	3.30	10.07	0.07	2.68	0.04	8.06	0.30			-31.3
10/17/2012	3	41.690747	33	31	15.1	5.90	2.29	2.16	2.44	6.19	0.30	7.85	2.31	8.64	0.09			-31.7
10/17/2012	4	41.619800	35	33	15.4	3.52	7.05	3.77	2.70	9.23	0.82	3.64	1.26	9.28	0.03			-29.5
10/17/2012	5	41.623092	36	34	15.7	4.19	4.08	1.31	3.72	6.99	0.23	3.98	0.44	9.02	0.62			-51.2
10/17/2012	6	41.540378	35	33	15.7	1.39	3.92	2.53	3.19	4.97	0.61	2.50	0.79	8.85	0.76			-41.7
10/17/2012	7	41.512458	36	34	15.8	1.75	4.81	1.10	2.31	7.49	1.11	2.70	0.21	12.91	4.56			-28.2
10/17/2012	8	41.437311	36	34	15.9	1.69	3.78	0.61	3.08	7.62	0.91	6.61	2.38	9.28	0.27			-42.0
10/17/2012	9	41.439353	36	34	15.9	1.82	2.57	0.22	1.67	6.40	0.92	6.06	0.09	13.33	3.21			-21.0
11/20/2012	1	41.768336	30	28	9.6	1.55	12.96	7.96	2.99	8.98	0.30	0.93	0.33	6.81	0.74			-24.0
11/20/2012	2	41.724222	31	29	9.3	2.34	15.72	7.19	3.02	8.83	0.09	1.81	0.08	7.18				-22.5
11/20/2012	3	41.690747	31	29	9.4	3.57	8.75	5.40	0.92	8.17	0.07	3.31	0.09					2.33
11/20/2012	4	41.619800	34	32	9.1	1.20	7.12	3.15	1.80	7.45	0.03	2.80	0.06	8.22	0.88			-15.6

Date	Stn	Latitude	Salinity (ppt)	Corrected Salinity (ppt)	Temp (°C)	[chl a] (µg/L)	$[NO_3^-]$ (µM)	$[NH_4^+]$ (µM)	$[PO_4^{3-}]$ (µM)	$\delta^{15}N\text{-}NO_3^-$	stdev	$\delta^{18}O\text{-}NO_3^-$	stdev	$\delta^{15}N\text{-}PM$	stdev	$\delta^{15}N\text{-}chla$	stdev	N*
11/20/2012	5	41.623092	35	33	10.1	5.74	5.68	3.14	1.48	8.99	0.26	3.00	0.96	7.92				-12.0
11/20/2012	6	41.540378	35	33	9.2	3.77	4.27	1.22	3.37	9.36	0.15	5.23	0.05	9.42	0.00			-45.5
11/20/2012	7	41.512458	36	34	10.8	0.91	3.37	1.96	2.06	6.40	0.13	0.84	0.14	7.54	0.37			-24.7
11/20/2012	8	41.437311	36	34	11.2	1.40	3.29	1.42	1.14	5.32	0.95	2.56	0.15	7.83	0.67			-10.6
11/20/2012	9	41.439353	37	35	11.9	1.40	2.87	1.29	1.53	4.23	0.07	-0.84	0.38	9.27	1.39			-17.4

Table A-5. Subsurface water data. Salinity was corrected between collection and analysis (see chapter 2).

