

2012

SPATIAL AND TEMPORAL PATTERNS IN NUTRIENT STANDING STOCK AND MASS-BALANCE IN RESPONSE TO LOAD REDUCTIONS IN A TEMPERATE ESTUARY

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**SPATIAL AND TEMPORAL PATTERNS IN NUTRIENT STANDING STOCK AND
MASS-BALANCE IN RESPONSE TO LOAD REDUCTIONS IN A TEMPERATE
ESTUARY**

BY

JASON SETH KRUMHOLZ

**A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
OCEANOGRAPHY**

UNIVERSITY OF RHODE ISLAND

2012

DOCTOR OF PHILOSOPHY DISSERTATION
OF
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DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
2012

ABSTRACT

The addition of excess organic matter into a system, commonly referred to as eutrophication (Nixon, 1995), is a widespread problem in estuaries throughout much of the world. To combat this trend, many management agencies are imposing regulations limiting the amount of nutrients (nitrogen and phosphorus) which can be discharged into coastal waters through wastewater treatment and agriculture. In 2005, the Rhode Island Department of Environmental Management (RIDEM) enacted legislation mandating that wastewater treatment facilities (WWTF) discharging their effluent into Narragansett Bay and its tributaries reduce the concentration of nitrogen in their effluent. This legislation will reduce wastewater nitrogen loading to the bay by 50% by 2014 with the ultimate goal of improving water quality, reducing hypoxia, and restoring lost ecosystem services (e.g. seagrass) to the bay. Early stages of this reduction took place between 2005-2009, reducing loadings at 11 WWTF's which discharge into the bay from 16-20mg/l total nitrogen to either 8 or 5mg/l.

Response of other estuaries to similar reductions in loading has been varied and complex, with relatively few ecosystems showing straightforward linear reductions in concentration, productivity, and chlorophyll with reduced load. The overall goal of this study is to quantify the impact of these initial loading reductions on the standing stock (Chapter 1), seasonal cycling (Chapter 2), and mass-balance (Chapter 3) of nitrogen and phosphorus in Narragansett Bay.

To accomplish this goal, we first reviewed data from a five-year study of surface nutrient concentration at 13 stations throughout Narragansett Bay (Chapter 1). Because Narragansett Bay is aligned along a north-south gradient of decreasing

urbanization and most sources of nutrients to the bay are located in or around the city of Providence, at the head of the estuary, we can establish down-bay relationships of nutrient constituents to see how their concentrations change spatially throughout the bay, and compare these relationships to past studies. We can also use established volume relationships to estimate the total standing stock of nutrients in the bay at any given time, and compare how this changes over the course of a year during the present survey and during past surveys. In response to a 30% reduction in the total annual load of dissolved inorganic nitrogen from all sources, which corresponds to a 17% reduction in total nitrogen, we saw measurable reductions in downbay concentrations and standing stocks approximately on par with these reductions. Phosphorus concentrations in the bay have declined dramatically (30-50%) in part due to recent loading reductions, but also in part due to management action in the 1980's and 1990's to remove phosphates from detergents and industrial surfactants. We also see changes in the way nitrate, nitrite, and ammonium are used on a downbay gradient, which we hypothesize are related to the loading reductions.

In order to fully understand the impact of load reductions on the ecosystem, we must also consider how the nutrients in the system have changed over the long-term, both in terms of annual cycling, and in terms of response to changing climate in the bay. This analysis constitutes the second chapter of the dissertation. Over the last 50-100 years, Narragansett Bay has grown measurably warmer, and weather patterns have changed, bringing increased cloud cover, more storms, and more precipitation. All of these changes impact the way nutrients enter the bay, and the way phytoplankton use the nutrients. We examined the impact of these potential changes using a long-term

weekly dataset of nutrient concentrations collected by the MERL lab at the University of Rhode Island Graduate School of Oceanography since 1978. We use both conventional statistics and a state-space model formulated in the computing language R (SSPIR). Our results show virtually no long-term trend or change in timing of seasonal cycling of nutrients or chlorophyll. However, we do see changes in the seasonal patterns of concentration of both nutrients and chlorophyll at the GSO station, with measurable changes in cumulative distribution function for phosphate, silicate, ammonium, and chlorophyll. We also observe statistically significant reductions over the course of the time series for nitrate, nitrite, ammonium, and phosphate, though it is difficult to ascribe causality to these changes. Model results were largely inconclusive, but show a marginally significant intervention effect attributable to the loading reduction in the ammonium signal at the GSO dock, with no significant long-term trend observed for any analyte.

Finally, we conduct a mass-balance nutrient budget assessment for nitrogen and phosphorus in Narragansett Bay (Chapter 3). Mass-balance is a common way of tracing the sources, sinks, and reservoirs of nutrients in a system, and seeing how these components might change with time. Nutrient budgets for Narragansett Bay have been compiled approximately every decade, but recent and future loadings compel a reanalysis to determine how the system is responding to initial stage reductions. We see a reduction in WWTF loading to the bay of just over 100 million moles of nitrogen and 4 million moles of phosphorus, which constitutes about 20 and 16 percent of the net annual load of nitrogen and phosphorus from all sources. However, much of this reduction is realized in tributary rivers, and variable riverine abatement rates in those

rivers mean that some of the net reduction is not felt by the bay proper. Furthermore, evidence from literature suggests that changes in bay sediment net denitrification rate may be offsetting some or all of the loading reductions.

ACKNOWLEDGMENTS

It is the academic tradition for acknowledgements to be listed at the end of a peer reviewed manuscript, yet the irrefutable and iron clad university of Rhode Island dissertation format template lists acknowledgements first. I would like to think that the reason for this is because without the support of so many people, no dissertation, least of all this one, could possibly be completed. Dissertation writing is a marathon, not a sprint, and no marathoner can be successful without a great support team. So, before we dive headlong into the results of several (many?) years of hard labor, I, like many before me, would like to take a moment to thank all of those who made this milestone possible for me.

Virtually every acknowledgement section (including the acknowledgement section of my advisor) begins with some sort of remark about the thesis advisor's unending patience, and here too I will not disappoint. My mentor, Dr. Candace Oviatt, has shown near infinite patience for the tortuous path down which we have traveled together in pursuit of this degree. Make no mistake, this has not been a flat and straight pavement marathon. This has been an up and down, through mud and rocks endurance event. Yet through all the highs and lows, your steady hand and composed demeanor have kept me on my feet and moving (generally) forwards with a smile on my face. I cannot thank you enough.

To the rest of my dissertation committee, Drs. Scott Nixon, Jeremy Collie, Art Gold, and Graham Forrester I also extend my sincerest gratitude. You have opened your doors to me, shared your research and life experiences with me, from DGS and IGERT to the BVI, to words of encouragement in the hallways of GSO and the

corridors of the YMCA, you have always been there for me, often with a wisecrack at the ready. I consider myself a better and more thorough researcher and scientist thanks to each of your influences.

The GSO community as a whole has been a remarkable place to spend the last several (many?) years. Virtually every door is open, and any faculty, staff or student is willing to help in any way possible. For this assistance, in whatever form it takes, from technical help to logistical help, to friendship and emotional support I am extremely grateful. To list each and every person who has contributed to the work on the following pages would take virtually as long as the manuscript itself. I am, however, particularly indebted to my group of GSO peers with whom I have walked this road, and with whom I have learned, that science, like floor hockey, is truly a team sport. Particular thanks among this group for guidance and technical assistance with this dissertation are due to Wally Fulweiler, Matt Horn, and Rich Bell.

Team MERL has been a fixture in my graduate tenure, and I could not be prouder of my time in MERL, nor think of a better group of individuals with which to work. I have benefited greatly from my association with dozens of MERL alumni from the very first pioneers in the 70's to those of us who still man the tiller and keep the ship afloat to this day. Particular thanks among this group are due to Chris Calabretta, Brooke Longval, Heather Stoffel, Edwin Requintina, Conor McManus, Jeff Mercer, Leslie Smith, Matt Schult, Chris Melrose and Kim Hyde. Also to MERL Interns and technicians who assisted with the data collection and analysis for my dissertation: Ashley Bertrand, Danielle Dionne, and Rossie Ennis.

I would also like to thank all the faculty, staff and students of the Coastal Institute IGERT program for your support and guidance. Being able to see the entire project through from the beginnings as a member of the ‘guinea pig’ class of Co-05 to offering graybacked veteran support for later cohorts was a tremendous experience. The skills and perspective I have acquired through this program have shaped my path through grad school and continue to shape my career goals. I am particularly indebted to the tireless work of Pete, Judith, Q, Deb, Jim, Candace, and Art, as well as the Co-05 and ‘06 cohorts with which I shared my ‘active duty’ rotation. Thank you for showing me what it means to be truly interdisciplinary.

There are many collaborators whose willingness to exchange data and ideas have greatly improved the quality of the manuscripts herein. I would like to thank Angelo Liberti and the scientific staff at RIDEM and NBC for sharing data and ideas, brainstorming, and helping shape the outputs of this work. I would also like to thank collaborators Claus Dethlefsen and Jamie Vaudrey.

Last, but certainly not least, I want to thank all of my friends and family. The unflinching support of my wife Emily and the exuberant smile of my wonderful son Charlie have been a constant ray of light. This victory is as much yours as it is mine, and I promise, as soon as this thing is done, to do better with the housework. Thanks to my dad, Alan, for his sense of humor and for helping me to focus on the important things, to my mom Robin, for always believing in me and encouraging me to follow my dreams, and to my brother, Steven, for never questioning my motives, but always questioning my methods, and being my unfailing allies for 32 (28) years. I love you all so much.

DEDICATION

This work is dedicated to my son Charlie. I hope that in some small way, we can contribute to the furthering of the science associated with sustainable use and management of marine ecosystems on behalf of yours and future generations. It is my sincerest hope that we will be able to devise sound management practices for the sustainable use of marine resources, such that the wonderful mysteries of the ocean will continue to yield a sufficient spawning stock of research questions to support sustainable harvest of dissertation topics for generations to come.

I fancy myself to be a decent writer of this sort of thing, but I think your friend Dr. Seuss says it best:

“... now that you’re here, the word of the Lorax seems perfectly clear. UNLESS someone like you cares a whole awful lot, nothing is going to get better. It’s not.”

-The Old Once-Ler

PREFACE

As described in the URI Graduate School guidelines for thesis preparation, this thesis is organized in a manuscript format. The body of the text is divided into three sections, corresponding to the format of journal articles. The first manuscript is submitted to *Estuaries and Coasts*, with co-author Candace Oviatt. The second manuscript will be formatted for *Northeastern Naturalist*, and will be submitted with co-authors Candace Oviatt, Rich Bell, and Claus Dethlefsen. The third manuscript will be submitted to *Estuarine Coastal and Shelf Science*, and will be co-authored by Candace Oviatt, Jaimie Vaudrey, Scott Nixon, and Rosmin Ennis. There are three appendices, divided into A) supplemental methods, B) Plant and River discharge calculations, C) Matlab and R scripts for code used within the chapters. The appendices provide additional background that was excluded from the chapters for brevity's sake.

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CHAPTER 1

CHANGES IN NUTRIENT STANDING STOCK IN A TEMPERATE ESTUARY WITH DECREASED NITROGEN AND PHOSPHORUS LOADING

ABSTRACT

We review the initial impact of decreased summer nitrogen and phosphorus loading between 2004 and 2007 into Narragansett Bay, RI. Biological nitrogen removal at 11 of 29 sewage treatment facilities which discharge their effluent either directly into Narragansett Bay or into its tributaries has reduced effluent nitrogen concentration at those plants by half or more during summer months. This results in a 30% decrease in the inorganic load and a 17% decrease in the total annual nitrogen load to the system. The reduction in load is visible in a reduction of the standing stock of dissolved inorganic nitrogen, but no statistically significant change in total nitrogen in the bay over time was detected. We do see significant differences in downbay patterns of dissolved and total nitrogen when compared by analysis of covariance (ANCOVA), as well as several interaction effects, which may be an indication that utilization patterns are changing. In contrast, dissolved inorganic phosphorus shows a consistent reduction throughout the bay, likely caused by a combination of legislative efforts in the 1990's and removal of phosphorus at several treatment plants which discharge into tributary rivers. Taken together, our data indicate that the early response of the ecosystem to reduction is within the bounds of what might be expected, particularly given high inter-annual variability in nutrient concentrations.

Keywords: Nitrogen, Phosphorus, Nutrients, Management, Hypoxia, Estuary

INTRODUCTION

In the 21st century anthropogenic pressure on coastal ecosystems continues to grow. Despite accounting for only 17% of the land in the continental United States, coastal counties account for over 153 million people (53%), a number which has increased by more than 30 million since 1980, an increase of roughly 28% (Crossett et al. 2004). Many of our nation's largest cities, particularly on the East coast, are positioned on or near estuaries, which brings great benefit in terms of commerce, industry, recreation, and tourism, but also great responsibility, as estuarine ecosystems are both highly productive, and highly sensitive to change. A recent review of literature on our nation's estuaries found 64 out of the 99 estuaries assessed exhibited moderate to high levels of anthropogenic enrichment, with 65% of systems for which data were available predicted to worsen by 2020 (compared to 19% predicted to improve) (Bricker et al. 2007). The same assessment found the Mid-Atlantic Region (Cape Cod to Virginia) to be the most impacted region in the country, with 20 out of 22 estuaries considered moderately or highly eutrophic, and eight systems declining since 1999, while only one (Gardiners Bay) improved (Bricker et al. 2007).

Fortunately, as awareness about anthropogenic impact on coastal water bodies grows, an increasing number of management organizations are beginning to consider measures to limit nutrient input to estuaries, in the hopes of addressing the many impacts of increased eutrophication, such as hypoxia, reduced water quality, loss of SAV (submerged aquatic vegetation), beach and fishing closures, etc. (Carstensen et al. 2006, Deacutis 2008, Duarte et al. 2009, Dam et al. 2010). The implementation of tertiary, or 'advanced' wastewater treatment techniques at wastewater treatment

facilities (WWTF's) (defined herein as processes, whether biological, chemical, physical or any combination of those, which remove nutrients from wastewater effluent prior to discharge), often referred to as biological nutrient (or nitrogen) removal (BNR), is one such method which is being implemented widely, as increases in technology and utilization drive the cost of this treatment down and its efficacy up (Lishman et al. 2000, Jeong et al. 2006). The efficacy of this management option to generate system wide improvements in water quality is a topic of great interest to scientists and managers alike.

Decreased nutrients have had dramatically different patterns in different ecosystems. While in some cases management strategies to reduce nutrient loading have resulted in rapid declines in nutrient standing stocks, in many cases the ecosystem responds either slowly, or less dramatically than anticipated (e.g. Artioli et al. 2008; Carstensen et al. 2006; Boynton et al. 2008; Nixon 2009), which is attributed to a wide range of causal factors, including sediment release, shifting baselines, and non-linear response types (e.g. Duarte et al. 2009, Taylor et al. 2011). The lack of predictable response is particularly evident with respect to the use of BNR in WWTF's to mitigate hypoxia in estuarine waters. While certain key physical parameters (e.g. residence time, stratification, temperature, etc.) are causally linked to hypoxia (e.g. Codiga et al. 2009, Rabalais et al. 2009, Bianchi et al. 2010), the direct link between changes in nutrient supply and reduced hypoxia is weak, ecosystem specific, and often nonlinear (Artioli et al. 2008, Kemp 2009).

Decreased nitrogen and phosphorus loading to the bay may cause a wide range of ecological impacts, ranging from straightforward to more complex. At the most

basic level, reduction of loadings may cause a subsequent drop in the standing stock and total annual budget of nitrogen and phosphorus in the bay, or it is possible that other terms of the nutrient budget (e.g. sediment and water column recycling) may change to preserve the overall standing stock and annual budget (Carstensen et al. 2006, Fulweiler et al. 2007, Duarte et al. 2009). While re-mineralization of sediment nutrients has been implicated as a possible mechanism for delayed response in some heavily impacted ecosystems (Carstensen et al. 2006, Clarke et al. 2006), in other ecosystems (Boynton et al. 2008), including a mesocosm study in Narragansett Bay (Oviatt et al. 1984) the sediments have a short memory, and the ecosystem responds rapidly to changes in nutrient loading. Reduction of nutrients may result in a decrease in primary productivity in some or all regions (Carstensen et al. 2006, Boynton et al. 2008), a change in nutrient ratios which may impact the frequency with which a given nutrient (N,P, or potentially even Si) is limiting and/or cause a shift in the phytoplankton species assemblage (de Vries et al. 1998, Turner et al. 1998, Tomasky et al. 1999, Artioli et al. 2008). Nutrient reduction may lead to a decrease in the extent or severity of hypoxia in the bay by reducing primary productivity, and therefore export of organic matter to the benthos, or alternatively, the supply of nutrients and organic matter may not be limited, and/or variability in hypoxia may be driven primarily by physical forcings (Robinson and Napier 2002, Codiga et al. 2009, Duarte et al. 2009, Kemp 2009). The combination of these many variables makes it difficult to predict how future oligotrophication of the bay will impact its ecology (e.g. Nixon 2009, Nixon et al. 2009)

With increased awareness of the potential impacts of low oxygen conditions in the Providence River Estuary, Upper Bay, and Greenwich Bay, Rhode Island Department of Environmental Management (RIDEM) has required that several of the major sewage treatment plants which serve Narragansett Bay be upgraded to tertiary sewage treatment, with most other large plants planning upgrades in the next few years (RIDEM 2005). The overall goal of RI General Law § 46-12-3(25), the driving force behind these changes, is to reduce nitrogen loading to the bay from WWTF's by 50%, a task which, based on percentage reductions achieved at the plants which have already upgraded, will be achieved once the largest plant discharging into the bay, located at Fields Point (Fig. 1-1) completes upgrades, presently scheduled to be sometime in late 2013 or 2014.

Plants that have upgraded use bacterially mediated coupled nitrification/denitrification to convert ammonium to nitrate and nitrite aerobically, then anaerobically to di-nitrogen gas, which is out-gassed to the atmosphere (Lishman et al. 2000, Jeong et al. 2006). This process has reduced rates of ammonium discharge at some plants by nearly an order of magnitude, and DIN concentrations by more than half during summer months (Liberti, unpublished data), since the rate of bacterially mediated denitrification is temperature dependent (e.g. Dawson and Murphy 1972, Lishman et al. 2000, Pell et al. 2008). The implementation of a combined sewer overflow reservoir in 2008 has further reduced nutrient input during high flow periods by delaying storm water runoff, and running it through treatment plants before discharge into the bay. The combination of these factors has reduced annual sewage

based total nitrogen loading by 27% (Table 1-1) which constitutes a reduction of approximately 15% of the annual TN load to the ecosystem(Nixon et al. 2008).

Phosphorus loading reductions have also markedly decreased over the past decades, but this reduction is due in large part to legislative changes during the 80's and 90's, in particular RI general law § 49-26-3, passed in 1995, which dramatically limited the use of phosphate in detergents (Litke 1999). Several of the WWTF's that discharge into tributary rivers rather than directly into the bay have undertaken phosphate removal efforts to reduce loading from their effluent. In many cases, these efforts have been highly successful, removing upwards of 80-90% of the phosphate from effluent (see Appendix B). However, the impact of this reduction on the overall phosphorus budget of the bay (see chapter 3) is not large, in part because WWTF's contribute a smaller percentage of the overall phosphorus budget of the bay than for nitrogen, and in part because the plants with the largest phosphorus reductions are not the largest in terms of volume or total phosphorus flux.

By reviewing the impact of this management action on the standing stocks of dissolved inorganic nitrogen and phosphorus (DIN and DIP) as well as total nitrogen and phosphorus (TN and TP) in the bay, we can gain a better understanding with respect to how the ecology responds, on the short term, to changes in nutrient loading and compare our results with those observed in other ecosystems. In this paper, we examine the short-term impact of a large ($\approx 30\%$ of annual sewage based N loading, (Table 1-1)) reduction in nutrient loading on nutrient standing stocks in Narragansett Bay, RI resulting from the implementation of advanced wastewater treatment at several facilities discharging either directly into the bay, or into tributary rivers.

STUDY SITE

Narragansett Bay, including Mount Hope and Greenwich Bays, but not the Sakonnet River (which is connected to the bay proper by only a very small channel and has very limited exchange) is a relatively shallow (average depth 8.6 meters) temperate estuary of approximately 328 km² (Pilson 1985a). Freshwater input is relatively low, approximately 100m³s⁻¹, and circulation is predominantly tidally driven, with ocean water typically moving in the east passage, and out the west passage (Kincaid et al. 2008). As a result of the combination of these factors, and the generally shallow depth of the bay (with the exception of the lower parts of the East Passage), Narragansett Bay is typically only weakly stratified throughout most of its mid to upper reaches, and salinity remains high (>20 psu) throughout virtually the entire estuary, and increases on a generally north-south gradient to roughly 32psu at the bay mouth (Pilson 1985a, Kincaid et al. 2008).

In Narragansett Bay a significant amount of historical baseline data exists on nutrient dynamics in the bay, through field studies (Nixon et al. 1995, Nixon et al. 2008), and through experimental treatments in the MERL mesocosms (e.g. Oviatt 1980, Nowicki and Oviatt 1990, Oviatt et al. 1995, Oviatt et al. 2002). Past research indicates that the bay is a nitrogen limited ecosystem, with a strong North-South gradient of nitrogen and phosphorus concentration caused by WWTF and river inputs, which are the two largest sources of these nutrients and which are concentrated in the Providence River and Upper Bay (e.g. Nixon et al. 1995, Oviatt et al. 2002). Previous nutrient budgets suggest that the bay was a net autotrophic ecosystem, and that the majority of the nutrients exported into Rhode Island Sound from the bay are in

inorganic form, rather than as organic material (Nixon et al. 1995). Compared to other temperate estuaries, Narragansett Bay has a relatively densely populated watershed, and about 63% of the total nutrient flux into the bay comes directly or indirectly (via rivers) from WWTF's (Nixon et al. 2008), as compared to an average for 74 temperate estuaries of about 36% (Latimer and Charpentier 2010).

Primary production in the bay has been estimated at about 320 gC/m² on a baywide average (Oviatt et al. 2002) and the community is phytoplankton dominated, traditionally experiencing a strong winter/spring diatom bloom, and several subsequent blooms throughout the summer which are lesser in intensity, duration and areal extent (Nixon et al. 1995, Oviatt et al. 2002, Smith et al. 2010). The frequency and intensity of this winter/spring bloom has declined over the past several years, and has not occurred at all in some years (e.g. Oviatt et al. 2002, Oviatt 2004, Smith et al. 2010), although in the last few years the ecosystem has experienced large winter diatom blooms correlated with colder winter water temperatures. Furthermore, average chlorophyll levels have also been generally trending downward, with a 70% drop reported for a mid-bay site since the early 1970's (Fulweiler and Nixon 2009), though again, with the return of the Winter/Spring diatom bloom, this trend may also be reversing in Narragansett Bay and other similar Northeast U.S. estuaries (e.g. Dam et al. 2010). Given some evidence of changes in NAO it is reasonable to suspect that New England may see more years with strong winter-spring blooms than without in the near future (e.g. Knight et al. 2005, Keenlyside et al. 2008).

In addition to the above mentioned loading reductions, significant changes in the climate and phenology of the bay over the last several decades have been

documented (Oviatt 2004, Melrose et al. 2009, Smith et al. 2010). Over the last century, we have seen an annual precipitation increase of over 30 cm/y (nearly a 30% increase) (Pilson 2008, Melrose et al. 2009), and the frequency of severe precipitation events has increased nearly 90% (Madsen and Figdor 2007). Over the last half century, average water temperature has increased by 1.2°C and the average number of cloudy days per year has increased by 61 (Melrose et al. 2009). These shifts in climate have impacted the way that nutrients cycle through the bay and are taken up by biota, sequestered in sediments, recycled, and flushed from the bay (Pilson 2008, Fulweiler and Nixon 2009, Nixon et al. 2009). In addition, the intermittency of the Winter/Spring bloom in many recent years, may contribute to variability in nutrient standing stocks during this time period (e.g. Li and Smayda 1998, Oviatt et al. 2002, Oviatt 2004, Fulweiler et al. 2007).

We aim to compare downbay concentration gradients and total standing stocks of nitrogen and phosphorus in the bay since the implementation of advanced wastewater treatment with past studies of the bay to determine if and how the WWTF upgrades have impacted the distribution and standing stocks of nutrients in the bay. We will also investigate how chlorophyll has responded to changes in nutrient stocks. This exercise will help us to understand which areas of the bay (if any) are most susceptible to changes from present and future reductions in nutrient load.

METHODS

Surface nutrient samples were collected from 2006-2010 (inclusive) at thirteen stations throughout the bay (Fig. 1-1) representing a broad geographical coverage including four stations each in the East and West Passages, three stations in the

Providence River Estuary, a station at the mouth of the bay south of Jamestown, and a station in Mt. Hope Bay. Samples were collected monthly on cruises using the RIDEM R.V. John Chafee, supplemented with additional biweekly summer (May-September inclusive) sampling using the Marine Ecosystem Research Laboratory (MERL) 20' Wellcraft. Surface samples were collected (by bucket), and stored in 1L opaque polycarbonate bottles on ice until returned to the MERL facility for processing. Since the cruise track did not go into Greenwich Bay, a small dataset of nutrients collected at the Greenwich Bay DEM fixed monitoring network site was used (Figure 1-1). Apart from the sporadic nature of the collection dates at this site, these samples were processed identically to regular cruise samples and run on the same instrument.

Immediately upon returning to the lab, a 40 ml aliquot from each station was filtered (by 0.45 micron nucleopore filter using a syringe) for dissolved inorganic nutrients (NO_2 , NO_3 , PO_4 , NH_3 , and SiO_4), and a 40 ml whole water aliquot was collected for total nutrients (TN and TP). Samples were frozen at -4°C prior to analysis. Total nutrient samples were extracted using the Alkaline Persulfate method (Valderrama 1981, Patton and Kryskalla 2003). Traditional colorimetric analysis techniques were used for each analyte modified slightly to achieve maximum accuracy and precision on each instrument (Table 1-2).

From 2006-2008 samples were analyzed on a Technicon autoanalyzer. Beginning in 2009, samples were analyzed on a newly purchased Astoria SFA autoanalyzer. A thorough intercalibration between the two instruments was conducted prior to the switch-over, with samples from 1/09-6/09 as well as additional

intercalibration test samples, run on both instruments. All analytes with the exception of nitrate and total nitrogen were directly comparable between instruments with no correction. Nitrate (and total nitrogen, which is run on the nitrate channel) required the implementation of an empirically derived correction factor, after which results were directly comparable.

In all cases, yearly averages were first computed by calculating monthly averages from each station, to avoid biasing toward the more heavily sampled summer period. In order to fill data gaps caused by missed sampling cruises or lost/damaged samples, gaps at a given station of less than 2 samplings were linearly interpolated. Infrequent gaps of more than 2 samplings were filled by averaging the values for all samples collected in the month in question during other years in the survey (See Appendix D for more details). This was done to avoid bias in yearly averages caused by the presence or absence of sampling in a given month (particularly December and January, where sampling was often infeasible due to weather, and concentrations are typically highest).

Data were natural log normalized (to meet the linearity assumptions of tests used) and spatial patterns in nutrient concentration on a downbay gradient were compared between the present study and past studies at similar sampling locations (Fig. 1-1) (Oviatt 1980, Oviatt et al. 2002). This analysis was performed with analysis of covariance (ANCOVA) in MATLAB, where distance downbay from Field's Point (the furthest north sampling station) is the covariate, and the slope and intercept of the linearized downbay gradient in concentration were compared both within the present study and between this study and past studies. Analysis of covariance essentially

functions as a combination of a regression and an analysis of variance (ANOVA), by removing the variance associated with the covariate (distance downbay) and then conducting an ANOVA. This can greatly increase the power of the ANOVA by removing the variability attributed to the covariate (in this case, an order of magnitude or more).

Standing stocks were calculated by multiplying surface nutrient concentration by volumes for each section of the bay derived from the General Ecosystem Model (GEM) box model (see Kremer et al. 2010). In cases where a model box did not have an associated station, or had more than one station the numerical average of stations in surrounding boxes, or the numerical average of all stations in the box was used, respectively. The GEM model does have separate surface and bottom boxes for each element, but we elected to use surface nutrient values only because only a very limited number of bottom samples were collected as part of this study, and no relationship could be established between surface and bottom values. Data from past studies (e.g. Kremer and Nixon 1978, Oviatt 1980) indicate that surface and bottom values are frequently very similar (since the water column is often well mixed), and in times when they vary, these datasets do not provide a consistent relationship between surface and bottom to justify developing an algorithm to calculate bottom values. A recent study by Hefner (2009) using data from two mid-bay stations confirmed that surface and bottom nutrient levels are highly correlated, and residuals were not easily explained.

Water samples from the DEM Buoy station in Greenwich Bay were used for both GEM boxes in Greenwich Bay, however, since sampling frequency at this station

(particularly in winter months) was highly sporadic, it was not feasible to calculate averages for each year of the study, rather, a single average was computed for the period of 2006-2009 by averaging all monthly samples collected in a given month (n=2-12) during the sampling period, and using these monthly averages to calculate annual and summer (June-Sept.) averages during the sampling period. Due to its comparatively low volume, these two boxes contribute less than 2% of the total baywide standing stock, so the lack of precision in this region is unlikely to significantly influence results.

Annual and summer standing stocks were compared to each other and to prior standing stocks estimated by applying the methods above to data from the 1979-1980 survey (Oviatt 1980) for inorganic nutrients and the 1998 survey (Oviatt et al. 2002) for total nutrients. Statistical comparisons were two tailed T-tests using SigmaPlot. Prior to analysis, the Shapiro-Wilk test was used to confirm normality. Because only one year of data was available for past studies, equal variance was assumed for these tests, while unequal variance was assumed when testing summer vs. annual standing stock.

Spatial maps of major nutrient constituents were calculated by Inverse Distance Weighting (IDW) interpolation of the combined shuttle cruise and buoy datasets. The interpolation does not consider circulation dynamics or local geography (e.g. changes in bathymetry) within the bay when determining values intermediate to the sampling stations. However barrier vectors were manually drawn at the latitudes of Aquidneck and Prudence Islands to prevent the software from interpolating across these landmasses. The resulting interpolation was masked with the RI state outline

(which includes 32 islands) from RIGIS.org. This analysis was carried out in ArcGIS 9.2 according to methods described by Peterson and colleagues (2010).

RESULTS

The changes in downbay concentration are perhaps easiest viewed by comparing absolute concentration before the data have been normalized to meet the assumptions of the statistical tests used. Compared to previous studies (e.g. Oviatt 1980)(Fig. 1-2), the bay shows a reduction in annual dissolved inorganic nitrogen of 15-20% which is a significant reduction at upper bay stations, and a reduction of 35-50% in ortho-phosphate, which is significant throughout the bay (Fig. 1-2). While TP had a similar pattern to DIP, TN shows no significant reduction, though one station (station 11 in the Providence River Estuary) does appear to be consistently lower than past studies. The decrease in DIN was most noticeable in the mid to upper bay region, although the furthest North station (immediately adjacent to the outfall from the Fields Point WWTF) did not show a measurable reduction (upgrades for this plant are scheduled for 2013). However, interannual variability in nutrient concentration was also greatest in this mid-upper bay region (Fig. 1-2). DIP followed a similar downbay pattern to DIN, but with less interannual variability.

Analysis of Covariance reveals more details regarding the overall nutrient dynamics on the downbay gradient (Fig. 1-3). While DIN does not show statistically significant changes in estimated slope or intercept parameters, the ammonium intercept, which is a measure of the level in the upper bay, drops significantly, while nitrate+nitrate has an increased slope but no change in intercept (Table 1-3). Both TN and TP show reduction in intercept, while total phosphorus also changes slope (Table

1-3). As expected, ANCOVA identifies a very strong correlation among all nutrient parameters with distance downbay (Table 1-4). Once the variability associated with the covariate is removed the ANOVA portion of the test reveals significant changes between studies for all parameters tested both as annual averages and during the summer with the exception of TN during the summer. There is also a significant interaction effect (change in slope over time) for nitrate+nitrite and TP, with the interaction effect for DIN as a whole approaching statistical significance. Silicate shows a significant change between studies, both in terms of slope and intercept, but this is driven almost entirely by changes in the station 12 (Fields Point) data. None of the other stations show significant changes.

The pattern in baywide standing stocks shows many of the same patterns seen in the downbay gradients. More specifically, a drop was present for all parameters except silicate, though this relationship was only statistically significant for phosphorus (Fig. 1-4, Table 1-5), though the decrease in DIN on an annual average basis approaches significance (T-test $df=4$, $T=2.17$, $P=0.09$). However, while the reduction in TN is not statistically significant, the average value for the study period is approximately 17% less than the average value calculated for the 1998 survey (Oviatt et al. 2002), which is similar in magnitude to the observed 17% loading reduction, so it is possible that we simply lack the statistical precision to detect this change in light of inter-annual variability. Of note, however, is that the improved reduction efficiency anticipated during the summer (to the impact of temperature on the coupled nitrification-denitrification process) is not evident at all in the standing stock of TN. Similarly, while DIN exhibited a 62% decrease in the summer compared to the annual

average, the rest of the constituents did not exhibit this pattern (Fig. 1-4, Table 1-4), and the reduction, when compared to past studies, is not significantly different (36% during summer vs. 34% on an annual basis).

Spatial patterns in nutrient dynamics showed expected trends when extrapolated across the entire bay (Fig. 1-5). Virtually all constituents mapped behaved similarly, decreasing exponentially with north south distance away from the Providence River Estuary and the major point sources of nutrients (WWTF's) therein. In general, concentration in the east passage was slightly lower than concentration in the west passage at equivalent latitude. Mount Hope Bay seemed to be a source of both Nitrogen and Phosphorus to the bay proper, with slightly higher concentrations inside than outside for all constituents, while Greenwich Bay appears to be a source only for elevated concentrations of DIN, with concentrations of DIP, TN, and TP roughly equivalent to, or even lower than surrounding waters (Fig. 1-5).

The ratio of N:P is commonly used as an indicator of potential nutrient limitation in marine ecosystems (Doering et al. 1995, de Vries et al. 1998, Tomasky et al. 1999, Guildford 2000). While not conclusive evidence of one type of limitation or another, DIN:DIP are frequently compared to the ratio of N:P in Redfield organic matter (16:1 N:P). A ratio below 16:1 is typically interpreted as an indication of nitrogen limitation, while ratios above 16:1 are considered indicative of phosphorus limitation (Oviatt et al. 2002, Artioli et al. 2008, Boynton et al. 2008, Nixon et al. 2008). For total nutrients (TN:TP) the inflection point between N and P limitation is typically higher and more variable. This has been attributed to the fact that organic and particulate nutrients are not as readily available for biological uptake and have

variable, but usually greater than 16:1 N:P ratios in nitrogen limited systems (e.g. Guildford 2000). When averaged over the year, the bay showed evidence of nitrogen limitation throughout (Fig.1-6), with ratio approaching, but never reaching 16:1 in Greenwich Bay and the Upper Bay, and below 4:1 throughout much of the mid and lower bay. Similarly, N:Si ratio is well below 1:1 through most of the bay, approaching 1:1 in the Providence River where both species are abundant. Comparing DIN:DIP to TN:TP ratios, demonstrates the large amount of nitrogen which is locked up in organic and particulate material, particularly in the Providence River Estuary and Greenwich Bay, but also in the Ohio Ledge region. Despite DIN:DIP ratios around 10:1, these areas showed TN:TP ratios well above 16:1 and in some places, above 20:1. 20:1 is the threshold indicated by a meta-analysis by Guildford and colleagues (2000) as the bottom cut-off for potential N/P co-limitation (Fig.1-6).

DISCUSSION

Nutrient reductions observed

While significant reduction in DIN compared to levels in the late 70's was evident, there is no evidence of a system-wide reduction in TN since 1998 which would be associated with WWTF upgrades. Unfortunately, no TN data from the 70's is available with which to compare, as this survey pre-dates the widespread adoption of the alkaline persulfate technique for colorimetric determination of TN (Valderrama 1981). Stoichiometric and regression based calculations by Oviatt (2008) suggest that a reduction in load of 20% would be minimally detectable under present conditions, and our result corroborates that conclusion. Concentrations of all nutrient constituents remained high in the upper bay year round, and both 2006 and 2009 demonstrated

high spatial and temporal extents of hypoxia in the bay (Codiga et al. 2009, Deacutis pers. comm.), indicating that at present, load reductions do not appear to be having a large enough impact on nutrient dynamics to measurably reduce the severity, aerial extent or duration of upper bay hypoxia.

Furthermore, it was difficult to discern if the reductions presently observed are even the direct result of activities at the WWTF's. Since BNR is most effective at warm temperatures (e.g. Dawson and Murphy 1972, Lishman et al. 2000, Pell et al. 2008), one would expect to see a much larger reduction during the summer months, and less so over the remainder of the annual cycle. In contrast, the data from this study (Fig. 1-4, Fig. 1-5) show a relatively consistent reduction over the summer and the entire year, when compared to past studies. The lack of a stronger reduction in the summer is particularly puzzling given that research in similar polyhaline ecosystems typically point to stronger nitrogen limitation during the summer months, with evidence of light or other factors becoming important in colder months (Hecky and Kilham 1988, Cloern 1999, Tomasky et al. 1999). A possible explanation of this is the observed decrease in net denitrification rates observed in the bay over the last several years (see Chapter 3, Fulweiler et al. 2007, Fulweiler and Nixon 2011).

One strong indication that at least some of the observed trends in nutrient patterns can be attributed to loading reduction comes from the percentage of DIN in the bay which was ammonium. Past studies have shown the majority ($\approx 60\%$) of the DIN in the Providence River Estuary and upper bay to be ammonium, with a decreasing percentage moving down bay (Kremer and Nixon 1975, Oviatt 1980) (Fig. 1-2). This pattern of decreasing proportion moving down bay is consistent with high

point source loading of sewage in the upper bay, since secondary treated sewage has very high ammonium concentration, but ammonium is preferentially selected by many plankton species. However, the present study shows lower ($\approx 40\%$) ammonium concentration in the upper bay, and no decrease moving down bay (Fig. 1-2e), which would be expected if tertiary treatment was converting much of the ammonium to nitrate and nitrite (whose concentrations have actually increased in the effluent streams of many plants which have upgraded). Furthermore, standing stocks of silicate remain unchanged, which reduces the likelihood that the observed reductions are caused by increased drawdown by diatom blooms.

Relationship with primary productivity

The nutrient observations can be compared to recent primary productivity measurements in the bay which have not decreased since the 2005 implementation of advanced wastewater treatment (Smith 2011). The present reduction constitutes about a 17% reduction in the total annual loading of nitrogen to the ecosystem (slightly higher as a fraction of summer N load) when the sewage load is considered alongside riverine, direct deposition, and runoff values (Table 1-1). Mesocosm experiments conducted at the MERL facility in the 1980's indicate log-linear response of primary productivity to nutrient loading, and indicated an 18% reduction in primary productivity in response to a halving of nutrient concentration at loading levels similar to those presently observed in the Providence River Estuary (Oviatt 1986). Another possible explanation for the lack of observed response is that many ecosystems, even those dominated by sewage inputs, may take several years to respond to load

reductions (e.g. Carstensen et al. 2006, Duarte et al. 2009). However, similar mesocosm experiments in the Narragansett Bay ecosystem show rapid response of sediment and water column to loading reduction (Oviatt et al. 1984).

The loading reduction does not directly result in a reduction of chlorophyll-a in the bay. Although others have reported a long-term decline in average chlorophyll in Narragansett Bay (e.g. Li and Smayda 1998, Fulweiler et al. 2007, Nixon et al. 2009) weekly data from the GSO dock station and data from a fixed buoy operated by RIDEM located at Bullocks Reach (in the southern reaches of the Providence River Estuary) both exhibit no change in annual average between the first and second half of the 00's (Two tailed equal variance T-Test: $df=5$ $T=-0.4$ $P=0.70$, $df=5$ $T=-2.05$ $P=0.10$ for BR and GSO respectively) or maximum chlorophyll (Two tailed equal variance T-Test: $df=5$ $T=-0.94$ $P=0.38$, $df=5$ $T=-0.96$ $P=0.37$ for BR and GSO respectively) which would be associated with the WWTF reductions; occurring primarily in 2005 and 2006 (Fig. 1-7). Furthermore, there is little long term change in GSO dock data collected by Pilson and colleagues in the late 70's and early 80's (see chapter 2, Pilson 1985b). If anything, chlorophyll has increased during the latter part of the 00's, though this is unlikely to have been caused by the WWTF reduction; more likely the return of large winter-spring blooms in these years.

Sources and sinks of nutrients

Applying a statistical technique to spatially average concentrations showed the location of primary sources and sinks of nutrients in the bay and an exponential decrease with distance down bay. Concentrations in the East Passage were slightly

lower than the West Passage, as the circulation patterns of the bay tend to bring oceanic water in the East passage, and advect fresher water from up the bay out the West passage (Kincaid et al. 2008, Rogers 2008). Mt. Hope Bay and the Taunton River were a source of nutrients to the bay proper, while Greenwich Bay may pulse nutrients into the ecosystem after storm events, but on an annual average, has concentrations similar to surrounding bay water for most constituents. On the whole, the circulation dynamics of the bay appeared to be exporting nutrients to Rhode Island Sound, although these nutrients appeared to be primarily in organic form, rather than inorganic (Fig. 1-5). However, caution should be taken in over-interpreting the results of this portion of the analysis, since the model does not take into consideration circulation, depth, wind, or other parameters, and simply extrapolates nutrient concentration based on distance between sampling points.

Discussion in the literature has regarded the role of sediment nutrient flux in Narragansett Bay, and how the contribution of the sediments to the overall nutrient budget of the bay may have changed over the past several decades (Fulweiler et al. 2007, Nixon et al. 2009, Fulweiler et al. 2010). Changes in sediment nutrient flux, particularly the observed reductions in net sediment denitrification, could potentially mask any observable changes resulting from decreased loading. When scaled up to a whole bay average, the results of Fulweiler and colleagues (2007) indicated that the sediments may now be contributing roughly 100 million moles of nitrogen during the summer period, compared with past studies which showed denitrification throughout the annual cycle (Seitzinger et al. 1984, Nowicki 1994b). This change is on the same order of magnitude as the presently observed reductions in sewage loading (90 million

moles, Table 1-1) and could explain the lack of a reduction in nutrient concentration and standing stock during the summer (Fig. 1-4).

Nutrient ratios

Similar caution should be used in interpreting N:P ratio data. The data indicated that the ecosystem as a whole, on an annual average, remained strongly nitrogen limited (based on DIN:DIP data, Fig. 1-6) as observed in past literature (e.g. Oviatt et al. 1995). While TN:TP ratios are typically not used as a metric for nutrient limitation, the difference between DIN:DIP and TN:TP indicated, in that for the most part, phosphorus behaved conservatively in the bay, with DIP:TP ratios remaining fairly constant down bay while DIN:DIP ratio decreased on a downbay gradient (presumably as N, the limiting nutrient, is consumed). In contrast, DIN:TN ratio (Fig. 1-6b) is not at all consistent, with large amounts of particulate and organic N observed in the Upper Bay, Greenwich Bay, and the Ohio Ledge area, changing the N:P ratio in these areas, a possible indication of higher nutrient utilization in these areas (Fig. 1-6). The pooling of organic material also may be related to the short residence time of water in the Providence River Estuary (Pilson 1985a) limiting the amount of biological activity which can take place in that region, and/or advecting large amounts of phytoplankton into the upper bay and Ohio Ledge. N:Si ratios follow a consistent north/south gradient, as silicate concentrations appear to fall off linearly rather than exponentially moving downbay (Fig. 1-2). While in the upper bay, N:Si ratio approaches 1:1, in most cases, both species are abundant in this region.

Analyzing the N:P ratios in the form of average of annual averages over a four year period smoothes the data a great deal, and tends to flatten out many of the finer scale details. DIN:DIP ratio, like everything else presented here, was highly variable, and while the smoothed data suggest that the bay is strongly nitrogen limited, there were several individual instances where DIN:DIP ratio exceeded 16:1, particularly in the winter (see Appendix D). This seasonal pattern is consistent with literature from other similar ecosystems (e.g. Fisher et al. 1999, Tomasky et al. 1999, Saito 2008), and suggests that, particularly in this time period (which includes the winter bloom period) both phosphorus and nitrogen may be of concern to management.

Comparison with other ecosystems

Direct comparison of the impact of nutrient reductions between ecosystems can be difficult, as many complex biological, chemical, and physical variables play a large role in how an ecosystem responds to a stimulus. It is, nevertheless, worth the exercise of placing the results observed here in the context of other ecosystems, with the caveat that this is intended merely as a reference, and not as an indication of relative success or failure of the management effort. To this end, we briefly compiled results and compared loading reduction, concentration reduction, and biological response (generally either chlorophyll or primary productivity) from several similar (predominantly temperate estuarine) ecosystems which have undergone nutrient loading reductions (Table 1-6).

In general, the results of this study fall well within the range of observed patterns in other ecosystems. For most ecosystems, response was less than the loading

reduction, and Narragansett Bay is no exception to this pattern. Most ecosystems do show some biological response (while not quantified in a method comparable with the other studies presented, Carstensen and colleagues show a correlation between TN and chlorophyll, and therefore, a consequent reduction (Carstensen et al. 2004, Carstensen et al. 2006)) though the range of observed responses is very large. Some general trends which emerge from this comparison are that highly eutrophic ecosystems require greater reduction to elicit response. Greening and Janecki (2006) broke down their analysis to different sections of Tampa Bay, and show less response in highly eutrophic sections of the bay, despite large loading reductions, with greater response in less impacted regions. Residence time may also be a concern, particularly for poorly mixed ecosystems. In general, polyhaline N limited ecosystems did not show significant time lags unless groundwater was a major contributor of loading, though sediment P release may be a larger concern.

CONCLUSION

In general, the results of this study suggest that nutrient concentrations and standing stocks are responding predictably to the instituted loading reductions, and that changes in observed concentrations and standing stocks represent a reduction proportional to the percentage reduction in loading to within the confidence intervals imposed by inter-annual variability in all sampled terms. This reduction is detectable at a statistically significant level for DIN, for which the reduction constitutes approximately 30% of the annual ecosystem budget, but for TN, for which the reduction constitutes only about 17% of the total annual ecosystem budget, some evidence of reduction can be seen in some tests, but not in others. Both total and inorganic phosphorus show statistically significant reductions of 35-50%, though these reductions are likely due just as much from legislative action removing phosphates from detergents and surfactants as to the limited phosphorus removal activities going on at the WWTF's.

While the nutrient standing stocks in the bay have responded to the implemented reduction, no observable reduction in annual average chlorophyll (Fig. 1-7) or primary productivity (Smith 2011) were observed. Past experiments in this ecosystem (Oviatt 1986) have indicated that nutrient levels in the upper bay are sufficiently high that concentrations would have to be reduced by half or more to elicit a response that might be detectable against the inter-annual variability (Oviatt 2008). While present reductions do not approach this level, once all plants discharging into the ecosystem have upgraded to tertiary treatment, we estimate that the annual nitrogen budget will be reduced by approximately 50% (Table 1-1), which would

justify a reanalysis of nutrient dynamics and primary productivity of the ecosystem at that time.

ACKNOWLEDGEMENTS

The authors would like to thank a great many people for assistance in collecting and analyzing the data presented here. Fieldwork and laboratory assistance was provided by many past and present MERL staff and interns, chiefly Chris Calabretta, Brooke Longval, Conor McManus, Jeff Mercer, Leslie Smith, Edwin Requintina, Heather Stoffel, Laura Reed, Hannah Williams, Ashley Bertrand and Rossie Ennis. We also thank Drs. Scott Nixon and Robinson Fulweiler for thoughtful discussions which greatly improved the manuscript. We also thank our funding sources: NOAA Bay Window Awards to Candace Oviatt and collaborators: NA04NMF4550409, NA05NMF4721253, NA07NMF4720287, NA09NMF4720259, and the NOAA Coastal Hypoxia Research Program (CHRP) NA05NOS4781201 to Candace Oviatt and collaborators, as well as a Coastal Institute IGERT program ‘grant in aid’ to Jason Krumholz.

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Table 1-1 Estimated major sources of Nitrogen (10^6 Moles N as TN) to Narragansett Bay, and potential future change resulting from impending management strategies. 2010 change values are from this study (Chapter 3).

Nitrogen Source	2003^a	2010 change	2014 potential change^b	Notes
Direct Sewage	170	143 (16% reduction)	up to 60% decrease	2014 value based on RIDEM estimates of loading: 3mg/l for major plants for 2014, 8mg/l for smaller plants. ^b
Indirect (into rivers) Sewage	193	120 (37% reduction)	up to 50-60% decrease	Assumes above plus MA compliance with proposed reductions. Does not account for riverine abatement.
Other riverine inputs & surface drainage	145	129 (11% Reduction)	?	may improve slightly due to reduction in ISDS usage, fertilizer restriction, and improved land-use practices. Changes may take years-decades to manifest.
Direct Atmospheric Deposition	30	30	?	unlikely to change significantly, but may decrease slightly due to air quality regulations.
Urban Runoff	37	62(67% increase)	up to 20-30% decrease	Increased precipitation and land-use changes. Potential future decrease from improvements in CSO abatement and land usage regulations.
TOTAL (10⁶ Moles/yr)	575	484^c	approx. 270-320	
^a Data from Nixon et al. 2008 ^b Estimates from Liberti, 2009 pers. comm. ^c assuming no change in un-estimated parameters.				

Table 1-2 Autoanalytic methodologies and empirically determined detection limits for each nutrient analyte

Analyte	Technicon Method (used 2006-2008)	Technicon MDL	Astoria Method (used 2009-present)	Astoria MDL
Nitrite	Greiss Reaction (NH ₄ Cl buffered Naphthethelene/Sulfanilimide (NED/SAN)) (Strickland and Parsons 1968, Technicon 1972a, Fox 1979)	0.02 µM	Greiss reaction (Imidazole Buffered NED/SAN) (Strickland and Parsons 1968, Fox 1979, Astoria-Pacific 2005)	0.02 µM
Nitrate	Greiss reaction (NED/SAN w/packed cadmium reduction) (Strickland and Parsons 1968, Technicon 1972a)	0.2 µM	Greiss reaction (NED/SAN w/ open tubular cadmium reduction) (Strickland and Parsons 1968, Astoria-Pacific 2005, Scott et al. 2005)	0.1 µM
Phosphate	Heteropoly Blue (molybdic+ascorbic) (Technicon 1971, Hager et al. 1972, EPA 1983c)	0.12 µM	Heteropoly Blue (molybdic + ascorbic acid) (EPA 1983c, Scott et al. 2005)	0.06 µM
Ammonia	Berthelot Indophenol blue (crystalline phenol+hypochlorite) (Solorzano 1969, Technicon 1973, EPA 1983a)	0.1 µM	Modified Berthelot (liquid phenol, hypochlorite, tartarate) (Solorzano 1969, Scott et al. 2005, Schmidt and Clement 2009)	0.05 µM
Silica	Silico-heteropoly blue (ascorbic, oxalic, molybdic) (Brewer and Riley 1966, Technicon 1972b)	0.06 µM	Silico-heteropoly blue (molybdic, tartaric, stannous chloride) (Sakamoto et al. 1990, Scott et al. 2005)	0.08 µM
Total Nitrogen	Alkaline Persulfate Oxidation + Greiss reaction (as above) (Technicon 1972a, Solorzano and Sharp 1980, Valderrama 1981)	1.1 µM	Alkaline Persulfate Oxidation + Greiss reaction (as above) (Solorzano and Sharp 1980, Valderrama 1981, Astoria-Pacific 2005)	0.5 µM
Total Phosphorus	Alkaline Persulfate Oxidation + Heteropoly Blue (as above) (Technicon 1971, Solorzano and Sharp 1980, Valderrama 1981)	0.12 µM	Alkaline Persulfate Oxidation + Heteropoly Blue (as above) (Solorzano and Sharp 1980, Valderrama 1981, Scott et al. 2005)	0.06 µM

Table 1-3 Parameter estimation by analysis of covariance (ANCOVA) comparing various nutrient parameters from the present study (2006-2010 average) with past studies (Oviatt 1980, Oviatt et al. 2002) over annual and summer (June-Sept.) periods with the covariate of distance south of Fields Point. Parameters are natural log transformed to meet assumptions of ANCOVA, so estimates are ln (concentration) in μM with variation between studies expressed as \pm . A p value below 0.05 (boldface) indicates a parameter which has changed significantly between studies

Analyte	Annual				Summer			
	Estimate	St. Err.	T	P	Estimate	St. Err.	T	P
DIN								
Slope	-0.063+/- 0.010	0.0056	1.70	0.10	-0.078+/- 0.004	0.010	0.42	0.68
Intercept	3.20+/-0.22	0.13	1.64	0.12	2.55+/-0.44	0.23	1.9	0.07
DIP								
Slope	-0.031+/- 0.002	0.0033	0.60	0.56	-0.045+/- 0.003	0.003	0.98	0.33
Intercept	.897+/-0.24	.078	3.08	0.006	1.33+/-0.54	0.070	7.61	>0.001
Ammonium								
Slope	-0.073+/- 0.000	0.0050	0.02	0.98	-0.074+/- 0.009	0.009	0.93	0.36
Intercept	2.62+/-0.41	0.12	3.43	0.003	1.89+/-0.68	0.22	3.07	0.006
Nitrate+Nitrite								
Slope	-0.052+/- 0.005	0.0051	2.93	0.008	-0.081+/- 0.0012	0.011	0.11	0.91
Intercept	2.56+/-0.09	0.12	0.73	0.48	1.67+/-0.22	0.26	0.86	0.40
Silicate								
Slope	-0.035+/- .006	0.002	3.76	0.001	-0.028+/-0.06	0.003	1.96	0.065
Intercept	3.37+/-0.18	0.03	4.69	>0.001	3.25+/-0.09	0.07	1.29	0.21
TN								
Slope	-0.041+/- .004	0.025	1.73	0.10	-0.041+/- 0.003	0.0027	1.07	0.29
Intercept	3.88+/-0.22	0.059	3.69	0.001	3.82+/-0.11	0.063	1.7	0.10
TP								
Slope	-0.043+/- 0.007	0.0021	3.5	0.002	-0.049+/- 0.007	0.0022	3.04	0.005
Intercept	1.19+/-0.36	0.050	7.17	>0.001	1.53+/-1.30	0.052	29.5	>0.001

Table 1-4 Statistical results of ANCOVA test comparing present (2006-2010 average) downbay gradient to past (Oviatt 1980, Oviatt et al. 2002) studies over the annual cycle and during the summer (June-Sept.) with covariate distance downbay from Fields Point. All values were ln transformed prior to analysis to meet criterion for normality (by Shapiro-Wikes test). Parameters with $P < 0.05$ are considered statistically significant and are presented in bold

Annual				Summer			
Analyte	df	F	P	Analyte	df	F	P
DIN							
Survey	1	31.9	>0.001	Survey	1	8.14	0.001
Distance	1	123	>0.001	Distance	1	65.2	>0.001
Survey*Distance	1	2.88	0.10	Survey*Distance	1	0.17	0.68
DIP							
Survey	1	43.6	>0.001	Survey	1	166	>0.001
Distance	1	88.8	>0.001	Distance	1	239	>0.001
Survey*Distance	1	0.36	0.56	Survey*Distance	1	0.97	0.33
Ammonium							
Survey	1	39.6	>0.001	Survey	1	17.6	>0.001
Distance	1	222	>0.001	Distance	1	65.7	>0.001
Survey*Distance	1	>0.1	0.98	Survey*Distance	1	0.87	0.36
Nitrate+Nitrite							
Survey	1	10.2	0.004	Survey	1	3.07	0.09
Distance	1	96.1	>0.001	Distance	1	54.5	>0.001
Survey*Distance	1	8.56	0.008	Survey*Distance	1	0.01	0.91
Silicate							
Survey	1	8.64	0.008	Survey	1	0.40	0.53
Distance	1	437	>0.001	Distance	1	86.3	>0.001
Survey*Distance	1	13.57	0.002	Survey*Distance	1	3.78	0.065
TN							
Survey	1	19.1	>0.001	Survey	1	2.37	0.13
Distance	1	271	>0.001	Distance	1	235	>0.001
Survey*Distance	1	2.99	0.09	Survey*Distance	1	1.14	0.29
TP							
Survey	1	68.3	>0.001	Survey	1	36.6	>0.001
Distance	1	409	>0.001	Distance	1	491	>0.001
Survey*Distance	1	12.2	0.002	Survey*Distance	1	9.84	0.005

Table 1-5 Statistical Results of standing stock analysis comparing total average standing stock of nutrients from present study (2006-2010 average) to past studies (Oviatt 1980, Oviatt et al. 2002). Results were tested using two tailed T-test with pooled variance. Negative T values indicate that the parameter decreased between studies, positive T values indicate an increase. Parameters with $T > T_{crit}$ (2.77 for past vs. present studies, 2.30 for annual vs. summer) are considered statistically significant and presented in bold

Past vs. Present Annual			
Analyte	Df	T	P
DIN	4	-2.17	0.09
DIP	4	-5.57	0.005
Silicate	4	0.48	0.66
TN	4	-1.01	0.37
TP	4	-2.84	0.04
Past vs. Present Summer			
Analyte	Df	T	P
DIN	4	-1.43	0.23
DIP	4	-3.49	0.03
Silicate	4	-0.15	0.89
TN	4	-0.23	0.83
TP	4	-1.12	0.33
2006-2010 Annual vs. Summer			
Analyte	Df	T	P
DIN	8	5.39	0.001
DIP	8	-0.42	0.69
Silicate	8	0.17	0.87
TN	8	-0.08	0.93
TP	8	-2.42	0.05

Table 1-6 Response of selected similar estuarine systems to reduction in nutrient loadings. For each ecosystem, response parameter, loading reduction, observed reduction of concentration, and biological response (generally either chlorophyll concentration or primary productivity) are presented (where available) along with the reference citation. NR: not reported NS: No Significant reduction observed

Ecosystem	Parameter	% load reduction	% conc. reduction	% biological response	reference
Narragansett Bay	DIN	30	34	NS	This study, Smith (2010), Oviatt et al. (2002)
	TN	17	17 (*NS)	NS	“
	TP	NR	28	NS	“
Lajalati Bay	TN	90	30-40	30-40	Clarke et al. (2006)
Pawtuxent R. Estuary	TN	10	NS	NS	Boynton et al. (2008)
Danish Straits	TN	50	Up to 44	NR	Carstensen et al. (2006)
	TP	80	22-57	NR	“
Gulf of Riga	TN	50	NR	NS	Duarte et al. (2009)
Odense Fjord	TN	33	NR	22	“
Helgoland	TN	50	NR	20	“
Marsdiep	TN	43	NR	30	“
Boston Harbor	TN	80-90	35	29,50**	Taylor et al. (2011)
	TP	80-90	32	29,50**	“
Tampa Bay	TN	60+	NR	20-60	Greening and Janecki (2006)
* result not statistically significant			** Chlorophyll-a, Primary Productivity		

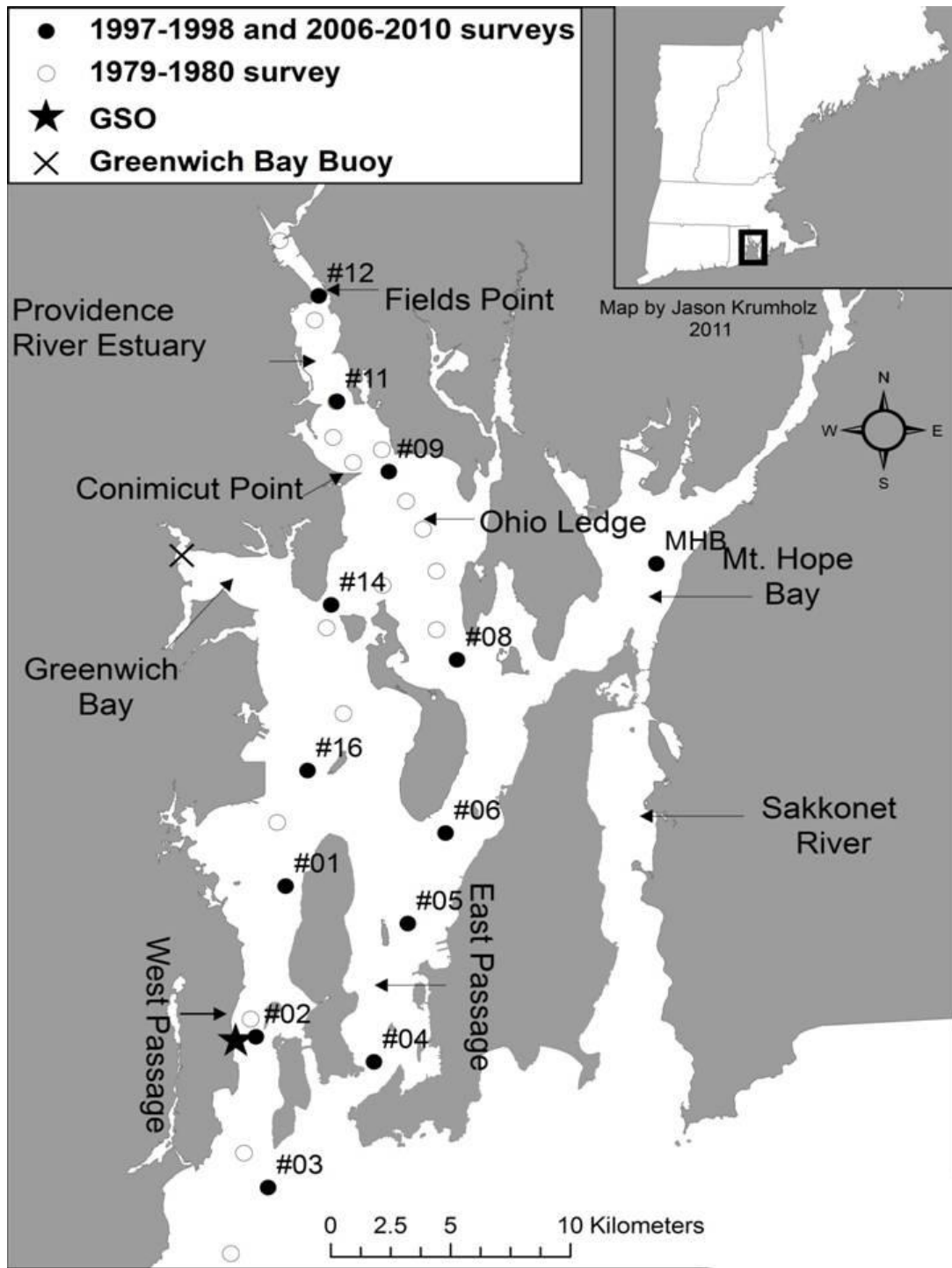


Fig. 1-1 Map of Narragansett Bay, Rhode Island. Solid dots indicate surface water sampling locations for this study, which were the same stations used by Oviatt et al. (2002). Hollow dots indicate sampling locations from Oviatt et al. (1980) used for comparison. The Graduate School of Oceanography (GSO) is marked with a star. Bay landmarks referred to in the manuscript are identified for reference

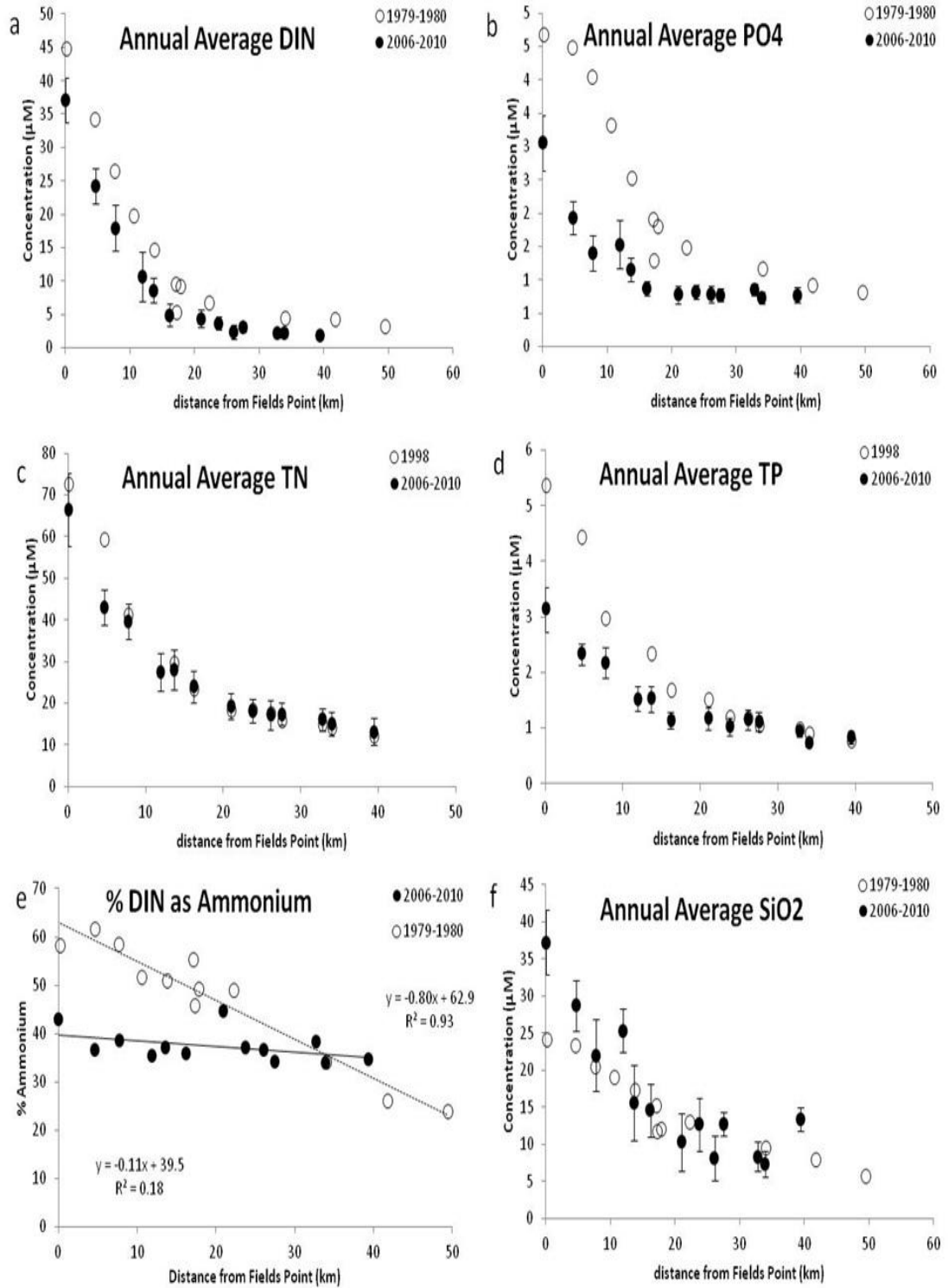


Fig. 1-2 Annual nutrient averages on a downbay gradient from Fields Point. Data from this survey (2006-2010) were compared with previous surveys (Oviatt et. al 2002, Oviatt 1980). Error bars are 1σ of annual averages

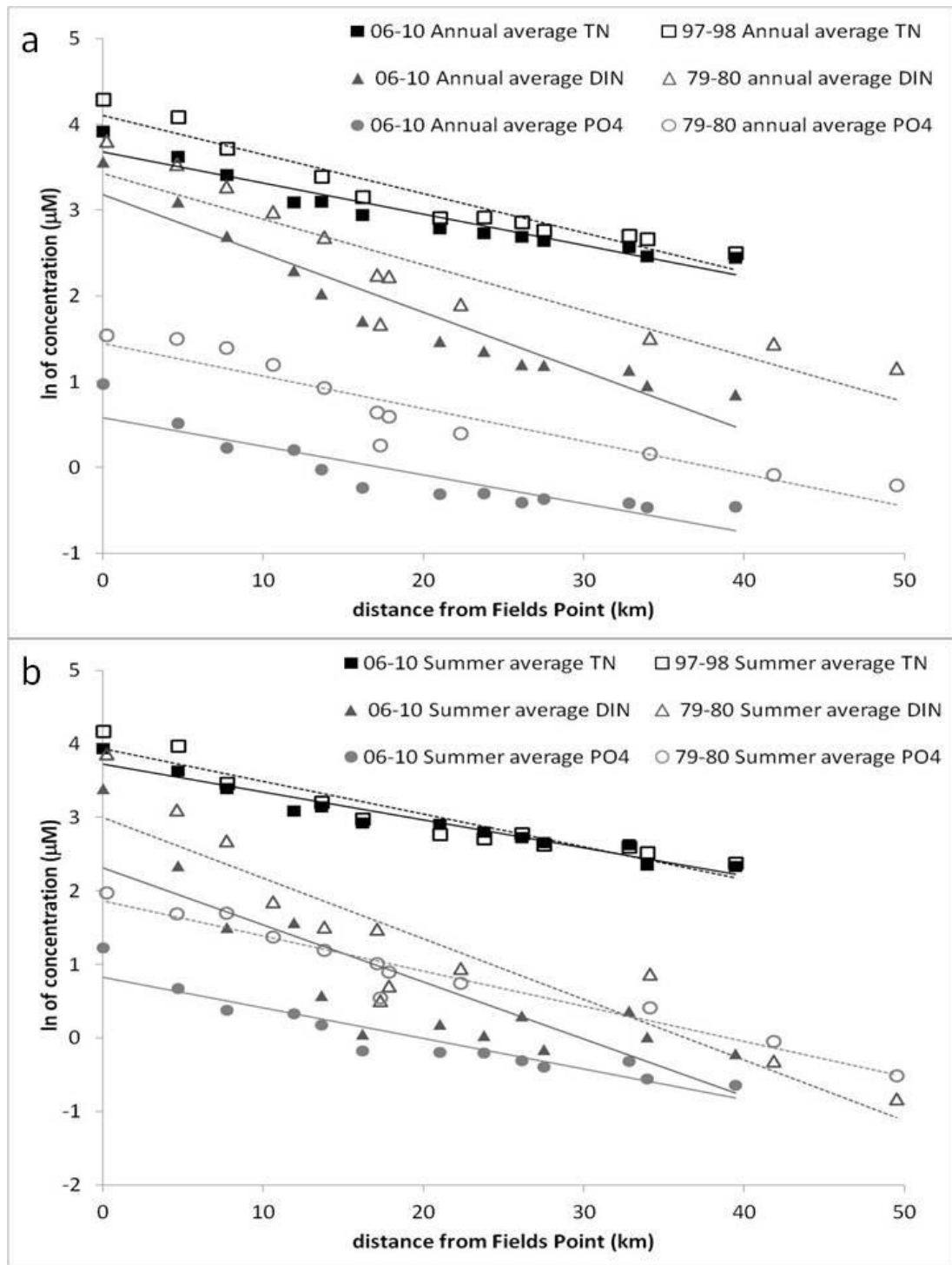


Fig. 1-3 Natural log of annual (a) and summer (June-September) (b) average total (TN) and dissolved (DIN) nitrogen and ortho-phosphate (PO_4) concentration on a downbay gradient during the present study (2006-2010) compared with past studies (Oviatt et al. 2002; Oviatt et al. 1980). Each relationship was compared by ANCOVA (Table 3 and 4)

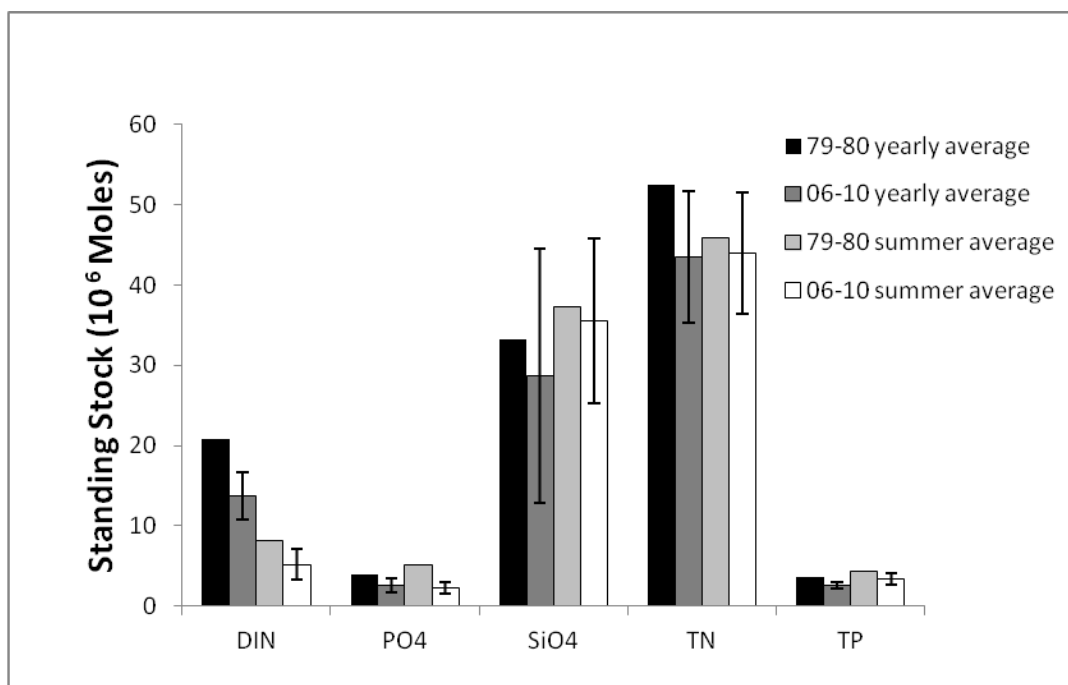


Fig. 1-4 Annual and summer standing stock of nutrients in Narragansett Bay. The 06-10 data were based on annual and summer (June-September) averages of monthly survey averages from this study. Historical TN & TP data from 1997-1998 survey (Oviatt et. al 2002), historical DIN, SiO₄ and PO₄ data from 1979-1980 survey (Oviatt 1980). Statistical results for this analysis can be found in Table 5

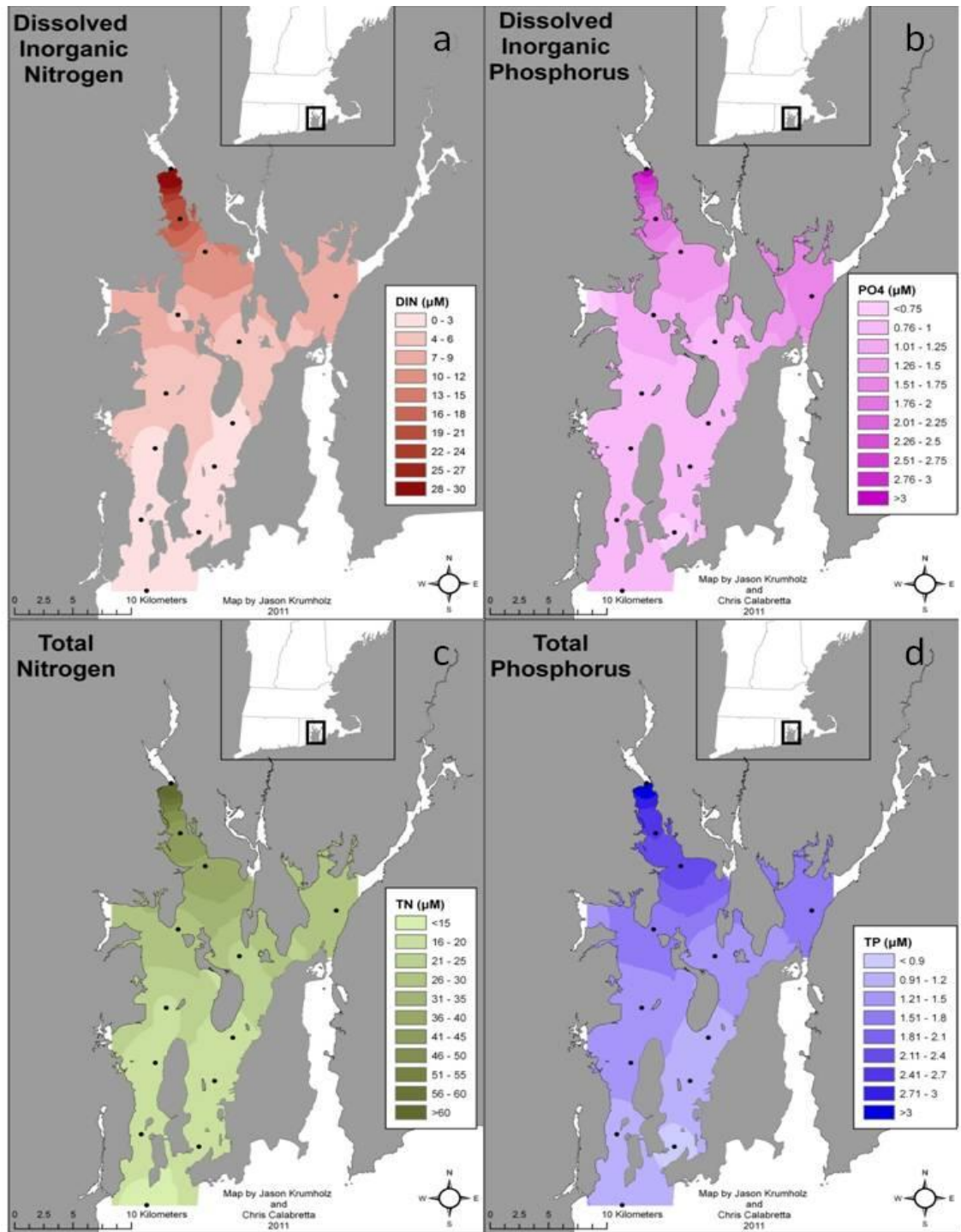


Fig. 1-5 Spatial maps of annual average surface nutrient concentration in Narragansett Bay for dissolved inorganic nitrogen (a) and Phosphorus (b) as well as total nitrogen (c) and phosphorus (d). Spatial interpolation was accomplished by inverse distance weighting of 2006-2010 annual averages of monthly average cruise and buoy data

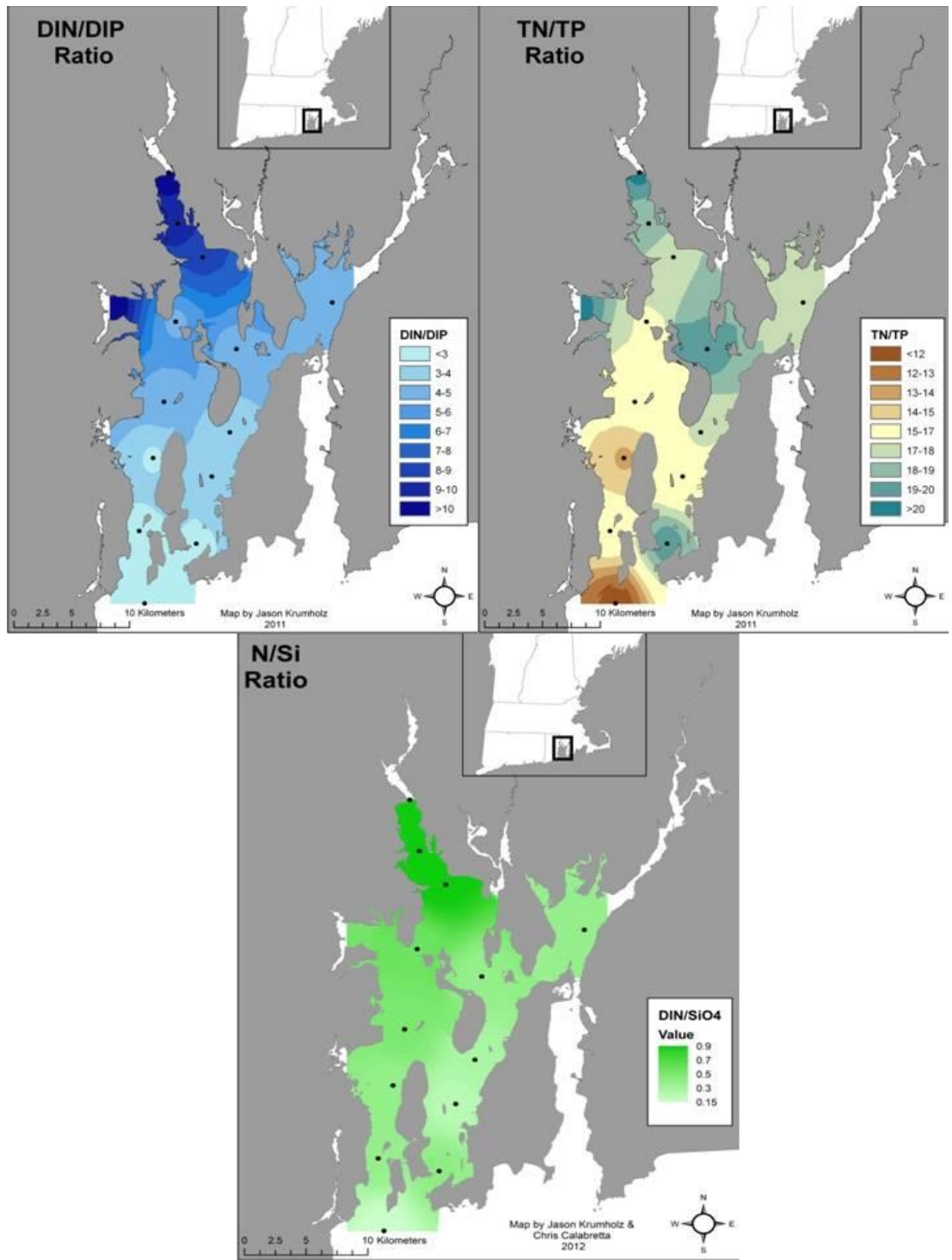


Fig.1-6 Spatial interpolation of dissolved inorganic (a) and total (b) nitrogen to phosphorus ratio and DIN:SiO₄ ratio (c) in Narragansett Bay. Values are 2006-2010 annual averages of monthly average cruise and buoy data. Spatial interpolation completed in ARC 9.2 using IDW technique

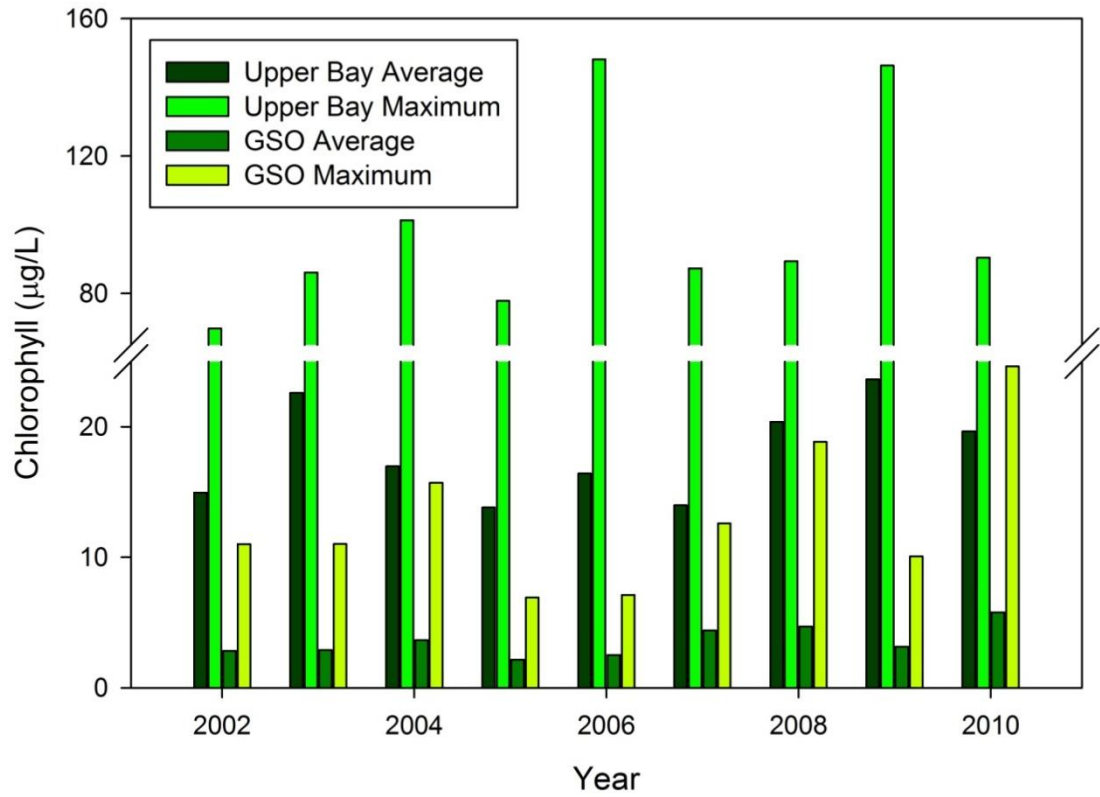


Fig. 1-7 Annual average and maximum chlorophyll-a levels at the GSO Dock station (measured weekly) (Fig. 1) and Bullock's Reach Buoy (Upper Bay) (Data from Heather Stoffel, www.narrbay.org). Upper bay data are seasonal (May-Oct) average and seasonal maximum of daily averages calculated from 15 minute in situ fluorescence data.

