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Improved Estimates of Tributary Nitrogen Load to Casco Bay, Maine

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IMPROVED ESTIMATES OF TRIBUTARY NITROGEN LOAD TO CASCO BAY, MAINE

By

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An Abstract of the Thesis Presented
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Over the past two decades, total nitrogen (TN) concentrations have increased in Casco Bay (CBEP 2015). The sources of the increased nitrogen are poorly understood but occur with simultaneous population growth and land use changes. The total riverine nitrogen load to Casco Bay was previously estimated by Liebman and Milstead (2012) using the United States Geologic Survey's (USGS) SPAtially Referenced Regression On Watershed attributes (SPARROW) model. The SPARROW model uses watershed characteristics, regional monitoring data and nitrogen source data to estimate nitrogen loading but was not validated using measurements of nitrogen in the Casco Bay watershed. This study attempts to estimate the nitrogen load from three rivers (Presumpscot, Royal and Capisic Brook), that together account for 78% of Casco Bay's watershed (87% of the freshwater flow) and generally represent two distinct types of sub basins in the larger watershed (i.e., forested and urban) (Liebman and Milstead 2012). The TN loading estimates from the three rivers were then extrapolated to provide an estimate for the total riverine load to Casco Bay and compared to the previously modeled TN load estimates. Additionally, the riverine TN load was compared to other known TN loads from the other major sources such as atmospheric deposition, combined sewage outfalls (CSO) and waste water treatment facility (WWTF) effluent.

Loading estimates for the three rivers were based on discharge and nitrogen concentration data from June 2017 – May 2018. We used Presumpscot River discharge from USGS gauge 01064118 near Westbook, Maine. Discharge for the Royal River was estimated using a historic watershed yield

relationship with the nearby Sheepscot River which is still gauged. Capisic Brook discharge was estimated using the USGS Streamstats model. Water samples were collected at least monthly with an attempt to collect at both high and low flows. Water samples were analyzed for TN, Nitrate/Nitrite, and Ammonium. Water samples were not collected from December – March; concentrations for that time period are based on a discharge-concentration relationship, if present, or are assumed to be the average concentration of all data.

Collectively, the rivers in this study load less TN than is discharged by the area's five largest WWTFs. Presumpscot River, while loading the greatest total mass of nitrogen (173 Mg N yr^{-1}), loads the least per hectare (1.16 kg ha^{-1}). Capisic Brook loads the most total nitrogen per hectare (7.71 kg N ha^{-1}) and Royal River loads more nitrogen than Presumpscot but less than Capisic (3.79 kg N ha^{-1}). Land use is correlated with the mass of nitrogen per hectare exported via the rivers. For example, Capisic Brook has the greatest percentage of developed land use types followed by Royal then Presumpscot. For comparison, if we assume the WWTF's discharge to their permit limit, the total nitrogen load from these three rivers accounts for less than half of the total nitrogen mass discharged into Casco Bay from WWTFs (902 Mg N yr^{-1}).

This study's findings suggest that while non-point loading from river systems in Casco Bay contribute to the nitrogen content in the bay, they load less nitrogen than the areas of WWTFs. The amount of developed and agricultural land is correlated with the amount of nitrogen delivered to the bay by a river, which means that population growth will increase diffuse and point source loading in the future. And finally, this study's estimates are in fair agreement with SPARROW's TN loading estimate. More specifically, all estimates are within the same order of magnitude, but SPARROW's estimates are a factor of two greater for the Presumpscot River and Capisic Brook. This study represents an important first step in understanding nitrogen loading to Maine's most populous watershed and can be used to prioritize management of the largest nitrogen sources.

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CHAPTER 1

INTRODUCTION

1.1 Nitrogen and Estuaries

Estuaries or near-coastal regions around the world experience eutrophication due to excessive land-derived nitrogen and other nutrients, leading to hypoxic zones that can reduce biodiversity, natural resources (e.g. fisheries production) and harm coastal economies (Nixon 1995; Vitousek et al. 1997). Increasing coastal populations exacerbate eutrophication by contributing greater nutrient loads to these already stressed marine environments (Breitburg et al. 2018). Anthropogenic nitrogen delivered to estuaries derive from many sources (e.g. agricultural operations, industrial emissions, and wastewater treatment facilities) and are delivered through various pathways (e.g. tributaries, atmospheric deposition, point source discharge) (Vitousek et al. 1997). Identifying and quantifying the sources of those nutrients and pathways is a fundamental step towards managing and mitigating the consequences.

1.2 Nitrogen in Casco Bay

The Casco Bay watershed, which includes Maine's most populous city, Portland, is home to nearly 20% of the state's total population, but accounts for only 3 percent of the state's total landmass (Casco Bay Estuary Partnership 2016). In 2015, Portland had the second largest percentage of growth among New England's 14 metro areas indicating that this already populous area is continuing to grow (Portland Press Herald 2015). And while much of the watershed is forested (65%), the 10 % of the area that is developed is close to the coast. A large and growing population concentrated in the coastal zone can lead to excessive nutrient loading to the adjacent receiving waters.

Perhaps due to relatively low temperatures and large tidal amplitude, water quality in Casco Bay, Maine is generally good although there is some cause for concern. Nitrogen concentrations have been trending up for the past decade, especially in more nearshore locations (Casco Bay Estuary Partnership, 2015). In 2009, 90% of the total nitrogen concentrations statewide in coastal waters were below 0.42 mg N L^{-1} but multiple locations within Casco Bay exceeded those values (Cadmus Group, 2009; Casco Bay Estuary Partnership, 2015). In recent years, summer algal blooms in Portland's Back Cove have been observed more frequently (Casco Bay Estuary Partnership, 2015). Additionally, management agencies in the region have observed epiphytes on submerged aquatic vegetation (A. Brewer, personal communication, March 27, 2019). Additionally, the Gulf of Maine, which circulates water into Casco Bay, is warming. Pershing et al. (2015) reported that the Gulf of Maine warmed faster than 99% of the world's oceans between 2004-2013. Warming waters can increase susceptibility to eutrophication by increasing stratification and respiration rates (Breitburg 2018). However, due to the factors that protect Casco Bay from poor water quality, very few measurements of nutrient loading from the landscape have ever been taken and the relative contribution of nitrogen from different sources and pathways is uncertain.

Land-derived nitrogen in Casco Bay originates from either point (discrete) or non-point sources (diffuse) and is delivered through multiple pathways (e.g. rivers, atmospheric deposition, combined sewage outfalls, and direct discharge). In the Casco Bay region, the Maine Department of Environmental Protection (ME DEP) identifies licensed point sources to include: waste water treatment facilities (WWTFs) that lack tertiary (nitrogen) treatment, combined sewage outfalls (CSOs) and small overboard discharges (ME DEP 2008). ME DEP identifies various land use activities, with delivery via rivers, and atmospheric deposition as non-point sources of nitrogen in Casco Bay (ME DEP 2008). The mass of nitrogen delivered from some of these sources to Casco Bay have been estimated (ME DEP 2008) or measured while others, like the riverine nitrogen load, have only been modeled (Liebman and Milstead 2012).

There are five WWTFs that discharge directly into Casco Bay; none of these facilities have tertiary treatment. The WWTFs monitor their daily discharge but, until recently, were not required to measure the nitrogen concentrations found in their effluent. Total nitrogen loads to Casco Bay via

WWTF effluent have been estimated assuming 20 mg N L^{-1}, based on literature values for nitrogen concentrations in similar effluents, and average annual effluent volumes (ME DEP 2008). The most recent and best estimate for total nitrogen loading into Casco Bay from the five WWTFs is ME DEP's 2008 estimate of between 758 Mg N yr^{-1} (based on design flow) and 903 Mg N yr^{-1} (based on average flow) (ME DEP 2008). ME DEP implemented nitrogen monitoring requirements for all WWTFs, upon MEDEP permit renewal (2017), and future estimates will include more accurate nitrogen concentrations.

In addition to the discharge of nitrogen containing WWTF effluent, Portland and other municipalities in the Casco Bay watershed utilize Combine Sewage Outfalls (CSOs) where sewage combines with stormwater during large rain events, transporting nitrogen directly to the Casco Bay (ME DEP 2008; ME DEP 2018). A ME DEP report (2008) estimated that CSOs deliver 6 Mg N yr^{-1} annually (a year = summertime) to Casco Bay based on the average summertime flow of 332 million gallons yr^{-1} and assumes nitrogen concentration of 5 mg N L^{-1}. Since the 2008 report, three CSOs have been abated; as of 2018, Portland had 30 functioning CSOs.

Previous studies have estimated that atmospheric deposition of total inorganic nitrogen directly to Casco Bay accounts for 30 – 40% of the overall nitrogen load to the bay (ME DEP 2008; Sonoma Technology 2003). In Sonoma Technology's 2003 report, the authors estimated total atmospheric deposition of inorganic nitrogen (dry plus wet) on the bay's surface to be 4.3 – 7.22 kg ha^{-1} yr^{-1}, depending on how dry deposition was calculated, totaling between 255 – 428 Mg yr^{-1} delivered directly to the bay's surface waters. Atmospheric deposition of nitrogen is continually monitored in Casco Bay by Maine Department of Environmental Protection (MDN Site ME96). Besides WWTF effluent, CSOs and atmospheric deposition, the other sources or pathways of nitrogen in Casco Bay have not yet been quantified (e.g. riverine load, ocean).

Rivers deliver nitrogen from upstream point and diffuse sources such as farms, golf courses, and septic tanks. The riverine load of nitrogen to Casco has previously been estimated using the USGS

SPAtially Referenced Regressions on Watershed attributes (SPARROW) model. The SPARROW model predicts average annual nitrogen load based on watershed and stream characteristics, USGS gauging data, monitoring data when available and land use. The nitrogen loading estimate for Casco Bay using the SPARROW model is based on 2002 land use, gauging stations outside of the watershed, and minimal nutrient data from within the watershed (Liebman and Milstead 2012; Moore 2011). The SPARROW estimate did not include nitrogen measurements at the fall-line of Casco Bay rivers and nor did it account for seasonal or annual variation. An investigation of all sources and pathways of nutrients, to better quantify their relative contribution, is a necessary step towards mitigating impacts in Casco Bay with targeted management. Given that there are no ground-truthed estimates of tributary nitrogen loading, estimating tributary nitrogen loading into Casco Bay is an important next step to understanding the origin(s) of elevated nitrogen concentrations and algal blooms observed in the bay.

1.3 Managing Nitrogen in Casco Bay

In addition to improving our understanding of the origin of nitrogen in Casco Bay, this study can help inform federally required water quality regulation standards in the State of Maine. In 1998, in response to the elevated levels of nitrogen and other nutrients in waters around the United States (US), and in accordance with the Clean Water Act, the Environmental Protection Agency (EPA) introduced a strategy to develop nutrient criteria for nitrogen and phosphorus in all water body types (EPA, National Strategy for the Development of Regional Nutrient Criteria, 1998). The EPA, acknowledging that nationwide criteria would be ineffective due to regional and climactic variability, set a requirement on states to establish their own criteria. As of 2019, like many other states, Maine does not have any water bodies with established numeric nutrient criteria.

Currently, Maine has draft nutrient criteria for inland waters (lakes, streams, and rivers) that have been reviewed by the EPA but no nutrient criteria are drafted for estuaries or nearshore regions. The EPA reviewed and tentatively accepted Maine's draft nutrient criteria for inland waters but recommended the addition of addressing how the criteria will affect downstream (estuarine and nearshore) waterbodies (EPA, 2011). Drafted nutrient criteria for coastal waters would help to inform and revise the inland waters criteria per EPA's recommendation but nutrient criteria for Maine's estuaries and marine systems has proven to be a more difficult task and are still not drafted despite the passing of targeted legislation in 2007. The LD 1297 Resolve, Regarding Measures to Ensure the Continued Health and Commercial Viability of Maine's Seacoast by Establishing Nutrient Criteria for Coastal Waters spurred action by ME DEP to focus on setting marine nutrient criteria but did not result in the actual drafting and establishment of coastal nutrient criteria.