ID	Latitude	Salinity (ppt)	Corrected Salinity (ppt)	Temp. (°C)	$[NO_3^-]$ (µM)	$[NH_4^+]$ (µM)	$[PO_4^{3-}]$ (µM)	$\delta^{15}N$-NO_3^- (‰)	stdev	$\delta^{18}O$-NO_3^- (‰)	stdev	$\delta^{15}N$-PM (‰)	stdev
6/20/12 1D	41.768336	27	26	20.8	1.71	2.75	1.66					16.49	0.69
6/20/12 2D	41.724222	31	29	18.5	1.82	6.98	2.42					15.91	0.00
6/20/12 3D	41.690747	30	28	19.5	0.34	2.03	1.44					17.62	1.89
6/20/12 4D	41.619800	31	29	18.9	0.28	1.46	2.13					17.17	1.55
6/20/12 5D	41.623092	33	31	18.5	0.2	1.26	0.91					22.10	5.89
6/20/12 6D	41.540378	31	29	19.6	nd	0.91	1.1					20.68	0.54
6/20/12 7D	41.512458	34	32	17.6	0.4	1.18	nd					25.33	1.52
7/3/12 1D	41.768336	29	28	22.6	1.4	5.63	2.5					22.20	0.59
7/3/12 2D	41.724222	31	29	20.9	1.08	6.14	2.12					17.95	
7/3/12 3D	41.690747	31	29	21	0.7	6.49	2.93					10.84	0.07
7/3/12 4D	41.619800	31	29	19	0.47	2.06	1.69					10.31	1.23
7/3/12 5D	41.623092	31	29	19.5	0.42	2.08	0.79					14.59	3.90
7/3/12 6D	41.540378	32	30	18.5	0.18	1.32	0.92					10.52	2.44
7/3/12 7D	41.512458	34	32	18.3	0.23	0.89	0.69					11.73	0.77
7/3/12 8D	41.437311	35	33	18	0.48	1.78	0.8					13.23	3.65
7/3/12 9D	41.439353	35	33	18.2	nd	1.48	1.67					9.71	1.41
8/20/12 1D	41.768336	29	28	24.4	2.47	15.00	6.41	15.04	0.30	8.99	0.95	8.58	0.77
8/20/12 2D	41.724222	30	28	23.5	1.87	8.48	3.66	22.42	0.76	13.33	2.91	14.54	2.14
8/20/12 3D	41.690747	30	28	23.4	1.64	12.36	4.58					14.69	0.05
8/20/12 4D	41.619800	31	29	23.1	0.11	1.25	1.62					12.80	0.83
8/20/12 5D	41.623092	30	28	21.8	1.29	4.77	2.61					9.48	6.29
8/20/12 6D	41.540378	31	29	23.6	0.52	3.31	1.84					11.63	2.89
8/20/12 7D	41.512458	32	30	19.7	1.6	2.35	3					12.39	2.49
8/20/12 8D	41.437311	34	32	16.9	5.61	5.99	2.06	8.63	1.53	5.52	0.70	15.99	3.03
8/20/12 8D	41.437311	34	32	16.9	5.61	5.99	2.06						

ID	Latitude	Salinity (ppt)	Corrected Salinity (ppt)	Temp. (°C)	$[NO_3^-]$ (µM)	$[NH_4^+]$ (µM)	$[PO_4^{3-}]$ (µM)	$\delta^{15}N$-NO_3^- (‰)	stdev	$\delta^{18}O$-NO_3^- (‰)	stdev	$\delta^{15}N$-PM (‰)	stdev
8/20/12 9D	41.439353	34	32	18.9	3.04	2.83	1.81					12.30	10.31
8/23/11 4D	41.619800	34	32	22.9	0.61	2.92	0.38						
8/23/11 5D	41.623092	34	32	23.6	2.08	6.22	1.46						
8/23/11 7D	41.512458	34	32	20.8	2.03	3.98	1.18						
8/23/11 8D	41.437311	33	31	21.4	1.22	3.16	nd						
8/23/11 9D	41.439353	34	32	17.1	3.15	4.83	1.16						
8-23-11 1D	41.768336	30	28	24.9	1.88	16.92	0.76	3.88	0.06	12.20	2.13		
8-23-11 2D	41.724222	31	29	22.4	1.34	7.72	4.16	10.61	2.15	14.74	0.55		
8-23-11 6D	41.540378	35	33	22.5	1.66	3.19	0.39	34.55	1.13	4.06	0.92		
8-23-11 3D	41.690747	31	29	23.9	1.5	10.11	1.59	16.65	1.80	11.45	5.51		
9/28/11 4D	41.619800	30	28	21.6	1.13	6.43	1.07						
9/28/11 5D	41.623092	32	30	21.5	0.4	1.18	1.46						
9/28/11 7D	41.512458	32	30	19.8	0.43	0.37	0.69						
9/28/11 8D	41.437311	34	32	19.3	0.47	0.99	nd						
9/28/11 9D	41.439353	35	33	19.5	nd	0.37	nd						
9-28-11 1D	41.768336	27	26	21.6	2.73	8.64	0.26	8.10	1.38	1.11	0.35		
9-28-11 2D	41.724222	30	28	21.5	1.77	10.03	0.93	8.38	0.09	0.69	0.80		
9-28-11 3D	41.690747	30	28	20.8	1.95	8.12	0.56	16.79	1.85	0.89	1.35		
9-28-11 6D	41.540378	32	30	19.9	1.33	4.01	0.21	28.42	0.16	6.94	1.34		

Table A-6. Macroalgae collection data.

