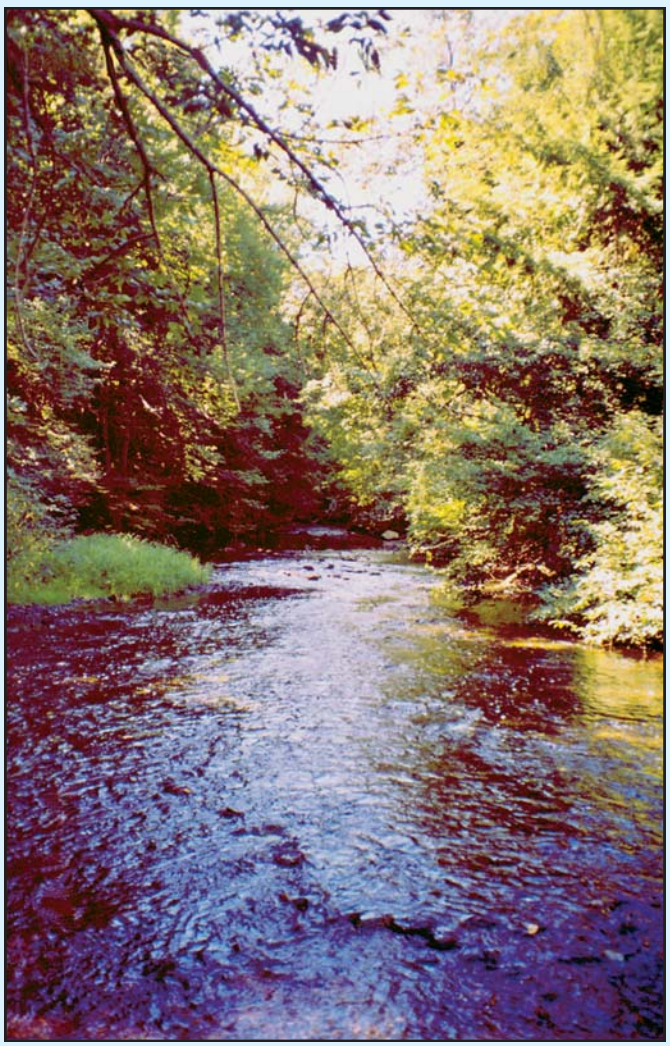
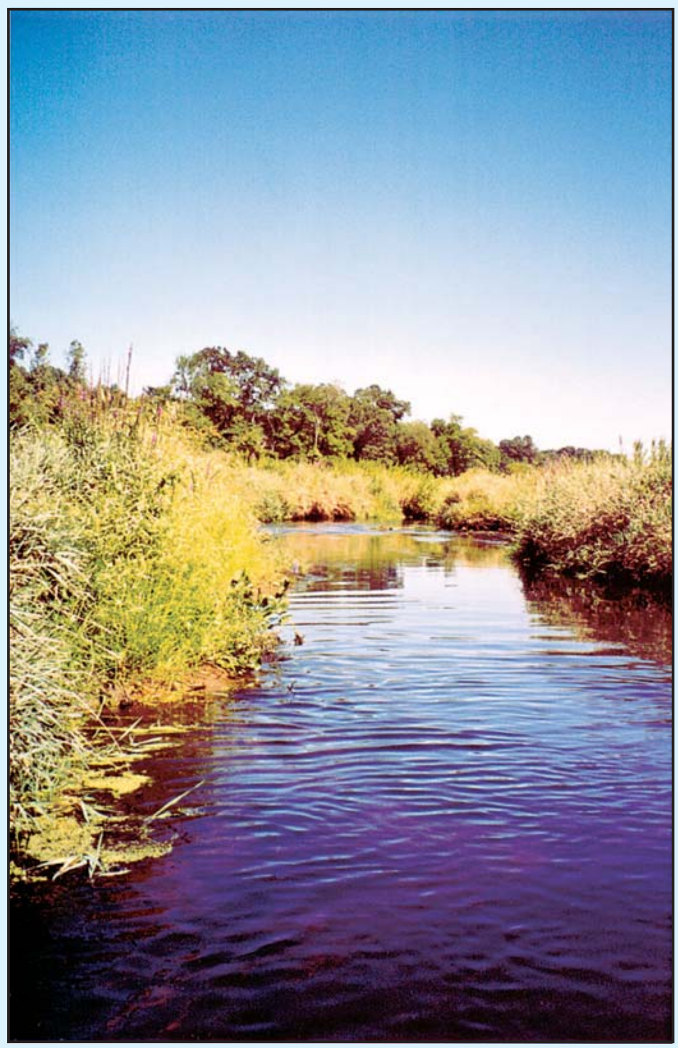
science for a changing world

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Nutrient and Chlorophyll Relations in Selected Streams of the New England Coastal Basins in Massachusetts and New Hampshire, June-September 2001

Water-Resources Investigations Report 03-4191





U.S. Department of the Interior
U.S. Geological Survey

Nutrient and Chlorophyll Relations in Selected Streams of the New England Coastal Basins in Massachusetts and New Hampshire, June-September 2001

By Melissa L. Riskin, Jeffrey R. Deacon, Matthew L. Liebman, *and* Keith W. Robinson

---

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 03-4191

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Pembroke, New Hampshire
2003

U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

For additional information write to:

District Chief
U.S. Geological Survey
New Hampshire/Vermont District
361 Commerce Way
Pembroke, NH 03275-3718
http://nh.water.usgs.gov

Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Building 810
Box 25286, Federal Center
Denver, CO 80225-0286

FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. (http://www.usgs.gov/). Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity *and* quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. (http://water.usgs.gov/nawqa/). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. (http://water.usgs.gov/nawqa/nawqamap.html). Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings. (http://water.usgs.gov/nawqa/natsyn.html).

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch

Associate Director for Water

CONTENTS

FIGURES

TABLES

CONVERSION FACTORS AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square mile (mi^2)	2.590	square kilometer (km^2)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F=1.8 °C+32.

Concentrations of nutrients are reported in milligrams per liter (mg/L).

Concentrations of phytoplankton are reported in micrograms of chlorophyll *a* per liter (μg/L).

Concentrations of periphyton are reported in milligrams of chlorophyll *a* per square meter (mg/m^2).

Water volumes are reported in milliliters (mL).

ABBREVIATIONS USED IN REPORT

EWI	Equal Width Increment
NAWQA	National Water-Quality Assessment Program
NECB	New England Coastal Basins
NWIS	National Water Information System
NWQL	National Water-Quality Laboratory
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Nutrient and Chlorophyll Relations in Selected Streams of the New England Coastal Basins in Massachusetts and New Hampshire, June-September 2001

By Melissa L. Riskin[1], Jeffrey R. Deacon[1], Matthew L. Liebman[2], and Keith W. Robinson[1]

ABSTRACT

The U.S. Environmental Protection Agency is developing guidance to assist states with defining nutrient criteria for rivers and streams and to better describe nutrient-algal relations. As part of this effort, 13 wadeable stream sites were selected, primarily in eastern Massachusetts, for a nutrient-assessment study during the summer of 2001. The sites represent a range of water-quality impairment conditions (reference, moderately impaired, impaired) based on state regulatory agency assessments and previously assessed nitrogen, phosphorus, and dissolved-oxygen data. In addition, a combination of open- and closed- canopy locations were sampled at six of the sites to investigate the effect of sunlight on algal growth. Samples for nutrients and for chlorophyll *a* from phytoplankton and periphyton were collected at all stream sites.

Total nitrogen (dissolved nitrite + nitrate + total ammonia + organic nitrogen) and total phosphorus (phosphorus in an unfiltered water sample) concentrations were lowest at reference sites and highest at impaired sites. There were statistically significant differences ($p < 0.05$) among reference, moderately impaired, and impaired sites for total nitrogen and total phosphorus. Chlorophyll *a* concentrations from phytoplankton were not significantly different among site impairment designations. Concentrations of chlorophyll *a* from periphyton were highest at nutrient-impaired open-canopy sites. Chlorophyll *a* concentrations from periphyton samples were positively correlated with total nitrogen and total phosphorus at the open- and closed-canopy sites. Correlations were higher at open-canopy sites ($p < 0.05$, rho = 0.64 to 0.71) than at closed-canopy sites ($p < 0.05$, rho = 0.36 to 0.40). Statistically significant differences in the median concentrations of chlorophyll *a* from periphyton samples were observed between the open- and closed-canopy sites ($p < 0.05$).