CHAPTER 2

AN ANALYSIS OF ANNUAL NUTRIENT CYCLING IN NARRAGANSETT

BAY, RI: 1978-2010

ABSTRACT

Annual patterns in nutrient cycling are important to furthering our understanding of how the biology, physics, and chemistry of estuarine ecosystems interact. We use a 40+ year long dataset of weekly water quality and nutrient parameters in Narragansett Bay to analyze long-term and seasonal nutrient trends which may be associated with climate change as well as to investigate changes attributable to recent reductions in nutrient inputs to the bay from implementation of advanced wastewater treatment at several facilities which discharge into the bay.

Comparing the beginning of this dataset to the five years of data available after nutrient plant upgrades (2006-2010, there are statistically significant decreases in concentrations of nitrate, nitrite, ammonium, and phosphate, no change in chlorophyll, and a statistically significant increase in silicate. We also observed changes in the cumulative distribution function of phosphate, ammonium, silicate and chlorophyll. While seasonal cycling was much stronger in the lower bay than the upper bay, no long-term changes in timing of the seasonal cycle in either region of the bay were evident.

INTRODUCTION

In many estuaries, nutrient mitigation strategies are being considered to slow or reverse the progression of anthropogenic eutrophication caused by large sewage, industrial, or agricultural loads (Carstensen et al. 2006, Clarke et al. 2006, Boynton et al. 2008, Vaudrey pers. comm., Nixon et al. 2008). However, the implications of these reductions are not uniform. While in some cases response is relatively linear and predictable- perhaps with a time lag (Carstensen et al. 2006, Artioli et al. 2008, Kemp 2009), in many cases, response is non-linear and for systems with a long history of eutrophication, rapid reductions may not produce the desired result (Duarte et al. 2009, Kemp 2009, Nixon 2009, Taylor et al. 2011).

Increased awareness of the adverse impacts of excessive nutrient loading, combined with falling cost of advanced wastewater treatment upgrades has led Rhode Island Department of Environmental Management (RIDEM) to require that several of the major sewage treatment plants which serve Narragansett Bay be upgraded to tertiary sewage treatment procedures. Between 2002 and 2006, eight plants which discharge into the bay or its tributaries upgraded to tertiary treatment, with three more upgrading between 2007 and 2010 and most other large plants planning upgrades in the next few years (RIDEM 2005). These advanced wastewater treatment procedures include bacterial nutrient removal, which has reduced DIN concentrations in the effluent of these plants by more than half during summer months (the rate of bacterially mediated denitrification is temperature dependent) (e.g. Dawson and Murphy 1972, Lishman et al. 2000, Pell et al. 2008). The implementation of a combined sewer overflow reservoir in 2008 has further reduced nutrient input during

high flow periods by delaying storm water runoff, and allowing it to be run through treatment plants before discharge into the bay. The combination of these factors has the potential to reduce total annual nitrogen loading by approximately 30% (Table 2-1).

Often it can be difficult to tease apart the impact of an intervention on an estuarine system in light of various other long-term anthropogenic and natural (e.g. decadal oscillations) variability. Given that most management interventions are not designed as scientific experiments, replication and other forms of scientific controls are often not practical, and in many cases, sufficient long-term baseline monitoring data are not available. Although recent advances in technology have brought automated in situ nutrient analysis within reach (if not quite firmly in hand), the monitoring of nutrients in coastal waters is still, for the most part, accomplished with colorimetric nutrient analysis techniques which have changed little over the past few decades. Modern technology, however, provides continually advancing capability to assimilate, analyze, and communicate data, and as interest in tracking the impacts of remediation activities grows, so too does the body of readily available datasets and tools designed for this purpose.

One such package is SSPIR (Dethlefsen and Lundbye-Christensen 2006), a State-space Model (SSM) package written for the computing language R (R Development Core Team 2005). SSM's are commonly used in the pollution literature for time series data with both an annual and long-term trend (Fanshawe et al. 2008, Lundbye-Christensen et al. 2009, Dadvand et al. 2011) and the SSPIR package allows the differentiation of seasonal cycle, long-term trend and one-time intervention (such

as caused by a legislative change or facility upgrade). This package is therefore ideal for this type of study, because it allows us to parse the various changes observed in the seasonal cycle and/or long-term trend separately, rather than perceiving the seasonal cycle as variability in the long-term trend.

In this study, we analyze changes in the annual cycling of nutrients in a temperate estuary (Narragansett Bay, RI) resulting from loading reductions to this system, but also in light of changes in climate and phenology of the region (e.g. Nixon et al. 2009, Fulweiler et al. 2010). The key questions we aim to answer are whether loading reductions at wastewater treatment plants in the upper bay have impacted the seasonal patterns of nutrient concentration in the upper bay, and whether these changes persist further down the estuary and/or impact the seasonal distribution of chlorophyll-a (a frequently used proxy for primary productivity) in the mid to lower bay region. We will also investigate whether long-term changes in the abundance or cycling of nutrients exist in the lower bay, presumably related to changes in climate and phenology.

STUDY SITE

Narragansett Bay is a 328-km² shallow phytoplankton based temperate ecosystem with a mean depth of about 8.6 m and a mean water residence time of 26 days (Pilson 1985a, Nixon et al. 1995). Freshwater input is only about 100 m³s⁻¹ (Pilson 1985a), resulting in a generally well-mixed system with relatively high salinity ranging from about 20psu in the surface waters at the head of the estuary to about 32psu at the mouth (Oviatt et al. 2002).

The watershed is home to approximately 2 million people, most of whom are concentrated in the northernmost urbanized portions of the watershed. As a result, the bay tends to have a generally north-south gradient in salinity, nutrient and other pollution loading, which in turn creates a similar gradient in eutrophication and primary productivity (Oviatt et al. 2002, Nixon et al. 2008, Oviatt 2008). In contrast to other similar estuaries, approximately 60-65% of the annual nitrogen load to Narragansett Bay comes from sewage (Nixon et al. 1995, Nixon et al. 2008) which is much higher than the average of 36% found by Latimer and Charpentier (Latimer and Charpentier 2010) for 74 New England Estuaries (including Narragansett Bay).

METHODS

Since the fall of 1976, water samples have been collected weekly from the end of the dock at the Graduate School of Oceanography, Narragansett, RI (Figure 2-1). Surface water samples were collected at approximately 9AM each Wednesday morning, irrespective of tide, although if significant precipitation or scheduling conflicts were anticipated, the sample was occasionally collected slightly early or late. Sampling commenced in August, 1976 and has continued virtually without interruption (two short periods, one in 1977 and 1983 had no samples for a few months) through the present. For the purposes of this analysis, only complete years (1978-2010, excluding 1983) were used, constituting a total of 1715 discrete samples over this 33 year period; slightly over 51 samples per year on average.

The sampling location has changed very little over the time period sampled. During 1977 and 1978, samples were collected by Niskin bottle from 2m depth at the

GSO pier. During the operational phase of the Marine Ecosystem Research Lab (MERL), water was collected from the indoor header tank supplying water to the mesocosm facility. The supply intake for this tank was located in approximately 2-3m of water under the dock (Pilson 1985b, Oviatt 2004). When this facility ceased full-time operation in June 1997, sampling returned to the pier, although samples are now collected by bucket from the surface, rather than by Niskin bottle.

Each sample was measured for temperature immediately by thermometer, then a one liter subsample was collected in an opaque polycarbonate bottle and returned to the MERL facility for analysis. Samples were analyzed immediately (after a 30 minute rest in a dark room) for fluorescence and a 10ml aliquot buffered with two drops of supersaturated magnesium carbonate buffer was filtered onto 25mm Whatman GFF filters for chlorophyll extraction (Yentsch and Menzel 1963) as modified by Lorenzen (1966). Prior to July 1984, all chlorophyll analysis was conducted with a Turner Model III fluorometer; from July of 1984 until August 2002, a Turner Designs Model 10 Series Field Fluorometer (Oviatt and Hindle 1994) was used. In August 2002 this instrument was replaced by a Turner Design Model 700, and in May, 2007 by a Turner model 10-AU. In each case, an intercalibration of the two instruments was performed. Specifics of the MERL application of this procedure can be found in the MERL methods manual (Oviatt and Hindle 1994). With a few small exceptions, most notably a switch from freezing chlorophyll filters for later extraction to immediate extraction in November, 2008 (MERL, unpublished) these methods have changed little over time. To correct the chlorophyll dataset, a correction factor was empirically derived using a set of side-by-side samples over the course of

a year, and put in place to account for possible differences resulting from the switch from freezing to immediate extraction (as per Graff and Rynearson 2011). Because the majority of the dataset used freeze-and-extract methodology, the most recent two years of data were corrected to resemble earlier data, rather than correcting 30+ years of data, even though it is likely that immediate extraction results are more accurate.

Separate 40 ml aliquots were withdrawn for salinity and dissolved inorganic nutrients. Salinity samples were sealed with parafilm and stored at room temperature awaiting analysis on a Guildline model 8400B Autosal salinometer. This model instrument has been continuously employed since the commencement of the dataset, although it was replaced partway through with a nearly identical model.

Nutrient samples were filtered through a 0.45 μ M nucleopore filter and stored frozen until analysis. For the majority of the sampling period, nutrients were analyzed on a Technicon model 2 Autoanalyzer (Technicon Industrial Systems, Tarrytown, NY). In 2009, nutrient analysis in the MERL facility switched to an Astoria SFA analyzer (Astoria-Pacific, Clackamas, OR). A thorough intercalibration between these two instruments was conducted to ensure continuity of data (See Appendix A). Colorimetric techniques used by the two instruments were similar, although some changes do exist (See Appendix A for a thorough review or *Table 1-2* for summary). Prior to 1982, Nitrite was not run separately, so only a ‘nitrate+nitrite’ measurement was available; however, this does not impact the determination of dissolved inorganic nitrogen because any nitrite present in the sample (generally a small amount of the total DIN (see Chapter 1)) would have been detected in the ‘nitrate+nitrite’ channel. Methodology for the preparation and storage of nutrient samples has not changed with

instrument switchover, with the exception that starting in 2009, salinity for upper bay samples was recorded for matrix matching purposes (matrix matching was not used for the Technicon, rather a salinity correction factor was applied when necessary, see appendix A) and is outlined along with standard operating protocols for the Technicon analyzer in the MERL manual (Oviatt and Hindle 1994). Seawater operating procedures for the Astoria analyzer can be found in Scott et al. (2005), and SOP for the MERL Astoria Analyzer can be found in Appendix A.

In order to correct for any potential bias caused by missed or lost samples, linear interpolation was used to fill any gaps in the dataset. Of the 10620 discrete values in the dataset, 639, or roughly 6% were interpolated. Most gaps occur in the early portions of the dataset and only 5 are more than 2 weeks in duration between samples.

Annual averages, minima, and maxima for each analyte were calculated and compared via regression analysis to examine long-term trends. Nutrient and chlorophyll data were also compared to climate variables such as precipitation at T.F. Green airport in Providence (NOAA 2008), and NAO to identify any long-term trends. These lower bay data were compared with similar data collected at several upper bay stations during similar time periods, using two separate discrete datasets. During 1979-1980 surface nutrient samples were collected from 17 stations around the bay (but not including the lower east passage) approximately biweekly as part of a separate study (Oviatt 1980). Similarly, from 2006-2010 surface water samples were collected from 13 stations throughout the bay for a separate project. However, the sampling methodology used in both of these data sets is virtually identical to the protocol used

for the GSO dock sample (for more detail, see Chapter 1) with the exception that no chlorophyll samples were taken, and all samples were run on the MERL autoanalyzers, so the data are comparable. However, because the sampling locations in these two studies do not line up exactly, and because nutrient concentrations in the Providence River Estuary are strongly spatially variable, it was necessary to average the values over a larger area in order to make these datasets comparable. By averaging over the entire Providence River Estuary (defined as from Fields Point south to Conimicut Point, encompassing 4 stations for the 79-80 survey, and 3 stations for the 2006-2010 survey) it is possible to directly compare these two datasets. Averaging in this way also eliminates any small scale spatial variability which could impact the results.

Data were compared across time and space with two-sided two-tailed Kolmogorov-Smirnov (KS) tests to determine if the distribution or magnitude of the nutrient data have changed over time. This test is commonly used to test the assumption of normalcy in a dataset by comparing a given dataset to a normal dataset with the same mean and standard deviation (often referred to as a one sided KS test). However, it can also be used to compare two observed distributions, and calculate the likelihood that those observations are drawn from the same larger dataset or are independent (two sided KS test).

The KS test is useful to determine whether the data are drawn from the same or statistically different distributions, but it does not distinguish between temporal shifts and magnitude shifts. To attempt to isolate any temporal changes, the data were normalized to cumulative percentage of observed nutrients over the course of a year,

such that on 12/31, 100% of each analyte has been realized. This allows us to view the percentage of the nutrients which can be found in each given season. This procedure creates a visualization whereby a constant concentration across the annual cycle would cause a straight line with slope approximately 2% per week, and a strong seasonal cycle would produce a sigmoid response. The normalized data were then tested again with the KS test to determine if any temporal shifts were statistically significant.

The time series analysis package SSPIR (Dethlefsen and Lundbye-Christensen 2006), written for R (2005) was used to parse the observed effects into long-term, seasonal, and intervention driven changes. SSPIR is a state-space model (SSM) which is similarly treated in R to a generalized linear model (GLM), with the exception that the SSM allows the parsing of time series terms (e.g. harmonic and unstructured seasonal patterns, interventions, etc...). The model is then fitted to the data using extended Kalman filtering (Dethlefsen and Lundbye-Christensen 2006).

Because of the high amount of interannual variability, and the strong serial autocorrelation in the data (correlation coefficient of timestep t with timestep $t-1$ was about 0.8), fitting a state-space model like SSPIR to the data is a good choice to try to increase the resolution. Because SSPIR cannot predict variance (and therefore provide a confidence interval around a prediction) it was necessary to calculate variance with another function. For this, we chose StructTS (Ripley 2002) and removed the annual cycle using 'sumseason' to average the past 52 (weekly) data points to white noise, which reduced the trend to a random walk, and produced appropriately uncorrelated residuals.

By separating the long-term trend from the intervention in this periodic dataset, we can isolate whether reductions at Upper Bay treatment facilities have a measurable impact on average nutrient concentrations, seasonal nutrient cycles, or chlorophyll levels at this lower bay station or whether this area of the bay is relatively insulated from upstream changes. To do this, we calculated the magnitude and confidence intervals for an intervention term on various nutrient analytes taking place in January 2006 (When the Bucklin point plant came online, although several other smaller plants upgraded within a few months of this time), and for comparison sake, a phosphate intervention term taking place in January 1995, immediately after legislation passed to reduce phosphate loadings from detergent (Litke 1999). This comparison will allow us to test the sensitivity of the model to the intervention term, because unlike DIN reductions, phosphorus reductions were gradual, beginning well before the passage of legislation, and continuing to gradually fall throughout the 90's and 00's. R-Code and specific application notes pertaining to the model can be found in Appendix C.

RESULTS

Virtually all nutrient components exhibited a seasonal cycle, with concentration highest in the late winter/early spring, falling off sharply with the winter-spring diatom bloom (or less sharply in years where this bloom is weak or absent), remaining lower through the summer, then rising again in the fall as primary productivity tapers off (Oviatt et al. 2002) (Figure 2-2). The absolute magnitude and timing of the yearly maximum was variable, and appeared to show little trend over time, with the possible exception of a lack of extremely high values during the last 5

years or so (Figure 2-2). Throughout the year, the ratio of N:P was typically well under the 16:1 Redfield ratio, an indication of nitrogen limitation, although at times during the summer, both nitrogen and phosphorus became quite low (Figure 2-2, 2-3).

A first pass comparison can be made by observing side-by-side, the annual cycle at the beginning of the dataset and the annual cycle from the most modern years, to detect whether a change in absolute magnitude or seasonal timing can be observed in either the GSO dock or Providence River Estuary datasets (Figure 2-3, 2-4 respectively). For the upper bay dataset, discreet sampling was done on a monthly (bi-weekly in the summer) basis at several stations in the Providence River Estuary both in 1979-1980 (Oviatt 1980) and from 2006-2010 (this study). To account for differences in sampling locations (due to proximity to nearby WWTF's, nutrient concentrations in the PRE were highly spatially variable) all stations within the area north of Conimicut Point and South of Fields Point (3 for the 2006-2010 survey and 4 for the 1979-1980 survey) were averaged.

Seasonal magnitudes and patterns of nitrogen constituents (nitrate, nitrite, ammonium) have not changed dramatically over time, though some small changes in seasonal pattern (most notably a sharper drop off of nitrate+nitrite in the modern data due possibly to the return of larger winter spring blooms) and magnitude (e.g. less ammonium in the fall in the modern data) may be observed (Figure 2-3). There was a dramatic reduction in the concentration of phosphate throughout the annual cycle. In contrast, silicate shows a small, but statistically significant increase in concentration, particularly during the summer months.

It is apparent from the data that there was a large amount of inter annual variability, both in range and in pattern. This was particularly true in the winter-spring period and in late summer, which is expected, because of variability associated with bloom dynamics during these periods, documented in past literature on the bay (e.g. Pilson 1985b, Oviatt et al. 2002, Smith et al. 2010), and observed in high variability in the chlorophyll data during those times of year (Figure 2-3). When taken as yearly averages, there was no long-term trend observed in the chlorophyll data, however, again possibly due to weakening of spring blooms (e.g Nixon et al. 2009) there is a slight downward trend in annual maximum chlorophyll over time (Figure 2-5).

Precipitation was a small but significant contributor to DIN and SiO_4 concentration in the bay, with a slight positive relationship between the average DIN concentration in a given month at the GSO dock, and the total precipitation fallen during that month ($R^2=0.02$, $df=359$, $F=6.6$, $P=0.01$), and similarly, over an annual cycle, for silicate ($R^2=0.22$, $df=30$, $F=8.2$, $P=0.007$) (Figure 2-6a,d). Because the sample was not collected when rain is falling, we chose not to attempt correlation on a shorter time scale than monthly for fear of biasing the result due to the sampling method. No relationship was found between PO_4 and precipitation or between NAO (December, January, February index) and nutrients at the GSO station, though NAO exhibits a slight negative correlation with chlorophyll ($R^2=0.14$, $df=32$, $F=5.17$, $P=0.03$). There were small but significant negative relationships between chlorophyll and nutrients ($R^2=0.13$, $df=383$, $F=58$, $P<0.001$ for DIN and $R^2=0.11$, $df=383$, $F=47$, $P<0.001$ for PO_4), though the relationship with DIN has both steeper (relative to Redfield) slope and higher R^2 (Figure 2-6).

By using the KS test to compare data from the beginning of the dataset to data after the onset of loading reductions (2006-2010) we can determine whether the upgrades, or other changes to the system, have altered the distribution of nutrients, either in timing (likely associated with climate change), or in magnitude (likely attributed to load reductions). One output visualization of the Kolmogorov-Smirnov test is to compare the cumulative frequency distribution (with frequency on the Y axis and concentration on the X) of the two datasets. This analysis for the GSO dock data, indicated that the nutrient analytes have responded differently over time. While nitrate and nitrite showed virtually identical curves to data from 30 years ago, ammonium showed a small but statistically significant drop across the entire range of observed values (Figure 2-7). DIN showed similar maximum magnitude, indicating that peak DIN concentrations have not changed over time, and a small but not statistically significant increase in the frequency of moderate values (between 2-4 μM), with a not statistically significant corresponding decrease in the frequency (but not magnitude) of high ($>8\mu\text{M}$) values.

In contrast, phosphate showed a continuous reduction across all dates, with the largest reduction ($>50\%$) present in the peak values. For example, 90% of observed phosphate values in the modern dataset are below 1.3 μM , while only about 50% of the historical values are below this threshold (Figure 2-7).

Silicate shows a statistically significant increase at the GSO site, and nearly statistically significant in the upper bay, with the increase appearing to result from more very high values in the recent data, rather than fewer low values (Figure 2-7, 2-8).

Chlorophyll also shows a statistically significant decline though this reduction appears to come exclusively from a drop in peak values (Figure 2-7, 2-5). While the KS test does not discriminate as to whether a statistically significant change is due to a drop in peak values, or a change in distribution, the associated K statistic shows the maximum difference observed between the two datasets, which in the case of chlorophyll, is located at the very peak of the distribution (Figure 2-7). Furthermore, regression analysis shows no change in annual average, but a measurable downward trend in annual maximum (Figure 2-5). Unfortunately, bloom dynamics in the lower bay are difficult to discern from this dataset because an observed chlorophyll peak may be due to favorable local conditions, or due to advection of a bloom from the upper bay, and the weekly sampling frequency is insufficient to reliably capture shorter events. Nevertheless, this portion of the bay has experienced a significant reduction in the frequency and magnitude of high chlorophyll values over the last few decades.

The upper bay data (Figure 2-4, 2-8) have similar absolute patterns to the lower bay data, though the concentrations are (expectedly) higher, and the seasonal variability is somewhat lower. For this dataset we also have total nutrients (from Oviatt et al. 2002), which show a significant decrease in very high TN events, and a nearly significant reduction in TP, which appears to be relatively constant across concentration (Figure 2-8)

We observed interesting patterns in the magnitude shifts in nutrients associated with the last few decades in Narragansett Bay, but in order to investigate whether changes in seasonality are observed, it was necessary to isolate and remove these

magnitude changes, in order to look strictly at the seasonal patterns (Figure 2-9). To do this, we normalized the maximum concentration observed in any given year to 1, and examined the cumulative fraction of the total nutrient load observed during the course of the year. A normalized cumulative percent contribution curve that is close to linear indicates consistent concentration throughout the year. Areas with steep slopes have disproportionately high concentrations, and vice versa. Some variables (e.g. nitrate) exhibit a much stronger seasonal cycle than others (e.g. chlorophyll, phosphate). In general, however, few changes between the datasets are observed. The spring bloom may be occurring slightly earlier (evidenced by an earlier drawdown of nitrate and DIN), and there may be a slightly stronger seasonal cycle in phosphate and ammonia, but none of these observations were statistically significant. On a seasonal basis, a much weaker cycling in the upper bay occurred than we observed in the lower bay, particularly in nitrate+nitrite, which was relatively constant in the upper bay, but showed a strong seasonal cycle in the lower bay (Figure 2-10, 2-9 respectively). In contrast, silicate shows very weak seasonal cycling in both parts of the bay, possibly because it does not flux into or out of the sediments as much as nitrogen.

Similarly to the lower bay, there were only very slight differences in seasonal pattern which can be observed between the datasets, none of which were statistically significant (Figure 2-10). Increased variability in the upper bay dataset may be related to variations in discharge associated with precipitation, but also may be an artifact of the way the data were handled. While the lower bay are weekly data points from a single source, the upper bay data are monthly averages of several stations located across a strong spatial gradient. In many cases, the concentration at Conimicut point

(the southernmost extent of stations categorized as ‘Providence River Estuary’) are half or less the value observed at Field’s Point (the northernmost extent and location of the outfall for the largest plant), a reduction due in part to dilution and in part, presumably to utilization.

None of the analytes showed a statistically significant (confidence interval not overlapping zero) intervention effect relating to a phosphorus reduction pinpointed in January 1995 at $\alpha=0.10$, and most estimated intervention terms (with the exception of phosphate) were very small, indicating minimal impact. Intervention terms for the DIN reduction associated with the WWTF upgrades were much larger, but so too are the associated confidence intervals. No intervention parameters were significant at $\alpha=0.05$, and only ammonium was significant at $\alpha=0.10$ (-0.54 ± 0.46 μM). The intervention term for chlorophyll was positive (though not statistically significant), indicating that, if anything, chlorophyll in the lower bay has increased since the reductions came online.

Another benefit of the model is that it can be used to compare the relative magnitudes of the various signals within the dataset (Figure 2-11). The model pulls out a seasonal signal of approximately 10 μM . With annual cycling removed by compiling a one year moving average, we can also display a long-term trend in the data (Figure 2-11a). While the time series shows some prolonged periods of relatively high DIN concentration in the 1990’s, and an extended period of low average values from 2003-2008, 2009 and 2010, the last two years of the model are quite high, which casts doubt on any long-term trend. While the model does show some interesting patterns, the remaining residual after long-term trend and seasonal cycle have been

removed is still quite large (Figure 2-11c); larger than the magnitude of the seasonal cycle and the long-term trend combined. This term also appears to show an annual pattern, a possible indication that not all of the annual signal is captured appropriately by the model.

DISCUSSION

When directly comparing the early and late parts of the dataset, there are some clear changes despite the large amount of interannual variability. Virtually every analyte (with the exception of chlorophyll) showed a statistically significant change from the early to the later part of the dataset (with NO_2 , NO_3 , DIN, NH_4 , and PO_4 decreasing, and SiO_4 increasing). The aspect most directly associated with the upgraded WWTF processing is the observed decrease in ammonium during the summer. These reductions significantly (up to 90% in some cases, see chapter 3) reduce ammonium loading from several of the plants discharging into the bay and its tributaries. This hypothesis is strengthened by the fact that the changes in ammonium were larger in the upper portions of the bay, nearer to the WWTF's (Figure 2-3, 2-4). The trend was weaker when considering DIN as a whole, as nitrate and nitrite have decreased only slightly in the lower bay, and not at all in the upper bay.

In contrast, the observed large reduction in phosphorus was likely less related to WWTF upgrades (though a few plants have implemented phosphorus reduction procedures), but rather due to changes in legislation removing phosphates from detergents which occurred throughout the 80's and 90's and continue into the present (e.g. Litke 1999). We suspect this because phosphate showed a gradual decline

throughout the dataset (Figure 2-7, 2-8, 2-12), rather than a punctuated drop in the highest values as observed with the nitrogen species (Figure 2-7, 2-8).

Unfortunately, the model cannot confirm the impact of legislation on phosphate concentrations result, as there was no significant response of phosphate to intervention either in the mid 1990's or 2005. The phosphate response should be more gradual because phasing out began before the passage of legislation, continued to reduce through the 90's and 00's, and may also have been delayed due to sediment remineralization (Pomeroy et al. 1965, Litke 1999, Carstensen et al. 2006).

We also observed an increase in dissolved silicate between the beginning and end of the survey period. It is possible that the observed increase in silicate in both the upper and lower bay (Figure 2-3, 2-4) is related to increased precipitation, as silicate concentration shows a positive correlation with total precipitation on an annual basis ($R^2=0.23$, $df=29$, $F=8.28$ $P=0.007$). It is also possible that this pattern was related to decreased diatom based primary productivity, and therefore decreased demand. The trend holds for both the upper and lower bay datasets (Figure 2-3, 2-4), reducing the likelihood that it is anecdotal or site related (e.g. increased sedimentation at GSO dock site). However, there is a great deal of interannual variability in silicate concentration, and while several other studies have shown a decrease in chlorophyll over time in Narragansett Bay (e.g. Fulweiler et al. 2007, Nixon et al. 2009), this dataset does not show any long-term reduction of average chlorophyll concentration in the bay (Figure 2-3, 2-5), though there may be some evidence of decrease in the intensity of blooms (Figure 2-5, 2-7). While a shift in the biological community of primary producers

might explain the observed trend, it is beyond the scope of this study to speculate on causality.

In the upper bay a steep reduction in maximum ammonium values occurred, likely caused by the removal of ammonium from the WWTF's. The biological nitrogen removal process used at these plants is typically coupled nitrification-denitrification, whereby the DIN in secondary treated wastewater is super-oxygenated and bacteria oxidize ammonium into nitrite then nitrate, after which the wastewater is allowed to become anoxic, and other bacteria convert it into nitrogen gas (N_2). If the aerobic process is run near to completion but the anaerobic portion is not, a dramatic reduction in ammonium discharge occurs (up to 90% for some plants during summer months), with little change, or even an increase in nitrate and nitrite discharge. This transformation explained the upper bay data (Figure 2-8), but the trend weakened in the lower bay as the relative contribution of ammonium to DIN decreased. This is somewhat puzzling, since typically ammonium is more readily bioavailable than nitrate or nitrite, however it is possible that decreased loading of ammonium paired with stable or even slightly increasing nitrate and nitrite loads may have increased the relative percentage of nitrate and nitrite taken up, simply because there was insufficient available ammonium.

The lack of a strong seasonal cycle in nitrate in the upper bay is a potential indication that nutrients were not limiting production in the upper bay. While concentrations in the lower bay were drawn down to near zero during the summer months when productivity was high, concentrations in the upper bay remained relatively constant throughout, as a steady supply of nutrients from the plants

exceeded that which can be utilized by the plankton during its short residence time of about 3 days in the Providence River Estuary (Pilson 1985a). This is confirmed by results from the GEM box model, which showed, in general, that light limited production in the Providence River Estuary during most of the year (Kremer et al. 2010, Vaudrey pers. comm.). Literature from other systems also provides evidence of light limitation under similar nutrient loads, especially in the winter time (e.g. Cloern 1999, Sin et al. 1999, Saito 2008). Furthermore, mesocosm experiments (Oviatt et al. 1986, Oviatt et al. 1995) showed decreased ‘return on investment’ with nitrogen loading at or near concentrations observed in the Providence River Estuary.

Although definite differences in seasonal cycling between the upper and lower bay occur, when we compare the seasonal patterns at the same site over time, there is little evidence of any changes. After standardizing to remove changes in absolute magnitude of nutrient concentration, we see no change in annual cycle over the dataset. This is an indication that the many other climate related factors which might be influencing nutrient dynamics in the bay by altering phenology have not, at least as of yet, impacted the seasonal cycling of nutrients.

The model results were relatively inconclusive in terms of discerning whether an instantaneous ‘intervention’ occurred in concentration associated with the plant reductions, rather than a gradual decrease or simply interannual variability. While the model predicts a decrease in all nitrogen species associated with the intervention, the residuals produced by the StructTS function which are used to calculate the confidence interval for the model were cripplingly large. As such, the only analyte with a 90% confidence interval not overlapping zero was ammonium (intervention

term $0.54\mu\text{M}\pm 0.46$). This is the analyte from which we would expect the greatest response, since the majority of the plant reductions is in the form of ammonium. While the state-space modeling approach may be an interesting and appropriate technique to parse trends and responses in this dataset, additional work is necessary before the model will provide further insight.

One possible issue is that because the residuals were estimated with StrucTS, which does not include an intervention term, variability associated with the reduction would be interpreted by StrucTS as ‘noise’, increasing the residuals from the model, and therefore, the variance in SSPIR. It is also possible that the ‘solution’ provided by StrucTS was a local maximum rather than the global maximum likelihood, artificially inflating our estimation of variance as well.

Another issue with the model is the high amount of variability in the data not captured by either the long-term trend, the seasonal cycle, or the intervention term. The model residuals appear to still have an annual signal in them as well, though perhaps the period of this signal is not exactly 52 weeks from year to year, which may explain why the model does not attribute this variability to the annual cycle term. We attempted to fit the annual cycle term using the ‘polytrig’ function in SSPIR, which would allow the periodic (seasonal) cycle to vary from year to year both in amplitude and in period, but could not get this function to work, and so settled for the simpler ‘sumseason’ command which uses a fixed amplitude and 52 week period. It is quite possible that the uncaptured variability in the seasonal cycle has to do with the timing of the winter-spring bloom. We suspect this because there is a downward spike in the residuals virtually every year in the February-March time frame, and the spike tends to

be smaller in years with no winter-spring bloom (e.g. 1998, 2005, 2006) (Figure 2-11), which we anticipate is indicative of nutrient drawdown correlated with the bloom. The ability to capture and incorporate some of this variability would greatly improve the utility, and probably the predictive capacity of the model.

CONCLUSION

Some marked changes have occurred in the way nutrients cycle in the bay over the last several decades. There is a strong decrease in phosphorus in both the upper and lower bay (Figure 2-3, 2-4, 2-7, 2-8), due to legislative changes removing phosphates in detergents, surfactants, and other industrial and household products. WWTF load modifications have resulted in significant reductions of ammonium and to a lesser degree DIN in both the upper and lower bay (Figure 2-3, 2-4, 2-7, 2-8). While the lower bay appears to have a stronger seasonal cycle, particularly for nitrate+nitrite, than the upper bay, neither location exhibits statistically significant shifts in timing or seasonal pattern (only magnitude) (Figure 2-9, 2-10). Furthermore, the WWTF reductions appear to have had no impact on chlorophyll concentrations in either the upper or the lower bay (Figure 2-3, 2-5). However, a statistically significant reduction in annual maximum chlorophyll value had occurred in the lower bay over the course of the entire dataset (Figure 2-5, 2-7).

ACKNOWLEDGEMENTS

This manuscript would not have been possible without the diligent efforts of literally dozens of MERL staff who have collected, analyzed, compiled, and intercalibrated this fantastic dataset over the last 40+ years. Thanks are also due to Heather Stoffel and Edwin Requintina for providing buoy data, and to the NOAA Nu-Shuttle team for support and logistical assistance. Particular thanks go to Brooke Longval for assistance intercalibrating nutrient autoanalyzers and to Jeff Mercer, Leslie Smith, Matt Schult and Conor McManus for their work intercalibrating and standardizing the long-term chlorophyll dataset. We also thank our funding sources: NOAA Bay Window Awards to Candace Oviatt and collaborators: NA04NMF4550409, NA05NMF4721253, NA07NMF4720287, NA09NMF4720259, and the NOAA Coastal Hypoxia Research Program (CHRP) NA05NOS4781201 to Candace Oviatt and collaborators, as well as a Coastal Institute IGERT program ‘grants in aid’ to Jason Krumholz.

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Table 2-1: Estimated major sources of Nitrogen (10^6 Moles N as TN) to Narragansett Bay, and potential future change resulting from impending management strategies.

Nitrogen Source	2003^a	2010 change	2014 potential change^b	Notes
Direct Sewage	170	143 (16% reduction)	up to 60% decrease	2014 value based on RIDEM estimates of loading: 3mg/l for major plants for 2014, 8mg/l for smaller plants. ^b
Indirect (into rivers) Sewage	193	120 (37% reduction)	up to 50-60% decrease	Assumes above plus MA compliance with proposed reductions. Does not account for riverine abatement.
Other riverine inputs & surface drainage	145	129 (11% Reduction)	?	may improve slightly due to reduction in ISDS usage, fertilizer restriction, and improved land-use practices. Changes may take years-decades to manifest.
Direct Atmospheric Deposition	30	30	?	unlikely to change significantly, but may decrease slightly due to air quality regulations.
Urban Runoff	37	62(67% increase)	up to 20-30% decrease	Increased precipitation and land-use changes. Potential future decrease from improvements in CSO abatement and land usage regulations.
TOTAL (10⁶ Moles/yr)	575	484^c	approx. 270-320	
^a Data from Nixon et al. 2008 ^b Estimates from Liberti, 2009 pers. comm. ^c assuming no change in un-estimated parameters.				

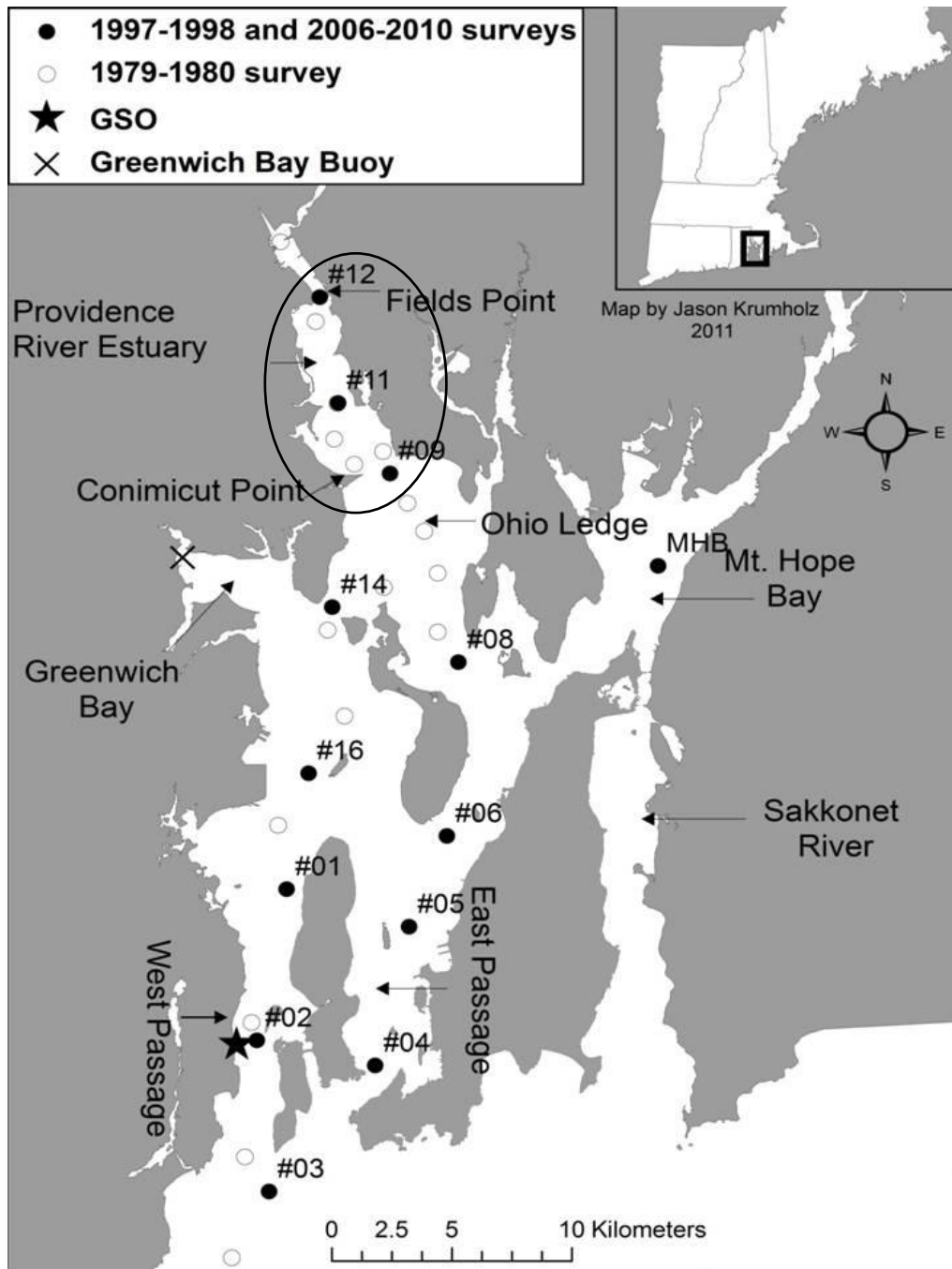


Figure 2-1: Map of Narragansett Bay and landmarks referred to in this manuscript. Sampling stations from the Providence River Estuary averaged in this manuscript to generate ‘upper bay’ values are enclosed in the circle.

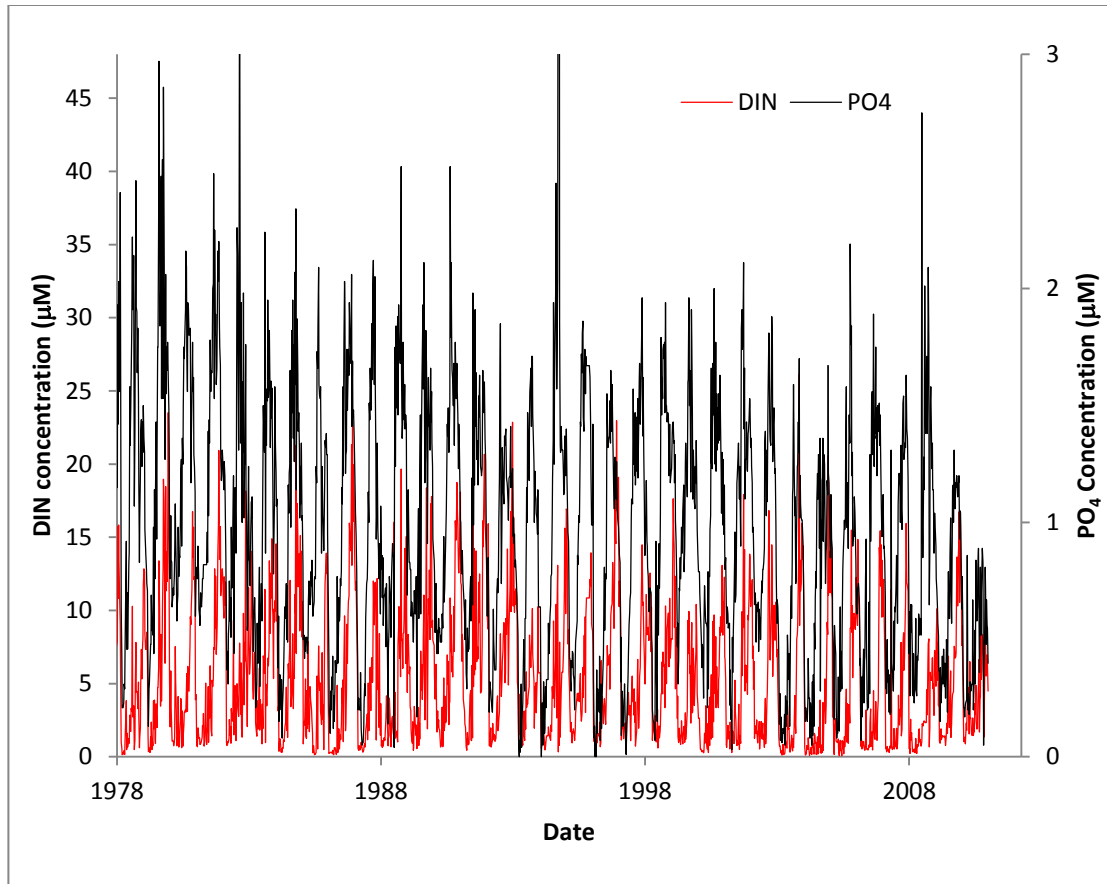


Figure 2-2: Weekly dissolved Inorganic nitrogen and phosphorus concentrations over the 35 year dataset at GSO Pier. Nitrogen (left axis) and phosphorus (right axis) axes are scaled at 16:1.

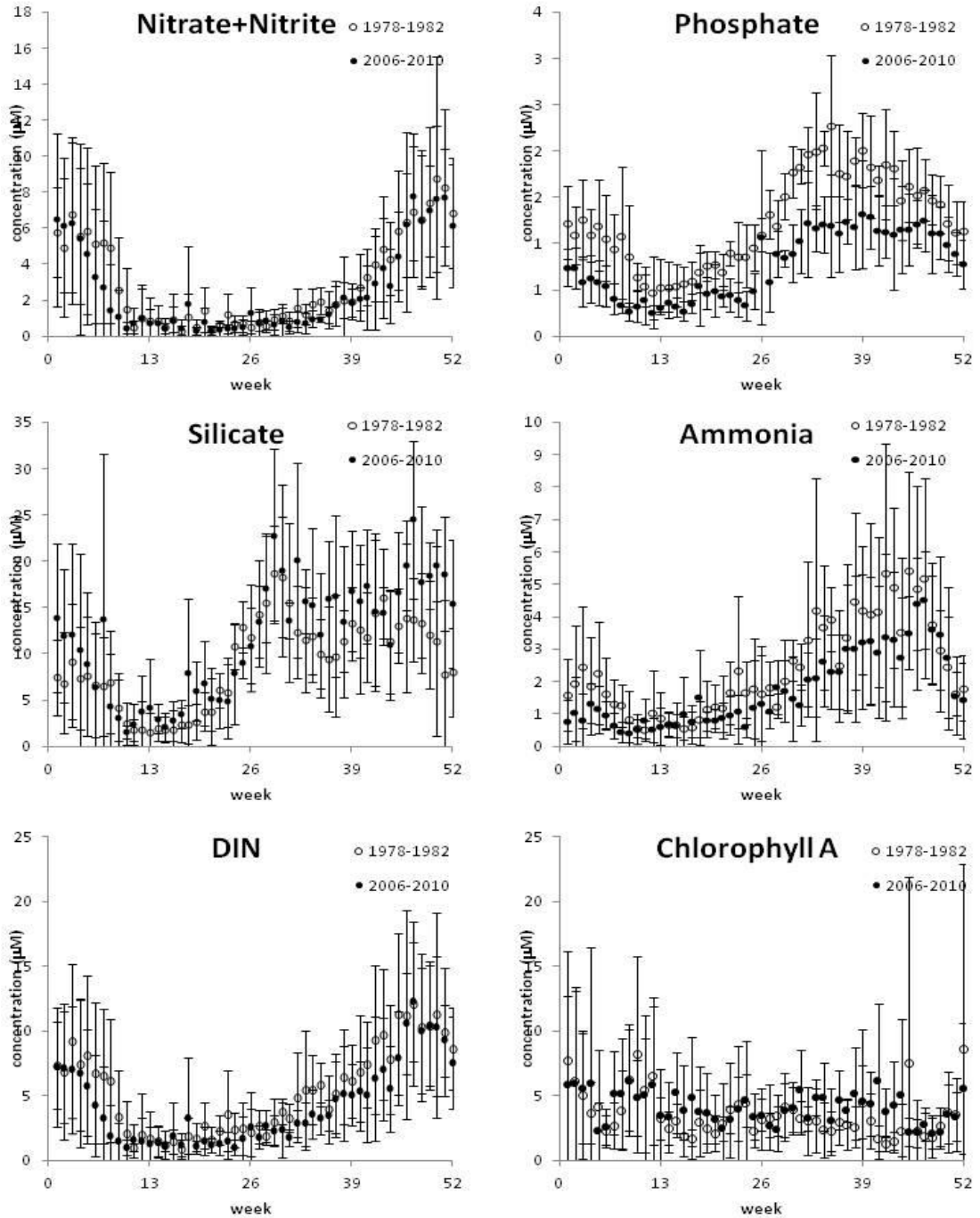


Figure 2-3: Seasonal cycle of nutrient analytes at GSO dock station. Data are annual averages by week for the periods 1978-1982 (inclusive) and 2006-2010 (inclusive). Error bars are the standard deviation of annual values for the given week within the 5 year survey period.

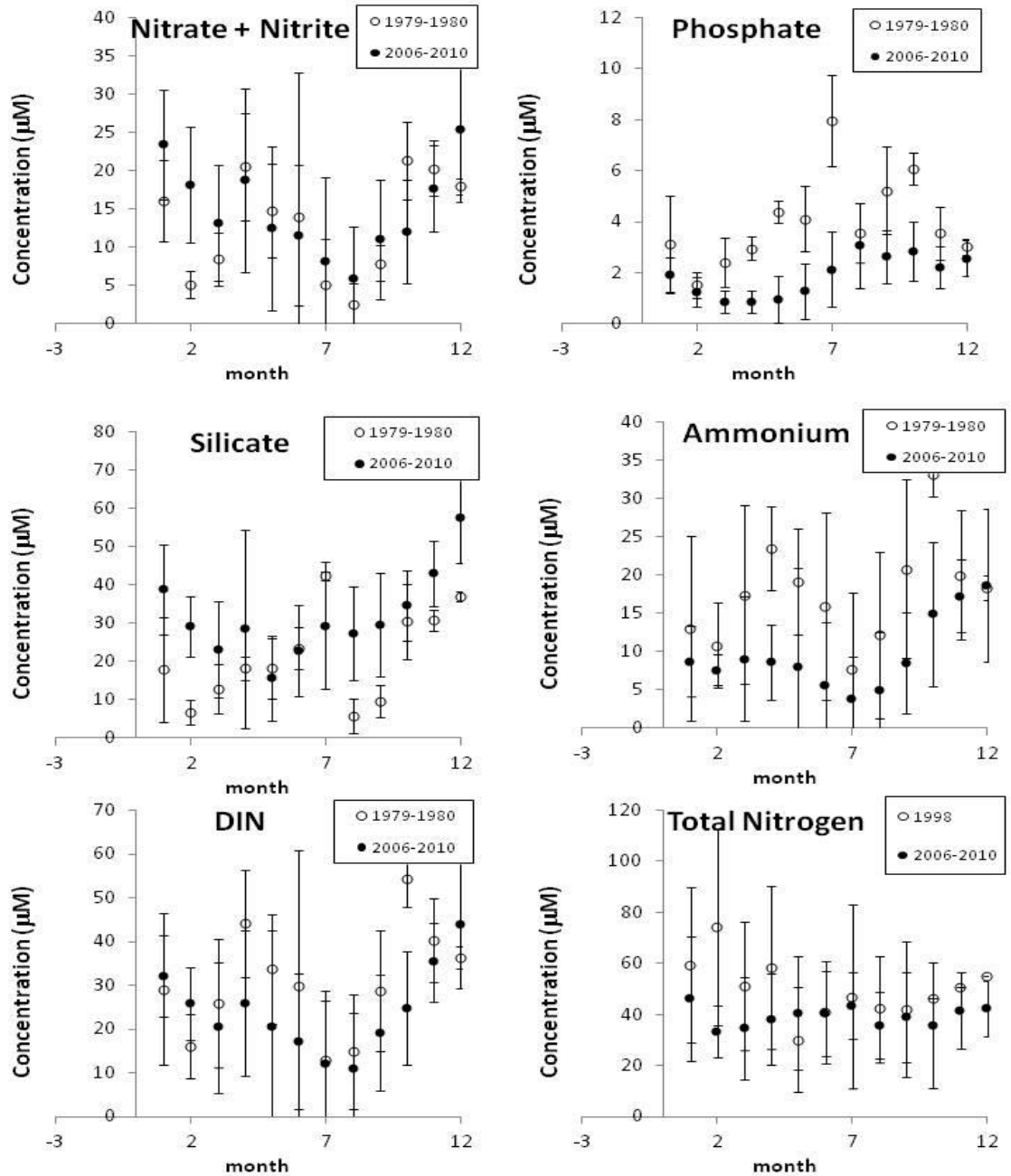


Figure 2-4: Seasonal cycle of nutrient analytes in the Providence River Estuary. Data are averages of all observed values at 3 (2006-2010) or 4 (1979-1980) stations between Conimicut Point and Fields Point during the given month (N= 3-12) for the 1979-1980 survey (Oviatt et al. 1980) and 2006-2010 (inclusive). Error bars are the standard deviation of all values for the given month within the survey period.

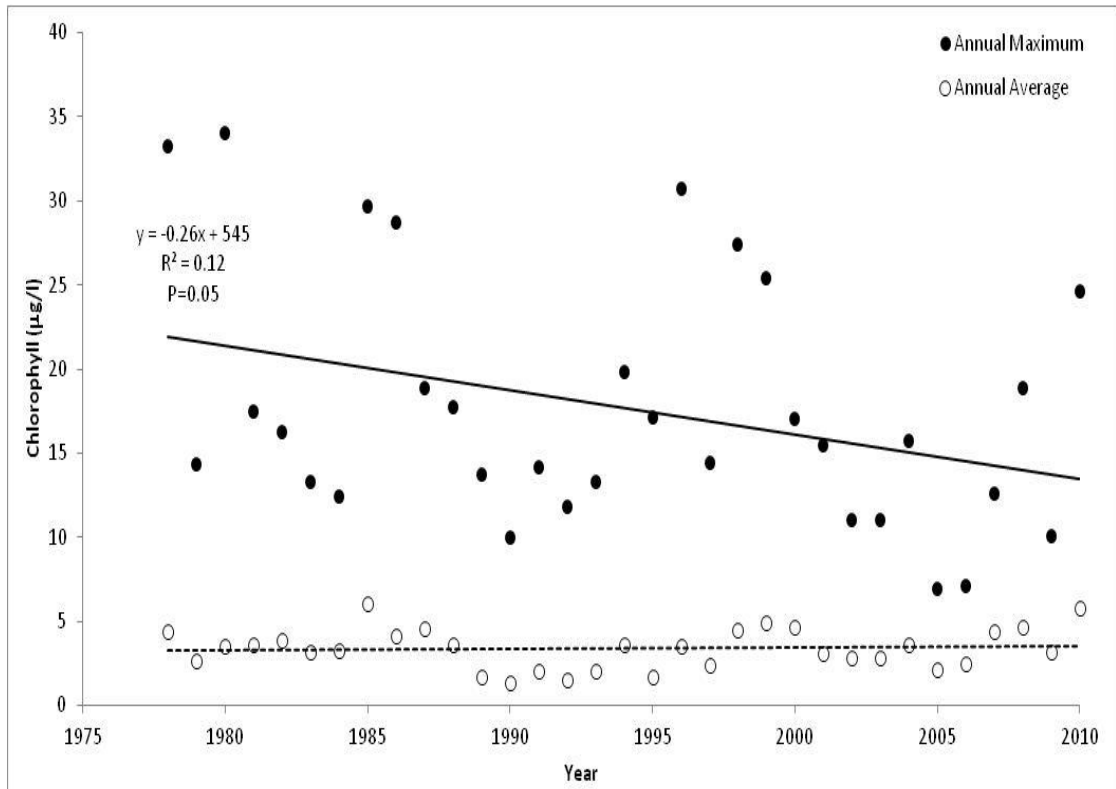


Figure 2-5: Annual average (solid bars) and maximum (hollow bars) chlorophyll at the GSO station over the course of the time series. Annual average chlorophyll shows no long-term trend, while annual maximum shows a slight downward trend of about 0.25 µg/l/y ($R^2=0.13$, $df=33$, $F=4.14$, $P=0.05$).

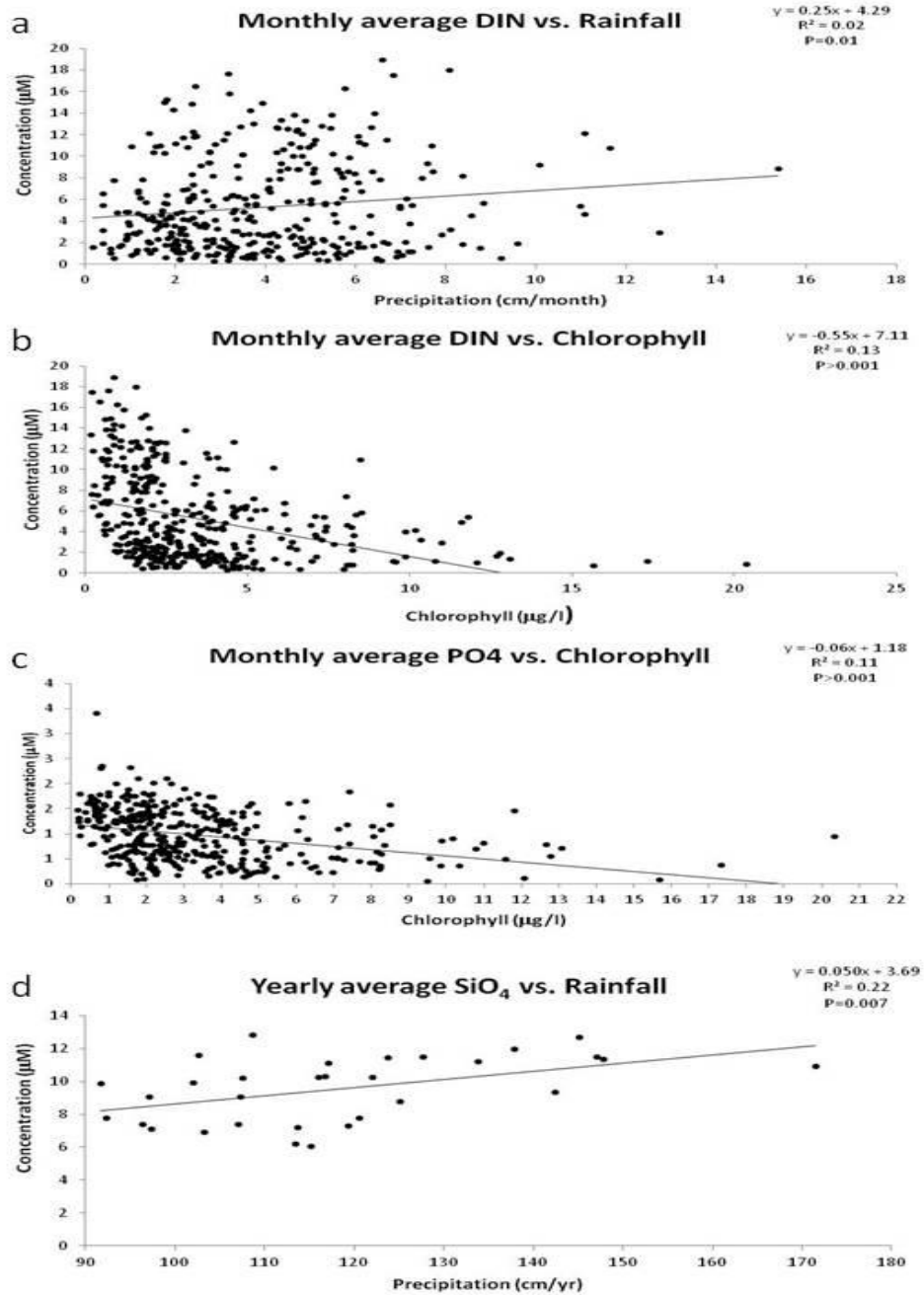


Figure 2-6: Relationships between monthly average DIN and precipitation (a) and chlorophyll (b), and between monthly average PO₄ and chlorophyll (c), and yearly average SiO₄ and chlorophyll (d) at the GSO dock station from 1978-2010. Concentration data are the average of all samples taken in that month, and precipitation data are the total monthly precipitation (in rainfall equivalent) at TF Green airport in Providence (NOAA 2011).

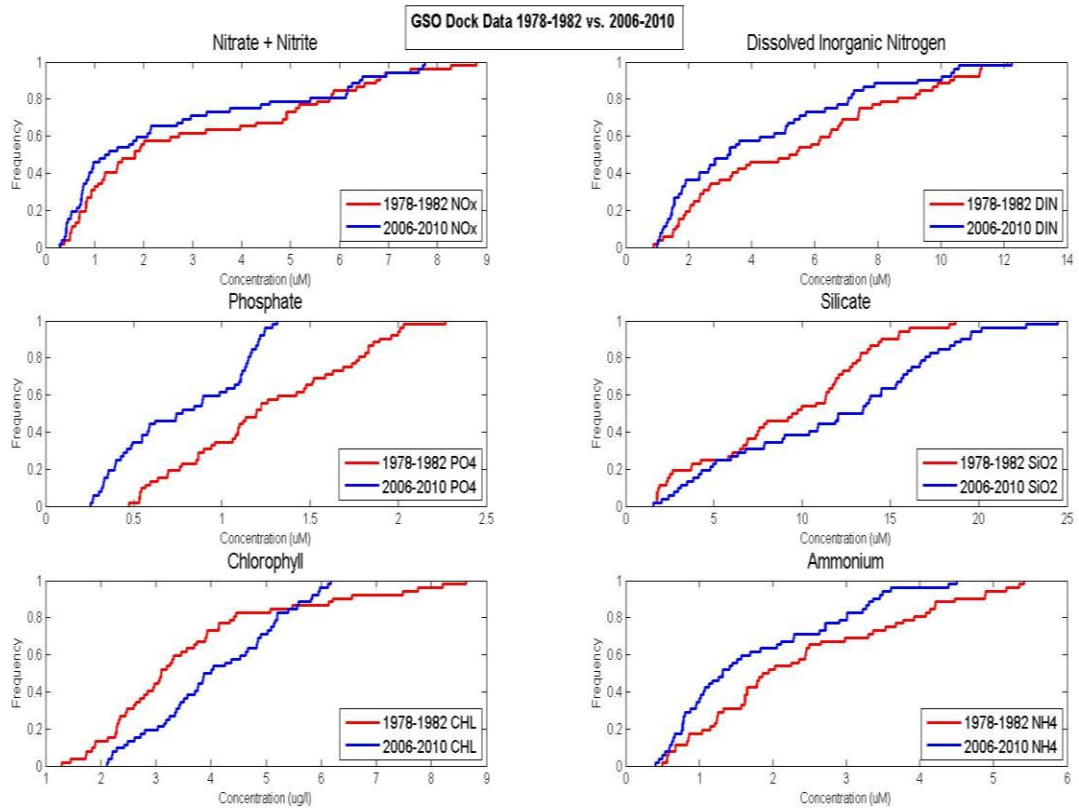


Figure 2-7: Comparison of Cumulative Distribution function of various nutrient analytes at GSO Dock station between 1978-1982 (inclusive) and 2006-2010 (inclusive). 2 sided 2 tailed Kolmogorov-Smirnov testing showed significant differences for Phosphate ($p < .001$, $K = 0.42$), Silicate ($p = 0.05$, $K = 0.36$), Ammonium ($p = 0.02$, $K = 0.26$), and Chlorophyll ($p = 0.005$, $P = 0.32$).

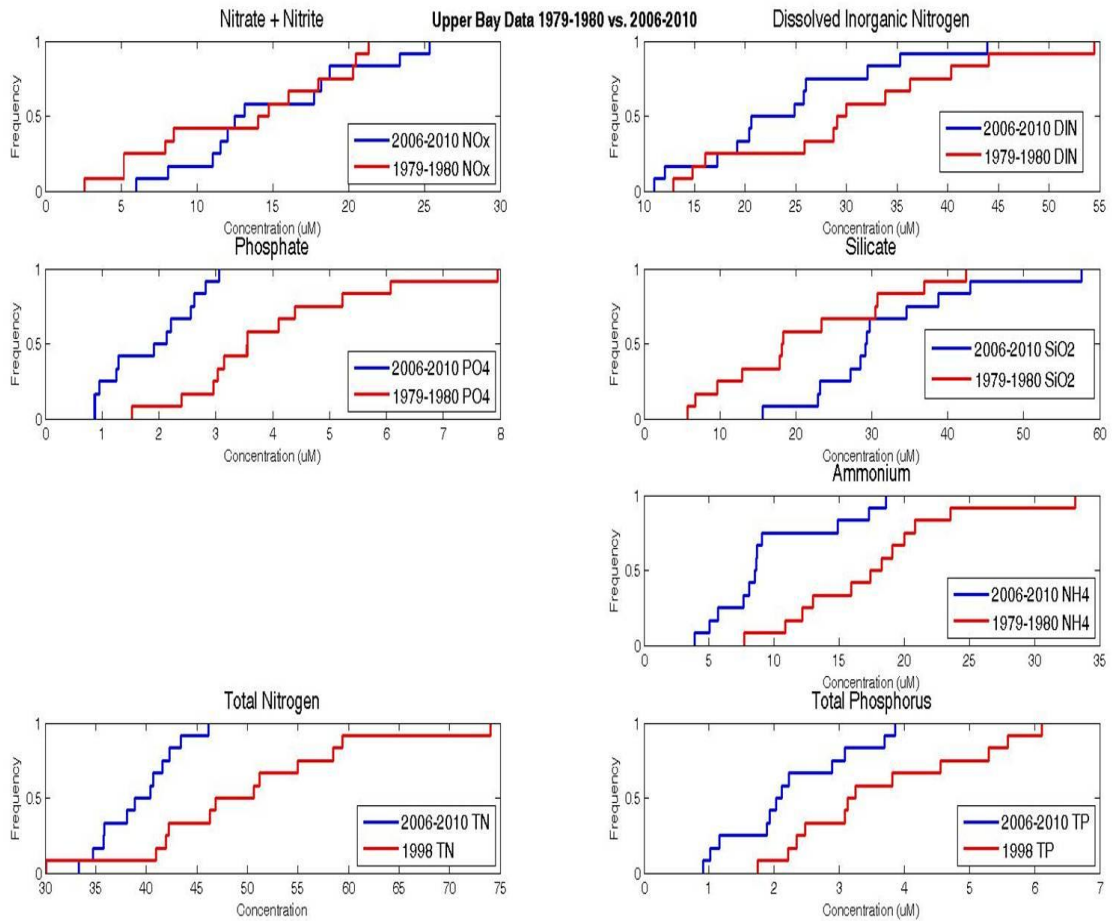


Figure 2-8: Comparison of Cumulative Distribution function of various nutrient analytes at Upper Bay stations in 1979-1980 and 2006-2010 (inclusive). 2 sided 2 tailed Kolmogorov-Smirnov testing showed significant differences for Phosphate ($p < .001$, $K = 0.75$), Ammonium ($p = 0.004$, $K = 0.66$), and Total Nitrogen ($p = 0.004$, $K = 0.66$), and nearly significant difference for Total Phosphorus ($p = 0.06$, $K = 0.5$) and Silicate ($p = 0.06$, $K = 0.5$).

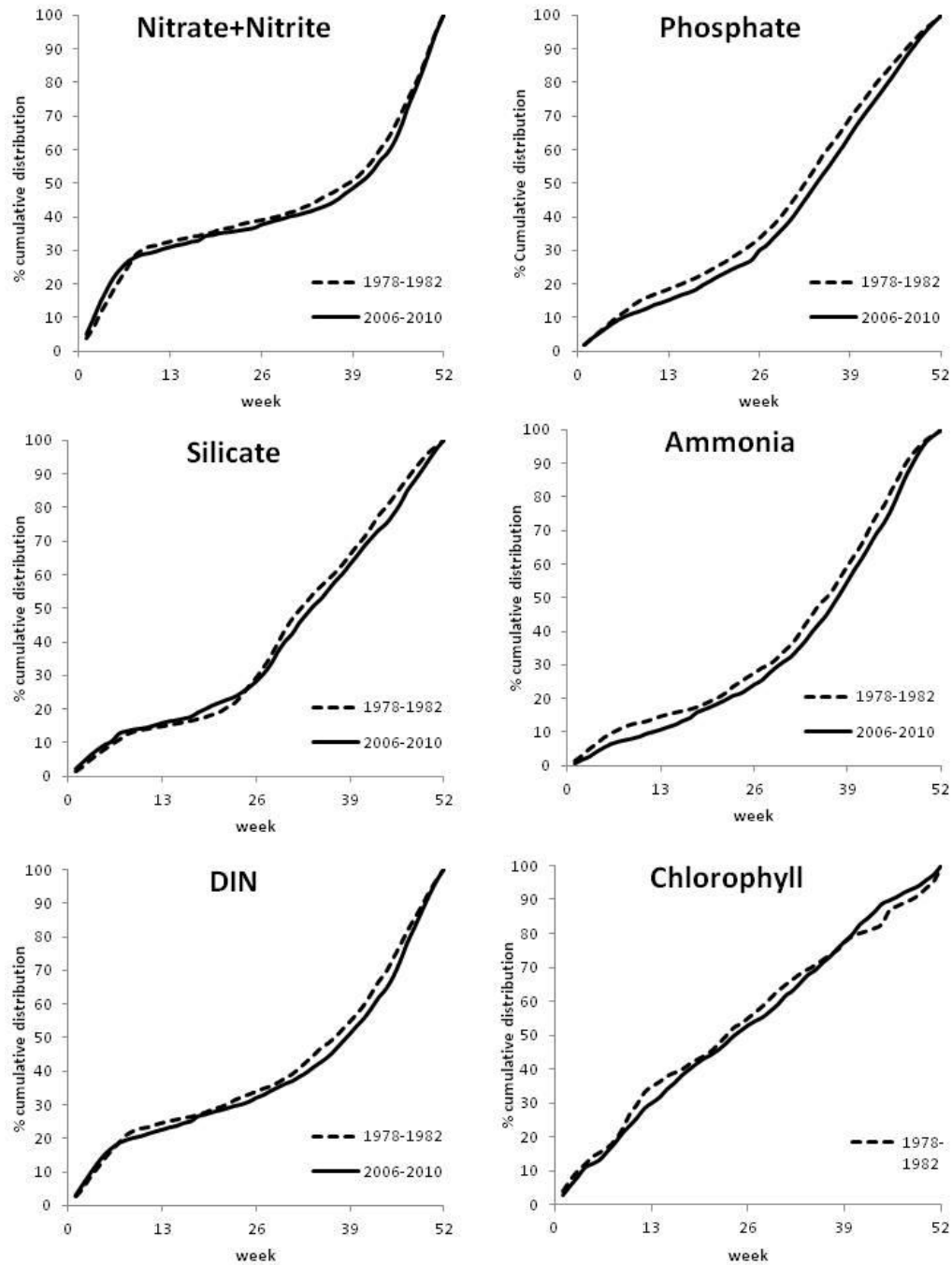


Figure 2-9: Normalized (to % of total observed) seasonal nutrient patterns at GSO Dock Station during the periods 1978-1982 (inclusive) and 2006-2010 (inclusive). Data are annual averages of values in a given week. Y-axis labels are cumulative percent contribution for that analyte at that time of year.

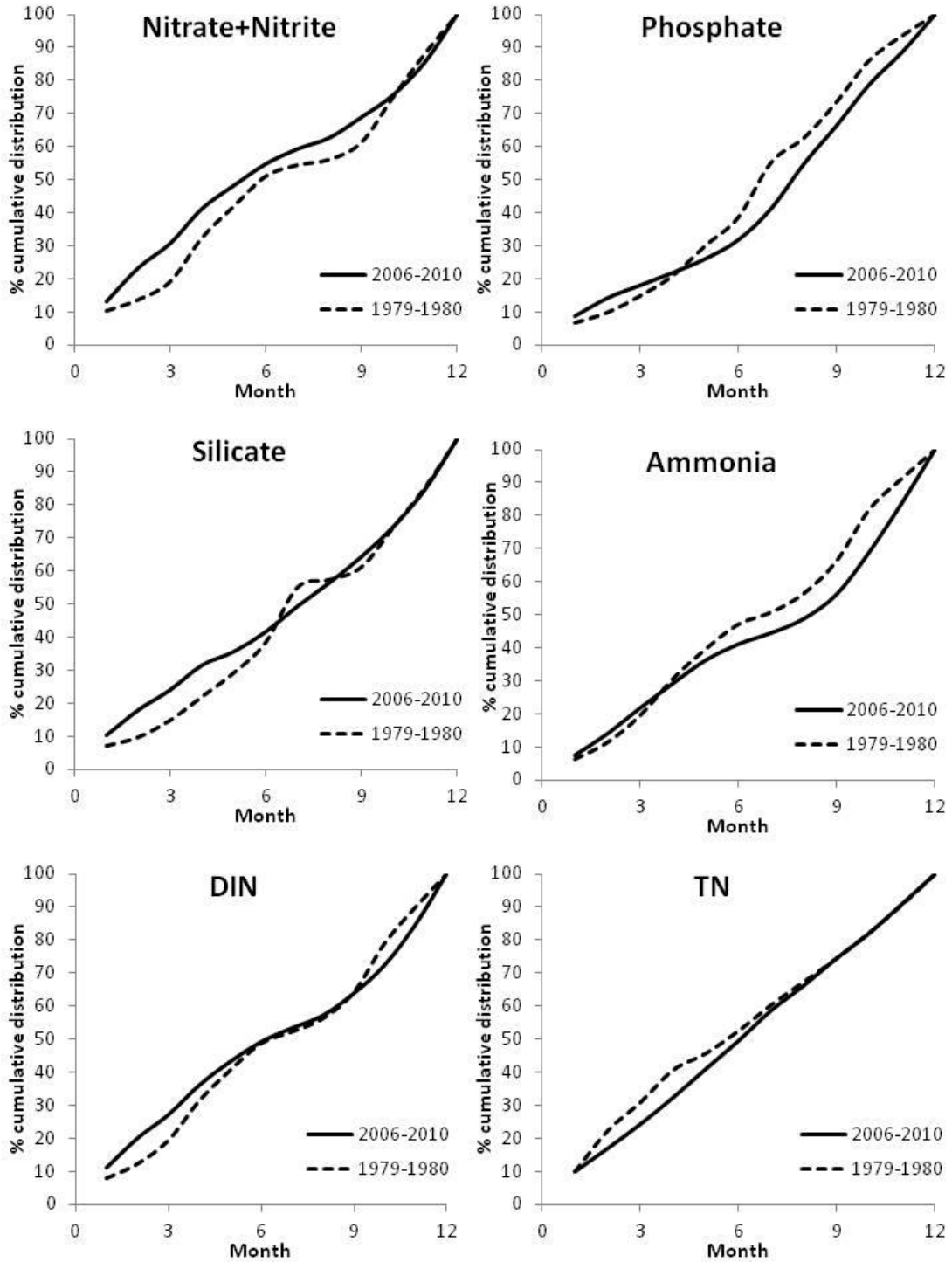


Figure 2-10: Normalized (to % of total observed) seasonal nutrient patterns for the average of 4 (1979-1980) or 3 (2006-2010) stations in the Providence River Estuary (Between Conimicut Point and Fields Point) during 1979-1980 and 2006-2010 (inclusive). Data are average of monthly averages for each year surveyed. Y-axis labels are cumulative percent contribution for that analyte at that time of year.

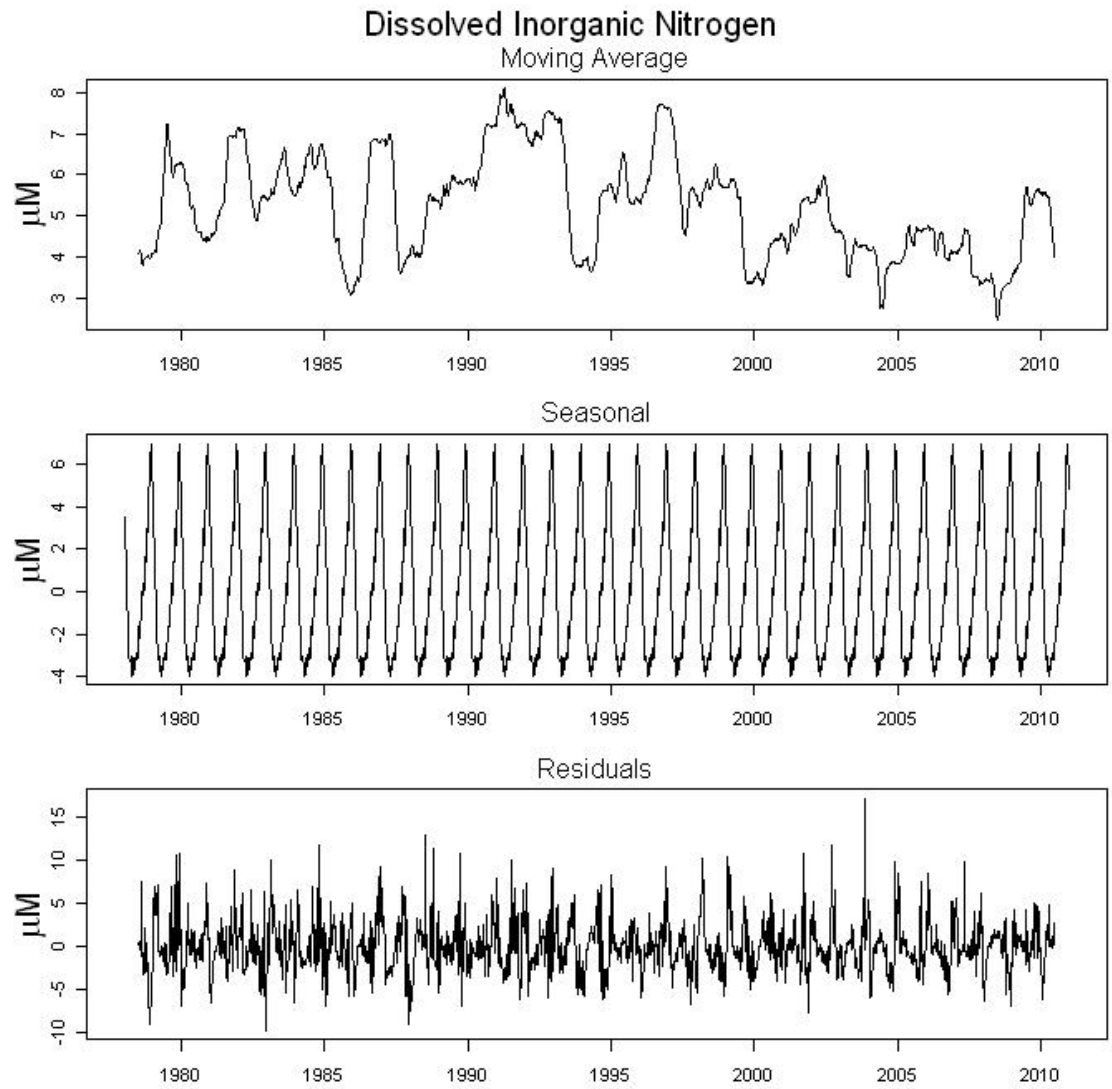


Figure 2-11: SSPIR model results for dissolved inorganic nitrogen showing 52 week moving average (top), seasonal cycle (middle) and residual signal (bottom) of the modeled trend.