In 2008, in fulfillment of LD 1297, Maine Department of Environmental Protection (ME DEP) and the EPA contracted Battelle to create a conceptual plan for establishing nutrient criteria for marine and estuarine waters in Maine. In their report, Batelle suggested that there was insufficient data to set criteria at the time and that a database needed to be established to organize current and future data. To establish criteria, Batelle recommended the continuation of nutrient monitoring statewide and expanding monitoring sites in Casco Bay. Later in 2008, in accordance with the LD 1297, the Maine DEP published a report outlining (1) a conceptual plan for establishing criteria, (2) summary of point and non-point sources of nutrients, (3) summary of technologies and costs associated with mitigating waste water nutrients and (4) plan and timeline for setting nutrient criteria (ME DEP, 2008). The report also highlighted multiple issues associated with the development of nutrient criteria for marine and estuarine waters that needed to be resolved before criteria could be adopted (e.g. classification of water body type, seasonality, data sufficiency and acquisition). Lack of funding to support increased monitoring, modeling and general staffing deficiencies were also mentioned as reasons for a delay in establishing criteria. Despite the hurdles, ME DEP's plan set a goal of submitting draft criteria in 2012 (ME DEP, 2008).

In 2012, ME DEP submitted a revised timeline for the development of marine nitrogen. In this revision they identified key decisions that would help with establishing the nutrient criteria. The key decisions included (1) establishing a stakeholder Technical Advisory Committee, (2) deciding if existing data was sufficient for establishing criteria and if not, identify how much more data needed to be collected, (3) adding data to the nutrient database to create a comprehensive dataset to support a criteria decision, (4) deciding the correct approach (i.e. effects-based approach or data distribution) and (5) determining if state wide or regional criteria are more appropriate (ME DEP, 2012). This revision extended the deadline for submission of draft criteria until December 2015. As of 2019, nutrient criteria for marine waters in Maine are still not drafted, but ME DEP is making continued progress towards understanding the causes and consequences of nitrogen and other nutrients in Casco Bay.

A statute of Maine legislation (MRS 38 410-F) requires the monitoring of waterbodies for contaminants and environmental impact. In the summer of 2017, ME DEP undertook a water quality and habitat monitoring effort in Casco Bay to fulfill requirements of MRS 38 410-F which requires monitoring contaminants, the impact of those contaminants, and assessing marine habitats (State of Maine, 2019). During the 2017 field season they specifically monitored around Waste Water Treatment facilities to assist facilities with the inclusion a “Nitrogen” section in their National Pollution Discharge Elimination System (NPDES) Permit revisions (ME DEP 2017). The additional nitrogen section of WWTFs’ NPDES requires increased monitoring of nitrogen (weekly) and annual reporting.

This study’s baseline data provides a steppingstone upon which ME DEP and other stakeholders in Casco Bay can base future monitoring efforts to further inform policy and management decisions. Acknowledging funding limitations associated with increased monitoring, we also compare our measurements with the best available modeled estimates of nitrogen loading to examine how well the modeled loading estimate agrees with the measured estimates.

1.4 Study Objectives

The objectives of this study were to 1) estimate nitrogen loading from three representative streams/rivers that enter the Casco Bay region, 2) compare the study TN load observations with SPARROW TN load estimates and 3) compare riverine TN loading estimate to the known loading from waste water treatment plants in the Casco Bay region.

CHAPTER 2

METHODS

This study estimated nitrogen loading from three sub basins within the larger Casco Bay watershed; the Presumpscot and Royal River, the two largest sub basins within the Casco Bay watershed and a small urban sub basin, Capisic Brook (Figure 1). Together, the Presumpscot and Royal River sub basins cover nearly 2000 km^2 (78% of Casco Bay's total drainage area) and are the largest freshwater sources within the Casco Bay watershed. The remainder of Casco Bay's watershed consists of a few smaller river basins (i.e., the Fore, Cousins and Harraseeket Rivers) and numerous small, urban sub basins that drain directly into Casco Bay. Capisic Brook lies within the Fore River basin that drains to southern Casco Bay.

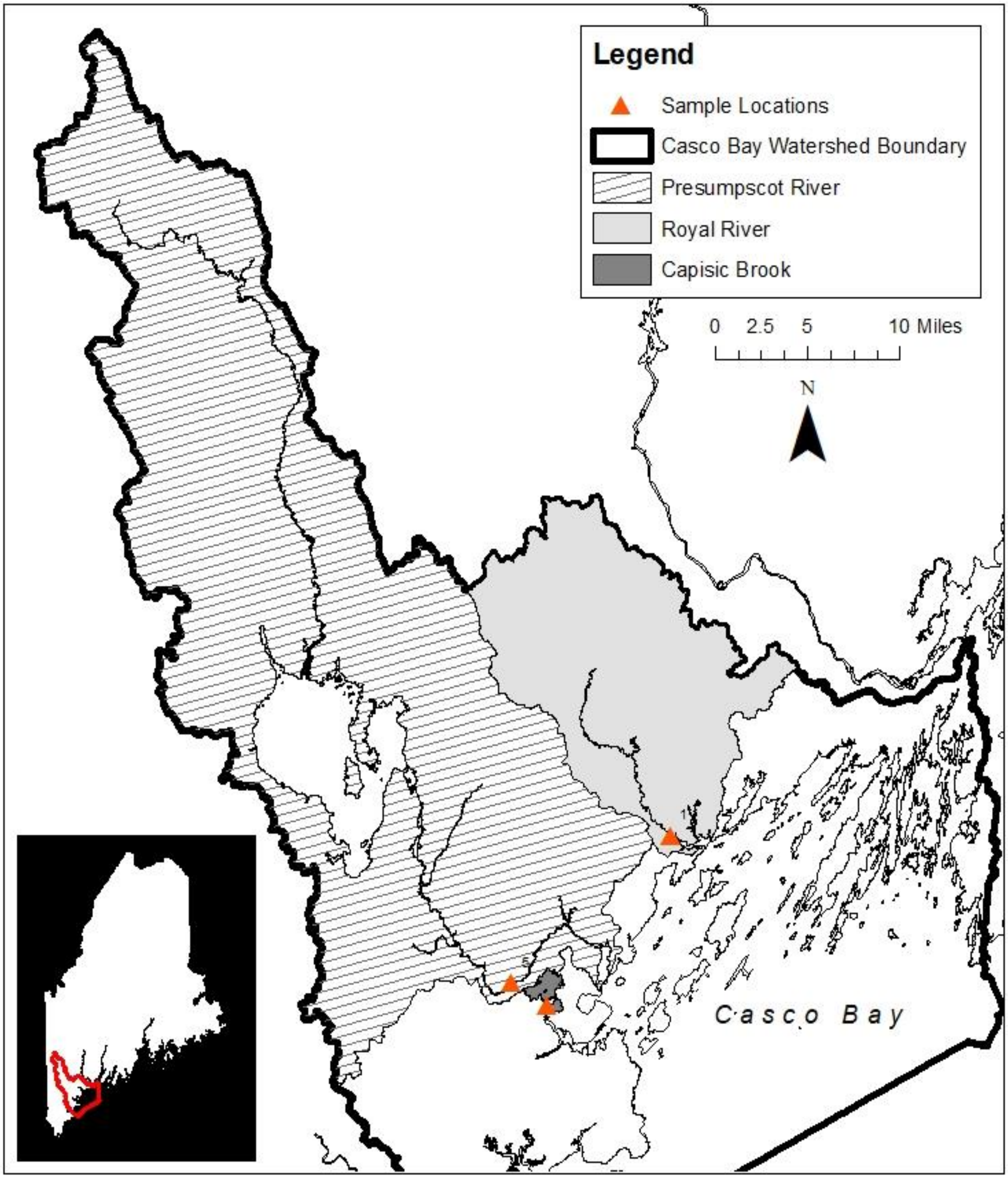

Figure 1. Map of Entire Casco Bay Watershed. Inset: The location of the Casco Bay watershed in Maine. Main Figure: Casco Bay watershed and Estuary showing location of study sample sites.

2.1 Study Site Descriptions

The Casco Bay watershed (2550 km^2), located in the south western region of Maine, drains the western lakes and mountain region to the coastal lowlands (Figure 1, inset). The basin is forest dominated (65%) with 10% urban land use and only 8% of land use being agricultural; the remainder of the land cover is a mix of wetland, scrub, grass and barren land (11%, 4%, 1% and 1% respectively) (CBEP 2015). Soils within the watershed experience slow infiltration with 75% of soils having a Hydrologic Soil Group classification of C to D (poorly to very poorly drained); 12.6% of the soils in the watershed are hydric soils (Table 1). The climate of the region is humid continental (Huntington and Billmire 2013; Peel et al. 2007) and receives about 116 cm of precipitation annually with minimal monthly variation (~10 cm per month) (Figure 2). Temperatures range from about -5 C° in the winter to about 20 C° in late summer (NOAA NCDC).

Table 1.

Summary of Physical Characteristics of Study Watersheds

		Land use, % of subbasin area				Hydrologic soil class, % of subbasin area				% Hydric	Mainstem Dams	CFOs
Basin	Area, km^2	Forest	Agriculture	Urban	Other	A	B	C	D			
Casco Bay										12.6		
Presumpscot	1,494	61.2	5.8	7.9	25.2	26.2	2.7	34.5	12.2		8	5
Royal	360	61.7	11.4	9.6	17.3	20.1	5.1	41.6	28.5		2	0
Capisic	5.2	10.5	0.7	81.7	7.1	23.2	2.8	33.5	27.9		0	1
Sheepscot	375	65.9	6.5	4.7	22.8	5.4	1.3	47.1	33.1			