Total nitrogen and total phosphorus data from moderately impaired and impaired sites in this study exceeded the preliminary U.S. Environmental Protection Agency nutrient criteria values for the coastal region of New England. In an effort to establish more appropriate nutrient and chlorophyll criteria for streams in the New England coastal region, relations between total nitrogen and total phosphorus to periphyton chlorophyll *a* in wadeable streams from this study were quantified to present potential techniques for determining nutrient concentrations. Linear regression was used to estimate the total nitrogen and total phosphorus concentrations that corresponded to various chlorophyll *a* concentrations. On the basis of this relation, a median concentration for moderately enriched streams of 21 milligrams per square meter

---

[1]U.S. Geological Survey.

[2]U.S. Environmental Protection Agency.

(mg/m^2) of periphyton chlorophyll *a* from the literature corresponded to estimated concentrations of 1.3 milligrams per liter (mg/L) for total nitrogen and 0.12 mg/L for total phosphorus. The median concentration for periphyton chlorophyll *a* from the literature is similar to the 50th-percentile concentration of periphyton chlorophyll *a* (17 mg/m^2) calculated with the data from open-canopy sites in this study. The 25th-percentile concentration for periphyton chlorophyll *a* of all open-canopy sites (5.2 mg/m^2) and the 75th-percentile concentration for periphyton chlorophyll *a* of open-canopy reference sites (16 mg/m^2) also were plotted to provide additional estimates and methods for developing total nitrogen and total phosphorus criteria.

The 25th-percentile concentrations of total nitrogen and total phosphorus were calculated based on all sites in this study and were used as another potential criteria estimation. A concentration of 0.64 mg/L for total nitrogen and 0.030 mg/L for total phosphorus were calculated. As another possible method to develop threshold concentrations, the 10th-percentile concentrations of total nitrogen and total phosphorus were calculated based on all the impaired sites in this study. A concentration threshold of 0.73 mg/L for total nitrogen and 0.036 mg/L for total phosphorus were calculated. Ultimately, a combination of these techniques may be appropriate for water-resources managers to use to set regional nutrient criteria to limit undesirable levels of algal growth in streams.

NTRODUCTION

Nutrients are essential to the health and diversity of surface waters. In excessive amounts, however, they can be harmful. Chronic symptoms of excessive nutrient enrichment include algal blooms, low dissolved oxygen, fish kills, turbid water, and loss of desirable flora and fauna. Human activities that may affect levels of algal biomass include (1) discharge of nutrient-rich wastewater; (2) development that increases impervious surfaces in the drainage basin; (3) reduction of flows; (4) removal of streamside vegetation, which increases light and the flux of nutrients and sediment from riparian zones because of reduced uptake from plants; and (5) construction of residential development with individual septic systems (U.S. Environmental Protection Agency, 2000a).

Factors that control the response of algal biomass to nutrient inputs include hydrologic disturbance, days of algal accrual (Biggs, 2000), light availability (Spahr and Deacon, 1998), turbidity, consumption of algae by invertebrate grazers (Deacon and Spahr, 1998), and possible toxic responses associated with herbicides and other organic contaminants. The importance of any one or any combination of these factors in limiting the growth of algae appears to vary among streams. Nutrient concentrations and light availability, however, often are regarded as the most important factors affecting the primary production in streams that may result in excessive algal growth (Mosisch and others, 1999). Light can be a limiting factor in small streams where there is dense riparian cover. Kjeldsen (1996) found that differences in algal growth between a shaded stream reach and an unshaded stream reach were highly significant ($p < 0.05$) if the sampling reaches differed only with respect to light availability but the water chemistry and other physical factors remained the same. Welch and others (1992) found that lower than expected algal biomass levels were associated with riparian shading and high macroinvertebrate-grazer densities.

Approaches for assessing the effects of nutrients on algae in streams and rivers are not as well developed as the approaches for lakes. For lakes and reservoirs, a strong quantitative framework has been developed over the past three decades that allows prediction of algal biomass and other water-quality parameters from nutrient loading and nutrient concentrations; however, there is no generally accepted system for classifying streams and rivers (Reckhow, 1979). The U.S. Environmental Protection Agency (USEPA) has developed guidance to assist states in developing nutrient and algal criteria for rivers and streams to protect water quality for designated uses from impairment (U.S. Environmental Protection Agency, 2000a).

Nutrient concentrations that lead to water-quality degradation and impairment of designated use (for example, recreation and aquatic life) differ because of regional variations in geology, climate, and soil types. To be most effective, therefore, water-quality criteria need to take into account ecoregional variations (U.S. Environmental Protection Agency, 2000a). Currently (2003), most states use qualitative criteria based on “best professional judgment” to assess impairment. To control nutrient loading to streams more effectively, however, quantitative nutrient criteria would be valuable to water-resources managers. The numerical criteria could translate qualitative criteria into quantitative endpoints and range along the transition from a desirable mesotrophic (moderately enriched) condition to an undesirable eutrophic condition.

The USEPA has established preliminary recommendations for reference concentrations of total nitrogen and total phosphorus in rivers and streams for ecoregions of the country. These concentrations represent the 25th-percentile concentrations of nitrogen and phosphorus for all sites, which are expected to prevent nuisance algal growths. Concentration thresholds based on the 25th percentile from all sites for USEPA subecoregion 59 (the region of this study) are 0.57 milligram per liter (mg/L) for total nitrogen (dissolved nitrite + nitrate + total ammonia + organic nitrogen) and 0.024 mg/L for total phosphorus (phosphorus in an unfiltered water sample) (U.S. Environmental Protection Agency, 2000b). Another method is to choose the 75th percentile of concentrations of total nitrogen and total phosphorus from a reference population of streams that are minimally affected. Analyses of national nutrient data to date indicate that the 25th percentile from an entire population roughly approximates the 75th percentile for a reference population (U.S. Environmental Protection Agency, 2000b). Although the USEPA did not publish preliminary recommendations for concentrations of periphyton chlorophyll *a* to maintain suitable levels of algal growth in streams, according to Biggs (1996), streams with chlorophyll *a* concentrations of 100 milligrams per square meter (mg/m^2) or greater for periphyton are generally characterized as eutrophic.

Currently, because of the lack of nutrient and algal data for New England streams, it is difficult to define a precise range of nitrogen and phosphorus concentrations that would promote excessive algal growth and result in water-quality impairments. In an effort to define such a range for the New England Coastal Basins (fig. 1), the U.S. Geological Survey (USGS) National Water-Quality Assessment Program (NAWQA) performed a study from June through September 2001 to derive more quantitative relations between total nitrogen and total phosphorus to periphyton chlorophyll *a* in wadeable streams in the Northeastern Coastal Zone (fig. 1).

Purpose and Scope

The objective of this report is to develop potential methods that could guide water-resource managers in the development of nutrient criteria for New England streams on the basis of water-quality data collected at sites in the New England Coastal Basins study area. This report (1) summarizes water-quality data at selected wadeable streams, (2) examines the response of algae to nutrients and incident light (as measured by tree canopy) from June through September 2001, and (3) provides potential methods for nutrient-criteria development. The results presented are relevant only to the data analysis performed in this study. However, examples are presented in this report of how nutrient criteria could be developed by water-resource managers for the Northeastern Coastal Zone.

Description of Study Area

The New England Coastal Basins (NECB) study area is a 23,000 square mile (mi^2) area that encompasses central Maine, eastern New Hampshire, eastern Massachusetts, and Rhode Island. Major rivers in the NECB study area include the Kennebec, Androscoggin, Saco, Merrimack, Charles, and Blackstone Rivers. Land use in the NECB study area consists of 74 percent forest, 11 percent urban development, 8 percent surface-water bodies, and 6 percent agriculture (Flanagan and others, 1999). A more detailed description of the physical and cultural settings of the NECB study area is found in Flanagan and others (1999). All sites for this specific investigation were in subecoregion 59 of the NECB, which is the Northeastern Coastal Zone (fig. 1).