Sample ID	Date Collected	Scientific Name	Macroalgae color	Latitude	Longitude	Mean $\delta^{15}N$ (‰)	St. Dev	Mean $\delta^{13}C$ (‰)	St. Dev
N. tip of Coanicut Island									
2	7/15/2008	*Cladophora albida*	Green	41.57413	71.37161	10.60		-17.17	
3	7/15/2008	*Ulva* spp.	Green	41.57413	71.37161	11.36	0.21	-18.89	0.07
4	7/15/2008	*Codium fragile*	Green	41.57413	71.37161	10.45	0.09	-12.93	0.27
North Point									
1	7/15/2008	*Codium fragile*	Green	41.681889	71.3023056	10.64	0.05	-13.42	0.10
2	7/15/2008	*Ceramium virgatum*	Red	41.681889	71.3023056	10.34	0.07	-14.07	0.27
4	7/15/2008	*Ulva* spp.	Green	41.681889	71.3023056	11.05	0.17	-20.05	0.02
5	7/15/2008	*Ulva* spp.	Green	41.681889	71.3023056	14.31	0.02	-17.97	0.03
Hope Island									
1	7/15/2008	*Cladophora sericea*	Red	41.59662	71.3695	11.19	0.01	-20.20	0.04
3	7/15/2008	*Ulva* spp.	Green	41.59662	71.3695	10.06	0.07	-19.66	0.00
4	7/15/2008	*Codium fragile*	Green	41.59662	71.3695	9.49	0.03	-16.22	0.24
5	7/15/2008	*Ceramium virgatum*	Brown	41.59662	71.3695	10.65	0.09	-18.18	0.25
Patience Island									
1	7/15/2008	*Ulva* spp.	Green	41.6502361	71.3603139	14.57	0.14	-19.41	0.04
3	7/15/2008	*Grateloupia turuturu*	Brown	41.6502361	71.3603139	12.17	0.12	-18.24	0.07
Rumstick Point									
1	7/15/2008	*Grateloupia turuturu*	Brown	41.7062889	71.3021306	10.43	0.07	-17.23	0.13
2	7/15/2008	*Polysiphonia* spp.	Red	41.7062889	71.3021306	9.61	0.04	-20.08	0.01
3	7/15/2008	*Codium fragile*	Green	41.7062889	71.3021306	10.44	0.04	-14.85	0.14
4	7/15/2008	*Ulva* spp.	Green	41.7062889	71.3021306	10.74	0.02	-18.65	0.12
5	7/15/2008	*Ulva* spp.	Green	41.7062889	71.3021306	11.01	0.01	-17.17	0.02

Sample ID	Date Collected	Scientific Name	Macroalgae color	Latitude	Longitude	Mean $\delta^{15}N$ (‰)	St. Dev	Mean $\delta^{13}C$ (‰)	St. Dev
Prudence Island N.									
1	7/15/2008	*Neosiphonia harveyi; polysiphonia*	Red	41.6443167	71.3527833	11.23	0.01	-23.03	0.01
2	7/15/2008	*Ulva* spp.	Green	41.6443167	71.3527833	14.14	0.04	-18.84	0.07
Hog Island									
1	7/15/2008	*Ulva* spp.	Green	41.6374667	71.2736778	9.43	0.03	-15.47	0.02
2	7/15/2008	*Grateloupia turuturu*	Brown	41.6374667	71.2736778	10.40	0.06	-18.21	0.04
Dyer Island									
1	7/15/2008	*Ceramium virgatum*	Red	41.5801167	71.2989583	9.58	0.06	-21.95	0.04
2	7/15/2008	*Codium fragile*	Green	41.5801167	71.2989583	9.23	0.05	-16.37	0.06
3	7/15/2008		Red	41.5801167	71.2989583	9.12	0.03	-21.64	0.05
4	7/15/2008	*Ulva* spp.	Green	41.5801167	71.2989583	10.54	0.00	-22.58	0.05
5	7/15/2008	*Ulva* spp.	Green	41.5801167	71.2989583	9.67	0.08	-21.25	0.03
6	7/15/2008	*Cladophora sericea*	Green	41.5801167	71.2989583	10.29	0.03	-16.60	0.04
Prudence N. of Nag									
1	7/15/2008	*Neosiphonia harveyi*	Red	41.6328	71.34959	11.74	0.02	-22.29	0.03
2	7/15/2008	*Grateloupia turuturu*	Brown	41.6328	71.34959	12.03	0.04	-18.56	0.01
3	7/15/2008	*Ulva* spp.	Green	41.6328	71.34959	11.75	0.10	-19.75	0.02
4	7/15/2008	*Bryopsis plumosa*	Green	41.6328	71.34959	12.47	0.10	-18.35	0.04
T-Wharf									
1	7/15/2008	*Ulva* spp.	Green	41.5784278	71.3210139	11.58	0.03	-20.38	0.10
2	7/15/2008	*Ceramium virgatum*	Red	41.5784278	71.3210139	11.28	0.05	-14.65	0.14
Conimicut Point									
1	7/15/2008	*Ulva* spp.	Green	41.7169389	71.3450639	7.63	0.07	-16.87	0.02