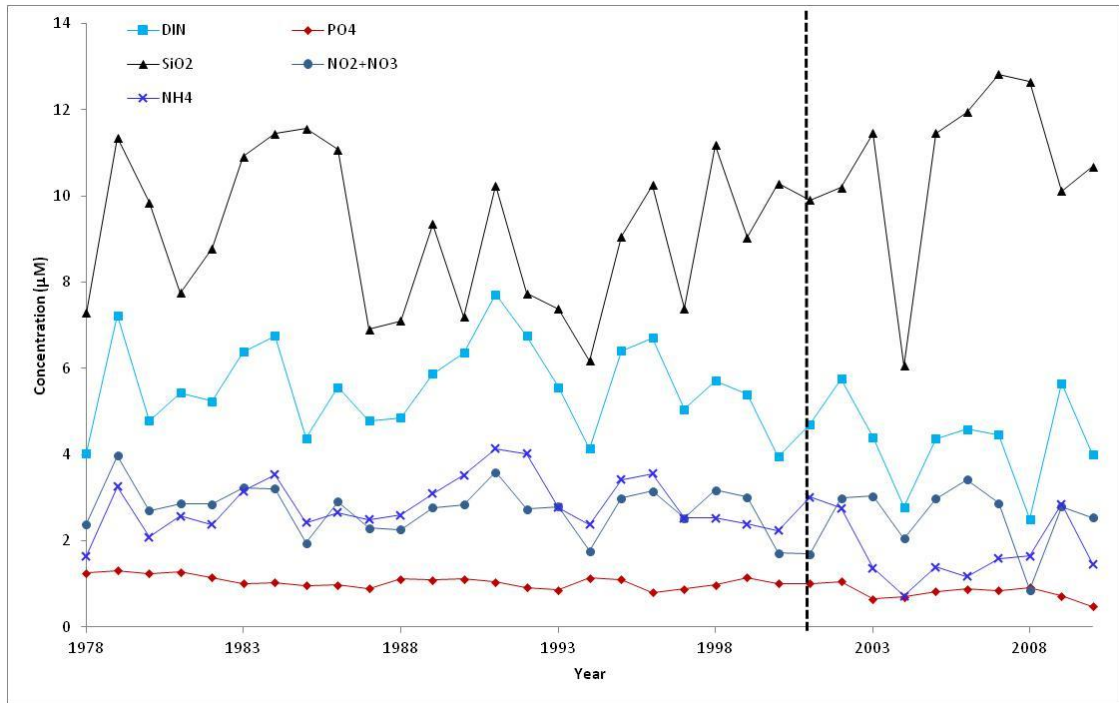


Figure 2-12: Annual average of nutrient analytes at GSO dock station 1978-present. Dashed line shows beginning of implementation of advanced wastewater treatment. Only phosphate shows significant reduction (regression $R^2=0.44$, $df=27$, $F=20.7$, $P>0.001$) prior to the implementation of wastewater treatment. All analytes except silicate show significant reduction between pre and post treatment year

CHAPTER 3

AN ASSESSMENT OF THE IMPACT OF NUTRIENT LOADING REDUCTIONS ON THE ANNUAL MASS-BALANCE OF NITROGEN AND PHOSPHORUS IN NARRAGANSETT BAY

ABSTRACT

Narragansett Bay is a relatively well mixed, high salinity estuarine ecosystem with low fresh water inflow. Much of the shoreline is developed, and most of the sources of nutrient load to the bay are located in the head of the estuary. Recently, several wastewater treatment facilities which discharge into the bay or its tributaries have upgraded to advanced wastewater treatment, with upgrades at the remaining plants following within 2-4 years. We review the mass-balance of nitrogen and phosphorus in the bay, examining the contribution of inorganic and total nitrogen and phosphorus to the bay from atmospheric deposition, river loading, wastewater treatment plants, groundwater and urban run-off, and loss terms from fisheries, denitrification, sediment burial, and export. For the first time in a mass-balance of this system, we attempt to calculate flux across the bay/sound interface rather than estimating it by difference.

Our results show a total load to the system of 488 million moles total nitrogen (TN) and 25.8 million moles total phosphorus (TP) per year. This works out to about 1.48 moles and 0.078 moles of TN and TP per square meter per year respectively, a value which falls near the center of the range of similar urban estuaries (e.g. Bricker et al. 2007, Boynton et al. 2008), though the overall N:P of inflows is nearly 19:1, while

most similar systems are below 16:1 (Boynton et al. 2008). The reduction in total system loading from sewage of roughly 100 million moles TN and slightly more than 4 million moles TP, constitutes reductions of roughly 28% and 22% of sewage based nitrogen and phosphorus respectively, which translates to roughly 17% of the total load of both nitrogen and phosphorus to Narragansett Bay from all sources. Most of these reductions reach the bay, though some of the upgrades to plants in the Blackstone River are mitigated before that river meets the estuary proper. Sewage, whether directly or indirectly discharged into the bay, accounts for just over half of the TN and TP discharged to the system, a reduction when compared to past studies. Our estimates of offshore flux indicate that approximately 65% of the TN load, but slightly higher than 100% of the annual TP load are fluxed offshore from the bay. The former estimate is in line with past estimates, but the latter, if correct, may indicate that the system is not at steady state with regard to P.

INTRODUCTION

The compilation of elemental mass-balances for estuarine systems is a topic which has been of interest to science for over a century since James Johnstone compiled a nitrogen budget for the North Sea (Johnstone 1908). Concern over eutrophication in Narragansett Bay, similarly, has roots stretching back over a century to the pioneering work of George Field and colleagues at the RI College of Agriculture experimental station (Field 1898), and perhaps even further to the work of Justus von Liebig in the mid 19th century. Furthermore, most modern nutrient budgets address many of the same components addressed by Johnstone (1908) in his initial attempts (though often our estimates are somewhat better constrained). Yet this tool continues to be of great interest to scientists and managers alike, with the Thompson ISI web of knowledge (apps.webofknowledge.com) reporting 384 marine or freshwater nutrient mass-balances published in the last three years (2009-2011) alone.

The question of why nutrient mass-balances (nutrient budgets herein) have garnered attention through the years and yet, have remained fundamentally unchanged in their execution, has to do primarily with the fact that a mass-balance is rooted in simple arithmetic and basic physical properties. A body of water must, over the long-term, balance what comes in and what goes out, and the physical vectors for these fluxes have changed little over the last century. Nutrients enter the estuary through flow from tributary rivers, and in the case of nitrogen, through direct deposition from the atmosphere. The standing stock within the estuary exchanges nutrients with the sediments through burial and resuspension/remineralization, and with the open ocean

through tidal flushing and circulation. Biota can assimilate nutrients, changing their form (from inorganic to organic) and, to a limited degree, can export nutrients from the system via advection, migration, or anthropogenic capture. Recently, we have also begun to consider the ability of biota to export and import nitrogen into the system via nitrogen fixation and/or denitrification, though the magnitude of this flux can be very variable and is often not well constrained (e.g. Lipschultz and Owens 1996, Larsson 2001, Fulweiler and Nixon 2011).

While the principles of nutrient mass-balance have changed little over the last century, the level of technology with which the problem can be approached has dramatically increased over the last few decades. While traditionally most nutrient budgets have assumed a closed system, and calculated at least one major term of the budget by difference, increasing availability of computer driven circulation models such as the Regional Ocean Model System (ROMS) has made estimation of flux at the ocean estuary interface (typically the most difficult of the terms to estimate) more feasible. Availability of GIS based tools has also greatly improved the accuracy of estimating fluxes from the watershed such as urban runoff, atmospheric deposition, and land-use changes.

Contemporary with these improvements in technology, management attitudes with respect to nutrient loadings in marine systems have begun to shift as well. Up until a few decades ago, estuaries around the world were on a general trend of eutrophication, predominantly at the hands of anthropogenic processes such as fertilizer use, wastewater disposal, and increases in impervious surface (Clarke et al. 2006, Bricker et al. 2007, King et al. 2008). Recently, however, a sharp increase in

the number of management actions to curtail, and in some cases reverse, this trend of eutrophication has renewed interest in conducting mass-balances in these systems to determine the impact of these management actions on the various exchanges of nutrients within the estuary and the response of the system to load reductions (e.g. Carstensen et al. 2006, Artioli et al. 2008, Boynton et al. 2008, Eyre et al. 2011).

This manuscript aims to update the nitrogen and phosphorus budget for Narragansett Bay, a temperate New England estuary. Past budgets for this system have been conducted approximately once per decade (e.g. Nixon et al. 1995, Nixon et al. 2008). The most recent budget was published in 2008, using a combination of data collected during the 2003-2004 field season and ‘carry over’ data from the 1995 budget, most of which were collected in the 1980’s. Recently, Rhode Island Department of Environmental Management (RIDEM) has required that several of the major wastewater treatment facilities (WWTF) which serve Narragansett Bay be upgraded to tertiary sewage treatment, with most other large plants planning upgrades in the next few years (RIDEM 2005). The overall goal of RI General Law § 46-12-3(25), the driving force behind these changes, is to reduce nitrogen loading to the bay from WWTF’s by 50%, a task that, based on percentage reductions achieved at the plants which have already upgraded, will be achieved once the largest plant discharging into the bay, located at Fields Point (Figure 3-1) completes upgrades, presently scheduled to be sometime in late 2013 or 2014. RIDEM is also imposing phosphorus loading limits on plants which discharge into tributary rivers of the bay.

While nitrogen reduction is typically accomplished by bacterially mediated coupled nitrification/denitrification (Lishman et al. 2000, Jeong et al. 2006),

phosphorus reduction is typically accomplished by chemical scavenging, though more advanced biological techniques may be on the horizon (Strohm 2006). These processes result in very different limits being imposed for the different nutrients. Because the bacterial nitrogen removal process is often temperature dependent, both in nature and in WWTF's (Nowicki 1994a, Lishman et al. 2000) most plants discharging into the bay are required to reduce total nitrogen load in effluent to either 8 or 5 mg/l (0.6 or 0.4 millimolar) during the active (May-October) season, and to the maximum extent possible during the colder winter months (Liberti, pers. Comm). During the active season, this is typically a reduction of 60-70% from the concentration before upgrade (see appendix B). In contrast, phosphorus is chemically scavenged from the wastewater, which is a process that is not temperature dependent and capable of much higher removal rates. Many plants which are upgrading to remove phosphorus have or soon will have limits of 0.1 mg/l (3.2 mM), a reduction of 90% or more. This changes the molar ratio of N:P in effluent at these plants from about 7:1 to somewhere between 22-35:1.

In light of these changes, a re-assessment of the nitrogen and phosphorus budget of the bay is justified. The main question we aim to answer through this exercise is whether other parameters of the budget have also changed in response to reductions from the WWTF's. As such, we have made efforts to update estimates of as many parameters of the budget as possible while adhering to the general framework laid by the most recent (Nixon et al. 2008) system budget, so as to isolate sources of change to the system from changes to our estimates of system parameters resulting from improved estimation techniques (which also occur).

We reassessed loading of nitrogen and phosphorus from rivers, wastewater treatment plants, groundwater and urban run-off. We also reassessed the role of the sediments as a source/sink of nitrogen, export resulting from secondary production (fish), and attempt to close the budget by using the EcoGEM model (Kremer et al. 2010) to predict the flux of nitrogen and phosphorus across the bay/sound interface. However, in many cases, sufficient data for a new parameter estimate were not available. In these cases, parameters were carried over from the most recent budget, rather than risking estimation based on incomplete or insufficient data.

STUDY SYSTEM

For the purposes of this paper, we will adhere to the convention used in past budgets, of defining the bay as all of the portions of the bay proper, the East and West Passages, Mount Hope and Greenwich Bays (as well as many smaller bays and harbors), and the Providence River Estuary. All of these sections of the bay exchange freely with each other and with Rhode Island Sound on the southern boundary (Figure 3-1). Similarly, we choose to exclude the Sakonnet river, as have past budgets, because its exchange with the bay proper is limited to a very small breachway and it receives little direct input of fresh water or sewage (Nixon et al. 1995).

When considered in this way, the bay has an area of 328 km² with an average depth of about 8.6 meters and a watershed to surface area ratio of roughly 11:1 (Chinman and Nixon 1976, Pilson 1985a). Circulation in the bay is predominantly tidally driven, with the mean flow direction in the East Passage and out the West

Passage (Kincaid et al. 2008, Rogers 2008). Freshwater input is small, presently averaging about 103.8 m³/s (Spaulding and Swanson 2008), which is virtually identical to the value used by Nixon and colleagues in past budgets of 105 m³/s which was calculated by Pilson in the 80's (Pilson 1985a). A more detailed description of the ecology of the bay can be found in Kremer and Nixon (1978) or Desbonnet and Costa Pierce (2008).

When compared to other similar temperate estuaries, Narragansett Bay is generally considered moderately eutrophic (e.g. Bricker et al. 2007), with a nitrogen and phosphorus load per square kilometer which ranks 11th and 10th highest out of 35 estuaries surveyed by Boynton and colleagues (2008) and 8th in nitrogen load/km² among 33 systems surveyed by Latimer and Charpentier (2010). Prior to upgrades, Narragansett Bay received approximately 65% of its nitrogen load from sewage discharged either directly into the bay or into its tributaries (Nixon et al. 2008), which is nearly double the average of 36% found by Latimer and Charpentier (2010). This loading makes it an excellent candidate for assessing the impact of load reductions from WWTF's on components of the system budget.

METHODS/DATA SOURCES

STANDING STOCKS AND WATER COLUMN CONCENTRATIONS

Water column nutrients in the bay were measured from monthly surface water collection at 13 stations throughout the bay (Figure 3-1) from 2006-2010 collected as part of the CHRP/NuShuttle and MERL sampling cruise and augmented with data

from QA/QC samples collected sporadically at the Greenwich Bay fixed buoy station. To buffer against interannual variability, which can be significant, typically the average of 2006-2010 annual averages is presented, with confidence interval given as the standard deviation of annual averages. In virtually all cases, the natural variability exceeds any sources of measurement error by at least two orders of magnitude (see appendix A), so it was deemed unnecessary to propagate sources of error. Standing stocks were calculated using volume estimates from the GEM box model (Kremer et al. 2010). For greater detail on the methodologies associated with the collection and analysis of these data, and the compilation of standing stock values, please refer to Chapter 1 and Appendices A and D.

RIVERS

Data for river concentrations of phosphate (PO_4), nitrite (NO_2), nitrate (NO_3), ammonium (NH_4), and total nitrogen (TN) were provided by the Narragansett Bay Commission (NBC). Data were collected approximately biweekly during the time period of 2006-2010, with a total of 107 samples collected during these five years (slightly more than 21 per year on average). Samples were collected from 15 stations on rivers discharging into the bay. However, for this study, only the stations closest to the mouth of the Blackstone, Pawtuxet, Taunton, Woonasquatucket, Moshassuck, and Ten Mile rivers were used (Figure 3-2). Combined, these five rivers account for nearly 80% of the flow entering the bay (Ries et al. 1990, Nixon et al. 1995). These data were analyzed by NBC personnel, using standard colorimetric autoanalysis techniques (NBC 2008). An intercalibration between the instrument used for these

samples, and the one used for the water column samples was conducted in 2005 to ensure inter-comparability of data (NBC 2008).

To estimate flux requires flow and concentration. Daily average flow data for the rivers in question are available for download on the USGS website:

<http://waterdata.usgs.gov/ma/nwis/current/?type=flow>. Flow was corrected for ungauged area below the monitoring stations using ratios calculated by Pilson (1985a) and Boucher (1991) as per Nixon and colleagues (1995, 2008). To arrive at daily flux by combining daily flow measurements with periodic concentration values, there are a number of techniques used in literature. In this case, we chose Beale's unbiased estimator (Beale 1962) for several reasons: flow and concentration are weakly correlated, flow data are positively skewed, and the sample size in any given year is relatively small (<50). Comparisons of results using different estimation techniques to estimate flux in this way show Beale's to be well suited to these types of data, and in most cases, show little difference between techniques (Tin 1965, Fulweiler 2003). Furthermore, Beale's estimator was used by Nixon and colleagues in past budgets, so given no indication that a different technique would produce superior results, Beale's is the logical choice. Briefly, Beale's estimator works by comparing the flow on measured days to the mean flow, and correcting the estimated flux for any bias imposed by the less regular concentration sampling régime. A more thorough review of the application of Beale's estimator can be found in Dolan et al. (1981) or Fulweiler(2003).

There is a significant amount of interannual variability in river load, based in large amount due to variability in precipitation. To arrive at a better estimate of the average loading to the bay from this source, we calculated the average loading from each river from a three year period, 2008-2010, and compared this loading to the most recent published values from Nixon et al. (2003-2004 for all rivers but the Taunton, for which Nixon and colleagues used a dataset from the 80's). We were able to make direct comparisons for dissolved and total nitrogen, and dissolved inorganic phosphorus; unfortunately, we did not have data for total phosphorus in this dataset. To arrive at an estimate of this parameter for the budget, we calculated the average ratio of total phosphorus to inorganic phosphorus from the several surveys presented in Nixon et al. (2008, table 5.9) for each river. Finding relatively consistent relationships (RSD<30% in all cases) we used this value to extrapolate total phosphorus from inorganic. However, Nixon and colleagues were unable to get data from the Taunton River at that time.

TREATMENT PLANTS

There are 29 WWTF's that discharge their effluent into Narragansett Bay. Of those, 10 discharge their effluent directly into the bay and 19 discharge into tributary rivers which subsequently drain into the bay. A total of 21 of the plants including four of the five largest plants, discharge either directly into the Providence River Estuary or into its tributaries, with four discharging into the Taunton River and Mt. Hope Bay and one into Greenwich Bay. The remainder discharge directly into the mid or lower bay. For the purposes of calculating total nutrient load to the bay, plants discharging into rivers are considered as part of the flux from those respective rivers (to avoid

double counting and allow for river abatement). RIDEM was able to provide data for discharges from 17 of these plants including 8 out of the 10 plants which discharge directly into the bay. In most cases, these data were collected weekly, though larger plants were sampled more often, and smaller plants as infrequently as every other month. In all cases samples were 24-hour average composites of samples collected every 30 minutes. (NBC 2008 Liberti pers. comm., see appendix B for more details) Beale's estimator (Beale 1962) was again used to calculate flux from flow and concentration data provided.

Where data were not available, we adjusted numbers from past budgets to account for changes in population served by those plants. In some cases, past budgets had estimated data using an average value of N and P load per person multiplied by the number of people served by the plant. In these cases, we used the same technique, but we found that the average load per person per day (even among plants which have not upgraded) has changed since Nixon and colleagues estimated it, so we revised the estimated load from 0.9 and 0.035 moles of N and P per person per day (Nixon et al. 2008) to 0.8 and 0.045 moles of N and P, respectively, per person per day (Appendix B).

Because most plants which upgraded did so in the 2005-2006 time frame, we compare annual averages from the years 2008-2010 to annual averages from 2000-2003 (from Nixon et al. 2008) to ascertain the impact of advanced treatment on loadings. A few plants (North Attleboro in 2008 and Worcester in 2009) upgraded after the others, and for those plants, we calculate the 'post upgrade' averages using only the available data after the upgrade was completed. For plants where 2000-2003

data were available, we recalculated fluxes to ensure that our methods were comparable to Nixon and colleagues, and found excellent agreement, typically to within rounding error.

ATMOSPHERIC DEPOSITION

Atmospheric deposition onto the watershed of Narragansett Bay is accounted for in river loading, therefore only the direct wet and dry deposition of nitrogen and phosphorus onto the surface bay are of concern. These loadings were estimated by Nixon and colleagues from data collected at the Graduate School of Oceanography (for P) in the late 1970's and on Prudence Island (for N) in the 1980's (Nixon et al. 1995) and have in the past generally been found to be a small (<5%) portion of the overall budget. While no new direct measurements of deposition were made for this study, we did compare the results from these studies to more recent estimates of deposition rates from the New England area (Howarth et al. 2007, Howarth 2008) and found the results to be similar. While environmental regulations have improved the emissions of NO_x from automobile and industrial exhaust, the number of car miles driven on New England roads has increased 70% since 1970 (Howarth 2008), resulting, it seems, in an overall deposition figure which has likely changed little since it was last measured. Furthermore, while direct deposition is a major factor in some systems, contributing 4-35% of the load incident on 40 major coastal watershed surveyed by Alexander et al. (2001), it is a relatively minor player in Narragansett Bay, despite a relatively high flux per unit area (Howarth 2008). For these reasons, lacking more recent direct measurements, and with no evidence suggesting that

loading from this vector has changed significantly in the intervening time-span, we chose to carry over estimates of direct deposition from past budgets.

URBAN RUN-OFF

A previous study of nutrient loading from various land-use types during 12 storms over the course of 1979-1980 (Carter 1982) has provided the basis of estimates of urban run-off for the last several mass-balances conducted. While this study has the distinct benefit of being conducted in the Narragansett Bay watershed, the amount of data available and the number of land-use types surveyed was very limited, with the flux per acre coefficients for many land-use types determined by only a few data points. An estimate of flux from urban run-off was calculated by multiplying the coefficients determined by Carter (1982) by the long-term average precipitation at the time of 1.19 m/y, and by the approximate number of acres of each land-use type in cities and towns which discharge their stormwater directly into the bay (Nixon et al. 1995). This estimate of the flux from urban run-off has been used, essentially without revision, for the last 30 years.

We made several adjustments to this value. First, we used the identical method to Nixon et al. (1995), adjusting only for changes in land-use and precipitation. Land-use was adjusted by comparing present and historical GIS land-use coverage in the towns surveyed using ArcGIS 9.2, and precipitation was adjusted to the 10 year average between 2000-2010. Next, we considered all land-use types occurring within the areas which discharge directly to the bay. Though the majority of land-use types in terms of acreage are covered by the four categories used in Carter's survey (Residential, Commercial, Industrial, and Highway), remaining land-use types are

ignored in that study, and subsequently in acreage estimates used by Nixon et al. (Carter 1982, 1995). Rather than ignoring these other land use types (e.g. mixed use, transitional, institutional, and open space) we assigned each to the land-use category from Carter's work which most closely approximated it. With the exception of open space, we were able to arrive at a reasonable analogue from Carter's work (sometimes averaging her coefficients for areas zoned as mixed use). For areas zoned as open space, we used the nationwide average coefficient from an NRC report (NRC 2008) on urban storm water. Finally, we considered the variability inherent in this prediction by comparing the results derived from using the coefficients determined by Carter (1982) to results derived if the NRC coefficients (NRC 2008) were used for all land-use types. While the NRC coefficients gain several additional coverage types, and benefit from a large number of samples within each coverage, these samples are nationwide averages, and the amount of nutrient in urban storm water run-off is very system specific. Thus, while it is impossible to tell which set of coefficients is more 'correct', this analysis at least gives us an idea of the variability inherent in our ability to estimate this term of the budget.

PRIMARY PRODUCTION

While primary production does not, in itself, change the amount of nutrients coming into or out of the bay, it is an important vector for moving nutrients between the various pools and sinks (e.g. transforming inorganic nutrients to organic, moving nutrients from the water column to the sediment, etc...) and also is highly relevant to the discussion of loading reductions from a management perspective. A very robust survey of primary productivity in Narragansett Bay over an annual cycle was

conducted by Oviatt and colleagues in 1998 (Oviatt et al. 2002). Data collected by Smith (2011) in 2006-2008 do not show conclusive evidence of changes in primary productivity since the 1998 survey at 5 stations in the Providence River estuary and the West Passage. Since the latter survey occurs after the majority of the WWTF upgrades (including the largest, at the Bucklin Point facility in East Providence) we assume that primary productivity in the bay has not changed significantly since 1998, and therefore because the 1998 study has greater spatial coverage, we use the regressions established therein.

DENITRIFICATION

It is fortunate that Narragansett Bay has been the site for several studies on the net flux of nitrogen into and out of estuarine sediments. The estimates used by Nixon et al. (Nixon et al. 1995, Nixon et al. 2008) are built upon a series of studies conducted in the bay (Seitzinger et al. 1984, Nowicki and Oviatt 1990, Nowicki 1994a) and at the MERL mesocosm facility at the Graduate School of Oceanography which established in situ denitrification rates, and extrapolated those values using regressions between temperature and denitrification rate established by mesocosm study.

More recently, Fulweiler and colleagues have measured denitrification at the same mid-bay station as well as several other stations throughout the bay, and observed dramatic differences in sediment nitrogen and phosphorus flux (e.g. Fulweiler et al. 2007, Fulweiler et al. 2010, Fulweiler and Nixon 2011). In 2005 and 2006, they noted a large reduction in denitrification rate, with the sediments serving as a net source (nitrogen fixation) rather than a sink (denitrification) of nitrogen during parts of the year (Fulweiler et al. 2007). Furthermore, Fulweiler and colleagues noted

a lack of the previously established pattern of spatial and temporal relationships in denitrification rate in the bay (Fulweiler et al. 2010, Fulweiler and Nixon 2011). We revise estimates of net sediment nitrogen flux calculated in past budgets by re-estimating baywide flux using data from these manuscripts.

SEDIMENTS

As with many such systems (Carstensen et al. 2006, Clarke et al. 2006, Boynton et al. 2008), the sediments of Narragansett Bay are a key storage term in the nutrient budget, since most of the sediment that enters the bay likely remains within the system (Nixon et al. 1995). Mesocosm experiments in the MERL facility have shown the sediments of Narragansett Bay to have generally short ‘memory’ and rapidly achieve equilibrium with overlying water via remineralization within an annual cycle (Kelly and Nixon 1984, Oviatt et al. 1984, Kelly et al. 1985).

However, long-term burial in the sediments is a form of export from the system which must be considered. Nixon and colleagues estimated the amount of N and P buried in this way by multiplying sedimentation rate determined from radiometric dating of ^{210}Pb and ^{137}Cs as well as other organic pollutants and metals in sediment cores (Corbin 1989) with measurements of N and P in sediments below the zone of biological activity (e.g. Nixon et al. 1986, Nixon et al. 1995). While it would be ideal to have revised estimates of this parameter, sedimentation rates in the bay do not appear to have changed dramatically (Hartmann et al. 2005). Furthermore, given the amount of time it takes for sediments in the bay (and the nutrients they contain) to be buried (Nixon et al. 1986, Corbin 1989), it seems unlikely that the concentration of nutrients in the sediment being buried would have changed significantly as a result of

loading reductions which occurred only a few years ago. Therefore, carrying over estimates of sediment nutrient burial seems to be a reasonable assumption.

As a point of reference, we can also estimate the ‘standing stock’ of nutrients stored in the sediments which is theoretically bioavailable. Using published estimates of N and P concentration in bay sediments from mesocosm work by Nowicki and Oviatt (1990), and assuming that sediments are bioavailable down to a depth of 10 cm and that concentrations measured by Nowicki and Oviatt remain constant throughout this bioturbated layer, we can arrive at a cursory estimate of the amount of nitrogen and phosphorus are in short term storage in the bioavailable sediments at any given time, using concentrations from Nowicki and Oviatt’s 8X enriched experiment for the Providence River Estuary, and the control sediments for the rest of the bay (Nowicki and Oviatt 1990).

FISHERIES LANDINGS

Export of nutrients from the bay from fish and fisheries landings is extremely difficult to quantify. Most of the commercially captured finfish species in the bay are migratory, spending only part of the year within the bay. Thus, it is a grossly inappropriate assumption to calculate finfish (or even lobster) landings in the bay, determine the amount of nitrogen in that biomass, and assume it is an export of bay sourced nitrogen. In past budgets, Nixon and colleagues have been limited to estimating hard clam landings (the only major sessile species harvested in the bay) as a source of export.

Recently Longval (2009) calculated biomass spectra for the Narragansett Bay fish community. As part of this study, she compared the biomass spectra across a

seasonal cycle. In this analysis, a clear peak in biomass exists which matches size with several very common small age 0 fish (typically species such as scup, butterfish, and clupeids) which recruit in the spring and grow over the course of the summer. By comparing the biomass in this peak when the fish first recruit to the net (1cm mesh) in the spring to the biomass in the same peak in the fall, one can achieve a rudimentary, albeit highly conservative estimate of fish biomass which can directly be attributed to Narragansett Bay, virtually all of which is exported from the bay, either as fisheries landings, or in the stomachs of other fish which either move offshore, or are captured. We therefore supplement a revised hard clam harvest estimate with the estimate of fish biomass export achieved in this way.

BOUNDARY FLUXES

We attempt herein to model, rather than calculating by difference, the flow of nutrients across the bay/sound interface, and thus, to ‘close’ the total system budget. Fully closed nutrient budgets are becoming more common as more advanced computer simulations improve our ability to model water flow in and out of a system. In this case, we use the GEM model (Kremer et al. 2010) to handle nutrient movement, into and out of the 15 model boxes (Figure 3-3) which are parameterized for flow into and out of Narragansett Bay by the ROMS circulation model (e.g. Kincaid et al. 2008, Rogers 2008). Circulation data exist only for 2006, so we use nutrient data for this year to estimate flux.

We have a robust dataset of water column concentration from monthly sampling, however because this dataset was collected from the back of a moving boat, it was not possible to sample bottom water on a regular basis. We used two past

datasets of surface and bottom nutrients, one from 1972-72 and one from 1979-1980 (Kremer and Nixon 1975, Oviatt 1980) to develop relationships between surface and bottom concentrations in the lower east and west passages and from this, were able to estimate bottom concentrations from our surface data (Figure 3-4). While the relationship between surface and bottom is generally complex and variable on any given day, particularly in the southern portions of the bay, where concentrations tend to be very low, there does appear to be a clear seasonal pattern which we were able to discern by combining these two datasets (Figure 3-4).

The GEM model shows that, over the course of one day, virtually no water exchanges between the sound and anywhere past the south end of Prudence Island, so it was only necessary to extend these relationships to the lower east and lower west passages, for which these two surveys have a reasonable density of data.

Having established a parameterization for the surface and bottom boxes of the GEM model for the bay/sound boundary and the lower east and west passages, we first calculated the amount of nitrogen and phosphorus which flux into the bay on an annual basis by setting the concentration in all bay boxes to zero, and initializing the model with appropriate conditions for the sound. We ran the model for one day, ‘captured’ the amount of nutrients in each box in the bay, reset the bay concentrations to zero, and advanced the model one day. We repeated the process for the entire year of 2006 (the ROMS model is parameterized with 2006 weather and forcing data). The sum of these gives us an estimate of the flux in from the sound to the bay. We then reversed the process, parameterizing bay boxes with modeled nitrogen and phosphorus concentrations, and setting the boundary condition to zero. By monitoring the net

change in nutrients over the course of each day, we can calculate the amount of nutrients the model is exporting from the system on that day. This can again be summed for the year and subtracted from total import to provide an estimate of net total flux into or out of the bay.

In order to assess the variability associated with the assumptions we are forced to make with respect to this calculation (most notably the extrapolation of bottom concentration from surface) we parameterize the model using several different estimation techniques and ran it to get a range of estimates. We also ran the model with the 2006-2010 average concentrations in addition to the 2006 data to see how much interannual variability changes this estimate, with the caveat that when using 2006-2010 data rather than only the 2006 data the weather forcing no longer lines up with nutrient concentrations which accurately correspond to those conditions.

RESULTS

INPUTS

DIRECT DEPOSITION

Nixon et al. estimated 30 +/- 6 million moles of nitrogen per year deposited directly on the surface of the bay. Using Howarth's (2008) regional estimate of 1200 KgN/km²/y and a bay area as above of 328 km² yields a very similar estimate of 28 million moles. This vector is therefore still responsible for roughly 5% of the annual total nitrogen budget of the bay (Table 3-1). Assuming ratios of DIN:TN are similar to those observed in 1995, approximately 80% of this is in dissolved inorganic form. Phosphorus flux measurements exist only from a 1977 dataset by Graham (Graham

1977 in Nixon et al. 1995), who measured $390 \mu\text{mol}/\text{m}^2/\text{y}$ incident on the lower West Passage. Assuming this rate is consistent across the bay yields an estimate of 0.13 million moles of phosphorus deposited in this way. While this is perhaps not the best assumption, this rate is roughly comparable to literature values (e.g. Davis and Ogden 1994, Jassby et al. 1994) which also do not show a great deal of spatial or temporal variability within the same system (Jassby et al. 1994) and the total flux of phosphorus by this method constitutes less than 1% of the phosphorus budget (Table 3-1), so the budget is highly insensitive to changes in this parameter.

RIVERS

Rivers are the single largest contributor of both nitrogen and phosphorus to the bay when sewage discharged into the rivers is considered as part of the river flow. However, due in part to improvements in plant efficiency on the rivers, and presumably in part to changes in the watershed not well measured in this study (e.g. vegetated buffer strips, reduced fertilizer use on lawns and agriculture, less phosphates in detergents, etc...), the nutrient load coming down most of the rivers has declined dramatically since the last assessment (Table 3-2). The Taunton was not measured directly in the most recent budget, so our comparison here is with data from the late 80's (Boucher 1991, Nixon et al. 1995), but shows a reduction of more than 50% in nitrogen and nearly 90% in phosphorus. A large portion of this difference is due to the fact that the previous estimates relied on a large correction factor to scale flows at the Bridgewater gauge station up for 250 square miles of watershed below this station. While we use this technique for the other rivers, we do not feel that it is appropriate for the Taunton because of vast concentration differences between the Taunton at the

mouth and the Taunton at Bridgewater. Instead, we add these 250 square miles to the ‘ungauged flow’ term initially proposed by Reis et al. (1990) and employed in both recent budgets (Nixon et al. 1995, Nixon et al. 2008). If we were to apply the same correction factor used in past studies, we would get 82.1 million moles TN and 1.23 million moles TP, a 30 and 77% reduction respectively.

Most other rivers show modest reductions in TN load, which are typically associated with, and less than or equal to reductions that took place at plants discharging into those rivers, though the Ten Mile River shows a slight increase (Table 3-2). Similarly, phosphate reductions in the Pawtuxent and Ten Mile can be attributed to permit limits for phosphorus discharge on those rivers, while the Blackstone, which has no such limits at this time, shows an increase in P loading. The smaller rivers which do not have any plants on them (Moshassuck and Woonasquatucket), also show significant P loading reductions. Though the source of these reductions is not clear, the magnitude of flux from those rivers is very small, and thus, the change in the budget from these vectors is small in light of other changes.

WASTEWATER TREATMENT FACILITIES

Of the 29 facilities which discharge into the bay and its tributaries, 11 plants have upgraded to advanced wastewater treatment for nitrogen since the last assessment (Bucklin Point, East Providence, East Greenwich, Woonsocket, Smithfield, Cranston, Warwick, West Warwick, and Burrillville in Rhode Island, and Worcester, and North Attleboro in Massachusetts). Three of those plants (Bucklin Point, East Providence and East Greenwich) discharge directly into the bay, while the rest discharge into the tributary rivers. In that same time period, five plants (Woonsocket, Smithfield,

Cranston, Warwick, and West Warwick) discharging into tributary rivers, have undergone upgrades to remove phosphorus from effluent. This removal has resulted in a reduction in the total sewage load to the bay of approximately 100 million moles of TN and 4.2 million moles of TP (Table 3-3, Figure 3-4). About three fourths of the nitrogen reduced, and all of the phosphorus reduction comes via the tributary rivers, with only about 27 million moles of TN per year in reductions at plants that discharge directly into the bay, and a slight increase in TP load at those same plants (Table 3-3). A thorough review of the plant-by-plant loading, permit levels, and upgrade status for each plant can be found in appendix B.

From a budget standpoint (Table 3-1) it is important to distinguish between the two sources (because reduction from plants discharging into tributaries is realized in the river value, not in the sewage value for the overall budget). For the purpose of presenting and discussing results, we felt it would be easier to discuss all plant discharges together. In examining the plant discharges, we wanted to determine whether the reductions we see in total load can be conclusively attributed to advanced wastewater treatment practices at the upgraded plants. As such, we looked at the change over time in total, active season, and inactive season discharge from plants which have, and have not upgraded (Figure 3-4, Figure 3-5, Figure 3-6). While there is a fair amount of interannual variability, we universally see a clear and statistically significant improvement among plants upgraded for nitrogen removal, both individually and as a group, as these plants mirror the un-upgraded plants for the first few years of the dataset before diverging as the upgraded plants come online in 2005-2009 (Figure 3-4). As more plants continue to come online, and several plants with

early stages of reduction continue upgrades to meet permit limits of 5 or even 3mg/l, we can expect the total contribution from sewage to drop even further.

Contrary to expectations, there is minimal difference between ‘active’ (Figure 3-5B) and ‘inactive’ (Figure 3-5C) season loading reductions among plants which upgraded for nitrogen reduction. While these plants are only bound to their permit limits during the warmer months, they are required to operate advanced wastewater treatment to ‘maximum extent’ during the rest of the year, which appears to, at least on average, approach the efficiency achieved during warmer months(Figure 3-5D). With phosphorus, on the other hand, because removal is done by chemical scavenging, and is not mandated in the colder months, a clear difference can be seen in the amount of reduction achieved during active (Figure 3-6B) vs. inactive season (Figure 3-6C) despite a fair amount of noise in this signal (Figure 3-6D). While fewer plants have phosphorus limits, those limits typically specify reductions of 80-90% vs. untreated water, so the net effect is similar percentage wise. With several other plants preparing to remove phosphorus down to 0.1 or 0.2 mg/L (Liberti, pers. Comm.), the reduction in the coming years could be even more significant.

The data presented here include data from the 2010 year. In late March of 2010, Rhode Island received a massive rainstorm, which dumped more than 8” of rain on parts of the state (NOAA 2011). As a result of this storm (considered a 100-year storm), virtually all plants violated their permits for a short period of time. Due to severe flooding on the Pawtuxent river, three plants; Cranston, Warwick, and West Warwick were forced to close for several days, and discharged a large volume of minimally treated sewage into the bay until they became operational again, after which

they still required up to a few months to get tertiary treatment systems back online and fully operational. Reductions at these plants were much greater during the 2008 and 2009 seasons. However, because high flow events do happen from time to time, we decided not to remove 2010 from consideration in our analysis, but rather to simply note its impact on plant discharges.

URBAN RUN-OFF

Nixon and colleagues (1995) partitioned the un-gauged flow determined by Ries et al. (1990), by calculating the portion of un-gauged acreage which falls within these qualifications ($6-9\text{m}^3/\text{s}$), and separating it from the roughly $25\text{m}^3/\text{s}$ of unmeasured flows determined by Ries (1990). They then assigned coefficients from Carter (1982) for each of four land-use types (industrial, residential, commercial, and highway) to the acreage from each of the municipalities above. Doing so yielded a contribution of 37 million moles TN and 4 million moles TP from this vector. This component of the budget was used 'as is' in the more recent budget by Nixon and colleagues (Nixon et al. 2008).

Adhering to all of the conventions and assumptions laid out by Nixon et al., and adjusting only for changes in precipitation and changes in land-use yields 28% and 25% increases in total nitrogen and phosphorus loadings, respectively. However, since 2008, the Narragansett Bay Commission (NBC) has been collecting stormwater in the first phase of a stormwater reduction project, which directs 14 combined sewer overflows (CSO) into a large underground tunnel during storm events, for later treatment at the Fields Point treatment plant, rather than discharging it via the combined sewer overflows (CSO) directly into the bay. At present, the Fields Point

has not upgraded to advanced treatment, so this process has little impact on the total nitrogen and phosphorus discharged into the bay (though secondary treatment does remove some nutrients). However, because this water is now diverted through the plant, it was counted in our direct sewage discharge, and so, should be removed from the urban run-off estimate. Based on preliminary data from NBC (Comeau, pers. comm), the tunnel treats about 4 million cubic meters of water per year, which amounts to <1% of the stormwater load to the bay by volume, but the concentration is quite high. While the monitoring program within the tunnel is preliminary, we estimated that it diverts 2.5 million moles of TN and about 250,000 moles TP per year from the CSO's into the Field's Point plant. Subtracting this amount gives a net increase in urban stormwater of 22% or 8.1 million moles of TN and an increase of 19% or 0.75 million moles of TP (Table 3-4C).

Further modification of the urban run-off figure comes from a re-analysis of the approximately 140,000 acres falling within cities and towns which discharge their run-off directly into the bay. Carter (1982) considers in her analysis only acreage which fits into the land-use categorizations she sampled. This leaves a large amount of acreage unassigned. Much of this land is open space, which has very low per acre coefficients (NRC 2008) (Table 3-4A), but some of it falls into categories such as transitional area, mixed use, transportation (railroad tracks, bus terminals, port facilities) and institutional usage (e.g. schools, courthouses, etc...) (Table 3-4B). We assigned these acreages to the coefficient most closely resembling their usage, and added coefficients from the NRC stormwater report (NRC 2008) where necessary. This results in a large increase in the loading of both nitrogen and phosphorus, caused

in large part from the additional acres surveyed in this way, but also from the improvements in the accuracy of the GIS techniques used to conduct the assessment, and the improved classification provided by having additional coefficients. The change calculated from this step is approximately 38 million additional moles of TN and 2 million additional moles of TP. However, since these changes represent improved accuracy, and not a change in the actual loading to the bay, they should be considered separately from the above discussed changes, which do represent an increased loading to the bay. We therefore present the urban run-off figure as a range, with calculation from Nixon et al. modified for land-use change, precipitation, and CSO abatement as the low end, and our modified calculation as the high end (Table 3-1).

GROUNDWATER

Estimates of nutrient contribution from groundwater have not been included in past budgets. However, groundwater can be a locally important phenomenon worthy of some, if cursory, consideration. Particularly in older neighborhoods with high densities of septic tanks, of which some may be old and leaky (modern septic systems contribute much less nitrogen to groundwater), groundwater nitrate concentrations may be an order of magnitude elevated from surface water flows (Valiela and Costa 1988, Nowicki and Gold 2008).

This is locally true in Greenwich Bay, where recent efforts at sewerage large portions of the population are underway, but for a long time, residents living very near to the water were reliant on septic systems and ISDS for disposal of wastewater. Urish and Gomez (Urish and Gomez 2004) estimate the groundwater flux of nitrogen

into this embayment using three different sets of attenuation coefficients, and arrive at an estimate of 47-57 metric tons of N, or 3.5-4.1 million moles. This value is roughly consistent with a budget for Greenwich Bay of 10-16 million moles N, of which slightly more than ½ is sourced from the bay proper (DiMilla et al. 2011). While in the grand scheme of the budget, this constitutes less than 1% of the total flow of N into the bay, it should be noted that this value is 4-5 times larger than the flow from the East Greenwich WWTF (which has recently upgraded). Groundwater is not thought to be a significant contributor of phosphorus in most situations, due to the high capacity of soil to absorb phosphorus.

OUTPUTS

DENITRIFICATION

Sediment denitrification (the microbial conversion of DIN to N₂O and N₂ gas) is particularly difficult to quantify because it does not follow easily predictable patterns. While some systems at some times show clear relationships between denitrification rate and temperature and/or organic material loading (Jorgensen 1989, Nowicki and Oviatt 1990, Seitzinger and Giblin 1996, Cabrita and Brotas 2000, Lishman et al. 2000), recent studies have repeatedly shown no clear correlation with either in Narragansett Bay (Fulweiler et al. 2007, Fulweiler and Nixon 2009, Fulweiler et al. 2010, Fulweiler and Nixon 2011) and even the first direct measurements of denitrification in Narragansett Bay showed no impact of increased organic matter loading or temperature (Seitzinger et al. 1984).

Earlier budget estimates attributed 85-170 million moles of N loss to denitrification (Nixon et al. 1995). There is strong evidence suggesting that this

number has gone down significantly, though by how much is uncertain. Data collected by Fulweiler and colleagues for 2005, when extrapolated over the entire bay, suggest an average net denitrification rate of about $40\mu\text{mol}/\text{m}^2/\text{h}$ (Fulweiler et al. 2007, Fulweiler and Nixon 2011). This number scales up to just under 80 million moles per year if extrapolated across the soft bottomed area of the bay and through the entire year. In the summer of 2006, however, Fulweiler and colleagues observed strong net nitrogen fixation, and postulated that if the rates observed in that summer were paired with denitrification at the rate observed in 2005 during the remaining 9 months of the year, the net result would be fixation of 40 million moles over the course of the year. The summer of 2006 was a year with no winter/spring diatom bloom in the bay and relatively low average chlorophyll in the mid-bay where these samples were collected (see Chapter 1). The working hypothesis of the authors was that reduction in flux of organic material to the benthos as a result of decreased chlorophyll and the lack of a large winter/spring bloom, coupled with warming water is facilitating these changes (e.g. Nixon 2009, Nixon et al. 2009, Fulweiler et al. 2010). However, we have recently had several years with strong winter/spring blooms, and average chlorophyll in our lower bay dataset (see chapter 2) shows no trend with time (due in part to high annual values in 2008, 2009, and 2010). So it is possible that the 2006 values observed by Fulweiler et al. are ‘worst case’ numbers. However, it is also possible that they are indicative of the future, since 2006 is also the first summer during which many of the upgraded plants discharged reduced effluent loads into the bay. Fulweiler and colleagues have continued this sampling program, but the data are not yet available for publication. It will be interesting to see how this

term of the budget refines itself as more data become available. For the time being, we see no alternative other than to use the 2005 and 2006 measurements as a range, which yields an estimate of -20 ± 60 million moles TN per year contributed by net sediment processes.

BURIAL

The loss of nutrients through burial in the sediments is an important term of the budget, but one which is difficult to quantify. The benthos of Narragansett Bay is very active, and much of the organic material which falls to the bottom is recycled and returned to the system. Mesocosm studies at the MERL facility have shown that nutrients in the sediment are rapidly returning to the overlying water even from heavily enriched sediments (Oviatt et al. 1984, Nowicki and Oviatt 1990). More recent measurements of sediment nutrient flux by Fulweiler et al. confirm the trend of rapid release of nutrients from the sediment, particularly the release of phosphate in low oxygen conditions, which are becoming more common in the Upper Bay regions (Melrose et al. 2007, Codiga et al. 2009, Smith 2011) where phosphate concentrations are also the highest (Fulweiler et al. 2010).

Quantification of burial requires an estimate of sedimentation rate, coupled with measurements of nitrogen and phosphorus concentration in the zone of sediments below bioturbation. Nixon et al. (1995, 1986) make this calculation based on two studies of deposition rates at different areas in the bay (Santschi et al. 1984, Corbin 1989). Because these studies measure carbon, not nitrogen, established C/N ratios in accumulating sediments (Nixon and Pilson 1984, Frithsen et al. 1985) were used to estimate N burial. This indirect method was chosen because of a paucity of direct

nitrogen measurements in sequestered sediment. By this technique, Nixon and colleagues estimated a burial rate of 45-100 million moles per year for nitrogen. Data for phosphorus burial in the bay are similarly limited by lack of available sedimentation rate data (see Nixon and Pilson 1984, Nixon et al. 1995), but do align with reported values for other similar systems (Lukkari et al. 2009, Hartzell et al. 2010, Eyre et al. 2011), and thus with similar caution as originally urged by Nixon and colleagues (1995), we can adopt their estimate of 5-8 million moles per year for phosphorus burial. While Nixon et al. (1995) lament the lack of resolution in estimating these parameters, there is not sufficient supplementary data readily available to justify a reanalysis. Furthermore, given the relatively long amount of time it takes sediment to settle below the zone of bioturbation, it is unlikely that burial rates have changed in response to WWTF upgrades which are only a few years old. Over time, it is possible that decreased loading could reduce nutrient flux to the benthos, and therefore decrease burial rates, but for the time being, we can carry over the estimates from the past budget with some confidence that they are reasonably accurate.

FISHERIES

A remaining export of biomass comes from the fishery. Nixon et al. (1995) estimate nitrogen removal from the quahog fishery by calculating the meat weight of landings, and using a percentage (2.7%) of biomass N determined from literature, and 16:1 N:P ratio to estimate removal by this vector (Nixon et al. 1995). Though hard clam landings have been very variable, landings over the last few years for which we were able to get data average to about 1.85 million kilograms per year, up very slightly

from the earlier estimate of 1.75, resulting in a net removal of 3.5 million moles of N and 0.22 million moles of P by this vector.

We also estimate removal from growth of fish biomass which can be directly ascribed to growth in the bay. To do this, we account only for the growth in biomass of age 0 fish which come into the bay in the spring, and grow over the course of the summer. Using biomass data summarized from the DEM monthly fish trawl in the bay by Longval (2009), we estimate that biomass growth from this vector is approximately $0.95\text{gC}/\text{m}^2/\text{y}$ wet biomass. Since this is a baywide average of sampling stations roughly evenly distributed throughout the bay, we can scale it up over the area of the bay to get approximately 311 metric tons of fish biomass per year supported in this way. Furthermore, because we are using biomass rather than abundance, this estimate accounts for loss due to mortality and assimilation efficiency. To convert this to nitrogen, we used a biomass:carbon ratio of 3:1 and Redfield C:N:P, which works out to 2.3% N by weight. This value is similar to the value found by Nixon et al. (1995) for Quahog and is also roughly comparable to values found in a similar study on fish nutrient export in coastal Louisiana (Deegan 1993). By this calculation, 7.5 million moles of N and 0.45 million moles of P are exported by this vector. While this is a conservative estimate, at the very least, it makes some attempt at quantifying the role of secondary production on nutrients. Combined with the hard clam data, this sums to 11 million moles of TN and 0.67 million moles of TP.

EXPORT

Flux across the bay/sound interface has historically been extremely difficult to quantify. Past budgets have, at least in some part, calculated this term by difference,

assuming that the system is, on average, at steady state. Nixon et al. (1995) estimated inflow of nitrogen and phosphorus from the sound to be 115 and 27 million moles of nitrogen and phosphorus, respectively, by calculating inflow volume using a salt balance model (Pilson 1985b) and concentration using the bottom water concentration in the lower East Passage from a yearlong survey in the early 70's (Kremer and Nixon 1975). Outflow of organic nutrients was calculated by estimating export of carbon from primary production (whose creation and burial are easier to quantify) and using the Redfield ratio to estimate N and P loss at 90-185 million moles of N and 7-14 million moles of P per year, plus an additional 72 and 2.4 million moles N and P, respectively, from riverine DOM. The budget is then 'balanced' by difference, assuming inorganic export of the remainder of the inputs of nitrogen and phosphorus to the bay, or 240-470 million moles N and 41-51 million moles TP (Nixon et. al 1995, Table 21).

We attempt herein to use a modeling approach to more accurately quantify these fluxes. The GEM Box model (Kremer et al. 2010) was designed as an eco-physical model to simulate property exchange in Narragansett Bay in order to look at the drivers of hypoxia in the bay. However, it uses the highly accurate ROMS model for property exchange and flow between a series of model boxes which correspond well to the stations sampled in this study (Figure 3-3). By parameterizing the GEM model with the river and plant loadings above, and parameterizing the bay/sound boundary using data from station 3 in Chapter 1, we can generate estimates of exchange between elements, and therefore, produce an estimate of flux into and out of the bay.

The modeled nitrogen concentration in the 15 bay boxes (Figure 3-3) does an excellent job of paralleling measured concentrations from our baywide survey. To test this, we calculated Relative Operating Characteristic (ROC) scores comparing measured and modeled nitrogen and phosphorus at each station over the entire year at 19 evenly divided thresholds between the minimum and maximum value observed in each GEM box. The summed ROC scores for the entire model (all boxes, across the entire year) are .92 for nitrogen and .96 for phosphorus, where 1.0 is a perfect match, and a score above 0.5 is indicative of a skilled model (Figure 3-7).

Doing so yields inflow estimates of 251 million moles DIN and 75 million moles DIP per year, both significantly higher than estimates of 115 and 27 million moles N and P respectively put forth by Nixon et al. (1995) in previous budgets. However, similar to past budgets, the model predicts net fluxes out of the bay for both N and P, calculating net export of 102 and 283 million moles inorganic and total nitrogen, and 29.8 and 32 million moles inorganic and total phosphorus respectively. This calculation indicates that significantly less nitrogen and more phosphorus are fluxed out of the bay in inorganic form than estimated by Nixon et al. (1995) but upholds the conclusions of that study that the vast majority of both N and P incident on the bay are exported to the sound in one form or another, and that most of the P export is inorganic. Using these estimates to close the budget, we are very close to balancing the nitrogen budget for the bay, with inputs and outputs overlapping to within the significant margin of error necessary with this type of calculation. However, our estimate of net phosphorus export makes the bay slightly net negative

for phosphorus, as total load to the system as quantified above, is only about 25 million moles.

STORAGE TERMS

A thorough review of the standing stock of nutrients stored in the water column of the bay can be found in Chapter 1. Relative to the magnitude of other terms in the budget, the water column standing stocks are small; 15 and 45 million moles of DIN and TN respectively, and 2.5 and 3 million moles of DIP and TP respectively. With standing stock and input, we can make a cursory estimate at residence time, arriving at a residence time of 15.5, 33, 67, and 42 days for DIN, TN, DIP, and TP respectively. Compared to a residence time of about 30 days for water in the bay (Pilson 1985a), DIN appears to be rapidly assimilated, while phosphorus (both inorganic and organic) may be being retained in the bay for longer than the average residence time of water, possibly either through recycling, or sediment flux and resuspension.

The storage terms in the sediment were much larger than in the water column. Our ability to estimate this from existing data is limited, as we have only very limited data on nutrient concentration in the surficial sediments from mesocosm experiments. However, when we scale these concentrations up to account for the top 10 centimeters across the bay, we estimate approximately 1770 million moles TN are and 377 million moles TP are stored in this reservoir. There is a tremendous amount of uncertainty associated with these terms, as we do not know if concentration is constant throughout the bioavailable sediments, and we have only 2 data points, both of which come from

mesocosm and not in situ data. However, the resolution here is sufficient to arrive at the conclusion that the short term storage in sediments far exceeds the annual inflow for both N and P and thus, the reservoir is more than large enough to potentially buffer short term changes in supply, or even mask a management intervention for a short period of time.

DISCUSSION

INPUTS

DEPOSITION

Though only nutrients which fall directly onto the bay's surface are quantified here as a budget term, and this term is a relatively small contributor to the overall budget of the bay, less than 10% of the nitrogen budget and less than 1% of the phosphorus budget, atmospheric deposition onto the watershed is an important part of the budget. Its predominant manifestation is in the rivers term, and we can estimate its magnitude by subtracting the plant discharges from the total river flow numbers. Of the 221 million moles ascribed to river flow, a maximum of 118 million moles can be ascribed to plant discharges, and this assumes no loss term for utilization or burial ascribed to the stream flow. Similarly for phosphorus, of the 9.35 million moles which enters the bay through the rivers, only half could possibly come from the plants, and phosphorus in freshwater systems is typically taken up very quickly. The remainder in both cases is caused by processes in the watershed, either deposition on the watershed and subsequent run-off or other anthropogenic processes (e.g. fertilizer, septic systems, run-off from roads, etc...)

In reality, the fraction of this river flow due to watershed processes is likely even higher. We can make a first pass approximation of this in rivers which experienced upgrades, such as the Blackstone. Between measurements made by Nixon and colleagues in 2003-2004 and those made by NBC in 2006-2010, approximately 50 million moles/year of nitrogen were removed from effluent discharged from this river (Table 3-3), yet we see only a 15 million mole reduction (approximately) in flux to the bay (Table 3-2). The difference is somewhat mitigated by the observed 10% increase in flow, to which we can, estimating by percentages, attribute an additional 7.5 million moles of loading. Even still, our results indicate that at most half of impact of the reductions implemented is felt by the bay proper. This is an indication that the 50% riverine abatement estimate used by the DEM in assessing the impact of reductions may be close to accurate for the Blackstone (RIDEM 2005). In comparison, the Pawtuxent River, the only other river which had substantial upgrades to its plants, shows reductions in nitrogen and phosphorus which almost exactly match the plant reductions of about 20 million moles per year nitrogen and 2 million moles per year phosphorus, a potential indication of very little abatement. This is not surprising, since the travel time on the Blackstone from Worcester to Narragansett Bay allows much more time for biological, physical and chemical processes than the short run down the Pawtuxent from Cranston and Warwick to the bay.

RIVERS

As mentioned earlier, the rivers are the primary vector of nutrients into the bay, despite relatively low total freshwater input compared to other similar systems

(Bricker et al. 2007). Most of our river calculations seem in line with what we expect to see given the plant reductions, tempered slightly by increases in precipitation which have, on average, increased flow by around 10%. There are two discrepancies in river estimates between our work and past budgets which warrant attention. The first is the order of magnitude reduction in phosphorus load in the smaller rivers. While we expect reduction in phosphorus load in the Pawtuxent and Ten Mile loadings (and soon the Blackstone) due to plant upgrades on those waterways, no such upgrade occurs on the Moshassuck or Woonasquatucket rivers, and flow between the surveys seems relatively consistent. It is difficult to establish a firm causal mechanism here, as we are not aware of any management action to reduce loadings in these stream reaches. However, the contributions of these rivers to the overall budget are very small, so the resolution of our data may be limited. Despite order of magnitude phosphorus reductions in both of these rivers, this change accounts for only 1-2% of the phosphorus budget.

The other, and far more significant difference is the Taunton River. The discrepancy in measurement comes in part from the fact that Nixon et al. (1995, 2008) scaled up the flow of the Taunton to account for the large un-gauged area between the measurement station, at State Farm in Bridgewater MA, and the mouth of the river. By land area, slightly more than half of the watershed is un-gauged because the river has tidal influence for about 10 miles from its mouth. This results in increasing the flow from the Bridgewater gauge by about 40%, as calculated by (Boucher 1991). We elected not to scale this flow up primarily because the Taunton River at Bridgewater, where it was sampled both for flow and for concentration, during low flow periods is

more than half sewage effluent by volume. Even during high flow periods, the effluent from the Brockton WWTF, at a relatively constant 17-20 million gallons per day, is close to 10% of the total flow of the river. Therefore, we feel it may not be accurate to apply concentration data taken at the Bridgewater gauge, and assume that it will hold constant as the volume essentially doubles with 300 square miles of un-gauged area below this station. This is much less of a concern for other rivers, where the volume of effluent is small compared to the volume of water, and the ratio of gauged to un-gauged area is small (for most of the other rivers, the ratio of gauged to total area is <1.2).

When we calculate the Taunton River using Boucher's (1991) coefficient, we get 82 million moles TN and about 1.22 million moles TP. This TN estimate is still a 30% reduction over Nixon et al. and the phosphorus reduction is still about 77% of the earlier estimate. These numbers are probably a more accurate representation of the change which has gone on over time in that system. We expect the large phosphorus reduction, since Nixon et al.'s values are from data collected in the 1980's, before large scale reductions in phosphorus load became mainstream (Litke 1999). However, for the purpose of attempting to quantify as accurately as possible the total flows into and out of the system, we believe that adding the un-gauged portion of the Taunton River to our 'unmeasured drainage' term, and representing it with the average load per acre across the entire system provides a more accurate picture of the actual contribution from the Taunton, though we admit there is a fair amount of uncertainty either way on this matter.

WASTEWATER TREATMENT PLANTS

The flows from the treatment plants are perhaps the easiest to quantify, and the most data-rich portion of the assessment. There were very few ‘surprises’ in this analysis either. Most plants with upgrade permits in force met or exceeded their targets virtually without fail. Many plants did almost as well during the winter as they did during the summer. This was a bit of a surprise, because we expected a temperature-dependent relationship here (e.g. Lishman et al. 2000, Jeong et al. 2006), but we hypothesize that since the tanks are generally underground, and receiving water also from underground and/or partially indoor facilities, the water in these tanks may be fairly well insulated, and remain warmer than expected despite cold air temperatures, which would improve efficiency.

We elected to use 2010 data from Warwick, and West Warwick, even though those plants were physically flooded for a prolonged period of time, and not fully back online for several months after the large flood in late March. The 2010 average numbers from these two plants are 50% higher for total nitrogen, and nearly double for total phosphorus compared to 2008 and 2009. Over the long-term, we expect most years to be more like 2008 and 2009, and hopefully these plants will implement procedures which will assist them in recovering quickly from flood events when they do occur, minimizing excess flux. However, if the past 50 years have been any indication, the climate of Narragansett Bay is shifting towards increased precipitation and increased storms (Madsen and Figdor 2007, Pilson 2008, Smith et al. 2010), so removal of these data as a ‘fluke’ seems shortsighted.

URBAN RUN OFF

The impact of industrialization and build up in nearshore communities is felt in the nutrient mass-balance through the urban run-off term. Precipitation that falls on these areas, with high amounts of impervious surface, is collected in sewers and discharged directly into the bay, rather than moving gradually through the water table, where much of the nutrient load may be alleviated. This is true of nearshore communities throughout the Providence area, as well as Fall River, Newport, East Greenwich and North Kingstown.

This term of the budget also is more complex than the analysis suggests. Much of the trick with urban run-off involves effectively partitioning the run off so that it is not double counted as part of either a WWTF discharge or in the 'unmeasured flow' term associated with the rivers. Nixon et al. (1995) thoroughly review the assumptions that go into the parceling of space so as to avoid, or at least minimize double counting here, with the only major change that has occurred on this front being the institution of the CSO catchment tunnel, which actually diverts a significant portion of what was formerly part of this term of the budget into the 'direct plant discharge' term. Even so, the combination of land-use change and increased precipitation causes this term to rise.

The reassessment of acreage not originally assessed by Carter (1982), and therefore by Nixon et al. (1995, 2008) is difficult, because the decision to use nationwide coefficients specific to a land-use type rather than a more generic coefficient that is more specific to the watershed is a difficult trade off, and can be argued either way. For the most part, there is reasonable agreement in coefficients

between the two studies, but there are some exceptions, notably the phosphorus coefficient associated with highways, which in the case of the earlier study, is based only 3 data points (Table 3-4B). The other issue arises from the consideration of land use types not measured by Carter. We felt it necessary to provide some value for these previously unconsidered acres, and when we did a sensitivity analysis by varying how we assign coefficients (Dionne et al. 2009), we found the overall estimate to be relatively insensitive to how we handled this issue. However again here, a large part of the difference between our assessment and the past assessment is due to a change in methodology, so the increase in actual load from this source since it was last assessed in the 80's is probably about 20%.

One interesting thing to point out is that road miles are a large driver of load from this vector, since the runoff coefficients from this land use type are so high. One thing that neither our assessment nor Nixon et al.'s work takes into consideration is the recent trend towards the creation of vegetated buffer strips and retention wetlands. In virtually all systems studied with low to moderate loading rates (Narragansett Bay would be considered moderate, as compared to dense agriculture or concentrated feed lot operations, which would be considered high), this technique reduced N and P load by more than 90%, in some cases as high as 99% (Haycock 1993, Lee et al. 1998, Greenway et al. 2001). This is particularly true during the growing season, but even in winter, buffer strips with trees are >95% efficient for nitrogen removal, while grass is 84% efficient for nitrogen removal and up to 50% efficient in phosphorus removal, even during simulated heavy rain events, presumably due in large part to subsoil microbes as well as above ground biomass (Haycock 1993, Lee et al. 1998). These

advances in urban planning could explain some of the reductions in the smaller rivers, and could mitigate future land-use changes as the upper bay SAMP continues to prioritize vegetated buffers (SAMP 2005).

Retention wetlands also have great potential for mitigation. Greenway and colleagues (2001) show that >25 % of TP and 80-85% of TN can be removed by constructed wetlands, while Lin et al. (2002) show similar patterns with even higher rates of P removal. Small 'wetlands' are an ancillary result of digging borrow pits to create overpasses, but if these wetlands are managed (with appropriate drainage and above-ground biomass removal) they can sequester as much as 1.5 tons of carbon per hectare per year (McCarty and Ritchie 2002). A meta analysis of nitrogen uptake rates in retention wetlands (Crumpton et al. 2008) shows wide range of nitrate consumption rates, from 200-1200kgN/ha/y with a mean of 400 though some of this is likely due to denitrification.

While these numbers sound enticing, it seems logical to ask whether these retention wetlands can offset the additional nutrients incident on a system from a construction project. To accomplish this, we analyzed a recent construction project in North Kingstown RI, where several small retention wetlands which, were periodically mowed, were created adjacent to new overpasses associated with an expansion of route 403 coming from the Quonset Point port facility (Figure 3-8). We used Google Earth to measure the amount of newly constructed highway (4 additional lanes in some places and expansion from 2 lanes to 4 lanes in others), and to map and quantify the areas of wetlands created (Figure 3-8). If we apply our highway urban run-off coefficient, our annual rainfall of about 127cm/yr puts about 500-700 moles N and 40-

50 moles TP on an acre of highway, while Crumpton et al. (2008) measured that an acre of wetland could remove (average) 11,500 moles TN. The N:P ratio in live marsh grass is close to 16:1 (Dame 1991), but literature suggests that a significant amount of the N removal from marshes is the result of denitrification, not above ground biomass growth (Valiela and Teal 1977, Dame 1991, Mitsch and Gosselink 1993). In the case of natural salt marshes, probably most of the vegetative uptake is recycled (since little of this organic matter is exported), but in constructed wetlands, the plant material is mowed and composted. Lacking estimates of the amount of biomass removed by mowing, if we estimate denitrification to be responsible for 50% of the N loss, and an N:P ratio of 16, 350 moles TP would be removed in this way. Our Google earth calculation suggests that the Route 403 expansion in North Kingstown adds 27,000 m² of created wetland or about 6.7 acres across several small ponds, and about 1.3 million square feet of roads assuming 12 foot lanes, which is about 30 acres. This gives us a total increased load from construction of 18,000 moles N and 1350 moles P, while the wetland could remove 77,000 moles N and 2400 moles P; in this case several times more than the road adds. A similar study on retention ponds in Saskatchewan showed that a pond of roughly 9,000 square meters (2.2 acres) removed approximately 18,000 moles of nitrate per year (Wang et al. 2008), which is similar in magnitude to the estimate presented here.

In fact, the role of wetlands in general as a nutrient sink may be a mitigation pathway deserving more attention. Heffner and Nixon are presently calculating rates of nitrogen removal from salt marshes exposed to varying levels of anthropogenic nitrogen loading, but these data are not ready for publication, and the total acreage of

salt marsh in the bay proper is small, slightly less than 1500 hectares (Wigand 2008) perhaps leading to why this term has not been included in past budgets of Narragansett Bay, despite inclusion in budgets of many other systems (Woodwell et al. 1977, Woodwell et al. 1979, Boynton et al. 2008, Eyre et al. 2011). If we were to make a first-pass approximation at the amount of nitrogen which could be removed in this way, we might use the low end figure from Crumpton et al. (2008) of 200kgN/ha/y, which would give us a removal term of about 20 million moles per year, a small but significant contributor to the budget. Thus, the restoration of natural wetlands may be a management strategy worth considering moving forward.

Another factor which has received a great deal of attention is the new CSO collection tunnel. At present, all this tunnel does from a nutrient budgeting perspective is move about 2.5 million moles per year of TN and about 0.25 million moles of TP from the urban run-off term to the direct sewage term because the Fields Point plant has not instituted advanced treatment yet. In practice, the impact on the ecosystem may be more pronounced, because it will delay these nutrients (and the freshwater in which they are suspended) from entering the bay during a time of already high freshwater flux, and therefore may slightly reduce the extent or severity of hypoxia which typically follows large rainfall events.

In theory, once the Fields Point plant upgrades, this will result in a net removal of about 2 million moles of nitrogen per year. Further upgrades to the CSO system will capture 15 more overflows within the next 3 years, and create a second tunnel which feeds the Bucklin Point plant, intercepting another 17 CSO's by 2021. All told, the system could capture and treat as much as half of the stormwater nitrogen

incident on the Providence metro area, resulting in a reduction of 10 million moles TN or more. It should be pointed out that the primary goal of the retention project is not nutrient removal, but rather reducing beach and fishing closures, by reducing the discharge of untreated wastewater and its bacterial load, so analyzing this reduction on a ‘cost per mole’ basis does not capture the full benefit of the tunnel.

GROUNDWATER

Compared to many other systems, particularly those with large agricultural inputs, the groundwater contribution to Narragansett Bay is very small (Boynton et al. 2008, Kincaid et al. 2008, Nowicki and Gold 2008). Based on salinity budget measurements, Pilson estimated this avenue to account for less than 10% of the total freshwater to the bay (Pilson 1985a). This falls roughly in line with estimates made by Kincaid and colleagues using the ROMS model (Kincaid et al. 2008). Furthermore, some of this may be captured in the ‘unmeasured flows’ estimated by Ries (1990), which are included in above and past mass-balance calculations. By subtracting the sewage estimate from the river load and adding the urban run-off number to the remainder, we can roughly quantify the amount of nutrients which freshwater flows bring into the bay at about 150 million moles TN, 10% of which is about 15 million moles. Our only quantifiable source of groundwater comes from Greenwich Bay, which we estimate at 4 million moles TN. Some of the remaining groundwater is likely counted by the ‘unmeasured flows’ term (which we used to scale up observed flows to match predicted flows). In general, while we may be underestimating this term somewhat, the magnitude of the discrepancy is not a major concern within the scope of the budget writ large.

OUTPUTS

SEDIMENT FLUX

Narragansett Bay is extremely fortunate to have a rich history of denitrification studies measuring flux of nitrogen to and from the sediment (Seitzinger et al. 1984, Nowicki and Oviatt 1990, Nowicki 1994b, Fulweiler et al. 2007). This biological process has traditionally been viewed as an important removal mechanism by which 13-26% of the annual input is removed from the bay (by conversion to N₂ gas) (Nowicki 1994b, Nixon et al. 1995, Fulweiler et al. 2007). However, recent changes to the bay, brought presumably by changes in climate and phenology (e.g. Nixon 2009, Nixon et al. 2009, Fulweiler et al. 2010) and possibly in part by decreased loading have altered the net denitrification rates in the bay.

This term of the budget also has perhaps the most uncertainty associated among any of the terms we can directly measure. Measurements of denitrification in the bay, both past and present appear to be patchy, variable, and not well correlated to other physical processes in the bay (e.g. organic material loading or temperature) (Seitzinger et al. 1984, Nowicki 1994b, Fulweiler et al. 2007, Fulweiler et al. 2010, Fulweiler et al. 2011). Even as the amount of data on this topic has increased rapidly over the last few years, it has served mostly to help us realize how much more we need to do in order to truly understand the benthic-pelagic coupling in this ecosystem.

With that being said, there are certainly enough data available to make a reasonable estimate at the contribution of this term. However, it also seems likely that the denitrification rate in the bay is not constant, and is likely to vary greatly from season to season, based on the amount of organic matter fluxed to the benthos in any

given year (Nowicki and Oviatt 1990, Fulweiler and Nixon 2009, 2011) and the availability of oxygen during summer months, which is also variable (Melrose et al. 2007, Codiga et al. 2009). The two years sampled by Fulweiler et al. (2007) and presented in this study, 2005 and 2006 both represent years with no winter-spring bloom, and 2006 was one of the most severe years on record for hypoxia in terms of spatial extent, severity, and duration (Codiga et al. 2009, Smith 2011). In contrast, very large blooms occurred in 2009 and 2010, with blooms smaller but still present in 2008. This may cause the estimate of denitrification to more closely resemble earlier measurements by Seitzinger, Nowicki, and colleagues (Seitzinger et al. 1984, Nowicki 1994b). However, the opposite can also be argued; that because 2006 was the first year after loading reductions, we ought to expect that conditions in this year would be the norm moving forward. We therefore provide a large range (-20 ± 60 million moles) for the estimate of denitrification, but our range does not overlap with the estimate of Nixon and colleagues of 85-170 million moles denitrification (Table 3-1). If net sediment N flux truly varies from the maximum of the range calculated in this study (40 million moles net nitrogen fixation) to the minimum of the range calculated by Nixon and colleagues (170 million moles net denitrification), it would be the single largest term in the nutrient budget. Even our estimate of the interannual variability in this term (-20 ± 60 million moles), which may well be too small, makes this the third largest term in the budget, and something we should keep our eye on closely as we move into the future.

It should also be noted that the change in estimates of denitrification between Nixon's estimate; 130 ± 45 million moles and the present estimate; 20 ± 60 million

moles, is almost exactly the same magnitude as the reduction in loading of nitrogen to the bay associated with upgrades to wastewater treatment facilities (Table 3-1). It is difficult to establish a positive causal link between these two factors, and it is entirely possible that this similarity is a coincidence, but it is also possible that changes in the flow of nitrogen into and out of the sediments may ‘counteract’ a significant portion of continued reduction efforts, whether causally or driven by another (e.g. climate) factor.

Especially given the present and pending phosphorus reductions, this could have interesting implications for the N:P ratios in the bay. While presently, the bay remains nitrogen limited on average, the ratio of N:P approaches or exceeds 16 particularly during winter months in the upper portions of the bay, though both species are typically abundant during this time of year (see chapter 1). If total N loads to the system remain constant (e.g. reductions to the load are balanced by changes in sediment flux) while P load continues to drop, this may tip the scales even further towards phosphorus limitation.

Another interesting corollary of this research is that while we expected to find a proportionately larger impact on standing stocks during the summer as a result of WWTF upgrades, we found similar magnitudes of decrease when comparing summer and annual totals (see Chapter 1). If indeed the benthos is contributing a significant amount of nitrogen to the water column by fixation (or even denitrifying less) during the summer, this could explain why the decreased loads during the summer are not evident in the standing stocks.

The lack of phosphorus balance in the bay is a key point of discussion, and the sediments are the lynchpin which might enable this phenomenon. The sinks of phosphorus we document in this study are actually about 25% less than found by Nixon et al. (1995). However, our total sources of phosphorus over the same time period have dropped by more than half. If indeed sinks of phosphorus exceed sources at this time by the 15 million moles estimated (Table 3-1), these losses are likely coming from the large reservoir of phosphorus stored in the sediments.

Flux from the sediments of phosphorus is traditionally considered to be net zero, whereby flux from water column to sediment is balanced by burial and remineralization. Mesocosm studies using Narragansett Bay sediments confirm this trend, showing sediment and water column reaching relative equilibrium within 6 months of a disturbance (Oviatt et al. 1984, Nowicki and Oviatt 1990, Nowicki 1994b). However, it is worth considering that the year of data used for the bay/sound modeling flux is the year during which most of the plants which upgraded completed their upgrades. Thus, any short term imbalance resulting from this reduction in supply would be reflected in our results. Furthermore, 2006 was a particularly severe year for hypoxia in the bay, and hypoxic conditions are well known to flux phosphorus from sediment to water column (Nowicki and Oviatt 1990, Fulweiler et al. 2010), which could cause additional short term flux out of the bay from the sediment storage term.

In addition to their nitrogen measurements, Fulweiler and colleagues also measured net sediment phosphate flux at 3 stations in the Providence River estuary, Greenwich Bay, and the Upper Bay (Fulweiler et al. 2010). This relationship does show weak temperature dependence, with the strongest fluxes out of the sediment at

warm ($>20^{\circ}\text{C}$) water temperatures, and flux dropping to essentially zero in cold ($<10^{\circ}\text{C}$) water. Fitting the regression applied by Fulweiler et al. to average annual water temperature data for the bay, we can calculate that the sediments of the Providence River estuary might supply some 4.2 million moles of inorganic phosphorus to the water column over the course of 2006, with net flux from Greenwich Bay of only a few thousand moles, and the Upper Bay station close to zero (Fulweiler et al. 2010). The authors do not measure flux from the lower bay, but their measured flux from the Providence River Estuary alone would account for more than half of the ‘missing’ phosphorus in our budget (Table 3-1). This may be a key area for future study, because if the ecosystem truly is ‘balancing the budget’ by exporting several million moles of phosphorus from sediment storage per year, there could be further changes in productivity and N:P ratio once the system reaches equilibrium, especially given additional future loading reductions.

FISHERIES

Our estimates to quantify fisheries removal herein are preliminary and certainly conservative. There are a number of literature attempts to quantify the impact of fish and fish biomass on nutrient dynamics (Vanni et al. 1997, Vanni 2002, Sereida et al. 2008), mostly for freshwater systems. However Deegan (1993) attempted to quantify the role of fish biomass export on an estuarine nutrient budget in Louisiana, arriving at an estimate of about 3.1 grams N/m^2 and about 0.9 grams P/m^2 , which constituted about 5-10% of the total nutrient budget of that system. Our estimate of fish export is between 2-3% of the total inputs to the system. If we were to assume the same rate of export as Deegan found, Narragansett Bay would export

about 70 million moles of TN and 9.5 million moles of TP per year as fish biomass (Deegan 1993). This export would represent about 22 grams carbon/m² according to Deegan's calculations, which is less than 10% of the total primary productivity in the bay of 323 gC/m²/y as estimated by Oviatt and colleagues (Oviatt et al. 2002).

The key difficulty in estimating fish export from this system is that much of the fish biomass is not year round resident. Virtually all of the biomass of fish leaves the bay in the winter, migrating offshore and/or south. Species like bluefish and striped bass, which constitute the majority of the recreational catch, are highly mobile, and even more site associated demersal fish like tautog, black seabass, and scup tend to move into deeper water during the winter. The other major fishery in the bay which may be easily quantifiable is for lobster, which is responsible for about 1,700 metric tons of landings (RIDFW 2008), but these animals also are mobile, and a portion of their diet is thought to come from lobster pots, which are typically baited with skate, herring, or other fish whose source is unknown (Saila et al. 2002).

BURIAL

Especially as the inputs to the system continue to change over the next years and decades, it may be wise to systematically reevaluate whether the rate of nutrient removal from the system by burial is changing. Based on recent estimates of sedimentation rate in the bay which range from 0.5-2cm/y (Hartmann et al. 2005), it would take a minimum of 5-10 years for sediment to settle out of the top 10-20 cm, which is typically the zone considered to be most biologically active (Calabretta and Oviatt 2008, Shumchenia and King 2008). Since the majority of upgrades did not

occur until 2005, it may still be too early to detect any change which is occurring in all but the most sensitive locations in the bay.

FLUSHING

Estimates of exchange across the bay/sound interface are limited not by the modeling capacity, but by the relative paucity of data used to inform the process. While we are quite confident in the ability of the GEM model to provide reasonable estimates of water exchange between the bay and the sound and circulation within the bay (Figure 3-8), our nutrient data are on a much coarser scale than the model truly needs.

We have only one station representing RI sound, and two stations representing the lower east and west passages respectively. Each station was sampled 12 times during the year 2006, and the samples are surface only. From this, we must create a matrix of daily surface and bottom nutrient concentration estimates to parameterize the flux into the model, which, by the nature of their being estimates, do not really ‘line up’ with any particular weather events associated with the circulation parameterization of the model (e.g. if the modeled weather data dictate a wind shift from the North to the South on a given day, this will intensify the flow up the East Passage of the bay, bringing in more nutrients from the Sound, but if we did not sample that day, we may be using inappropriately interpolated concentrations to parameterize those fluxes.

Furthermore, we are estimating bottom concentrations from averaged relationships derived between surface and bottom concentration from two surveys several decades ago, and these relationships are very variable (Table 3-5). We must assume that the relative relationships between surface and bottom concentrations have

not changed with time, which is probably a reasonable assumption, but one on which we do not have enough data to conclusively comment either way. However, even after this assumption is considered, there are still problems associated with this technique. While the actual relationship between surface and bottom concentration is likely to be correlated to weather, wind, river flow, tide and other factors which are considered by the model, the concentration relationships we are using would be blind to these variations. This could bias the model one way or the other.

The model appeared to be relatively insensitive to changes in the estimation technique used to extrapolate bottom water concentrations from surface, with the net flux across the boundary changing by a maximum of 4% for nitrogen and 2% for phosphorus across the three estimation techniques we attempted. Interannual variability was a larger concern, causing a change of about 10% between the 2006 data and the 2006-2010 average concentration values. Even this is likely an underestimate of interannual variability, since this controls only the sound concentration, and weather and circulation as well as load from rivers and plants is still driven by the model, which, in this case remains parameterized with 2006 data. As discussed earlier, 2006 was a year with high precipitation (137 cm as opposed to a 10 year average of about 119), and high spatial hypoxia extent (Codiga et al. 2009). Therefore the forcings associated with this year may overestimate flux from the bay to the sound relative to a more ‘average’ year.

Because of the way the model runs, we were also forced to either treat TN as a conservative tracer, and not allow its uptake at all by biology, or treat it identically to DIN, and allow it to be immediately taken up by the biology in the model. We also do

not have appropriate particulate nitrogen (PN) data to parameterize the modeled river flows, and therefore had to use a ratio of TDN:TN derived from previous work (Dionne et al. 2009). Though PN is a relatively small contributor, these assumptions are the cause of the larger uncertainty in the TN flux.

Our fluxes for DIN calculated by the GEM model seem entirely reasonable. Exchange across the bay/sound boundary is much larger than estimated by Nixon et al. (1995) (Figure 3-9), likely because the model considers nutrients flowing in and out with the tidal cycles, while Nixon et al. measure only net transport in and out. However net flux out of the system is slightly less than calculated by Nixon, totaling just over 100 million moles. This could be an artifact of the totally different methodology, or it could be a reflection of reductions in loading. We do see changes in the way DIN constituents behave on a downbay gradient after the reduction (see Chapters 1,2), particularly ammonium, so it would not be unreasonable to attribute some or all of this reduction to actual decreases in the concentration of water leaving the bay (and/or increases in the concentration entering from increased regional atmospheric deposition).

On the other hand, phosphorus fluxes across the bay/sound interface of about 30 million moles, 90% of which is in inorganic form, are dramatically different than past estimates of 50-70 million moles export across this boundary (Figure 3-9), though Nixon's (1995) results also suggest that the vast majority of the export (about 80% in that study) is inorganic. The GEM model ascribes a much larger portion of the total phosphorus budget of the bay to import from offshore, and consequently, predicts much higher export, though net export is actually lower than calculated by Nixon et al.

(1995) (Figure 3-9). The model estimates that the flux of phosphorus out of the system is approximately 25% greater than the combined fluxes of phosphorus into the system from all sources. While we have few other quantifiable fluxes out of the system, and thus, expect a great deal of the phosphorus incident on the system to export to the sound one way or another (organically or inorganically), we would ideally have more data to try to determine whether these measurements are accurate, because it is important to understand whether we have captured a short term imbalance in the budget, whether there is continued consistent loss from the sediment storage reservoir into the water column, or whether we are missing another source of phosphorus to the bay, especially given recent management efforts to control phosphorus loading to the bay.