Thirteen wadeable stream sites, primarily in eastern Massachusetts, were selected on the basis of previous nitrogen, phosphorus, and dissolved oxygen data. Six of the 13 sites were classified as impaired because of existing nutrient problems, low levels of dissolved oxygen, or extensive algal growth. Five of

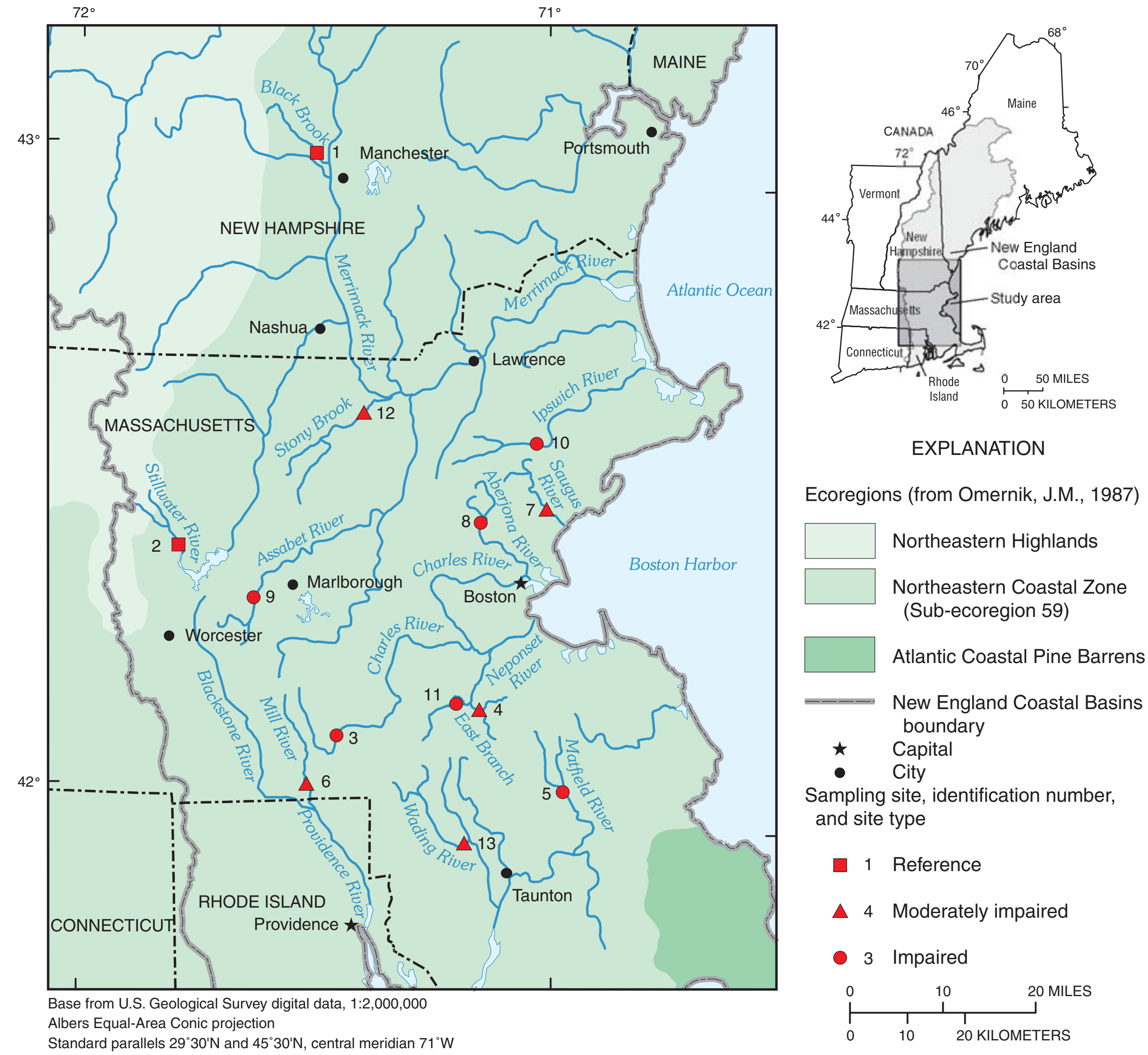


Figure 1. Sampling sites, site-identification numbers, and site types in the New England Coastal Basins study area in Massachusetts and New Hampshire. (Site identification numbers are show in table1.)

these sites were considered impaired, or not meeting narrative standards, on the basis of the State's 305(b) water-quality report or Clean Water Act 303(d) list (U.S. Environmental Protection Agency, 2002; Commonwealth of Massachusetts, 1999). The sixth site was classified as impaired because previous water samples collected at that site had nutrient concentrations that greatly exceeded preliminary standards. Five additional sites were selected on the basis of previous water-quality data (Karen Beaulieu, U.S. Geological Survey, written commun., 2002). Water samples collected at these sites were categorized as moderately impaired because their total nitrogen and total phosphorus concentrations slightly exceeded preliminary standards for subecoregion 59. Two additional sites were selected to represent reference conditions (table 1, fig. 1).

Riparian zones dominated by trees that provided substantial canopy cover (closed canopy) characterized all 13 sites. Additional locations with increased patchiness of riparian-tree cover provided an unshaded stream-sampling area (open canopy) at 6 of the 13 sites where supplementary periphyton samples were collected to compare with data from the closed-canopy sites.

Table 1. Selected characteristics for the study sites in the New England Coastal Basins study area in Massachusetts and New Hampshire

[No., number; fig., figure; mi^2, square mile; --, no impairment designation; latitude and longitude are given in degrees °, minutes ′, and seconds ″]

Site No. (fig. 1)	Site name	USGS station No.	Site type	Impairment justification	Canopy	Latitude	Longitude	Drainage area (mi^2)
1	Black Brook, Dunbarton Road near Manchester, N.H.	01090477	Reference	--	Open[4] Closed[5]	43°01′31″	71°30′17″	20.72
2	Stillwater River near Sterling, Mass.	01095220	Reference	--	Open Closed	42°24′39″	71°47′30″	31.6
3	Charles River at Maple Street at North Bellingham, Mass.	011032058	Impaired	305b report[1] 303d list[2]	Closed	42°07′11″	71°27′10″	21.0
4	East Branch Neponset River at Canton, Mass.	01105504	Moderately impaired	Nutrients exceed standards[3]	Closed	42°09′31″	71°09′17″	28.13
5	Matfield River at North Central Street at East Bridgewater, Mass.	01106468	Impaired	Nutrients greatly exceed standards	Open Closed	42°02′01″	71°58′21″	30.61
6	Mill River at Summer Street near Blackstone, Mass.	01112262	Moderately impaired	Nutrients exceed standards	Open Closed	42°02′27″	71°30′56″	28.46
7	Saugus River at Saugus Ironworks at Saugus, Mass.	01102345	Moderately impaired	Nutrients exceed standards	Closed	42°28′05″	71°00′27″	23.3
8	Aberjona River (head of Mystic River) at Winchester, Mass.	01102500	Impaired	303d list	Closed	42°26′50″	71°08′22″	24.1
9	Assabet River at Allen Street at Northborough, Mass.	01096710	Impaired	305b report 303d list	Open Closed	42°19′46″	71°37′48″	29.5
10	Ipswich River at South Middleton, Mass.	01101500	Impaired	305b report 303d list	Closed	42°34′10″	71°01′39″	44.5
11	Neponset River at Norwood, Mass.	01105000	Impaired	305b report 303d list	Closed	42°10′39″	71°12′05″	34.7
12	Stony Brook at School Street at Chelmsford, Mass.	01096544	Moderately impaired	Nutrients exceed standards	Open Closed	42°37′04″	71°24′08″	41.6
13	Wading River (head of Threemile River) near Norton, Mass.	01109000	Moderately impaired	Nutrients exceed standards	Closed	41°56′51″	71°10′38″	43.3

[1] U.S. Environmental Protection Agency, 2002, Waterbody system database for the Clean Water Act for 305(b) reporting.
[2] Commonwealth of Massachusetts, Final Massachusetts section 303(d) list of waters, 1998.
[3] Previous data shows that site exceeded U.S. Environmental Protection Agency preliminary standards.
[4] Sampling site located in an open-canopy section of the stream.
[5] Sampling site located in a closed-canopy section of the stream.

Acknowledgments

The authors thank Karen Beaulieu, Kimberly Campo, and Maureen Thomas for their assistance with field work. The authors also thank Stephen Porter, USGS Denver, Colo., and Jacob Gibs, USGS West Trenton, N.J., for their critical review of the manuscript. Appreciation is extended to the following USGS employees: Ann Marie Squillacci for manuscript preparation, Laura Hayes and Anita Cotton for graphics assistance, and Matthew Cooke and Mary Ashman for editorial review of this report.

DATA-COLLECTION AND ANALYSIS

This study was designed to measure nutrient and chlorophyll *a* concentrations for a range of wadeable sites from reference to nutrient-impaired conditions and to compare data from open- and closed-canopy sites in the same stream. Samples for nutrients and chlorophyll *a* from phytoplankton and periphyton were collected at all 13 sites. Seven field-blank and 10 field-replicate samples were collected throughout the sampling period for nutrients and chlorophyll *a*. Total nitrogen, total phosphorus, and periphyton chlorophyll *a* are the primary constituents discussed in this report. Statistical analyses were completed on the nutrient and algal data.