Sample ID	Date Collected	Scientific Name	Macroalgae color	Latitude	Longitude	Mean $\delta^{15}N$ (‰)	St. Dev	Mean $\delta^{13}C$ (‰)	St. Dev
2	7/15/2008	*Ulva* spp.	Green	41.7169389	71.3450639	9.15	0.05	-15.05	0.02
3	7/15/2008	*Fucus* spp.	Brown	41.7169389	71.3450639	10.18	0.08	-15.03	0.04
Fox Island									
1	7/17/2008	*Spyridia filamentosa*	Red	41.5547278	71.4191944	11.29	0.10	-16.11	0.01
2	7/17/2008	*Ceramium strictum*	Red	41.5547278	71.4191944	11.11	0.04	-18.18	0.02
3	7/17/2008	*Cystoclonium purpureum*	Red	41.5547278	71.4191944	12.83	0.00	-17.67	0.03
4	7/17/2008	*Cladophora sericea*	Green	41.5547278	71.4191944	11.16	0.04	-17.02	0.03
5	7/17/2008	*Ulva* spp.	Green	41.5547278	71.4191944	11.00	0.21	-20.62	0.10
6	7/17/2008	*Codium fragile*	Green	41.5547278	71.4191944	10.57	0.09	-15.80	0.01
Plum Island									
1	7/17/2008	*Ulva* spp.	Green	41.580275	71.405225	10.53	0.08	-17.03	0.04
3	7/17/2008	*Condrus crispus*	Brown	41.580275	71.405225	10.34	0.09	-20.33	0.17
4	7/17/2008	*Grateloupia turuturu*	Brown	41.580275	71.405225	11.09	0.10	-16.95	1.06
Field's Point									
1	7/19/2008	*Fucus distichus*	Brown	41.787125	71.379125	7.25	0.16	-12.63	0.01
2	7/19/2008	*Ulva* spp.	Green	41.787125	71.379125	13.98	0.07	-8.59	0.03
3	7/19/2008	*Ulva* spp.	Green	41.787125	71.379125	12.31	0.06	-13.29	0.09
Rocky Point									
1	7/19/2008	*Grateloupia turuturu*	Brown	41.6917389	71.3633389	13.45	0.03	-17.22	0.00
Bullock's Reach									
3	7/19/2008	*Ulva* spp.	Green	41.7382472	71.3812278	11.85	0.03	-11.59	0.12
Rose Island									
2	7/27/2008	*Ulva* spp.	Green	41.4982111	71.3411083	9.05	0.01	-18.30	0.09
3	7/27/2008	*Bryopsis plumosa*	Green	41.4982111	71.3411083	9.27	0.08	-20.05	0.01

