THE TEMPORAL AND SPATIAL RELATIONSHIP BETWEEN PHOSPHORUS AND NITROGEN CONCENTRATIONS, ALGAL GROWTH, AND NUTRIENT SOURCES IN THE MEDUXNEKEAG RIVER WATERSHED

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Elizabeth A. Fretwell

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Advisory Committee:

D. Bryan Dail, Assistant Professor Soil Microbiology, Co-Advisor

Katherine E. Webster, Assistant Professor of Biological Sciences, Co-Advisor

Susan H. Brawley, Professor of Plant Biology

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Thesis Advisors: Dr. D. Bryan Dail and Dr. Katherine E. Webster

An Abstract of the Thesis Presented
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Excess nutrients from both point and non-point sources commonly impair rivers and contribute to the formation of nuisance algal blooms that can cause aesthetic issues and decrease dissolved oxygen concentrations. The Meduxnekeag River in Aroostook County, Maine has historically experienced nuisance filamentous algal blooms and low dissolved oxygen concentrations during summer months, raising concern about possible nutrient enrichment within the river. In addition to nutrient inputs from agriculture, the river receives effluent from a starch plant and then flows through downtown Houlton, where it receives stormwater runoff and effluent from a wastewater treatment plant (WWTP). The primary objectives were to determine spatial and temporal trends in nutrient concentrations and loads, assess algal coverage within the river and determine its relationship to nutrient concentrations, and to determine which nutrient sources within the watershed pose the greatest risk to the water quality.

I investigated the relationship between nutrients, algal growth, and land use within the Meduxnekeag River watershed. Fourteen sites in a 34 kilometer reach of the river were sampled biweekly in 2004 and 2005 from May until October. Sampling included the collection of water samples for analysis of nitrogen (N) and phosphorus (P) and assessments of filamentous algal coverage at each site. The C:N:P ratio was determined for water and algal samples. I used a general linear model to determine if nutrient concentrations accounted for a significant amount of the variability in algal coverage among sites. Nutrient loads were calculated for each site based on discharge information from three gauges within the study area, and loads were related to nutrient sources within the watershed.

Both TP and NO_3^- concentrations increased downstream. For all sites, the mean total P (TP) concentration was 11.8 μg/L and the mean nitrate (NO_3^-) concentration was 0.175 mg/L. Soluble reactive P was close to or below detection in more than half of the samples and ammonium was below detection in most samples. Area-weighted load data indicated that the WWTP was the single largest source of TP and NO_3^-, but unweighted data suggested that cumulatively, agricultural land within the watershed contributed more than three times the amount of TP as the WWTP.

A nuisance bloom did not occur in either study year; the highest mean algal coverage at a site was only 16% (0-43%) and much less than the 30% coverage typically considered as nuisance level. Despite the steady increase in both NO_3^- and TP concentrations downstream, the major pattern in algal coverage was for significantly *higher* values upstream than downstream. Neither N nor P accounted for a significant amount of variability in algal coverage. Although nutrient ratios suggested P limitation,

longitudinal patterns in algal coverage suggested that nutrients were not the primary limiting factor. Other factors such as light, substrate, and flow may be limiting algal growth in the river.

The study determined the relative contribution from different sources within the watershed but also established that the entire study area had low average nutrient concentrations. Within the past few years, agricultural practices within the watershed have improved, and the WWTP decreased the P content of its effluent. These changes could have lowered nutrient concentrations below the river's threshold for nuisance blooms and highlight the importance of effective watershed management, although further monitoring is warranted. This suggests that while the WWTP and agricultural land are the dominant nutrient sources within the watershed, current management of point and non-point sources is effectively maintaining low nutrient concentrations within the river.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
C	Carbon
DIN	Dissolved Inorganic Nitrogen
DIP	Dissolved Inorganic Phosphorus
DO	Dissolved Oxygen
EPA	Environmental Protection Agency
GIS	Geographic Information System
GLM	General Linear Model
HDPE	High-Density Polyethylene
HBMI	Houlton Band of Maliseet Indians
MDEP	Maine Department of Environmental Protection
N	Nitrogen
N_2	Nitrogen Gas
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
P	Phosphorus
PP	Particulate Phosphorus
SRP	Soluble Reactive Phosphorus
TDN	Total Dissolved Nitrogen
TDP	Total Dissolved Phosphorus
TMDL	Total Maximum Daily Load
TP	Total Phosphorus

USGS	United States Geological Survey
WWTP	Wastewater Treatment Plant

Chapter 1

INTRODUCTION

The nutrient chemistry of undisturbed rivers reflects precipitation inputs and contributions from local geology and the influence of plant and soil processes upon these inputs (Allan 1995), but anthropogenic activities can elevate nutrient concentrations and affect ecosystem processes. In the 2000 National Water Quality Inventory, 39% of the surveyed rivers failed to meet one or more designated uses, which include recreation, aquatic life support, fisheries and fishing, drinking water supply, and agriculture (EPA 2000). Rivers can become physically degraded by habitat destruction and channel alteration, and their water quality can be affected by pollution from point and non-point sources.

Point source pollution comes from a specific site, such as an industrial facility or municipal sewage treatment plant, whose discharges are usually regulated. Non-point source pollution is usually associated with land use and cannot be easily traced to single source points. Non-point sources include atmospheric deposition, agricultural runoff, and urban runoff. Runoff transports sediment, bacteria and other microorganisms, pesticides, metals, and nutrients from the land into rivers and is difficult to regulate because it can come from extensive areas of land. While point source discharges are typically regulated, in urban areas they can contribute more nutrients than non-point sources (Carpenter et al. 1998). However, in the majority of rivers, non-point source pollutants from both urban and agricultural areas are the leading cause of impairments (EPA 2000).

The most common result of runoff entering the nation's surface waters is eutrophication (EPA 1996). Eutrophication is a process by which a body of water

becomes enriched with dissolved nutrients, and it is often associated with an increased growth of algae and aquatic plants, which causes aesthetic issues, kills other biota by reducing dissolved oxygen (DO) levels, and degrades habitat (Carpenter et al. 1998, Dodds and Welch 2000). In response to the large-scale eutrophication of surface waters, the EPA has set maximum acceptable levels of nutrients in streams and rivers and made recommendations for nutrient criteria that differ by ecoregion. However, these criteria are provided with the caveat that they be considered with regard to local conditions.

BACKGROUND

The Meduxnekeag (muh-DUHKS-nuh-keg) is a 56 km river which flows north from Maine into New Brunswick, Canada and is part of the St. John River system. The watershed drains a total area of 1,326 km^2, 1,098 km^2 of it in Maine. The river is comprised of three branches: the mainstem, North Branch, and South Branch. Feeder streams flow into Lake Meduxnekeag, but the lake is generally considered the headwater. A 20-mile segment of the Meduxnekeag River in Aroostook County, Maine, that flows through Houlton Band of Maliseet Indian (HBMI) tribal lands has historically experienced substantial filamentous algal blooms during summer months, raising concern about nutrient enrichment within the river. The watershed contains multiple nutrient sources, both point and non-point, as well as a range of land cover types from forested to agricultural to urban. Increased nitrogen (N) loading, largely in the form of nitrate (NO_3^-) and organic N has been observed in a stretch of the river adjoining the town of Houlton, Maine (Schalk and Tornes 2005). The Meduxnekeag is considered a Class B river (i.e. good water quality) but has had non-attainment problems in regards to DO and excess nutrients. A Total Maximum Daily Load (TMDL) study cited the algal blooms as a direct

cause of depressed DO levels in a 10-kilometer stretch of the river (MDEP 2000).

The Meduxnekeag River watershed contains the some of the most intensively farmed land in southern Aroostook County. Two-thirds of the agricultural land is in potato production, and the rest is used for hay production, dairy and beef cattle, and for other types of crops and livestock (SASWC 1993). Lake Meduxnekeag is not known to have significant water quality issues (SASWC 1993), but the segment affected by algal blooms starts less than one km downstream of the lake. The river receives inputs from multiple sources including a starch processing plant, stormwater runoff from Houlton, agricultural lands, and a wastewater treatment plant (WWTP) before flowing through HBMI land beginning at river km 30. Both point and non-point sources are suspected of contributing excess nutrient loads to the river, but historical nutrient data are limited. The HBMI has monitored 10 sites on a weekly basis for a 12 to 14 week period every summer since 1995. Its monitoring program includes total suspended solids, *E. coli*, pH, temperature, turbidity, conductivity, alkalinity, and DO. Nitrogen and phosphorus (P) measurements, however, are limited to those collected for the TMDL study (MDEP 2000) between 1995 and 1997 and those collected in 2003 for a USGS sediment study (Schalk and Tornes 2005).

One goal of the USGS study by Schalk and Tornes (2005) was to investigate nutrient dynamics in surface waters and sediments in order to better understand temporal and spatial variability and how this might relate to algal blooms. They measured nutrient concentrations in bed-sediment at four stations and in the water column at five stations within the mainstem and its tributaries. Relative to other studies in the region, they found low P concentrations in the sediment, mid-range P concentrations in the water, and high

N in surface waters (both organic-N and NO_3^-). No significant algal blooms occurred during the study year (2003), so comparisons of algal blooms and nutrients in the surface water or bed sediments along this reach could not be made.

Section 303(d) of the Clean Water Act requires that pollution loads to a water body not supporting beneficial uses or meeting state water quality standards be amended to enable the water body to comply with standards and satisfy its beneficial uses (Watson and Gestring 1996). To improve the water quality of a river, the current status and causes leading to its impairment need to be understood. The limited amount of information regarding nutrients in the Meduxnekeag River and the intermittent nature of the algal blooms has been such that effective management of the blooms, through nutrient management, has been difficult for this watershed.

The recurring algal blooms in the Meduxnekeag River, its unknown nutrient status, and the mixed land uses within the watershed make the river a very interesting yet challenging system to study. Previous research in other waterways indicates that point sources, such as the WWTP and the starch plant, can be major contributors of nutrients, but the extent of agriculture in the watershed makes non-point source pollution just as important a potential source (Dillon and Kirchner 1975, Edwards et al. 2000, Donohue et al. 2005). The causes of algal blooms require further investigation, including any temporal or spatial patterns that may be associated with them that would better identify proximate causes of the blooms. In this study, I investigated algal–nutrient relationships, the trophic status of the river, and nutrient sources within the watershed that might contribute to the proliferation of algal blooms.

OBJECTIVES

The overarching goal of this project was to gain a broader understanding of the Meduxnekeag River and potential factors that lead to excessive algal growth by examining the spatial and temporal relationships between P and N concentrations, algal growth, and nutrient sources in the watershed. I evaluated the underlying causes of the eutrophication by collecting two years of P and N data, assessing temporal and spatial changes in the algae, and comparing nutrient data to filamentous algal growth. To address the overarching goal, I set two objectives, each with a corresponding hypothesis:

1) Objective: Determine the spatial and temporal phosphorus and nitrogen trends in the Meduxnekeag River and describe how they correlate to point and non-point nutrient sources in the watershed.

   Hypothesis: Spatial and temporal land use related differences in the nutrient concentrations in the river will allow identification of the primary nutrient sources. I predicted that the primary nutrient sources will be associated with either a point source or with land that is primarily used for agriculture and will be indicated by distinct changes in surface water chemistry.

2) Objective: Investigate spatial and temporal patterns in filamentous algal growth and determine if algal coverage positively covaries with nutrient concentrations.

   Hypothesis: Spatial patterns in algal growth will reflect spatial patterns in the nutrient data; sites with the highest average percent coverage will be the sites with the highest P concentrations. I expected the system to be either limited by P or co-limited by N and P. I predicted that temporal changes in nutrient

limitation will be more apparent than spatial changes in nutrient limitation but that the N:P ratio would decrease longitudinally as the percent of land in agriculture decreased. I expected the N:P ratio to be highest in late spring and decrease when flows were the lowest (i.e. midsummer).

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Chapter 2

LITERATURE REVIEW

NUTRIENTS

Nutrient Dynamics and River Eutrophication

Nitrogen (N) and phosphorus (P) are the primary nutrients of concern in relation to water quality issues because they can stimulate primary productivity. The major forms of N and P found in natural waters are listed in Table 1. Nitrogen is present in the environment as organic nitrogen (i.e. bound to organic matter), nitrogen gas (N_2), nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+). Organic nitrogen exists in both a dissolved and a particulate form in aquatic environments. Organic nitrogen includes urea, proteins, individual amino acids, as well as other, more complex biomolecules and it is found within living organisms and decaying plant and animal tissues. The sum of NH_4^+, NO_3^-, and NO_2^- is usually referred to as dissolved inorganic nitrogen (DIN). Although N_2 is inorganic and sparingly soluble in water, it is not considered DIN as it is generally not biologically available.

Primary producers, such as algae, preferentially take up NH_4^+ but also use NO_3^-, and rarely, NO_2^- (Dodds 2002). Nitrification-denitrification pathways result in the loss of NH_4^+, and it is regenerated by excretion and decomposition (see Figure 1). Nitrate is commonly used as a measure of available N because it is the most oxidized form, organic N can be hard to measure, and NH_4^+ is often converted to NO_3^- or taken up by terrestrial vegetation before it reaches open water (Dodds 2002). Ammonium that leaches from land to streams can be exported as such or converted to NO_3^- via nitrification in-stream (Mulholland et al. 2000, Tank et al. 2000).

Table 1. Major forms of nitrogen and phosphorus in natural waters. Nitrogen is also present as dissolved N_2 gas but is not listed in the table (adapted from Allan 1995).

Nitrogen		
Dissolved inorganic nitrogen (DIN)	Total dissolved nitrogen (TDN)	Total nitrogen (TN)
NO_3^- nitrate		
NO_2^- nitrite		
NH_4^+ ammonium		
Dissolved organic nitrogen (DON)		
Particulate organic nitrogen (PON)		
Phosphorus		
Dissolved inorganic phosphorus (DIP or SRP)	Total Dissolved/soluble phosphorus (TDP or TSP)	Total phosphorus (TP)
PO_4^{-3} orthophosphate		
Dissolved organic phosphorus (DOP)		
Particulate organic phosphorus (POP)		
Particulate inorganic phosporus (PIP)		

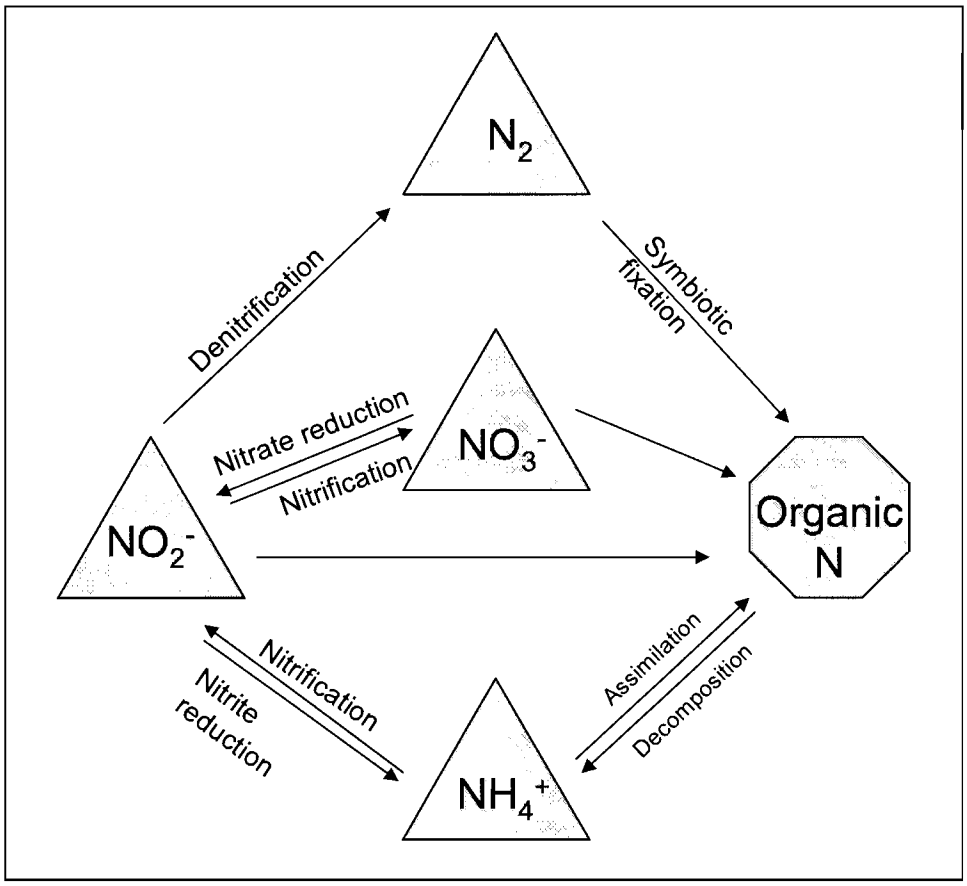

Figure 1. Simplified version of the N cycle.

Nitrate and NH_4^+ are the dominant forms of DIN in oxygenated and anoxic waters, respectively.

Phosphorus fractions commonly measured in water quality studies are orthophosphates, total inorganic phosphate, and total phosphorus (TP) (Chapman et al. 1996). Organic P is composed of a dissolved fraction and a particulate fraction, but unlike N, P is primarily found in only one inorganic form. Phosphate (PO_4^{-3}), the only inorganic form of P in natural waters, is generally considered the bioavailable fraction and is also referred to as orthophosphate, dissolved inorganic phosphorus (DIP), or soluble reactive phosphorus (SRP). Phosphate concentrations are often below detectable limits in natural waters (Dodds 2002). Soluble reactive P assimilated by plants and microbes is transformed into dissolved (DOP) and particulate organic phosphorus (POP). Phosphorus may then be excreted or released during cell lysis as SRP or as dissolved organic P (DOP), which is then broken down to SRP by bacterial activity.

Some organisms, including many species of cyanobacteria, have phosphatase enzymes that make DOP biologically available. The role of organic P in aquatic systems and in dissolved P transfer is not well understood. Concentrations of SRP in heavily fertilized and manured soils and that of particulate P (PP) in runoff from tilled land are generally much higher than organic P; however, organic P can constitute a varying fraction of TDP depending on its source, and some organic P compounds are more susceptible to leaching than SRP (Turner 2005).

Phosphorus availability is also influenced by physical-chemical transformations. At high SRP concentrations, precipitation of P as iron and aluminum phosphates occurs, while at low SRP concentrations, organic and inorganic compounds adsorb to sediment

(Allan 1995). Soluble reactive P, polyphosphates, and DOP only precipitate with metals such as iron and aluminum under oxic conditions. In acidified watersheds, the mobility and solubility of aluminum increases, and this change can result in lower P concentrations as more P becomes bound to aluminum (Kalff 2003). Under anoxic conditions, this redox process is reversed and P dissociates from metals.

Transport

Nutrients may be transported to a stream in surface runoff, subsurface flow, base flow, and directly from litterfall; subsurface and base flows are the most common pathways (Brooks et al. 2003). Dissolved NO_3^- readily leaches from soil and is transported in runoff, particularly during heavy rain events and snowmelt (Blum 1956, Piatek et al. 2005). In stream systems with low N, atmospheric deposition can be a significant source of nutrient inputs (Dodds 2002). In many streams, however, agricultural soils are also a significant source of N (Jarvet et al. 2002). Globally, more nutrients are added as fertilizer than are removed as produce (Carpenter et al. 1998). At the watershed scale, depending on the timing of fertilizer additions and soil type, much of the N can be leached and affect ground and surface waters (Carpenter et al. 1998). Considering all land uses, sediment-associated transport contributes approximately 57 percent of total N (TN) exported to oceans by rivers (Walling et al. 2001).

Phosphorus can be dissolved in surface runoff or leached through the soil, but it is often bound to particulate matter and transported to streams with eroding sediment (Barrows and Kilmer 1963). Most of the P transported from grasslands and forests is soluble, and most of the P transported from agricultural fields is particulate (Lemunyon and Gilbert 1993). Around 90 to 95 percent of the TP exported by rivers is associated

with suspended solids that are largely transported to rivers in surface runoff (Froelich 1988, Walling et al. 2001). In addition, the concentration of P in runoff tends to be higher than in the source soil because water and wind tend to move smaller, less dense particles with a high proportion of clay and organic matter laden with P (Lemunyon and Daniel 2002). Although the concentration of P in runoff may be higher than in the source soil, it is not necessarily bioavailable. Sharpley et al. (1985) found that bioavailable P levels were three times greater than that of the source soil, but Owens and Walling (2002) estimate that only 10 to 20 percent of the PP transported to rivers is bioavailable. Because estimates of the bioavailability of PP largely differ and much sediment is transported to rivers in surface runoff, it is important to effectively manage erosion within watersheds.

Cycling and Availability

Although streams are open systems that receive large nutrient inputs from their watersheds, in-stream cycling is very important to stream productivity. Nutrient cycling generally describes the uptake of available dissolved forms of elements by biota, transfer through food chains from one organism to another, release by excretion or decomposition into the pool of dissolved available nutrients, and element reassimilation by organisms (Allan 1995, Mulholland 1996). In lotic systems, the cycling is more often referred to as spiraling because the cycle involves downstream transport. Nutrient cycling is quantified by uptake rate and distance traveled by an atom in completing a cycle. Nutrient turnover depends on the size of the nutrient pool, rate of uptake and remineralization of nutrients by organisms, and the water velocity. For example, stream NH_4^+ pools can be completely remineralized in as little as six minutes from the time of assimilation (Dodds et al. 2000).

Because of its ability to rapidly restore nutrient pools, remineralization is the main short-term source of nutrients for primary producers (Dodds 2002).

Discharge can influence the spiraling length and affect dissolved inorganic nutrient concentrations (Newbold et al. 1981). During periods of low discharge, the contact time between the water and substrate increases, and this decreases the spiraling length by increasing the amount of nutrient uptake (Butturini and Sabater 1998). Inorganic nutrients are often under high demand and turnover rapidly, and thus are efficiently recycled. Therefore, even if supply is high, the in-stream concentration of inorganic nutrients may be low (Dodds 2003). For example, SRP concentrations may be low despite the desorption of SRP from sediments during low flows (Olley and Caitcheon 2000, Bowes et al. 2003). To complicate matters, SRP concentrations can be difficult to estimate because they are not necessarily proportional to TP concentrations. Dodds (2003) found that the proportion of SRP decreases as TP increases.

Low flow conditions can also affect the availability of organic P and N fractions. Particulate P is not generally considered bioavailable because it is suspended and transported downstream, but during low flows, PP retained by within-channel sediment deposition becomes available for utilization by sediment microorganisms (Sharpley et al. 1994, Bowes et al. 2003). During low flow, most of the organic N present is largely derived from in-stream or autochthonous sources (Edwards et al. 2000). Thus, a large source of in-stream nutrient variability may result from flow dynamics.

Land Use Effects on Nutrients

Watershed area and land cover often correlate to mean nutrient concentrations in streams (Osborne and Wiley 1988), but the strength of the correlation depends on the

land cover type. Nutrient levels are often elevated in streams draining urban and agricultural areas, particularly when compared to forested watersheds (Dillon and Kirchner 1975, Omernik and McDowell 1977, Hirose and Kuramoto 1981, Meador and Goldstein 2003). Forested streams generally have nutrient concentrations 15 times lower than those in agricultural or urban streams (Omernik and McDowell 1977). In small agricultural watersheds, the rate of fertilization is often the most important factor in N runoff, but in larger watersheds with mixed land uses, the spatial pattern of land use in the watershed more strongly influences nutrient concentrations in runoff (Mander et al. 2000).

Both agricultural and urban land cover types can contribute to high N and P concentrations in streams. The percent of agricultural land in a watershed is often correlated to NO_3^- (Edwards et al. 2000, Hakala et al. 2002, King et al. 2005) and, less commonly, to TP (Hakala et al. 2002, Buck et al. 2004). Streams in agricultural watersheds usually remain in good health until agriculture makes up more than 30 to 50% of the land use (Allan 2004). Urban runoff is not well retained by soil particles and can discharge high levels of SRP, TP (Dillon and Kirchner 1975, Owens and Walling 2002), and NO_3^- (Hirose and Kuramoto 1981,Taylor et al. 2005) to surface waters. Even if urban land cover comprises a small percent of a watershed, it can have a disproportionately large influence on water quality (Allan 2004).

Land use effects on water quality may override physical watershed characteristics such as geology and soil type. Water chemistry may be more strongly correlated to land use than to bedrock geology or soil association (Smart et al. 1985). The scale of land use can also be a factor influencing water quality. For instance, land use at the watershed

level is a larger determinant of nutrient concentrations in large streams (e.g. 4th order), while local land uses and other factors are more important in small streams (e.g. 2nd order) (Allan et al. 1997, Buck et al. 2004).

ALGAL GROWTH

Periphyton Growth Factors

Although the term periphyton is sometimes used to describe the entire microflora (e.g. microscopic algae, bacteria, and fungi) on the substrata (Stevenson 1996), I use benthic algae and periphyton interchangeably to refer to the micro- and macroscopic algae living on or in association with the substrata. Factors such as light, nutrients, temperature, stream velocity, substrate availability, and grazing all affect periphyton growth rates. Generally, light, nutrients, and temperature control biomass accrual, whereas disturbance and grazing control biomass losses (Biggs 1995).