Sample Collection

Each of the 13 sites was sampled on 5 occasions between June through September 2001. Streams were sampled during the summer in an effort to capture changes in biomass throughout the "growing season." The equal-width increment (EWI) technique was used to obtain a representative water sample at each site. The samples were then processed in the field according to standard surface-water-collection protocols (Shelton, 1994). Samples were packed on ice and sent to the USGS National Water-Quality Laboratory (NWQL) in Denver, Colo., for analysis. Inorganic constituents were analyzed using methods cited in Fishman (1993) and Fishman and Friedman (1989). Field measurements for each sample included water temperature, dissolved oxygen, pH, specific conductance, and stream discharge. Field measurements, nutrients, and major ion data are stored in the USGS National Water Information System (NWIS) and published in the USGS Annual Water Data Report (Coakley and others, 2001; and Socolow and others, 2001).

Chlorophyll *a* was measured in phytoplankton and periphyton samples to estimate the algal biomass at the sampling sites. Phytoplankton measurements were determined by filtering 500 mL of water through a glass-fiber filter. The filter was then wrapped in foil, placed in a petri dish, and immediately put on dry ice for shipment to the USGS NWQL for chlorophyll *a* determination (Porter and others, 1993). Chlorophyll *a* in phytoplankton was analyzed by methods in Arar and Collins (1997). Periphyton samples were collected from five representative rocks in riffle areas by scraping the algae from the rock surface. The scraped area was estimated by fitting an equivalent area of aluminum foil to the scraped section, using the foil-template method (Porter and others, 1993). Two subsamples of algal slurry were filtered, stored on dry ice, and sent to the USGS NWQL for chlorophyll *a* and ash-free dry-mass determinations (Arar and Collins, 1997).

At each site, the open-canopy angle was used to assess the amount of direct sunlight reaching the stream. The left and right canopy angles were measured with a handheld clinometer and the percentage of open canopy was calculated (Fitzpatrick and others, 1998).

Quality Assurance

Field blanks provide information on the potential for bias due to contamination of analytical results by sample collection, processing, shipping, and analysis. A field-blank sample is processed with water free of the analytes of interest. The blank water is passed through all the sampling equipment, processed as a regular water-quality sample, and analyzed for all water-quality constituents. Analytical results from the seven field-blank samples indicated that concentrations for constituents discussed in this report were less than the laboratory reporting level.

Replicate samples provide information on the variability of analytical results caused by sample collection, processing, shipping, and analysis. Differences in concentrations between environmental and replicate samples for nutrients were generally less than 0.01 mg/L. Differences in concentrations between environmental and replicate samples for periphyton chlorophyll *a* were less than 2 mg/m^2.

Statistical Methods

A Spearman rho correlation test was used to determine relations between nutrient concentrations in the water column to chlorophyll *a* concentrations in phytoplankton and periphyton. Correlations were considered significant if the probability was less than 5 percent ($p < 0.05$). The Kruskal-Wallis statistical test (Helsel and Hirsch, 1992) with an alpha value of 0.05 was performed on nutrient concentrations and chlorophyll *a* concentrations to determine if there were significant differences among the groups of data for each of the three site types. If results from the Kruskal-Wallis test indicated significant differences, a Tukey's multiple comparison test (Helsel and Hirsch, 1992) was used to determine which site types differed significantly. Linear regression analysis was used to determine the relation between total nitrogen or total phosphorus and chlorophyll *a* concentrations. All statistical analyses were performed using Statview Statistical Software (SAS Institute, Inc., 1998).

CHARACTERIZATION OF NUTRIENTS AND CHLOROPHYLL

Median concentrations of total nitrogen and total phosphorus exceeded the preliminary recommended criteria set by the USEPA for subecoregion 59 at 11 of the 13 sites. Periphyton chlorophyll *a* data from the six open-canopy sites were selected to determine the association between total nitrogen and total phosphorus concentrations and chlorophyll *a* concentrations because these sites represented areas of greatest nutrient and algal concentrations.

Nutrients

Summary statistics for nutrients are listed in table 2. Selected percentile statistics for total nitrogen and total phosphorus are summarized in table 3. The two reference sites were the only streams with median nutrient concentrations less than the USEPA preliminary recommendations for total nitrogen and total phosphorus (figs. 2 and 3). Median total nitrogen and total phosphorus concentrations were significantly different ($p < 0.05$) among all three site types (figs. 2 and 3). Among the streams sampled, concentrations of total nitrogen and total phosphorus were highest at the Matfield and Assabet Rivers. It is well documented that point sources are the major impact to the Assabet River especially during the summer low flow (ENSR International, 2000). In addition, a wastewater-treatment plant upstream of the Matfield River site may be the primary source of nutrient loading to this water body. Nutrient concentrations were also high at the Aberjona River, which may be a result of the heavily urbanized drainage basin. Eleven of the sites were nitrogen and phosphorus limited and two sites were only phosphorus limited based on ratios of dissolved nutrient concentrations.

Chlorophyll

Summary statistics for chlorophyll *a* from phytoplankton and periphyton samples and ash-free-dry mass are listed in table 2. Selected percentile statistics for periphyton chlorophyll *a* are summarized in table 3. Chlorophyll *a* concentrations were higher at the open-canopy sites than the closed-canopy sites (table 3). There were no significant relations between chlorophyll *a* in phytoplankton and total nitrogen and total phosphorus. However, chlorophyll *a* concen-trations from periphyton samples increased significantly with total nitrogen and total phosphorus concentrations at the open- and closed-canopy sites. Correlation coefficients were higher at the open-canopy sites (rho = 0.64 to 0.71) than at the closed-canopy sites (rho = 0.36 to 0.40). This indicates that light affected the algal biomass and the relation between nutrient and chlorophyll *a* concentrations. There was no significant temporal variation in phytoplankton or periphyton samples collected throughout the sampling period.

Median concentrations of periphyton chlorophyll *a* were highest at nutrient-impaired sites (table 2). There were significant differences ($p < 0.05$) in median periphyton chlorophyll *a* concentrations among all three site types for open-canopy sampling sites (fig. 4). There were significant differences between reference and impaired sites and between moderately impaired and impaired sites at the closed-canopy sampling locations, but not between reference and moderately impaired sites (fig. 5). Concentrations of chlorophyll *a* from periphyton were significantly higher ($p < 0.05$) at open-canopy sites than at closed-canopy sites. Chlorophyll *a* concentrations from phytoplankton were not significantly different among site designations. This suggests that periphyton may be a better indicator of eutrophication than phytoplankton in wadeable NECB streams, regardless of canopy conditions.

Comparison of periphyton chlorophyll *a* concentrations from the six sampling sites that had open- and closed-canopies indicated that open-canopy sites had higher concentrations of chlorophyll *a* among all three site types (fig. 6). Periphyton chlorophyll *a* concentrations from samples collected at closed-

Table 2. Summary of selected nutrient and chlorophyll *a* concentrations (open- and closed-canopy sites) for the study site types in the New England Coastal Basins study area in Massachusetts and New Hampshire

[Sites sampled five times between June 1 and September 30, 2001; mg/L, milligrams per liter; Min, minimum; Max, maximum; µg/L, micrograms per liter; mg/m^2, milligrams per square meter; g/m^2, grams per square meter; <, less than]

Site type	Total nitrogen (dissolved nitrite + nitrate + total ammonia + organic nitrogen) (mg/L)			Dissolved inorganic nitrogen (dissolved nitrite + nitrate + dissolved ammonia) (mg/L)			Total phosphorus (phosphorus in an unfiltered water sample) (mg/L)			Dissolved phosphorus (mg/L)			Dissolved ammonia (mg/L)		
	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Reference	0.32	0.44	0.54	0.07	0.13	0.22	0.006	0.019	0.043	< 0.006	0.009	0.013	< 0.041	< 0.041	< 0.041
Moderately impaired	.49	.78	2.2	.12	.26	1.5	.016	.039	.072	.009	.017	.041	< .041	< .041	.074
Impaired	.64	2.2	10	.08	1.5	9.2	.024	.055	.905	< .006	.025	.899	< .041	< .041	2.5

Site type	Dissolved nitrite + nitrate (mg/L)			Dissolved nitrite (mg/L)			Orthophosphate (mg/L)			Nitrogen ammonia + organic total (mg/L)			Nitrogen ammonia + organic dissolved (mg/L)		
	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Reference	<0.047	0.090	0.202	< 0.006	< 0.006	< 0.006	< 0.020	< 0.020	< 0.020	0.23	0.34	0.41	0.11	0.27	0.33
Moderately impaired	.086	.231	1.4	< .006	< .006	.056	< .020	< .020	< .020	.28	.49	2.0	.23	.36	1.1
Impaired	.055	.921	6.7	< .006	.014	.436	< .020	< .020	.812	.35	.66	3.8	.31	.58	3.7