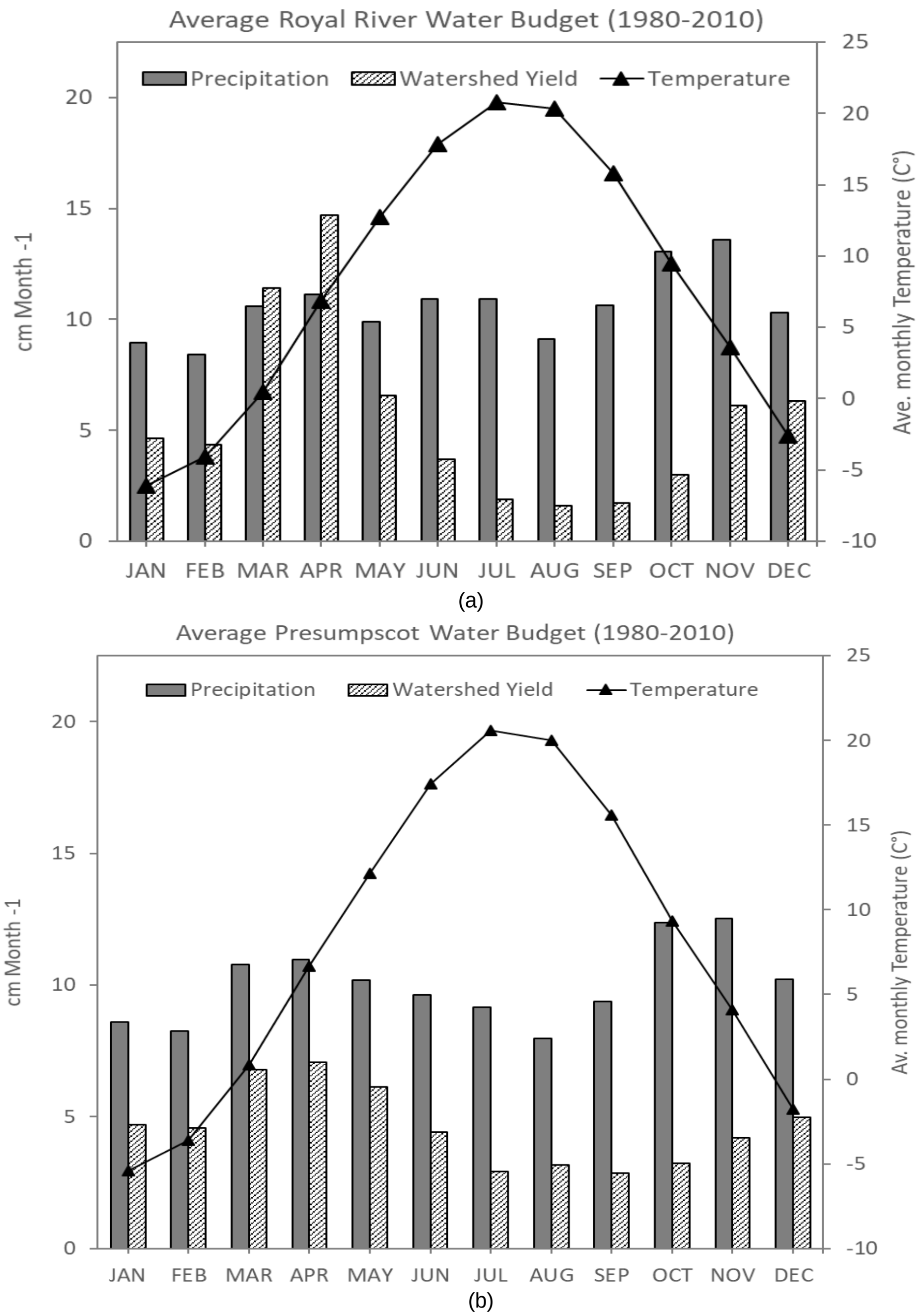

Figure 2. 30 Year Climatological Average Hydrology. (a) Long-term precipitation records (cm month^{-1}) and temperature for the Royal River based on daily data collected at the NWS observer station at Gray, Maine. Watershed yields for Royal River are based on discharge from Royal River at Yarmouth Maine (USGS 01060000). (b) Long-term precipitation records (cm month^{-1}) and temperature for the Presumpscot River based on daily data collected at the cooperative NWS station at Portland Jetport, ME. Watershed yields for Presumpscot River are based on discharge from Presumpscot River at Westbrooke, Maine (USGS 01064118). Water yield is discharge (m^3 month^{-1}) normalized to watershed area (m^2)

The Presumpscot basin (1,494 km^2) is the largest catchment in the watershed. Land use is forest dominated (61%) with 8% urban land use and only 5% of the basin is agricultural (Table 1); other land cover includes open water and wetlands, shrub, grass and barren land (21.9%, 3.2%, 0.6%, and 0.3%, respectively) (NLCD 2011). The relatively large open water percentage of land use is due to the presence of Lake Sebago, the deepest and second largest lake in Maine. Eight dams impede and control the flow of the main stem of the Presumpscot River from Sebago Lake, to seven miles upstream of where the river discharges into Casco Bay (Figure 3).

The Royal River (360 km^2) is predominately forested (62%) with agriculture and urban land uses accounting for 11% and 10% of the land use, respectively (Table 1); the remainder is a mix of open water and wetland, barren land and shrub (14.3%, 0.7% and 2.3% respectively) (NLCD 2011). Two dams are found along the main stem of the Royal River; the most downstream dam (Bridge Street) is a minimal use hydroelectric dam used to power the Sparhawk Mill business center (Figure 3). The more upstream dam (East Elm Street Dam) is not active and has fallen into disrepair; during low flow an impoundment can form behind the East Elm Street Dam (www.mainerivers.org).

Capisic Brook (5.2 km^2) is the smallest and most urban sub basin characterized in this study. Urban land use accounts for 81% of the total land use with about 10% forest and a negligible amount of agriculture (0.7%); barren, shrub and wetlands make up the remainder of the land cover (1.1%, 2.3% and 3.7 respectfully) (NLCD 2011). There is one functioning combined sewage outflow in the Capisic basin (ME DEP 2018) (Figure 3). Capisic Brook is classified as an impaired stream by the ME DEP and has an active Watershed Management Plan addressing its impairment.

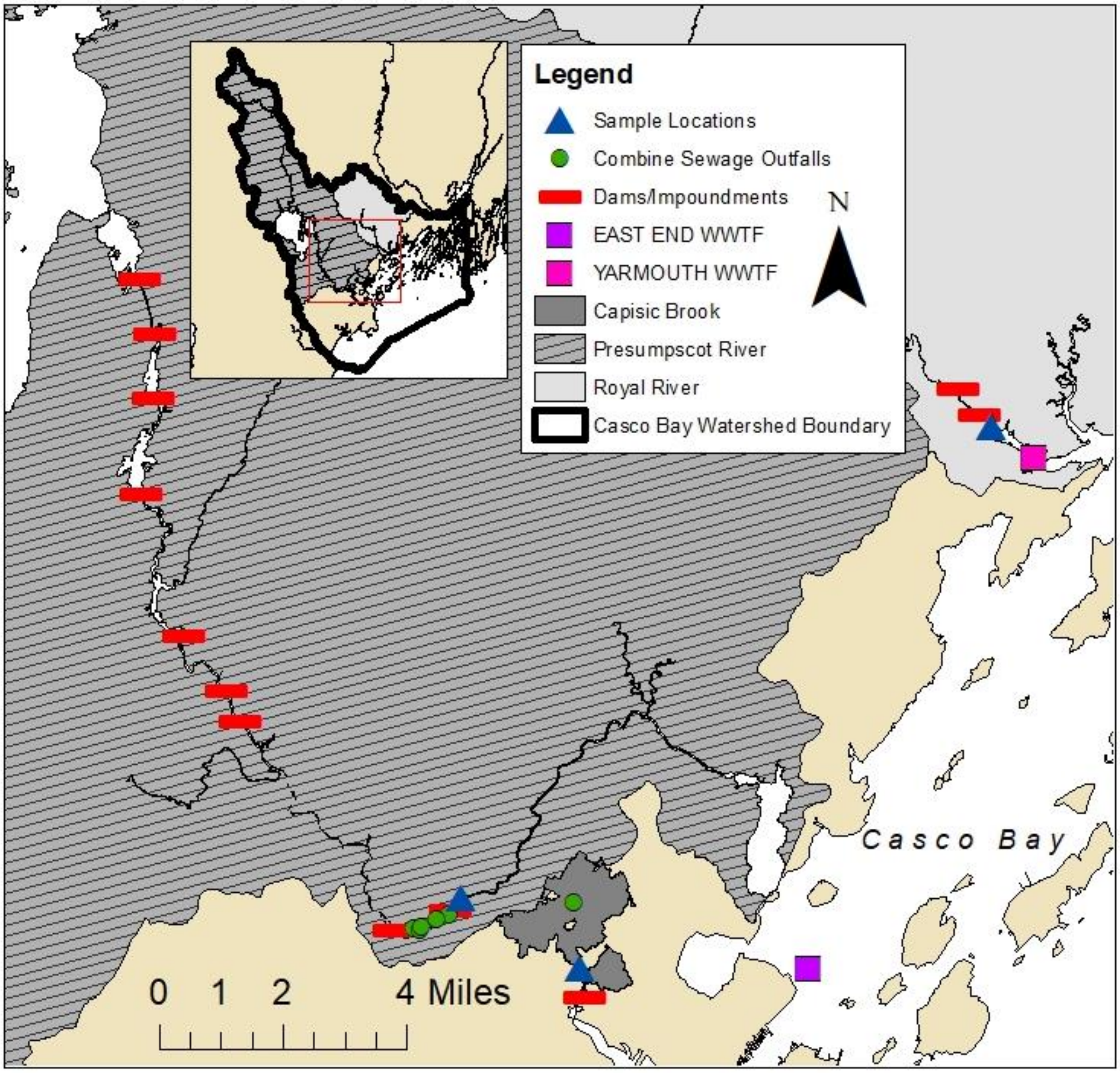

Figure 3. Lower Casco Bay Watershed with Key Features. Inset: Location of the lower Presumpscot River, Royal River and Capisic Brook within the great Casco Bay watershed. Main Figure: Location of nine dams along the lower Presumpscot River, two along the Royal River and dam downstream of Capisic Brook sample location.

2.2 Hydrology

We obtained surface water discharge data from three sources. Daily and monthly discharge data were downloaded from the United States Geologic Survey's (USGS) website for the gauging site near Westbrook, Maine (01064118) along Presumpscot River. The gauge's watershed is 1,494 km^2 and has been gauged since 1975 by the USGS, with a mean annual flow of 26.1 $m^3 s^{-1}$ and large variation due to seasonal dynamics related to temperature, precipitation, and snow cover.

There was no direct measurement of discharge from the Royal River during the study period. However, we were able to estimate discharge for Royal River by comparing historic monthly water yields with those of nearby Sheepscot River. Sheepscot River is outside of Casco Bay's watershed but has similar watershed characteristics to the Royal River (Table 1). Royal River was gauged by the USGS from 1949 to 2004 at Yarmouth, Maine (01060000), just above Casco Bay's head of tide at the same location as this study's Royal River Sample Site (Figure 3). Sheepscot River is currently gauged by the USGS at North Whitefield, Maine (01038000) and has been gauged since 1938. A monthly yield relationship between Sheepscot and Royal River was created using average monthly discharge data from each river during 42 years of overlapping data, 1951 to 1993. As an example, the water yield relationship for the month of May was:

$$Y_{RYL} = 1.1005Y_{SHP} - 0.0065 \quad (1)$$

with an R^2 of 0.59. Where Y_{RYL} is the predicted water yield of Royal River and Y_{SHP} is the measured water yield of Sheepscot River. The monthly yield relationship was then validated using the remaining 11 years of overlapping data, 1994 to 2003. Royal River discharge for the 2017-2018 study period was then calculated using Sheepscot and Royal River yield relationship. There is large hydrologic variability in the water yields at the monthly time scale due to the spatial variability in rainfall and some watershed characteristics. Root mean square error calculated for the validation years indicates that variability is around 24%.

Capisic Brook's discharge is also not gauged. Consequently, an average annual discharge estimate was obtained using USGS's Stream Stats web application that allows users to delineate a watershed and outputs watershed characteristics and streamflow estimates. The Stream Stat's streamflow estimate for Capisic Brook is based on USGS regression equations for annual streamflow in ungauged rivers in Maine (Dudley 2015). The regression equations are derived from the relationship between the measured stream flow of 24 gauged rivers in Maine and New Hampshire and eight explanatory land characteristics with drainage area, mean basin elevation and fraction of soil and gravel aquifer being the most significant (Dudey 2015). There is unknown error associated with the annual streamflow estimate for urbanized streams as the regression equations are based on more rural watersheds (Dudley 2015). To address the unknown error an annual TN load calculation will first be calculate using the Stream Stat's derived discharge and later using the same discharge SPARROW used to calculate Capisic Brook's TN load.

2.2.1 Discharge Estimation Error

Error associated with USGS measured discharges can be found in USGS's Report 92-144. Most USGS measured discharge measurements have a standard error range of 3-6 percent (Sauer and Meyer 1992). Ten years of overlapping, monthly Sheepscot and Royal River discharge data was used to validate the water yield relationship method used to estimate discharge for the Royal River. A Root Mean Square Error was then calculated to determine the difference between the model predicted Royal River discharge and the actual Royal River discharge for those 10 years.

Error associated with the annual discharge for Capisic Brook is based on the error associated with the USGS Stream Stats program. The Capisic Brook discharge estimated by USGS Stream Stats is based on Dudley (2015) which uses regression analysis to estimate error in annual streamflow for ungauged rivers in Maine.

2.3 Sampling Program

On Presumpscot River, water was sampled at the United States Geologic Survey (USGS) gauge 01064118 at Westbrook, Maine. This location is seven miles upstream of where the river meets Casco Bay and discharge is continuously monitored (Figure 2.1). Royal River's sampling site (Figure 2.1) was located at a historic USGS gauge 01060000 at Yarmouth Maine, just above the fall line. Capisic Brook's sample location was upstream of Capisic's dammed pond (Figure 2.1) (reducing the likelihood of sampling water that had more opportunity to denitrify); after the dam, Capisic meets the tidal Fore River.

During the summer of 2017 (May-September), water samples were obtained every one to two weeks, with a total of about 15 sample dates per site. Following the summer sampling (October 2017 to May 2018), water collection was done at least once a month when ice did not cover the river. In total, about 25 samples were collected per site over the course of one year. Samples were collected at varying discharge levels with an effort to capture some storm or freshet discharge events, in addition to base flow.