Algal community composition is often determined by whether accrual or loss processes are dominating the system. Accrual processes tend to dominate with low to medium flood frequency and grazing, and a medium to high resource supply, resulting in erect, stalked diatoms and/or communities dominated by filamentous green algae such as *Cladophora glomerata* (Biggs 1996). If the disturbance frequency and resource supply are low to moderate, the communities tend to be comprised of filamentous cyanobacteria, red algae, and a limited number of diatoms. Conversely, loss processes limit growth if the flood frequency is medium to high, or if there is heavy grazing, and low growing diatoms such as *Cocconeis placentula* dominate the substrate.

Grimm and Fisher (1986) suggested that nutrients regulate periphyton accrual in streams but that maximal standing crops are a function of flood frequency. Even when

nutrient concentrations are high, flood events, grazing, and light limitation can lower algal biomass (Dodds 2002). Lohman et al. (1992) concluded that effects of enrichment may be obscured by flood events, and that disturbance events may explain the mixed results in studies investigating nutrient-biomass relationships.

Substrate type is a factor in both algal colonization and the magnitude of loss of biomass following disturbance events. For instance, substrate type can influence the magnitude of temporal variance in algal biomass (Biggs et al. 1999, Lavoie et al. 2004). Unstable substrate, such as large gravel, limits biomass development, and if other growth-limiting conditions are similar, biomass may be an order of magnitude lower on small cobble as compared to large gravel (Welch et al. 1992). In an algal-based water quality assessment, Potopova and Charles (2005) found species composition, biovolume, and abundance were all affected by substrate type. They concluded that restricting sampling to one substrate type is less important in studies based on the autoecology of many algal taxa or in studies inferring water chemistry than in studies estimating algal diversity, total algal biovolume, or abundance of specific taxa. Nonetheless, they recommended sampling standard substrates where possible to eliminate the influence of substrate, particularly in studies within a small watershed or single water body.

Light levels can affect algal growth rates and nutrient uptake. Typical saturation light levels for periphyton are 20 to 30% of incident photosynthetically active radiation (Carr et al. 2005). Light limiting conditions decrease the photosynthetic rate, causing a decline in the uptake rate of nutrients (Son and Fujino 2003). Several cloudy days can induce detachment and disappearance of certain algae (Blum 1956). High light levels cause an increased demand for P (Qian 2000) but can also decrease photosynthetic

activity by causing photoinhibition (Graham and Wilcox 2000). The upper layers of thick algal mats may reduce the quality of light transmitted into lower layers, but limited research has been conducted on the distribution of light within benthic algal communities (Hill 1996).

During flood-free periods, nutrients are influential in determining biomass (Lohman et al. 1992, Biggs 1995). Similarly, Leland and Porter (2000) suggest that under stable flow conditions, resource availability (i.e. nutrient supply, substrate, and light) is of equal or greater importance than disturbance regime. In an analysis of data from over 350 temperate stream sites around the world, about 40% of variance in algal biomass was explained by nutrient availability (Dodds et al. 2002). Although other factors, such as light, grazing, and disturbance regime, may decouple nutrient enrichment from algal biomass, they are not easily controlled at most sites, leaving a reduction in nutrient inputs as the most feasible management alternative (Dodds and Welch 2000).

Because land cover influences nutrient concentrations in streams (Osborne and Wiley 1988), it can influence algal growth and can also be a strong predictor of biological and habitat integrity (Allan et al. 1997). Smart et al. (1985) found that algal chlorophyll values correlated more strongly to land cover than to bedrock geology or soil association. In addition to influencing algal biomass, land cover can be a larger determinant than basin geology in the *distribution* of benthic algae (Leland and Porter 2000).

Nutrient Limitation

Primary producers require certain ratios of nutrients for optimal growth, and limitation occurs when production of biomass is restrained by the nutrient supply. Algae in streams are generally limited by either N or P, and in some cases, by both nutrients.

Historically, P was considered the primary limiting nutrient in freshwater ecosystems (Vollenweider 1968), particularly in the northern half of the United States (Borchardt 1996). More recently, N limitation has been observed in a variety of streams (Edwards et al. 2000, Francoeur 2001).

Dissolved and cellular nutrient ratios are often used to predict which nutrient limits algal production (Bothwell 1985, Francoeur et al. 1999). Redfield (1958) found the atomic ratio of cellular C:N:P for balanced growth to be 106:16:1. This ratio was determined for oceanic phytoplankton, however, and may differ slightly for other primary producers such as benthic microalgae and macroalgae, and even among species (Hillebrand and Sommer 1999, Sterner and Elser 2002). Nutrient limitation can be more problematic to determine in periphyton than in phytoplankton because periphyton are attached to a substrate rather than floating in water column (Aloi 1990). Diatoms generally have a lower optimal N:P than green algae (Rhee and Gotham 1980). Because advective transport of nutrients is more efficient in delivering nutrients to attached forms than nutrient diffusion, a periphyton assemblage can influence the movement of water, and thus, limit growth by reducing the transfer of nutrients into the assemblage (Steinman et al. 1992, Vogel 1994).

Nutrient ratios suggest which nutrient(s) *may* be limiting but do not necessarily indicate if nutrients *are* limiting (Francoeur et al. 1999). When assessing nutrient limitation, the stream nutrient concentration should be considered in addition to the nutrient ratio (Bothwell 1985, Stelzer and Lamberti 2001), and nutrient limitation bioassays should be performed if possible (Dodds 2002, 2003). Bioassays are important because they directly test the response of algae to differing nutrient environments. In

Minnesota, algal growth responses following nutrient additions in three rivers did not correlate to responses expected based on the N:P ratio of water samples (Kutka and Richards 1997). Atomic ratios are not always reliable because primary producers can alter their stoichiometry and acquire and store cellular components when resources are not limiting through luxury consumption. Therefore, solely measuring the cellular stoichiometry may not identify the true limiting factor. Determining nutrient limitation can be helpful but does not provide the predictive relationships between stream nutrient concentrations and algal biomass needed to manage eutrophication and to understand ecosystem-level relationships between nutrient loading and algal biomass (Dodds et al. 2002).

Nutrient Uptake and the Relationship of Algal Growth to Nutrient Concentrations

Biologically available nutrients are primarily found in the dissolved pool within the water column, but because primary producers are predominantly benthic in streams, they must assimilate nutrients close to the sediments (Mulholland 1996). Although some algae can thrive at low nutrient concentrations, filamentous algae, particularly when in large mats, need higher concentrations of nutrients for optimal growth. For instance, Horner et al. (1983) found that the green alga, *Mougeotia* sp., increases in biomass at SRP concentrations up to 25 μg/L, beyond which no additional growth occurs despite increasing P supply. In laboratory channels, Seeley (1986) found filamentous green algae were saturated at about 15 μg/L SRP.

Because the surface to volume ratios are high for stream beds, benthic algae that colonize these surfaces can assimilate and turnover P at rates that are typically as high as those reported for lakes and higher than those measured in the ocean (Mulholland 1996).

Nutrient uptake can also cause longitudinal or downstream increases in nutrient limitation and increase the need for efficient nutrient cycling to meet algal nutrient demands. Downstream of groundwater nutrient sources in Arizona, Grimm et al. (1981) observed nutrient decreases of up to 90% in stream reaches of differing lengths (80 to 6000 meters). Net N retention and rates of spatial decline in stream N concentration have also been observed during the regrowth of benthic algal communities following flood events (Mulholland 1996).

Strong correlations between maximum algal biomass and SRP and TP have been found in both artificial troughs (Bothwell 1989) and rivers (Aizaki and Sakamoto 1988). Total P can be predictive of algal abundance in a river receiving high P loads (Leland and Porter 2000). Dodds et al. (2002) compared data from almost 300 sites in over 200 rivers within North America and New Zealand and found a strong correlation between mean and maximum concentrations of benthic chlorophyll and TN and TP. The relationship was much stronger relative to TN and TP than DIN, and SRP was significantly correlated only with maximum benthic chlorophyll. Lohman et al. (1992) found a positive correlation between benthic chlorophyll *a* and log-transformed TP and TN at 22 sites in 12 streams in the northern Ozarks, Missouri. The predictive power of SRP has been proposed (Nolan et al. 1995), but generally, inorganic nutrient concentrations are not as strongly correlated to algal biomass as TP and TN (Welch et al. 1988, Biggs and Close 1989, Dodds et al. 1997). Moreover, Dodds (2003) advised against determining nutrient demand solely from inorganic nutrient concentrations, particularly when these concentrations are low.

Temporal and Spatial Changes in Algal Growth

Because disturbance regimes (e.g. flood events), light intensity, nutrient supply, and grazing can vary with time, many studies have investigated temporal changes in algal growth. Temporal variability is much greater in rivers than in lakes. Dodds et al. (1998) found a ratio of peak-to-mean seasonal biomass of 4.5 in 176 stream sites in North America and New Zealand much higher than the ratio of 1.7-2.6 for lakes. Periods of high biomass may last for less than two weeks (Biggs and Close 1989, Walton et al. 1995), but can extend to six to eight weeks if nutrient availability is stable and flood disturbances are infrequent (Biggs 1995).

In the longer term, over 2-15 months, biomass and community composition reflect the frequency of flood disturbances, nutrient supply, and light intensity (Biggs 1996). Depending on which factor is more controlling, streams exhibit three main biomass patterns: 1) relatively constant, low biomass; 2) cycles of accrual and sloughing with extended periods of flow stability and accumulation of biomass; and 3) seasonal growth with intervening periods of moderate to low biomass.

Algal distribution and coverage can vary seasonally and annually. Seasonality is better defined at sites with a flood frequency less than 15 per year (Biggs 1995). Flood events can be less important controls on algal biomass in nutrient-poor watersheds (Biggs 1995). Rosemond et al. (2000) studied the response of algal populations to changes in light, nutrients, and grazers, and found that although all factors were limiting or near-limiting throughout the year, the relative importance of each factor shifted seasonally. Francouer et al. (1999) found seasonal variation in benthic algal biomass accrual as a result of nutrient amendment. Nutrient stimulation of growth was the greatest in the summer and the least in the winter. Accrual of taxa such as *Cladophora* and *Spirogyra* is

generally limited to stable flow periods in specific seasons (Biggs 1996). Many benthic taxa such as *Cladophora* have a basal portion or holdfast that allows them to persist from year to year (Blum 1956). Severe disturbance can reset algal communities and act as a selective agent for subsequent community development. In the upper Clark Fork River, Montana, where the filamentous green alga *Cladophora glomerata* causes nuisance blooms, algal growth is low and slow to recover in the year following ice flows or high spring flows that move rocks or scour holdfasts (Watson and Gestring 1996). In addition to flood events, seasonal differences in nutrient limitation may be mediated by other climate factors such as water temperature (Francoeur et al. 1999).

Spatial heterogeneity in algal growth, which reflects differences in shear stress, nutrient mass transfer, and substratum type, can occur between pool, run, and riffle habitats in unshaded streams (Stevenson 1996). Sobczak and Burton (1996) found a greater spatial variation in algal biomass in riffle habitats. Even when light, nutrient supply and temperature are stable, patchy distribution occurs at the small scale of an individual substrata or a stream reach because of variations in growth and losses resulting from spatial variations in water velocity and scour (Biggs et al. 1998). Because disturbance events are the major cause of biomass loss on a larger scale (Biggs 1996), spatial patterns are best detected after prolonged periods of stable flow (Biggs 2000b).

In enriched streams, algal communities often develop high biomass in low velocity runs and pools, and such communities are usually dominated by filamentous green algae. In streams with low to moderate nutrient levels, riffles usually have the highest biomass because of greater nutrient mass transfer (Biggs and Hickey 1994). The River Continuum Concept (Vannote et al. 1980) proposes that benthic algal biomass will

increase downstream from headwater to midcatchment as the channel widens and shading is reduced and then decrease in the lower regions of the catchment as depth and turbidity increase. Although this trend has been seen in some streams with forested headwaters, local watershed features and inputs can cause quite different patterns, such as higher benthic algal productivity in headwater reaches of non-forested prairie watersheds (Wiley et al. 1990).

Nuisance Algae

Benthic algae are the main source of energy for higher trophic levels in many unshaded temperate streams and in rivers with low turbidity (Minshall 1978, Giller and Malmqvist 1998, Biggs 2000a), but they can accumulate excessively and disrupt aquatic food webs by altering habitat, flow regimes, and DO. Large accumulations of algae, referred to as nuisance blooms, tend to become most problematic during periods of low flow. These blooms are considered a nuisance because they can cause a myriad of problems including clogging water supply intakes, altering the substrate and stream flow, interfering with recreational activities such as fishing, and decreasing DO to a level dangerous for biota. The level of growth that qualifies as a nuisance is difficult to define because it depends on the water use being considered. For example, aesthetic problems can arise at a lower biomass than that which affects DO and benthic fauna (Welch et al. 1989). Nuisance biomass levels are difficult to define because certain algal groups such as filamentous green algae may become a nuisance at a lower biomass than algal groups such as diatoms (Dodds and Welch 2000).

As a result of the difficulty in defining nuisance blooms, both biomass and percent coverage are used as indices of nuisance conditions and are included in

recommendations to limit nuisance algal growths. Horner et al. (1983) and Welch et al. (1988) set chlorophyll *a* exceeding 100-150 mg/m^2 or greater than 20% coverage of filamentous algae as excessive growth. In a survey of over 400 streams in New Zealand, Biggs and Price (1987) found that when filamentous algal coverage exceeded 40%, it became very noticeable from the riverbank, and when it exceeded 55% coverage, it covered most of the bed sediments. The New Zealand Periphyton Guideline (Biggs 2000) recommends less than 30% coverage by filamentous algae greater than 2 cm long to avoid nuisance levels of algal growth.

The differing recommendations reflect the growing concern over nuisance blooms and the increasing pressure to develop nutrient criteria and set periphyton guidelines. Currently, data are insufficient to predict the threshold when changes in nutrient loads will shift benthic algal communities to nuisance levels (Dodds and Welch 2000). Because the relative importance of factors limiting growth differs among lotic systems, nutrient criteria for controlling nuisance algal blooms must be considered on a site-specific basis.

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Chapter 3

THE RELATIVE IMPORTANCE OF POINT AND NON-POINT CONTRIBUTIONS TO TEMPORAL AND SPATIAL NUTRIENT TRENDS WITHIN THE MEDUXNEKEAG RIVER

INTRODUCTION

The nutrient chemistry of undisturbed rivers reflects precipitation inputs and contributions from local geology and the influence of plant and soil processes upon these inputs (Allan 1995), but anthropogenic activities can elevate nutrient concentrations and affect ecosystem processes. The 2000 National Water Quality Inventory indicated the extent to which the nation's rivers have been altered: 39% of the surveyed rivers failed to meet one or more of the designated uses of recreation, aquatic life support, fish consumption, drinking water supply, and agriculture (EPA 2002). Excess nutrients are one of the most common causes of impairment (EPA 2002) and are frequently associated with an increase in algal growth to a level that degrades habitat and stresses biota by reducing dissolved oxygen (DO) concentrations (Carpenter et al. 1998, Dodds and Welch 2000).

Nitrogen (N) and phosphorus (P) are the primary nutrients of concern in relation to water quality issues because they stimulate primary productivity. Primary producers preferentially take up N as ammonium (NH_4^+), but also use nitrate (NO_3^-) and, rarely, nitrite (NO_2^-). Nitrate is commonly used as a measure of available N because it is the most mobile form and because NH_4^+ is often converted to NO_3^- or taken up by vegetation (Dodds 2002). Organic N, both particulate and dissolved, can be difficult to measure and is of unknown or complex bioavailability (Dodds 2002). Nitrate readily leaches into soil

and is transported in surface runoff and subsurface flow, particularly during heavy rain events and snowmelt (Blum 1956, Osborne and Wiley 1988, Murdoch and Stoddard 1992). Because the concentration of soluble reactive P (SRP), the only inorganic form of P in natural waters, is often below detectable limits in natural waters (Dodds 2002), total P (TP) and total dissolved P (TDP), which contains both organic and inorganic fractions, are frequently measured to indicate available P in a river. The difference between TP and TDP is particulate P (PP). Phosphorus can be dissolved in surface runoff or leached through the soil, but it is often bound to particulate matter and transported to streams with eroding soils (Barrows and Kilmer 1963).

Algal growth in streams can be limited by N, P, both N and P, or by other factors such as light, temperature, or invertebrate grazing. Historically, P has been considered the primary limiting nutrient in freshwater ecosystems (Vollenweider 1968), particularly in the northern half of the United States (Borchardt 1996). More recently, N limitation has been observed in a variety of streams (Edwards et al. 2000, Francoeur 2001). Dissolved nutrient ratios in the water column are often used to predict which nutrient will limit algal production (Edwards et al. 2000, Qian 2000, Vieux and Moreda 2003). Redfield (1958) found the cellular ratio of atomic N:P for balanced algal growth to be 16:1. For ambient nutrient ratios, N is potentially limiting when the ratio of dissolved inorganic nitrogen (DIN) to SRP is much less than 16 and P is potentially limiting when the ratio is much greater than 16 (Qian 2000). The nutrient ratio of the water column does not account for uptake and remineralization and may not be a true representation of supply, particularly for sessile algae (Dodds 2003), but this index is among the indicators of potential limitations of primary productivity.

Although the greatest export of TP and NO_3^- to rivers is frequently associated with snowmelt and peak annual discharge in the winter and spring (Osborne and Wiley 1988, Moreau et al. 1998, Edwards et al. 2000, May et al. 2001, Hakala et al. 2002, Bowes et al. 2003), the relationship between flow and concentrations and loads of TP and NO_3^- tends to differ in the summer. Total P and PP export, a function of P concentration and water flux, are positively related to storm flows and often reach a maxima on the rising limb or near the peak of the hydrograph (May et al. 2001, Bowes et al. 2003, Donohue et al. 2005). For instance, in 11 rivers in western Ireland, TP and PP concentrations were greatest during summer high flow events despite significantly higher flows in the winter and spring (Donohue et al. 2005). However, because NO_3^- easily leaches from watershed soils and is transported with subsurface flow, NO_3^- concentrations are often highest at base flow and diluted at high flows (Moreau et al. 1998, Edwards et al. 2000, Vieux and Moreda 2003).

Dissolved and particulate fractions of P and N are transported to rivers via point sources such as wastewater treatment plants (WWTP) and non-point sources such as urban areas and agricultural land. While point source discharges are typically regulated, in urban areas they can contribute more nutrients than non-point sources (Carpenter et al. 1998). For the majority of rivers, however, non-point source pollution from urban and agricultural areas is the leading cause of impairment (EPA 2002). Early management efforts focused on point sources, but after point sources were controlled and enrichment still remained an issue, the focus shifted to non-point sources (Carpenter et al. 1998). More recently, the need to address enrichment on a watershed scale and include contributions from both source types has been recognized (Osborne and Wiley 1988,

Vieux and Moreda 2003).

Nutrient concentrations usually increase downstream as the contributing watershed area increases (Allan 1995), but the relative concentrations and rate of increase differ between areas of different land use. Nitrogen and P levels in agricultural and urban streams are typically 15 times more than in forested streams (Omernik and McDowell 1977). Therefore, urban and agricultural areas can be major non-point sources of N and P (Dillon and Kirchner 1975, Edwards et al. 2000, Donohue et al. 2005). Urban runoff is not well retained by soil particles and can discharge high levels of SRP, TP (Dillon and Kirchner 1975), and NO_3^- (Hirose and Kuramoto 1981,Taylor et al. 2005) to surface waters. For example, in Missouri Ozark streams, TP, TDP, and NO_3^- were higher in streams draining urban areas than in streams draining pastures or forests (Smart et al. 1985). The percent of agricultural land in a watershed is often correlated to NO_3^- (Edwards et al. 2000, Hakala et al. 2002, King et al. 2005) and sometimes correlated to TP (Hakala et al. 2002, Buck et al. 2004).

I focused this study on an analysis of nutrient inputs to the Meduxnekeag River, Aroostook County, Maine. The watershed contains multiple nutrient sources, both point and non-point, as well as a range of land cover types from forested to agricultural to urban. Further, the portion of the river I studied has historically experienced nuisance filamentous algal blooms during summer months, raising concern about nutrient enrichment within the river. My primary objectives were to define the nutrient status of the Meduxnekeag River, determine spatial and temporal trends in concentration and species of P and N, and identify areas of the watershed that contribute nutrients that pose the greatest risk to water quality. My results suggest that inputs from point sources are

overshadowing inputs from individual agricultural subwatersheds but that agricultural inputs at the watershed scale are an important source of N and P.

METHODS

Study Area

The Meduxnekeag River is a part of the St. John River system that flows north from Maine into New Brunswick, Canada. The watershed drains a total area of 1,326 km^2, 1,098 km^2 of it in Maine. The river is comprised of three branches: the mainstem, North Branch, and South Branch. The North Branch is part of the Meduxnekeag watershed but not part of my study reach (Figure 2). Feeder streams flow into Lake Meduxnekeag, but the lake is generally considered the headwater. I monitored 34 km of the mainstem of the Meduxnekeag River from its headwater to just downstream of its confluence with Big Brook, an area that encompasses 707 km^2 of drainage (Figure 2).

The Meduxnekeag River watershed is a mosaic of different land cover types comprised of 74% forest, 13% row crops, 6% wetlands, 2% pasture, 2% open water, and 1% each of residential, commercial, and urban/recreational grass (Figure 3). The watershed contains the most intensively farmed land in southern Aroostook County (SASWC 1993). Two-thirds of the agricultural land is in potato production, with the rest used for hay production, dairy and beef cattle, other types of crops and livestock. In addition to nutrient inputs from agriculture, the study reach receives effluent from a starch plant and then flows through downtown Houlton where it receives stormwater runoff and effluent from a WWTP. In the 2000 U.S. Census, Houlton had a population of 6,476 (US Census 2000).

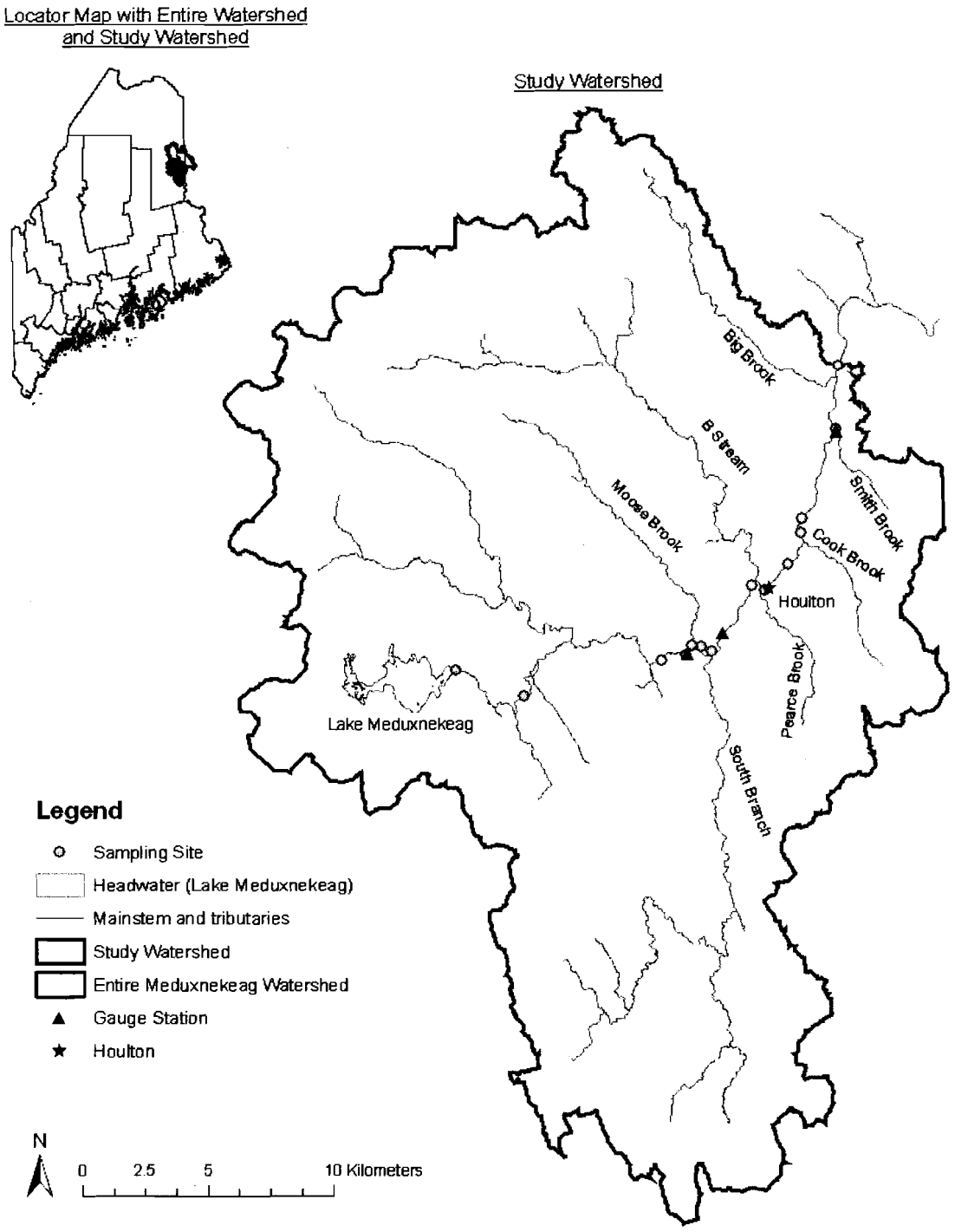

Figure 2. The location of the study area within Maine (inset map) and the Meduxnekeag watershed. Included are the headwater lake, the mainstem of the Meduxnekeag, the South Branch of the river, and the major tributaries. Only tributaries of concern to the study are labeled. The 14 sampling sites are indicated by the solid circles, stream flow gauges are triangles, and major towns are indicated by a star.