Sample ID	Date Collected	Scientific Name	Macroalgae color	Latitude	Longitude	Mean $\delta^{15}N$ (‰)	St. Dev	Mean $\delta^{13}C$ (‰)	St. Dev
Dutch Island									
1	7/27/2008	*Condrus crispus*	Brown	41.4964341	71.4044472	10.79	0.13	-21.59	0.17
2	7/27/2008	*Grateloupia turuturu*	Brown	41.4964341	71.4044472	12.07	0.02	-18.59	0.01
4	7/27/2008	*Ulva* spp.	Green	41.4964341	71.4044472	11.51	0.02	-17.58	0.05
Beavertail Point									
1	7/27/2008	*Condrus crispus*	Brown	41.4507556	71.4004167	8.13	0.06	-23.80	0.17
2	7/27/2008	*Polysiphonia* spp.	Red	41.4507556	71.4004167	9.04	0.09	-20.33	0.32
Castle Rock									
2	7/27/2008	*Fucus* spp.	Brown	41.4571306	71.3591028	8.16	0.03	-12.46	0.16
3	7/27/2008	*Polysiphonia fucoides*	Brown	41.4571306	71.3591028	7.72	0.02	-23.16	0.03
4	7/27/2008	*Ascophyllum nodosum*	Green	41.4571306	71.3591028	9.10	0.10	-18.35	0.21
7	7/27/2008	*Condrus crispus*	Red	41.4571306	71.3591028	8.35	0.19	-22.67	0.05
Gould Island W.									
1	7/27/2008	*Cystoclonium purpureum*	Red	41.53557	71.34649	10.80	0.05	-14.79	0.01
2	7/27/2008	*Bryopsis plumosa*	Green	41.53557	71.34649	11.47	0.13	-18.17	0.02
3	7/27/2008	*Champia parvula*	Red	41.53557	71.34649	10.68	0.03	-15.67	0.01
5	7/27/2008	*Grateloupia turuturu*	Brown	41.53557	71.34649	10.58	0.03	-16.34	0.01
Gould Island E.									
1	7/27/2008	*Ceramium virgatum*	Red	41.53364	71.34236	10.46	0.03	-15.12	0.20
Graduate School of Oceanography									
1	7/27/2008	*Codium fragile*	Green	41.4921417	71.4189139	12.23	0.10	-14.30	0.01
2	7/27/2008	*Fucus spiralis*	Brown	41.4921417	71.4189139	10.84	0.02	-11.56	0.02
3	7/27/2008	*Ulva* spp.	Green	41.4921417	71.4189139	11.27	0.00	-17.44	0.01
4	7/27/2008	*Ulva* spp.	Green	41.4921417	71.4189139	11.17		-17.64	

Sample ID	Date Collected	Scientific Name	Macroalgae color	Latitude	Longitude	Mean $\delta^{15}N$ (‰)	St. Dev	Mean $\delta^{13}C$ (‰)	St. Dev
5	7/27/2008	*Agardhiella subulata*	Red	41.4921417	71.4189139	11.37	0.00	-18.38	0.13
6	7/27/2008	*Grateloupia turuturu*	Brown	41.4921417	71.4189139	12.00	0.05	-17.53	0.01
7	7/27/2008	*Agardhiella subulata*	Red	41.4921417	71.4189139	11.86	0.00	-18.81	0.02
8	7/27/2008	*Ceramium virgatum; Ulothrix flacca*	Red	41.4921417	71.4189139	11.11	0.00	-18.57	0.31
Whale Rock									
1	7/27/2008	*Laminaria* spp. *Or Saccharina* spp.	Brown	41.4443528	71.4236583	9.50	0.09	-14.27	0.22
3	7/27/2008	*Grateloupia turuturu*	Brown	41.4443528	71.4236583	9.88	0.00	-19.88	0.04

Table A-7. Hard clam (*Mercenaria mercenaria*) collection data. Samples were numbered sequentially, and sorted by sample location.

Sample ID	Date Collected	Latitude	Longitude	L (mm)	W (mm)	Mean $\delta^{15}N$ (‰)	St. Dev
Calf Pasture							
1	8/1/2012	41.63002778	71.39763889	71	64	13.29	0.05
2	8/1/2012	41.63002778	71.39763889	100	84	13.28	0.09
3	8/1/2012	41.63002778	71.39763889	96	78	13.02	0.25
4	8/1/2012	41.63002778	71.39763889	91	77	13.55	0.15
5	8/1/2012	41.63002778	71.39763889	83	67	13.11	0.02
6	8/1/2012	41.63002778	71.39763889	77	63	13.22	0.04
7	8/1/2012	41.63002778	71.39763889	70	63	12.88	0.09
8	8/1/2012	41.63002778	71.39763889	70	58	12.97	0.09
9	8/1/2012	41.63002778	71.39763889	79	64	13.12	0.25
10	8/1/2012	41.63002778	71.39763889	72	61	13.14	0.01
11	8/1/2012	41.63002778	71.39763889	79	64	13.25	0.30
12	8/1/2012	41.63002778	71.39763889	95	84	13.79	0.14
North Kingstown							
13	8/1/2012	41.65438889	71.40300000	75	65	14.36	0.13
14	8/1/2012	41.65438889	71.40300000	79	59	12.99	0.11
15	8/1/2012	41.65438889	71.40300000	80	65	13.68	0.02
16	8/1/2012	41.65438889	71.40300000	69	57	13.62	0.04
17	8/1/2012	41.65438889	71.40300000	63	52	14.05	0.09
18	8/1/2012	41.65438889	71.40300000	92	80	13.55	0.08
19	8/1/2012	41.65438889	71.40300000	92	78	14.07	0.04
20	8/1/2012	41.65438889	71.40300000	65	54	12.63	0.15
21	8/1/2012	41.65438889	71.40300000	57	50	12.50	0.18
22	8/1/2012	41.65438889	71.40300000	93	76	14.39	0.21
23	8/1/2012	41.65438889	71.40300000	59	53	14.60	0.01
24	8/1/2012	41.65438889	71.40300000	88	78	13.75	0.23