Here again, a conceivable mechanism for the imbalance might be sediment regeneration. If for many years, phosphorus inputs have greatly exceeded readily quantifiable outputs (as postulated in past budgets), it seems logical that a large storage term of phosphorus would exist in the sediments of the bay, which could conceivably take a while to flux out in response to reduced loadings. This has been shown true in many other estuarine systems (e.g. Carstensen et al. 2006, Artioli et al. 2008, Boynton et al. 2008, Lukkari et al. 2009), but most of those systems have lower salinity than observed in Narragansett Bay, and past mesocosm experiments in this system (e.g. Oviatt et al. 1984, Kelly et al. 1985, Nowicki and Oviatt 1990) have shown rapid response of the system to changes in loading, such that it would seem unlikely that phosphorus deposited in the the 1980's and earlier when loading was much higher would still be remineralizing and contributing to flux out of the system at

this point. It is, however, possible that our measurements captured a short term event, and in reality, fluxes from the bay into the sound are somewhat lower.

COMPARISONS WITH OTHER SYSTEMS

Narragansett Bay appears to respond similarly to nutrient loading reduction as other similar systems for which budgets have been compiled (e.g. Artioli et al. 2008, Boynton et al. 2008, Duarte et al. 2009). It is difficult to tell at this early and intermediate stage in the reduction process what the ultimate impact on the system will be. Many systems with smaller reductions in load have shown no or minimal biological response (Carstensen et al. 2006, Artioli et al. 2008, Duarte et al. 2009) to the reduction. At this point, Narragansett Bay shows no measurable decline in chlorophyll (see chapter 1, 2) or primary productivity (Smith 2011) as a result of the load reductions. In contrast, systems with dramatic loading reductions almost always show biological response (Greening and Janicki 2006, Taylor et al. 2011), so it is possible that as loading reductions approach the 50% threshold predicted by RIDEM (RIDEM 2005) we will begin to see reduction of chlorophyll and primary productivity (Oviatt 2008).

Narragansett Bay falls in the middle of many similar systems in terms of nitrogen and phosphorus loadings (Figure 3-10) in terms of load per acre. While our study shows the system to be nitrogen limited on the large scale, and this result is consistent with past studies of Narragansett Bay (e.g. Nixon et al. 1995), the present N:P ratio of loading to the bay is 19:1. Proposed reductions will bring the system more in line with a 16:1 input ratio of N:P. Continued management efforts to reduce phosphorus from several additional plants stand to remove 2-3 million additional

moles of phosphorus from the bay, at which point, the phosphorus load to the bay will be only about 110% of prehistoric levels, while nitrogen load will still be in the vicinity of 4 times prehistoric estimates (Nixon 1997).

CONCLUSION

In compiling the budget of clearly defined inflows to the bay, marked reductions in the contribution of sewage to the total nitrogen and phosphorus budget of the bay occurred (Figure 3-4, 3-5). Of the 11 plants in the bay which have upgraded their systems, virtually all plants are meeting or falling below permitted concentrations throughout the year, with only a few very short violations (see appendix B). Many plants are exceeding expected reduction levels during the winter months. The combination of these factors has resulted in a reduction in the sewage load to the bay of just over 100 million moles, or about 27% of the total 2003 sewage nitrogen load to the bay as estimated by Nixon et al. (2008) (Table 3-3). Given the excellent performance relative to targets of plants which have upgraded to date, there is little reason to believe that planned upgrades to other plants scheduled for 2012, 2013, and 2014 will not combine to reach the targeted 50% nitrogen load reduction set out by RIDEM (RIDEM 2005).

Several of the upgraded plants are located along rivers, which seem to have highly variable abatement rates. While virtually all of the reductions calculated for plants discharging into the Pawtuxent River are realized in reduction in flux from that river, only about 30% of the nitrogen reductions calculated for the Blackstone River (about 50 million moles per year) are realized in reduction in annual flux for this river

(about 15 million moles per year reduction) (Table 3-2, Table 3-3). While some of the decreased effluent discharge is mitigated by increased flow, driven by increased precipitation, it is clear that if the overall goal is reduction of load delivered to the bay proper, management effort should be focused on plants discharging either directly into the bay, or into tributaries which drain rapidly into the bay. This observation, however, does not take into consideration the improvement in ecosystem function which might be realized within these rivers by reducing load discharged into them.

Fluxes of nutrients from the sediment to the water column appear to have changed dramatically over time. Recent estimates are highly variable, but show significantly lower rates of denitrification and phosphorus flux in all observed cases than past estimates (Table 3-1, Fulweiler et al. 2007, Fulweiler et al. 2010, Fulweiler and Nixon 2011). The magnitude of the denitrification decrease approximately parallels the observed decrease in nutrient load to the bay proper from advanced wastewater treatment. Whether a result of changes in climate and/or phenology, or a direct result of loading reductions, the sediments, which were formerly a sink through denitrification for approximately 20% of the nitrogen incident on the system, now appear to be close to neutral in terms of net nitrogen flux. This change has the ability to mask or mitigate a great deal of the impact of present and future loading reductions if the sediments continue to be net neutral over an annual cycle.

The fluxes of nutrients across the bay/sound interface remain difficult to quantitatively estimate, but the flux of nitrogen from the bay into the sound may have decreased in response to loading reductions (Table 3-1).

Biological parameters (primary productivity, fish export, etc...) do not appear to have changed at this time (see chapters 1 &2, Oviatt 2008, Longval 2009). This is not surprising, given the small magnitude of loading reduction, logarithmic relationship between nutrient load and productivity, and response of the system (e.g. less denitrification, less river abatement, less flux across the bay/sound interface) to load reductions. It seems that, for the present time at least, there are still ample nutrients to support the sustained level of primary productivity observed before reductions. However, future reductions may be large enough to have an impact.

ACKNOWLEDGEMENTS

This manuscript would not have been possible without the diligent efforts of literally dozens of GSO staff who have collected, analyzed, compiled, and intercalibrated these fantastic datasets over the last 40+ years. Particular thanks to the staff at GSO's MERL Lab and the Narragansett Bay Commission and Rhode Island Department of Environmental Management for sharing data and ideas. We also thank Wally Fulweiler for insightful conversation and sharing data used herein. We also thank our funding sources: NOAA Bay Window Awards to Candace Oviatt and collaborators: NA04NMF4550409, NA05NMF4721253, NA07NMF4720287, NA09NMF4720259, and the NOAA Coastal Hypoxia Research Program (CHRP) NA05NOS4781201 to Candace Oviatt and collaborators, as well as a Coastal Institute IGERT program 'grants in aid' to Jason Krumholz.

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Table 3-1: Nutrient budget for Narragansett Bay with sources for each flux. Units are in millions of moles nitrogen and phosphorus. Positive numbers indicate a source of nutrients to the bay, negative numbers represent sinks. Confidence intervals on river and plant loading are standard deviation of annual averages since upgrade (see appendix B for calculation).

Source	DIN	TN	DIP	TP	Notes
Direct Deposition	24± 5	30 ±6	-	0.13	Nixon et al. 1995
Rivers	173±43	249±62	4.7±1.2	10.54±2.6	Calculated, TP estimated by ratio
Direct Sewage Discharge	100±12	143±17	4.18±0.5	9.4±1.1	Calculated, DIP estimated by ratio
Urban Run-off	29±9	62±17	2.8±0.5	5.8±1	Reassessed based on Nixon et al. 1995
Groundwater	4	4	-	-	Urish and Gomez 2004
TOTAL INPUTS	330±46	488±67	11.7±1.4	25.8±3	
Denitrification	-20 ±60	-20 ± 60			Fulweiler et al. 2007, 2010, 2011
Burial	-	-70±26	-	-6.5±1.5	Nixon et al. 1995
Fisheries export	-	-11	-	0.65	Calculated from Longval 2009
Net Export to Sound	-102±12	-283±60	-29.8±3.3	-32±3.5	Calculated using GEM
TOTAL OUTPUTS	-122±62	-384±94	-29.8±3.3	-39.1±4.0	
STORAGE TERMS					
Standing Stock	15±3	45±8	2.5±.9	3±.4	Chapter 1
Sediments		1770±590		377±112	Calculated from Nowicki and Oviatt (1990)

Table 3-2: Comparison of river flow and nutrient flux from rivers between this survey and the 2003-2004 survey presented by Nixon et al. (2008). Units are millions of m³/day for flow and millions of moles per year for flux.

	2003-2004		2008-2010	
	N	P	N	P
Blackstone River				
Mean Daily Flow	2.57		2.76	
Dissolved Inorganic	68.88	1.69	59.34	2.18
Total	98.63	3.87	84.73	5.36 ^a
Pawtuxet River				
Mean Daily Flow	1.00		1.11	
Dissolved Inorganic	44.61	1.96	25.67	0.77
Total	59.29	3.61	36.78	1.63 ^a
Woonasquatucket River				
Mean Daily Flow	0.28		0.29	
Dissolved Inorganic	6.62	0.16	4.10	0.03
Total	8.59	0.32	5.72	0.10 ^a
Moshassuck River				
Mean Daily Flow	0.19		0.12	
Dissolved Inorganic	3.50	0.07	2.04	0.01
Total	4.77	0.13	2.68	0.02 ^a
Ten Mile River				
Mean Daily Flow	0.35		0.33	
Dissolved Inorganic	9.86	0.24	11.84	0.08
Total	14.07	0.81	14.39	0.27 ^a
Taunton River				
Mean Daily Flow	2.58 ^c		1.59	
Dissolved Inorganic	86 ^c	3.3 ^c	23.53	0.35
Total	117 ^c	5.3 ^c	37.68	0.56 ^b
Unmeasured Flow				
Mean Daily Flow	1.48 ^d		2.90 ^e	
Dissolved Inorganic	48.3	1.6	46.8	1.27
Total	66.5	3.1	67.3	2.85
GRAND TOTAL				
Mean Daily Flow	8.43		9.10	
Dissolved Inorganic	267.8	9.05	173.3	4.70
Total	368.9	17.13	249.3	10.54

^aCalculated from the average ratio of inorganic to total phosphorus (Nixon et al. 2008)

^bCalculated from the average of the average ratios of inorganic to total phosphorus (Nixon et al. 2008)

^c data from (Boucher 1991) as presented in (Nixon et al. 1995)

^d based on calculation of area of gauged to ungauged river area by (Ries et al. 1990) as modified by (Nixon et al. 1995)

^e based on Ries et al. (1990) plus flow from 304 mi² of un-gauged flow in Taunton basin.

Table 3-3: Average wastewater treatment facility discharge for the time period from 2007-2010 at wastewater treatment facilities discharging into the bay or its tributaries. All values with the exception of flow, which is in millions of gallons per day, are in millions of moles per year.

PLANT	Flow	NH ₄ ⁺	NO ₂	NO ₃	DIN	TN	TP
<i>Discharges to:</i>							
Narragansett Bay							
Field's Point	44.45	37.40	3.23	5.84	46.47	63.50	3.19
Bucklin Point	21.37	1.27	0.23	13.70	15.20	18.90	3.14
Newport	9.20	<i>Nutrients</i>	<i>not</i>	<i>monitored</i>		10.50	0.59
East Providence	7.11	3.28	0.13	2.93	6.34	7.53	0.52
Bristol	3.57	1.94	0.17	1.93	4.04	6.27	0.18
Warren	1.92	1.35	0.02	0.22	1.59	1.86	0.05
East Greenwich	1.07	0.86	0.01	0.46	1.33	0.87	0.42
Quonset Point	0.47		0.04	0.46		0.73	0.10
Jamestown		0.05	0.00	0.10	0.15	0.16	0.02
Fall River*		22.90			24.95	33.20	1.15
Total		69.04	3.83	25.64	100.06	143.52	9.37
Blackstone River							
Worcester ¹	31.09	3.01			14.02	16.60	1.07
Woonsocket	7.48	0.97	0.06	3.24	4.27	4.99	0.56
Smithfield	2.01	0.18	0.07	1.04	1.29	1.46	0.02
Grafton*		2.00			3.34	3.28	0.14
Millbury*		1.96			2.42	2.44	0.24
Northbridge*		1.48			1.91	3.06	0.17
Burrillville	0.85	0.99	0.07	0.23	1.29	1.40	0.02
Hopedale*		0.13					0.02
Leicester*		0.03					0.00
Douglas*		0.10			0.14	0.20	0.02
Upton*		0.07			0.08	0.12	0.00
Total		10.92	0.20	4.51	28.75	33.55	2.27
Ten Mile River							
Attleboro	4.07	0.45				7.67	0.02
North Attleboro	4.28	0.41				2.98	0.03
Total		0.86				10.65	0.06

Table 3-3 continued.

PLANT	Flow	NH₄⁺	NO₂	NO₃	DIN	TN	TP
Pawtuxent River							
Cranston	11.33	3.96	0.12	5.98	10.06	12.50	0.43
West Warwick	6.00	1.01	0.36	5.37	6.74	8.03	0.45
Warwick	5.00	1.43	0.06	2.39	3.88	4.75	0.21
Total		6.40	0.54	13.74	20.68	25.28	1.09
Taunton River							
Brockton*		15.72			27.56	36.51	0.83
Taunton*		2.04				4.18	0.29
Somerset*		2.68			3.44	8.28	0.17
Total		20.43			30.99	48.97	1.28
GRAND TOTAL						262.0	14.1

[†] Flow value is the average of flows from 2009-2010 instead of 2007-2010 as there was no flow data available for 2007 and 2008.

* Parameter values were calculated by scaling previous values, 2000-2003 (Nixon, 2008), by the population change from 2000-2010.

Table 3-4: Changes in urban run-off attributable to different sources of variability. A: Land use coefficients from Carter 1982 (used by Nixon et al.) and from NRCDS 2008 (used by this study) in moles per acre per centimeter of rain. B: Total acreage (in thousands of acres) of each land use type which discharges to Narragansett Bay as calculated in the two studies. C: Changes in urban runoff attributable to different vectors. All changes are relative to urban run-off figures presented in Nixon et al. (1995) and based upon the central assumptions presented therein.

Table 3-4A	Res.	Com.	Ind.	Hwy	Inst.	open
Nitrogen						
Carter 1982	3.23	3.53	1.33	5.5	-	-
NRCDS 2008	4.58	4.96	5.34	6.49	4.20	1.53
Phosphorus						
Carter 1982	0.16	0.028	0.21	6.1	-	-
NRCDS 2008	0.26	0.39	0.26	0.26	0.39	0.026

Table 3-4B	Res.	Com.	Ind.	Hwy	Inst.	open	other	TOTAL
Nixon 1995	33.2	6.88	29.75	3.31*	-	-	-	73.14
Present	64.65	6.97	7.80	3.54	4.61	37.4	15.1	140.1

*Our estimate of 1990 loadings corrects an mathematical error in Nixon et al. (1995) which incorrectly publishes this value as 8.49

Table 3-4 C: Changes to estimates of Urban Run-off into Narragansett Bay		
Constituent	% Change TN	% Change TP
Increased precipitation 10 year avg. 2000-2010 vs. Nixon et al. 1995	9	9
Land-use Change Primarily from increased # of lane-miles of roads & highways offset by loss of industrial acreage	19	14
CSO retention tunnel Based on phase one, complete 11/2008	-6	-6
TOTAL ATTRIBUTABLE TO CHANGES IN LOADING	22%	17%
Changes in Assessment Method: Use of GIS to categorize previously unconsidered sewered acreage, change to NRCDS coefficients.	102	52
TOTAL	124% increase	71% increase

Table 3-5: Conversion factors used to estimate bottom nutrient concentration in Rhode Island Sound from surface concentration. Conversion factors were established by comparing known surface and bottom concentrations from a 1972-1973 survey (Kremer and Nixon 1974) and a 1979-1980 survey (Oviatt 1980) and are the mean of all bottom/surface ratios for the given month at all stations located at the mouth of the bay in each study.

Month	NH4	PO4	DIN	NO2+NO3
Jan	0.49	0.89	0.95	0.98
Feb	0.58	1.08	1.01	1.06
Mar	0.78	1.22	0.62	1.34
Apr	1.14	1.10	0.62	0.48
May	1.48	1.02	0.74	0.76
Jun	1.79	0.92	2.36	2.36
Jul	2.82	0.85	3.09	2.86
Aug	2.38	1.07	2.35	1.84
Sept	0.92	0.99	1.01	0.98
Oct	1.00	0.91	0.86	0.73
Nov	0.38	0.68	0.42	0.43
Dec	0.34	0.82	0.61	0.69

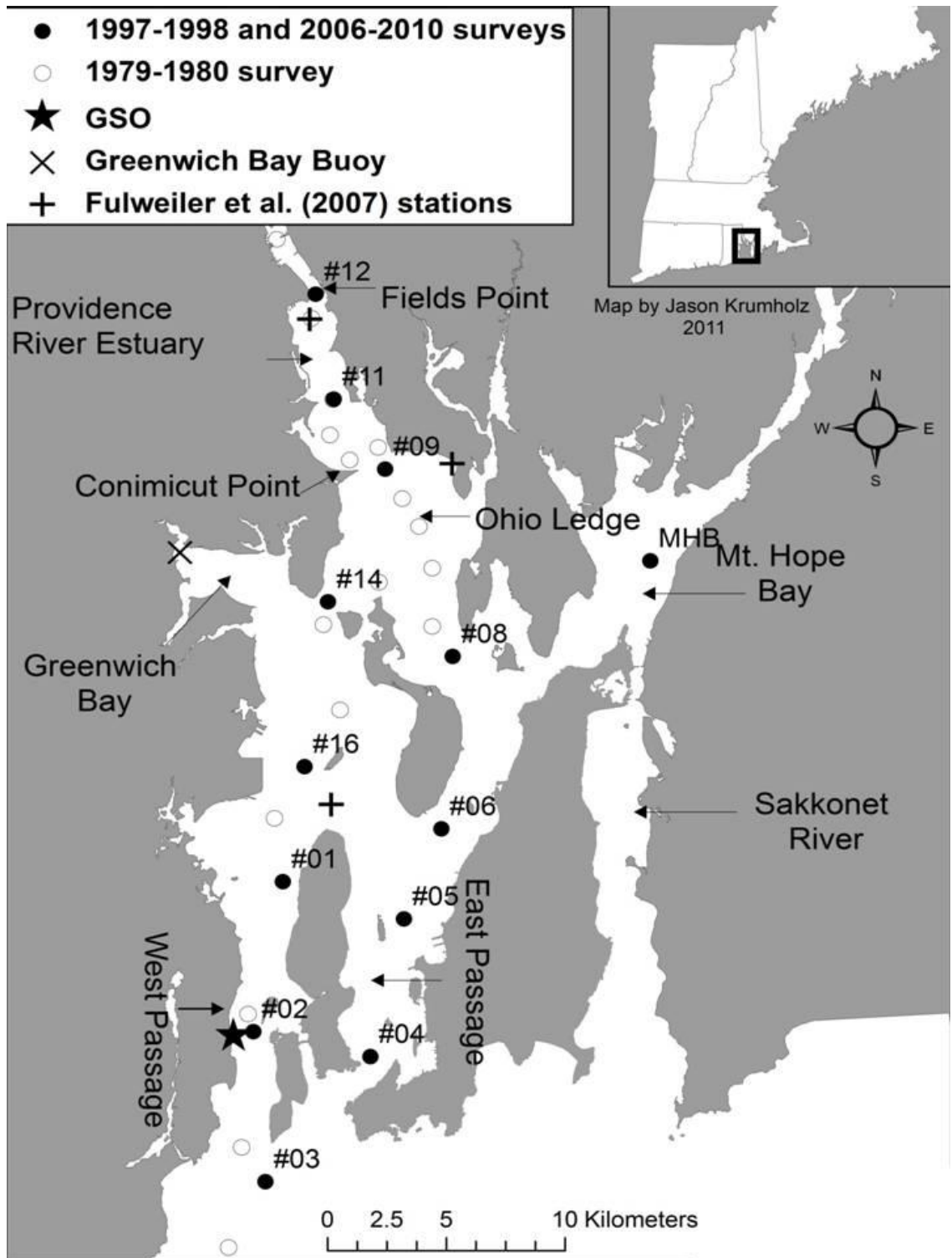


Figure 3-1: Map of Narragansett Bay showing the sampling stations and landmarks used by various studies cited within this manuscript.

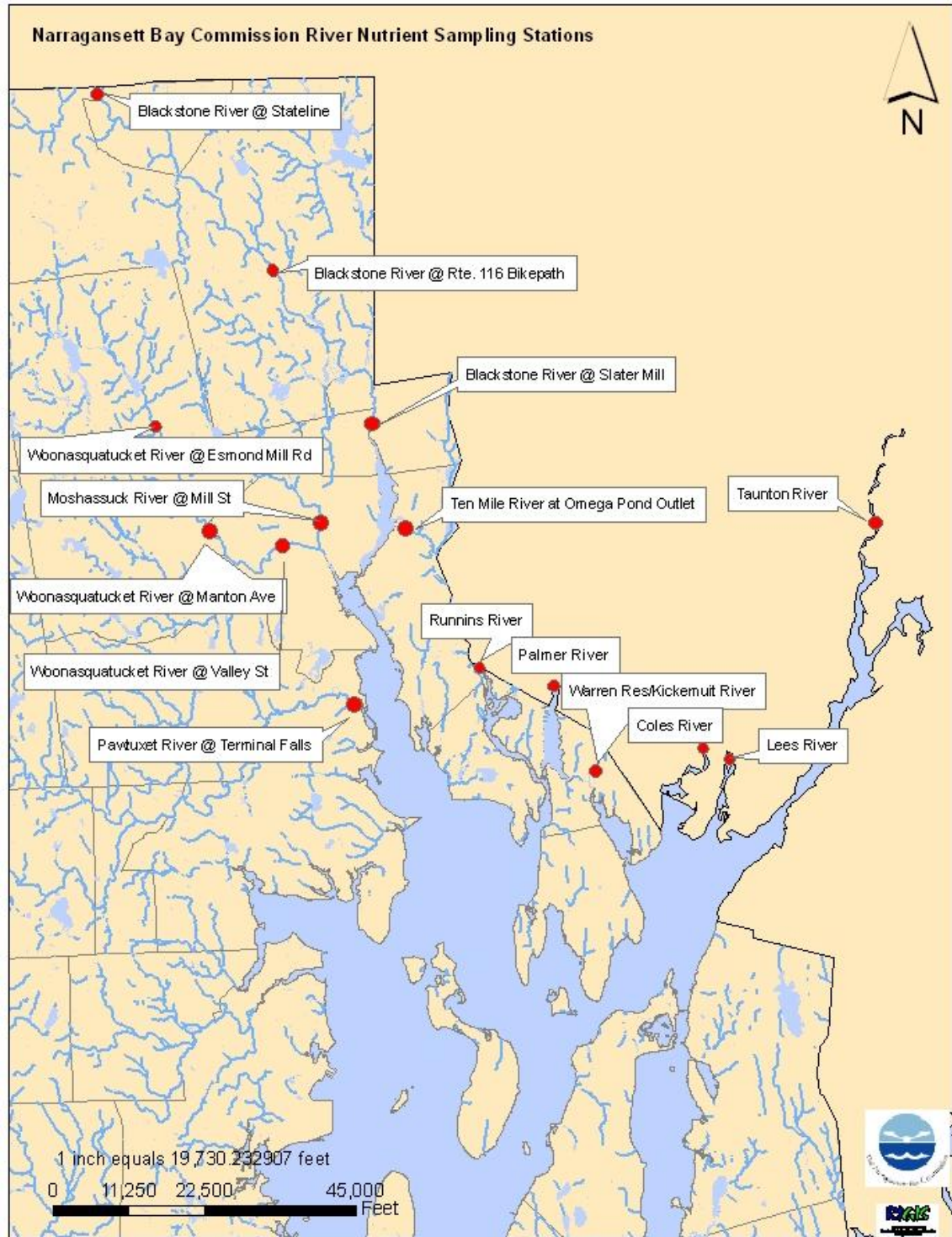


Figure 3-2: Map of Upper Narragansett Bay showing river sampling stations used by the Narragansett Bay Commission for nutrient sampling.

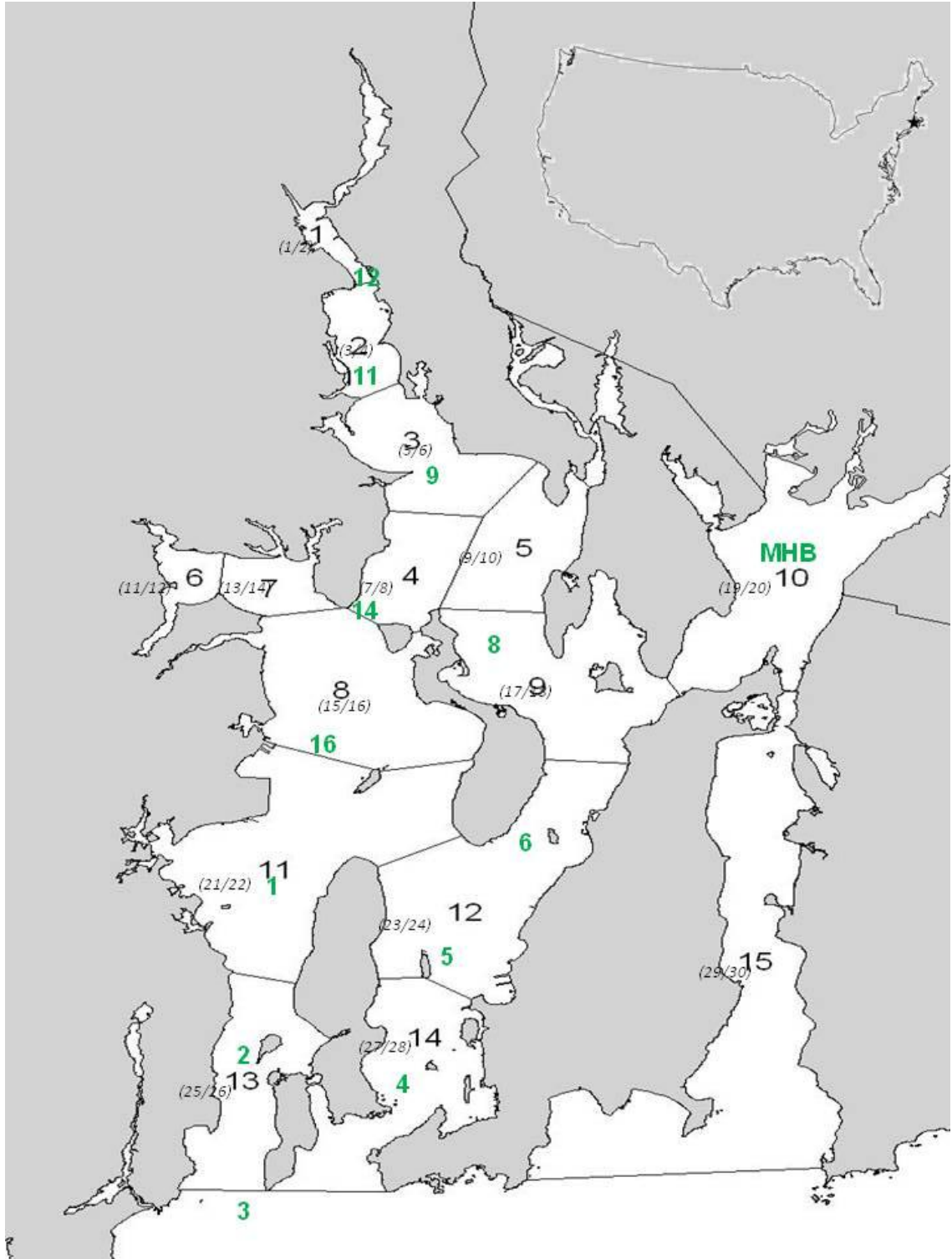


Figure 3-3: Map of boxes and elements used by the GEM model to calculate flux across the bay/sound interface (from Kremer et al. 2010). Sampling stations from the 2006-2010 CHRP/Nu-Shuttle survey are provided for reference.

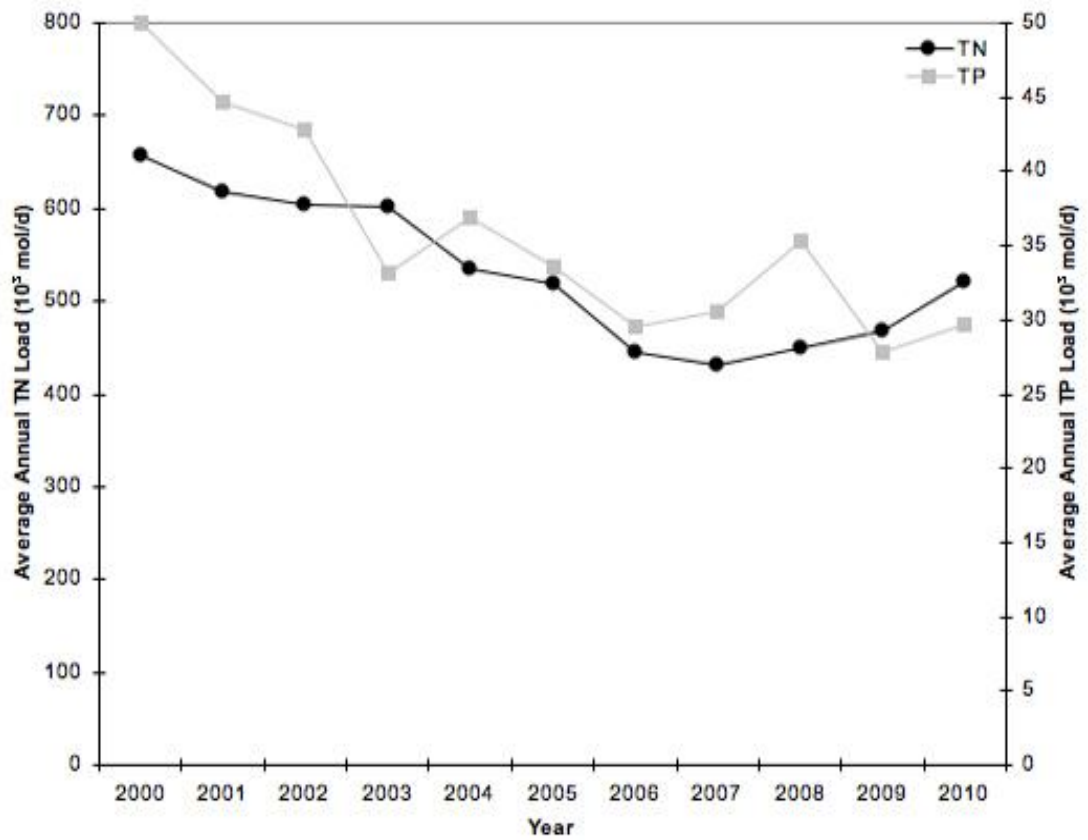


Figure 3-4: Estimated average daily total nitrogen (black, left axis) and phosphorus (grey, right axis) load to Narragansett Bay from sewage for the years 2000-2010. This load includes estimates from all plants discharging into the bay and tributary rivers. Units are thousands of moles per day.

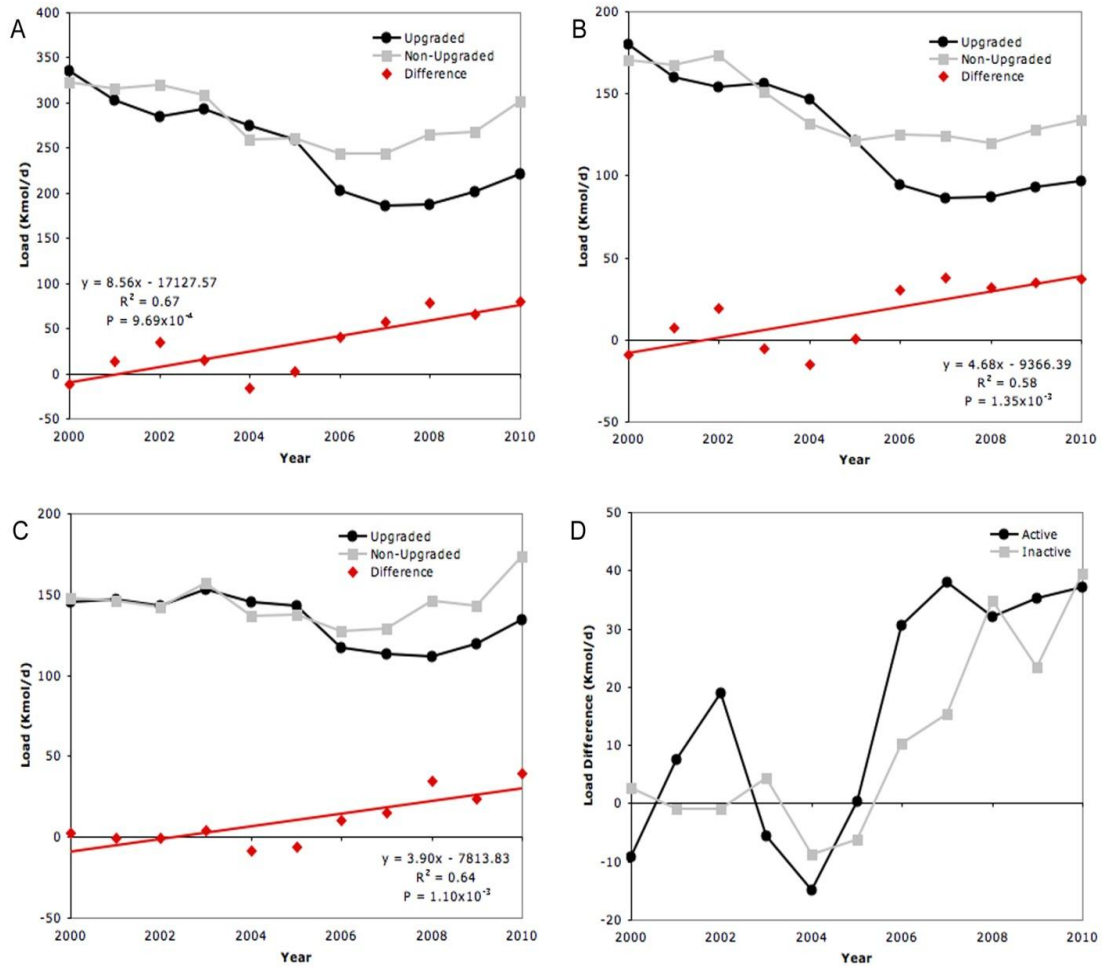


Figure 3-5: Total nitrogen (TN) load at 17 WWTF's for which data were available in thousands of moles per day. A) Annual TN load from facilities which underwent upgrades (black) and those which did not (grey) with the difference between the two (red). B) Active season (May-Oct.) TN load discharged from upgraded (black) and un-upgraded (grey) facilities with the difference in red. C) Inactive (Nov.-April) season difference (red) between upgraded (black) and un-upgraded (grey) plants. D) Improvement during active (May-Oct., black) relative to inactive (Nov.-Apr., grey) season difference among upgraded plants.

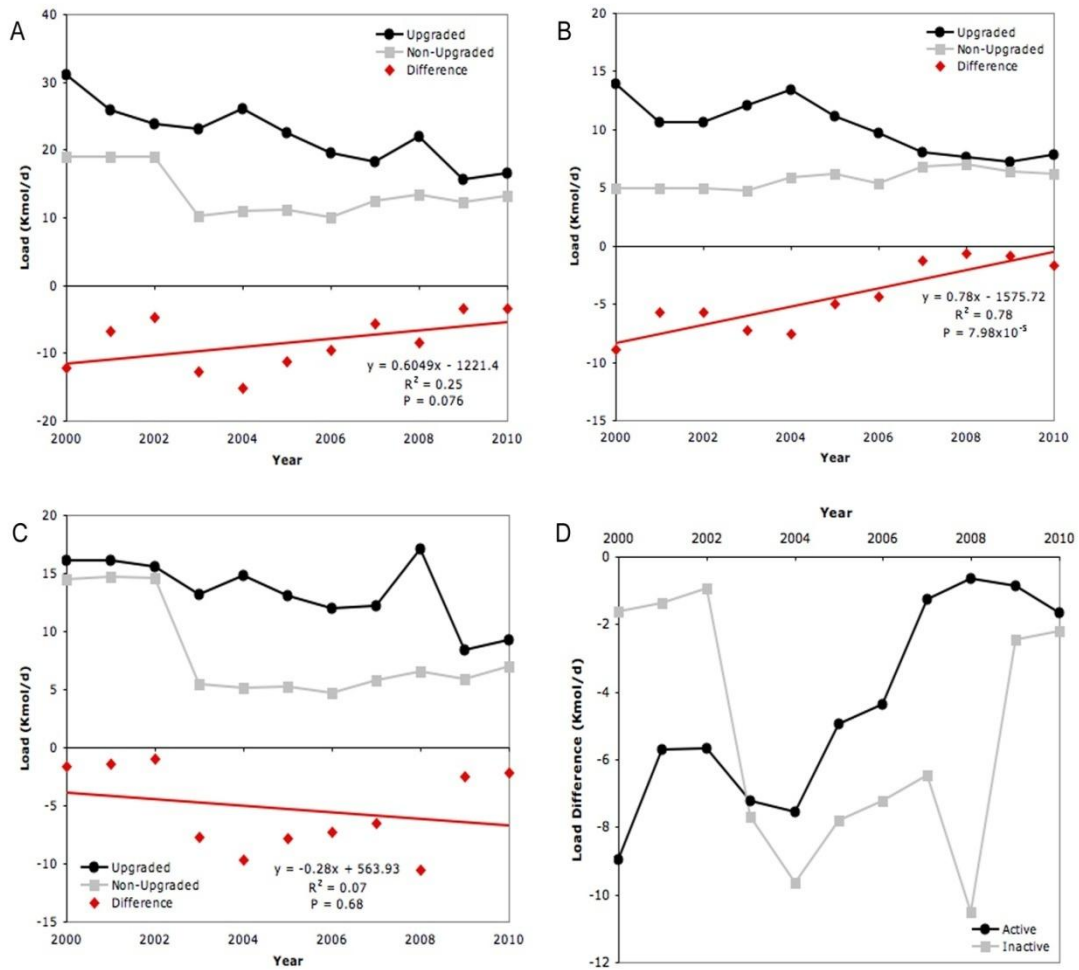


Figure 3-6: Total phosphorus (TP) load at 17 WWTF's for which data were available, in thousands of moles per day. A) Annual TP load from facilities which underwent upgrades (black) and those which did not (grey) with the difference between the two (red). B) Active season (May-Oct.) TP load discharged from upgraded (black) and un-upgraded (grey) facilities with the difference in red. C) Inactive (Nov.-April) season difference (red) between upgraded (black) and un-upgraded (grey) plants. D) Active (May-Oct., black) vs. inactive (Nov.-Apr., grey) season difference among upgraded plants.

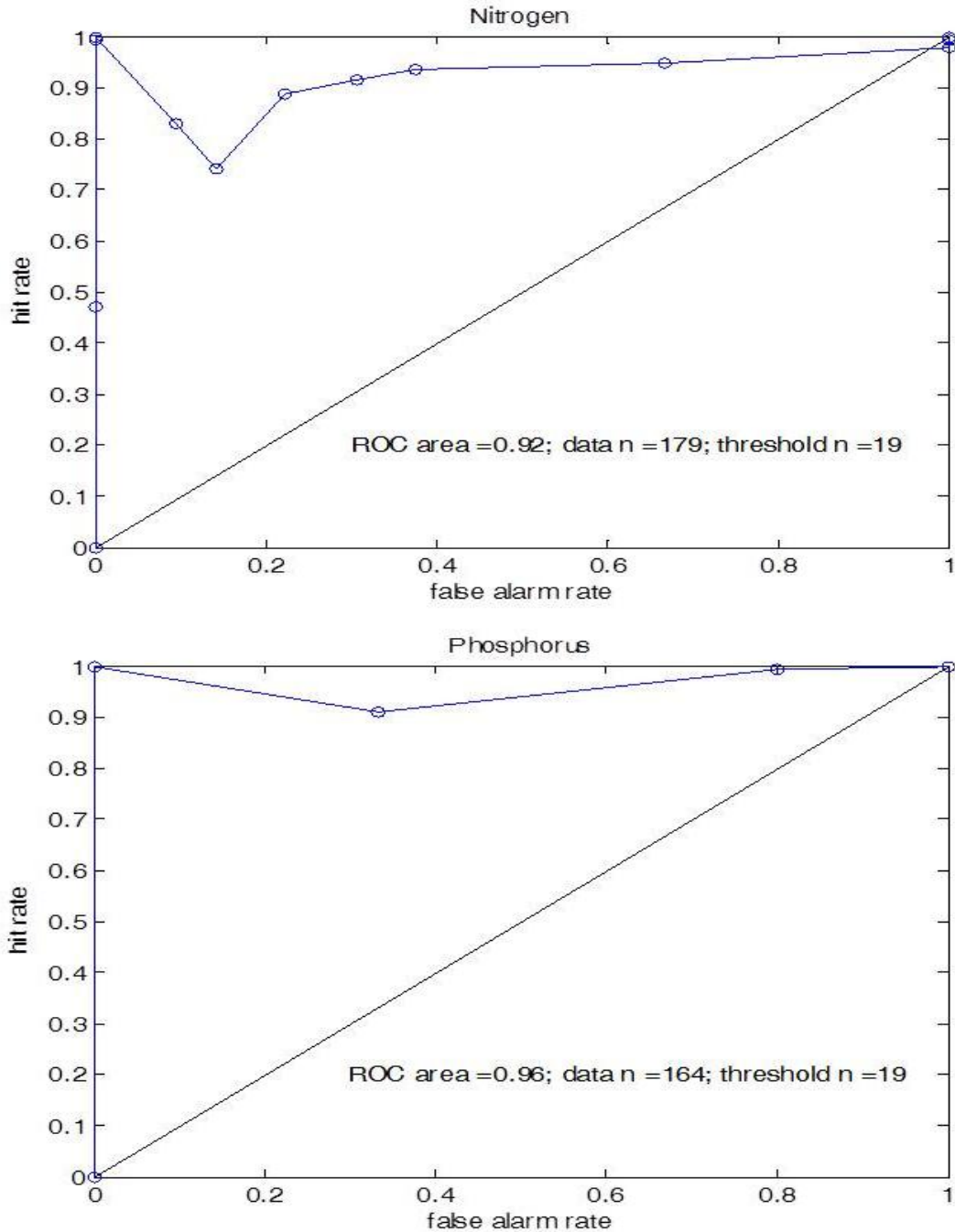


Figure 3-7: Relative Operating Characteristic (ROC) scores for GEM box modeled nitrogen and phosphorus concentration relative to observed concentration (Chapter 1). Scores presented are cumulative for all boxes, across the entire year (15 boxes, 12 months) and represent the model's ability to correctly match the observed data relative to 19 threshold concentrations. The area under the ROC curve is an indication of model skill, ranging from 0-1 where 1 is perfect and >0.5 (black line) is considered skilled.

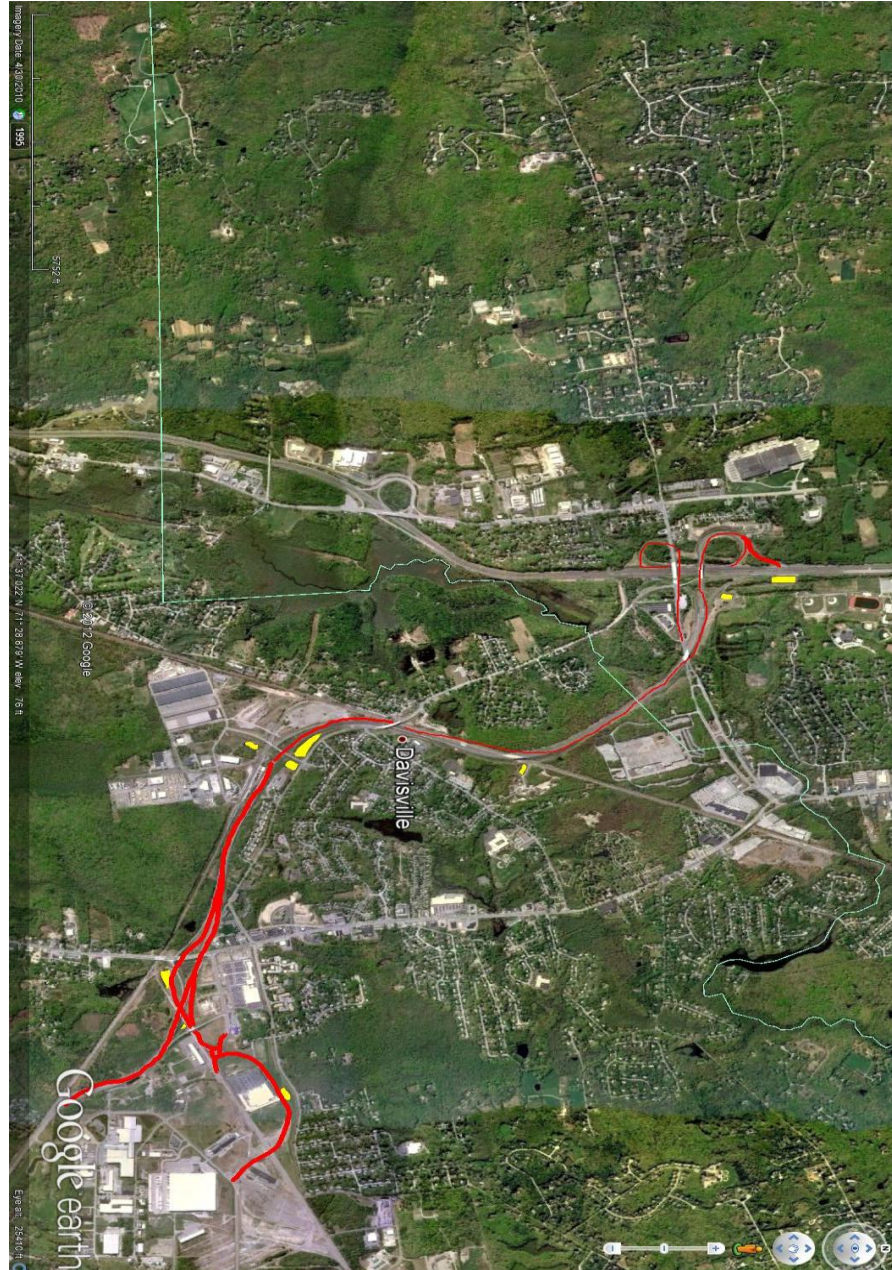


Figure 3-8: Map of areas of North Kingstown, Rhode Island impacted by recent construction of an extension for route 403. Newly created treatment wetlands are shown in yellow, while newly created roads are shown in red, with a thick red line indicating the addition of 4 new lanes of road, and a thin red line indicating expansion from 2 to 4 lanes.

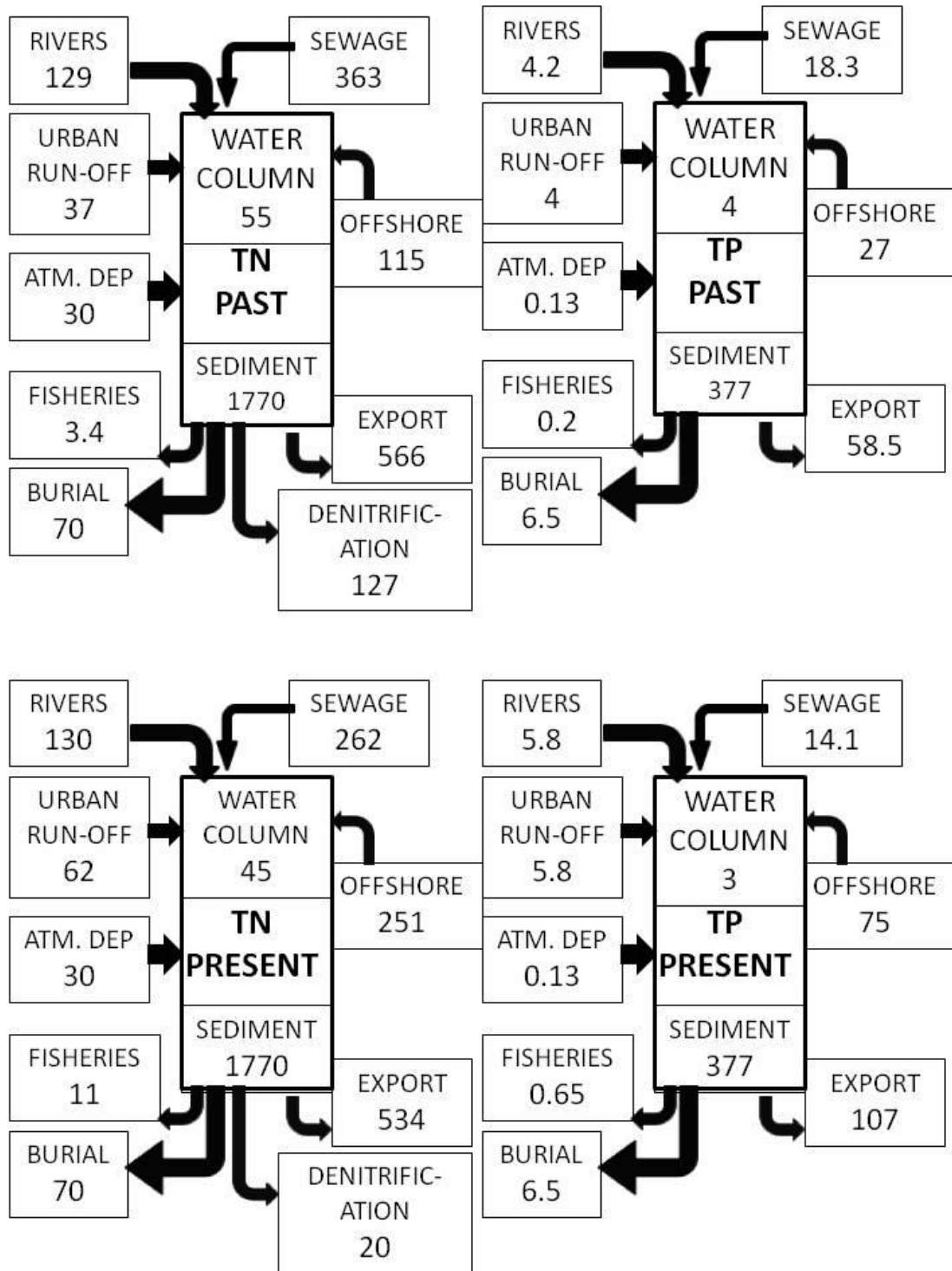


Figure 3-9: Box diagram of sources and sinks of nutrients to Narragansett Bay past and present. Past data are most recent available estimates from previous budgets by Nixon and colleagues (1995, 2008). Present data are 2006-2010 average, except export which is for 2006. Sewage value includes direct and indirect discharge, and river loading here is estimated as total river loading – sewage discharge into rivers. Export is presented as gross export. All units are millions of moles per year.

Total Nitrogen and Phosphorus Loadings in Various Estuaries

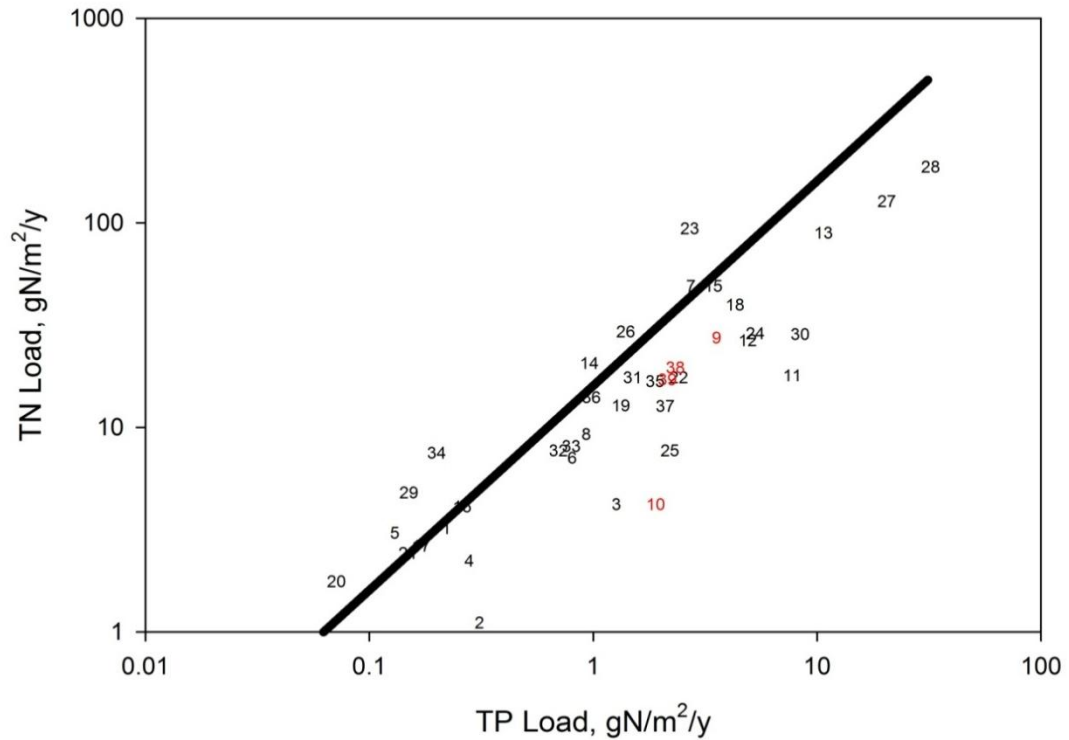


Figure 3-10: Total nitrogen and phosphorus loadings to various ecosystems. Figure adapted from Boynton et al. 2008. Narragansett Bay points are shown in red, with point 9 representing the 1995 Nixon et al. budget, point 10 indicating estimates of prehistoric load to Narragansett Bay by Nixon et al. 1997, point 38 representing this survey, and point 39 representing the projected loadings for Narragansett Bay for 2014 once additional WWTF upgrades are complete. The line represents a 16:1 N:P loading ratio.

APPENDIX A

Supplemental Methods

This Appendix contains 3 sections. The first details the autoanalytic methodologies used on the two instruments presented in the study, their differences from each other and from the literature on which they were based. The second details the intercalibration procedure for the two instruments. The third is a Standard Operating Protocol and troubleshooting guide for the Astoria Analyzer, provided for reference purposes.

SECTION 1: AUTOANALYTIC METHODOLOGIES

Nitrate/Nitrite

Both the Astoria and Technicon autoanalyzers use a very similar chemical reaction to measure nitrate and nitrite. In both instruments, nitrite is detected by the formation of an azo dye during the Greiss reaction- the diazotization of Sulfanilimide (SAN) and subsequent coupling with N-1 naphthylethylenediamine (NED)(Fox 1979). This reaction takes place in a buffered acidic medium. The absorbance of the resulting dye is read at 540nm on both instruments. Nitrate is measured by reducing nitrate to nitrite using cadmium coated with copper (Wood et al. 1967)

This methodology was developed throughout the 1960's and is reviewed by (Strickland and Parsons 1968). The respective manufacturers detail their specific variations on this methodology used by each instrument (Technicon 1972a, Astoria-Pacific 2005), the recommended techniques for each instrument are followed exactly except that the Imidazole buffer called for in the Astoria Pacific methodology is replaced with the Ammonium Chloride/Ammonium Hydroxide buffer used in the

Technicon methodology. A comparison between the two buffers showed no increased precision with the Imidazole buffer, and since it is expensive and difficult to prepare, we retained the original method. Thus, the only differences between the two methods are as follows:

- 1) The Astoria technique uses a slightly lower concentration of the SAN reagent
- 2) Both the NED and SAN reagents are filtered at 0.45 μm before use in the Astoria, while the Technicon procedure only calls for the filtration of NED
- 3) The Technicon methodology calls for a single mixed NED/SAN reagent (50/50) while the Astoria method calls for the reagents to be separated, but injects them sequentially in a 1:1 ratio.
- 4) The Astoria methodology calls for a small amount of surfactant (Brij-35 or TX-10) to be added to the SAN and the buffer, while the Technicon does not use surfactants.

These methodologies differ significantly from the standard EPA methodology for colorimetric determination of nitrate/nitrite in that they lack EDTA in the buffer, and use much lower ratio of reagent/sample (EPA 1983b). However, the use of EDTA was shown to be problematic, and the lower reagent concentrations reduce the blank value, and thus, are commonly used for the determination of low level nitrate/nitrite (Strickland and Parsons 1968, Grasshoff et al. 1983).

Phosphate

The phosphate methodology used by both instruments is very similar, and is essentially unchanged from the recommended Technicon Industrial Method (Technicon 1971). This methodology is based on the formation of phosphomolybdic acid (by mixing phosphate ions with molybdic acid in an acidic medium). The

phosphomolybdic acid is subsequently reduced. This reaction produces heteropoly blue, which can be read at 660nm or 880nm. The reduction is typically accomplished using ascorbic acid, however alternate methodologies call for hydrazine sulfate or stannous chloride. The method was initially described by (Murphy and Riley 1962), and modified for use on autoanalyzers by (Hager et al. 1972). This method is very similar (stoichiometrically identical) to the established EPA procedure for autoanalytic phosphate measurement (EPA 365.1), with the only minor difference being the diameter of the diluent line, which is slightly different between the EPA method, the Technicon method, and the Astoria method (EPA 1983c)

Astoria Pacific has methodologies for both ascorbic acid reduction (A205) and hydrazine (A204) (Scott et al. 2005) but in order to maintain maximum continuity in the transition between instruments, it was deemed best to continue using ascorbic acid reduction, since the only major downside of this methodology is that the reagent is relatively unstable, and must be prepared daily. Although both instruments use essentially identical reagent chemistries, the following minor differences exist:

- 1) The Astoria reagent has a small amount of surfactant (SLS) added, while the Technicon reagents do not use surfactant.
- 2) The Technicon procedure calls for 4.9N Sulfuric Acid, while the Astoria procedure calls for 5.0N acid.
- 3) The Astoria reagent is filtered at 0.45µm before use.
- 4) The Astoria uses an 880nm filter while the Technicon uses an 820nm filter

Ammonia

There are a wide range of commercially available techniques for the measurement of Ammonia. Both the Astoria and the Technicon use methods based on the Berthelot reaction. In this reaction, hypochlorite (bleach), alkaline phenol, and ammonia are combined and heated in a heat bath at 65°C to produce indophenol blue. The intensity of this colorimetric reaction is intensified by the addition of sodium nitroferricyanide (also referred to as nitroprusside).

Both the Astoria and Technicon methods are based on the technique detailed by (Solorzano 1969). MERL uses a Solorzano modified version (order of reagents flipped) of the original Technicon method (Technicon 1973) on the Technicon analyzer. MERL procedure uses two reagents; a combined phenol/nitroferricyanide reagent, and a sodium citrate/sodium hydroxide/sodium hypochlorite complexing reagent. The air line for this cartridge is scrubbed through a 10% sulfuric acid solution to remove airborne ammonia contamination (a major problem). On the Astoria analyzer, MERL uses a modification of Astoria method A026 (Scott et al. 2005). The Astoria method is similar to the Technicon method stoichiometrically, except that it calls for a third reagent. In this case, a weaker nitroferricyanide/phenol reagent, a separate sodium hydroxide/sodium hypochlorite reagent, and a complexing reagent of sodium citrate, potassium sodium tartarate, and sodium hydroxide are used. The addition of tartarate to the complexing reagent is intended to remove any crystallization of calcium and/or magnesium which can occur during the reaction process, and which interferes with the reading as the sample passes through the flowcell. While the Technicon does not appear to suffer from this problem even

without the tartarate (Oviatt and Hindle 1994), the Astoria was experiencing irregular baselines and random spikes attributed to the precipitation of calcium by this reaction. To combat this, the amount of hydroxide used in the reagents was reduced by half from the published values, in order to lower the pH of the reaction and inhibit crystallization. This modification is based on work done by Dr. Christopher Schmidt at Texas A&M (Schmidt and Clement 2009). To combat airborne interference, this cartridge is injected with ultrapure (99.95%) N₂ gas, rather than air.

The differences between the MERL Technicon and Astoria methods can be summarized as follows:

- 1) The Astoria method uses a potassium sodium tartarate addition to the complexing reagent to prevent crystallization. The Technicon does not experience this problem
- 2) The Astoria method separates the hypochlorite from the complexing reagent
- 3) The Astoria method uses a weaker mixture of phenol/nitroferricyanide
- 4) The Astoria method uses dinitrogen gas rather than scrubbed air to segment flow
- 5) The Astoria method uses a small amount of surfactant (TX-10 or Brij-35) added to the complexing reagent. The Technicon does not require surfactant.
- 6) The Astoria measures at 640nm, the Technicon measures at 630nm

Silicate

The Technicon and Astoria use different methods for the analysis of silicate in seawater. The MERL method for the Technicon is based on Technicon method 186-72W (Technicon 1972b). This involves the reaction of silica with an acidic molybdate solution to produce silico-molybdic acid, which are reduced (similarly to colorimetric ortho-phosphate methods) to produce a heteropoly blue complex. This method was

first tuned for autoanalysis by Brewer and Riley (Brewer and Riley 1966). The Technicon method calls for the addition of oxalic acid prior to the reaction with molybdate to eliminate interference from ortho-phosphate (since the colorimetry for phosphate is very similar), and uses ascorbic acid as the reductant.

The Astoria method uses Astoria method A026 (Scott et al. 2005) wherein a similar ammonium molybdate solution to form silico-molybdic acid. Subsequently, tartaric acid is used to destroy any phospho-molybdic acid compounds which have formed (essentially different ways of dealing with the same phosphate interference problem). Stannous chloride is then used as the reducing agent. This method is discussed in detail by Sakamoto et al. (Sakamoto et al. 1990) Both instruments read the resulting silicoheteropoly blue at 820 nM.

The Ascorbic/Oxalic/Molybdic technique used by the Technicon is far more popular among general use (Gilbert and Loder 1977, Gordon et al. 1993), however, this technique does not appear to be compatible with the surfactant (SLS) required for the Astoria to run smoothly. After several attempts to modify this technique to achieve consistent results, it was abandoned in favor of the above discussed method. In summary, methods differences between the Astoria and the Technicon are as follows:

- 1) The Astoria uses tartaric acid rather than oxalic to eliminate phosphate interference
- 2) The Astoria uses stannous chloride rather than ascorbic acid as the reductant
- 3) The Astoria uses surfactant (SLS) in the molybdic acid reagent. The Technicon uses no surfactant
- 4) All Astoria reagents are filtered at 0.45mM. Technicon reagents are not filtered.

Total Nitrogen (TN)/Total Phosphorus (TP)

The analysis of total nitrogen and total phosphorus is accomplished by the use of a persulfate oxidation reaction conducted on whole (unfiltered) seawater. 22.5ml of seawater is digested by boiling for 30 minutes with 2.5 ml of potassium persulfate/boric acid/sodium hydroxide oxidizing reagent. This breaks down organic nutrients, converting them to dissolved inorganic form, at which point they are run on the autoanalyzer in an identical fashion to Nitrate and Ortho-Phosphate. This method was initially described by Valderrama (Valderrama 1981), and is used frequently for seawater (Grasshoff et al. 1983).

The measurement of TP in seawater using this technique is fairly robust, however the measurement of TN by this technique has been the subject of some debate. Prior to the use of the alkaline persulfate digestion, the primary technique in use was the Kjeldahl digestion, which is rapid and robust, but has several key drawbacks, most notably, the toxicity of the reagents, and the fact that the resultant value (often referred to as TKN, or total Kjeldahl nitrogen) is a measure of ammonia plus organic nitrogen, and does not include nitrate and nitrite, two major inorganic constituents which are captured by the alkaline persulfate methodology. The major drawback of the alkaline persulfate technique is that it is dependent on a high and consistent conversion rate of ammonia and organics into nitrate and nitrite. This conversion efficiency is highly sensitive to the temperature and time of the extraction process, and incomplete extraction, if not appropriately corrected for, can bias results. Furthermore, because the estuarine TN values are significantly higher than typical estuarine nitrate values (TN values in upper Narragansett Bay routinely exceed 60mM

and can reach 100mM, while nitrate values rarely exceed about 20mM), issues with nonlinearity of standards and cadmium reduction efficiency can emerge, as well as the potential for depletion of the cadmium column during the run day, causing efficiency loss (Scott et al., 2005; Scott, pers. comm.). USGS recently compared the two techniques, and found that while TP and TKP reliably produce consistent values, TN (minus nitrate and nitrite) and TKN do not always agree, particularly at high nutrient levels. The cause for this discrepancy is uncertain, but the reports suggests that this is likely due to nitrate interference in the TKN methodology, but potentially due to extraction efficiency problems with the alkaline persulfate technique (Patton and Kryskala, 2003).

SECTION 2: INTERCALIBRATION RESULTS

Nitrite/Nitrate

Intercalibration of nitrite was relatively straightforward. The relationship is approximately 1:1, and the R^2 is around 0.99 (Figure A-1). It should be noted that the tightness of the fit sometimes breaks down somewhat at low (< 0.3mM) concentrations, with the Astoria showing detectable levels of nitrite, while the Technicon values are near the detection limit (Figure A-2). This may be a factor of increased low range sensitivity in the Astoria technique, which is more precise, and uses a higher SAN concentration. In all cases (with and without high point), the relationship is not significantly different from 1:1 by ANCOVA.

Intercalibration of nitrate on the other hand, was extremely problematic. On any given day of intercalibration, the relationship between the two machines is

typically fairly strong ($R^2 < 0.9$), but the slope is inconsistent, and not close to 1:1. During some run days, the slope even appears to change mid-run (Figure A-3). These mid-run changes do not appear to be precipitated by any change in methodology, and are likely due to a rapid change in Cadmium reduction efficiency, perhaps caused by a blockage in the Technicon column. The shift is not likely to have been precipitated by a change in the efficiency of the Astoria unit, since during the run day, that instrument performs regular tests of its cadmium efficiency, all of which were within specification.

The Technicon always produces higher values, with slope varying from approximately 1.3:1 up to 1.8:1, and averaging about 1.6:1. To test whether one instrument or the other was the source of the problem, identical samples were run on both instruments as well as a Teledyne model 2003 Nitrous Oxide sensor, which uses a vanadium/sulfate reduction (as per (Braman and Hendrix 1989) which eliminates the potentially troublesome cadmium reduction step. This instrument is much more precise and accurate than either the Technicon or the Astoria (although it is very time consuming and cannot be used in segmented flow autoanalysis). Results from this inter-comparison suggest that the newer Astoria analyzer was producing reasonably accurate results, while the Technicon appeared to be severely overestimating, especially at higher concentrations (Figure A-4).

Given the relative reliability of nitrite results, it was deduced that the likely culprit for this variability is the Cadmium reduction process. Approximately four years ago, the Technicon was switched from Cadmium columns intended for use on that machine to columns designed for a Lachat brand analyzer, with a much lower

inner diameter. This was done without any sort of intercalibration or testing. It is hypothesized that this lower inner diameter results in incomplete reduction of standards at higher concentrations, producing an artificially shallow standard curve, and causing over-estimation of actual nitrate levels in samples with high concentrations. This is further complicated by the fact that the analyst applied a 'correction' to all nitrate data based on a one point 'check' of cadmium reduction efficiency. Given that the loss of efficiency appears to be dependent on concentration, this may have caused an underestimate of samples with low concentrations.

In order to test this hypothesis, old Technicon Cadmium columns were repacked according to the procedure detailed in the MERL manual (Oviatt and Hindle 1994). When the Cadmium efficiency 'correction' was removed, a relationship of 1.05:1 was observed, with an R^2 of <0.99 (Figure A-5). This relationship is not significantly different from 1:1 by ANCOVA. This provides strong evidence that the combination of incomplete reduction from the smaller diameter coil and an incorrectly applied 'correction' are the source of the disagreement between instruments.

However, in order to use the data which was run on the Technicon (which is essential for the compilation of nutrient budgets, and the comparison of present nutrient standing stocks with those of the previous decade), it was necessary to derive an empirical correction factor which relates concentration on the Technicon (using Lachat Cadmium columns) to appropriate values. In order to do this, it was necessary to go back to the raw data sheets, and re-calculate the Cadmium efficiency 'correction' for each run day, and then remove this correction from the data, after which Astoria and Technicon values were compared across the pooled intercalibration samples

(approximately 200), and a consistent correction factor was determined (Figure A-6). A linear regression for the slope of the correction factor has intercept not significantly different from zero ($P=0.50$) and a highly statistically significant slope ($P<0.0001$). Analysis of covariance shows corrected data have a relationship not significantly different from 1:1 against the Astoria data.

Phosphate

The intercalibration of ortho-phosphate between the two instruments proceeded very smoothly. The relationship between the two instruments is consistent, very close to 1:1, and displays good correlation across the entire range of samples measured (Figure A-7). This relationship is not different from 1:1 by ANCOVA. This seems logical given that the two chemistries are virtually identical, and this technique is used almost unilaterally, with little variation, for colorimetric analysis of Ortho-phosphate in seawater; a surefire indication of its reliability.

Ammonia

The intercalibration of ammonia between the Technicon and the Astoria has met with somewhat mixed results. Once the Astoria technique was modified to remove any interference from precipitates, the relationship is approximately 1:1, especially at higher levels and the correlation is reasonable (R^2 approximately 0.98) (Figure A-8). However there is a bit of variability and noise in the data. On different run days, the relationship can be slightly greater or less than 1:1, and the R^2 can be as low as 0.97 (Figure A-8). At present, the only explanation for this variability is the inherent noise in this analytical technique. Ammonia baselines are noisy and tend to drift on both instruments, and attempts to correct for this are not always completely

successful. Furthermore, even with the nitroferricyanide, the absolute amplitude of the signal (intensity of the color reaction) is low on both instruments (the absorbance peak of the high ammonia standard is less than 10% as intense as the nitrate high standard).

Another possible explanation for the variation is that colorimetric ammonia determination is slightly salinity dependent. Because the Astoria uses a 'matrix matching' analysis technique (where the rinse water is approximately the same salinity as the sample), it would be susceptible to variation if the salinity of the sample varies significantly from the salinity of the rinse water. Similarly, the Technicon might experience variability if the salinity of the standards were different from the salinity of the sample (it can be corrected with an equation. To correct for this, we have begun testing samples for salinity, and will alter the Astoria matrix as necessary to account for low salinity samples.

In order to determine whether the difference between the instruments is variable (and therefore uncorrectable in an intercalibration) or whether one machine consistently reads higher or lower than the other, additional intercalibration samples were run on three additional separate days. Once salinity corrected, data above 3X MDL (deemed by the EPA to be the functional reporting limit) show a very strong relationship not statistically different from 1:1 (Figure A-9). While the Astoria appears to be able to resolve samples significantly below this concentration, replication on the Technicon at very low concentrations becomes problematic and the correlation between instruments is poor.

Silicate

Despite significant differences in the methodology, silicate intercalibration proceeded smoothly. The relationship is very close to 1:1 (it improves further with the reduction of the two outliers) and the correlation is good ($R^2 > .99$). This relationship is not statistically different from 1:1 (Figure A-10). Two outliers are present in the dataset, which were sequential samples when run, but since no concrete explanation can be arrived at for why these samples deviate from the expected pattern, they are not excluded from the analysis.

Total nitrogen (TN)/Total phosphorus (TP)

Given the fact that, from an autoanalytic standpoint, the measurement of TN/TP is identical to the measurement of nitrate and phosphate, one would expect to get similar results for the intercalibration of TN and TP to the results achieved for nitrate (highly problematic) and phosphate (extremely reliable). For the most part, this is the case, although the measurement of TN/TP proves to introduce significantly more variability in the data, lowering R^2 values for both TN (Figure A-11) and TP (Figure A-12). The significantly greater than 1:1 relationship on the nitrate channel persists, as expected, into TN analysis. What is rather unexpected is the degree of variability in TN observed in this intercalibration. While each individual run day produces a relatively strong correlation between the Astoria and Technicon results (individual R^2 values range from approximately 0.91-0.98), the slope of the relationship is highly variable (ranging from almost exactly 1:1, to as high as 2:1), resulting in a very weak relationship when the data is pooled, which is not only poorly correlated ($R^2=0.57$),

but also shows signs of a potential baseline or blanking problem (intercept 5.1mM) (Figure A-11).

In attempting to account for the increased variability caused by the TN/TP procedure over the inorganic analogues, and other inconsistencies observed in preliminary data analysis (e.g. some samples with Ortho-P values higher than TP) a thorough review of MERL TN/TP procedures compared to recommended literature procedures (Grasshoff et al. 1983, Oviatt and Hindle 1994) was conducted. The following inconsistencies were identified:

- 1) Protocols call for vials to be dried at 200°C after cleaning. Present MERL procedures utilize a 60°C oven for this purpose
- 2) Literature protocols call for the use of fructose 1-6-diphosphate (TP) and glycine (TN) standard curves rather than traditional sodium nitrate and potassium phosphate standards used for DIN analysis. Using an organic standard corrects for extraction efficiency losses during the extraction process (typically nonlinear). MERL uses inorganic standards with a one point extraction efficiency check, and does not apply a correction.
- 3) Literature recommends pre-diluting any samples expected to have TN above 50mM as extraction efficiency falls off at this point. MERL does not pre-dilute samples anticipated to be above this threshold (e.g. Fields Point station).
- 4) Literature also recommends multiple recrystallizations of Potassium Persulfate, and that persulfate be stored in a vacuum jar with sulfuric acid and potassium permanganate to scavenge organics

These deviations from protocol are likely to cause two potential problems. Failure to properly clean vials before extraction could cause blanks to be too high, and indeed, upon inspection MERL TN blanks range from about 2-10mM TN as compared to literature values of 1-2 mM, and MERL TP blanks range from about 0.3-1.0 as compared to literature values of 0.3-0.5mM (Grasshoff et al. 1983, Oviatt and Hindle 1994, Patton and Kryskalla 2003). Given that the low end of observed MERL blank values is in line with literature values, and only 1-2 blanks were run for each run day, sometimes with significant variability between the blanks, it can only be assumed that different vials possess different amounts of contamination, and as such contamination variability could be passed along to the sample, which would more than explain the approximately 5% loss of correlation between total nutrient and dissolved nutrient intercalibrations. While this problem cannot be corrected for in the existing dataset, it can be rectified moving forward, to improve the precision of our measurements. Further experimentation on this matter revealed that with 3 recrystallizations and proper storage of persulfate, MERL blanks can be brought into the 2mM range

The use of improper standards is perhaps a more serious problem. A preliminary analysis comparing inorganic to organic standards was conducted to assess the severity of the potential loss. As suggested in the literature, TN samples above approximately 50mM TN showed decreased extraction efficiency. No such problem was observed for TP extraction efficiency, which remains reliable and linear up to approximately 50mM (much higher than the highest observed field values). TN standards of 12, 24, 36, and 48mM closely paralleled equivalent DIN standards, but by 200mM, extraction efficiency loss was about 30% (Figure A-13). This means that

high TN values in the existing dataset will be under-represented, and any loss or change in extraction efficiency from day to day would not be corrected for in the data.

Conclusion

With some minor modifications to procedure, we were able to successfully intercalibrate all analytes between the two instruments. Nitrite, phosphate, ammonium, silicate and total phosphorus can be directly compared between instruments without the need for a correction factor. These channels show strong regression relationships with high R^2 and statistically significant slopes, with intercepts not significantly different from zero. All also showed no significant difference in slope between the established relationship and a 1:1 line (Figure A-14).

Nitrate and TN data required significant additional attention, however once an erroneously applied cadmium correction coefficient was removed from the data, and dilutions were appropriately treated, the data show a reliable and correctable pattern of underestimation by the Technicon in both TN and nitrate (which is to be expected since they run on the same channel). Once a correction factor is applied to the Technicon data they show reasonable comparability with the associated Astoria data, and have slope and intercept not significantly different from 1:1.

After intercalibration, all analytes showed EPA Method Detection (Ripp 1996) limits similar to literature values (Grasshoff et al. 1983) (Table A-1).

**SECTION 3: STANDARD OPERATING PROCEDURE (SOP) FOR MERL
NUTRIENT SAMPLE ANALYSIS USING ASTORIA 5 CHANNEL SFA**

Procedure compiled 3/2012 by:

Jason Krumholz

Rosmin Ennis

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Preface

This appendix is designed to serve as an operational guide for daily use, maintenance, and routine troubleshooting of the MERL Astoria-Pacific 5 channel Segmented Flow Nutrient Analyzer. While many parts of this document are specific to the MERL lab set-up and designed to aid in transitioning the use of the instrument between operators and technicians, many portions may be of use to others using this, or a similar colorimetric nutrient analyzer. See earlier sections of this Appendix for more specifics about the colorimetric techniques used on this instrument.

I. SAMPLE COLLECTION AND STORAGE

Prior to Collecting Samples

1. Build Nutrient Filters
 - a. Rinse all parts of the filter with DI water.
 - b. Place the circular disk onto the large piece and press an O ring into the groove around the circular disk.

- c. Use tweezers to place a polycarbonate 0.45 micron filter (part # K04CP04700) onto the circular disk.
 - d. Press the round piece with a “tail” on top of the filter and O ring and screw on the last piece tightly.
 - e. Be sure to build at least 13 nutrient filters.
2. Labeling Bottles: There are 13 stations from which samples are collected. Two samples are collected from each station: one filtered sample for Dissolved Inorganic Nutrient (DIN) analysis and one whole water (unfiltered) sample for Total Nutrient (TNTP) analysis.
- a. Gather 26 clean nutrient bottles (translucent HDPE with Polypropylene screw caps, Fisher ID 02-895A). Inspect all bottles for damage; bottles should be full of DI water. A bottle that is less than full has a high probability of having a leak.
 - b. Use one color of tape for DIN and another color for TNTP (makes them easier to separate later and prevents mistakes). Put a ring of tape around each bottle about halfway up ensuring that the tape ring goes at least 1.5 times around the bottle so it won't come off when the bottle gets wet.
 - c. Label each bottle with permanent marker with the following information: the cruise date (mm/dd/yyyy), the sample type (DIN or TNTP) and the station number
 - d. The station numbers we use are 1, 2, 3, 4, 5, 6, 8, 9, 11, 12, 14, 16, and MHB (Mount Hope Bay). These station numbers are chosen to line up

with a previous study, but we don't use all of the sampling sites from the previous study, so some numbers are missing.

3. Sample bottles are 1L opaque HDPE narrow mouth bottles (Fisher part No.:312004-0032). Samples bottles are stored full of DI water in a cooler in the hallway. During collection, samples are stored on ice before being returned to the lab for filtration

Filtering Nutrient Samples

1. Take the first station's brown sample bottle and invert it 5 times.
2. Place the tube attachment of the syringe inside the brown bottle. Do not remove it until you switch bottles.
3. Connect the syringe to the tube and draw about 20 ml of water into the syringe and rinse it. Repeat this two more times.
4. Empty the DI water from the first station's corresponding clear sample bottles. Place a nutrient filter on top of your clear DIN sample bottle for that station. Draw a full pull of water into the syringe and filter 1/3 of the contents of the syringe into the clear DIN sample bottle. Shake the water in the bottle and pour it out. Repeat this 2 more times with the remainder of the water in the syringe.
5. Draw a full pull of water into the syringe and filter into the clear DIN sample bottle to fill it until about where the top of the tape is being sure to leave room for the water to expand as it freezes.
6. **TNTP samples are NOT filtered.** They are rinsed 3 times with water directly from the brown sample bottle and filled with water directly from the brown

sample bottle. Once again, they are filled to the top of the tape leaving enough room to allow for expansion during freezing.

7. Repeat steps 1 – 6 for the 12 other stations, but change your nutrient filter between each station.
8. If the nutrient filter is severely leaky, first try tightening the cap. If that fails, get a new filter. If you run out of filters, you can rinse and rebuild one of the ones that leaked, making sure to rinse it thoroughly with DI water **then with sample** before proceeding.
9. The analyst for the ASTORIA nutrient analyzer needs to know the salinity of the samples being run (i.e. if it is below about 20 ppt). After you have finished filtering, take a small amount of water (~0.5 ml) from the brown station 12 bottle (the furthest north station) with a pipette and place it on the refractometer to measure salinity. If the salinity is below 20 ppt, take a small piece of tape, write the salinity on it, and place it over the top of the DIN and TNTP vials from that station. Continue measuring salinity at downbay stations until one of them is >20ppt. The downbay station order is: 12, 11, and 9, then 8, 14, and MHB, then 6 and 8. If station 9 is below 20 ppt, measure 8, 14, **and** MHB, if one of those is below 20 ppt, measure 6 **and** 8. Typically, either all of the stations will be OK, or only station 12 will be below 20 ppt. If you believe more than station 12 and 11 to be below 20 ppt, find someone to double check and make sure you're using the refractometer right before proceeding.

Storing Nutrient Samples

1. All samples are placed into the nutrient freezer. Check all caps for tightness before placing in freezer.
2. Put DIN samples on the DIN shelf, TNTP samples on the TNTP shelf, and buoy samples, if applicable, on the door.
3. Log samples (quantity and date) put in the freezer on the door so that if a station was not sampled on a given cruise day someone doesn't spend 30 minutes going through the freezer looking for the missing sample.