Site type	Chlorophyll *a* from phytoplankton (µg/L)			Chlorophyll *a* from periphyton (mg/m^2)			Ash-free dry mass (g/m^2)		
	Min	Median	Max	Min	Median	Max	Min	Median	Max
Reference	0.40	1.3	5.5	1.4	5.4	22	1.6	6.4	17
Moderately impaired	.30	1.2	16	.50	5.2	59	2.7	8.4	39
Impaired	.30	1.4	22	.30	17	166	2.4	15	70

Table 3. Percentile statistics of total nitrogen, total phosphorus, and periphyton chlorophyll *a* concentrations for the study sites in the New England Coastal Basins study area in Massachusetts and New Hampshire

[n, number of samples; mg/L, milligrams per liter; mg/m^2, milligrams per square meter]

	Minimum	25th percentile	50th percentile	75th percentile	Maximum	n
Total nitrogen (mg/L)	0.32	0.64	0.90	2.1	10	65
Total phosphorus (mg/L)	.006	.030	.044	.065	.905	65
Periphyton chlorophyll *a*[1] (mg/m^2)	2.2	5.2	17	41	166	30
Periphyton chlorophyll *a*[2] (mg/m^2)	.30	3.3	6.0	15	52	65

[1] Open-canopy sites.
[2] Closed-canopy sites.

canopy reference and moderately impaired sites were less than the median literature value for moderately enriched streams (21 mg/m^2) (Biggs, 1996). Chlorophyll *a* concentrations from most samples collected at closed-canopy impaired sites had concentrations greater than the median literature value for moderately enriched streams. Chlorophyll *a* concentrations from samples collected at open-canopy sites had higher ranges of chlorophyll *a* concentrations than those at closed-canopy sites for all three site types. Generally, most of the chlorophyll *a* concentrations from open-canopy reference and moderately impaired sites had concentrations less than the median literature value for moderately enriched streams (fig. 6). Chlorophyll *a* concentrations from open-canopy impaired sites, however, were generally between the median literature value for moderately enriched and enriched streams (fig. 6). Nutrient concentrations, types of substrate, and stream velocities were similar between the closed- and open-canopy sampling locations at the same site, indicating that light is affecting algal biomass as measured by chlorophyll *a*.

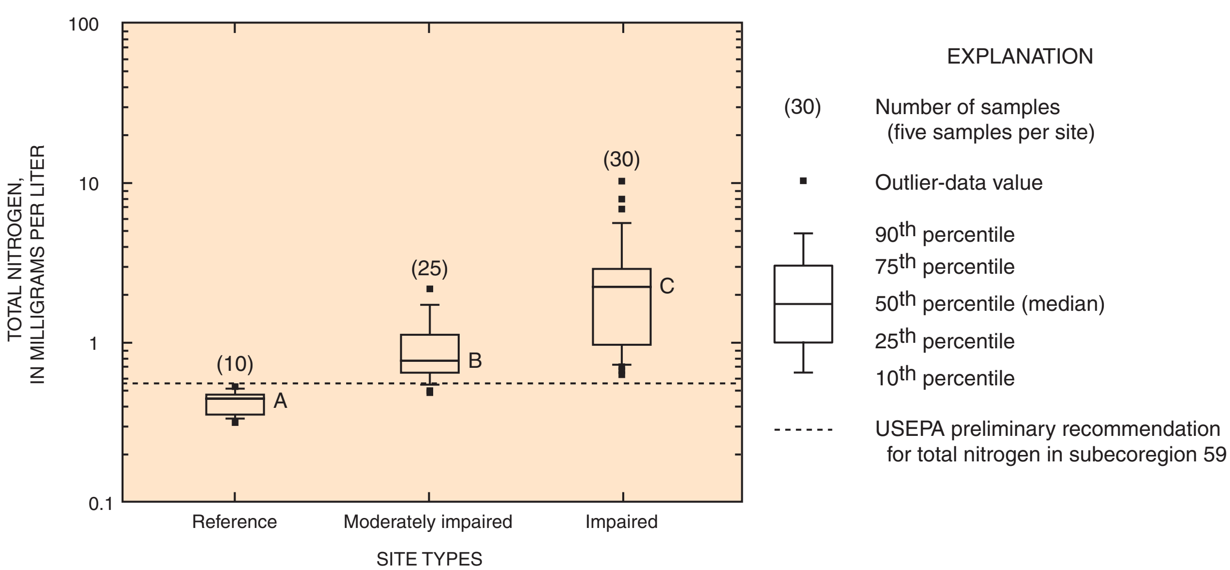


Figure 2. Total nitrogen concentrations among site types in New England Coastal Basins study area. [Result of Tukey's multiple-comparison test [Helsel and Hirsch, 1992] among groups are presented as letters, and concentrations with at least one letter in comon do not differ significantly; for example, concentrations among all three groups differ significantly.

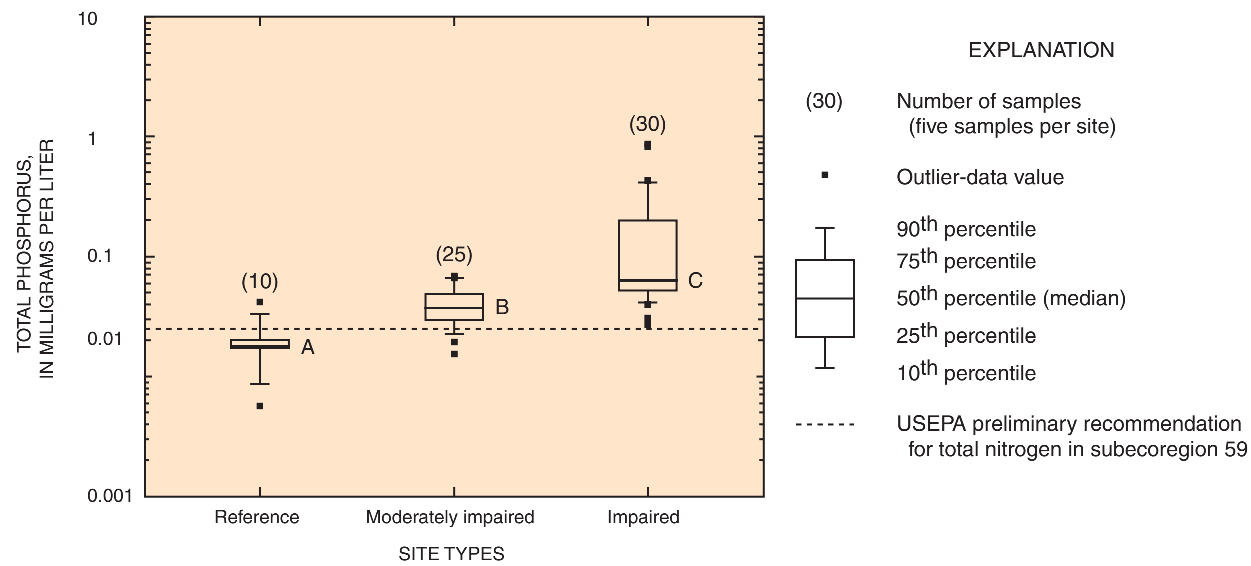


Figure 3. Graph showing Total phosphorus concentrations among site types in the New England Coastal Basins study area. (Results of Tukey's multiple-comparison test [Helsel and Hirsch, 1992] among groups are presented as letters, and concentrations with at least one letter in common do not differ significantly; for example, concentrations among all three groups differ significantly.)