Sample ID	Date Collected	Latitude	Longitude	L (mm)	W (mm)	Mean $\delta^{15}N$ (‰)	St. Dev
Providence River							
25	9/7/2012	41.76083333	71.36716667	75	62	14.51	0.03
26	9/7/2012	41.76083333	71.36716667	81	70	14.13	0.05
28	9/7/2012	41.76083333	71.36716667	74	59	14.41	0.01
29	9/7/2012	41.76083333	71.36716667	71	61	14.48	0.03
30	9/7/2012	41.76083333	71.36716667	71	59	14.41	0.08
31	9/7/2012	41.76083333	71.36716667	76	59	14.22	0.01
32	9/7/2012	41.76083333	71.36716667	77	65	14.00	0.07
33		41.76083333	71.36716667	75.00	57	14.02	0.06
34	9/7/2012	41.76083333	71.36716667	68	57	13.77	0.05
35	9/7/2012	41.76083333	71.36716667	77	64	14.56	0.09
36	9/7/2012	41.76083333	71.36716667	72	60	14.20	0.41
Rocky Point							
37	9/7/2012	41.69900000	71.35185000	92	79	13.83	0.01
38		41.69900000	71.35185000	75	66	13.74	0.70
39	9/7/2012	41.69900000	71.35185000	87	72	14.24	0.09
40	9/7/2012	41.69900000	71.35185000	80	63	13.89	0.05
41	9/7/2012	41.69900000	71.35185000	71	61	14.35	0.12
42	9/7/2012	41.69900000	71.35185000	80	70	13.79	
43	9/7/2012	41.69900000	71.35185000	79	67	14.18	0.24
44	9/7/2012	41.69900000	71.35185000	84	67	14.24	0.05
45		41.69900000	71.35185000	91	78	13.91	0.08
46	9/7/2012	41.69900000	71.35185000	90	78	14.19	0.17
48	9/7/2012	41.69900000	71.35185000	76	64	14.03	0.33
49	9/7/2012	41.69900000	71.35185000	72	64	14.20	0.01
Prudence Island							
50	9/7/2012	41.63425000	71.32703333	89.00	77	13.19	0.08

Sample ID	Date Collected	Latitude	Longitude	L (mm)	W (mm)	Mean $\delta^{15}N$ (‰)	St. Dev
51	9/7/2012	41.63425000	71.32703333	59	50	12.49	0.03
52	9/7/2012	41.63425000	71.32703333	82	68	13.15	0.04
53	9/7/2012	41.63425000	71.32703333	72	64	13.86	0.03
55	9/7/2012	41.63425000	71.32703333	88	75	13.49	0.06
56	9/7/2012	41.63425000	71.32703333	84	70	13.44	0.03
57	9/7/2012	41.63425000	71.32703333	76	62	13.75	0.83
58	9/7/2012	41.63425000	71.32703333	46	38	14.06	0.34
59	9/7/2012	41.63425000	71.32703333	59	49	13.14	0.05
60	9/7/2012	41.63425000	71.32703333	58	46	13.20	0.22
61	9/7/2012	41.63425000	71.32703333	78	63	13.24	0.19
Hog Island							
62	9/7/2012	41.63560000	71.27815000	110	98	13.71	0.05
64	9/7/2012	41.63560000	71.27815000	107	89	13.15	0.36
65	9/7/2012	41.63560000	71.27815000	104	86	13.55	0.11
66	9/7/2012	41.63560000	71.27815000	92	79	13.47	0.01
67	9/7/2012	41.63560000	71.27815000	103	85	12.93	0.06
69	9/7/2012	41.63560000	71.27815000	94	82	12.86	0.17
70	9/7/2012	41.63560000	71.27815000	64	52	12.62	0.83
71	9/7/2012	41.63560000	71.27815000	94	80	13.48	0.02
72	9/7/2012	41.63560000	71.27815000	94	84	13.82	0.90
73	9/7/2012	41.63560000	71.27815000	99	88	13.03	0.33
Conditional Area B							
74	9/10/2012	41.67458333	71.33950000	81	69	13.91	0.06
75	9/10/2012	41.67458333	71.33950000	60	49	13.75	0.10
76	9/10/2012	41.67458333	71.33950000	65	54	13.80	0.14
77	9/10/2012	41.67458333	71.33950000	69	56	13.67	0.00
78	9/10/2012	41.67458333	71.33950000	68	57	13.70	0.17