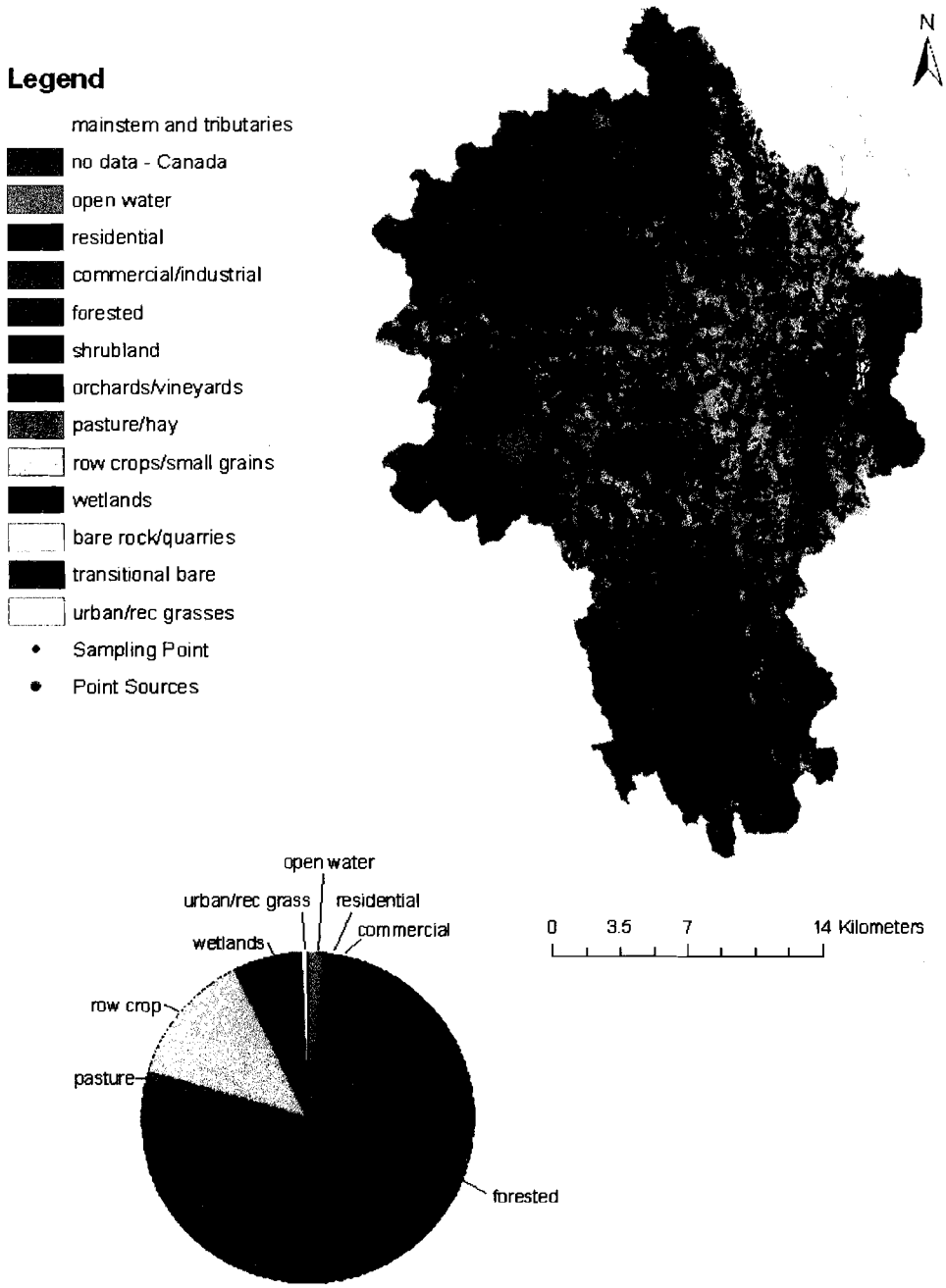

Figure 3. Land cover composition of the Meduxnekeag watershed. Closed blue circles indicate sampling sites and closed red circles indicate point sources. The horizontal brown line in the middle of the watershed is Interstate 95. The pie chart shows the percent of each land cover type in the watershed.

The Houlton Band of Maliseet Indians (HBMI) has monitored 10 sites on a weekly basis every summer since 1995 for total suspended solids, *E. coli*, pH, temperature, turbidity, conductivity, alkalinity, and DO. Nutrient data were collected for a Total Maximum Daily Load (TMDL) study between 1995 and 1997 (MDEP 2000) and for a sediment study in 2003 by Schalk and Tornes (2005). The TMDL study focused on P loading from point sources and did not directly address non-point sources or N inputs. The sediment study included storm event sampling, and it assessed organic compounds, mercury, and nutrient concentrations in the water column and bed sediments but was limited to a few sites and sampling dates.

Site Selection and Location

Water samples were collected from 14 sites (Figure 2) on a biweekly basis from May through October in 2004 and 2005 for a total of 11 sampling trips per season. The monitoring sites were selected to bracket point sources and tributaries to the mainstem (Figure 2, Table 2). Sites were coded based on their river km location ($\pm$0.3 km) as identified by the HBMI. I included eight pre-existing HBMI sites to take advantage of its ongoing monitoring activities. The 18 sites sampled in 2004 included sites that bracketed potential sources. Based on cluster analysis, I was able to eliminate one site from each of four sets of adjacent sites that had generated data that were not significantly different than retained sites for all N and P analytes. This reduced my final set of sampling sites to 14.

Table 2. Sampling locations by river km, approximate site location in relation to tributaries and point sources, and suspected source type.

Site Name (by river km)	Approximate site location (in relation to point sources and tributaries)
0.2	Headwater at outlet of Meduxnekeag Lake – REFERENCE
5.0	General non-point source site – agricultural inputs
14.6	General non-point source site – agricultural inputs
16.4	Upstream of a starch plant – agricultural inputs
16.6	Downstream of a starch plant – point source
16.7	Downstream of Moose Brook – agricultural inputs
18.0	Downstream of South Branch – agricultural inputs
21.9	Upstream of B Stream – urban and agricultural inputs
22.4	Downstream of B Stream and Pearce Brook – agricultural inputs
23.7	Downstream end of town; general non-point source site – urban inputs
25.7	Upstream of a WWTP – urban and agricultural inputs
26.4	Downstream of a WWTP – point source
30.4	Downstream of Smith Brook – agricultural inputs
34.1	Downstream of Big Brook – agricultural inputs

Sampling Methods

Water temperature, DO, and conductivity were measured at each sampling site with a YSI model 556 field meter. Grab samples for nutrient analysis were collected at mid-depth in the main channel directly into 500 milliliter (mL) acid-washed amber high-density polyethylene (HDPE) bottles that were then kept on ice before being frozen upon return to the laboratory. All parameters were measured at all sites in 2004, but due to time and resource constraints, TDP was only measured at a subset of sites for the 2005 season (sites 0.2, 5.0, 22.4, 26.4, and 34.1). Time of collection and any additional comments (e.g. weather or problems encountered) were recorded in a field notebook. Because my goal was to investigate nutrient concentrations and load, and relate that to sources within the watershed, the DO and conductivity data were not analyzed further, but served to compare sampling conditions that roughly coincided spatially and temporally with those made as part of the HBMI monitoring program.

Analytical Methods

Approximately half of each sample was filtered on the day of collection through a 0.45μm filter into a 250 mL acid-washed amber HDPE bottle. This aliquot was analyzed for SRP, TDP (in a subset of samples), NO_3^-, and NH_4^+. The remaining sample in the 500 mL bottle was used for TP analysis. All forms of P were analyzed colorimetrically using the ascorbic acid method after initial fractionations or other treatments to partition the P form. Ammonium was analyzed colorimetrically with the automated phenate method, and NO_3^- was analyzed colorimetrically with the automated cadmium reduction method. Methods were based on those described by the American Public Health Association (APHA et al. 1998). The detection limit was 1.0 μg/L for all forms of P, 0.010 mg/L for

NO_3^-, and 0.050 mg/L for NH_4^+. Quality control included field duplicates, lab replicates, spike recovery, reagent blanks, and laboratory standards (Table 3).

Table 3. Field and laboratory quality control (QC) requirements.

QC Sample or Procedure	Frequency	Data Quality Indicator	Measurement Performance Criteria
Laboratory Replicate	1 per 10–15 samples	Precision	± 1.0 µg/L for < 20 µg/L P ± 5% for > 20 µg/L P
			± 5% for 0.1- 10 mg/L N
Laboratory Blank	1 per batch	Accuracy	± 1.0 µg/L P
			≤ .01 absorbance for N
Sample Spike and Blank Spike	1 of each per batch	Bias	85-115% recovery with 10 or 20 µg/L P spike
			85-115% recovery with 1 or 2 mg/L N spike
Initial Quality Control Check Standard	1 per batch immediately after standards	Accuracy	± 1.0 µg/L for < 20 µg/L P ± 5% for > 20 µg/L P
			± 5% for 0.1- 10 mg/L N
Continuing Quality Control Check Standard	1 per 10-15 samples	Accuracy	± 1.0 µg/L for < 20 µg/L P ± 5% for > 20 µg/L P
			± 5% for 0.1- 10 mg/L N
Field Duplicate	1 per team per sampling trip	Precision	± 1.0 µg/L for < 20 µg/L P ± 5% for > 20 µg/L P
			± 5% for 0.1- 10 mg/L N

Nutrient Load Calculation

Nutrient loads were determined by multiplying the sample concentration by the mean daily discharge on that date, yielding a total mass in kg per day at each site. For each sampling date, loads from a given site's subwatershed were calculated by subtracting the load for the nearest upstream site from the load at that site (Bowes et al. 2003). For instance, if a downstream site had a load of 15 kg/day and the nearest upstream site had a load of 5 kg/day, the subwatershed for the downstream site would have a load of 10 kg/day. Therefore, the load data presented here represent the mass of nutrients supplied

by the subwatershed only. I normalized load data by dividing by subwatershed area, thus allowing me to compare export on a per square-kilometer basis.

Some load differences resulted in negative loads, indicating that the nutrient load either settled out or was assimilated by biota within the reach. Because the study focused on defining the nutrient status of the river and indicating subwatersheds (of the overall Meduxnekeag watershed) contributing the largest nutrient loads, sites with a negative load difference were considered to be contributing a negligible amount to the Meduxnekeag River's total load, and no further attempt was made to explain the mechanisms behind the negative load. A brief comparison of subwatersheds with negative loads will be made to algal coverage in Chapter 3.

Mean daily discharge was determined using data from three USGS flow gauges located within the study area (Figure 4). Gauges are located between sites 16.4 and 16.6, close to site 18, and at site 30.4. The most downstream gauge was not installed until 2005. Discharge for each sampling date was estimated for ungauged sites based on streamflow measurements and estimates of watershed areas delineated using ArcHydro in ArcGIS 9.0®. A site's discharge was determined by multiplying the proportion of its watershed area relative to the total watershed area of the nearest downstream gauge by the discharge at that gauge station (Moreau et al. 1998) as follows:

$$\text{Discharge}_A = \text{Discharge}_B * (\text{watershed area}_A / \text{watershed area}_B),$$

where B is the downstream gauged watershed and A is the watershed of interest.

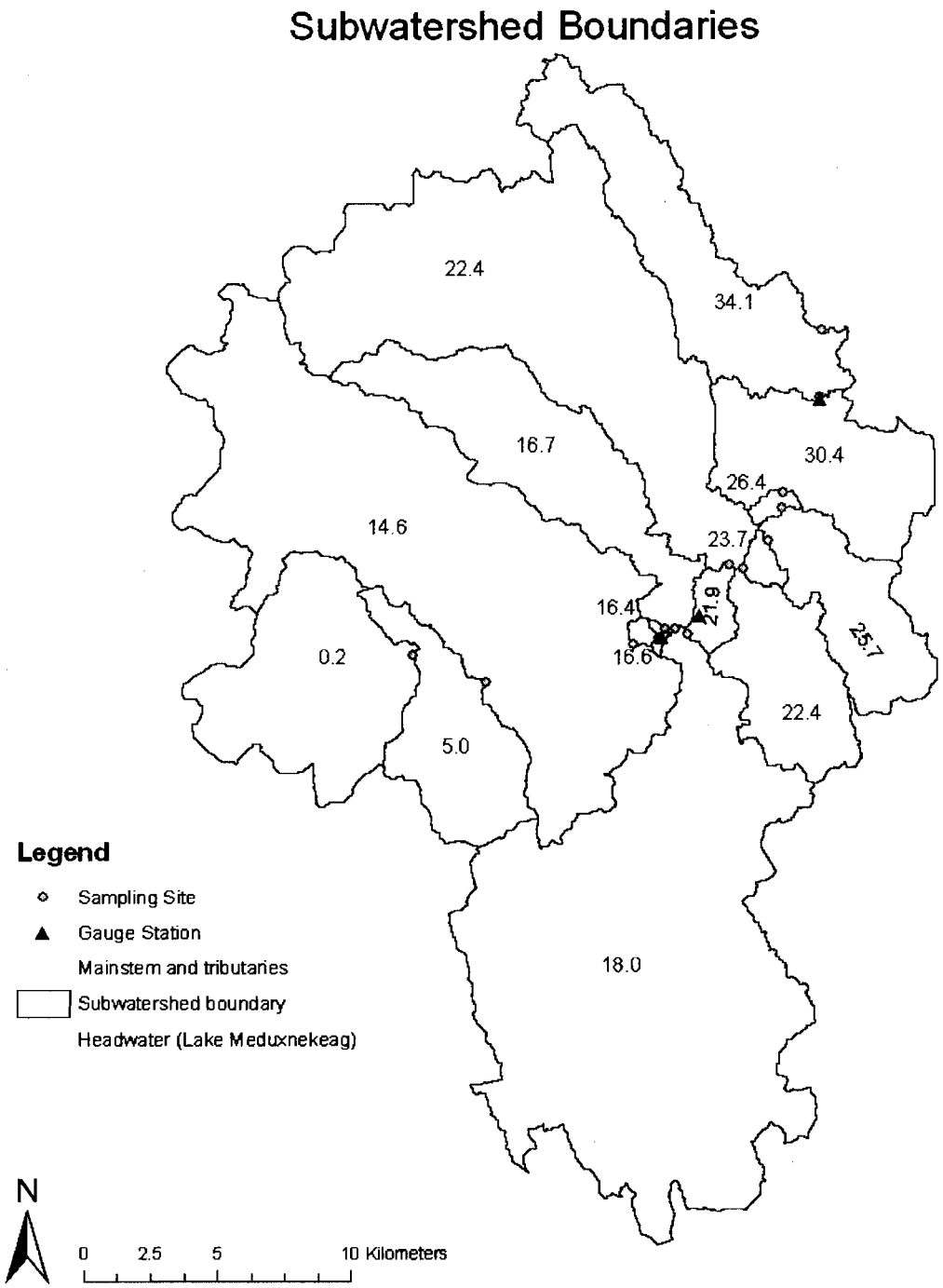

Figure 4. Site locations and their respective subwatersheds. Circles indicate site locations, triangles are gauges, and the numbers refer to site/subwatershed names by river km.

Watershed Land Cover

I used GIS tools to determine the land cover composition of the study watershed and the site subwatersheds in terms of categories such as row crop, forested, and wetland. Land cover data were part of the USGS National Land Cover Dataset, which was compiled from images obtained in 1992 at a spatial resolution of 30 m. Subwatersheds including point sources were small and tightly bracketed by upstream sites so as to restrict load calculations to the point source alone, assuming no contributions from other sources. Land cover composition was used for a comparison of high and low normalized load sites and a comparison of aggregated load contributions from point sources and different non-point sources. Positive non-normalized load data were grouped for non-point sources by the dominant land cover percentage ($\geq$10%) in each subwatershed other than forest, which included agricultural, urban, and agricultural/urban.

Data Analysis

Nutrient measurements below the detection limits were replaced with half the value of the detection limit as follows: 0.5 μg/L for all forms of P, 0.005 mg/L for NO_3^-, and 0.025 mg/L for NH_4^+. Missing data include TP data from September 2004 due to a laboratory mishap and NO_3^- from late September 2004 due to quality control issues. Ammonium was excluded from further data analysis because it was at or below the analytical detection limit 89% of the time in 2004 and 94% of the time in 2005. Soluble reactive P fell below the detection limit 44% of the time whereas all other nutrient variables had values that fell below the detection limit no more than 5% of the time.

Nutrient limitation was assessed through determination of the inorganic nutrient ratio of the water samples (molar NO_3^-:SRP). Ammonium was not included in the ratios

because it was commonly below detection. Where NO_3^- or SRP concentrations were below detection, nutrient ratios were not calculated because ratios are a less reliable indicator of nutrient availability at extremely low concentrations (Dodds 2003).

No statistical analysis was performed on the concentration data because the sample concentrations were not independent of each other. Load data were considered independent, however, because the contribution from upstream subwatersheds was subtracted out during load determination for each site. To meet assumptions of normality and constant variance, all load data were square-root transformed. If a load estimate was negative, the square root of its absolute value was taken and then the negative sign was added back to it. Transformed TP and NO_3^- loads were each set as the response variable in two different general linear models (GLM) testing the variation explained by site and time. In one model, site and sample date were categorical predictor variables. Dates were assigned a number based on their trip number (i.e. 1-22). In the other model, site and month were categorical predictor variables. The normalized load data were tested with both models but the non-normalized data were only tested with site as the predictor variable. Two extreme values were removed from both the TP dataset and the NO_3^- dataset before statistical analysis of the load data because they were outside of the 95% confidence interval for the load data from the site and large enough to skew the data distributions. The extreme values were from sites 26.4, 30.4, and 34.1. For predictor variables found to be significant in the GLM analysis, contrasts and Tukey's multiple comparisons were conducted to test for specific differences among sites or among dates or months. Data were analyzed with SYSTAT® version 11.

RESULTS

Nutrient Concentrations

Based on all observations within the Meduxnekeag River, the mean concentration was 11.8 μg/L for TP and 0.175 mg/L for NO_3^- (Table 4). The reference site had a mean TP concentration of 6.1 μg/L and a mean NO_3^- concentration below the detection limit. All P fractions were measured at all sites in 2004 (Figure 5). Despite different land use influences along the along the study reach, no temporal patterns were observed for the P fractions and all showed the same longitudinal trend as TP. The concentration of each fraction increased slightly after the reference site and then at site 26.4 (the WWTP). Particulate P comprised a consistent percent of TP ranging from 44-58%. Concentrations of TDP and PP measured at a subset of sites in 2005 showed no temporal pattern and the same longitudinal trend as those in 2004.

Table 4. Summary statistics for all sites over both sample years (see Appendix A for data split by site and year). The top of the table contains statistics for all sites but the reference site and the bottom of the table contains statistics for just the reference site. Total dissolved P was measured at all sites in 2004 but at a subset of five in 2005. Values marked as < DL were below the detection limit.

	TP (µg/L)	SRP (µg/L)	TDP (µg/L)	PP (µg/L)	NO_3^- (mg/L)
	All Sites				
N	255	269	182	155	268
Minimum	4.3	< DL	2.2	< DL	0.010
Maximum	46.3	14.6	21.4	37.8	1.310
Median	10.9	1.1	5.1	5.2	0.136
Mean	11.8	1.4	5.4	5.9	0.175
Standard Deviation	4.7	1.5	2.4	3.7	0.143
	Reference Site				
N	20	21	22	20	21
Minimum	4.2	< DL	1.4	< DL	< DL
Maximum	8.9	1.7	4.9	5.7	0.024
Median	5.8	< DL	2.6	3.1	< DL
Mean	6.1	< DL	2.8	3.3	< DL
Standard Deviation	1.4	< DL	< DL	1.6	< DL

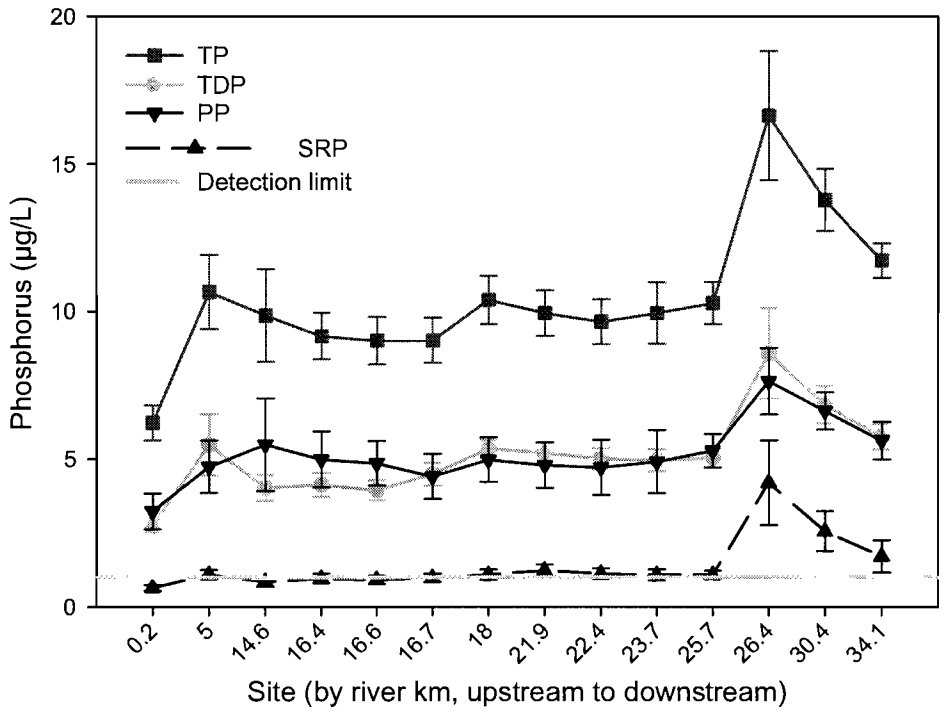

Figure 5. Mean (and standard error) for P fractions at all sites in 2004. Squares are TP, closed circles are PP, upside-down triangles are TDP, dashed line with triangles is SRP, and solid gray line is the detection limit (1.0 µg/L).

Inter-annual Spatial Patterns

Nitrate and TP concentrations exhibited similar longitudinal patterns (Figure 6). Phosphorus concentrations increased downstream with a sharper increase in 2005 than in 2004. Total P concentrations were consistently lowest at the reference site and then had more substantial increases at sites 5, 14.6, 18, and 26.4 (Figure 6a). Site 26.4, immediately downstream of the WWTP, had a higher spike in 2004 than in 2005. The spatial trends were more similar between years for NO_3^- concentrations than for TP concentrations (Figure 6b). In both years, NO_3^- concentrations were lowest at the reference site, increased slightly at site 5, and then increased steadily until peaking at the WWTP. The range of concentrations for TP and NO_3^- were both greater in 2005 than in 2004.

Inter-annual Seasonal Comparison

Total P and NO_3^- concentrations did not show a consistent seasonal pattern between years (Figure 7). In both years, TP concentrations were at the lower end of the range in May and early June, and NO_3^- concentrations were lowest in late August through early October (Figure 7). Other than nutrient concentrations being low in the same months each year, concentrations were very different among dates.