At each sampling site, surface water samples were taken mid-stream using two, one-liter, dark, open mouth Nalgene bottles; two bottles were collected to account for field error. The collected water was then transferred into cleaned (RBS Cleaning Agent or ash cleaned) vials for future nitrogen analysis. In transit, water samples were stored in a watertight container on ice then transferred to a freezer until analyzed. Water samples were analyzed for Total nitrogen (TN), Nitrate/Nitrite (NO_3/NO_2) and Ammonium (NH_4). TN was measured using a Shimadzu TOC-VCPH/CPN Total Organic Carbon Analyzer outfitted with a Total Nitrogen Analyzer Unit (TOC/TN). Nitrate, nitrite and ammonium were measured using a Lachat QuickChem Nutrient Analyzer. All samples were analyzed in the BioGeoChemistry lab at University of Maine's Darling Marine Center. Organic nitrogen was calculated by subtracting the summed dissolved inorganic nitrogen values ($NO_3/NO_2 + NH_4$) from the total nitrogen concentration.

Some sampling events on the Royal and Presumpscot River were completed in coordination with Maine Department of Environmental Protection's (ME DEP) in-bay sampling near the mouths of each river.

2.3.1 Nitrogen Sampling and Analysis

Two separate water grab samples were taken at each site and transferred to three sets of vials to account for field and analytical error, respectively, associated with nitrogen sampling. Occasionally, during sample analysis, a blank (filled with DI water) vial was run to further account for analytical error.

2.4 Estimating Nitrogen Loads and Export Coefficients

Before calculating an annual total nitrogen load for each river, we explored the relationship between total nitrogen concertation and discharge. For the Presumpscot River, when including the single high flow event, there was a discharge-TN Concentration relationship. There was, however, too little data in between the baseflow events and the high flow event to validate the discharge-concentration relationship. Therefore, given no significant correlation between total nitrogen concentration and discharge, we used the average total nitrogen concentration of all collected samples as representative of the entire year.

For both the Royal River and Presumpscot River, where there was no significant relationship between discharge and TN concentration relationship, a monthly nitrogen load was calculated by multiplying the average monthly nitrogen species concentration by the average monthly discharge. The monthly nitrogen loads were then summed over the study year to estimate an annual load for the study period. The average nitrogen concentration over all samples was used as the average monthly nitrogen concentration for months were no water samples were collected (December - April) due to freezing or dangerous conditions. An annual nitrogen load for Capisic Brook was calculated by multiplying the average annual discharge by the average nitrogen concentration of all samples.

The relative watershed size and annual discharge of each river influences the annual total nitrogen load. To account for the difference in discharge and watershed size an export coefficient was calculated, standardizing each watershed's annual load by watershed area (kg N ha^{-1} y^{-1}). In addition to allowing for better comparison between the total nitrogen loading of each river and to other values in the watershed literature, the export coefficients can relate N export to land uses.

2.4.1 Load Estimation Error

The annual TN load for the Presumpscot and Royal River were calculated using monthly average discharge and the average monthly N concentration; error associated with the river's estimated TN load was calculated using the root mean square error. The error was propagated according to Bevington (1969) to determine a range for the TN load.

$$\sigma_x = x\sqrt{\frac{\sigma_u^2}{u^2} + \frac{\sigma_v^2}{v^2}} \qquad (2)$$

Where σ_x is the fractional uncertainty associated with the daily TN load calculation (g day^{-1}), x is the calculated daily total nitrogen load (g $month^{-1}$), σ_u is the root mean square error of the nitrogen concentration (g m^{-3}), u is the monthly average N concentration (g m^{-3}). σ_v is the error associated with the average monthly discharge (m^3 $month^{-1}$) and v is the average monthly discharge (m^3 $month^{-1}$). The error associated with the monthly TN load, as determined through equation 1, was then summed for the study year, providing a total error estimate for the annual TN load of the Presumpscot and Royal River.

2.5 Comparing Total Nitrogen Loading Estimates

Riverine TN load estimates to Casco Bay was compared to other TN load estimates, including previous riverine total nitrogen loading estimates and the TN load from other sources and pathways (i.e., WWTFs and atmospheric deposition). A previous riverine total nitrogen load estimates comes from a draft report from the US Environmental Protection Agency (US EPA) Region 1 which uses the USGS SPARROW (SPAtially Referenced Regressions on Watershed attributes) model to estimate the TN load from each river draining to Casco Bay (2012). Briefly, this SPARROW model estimates stream segment nutrient (including TN) and sediment loading based on land use, nearby monitoring data (nutrient concentrations and discharge), and watershed characteristics (Moore 2011). The SPARROW model has been published widely and validated but not with Casco Bay specific data (Moore 2011).

The TN load from wastewater treatment facilities in Casco Bay was gathered from a report published by ME DEP (2008). The WWTF load was estimated by assuming each WWTF discharged at the daily design flow rate and with an assumed concentration of 20 mg N^{-1} (ME DEP 2008). The TN load from combined sewage outfalls (CSOs) was calculated using measured volumes from ME DEP's annual CSO Activity and Volumes report for the study period and a TN concentration of 0.5 mg N L^{-1} based on ME DEP's 2008. Atmospheric deposition was obtained from the National Atmospheric Deposition Program and Maine DEP's Casco Bay site at Wolfe's Neck Farm (NTN site ME 96) on the northeast side of Casco Bay.

CHAPTER 3

RESULTS

3.1 Hydrology

Annual precipitation during the study period in the Presumpscot River was 94 cm, 26 cm lower than the 30-year climate mean data (120 cm). Average monthly precipitation was more variable (12.2 cm; minimum: 2.6 cm in July 2017, maximum: 14.8 cm in April) than the typical ~4 cm variability between months (minimum: 8 cm in August, maximum: 12.5 cm in November) seen in the 30-year climate mean data (comparing Figure 2 (b) and Figure 4 (a)). Monthly mean stream discharge for the Presumpscot River during the study period exhibited similar behavior to the historical monthly average discharge with peak monthly average discharge during the spring freshet, in April and May, and low discharges in late summer (comparing Figure 2 (b) and Figure 4 (a)). The Presumpscot River exhibited less variation than the Royal River in discharge throughout the year, likely due to flow control by dams (MacDonald 1994). Temperatures in the watershed were slightly higher than normal seasonal conditions when compared to the 30-year climate mean with temperatures in January-March and August-October exhibiting higher than average monthly temperatures. Given the climatological context, 2017 could be hydrologically described as a more seasonably variable, but overall a dry year, in the Presumpscot watershed.

Mean monthly discharge for the Royal River was consistent with the climatological mean pattern. The highest discharge in April, around spring freshet with low discharge in the late summer and an increase again towards winter (Figure 2 (a)). Precipitation in the Royal River basin, like Presumpscot, was more seasonably variable (mean: 8.9; minimum 3.5 cm in July, maximum: 15.3 cm in May) than the climatological mean (mean: 10.6; minimum: 8.4 cm in February, maximum: 13.6 cm in November). The high spring discharge is driven by snow/ice melt rather than precipitation; in the summer evapotranspiration drive discharge down relative to precipitation. Overall, annual precipitation for 2017 in the Royal River watershed was lower (106.4 cm) than the climatological mean (127.6 cm).

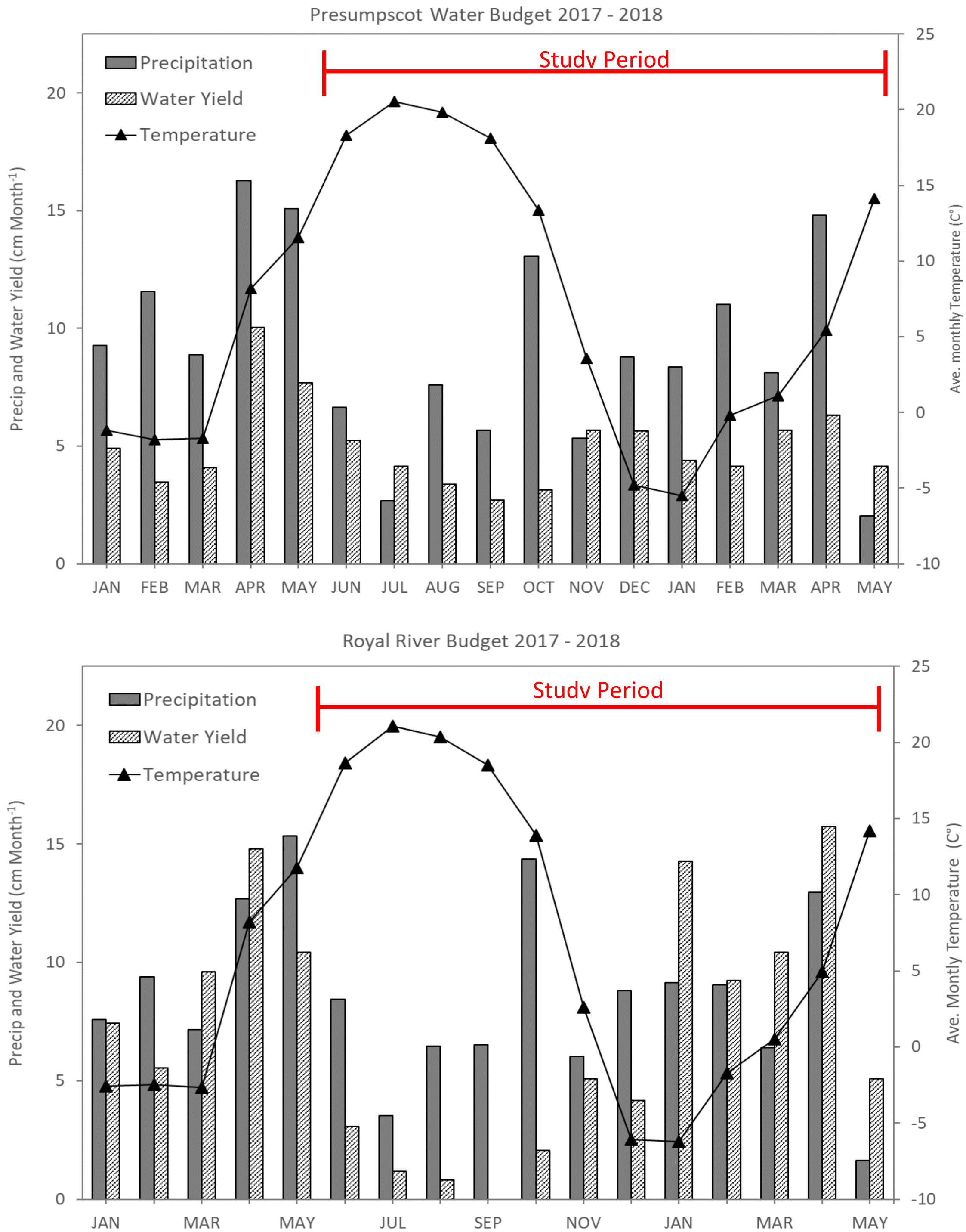

Figure 4. Study Period Hydrology. (a) January 2017 – May 2018 precipitation record (cm month^{-1}) and temperature for the Presumpscot River based on daily data collected at the cooperative NWS station at Portland Jetport, ME. ME. Watershed yields for Presumpscot River are based on discharge from Presumpscot River at Westbrooke, Maine (USGS 01064118). (b) January 2017 – May 2018 precipitation records (cm month^{-1}) and temperature for the Royal River based on daily data collected at the NWS observer station at Gray, Maine. Watershed yields for Royal River is estimated based on the historic monthly watershhed yield relationship between Royal River and the Sheepscot River. Water yield is discharge (m^{3} month^{-1}) normalized to watershed area (m^{2})

Annual discharge for Capisic Brook was estimated using the USGS Stream Stats estimate. There is one functioning CSO (CSO No. 042 at Warren Ave.) in the Capisic Brook watershed and in the 14 storm events when it became active in 2017, it discharged a total of 2.7 million gallons of combined sewage (ME DEP 2018). Precipitation and temperature patterns observe in the Capisic Brook watershed were consistent with those observed in Presumpscot River.