Sample ID	Date Collected	Latitude	Longitude	L (mm)	W (mm)	Mean $\delta^{15}N$ (‰)	St. Dev
79	9/10/2012	41.67458333	71.33950000	70	61	13.31	0.05
80	9/10/2012	41.67458333	71.33950000	67	55	13.58	0.12
81	9/10/2012	41.67458333	71.33950000	75	60	13.68	0.08
82	9/10/2012	41.67458333	71.33950000	83	66	13.56	0.15
83	9/10/2012	41.67458333	71.33950000	80	67	13.77	0.02
85	9/10/2012	41.67458333	71.33950000	59	51	13.67	0.04
Bissel Cove							
86	9/7/2012	41.54200000	71.41940000	87	73	14.75	0.01
87	9/7/2012	41.54200000	71.41940000	86	77	14.41	0.05
88	9/7/2012	41.54200000	71.41940000	88	76	14.23	0.07
89	9/7/2012	41.54200000	71.41940000	93	78	14.28	0.03
90	9/7/2012	41.54200000	71.41940000	93	82	14.19	0.05
91	9/7/2012	41.54200000	71.41940000	82	70	14.25	0.01
92	9/7/2012	41.54200000	71.41940000	94	79	14.85	0.05
93	9/7/2012	41.54200000	71.41940000	81	73	14.59	0.05
94	9/7/2012	41.54200000	71.41940000	102	89	14.11	0.10
95	9/7/2012	41.54200000	71.41940000	96	79	14.49	0.00
96	9/7/2012	41.54200000	71.41940000	85	74	14.11	0.08
Potowamut							
98	9/10/2012	41.66750000	71.39383333	74	63	13.93	0.07
99	9/10/2012	41.66750000	71.39383333	81	67	14.34	0.12
100	9/10/2012	41.66750000	71.39383333	83	69	14.11	0.01
101	9/10/2012	41.66750000	71.39383333	82	68	14.74	0.03
102	9/10/2012	41.66750000	71.39383333	85	69	14.64	0.05
103	9/10/2012	41.66750000	71.39383333	64	52	14.25	0.04
104	9/10/2012	41.66750000	71.39383333	82	69	13.81	0.04
105	9/10/2012	41.66750000	71.39383333	83	73	13.71	0.03

Sample ID	Date Collected	Latitude	Longitude	L (mm)	W (mm)	Mean $\delta^{15}N$ (‰)	St. Dev
106	9/10/2012	41.66750000	71.39383333	74	59	13.62	0.03
107	9/10/2012	41.66750000	71.39383333	82	69	13.53	0.07
108	9/10/2012	41.66750000	71.39383333	79	67	13.79	0.14
109	9/10/2012	41.66750000	71.39383333	74	64	13.71	0.06
Greenwich Cove							
110	9/10/2012	41.66933333	71.44215000	72	61	13.80	0.02
111	9/10/2012	41.66933333	71.44215000	65	52	14.64	0.06
112	9/10/2012	41.66933333	71.44215000	63	52	13.42	0.06
113	9/10/2012	41.66933333	71.44215000	62	49	13.73	0.13
	9/10/2012	41.66933333	71.44215000				
115	9/10/2012	41.66933333	71.44215000	60	50	13.85	0.03
116	9/10/2012	41.66933333	71.44215000	64	55	14.18	0.01
117	9/10/2012	41.66933333	71.44215000	56	47	14.63	0.04
118	9/10/2012	41.66933333	71.44215000	66	57	13.34	0.08
119	9/10/2012	41.66933333	71.44215000	58	44	13.94	0.03
120	9/10/2012	41.66933333	71.44215000	74	62	14.67	0.02
121	9/10/2012	41.66933333	71.44215000	70	62	13.96	0.13
Dyer Island							
138	10/23/2012	41.57783333	71.29836111	80	68	13.77	0.00
139	10/23/2012	41.57783333	71.29836111	75	65	13.60	0.25
140	10/23/2012	41.57783333	71.29836111	90	82	13.25	0.03
141	10/23/2012	41.57783333	71.29836111	85	71	13.50	0.01
142	10/23/2012	41.57783333	71.29836111	66	56	13.49	0.01
143	10/23/2012	41.57783333	71.29836111	81	73	13.53	0.15
145	10/23/2012	41.57783333	71.29836111	70	55	13.37	0.01
148	10/23/2012	41.57783333	71.29836111	90	79	13.09	0.03
T-Wharf							