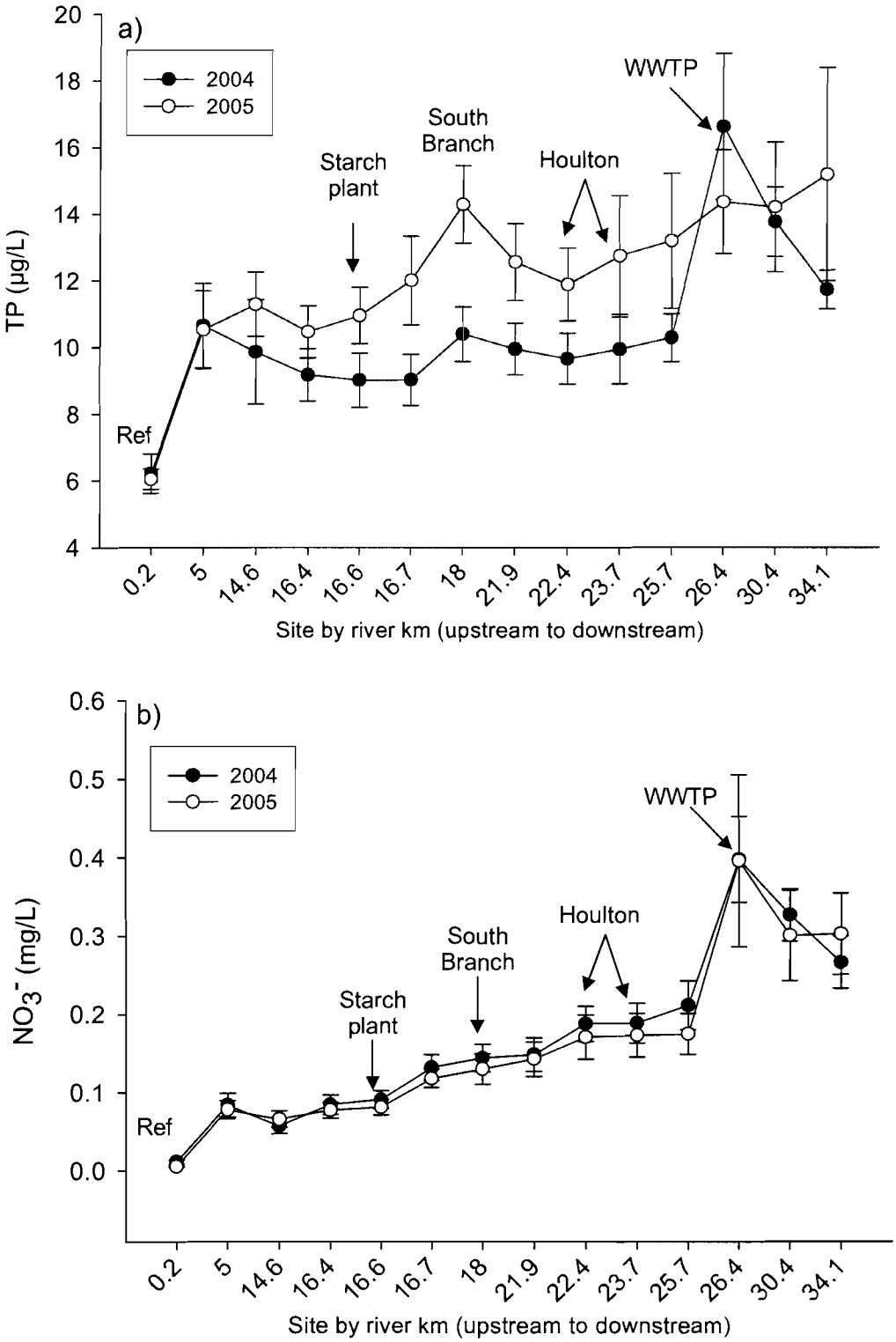

Figure 6. Mean (and standard error) of (a) TP in µg/L and (b) NO_3^- in mg/L by site in 2004 (filled circles) and 2005 (open circles). Selected tributaries and nutrient sources are indicated. Ref refers to the reference site (n = 9-11 for each data point).

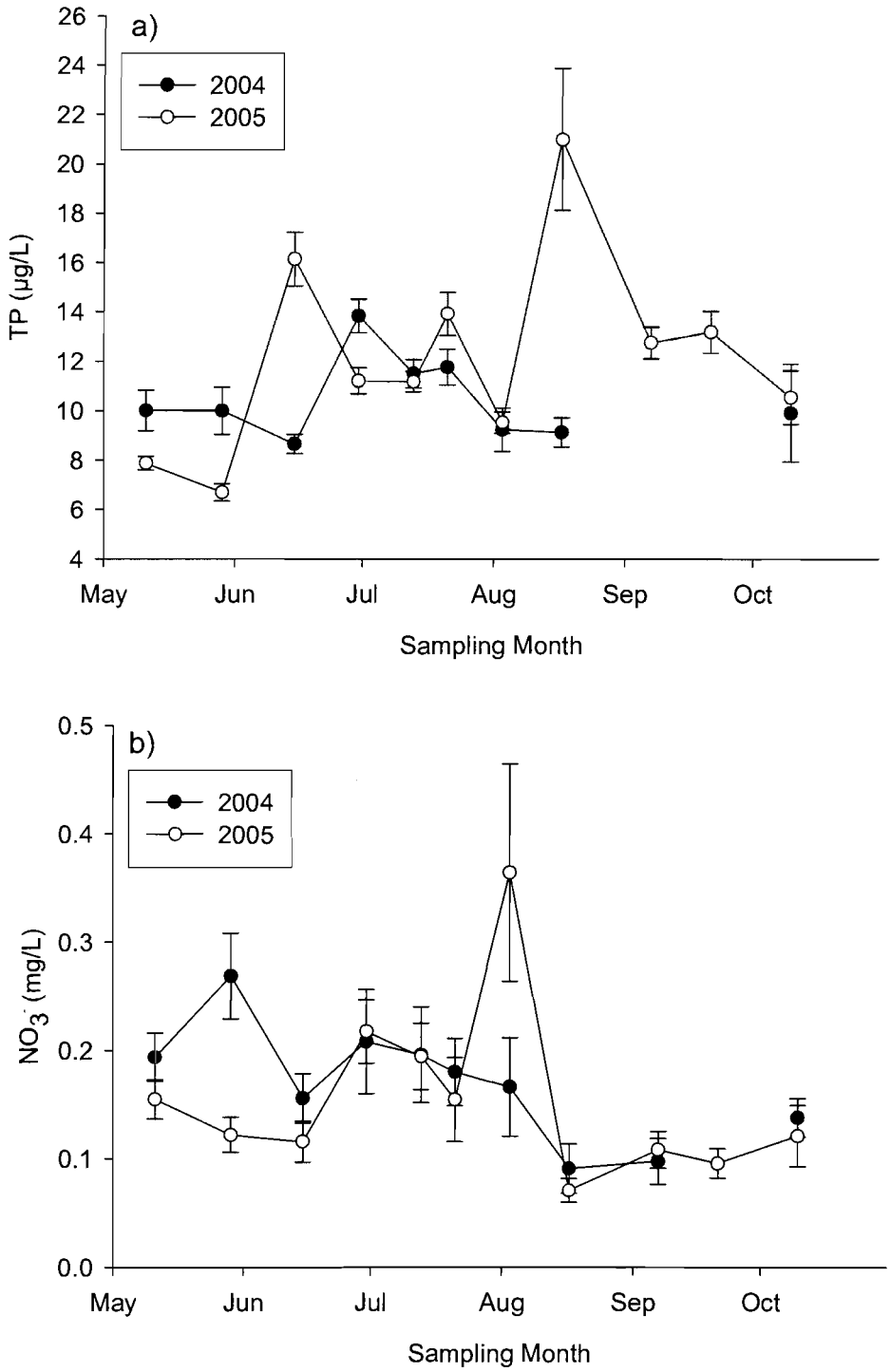

Figure 7. Mean concentrations and standard error bars across sites for each sampling date. Solid symbols are 2004 and open symbols are 2005. a) TP (µg/L); no data for September 2004 and b) NO_3^- (mg/L); no data for late September 2004.

NO_3^-:SRP Ratios

The molar ratio of NO_3^- to SRP in the water column was determined for all sites except the reference site (0.2), where concentrations of both NO_3^- and SRP were below the detection limit (Figure 8). Similar to the trend in NO_3^- concentrations, the NO_3^-:SRP ratio increased in a downstream direction. Because SRP concentrations generally did not change much longitudinally, increasing NO_3^- concentrations drove the downstream increase in NO_3^-:SRP ratios. With the exception of a few sites (5, 14.6, 26.4, and 30.4), the ratios were lower in 2005 than in 2004. All sites had ratios both years that were well above the Redfield ratio (16:1). Except for sites 5.0 and 14.6, NO_3^-:SRP ratios exceeded 100:1, indicating extreme P limitation.

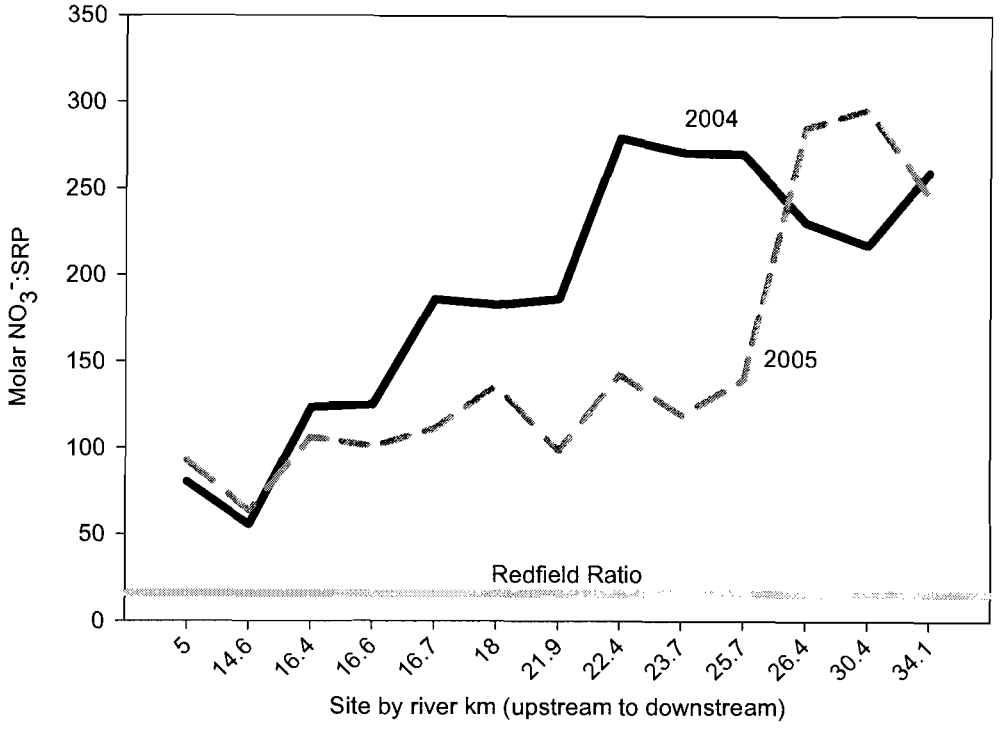

Figure 8. Molar ratios of NO_3^- to SRP in the water column. The solid black line is 2004, the dashed gray line is 2005, and the solid gray line is the Redfield ratio (16:1). Tabular values are provided in Appendix B.

Watershed Hydrology

Seasonal and Inter-annual Variability in Hydrology

The mean daily discharge for the sampling months May through October was different between sampling years and from the historical mean for 43 years of record (Figure 9). The daily discharge in 2004 was generally lower than the historical mean except for August and September. This pattern differed in 2005, which had more storm events than 2004; discharge was below the historical mean in July and August but there were several peaks above the historical mean in the other sampling months. Discharge on sampling dates ranged from 1.2-6.8 m^3/s in 2004 and from 0.4-16.6 m^3/s in 2005, when my sampling captured more storm events. The top four discharge sampling dates in 2005 exceeded the maximal sampling discharge measured in 2004.

Relationships between Concentration and Flow

Total P concentrations did not have a consistent relationship with flow (Figure 10a). In contrast, NO_3^- concentrations were inversely related to flow (Figure 10b). Concentration-flow relationships for a point source site (26.4), an urban site (23.7), and an agricultural site (18) differed for TP and NO_3^-. TP concentrations at the point source site were not related to flow. Both the urban and agricultural site had a weakly inverse relationship with flow, but concentrations peaked on two dates when flow was around 9 m^3/s and 16 m^3/s (Figure 10a). These sampling dates, June 15 and August 31, 2005, were either on the rising arm of a storm event or near the peak of a storm event (Figure 9). This suggests that most TP was exported from agricultural and urban land within this region of the hydrograph.

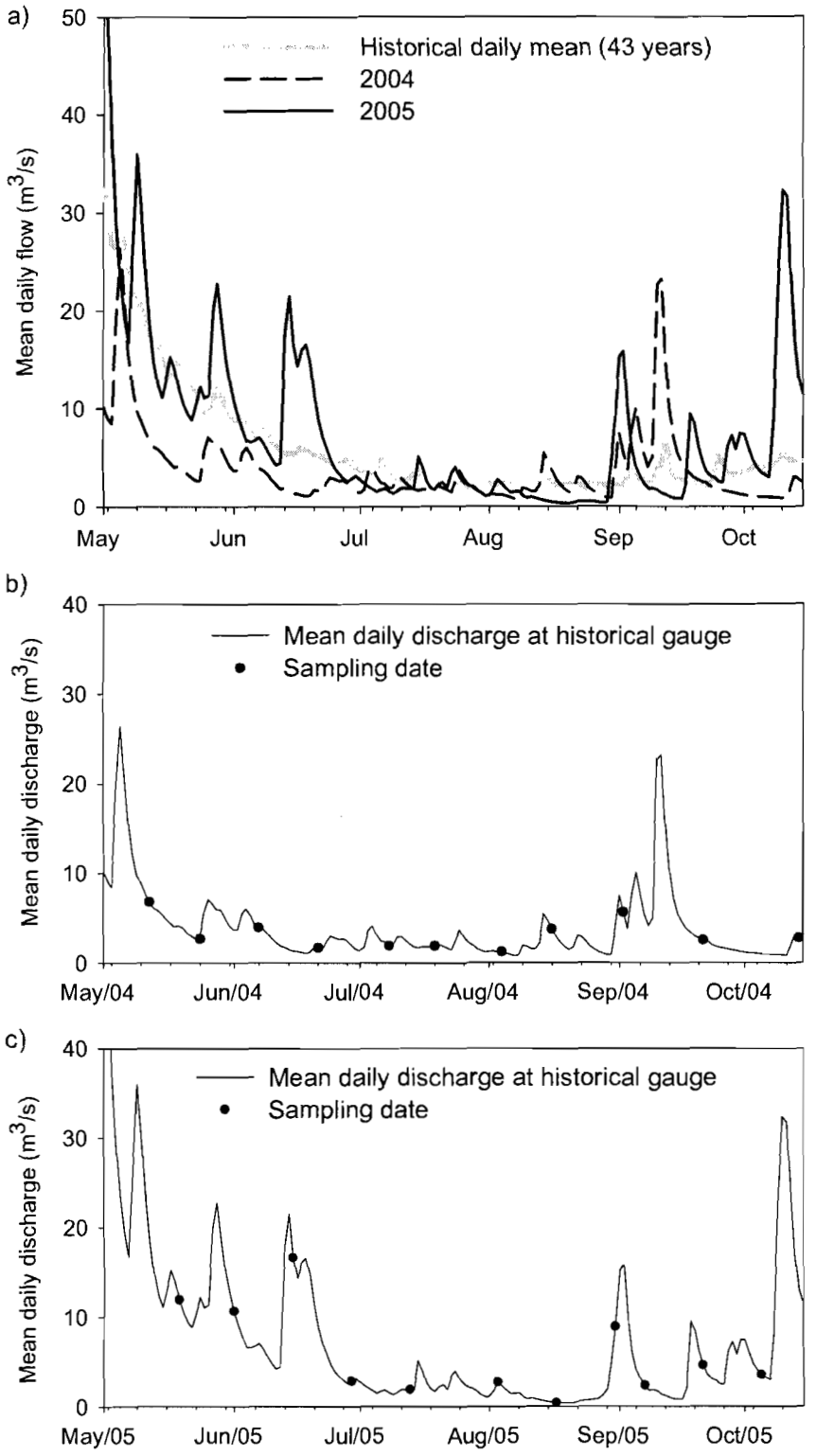

Figure 9. a) Historical daily mean discharge over 43-years compared to discharge during sampling years, b) Mean daily discharge for the 2004 sampling season, and c) Mean daily discharge for the 2005 sampling season. Sampling days are depicted with black dots.

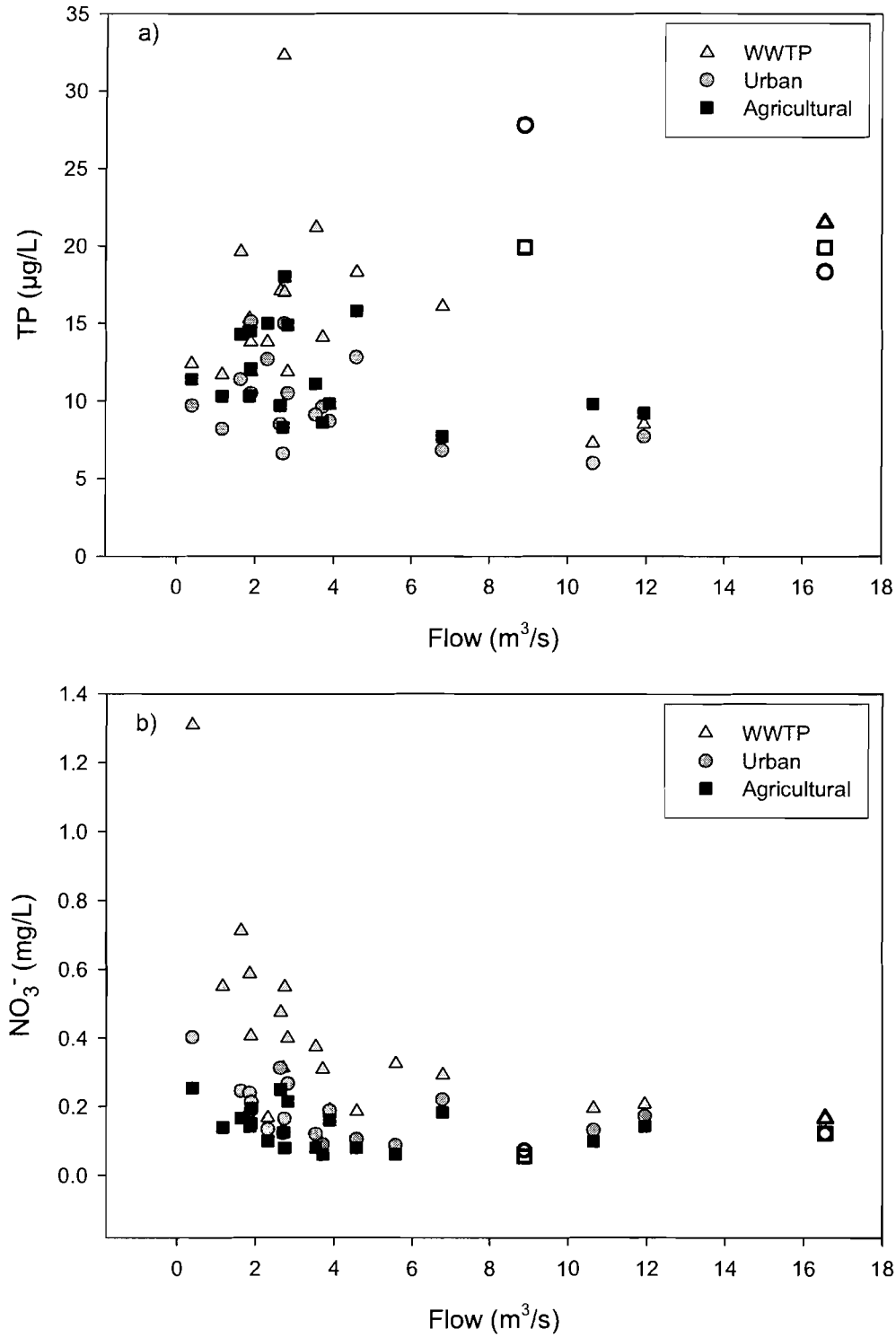

Figure 10. Flow versus a) TP (µg/L) and b) NO_3^- (mg/L). Gray triangles represent the point source site (26.4), gray circles represent the urban site (23.7), and black squares represent the agricultural site (18). Flows on the rising limb or near the peak of a storm event (June 15 and August 31, 2005) are indicated by open symbols corresponding to site type.

Additional sampling dates that coincided with the rising arm or the peak of a storm event would be needed to confirm this aspect of the TP-flow relationship. Nitrate concentrations at the point source site, urban site, and agricultural site were all inversely related to flow, including the sampling dates where the flow relationship differed for TP at the urban and agricultural site.

Nutrient Loads

Normalized Loads

A significant amount of variation in normalized loads for TP and NO_3^- was explained by differences among sites ($p < 0.001$) while sample date and month were not significant. Based on Tukey's pairwise comparison test, the TP and NO_3^- contribution from site 26.4, the WWTP, was significantly higher than any other site. The mean normalized TP load at site 26.4 was 1.5 kg/km^2/day, a value seven times greater than the next highest contributor (Figure 11a). For NO_3^-, the mean normalized load from site 26.4 was 47.0 kg/km^2/day, which was 23 times greater than the next highest site (Figure 11b). For all other sites, normalized loads for TP and NO_3^- were not significantly different. The average normalized load for other [positive-loading] sites was 0.05 kg/km^2/day for TP and 0.6 kg/km^2/day for NO_3^-. Total P load increases were associated with the starch plant (site 16.6) and with Houlton (site 23.7), while NO_3^- loads increased at an agricultural site and the starch plant (sites 16.4 and 16.6, respectively). Normalized loads were less than zero for TP at sites 16.4 and 21.9 with a mean of -0.1 kg/km^2/day and for NO_3^- at sites 30.4 and 34.1 with a mean of -0.07 kg/km^2/day.

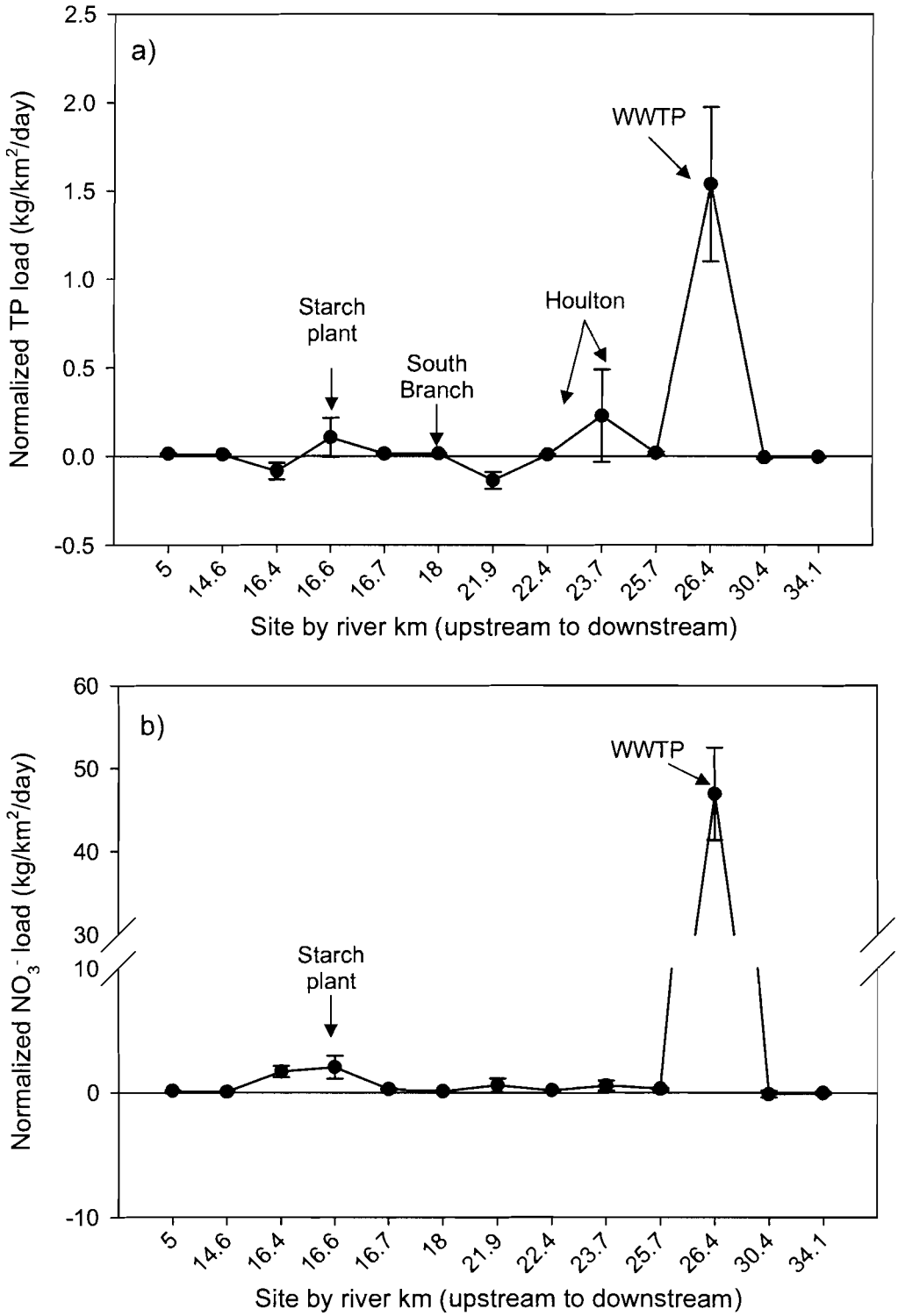

Figure 11. Mean nutrient loads (kg/km^2/day) normalized by watershed area with standard error bars. Some nutrient sources are indicated. a) TP load and b) NO_3^- load. The y-axis in (b) is split from 10-30 kg/km^2/day.