3.2 Water Quality – Nitrogen Concentrations

The highest concentrations of TN were found in Capisic Brook (mean 0.95 mg N L^{-1}) while the lowest concentrations were found in Presumpscot River (mean 0.23 mg L^{-1}); Royal River's mean total nitrogen concentration was 0.51 mg L^{-1} (Table 2). The composition of the total nitrogen found in each stream varied however, with the dominating forms shifting in some months organic to inorganic species.

Organic nitrogen dominated the total nitrogen concentrations in Presumpscot River but did not consistently dominate in the Royal River or Capisic Brook. In the Royal River, organic nitrogen initially dominated but began to shift towards nitrate/nitrite beginning in July. In July the ratio of organic to inorganic nitrogen crept towards 1:1 but shifted to inorganic dominance in September and October and back to organic dominated in November. In Capisic Brook, all months but November and August were dominated by inorganic nitrogen with nitrate/nitrite being the primary species.

In all streams, ammonium concentrations were the least abundant nitrogen form present. Ammonium concentrations ranged from 0.004 mg N L^{-1} in Presumpscot River to 0.091 mg L^{-1} in Capisic Brook. The average concentrations of ammonium in Presumpscot River, Royal River and Capisic Brook were 0.018, 0.024 and 0.062 mg L^{-1}, respectively (Table 2). During the study period, two CSO overflows in Capisic Brook coincided with sampling dates. However, nitrogen concentrations on those two sample days were not significantly different than days when the CSO did not overflow.

Table 2. Average Nitrogen Concentrations for Study Watersheds. Average monthly nitrogen [total nitrogen, inorganic nitrogen (nitrate/nitrite and ammonium) and organic nitrogen] concentrations for study rivers during 2017 sample season. Bold concentrations highlight nitrogen species dominating

River	Sample Month	Total Nitrogen (TN) mg/L	Nitrate/Nitrite (NO_x) mg/L	Ammonium (NH_4+) mg/L	Organic Nitrogen mg/L
Presumpscot					
	April	0.556	0.108	0.007	0.441
	May	--	--	--	--
	June	0.179	0.049	0.024	**0.106**
	July	0.203	0.040	0.024	**0.139**
	August	0.190	0.015	0.008	**0.166**
	September	0.183	0.013	0.010	**0.159**
	October	0.222	0.041	0.004	**0.176**
	November	0.238	0.053	0.007	**0.179**
	AVERAGE	0.223	0.040	0.017	**0.171**
Royal					
	April	0.593	0.088	0.013	**0.492**
	May	0.323	0.088	0.021	**0.213**
	June	0.402	0.113	0.029	**0.297**
	July	0.563	0.206	0.035	**0.322**
	August	0.523	0.243	0.016	**0.278**
	September	0.485	**0.278**	0.029	0.179
	October	0.561	**0.386**	0.011	0.164
	November	0.520	0.119	0.013	**0.388**
	AVERAGE	0.506	0.212	0.023	**0.283**
Capisic					
	April	1.265	0.485	0.068	0.711
	May	--	--	--	--
	June	0.877	0.370	0.091	**0.415**
	July	1.021	0.450	0.090	**0.480**
	August	0.931	0.413	0.039	**0.479**
	September	0.902	0.424	0.049	**0.428**
	October	0.780	**0.416**	0.020	0.344
	November	0.892	0.276	0.076	**0.541**
	AVERAGE	0.945	0.414	0.062	**0.469**

3.3 Nitrogen Loads and Export Coefficients

3.3.1 Total Nitrogen Load and Export Coefficients

The Presumpscot River's annual total nitrogen load is largest but exported the least nitrogen per hectare when standardized by watershed area (Table 3). Over the study year (June 2017 – May 2018), the annual total nitrogen load from the Presumpscot River was 173 Mg TN yr^{-1} ± 96 Mg TN yr^{-1} (Table 3). Presumpscot River's TN load per hectare, however, was 1.16 kg N ha^{-1} yr^{-1} (Table 3).

Table 3. TN Load and Export Coefficient of each Study River. Summarizes each river's estimated annual (June 2017 to May 2018) Total Nitrogen (TN) load calculated by multiplying observed concentrations and measure or estimated discharge (column 1). Column 2 is the TN load estimate standardized by watershed area. This value is referred to as the export coefficient and relates the loading estimates to land use in the watershed.

River	Study TN Load Estimation (Mg TN yr^{-1})	TN Export Coefficient (kg ha^{-1} yr^{-1})
Presumpscot	173	1.16
Royal	137	3.79
Capisic	4	7.71

The Royal River's annual total nitrogen load was less than Presumpscot River's, but the Royal River loaded 2.5 times more per unit area. The annual total nitrogen load for the Royal River was 137 Mg TN yr^{-1} ± 40 Mg TN yr^{-1}) and Royal River's annual total nitrogen load per hectare was 3.79 kg ha^{-1} yr^{-1} (Table 3).

Capisic Brook, annually, loaded the least total nitrogen but loaded the most per hectare, loading more than five times more total nitrogen per hectare than the Presumpscot River (Table 3). Based on the average total nitrogen concentration of all Capisic Brook samples and the average annual discharge estimated by USGS StreamStats; Capisic Brook's annual total nitrogen load was 4 Mg TN yr^{-1}; per hectare, Capisic Brook exports 7.71 kg ha^{-1} yr^{-1} (Table 3).

3.3.2 Annual Load Nitrogen Composition

The annual load of total nitrogen delivered from each river also varied in composition. In all rivers, the total nitrogen load composition is dominated by organic nitrogen (Figure 5). Annually, 77% of Presumpscot River's total nitrogen load was composed of organic nitrogen (1.13 kg Organic N ha^{-1} yr^{-1}), 64 % of Royal River's nitrogen load (2.42 kg Organic N ha^{-1} yr^{-1}) and 50% of Capisic Brooks' nitrogen load was organic nitrogen (3.96 kg Organic N ha^{-1} yr^{-1}).

The mass of inorganic nitrogen (nitrate/nitrite [NO_{3+2}-] + ammonium [NH_4+]) in the total nitrogen load increased as the percentage of developed land use increases. Unsurprisingly, Capisic Brooks' developed watershed (81.7 % urban land use, Table 1), loaded the most inorganic nitrogen per hectare, annually (3.81 kg NO_{3+2}- + NH_4 ha^{-1} yr^{-1}) followed by Royal River (9.6 % urban land use; 1.42 kg NO_{3+2}- + NH_4 ha^{-1} yr^{-1}) and Presumpscot River (7.9 % urban land use; 0.34 kg NO_{3+2}- + NH_4 ha^{-1} yr^{-1}) (Table 1 and Figure 5, respectively). Ammonium maked up a small portion of the inorganic nitrogen mass loaded from each river; Capisic Brook loaded the most ammonium (0.5 kg NH_4 ha^{-1} yr^{-1}), Royal River loaded 0.15 kg NH_4 ha^{-1} $yr^{-1}$and Presumpscot loaded the least ammonium (0.07 kg NH_4 ha^{-1} yr^{-1}).

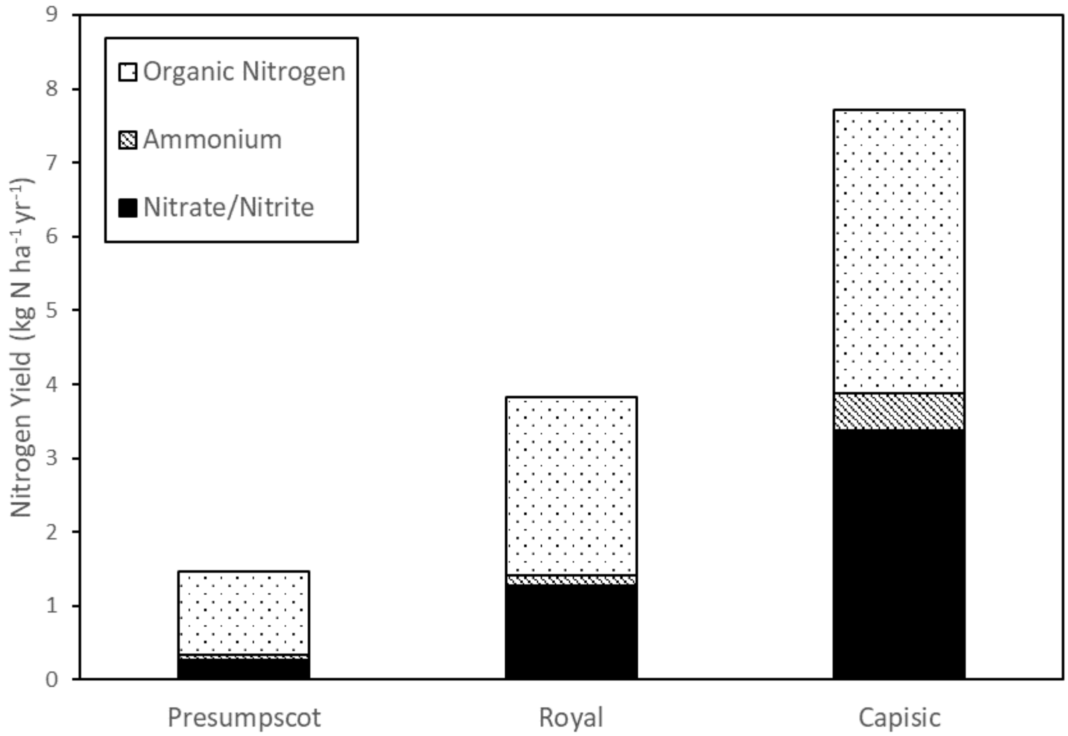

Figure 5. Nitrogen Yield by Nitrogen Species. Nitrogen composition of each river's annual (June 2017 – May 2018) total nitrogen load per hectare. Organic Nitrogen dominates the composition of each river's total nitrogen load and the presence of Nitrate/Nitrate increases with percent urban land use (urban land use increase from left to right. Green diamond denotes the average total nitrogen load per area based on measurements collect during the study perriod while the Capisic column sums total nitogen based on the averages of the measurements of the other forms of nitrogen. The measure average total nitrogen per hectare (green diamond) does not equal the total nitrogen based on the sum of the average of the other species of nitrogen.

CHAPTER 4

DISCUSSION

4.1 Watershed Characteristics

4.1.1 Hydrology

Because local hydrology and watershed characteristics of the three rivers have an influence on the nitrogen loading for each river, we consider some of the potential hydrological and watershed influences on our river and sample year. Lower precipitation during the study year (June 2017 to May 2018) did not influence the differences in watershed yields (or discharge) between the rivers, but it almost certainly influenced the nitrogen exported from each river. Wetter years are typically associated with an increased export of nitrogen from watersheds either due to flushing after storage of nitrogen in the landscape during dry years (McIsaac 2001) or decreased nitrogen sinks associated with wetter landscapes (Howarth et al. 2006). The lower precipitation during the study period could imply that nitrogen exported from the rivers would be lower than would be exported under average or greater than average precipitation. As our climate continues to change and precipitation continues to increase in Maine (Fernandez et al. 2015), nitrogen exported from the watershed could increase. Quite simply, additional years of investigation are needed to better understand the influence of precipitation on the export of nitrogen from watersheds into Casco Bay.

4.1.2 Temperature

Temperature in combination with soil infiltration and water table in each watershed have an influence on the delivery of water and land-derived nitrogen delivered to each river. The soils vary in their composition, depending on distance from the shore and slope. The soil infiltration capacity and drainage also vary spatially. In the Presumpscot and Royal River watershed, the soils are predominately loamy with areas of clay (Ferwerda et al. 1997). This is particularly true downstream of Sebago Lake and closer to where the watersheds meet the bay (Ferwerda et al. 1997). Water tables in the loamy or clay areas are higher from about November to May/June (Ferwerda et al. 1997), suggesting that infiltration is limited by evapotranspiration in the summer (Ferwerda et. al 1997). When the water table is high, there is a greater hydraulic gradient for delivery of groundwater and associated nutrients to the rivers via subsurface flow. When soils are saturated, overland flow will likely increase during rain events and overland flow is also likelier to occur when soils are exceptionally dry and hardened. During the summer high evapotranspiration removes soil water and reduces groundwater infiltration causing the water table to decrease. As a result, the water yield declines in the summer months, despite precipitation.