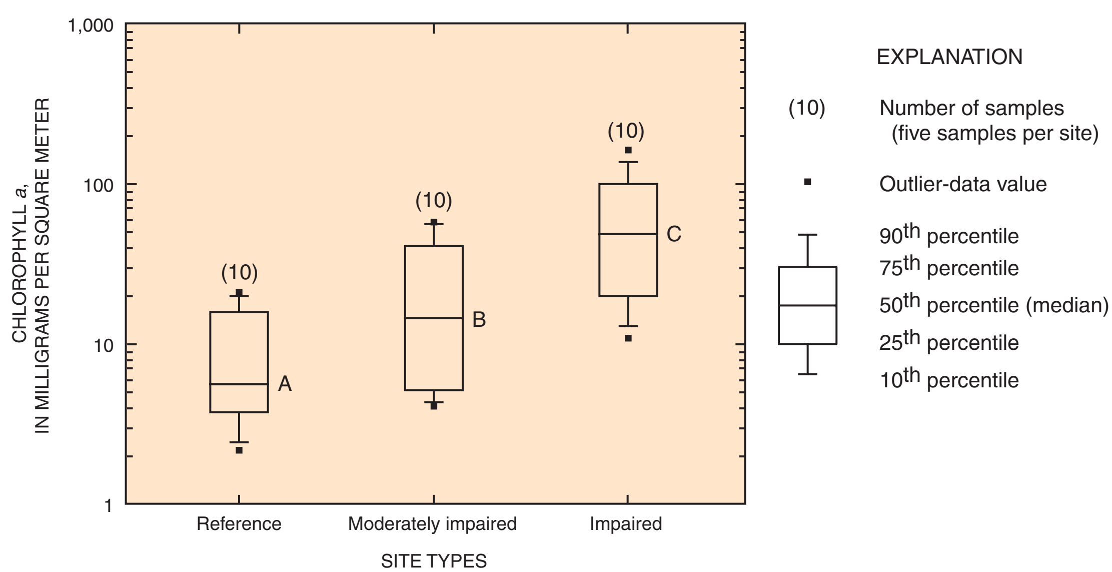


Figure 4. Graph showing Chlorophyll *a* from periphyton samples among site types at the open-canopy locations in the New England Coastal Basins study area. (Results of Tukey's multiple-comparison test [Helsel and Hirsch, 1992] among sites are presented as letters, and concentrations with at least one letter in common do not differ significantly; for example, concentrations among all three groups differ significantly.)

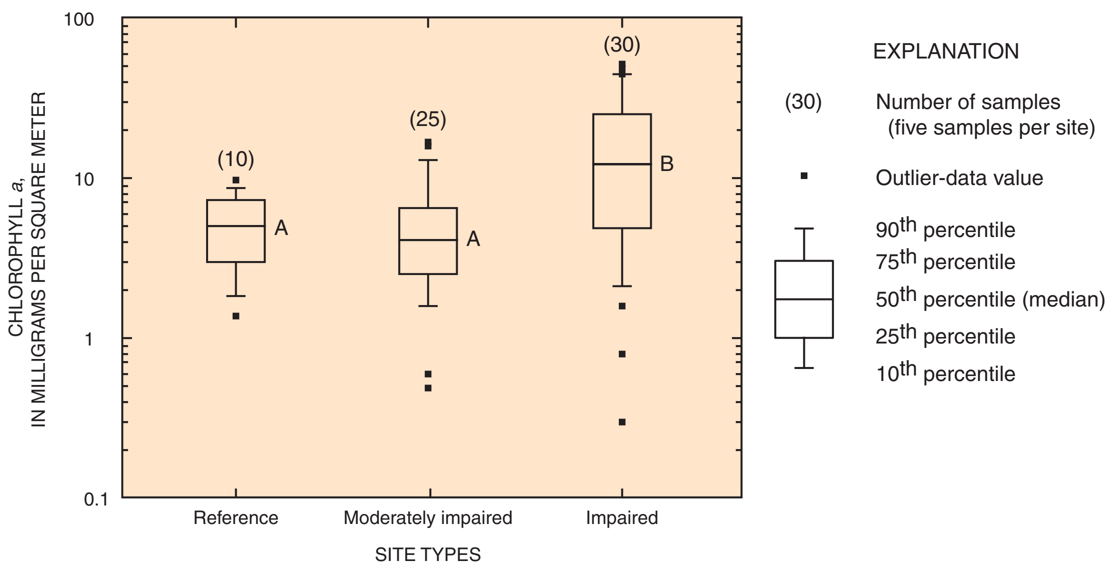


Figure 5. Graph showing Chlorophyll *a* from periphyton samples among site types at the closed-canopy locations in the New England Coastal Basins study area. (Results of Tukey's multiple-comparison test [Helsel and Hirsch, 1992] among sites are presented as letters, and concentrations with at least one letter in common do not differ significantly; for example, concentrations between the reference and moderately impaired sites do not differ significantly.)

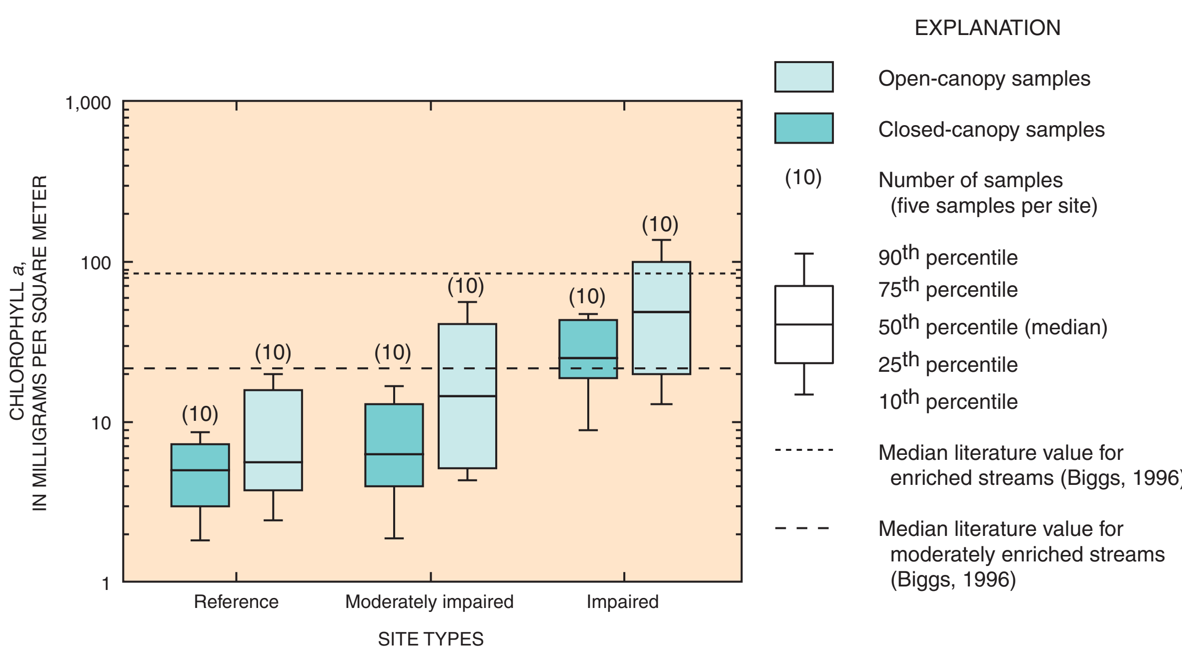


Figure 6. Graph showing Chlorophyll *a* from periphyton samples among site types at the six sites with open- and closed-canopy sampling locations in the New England Coastal Basins study area.

APPLICATION OF NUTRIENT AND CHLOROPHYLL *a* DATA TO IN-STREAM CRITERIA DEVELOPMENT BY WATER-RESOURCES MANAGERS

The nutrient and chlorophyll data collected for this study can provide information useful for nutrient-criteria development. One approach is to use linear regression to estimate the total nitrogen and total phosphorus concentrations that corresponded to various chlorophyll *a* concentrations at open-canopy sites (figs. 7 and 8). The periphyton chlorophyll *a* concentration at which a stream is considered mesotrophic can be identified on the regression line, and the corresponding nutrient concentrations may be applicable as estimates for setting nutrient criteria. The mesotrophic concentration should be used rather than the eutrophic concentration because this criterion is intended to prevent the adverse effects of nutrient enrichment. Biomass data from multiple studies including Lock (1981), Horner and others (1983),Bott and others (1985), and Biggs and Price (1987) were summarized by Biggs (1996) to determine typical algal biomass concentrations for different site types according to levels of nutrient enrichment. On the basis of these data, the median concentration of periphyton chlorophyll *a* from moderately enriched streams (mesotrophic) was determined to be 21 mg/m^2, which is similar to the 50th-percentile concentration of periphyton chlorophyll *a* (17 mg/m^2) calculated with the data from all open-canopy sites in this study. An estimated concentration of 1.3 mg/L for total nitrogen and 0.12 mg/L for total phosphorus corresponded to the periphyton chlorophyll *a* concentration (21 mg/m^2) for moderately enriched streams (figs. 7 and 8).