Non-normalized Loads

Non-normalized TP and NO_3^- loads (GLM; $p < 0.001$) varied significantly by site. Unlike patterns for concentration, non-normalized loads did not consistently increase downstream. The subwatershed containing the South Branch of the river (site 18) contributed the highest TP load (Figure 12a), averaging 2.6 kg/day. Other high TP loading sites, 14.6, 22.4, and 26.4, were associated with agricultural land, Houlton, and the WWTP, respectively. The subwatersheds that had significantly lower TP loads than all high loading sites were 16.4, 16.6, 21.9, 30.4 and 34.1, associated with either the starch plant (site 16.6) or various tributaries. The WWTP (site 26.4) had a significantly higher NO_3^- load at 62.8 kg/day than all other sites (Figure 12b). With the addition of site 16.7, other high NO_3^- loading sites coincided with high loading TP sites. The highest non-normalized TP and NO_3^- loads were from the South Branch, runoff from Houlton, agricultural land, and effluent from the WWTP. With the inclusion of site 23.7, NO_3^- sites with significantly lower loads than higher loading sites also coincided with low TP loading sites.

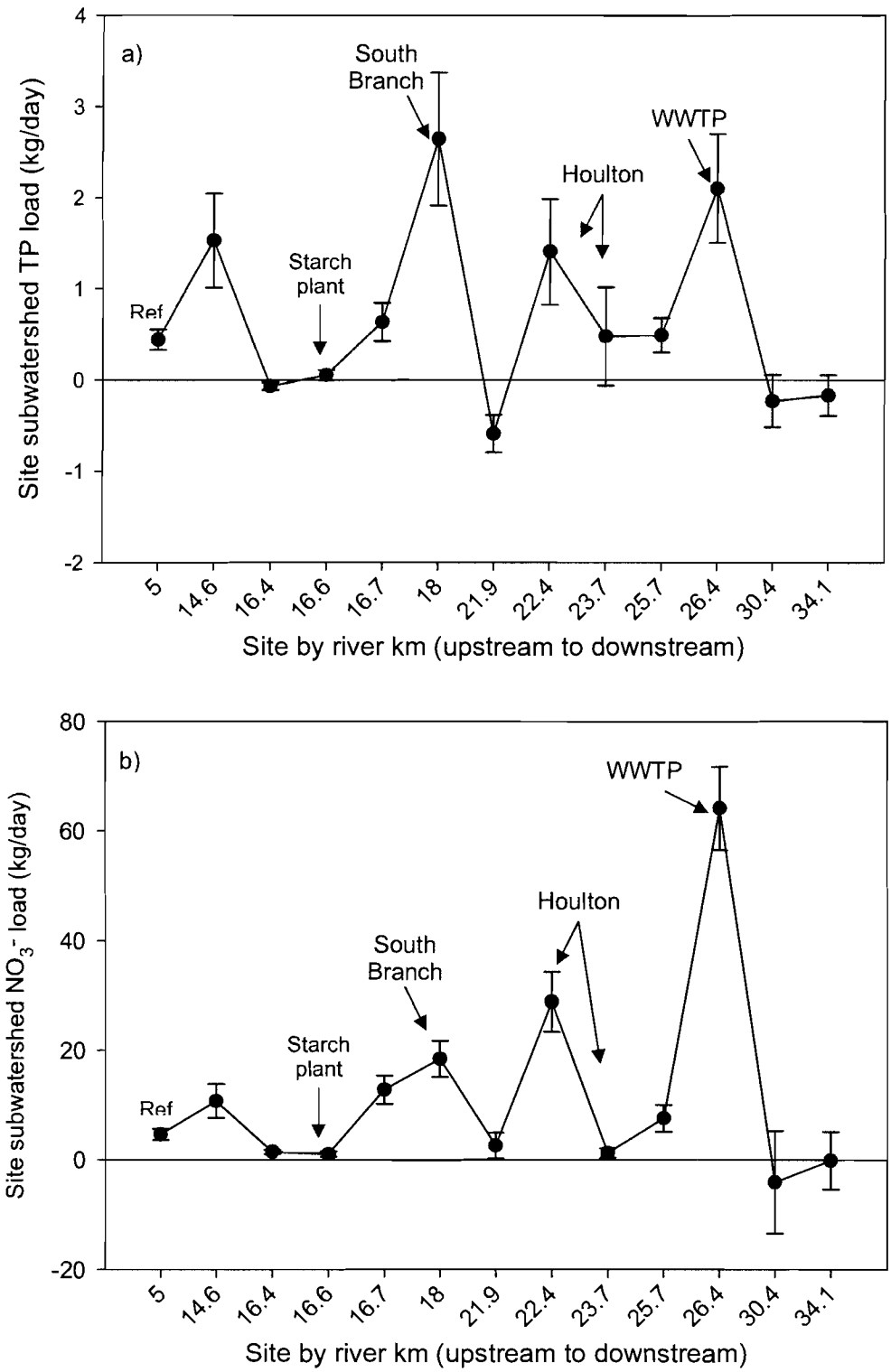

Figure 12. Mean and standard error for all load (kg/day) estimates measured during the study period for a) TP and b) NO_3^-. Loads were not corrected for watershed size. Some potential sources are indicated.

Land Cover in the Site Subwatersheds

In order to prioritize the sources contributing the most enrichment to the river, loads need to be related to land cover within each site subwatershed. To do this, I first compared land cover composition in non-point source dominated site subwatersheds where normalized TP and NO_3^- loads increased to those with lower loads. Then, I compared overall (i.e. non-normalized) load contributions from each source type.

Land cover class percentages in the low-loading site subwatersheds (14.6, 16.7, 18, and 22.4) were all very similar so were averaged for comparison with the high-loading site subwatersheds (Figure 13 and Table 5; see Appendix A for all percentages). Land cover composition in the low-loading subwatersheds was predominately forested (77%), similar to that of the entire the study watershed. The subwatersheds with high NO_3^- loads (16.4 and 21.9) were less forested (31 and 38%, respectively) and had 31% and 58% of total area in row crops, which is roughly two to five times that in low loading subwatersheds. The high-loading subwatershed 21.9 also had over 15% urban, including residential and commercial land cover. The urban site, 23.7, which contributed high loads of both TP and NO_3^-, was very different than other non-point source watersheds in that it had a small percentage of forest (16%) and was predominantly residential and commercial (69%). The only other subwatershed that had high TP loads was 25.7, which had a similar amount of agriculture to the low loading subwatersheds but was slightly urban with about 11% commercial and residential land cover.

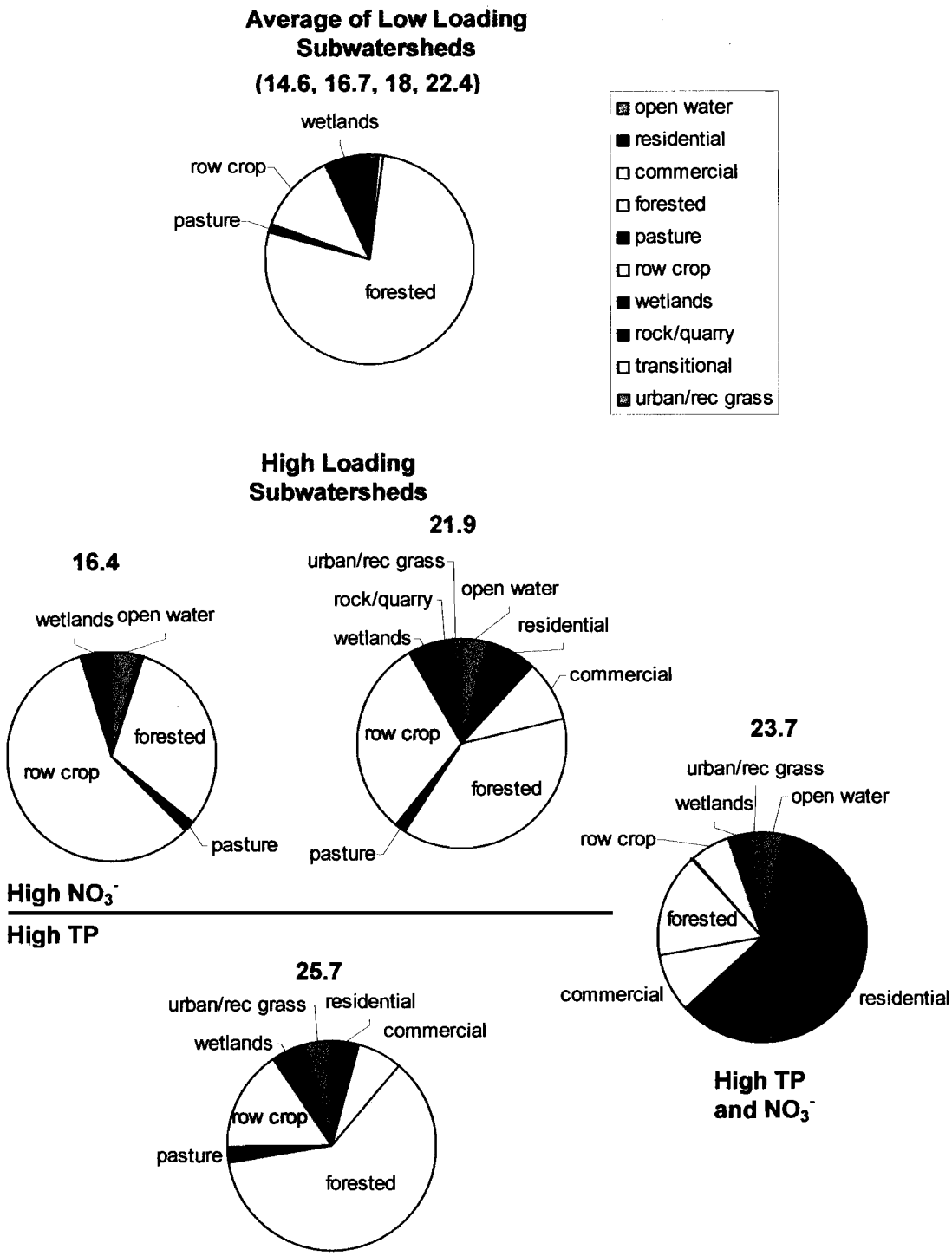

Figure 13. Land cover classes within normalized high and low non-point source loading site watersheds. Classes that comprise less than 1 percent of land cover are not labeled here but are presented in Table 5. Site 25.7 has 8 km^2, 33% of its watershed area, in Canada; this acreage was omitted from the land cover percentages. Graphs above the black line had high NO_3^- loading and graphs below the black line had high TP loading. Site 23.7 was high for both.

Table 5. The watershed area for each site subwatershed, source/dominant land cover type, and mean normalized and non-normalized loads for each site. Point source rows are in gray (site 16.6 and 26.4). Sites with a negative load are indicated with an asterisk.

Site	Source/ dominant land cover type	Site Watershed Area (km^2)	Normalized TP load ($kg/km^2/day$)	Non-normalized TP load ($kg/km^2/day$)	Normalized NO_3^- load ($kg/km^2/day$)	Non-normalized NO_3^- load ($kg/km^2/day$)
5	agricultural	28.9	0.015	0.442	0.160	4.62
14.6	agricultural	147.4	0.010	1.53	0.073	10.7
16.4	agricultural	0.8	*	*	1.69	1.43
16.6	starch plant	0.5	0.106	0.052	2.03	1.01
16.7	agricultural	45.9	0.014	0.634	0.279	12.8
18	agricultural	178.9	0.015	2.64	0.103	18.5
21.9	urban/ agricultural	4.3	*	*	0.596	2.58
22.4	agricultural	142.1	0.010	1.40	0.203	28.9
23.7	urban	2.1	0.230	0.474	0.585	1.21
25.7	urban/ agricultural	24.6	0.020	0.490	0.306	7.53
26.4	WWTP	1.4	1.54	2.10	47.0	64.1
30.4	agricultural	35.4	*	*	*	*
34.1	agricultural	47.1	*	*	*	*

Table 6. Percent composition by land cover class for each high loading site watershed and averaged for the low loading site watersheds. Point source subwatersheds are not shown because land cover is not important for these small subwatersheds.

Land cover class	Low loading site average	16.4 (high NO_3^-)	21.9 (high NO_3^-)	23.7 (high N & P)	25.7 (high TP)
open water	0.74	4.3	4.3	3.2	0.34
residential	0.68	0.85	7.6	59.8	3.9
commercial	0.86	0.00	9.3	9.1	6.8
forested	77	31	38	16	61
shrub	0.01	0.00	0.00	0.00	0.00
orchards	0.00	0.00	0.00	0.00	0.01
pasture	1.4	1.5	1.7	0.45	2.1
row crop	13	58	31	5.9	16
wetlands	6.2	4.4	5.1	3.1	4.9
rock/quarry	0.05	0.00	1.8	0.09	0.07
transitional	0.21	0.00	0.12	0.09	0.06
urban/rec grass	0.34	0.32	1.3	2.2	4.5

Non-normalized Loads by Source Type

A summation of positive non-normalized loads by site type (i.e. point source, agricultural, urban, or agricultural/urban) showed the total contribution of each source type to the overall daily TP and NO_3^- load in the watershed (see Tables 5 and 7). For both TP and NO_3^-, urban subwatersheds made the smallest contribution followed by agricultural/urban subwatersheds. Subwatersheds that were primarily agricultural, however, contributed three times as much TP as the point source subwatersheds. Similar to the results for normalized loads, point sources, largely because of effluent from the WWTP, contributed a greater load than all other source types combined.

Table 7. Summed non-normalized TP and NO_3^- loads by each dominant source type in the watershed. For non-point sources, dominance was considered ≥10% for a particular source type. Sources were grouped according to categories in Table 5. Negative loads were not included.

Source type	Sum of non-normalized TP loads (kg/day/km^2)	Sum of non-normalized NO_3^- load (kg/day/km^2)
Agricultural	6.7	29
Urban	0.47	2.4
Agricultural/urban	0.49	10
Point source	2.2	65

DISCUSSION

Despite being the most intensively farmed watershed in Aroostook County, the WWTP was the single largest source of TP and NO_3^- to the Meduxnekeag River. Also, even though several tributaries and agricultural non-point source sites increased concentrations and contributed significant overall loads, urban runoff from Houlton and effluent from the starch plant were more important sources when the area of their

contributing watersheds was considered. This finding illustrates the disproportionate effect that point sources and small urban areas can have on water quality (Allan 2004).

The results of this study are similar to the findings of the TMDL (MDEP 2000) and the sediment studies (Schalk and Tornes 2005). Both found the most enrichment occurring in the vicinity of Houlton, and particularly downstream of the WWTP. In the TMDL study, mean TP and SRP concentrations averaged 32.0 and 92.3 μg/L and 13.0 and 76.7 μg/L downstream of the WWTP in 1993 and 1995, respectively, prior to initiation of P treatment by the WWTP in 1997. In contrast, I measured substantially lower mean TP and SRP concentrations (15.5 and 3.4 μg/L, respectively) downstream of the WWTP. These values were slightly lower than concentrations measured in 1997 for the TMDL (20.8 and 5.0 μg/L, respectively). This illustrates the substantial load reductions that can occur when a WWTP increases its treatment level (Neal et al. 2000). The similarity between the post-P treatment concentrations in the TMDL and my measurements suggests that concentrations downstream of the WWTP have been stable, and possibly declining, since the treatment level was improved. Despite this large reduction in P discharge, the WWTP is still the most significant source of N and P in the Meduxnekeag watershed.

It is difficult to compare loading within the watershed to other studies because most loading studies include intensive storm-related loading and extrapolate loads to an annual scale (Moreau et al. 1998, May et al. 2001, Jarvet et al. 2002). However, compared to other rivers, nutrient concentrations in the Meduxnekeag River were low. Mean concentrations of TP and NO_3^- corresponded to levels from forested watersheds in other studies or areas categorized as nutrient-poor (Edwards et al. 2000, Hakala et al.

2002, Jarvet et al. 2002, Vieux and Moreda 2003, Buck et al. 2004, Donohue et al. 2005, Hively et al. 2005, Taylor et al. 2005). The relatively low nutrient concentrations could be because the study watershed is predominantly forested. Because SRP may be actively and efficiently cycled, and NH_4^+ may be quickly assimilated or converted to NO_3^-, the non-detectable levels of SRP and NH_4^+ I measured are commonly observed elsewhere (Dodds et al. 2002, Taylor et al. 2005). The percent of PP in the Meduxnekeag was less variable temporally and spatially compared to other studies (May et al. 2001, Bowes et al. 2003, Hively et al. 2005). Perhaps more PP settled out in certain areas of the river or the sampling did not coincide with enough high discharge events to capture variability in PP.

The concentration-flow relationship of TP and NO_3^- differed depending on the source type. Concentrations of TP at point source sites did not correspond to flow. This was probably because the WWTP did not continuously discharge each day, and when it did discharge, the concentration of the effluent varied. The lack of relationship between flow and concentration at the starch plant was likely because it had flow restrictions in its permit that frequently restricted summer discharge (MDEP 2000). Similar to other studies, higher TP concentrations were seen at high flow for the agricultural and urban non-point source sites, particularly for sampling days that were on the rising arm or near the peak of a storm event (Moreau et al. 1998, Vieux and Moreda 2003). Some studies have found suspended sediment within the river increases TP concentrations at higher flows (Donahue et al. 2005). However, a dilution effect occurred at lower flows and even at higher flows that were not on the rising arm of a storm event, suggesting that non-point source sites were a larger source of TP near the peak of storm events. Nitrate concentrations, which tend to be diluted at high flows (Moreau et al. 1998, Edwards et al.

2000, Vieux and Moreda 2003), were highest during baseflow for both point and non-point source sites in the Meduxnekeag River. The WWTP does not have NO_3^- limits in its permit (MDEP 2000) and may have discharged effluent with a consistently high NO_3^- concentration, resulting in its inverse relationship with flow. Because TP is primarily transported in runoff with eroding soils, while NO_3^- is very soluble and mobile, different relationships between concentration and flow are not unexpected. This, combined with the number of high discharge dates in 2005, may explain why TP and percent PP concentrations were higher and more variable in 2005, while NO_3^- concentrations were lower and less variable.

The ratio of NO_3^- to SRP in the water column suggests the Meduxnekeag is P limited, a common observation in freshwaters in the northeast (Borchardt 1996). Nitrogen limitation is unlikely when the N:P ratio is close to 100 (Dodds 2003), as was the case in the Meduxnekeag. If the river was P limited, management efforts should focus on reducing P loads. However, because higher N loading subwatersheds corresponded to high P loading subwatersheds, both elements could feasibly be targeted within the same subwatersheds.

Although the WWTP contributed the highest normalized nutrient loads to the river, sites 23.7 and 25.7, which were downstream of Houlton, illustrated the influence of non-point urban sources. Considering the land cover composition at the high loading sites, higher percentages of agricultural land appeared to be more closely related to NO_3^- loads than TP loads, similar to findings by others (Edwards et al. 2000, Hakala et al. 2002, King et al. 2005). The similarities in land cover composition between the higher and lower TP loading subwatersheds could be part of the reason for the small longitudinal

difference among normalized TP loads. Also, because site 25.7 was a mix of agricultural and urban land cover, the relative load contribution of one cover type may have obscured the influence of the other cover type, as observed previously by King et al. (2005).

On an areal basis, agricultural sites did not contribute as much as the WWTP to the nutrient loads, but when their unweighted loads were considered as a whole, they were the largest cumulative source of TP. Total P concentrations at agricultural sites were highest on the rising arm or near peak of storm events. Thus, agricultural sites could be sources during discrete events such as inorganic fertilizer additions followed by a storm, but these events were not specifically targeted by sampling during this study. The risk of loading from the agricultural subwatersheds was likely increased during storm events because runoff occurs faster at non-field areas compared to fields and forested areas, and the potential loading contribution of small hydrologically active non-field areas with high soil P is high (Hively et al. 2005).

My results showed that despite advances in P treatment, WWTPs can still have a disproportionate effect on water quality. However, my results also highlight the importance of considering input sources on the watershed scale. While the WWTP was the single largest source, agricultural sources contributed a total load more than three times that of the WWTP. Despite this, the entire study reach had low average nutrient concentrations. The mean TP concentration was similar to the EPA's recommended nutrient criteria for streams (EPA 2001), and although NO_3^- was almost double the recommended criteria, it is not limiting in the system and concentrations were much lower than those that pose a known health risk. This suggests that while there are certainly substantial nutrient sources within the watershed and ways to decrease inputs

from those sources, the EPA's nutrient criteria are too conservative for the Meduxnekeag and current management of point and non-point sources is effectively maintaining low nutrient concentrations within the river.

If additional nutrient reductions were desired, I would recommend focusing management efforts on the WWTP, Houlton, and agricultural subwatersheds. Normalized nutrient loads increased slightly at the starch plant, but I would not recommend making the starch plant a high priority for P reductions. Phosphorus concentrations and the unweighted load changed minimally at that site and because of flow-related discharge restrictions, the starch plant infrequently discharges to the river in the summer (MDEP 2000). The most recent permit for the WWTP set new effluent limits starting in July 2006 and required the development of an alternatives analysis for not discharging into the river during the summer and for increased treatment technology (pers. comm., Miller 2006). These permit requirements suggest that load reductions will continue to occur at the WWTP and may even be eliminated in the summer at some point. My results suggest that P reduction should be the priority, and based on the substantial TP contribution from agricultural land, agricultural land should be the priority for P reductions. Because normalized P loads were similar, and more than 90% of the P exported from watersheds typically comes from less than 10% of the land area (Pionke et al. 1997), watershed assessments should be performed to determine the specific subwatersheds with the most severe erosion problems prior to developing a nutrient management plan for those areas. Because my results suggested that TP export from agricultural land increases during storm events, most of the high flows occurred in 2005, and the study did not include intensive storm sampling, I would recommend conducting storm sampling to validate

assessments of subwatersheds with a high risk of erosion (Hilton et al. 2002). There are several storm sewers in Houlton, and within subwatershed 22.4, which was a major portion of agricultural unweighted loads. Storm sewers would be an easy urban item to target because they collect nutrients from a diffuse area and can be retrofitted with different types of stormwater filters.

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Chapter 4

LONGITUDINAL AND TEMPORAL PATTERNS IN FILAMENTOUS ALGAE IN THE MEDUXNEKEAG RIVER: WHAT ROLE DO NUTRIENTS PLAY?

INTRODUCTION

Filamentous algal proliferations often reach nuisance levels within enriched streams (Welch et al. 1992, Dodds et al. 1997). Such proliferations can cause aesthetic issues, stress biota by reducing dissolved oxygen (DO) levels, degrade habitat, and effect faunal biodiversity (Carpenter et al. 1998, Dodds and Welch 2000). Because the nutrients nitrogen (N) and phosphorus (P) often limit algal growth, and other growth-limiting factors such as temperature, light, invertebrate grazing, and flooding are difficult to control, much research has focused on defining the relationship of N and P to algal growth in lotic systems (Aizaki and Sakamoto 1988, Biggs and Close 1989, Welch et al. 1989, Dodds et al. 1997, Dodds et al. 2002, Son and Fujino 2003).

An initial step in defining the relationship between nutrients and algal growth is assessing nutrient limitation. Historically, P was considered the primary limiting nutrient in freshwater ecosystems (Vollenweider 1968), particularly in the northern half of the United States (Borchardt 1996). More recently, however, N limitation has been observed in a variety of streams (Edwards et al. 2000, Francoeur 2001). A variable nutrient addition bioassay is a common tool used to confirm nutrient limitations (Grimm and Fisher 1986, Francoeur 2001, Dodds et al. 2002, Dodds 2003); however, the N:P ratio of stream waters and cellular nutrients is a more rapid means of assessing nutrient limitation (Bothwell 1985, Freeman 1986, Welch et al. 1989, Stelzer and Lamberti 2001). Redfield

(1958) found the atomic ratio of cellular macronutrients C:N:P for balanced growth to be 106:16:1. This ratio was determined for oceanic phytoplankton but has been used as a standard for assessing nutrient limitations in algae from varied habitats. However, the optimal C:N:P ratio may differ slightly for other primary producers such as benthic microalgae and macroalgae, and among species (Hillebrand and Sommer 1999). Based on a review of the literature, Kahlert (1998) concluded that the optimal cellular C:N:P ratio for maximum growth of freshwater benthic algae was 158:18:1. For a more conservative estimate of limitation, she recommended the use of an optimal range for C:N:P of 99-369:11-32:1 rather than a threshold.

Determining nutrient limitation is important, but understanding the relationship between nutrient concentrations and algal biomass is a key for effective management of eutrophication (Dodds et al. 2002). However, the development of nutrient models that are predictive of algal growth has had mixed success. Mean and maximal biomass in some rivers and streams is significantly correlated to total P (TP), total N (TN), and soluble reactive P (SRP) (Aizaki and Sakamoto 1988, Biggs and Close 1989, Lohman et al. 1992, Dodds et al. 2002). In some lotic systems, however, the relationship between N and P and algal growth has been weak or non-existent (Welch et al. 1988, Welch et al. 1992). This has been attributed to co-limitation by other factors such as light and snail grazing or even to seasonal shifts in limiting factors (Rosemond et al. 2000). For instance, Welch et al. (1988) attributed the lack of relationship between algal biomass and nutrient concentrations in seven New Zealand streams to inter-stream differences in SRP uptake and recycling rates, riparian shading, substrate stability and size, suspended solids, and invertebrate grazing pressure; other pollutants may reduce or eliminate grazing pressures

by removing sensitive aquatic macroinvertebrate insects that typically limit algal growth. Differences in nutrient uptake by algae can cause a longitudinal decrease in inorganic nutrient concentrations that is counteracted by increased P cycling downstream such that overall biomass does not change (Mulholland and Rosemond 1992). Floods can also obscure the effects of enrichment on algal growth by periodically reducing the standing crop (Biggs and Close 1989, Lohman et al. 1992, Biggs 1995).