In the upper reaches of Presumpscot River's watershed, near Sebago Lake, the soils have much higher infiltration capacity and are loamy with some sandy areas all underlain by loose or loamy till. Here too some areas have seasonably high water tables while other areas have no consistent water table (Ferwerda et. al 1997). Further upstream of Sebago lake, soils again become less permeable, suggesting greater surface flow delivery during rain events or subsurface delivery when the water table is seasonably high (Ferwerda et. al 1997). Aside from the natural characteristics of the watershed, anthropogenic alteration has influenced the watershed and, in many ways, facilitating increased flow and nitrogen concentrations.

4.1.3 Land Use

Anthropogenic alteration of the rivers and their watersheds likely influenced the observed nitrogen concentrations and these loading estimates. Watersheds with a higher proportions of land use in agriculture and impervious surfaces are known to have higher nitrogen concentrations and would be expected to load excess nitrogen (Galloway et al. 1995, Boyer et al. 2002). This study's findings are consistent with that understanding as the mostly forested watershed (Presumpscot River) loads less per hectare than the small urbanized watershed (Capisic Brook) (Table 1 and Table 3).

In addition to natural lakes, dams and their impoundments have the potential to remove nitrogen added to the watershed (Zhang et al. 2015). Sebago Lake and mainstem dam control may influence removal of nitrogen added to Presumpscot River's watershed. Nitrogen removal rates are generally larger in lower order streams than higher order streams (Seitzinger et al. 2002). In addition, dams on low order streams remove more nitrogen than dams found on higher order streams (Gold et al. 2016). While dammed reservoirs have the potential to act as a sink for settling organic nitrogen, retention is dependent upon residence times (Gotteye 2019). Given these findings, it is unlikely that the dams on the main stem of the Presumpscot River have a significant influence on the removal of nitrogen from the upstream watershed due to its high order and short residence times behind the, mostly, hydroelectric dams. Further investigation into the influence of Sebago Lake and the dams/impoundments on the Presumpscot River would help to understand the effect dams have on the nitrogen concentrations found in the Presumpscot River and provide insight into how an increase in urbanization or agriculture might affect the river's load into Casco Bay.

The Royal River, with a percentage of forested land cover similar to the Presumpscot, has a slightly larger percentage of agricultural and urban land use (Table 1). There is no large lake and only two dam remnants along the main stem of the Royal River. Given the lack of influence of main stem impoundments on nitrogen removals (Gold et al. 2016), it is likely that the increased urban and agricultural land use (i.e., Royal River has roughly twice as much agriculture in the watershed than the Presumpscot) is the main reason for the Royal River's higher nitrogen concentrations and per hectare loading.

From a land use perspective, it is expected that Capisic Brook would have the highest concentrations of nitrogen found in the stream. In fact, Capisic Brook exhibited the highest concentrations of nitrogen. Not only does this watershed have a high percentage of impervious urban surface (NLCD 2011), but it also includes a combined sewage outfall (CSO). Given that there was no significant difference in nitrogen concentrations between days when the CSOs overflowed and days it did not overflow, it is unlikely that the CSOs are a large factor in Capisic Brook's annual nitrogen load.

Despite no clear signal from the CSO, the nitrogen concentrations in this urban watershed are higher than both Presumpscot and Royal, suggesting that other land use (e.g., lawn fertilizers, development) influences the nitrogen concentrations in the rivers and loading to Casco Bay.

4.2 Nitrogen Concentrations, Loading and Export Coefficient

4.2.1 **Total Nitrogen Concentrations and Composition**

The average total nitrogen concentrations in the two mostly forested watersheds (Presumpscot and Royal) are within the normal range of nitrogen concentrations expected of forested watersheds in the northeastern United States. Clark et al. (2000) found that total nitrogen concentrations in undeveloped watersheds range from 0.20 to 0.50 mg N L^{-1} (25^{th} -75^{th} percentile); Presumpscot and Royal Rivers concentrations span that range (0.20 mg N L^{-1} and 0.48 mg N L^{-1}, respectively). Increased development (urban and agriculture) in Royal River's watershed influence on average total nitrogen concentration at the upper end of the total nitrogen concentration range for undeveloped watersheds.

Nitrogen concentrations in Capisic Brook exceed the TN concentration recommended by the US EPA (0.32-0.63 mg N L^{-1}) but are not as high as concentrations observed in agriculturally dominated watersheds (5-10 mg N L^{-1}). The heavily urbanized Capisic Brook watershed has TN concentrations (0.9 mg N L^{-1}) much higher than expected in an undeveloped stream and exceed the US EPA's recommended TN values of 0.38 mg N L^{-1} (or range of 0.32-0.63 depending on subregion) for streams in the northeast US (aggregated ecoregions 8) (US EPA 2000). Rhe Capisic Brook's TN concentrations are elevated locally, but low compared to those observed in heavily farmed watershed like the Choptank River (2.0 mg N L^{-1}) in Maryland and even the Susquehanna River (1.5 mg N L^{-1}) where agriculture and urbanized land use account for only 30% of the watershed's land use (Fisher et al. 1998).

The composition of the total nitrogen in the rivers can provide valuable insight into its sources in the watershed. This information in turn is key to informing watershed management. Broadly, the various species of nitrogen can be divided into two subgroups: inorganic and organic nitrogen. Inorganic nitrogen such as nitrate, nitrite and ammonium typically originate from more anthropogenic sources such as emissions, fertilizers, septic tanks or waste water treatment facilities (Boyer 2002; Xia 2018). The inorganic forms of nitrogen are the most biologically available to primary producers, and in excess can lead to blooms in downstream estuarine systems. Organic nitrogen is naturally found in surface waters and is sourced from living or dead organisms. Organic N can also be supplemented by anthropogenic sources (e.g. CSOs, MPCA, 2013). Typically, in riverine waters where nitrogen is low, organic N accounts for most of the nitrogen, especially where the watershed is heavily forested (MPCA 2013). Where concentrations of TN in riverine waters are high, inorganics, especially nitrate, typically make up most of the TN (e.g., Fisher et al. 1998).

The Presumpscot and Royal rivers, are mostly consistent with what we expected in low-N waters. The Royal River tends towards a relatively equal distribution of inorganic and organic nitrogen. On all sampling occasions, on the Presumpscot River, organic nitrogen is the dominate form of nitrogen, making up 54 to 90% of the total nitrogen. On the Royal River, organic nitrogen dominated about half the time except on 4 occasions when the percentage of organic nitrogen ranged from 10-37% (Table 2). The low inorganic nitrogen observations came in late summer to fall (7/28, 8/31, 9/18 and 10/13) when riverine water yields were low and there was no apparent correlation with precipitation. It is possible that the inorganic nitrogen was delivered via groundwater sourced base flows and the inorganic nitrogen could be from natural sources, previous agriculture (legacy nitrogen) or septic tanks, which leach NO_3^- when working properly and NH_4^+ when failing (NESC 2012).

The concentration and the composition of nitrogen in the Presumpscot and Royal Rivers are related to their land uses. The Presumpscot has less agriculture and urban area and a low total nitrogen composed of mostly organics (Figure 6A). The Royal, with more agriculture and urban area has slightly higher total nitrogen, mainly composed or organic nitrogen (Figure 6A). Capisic Brook, the urban watershed, varies considerable from these two watersheds, consistent with what can be expected given the urban land use and high total nitrogen concentrations (Figure 6B).

Capisic Brook's inorganic and organic composition, on average, represent equal fractions of the TN. However, on some sampling occasions as seen in the Royal River, inorganic nitrogen concentrations dominated the nitrogen concentration composition. This occasional shift is consistent with what is expected of riverine waters where high TN is observed (MPCA 2013, Fulweiler and Nixon 2005). Additionally, nitrogen was less organic (49-63%) compared to Presumpscot and Royal. When attempting to qualitatively relate these the TN concentration in river draining watersheds to their land use, the composition of the total nitrogen is also important to consider.

In all rivers, the NH_4+ concentrations were the least abundant form of nitrogen analyzed. This finding could be due to little NH_4^+ inputs; high ammonium levels are typically found near high sources of human or animal waste or fertilizer (Boyer 2002; Dentener & Crutzen 1994). Additionally, NH_4+ is quickly consumed by stream periphyton and also transformed into nitrite and nitrate through nitrification (Boyer 2002; Dentener & Crutzen 1994). Unsurprisingly, Capisic Brook had the highest concentrations of ammonium followed by Royal, then Presumpscot (Table 2 and Figure 6). The nitrate/nitrite concentrations of Capisic Brook are also the highest which is consistent with what is expected of urban watersheds. Royal River nitrate concentrations are slightly higher than expected for a mostly forested watershed, but the presence of agriculture and urban areas likely raises the nitrate concentrations (Boyer 2002; Fisher et al. 2006). The predominately forested Presumpscot River had the lowest nitrate concentrations (0.035 mg NO_3-N L^{-1}).

Nitrogen concentrations found in the rivers that drain to Casco Bay are low. Concentrations found in rivers that drain to Chesapeake Bay (a more southern but still temperate estuary) are 1.5 – 4 1.5 mg TN L^{-1} (Fisher et al 2006), whereas concentrations found in similar rivers in New England are lower. For context, total nitrogen concentrations found in the Choptank River, an agriculture dominated watershed (58% agriculture, 33% forested and 9 % urban) that drains to the Chesapeake Bay, averages around 1.5 mg TN L^{-1} (Fisher 2010; McCarty et al. 2008). The Patuxent River, a mixed land use but urban and agriculturally dominated stream (33 % urban, 32 % forest, 25 % agriculture), averaged 1.3 mg TN L^{-1} (Homer 2011; USGS 2016). These two watersheds provide examples of nitrogen concentrations found in rivers draining to an estuary that experiences eutrophication and seasonal hypoxia. While the largest rivers in Casco Bay do not have total nitrogen concentrations nearly this high continued population increases and land use changes could bring nitrogen concentrations closer to those seen in Chesapeake Bay tributaries, especially given the concentrations seen in Capisic Brook (1.1 mg L^{-1}). Another apt comparison is to nitrogen concentrations found in watersheds similar, geographically and climatologically, to Casco Bay.

For example, Pawcatuck Watershed drains to Little Narraganset Bay in Rhode Island and is similar in characteristics to Presumpscot and Royal River watersheds with over 60% forested area, less than 10% each of agricultural and urban land use (Fulweiler and Nixon 2005). Narraganset Bay also experiences symptoms of eutrophication and associated anoxic and hypoxic events (Desbonnet and Banister 1994; Jordan 1998; Fulweiler and Nixon 2005). The concentrations of nitrogen found in the Pawcatuck River and the loading of nitrogen from the watershed to the bay has been quantified and serves as another point of context for this study. Over a one-year period of monitoring in 2002, total nitrogen concentrations averaged ~0.76 mg L^{-1}. Organic nitrogen and inorganic nitrogen had a negative, inverse relationship acting similar to the Royal River's nitrogen concentrations (Fulweiler and Nixon 2005). The Royal River and Presumpscot River have average total nitrogen concentrations below those observed in the Pawcatuck River suggesting that while the land use is similar the nitrogen added to the various land uses in Rhodes Island may be different, or Maine watersheds are better able to attenuate nitrogen.

4.2.2 Nitrogen Loading and Export Coefficients

The largest river (Presumpscot) had the largest absolute load, but the smallest watershed (Capisic Brook) loaded the most on a per hectare basis (Table 3). Each watershed's per hectare nitrogen loading, often called the export coefficient, relates the nitrogen found leaving the watershed to the watershed's land use. Beaulac (1982) and Reckhow et. al (1980) compiled nitrogen export coefficients for agricultural, forest and urban landscapes providing a quantitative gauge of the anthropogenic influence from non-point sources within the watershed (Fisher et al. 2006). Comparing the nitrogen export coefficients of the three rivers in this study to values outlined by Beaulac (1982) and Reckhow et. al. (1980) can provide insight into whether these watersheds are exporting nutrients consistent with their dominant land use.