The allowable or desired concentrations of nutrients and chlorophyll *a* may depend on the designated use or existing quality of a water body. Lines representing the 25th percentile of periphyton chlorophyll *a* from all open-canopy sites in this study (5.2 mg/m^2) and the 75th percentile value for open-canopy reference sites (16 mg/m^2) also were plotted on figures 7 and 8 to provide additional total nitrogen and total phosphorus concentrations. An estimated concentration of 0.45 mg/L for total nitrogen and 0.027 mg/L for total phosphorus corresponded to the periphyton chlorophyll *a* concentration of 5.2 mg/m^2 (25th percentile from the open-canopy sites) and an estimated concentration of 0.90 mg/L for total nitrogen and 0.075 mg/L for total phosphorus corresponded to the periphyton chlorophyll *a* concentration of 16 mg/m^2 (75th percentile value for open-canopy reference sites). It is reasonable to assume that the data for impaired open-canopy sites would represent conditions most favorable for the growth of nuisance algae. If nutrient criteria were established from data collected under these conditions, it could also be applied to other conditions (closed-canopy sites) that are less favorable for the growth of nuisance algae because of light limitation, and could be considered a conservative limit.

The concentrations of total nitrogen and total phosphorus obtained using several potential methods for nutrient criteria development using data in this study are summarized in table 4. These methods are some of the possible techniques that can be used by water-resources managers; depending on the designated use of a specific area, other calculated percentiles or estimates might be more appropriate.

The resulting total nitrogen and total phosphorus concentrations are generally similar for the various approaches. The lowest total nitrogen and total phosphorus concentrations were the subecoregion 59 preliminary criteria developed by the USEPA (0.57 mg/L for total nitrogen and 0.024 mg/L for total phosphorus) and the estimated total nitrogen and total phosphorus concentrations that corresponded to the 25th percentile of chlorophyll *a* from all open-canopy sites in this study (0.45 mg/L for total nitrogen and 0.027 mg/L for total phosphorus). The highest total nitrogen (1.3 mg/L) and total phosphorus (0.120 mg/L) concentrations corresponded to the estimated concentration from the median literature concentration of chlorophyll *a* from moderately enriched streams (21 mg/m^2). A combination of these methods may aid in the selection of an appropriate range of total nitrogen and total phosphorus concentrations to be used for nutrient criteria development in wadeable New England Coastal streams.

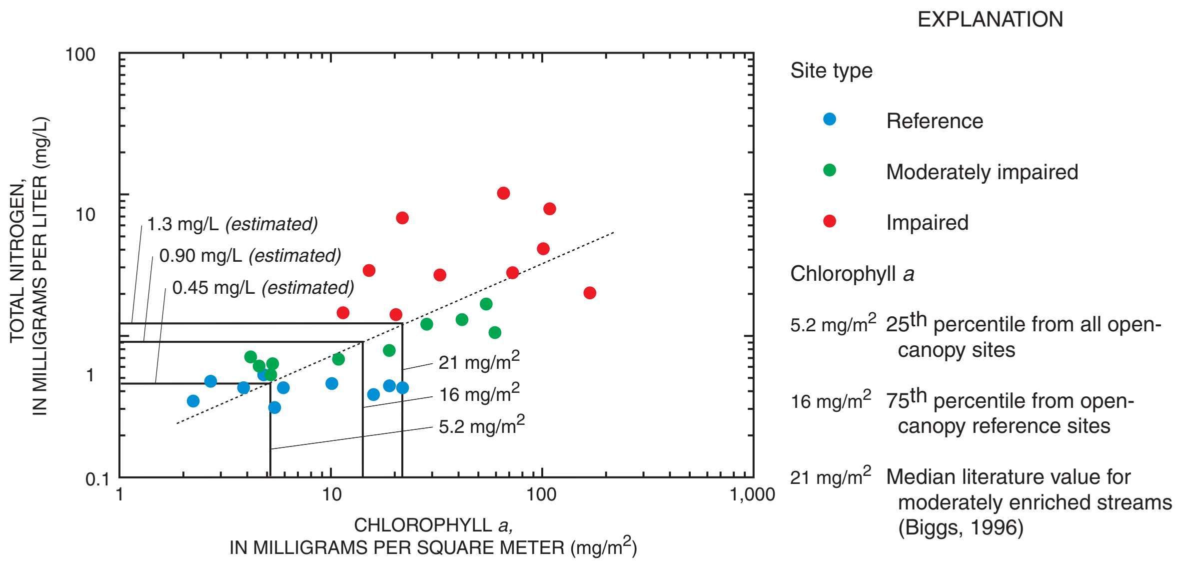


Figure 7. Graph showing Relation between total nitrogen and periphyton chlorophyll *a* concentrations for the six open-canopy sites sampled five times from June through September 2001 in the New England Coastal Basins study area in Massachusetts and New Hampshire.

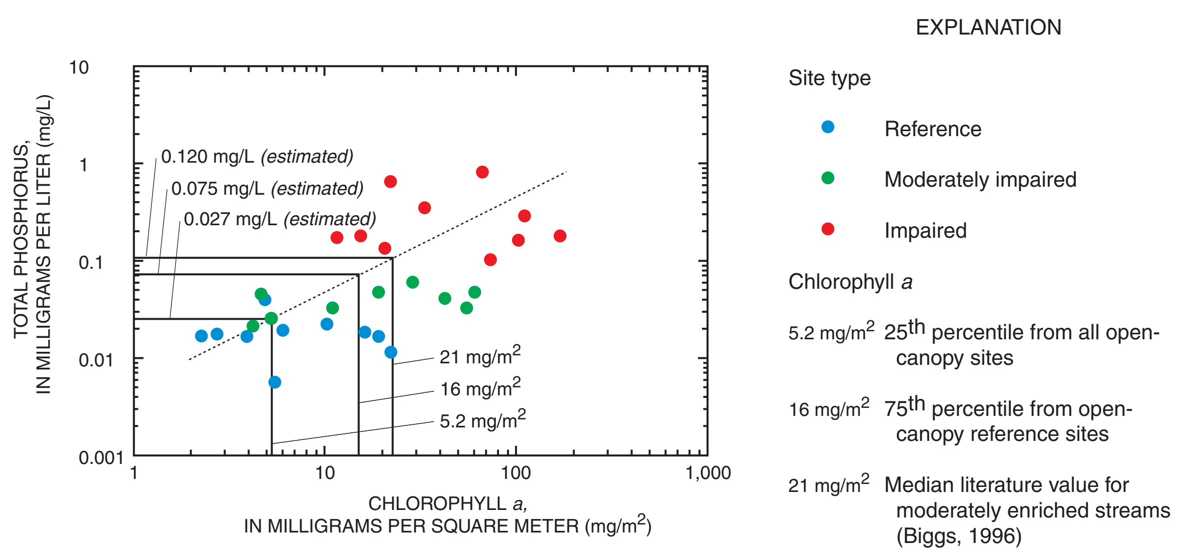


Figure 8. Graph showing Relation between total phosphorus and periphyton chlorophyll *a* concentrations for the six open-canopy sites sampled five times from June through September 2001 in the New England Coastal Basins study area in Massachusetts and New Hampshire.

Table 4. Summary of total nitrogen and total phosphorus concentrations for potential methods of nutrient criteria development in the Northeastern Coastal Zone in Massachusetts and New Hampshire

[mg/L, milligrams per liter]

Criteria method	Total nitrogen (mg/L)	Total phosphorus (mg/L)
Subecoregion 59 preliminary criteria.	0.57	0.024
25th percentile-all sites in this study.	.64	.030
10th percentile-impaired sites in this study.	.73	.036
Estimated concentrations of total nitrogen and total phosphorus[1]		
Estimated concentration at the 25th percentile of chlorophyll *a* from all open-canopy sites.	.45	.027
Estimated concentration at the 75th percentile of chlorophyll *a* from all open-canopy reference sites.	.90	.075
Estimated concentration at the median literature concentration for chlorophyll *a* for moderately enriched streams.	1.3	.120

[1] Concentrations of total nitrogen and total phosphorus are estimated from chlorophyll *a* concentrations in this study (figs. 7 and 8).

SUMMARY AND CONCLUSIONS

The U.S. Environmental Protection Agency is currently developing guidance to assist state water-resources managers with establishing nutrient and algal criteria to prevent streams and rivers from becoming impaired and to preserve them for designated water uses (such as the protection of wildlife). Nutrient levels differ among regions because of variations in geology, climate, soil, and other physical factors. Therefore, for the criteria to be most effective, ecoregional variations need to be considered.