Sample ID	Date Collected	Latitude	Longitude	L (mm)	W (mm)	Mean $\delta^{15}N$ (‰)	St. Dev
149	10/23/2012	41.58033333	71.32036111	95	84	13.40	0.07
150	10/23/2012	41.58033333	71.32036111	73	64	13.03	0.05
151	10/23/2012	41.58033333	71.32036111	77	69	13.00	0.04
152	10/23/2012	41.58033333	71.32036111	98	82	13.25	0.11
153	10/23/2012	41.58033333	71.32036111	52	40	12.56	0.02
155	10/23/2012	41.58033333	71.32036111	69	65	12.29	0.05
157	10/23/2012	41.58033333	71.32036111	47	41	12.38	0.13
158	10/23/2012	41.58033333	71.32036111	62	52	13.42	0.01
159	10/23/2012	41.58033333	71.32036111	69	60	13.39	0.03
160	10/23/2012	41.58033333	71.32036111	84	78	13.16	0.01
Wickford							
161	10/23/2012	41.57111111	71.43261111	98	84	14.18	0.05
162	10/23/2012	41.57111111	71.43261111	109	95	14.40	0.04
163	10/23/2012	41.57111111	71.43261111	91	71	14.36	0.01
164	10/23/2012	41.57111111	71.43261111	110	88	13.64	0.04
166	10/23/2012	41.57111111	71.43261111	101	90	14.42	0.01
168	10/23/2012	41.57111111	71.43261111	84	78	13.71	0.06
169	10/23/2012	41.57111111	71.43261111	91	81	13.81	0.03
170	10/23/2012	41.57111111	71.43261111	90	79	14.29	0.01
Bristol							
174	10/23/2012	41.65627778	71.29683333	81	70	13.85	0.03
175	10/23/2012	41.65627778	71.29683333	59	52	13.14	0.10
177	10/23/2012	41.65627778	71.29683333	53	60	12.64	0.04
178	10/23/2012	41.65627778	71.29683333	85	70	13.42	0.01
179	10/23/2012	41.65627778	71.29683333	45	40	12.87	0.03
180	10/23/2012	41.65627778	71.29683333	48	42	13.01	0.03
181	10/23/2012	41.65627778	71.29683333	46	42	12.84	0.11

Sample ID	Date Collected	Latitude	Longitude	L (mm)	W (mm)	Mean $\delta^{15}N$ (‰)	St. Dev
182	10/23/2012	41.65627778	71.29683333	84	72	12.75	0.00
Brenton Cove							
184	10/23/2012	41.47752778	71.33350000	80	67	13.24	0.02
186	10/23/2012	41.47752778	71.33350000	82	76	13.36	0.03
187	10/23/2012	41.47752778	71.33350000	68	55	12.53	0.05
188	10/23/2012	41.47752778	71.33350000	83	68	13.06	0.02
189	10/23/2012	41.47752778	71.33350000	69	58	13.68	0.05
190	10/23/2012	41.47752778	71.33350000	82	79	13.80	0.04
191	10/23/2012	41.47752778	71.33350000	72	68	13.24	0.09
192	10/23/2012	41.47752778	71.33350000	61	50	12.65	0.00
193	10/23/2012	41.47752778	71.33350000	75	71	13.49	0.06
194	10/23/2012	41.47752778	71.33350000	86	71	13.09	0.02
Graduate School of Oceanography							
196	10/23/2012	41.48738889	71.41805556	99	98	14.38	0.01
197	10/23/2012	41.48738889	71.41805556	86	84	13.94	0.09
198	10/23/2012	41.48738889	71.41805556	97	80	14.13	0.07
199	10/23/2012	41.48738889	71.41805556	86	71	14.15	0.01
201	10/23/2012	41.48738889	71.41805556	82	95	13.63	0.23
202	10/23/2012	41.48738889	71.41805556	91	80	13.32	0.04
204	10/23/2012	41.48738889	71.41805556	94	81	14.37	0.02
205	10/23/2012	41.48738889	71.41805556	84	72	13.69	0.11
206	10/23/2012	41.48738889	71.41805556	101	87	13.79	0.01

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