Forests typically have the lowest nitrogen export coefficients, exporting around 1 kg N ha^{-1} yr^{-1} (Fisher et al. 2006; Clark et al. 2000) while urban areas export around 10 kg N ha^{-1} yr^{-1} and agricultural lands can export 5-16 kg N ha^{-1} yr^{-1} (Fisher 2006; Beaulac and Reckhow 1982). The respective estimated export coefficients of each watershed reveal that Presumpscot River is exporting nitrogen (1.5 kg N ha^{-1} yr^{-1}) at a rate consistent with forest as its major land use (Figure 6). Royal River, which is mostly forested, is exporting 3 times (3.79 kg N ha^{-1} yr^{-1}) the expected export from a forested watershed, suggesting an anthropogenic effect on the nitrogen export from other land uses (Figure 6). Capisic Brook is exporting much more than a forested watershed but about as much is expected of an urban watershed (5.31 kg N ha^{-1} yr^{-1}) (Figure 6).

Figure 7 puts the study river's nitrogen yield or nitrogen export coefficient into wider context. Capisic Brook, in orange, is exporting nitrogen as expected of a urban watersheds reviewed by Reckhow et al. (1980). Presumpscot River is exporting slightly less nitrogen than an average forested watershed. The Royal River is exporting more than the average forested watershed but less than the average urban watershed, reflecting the relatively mixed land use occurring in this sub basin.

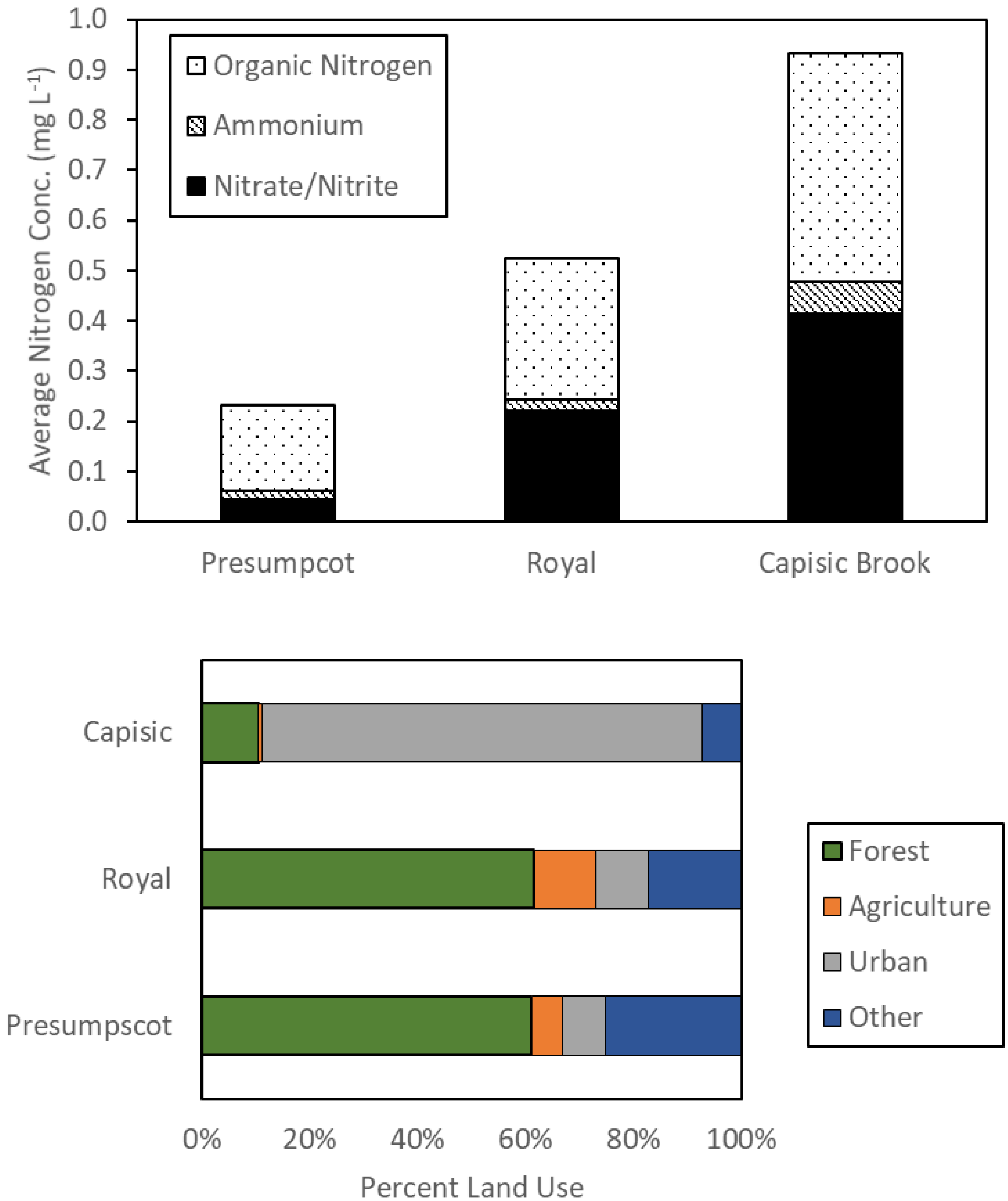

Figure 6. Comparing Nitrogen Yield and Watershed Land Use. Top: The composition of Total Nitrogen broken down by species. Bottom: Percent of each land use in each watershed. Other is a mix of wetlands, water, barren land or shrub.

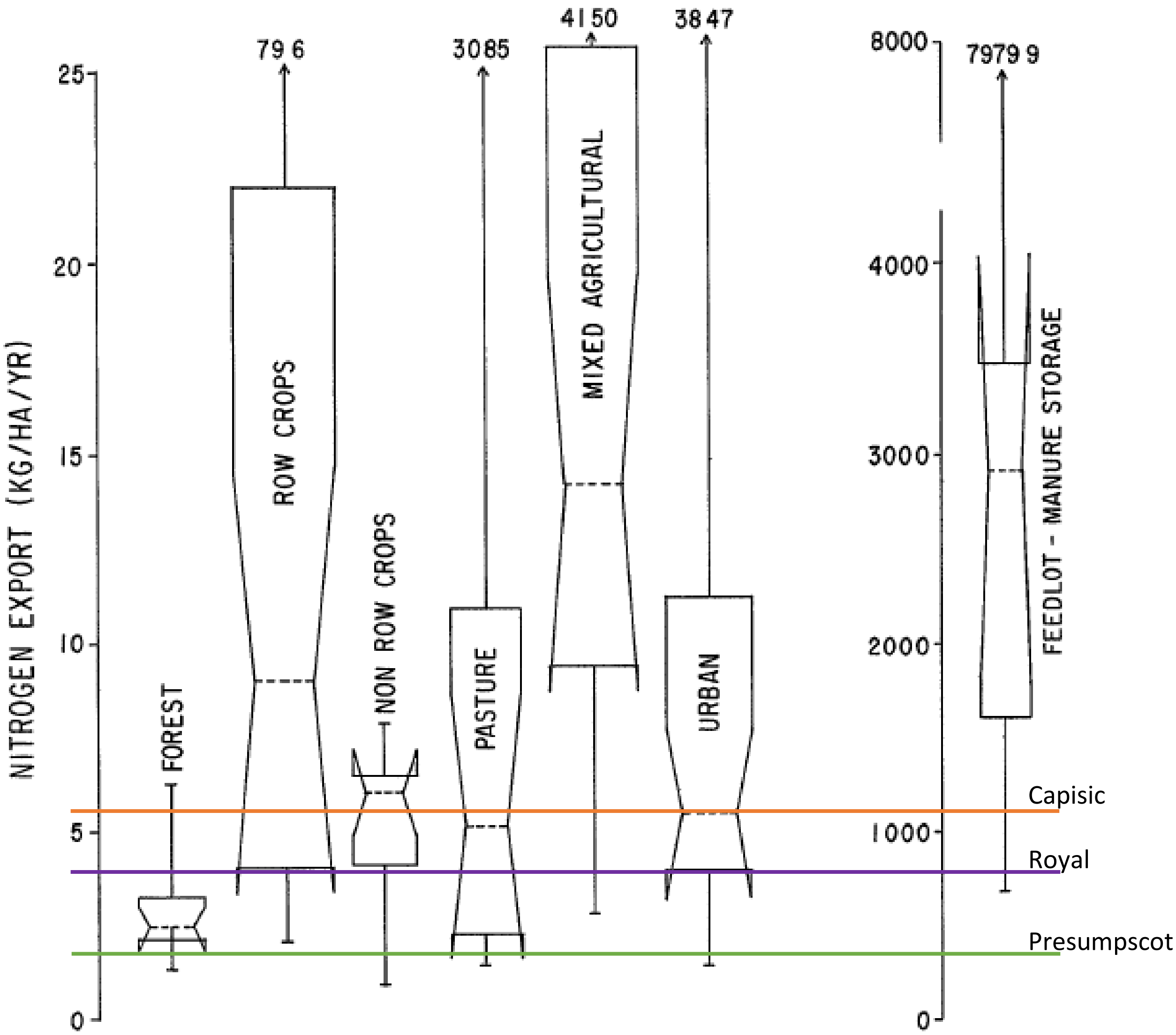

Figure 7. Casco Bay River N Yields Compared to Literature Values. Literature accepted nitrogen export coefficients with the nitrogen export coefficients for each river of this study, overlaid. Original plot is from Reckhow et al. 1980

4.3 Comparing SPARROW and Study Nitrogen Load Estimates

Nitrogen loads for the all the rivers that drain to Casco Bay have previously been estimated using the Northeast (NE) SPARROW (SPAtially Referenced Regression On Watershed attribute) model (Leibman et al. 2012). This model estimates the load of nitrogen from a watershed to a water body based on watershed characteristics, nutrient sources and available monitoring data. However, the monitoring data that informs the NE SPARROW model are from nearby watersheds, outside of Casco Bay's watershed and the watershed characteristics are 17 years old. We compare our estimated loading values to those of the Casco Bay SPARROW Model to investigate differences, refine the SPARROW estimates and improve its usefulness for management decisions in the Casco Bay region.

Comparing the NE SPARROW model estimated nitrogen loads at this study's sample sites, we determine that they generally agree with this study's nitrogen loading estimates (Table 4, column 2). All the nitrogen loading estimates from this study and the NE SPARROW Model are within a factor of two. However, in the case of the Presumpscot River and Capisic Brook, SPARROW's estimates are greater than the study estimates. In the Royal River, SPARROW underestimates the nitrogen load compared to our estimates. For the Presumpscot River, the NE SPARROW estimates an annual load of 451 Mg yr^{-1}, about double this study's nitrogen load estimate. For the Royal River, the NE SPARROW model's annual TN load estimate is 98 Mg yr^{-1} which is about 30% less than this study's TN loading estimate (Table 4, column 2). And finally, the NE SPARROW model's TN load estimate for Capisic Brook is 6 Mg yr^{-1}, 1.5 times this study's total (Table 4, column 2).

The differences in the SPARROW and study nitrogen loading estimates suggests that SPARROW may be overestimating the concentration of nitrogen from the Presumpscot and Capisic or underestimating the removal of nitrogen within the watershed. Using the SPARROW model, Smith et al. (1997), like Seitzinger et al. (2002) and Goyette et al. (2019), found that reservoirs (i.e. dams) do not significantly retain total nitrogen indicating that the lack of considering dam attenuation is not a factor

Table 4. Study TN v. SPARROW TN Load Estimates. Study Total Nitrogen Load estimate for each river (column 1) compared to Total Nitrogen Load estimate for each river based on Northeast SPARROW Model (column 2). Column 4 is a revised TN load estimate using study nitrogen concentrations and SPARROW discharge. Column 3 is the percent difference between the study TN load estimate and the SPARROW TN load estimate. Column 5 is the difference between the revised TN load estimate and the SPARROWTN load estimate.