Cleaning Filters

1. Take apart the nutrient filter apparatus.
2. Throw away the polycarbonate filter.
3. Rinse all plastic pieces and O ring 3 times.
4. Place all the plastic pieces into a 10% hydrochloric acid bath.
5. Place the O ring into a beaker with DI water as it will disintegrate in the acid bath.
6. Take all plastic pieces out of the acid bath after at least 24 hours. Rinse 3 times with DI water and set out to dry in a clean place.
7. ONCE DRY, PUT AWAY. DO NOT LEAVE INDEFINITELY ON THE COUNTER!!!

II. SAMPLE PREPARATION

Preparing DIN Samples: DIN samples do not require any special treatment prior to analysis. DIN samples remain frozen until the day of analysis.

Preparing TNTP Samples:

1. Recrystallizing Potassium Persulfate: Be sure to make recrystallized potassium persulfate before the day you need to do the TNTP extraction. The glassware, thermometer, and funnel need to be washed in an acid bath, rinsed with ultrapure DI water, and dried in a drying oven prior to TNTP extraction.
 - a. Dissolve 48 g of potassium persulfate in 300 ml ultrapure DI water in a 1500 ml Erlenmeyer flask. You can double this recipe if desired.
 - b. Heat to 65°C, hand stirring and swirling until all potassium persulfate has dissolved. While solution is heating, create an ice bath large enough to fit the flask.
 - c. Continue to heat with swirling and bring temperature up to 75°C.
 - d. Remove and place immediately in the ice bath. Cool solution to <10°C. Crystals should form.
 - e. Using a 3" Buckner funnel with a #42 Whatman Qualitative filter cut down to size, first rinse the filter through the funnel with ultrapure DI water then pour potassium persulfate crystals and remaining liquid through the funnel with vacuum (5 psi) to draw off the water. Note: When doubling recipe the solid will almost completely fill the funnel.
 - f. Scoop the remaining crystals out of the beaker, rinsing with a small amount of ultrapure DI water if necessary (adding water reduces the return).
 - g. Dry and fluff crystals in funnel for 5min.

- h. Transfer to clean dish and put in desiccator or 60°C oven until dry (approx. 24 hrs/overnight in oven).
- i. Store crystals in a dessicator jar to prevent accumulation of moisture. Ideally, add a small dish of 36N sulfuric acid and a small dish of potassium permanganate to the dessicator jar to scavenge any impurities out of the air.

NOTE: To maximize purity, potassium persulfate should be recrystallized a minimum of 2 times, preferably 3 times. After each recrystallization, estimate the percent return and reduce the amount of water added when starting the process proportionately, otherwise it may be difficult to get all the crystals out of solution with an ice bath. A saltwater ice bath can ameliorate this issue somewhat. Ideally, there should be just enough water in the flask so that the last of the crystals dissolve right at 75°C.

2. Cleaning and Drying TNTP Vials

- a. Create a water bath and begin heating to 80°C while the vials are prepared as it takes a while to get to the correct temperature.
- b. Set up TNTP vials into racks and get the beaker of TNTP vial caps. For each run you will need enough vials for your samples, extraction standards (2N & 2P), and blanks (2). It is always a good idea to do extra vials than you will need to allow for breakage and extras.
- c. Make up a solution of potassium persulfate in a volumetric flask to be used for cleaning.

Recipe: 25 g potassium persulfate (does not have to be recrystallized)

15 g boric acid

175 ml 1M NaOH

Fill to 500 ml with ultrapure DI water

- d. Pour some of the potassium persulfate solution into a clean beaker from which to pipette.
- e. Pipette 3.5 ml of the potassium persulfate solution into each TNTP vial and screw on the cap. Keep any extra potassium persulfate solution in a bottle for future cleanings.
- f. Place TNTP vials in the water bath when it reaches 80°C.
- g. Bring water bath to a boil (100°C). This is a critical time for the TNTP vials so make sure the vials are put in when the water bath is 80°C and then bring it up to a boil. It is during this time period that crucial chemical reactions occur so it is best not to mess it up.
- h. Start a timer for 15 minutes when the water comes to a boil.
- i. At the end of 15 minutes, remove the vials from the water bath and let them cool to room temperature.
- j. Empty the contents into a hazardous waste receptacle and rinse vials with DI water.
- k. Turn the TNTP vials upside down in the rack and place them in the drying oven.
- l. Place the caps in a 10% hydrochloric acid bath for about 8 hours. After acid washing, check the integrity of the caps and discard any that are showing excessive signs of wear.

3. Extracting TNTP Samples

- a. Remove TNTP samples out of the nutrient freezer and thaw them. This can be accomplished by placing the sample bottles in a **warm** water bath or by running them under warm water. Be sure to check the tightness of the sample bottle caps, ensure there are no cracks in the sample bottle, and not to submerge the bottles to prevent contamination of the sample. Make sure they are completely thawed before proceeding. After thawing, rinse the sample bottles with DI water and dry them before pouring sample out. Even a single drop of tap water can severely contaminate a sample.
- b. Create a water bath and begin heating to 80°C while the samples are prepared as it takes a while to get to the correct temperature.
- c. Make up a solution of potassium persulfate in a volumetric flask to be used for extraction.

Recipe: 12.5 g **recrystallized** potassium persulfate

7.5 g boric acid

87.5 ml 1M NaOH

Fill to 250 ml with ultrapure DI water

NOTE: This recipe is sufficient for nearly 100 samples. For smaller batches, it can be reduced proportionately.

Useful variation: 10 g **recrystallized** potassium persulfate

6 g boric acid

70 ml 1M NaOH

Fill to 200 ml with ultrapure DI water

- d. Mix on a heated stir place on medium heat until potassium persulfate has dissolved completely.
- e. Remove clean TNTP vials from the oven and gather **completely** dry acid washed caps. Rack TNTP vials and be sure to write down which vials correspond to which samples.
- f. Take the thawed sample bottle and gently agitate to mix the sample. Unscrew the cap and wipe the neck of the bottle with a kimwipe to remove any remaining DI water. This is to ensure the sample is not contaminated.
- g. Fill TNTP vials with 22.5 ml of sample (up to the etched line).
- h. Pour recrystallized potassium persulfate solution into a clean beaker and pipette 2.5 ml of the recrystallized potassium persulfate solution into each vial and screw on the cap.
- i. FOR BLANKS: fill 2 additional vials to the line with artificial seawater (or ultrapure DI water for freshwater analysis), add 2.5 ml of the recrystallized potassium persulfate solution, and screw on the cap.
- j. FOR EXTRACTION STANDARDS: reserve 2 vials each for phosphorus and nitrogen extraction standards.
 - i. Phosphorus: Add 200 μ l of 1000 μ M fructose 1, 6-diphosphate stock to a 100 ml volumetric flask and fill to the line with artificial seawater (or ultrapure DI water for freshwater analysis). Mix the solution then add 22.5 ml (to the etched line)

to the corresponding P standard TNTP vials. Pipette 2.5 ml of the recrystallized potassium persulfate into the vials and screw on the caps. This makes a 2mM extraction standard check

ii. Nitrogen: Add 2 ml of 1000 μ M glycine stock to a 100 ml volumetric flask and fill to the line with artificial seawater (or ultrapure DI water for freshwater analysis). Mix the solution then add 22.5 ml (to the etched line) to the corresponding N standard TNTP vials. Pipette 2.5 ml of the recrystallized potassium persulfate into the vials and screw on the caps. This makes a 20mM extraction standard check

- k. Keep any extra recrystallized potassium persulfate solution in a bottle to use for TNTP vial cleanings in the future.
- l. Place TNTP vials in the water bath when it reaches 80°C
- m. Bring the water bath to a boil (100°C). This is a critical time for the samples so make sure they are put in when the water bath is 80°C and then bring it up to a boil.
- n. Start the timer for 30 minutes when the water comes to a boil.
- o. After 30 minutes have passed, turn off the heat for the water bath and let the TNTP vials cool gradually to room temperature.
- p. Remove from the water bath and tighten caps. Samples are stable at room temperature for at least 30 days after extraction.

4. Vial Care between Extractions

- a. Discard extra sample in waste container.

- b. Triple rinse caps and vials with DI water.
- c. Vials should be acid washed after every usage.

III. SAMPLE ANALYSIS

Prior to Run Day:

1. Make sure the DI water pump is functioning properly. It should read about 18.
2. Check all chemicals used to make nutrient reagents to ensure they have not gone bad. If any have gone bad, remake them. The most common chemicals to go bad are:
 - a. Stock molybdic acid- commonly precipitates along walls of bottle, check bottle carefully the day before, generally cannot be re-heated to get back into solution.
 - b. Ammonium molybdate- commonly precipitates along walls of bottle, check bottle carefully the day before, generally cannot be re-heated to get back into solution.
 - c. SLS: If crystals have precipitated, place on heat and stir until they go back into solution.
3. The chemicals used to remake nutrient chemicals can be found in Table A-2:
4. Nutrient chemicals are made as can be found in Table A-3:

On the Run Day:

1. Starting the Machine
 - a. Dump, rinse, and refill water reservoir with ultrapure DI water and place lines in bottle.
 - b. Latch all the platens down on the machine.

- c. Lock the auxiliary pump in the back and turn it on.
- d. Open the nitrogen gas.
- e. Turn on the surge protector.
- f. Run machine for 7 minutes.

2. Rinsing the Machine

NOTE: Rinse line goes through all of these steps, but not the coolant reservoir line, which always stays in water.

- a. Run the machine on water for 7 minutes and check for a regular bubble pattern before proceeding to the next step.
- b. Run the machine on 10% hydrochloric acid for 5 minutes.
- c. Run the machine on ultrapure DI water for 5 minutes.
- d. Run the machine on Chemwash for 5 minutes.
 - i. While the machine is running on Chemwash, turn on the computer, open FasPac II, and create a new run.
 - ii. Click the hand icon to connect the computer to the machine. A green light indicates they are connected.
 - iii. Fill SR 20 with Chemwash and under “System”, click “Clean System”. When done cleaning (sampler returns to original position), clean again.
- e. Once cleaned, place machine in start up/shut down mode until ready for reagents (usually exceeds the 7 min needed to be online).

3. Conditioning the Cd Column

NOTE: Remember to only put the Cd column line on when the reagents/standards/samples go on. No water can go through the Cd column.

- a. Cd column is online when the colored lines are hooked up together (Green-Green and Red-Red).
- b. To clean, first hook up green end to waste tube.
 - i. Inject 10 ml ultrapure DI water into red end of Cd column.
 - ii. Inject 10 ml 2% CuSO_4 over 30 seconds. **If you push through too slow the column will clog, but if you push too fast the column won't clean/react with chemicals inside the column.**
 - iii. **QUICKLY/AS FAST AS REASONABLY POSSIBLE** put buffer through the column. Buffer should be injected both forward and backward. This requires you to switch the waste end to the red end.

4. Make Reagents (Table A-4)

- a. Rinse all reagent bottles with DI water.
- b. Reagents should be made while machine is being rinsed and the Cd column is being cleaned.
- c. Recipe quantities are for an 8 hour run day. Typically if you plan to run longer, multiply the NED, SAN, Ammonium complexing reagent and silicate molybdate and Tartaric reagents by 1.5.
- d. NOTE: the Stannous chloride and phenol reagents tend to be marginally stable. On a good day, you can get 12 hours out of them,

but you need to watch them vigilantly for decay in amplitude of your check standard after about 6-8 hours.

NOTE: Astoria Pacific calls for the use of an imidazole buffer for this analyte to preserve Cd column life. We found this buffer to produce undesirable results in saltwater use, and have defaulted back to the Ammonium Chloride buffer used in the Technicon method. However, to improve column life, we always flush and store the column filled with the imidazole buffer after each run (see Table A-4 for recipe).

NOTE: While the Ammonium Chloride buffer works well in most cases, for extremely high values, such as porewater samples, or samples with pH significantly different from 8, it isn't strong enough and can severely damage the column. In these cases we have had good luck with a buffer composed of 85g ammonium chloride (NH₄Cl), and .1g EDTA mixed to a total volume of 900 ml then adjusted with Sodium Hydroxide (NaOH) to a pH of 8.5.

5. Put all Reagents Online

- a. Before putting reagents online, turn on the heat baths.
- b. For silicate, the stannous chloride reagent goes on after (5 min delay) the molybdate and tartaric acid reagents.
- c. Once the reagents have been online for a few minutes, put the Cd column online.
- d. At this time, switch the rinse from ultrapure to ASW.
- e. If you have not done so already, initialize FasPac and connect to the instrument. Display all signals and Zero all signals so you can see your

baseline. Expect a baseline jump when the machine goes to reagents/ASW. Sometimes there is also bubble introduction into the flow cells from this process. This is the first culprit if you do not have stable baselines. Once all baselines are stable, proceed to step 7 (step 6 is done concurrently to step 5)

- f. The Ammonium channel tends to produce a lot of crystalline precipitate which partially obscures the flowcell and impairs baseline detection when it first goes onto ASW carrier. This USUALLY resolves in about 15-20 minutes, sometimes it takes as long as 30 minutes. It is not really well known why this takes so long to stabilize. It has been empirically shown that vigilant watching, cursing, yelling, and threats extend this time exponentially, while soft music, encouragement, and simply walking away to check your e-mail tend to shorten it.

6. Make Standards (Table A-5)

- a. Rinse standard bottles with DI water
- b. Standards should be made while the machine is being put on the reagents. Standards should be made as follows (values in ml of 1000mM stock added to each 100ml **plastic** volumetric)
- c. Standard bottles are then filled with artificial seawater (ultrapure DI water for freshwater samples) and inverted several times to mix.

7. Put Standards Online

The instrument uses specific 'identifiers' to recognize specific types of samples, for a complete list of the available identifiers, see the FasPac manual. The identifiers commonly used are described here, it is important to note that the format is case sensitive.

SYNC = Synchron standard. Used to line up the timing on different channels and account for differences in transit time. Typically a high standard with all analytes being run in it.

W= baseline check. A water (ASW or ultrapure DI) sample for which you want the instrument to reset the baseline.

w= A blank for which you do NOT want the instrument to reset the baseline to zero, used often when you're going from a high standard to a low standard and want to eliminate the possibility of carryover. NOTE: the difference in case between w and W has a huge difference in how the machine interprets.

CO= Carryover check. A water (ASW or DI) sample placed immediately following a high standard. This preprogrammed identifier calculates the percentage of the amplitude of the previous peak which 'carries over' into the next peak. If automatic carryover correction is enabled, it will use this value to correct subsequent high samples followed by low samples

NOX%= preprogrammed identifier for cadmium efficiency check. This is a high nitrite sample (red 4) placed immediately after a high nitrate (black 4) sample. The instrument calculates the percentage return on the cad column and (if enabled) can perform a range of actions if this value is outside of an acceptable parameterization (e.g. 95%)

C1, C2, ...CX = preprogrammed identifiers for calibrants. In our case, C1 is a zero standard (ASW of the appropriate matrix or Ultrapure DI), C2-C6 are the black (mixed) standards in order, and C7-C10 are the red (nitrite) standards in order. The instrument reuses C1 as the zero standard for both curves. TNTP uses a single mixed curve. The values of the calibrants can of course be changed in the System menu. See the FasPac Manual for more details here.

The racking order for the standards with # of reps in parentheses () can be found in Table A-6.

8. Check Calibrants

- a. The software options for monitoring check calibrants are severely buggy, and my recommendation is to turn them off and manually monitor your check calibrants. Should you choose to enable calibrant checks, be aware that the instrument will occasionally restart a run with no warning or explanation. Without extreme vigilance, this will cause the instrument to draw the first sample tube dry and introduce air into the lines, which will cause FAR more problems for you than monitoring your own check calibrants.
- b. For DIN runs, typically the CC1 (check cal 1) identifier is used for the mixed high standard (black 4) and the CC2 identifier is used for a cad check (red 4). CC1 is racked in slot 1:1 and CC2 in slot 1:2 with the initialization marker (right click to set) set on 1:1. I allow the instrument to set the check cal frequency (20) and wash frequency (20) in the system menu, but uncheck 'monitor check calibrants'. This

means that you must manually inspect the run to make sure your check calibrants are within bounds.

- c. For TN runs, I use the same identifiers for check calibrants, but rack them in the Standards rack (typically in the open SR17 and SR18 spots). This allows the analyst to easily line up the sample ID's from the extraction sheet with the sample ID's in the sample table, minimizing the chance for confusion and a sample to get mis-racked. If you do this, you must reset the initialization block marker (right click) onto SR17 (if not already done) and make sure you set the 'first CC row' to SR17 in the system menu or the instrument will malfunction.
- d. Because the instrument takes up about 2-3 ml per sample, you can get about 4 checks from a 16 ml vial (the bottom 2ml are unusable- the needle doesn't go that far down) before it needs to be refilled. Monitor this closely, as if these vials run dry, you will inject air into the instrument, which puts unnecessary wear on the cd column and can ruin your bubble pattern and your day very easily.

9. Preparing and Racking Samples

- a. If DIN samples are being run, begin thawing samples under warm water. Be sure all caps are tight before thawing, and that the water does not come up to the caps. A single drop of tap water can severely contaminate a sample. Once thawed, rinse in DI water and dry thoroughly to remove any tapwater from the sample.

- b. If TNTP samples are being run, make sure extracted sample tubes are in the correct order according to the sample sheet.
- c. Once DIN samples are thawed, rinse in DI water, dry bottles completely, and order them.
- d. Place an appropriate amount of tubes in the plastic racks.
- e. Gently mix samples (DIN or TNTP) and begin pouring into tubes in order going down each column working from left to right.
- f. The machine batch downloads data from the sample table (in FasPac) to the instrument every 4 samples. This means that you must have the sample table filled in at least 4 samples ahead of where the sampler is sampling at all times (or the instrument will malfunction). The transit time for the longest line (ammonium) is about 7 minutes. The default sample time is 35 sec. with a 55 sec. wash, so this means that you must be racked at least 15 replicates (5 samples in triplicate) ahead of what you see on the screen for results, or you will crash the software.

10. During the Run

- a. Make sure you are either manually inserting, or using FasPAC to control autowashes (capital W's if doing it manually) to monitor baseline and check standards to monitor colorimetric response and Cd column efficiency.
- b. If Cd column efficiency falls well below 95%, you can pause the run (use the PAUSE command), make sure you put it into the sample table at least 4 samples ahead of where the machine is presently sampling),

reactivate the column and continue, or abort the run at the analyst's discretion

- c. **DILUTIONS AND RERUNS:** If you have offscale samples that need to be diluted and re-run, or other problems (e.g. bubbles) cause you to lose a sample, you can add it to the end of the sample run. If you are planning on doing this, make sure you either get the re-runs entered into the end of sample table before the machine gets close to the end of the run (see 9F above) or put a string of 5-6 waters at the end of the sample table, which will allow time for all of the samples to get through the flowpath, and for the analyst to figure out which samples require dilution and get them into the sample table. Make sure you put them in the sample table FIRST, then dilute the sample and put it in the rack. The FasPAC sample table has a column for 'total dilution' which, if you use it to enter your dilution factor, will automatically calculate the correct concentration. We have found the various colorimetries to be relatively linear up to about 100 mM, thus, while samples still need to be rerun if they are more than about 120% of the high standard, the concentration of the original sample can be used to estimate the dilution factor (e.g. if your curve goes from 0-8mM, and the original sample runs through at 40mM, a 10X dilution is ideal.) Dilutions can be done to a total volume of 10ml (to simplify math) and the instrument can still get 3 replicates reliably. We have not had much luck with dilutions past about 20X. In these cases, the recommended

procedure would be to refreeze the sample and rerun it with a higher standard curve.

11. Shutting Down the Machine

- a. Take the Cd column offline
- b. Take the stannous chloride offline and put line in start up/shut down
- c. Turn off the heat baths
- d. Flush the Cd column with Imidazole buffer and store it closed (attach inflow line to outflow line) and filled with Imidazole buffer.
- e. Move the rest of the reagents to start up/shut down **EXCEPT** for the tartaric acid and molybdate reagents.
- f. Take the tartaric acid and molybdate reagents off after 5 minutes.
- g. Let the machine run on start up/shut down for about 7 minutes.
- h. Run machine on 10% HCl for 7 minutes.
- i. Run machine on ultrapure DI water for 7 minutes.
- j. Run machine on Chemwash for 7 minutes.
- k. Run machine on water for 7 minutes.
- l. Run machine dry.

NOTE: If running again in the near future, Steps H-L are unnecessary. Run the machine on start-up/shut down solution for about 15 minutes, followed by water for 7 minutes and shut it down.

- m. Detach platens on main and accessory pump
- n. Close nitrogen pillow
- o. Turn off main power switch

- p. Place catch cup under sampler incase water backflows
- q. Leave all reagent lines in the water beaker (if running soon) or a clean dry covered container (if pumped dry)
- r. OPTIONAL: detach all pump tubes from the right side stretcher to take the tension off the tubes. This can extend their life, especially if you're not planning on running again soon.

12. Run Day Troubleshooting

NOTE: Use this section like a dichotomous key. Find the problem you are having, and drill down. I've organized by most likely to least likely issues for each situation.

- a. UNSTABLE BASELINE
 - i. Check for bubbles in the flow cells
 - 1. Clear bubbles from flowcells
 - ii. Check for good bubble pattern, capsule shaped bubbles at even intervals. Approximately even ratio of bubble/sample
 - 1. Make sure all reagents in the problematic sample are delivering (remove straw from solution, introduce a bubble and follow it through the system)
 - 2. Make sure there's not a leak or a fitting that's allowing air into the system (evident from jerky bubble motion)
 - 3. Try turning up the accessory pump a little to deliver more flow.
 - 4. Consider replacing the offending pump tube

5. Call technical support
- iii. Is there junk (crystals) in the ammonia flow cell
 1. Wait 30 minutes and try again
 2. Wait 15 more minutes and try again
 3. Test pH coming out of heat bath, should be about 9-10
 - a. Remake complexing reagent and adjust pH to 10
 - iv. Are all of the filters in the flowcells in good condition?
 1. If not, replace them. Refer to brown maintenance manual or call technical support for assistance.
 - v. Walk away for 15 minutes
 1. Sometimes the machine just takes a while to figure itself out in the morning. If this fails, proceed to vi.
 - vi. Call technical support
- b. NO/INSUFFICIENT SYNC PEAK
 - i. Are all of the lights OK (unlikely but easy to fix)?
 1. Go to 'system> show light %' and compare light percentages to recent runs to make sure the lights are still good
 - a. If it's too high or low, you can loosen the set screw and adjust the position of the light to get it within nominal range
 - b. If you still have no/insufficient light, consider replacing the fiber optic

ii. Were all reagents made correctly?

1. Is phosphorus reagent (if PO₄ is the problem) a nice straw yellow?

a. Remake (once), if that fails, proceed to b.iii

2. Did you reactivate the Cd column this AM (if NO₂ is good but NO₃ is bad)

a. If no, do that now, if yes, go to b.iv

iii. Is it a flow path problem?

1. Are all reagents on the offending channel drawing appropriately (see a.ii.1 above)

a. If not, check for a clog in the straw or one of the fittings

2. Is sample being delivered efficiently

a. Look for backflow in offending lines, introduce a bubble by removing the sample needle from the washpot and follow it through the system

b. The flowpath of sample is

NH₄>SIO₄>NO₂>NO₃>PO₄. If the

interruption is in line with this (e.g. you have

NH₄, SIO₄, and NO₂ but no NO₃ or PO₄) this is

the likely problem, inspect the flowpath for leaks

and clogs, clean all metal fittings, replace if

necessary. If not (e.g. you have all but NH_4 or SiO_4) this is not the problem.

iv. Is one of the reagents bad?

1. Check for precipitate in reagent bottle. As above, the most likely offenders for this are (in order)
 - a. Either of the molybdate reagents (silicate or Phosphate)
 - b. The Citric acid (phosphate)
 - c. The complexing reagent (ammonium)
 - d. Not likely a reagent problem (NO_2 , NO_3)

v. Is the Cd column bad (NO_2 , NO_3)

1. Check the pH of the sample coming out of the column. This can be problematic for anoxic, very high concentration, or poorly buffered (freshwater) samples. It should be around 2. If not (usually too low), adjust the buffer so the pH is around 2 or slightly above.
2. Reactivate the column
 - a. First do the daily reactivation again (water, copper, buffer). If that fails:
 - b. Do the more aggressive reconditioning in the brown troubleshooting manual. If that fails

- c. Consider replacing the column, especially if it's over 200 hours old. Remember to activate and 'burn in' a new column before use
- vi. Are all the stocks/standards good?
 1. They're good for a year, and don't tend to go 'all the way' bad. If you're off by 10% or so, consider remaking your standards, or stocks, if they're old
 2. If you're not getting any peak at all, this is unlikely to be the problem. Attempt all other troubleshooting methods (e.g. flowpath or reagent issues) before proceeding to 3 below.
 3. If you're not getting any peak at all, and the stocks are appropriate age, consider attempting a benchtop titration to see if you get any color (use straight 1000uM stock, you're looking for blue for PO₄ and SiO₄, and pink for nitrogen species). If not, remake the stock.

c. FLOWPATH/BUBBLE PATTERN ISSUES

- i. Consider a.ii and b.ii above
- ii. Can you trace the problem to a specific line?
 1. Check all reagents to that line to make sure they're delivering
 2. Make sure the Nitrogen pillow is open and full

3. Make sure the air line pump tube (for lines not on the N2 pillow) are not obstructed and are in good condition
- iii. Are all/multiple lines malfunctioning
 1. In this case it's probably a sample line issue, see B.iii.2 above
 2. Check to make sure the needle is properly positioned in the washpot and not drawing up too many bubbles
 - a. Adjust the needle, or if there's too much air in the washpot, try turning up the accessory pump a little
 - b. Make sure none of the lines going into or out of the accessory pump are kinked or trapped under anything, even a small restriction can be deadly here.
 3. Walk away for 15 minutes and see if the problem persists
 - a. Seriously, sometimes the machine just takes a while to sort itself out.
 - b. Call tech support.
 - d. CADMIUM COLUMN ISSUES
 - i. Did you remember to activate it this morning?
 1. If not, activate it and start over
 - ii. Is it clogging, tearing up bubbles excessively, or back flowing?

1. Flush extensively with imidazole buffer in BOTH directions
 2. Try cleaning out the edges of the column with the paperclip probe tool (a piece of 0.020 wire rubber banded to a ½ paperclip)
 3. Check/replace the PE tubing coming in and out of the column, the fittings which link that tubing to the column (0.90 PE with 0.33 silicone sheathed inside) and the pins that connect it to the PE tubing on the system. Clean and replace if necessary
 4. Perform a more extensive cleaning procedure from the brown troubleshooting manual
 5. If it's old, consider replacing it. If not, call tech support
- iii. Is the efficiency dropping off rapidly?
1. Try the harsh reactivation step in the brown binder
 2. Test the pH of the sample coming out of the column to make sure it's 2ish.
 3. If you are running porewater, brackish samples, potentially anoxic samples, or potentially very high concentration seawater samples, switch buffers to the ammonium chloride/EDTA buffer and see if that helps
 4. Consider replacing the column if old, otherwise call tech support

Machine Maintenance

1. 50 hour preventative maintenance. (NOTE: This needs to be performed EVERY 50 hours, sometimes a little earlier, sometimes a little later. Usually you will notice pump tubes starting to go bad. If you can replace 1 and get a run day in, go for it, if more than 1 is bad, you should probably scrap the run day and do the maintenance, because it's likely that others will go bad during the run day and ruin your data
 - a. Run warm 20% contrad (heat to 65C in water bath) through all lines except sample rinse line and ammonium waterbath line to clean the glass coils and flowcells.
 - b. Run water through the system for 30 minutes to flush the contrad
 - c. Clean the platens by removing them and cleaning them with ethanol then with lubricant (tri Flow silicone lubricant, ordered from Astoria)
 - d. Clean the rollers by undoing one side of the tubes for each roller and holding a Kimwipe with ethanol over them as they move. Repeat with lubricant.
 - e. Change all pump tubes.
 - i. Be sure to trim pump tubes to appropriate length to avoid (minimize) the massive tangle of tubes. Trim with the GREEN or YELLOW cutters or a razor blade.
 - ii. The pump tubes can be dipped in ethanol to ease putting them back on, and can also be stretched a little with the probe tool or WHITE pliers.

- f. Change all Poly Flow (bluish tubing)
 - i. You have to use Astoria brand poly flow. You cannot substitute generic .034 PTFE tubing (I tried, I know it's much cheaper, trust me)
 - ii. It must be trimmed with a razor or guillotine, NO cutters
 - iii. You can ease replacement by priming the tip with the probe tool
 - iv. If the tube kinks, you need to trim it off at the kink and try again. For this reason, it's often a wise idea to cut the tube a bit longer than you think you need!
- g. Clean autosampler
 - i. Clean any salt stains and wipe down the sampler with water or ethanol.
 - ii. Use Tri-Flow to oil the sample arm gears and the crossbeam
- h. Clean instrument
 - i. Inspect under cartridges for leaks
 - ii. Inspect flowcells, 'coffins' and sliders. Oil sliders with tri-flow making sure not to get any oil on the flowcell!
 - iii. Wipe off all surfaces with water and/or ethanol to clean any spills
 - iv. Inspect all glass/glass junctions, fittings etc. for cracking, wear, or damage
- i. Rotate platens to ensure they wear evenly
- j.

2. TWICE PER YEAR

- a. Clean all reagent, rinse, and ASW bottles by filling partly with 10% bleach. Let sit for 30 minutes then dump and rinse with DI water. Fill bottle partly with 10% hydrochloric acid. Let sit for 30 minutes then dump and rinse with DI water.
- b. Change all PE (grey) tubing. (note, this can be done at discretion when it appears worn, stretched out, or overly stained, between once and twice per year)
 - i. Make sure you use a razor or the YELLOW cutters to cut PE.
You can use Astoria brand or generic 0.34 Polyethelene tubing
 - ii. You can ease the replacement by dipping in ethanol, but try not to use the tool, this will only increase the frequency with which the tubes have to be changed
 - iii. It doesn't matter if PE kinks (unlike PolyFlow)
- c. Carefully inspect all junctions and fittings, replace worn junctions, inspect and replace any worn, stained, or skuzzy reagent straws,
- d. Carefully remove and flush out flowcells with warm contrad then water to remove any accumulated sediment.
- e. Inspect (replace if worn/skuzzy) the coiled sample line. Typically this has a lifespan of about one year. Be sure to mark it's in service date
- f. Inspect all platens for excessive wear. Replace as necessary. Platens have a lifespan of 500-1000 hours depending on usage

- g. Inspect all stocks, reagents, surfactants, and dry chemicals and replace any that have expired. Stocks and wet chemicals are good for 1 year, dry chemicals are good for 5 years. Surfactants vary. **BRIJ-35 (Astoria proprietary surfactant used for ammonia) actually does go bad, and has to be replaced if expired.** TX-10/100 seems to be more reliable.

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Table A-0-1. Autoanalytic methodologies and empirically determined EPA detection limits for each nutrient analyte.

Analyte	Technicon Method (used 2006-2008)	Technicon MDL	Astoria Method (used 2009-present)	Astoria MDL
Nitrite	Greiss Reaction (NH ₄ Cl buffered Napthyethelene/Sulfanilimide (NED/SAN)) (Strickland and Parsons 1968, Technicon 1972a, Fox 1979)	0.02 mM	Greiss reaction (Imidazole Buffered NED/SAN) (Strickland and Parsons 1968, Fox 1979, Astoria-Pacific 2005)	0.02 mM
Nitrate	Greiss reaction (NED/SAN w/packed cadmium reduction) (Strickland and Parsons 1968, Technicon 1972a)	0.2 mM	Greiss reaction (NED/SAN w/ open tubular cadmium reduction) (Strickland and Parsons 1968, Astoria-Pacific 2005, Scott et al. 2005)	0.1 mM
Phosphate	Heteropoly Blue (molybdic+ascorbic) (Technicon 1971, Hager et al. 1972, EPA 1983c)	0.12 mM	Heteropoly Blue (molybdic + ascorbic acid) (EPA 1983c, Scott et al. 2005)	0.06 mM
Ammonia	Berthelot Indophenol blue (crystalline phenol+hypochlorite) (Solorzano 1969, Technicon 1973, EPA 1983a)	0.1 mM	Modified Berthelot (liquid phenol, hypochlorite, tartarate) (Solorzano 1969, Scott et al. 2005, Schmidt and Clement 2009)	0.05 mM
Silica	Silico-heteropoly blue (ascorbic, oxalic, molybdic) (Brewer and Riley 1966, Technicon 1972b)	0.06 mM	Silico-heteropoly blue (molybdic, tartaric, stannous chloride) (Sakamoto et al. 1990, Scott et al. 2005)	0.08 mM
Total Nitrogen	Alkaline Persulfate Oxidation + Greiss reaction (as above) (Technicon 1972a, Solorzano and Sharp 1980, Valderrama 1981)	1.1 mM	Alkaline Persulfate Oxidation + Greiss reaction (as above) (Solorzano and Sharp 1980, Valderrama 1981, Astoria-Pacific 2005)	0.5 mM
Total Phosphorus	Alkaline Persulfate Oxidation + Heteropoly Blue (as above) (Technicon 1971, Solorzano and Sharp 1980, Valderrama 1981)	0.12 mM	Alkaline Persulfate Oxidation + Heteropoly Blue (as above) (Solorzano and Sharp 1980, Valderrama 1981, Scott et al. 2005)	0.06 mM

Table A-2. Chemicals used to make nutrient chemical listed by name with its manufacturer and number.

Chemical	Company	Number
Ammonium Molybdate	Fisher	A674
5.0 Sulfuric Acid	Ricca	8325
Ascorbic Acid	Fisher	A61
Potassium Antimony Tartrate	Aldrich	244791
Sodium Dodecyl Sulfate	Fisher	BP166
Ammonium Chloride	Fisher	A661
N-1-Naphthylethylenediamine	Sigma-Aldrich	222488
Sulfanilamide	Sigma	S9251
Ammonium Hydroxide	Fisher	A669
Sodium Hydroxide	Fisher	S318
Sodium Hypochlorite Solution	Fisher	SS290
Sodium Citrate	Fisher	S279
Potassium Sodium Tartrate	Fisher	S387
Sodium Nitroferricyanide	Fisher	S350
Phenol Liquid	Fisher	A931I
36N Sulfuric Acid	Fisher	
Tartaric Acid	Fisher	A314
Chloroform	MP	194002
Hydrochloric Acid	Fisher	A144C
Stannous Chloride	Fisher	T142
Sodium Chloride	Fisher	S271
Magnesium Chloride	Fisher	M63

Table A-3. Procedure for making nutrient chemicals.

NO₂ + NO₃ REAGENTS	
Ammonium Chloride	<ol style="list-style-type: none"> 1. 30 g Ammonium Chloride/L ultrapure DI water 2. Mix with stir bar 3. Store on shelf
Naphthylethylene (NED)	<ol style="list-style-type: none"> 1. 1.0 g N-1-Naphthylethylenediamine/L ultrapure DI water 2. Filter at 0.045 µm 3. Store in small chemical fridge
Sulfanilamide (SAN)	<ol style="list-style-type: none"> 1. 10 g Sulfanilamide/L 10% HCl 2. Filter at 0.045 µm 3. Store in small chemical fridge
Ammonium Hydroxide	Straight from bottle in chemical fridge
NH₄ REAGENTS	
0.125N Sodium Hydroxide	<ol style="list-style-type: none"> 1. 5.0 g Sodium Hydroxide/L ultrapure DI water 2. Mix with stir bar 3. Store on shelf
Sodium Hypochlorite Solution	Straight from bottle in small chemical fridge. Use fisher (or similar) brand hypochlorite. Do not use household bleach.
Ammonia Complexing Reagent	<ol style="list-style-type: none"> 1. 56 g Sodium Citrate + 0.75 g hydroxide + 9.6 g Potassium Sodium Tartrate/500 mL ultrapure DI water 2. Filter at 0.045 µm 3. Store in small chemical fridge
Sodium Nitroferricyanide	<ol style="list-style-type: none"> 1. 0.5 g Sodium Nitroferricyanide/L ultrapure DI water 2. Mix with stir bar 3. Store in small chemical fridge
Phenol liquid	Straight from bottle in enclosed section of chemical shelf
SiO₄ REAGENTS	
Stock Molybdic Acid	<ol style="list-style-type: none"> 1. 10.8 g Ammonium Molybdate + 2.8 mL 36 N Sulfuric Acid/L ultrapure DI water. Add Ammonium Molybdate and 700-800 mL ultrapure then add acid and remaining ultrapure DI water. 2. Filter at 0.045 µm 3. Store in chemical fridge
Tartaric Acid	<ol style="list-style-type: none"> 1. 200 g Tartaric Acid/L ultrapure 2. Add 2 drops of chloroform 3. Store in small chemical fridge
10% Hydrochloric Acid	<ol style="list-style-type: none"> 1. 100 mL HCl/900 mL ultrapure DI water. Fill with ultrapure then add acid.

	2. Store on shelf
Stannous Chloride	1. 50 g Stannous Chloride + 50 mL HCl/250 mL ultrapure DI water. Add some ultrapure DI water to Stannous Chloride then add acid and remaining ultrapure. 2. Store in freezer
PO₄ REAGENTS	
Ammonium Molybdate	1. 40 g Ammonium Molybdate/L ultrapure DI water 2. Mix with stir bar 3. Filter at 0.045 µm 4. Store in chemical fridge
4.9N Sulfuric Acid	1. 20 mL ultrapure DI water filled to 1L with 5.0N Sulfuric Acid 2. Store on shelf
Ascorbic Acid	1. 54 g Ascorbic Acid/L ultrapure DI water 2. Store in small chemical fridge
Potassium Antimony Tartrate	1. 0.68 g Potassium Antimony Tartrate/500 mL ultrapure DI water 2. Mix with stir bar 3. Store on shelf
SLS	1. 15 g Sodium Dodecyl Sulfate/85 mL ultrapure. Be sure to wear a mask. 2. Mix with stir bar 3. Store on shelf
OTHER	
Artificial Seawater (28 psu)	1. 51 g Sodium Chloride + 16 g Magnesium Sulfate/2L ultrapure DI water 2. Mix with stir bar 3. Store on shelf 4. This makes 28PSU artificial seawater. For other salinities adjust accordingly
Start-up/Shut-down	Add the following surfactants to 250 ml ultrapure DI water: 1. Nitrate,Nitrite, TN: 3.5 ml TX-10 2. Phosphate (and TP) and Silicate: 10ml SLS 3. Ammonium: 1ml Brij-35 (30 drops)
ChemWash	1. 40 g Sodium Hydroxide/ 1L ultrapure DI water 2. Stir with stir bar 3. Add 4 ml Triton X100
Imidazole Buffer	1. 34 g Imidazole + 30 ml Stock Ammonium Chloride – Copper Sulfate/2L ultrapure DI water 2. Fill with about 1.5 ml ultrapure DI water 3. Add about 67 ml 10% Hydrochloric Acid 4. Fill to top with remaining ultrapure DI water

Table A-4. Procedure for making nutrient reagents.

NH₄		SiO₄	
Hypochlorite		Molybdate	
60 ml	0.125 Sodium Hydroxide	100 ml	Molybdic Acid Reagent
1.2 ml	Sodium Hypochlorite Solution	6.5 ml	SLS
Citrate/Tartrate/Hydroxide		Tartaric Acid	
100 ml	Complexing Reagent	60 ml	Tartaric Acid
20 drops	Brij		
Nitroferricyanide/Phenol		Stannous Chloride	
60 ml	Sodium Nitroferricyanide	60 ml	10% HCl
1.2 ml	Phenol liquid	1.2 ml	Stannous Chloride
NO₂+NO₃		PO₄	
Ammonium Chloride Buffer*		ADD IN ORDER	
50 ml	Ammonium Chloride	10 ml	Ammonium molybdate
100 ml	Ultrapure DI water	33 ml	4.9 Sulfuric Acid
0.25 ml	Ammonium Hydroxide	6.65 ml	Ascorbic Acid
1.33 ml	TX-10	6.65 ml	Potassium Antimony Tartrate
		10 ml	Ultrapure DI water
NED		<hr/>	
60 ml	Napthyethylene (NED)	FILTER @ 0.45 μM	
		5.5 ml	SLS
SAN			
80 ml	Sulfanilamide (SAN)		
1.6 ml	TX-10		

Table A-5. Guide for making nutrient standards. All values are in ml.

DIN	1	2	3	4	4.5	5	SYNC
PO ₄	0.2	0.4	0.6	0.8	1.0		0.8
SiO ₄	0.5	1.0	1.5	2.0	4.0		2.0
NO ₂ +NO ₃	0.3	0.6	0.9	1.2	1.8		0.0
NH ₄	0.2	0.4	0.6	0.8	1.0		0.8
NO ₂	0.1	0.2	0.3	0.4	0.6	1.2	1.2
TNTP	1	2	3	4	4.5	5	SYNC
NO ₂ +NO ₃	1.2	2.4	3.6	4.8	7.2		
PO ₄	0.2	0.4	0.6	0.8	1.0		0.8
NO ₂						4.8	4.8

Table A-6. Racking order for nutrient standards with the number of reps in parentheses ().

Rack Position	DIN	TNTP
SR1	SYNC (1)	SYNC (1)
SR2	CO (1)	CO (1)
SR3	W (1)	W (1)
SR4	w (1)	w (1)
SR5	B4 (2)	B4 (2)
SR6	NOX% (2)	NOX% (2)
SR7	W (1)	W (1)
SR8	w (1)	w (1)
SR9	C1 (2)	C1 (2)
SR10	C2 (2)	C2 (2)
SR11	C3 (2)	C3 (2)
SR12	C4 (2)	C4 (2)
SR13	C5 (2)	C5 (2)
SR14	C6(2)	C6(2)
SR15	C7(2)	C7(2)
SR16	C8 (2)	W
SR17	C9(2)	CC1
SR18	C10(2)	CC2
SR19	W	

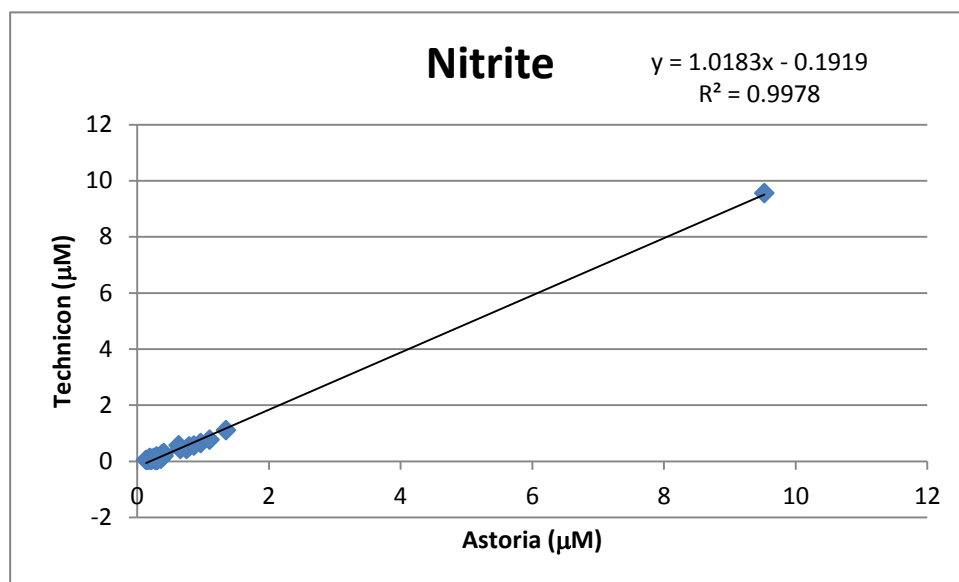


Figure A-1 Comparison of Nitrite values between Astoria and Technicon Autoanalyzers. Data run 11/30/2009

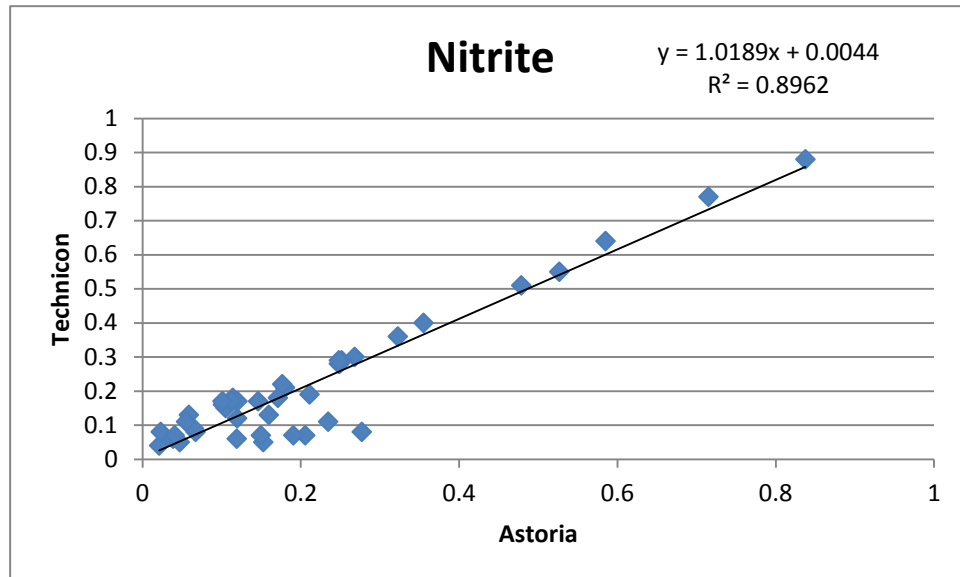


Figure A-2 Low range Nitrite comparison between Astoria and Technicon Autoanalyzer. Samples run 11/4/2009. While the overall relationship remains solid, the Astoria appears to be able to detect lower levels than the Technicon.

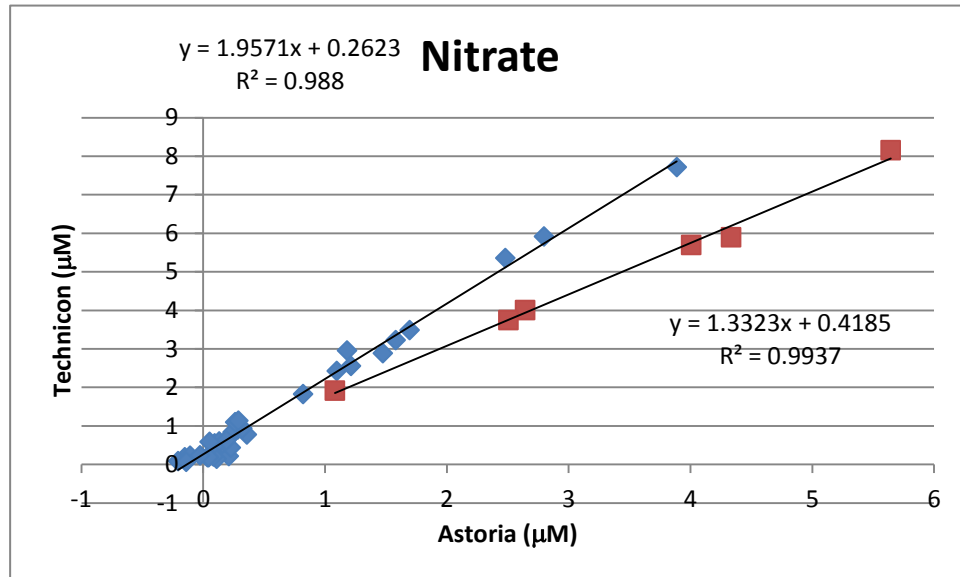


Figure A-3 Intercomparison of Nitrate data between Technicon and Astoria Autoanalyzers on 11/4/2009. Squares represent the first six samples run during this day, and diamonds represent remaining samples. High correlation on both 'sets' indicates a possible rapid shift in Cd reduction efficiency on the Technicon.

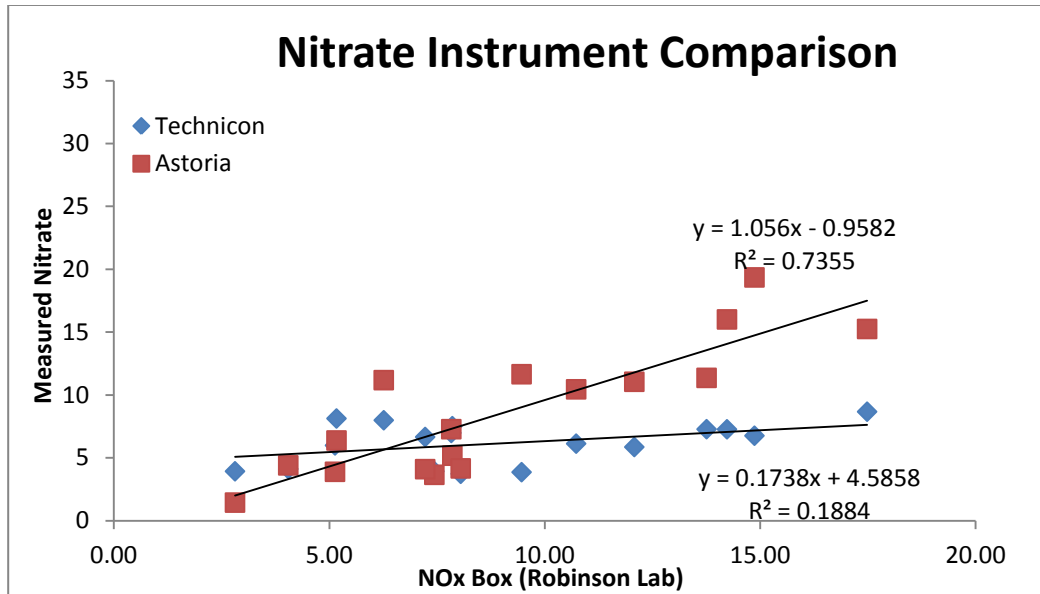
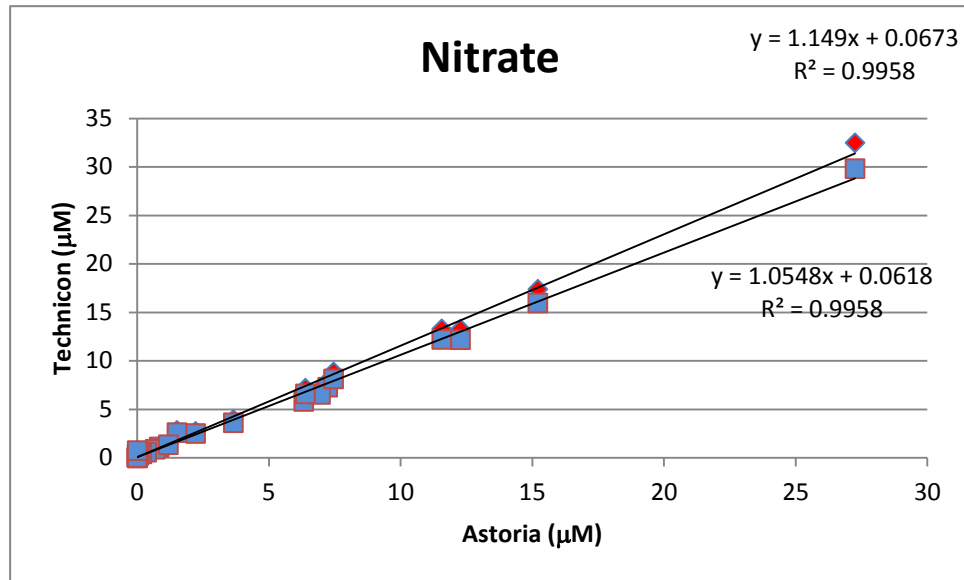


Figure A-4 Comparison of MERL measured nitrate+nitrite for both instruments to measurements on Teledyne instruments nitrous oxide sensor.



FigureA-5: Intercalibration data from 11/30/2009 showing Technicon values against Astoria values after the Technicon was retrofitted with a refurbished old style Cadmium column. Diamonds show data with a one point 'correction' for Technicon Cd efficiency. Squares show data without the correction.

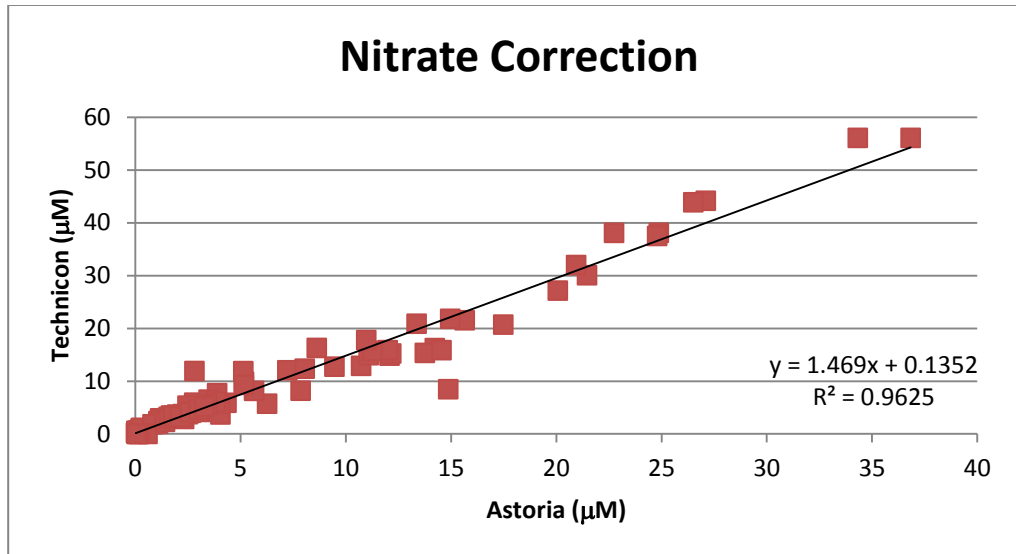


Figure A-6. Final pooled corrected nitrate data for all intercalibration samples run showing relationship between Astoria (X) and Technicon (Y) results once the erroneous cad efficiency correction was removed.

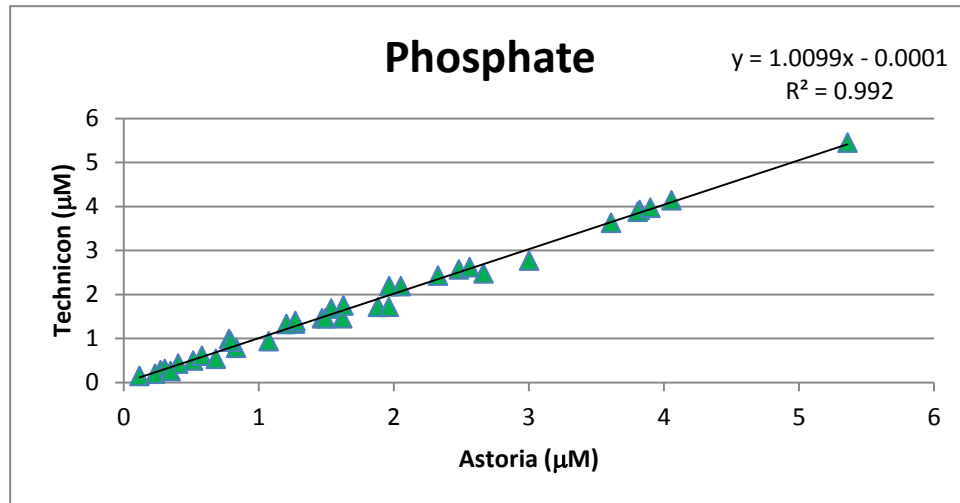


Figure A-7: Sample intercalibration curve for Ortho-Phosphate from intercalibration data run 10/28/2009.

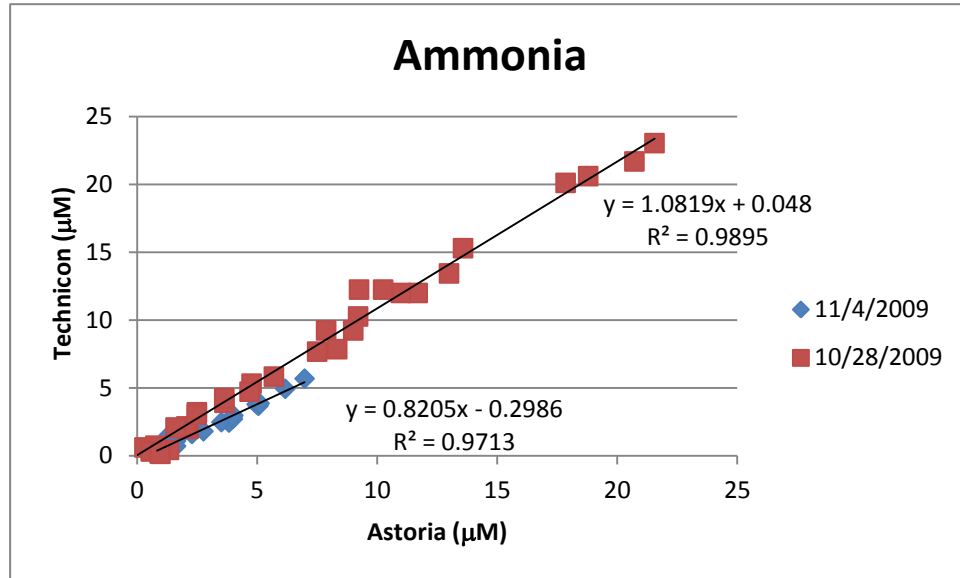


Figure A-8. Intercalibration of ammonia between Astoria and Technicon autoanalyzers. Data from 11/4/09 in blue diamonds, data from 10/28/09 in red squares.

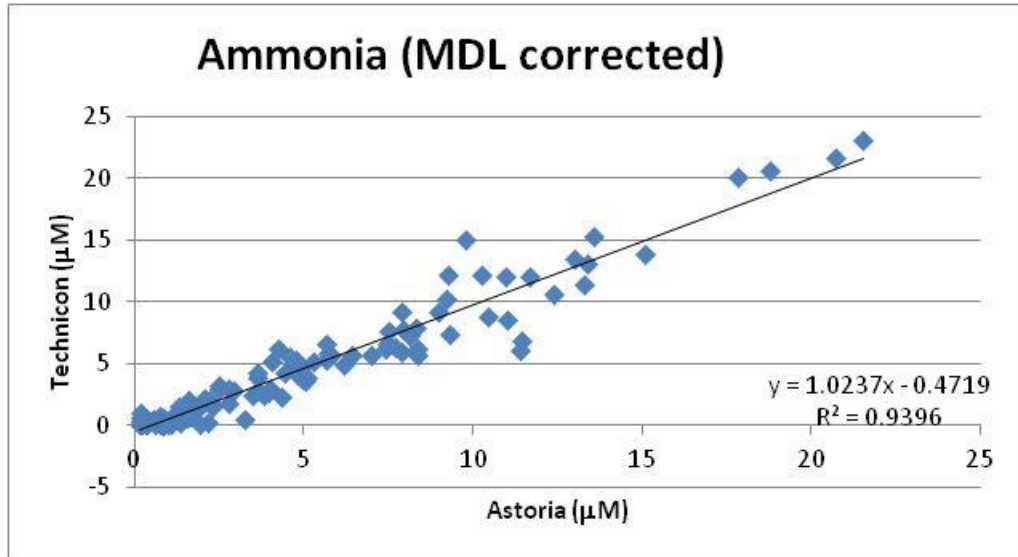


Figure A-9. Pooled and salinity corrected intercalibration data for Astoria vs. Technicon ammonium channels. These data were corrected such that values below the EPA reporting limit of 0.3mM are not considered in the analysis

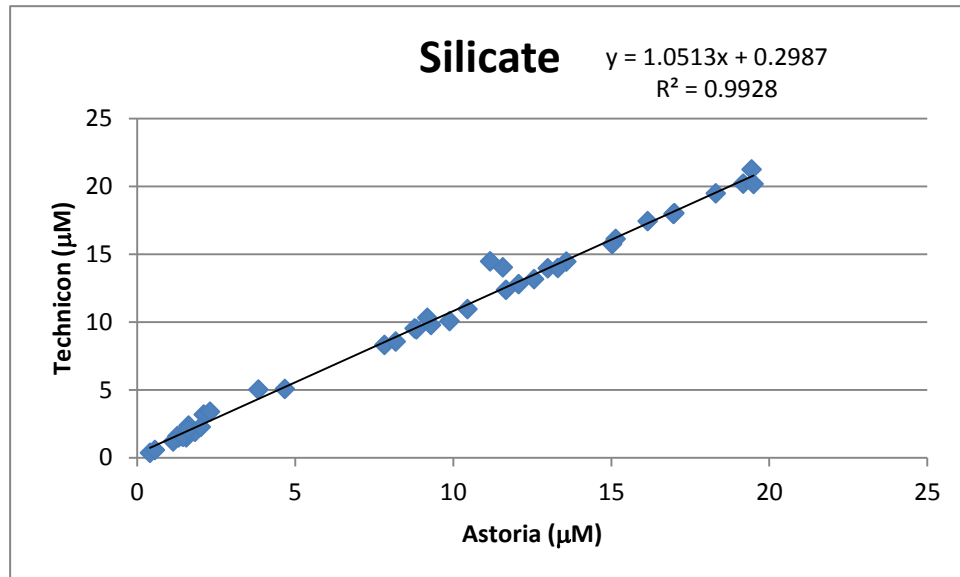


Figure A-10. Intercalibration results between Technicon and Astoria autoanalyzers for silicate. Samples run on 11/4/2009.

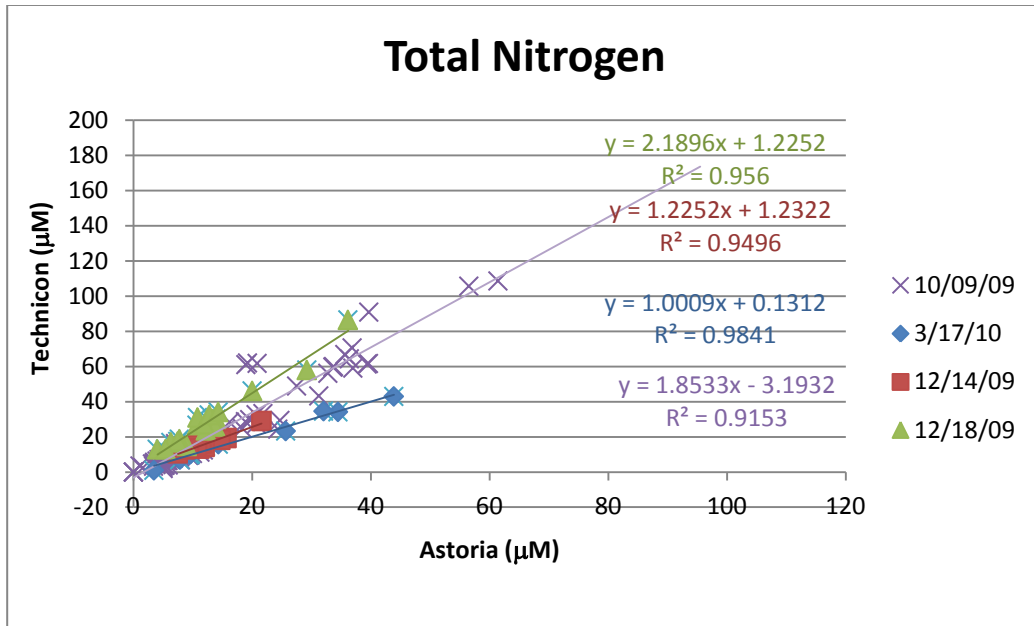


Figure A-11. Intercalibration of Total Nitrogen (TN) between Astoria and Technicon autoanalyzers with samples broken down by date run. R² of pooled sample is 0.57 with equation $Y=1.27X+5.11$

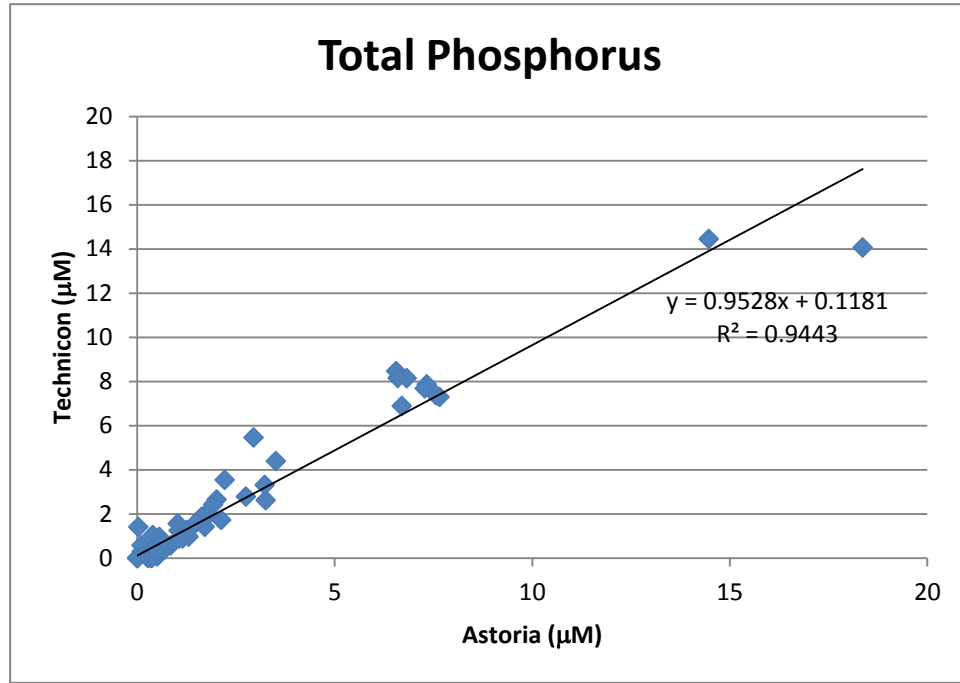


Figure A-12. Intercalibration of Total Phosphorus (TP) between Astoria and Technicon autoanalyzers. Samples run 10/09/2009.

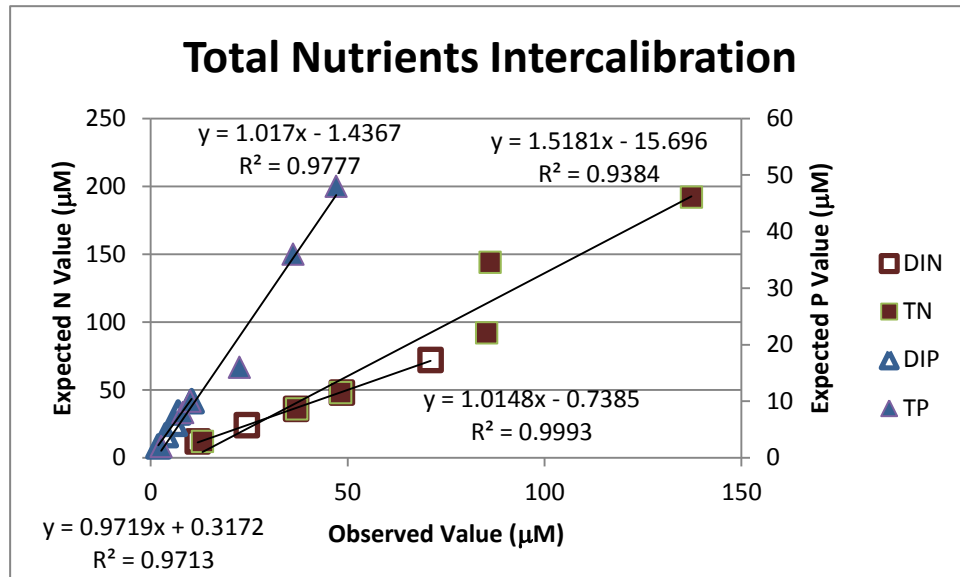


Figure A-13. Total nutrients vs. dissolved nutrients standards tests. TN/DIN is on the left Y-axis, while TP/DIP is on the right Y-axis. Dissolved nutrients are hollow markers, total nutrients are filled. Data run 12/14/2009

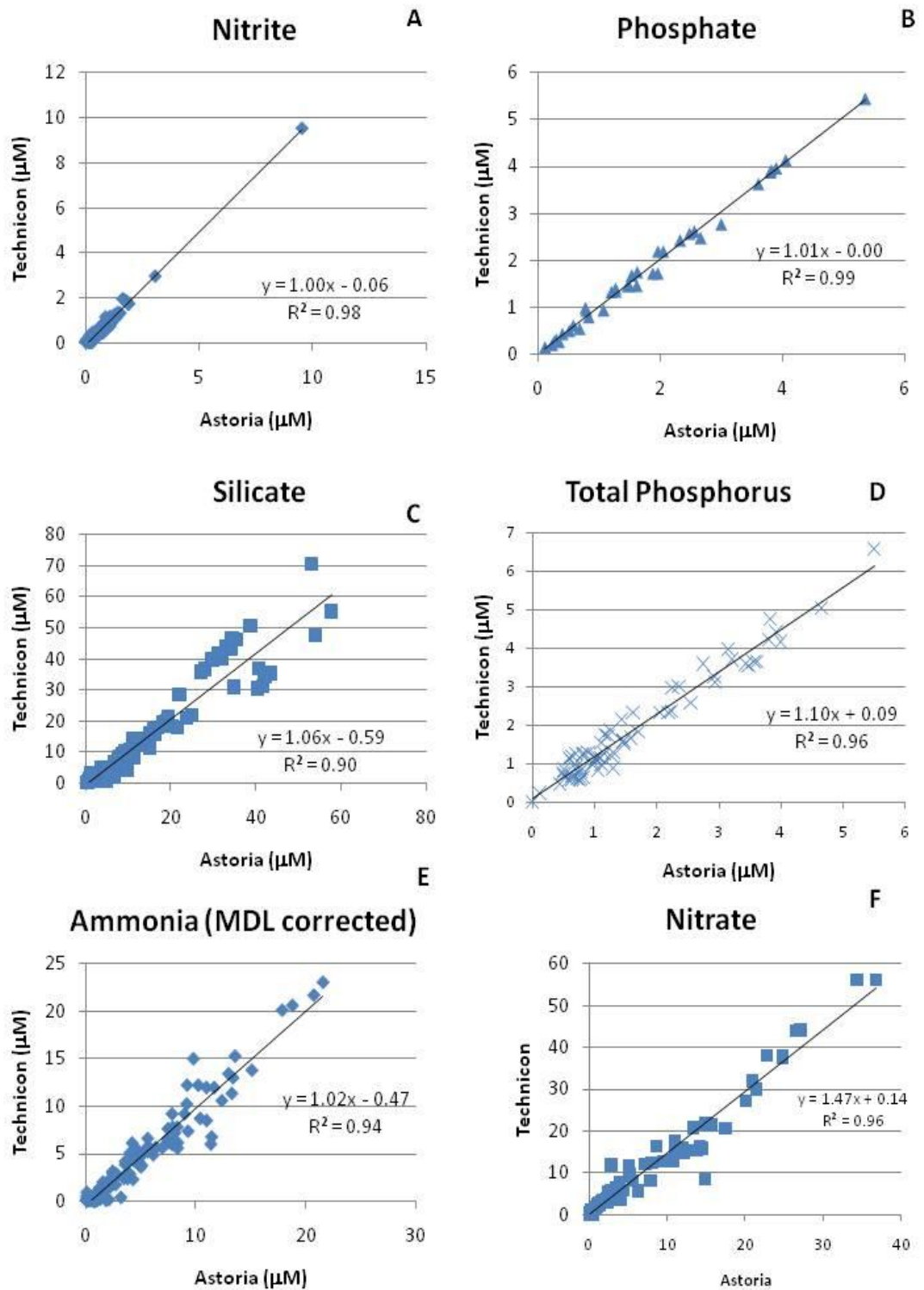


Figure A-14 Summary of pooled intercalibration data for all analytes measured. All concentrations are in μM with Astoria values on the X axis and Technicon values on the Y. Nitrate data include both nitrate and TN data run on the same channel.

APPENDIX B

NUTRIENT INPUT FROM WASTEWATER TREATMENT FACILITIES IN THE NARRAGANSETT BAY WATERSHED, 2000 – 2010

Preface

This appendix is based in large part upon the results of an independent study project by Rosmin Ennis undertaken under the supervision of Jason Krumholz and Candace Oviatt in the spring of 2011.

Executive Summary

Wastewater treatment facilities (WWTF) have been the primary source of nitrogen and phosphorus into Narragansett Bay for many years. Upgrades to 10 facilities in the Narragansett Bay watershed have been completed in the first stage of a project with the overall goal of reducing nitrogen and phosphorus loading to the Bay from WWTF by 50%. As expected, after upgrade, the majority of those facilities showed a reduction in nitrogen and/or phosphorus when compared to their load prior to upgrade and to those facilities that have not yet upgraded. With this in mind, there are a few additional main points of our study that should be highlighted.

The Bucklin Point facility in East Providence, RI reduced total nitrogen in effluent by about 50%. This reduction has been relatively consistent year-round since upgrade completion.

The Worcester and Woonsocket plants have shown large reductions in total nitrogen since implementation of advanced treatment, but are significantly upstream from Narragansett Bay proper, so it is difficult to tell at this stage what impact the reductions may have on the riverine abatement rate in the Blackstone River and therefore the overall impact on the downstream system; especially for the Worcester plant, which first upgraded in 2009.

The North Attleboro, MA facility has shown a large reduction in total phosphorus since its upgrade completion in 2008; however, the full impact of the upgrade is uncertain due to how recently it was completed. The Attleboro, MA facility showed an equally large reduction in total phosphorus in 2007-2010 when compared to 2000-2003. All facilities on the Pawtuxet River (Cranston, Warwick, and West Warwick) showed a large reduction in total phosphorus since their upgrade completions. However, a similar reduction in their total nitrogen loads was not observed most likely due to their difficulties with flooding in 2010. When this year of data is removed, all facilities' total nitrogen reductions improved.

Overall it appears that the upgraded facilities are indeed reducing their total nitrogen and total phosphorus loads to Narragansett Bay. However, the majority of these facilities are on rivers that discharge into Narragansett Bay not the Bay itself, which makes the full effect of the upgrades on the total load to the Bay difficult to determine.

Introduction

History of Nutrient Introduction into Narragansett Bay

Human interactions with the Narragansett Bay have had noticeable impacts on the ecosystem. Since the dawn of the Industrial Revolution in the mid 1800s, humans have been dredging the bottom of the Bay, inadvertently or purposefully introducing exotic species, and polluting the waters through the discharge of numerous chemicals and excess nutrients in the form of human and animal waste and agricultural fertilizers (Nixon et al., 2005; Nixon et al., 2008; Hamburg et al., 2008).

Prior to the Industrial Revolution, nutrient concentrations in Narragansett Bay were relatively low (Nixon et al., 2008). This kind of environment allowed vast eelgrass meadows to thrive, as eelgrass meadows are very sensitive to nutrient inputs (Nixon et al., 2008). However, a community shift occurred after the rapid industrialization, nitrogen pollution, and population growth associated with the Industrial Revolution (Nixon et al., 2008; Hamburg et al., 2008; Kelly 2008). The majority of these meadows quickly disappeared indicating an increase in nutrient concentrations in Narragansett Bay (Nixon et al., 2008).

The explosive population growth of the 19th century increased the demand for protein rich food imported from nearby areas, which in turn increased the amount of nitrogen in human waste (Nixon 1995; Hamburg et al., 2008). When coupled with the almost 55,000 people connected to established sewer systems in 1889, the amount of nitrogen being discharged into the Narragansett Bay and its major tributaries steadily

increased and has continued to do so with population growth (Nixon et al., 2005; Nixon et al., 2008; Hamburg et al., 2008; King et al., 2008). Traditional agricultural practices also changed during the 19th century from the use of no synthetic fertilizers to their use on almost every farm (Hamburg et al., 2008). However, although synthetic fertilizers and other non-point sources of pollution are important when discussing the history of nitrogen introduction in Narragansett Bay, the single largest contributor of nitrogen to the Bay is sewage, which until very recently contributed about 65% of the Bay's total load of nitrogen (Nixon et al., 2008). This increased loading of nitrogen into Narragansett Bay quickly exhibited unwanted effects on the ecosystem.

Excess Nutrient Input Leads to Eutrophication

Phosphorus and primary production limiting nitrogen are essential nutrients in the maintenance of a healthy estuarine system (Latimer and Charpentier 2010; RI DEM 2005; Oviatt 2008; Bowen and Valiela 2001; Caraco and Cole 1999). However, the amount of reactive nitrogen in aquatic systems has increased every year until recently due to anthropogenic practices and is causing eutrophication, an increase in the input of organic matter to an ecosystem (Nixon et al., 2008; Latimer and Charpentier 2010; King et al., 2008; Caraco and Cole 1999; Howarth and Marin 2006).

Eutrophication is detrimental to aquatic ecosystems because it promotes increased algal growth, which prevents sunlight from penetrating the water column to sustain benthic plants (Bowen and Valiela 2001; RI DEM 2005). Decomposing algae

strip the water of its dissolved oxygen, creating hypoxic or anoxic conditions leading to fish kills and possible changes in food web structures (Latimer and Charpentier 2010).

The occurrence of eutrophication in Narragansett Bay due to anthropogenic nutrient input has been increasing over the last century. Previous studies have determined that nitrogen input to coastal waters is greatest in areas of agricultural and urban activity (Howarth and Marino 2006). Observed trends in carbon and nitrogen concentrations also provide strong evidence that eutrophication is occurring in the upper Narragansett Bay due to anthropogenic causes (King et al., 2008). Additionally, studies of ^{15}N in the Bay have suggested eutrophication and decreased dissolved oxygen concentrations as a result of sewage discharge (King et al., 2008).

Advances in Wastewater Treatment and Reduction of Nitrogen

The establishment of sewer systems and sewage treatment facilities in the Narragansett Bay watershed in the late 1880s brought waste from a large number of people to one central location for discharge into the water (Nixon et al., 2005). Previously, waste had been left in the soil on land as fertilizer (Nixon, et al., 2005; Hamburg et al., 2008). However, the newly established wastewater treatment facilities received raw sewage and did little other than undertake rudimentary treatment methods aimed at protecting public health and safety (Latimer and Charpentier 2010). The introduction of secondary treatment in the 1970's, and subsequently tertiary treatment in the 2000's has provided better options for treatment of wastewater prior

to its discharge into the Bay (Nixon et al., 2008). Primary treatment, or more simply disinfection, of wastewater was the first advance in wastewater treatment followed by secondary treatment, more advanced filtration and removal of suspended solids (Hamburg et al., 2008). By the late 20th century, all public sewage treatment facilities were equipped for secondary treatment of wastewater. However, wastewater treatment facilities are currently the largest source of nitrogen to Narragansett Bay and further reduction in nitrogen is needed (RI DEM 2005).

The motivation to further reduce nitrogen was accelerated by the occurrence of intense algal blooms and fish kills associated with eutrophication in 2003 (Oviatt 2008). Rhode Island General Law now requires the Department of Environmental Management (DEM) to not only reduce nitrogen loadings from wastewater treatment facilities by 50% by 2014 and provide reports of their reduction status, but also to implement a plan of action designed to manage excess nutrients and their effects on Rhode Island water to prevent eutrophic conditions (RI DEM 2005; Section 46-12-2; Section 46-12-3). Additionally, the Federal Clean Water Act requires each state to create a schedule for water quality restoration in impaired waters (RI DEM 2005).

Further reduction of nitrogen has been accomplished by the development of tertiary treatment methods (Hamburg et al., 2008). The addition of anaerobic denitrification by bacterial growth as the last step in wastewater treatment converts nitrate to inert nitrogen gas, which is released from the facility into the atmosphere (RI DEM 2005; Nixon et al., 2008). The reduction of nitrogen in discharged effluent is anticipated to reduce the amount of primary productivity thereby restoring habitable dissolved oxygen concentrations to the benthic community and sediments (Nixon et

al., 2008). In recent years, there has been a decrease in the amount of nitrogen discharged into Narragansett Bay due to the establishment of tertiary treatment at several facilities and stricter environmental regulations (King et al., 2008). However, some of the larger wastewater treatment facilities still remove only a small amount of the total nitrogen they collect in untreated sewage (Hamburg et al., 2008).

It is difficult to determine how the reduction of nitrogen in wastewater effluent will translate to Narragansett Bay as a whole because the Bay has been changing dramatically over the years (Nixon et al., 2008). Long-term upward trends in temperature of almost 1°C have put stress on the ecosystem (Pilson 2008; Hamburg et al., 2008). Increases in precipitation and river flow into the Bay have also increased over the last century (Pilson 2008). Freshwater input from the Bay's major tributaries largely influence residence time of water and dissolved substances in the Bay (Pilson 1985; 2008). Nutrient cycling and retention in the coastal environment must be assessed prior to determining the allowable amount of nutrients discharged into the water (Doering et al., 1990). Topography, geology, and oxygen concentration in the water, among other factors, must also be taken into account because they influence the retention of nitrogen in a system (Caraco and Cole 1999).