Thirteen stream sites, primarily in eastern Massachusetts, were selected for a nutrient-chlorophyll assessment study. The sites represent a range of water-quality impairment conditions (reference, moderately impaired, impaired) based on state regulatory agency assessments and previously assessed nitrogen, phosphorus, and dissolved-oxygen data. In addition, a combination of open- and closed-canopy sections were sampled at six of the sites to investigate the effect of sunlight on algal growth. Among the sites sampled, median nutrient concentrations were lowest at the two reference sites and highest at the six impaired sites. When sites were grouped by site type, there were statistically significant differences ($p < 0.05$) among all site types for total nitrogen and total phosphorus.

The chlorophyll *a* concentrations from periphyton samples were positively correlated with total nitrogen and total phosphorus concentrations at the open- and closed-canopy sites. Correlations were higher at the open-canopy sites than at the closed-canopy sites because light stimulates the production of algal biomass and enhances algal-nutrient relations. Median concentrations of chlorophyll *a* from periphyton were highest at impaired sites and were significantly higher at open-canopy sites than at sites with closed canopies. Results of analysis of periphyton chlorophyll *a* concentrations from the six sites that had open- and closed-canopy sampling locations indicated that open-canopy sites had higher concentrations of chlorophyll *a* among all three site types. Nutrient concentrations, types of substrate, and stream velocities were similar between the closed- and open-canopy locations at the same site, indicating that light was affecting algal biomass as measured by chlorophyll *a*.

Linear regression was used to estimate the total nitrogen and total phosphorus concentrations that corresponded to various chlorophyll *a* thresholds. Nutrient concentrations were plotted as a function of chlorophyll *a* concentrations. A regression line was drawn and used to estimate concentrations of total nitrogen and total phosphorus from concentrations of chlorophyll *a*. On the basis of a median value in the literature for periphyton chlorophyll *a* of 21 mg/m^2 for moderately enriched streams, total nitrogen and total phosphorus for this ecoregion (subecoregion 59) were estimated from a regression line using the literature value to yield concentration thresholds of 1.3 mg/L for total nitrogen and 0.12 mg/L for total phosphorus. Lines representing the 25th percentile of periphyton chlorophyll *a* concentrations for all of the open-canopy sites in this study (5.2 mg/m^2) and the 75th-percentile value for open-canopy reference sites (16 mg/m^2) also were plotted to provide additional nutrient limits based on allowable levels of algae. The 25th-percentile total nitrogen and total phosphorus concentrations were calculated with all of the study data as a possible additional threshold. From these data, concentrations of 0.64 mg/L for total nitrogen and 0.030 mg/L for total phosphorus were obtained. As another possible method of threshold development, the 10th-percentile concentrations of total nitrogen and total phosphorus were calculated using all of the impaired sites in this study. Concentration thresholds of 0.73 mg/L for total nitrogen and 0.036 mg/L for total phosphorus were obtained. These nutrient concentrations derived from current data (2001) may contribute to development of a potential set of regional nutrient criteria. The combination of these methods may aid in the selection of an appropriate range of total nitrogen and total phosphorus concentrations to be used by water-resources managers for nutrient criteria development.

REFERENCES CITED

Arar, E.J., and Collins, G.B., 1997, U.S. Environmental Protection Agency Method 445.0, In vitro determination of chlorophyll *a* and pheophytin *a* in marine and freshwater algae by fluorescence, revision 1.2: Cincinnati, Ohio, U.S. Environmental Protection Agency National Exposure Research Laboratory, Office of Research and Development.

Biggs, B.J.F., 1996, Patterns in benthic algae of streams, *in* Stevenson, R.J., and others, eds., Algal Ecology Freshwater Benthic Systems: New York, Academic Press, p. 31-51.

———2000, Eutrophication of streams and rivers: dissolved nutrient-chlorophyll relationships for benthic algae: Journal of American Benthological Society, v. 19, no. 1, p. 50-67.

Biggs, B.J.F., and Price, G.M., 1987, A survey of filamentous algae proliferations in New Zealand Rivers: Journal of Marine and Freshwater Research, v. 21, p. 175-191.

Bott, T.L., Brock, J.T., Dunn, C.S., Naiman, R.J., Ovink, R.W., and Petersen, R.C., 1985, Benthic community metabolism in four temperate stream systems, An inter-volume comparison and evaluation of the river continuum concept: Hydrobiologia, v. 123, p. 3-45.

Coakley, M.F., Ward, S.L., Hilgendorf, G.S., and Kiah, R.G., 2001, Water Resources Data, New Hampshire and Vermont, Water Year 2001: Water-Data Report NH-VT-01-1, 194 p.

Commonwealth of Massachusetts, Executive Office of Environmental Affairs, 1999, Final Massachusetts section 303(d) list of waters 1998: Department of Environmental Protection, Division of Watershed Management, variously paged.

Deacon, J.R., and Spahr, N.E., 1998, Water-quality and biological community characterization at selected sites on the Eagle River, Colorado, September 1997 and February, 1998: U.S. Geological Survey Water-Resources Investigations Report 98-4236, 8 p.

ENSR International, 2000, SuAsCo Watershed Assabet River TMDL study phase one draft final report for the Army Corps of Engineers and Massachusetts Department of Environmental Protection: Document no. 9000-259-100: variously paged.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Fitzpatrick, F.A., Waite, I.R., D'Arconte, P.J., Meador, M.R., Maupin, M.A., and Gurtz, M.E., 1998, Revised methods for characterizing stream habitat in the National Water-Quality Assessment Program: U.S. Geological Survey Water-Resources Investigations Report 98-4052, 67 p.

Flanagan, S.M., Nielsen, M.G., Robinson, K.W., and Coles, J.F., 1999, Water-quality assessment of the New England Coastal Basins in Maine, Massachusetts, New Hampshire, and Rhode Island—Environmental settings and implications for water quality and aquatic biota: U.S. Geological Survey Water-Resources Investigations Report 98-4249, 62 p.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: New York, Elsevier Science Publishers, 552 p.

Horner, R.R., Welch, E.B., and Veenstra, R.B., 1983, Development of nuisance periphytic algae in laboratory streams in relation to enrichment velocity, *in* Wetzel, R.G., ed., Periphyton of Freshwater Ecosystems: The Hague, Dr. W. Junk Publishers, p. 121-134.

Kjeldsen, K., 1996, Regulation of algal biomass in a small lowland stream, Field experiments on the role of invertebrate grazing, phosphorus and irradiance: Freshwater Biology, v. 36, p. 535-546.

Lock, M.A., 1981, River epilithion, A light and organic energy transducer, *in* Lock, M.A., and Williams, D.D., eds., Perspectives in Running Water Ecology: New York and London, Plenum, p. 3-40.

Mosisch, T.D., Bunn, S.E., Davies, P.M., and Marshall, C.J., 1999, Effects of shade and nutrient manipulation on periphyton growth in a subtropical stream: Aquatic Botany, v. 64, no. 2, p. 167-177.

Omernik, J.M., 1987, Ecoregions of the conterminous United States: Annuals of the Association of American Geographers, v. 77, p. 118-125.

Porter, S.D., Cuffney, T.F., Gurtz, M.E., and Meador, M.R., 1993, Methods for collecting algal samples as part of the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 93-409, 39 p.

Reckhow, K.H., 1979, Quantitative techniques for the assessment of lake quality: Office of Water, U.S. Environmental Protection Agency, EPA 440-5-79-015, variously paged.

SAS Institute, Inc., 1998, Statview Reference Guide: Cary, N.C., version 5.0, 528 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.

Socolow, R.S., Leighton, C.R., Whitley, J.F., Ventetuolo, D.J., 2001, Water Resources Data, Massachusetts and Rhode Island, Water Year 2001: Water-Data Report MA-RI-01-1, 307 p.

Spahr, N.E., and Deacon, J.R., 1998, Water-quality characteristics of the Slate and East Rivers, Colorado, during the winter recreational season, December 1996: U.S. Geological Survey Open-File Report 98-279, 9 p.

U.S. Environmental Protection Agency, 2000a, Nutrient criteria technical guidance manual—Rivers and streams: Office of Water, U.S. Environmental Protection Agency, EPA 822-B-00-002, variously paged.

———2000b, Ambient water quality criteria recommendations—Information supporting the development of state and tribal nutrient criteria—Rivers and Streams in Nutrient Ecoregion XIV: Office of Water, EPA 822-B-00-022, variously paged.

———2002, Waterbody system database for the Clean Water Act for 305 (b) reporting: variously paged.

Welch, E.B., Quinn, J.M., and Hickey, C.W., 1992, Periphyton biomass related to point-source nutrient enrichment in seven New Zealand streams: Water Resources, v. 26, no. 5, p. 669-675.