	Study TN Load (Mg/yr)	SPARROW TN Load (Mg/yr)	Percent Difference Between Study and SPARROW TN Load	Revised Study TN Load (Study Concentration and SPARROW Discharge) (Mg/yr)	Percent Difference Between Revised Study TN Load and SPARROW
Presumpscot	173	451	89%	213	21%
Royal	137	98	33%	127	8%
Capisic	4	6	40%	3	29%

in the difference in TN yields. One major difference in these two loading estimates is the discharge used to calculate the load. We used actual discharge for the study year for Presumpscot River and used Royal River's estimated discharge based on known discharge in the Sheepscot River but in a dry year. We used USGS's Stream Stats' annual discharge estimate for Capisic Brook that is based on USGS regression equations for annual streamflow in ungauged rivers in Maine (Dudley 2015). To better compare the values, we have recalculated this study's loading estimates using the same discharge that the NE SPARROW used for its loading estimates (Table 4, column 4).

A recalculation of this study's TN loading estimates, using the discharge values used in the Casco Bay SPARROW model brings the TN loading values of Presumpscot and Royal River closer. Even when my results are recalculated using SPARROW's discharge, SPARROW's Presumpscot TN loading estimate is still a factor of two greater than this study's estimate suggesting discharge was not responsible for the difference in values. The Royal River estimates, however, are closer with the recalculation (within 30% of one another) suggesting the nitrogen sources, watershed characteristics and nitrogen attenuation SPARROW is using for its estimate are likely close to reality (assuming this study's values are a true representation of actual loading). Capisic Brook's study TN load estimate and recalculated TN using study concentrations and SPARROW's discharge suggests (Column 4 of Table 4) SPARROW's nitrogen values are much higher than those seen in the watershed or there is more attenuation occurring than accounted for by SPARROW. Updating the land use used in the Northeast SPARROW and reassessing the nitrogen values attributed to each land use in Casco Bay could help to refine the SPARROW's total nitrogen loading estimates for Casco Bay. Additional years of observations would significantly improve our ability to understand interannual variability of nitrogen concentrations seen in Casco Bay rivers. Additional monitoring of Casco Bay Rivers to help refine our understanding of riverine loading into Casco Bay in addition to refining the SPARROW Model for Casco Bay would provide better tools and data for decision makers tasked with managing nitrogen in Casco Bay.

4.4 N Loading Compared to Other Known N Loading

Given the somewhat elevated nitrogen concentrations found in Casco Bay, it's important to investigate all the possible sources of that nitrogen. This study provides an estimate for the contribution of three rivers that drain directly to Casco Bay, accounting for much of the non-point source loading from the watershed. While these rivers deliver over 80% of the freshwater to Casco Bay, but their total nitrogen loads, alone don't provide a total annual load from all rivers in to the bay. By extrapolating the data from this study, the total riverine nitrogen load to Casco Bay would be about 488 Mg yr^{-1} (Table 6) with the remaining river contributing 128 Mg TN yr^{-1}.

To make this extrapolation, we used SPARROW's discharge values for each river in Casco Bay, besides the study rivers, and multiplied it by the average TN concentration of either the Royal River or Capisic Brook. To determine which study river's average concentration to use, the land use of each watershed was investigated. If urban land use accounted for greater than 50 percent of the watershed's total land use, Capisic Brook's average TN concentration was used to calculate that river' TN load. If forest area dominated the watershed's land use Royal River's TN concentration.

We can compare the total Casco Bay riverine load to the loading from Waste Water Treatment Facilities (WWTFs) and atmospheric deposition. We caution that there is significant uncertainty in this estimate due to the lack of data. One major source of potential uncertainty is the discharge estimate used for each river. The flow is based on the NE SPARROW which is not representative of the actual flows observed over this study period. But even this estimate enables understanding the relative contribution of all these sources and provides insight into where nitrogen management could be focused.

Five WWTFs that drain directly to Casco Bay. These facilities are limited to secondary treatment and do not actively remove dissolved nitrogen from their treated discharge. These facilities monitor and report their annual nitrogen load and in 2008 collectively discharged 902 Mg of total nitrogen to Casco Bay (Leibman et al. 2012; ME DEP 2008) (Table 5), nearly three times the estimated total nitrogen loading from the three rivers in this study. Assuming no major facility changes have occurred, it's reasonable to assume that the Casco Bay facilities loaded approximately the same quantity in 2017, during this study period (Table 5).

In 2008, Portland Water District's East End Facility, which releases its effluent downstream of the mouth of Presumpscot River, loaded 546 Mg y^{-1}, two and a half times Presumpscot River's estimated load (173 Mg y^{-1}) (Purple Square, Figure 3). Yarmouth's WWTF, which is down stream of this study's sample site along the Royal River (Pink Square, Figure 3), loaded 36 Mg y^{-1} of nitrogen to Casco Bay, about one third of Royal River's estimated load (137 Mg y^{-1}). There is no apt comparison of a specific WWTF to Capisic Brook because it is a smaller stream that drains to the Fore River Estuary. This closer

Table 5. Study TN Load, SPARROW TN and WWTF TN Load.
(a) Study TN Load Estimates and SPARROW TN Load Estimate for each river with summed total of all rivers TN load to Casco Bay. (b) 2008 TN Load of each Wastewater Treatment Facility that drains directly to Casco Bay to total summed TN Load at bottom.

A.

	TN Load Estimation (Mg yr^{-1})	SPARROW TN Load Estimate (Mg yr^{-1})
Presumpscot	173	451
Royal	137	98
Capisic	4	6
TOTAL	314	555

B.

	TN Loads (Mg yr^{-1})
Portland Water District	546
South Portland	256
Falmouth	42
Yarmouth	36
Freeport	20
TOTAL	902

look at the specific river and nearby WWTFs suggests that broadly speaking, WWTFs contribute more nitrogen to Casco Bay but that not all areas of the bay are equally affected by WWTFs. Royal River is an example of a river contributing more than nearby WWTF.

Wastewater Treatment Facilities and river, however, are not the only quantifiable sources of nitrogen to Casco Bay; atmospheric deposition and Combined Sewage Outfalls (CSOs) also contribute nitrogen to the bay. Maine DEP estimates that atmospheric nitrogen accounts for 30-40% of the nitrogen delivered to Casco Bay (ME DEP 2008). In 2017, based on National Atmospheric Deposition Program's data collected by ME DEP at Wolfe's Neck Farm in Casco Bay, 138 Mg of nitrogen was

Table 6. Comparing TN Load of All Casco Bay Sources and Pathways. Total Nitrogen load to Casco Bay, by source or pathway. WWTFs and Rivers load the most nitrogen to Casco Bay, CSOs and OBDs deliver the least amount of nitrogen and Atmospheric Deposition delivers less than 1% of the total nitrogen that enters Casco Bay. This information is helpful for prioritizing management decisions.

	Annual nitrogen Load ($Mg\ yr^{-1}$)	Percentage of Total Nitrogen Load
WWTF	902	60
Casco Bay Rivers	441	30
Combined Sewage Outfalls	6	< 1
Atmospheric Deposition	138	9
Overboard Discharges	0.98	< 1
Total	1,488	

delivered to the surface waters of Casco Bay. This calculation is lower than a 2003 study that estimated atmospheric nitrogen deposition to be between 255 – 428 Mg yr^{-1} accounting for less than 10 percent of the nitrogen delivered to Casco Bay (Table 6) (Casco Bay Air Deposition Study Team 2003). Atmospheric deposition loads less nitrogen to Casco Bay than either the rivers and WWTFs.

In 2017, the City of Portland had 30 functioning Combined Sewage Outfalls (CSOs). Many drain directly to Casco Bay and overflowed at least once during the study period. Overflow event dates and discharge volumes are recorded and reported annually by Maine DEP but no nitrogen concentration data are available. Collectively, over the 38 overflow events in 2017, the CSOs discharged 6.62×10^5 m^3 of water and an unknown quantity of nitrogen directly into Casco Bay. It is not unreasonable to assume that concentrations of CSOs is similar Capisic Brook's total nitrogen concentration (0.9 mg L^{-1}). By this admittedly crude assumption, in 2017 the CSO's would be contributing 6 Mg yr^{-1} (delivering more nitrogen than Capisic Brook) into Casco Bay (Table 6F). This, of course, is only an approximation with unknown errors. While the City of Portland has a continued effort to eliminate the CSOs, to better understand the true loading of nitrogen from the CSOs, monitoring during overflow events is needed. Besides the rivers, WWTF, atmospheric deposition and CSOs, there are a few potential sources that have not been quantified or are not fully understood (e.g. remineralized nitrogen from the ocean, Kennebec River).

Another source of human waste derived nitrogen is overboard discharges (OBDs) from homes directly into nearby waterbodies. Casco Bay has approximately 23 active overboard discharges that release directly into Casco Bay (as opposed to upstream waterbodies that eventually flow to Casco Bay) (ME DEP 2017). All but one of these OBDs are residential systems that discharge an average of 500 gallons day^{-1}; a commercial OBD that services multiple homes on an island discharges about 35,000 gallons day^{-1} (ME DEP 2017). Given that the OBDs do treat the sewage, like WWTFs lacking nitrogen removal, we assume they discharge concentrations of nitrogen like WWTFs (20 mg L^{-1}) (ME DEP 2008). If all the OBDs were functioning year-round, collectively, they would load about 0.99 Mg yr^{-1} into Casco Bay (Table 6). Overboard discharges load a minor amount of nitrogen compared to other sources into Casco Bay and are thus not monitored by ME DEP for nutrient but could have more local implications (ME DEP 2008).

Considering the open nature of Casco Bay and the dominate circulation of the Gulf of Maine (east to west) we would be remiss not to mention the possible contribution deep ocean sourced nutrients could have on the nitrogen budget of Casco Bay. Winter-spring phytoplankton blooms have been known to occur throughout the Gulf of Maine due to the delivery of nutrient rich, deep ocean water to the surface waters via numerous processes (i.e. upwelling, tidal mixing, convective overturn, etc) (Thomas et al., 2003; Rebuck, 2011; Rebuck and Townsend, 2014; Townsend et al. 2015). Investigating further ocean, or Gulf of Maine, sourced nitrogen, in addition to understanding the circulation dynamics of the bay would help to better understand how the nitrogen budget is influenced by the bay's circulation.

It is clear that while the nitrogen loading from tributaries in Casco Bay is large, collectively, it is not as large as other, more easily managed loads of nitrogen like those coming from area WWTFs. But at a smaller scale, some rivers, like the Royal, are loading more nitrogen than the nearest WTTF. It will be important not to ignore these smaller scale findings with broad management approaches. Understanding the relative magnitude of loading can help to prioritize future management strategies in the region. The implications of these findings on future policy and management prioritization is further discussed in the next section.

4.5 Policy Implications and Management Prioritization

We present here the first study to estimate riverine nitrogen load to Casco Bay based on stream discharge and nitrogen measurements. This baseline data are not only informative but also useful in comparing modeled estimates based on common nitrogen export coefficients for different land uses.

Considering the limitation of measuring all streams in Casco Bay for their nitrogen loads, understanding how the measured estimates compare to modeled estimates creates an opportunity for the use of models in future research and management decision making. The measured and modeled loads were within a factor of two and can help to support current and future strategies aimed at managing and minimizing nitrogen inputs to Casco Bay and avoiding the ecological and economic consequences of eutrophication.

We have provided some insight into determining the efficacy of modeled approaches (SPARROW) for estimating nitrogen loads and helped to identify the relative load of different sources (WWTFs, atmospheric deposition and CSOs) compared to riverine load, and that together, those two outcomes can help guide future research and ultimately policy and management decisions in Casco Bay. More specifically, this research would be especially useful for Maine's effort of creating nutrient criteria for marine waters and linking it to nutrient criteria for fresh waters and helping stakeholders determine if the SPARROW model for Casco Bay is acceptable for use in decision making related to establishing nutrient criteria.

CONCLUSION

The three rivers in this study are delivering nitrogen to Casco Bay but collectively loaded less than the known effluent from Waste Water Treatment Facilities (WWTFs). The more urbanized watersheds load more per hectare. Estimates of loading made by a Casco Bay-specific SPARROW Model are in agreement but SPARROW's estimates are often a factor of two higher.

The findings and other discussion points from this research serve as a good starting point for future management prioritization. Ideally, these estimates, coupled with the other known loading in Casco Bay can be useful to state and local government and other stakeholder to help prioritize management of nitrogen in order avoid situations like Chesapeake Bay and the Gulf of Mexico.

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