Objectives

The primary objective of this study is to determine the load of nitrogen in the form of nitrite (NO₂), nitrate (NO₃), ammonium (NH₄⁺), and total nitrogen (TN) in the discharged effluents of wastewater treatment facilities (WWTF) in the Narragansett

Bay watershed. The load of phosphorus in the form of total phosphorus (TP) was also determined for the same WWTF. The load of nitrogen and phosphorus forms were also determined for the six major rivers that discharge into the Narragansett Bay.

Many methods exist to calculate annual loads based on measurements of flow and concentration. Although most ratio estimators are virtually equal when using a large sample size, in this study, Beale's unbiased ratio estimator (Beale 1962) was deemed the most suitable for several reasons. Beale's unbiased ratio estimator is ideally used in situations in which there are limited concentration data, but daily flow data are available (Dolan et al., 1981). Beale's unbiased ratio estimator also places different emphasis on concentration values based on their deviation from the mean, therefore, creating an almost unbiased estimate in cases where the distribution of values is not normal (Dolan et al., 1981; Tin 1965). An unbiased estimate is useful to data sets with samples from different times of the year, as there may be great variation throughout the year. It was also determined through comparison to other methods, means over a time period or log-linear regressions, by Dolan et al. (1981), that Beale's unbiased ratio estimator is superior in removing bias while still retaining high precision and accuracy (Dolan et al., 1981). Finally, Beale's unbiased ratio estimator has been used before in similar kinds of studies (Nixon et al., 1995; Nixon et al., 2008; Fulweiler 2003).

These load values will then be examined to determine the effectiveness of nitrogen reduction in WWTF upgraded to tertiary treatment methods and how this reduction translates to changes in concentrations of these nutrients in Narragansett Bay

and its major tributaries. It is expected that WWTF upgraded to tertiary treatment methods will discharge lower loads of nitrogen into Narragansett Bay.

Methods

Data Contribution

Total nitrogen (TN), ammonium (NH_4^+), nitrite (NO_2), nitrate (NO_3), and total phosphorus (TP) concentrations in effluent discharged from wastewater treatment facilities (WWTF) in the Narragansett Bay watershed and nutrient loading of rivers emptying into Narragansett Bay were examined in this study. Facility flow data associated with each parameter measurement were also considered. All WWTF data was in the form of MS Excel files. Angelo Liberti and Deb Merrill of the Rhode Island Department of Environmental Management (RI DEM) contributed all Rhode Island WWTF data as well as all data for the Attleboro, North Attleboro, and Worcester facilities. All remaining facilities were estimated from previous measurements. All data concerning the nutrient loading of rivers emptying into Narragansett Bay was processed and contributed by Steve Granger of the University of Rhode Island's Graduate School of Oceanography.

Data Processing

The data contributed by the RI DEM contain many different parameter and flow measurement intervals (ie. daily, weekly, monthly, etc.). For consistency, the monthly average of each parameter and flow from each facility was used for analysis. In some cases, the monthly average is the average of several measurements taken over the course of each month. All flow values were the monthly average of continuous flow measurements (Table B-1).

All relevant flow and parameter data were isolated from the RI DEM data and separated into its own MS Excel file by facility. From there, all flow data was converted from millions of gallons per day (Mgal/d) as it was in the RI DEM data to liters per day (L/d) and then to cubic meters per day (m^3/d). All parameter concentration data was converted from milligrams per liter (mg/L) as it was in the RI DEM data to moles per liter (mol/L). A flux value in moles per day (mol/d) for each month was determined from flow (L/d) and parameter concentration (mol/L). All monthly flux values were moles of nitrogen per day for all nitrogen related parameters and moles of phosphorus per day for all total phosphorus (TP) measurements.

Once flux values had been calculated from parameter concentration and flow (L/d) for all years of available data, an annual load in kilomoles per year (Kmol/y) was determined by using a Beale's unbiased ratio estimator macro in MS Excel (modified from Ganger, pers. comm.). The same process was repeated for both the active treatment season, defined by the RI DEM as May to October, and the inactive treatment season, defined as November to April. Each seasonal load (Kmol/season)

was calculated by using only each season's months of data with the Beale's macro then converting to kilomoles per day (Kmol/d) then multiplying by the number of days in each season to arrive at a seasonal load in kilomoles per season. This process was repeated with available data for all WWTF.

Estimating Missing Data

The data contributed by the RI DEM did not contain data for every year from 2000-2010 for all WWTF. It also did not include all facilities being examined in this study as was previously described. This problem was solved in one of two ways: scaling available load data by population change or by using a multiplication factor with population. The cities and towns served by each facility were provided by the RI DEM website. The annual total populations of the cities and towns served by each facility from 2000-2010 were found on the U.S. Census Bureau website. The actual population of the total served by each facility in 2000 was provided by the RI DEM website. The percent of the total population for each city or town served in 2000 was calculated from these values. This percentage was used for the remaining years in the decade to calculate the actual population served by each facility for each year from 2000-2010. The population change from one year to the next from 2000-2010 was then calculated from the annual actual population served by each facility. This technique assumes that growth occurs proportionally in sewered and unsewered areas, which, for the most part, is likely to be a robust assumption. Furthermore, population

change rates were generally low (ranging from -3.8% -2.9%), so the sensitivity of the overall loading estimate to this parameter is low.

For facilities included in the data provided by the RI DEM, individual years of missing load data from 2000-2010 were estimated by scaling the previous year of available load data by the change in population served by the facility. For the Massachusetts facilities that were not included in the RI DEM data, individual years of load data were not estimated. Instead, a 2007-2010 annual load average was estimated by scaling the 2000-2003 annual load average calculated by Nixon (2008) by the change in population served by each facility from 2000-2010.

The RI DEM data did not include total nitrogen or total phosphorus data for all facilities. For those facilities that had no data for total nitrogen or total phosphorus, annual and seasonal loads for total nitrogen or total phosphorus were calculated by using a multiplication factor of 0.8 moles of nitrogen per person per day or 0.045 moles of phosphorus per person per day. Similar multiplication factors (0.9 mol N/person/day and 0.035 mol P/person/day) were previously calculated by Nixon, et al. (2008) using earlier data. The multiplication factors used in this study were calculated in the same way using available data from this study. The appropriate multiplication factor was multiplied by the actual population served by the facility with missing data to get a daily load. The daily load was then multiplied by the number of days in the year, 365, or in each season to arrive at an annual load in moles per year or a seasonal load in moles per season.

Data Analysis

All load values were formatted into tables and graphs were created using MS Excel. “Pre” and “post” values were calculated from these tables to illustrate the effect upgrade completion has had on the load of upgraded and non-upgraded facilities. “Pre” values are defined as the average of load values from 2000-2004, except at the Burrillville (2000-2001) and Woonsocket (2000-2002) facilities, which upgraded in 2002 and 2003, respectively. The Burrillville and Woonsocket facilities use different years to avoid averaging over the year of upgrade completion. “Post” values are defined as the average of load values from 2007-2010, except at the Worcester and North Attleboro facilities. The Worcester facility upgraded in 2009, so the only “post” value is the 2010 load. “Post” values for the North Attleboro facility were the average of 2009 and 2010 data to avoid averaging over the year of upgrade completion. The percent difference between the pre and post loads were also calculated. T-tests were used to determine significance between the pre and post both annual and seasonal load values and any other load difference.

Results

The results presented below are the most interesting and relevant results to this study. Results are first presented as the total load to Narragansett Bay and subsequently divided by the body of water into which each facility discharges. Dotted lines in figures indicate that the load value was estimated from population data and

recent load values. Several facilities show load reductions immediately prior to upgrade completion, which can most likely be attributed to the facilities' ability to begin reducing before the upgrade was officially reported complete (Liberti, pers. comm.; Travers, pers. comm.). A complete record of the status and trends of all plants for which data are available can be found in the appendix.

Total Sewage Discharge to Narragansett Bay

The average annual total sewage nitrogen from 2007-2010 discharged from each facility was added together to achieve an average grand total amount of nitrogen discharged into Narragansett Bay annually during that time period. The same was repeated for the average annual total sewage phosphorus discharged from each facility from 2007-2010. The average grand total amount of sewage nitrogen discharged into Narragansett Bay per year from 2007-2010 was 262.0 million moles and the average grand total amount of sewage phosphorus discharged per year was 14.1 million moles (Table B-2). This nitrogen load is 101.5 million moles, or 38.5%, less than the grand total nitrogen load calculated for 2003 and the phosphorus load is 4.2 million moles, 27.7% less (Nixon et al. 2008).

The average annual and active season total nitrogen concentrations from 2000-2004 and 2007-2010 were calculated for all facilities that had total nitrogen concentration data available. The Worcester, Woonsocket, Burrillville, and North Attleboro used 2010, 2000-2002, 2000-2001, and 2009-2010 averages, respectively, to avoid averaging over upgrades. These values were compared to existing and future

nitrogen limits. The Bucklin Point and North Attleboro facilities are the only two that were in compliance with their nitrogen limits throughout the year and specifically during the active season after their upgrades were completed. The East Greenwich and Cranston facilities were in compliance with their limits only during the active season after their upgrades were completed. Due to flooding in 2010, all facilities on the Pawtuxet River (Cranston, West Warwick, Warwick) were examined more closely. Only average annual total nitrogen concentrations from 2007-2009 were calculated for all three facilities as the flood occurred in March, which is not included in the active season. The average annual total nitrogen concentrations from 2007-2009 for the Cranston, West Warwick, and Warwick facilities were 11.2 mg/L, 12.3 mg/L, and 8.3 mg/L, respectively. Many facilities have nitrogen limits set to go into effect in several years and it can be seen that these facilities have already begun total nitrogen concentration reductions to meet those limits by their deadlines (Table B-3).

The average annual and active season total phosphorus concentrations from 2000-2004 and 2007-2010 were calculated for all facilities with available total phosphorus concentration data. The Worcester, Woonsocket, Burrillville, and North Attleboro used 2010, 2000-2002, 2000-2001, and 2009-2010 averages, respectively, to avoid averaging over upgrades. These values were compared to existing and future phosphorus limits. The Smithfield and Cranston facilities are the only two that were in compliance with their phosphorus limits throughout the course of the year and, more specifically, during the active season after their upgrades were completed. The Warwick facility was in compliance with its phosphorus limit during the year and the Woonsocket facility was in compliance with its phosphorus limit during the active

season. Due to flooding in 2010, all facilities on the Pawtuxet River (Cranston, West Warwick, Warwick) were examined more closely. Only average annual total phosphorus concentrations were calculated as the flood occurred in March. These facilities have average annual total phosphorus concentrations of 0.89 mg/L, 1.4 mg/L, and 0.62 mg/L, respectively, from 2007-2009 (Table B-4).

The annual total nitrogen load of upgraded facilities was on average 7% higher than that of non-upgraded facilities from 2000-2004. However, the annual total nitrogen load of upgraded facilities was significantly less, by about 70%, than that of non-upgraded facilities from 2007-2010 ($df = 7$, $T = -3.31$, $P = 9.68 \times 10^{-4}$). The average total nitrogen load difference between upgraded and non-upgraded facilities during the active season and the inactive season was 1.54×10^4 moles per day and 1.03×10^4 moles per day, respectively. The average total nitrogen load difference during the active season was not significantly different than the average total nitrogen load difference during the inactive season ($df = 20$, $T = 0.26$, $P = 0.523$; Fig. B-1).

The average total phosphorus load difference between upgraded and non-upgraded facilities during the active season and the inactive season was 4.45×10^3 moles per day, and 5.28×10^3 moles per day, respectively. The average total phosphorus load difference during the active season was not significantly different than the average total phosphorus load difference during the inactive season ($df = 20$, $T = 0.18$, $P = 0.558$; Fig. B-2).

Direct Discharge to Narragansett Bay

After its upgrades were completed in 12/2005, the Bucklin Point facility significantly reduced its average annual total nitrogen load ($df = 7$, $T = 5.79$, $P = 3.11 \times 10^{-6}$; Fig. B-3). Bucklin Point also significantly reduced its annual ammonium load ($df = 7$, $T = 11.71$, $P = 2.67 \times 10^{-7}$) while its annual nitrate load significantly increased after upgrades were completed ($df = 7$, $T = -7.49$, $P = 5.60 \times 10^{-6}$; Fig. B-4). The Bucklin Point facility also significantly reduced its active season nitrite load ($df = 7$, $T = 2.46$, $P = 0.005$; Fig. B-5). Load reductions during the active and inactive season showed a similar pattern to annual load reductions for all parameters.

Although the East Greenwich facility did not significantly reduce its average annual total nitrogen load after upgrades were completed, it did significantly reduce its average active season total nitrogen load by about 40% more than the annual reduction ($df = 7$, $T = 4.34$, $P = 1.96 \times 10^{-4}$; Fig. B-6). The East Greenwich facility also significantly reduced its annual nitrite load after upgrades were completed ($df = 7$, $T = 1.55$, $P = 0.039$; Fig. B-7). Both active and inactive season nitrite load reductions followed a similar pattern to the annual load reduction. The East Greenwich facility significantly reduced its average active season nitrate load ($df = 7$, $T = 2.74$, $P = 0.003$), but it significantly increased during the inactive season ($df = 7$, $T = -2.46$, $P = 0.005$; Fig. B-8). Additionally, it should be noted that the East Greenwich facility experimented with nitrogen removal during June and July of 2005, which may account for early reductions observed before upgrade construction was completed (Travers, pers. comm.).

Discharge to the Blackstone River

Upon upgrade completion, the Burrillville facility significantly reduced its average active season total sewage nitrogen ($df = 4$, $T = 2.17$, $P = 0.037$) and total sewage phosphorus loads ($df = 4$, $T = 2.03$, $P = 0.045$; Fig. B-9). However, during the inactive season, the Burrillville facility significantly increased its average ammonium load ($df = 4$, $T = -2.28$, $P = 0.032$; Fig. B-10).

The Woonsocket facility significantly reduced its average annual nitrite load after upgrades were completed in 9/2001 ($df = 5$, $T = 5.95$, $P = 2.85 \times 10^{-4}$; Fig. B-11). Both the active and inactive season load reductions were similar to the annual reduction. The Woonsocket facility also significantly reduced its inactive season ammonium load with similar reductions during the active season and the year overall ($df = 5$, $T = 2.09$, $P = 0.025$; Fig. B-12).

After upgrades were completed in 6/2006, the Smithfield facility significantly reduced its annual total nitrogen load ($df = 7$, $T = 3.05$, $P = 0.002$; Fig. B-13). Both the active season and inactive season total nitrogen load reductions followed a similar pattern to annual reductions. The Smithfield facility also significantly reduced its annual ammonium load ($df = 7$, $T = 7.57$, $P = 5.20 \times 10^{-6}$), but its annual nitrate load significantly increased after upgrades were completed ($df = 7$, $T = -6.25$, $P = 1.87 \times 10^{-6}$; Fig. B-14). A similar reduction pattern in ammonium and nitrate was seen seasonally. A significant reduction in average annual total phosphorus discharged

from the Smithfield facility occurred after upgrades were completed ($df = 7$, $T = 10.03$, $P = 7.72 \times 10^{-7}$; Fig. B-15).

Significant changes in the average annual or seasonal loads for any parameter from the Worcester facility could not be determined as this facility recently upgraded to advanced wastewater treatment in 2009. However, a large reduction in ammonium and total phosphorus occurred after the upgrade was completed (Fig. B-16). It should be noted that the Worcester facility participated in nutrient removal training and assistance during 2007 and 2008, which is most likely the cause of reductions seen prior to the upgrade being reported complete (Travers, pers. comm.).

Discharge to the Pawtuxet River

Due to excessive flooding in 2010, all facilities that discharge to the Pawtuxet River were evaluated for two sets of years after upgrades were completed: 2007-2010 and 2007-2009. The purpose is to illustrate the effect the flood had on post upgrade load values.

After upgrades were completed in 11/2004, the Warwick facility significantly reduced its average annual total nitrogen load ($df = 7$, $T = 3.09$, $P = 0.001$; Fig. B-17). Seasonal total nitrogen load reductions followed a similar pattern to annual reductions. The Warwick facility significantly reduced its average annual ammonium load after upgrades were completed and both seasons showed comparable reductions ($df = 7$, $T = 2.83$, $P = 0.002$; Fig. B-18). Average annual nitrite loads were significantly reduced ($df = 7$, $T = 2.35$, $P = 0.006$) while average annual nitrate loads significantly increased

after upgrades were completed ($df = 7$, $T = -1.86$, $P = 0.019$; Fig. B-19). The Warwick facility also significantly reduced its average annual total phosphorus load upon upgrade completion ($df = 7$, $T = 3.32$, $P = 0.001$; Fig. B-20). When flooding is accounted for, the average total nitrogen, ammonium, nitrite, and total phosphorus loads after upgrades were completed both annually and seasonally were on average about 10% lower than when 2010 load values were included. The average nitrate load after upgrades were completed both annually and seasonally was about 10% higher than when 2010 load values were included. Additionally, it should be noted that the Warwick facility underwent several nitrogen removal trial periods from 2001-2003, which may account for reductions observed prior to upgrade construction completion (Travers, pers. comm.).

Although it completed upgrades in 1/2006, the Cranston facility did not significantly reduce its average annual total nitrogen load ($df = 7$, $T = 1.16$, $P = 0.101$). However, its average active season total nitrogen load was significantly reduced ($df = 7$, $T = 2.33$, $P = 0.007$; Fig. B-21). Additionally, the Cranston facility significantly reduced its average total phosphorus load year round ($df = 7$, $T = 2.69$, $P = 0.003$; Fig. B-22). When flooding is accounted for, the Cranston facility still did not significantly reduce its average annual total nitrogen load ($df = 7$, $T = 1.16$, $P = 0.143$).

The West Warwick facility significantly reduced its average annual ammonium load ($df = 7$, $T = 2.56$, $P = 0.004$) while its average annual nitrate load significantly increased after upgrades were completed in 7/2005 ($df = 7$, $T = -4.39$, $P = 1.81 \times 10^{-4}$; Fig. B-23). Seasonal ammonium and nitrate loads had comparable reductions to the

annual load reductions. When flooding is taken into account, all parameter load reductions were relatively unchanged with the exception of active season total phosphorus, which was significantly reduced ($df = 7$, $T = 1.28$, $P = 0.023$).

Discharge to the Ten Mile River

The upgrades completed at the North Attleboro facility in 2008 have not yet shown any significant change for any parameter either annually or seasonally, though mean values for total nitrogen and ammonium in upgraded years show an 8% increase and 25% reduction, respectively, over mean values pre-upgrade. However, the average annual total phosphorus discharged from the facility has dramatically decreased by an average of 75% annually and during the active season since upgrade completion (Fig. B-24).

River Loading

The grand total dissolved inorganic and total nitrogen load from all rivers combined was each on average about 25% less in 2008-2010 than the load from 2003-2004. The Pawtuxet, Woonquatucket, Moshassuck, and Taunton Rivers reduced both their dissolved inorganic and total nitrogen by an average of 30%, 36%, 43%, and 35%, each, respectively, in 2008-2010 when compared to 2003-2004. The grand total dissolved inorganic phosphorus and total phosphorus load from all rivers combined was on average 45% and 83% less, respectively, in 2008-2010 than the load in 2003-

2004. In 2008-2010, the Blackstone River increased its dissolved inorganic and total phosphorus loads by about 50% and 40%, respectively. The Pawtuxet River reduced its dissolved inorganic and total phosphorus loads by over 50% each in 2008-2010. The Woonasquatucket, Moshassuck, and Taunton Rivers reduced their dissolved inorganic and total phosphorus loads by about 80% each. The Ten Mile River reduced its dissolved inorganic and total phosphorus load by about 70% each (Table B-5).

Discussion

Advanced wastewater treatment for the removal of nitrogen is a two part process that includes aerobically converting ammonium to nitrite then to nitrate, or nitrification, then anaerobically converting nitrate to nitrogen gas, or denitrification (“Nitrogen Removal from Wastewater”; RI DEM, 2005). A common trend observed among upgraded facilities that utilize this process to remove nitrogen was a dramatic decrease in their ammonium loads with a large increase in their nitrate loads. This most notably occurred at the Bucklin Point, Smithfield, Warwick, and West Warwick facilities, all of which had significant reductions in ammonium loads with significant increases in nitrate loads. Additionally, the Warwick facility significantly reduced its nitrite load while its nitrate load significantly increased. This occurrence is most likely caused by the nitrification-denitrification process described above (“Nitrogen Removal from Wastewater”; RI DEM, 2005). However, the nitrate loads of three out of the four previously mentioned facilities had quite substantial increases, some by several orders of magnitude. It could be speculated that the increase in nitrate

observed at these facilities is due to an insufficient holding time of wastewater that does not allow for effective denitrification of nitrate. When this phenomenon is evaluated by examining DIN ($\text{NH}_4^+ + \text{NO}_2 + \text{NO}_3$) discharge from facilities where it was most common, it was found that DIN discharge significantly decreased in almost all cases, meaning the ammonium reduction was greater than the nitrate increase. Despite this observation, the reduction of ammonium and nitrite and increase in nitrate is indicative that the process of advanced wastewater treatment is functioning properly (“Nitrogen Removal from Wastewater”; RI DEM, 2005).

The total nitrogen load per year from all facilities combined in 2007-2010 was almost 40% lower than the total nitrogen load per year from all facilities combined calculated for 2000-2003 by Nixon et al. (2008). This reduction is likely attributed to the completion of upgrades as completed facilities accounted for almost 90% of the total load reduction in 2007-2010. The Worcester facility alone accounts for about half of the total load reduction. However, it is difficult to tell if this large reduction is due to the upgrade or annual variation as this facility was completed very recently in 2009. However, the Bucklin Point facility showed a consistent year round total nitrogen reduction of about half, which accounts for almost 20% of the grand total load reduction. Additionally, this facility is in now compliance with Rhode Island General Law stating that wastewater treatment facilities must reduce their nitrogen load by 50% (Section 46-12-2).

It should be noted that the Warwick facility has also consistently shown a significant reduction of its total nitrogen load, but due to the large flood in 2010, which overwhelmed all facilities on the Pawtuxet River (Warwick, Cranston, and

West Warwick), it is not in compliance with Rhode Island General Law. However, prior to flooding in 2010, the Warwick facility was in compliance with Rhode Island General Law with an annual nitrogen reduction of about 50% (Section 46-12-2). The Cranston and West Warwick facilities follow a similar reduction pattern but neither are in compliance either annually or seasonally, with or without the flood.

The total phosphorus load per year from all facilities combined in 2007-2010 was about 30% less than the total phosphorus load per year from all facilities combined calculated for 2000-2003 by Nixon et al. (2008). This reduction is largely due to the efforts of upgraded facilities to remove phosphorus from their effluent as they accounted for over 90% of the grand total phosphorus load reduction. The most successful of these facilities were the Smithfield, Cranston, Warwick, and Worcester facilities, which had consistent reductions of about 90%, 70%, 60%, and 50%, respectively, year round. Of those facilities, the Smithfield, Cranston, and Warwick facilities have phosphorus permits issued. The reductions of the Worcester, Smithfield, and Cranston facilities are especially noteworthy as they are the largest and third largest facilities on the Blackstone River and largest on Pawtuxet River.

Several facilities on the rivers that drain to Narragansett Bay showed significant decreases in their average annual total nitrogen and total phosphorus loads after their upgrades were completed. Phosphorus is essential to river ecosystems as it is the limiting nutrient for primary productivity (Kelly 2001); therefore, facilities located on rivers in the Narragansett Bay watershed also focused on removing phosphorus from their effluent (RI DEM 2005). As mentioned earlier, the Worcester, Woonsocket, and Smithfield facilities on the Blackstone River had large decreases in

their total phosphorus loads. The Cranston, Warwick, and West Warwick facilities located on the Pawtuxet River also had large reductions in their total phosphorus loads. On the Ten Mile River, the North Attleboro and Attleboro facilities both largely reduced their total phosphorus loads. Although they were not as great, most of these river facilities also had reductions in their total nitrogen loads. However, it is very difficult to tell the impact that these reductions will have on the overall Narragansett Bay ecosystem as only about 50% of river phosphorus loads reach Narragansett Bay proper (Nixon et al., 1995). Attenuation of sewage phosphorus in the Blackstone River removes about 25% of the total phosphorus load discharged (Nixon et al., 2008). Additionally, phosphorus reaching Narragansett Bay from the Pawtuxet and Ten Mile Rivers may not be purely from sewage as it has been observed that there are additional sources of phosphorus, such as storm water runoff, in these rivers (Nixon et al., 2008; RI DEM 2005). Discharged sewage nitrogen also has the ability to be released to the atmosphere through denitrification or stored in river sediments, which makes it difficult to determine the source of nitrogen entering Narragansett Bay (Nixon et al., 2008). Therefore, upgrades completed on rivers may have an immediate impact on the river in which they discharged but the impact they have on the Narragansett Bay system may be less apparent as of yet.

The wastewater treatment facilities examined in this study commonly enforce limits for nitrogen and/or phosphorus concentrations in effluent prior to discharge during the summer months of May to October, or the active season as it is referred to in this study (RI DEM 2005). Concentration limits are enforced during this time period because it is thought that greatest reductions will occur during this time

reducing primary productivity so that benthic dissolved oxygen concentrations will rise to prevent anoxia (Nixon et al., 2008). It was anticipated that upgraded facilities would dramatically reduce their loads during the active season because the process of advanced wastewater treatment is temperature dependent (“Nitrogen Removal from Wastewater”). Warmer temperatures increase the efficiency of the nitrification-denitrification process meaning increased nitrogen reduction (“Nitrogen Removal from Wastewater”). However, no significant difference was observed during the active and inactive seasons. Since there was no significant difference between load reductions during the two seasons, there may be other factors that influence the efficiency of nitrogen reduction. It could be speculated that there is no significant difference in seasonal loads because the underground cement wastewater holding tanks are well insulated and seasonal changes in the surrounding environment have little effect on the temperature of the wastewater. Whatever the reason may be, inactive season load reductions from upgraded facilities have been more efficient than originally expected.

Although facility upgrades accounted for the majority of the large nitrogen and phosphorus reductions to Narragansett Bay, it is difficult to tell the full effect these reductions will have on the Narragansett Bay ecosystem. Management strategies aim to reduce nutrient concentrations as much as possible to return Narragansett Bay to its condition before human nutrient introduction (Nixon et al., 2008). However, Narragansett Bay is a very dynamic ecosystem that has been affected by a multitude of environmental changes and natural fluctuations since the human introduction of nutrients, such as temperature changes, freshwater input, and chlorophyll

concentrations (Nixon et al., 2008; Pilson 2008; Hamburg et al., 2008; Duarte et al., 2009). These changes have shifted the original state of Narragansett Bay to something different that may not be attainable even with reductions in nutrient inputs (Duarte et al., 2009; Oviatt et al., 1984). A complete reversal may not occur once wastewater treatment facilities reduce their nutrient input or it may occur to a lesser degree after several years (Duarte et al., 2009). Therefore, the original state of Narragansett Bay should not be the ultimate goal of reducing nitrogen and phosphorus loads from wastewater treatment facilities, yet maintaining the Narragansett Bay ecosystem in a state that provides worthwhile ecosystem services (Duarte et al., 2009). Despite the frustration that Narragansett Bay may not revert to its original state, it has been argued that Narragansett Bay has been stable for almost 100 years and completely removing all nutrients could in fact be detrimental (Nixon et al., 2008). However, reasonable nitrogen and phosphorus reductions in wastewater treatment facility effluent are important, as they will prevent any further degradation to the Narragansett Bay ecosystem.

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Table B-1. All WWTF included in this study are listed below by the body of water into which they discharge. Facilities that have upgraded to advanced wastewater treatment for the removal of nitrogen are noted below with the year in which they upgraded. All parameters included in the RI DEM dataset are listed below. The frequency of measurements for each parameter is listed in its respective column followed by the years of data included in the RI DEM dataset. “Active” refers to the active season, May to October, and “inactive” refers to the inactive season, November to April. **W = weekly, 3W = 3x/week, 2W = 2x/week, M = monthly, 2M = 2x/month.**

<i>Discharges to:</i>	Upgraded	TN	NH₄⁺	NO₂ & NO₃	TP
Narragansett Bay					
Field's Point	Sched. 12/2013	W 2002-05 3W 2005-10	2W 2002-10	W 2002-05 3W 2005-10	W 2002-10
Bucklin Point	2006	W 2002-05 3W 2005-10	2W 2002-10	W 2002-05 3W 2005-10	W 2002-10
Newport			<i>No data</i>		
East Providence	Sched. 9/2012	W 2002-10	M 2002-07 W 2007-10	W 2002-10	W 2002-04
Bristol		2M 2000-10	2M 2001-04	2M 2000-10	2M 2000-04
Warren	Sched. 12/2015	W 2003-04	W 2003-04	W 2003-04	
East Greenwich	3/2006	W active 2M inactive, 2000-10		W active 2M inactive, 2000-10	
Quonset Point		2000-04	2000-04	2000-04	2000-04
Jamestown		2001-03	2000	2000-03	2000
Fall River, MA			<i>No data</i>		
Blackstone River	Upgraded	TN	NH₄⁺	NO₂ & NO₃	TP
Worcester	2009	3W active 2W inactive, 2009-10	3W 2000-02, 2009-10		3W Apr-Oct 2000-02, 2009-10, M Nov-Mar 2000-08, 2W Nov-Mar 2008-10
Woonsocket	2002	3x/week 2000- 10, M Nov- Mar 2008-10	3W Jun-Oct W Nov-May 2000-10	3W 2001-10 M Nov-Mar 2008-10	3W 2000-10
Smithfield	6/2006	3W active M inactive	3W Jun-Oct W Nov-May	3W 2000-07 M inactive	3W Jun-Sep W Oct-May

Grafton		2007-10	2000-10	2007-10	2001-10
Millbury			<i>No data</i>	<i>No data</i>	
Northbridge			<i>No data</i>	<i>No data</i>	
Burrillville	2001	W 2000-10 3W active 2006-10	W 2000-10 3W active 2006-10	W 2000-10 3W active 2006-10	W 2000-10 3W active 2006-10
Hopedale			<i>No data</i>	<i>No data</i>	
Leicester			<i>No data</i>	<i>No data</i>	
Douglas			<i>No data</i>	<i>No data</i>	
Upton			<i>No data</i>	<i>No data</i>	
Ten Mile River	Upgraded	TN	NH₄⁺	NO₂ & NO₃	TP
Attleboro		3W active W inactive 2008-10	3W active 2W inactive 2000-10		3x/week 2000-10, 2W Nov-Mar 2009-2010
North Attleboro	2008	3W active W inactive 2007-10	2W 2000-10		2x/week 2000-10, 3W Apr-Oct 2008-2010
Pawtuxet River	Upgraded	TN	NH₄⁺	NO₂ & NO₃	TP
Cranston	1/2006	W Jun-Sep 2M Oct-May 2000-10	W 2000-10	W Jun-Sep 2M Oct-May 2000-10	W 2000-10
West Warwick	7/2005	W Jun-Oct 2M Nov-May 2000-10	W 2000-10	W Jun-Oct 2M Nov-May 2000-10	W 2000-10
Warwick	11/2004	W Jun-Oct 2M Nov-May 2000-10	W 2000-10	W Jun-Oct 2M Nov-May 2000-10	W 2000-10
Taunton River	Upgraded	TN	NH₄⁺	NO₂ & NO₃	TP
Brockton			<i>No data</i>	<i>No data</i>	
Taunton			<i>No data</i>	<i>No data</i>	
Somerset			<i>No data</i>	<i>No data</i>	

Table B-2. The average value from 2007-2010 for each parameter discharged per year from each facility in the Narragansett Bay watershed is displayed below. All values with the exception of flow are in millions of moles per year. Flow values are in thousands of cubic meters per day. "NO₂ + NO₃" is the sum of nitrite (NO₂) and nitrate (NO₃). "DIN" is the sum of ammonium (NH₄⁺), nitrite (NO₂), and nitrate (NO₃). Nutrients were not monitored at the Newport facility. * indicates that parameter values were calculated by scaling previous values, 2000-2003 (Nixon, 2008), by the population change from 2000-2010.

<i>Discharges to:</i>	Flow	NH₄⁺	NO₂	NO₃	NO₂+NO₃	DIN	TN	TP
Narragansett Bay								
Field's Point	168.3	37.40	3.23	5.84	9.07	46.47	63.50	3.19
Bucklin Point	80.9	1.27	0.23	13.70	13.93	15.20	18.90	3.14
Newport	34.8	<i>Nutrients</i>	<i>not</i>	<i>monitored</i>			10.50	0.59
East Providence	26.9	3.28	0.13	2.93	3.06	6.34	7.53	0.52
Bristol	13.5	1.94	0.17	1.93	2.10	4.04	6.27	0.18
Warren	7.3	1.35	0.02	0.22	0.24	1.59	1.86	0.05
East Greenwich	4.1	0.86	0.01	0.46	0.47	1.33	0.87	0.42
Quonset Point	1.8		0.04	0.46	0.50		0.73	0.10
Jamestown		0.05	0.00	0.10	0.10	0.15	0.16	0.02
Fall River*		22.90			2.05	24.95	33.20	1.15
Total		69.04	3.83	25.64	31.51	100.06	143.52	9.37
Blackstone River								
Worcester ¹	117.7	3.01			11.01	14.02	16.60	1.07
Woonsocket	28.3	0.97	0.06	3.24	3.30	4.27	4.99	0.56
Smithfield	7.6	0.18	0.07	1.04	1.11	1.29	1.46	0.02
Grafton*		2.00			1.34	3.34	3.28	0.14
Millbury*		1.96			0.46	2.42	2.44	0.24
Northbridge*		1.48			0.43	1.91	3.06	0.17
Burrillville	3.2	0.99	0.07	0.23	0.30	1.29	1.40	0.02
Hopedale*		0.13						0.02
Leicester*		0.03						0.00
Douglas*		0.10			0.05	0.14	0.20	0.02
Upton*		0.07			0.01	0.08	0.12	0.00
Total		10.92	0.20	4.51	18.00	28.75	33.55	2.27
Ten Mile River								
Attleboro	15.4	0.45					7.67	0.02
North Attleboro	16.2	0.41					2.98	0.03
Total		0.86					10.65	0.06
Pawtuxet River								
Cranston	42.9	3.96	0.12	5.98	6.10	10.06	12.50	0.43
West Warwick	22.7	1.01	0.36	5.37	5.73	6.74	8.03	0.45
Warwick	18.9	1.43	0.06	2.39	2.45	3.88	4.75	0.21
Total		6.40	0.54	13.74	14.28	20.68	25.28	1.09
Taunton River								
Brockton*		15.72			11.84	27.56	36.51	0.83
Taunton*		2.04					4.18	0.29
Somerset*		2.68			0.76	3.44	8.28	0.17
Total		20.43			12.60	30.99	48.97	1.28
GRAND TOTAL							262.0	14.1

¹ Flow value is the average of flows from 2009-2010 instead of 2007-2010 as there was no flow data available for 2007 and 2008.

Table B-3. Average annual and active season total nitrogen concentrations during 2000-2004 and 2007-2010 for all facilities with nitrogen concentrations available. Nitrogen limits, when applicable, are listed below the average concentrations for each time period. All values are in mg/L. Gray shading indicates compliance with the limit, while yellow shading indicates non-compliance with limits currently in effect.

<i>Discharges to:</i>	ANNUAL		ACTIVE	
	2000-2004	2007-2010	2000-2004	2007-2010
Narragansett Bay				
Field's Point	14.8	13.6	14.8	13.5
	5.0	mg/L ^a	5.0	mg/L ^a
Bucklin Point	15.4	7.8	15.9	7.6
	8.0	mg/L ^b	8.0	mg/L ^b
East Providence	15.3	11.3	15.0	11.8
	5.9	mg/L ^c	5.9	mg/L ^c
Bristol	24.6	25.0	27.6	27.0
Warren	12.7	no data	14.6	no data
			5.0	mg/L ^d
East Greenwich	10.5	8.1	9.8	3.8
	5.0	mg/L	5.0	mg/L
Quonset Point	16.3	no data	16.7	no data
Jamestown	7.7	no data	7.7	no data
Blackstone River				
Worcester	no data	6.0	no data	6.3
	5.0	mg/L ^e	5.0	mg/L ^e
Woonsocket	17.0	6.7	16.9	5.9
	5.0	mg/L ^f	5.0	mg/L ^f
Smithfield	19.3	7.9	19.3	7.9
	max	extent	max	extent
Burrillville	16.8	15.8	14.4	10.4
	max	extent	max	extent
Ten Mile River				
Attleboro	no data	21.8	no data	23.5
	8.0	mg/L ^e	8.0	mg/L ^e
North Attleboro	no data	6.8	no data	6.5
	8.0	mg/L ^g	8.0	mg/L ^g
Pawtuxet River				
Cranston	16.2	11.0	15.0	8.0
	8.0	mg/L	8.0	mg/L
West Warwick	15.3	13.5	15.4	10.6
	8.0	mg/L	8.0	mg/L
Warwick	20.5	9.6	19.0	9.4
	8.0	mg/L	8.0	mg/L

^a Planned to be completed 12/6/13.

^b Nitrogen limit of 5.0 mg/L planned to be completed 3/1/14.

^c Planned to be completed 9/1/12.

^d Nitrogen limits of 5.0 mg/L (May-Oct) and 14.3 mg/L (Nov-Apr) planned to be completed 12/1/15.

^e Was planned to be completed by the end of 2011.

^f Nitrogen limit of 3.0 mg/L planned to be completed 3/31/14.

^g Planned to be completed by the close of 2012.

Table B-4. Average annual and active season total phosphorus concentrations during 2000-2004 and 2007-2010 for all facilities with phosphorus concentrations available. Phosphorus limits, when applicable, are listed below the average concentrations for each time period. All values are in mg/L. Gray shading indicates compliance with the limit, while yellow shading indicates non-compliance with limits currently in effect.

<i>Discharges to:</i>	ANNUAL		ACTIVE	
	2000-2004	2007-2010	2000-2004	2007-2010
Narragansett Bay				
Field's Point	1.2	1.4	0.9	1.6
Bucklin Point	2.2	2.4	1.7	2.3
East Providence	2.6	<i>no data</i>	2.9	<i>no data</i>
Bristol	1.3	<i>no data</i>	1.3	<i>no data</i>
Warren	<i>no data</i>	<i>no data</i>	<i>no data</i>	<i>no data</i>
East Greenwich	13.5	<i>no data</i>	<i>no data</i>	<i>no data</i>
Quonset Point	<i>no data</i>	<i>no data</i>	<i>no data</i>	<i>no data</i>
Jamestown	4.7	<i>no data</i>	<i>no data</i>	<i>no data</i>
Blackstone River				
Worcester	1.4	0.6	1.5	0.9
Woonsocket	3.6	1.6	3.8	0.5
		1.0 mg/L ^a		1.0 mg/L ^a
Smithfield	3.2	0.2	3.2	0.2
		0.2 mg/L		0.2 mg/L ^b
Burrillville	0.8	0.6	0.9	0.7
Ten Mile River				
Attleboro	0.4	0.1	0.4	0.1
North Attleboro	0.7	0.1	0.7	0.1
Pawtuxet River				
Cranston	3.5	<0.1	3.5	0.7
		1.0 mg/L ^c		1.0 mg/L ^c
West Warwick	2.8	1.7	3.1	1.3
		1.0 mg/L ^d		1.0 mg/L ^d
Warwick	2.9	1.0	3.4	1.1
		1.0 mg/L ^e		1.0 mg/L ^e

^a Phosphorus limit of 0.1 mg/L planned to be completed 3/31/14.

^b Phosphorus limit planned for April – October as of 12/20/12.

^c Phosphorus limit of 0.1 mg/L planned to be completed 3/31/13.

^d Phosphorus limit of 0.1 mg/L planned to be completed 4/1/14.

^e Phosphorus limit of 0.1 mg/L planned to be completed 9/30/13.

Table B-5. Flow, nitrogen, and phosphorus discharged from rivers that drain to Narragansett Bay in 2003-2004 (Nixon, et al., 2008) and from 2008-2010. All flow values are in millions of cubic meters per day and nitrogen and phosphorus values are in millions of moles per year.

	2003-2004		2008-2010	
	N	P	N	P
Blackstone River				
<i>Mean Daily Flow</i>	2.57		3.14	
<i>Dissolved Inorganic</i>	68.88	1.69	67.32	2.48
<i>Total</i>	98.63	3.87	96.13	5.36 ^a
Pawtuxet River				
<i>Mean Daily Flow</i>	1.00		1.28	
<i>Dissolved Inorganic</i>	44.61	1.96	29.73	0.89
<i>Total</i>	59.29	3.61	42.60	1.63 ^a
Woonasquatucket River				
<i>Mean Daily Flow</i>	0.28		0.29	
<i>Dissolved Inorganic</i>	6.62	0.16	4.10	0.03
<i>Total</i>	8.59	0.32	5.72	0.07 ^a
Moshassuck River				
<i>Mean Daily Flow</i>	0.19		0.12	
<i>Dissolved Inorganic</i>	3.50	0.07	2.04	0.01
<i>Total</i>	4.77	0.13	2.68	0.02 ^a
Ten Mile River				
<i>Mean Daily Flow</i>	0.35		0.33	
<i>Dissolved Inorganic</i>	9.86	0.24	11.84	0.08
<i>Total</i>	14.07	0.81	14.39	0.27 ^a
Taunton River				
<i>Mean Daily Flow</i>	2.58 ^c		3.46	
<i>Dissolved Inorganic</i>	86.00 ^c	3.30 ^c	51.25	0.76
<i>Total</i>	117.00 ^c	5.30 ^c	82.09	1.22 ^b
Unmeasured Flow				
<i>Mean Daily Flow</i>	1.48 ^d		1.48 ^e	
<i>Dissolved Inorganic</i>	48.30	1.60	27.70	0.75
<i>Total</i>	66.50	3.10	39.80	1.65
GRAND TOTAL				
<i>Mean Daily Flow</i>				
<i>Dissolved Inorganic</i>	267.80	9.05	193.98	5.00
<i>Total</i>	368.90	17.13	283.41	2.87

^a Calculated from average ratio of inorganic to total phosphorus (Nixon, et al., 2008).

^b Calculated from the average of the average ratios of inorganic to total phosphorus (Nixon, et al., 2008).

^c Data from (Boucher, 1991) as presented in (Nixon, et al., 1995).

^d Based on calculation of area of gauged to ungauged river area by (Ries, et al., 1990) as modified by (Nixon, et al., 1995).

^e Based on Ries, et al., (1990) plus flow from 304 mi² of un-gauged flow in the Taunton basin.

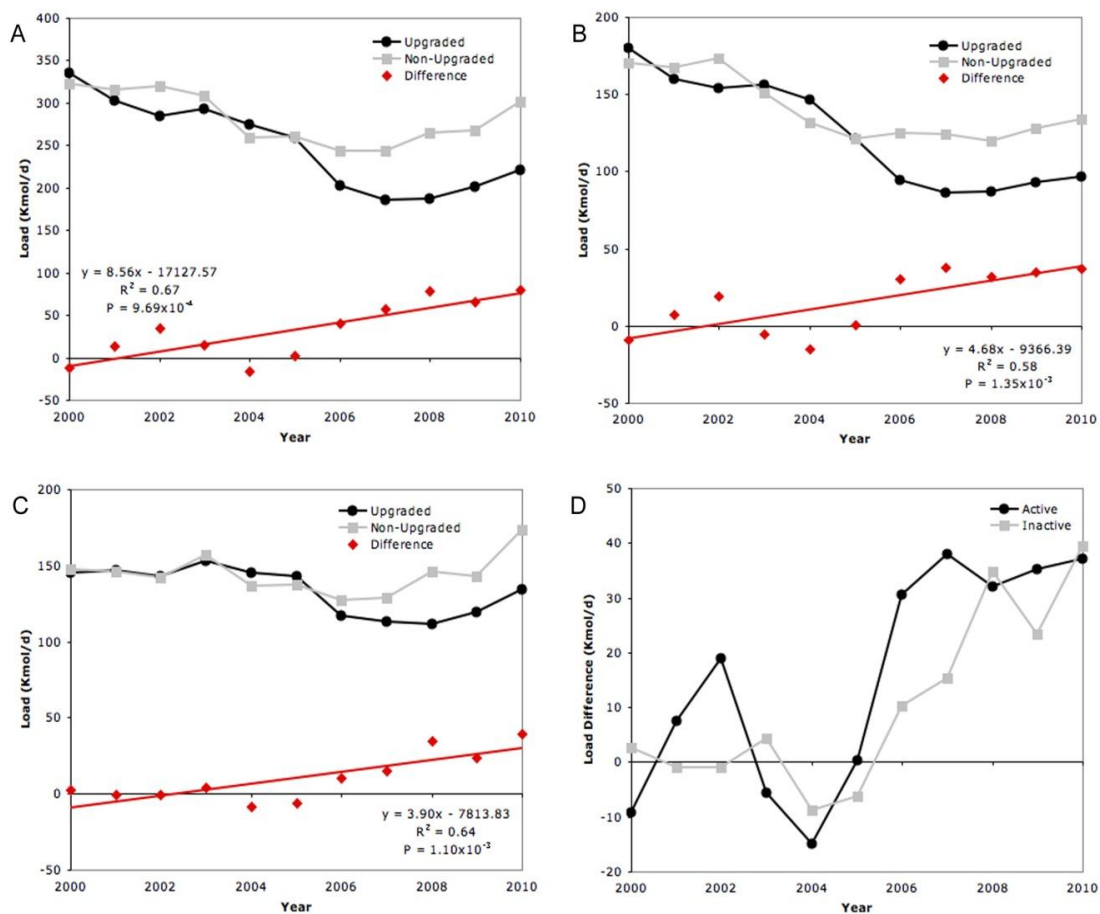


Figure B-1. Total nitrogen load from 2000-2010. (A) Annual total nitrogen load discharged from upgraded facilities (black) and non-upgraded facilities (gray) with the difference between the two (red). (B) Active season total nitrogen load discharged from upgraded facilities (black) and non-upgraded facilities (gray) with the difference between the two (red). (C) Inactive season total nitrogen load discharged from upgraded facilities (black) and non-upgraded facilities (gray) with the difference between the two (red). (D) The difference in total nitrogen between upgraded and non-upgraded facilities during the active season (black) and the difference in total nitrogen between upgraded and non-upgraded facilities during the inactive season (gray).

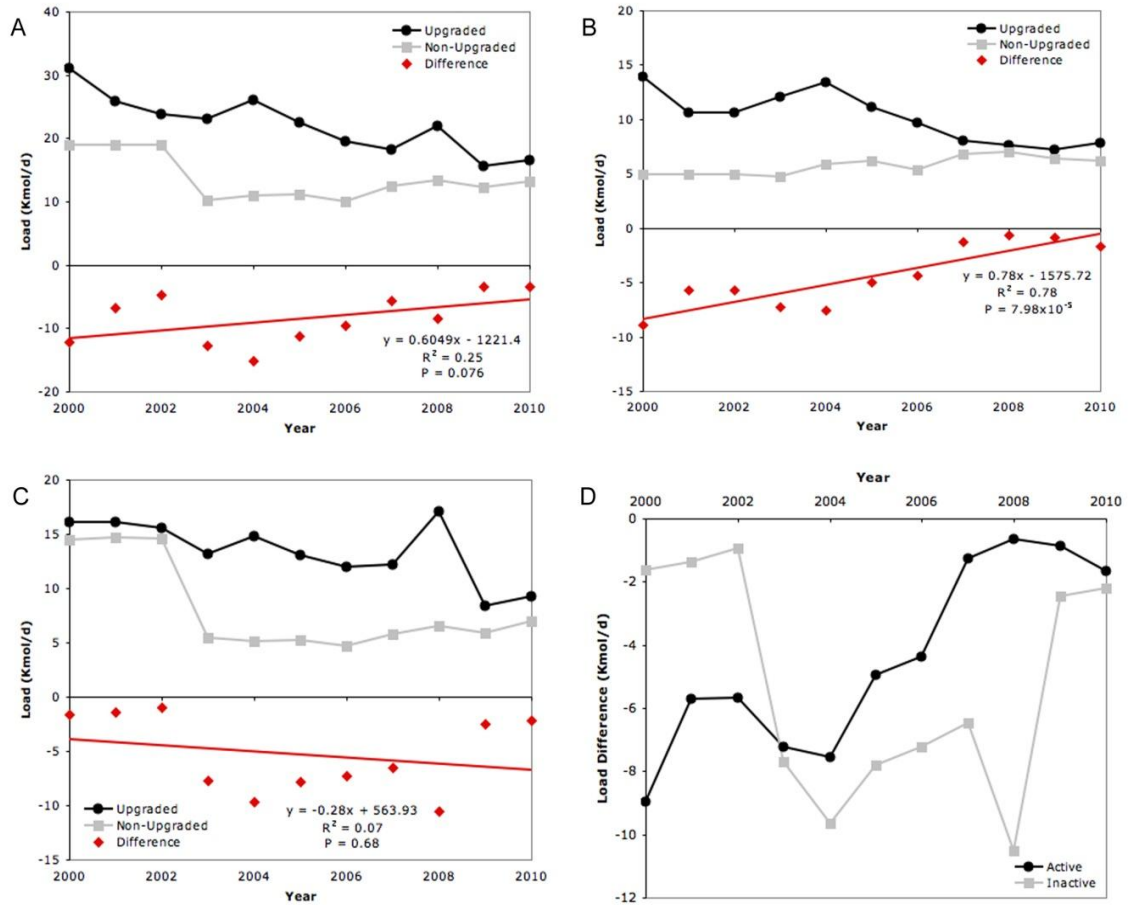


Figure B-2. Total phosphorus load from 2000-2010. (A) Annual total phosphorus load discharged from upgraded facilities (black) and non-upgraded facilities (gray) with the difference between the two (red). (B) Active season total phosphorus load discharged from upgraded facilities (black) and non-upgraded facilities (gray) with the difference between the two (red). (C) Inactive season total phosphorus load discharged from upgraded facilities (black) and non-upgraded facilities (gray) with the difference between the two (red). (D) The difference in total phosphorus between upgraded and non-upgraded facilities during the active season (black) and the difference in total phosphorus between upgraded and non-upgraded facilities during the inactive season (gray).

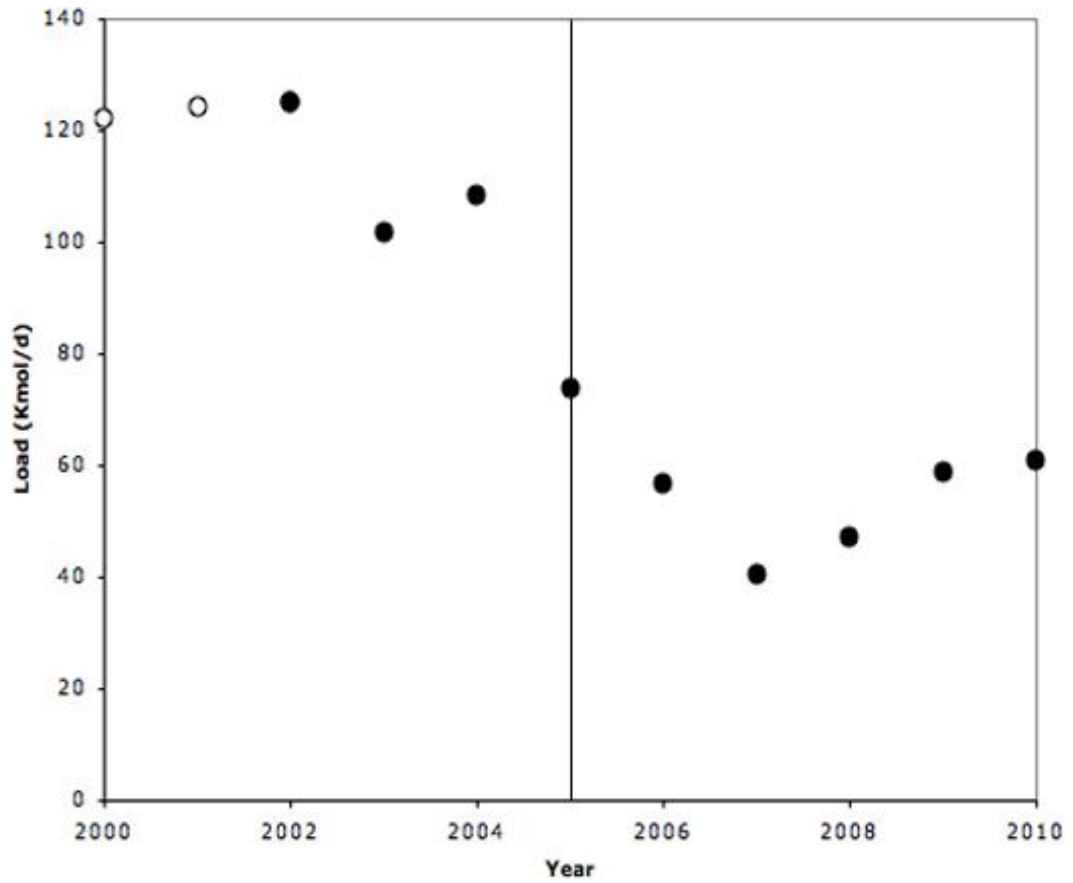


Figure B-3. Average annual total sewage nitrogen discharged from the Bucklin Point facility from 2000-2010. The vertical line represents upgrade completion in 12/2005. Open circles represent data that was estimated using population data and available load data. Closed circles represent actual data.

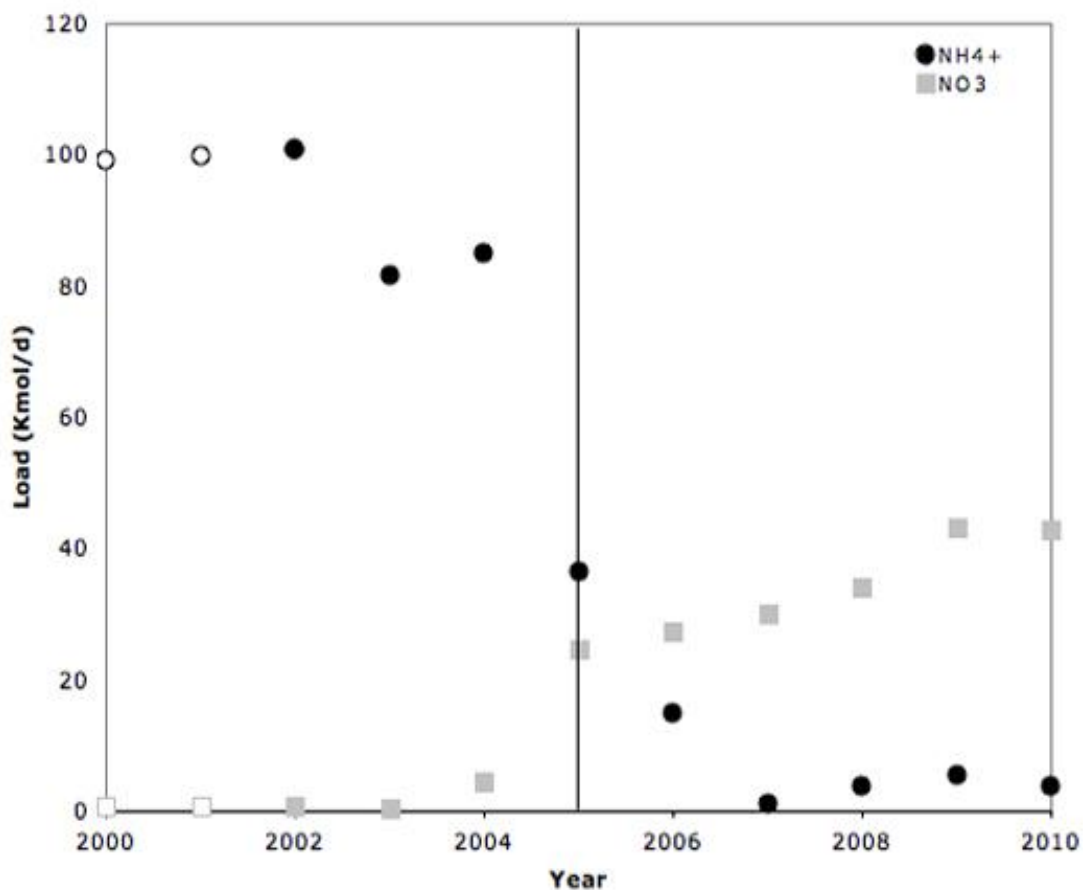


Figure B-4. Average annual sewage ammonium (NH_4^+) and nitrate (NO_3) discharged from the Bucklin Point facility from 2000-2010. The vertical line represents upgrade completion in 12/2005. Open points represent data that was estimated using population data and available load data. Closed points represent actual data.

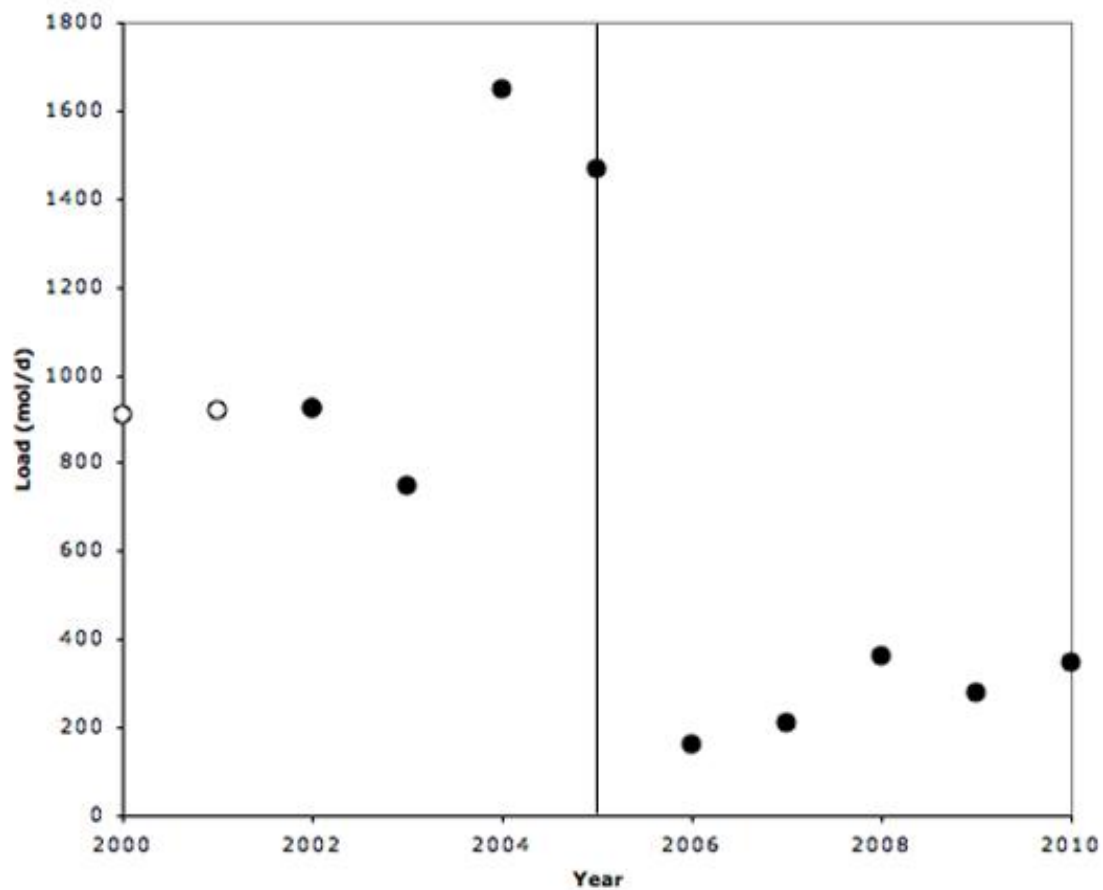


Figure B-5. Average active season sewage nitrite discharged from the Bucklin Point facility from 2000-2010. The vertical line represents upgrade completion in 12/2005. Open circles represent data that was estimated from population data and available load data. Closed circles represent actual data.

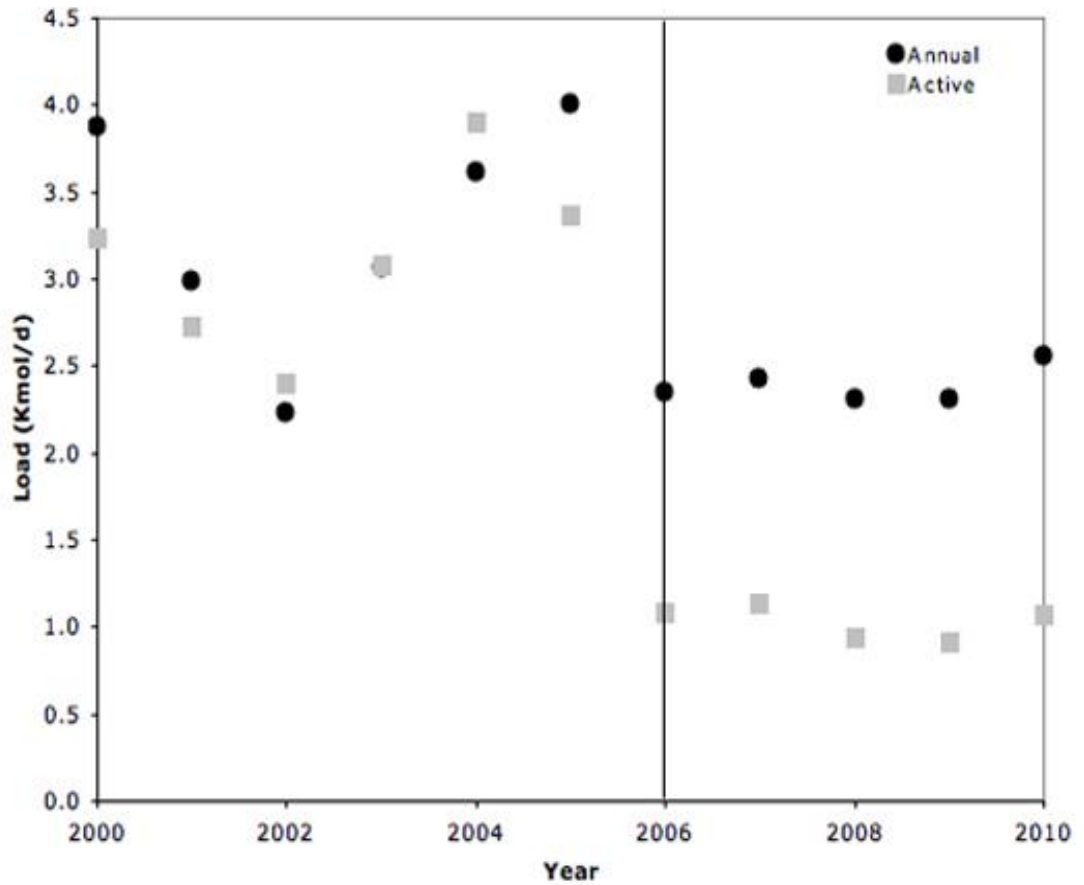


Figure B-6. Average annual and active season total sewage nitrogen load discharged from the East Greenwich facility from 2000-2010. The vertical line represents upgrade completion in 3/2006.

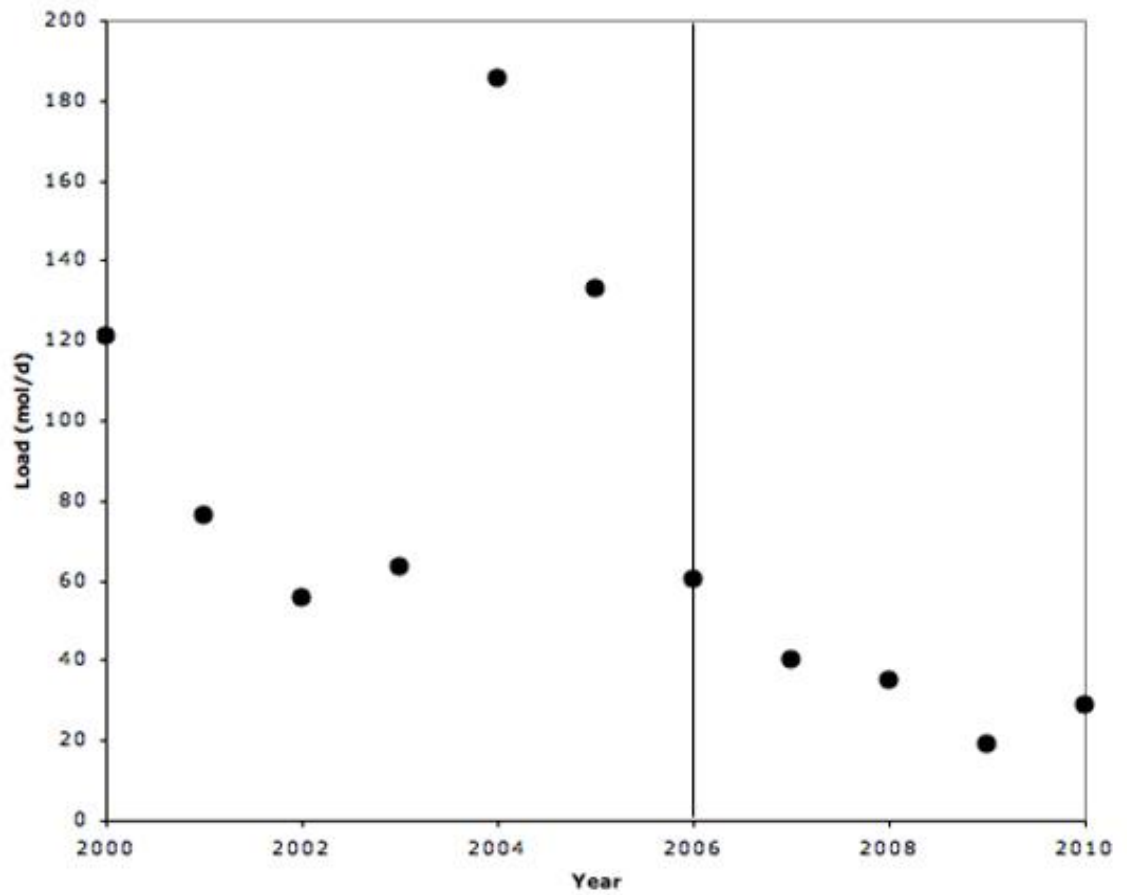


Figure B-7. Average annual sewage nitrite discharged from the East Greenwich facility from 2000-2010. The vertical line represents upgrade completion in 3/2006.

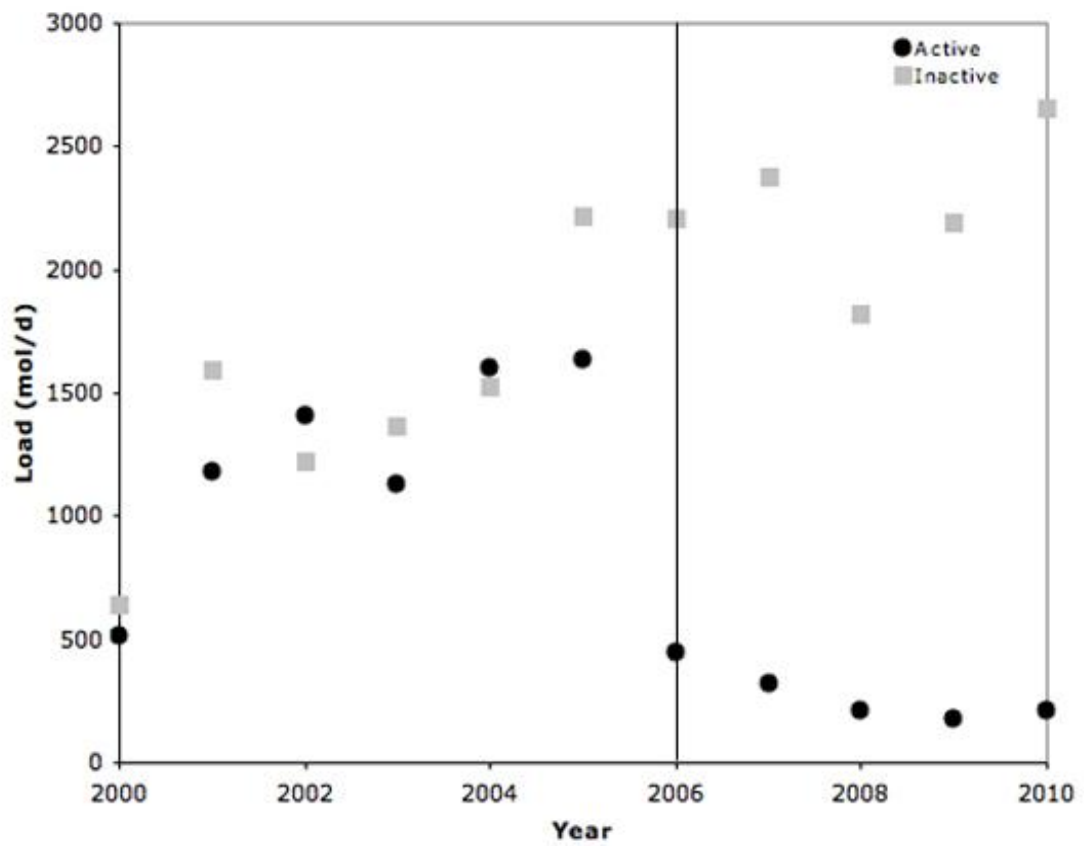


Figure B-8. Average active and inactive season sewage nitrate discharged from the East Greenwich facility from 2000-2010. The vertical line represents upgrade completion in 3/2006.

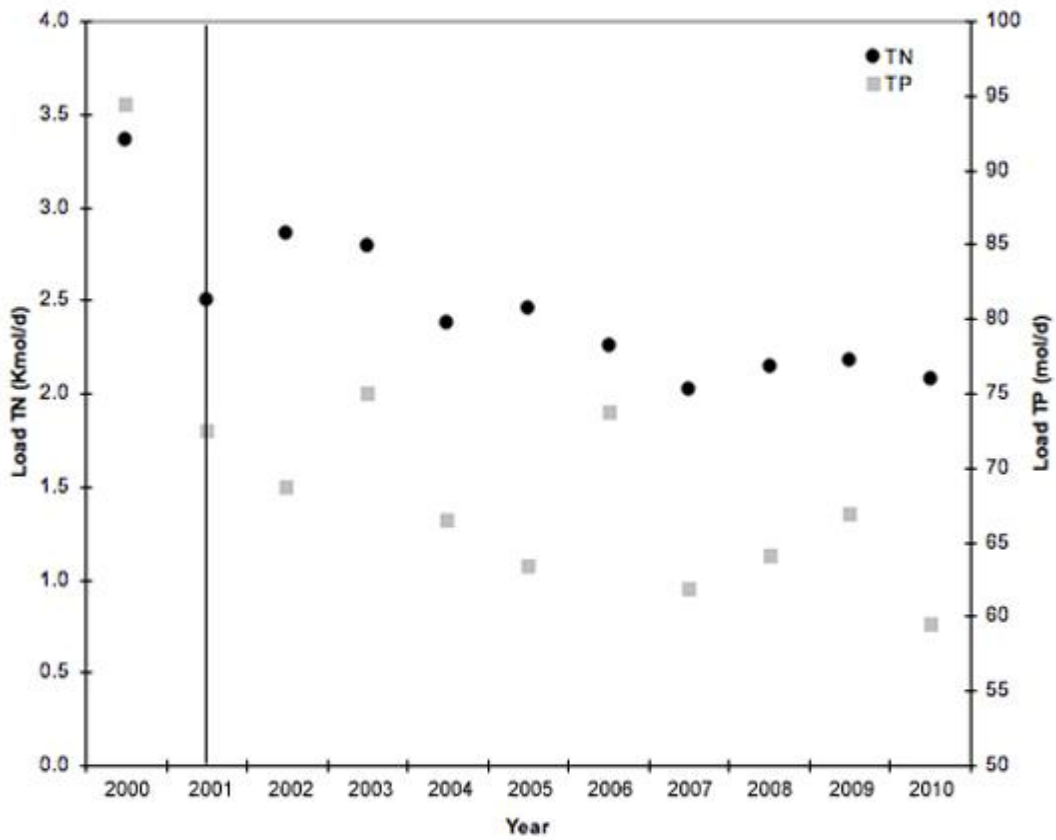


Figure B-9. Average active season total sewage nitrogen (TN) and phosphorus (TP) discharged from the Burrillville facility from 2000-2010. The vertical line represents upgrade completion during 2001.

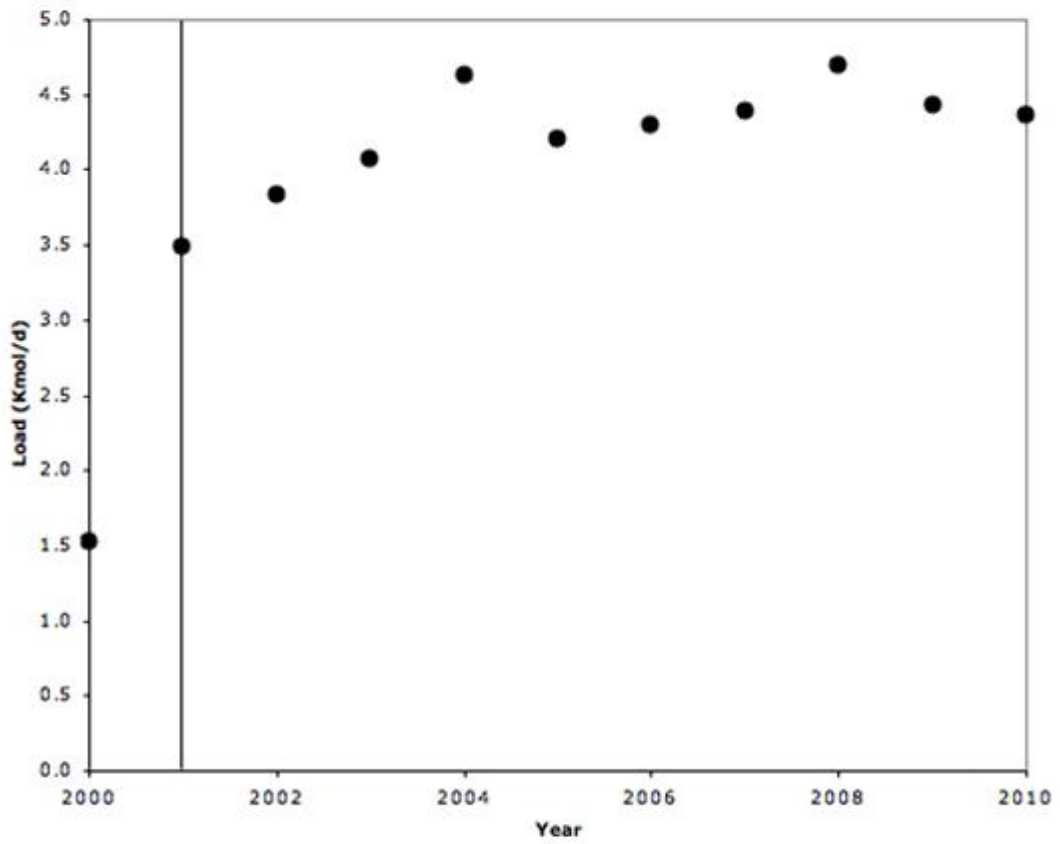


Figure B-10. Average inactive season sewage ammonium discharged from the Burrillville facility from 2000-2010. The vertical line represents upgrade completion during 2001.

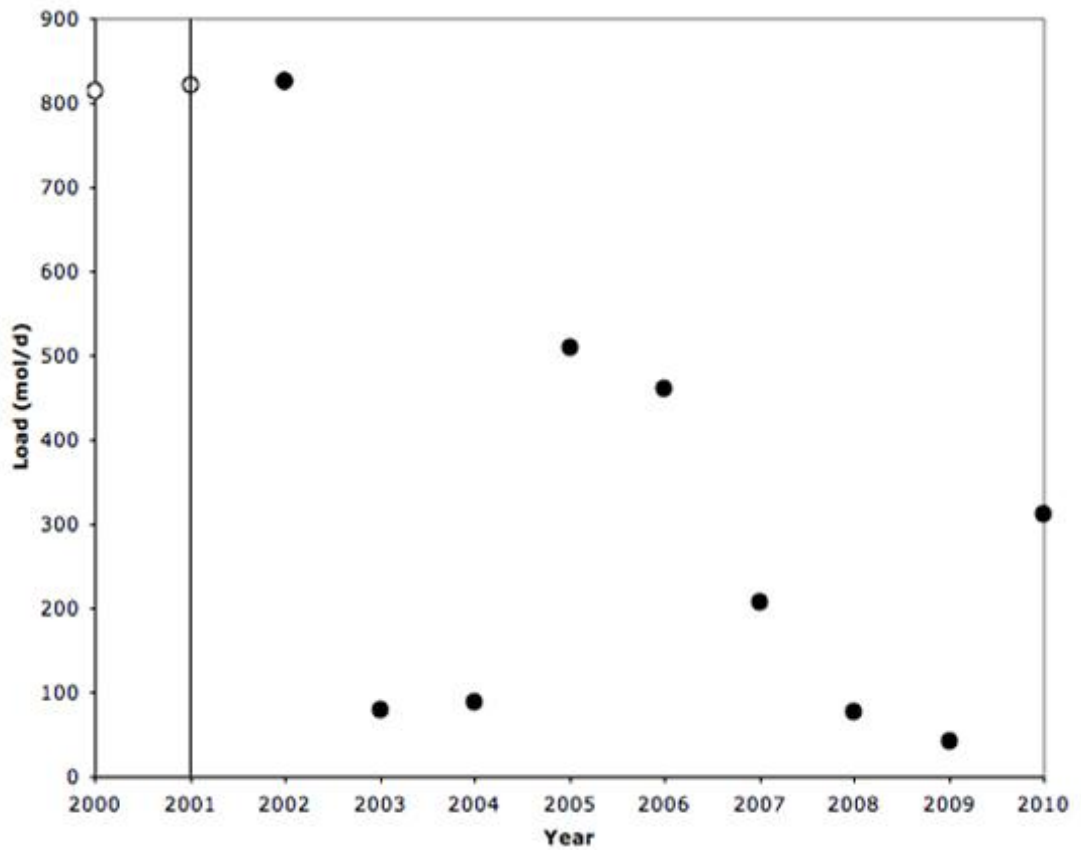


Figure B-11. Average annual sewage nitrite discharged by the Woonsocket facility from 2000-2010. The vertical line represents upgrade completion in 9/2001. Open circles represent data that was estimated with population data and available load data. Closed circles represent actual data.

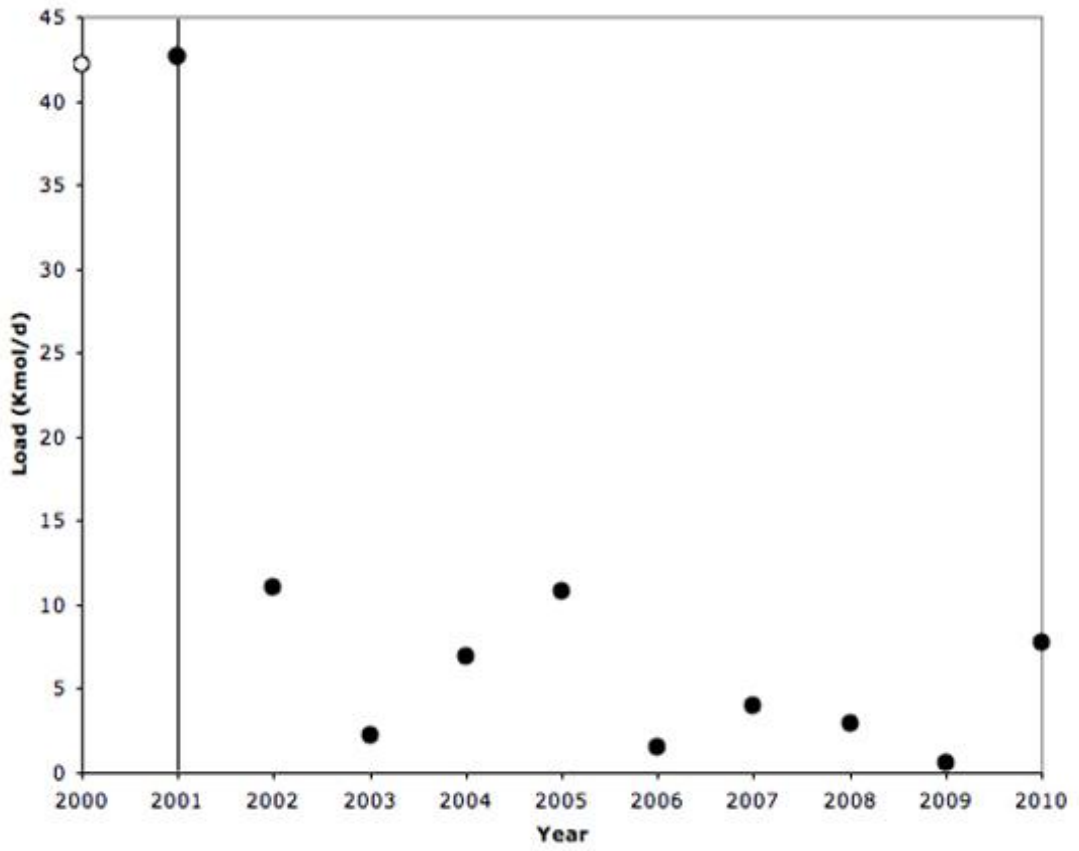


Figure B-12. Average inactive season sewage ammonium discharged from the Woonsocket facility from 2000-2010. The vertical line represents upgrade completion in 9/2001. Open circles represent data that was estimated from population data and available load data. Closed circles represent actual data.