Many of the models relating N and P concentration to algal growth are considered robust because they are based on studies in multiple streams (Biggs and Close 1989, Lohman et al. 1992, Welch et al. 1992, Leland and Porter 2000, Dodds et al. 2002). However, although these correlations are informative, it is still often difficult to extrapolate results to other systems because of variations in loading, in-stream cycling, and other controlling factors such as light and flood frequency. To manage excessive algal growth in a specific system, it may be more useful to develop nutrient criteria within the context of conditions within that system. Nutrient criteria have been suggested as a means to reduce nuisance algal blooms in Washington and Montana (Welch et al. 1989, Dodds et al. 1997). The EPA has recommended nutrient criteria for Maine as 12 μg/L for TP and 0.070 mg/L for NO_3^- (EPA 2001), but most criteria are suggested with the caveat that they be used as a starting point and considered in the context of local conditions.

The Meduxnekeag River in Aroostook County, Maine, historically experienced substantial filamentous algal blooms during summer (pers. comm., Ellis 2005). However, nutrient concentrations in relation to algal growth have not been quantified. The aim of

this study was to assess spatial and temporal trends in algal coverage, and relate those to nutrient sources, concentrations, loading, and limitation along the Meduxnekeag River.

METHODS

Study Area

The Meduxnekeag River is part of the St. John River system that flows north into New Brunswick, Canada. The river's watershed drains a total area of 1,326 km^2, 1,098 km^2 of it in Maine, and is comprised of three branches: the mainstem, North Branch, and South Branch. Feeder streams flow into Lake Meduxnekeag, but the lake is generally considered the headwater. Lake Meduxnkeag is not known to have significant water quality issues (SASWC 1993), but the segment of the river historically affected by algal blooms started less than 1 km downstream of the lake. Besides receiving nutrients from agricultural land throughout the watershed, the river receives effluent from a starch plant and then flows through downtown Houlton where it receives stormwater runoff and effluent from a WWTP (see Chapter 2). The Houlton Band of Maliseet Indians (HBMI) has tribal land along the river and has monitored 10 sites on a weekly basis every summer since 1995 for total suspended solids, *E. coli*, pH, temperature, turbidity, conductivity, alkalinity, and DO. The river has had non-attainment problems with respect to DO and excess nutrients (MDEP 2000).

Nutrient data were collected for a Total Maximum Daily Load (TMDL) study between 1995 and 1997 (MDEP 2000) and for a sediment study in 2003 (Schalk and Tornes 2005). The TMDL study cited nuisance algal blooms as a direct cause of depressed DO levels in a 10 km stretch of the river (MDEP 2000). One goal of the sediment study was to investigate nutrient dynamics in surface waters and sediments in

order to better understand temporal and spatial variability and how this might relate to algal blooms. To this end, nutrient concentrations in bed-sediment and in the water column within the mainstem and its tributaries were measured at a few sites over a few sampling days that included intensive storm event sampling. No substantial algal blooms occurred during the study year, so no comparisons of algal blooms and nutrients in the surface water or bed sediments could be made.

The river width ranges from 7 m at the headwater to 40 m in the lower sections. Mid-channel depth in the study area ranges from 0.25 m to 1.10 m. The riparian habitat within the watershed is a combination of grasses, shrubs, and trees, and the substrate within the river is a mix of bedrock, gravel, cobble, and sand. The pH of the river is typically between 7.0 and 8.0 (Schalk and Tornes 2005).

Site Selection and Location

I monitored 34 km of the mainstem of the Meduxnekeag River from its headwater at Lake Meduxnekeag to just downstream of its confluence with Big Brook, an area that encompasses 707 km^2 (see Figure 2). The monitoring area included 14 sampling sites (Figure 2) where algal assessments were performed and water samples were collected on a biweekly basis from May through October in 2004 and 2005, for a total of 11 sampling trips per season. The monitoring sites were selected to bracket point sources and tributaries to the mainstem (Table 2). Sites were named based on their approximate river km location ($\pm$0.3 km, provided by HBMI). Eight pre-existing HBMI sites were included to take advantage of ongoing monitoring efforts. Initially, a site on the North Branch was planned as a reference site (Appendix C), but site accessibility became difficult due to logging activities in the area. Nutrient concentrations and algal coverage at that site in

2004 were similar to those collected at the headwater site at the outlet of Meduxnekeag Lake, and the headwater site (0.2) was designated as the project reference site.

Algal Assessments and Sampling

To best characterize fluxes in algal biomass, the assessment reach within each sampling site was adjusted as much as possible to include both run and riffle habitat as suggested by Biggs and Price (1987) and Biggs (1996). Algal assessments were performed from the onset of noticeable filamentous green algae (typically in late June) until the last sampling date in September. Six assessments were performed in 2004 (July 8 – September 21) and again in 2005 (June 29 – September 21). Filamentous algae were collected and identified to genus (Canter-Lund and Lund 1995, John and Witton 2002, Wehr and Sheath 2003) at a subset of sites on two sampling dates in 2004 and three in 2005 to identify dominant taxa and to quantify any shifts in the composition of the filamentous algal communities.

An algal assessment method was adapted from methods described by Necchi et al. (1995) and Biggs and Kilroy (2000). To assess temporal and spatial patterns in algal growth, the percent coverage of filamentous green algae was estimated along four transects across the river width at each sampling site. The four fixed transects were established at randomly selected locations within a 20-meter reach at each site at the beginning of the 2004 sampling season. The percent filamentous algal cover was assessed at five equally spaced points along each transect. At each point, a 0.25 m^2 square was placed on the river bottom and the number of quadrants covered by algae was recorded (Figure 14). If all of the filamentous algae within the square filled one quadrant, a score of "1" was assigned (Figure 14). Scores of 2 to 4 represented 50 to 100% coverage,

respectively. A mean coverage for a given day was obtained for each sampling site by averaging coverage values measured across all 20 points in the 4 transects.

Water Chemistry

Water temperature, DO, and conductivity were measured at each sampling site with a field meter, and water samples were collected for the analysis of TP, TDP, SRP, NO_3^-, and NH_4^+. Water samples were collected mid-channel approximately 10 m downstream of the algal assessment reach (Figure 14). Time of collection and any additional comments (e.g. weather or problems encountered) were recorded in a field notebook. Daily TP and NO_3^- loads were calculated for each site. Additional details regarding collection and analytical methods of water samples and load calculations are provided in Chapter 3.

Because my goal was to investigate relationships between stream water chemistry and the potential for nutrient limitations on algae, the DO and conductivity data were not analyzed further, but served to compare sampling conditions that roughly coincided spatially and temporally with those made as part of the HBMI monitoring program. As discussed in greater detail in Chapter 3, SRP and NH_4^+ were often near or below the methodological limits of detection. TP data were not available for September 2004 due to a laboratory mishap, nor for NO_3^- for the late September sampling in 2004 due to failure to meet quality control limits.

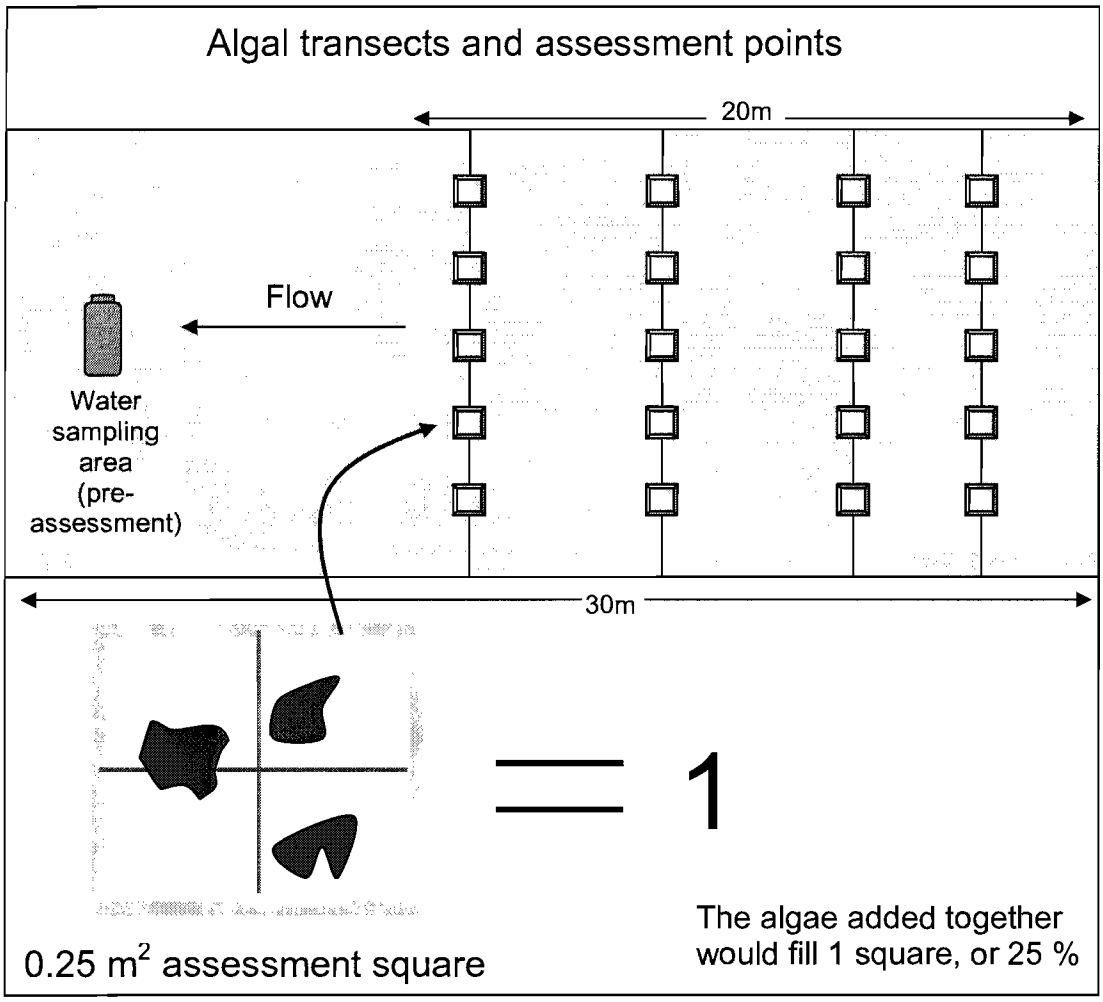

Figure 14. Conceptual drawing of site layout and algal assessment for measuring percent coverage at a given site and an example of how algal coverage was recorded.

Nutrient Limitation

Nutrient limitation was assessed through measurement of the inorganic nutrient ratio in river water samples (molar NO_3^-:SRP) and the C:N:P ratio of algal biomass. Where NO_3^- or SRP concentrations were below detection, nutrient ratios were not calculated because ratios are a less reliable indicator of nutrient availability at extremely low concentrations (Dodds 2003). C:N:P ratios were determined from filamentous algae collected at seven sites on three dates during the 2005 sampling season. Algal samples were collected within the 10 m reach between the water sampling point and algal assessment area (Figure 16). Samples were kept in river water in light-proof bottles in a cooler until transported to the lab. Algal samples were briefly rinsed with deionized water and visible detritus and organisms were removed. Algae were then freeze-dried at -80°C, homogenized in a ball mill, and analyzed for atomic C:N:P. Total C and N were analyzed by dry combustion with an autoanalyzer (APHA 1998). Total P was analyzed by the dry ash method described by Chapman and Pratt (1961). I used the optimal C:N:P ratio estimated by Kahlert (1998) for benthic algae for comparison with the cellular ratios of algae collected from the Meduxnekeag River.

Characterization of Site Habitat

During site selection, I attempted to choose sampling sites of similar depth and substrate type, but the river was very heterogeneous, both among and within sites. River width and mid-channel depth were measured at each site on numerous dates. Estimates of substrate composition were qualitatively determined from field observations but no quantitative measurements were taken in the field. Three USGS stream flow gauges are located within the study area and were used to estimate flows at sites because no direct

measurements of flow were made (see Figure 2 and Chapter 2). HOBO® light and temperature data loggers (Model # UA-002) were attached to cinder blocks and deployed mid-channel at nine sites at equivalent heights above the river substrates. The sensors were programmed to take measurements at 10-minute intervals from June to October 2005. Light data were not analyzed because of technical issues with some light sensors, and because a consistent relationship could not be determined between the HOBO® sensors and a photosynthetically active solar radiation sensor at one of the USGS gauges. Establishment of this relationship would have provided a stronger estimate of light availability relative to algal growth.

Data Analysis

A general linear model (GLM) was used to detect relationships between TP and NO_3^- concentrations and algal coverage. Algal coverage was square-root transformed to meet assumptions of normality and variance in the GLM analyses. Algal coverage at each site was always the response variable but was tested in a different way using three models. The first model used algal coverage values calculated as described above so each site had one value per sample date. The other two models used either the maximum or late season median (August-September) coverage measured at each site in each of the two years. The relationship between nutrients and algal coverage was tested in these alternative models because variability in algal growth within sites can make it difficult to assess the relationship between nutrient concentrations and growth if all data points are used (Biggs 2000). Predictor variables included site, year, log TP, log NO_3^-, change in degree days between assessment dates, site depth and width, and interactions between nutrients and year (Table 7). One iteration of the first model using all of the coverage

data was run using Julian day for the sample date, and another iteration was run using month for the sample date. Interactions between sample date and nutrient concentrations were included to determine if the relationship between nutrients and algal coverage varied at different time scales (e.g. Julian date, month, or year). The models were run in a forward and backward stepwise fashion iteratively. The parameters included in the model were modified until both directions resulted in a similar set of parameters. Analysis of variance (ANOVA) with a significance level of $p < 0.05$ was performed to test spatial and inter-annual differences in algal coverage. Statistical analyses were performed with SYSTAT® version 11.

Table 8. Predictor and response variables used in three general linear models.

Response Variables	**Predictor Variables**
Percent algal coverage (entire dataset) n = 132	Log TP
	Log NO_3^-
	Change in degree days since last assessment
	Year
	Julian date or month
	Interactions between nutrients and year and Julian date or month
Late season median algal coverage (1 value per site/year) n = 22	Mean log TP
	Mean log NO_3^-
	Site width
	Site depth
Maximum algal coverage (1 value per site/year) n = 22	Year
	Interactions between nutrients and year

RESULTS

Algal Community Composition

The dominant genera of filamentous collected in 2004 in order of abundance were *Spirogyra* sp., *Zygnema* sp., *Oedogonium* sp., and *Mougeotia* sp. Dominance order differed in 2005: *Oedogonium* sp., *Spirogyra* sp., *Cladophora* sp., *Microspora* sp., and *Mougeotia* sp. (Appendix E). At the beginning of each monitoring season, *Spirogyra* sp. was the most abundant taxon, but the communities rapidly diversified in composition to include the other genera listed above.

Algal Coverage

Algal coverage in the river was highly variable both among and within sites (Table 9, Figure 15a). The reference site (0.2) had a higher mean percent coverage than many of the downstream sites, particularly in 2004. Maximal coverage for all sites was 43% at site 16.4 in 2004 and 31% at site 25.7 in 2005. The highest median coverage in 2004 was 14% at site 16.4 and 16% at site 30.4 in 2005. Coverage percentages at sites 5, 18, and 21.9 were typically very close to zero. Algal coverage only exceeded the nuisance level of 30% for one assessment in 2004 and two assessments in 2005. Considering the rarity of coverage values greater than 30%, a nuisance bloom did not occur either year.

The longitudinal patterns in mean algal coverage were similar in 2004 and 2005 (Figure 15a). Algal coverage was close to 0% at site 5 and increased between sites 14.6 and 16.7 before decreasing to almost zero at site 18, where the South Branch joins the mainstem. Downstream of site 18, algal coverage increased steadily, with noticeable increases at site 23.7 in 2004 and at site 26.4 in 2005.

Table 9. Percent algal coverage at each sampling site in 2004 and 2005. Sites are characterized by nutrient source.

Site	Nutrient Source Type	Year	Mean	Median	Min	Max	Standard Deviation
0.2	reference	2004	10.2	9.4	0.0	22.5	9.1
		2005	9.9	8.1	5.0	20.6	5.7
5	agricultural	2004	0.2	0.0	0.0	1.3	0.5
		2005	3.3	0.6	0.0	10.0	4.7
14.6	agricultural	2004	11.0	9.4	1.3	28.8	9.4
		2005	15.0	11.9	2.5	31.3	12.6
16.4	agricultural	2004	16.2	14.4	0.0	43.4	14.6
		2005	15.1	13.1	6.3	30.0	9.0
16.6	starch plant	2004	12.7	11.9	10.0	16.3	3.1
		2005	14.6	14.4	7.5	21.3	5.4
16.7	agricultural	2004	8.2	6.9	2.6	15.0	4.8
		2005	14.5	11.3	6.3	26.3	9.0
18	agricultural	2004	0.0	0.0	0.0	0.0	0.0
		2005	1.5	1.3	0.0	3.8	1.7
21.9	urban/ agricultural	2004	0.4	0.0	0.0	2.5	1.0
		2005	4.4	0.6	0.0	21.3	8.4
22.4	agricultural	2004	1.7	1.3	0.0	5.0	1.7
		2005	8.1	11.3	0.0	16.7	7.6
23.7	urban	2004	6.5	4.4	1.3	18.8	6.9
		2005	9.2	5.0	2.5	20.0	7.4
25.7	urban/ agricultural	2004	4.9	3.9	0.0	11.3	5.2
		2005	8.3	2.5	1.3	31.3	12.9
26.4	WWTP	2004	3.7	1.9	0.0	15.0	5.7
		2005	14.6	14.7	2.5	26.3	11.9
30.4	agricultural	2004	3.9	1.9	0.0	13.2	5.1
		2005	14.1	16.3	2.1	28.8	10.8
34.1	agricultural	2004	5.0	3.1	0.0	15.0	5.6
		2005	11.6	12.5	5.0	17.5	4.7

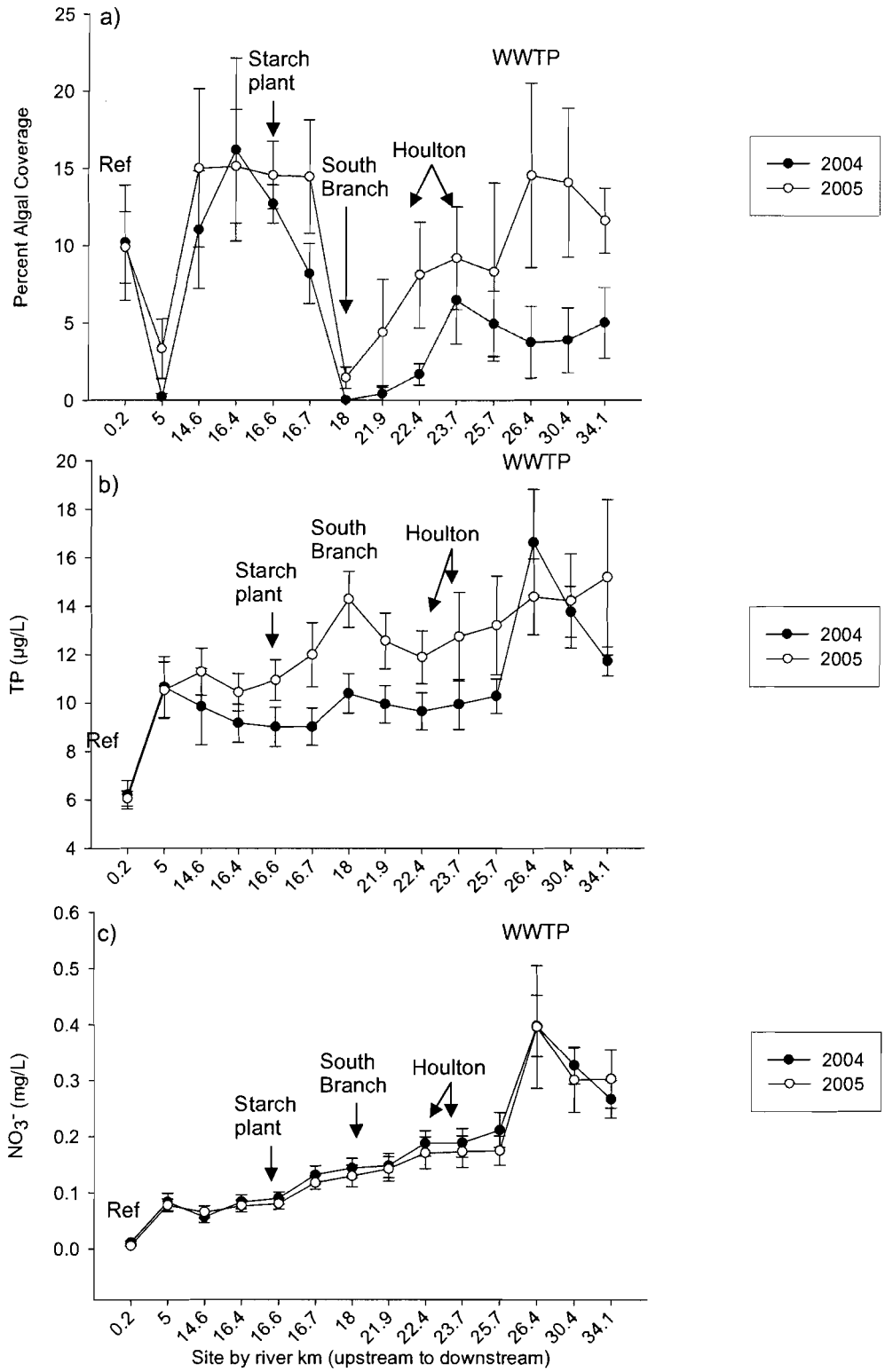

Figure 15. Mean percent algal coverage (a) and nutrient concentrations (b and c) for each site (with standard error). The location of nutrient sources are indicated. Solid circles represent 2004 and open circles represent 2005. a) Percent algal coverage, b) TP concentrations (µg/L), and c) NO_3^- concentrations (mg/L).

Algal coverage in both years was more similar at sites upstream of site 18. Because algal coverage sharply declined at site 18 before increasing again, I compared algal coverage at sites upstream and downstream of site 18. An ANOVA confirmed that coverage was significantly higher upstream of site 18 than downstream ($p<0.05$).

Seasonality in Algal Coverage in Relation to Flow

Algal coverage was significantly higher in 2005 than in 2004 (ANOVA; $p< 0.05$). Within-year variability for all sites was high (Figure 15a), however, and seasonal patterns differed between the two study years. In 2004, the highest percent algal coverage occurred in September and was almost double the coverage of July and August (Table 10). In 2005, algal coverage peaked in August but was not much higher than the mean of July and September.

Table 10. Mean and standard deviation of monthly algal coverage across the 14 sites for 2004 and 2005.

	2004		2005	
	Mean Algal Cover (%)	**Standard Deviation**	**Mean Algal Cover (%)**	**Standard Deviation**
July	4.5	6.0	9.7	7.6
August	4.8	6.9	11.0	10.7
Sept	8.5	9.0	8.3	8.1

High flow events have the potential to scour algae, thus affecting my estimates of algal coverage. Algal coverage did decline after the highest flow events in 2004 and 2005 (on September 11 and September 2, respectively), but I could not discern a flow threshold for scouring (Figure 16). For instance, in 2004, algal coverage declined after discharge peaked at 5.5 m^3/s on August 14 but was higher two weeks later after discharge had reached 7.5 m^3/s. The effect of flow on algal coverage was not related to season.

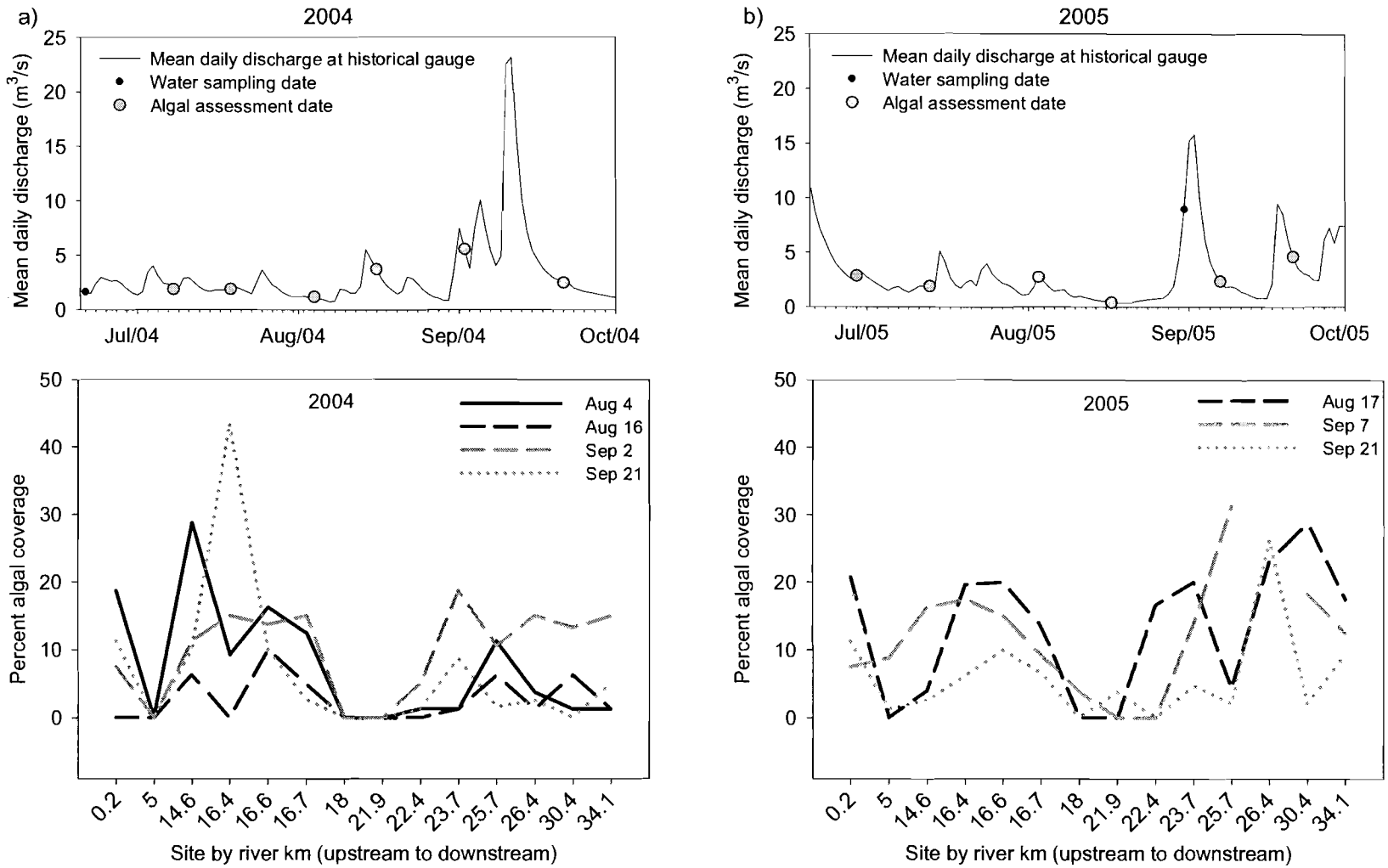

Figure 16. Hydrograph including algal assessment dates and site algal coverage percentages from several assessment dates. a) 2004 and b) 2005.

Although maximal algal coverage occurred in 2005 during a period of stable, low flow in July and August and consistently declined with higher flows in September, algal coverage in 2004 was highest in September, when most of the high flow events occurred (Table 10 and Figure 16). Flow-related declines in algal coverage were observed but were not consistent enough to explain within-year or seasonal variability in algal coverage.

Nutrient Concentrations and Loads

Longitudinal algal patterns did not covary with those for nutrients (Figure 15). Total P and NO_3^- concentrations were lowest at the reference site and increased downstream, whereas algal coverage was significantly higher above the South Branch (site 18) than below it. Although SRP concentrations were not compared to algal coverage because of detection limit issues, concentrations above the detection limit displayed no longitudinal or temporal trend other than to be slightly higher downstream of the WWTP (site 26.4, Figure 5). Not only did the general longitudinal nutrient pattern not correspond to algal growth, but peaks in nutrient concentrations, like those associated with the South Branch (site 18) and the WWTP (site 26.4), did not correspond to peak algal sites. Instead, algal coverage declined to near zero at intermediate sites such as 18 and 21.9.

The general linear models confirmed that nutrient concentrations did not account for a significant amount of the variability in algal coverage. Using maximum and late season (August-September) median algal coverage as compared to coverage values from the entire sampling season did not change the results of the model. Algal coverage also did not significantly vary with site width and depth. As mentioned earlier, in all model

iterations, year was the only significant predictor, indicating that year was the most important factor explaining algal coverage differences among sites.

As for nutrients, coverage was not related to longitudinal patterns in nutrient loads, which were calculated from nutrient concentrations and water flux (Figure 17). Sites that had low or negative TP and NO_3^- loads, suggesting nutrients were settling out or being immobilized, did not consistently have higher percentages of algal coverage. Also, sites which received high nutrient loads, and, thus a potentially larger pool of available nutrients, did not have consistently higher levels of percent algal coverage. For instance, site 18 had the highest TP load but had algal coverage estimates consistently close to 0% (Figure 17a). At site 26.4, which had the highest NO_3^- load, algal coverage was quite low (less than 5%) in 2004 but reached high values (15%) in 2005 (Figure 17b). These patterns suggest that multiple factors are influencing algal coverage patterns.

Nutrient Limitation

Cellular C:N:P ratios were determined for algae collected from seven sites in July, August, and September 2005 (Table 11). With the exception of algae from site 26.4 sampled on July 13, 2005, C:P and N:P ratios were much higher than the optimal range determined by Kahlert (1998). The cellular ratios of C:N were slightly higher than that of the optimal range. Mean NO_3^-:SRP ratios of the corresponding water samples also exceeded the optimal ratio, and most were over 100 except for site 14.6, which still had a mean over 50 (Table 12). Nutrient ratios in the river and in algal cells both suggest strong P limitation.

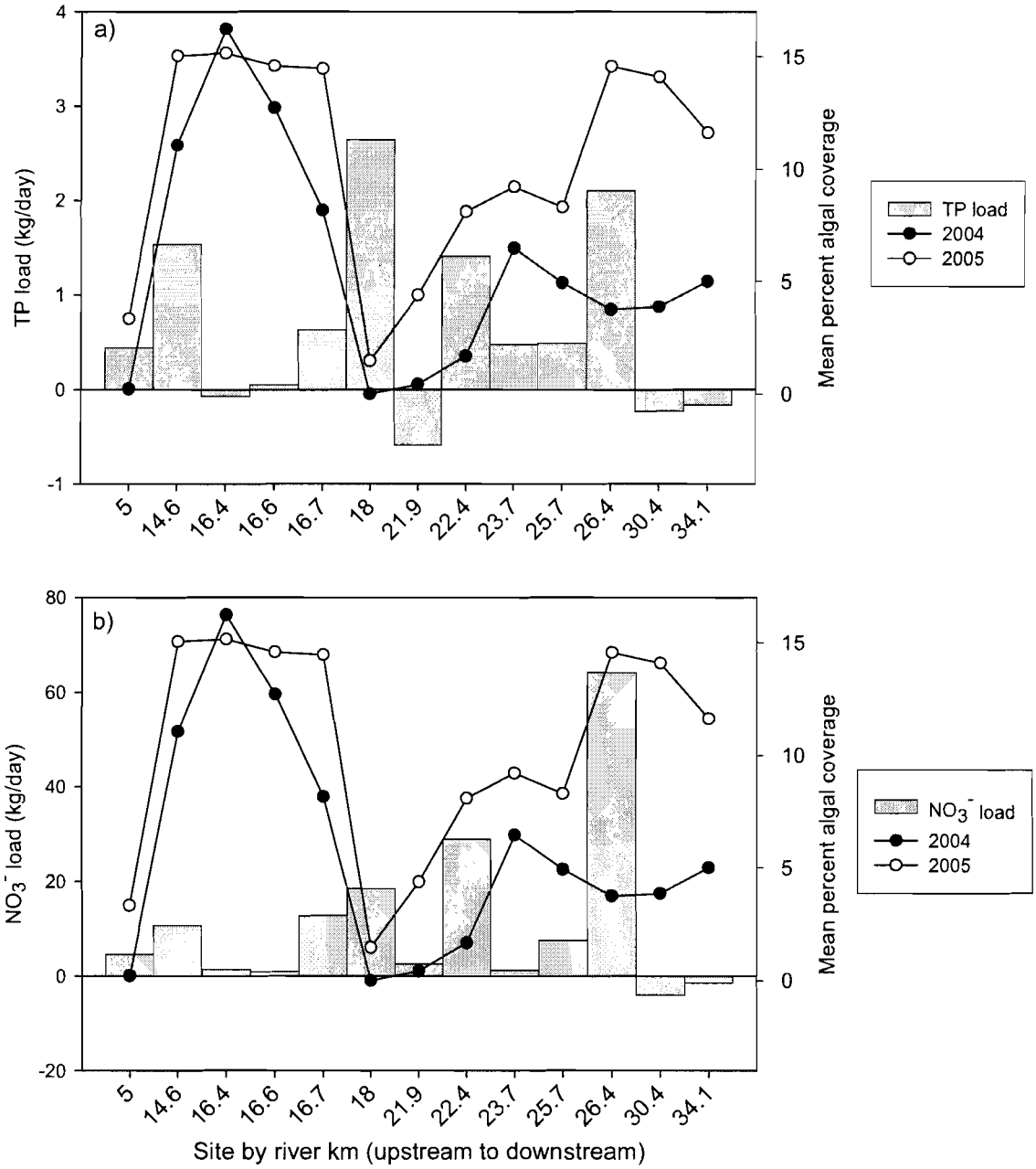

Figure 17. Mean percent algal coverage and unweighted mean daily nutrient loads for each site. Solid circles represent 2004 and open circles represent 2005. Gray bars represent loads averaged over the two years for a) TP (kg/day) and b) NO_3^- (kg/day).

Table 11. Cellular C:N:P ratios for algae by date[1] in 2005.

Site	Date	C	N	P	C:N
14.6	14-Jul	448	40	1	11
16.4	14-Jul	804	50	1	16
22.4	14-Jul	520	35	1	15
26.4	14-Jul	290	33	1	9
34.1	14-Jul	692	51	1	14
14.6	18-Aug	531	43	1	12
16.4	18-Aug	549	48	1	12
22.4	18-Aug	660	44	1	15
26.4	18-Aug	501	36	1	14
34.1	18-Aug	482	36	1	13
14.6	22-Sep	393	33	1	12
16.4	22-Sep	531	42	1	13
16.6 + 16.7	22-Sep	501	46	1	11
26.4	22-Sep	487	30	1	16
34.1	22-Sep	550	47	1	12
Overall Mean		529	41	1	13
Optimal Range		99-369	11-32	1	8-11

[1] Algae from sites 16.6 and 16.7 were combined because there was not enough biomass in the separate samples to complete the laboratory analysis.

Table 12. The minimum, maximum, and mean ratio of NO_3^- to SRP in water samples collected in 2004 and 2005. The sites correspond to the sites in Table 11 where algae were collected for C:N:P analysis.

		NO_3^-:SRP ratio		
Site	**Year**	**Min**	**Max**	**Mean**
14.6	2004	24	89	56
	2005	20	125	64
16.4	2004	61	187	123
	2005	45	195	106
16.6	2004	72	187	125
	2005	47	208	101
16.7	2004	125	281	186
	2005	53	202	112
22.4	2004	209	346	279
	2005	37	334	143
26.4	2004	33	468	231
	2005	54	956	285
34.1	2004	81	401	259
	2005	68	796	246

Consideration of Other Potential Growth Limiting Factors

Site Width, Depth, and Substrate

Differences in river width and depth can affect light availability, but mean algal coverage in the river was not strongly related to site depth or width (Figure 18). Also, no clear pattern was observed between mean algal coverage and substrate composition. The highest algal coverage values tended to occur at sites that were predominantly bedrock or cobble but this was not consistent (Figure 19a). The site with the highest percentage of sand had very low algal coverage, but no other trend with sand was apparent because other sites had much lower percentages of sand and little inter-site variation in the percentage of sand (Figure 19b).

Temperature

Differences in temperature can affect algal growth rates, but this was not a factor in the Meduxnekeag's algal coverage patterns. Mean monthly midday and midnight temperatures among the nine sites with data loggers differed by only 1 to 2 °C. Maximum midday temperatures occurred at sites 16.4 and 16.6. The midday temperature at the most downstream site was usually slightly lower than that measured at the most upstream sensor (site 14.6). July was the warmest month, followed by August, June, September, and October (Figure 20). The longitudinal temperature change was fairly constant among months, except for August. Sites upstream of site 18, where algal coverage was significantly higher than downstream, were generally slightly warmer than those downstream of site 18 but only by an average of 2°C (Figure 21).

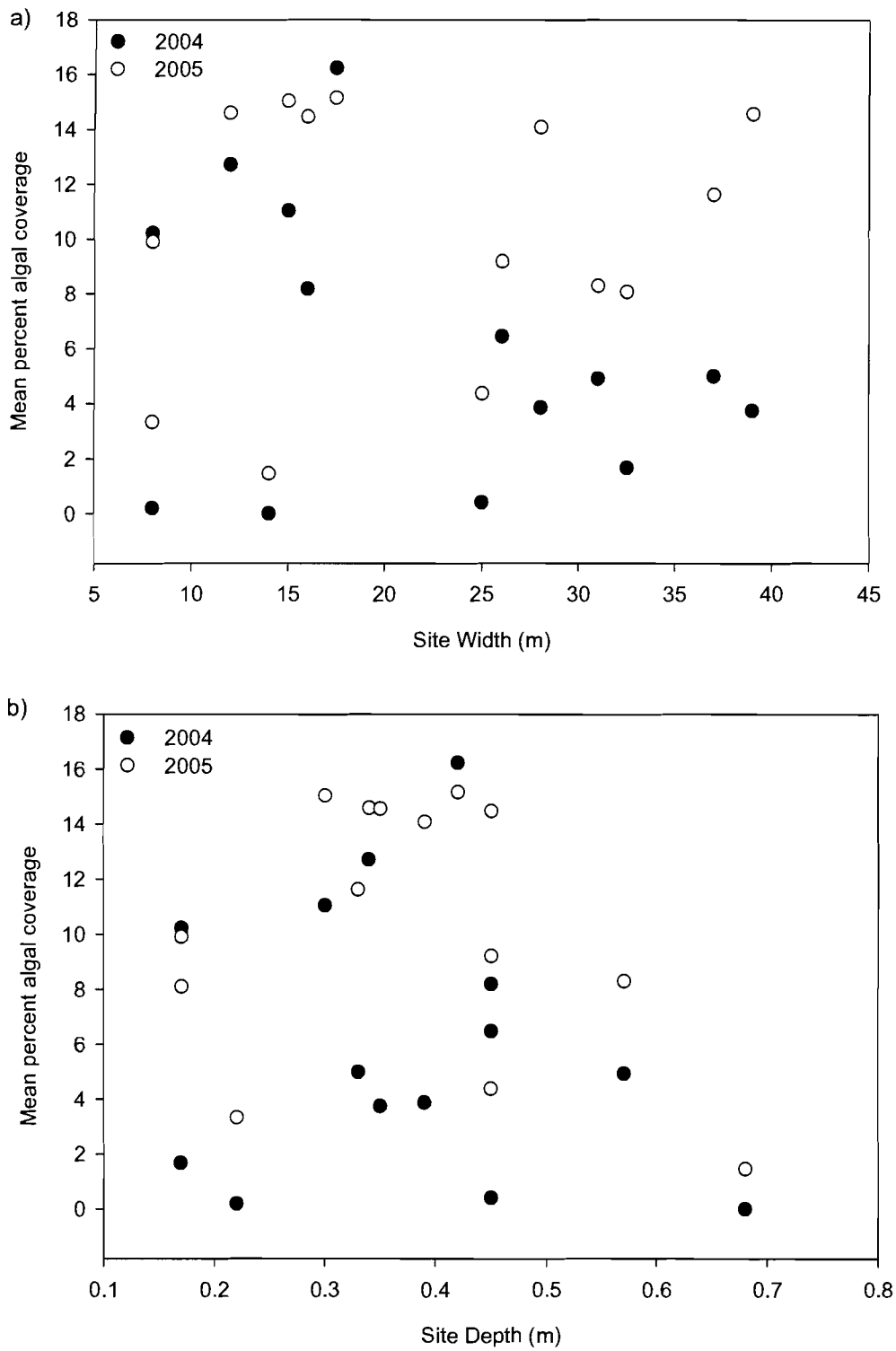

Figure 18. Mean percent algal coverage versus a) site width and b) site depth. Closed circles are from 2004 and open circles are from 2005.

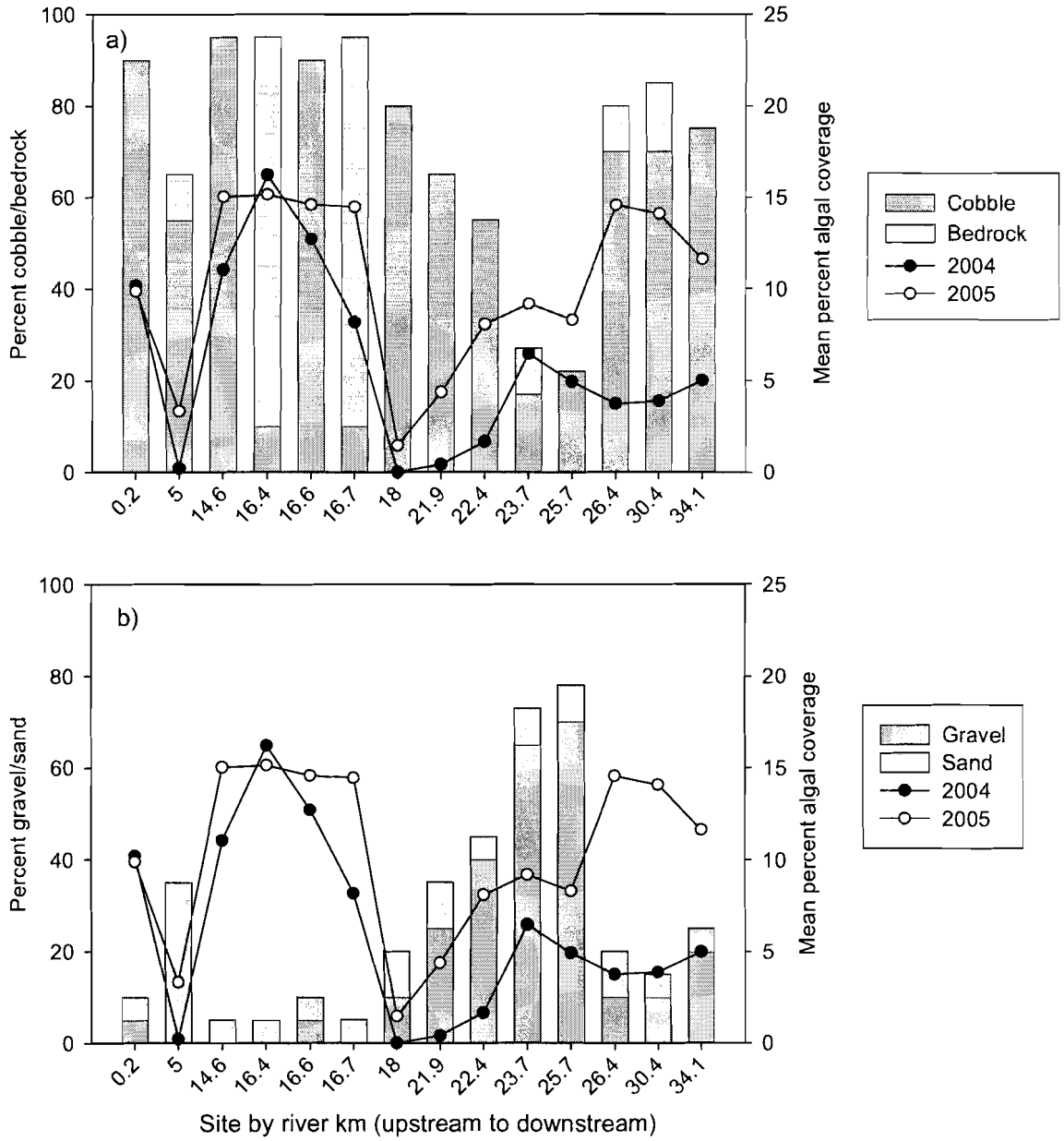

Figure 19. Approximate substrate composition per site and mean algal growth per year. Closed circles are algal coverage in 2004 and open circles are algal coverage in 2005. a) Cobble and bedrock and b) Gravel and sand.

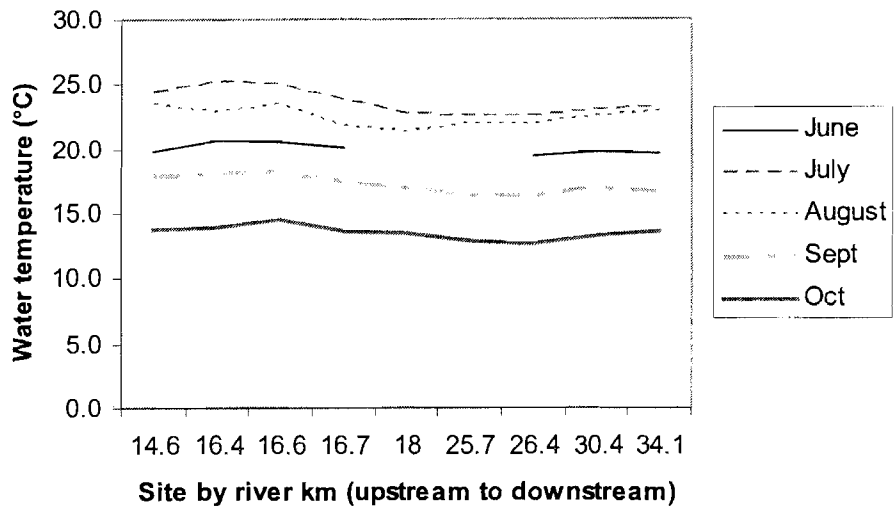

Figure 20. Monthly mean daytime temperature (°C) at the nine sites with temperature sensors.

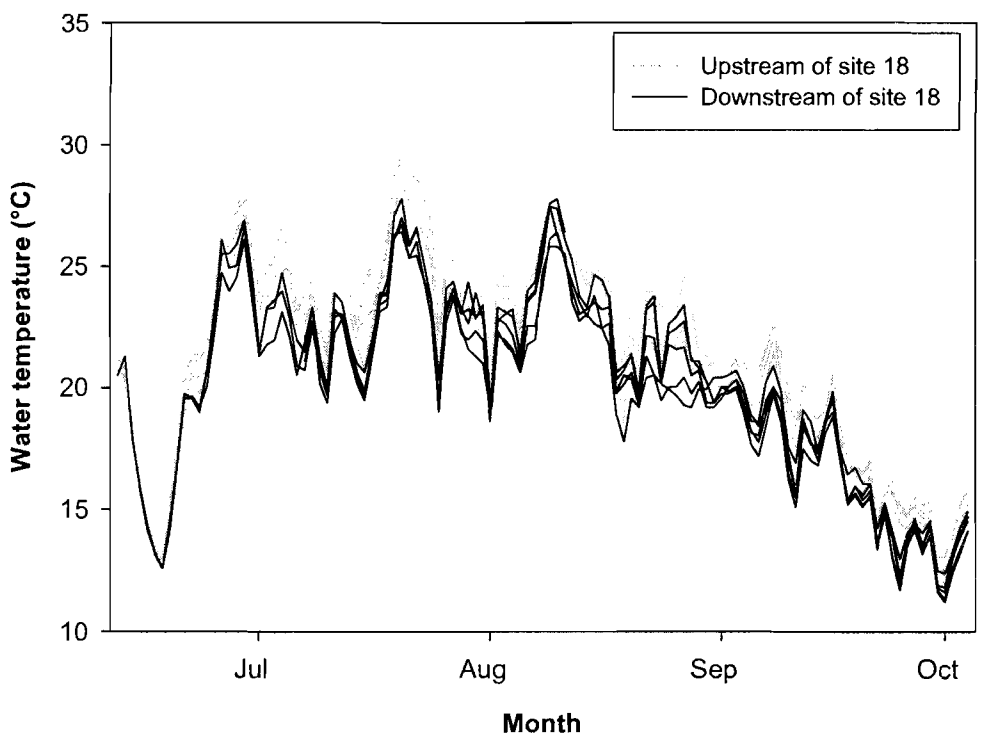

Figure 21. Daily temperatures (°C) at the nine sites with temperature sensors, coded by river location in relation to site 18. Sites upstream of site 18 are represented by gray shading and those downstream have black shading.

Climate Comparison of Study Years to Nuisance Bloom Years

Although nuisance algal blooms were an impetus for this study, they did not occur in either study year. To determine whether differences in weather might account for the low incidence of algae in 2004 and 2005, I compared weather conditions in the study years to 1998 and 2001, when the last major nuisance blooms occurred (pers. comm., Ellis 2005). There were no obvious differences in cooling degree days, air temperature, and precipitation either with the 30-year normal or the two nuisance bloom years (Figure 22). Cooling degree days are a measure of how far the daily average temperature is above 65 °F. Surprisingly, the cooling degree days in the nuisance bloom years (1998 and 2001) were lower than either the 30-year norm or the study years (Figure 22a). Air temperatures in the bloom years were higher in early spring months than those of the 30-year normal or the sampling years, however, bloom and non-bloom years were higher than normal from August onward (Figure 23b). It might be that higher early spring temperatures leads to early algal establishment, and this may result in a longer accrual period, higher resistance to scour, and higher biomass. Investigating these subtle seasonal differences was beyond the scope of my study. The weather data do support my result that nutrient availability alone did not explain in-stream differences in algal production in the two years of my study.