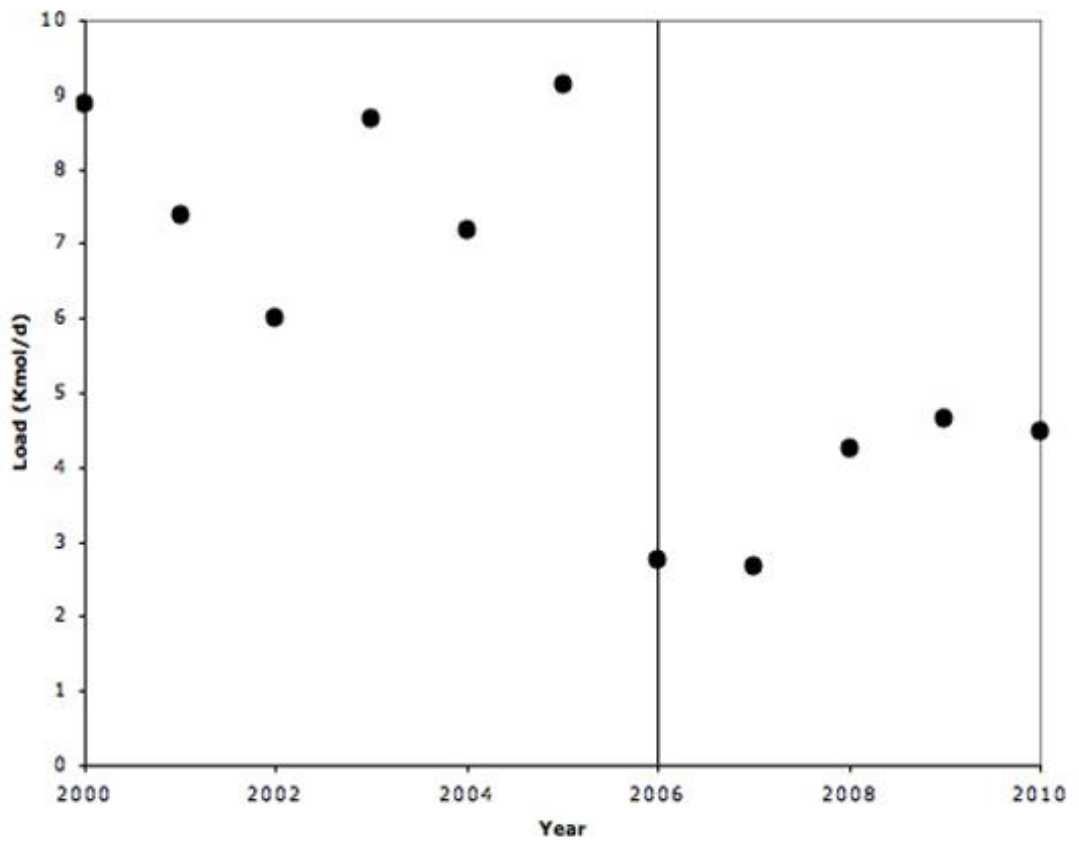


Figure B-13. Average annual total nitrogen discharged from the Smithfield facility from 2000-2010. The vertical line represents upgrade completion in 6/2006.

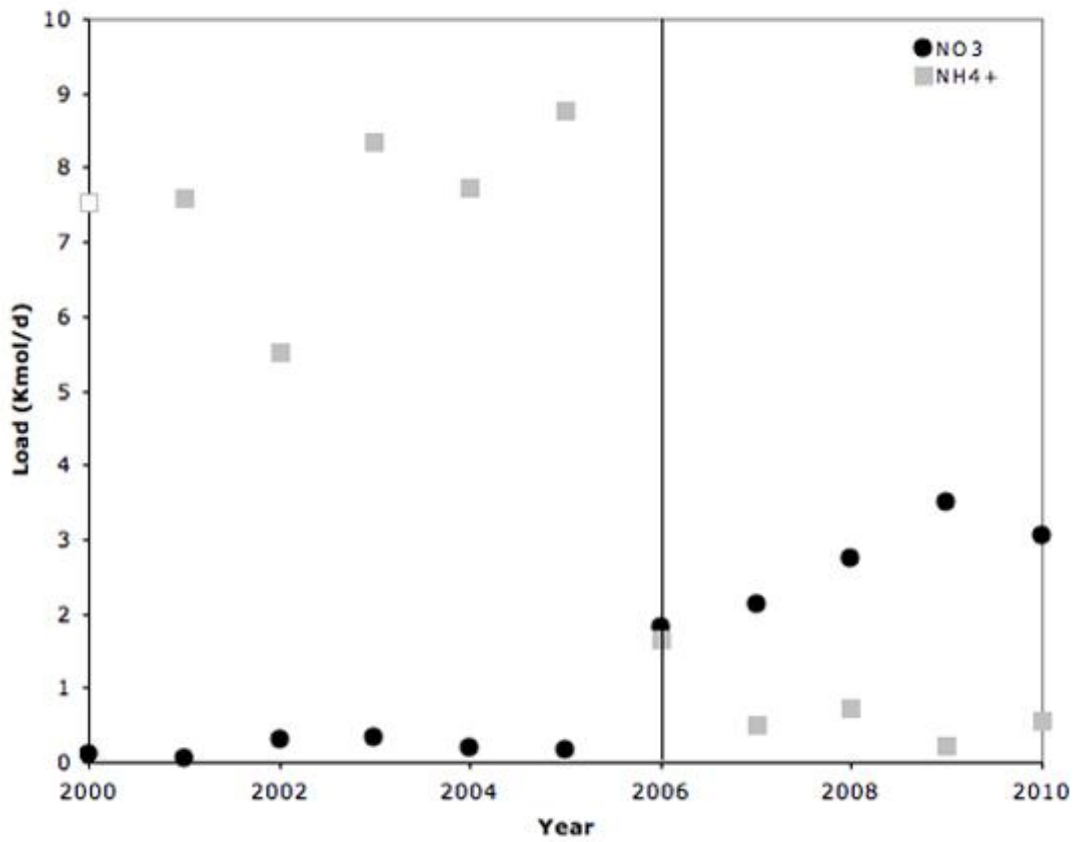


Figure B-14. Average annual ammonium (NH₄⁺) and nitrate (NO₃) loads discharged from the Smithfield facility from 2000-2010. The vertical line represents upgrade completion in 6/2006. Open points represent data that was estimated with population data and available load data. Closed points represent actual data.

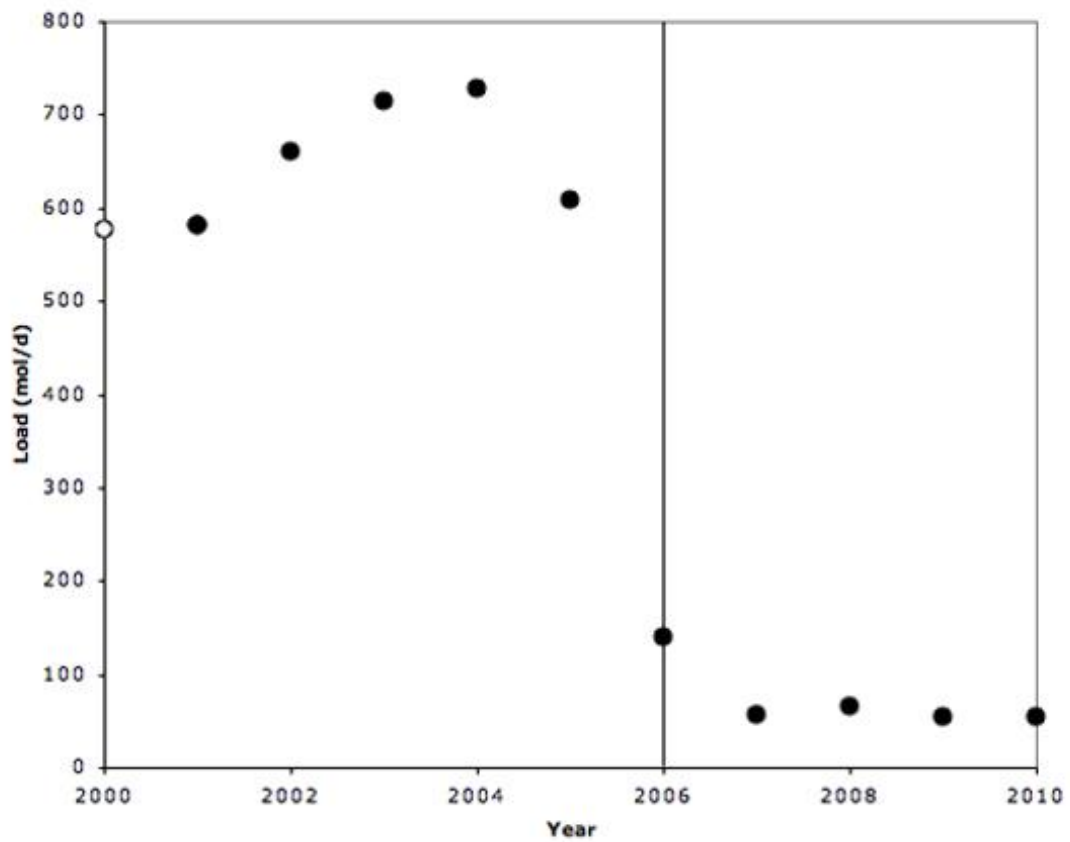


Figure B-15. Average annual total phosphorus discharged from the Smithfield facility from 2000-2010. The vertical line represents upgrade completion in 6/2006. Open circles represent data that was estimated from population data and available load data. Closed circles represent actual data.

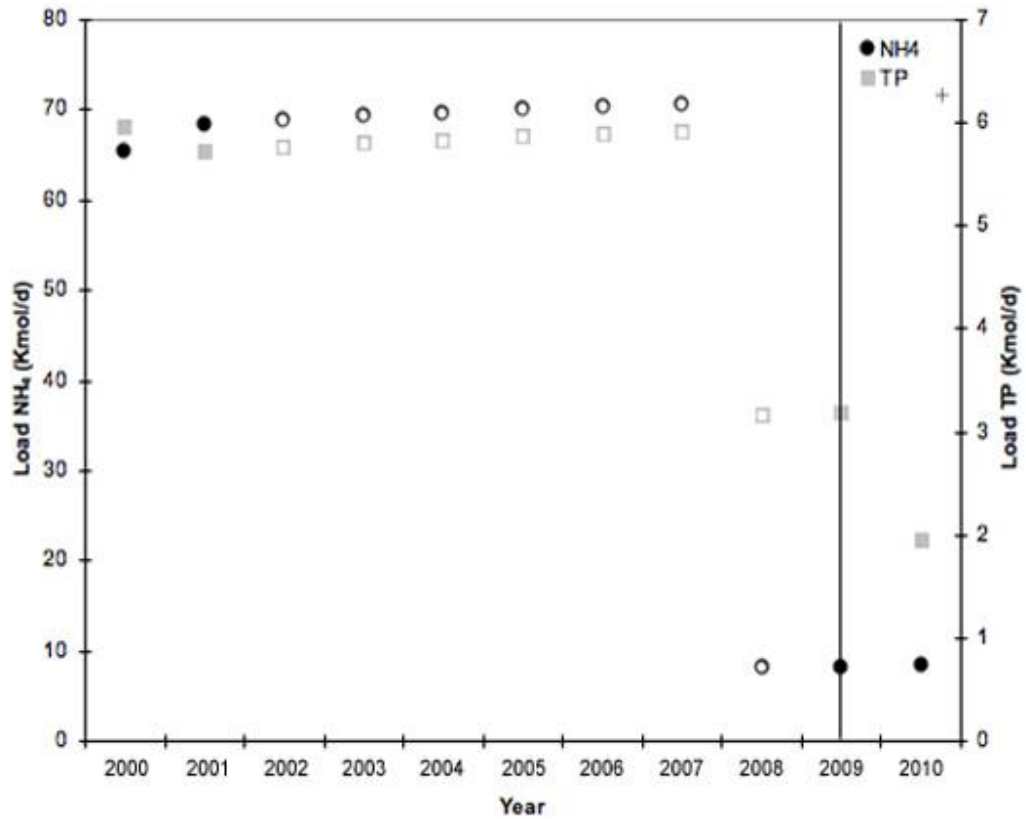


Figure B-16. Average annual sewage ammonium (NH₄⁺) and total sewage phosphorus discharged from the Worcester facility from 2000-2010. The vertical line represents upgrade completion in 2009. Open points represent data that was estimated with population data and available load data. Closed circles represent actual data.

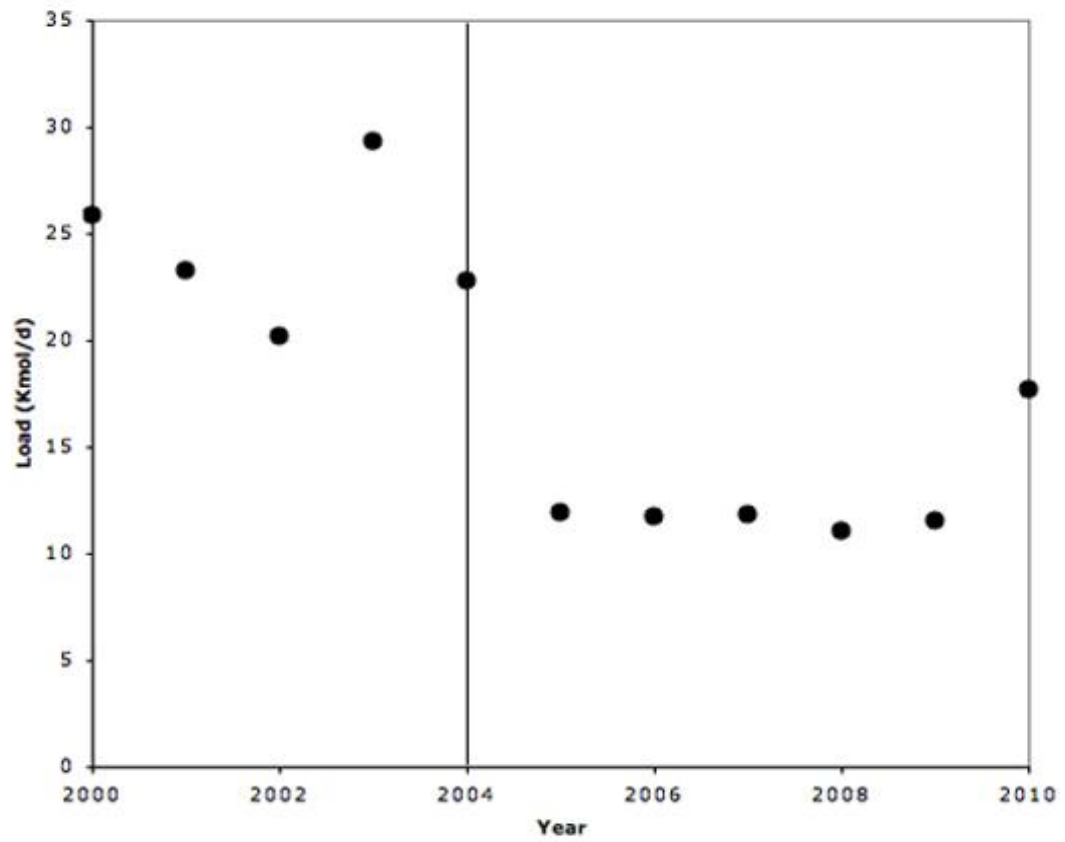


Figure B-17. Average annual total sewage nitrogen discharged from the Warwick facility from 2000-2010. The vertical line represents upgrade completion in 11/2004.

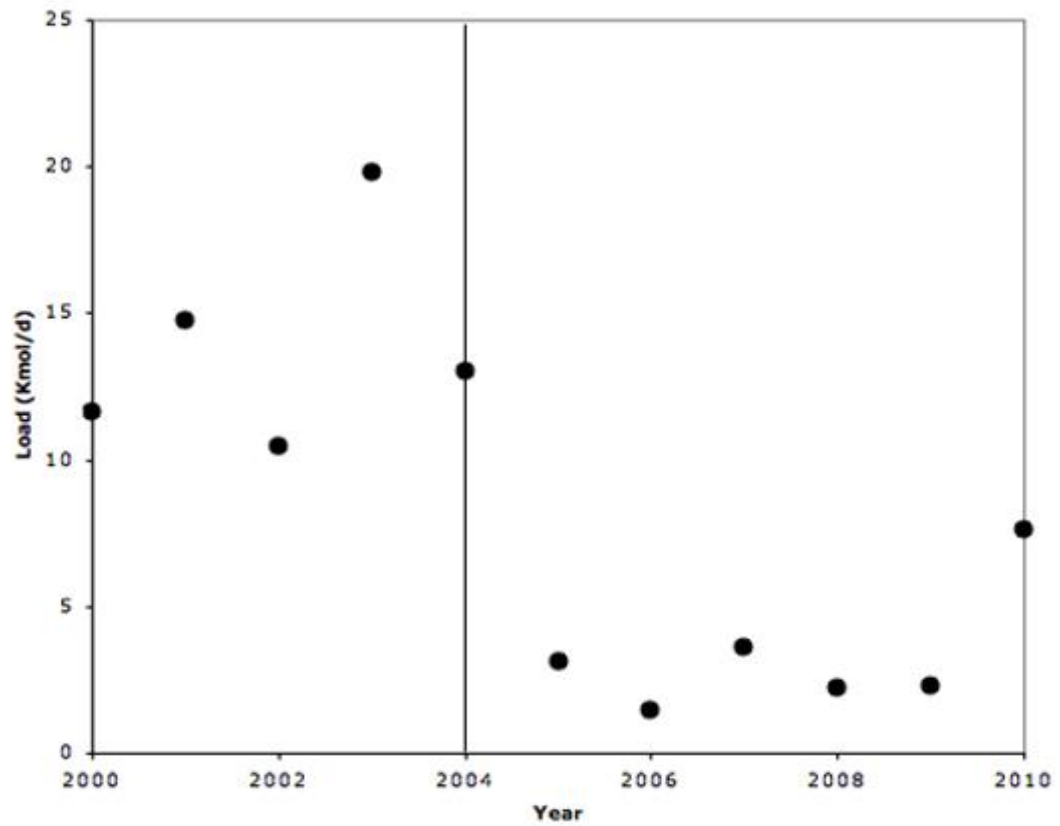


Figure B-18. Average annual sewage ammonium discharged from the Warwick facility from 2000-2010. The vertical line represents upgrade completion in 11/2004.

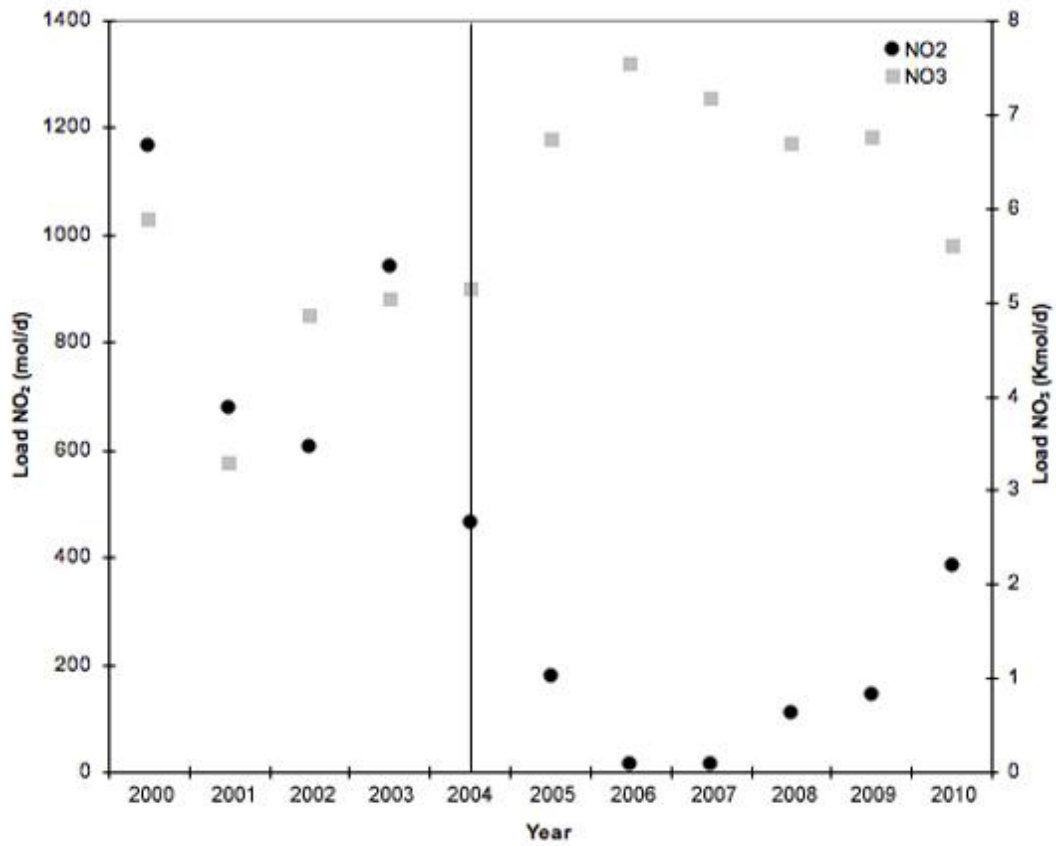


Figure B-19. Average annual nitrite (NO₂) load and nitrate (NO₃) load discharged from the Warwick facility from 2000-2010. The vertical line represents upgrade completion in 11/2004.

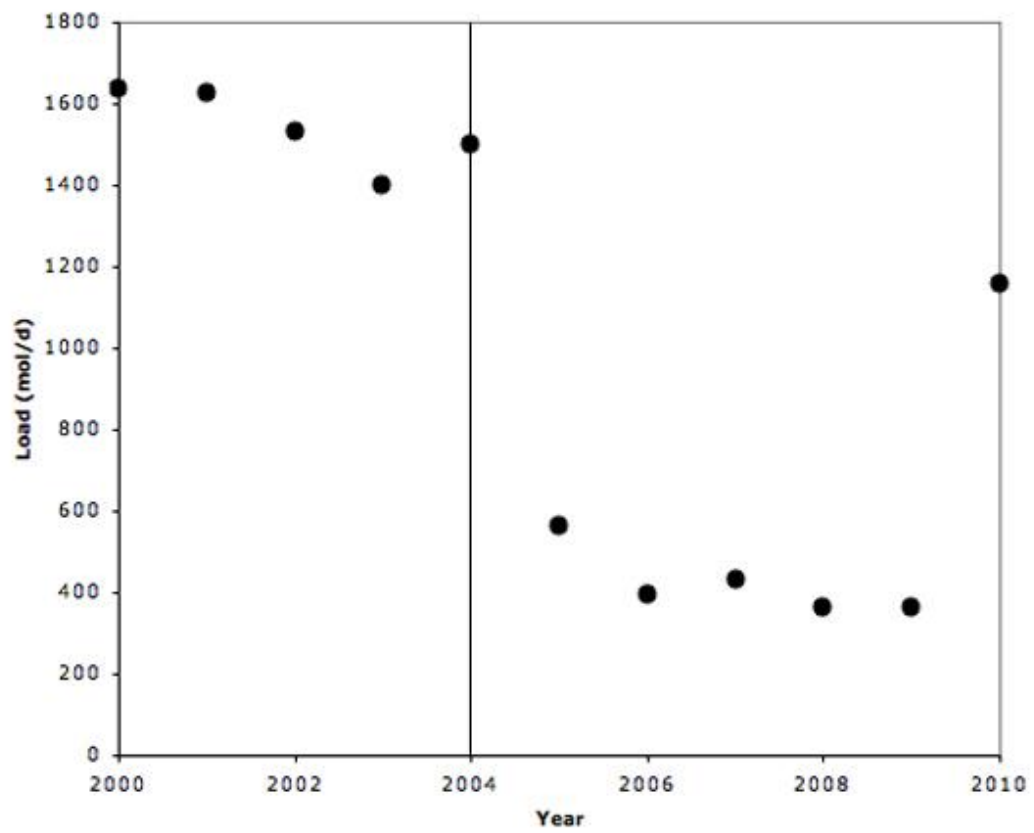


Figure B-20. Average annual total sewage phosphorus load discharged from the Warwick facility from 2000-2010. The vertical line represents upgrade completion in 11/2004.

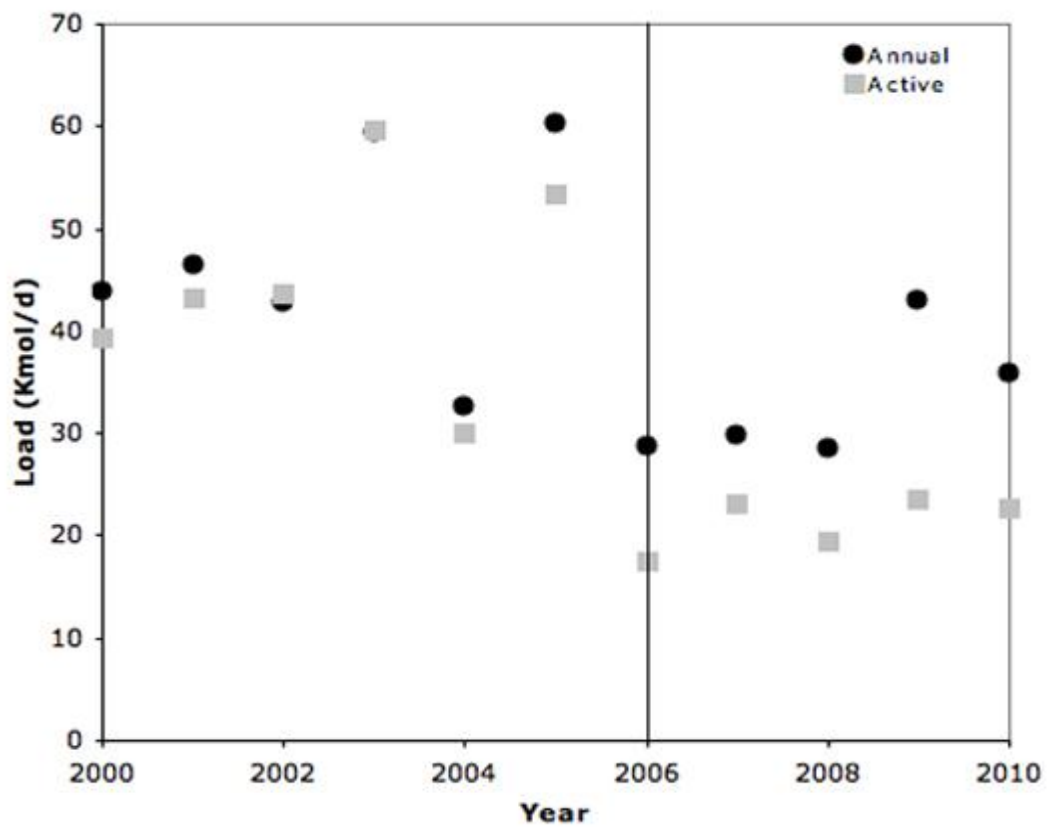


Figure B-21. Average annual and active season total nitrogen discharged from the Cranston facility from 2000-2010. The vertical line represents upgrade completion in 1/2006.

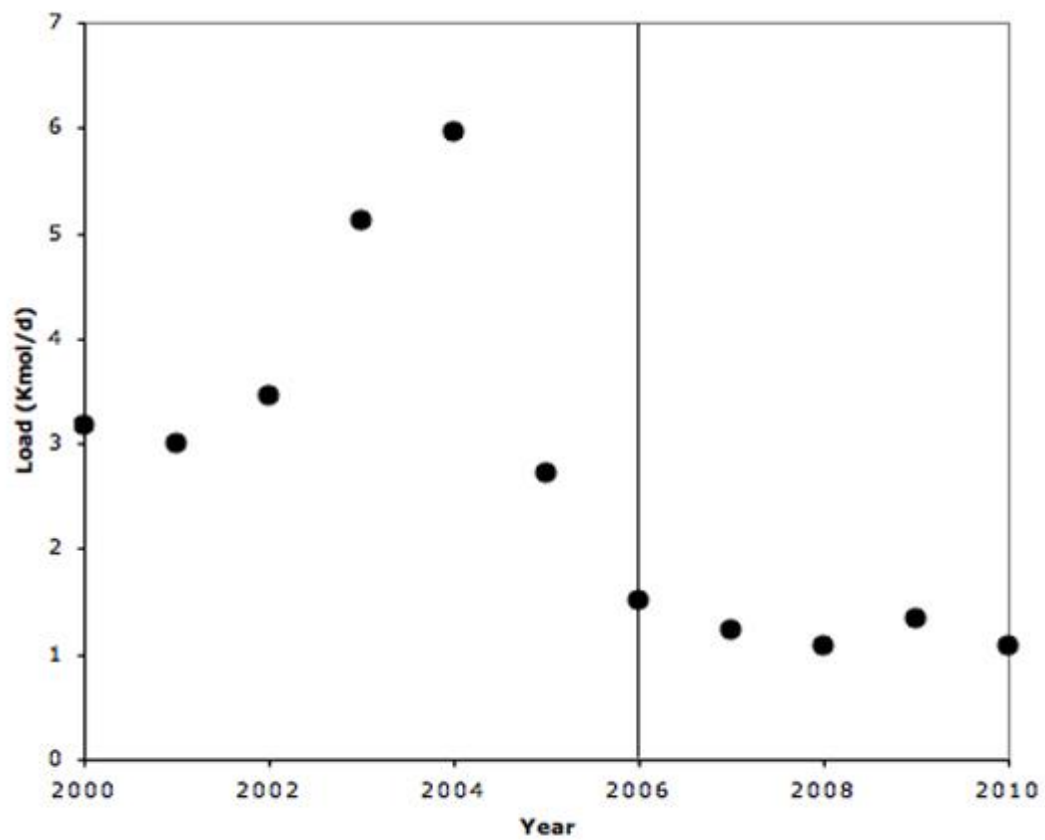


Figure B-22. Average annual total phosphorus load discharged from the Cranston facility from 2000-2010. The vertical line represents upgrade completion in 1/2006.

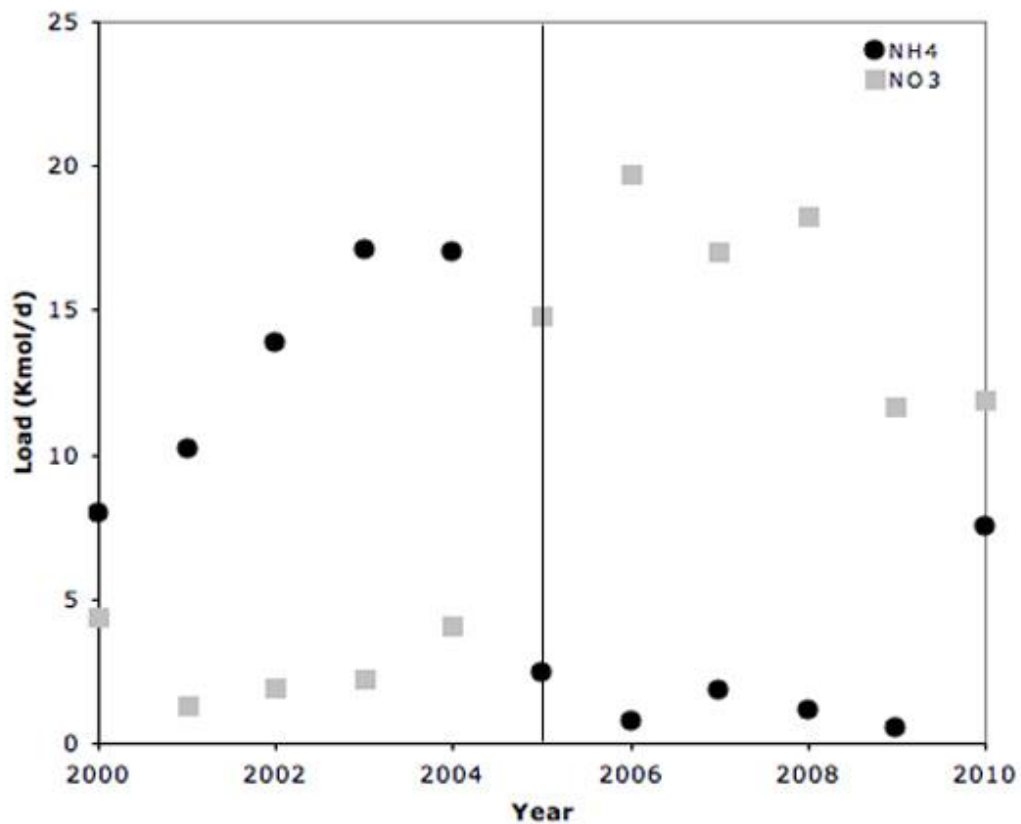


Figure B-23. Average annual ammonia (NH₄) and nitrate (NO₃) loads discharged from the West Warwick facility from 2000-2010. The vertical line represents upgrade completion in 7/2005.

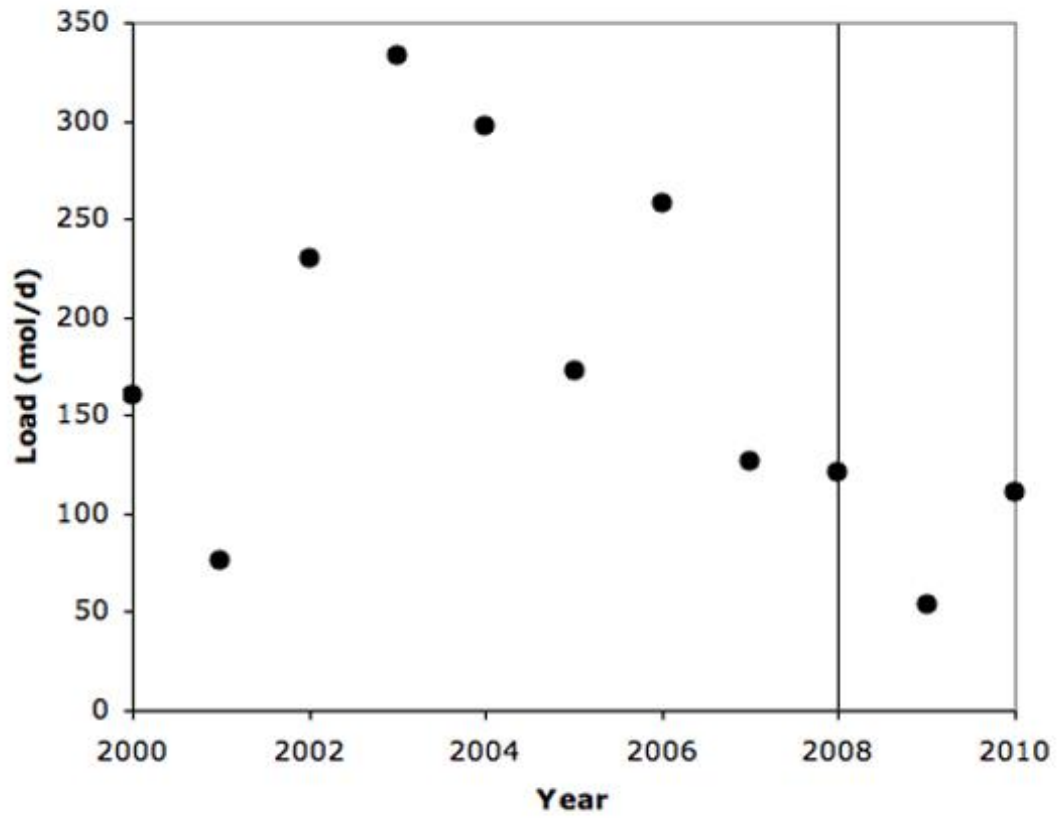


Figure B-24. Average annual total sewage phosphorus discharged from the North Attleboro facility from 2000-2010. The vertical line represents upgrade completion in 2008.

SUPPLEMENTAL FIGURES

Table B-6. Annual total nitrogen load discharged from each facility from 2000-2010.
All values are in millions of moles N per year.

<i>Discharges to:</i>	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
Narragansett Bay											
Field's Point	76.84 ^a	77.42 ^a	77.94	71.78	59.99	57.99	54.05	53.18	61.55	63.87	75.55
Bucklin Point	44.51 ^a	45.26 ^a	45.58	37.08	39.52	26.96	20.61	14.82	17.26	21.46	22.17
Newport ^b	11.21	11.17	11.14	11.07	10.96	10.70	10.91	10.46	10.39	10.35	10.64
East Providence	9.24 ^a	9.31 ^a	9.37	11.74	7.93	10.81	8.11	7.60	6.94	7.18	8.38
Bristol	8.97	5.94	6.81	6.44	5.49	5.47 ^c	5.46	7.61	7.40	6.04	4.03
Warren	3.10 ^d	3.11 ^d	3.12 ^d	3.10	1.93	1.91 ^c	1.89 ^c	1.88 ^c	1.87 ^c	1.85 ^c	1.83 ^c
East Greenwich	1.41	1.09	0.82	1.12	1.32	1.46	0.86	0.88	0.84	0.84	0.93
Quonset Point	0.98	1.00	0.78	0.94	0.75	0.74 ^c	0.73 ^c	0.73 ^c	0.73 ^c	0.73 ^c	0.73 ^c
Jamestown	0.11 ^e	0.11	0.09	0.16	0.16 ^d	0.16 ^d	0.16 ^d	0.16 ^d	0.16 ^d	0.16 ^d	0.15 ^d
Fall River*											
Blackstone River											
Worcester	15.74 ^f	15.85 ^f	15.98 ^f	16.11 ^f	16.22 ^f	16.33 ^f	16.41 ^f	16.45 ^f	16.88 ^f	16.93	16.55
Woonsocket	21.93	10.90	5.76	3.82	3.88	7.94	7.20	6.58	4.68	3.56	5.15
Smithfield	3.24	2.69	2.19	3.17	2.62	3.34	1.01	0.97	1.56	1.69	1.64
Grafton*											
Millbury*											
Northbridge*											
Burrillville	1.27	1.33	1.41	1.36	1.37	1.35	1.36	1.33	1.61	1.32	1.35
Hopedale*											
Leicester*											
Douglas*											
Upton*											
Ten Mile River											
Attleboro	7.19 ^f	7.26 ^f	7.35 ^f	7.39 ^f	7.38 ^f	7.38 ^f	7.39 ^f	7.41 ^f	7.41 ^f	7.45	8.42
North Attleboro	2.72 ^g	2.76 ^g	2.79 ^g	2.80 ^g	2.81 ^g	2.81 ^g	2.80 ^g	2.80 ^g	2.81	2.42	3.53
Pawtuxet River											
Cranston	16.04	16.95	15.59	21.65	11.88	21.97	10.50	10.90	10.42	15.69	13.06
West Warwick	5.82	5.28	6.27	9.28	12.41	7.81	8.76	8.90	7.96	5.38	9.86
Warwick	9.44	8.48	7.37	10.70	8.33	4.37	4.28	4.32	4.03	4.20	6.47
Taunton River											
Brockton*											
Taunton*											
Somerset*											

* Did not have annual data. 2007-2010 values were estimated by scaling 2000-2003 values (Nixon, et al., 2008) by population change.

^a Estimated with population data from the U.S. Census Bureau and load data from 2002.

^b Calculated assuming 0.8 moles nitrogen per person per day by 365 days per year.

^c Estimated with population data from the U.S. Census Bureau and load data from 2004.

^d Estimated with population data from the U.S. Census Bureau and load data from 2003.

^e Estimated with population data from the U.S. Census Bureau and load data from 2001.

^f Estimated with population data from the U.S. Census Bureau and load data from 2009.

^g Estimated with population data from the U.S. Census Bureau and load data from 2008.

Table B-7. Annual total phosphorus load discharged from each facility from 2000-2010. All values are in millions of moles P per year.

<i>Discharges to:</i>	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
Narragansett Bay											
Field's Point	4.94 ^a	4.97 ^a	5.01	2.04	2.41	2.57	2.09	3.07	3.41	2.96	3.30
Bucklin Point	3.24 ^a	3.27 ^a	3.29	2.23	2.56	3.01	3.04	2.68	4.69	2.38	2.79
Newport ^b	0.63	0.63	0.63	0.62	0.62	0.60	0.61	0.59	0.58	0.58	0.60
East Providence	0.88 ^a	0.89 ^a	0.89	0.62	0.53	0.53 ^c	0.52 ^c	0.52 ^c	0.52 ^c	0.52 ^c	0.51 ^c
Bristol	0.17 ^d	0.17	0.14	0.22	0.18	0.18 ^c	0.18 ^c	0.18 ^c	0.18 ^c	0.18 ^c	0.19 ^c
Warren ^e	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
East Greenwich	0.41	0.41 ^f	0.42 ^f	0.42 ^f	0.43 ^f	0.43 ^f	0.42 ^f	0.42 ^f	0.42 ^f	0.42 ^f	0.42 ^f
Quonset Point ^b	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Jamestown ^g	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.02
Fall River*											
Blackstone River											
Worcester	2.18	2.09	2.10 ^d	2.12 ^d	2.13 ^d	2.14 ^d	2.15 ^d	2.16 ^d	1.16 ^h	1.16	0.71
Woonsocket	2.93	1.19	0.11	0.16	0.24	0.65	0.24	0.21	0.73	0.71	0.59
Smithfield	0.21 ^d	0.21	0.24	0.26	0.27	0.22	0.05	0.02	0.02	0.02	0.02
Grafton*											
Millbury*											
Northbridge*											
Burrillville	0.03	0.03	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.03	0.02
Hopedale*											
Leicester*											
Douglas*											
Upton*											
Ten Mile River											
Attleboro	0.10	0.08	0.09	0.03	0.03	0.01	0.06	0.01	0.01	0.02	0.03
North Attleboro	0.06	0.03	0.08	0.12	0.11	0.06	0.09	0.05	0.04	0.02	0.04
Pawtuxet River											
Cranston	1.16	1.09	1.26	1.87	2.18	1.00	0.56	0.45	0.39	0.49	0.39
West Warwick	0.53	0.50	0.60	0.67	1.02	0.47	0.39	0.46	0.37	0.35	0.61
Warwick	0.60	0.59	0.56	0.51	0.55	0.21	0.14	0.16	0.13	0.13	0.42
Taunton River											
Brockton*											
Taunton*											
Somerset*											

* Did not have annual data. 2007-2010 values were estimated by scaling 2000-2003 values (Nixon, et al., 2008) by population change.

^a Estimated with population data from the U.S. Census Bureau and load data from 2002.

^b Calculated assuming 0.045 moles phosphorus per person per day by 365 days per year.

^c Estimated with population data from the U.S. Census Bureau and load data from 2004.

^d Estimated with population data from the U.S. Census Bureau and load data from 2001.

^e Estimated with population data from the U.S. Census Bureau and load data from 1996.

^f Estimated with population data from the U.S. Census Bureau and load data from 2000.

^g Estimated with population data from the U.S. Census Bureau and load data from 1994.

^h Estimated with population data from the U.S. Census Bureau and load data from 2009.

Table B-8. Active season total nitrogen load discharged from each facility from 2000-2010. All values are in millions of moles N per year.

<i>Discharges to:</i>	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
Narragansett Bay											
Field's Point	42.75 ^a	43.07 ^a	43.36	35.95	29.02	26.16	27.29	26.73	26.05	29.58	31.57
Bucklin Point	23.37 ^a	23.59 ^a	23.76	18.12	20.28	10.51	8.54	6.46	7.41	9.72	7.42
Newport ^b	5.65	5.63	5.62	5.58	5.53	5.39	5.50	5.28	5.24	5.22	5.37
East Providence	4.47 ^a	4.51 ^a	4.54	4.82	4.81 ^c	4.18 ^d	4.15	3.84	2.48	2.99	4.22
Bristol	4.02	2.34	4.30	3.20	3.20 ^c	3.18 ^d	3.16	4.05	4.38	3.47	2.27
Warren	1.72 ^c	1.73 ^c	1.73 ^c	1.72	1.72 ^c	1.70 ^c	1.69 ^c	1.68 ^c	1.67 ^c	1.65 ^c	1.63 ^c
East Greenwich	0.59	0.50	0.44	0.57	0.72	0.62	0.20	0.21	0.17	0.17	0.20
Quonset Point	0.52	0.51	0.38	0.48	0.48 ^c	0.48 ^c	0.47 ^c	0.47 ^c	0.47 ^c	0.47 ^c	0.47 ^c
Jamestown	0.07 ^e	0.07	0.05	0.11	0.11 ^c	0.11 ^c	0.11 ^c	0.11 ^c	0.11 ^c	0.11 ^c	0.10 ^c
Fall River*											
Blackstone River											
Worcester	7.63 ^f	7.69 ^f	7.75 ^f	7.81 ^f	7.86 ^f	7.91 ^f	7.95 ^f	7.97 ^f	8.18 ^f	8.21	7.57
Woonsocket	12.47	4.79	2.89	2.13	2.13	3.69	3.40	2.46	2.29	1.40	1.37
Smithfield	1.81	1.58	1.29	1.85	1.54	1.96	0.59	0.46	0.67	0.67	0.74
Grafton*											
Millbury*											
Northbridge*											
Burrillville	0.62	0.46	0.53	0.51	0.44	0.45	0.42	0.37	0.39	0.40	0.38
Hopedale*											
Leicester*											
Douglas*											
Upton*											
Ten Mile River											
Attleboro	3.05 ^g	3.08 ^g	3.12 ^g	3.14 ^g	3.13 ^g	3.13 ^g	3.13 ^g	3.14 ^g	3.14 ^g	3.16 ^g	3.16
North Attleboro ^b	5.13	5.21	5.26	5.27	5.29	5.30	5.29	5.29	5.30	5.31	5.44
Pawtuxet River											
Cranston	7.23	7.95	8.03	10.97	5.52	9.82	3.22	4.25	3.58	4.34	4.17
West Warwick	2.49	2.54	2.55	4.68	6.36	2.06	2.67	2.06	2.05	1.81	4.47
Warwick	4.30	3.90	3.67	5.15	3.34	1.91	2.09	1.91	1.79	1.80	3.44
Taunton River											
Brockton*											
Taunton*											
Somerset*											

* Did not have annual data. 2007-2010 values were estimated by scaling 2000-2003 values (Nixon, et al., 2008) by population change.

^a Estimated with population data from the U.S. Census Bureau and load data from 2002.

^b Calculated assuming 0.8 moles nitrogen per person per day by 184 days per summer season, 181 days per winter season, and 182 days per leap year winter season (2000, 2004, 2008).

^c Estimated with population data from the U.S. Census Bureau and load data from 2003.

^d Estimated with population data from the U.S. Census Bureau and load data from 2006.

^e Estimated with population data from the U.S. Census Bureau and load data from 2001.

^f Estimated with population data from the U.S. Census Bureau and load data from 2009.

^g Estimated with population data from the U.S. Census Bureau and load data from 2010.

Table B-9. Active season total phosphorus load discharged from each facility from 2000-2010. All values are in millions of moles P per year.

<i>Discharges to:</i>	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
Narragansett Bay											
Field's Point	0.75 ^a	0.76 ^a	0.76	0.95	1.35	1.48	1.14	1.74	1.81	1.58	1.50
Bucklin Point	0.80 ^a	0.81 ^a	0.81	1.11	1.23	1.56	1.50	1.09	1.23	1.14	1.14
Newport ^b	0.32	0.32	0.32	0.31	0.31	0.30	0.31	0.30	0.29	0.29	0.30
East Providence	0.49 ^a	0.49 ^a	0.49	0.24	0.24 ^c	0.24 ^c	0.24 ^c	0.24 ^c	0.24 ^c	0.24 ^c	0.23 ^c
Bristol	0.08 ^d	0.08	0.07	0.10	0.10 ^c	0.10 ^c	0.10 ^c	0.10 ^c	0.10 ^c	0.10 ^c	0.10 ^c
Warren ^e	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
East Greenwich ^f	0.39	0.40	0.40	0.40	0.41	0.41	0.40	0.40	0.40	0.40	0.40
Quonset Point ^b	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Jamestown ^g	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01
Fall River*											
Blackstone River											
Worcester	1.10	0.95	0.96 ^d	0.97 ^d	0.97 ^d	0.98 ^d	0.98 ^d	0.99 ^d	0.69 ^h	0.70	0.46
Woonsocket	1.66	0.59	0.05	0.09	0.12	0.37	0.15	0.10	0.12	0.04	0.06
Smithfield	0.10 ^d	0.10	0.10	0.13	0.13	0.11	0.01	0.01	0.01	0.01	0.01
Grafton*											
Millbury*											
Northbridge*											
Burrillville	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Hopedale*											
Leicester*											
Douglas*											
Upton*											
Ten Mile River											
Attleboro	0.06	0.05	0.05	0.02	0.02	0.01	0.04	0.01	0.01	0.01	0.01
North Attleboro	0.03	0.02	0.05	0.07	0.06	0.04	0.05	0.03	0.03	0.01	0.00
Pawtuxet River											
Cranston	0.44	0.49	0.82	0.94	1.04	0.44	0.26	0.18	0.16	0.19	0.13
West Warwick	0.23	0.26	0.27	0.37	0.58	0.08	0.09	0.07	0.08	0.09	0.34
Warwick	0.30	0.27	0.40	0.30	0.35	0.06	0.06	0.06	0.06	0.07	0.30
Taunton River											
Brockton*											
Taunton*											
Somerset*											

* Did not have annual data. 2007-2010 values were estimated by scaling 2000-2003 values (Nixon, et al., 2008) by population change.

^a Estimated with population data from the U.S. Census Bureau and load data from 2002.

^b Calculated assuming 0.045 moles phosphorus per person per day by 184 days per summer season, 181 days per winter season, and 182 days per leap year winter season (2000, 2004, 2008).

^c Estimated with population data from the U.S. Census Bureau and load data from 2003.

^d Estimated with population data from the U.S. Census Bureau and load data from 2001.

^e Estimated with population data from the U.S. Census Bureau and load data from 1996.

^f Estimated with population data from the U.S. Census Bureau and load data from 1999.

^g Estimated with population data from the U.S. Census Bureau and load data from 1994.

^h Estimated with population data from the U.S. Census Bureau and load data from 2009.

Table B-10. Inactive season total nitrogen load discharged from each facility from 2000-2010. All values are in millions of moles N per year.

<i>Discharges to:</i>	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
Narragansett Bay											
Field's Point	32.86 ^a	33.37 ^a	33.15	35.71	31.10	31.54	28.49	29.33	35.00	34.18	43.91
Bucklin Point	21.07 ^a	21.15 ^a	21.30	18.70	19.11	15.28	10.70	8.66	10.14	11.73	14.65
Newport ^b	5.59	5.54	5.52	5.49	5.47	5.31	5.41	5.19	5.18	5.13	5.28
East Providence	4.69 ^a	4.69 ^a	4.72	6.90	4.47	4.42 ^c	3.93	3.74	4.45	4.17	4.18
Bristol	4.91	3.57	2.50	3.23	3.10	3.07 ^c	3.05 ^c	3.05 ^c	3.06 ^c	3.02 ^c	3.11 ^c
Warren	1.39 ^d	1.39 ^d	1.39 ^d	1.39	1.08	1.06 ^c	1.05 ^c	1.05 ^c	1.05 ^c	1.03 ^c	1.02 ^c
East Greenwich	0.58 ^e	0.59	0.37	0.55	0.61	0.84	0.65	0.67	0.66	0.67	0.72
Quonset Point	0.45	0.48	0.40	0.46	0.42	0.41 ^c	0.41 ^c	0.41 ^c	0.41 ^c	0.41 ^c	0.41
Jamestown ^b	0.25	0.25	0.25	0.25	0.25	0.25	0.24	0.24	0.24	0.24	0.24
Fall River*											
Blackstone River											
Worcester	8.45 ^f	8.51 ^f	8.58 ^f	8.65 ^f	8.70 ^f	8.76 ^f	8.80 ^f	8.82 ^f	9.05 ^f	8.45 ^f	8.95
Woonsocket	3.68 ^g	3.69 ^g	3.72 ^g	3.77 ^g	3.78 ^g	3.75	3.79	4.08	2.41	2.15	3.73
Smithfield	0.87 ^h	0.87 ^h	0.88 ^h	0.89 ^h	0.90 ^h	0.90 ^h	0.89 ^h	0.89 ^h	0.89	1.02	0.90
Grafton*											
Millbury*											
Northbridge*											
Burrillville	0.66	0.87	0.88	0.85	0.93	0.89	0.94	0.94	1.21	0.91	0.96
Hopedale*											
Leicester*											
Douglas*											
Upton*											
Ten Mile River											
Attleboro	3.82 ⁱ	3.85 ⁱ	3.90 ⁱ	3.93 ⁱ	3.92 ⁱ	3.92 ⁱ	3.93 ⁱ	3.94 ⁱ	3.94 ⁱ	3.96	5.20
North Attleboro	1.48 ^h	1.50 ^h	1.52 ^h	1.52 ^h	1.53 ^h	1.53 ^h	1.52 ^h	1.52 ^h	1.53	1.40	2.02
Pawtuxet River											
Cranston	8.95 ^e	8.99	7.55	10.73	6.38	12.16	7.25	6.64	6.63	11.31	8.59
West Warwick	2.69 ^e	2.70	3.70	4.59	6.08	5.69	6.03	6.73	5.87	3.55	5.40
Warwick	4.58 ^e	4.58	3.70	5.54	5.00	2.45	2.18	2.40	2.25	2.40	3.04
Taunton River											
Brockton*											
Taunton*											
Somerset*											

* Did not have annual data. 2007-2010 values were estimated by scaling 2000-2003 values (Nixon, et al., 2008) by population change.

^a Estimated with population data from the U.S. Census Bureau and load data from 2002.

^b Calculated assuming 0.8 moles nitrogen per person per day by 184 days per summer season, 181 days per winter season, and 182 days per leap year winter season (2000, 2004, 2008).

^c Estimated with population data from the U.S. Census Bureau and load data from 2004.

^d Estimated with population data from the U.S. Census Bureau and load data from 2003.

^e Estimated with population data from the U.S. Census Bureau and load data from 2001.

^f Estimated with population data from the U.S. Census Bureau and load data from 2010.

^g Estimated with population data from the U.S. Census Bureau and load data from 2005.

^h Estimated with population data from the U.S. Census Bureau and load data from 2008.

ⁱ Estimated with population data from the U.S. Census Bureau and load data from 2009.

Table B-11. Inactive season total phosphorus load discharged from each facility from 2000-2010. All values are in millions of moles P per year.

<i>Discharges to:</i>	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
Narragansett Bay											
Field's Point	4.41 ^a	4.48 ^a	4.45	1.08	1.07	1.12	0.94	1.32	1.62	1.38	1.79
Bucklin Point	2.48 ^a	2.49 ^a	2.51	1.11	1.34	1.44	1.53	1.59	3.46	1.24	1.65
Newport ^b	0.31	0.31	0.31	0.31	0.31	0.30	0.30	0.29	0.29	0.29	0.30
East Providence	0.37 ^a	0.38 ^a	0.38	0.38	0.27	0.27	0.27	0.27	0.27	0.27	0.26
Bristol	0.09 ^c	0.09	0.08	0.12	0.11	0.11 ^d	0.11 ^d	0.11 ^d	0.11 ^d	0.11 ^d	0.11 ^d
Warren ^e	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
East Greenwich	0.21	0.21 ^f	0.21 ^f	0.21 ^f	0.22 ^f	0.22 ^f	0.21 ^f	0.21 ^f	0.21 ^f	0.21 ^f	0.21 ^f
Quonset Point ^b	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Jamestown ^g	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fall River*											
Blackstone River											
Worcester	1.09	1.12	1.13 ^c	1.14 ^c	1.15 ^c	1.15 ^c	1.16 ^c	1.16 ^c	1.19 ^c	0.26 ^h	0.26
Woonsocket	0.70 ⁱ	0.70 ⁱ	0.71 ⁱ	0.72 ⁱ	0.72 ⁱ	0.71 ⁱ	0.71 ⁱ	0.71 ⁱ	0.71	0.65	0.52
Smithfield	0.14 ^a	0.14 ^a	0.14	0.13	0.14	0.11	0.04	0.01	0.02	0.01	0.01
Grafton*											
Millbury*											
Northbridge*											
Burrillville	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Hopedale*											
Leicester*											
Douglas*											
Upton*											
Ten Mile River											
Attleboro	0.03 ^j	0.03 ^j	0.03 ^j	0.03 ^j	0.03 ^j	0.03 ^j	0.03 ^j	0.03 ^j	0.03 ^j	0.03 ^j	0.03
North Attleboro	0.02 ⁱ	0.02 ⁱ	0.02 ⁱ	0.02 ⁱ	0.02 ⁱ	0.02 ⁱ	0.02 ⁱ	0.02 ⁱ	0.02	0.01	0.04
Pawtuxet River											
Cranston	0.60 ^c	0.60	0.44	0.92	1.14	0.56	0.29	0.27	0.24	0.30	0.26
West Warwick	0.30	0.24	0.33	0.31	0.44	0.38	0.29	0.38	0.29	0.26	0.27
Warwick	0.32 ^c	0.32	0.16	0.22	0.20	0.14	0.08	0.09	0.07	0.07	0.13
Taunton River											
Brockton*											
Taunton*											
Somerset*											

* Did not have annual data. 2007-2010 values were estimated by scaling 2000-2003 values (Nixon, et al., 2008) by population change.

^a Estimated with population data from the U.S. Census Bureau and load data from 2002.

^b Calculated assuming 0.045 moles phosphorus per person per day by 184 days per summer season, 181 days per winter season, and 182 days per leap year winter season (2000, 2004, 2008).

^c Estimated with population data from the U.S. Census Bureau and load data from 2001.

^d Estimated with population data from the U.S. Census Bureau and load data from 2004.

^e Estimated with population data from the U.S. Census Bureau and load data from 1996.

^f Estimated with population data from the U.S. Census Bureau and load data from 2000.

^g Estimated with population data from the U.S. Census Bureau and load data from 1994.

^h Estimated with population data from the U.S. Census Bureau and load data from 2009.

ⁱ Estimated with population data from the U.S. Census Bureau and load data from 2008.

^j Estimated with population data from the U.S. Census Bureau and load data from 2010.

Table B-12. Nitrogen and phosphorus loads from rivers that drain to Narragansett Bay from 2006-2010. All nitrogen and phosphorus values are in millions of moles per year.

Blackstone River	NO₃+NO₂	NO₂	NO₃	NH₄	PO₄	SiO₂	TN	DIN	DON
2007	45.07	1.03	44.05	14.00	1.94	40.39	68.34	58.74	9.77
2008	75.25	1.52	73.72	20.60	2.45	66.28	146.16	90.98	55.19
2009	56.83	1.07	55.76	14.65	1.64	80.85	87.23	71.48	15.75
2010	34.29	0.67	33.67	6.59	3.34	56.81	55.00	39.51	14.93
Pawtuxet River									
2005	30.67	0.61	30.06	11.57	1.78	71.09	50.80	42.24	
2006	21.77	0.45	21.33	5.11	0.82	52.49	42.86	26.88	
2007	23.67	0.37	23.30	5.49	1.11	39.41	36.40	29.16	
2008	30.26	0.48	29.78	3.69	0.85	50.40	55.15	33.96	
2009	27.16	0.59	26.57	7.71	1.15	69.56	45.12	34.87	
2010	14.04	0.24	13.80	6.32	0.69	42.50	27.54	20.36	
Woonasquatucket River									
2006	2.67	0.05	2.63	0.71	0.15	3.01	6.68	3.38	3.26
2007	2.85	0.05	2.79	0.20	0.01	3.69	3.79	3.04	0.81
2008	3.78	0.06	3.72	0.60	0.04	3.59	6.19	4.38	1.78
2009	3.81	0.04	3.76	0.16	0.02	6.97	5.44	3.97	1.47
2010	3.66	0.09	3.57	0.29	0.04	6.22	5.52	3.96	1.57
Moshassuck River									
2006	1.06	0.03	1.03	0.39	0.01	1.44	2.77	1.45	1.35
2007	1.55	0.03	1.52	0.27	0.00	3.31	2.26	1.82	0.44
2008	1.85	0.03	1.82	0.36	0.01	3.63	2.88	2.21	0.67
2009	1.74	0.03	1.71	0.24	0.01	4.50	2.52	1.99	0.53
2010	1.59	0.02	1.57	0.32	0.01	3.43	2.63	1.91	0.72
Ten Mile River									
2006	9.63	0.19	9.43	1.21	0.11	5.92	15.31	10.88	4.52
2007	6.60	0.17	6.43	0.95	0.11	4.58	11.97	7.55	2.26
2008	12.47	0.12	12.35	0.62	0.11	7.91	16.60	13.09	3.52
2009	11.30	0.12	11.18	0.49	0.08	8.23	14.03	11.78	2.12
2010	9.86	0.22	9.65	0.78	0.06	6.93	12.52	10.65	2.49
Taunton River									
2006	23.97	0.69	23.27	9.82	0.99	23.86	97.04	33.94	62.09
2007	34.83	0.73	34.09	8.51	0.74	28.07	63.07	43.34	19.73
2008	44.55	0.61	41.14	9.34	0.75	31.64	78.59	53.88	24.71
2009	56.55	0.93	55.62	5.67	0.95	64.13	111.07	66.09	43.72
2010	29.07	0.68	28.48	4.40	0.58	22.33	56.60	33.76	23.27

Table B-13. Average and standard deviation of flow, nitrogen, and phosphorus for wastewater treatment facilities in the Narragansett Bay watershed from 2006-2010. All flow values are in cubic meters per day and all nitrogen and phosphorus values are in moles per year.

<i>Discharges to:</i> Narragansett Bay	Flow		DIN		TN		DIP^d		TP	
	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev
Field's Point	1.7x10 ⁵	4.2x10 ⁴	4.6x10 ⁷	7.6x10 ⁶	6.2x10 ⁷	9.1x10 ⁶	1.5x10 ⁶	9.1x10 ⁴	3.0x10 ⁶	5.2x10 ⁵
Bucklin Point	8.5x10 ⁴	2.7x10 ⁴	1.5x10 ⁷	3.3x10 ⁶	1.9x10 ⁷	3.1x10 ⁶	2.4x10 ⁶	2.7x10 ⁵	3.1x10 ⁶	9.1x10 ⁵
Newport	3.5x10 ⁴	1.1x10 ⁴			1.1x10 ⁷	2.3x10 ⁵	4.0x10 ⁵	2.8x10 ²	5.9x10 ⁵	1.3x10 ⁴
East Providence	2.7x10 ⁴	8.1x10 ³	6.7x10 ⁶	1.8x10 ⁶	7.6x10 ⁶	6.0x10 ⁵	4.5x10 ⁵	9.1x10 ¹	5.2x10 ⁵	6.8x10 ³
Bristol	1.4x10 ⁴	5.1x10 ³	3.9x10 ⁶	5.2x10 ⁵	6.1x10 ⁶	1.5x10 ⁶	1.2x10 ⁵	2.1x10 ¹	1.8x10 ⁵	2.0x10 ³
Warren	7.1x10 ³	2.8x10 ³	1.6x10 ⁶	1.8x10 ⁴	1.9x10 ⁶	2.5x10 ⁴	3.6x10 ⁴	1.2x10 ¹	5.2x10 ⁴	8.0x10 ²
East Greenwich ^a	4.1x10 ³	8.5x10 ²	1.3x10 ⁶	7.2x10 ⁴	8.7x10 ⁵	4.3x10 ⁴	2.9x10 ⁵	5.8x10 ⁻¹	4.2x10 ⁵	4.9x10 ²
Quonset Point	1.8x10 ³	4.7x10 ²			7.3x10 ⁵	2.2x10 ³	6.8x10 ⁴	9.3x10 ⁻¹	1.0x10 ⁵	3.0x10 ²
Jamestown			1.5x10 ⁵	9.5x10 ²	1.6x10 ⁵	1.4x10 ³	1.7x10 ⁴	1.9x10 ⁰	2.5x10 ⁴	2.2x10 ²
Fall River*										
Blackstone River										
Worcester ^b	1.1x10 ⁵	4.2x10 ⁴			1.7x10 ⁷		4.8x10 ⁵		7.1x10 ⁵	
Woonsocket	2.9x10 ⁴	8.9x10 ³	4.5x10 ⁶	1.2x10 ⁶	5.4x10 ⁶	1.5x10 ⁶	3.4x10 ⁵	1.3x10 ⁵	5.0x10 ⁵	2.5x10 ⁵
Smithfield ^a	7.6x10 ³	1.9x10 ³	1.3x10 ⁶	2.4x10 ⁵	1.5x10 ⁶	3.3x10 ⁵	1.4x10 ⁴	1.6x10 ²	2.1x10 ⁴	1.8x10 ³
Grafton*										
Millbury*										
Northbridge*										
Burrillville	3.2x10 ³	8.4x10 ²	1.3x10 ⁶	1.2x10 ⁵	1.4x10 ⁶	1.2x10 ⁵	1.6x10 ⁴	1.3x10 ²	2.4x10 ⁴	1.8x10 ³
Hopedale*										
Leicester*										
Douglas*										
Upton*										
Ten Mile River										
Attleboro	1.5x10 ⁴	4.3x10 ³			7.6x10 ⁶	4.5x10 ⁵	1.9x10 ⁴	1.6x10 ⁴	2.8x10 ⁴	2.1x10 ⁴
North Attleboro ^c	1.6x10 ⁴	4.4x10 ³			3.0x10 ⁶	7.8x10 ⁵	2.1x10 ⁴	7.0x10 ³	3.0x10 ⁴	1.5x10 ⁴
Pawtuxet River										
Cranston ^a	4.3x10 ⁴	1.0x10 ⁴	1.0x10 ⁷	2.4x10 ⁶	1.3x10 ⁷	2.4x10 ⁶	2.9x10 ⁵	5.0x10 ³	4.3x10 ⁵	4.6x10 ⁴
West Warwick	2.3x10 ⁴	6.3x10 ³	6.9x10 ⁶	1.8x10 ⁶	8.2x10 ⁶	1.7x10 ⁶	3.0x10 ⁵	2.4x10 ⁴	4.4x10 ⁵	1.0x10 ⁵
Warwick	1.9x10 ⁴	2.0x10 ³	3.8x10 ⁶	9.4x10 ⁵	4.7x10 ⁶	1.0x10 ⁶	1.3x10 ⁵	8.0x10 ⁴	2.0x10 ⁵	1.3x10 ⁵
Taunton River										
Brockton*										
Taunton*										
Somerset*										

* indicates facilities that do not have annual data.

^a Average and standard deviation values are for 2007-2010 to avoid averaging over upgrade completion.

^b Average nitrogen and phosphorus load values are 2010 load values as this is the only year of data available after upgrades were completed.

^c Average and standard deviation values are for 2009-2010 to avoid averaging over upgrade completion.

^d Average DIP load values for the Field's Point, Bucklin Point, and East Providence facilities were calculated using the ratio between DIP and TP values from earlier measurements (Nixon, et al., 1995). The ratio between DIP and TP for the remaining facilities was calculated by taking the average of the DIP to TP ratios of the Field's Point, Bucklin Point, and East Providence facilities. Average DIP load values for the remaining facilities were calculated using this average ratio.

Table B-14. Average and standard deviation of flow, nitrogen, and phosphorus for rivers that drain to Narragansett Bay from 2006-2010. All flow values are in millions of cubic meters per day and all nitrogen and phosphorus values are in millions of moles per year.

	Flow		DIN		TN		DIP		TP	
	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev
Blackstone River ^a	2.574	2.874	66.821	18.452	89.185	40.222	2.341	0.744	5.758	1.641
Pawtuxet River	1.071	1.366	29.047	6.333	41.413	10.272	0.923	0.199	1.949	0.943
Woonasquatucket River	0.225	0.266	3.744	0.603	5.526	1.094	0.052	0.058	0.172	0.069
Moshassuck River	0.115	0.163	1.877	0.310	2.612	0.241	0.006	0.001	0.014	0.002
Ten Mile River	0.320	0.333	10.780	2.226	14.087	1.922	0.095	0.024	0.028	0.000
Taunton River	1.502	1.516	45.340	13.191	81.273	22.824	0.804	0.168	1.290	

^a Average and standard deviation values are for 2007-2010.

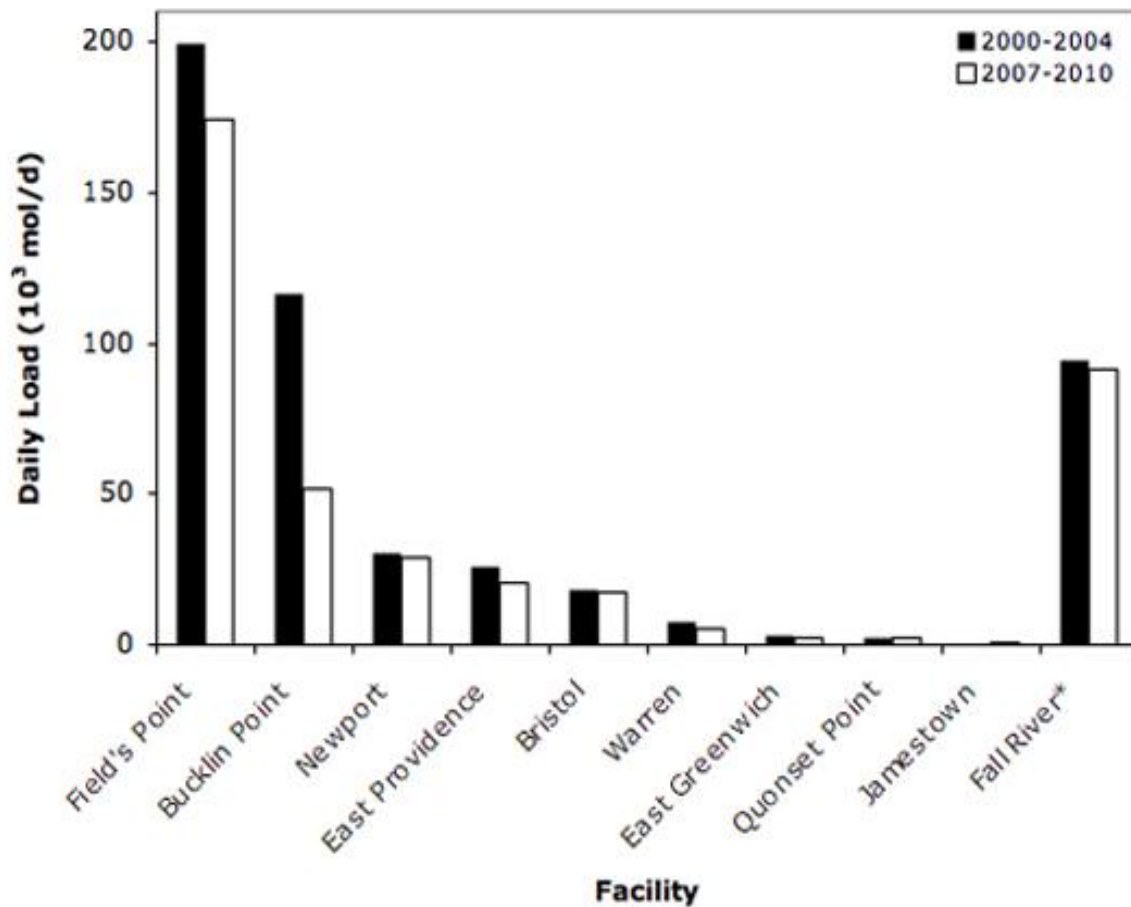


Figure B-25. Annual daily total nitrogen load from facilities that directly discharge to Narragansett Bay.

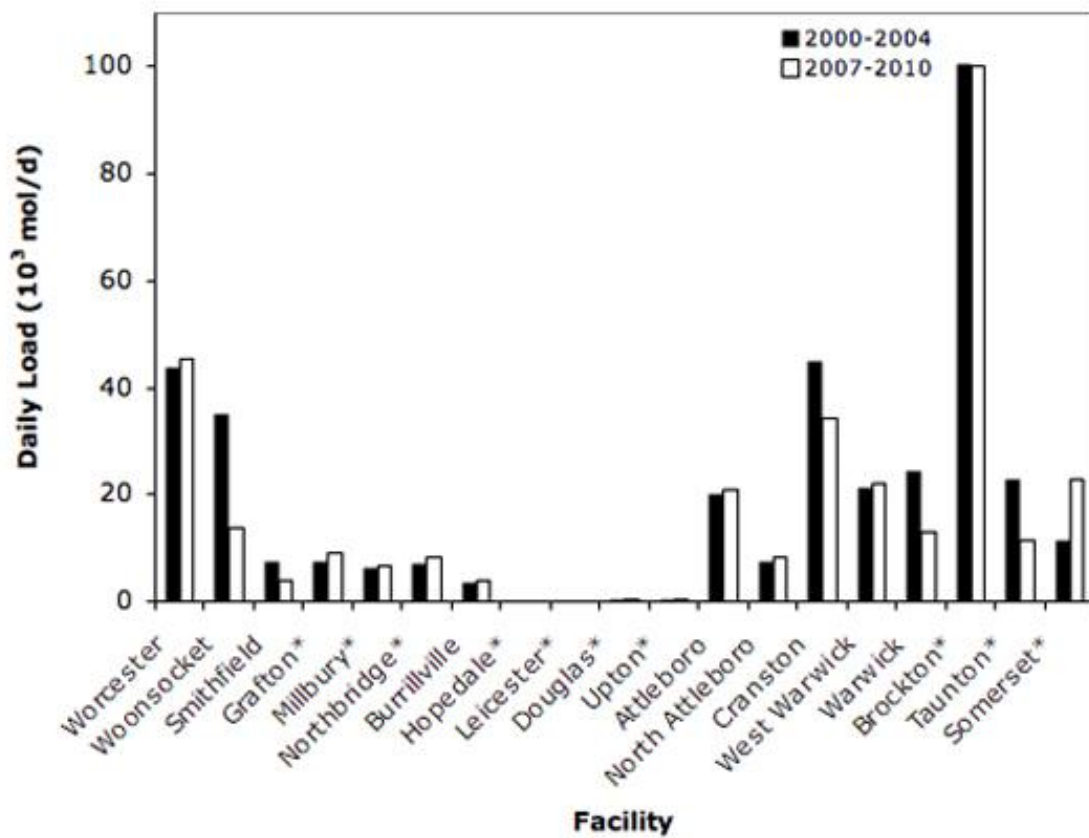


Figure B-26. Annual daily total nitrogen load discharged from facilities on rivers that drain to Narragansett Bay. * indicates that facilities were estimated with previous values (Nixon, et al., 2008) and population data.

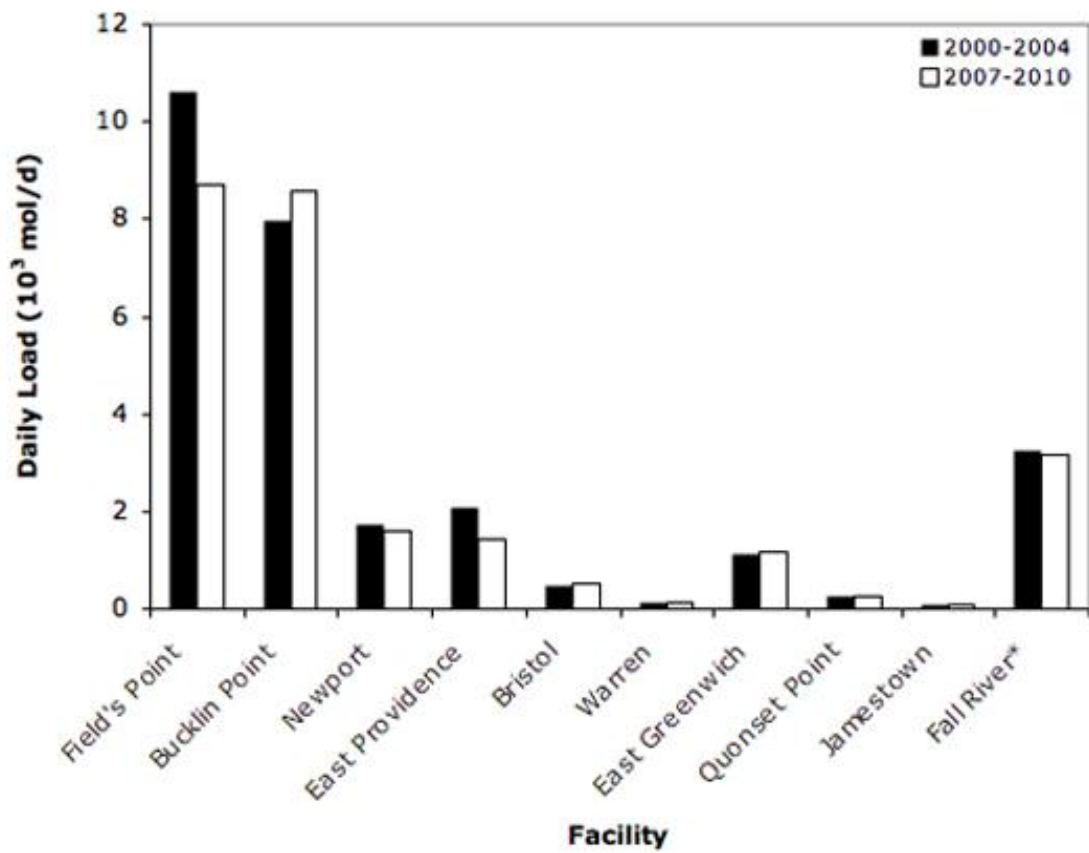


Figure B-27. Annual daily total phosphorus load from facilities that directly discharge to Narragansett Bay.

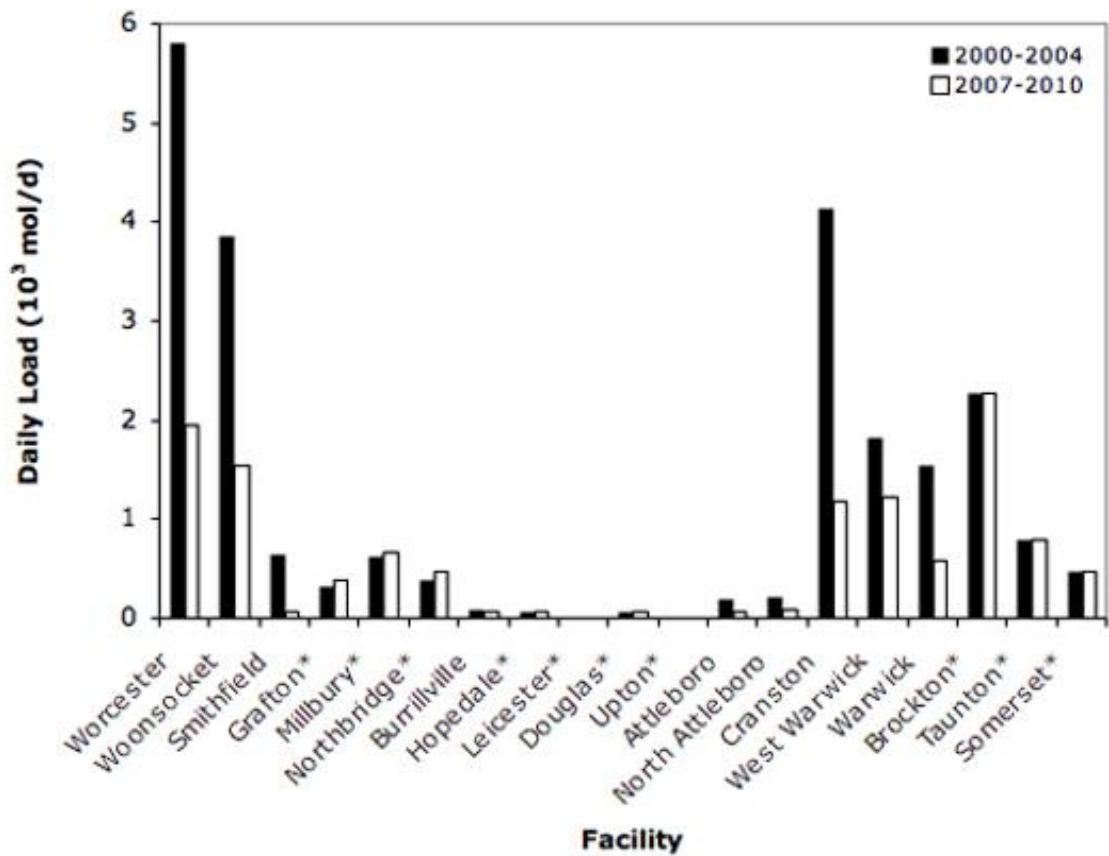


Figure B-28. Annual daily total phosphorus load discharged from facilities on rivers that drain to Narragansett Bay. * indicates that facilities were estimated with previous values (Nixon, et al., 2008) and population data.