Unfortunately, the river was not gauged during the 1998 and 2001 bloom years, thus hydrograph data could not be compared. As a surrogate, precipitation data from a nearby meteorological station were used to infer the potential for low and high flow events (NOAA 2006). Precipitation during the algal growing season was well below normal in 2001 but above normal in 1998 (Figure 22c). In addition, summer precipitation in both of my study years was less than precipitation in 1998.

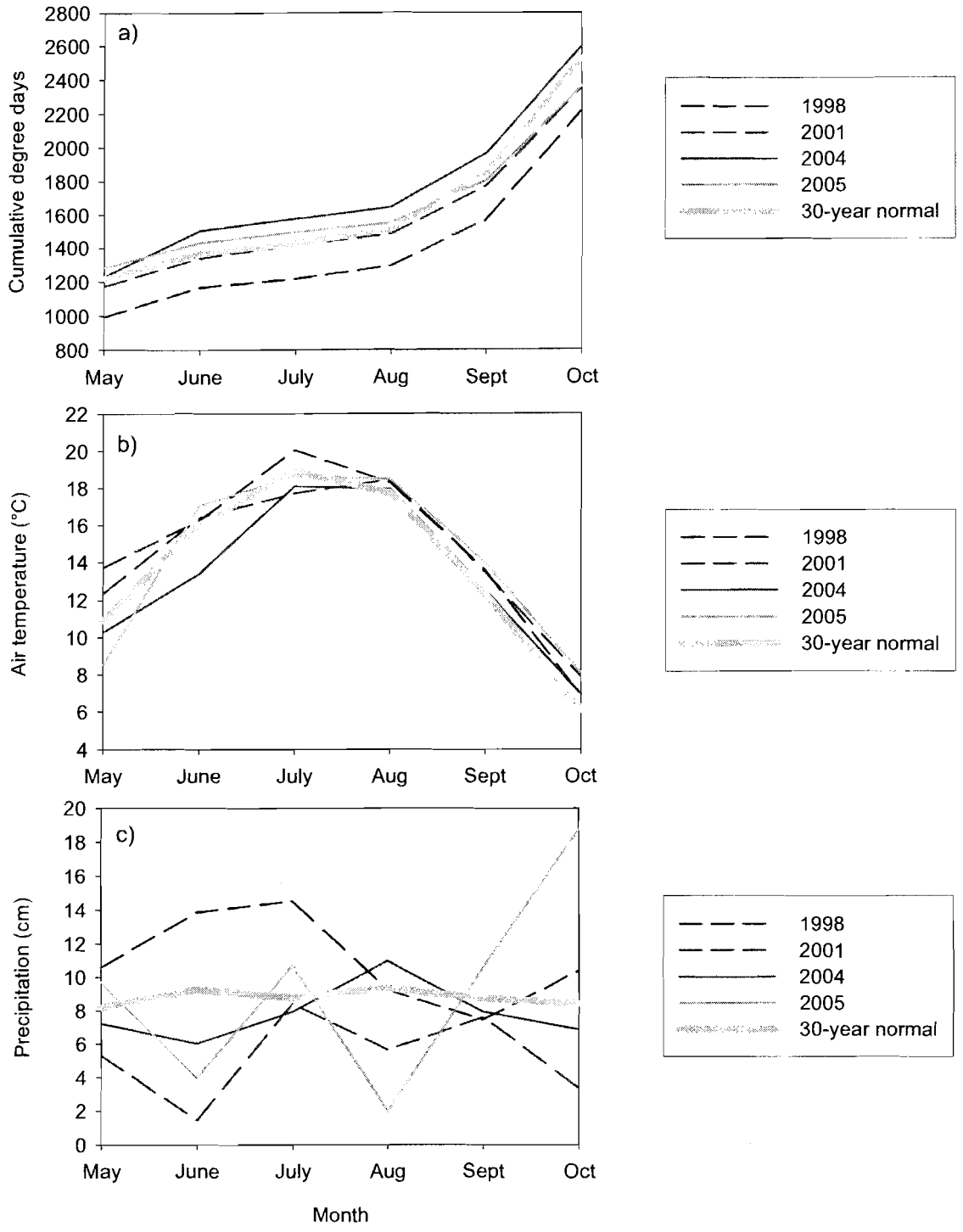

Figure 22. A climate comparison from May to October of the sampling years to the 30-year normal and 1998 and 2001, two years in which significant algal blooms occurred. a) cumulative cooling degree days, b) air temperature (°C), and c) precipitation (cm) (NOAA 2006).

Early season precipitation that might cause high flow events and reduce algal establishment did not show a clear trend from which to infer proximal cause of nuisance bloom years (Figure 22c). Overall, climatic differences between the sampling and bloom years did not suggest that weather was a factor controlling nuisance proliferations of algae.

DISCUSSION

Algal coverage patterns did not significantly correlate with nutrient concentrations within the Meduxnekeag River during the two seasons sampled for this study. Despite the steady increase in both NO_3^- and TP downstream, the major pattern was for significantly *higher* percent algal coverage upstream than downstream. The consistent inter-annual differences in coverage across sites caused year to be more predictive of coverage than nutrient concentrations, rather than any longitudinally-variable predictor. Longitudinal patterns in algal coverage suggest that nutrients were not the primary factor limiting algal coverage.

Water column and cellular N:P ratios suggested severe P limitation along the entire length of the Meduxnekeag that I studied. Similar findings of strong P limitation were reported by the MDEP (2000) in their TMDL study of the Meduxnekeag. Assuming P limitation, I would have expected coverage to be more substantial at sites with higher P concentrations. Total P concentrations and algal coverage were both higher in 2005, which suggests some overall effect of nutrients on algal coverage. Although the C:N ratios were slightly above the optimal range, N limitation is unlikely because both the ratio of NO_3^- to SRP in the water column and the cellular N:P ratios were very high (Dodds 2003).

My finding that nutrients provided little predictive capability to explain variation in algal coverage within the Meduxnekeag River is consistent with many other stream studies (Welch et al. 1988, Welch et al. 1992). Winter and Duthie (2000) found a significant correlation between *Cladophora* sp. cover and NO_3^- concentrations downstream of agricultural sites, but their study was limited to a stream with a maximum width of 2 m that received agricultural inputs from a 0.06 km^2 area. The stream in their study had stronger interactions with agricultural land than mine did and the watershed area was 0.005% the size of my study area. Some studies have had more success relating algal growth to nutrient concentrations when using a seasonal or annual mean (Lohman et al. 1992, Dodds et al. 2002), but my results did not change when I related median and maximum algal cover to mean nutrient concentrations over the sampling season. This was likely because algal coverage was so variable and nutrient concentrations had a very consistent longitudinal trend over time.

Previously, it was argued that significant algal blooms may modulate stream nutrient concentrations and take up nutrients so rapidly that stream concentrations do not reflect actual availabilities (Mulholland 1996), but I believe this was unlikely for two reasons. First, SRP concentration did not change seasonally and was not higher earlier in the sampling season when algal coverage was low or absent. Second, algal coverage was not any higher at sites that had small or negative nutrient loads. Even where nutrient concentration reflects availability and is related to algal growth or coverage, it usually explains roughly 40% of the variability in algal production because non-equilibrium conditions and other limiting factors are likely to dominate in rivers (Dodds et al. 2002).

Nutrients may increase growth rates but the combined effect of nutrients and other conditions can prevent any one factor from being an obvious limiting factor (Hillebrand and Kahlert 2001). Algal growth in the Meduxnekeag River could be limited or co-limited by other factors such as light or invertebrate grazing, and the limiting factors could shift seasonally (Welch et al. 1992, Rosemond et al. 2000). Temperature can have an important role in determining seasonal changes in primary productivity, particularly in forested or low nutrient streams (Son and Fujino 2003). Although water temperature was slightly lower at sites downstream of site 18, the difference was within 2°C and does not support temperature as a factor controlling spatial differences in algal cover. Light availability, which I was not able to account for, may be an additional limiting factor but is unlikely because higher algal growth occurred in the narrower headwater reaches of the river where shading was more prevalent. Invertebrate grazer density was not measured but can have a negative effect on algal biomass (Hillebrand and Kahlert 2001) and can even mask nutrient enrichment by keeping biomass at a fairly constant level (Rosemond 1994).

Substrate type, size, and stability can also limit development of algal biomass (Pringle 1990, Welch et al. 1992, Potapova and Charles 2005). Maximum algal proliferations have been observed at sites with open bedrock and cobble as compared to gravel and sand (Welch et al. 1992, Potapova and Charles 2005), and this was the case for the Meduxnekeag River. Welch et al. (1992) also measured lower algal growth at a site where the substrate changed from flat bedrock to a mix of bedrock, cobble, and boulder, and a tributary doubled flow. These changes are similar to the change in

substrate and flow conditions between site 16.7 and site 18, where filamentous algae were frequently absent.

Increased flow and substrate changes could very well be controlling factors at site 18, but flow effects were not consistent for all sites and flow is unlikely to be the limiting growth in the entire study area. A flow threshold for scouring algae was not observed and no seasonal flow effects were obvious. Flood disturbances can obscure the effects of enrichment on algal growth (Biggs and Close 1989, Lohman et al. 1992, Biggs 1995), but in watersheds with low nutrient concentrations like the Meduxnekeag, flood events are a less important controlling factor (Biggs 1995).

A difficulty in relating nutrient concentrations to algal blooms was that consistent nuisance algal coverage did not occur in either study year. Nuisance levels for filamentous algae have been defined as anywhere from 20 to 40% coverage and greater (Biggs and Price 1987, Welch et al. 1988, Biggs and Kilroy 2000). Site maxima in the Meduxnekeag River in 2004 and 2005 were only greater than 30% for a total of three assessments, and the annual mean for each site was equal to or below 16% coverage for both assessment seasons. Communications with the HBMI, who have monitored the river since 1995 and assisted with sampling for this study, confirmed that algal coverage in the study years was low for the river and much different than during historical nuisance blooms.

It is possible that nutrients were controlling algal growth in the past but local changes in land use practices have shifted limitation to another factor (Qian 2000). Agricultural practices within the watershed and effluent limitations for P at the WWTP have changed in the past 6 years, and may have reduced algal growth by decreasing

watershed nutrient inputs. The 2000 discharge permit issued by the MDEP for the WWTP mandated increased P removal, while the most recent permit in 2005 further increased the P restrictions for effluent (pers. comm., Miller 2006). Changes in agricultural practices since 2003 potentially affecting nutrient export include an increasing number of farmers applying winter cover crops and mulching to reduce surface runoff throughout the watershed (EPA 2005).

Historical blooms in the Meduxnekeag have been identified as *Cladophora*, a species which commonly forms nuisance blooms in enriched waters (Biggs and Price 1987, Jackson 1988, Dodds 1991). The filamentous green genera I found, however, are typically dominant in mesotrophic habitats (Biggs 2000, Biggs and Kilroy 2000). As a result of land use changes and additional P treatments, lower nutrient concentrations may have not only reduced algal growth but caused a shift in the filamentous algal community composition. Although the dominant genera I found can form nuisance blooms, *Cladophora* sp. is known more widely for causing them in a wide variety of freshwater ecosystems (Biggs 2000). Although changes in land use practices may have decreased nutrient concentrations below threshold levels for nuisance blooms, this is difficult to confirm without long-term data for nutrient concentrations, algal growth, and environmental forcing-factors such as light, temperature and flow.

Because nuisance blooms have been variable in occurrence and other factors besides nutrients may be potentially limiting algal growth, it would be premature to suggest nutrient criteria for the Meduxnekeag until more is known regarding the factors limiting and promoting algal production. Compared to the EPA's nutrient criteria, NO_3^- concentrations in the river were more than double the recommended concentration but the

mean TP concentration of 11.8 μg/L in the Meduxnekeag was very close to the recommended 12.0 μg/L. The criteria recommended by the EPA seem reasonable, and perhaps a little conservative, given the concentrations I measured and the corresponding level of algal coverage I observed.

Inter-annual variability in algal coverage was too high to detect any seasonal trends but my study did identify spatial trends in algal coverage within the river. Although coverage was not substantial in either year of the study, longitudinal trends were the same in both years. The data suggested severe P limitation within the river, and P may be seasonally limiting, as observed by Rosemond et al. (2000). Performing *in vitro* bioassays in several locations would confirm the P limitation suggested by both river nutrient and algal biomass nutrient ratios. A determination of nutrient limitation typically indicates whether concentrations of a particular nutrient should be reduced to limit growth. However, because there was no relationship between river P concentrations and algal coverage, reducing P concentrations alone may not control algal growth for this river.

The spatial trends I observed in algal coverage provide a useful starting point for future research. Other factors, such as grazers, light availability, and substrate, which were not closely examined for this study, should be assessed and compared among a subset of sites including those that had high and low coverage in my study. My study provides baseline data for a non-nuisance bloom year. If monitoring efforts continue in some capacity and another significant bloom occurs, the percent coverage that is considered a nuisance in the river could be quantified and data from that year could be compared to data from this study. Obviously, multiple causes of nuisance blooms might

be possible, but nutrient data from a nuisance bloom year would allow nutrient concentrations to be compared to a much broader range of algal coverage and help further define the relationship between nutrients and algal growth in the river.

This study provides another example of the spatial and temporal variability of algal growth in lotic systems, a prime reason why it is often difficult to relate nutrient concentrations to algal growth. Although nutrient ratios suggested severe P limitation, algal coverage in the river was not higher at sites with higher P concentrations. While nutrients are usually the easiest growth-limiting factor to control, the importance of other factors such as light, substrate, flow, and invertebrate grazing on algal growth may differ among sites and render it difficult to use nutrient control to reduce the occurrence of nuisance blooms. Nonetheless, the low nutrient concentrations and algal cover and corresponding change in land use practices within the watershed suggest that concentrations may have declined below the river's threshold for nuisance blooms, a results that highlights the importance of effective watershed management.

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APPENDICES

Appendix A

NUTRIENT CONCENTRATIONS

Table A1. Descriptive statistics for TP (µg/L) and NO_3^- (mg/L) concentrations at each sampling site in 2004 and 2005. Values with an asterisk (*) were below the detection limit.

		TP (µg/L)				NO_3^- (mg/L)			
Site	**Year**	**Mean**	**Min.**	**Max.**	**SD**	**Mean**	**Min.**	**Max.**	**SD**
0.2	2004	6.2	4.2	8.9	1.8	0.012	< DL	0.024	0.008
	2005	6.1	4.3	7.8	1.0	< DL	< DL	0.011	0.002
5	2004	10.7	4.3	17.4	3.8	0.084	0.010	0.174	0.049
	2005	10.5	5.7	20.1	3.9	0.078	0.035	0.155	0.038
14.6	2004	9.9	5.3	16.4	3.9	0.057	0.020	0.102	0.025
	2005	11.3	6.0	15.8	3.2	0.066	0.017	0.128	0.036
16.4	2004	9.2	6.7	14.7	2.4	0.085	0.040	0.150	0.039
	2005	10.5	6.0	15.0	2.6	0.077	0.042	0.135	0.034
16.6	2004	9.0	6.2	14.5	2.4	0.091	0.040	0.142	0.036
	2005	10.9	6.7	16.0	2.8	0.081	0.042	0.136	0.033
16.7	2004	9.0	6.9	14.3	2.3	0.132	0.050	0.202	0.051
	2005	12.0	5.7	20.4	4.4	0.118	0.060	0.183	0.039
18	2004	10.4	7.7	14.5	2.4	0.144	0.060	0.250	0.056
	2005	14.3	9.2	19.9	3.9	0.130	0.056	0.254	0.065
21.9	2004	9.9	6.8	14.1	2.3	0.149	0.066	0.282	0.068
	2005	12.6	6.5	19.1	3.8	0.143	0.055	0.294	0.073
22.4	2004	9.7	7.2	14.0	2.3	0.188	0.079	0.316	0.071
	2005	11.9	7.1	18.0	3.6	0.171	0.075	0.402	0.094
23.7	2004	9.9	6.6	15.1	3.1	0.189	0.088	0.313	0.076
	2005	12.7	6.0	27.8	6.1	0.173	0.073	0.402	0.093
25.7	2004	10.3	7.7	13.8	2.1	0.212	0.081	0.402	0.099
	2005	13.2	6.8	30.2	6.7	0.175	0.077	0.374	0.087
26.4	2004	16.6	9.7	32.3	6.6	0.398	0.191	0.712	0.173
	2005	14.4	7.3	21.5	5.0	0.396	0.167	1.310	0.347
30.4	2004	13.8	10.1	19.5	3.1	0.328	0.186	0.479	0.106
	2005	14.2	7.4	29.1	6.1	0.301	0.143	0.831	0.191
34.1	2004	11.7	12.5	8.7	13.7	1.8	0.267	0.296	0.101
	2005	15.2	12.5	8.4	46.3	10.6	0.303	0.254	0.151

Appendix B

MOLAR RATIOS

Table B1. Molar ratios of NO_3^- to SRP in the water column per site. Concentrations of both nutrients were too low to establish a ratio for Site 0.2.

Site	Year	Min	Max	Mean
5	2004	13.9	150.4	80.3
	2005	37.5	215.9	92.7
14.6	2004	23.6	89.1	55.6
	2005	20	125.1	63.6
16.4	2004	61.3	186.7	123.4
	2005	44.9	194.6	106.2
16.6	2004	71.5	186.7	125.0
	2005	46.7	208.4	100.9
16.7	2004	125.4	281.4	186.2
	2005	53.3	202	111.5
18	2004	128.9	224.3	182.9
	2005	44.3	298.8	136.0
21.9	2004	88.1	230.9	186.5
	2005	53.1	122.6	98.5
22.4	2004	209.1	345.9	279.3
	2005	37.1	334	142.6
23.7	2004	216.3	319.7	271.3
	2005	86	183.9	119.0
25.7	2004	196.8	330.1	269.7
	2005	65.5	222.2	139.6
26.4	2004	32.8	468.2	230.7
	2005	53.6	955.8	285.2
30.4	2004	59.9	398.4	217.3
	2005	68	1273.3	295.6
34.1	2004	81	400.7	259.4
	2005	68.1	795.8	246.3

Appendix C

NORTH BRANCH DATA

Table C1. Summary statistics for the original reference site on the North Branch of the Meduxnekeag. Samples were not analyzed for TDP in 2005 so TDP and PP values are only for 2004. Values marked as < DL were below the detection limit.

	TP (µg/L)	SRP (µg/L)	TDP (µg/L)	PP (µg/L)	NO_3^- (mg/L)
N	19	20	11	9	20
Minimum	3.7	0.5	2.1	1.0	< DL
Maximum	25.4	1.9	6.9	4.0	0.083
Median	6.6	0.5	3.0	2.3	0.040
Mean	7.5	0.7	3.6	2.3	0.041
Standard Deviation	4.7	0.5	1.4	0.9	0.025

Table C2. Summary statistics of percent algal coverage at the North Branch site split by study year.

Year	Mean %	Median %	Minimum %	Maximum %	Standard Deviation %
2004	4.2	1.9	0.0	15.0	5.8
2005	3.3	0.6	0.0	15.0	5.9

Appendix D

LAND COVER DATA

Table D1. Land cover composition by site subwatershed. Land cover data were part of the USGS National Land Cover Dataset. Numbers across the top correspond to site number by river km.

	0.2	**5**	**14.6**	**16.4**	**16.7**	**18**	**21.9**	**22.4**	**23.7**	**25.7**	**30.4**	**34.1**
open water	10	0.8	1.8	4.3	0.1	0.8	4.3	0.3	3.2	0.3	0.8	1.1
residential	0.1	1.1	0.2	0.8	0.2	0.5	7.6	1.8	60	3.9	2.4	1.2
commercial	0.1	0.3	1.3	0.0	1.0	0.1	9.3	1.0	9.1	6.8	3.6	0.9
forested	86	74	74	31	76	79	38	78	16	61	48	62
shrub	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
orchards	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
pasture	0.1	2.0	2.0	1.5	1.2	0.9	1.7	1.5	0.4	2.1	2.8	2.6
row crop	1.0	16	15	58	17	7.6	31	11	5.9	16	33	27
wetlands	2.9	4.7	5.3	4.4	3.9	10	5.1	5.6	3.1	4.9	7.0	4.5
rock/quarry	0.0	0.0	0.1	0.0	0.0	0.0	1.8	0.0	0.1	0.1	0.1	0.0
transitional	0.0	0.2	0.2	0.0	0.1	0.3	0.1	0.3	0.1	0.1	0.2	0.1
urban/rec grass	0.0	0.6	0.3	0.3	0.3	0.3	1.3	0.4	2.2	4.5	1.5	0.9

Appendix E

PHOTOMICROGRAPHS OF DOMINANT FILAMENTOUS ALGAL SPECIES

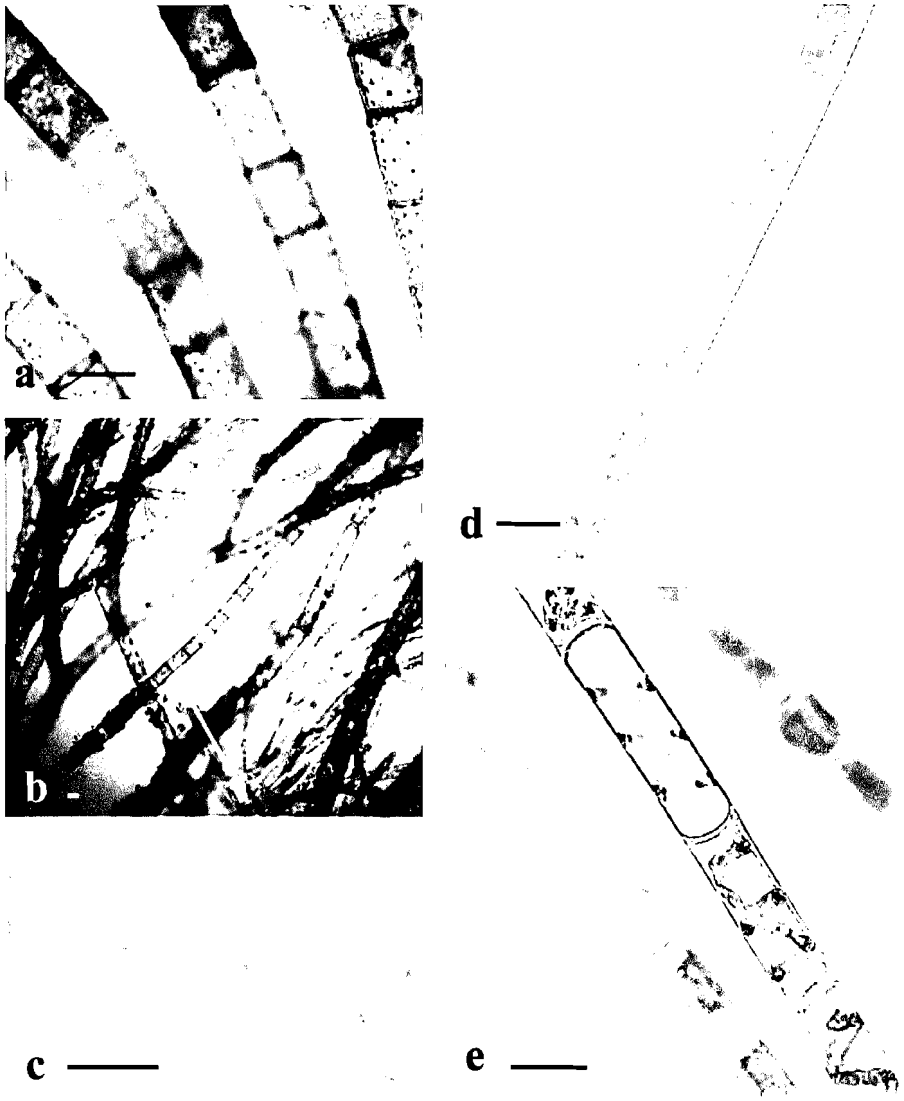

Figure E1. Photomicrographs of algae collected from the Meduxnekeag River (scale = 50μm). a) *Oedogonium*, b) *Cladophora* (except for the *Oedogonium* filament indicated by the arrow), c) *Mougeotia*, d) *Zygnema*, and e) *Spirogyra*. No image was available for *Microspora*.

BIOGRAPHY OF THE AUTHOR

Elizabeth ("Lisa") Fretwell was born in Richmond, Virginia, on September 19, 1979. She grew up outside of Richmond and graduated from James River High School in 1997. She then attended Virginia Tech in Blacksburg, Virginia, and graduated magna cum laude in December 2000 with a Bachelor's degree in Environmental Science. While at Virginia Tech, she interned at the North Carolina Aquarium on Roanoke Island, worked for a year at the Virginia Water Resources Research Institute, and spent a semester on exchange at the University of West Florida in Pensacola, Florida.

After graduation, she worked for an environmental consulting firm outside of Washington, D.C. developing floodplain maps, conducting environmental reviews, and working on various natural resource projects. She then moved to Maine in the summer of 2003 and received a research assistantship from the George Mitchell Center for Watershed and Environmental Research to pursue a graduate degree in Ecology and Environmental Science with a focus on water resources. She is a Certified Floodplain Manager and a member of the Association of State Floodplain Managers and the American Fisheries Society.

After receiving her degree, Lisa plans to move to the Upper Peninsula of Michigan and find a job in watershed management. Lisa is a candidate for the Master of Science degree in Ecology and Environmental Science from The University of Maine in May, 2006.