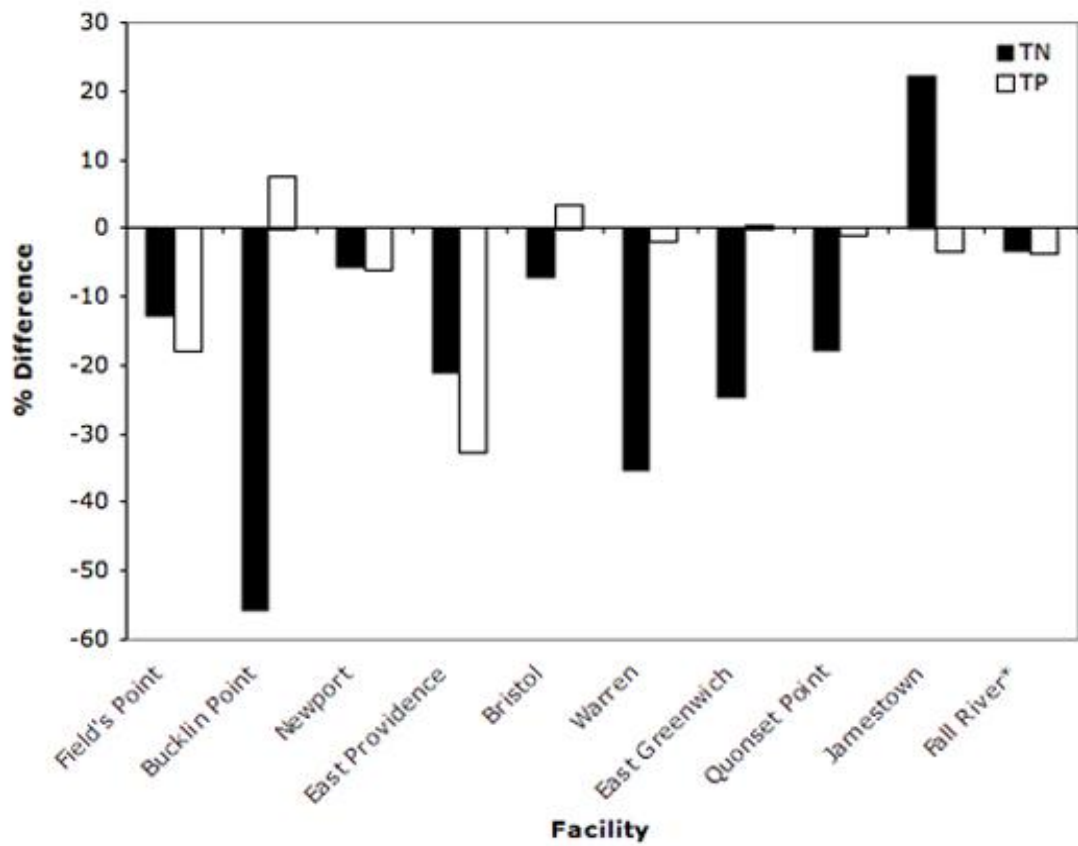


Figure B-29. Annual percent difference in total nitrogen and total phosphorus loads from facilities that directly discharge to Narragansett Bay in 2007-2010 relative to 2000-2004.

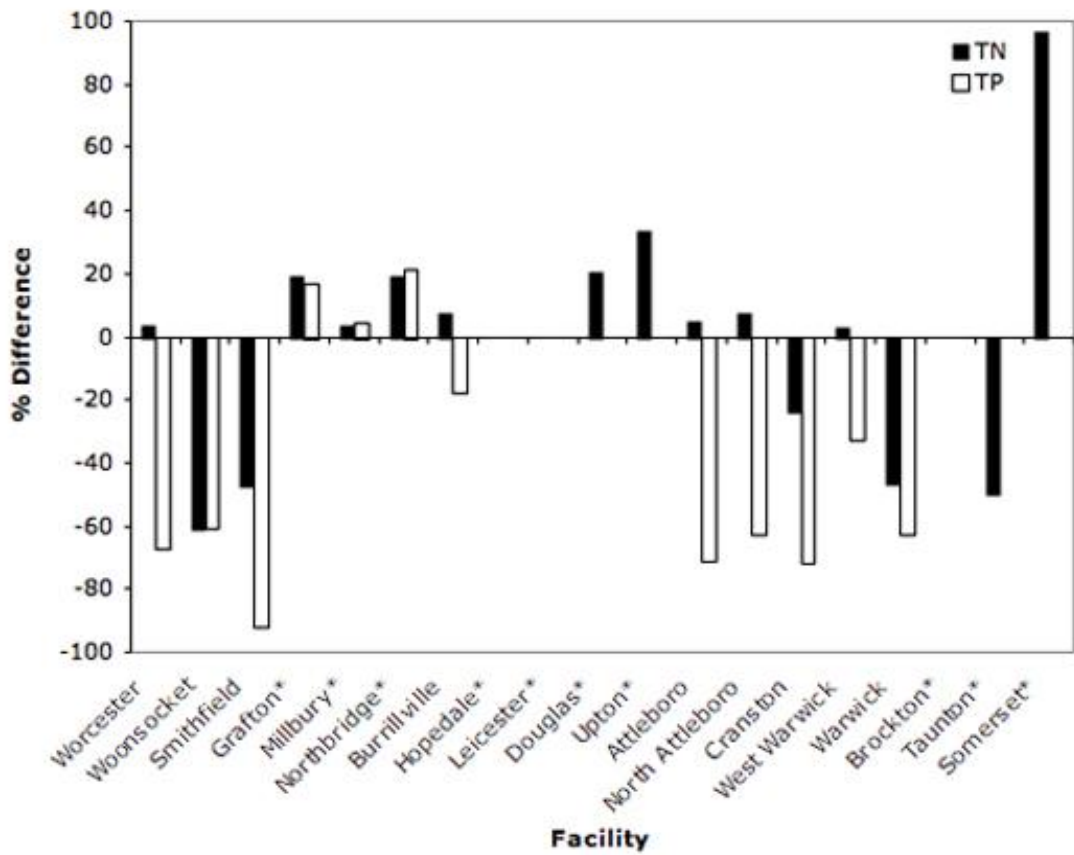


Figure B-30. Annual percent difference in total nitrogen and total phosphorus loads from facilities that discharge to rivers that drain to Narragansett Bay in 2007-2010 relative to 2000-2004.

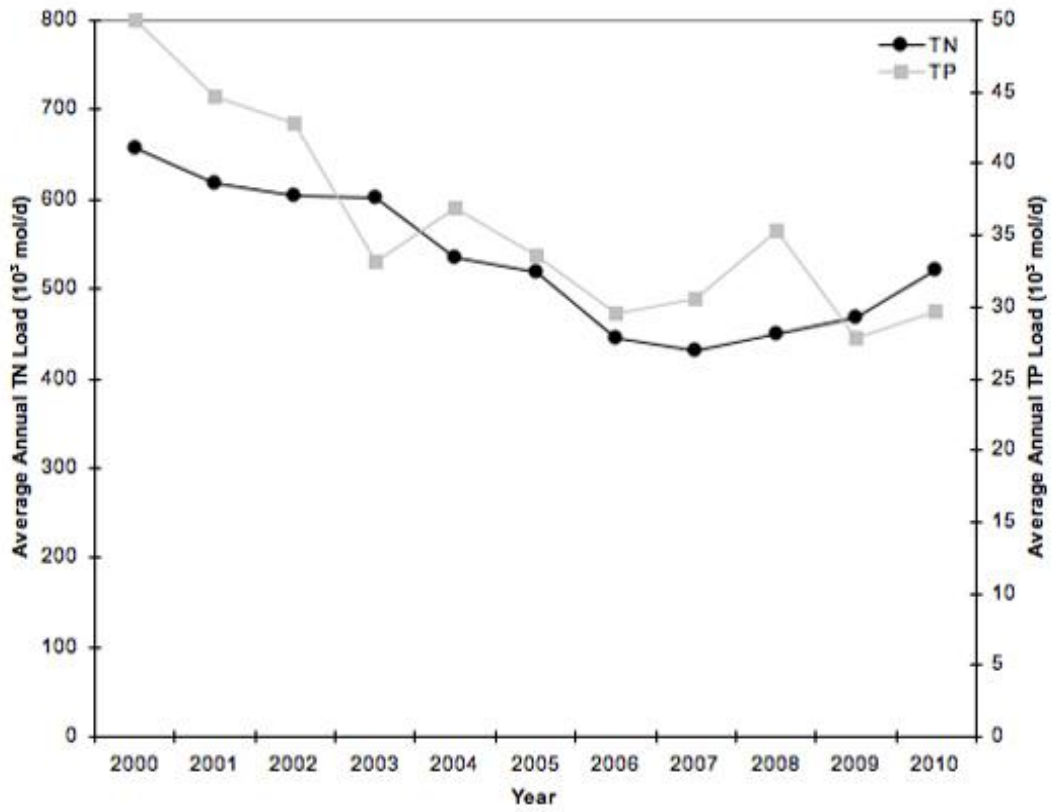


Figure B-31. Average annual total sewage nitrogen and total sewage phosphorus load discharged from all facilities combined over the 2000-2010 time period.

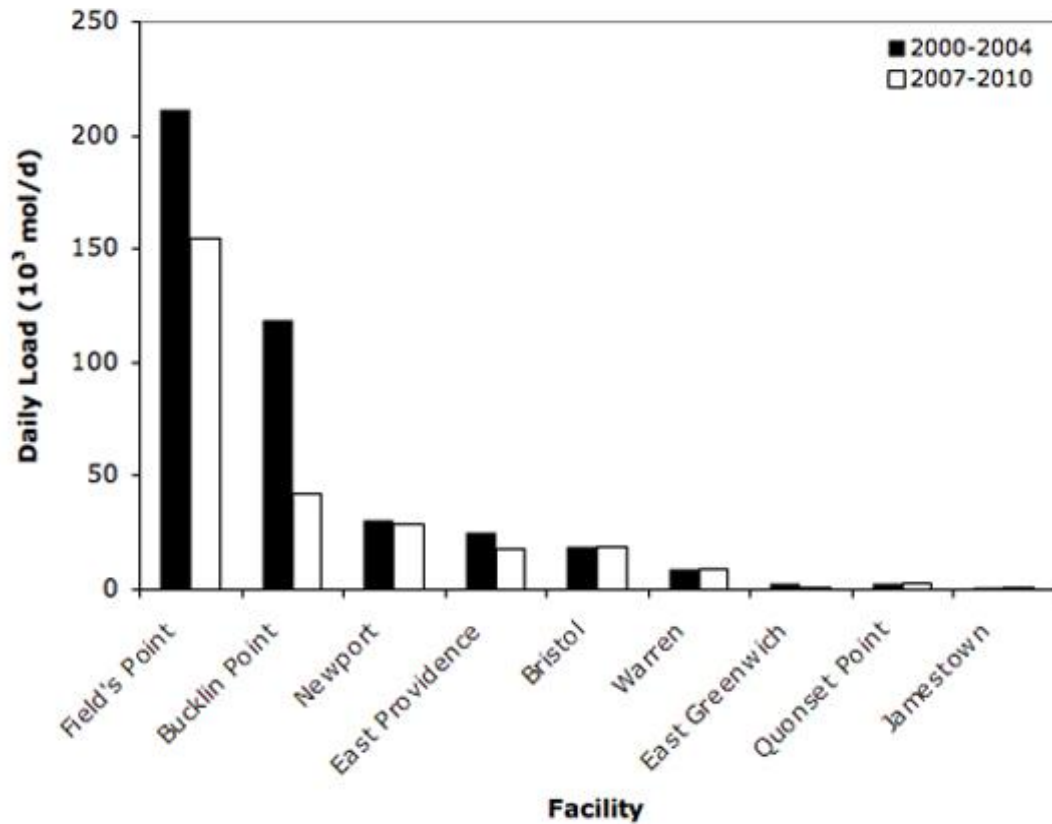


Figure B-32. Active season daily total nitrogen load from facilities that directly discharge to Narragansett Bay. The Fall River facility was not included as there was no seasonal data available.

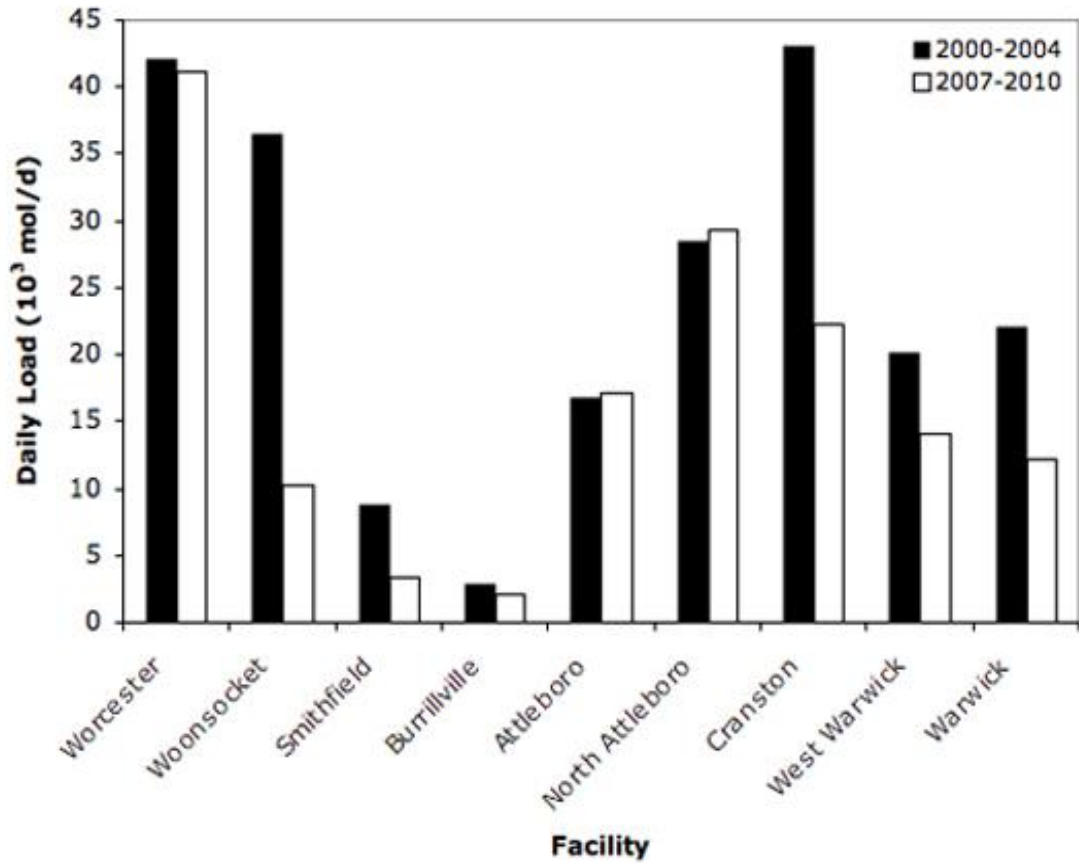


Figure B-33. Active season daily total nitrogen load discharged from facilities on rivers that drain to Narragansett Bay. The Grafton, Millbury, Hopedale, Leicester, Douglas, Upton, Brockton, Taunton, and Somerset facilities were not included as there was no seasonal data available.

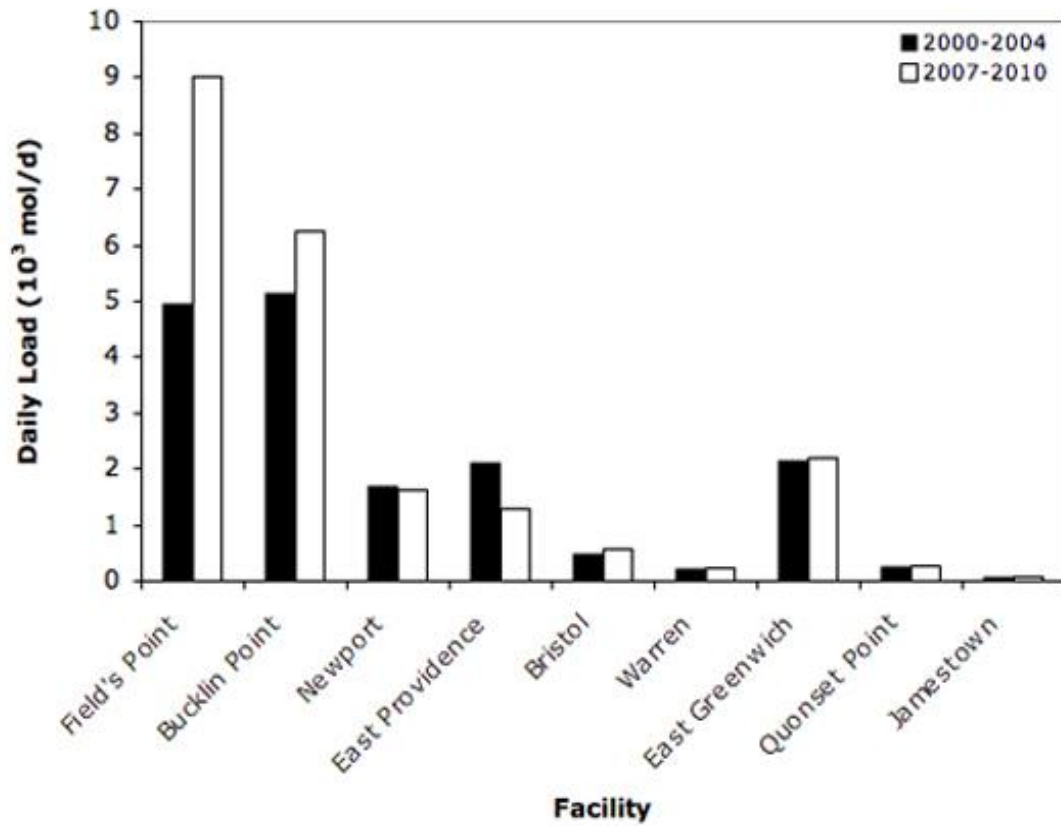


Figure B-34. Active season daily total phosphorus load from facilities that directly discharge to Narragansett Bay. The Fall River facility was not included as there was no seasonal data available.

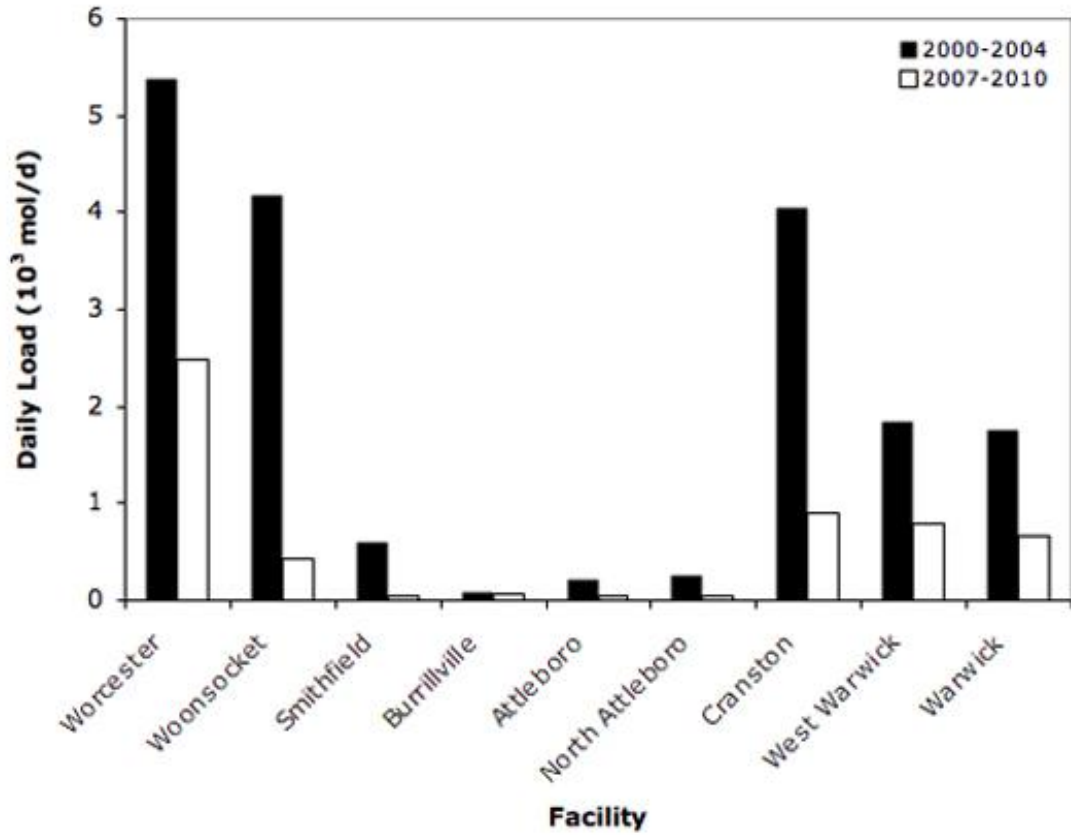


Figure B-35. Active season daily total phosphorus load from facilities discharged from facilities on rivers that drain to Narragansett Bay. The Grafton, Millbury, Hopedale, Leicester, Douglas, Upton, Brockton, Taunton, and Somerset facilities were not included as there was no seasonal data available.

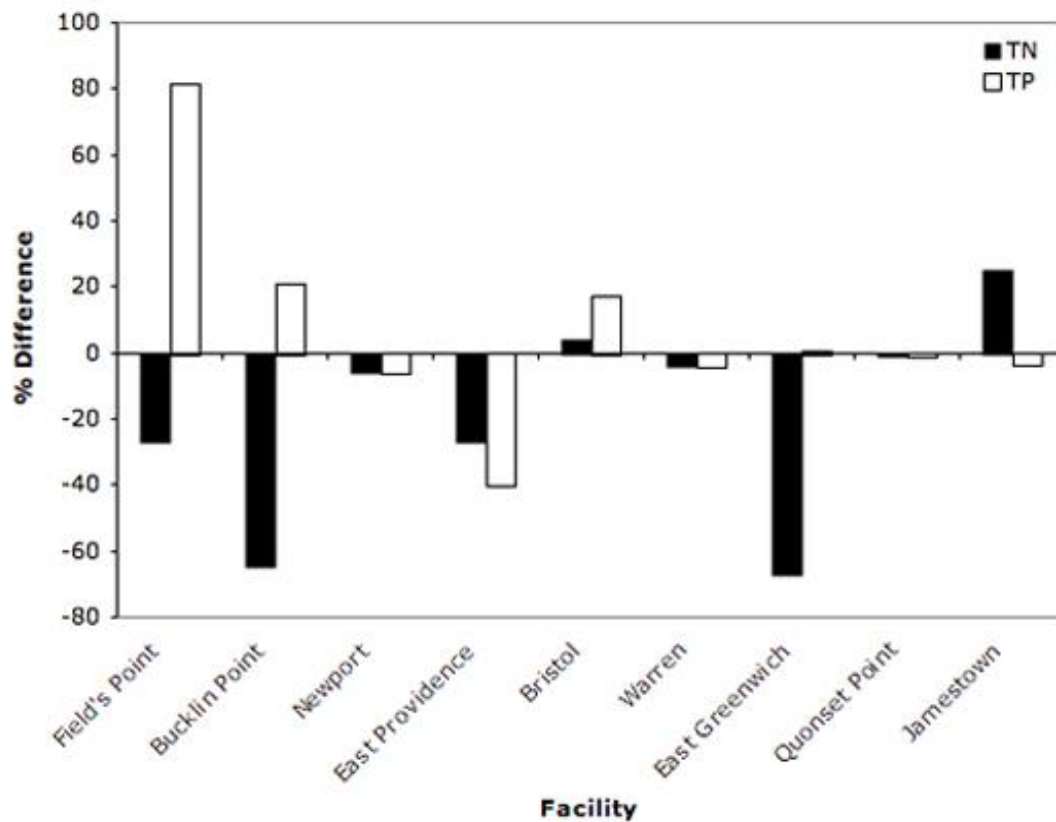


Figure B-36. Active season percent difference in total nitrogen and total phosphorus loads from facilities that directly discharge to Narragansett Bay in 2007-2010 relative to 2000-2004. The Fall River facility was not included as there was no seasonal data available.

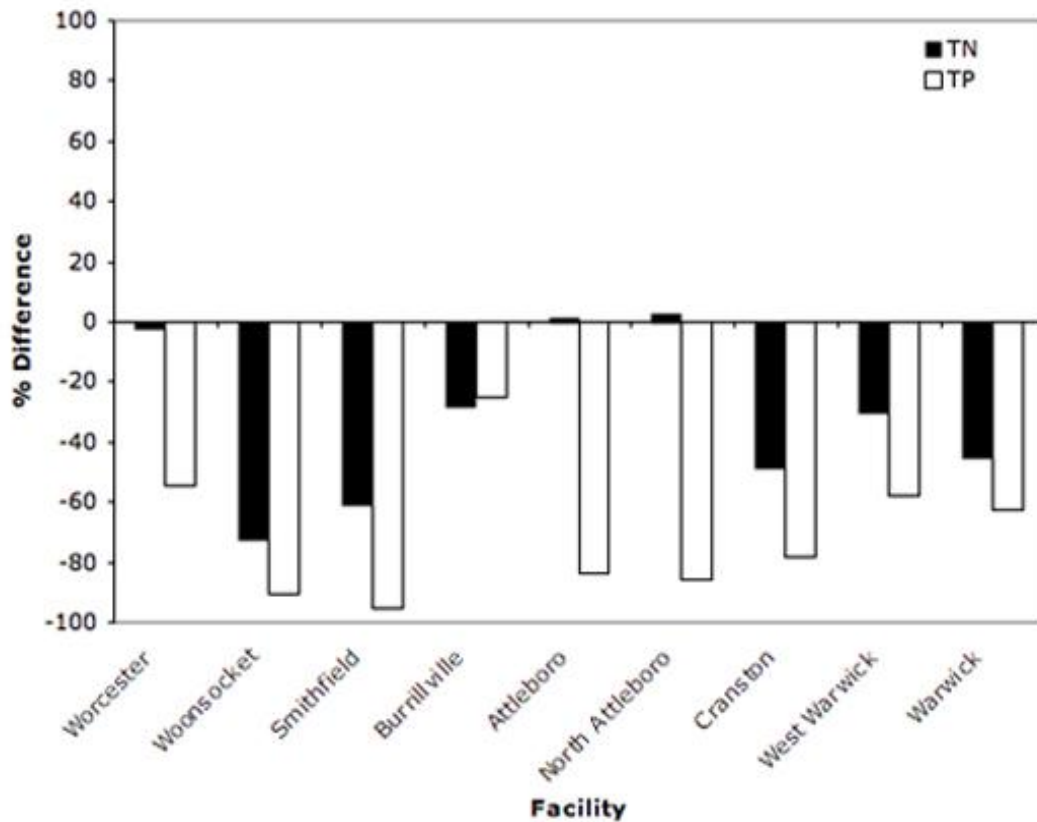


Figure B-37. Active season percent difference in total nitrogen and total phosphorus loads discharged from facilities on rivers that drain to Narragansett Bay in 2007-2010 relative to 2000-2004. The Grafton, Millbury, Hopedale, Leicester, Douglas, Upton, Brockton, Taunton, and Somerset facilities were not included as there was no seasonal data available.

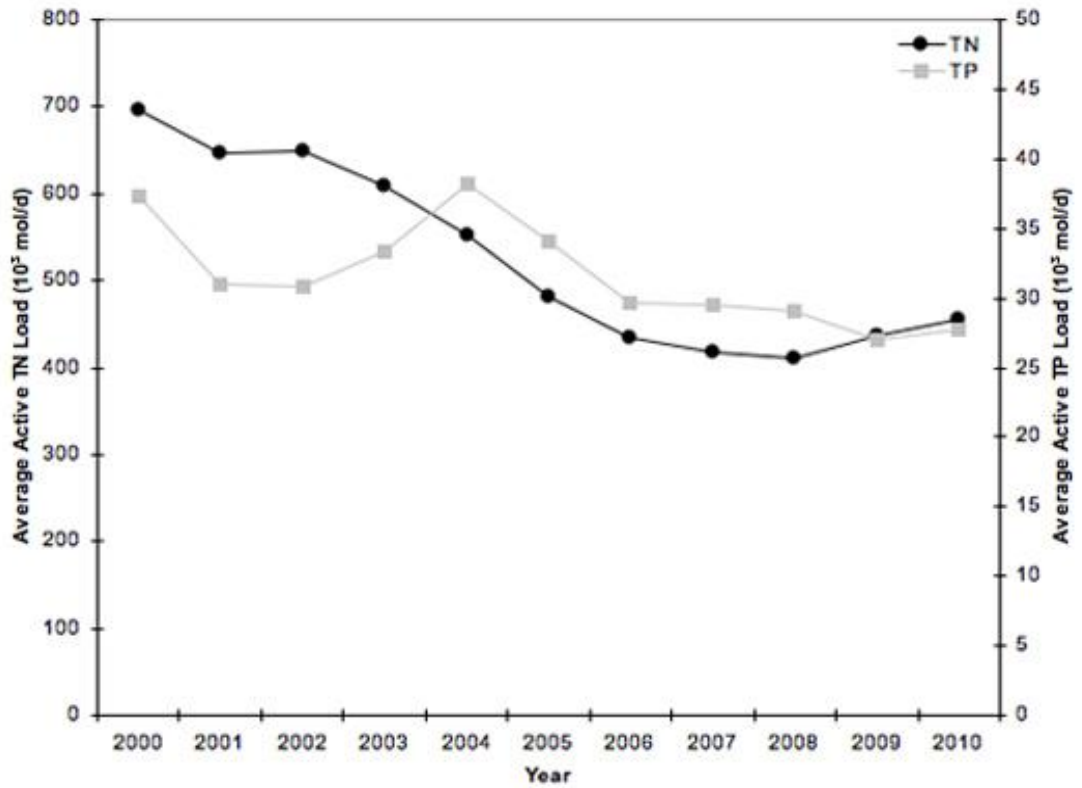


Figure B-38. Average active season total sewage nitrogen and total sewage phosphorus load discharged from all facilities with load data available combined over the 2000-2010 time period.

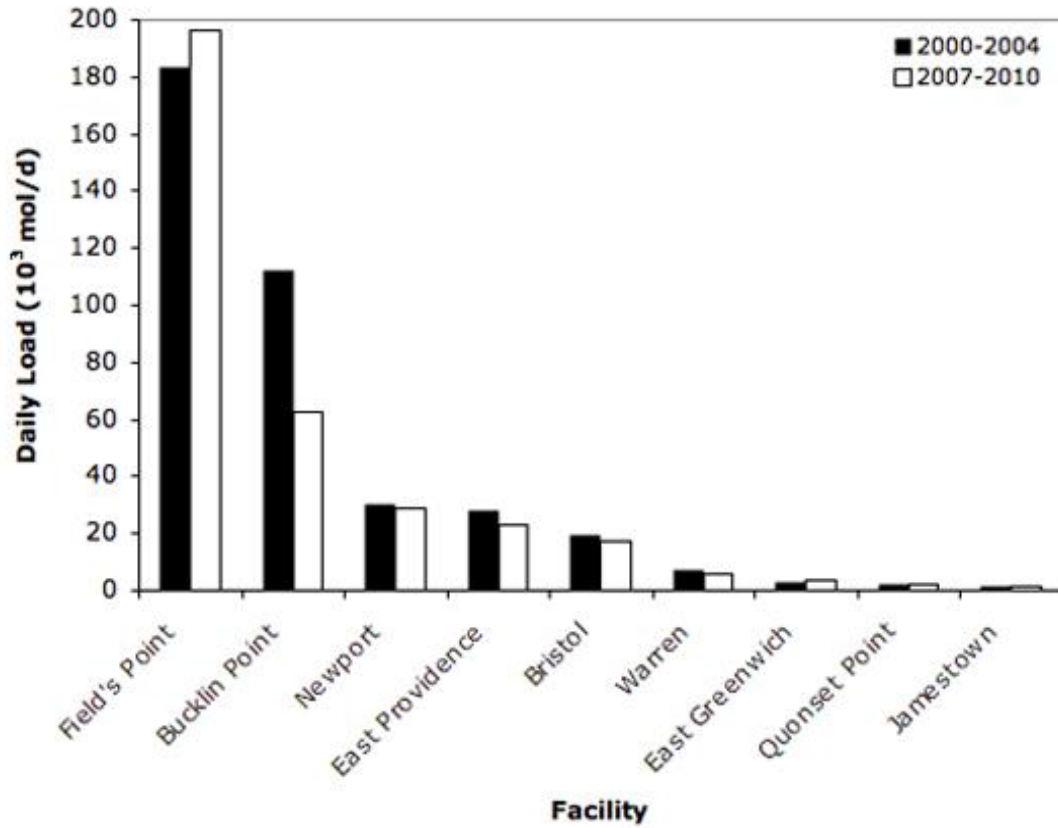


Figure B-39. Inactive season daily total nitrogen load from facilities that directly discharge to Narragansett Bay. The Fall River facility was not included as there was no seasonal data available.

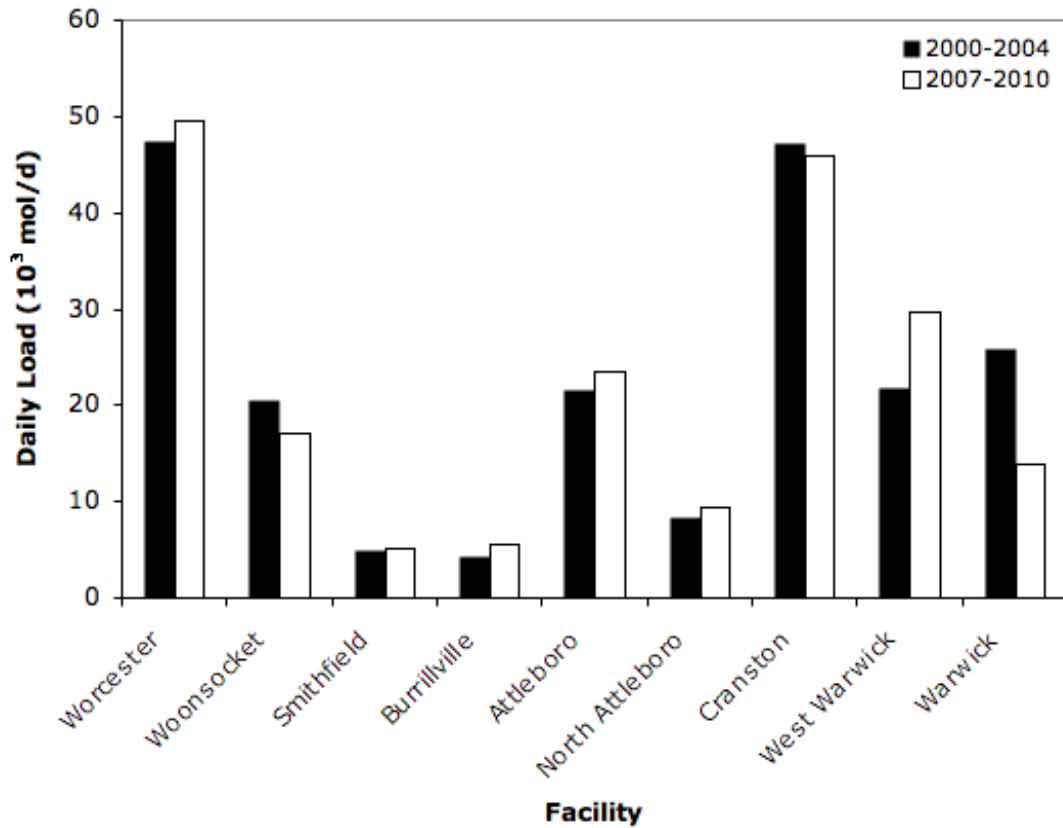


Figure B-40. Inactive season daily total nitrogen load discharged from facilities on rivers that drain to Narragansett Bay. The Grafton, Millbury, Hopedale, Leicester, Douglas, Upton, Brockton, Taunton, and Somerset facilities were not included as there was no seasonal data available.

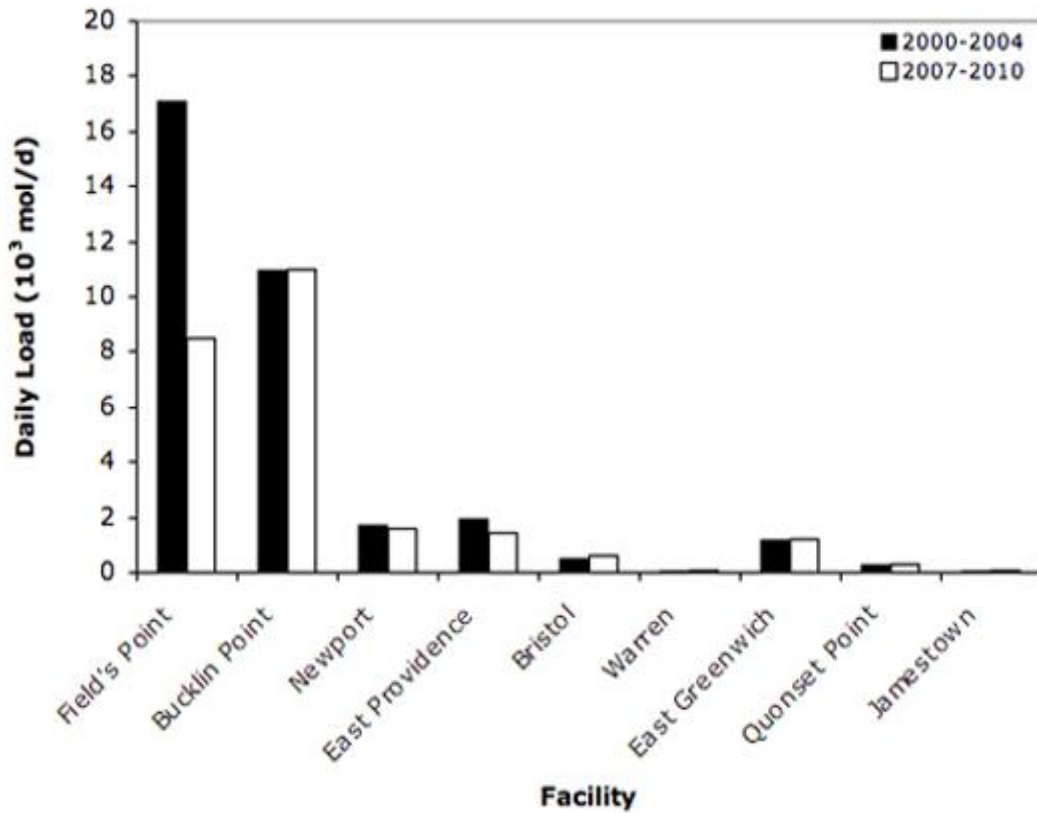


Figure B-41. Inactive season daily total phosphorus load from facilities that directly discharge to Narragansett Bay. The Fall River facility was not included as there was no seasonal data available.

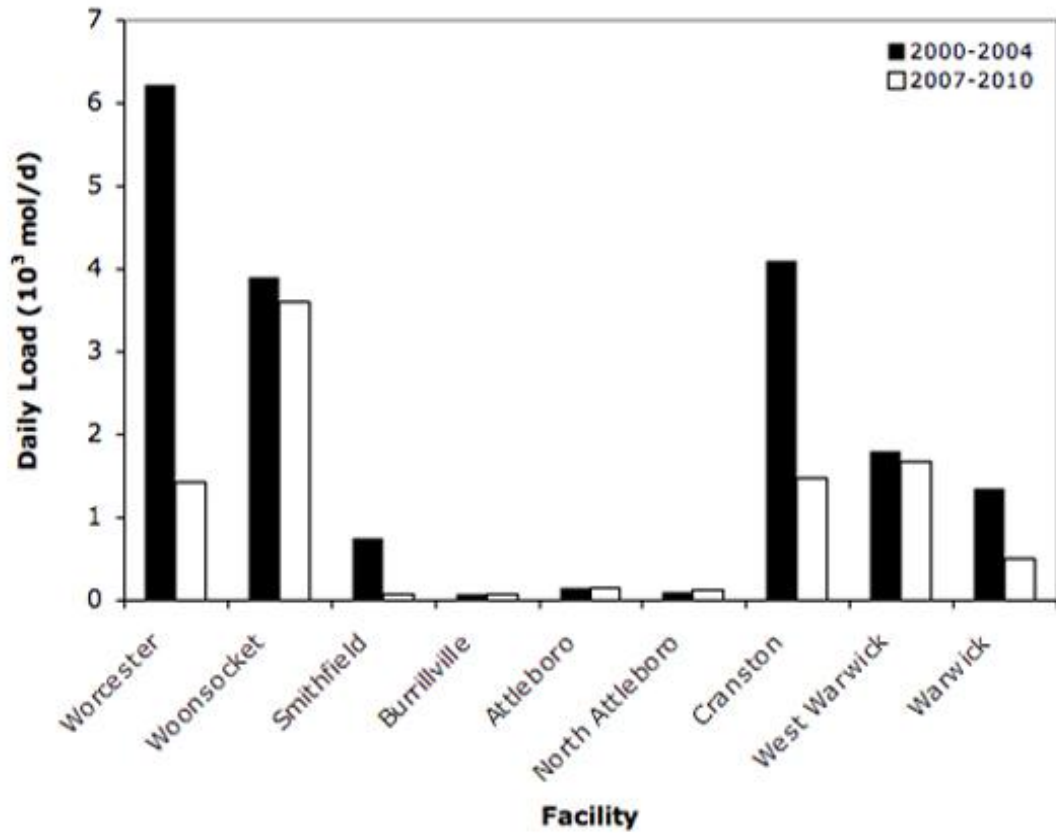


Figure B-42. Inactive season daily total phosphorus load discharged from facilities on rivers that drain to Narragansett Bay. The Grafton, Millbury, Hopedale, Leicester, Douglas, Upton, Brockton, Taunton, and Somerset facilities were not included as there was no seasonal data available.

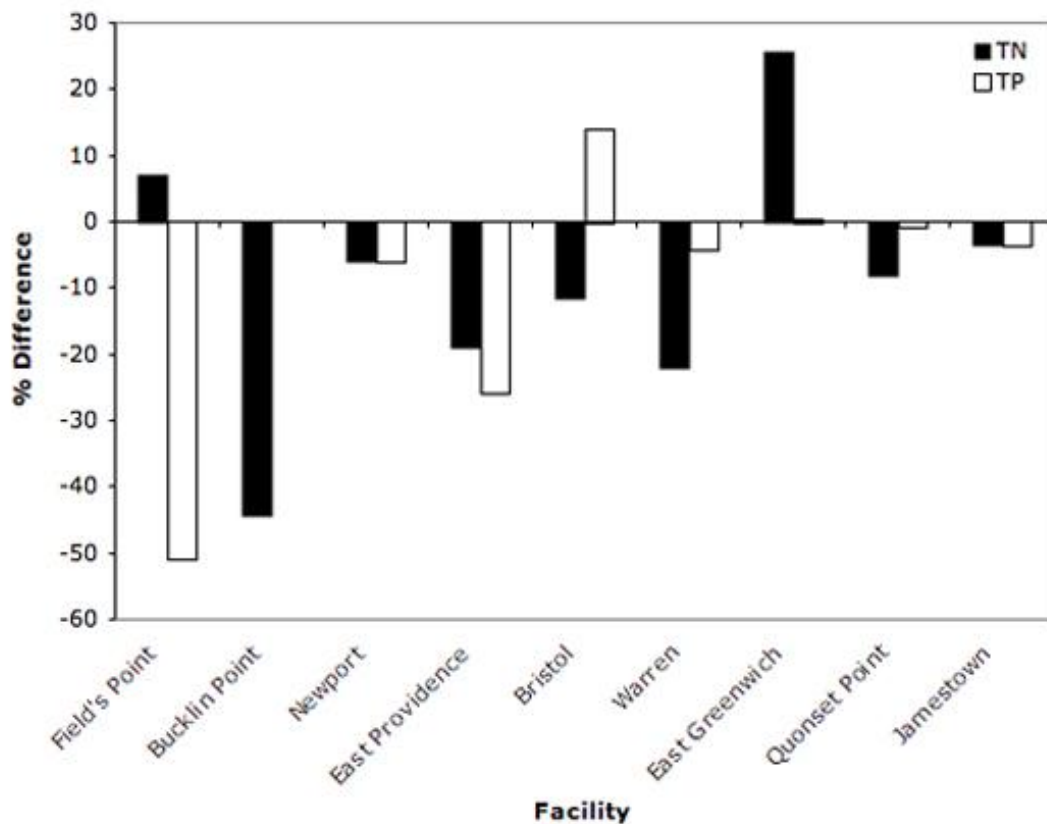


Figure B-43. Inactive season percent difference in total nitrogen and total phosphorus loads from facilities that directly discharge to Narragansett Bay in 2007-2010 relative to 2000-2004. The Fall River facility was not included as there was no seasonal data available.

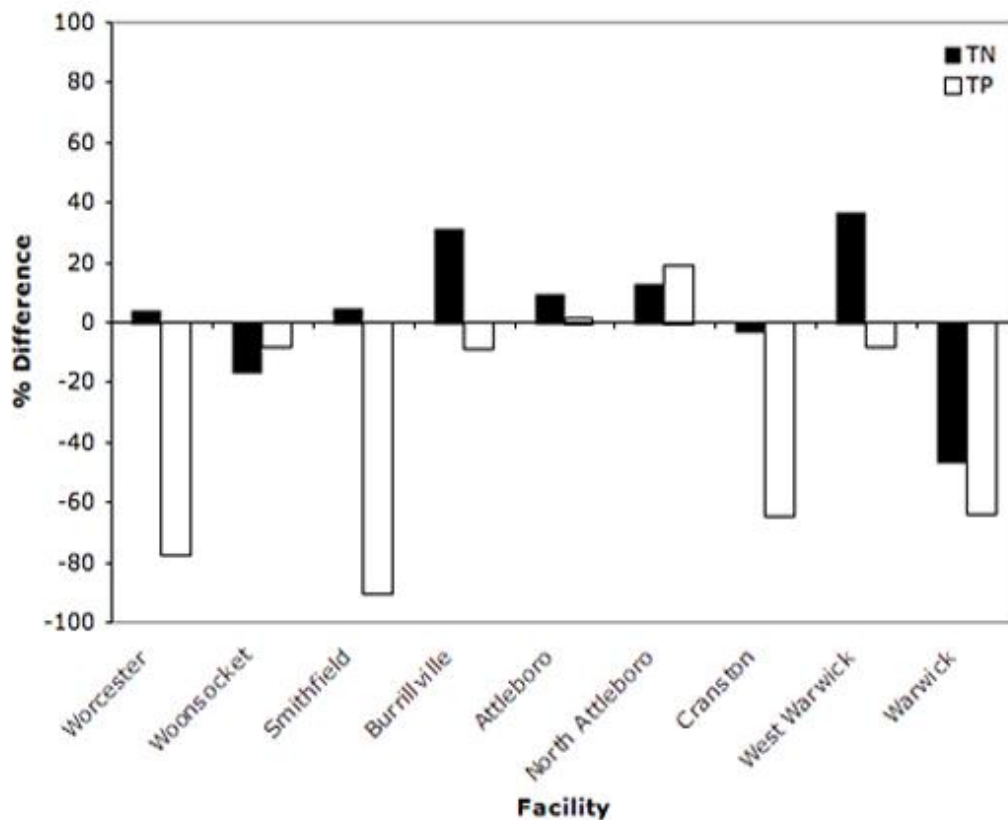


Figure B-44. Inactive season percent difference in total nitrogen and total phosphorus loads discharged from facilities on rivers that drain to Narragansett Bay in 2007-2010 relative to 2000-2004. The Grafton, Millbury, Hopedale, Leicester, Douglas, Upton, Brockton, Taunton, and Somerset facilities were not included as there was no seasonal data available.

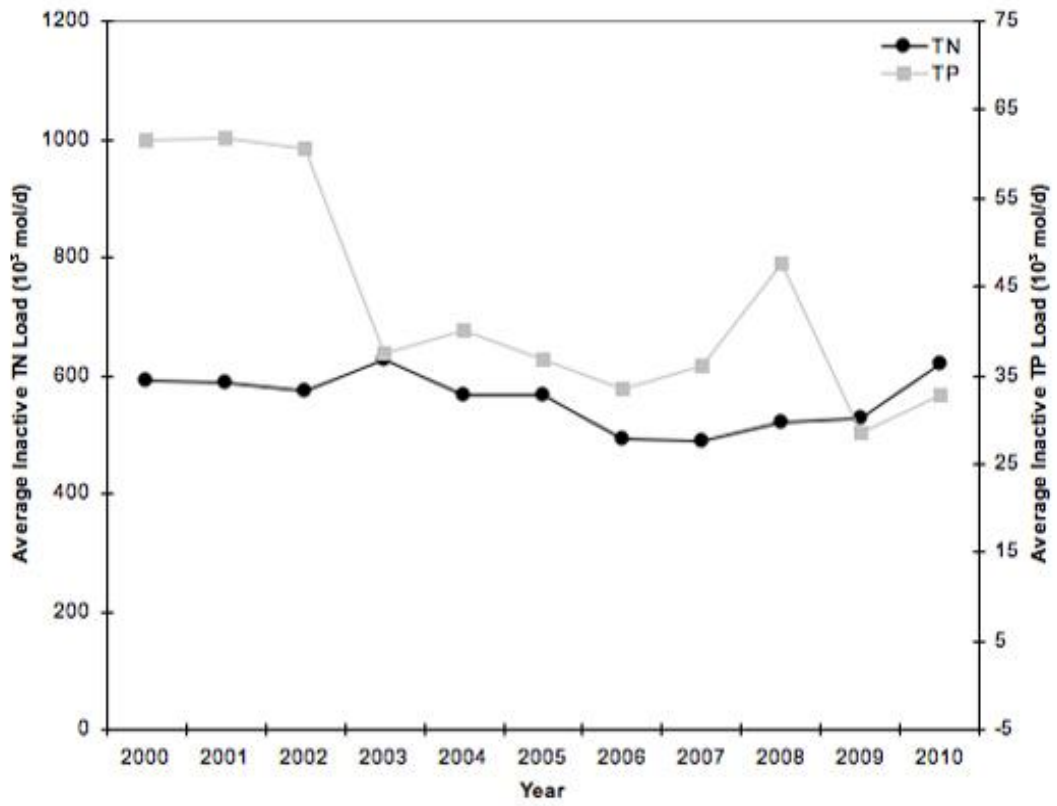


Figure B-45. Average inactive season total sewage nitrogen and total sewage phosphorus load discharged from all facilities with load data available combined over the 2000-2010 time period.

APPENDIX C

CODE FOR MATLAB AND R

ANALYSIS OF COVARIANCE IN MATLAB

This code was written with the assistance of Matt Horn

```
%First input your data
%Next rename them using the colheaders or textdata to identify what is
%what.
Year=data(:,1);
Distance=data(:,2);
DIN=data(:,3);
PO4=data(:,4);
NH3=data(:,5);
NOx=data(:,6);
SiO4=data(:,7);
%Clear extraneous data and keep your "data" which is equal to "raw"
clear colheaders textdata

%Take the log transform of 4 variables
ln_DIN=log(DIN);
ln_PO4=log(PO4);
ln_NH3=log(NH3);
ln_NOx=log(NOx);
ln_SiO4=log(SiO4);
%Use indexes to find the point identifier for given years - note... this is
%NOT the value... it's the location of those values in the matrix.
index1980=find(Year==1980);
index2006=find(Year==2006);
index2007=find(Year==2007);
index2008=find(Year==2008);
index2009=find(Year==2009);
index2010=find(Year==2010);

%%Make a matrix that is your year labels.
%yearlabel=char('1980','2006','2007','2008','2009','2010');

%Make an average that includes 2006-2010
temp_mean_ln_DIN=[ln_DIN(index2006) ln_DIN(index2007) ln_DIN(index2008)
ln_DIN(index2009) ln_DIN(index2010)];
temp_mean_ln_PO4=[ln_PO4(index2006) ln_PO4(index2007) ln_PO4(index2008)
ln_PO4(index2009) ln_PO4(index2010)];
temp_mean_ln_NH3=[ln_NH3(index2006) ln_NH3(index2007) ln_NH3(index2008)
ln_NH3(index2009) ln_NH3(index2010)];
temp_mean_ln_NOx=[ln_NOx(index2006) ln_NOx(index2007) ln_NOx(index2008)
ln_NOx(index2009) ln_NOx(index2010)];
temp_mean_ln_SiO4=[ln_SiO4(index2006) ln_SiO4(index2007) ln_SiO4(index2008)
ln_SiO4(index2009) ln_SiO4(index2010)];

mean_06_10_ln_DIN=mean(temp_mean_ln_DIN,2);
mean_06_10_ln_PO4=mean(temp_mean_ln_PO4,2);
```



```

mean_06_10_ln_NH3=mean(temp_mean_ln_NH3,2);
mean_06_10_ln_NOx=mean(temp_mean_ln_NOx,2);
mean_06_10_ln_SiO4=mean(temp_mean_ln_SiO4,2);
clear temp_mean_ln_DIN temp_mean_ln_PO4 temp_mean_ln_NH3 temp_mean_ln_NOX
temp_mean_ln_SiO4

%Plot up the raw data based upon year.
figure(1);clf;hold on;
subplot(5,1,1);
    plot(Distance(index1980),ln_DIN(index1980),'.k');hold on;
    plot(Distance(index2006),ln_DIN(index2006),'xr');hold on;
    plot(Distance(index2007),ln_DIN(index2007),'ob');hold on;
    plot(Distance(index2008),ln_DIN(index2008),'+g');hold on;
    plot(Distance(index2009),ln_DIN(index2009),'*m');hold on;
    plot(Distance(index2010),ln_DIN(index2010),'<k');hold on;
    plot(Distance(index2006),mean_06_10_ln_DIN,'cd');hold on;
    title('DIN');
    xlabel('distance (km)');ylabel('DIN')
    legend('1980','2006','2007','2008','2009','2010','06-10 mean')

subplot(5,1,2);
    plot(Distance(index1980),ln_PO4(index1980),'.k');hold on;
    plot(Distance(index2006),ln_PO4(index2006),'xr');hold on;
    plot(Distance(index2007),ln_PO4(index2007),'ob');hold on;
    plot(Distance(index2008),ln_PO4(index2008),'+g');hold on;
    plot(Distance(index2009),ln_PO4(index2009),'*m');hold on;
    plot(Distance(index2010),ln_PO4(index2010),'<k');hold on;
    plot(Distance(index2006),mean_06_10_ln_PO4,'cd');hold on;
    title('PO4');
    xlabel('distance (km)');ylabel('PO4')

subplot(5,1,3);
    plot(Distance(index1980),ln_NH3(index1980),'.k');hold on;
    plot(Distance(index2006),ln_NH3(index2006),'xr');hold on;
    plot(Distance(index2007),ln_NH3(index2007),'ob');hold on;
    plot(Distance(index2008),ln_NH3(index2008),'+g');hold on;
    plot(Distance(index2009),ln_NH3(index2009),'*m');hold on;
    plot(Distance(index2010),ln_NH3(index2010),'<k');hold on;
    plot(Distance(index2006),mean_06_10_ln_NH3,'cd');hold on;
    title('NH3');
    xlabel('distance (km)');ylabel('NH3')

subplot(5,1,4);
    plot(Distance(index1980),ln_NOx(index1980),'.k');hold on;
    plot(Distance(index2006),ln_NOx(index2006),'xr');hold on;
    plot(Distance(index2007),ln_NOx(index2007),'ob');hold on;
    plot(Distance(index2008),ln_NOx(index2008),'+g');hold on;
    plot(Distance(index2009),ln_NOx(index2009),'*m');hold on;
    plot(Distance(index2010),ln_NOx(index2010),'<k');hold on;
    plot(Distance(index2006),mean_06_10_ln_NOx,'cd');hold on;
    title('NOx');
    xlabel('distance (km)');ylabel('NOx')

subplot(5,1,5);
    plot(Distance(index1980),ln_SiO4(index1980),'.k');hold on;
    plot(Distance(index2006),ln_SiO4(index2006),'xr');hold on;
    plot(Distance(index2007),ln_SiO4(index2007),'ob');hold on;

```

```

plot(Distance(index2008),ln_SiO4(index2008),'+g');hold on;
plot(Distance(index2009),ln_SiO4(index2009),'*m');hold on;
plot(Distance(index2010),ln_SiO4(index2010),'<k');hold on;
plot(Distance(index2006),mean_06_10_ln_SiO4,'cd');hold on;
title('SiO4');
xlabel('distance (km)');ylabel('SiO4')

%ANCOVA-tron
%This version tests means
xval=[Distance(index1980); Distance(index2006)];%Distance
yval=[ln_SiO4(index1980); mean_06_10_ln_SiO4];%experimental variable
gval=[Year(index1980); Year(index2006)];% year
%this version tests years independently
%xval=[Distance(index1980);Distance(index2006);Distance(index2007);Distance(i
ndex2008);Distance(index2009);Distance(index2010);Distance(index2006)];
%DISTANCE
%yval=[ln_NOx(index1980);ln_NOx(index2006);ln_NOx(index2007);ln_NOx(index2008
);ln_NOx(index2009);ln_NOx(index2010);mean_06_10_ln_NOx]; %LN_DIN
%gval=[Year(index1980);Year(index2006);Year(index2007);Year(index2008);Year(i
ndex2009);Year(index2010);1;1;1;1;1;1;1;1;1;1;1;1;1;1;1]; %YEAR

[h,atab,ctab,stats] =
aoctool(xval,yval,gval,0.05,'Distance','ln_SiO4','Year');

multcompare(stats,0.05,'on','','intercept');% multiple comparison of
intercepts
%multcompare(stats,0.05,'on','','slope');% multiple comparison of slopes

```

Shapiro-Wilk Test in Matlab

This code was obtained through the Matlab File Exchange at:

<http://www.mathworks.com/matlabcentral/fileexchange/13964>

```
function [H, pValue, W] = swtest(x, alpha, tail)
%SWTEST Shapiro-Wilk parametric hypothesis test of composite normality.
% [H, pValue, SWstatistic] = SWTEST(X, ALPHA, TAIL) performs
% the Shapiro-Wilk test to determine if the null hypothesis of
% composite normality is a reasonable assumption regarding the
% population distribution of a random sample X. The desired significance
% level, ALPHA, is an optional scalar input (default = 0.05).
% TAIL indicates the type of test (default = 1).
%
% The Shapiro-Wilk hypotheses are:
% Null Hypothesis:      X is normal with unspecified mean and variance.
%   For TAIL = 0 (2-sided test), alternative: X is not normal.
%   For TAIL = 1 (1-sided test), alternative: X is upper the normal.
%   For TAIL = -1 (1-sided test), alternative: X is lower the normal.
%
% This is an omnibus test, and is generally considered relatively
% powerful against a variety of alternatives.
% Shapiro-Wilk test is better than the Shapiro-Francia test for
% Platykurtic sample. Conversely, Shapiro-Francia test is better than the
% Shapiro-Wilk test for Leptokurtic samples.
%
% When the series 'X' is Leptokurtic, SWTEST performs the Shapiro-Francia
% test, else (series 'X' is Platykurtic) SWTEST performs the
% Shapiro-Wilk test.
%
%   [H, pValue, SWstatistic] = SWTEST(X, ALPHA, TAIL)
%
% Inputs:
% X - a vector of deviates from an unknown distribution. The observation
%     number must exceed 3 and less than 5000.
%
% Optional inputs:
% ALPHA - The significance level for the test (default = 0.05).
%
% TAIL - The type of the test (default = 1).
%
% Outputs:
% SWstatistic - The test statistic (non normalized).
%
% pValue - is the p-value, or the probability of observing the given
%          result by chance given that the null hypothesis is true. Small values
%          of pValue cast doubt on the validity of the null hypothesis.
%
% H = 0 => Do not reject the null hypothesis at significance level ALPHA.
% H = 1 => Reject the null hypothesis at significance level ALPHA.
%
%
% References: Royston P. "Algorithm AS R94", Applied Statistics (1995) Vol.
44, No. 4.
% AS R94 -- calculates Shapiro-Wilk normality test and P-value
% for sample sizes 3 <= n <= 5000. Handles censored or uncensored data.
% Corrects AS 181, which was found to be inaccurate for n > 50.
%
```

```

%
% Ensure the sample data is a VECTOR.
%

if numel(x) == length(x)
    x = x(:);           % Ensure a column vector.
else
    error(' Input sample 'X' must be a vector. ');
end

%
% Remove missing observations indicated by NaN's and check sample size.
%

x = x(~isnan(x));

if length(x) < 3
    error(' Sample vector 'X' must have at least 3 valid observations. ');
end

if length(x) > 5000
    warning('Shapiro-Wilk test might be inaccurate due to large sample size (
> 5000). ');
end

%
% Ensure the significance level, ALPHA, is a
% scalar, and set default if necessary.
%

if (nargin >= 2) && ~isempty(alpha)
    if numel(alpha) > 1
        error(' Significance level 'Alpha' must be a scalar. ');
    end
    if (alpha <= 0 || alpha >= 1)
        error(' Significance level 'Alpha' must be between 0 and 1. ');
    end
else
    alpha = 0.05;
end

%
% Ensure the type-of-test indicator, TAIL, is a scalar integer from
% the allowable set [-1 , 0 , 1], and set default if necessary.
%

if (nargin >= 3) && ~isempty(tail)
    if numel(tail) > 1
        error('Type-of-test indicator 'Tail' must be a scalar. ');
    end
    if (tail ~= -1) && (tail ~= 0) && (tail ~= 1)
        error('Type-of-test indicator 'Tail' must be -1, 0, or 1. ');
    end
else

```

```

    tail = 1;
end

% First, calculate the a's for weights as a function of the m's
% See Royston (1995) for details in the approximation.

x      = sort(x); % Sort the vector X in ascending order.
n      = length(x);
mtilde = norminv((1:n)' - 3/8) / (n + 0.25));
weights = zeros(n,1); % Preallocate the weights.

if kurtosis(x) > 3

    % The Shapiro-Francia test is better for leptokurtic samples.

    weights = 1/sqrt(mtilde'*mtilde) * mtilde;

    %
    % The Shapiro-Francia statistic W is calculated to avoid excessive
rounding
    % errors for W close to 1 (a potential problem in very large samples).
    %
    W = (weights' * x) ^2 / ((x - mean(x))' * (x - mean(x)));

    nu      = log(n);
    u1      = log(nu) - nu;
    u2      = log(nu) + 2/nu;
    mu      = -1.2725 + (1.0521 * u1);
    sigma   = 1.0308 - (0.26758 * u2);

    newSFstatistic = log(1 - W);

    %
    % Compute the normalized Shapiro-Francia statistic and its p-value.
    %
    NormalSFstatistic = (newSFstatistic - mu) / sigma;

    % the next p-value is for the tail = 1 test.
    pValue = 1 - normcdf(NormalSFstatistic, 0, 1);

else

    % The Shapiro-Wilk test is better for platykurtic samples.

    c = 1/sqrt(mtilde'*mtilde) * mtilde;
    u = 1/sqrt(n);

    PolyCoef_1 = [-2.706056 , 4.434685 , -2.071190 , -0.147981 , 0.221157
, c(n)];
    PolyCoef_2 = [-3.582633 , 5.682633 , -1.752461 , -0.293762 , 0.042981
, c(n-1)];

```

```

PolyCoef_3 = [-0.0006714 , 0.0250540 , -0.39978 , 0.54400];
PolyCoef_4 = [-0.0020322 , 0.0627670 , -0.77857 , 1.38220];
PolyCoef_5 = [0.00389150 , -0.083751 , -0.31082 , -1.5861];
PolyCoef_6 = [0.00303020 , -0.082676 , -0.48030];

PolyCoef_7 = [0.459 , -2.273];

weights(n) = polyval(PolyCoef_1 , u);
weights(1) = -weights(n);

% Special attention when n=3 (this is a special case).
if n == 3
    weights(1) = 0.707106781;
    weights(n) = -weights(1);
end

if n >= 6
    weights(n-1) = polyval(PolyCoef_2 , u);
    weights(2) = -weights(n-1);

    count = 3;
    phi = (mtilde'*mtilde - 2 * mtilde(n)^2 - 2 * mtilde(n-1)^2) /
...
        (1 - 2 * weights(n)^2 - 2 * weights(n-1)^2);
else
    count = 2;
    phi = (mtilde'*mtilde - 2 * mtilde(n)^2) / ...
        (1 - 2 * weights(n)^2);
end

%
% The vector 'WEIGHTS' obtained next corresponds to the same coefficients
% listed by Shapiro-Wilk in their original test for small samples.
%

weights(count : n-count+1) = mtilde(count : n-count+1) / sqrt(phi);

%
% The Shapiro-Wilk statistic W is calculated to avoid excessive rounding
% errors for W close to 1 (a potential problem in very large samples).
%

W = (weights' * x) ^2 / ((x - mean(x))' * (x - mean(x)));

%
% Calculate the significance level for W (exact for n=3).
%

newn = log(n);

if (n > 3) && (n <= 11)

    mu = polyval(PolyCoef_3 , n);

```

```

sigma    =    exp(polyval(PolyCoef_4 , n));
gam      =    polyval(PolyCoef_7 , n);

newSWstatistic =    -log(gam-log(1-W));

elseif n >= 12

mu       =    polyval(PolyCoef_5 , newn);
sigma    =    exp(polyval(PolyCoef_6 , newn));

newSWstatistic =    log(1 - W);

elseif n == 3
mu       =    0;
sigma    =    1;
newSWstatistic =    0;
end

%
% Compute the normalized Shapiro-Wilk statistic and its p-value.
%

NormalSWstatistic      =    (newSWstatistic - mu) / sigma;

% The next p-value is for the tail = 1 test.
pValue      =    1 - normcdf(NormalSWstatistic, 0, 1);

% Special attention when n=3 (this is a special case).
if n == 3
pValue      =    1.909859 * (asin(sqrt(W)) - 1.047198);
NormalSWstatistic =    norminv(pValue, 0, 1);
end

end

% The p-value just found is for the tail = 1 test.
if tail == 0
pValue      =    2 * min(pValue, 1-pValue);
elseif tail == -1
pValue      =    1 - pValue;
end

%
% To maintain consistency with existing Statistics Toolbox hypothesis
% tests, returning 'H = 0' implies that we 'Do not reject the null
% hypothesis at the significance level of alpha' and 'H = 1' implies
% that we 'Reject the null hypothesis at significance level of alpha.'
%

H = (alpha >= pValue);

```

```

                2 sided 2 tailed Kolmogorov Smirnov test in Matlab
%Script for Importing and running data for 2 sided Kolmogorov Smirnov
%distribution test%
%Jason Krumholz September, 2011
%1 Import the data to a matrix of 12 rows by X columns called 'data'
%Name the variables
NOx0610=data(:,2);
DIN0610=data(:,3);
PO40610=data(:,4);
SiO20610=data(:,5);
NH30610=data(:,6);
TN0610=data(:,7);
TP0610=data(:,8);
NOx7980=data(:,9);
DIN7980=data(:,10);
PO47980=data(:,11);
SiO27980=data(:,12);
NH37980=data(:,13);
TN1998=data(:,14);
TP1998=data(:,15);
[hNOx,pNOX,kNOX] = kstest2(NOx0610,NOx7980)
[hDIN,pDIN,kDIN] = kstest2(DIN0610,DIN7980)
[hPO4,pPO4,kPO4] = kstest2(PO40610,PO47980)
[hSiO2,pSiO2,kSiO2] = kstest2(SiO20610,SiO27980)
[hNH3,pNH3,kNH3] = kstest2(NH30610,NH37980)
[hTN,pTN,kTN] = kstest2(TN0610,TN1998)
[hTP,pTP,kTP] = kstest2(TP0610,TP1998)
%Plot cumulative distribution frequencies
figure
subplot(4,2,1)
A0610 = cdfplot(NOx0610);
hold on
A7980 = cdfplot(NOx7980);
set(A0610,'LineWidth',2,'Color','r');
set(A7980,'LineWidth',2);
legend([A0610 A7980], '2006-2010 NOx', '1979-1980 NOx', 'Location', 'SE');
subplot(4,2,2)
B0610 = cdfplot(DIN0610);
hold on
B7980 = cdfplot(DIN7980);
set(B0610,'LineWidth',2,'Color','r');
set(B7980,'LineWidth',2);
legend([B0610 B7980], '2006-2010 DIN', '1979-1980 DIN', 'Location', 'SE');
subplot(4,2,3)
C0610 = cdfplot(PO40610);
hold on
C7980 = cdfplot(PO47980);
set(C0610,'LineWidth',2,'Color','r');
set(C7980,'LineWidth',2);
legend([C0610 C7980], '2006-2010 PO4', '1979-1980 PO4', 'Location', 'SE');
subplot(4,2,4)
D0610 = cdfplot(SiO20610);
hold on
D7980 = cdfplot(SiO27980);
set(D0610,'LineWidth',2,'Color','r');
set(D7980,'LineWidth',2);
legend([D0610 D7980], '2006-2010 SiO2', '1979-1980 SiO2', 'Location', 'SE');

```



```

subplot(4,2,7)
E0610 = cdfplot(TN0610);
hold on
E7980 = cdfplot(TN1998);
set(E0610, 'LineWidth', 2, 'Color', 'r');
set(E7980, 'LineWidth', 2);
legend([E0610 E7980], '2006-2010 TN', '1998 TN', 'Location', 'SE');
subplot(4,2,6)
G0610 = cdfplot(NH30610);
hold on
G7980 = cdfplot(NH37980);
set(G0610, 'LineWidth', 2, 'Color', 'r');
set(G7980, 'LineWidth', 2);
legend([G0610 G7980], '2006-2010 NH4', '1979-1980 NH4', 'Location', 'SE');
subplot(4,2,8)
F0610 = cdfplot(TP0610);
hold on
F7980 = cdfplot(TP1998);
set(F0610, 'LineWidth', 2, 'Color', 'r');
set(F7980, 'LineWidth', 2);
legend([F0610 F7980], '2006-2010 TP', '1998 TP', 'Location', 'SE');

```

SSPIR code in R

This code was written with the assistance of Claus Dethlefsen and Rich Bell.

```
# 7/15/11

# Krumholz nutrient data

# we shall try with SSPIR

library(sspir)

t98 <- read.table("T98interpolated.csv", header=T, sep=',', stringsAsFactors=F)
head(t98)

# pick out essential info
fav <- c("CHLa", "NO2.NO3", "PO4", "NH4", "DIN", "Nint", "Pint")
t98.small <- t98[,fav]
# (I found an NA in "SiO2" so I left this one out)

tt <- 1:nrow(t98.small)
t98.small$tt <- 1:nrow(t98.small)
t98.small$s1 <- sin(t98.small$tt*2*pi/52)
t98.small$c1 <- cos(t98.small$tt*2*pi/52)
t98.small$s2 <- sin(t98.small$tt*2*2*pi/52)
t98.small$c2 <- cos(t98.small$tt*2*2*pi/52)
t98.small$s3 <- sin(t98.small$tt*3*2*pi/52)
t98.small$c3 <- cos(t98.small$tt*3*2*pi/52)
t98.small$s4 <- sin(t98.small$tt*4*2*pi/52)
t98.small$c4 <- cos(t98.small$tt*4*2*pi/52)
t98.small$Nint <- as.factor(t98.small$Nint)
t98.small$Pint <- as.factor(t98.small$Pint)

t98.ts <- ts(t98[,fav], frequency = 52, start = c(1978, 1))
plot(t98.ts[,fav])

require(graphics)
t98.decomp <- decompose(t98.ts[,fav], type="additive")
plot(t98.decomp$trend) # moving average

library(rms)
n.group <- 1
d <- datadist(t98.small)
options(datadist="d")

describe(t98.small)
```

```

# inspect a histogram of the CHLa
hist(t98.small$CHLa)
hist(log(t98.small$CHLa))
# use log instead of raw measurements.
par(mfcol=c(5,2))
for (i in 1:5) hist(t98.small[,i])
for (i in 1:5) hist(log(t98.small[,i]))
par(mfrow=c(1,1))

## ordinary least squares models
# just trend and interventions
# trend is a restricted cubic spline with 7 knots
m1 <- ols(log(CHLa)~rcs(tt,7)+Nint+Pint,data=t98.small)
m1 <- ols(log(DIN)~rcs(tt,7)+Nint+Pint,data=t98.small)
m1 <- ols(log(PO4)~rcs(tt,7)+Nint+Pint,data=t98.small)

anova(m1)
summary(m1)
# Nint: 0.35 (0.05;0.66) ie (exp(0.35)-1)*100%=42% increase, p=2%
# Pint: -0.26 (-0.57;0.05) ie 23% decrease, p=11%

# adjust for one sine-cosine
m2 <- ols(log(CHLa)~rcs(tt,7)+c1+s1+Nint+Pint,data=t98.small)
m2 <- ols(log(NH4)~rcs(tt,7)+c1+s1+Nint+Pint,data=t98.small)
m2 <- ols(log(DIN)~rcs(tt,7)+c1+s1+Nint+Pint,data=t98.small)
m2 <- ols(log(PO4)~rcs(tt,7)+c1+s1+Nint+Pint,data=t98.small)

anova(m2)
summary(m2)
# Nint: 0.28 (-0.02;0.59) ie 32% increase, p=7%
# Pint: -0.32 (-0.62;-0.01) ie 27% decrease, p=4%

# adjust for four sine-cosines
m3 <- ols(log(CHLa)~rcs(tt,7)+c1+s1+c2+s2+c3+s3+c4+s4+Nint+Pint,data=t98.small)
m3 <- ols(log(DIN)~rcs(tt,7)+c1+s1+c2+s2+c3+s3+c4+s4+Nint+Pint,data=t98.small)
anova(m3)
summary(m3)
acf(resid(m3))
# Nint: 0.24 (-0.06;0.53) ie 27% increase, p=12%
# Pint: -0.35 (-0.66;-0.05) ie 30% decrease, p=2%
# note that the autocorrelation function of the residuals looks
# "terrible". There is a strong serial correlation. That's why the
# simple models do not work and we turn to time series models, such as
# state space models.

# A "simple" state space model is the Basic Structural Model, built in

```

```

# to R. It includes level, slope, "sum-to-season" and residuals. It is
# very efficient at maximizing the likelihood and estimating the
# variance parameters.
t98.i <- StructTS(log(t98.ts[,1]),type="BSM")
plot(cbind(fitted(t98.i),resids=resid(t98.i)))
print(t98.i$coef)
acf(resid(t98.i))
#level  slope  season  eps
#0.1867393 0 5.350514e-06 0.2672746
phihat <- c(0.1867393, 0, 5.350514e-06, 0.2672746)
# note that the slope variance parameter is estimated to 0, meaning
# that the slope is not time-varying. Thus the trend reduces to a
# local level model.

# the bad thing about StructTS is that it cannot handle covariates.
# That's why we turn to sspir and formulate the same model as BSM in
# StructTS but add the two covariates Nint and Pint.

# The bad thing about sspir is that it does not estimate the variance
# parameters. You need to use some kind of numerical maximization
# algorithm and it might take forever. We thus just take the estimated
# parameters from StructTS and plug in. This is not quite legal since
# the parameters are estimated without taking the covariates into
# account. We ignore that for now.... If you were to do it right, you
# would take this as initial values and then find the
# phi-configuration that maximizes kfs(yourmodel)$loglik

#####

#      Chl a is dependent variable

## the big model with timevarying season and trend.
## variance parameters are taken from the BSM model from StructTS

sm1 <- ssm( log(t98.ts[,1]) ~ -1+tvar(polytime(tt,1)) + tvar(sumseason(tt,52)) +
  t98.ts[,6] + t98.ts[,7],fit=FALSE)
phi(sm1)[c(4,1,2,3)] <- phihat
sm1.fit <- kfs(sm1)
Nint <- sm1.fit$m[1,54] # since it is static, all m's are the same
Pint <- sm1.fit$m[1,55]
# Nint: 0.23, ie 26% increase
# Pint: 0.51, ie 67% increase
sdNint <- sqrt(diag(sm1.fit$C[[1]])[54])
sdPint <- sqrt(diag(sm1.fit$C[[1]])[55])

```

```

# thus a 95% confidence interval can be obtained:
(exp(c(Nint - 1.96*sdNint, Nint + 1.96*sdNint))-1)*100
#very wide ...

# local level model for the trend
sm2 <- ssm( log(t98.ts[,1]) ~ tvar(1) + tvar(sumseason(tt,52)) +
  t98.ts[,6] + t98.ts[,7],fit=FALSE)
phi(sm2)[c(4,1,3)] <- phihat
sm2.fit <- kfs(sm2)
Nint <- sm2.fit$m[1,53]
Pint <- sm2.fit$m[1,54]
# Nint: 0.07, ie 7% increase
# Pint: -0.54, ie 42% decrease
sdNint <- sqrt(diag(sm2.fit$C[[1]])[53])
sdPint <- sqrt(diag(sm2.fit$C[[1]])[54])
# thus a 95% confidence interval can be obtained:
(exp(c(Nint - 1.96*sdNint, Nint + 1.96*sdNint))-1)*100
(1-exp(c(Pint - 1.96*sdPint, Pint + 1.96*sdPint)))*100

#####

#      Nitrogen as dependent variable

bad.egg<-which(log(t98.ts[,4])==min(log(t98.ts[,4])))
t98.ts[bad.egg,4]<-0.05
tt<-1:1716

## the big model with timevarying season and trend. for N and P
## variance parameters are taken from the BSM model from StructTS

sm1 <- ssm( log(t98.ts[,5]) ~ -1+tvar(polytime(tt,1)) + tvar(sumseason(tt,52)) +
  t98.ts[,6] + t98.ts[,7],fit=FALSE) #      DIN

sm1 <- ssm( log(t98.ts[,4]) ~ -1+tvar(polytime(tt,1)) + tvar(sumseason(tt,52)) +
  t98.ts[,6] + t98.ts[,7],fit=FALSE) #      NH4

phi(sm1)[c(4,1,2,3)] <- phihat
sm1.fit <- kfs(sm1)
Nint <- sm1.fit$m[1,54] # since it is static, all m's are the same
Pint <- sm1.fit$m[1,55]
# Nint: 0.50,
# Pint: -0.07
sdNint <- sqrt(diag(sm1.fit$C[[1]])[54])
sdPint <- sqrt(diag(sm1.fit$C[[1]])[55])
# thus a 95% confidence interval can be obtained:

```

```

(exp(c(Nint - 1.645*sdNint, Nint + 1.645*sdNint))-1)*100
#very wide ...

(exp(Nint)-1)*100    #    %=42% increase, p=2%

(exp(-0.54)-1)*100
#####

#    Nitrogen as dependent variable, w/o 2010 data

x.2009<-t98.ts[1:1664,]
par(family='serif',mfrow=c(3,3),mar=c(2,2,2,2))
for(i in 1:length(x.2009[1,]))
plot(x.2009[,i],typ='l',main=colnames(x.2009)[i])
}
tt<-1:1664
## the big model with timevarying season and trend. for N and P
## variance parameters are taken from the BSM model from StructTS

sm1 <- ssm( log(x.2009[,5]) ~ -1+tvar(polytime(tt,1)) + tvar(sumseason(tt,52)) +
  x.2009[,6] + x.2009[,7],fit=FALSE)
phi(sm1)[c(4,1,2,3)] <- phihat
sm1.fit <- kfs(sm1)
Nint <- sm1.fit$m[1,54] # since it is static, all m's are the same
Pint <- sm1.fit$m[1,55]
# Nint: 0.54
# Pint: -0.70
sdNint <- sqrt(diag(sm1.fit$C[[1]])[54])
sdPint <- sqrt(diag(sm1.fit$C[[1]])[55])
# thus a 95% confidence interval can be obtained:
(exp(c(Nint - 1.96*sdNint, Nint + 1.96*sdNint))-1)*100
#very wide ...

##### NH4

#    Nitrogen as dependent variable, w/o 2010 data

x.2009<-t98.ts[1:1664,]
par(family='serif',mfrow=c(3,3),mar=c(2,2,2,2))
for(i in 1:length(x.2009[1,]))
plot(x.2009[,i],typ='l',main=colnames(x.2009)[i])
}
tt<-1:1664

```

```

## the big model with timevarying season and trend. for N and P
## variance parameters are taken from the BSM model from StructTS

sm1 <- ssm( log(x.2009[,4]) ~ -1+tvar(polytime(tt,1)) + tvar(sumseason(tt,52)) +
  x.2009[,6] + x.2009[,7],fit=FALSE)
phi(sm1)[c(4,1,2,3)] <- phihat
sm1.fit <- kfs(sm1)
Nint <- sm1.fit$m[1,54] # since it is static, all m's are the same
Pint <- sm1.fit$m[1,55]
# Nint: -1.66
# Pint: --1.020
sdNint <- sqrt(diag(sm1.fit$C[[1]])[54])
sdPint <- sqrt(diag(sm1.fit$C[[1]])[55])
# thus a 95% confidence interval can be obtained:
(exp(c(Nint - 1.96*sdNint, Nint + 1.96*sdNint))-1)*100
#very wide ...

plot((log(x.2009[,4])),typ='l')

bad.egg<-which(log(x.2009[,4])==min(log(x.2009[,4])))

x.2009[bad.egg,4]<-0.05

t98.ts[bad.egg,]

plot(lowess(log(x.2009[,4])),typ='l')

```

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