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# Alternation of Factors Limiting Phytoplankton Production in the Cape Fear River Estuary

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**ABSTRACT: Phytoplankton nutrient limitation experiments were performed from 1994 to 1996 at three stations in the Cape Fear River Estuary, a riverine system originating in the North Carolina piedmont. Nutrient addition bioassays were conducted by spiking triplicate cubitainers with various nutrient combinations and determining algal response by analyzing chlorophyll *a* production and $^{14}C$ uptake daily for 3 d. Ambient chlorophyll *a*, nutrient concentration, and associated physical data were collected throughout the estuary as well. At a turbid, nutrient-rich oligohaline station, significant responses to nutrient additions were rare, with light the likely principal factor limiting phytoplankton production. During summer at a mesohaline station, phytoplankton community displayed significant nitrogen (N) limitation, while both phosphorus (P) and N were occasionally limiting in spring with some N + P co-limitation. Light was apparently limiting during fall and winter when the water was turbid and nutrient-rich, as well as during other months of heavy rainfall and runoff. A polyhaline station in the lower estuary had clearer water and displayed significant responses to nutrient additions during all enrichment experiments. At this site N limitation occurred in summer and fall, and P limitation (with strong N + P co-limitation) occurred in winter and spring. The data suggest there are two patterns controlling phytoplankton productivity in the Cape Fear system: 1) a longitudinal pattern of decreasing light limitation and increasing nutrient sensitivity along the salinity gradient, and 2) a seasonal alternation of N limitation, light limitation, and P limitation in the middle-to-lower estuary. Statistical analyses indicated upper watershed precipitation events led to increased flow, turbidity, light attenuation, and nutrient loading, and decreased chlorophyll *a* and nutrient limitation potential in the estuary. Periods of low rainfall and river flow led to reduced estuarine turbidity, higher chlorophyll *a*, lower ambient nutrients, and more pronounced nutrient limitation.**

## Introduction

The Cape Fear River Estuary (34°N, 77°57′W), receives drainage from the largest river basin in North Carolina, encompassing 23,310 km$^2$ and containing 27% of the state's population (North Carolina Department of Natural Resources 1983; Pietrafesa and Janowitz 1988). Heavy use of surface water resources has led to considerable water quality degradation in this region. Agricultural runoff and urban runoff from the increasing population are considered to be two primary causes of stream degradation in this system (North Carolina Department of Environment, Health, and Natural Resources 1996). The Cape Fear River basin is also the most heavily industrialized river basin in the state, with numerous point source discharges upstream and a major harbor and state port in Wilmington (North Carolina Department of Environment, Health, and Natural Resources 1996). The ultimate receiving area for these various effluents is the Cape Fear River tidal basin, a 45-km-long stretch of the lower river and estuary ranging from the freshwater river upstream of Wilmington to the polyhaline estuary mouth (Fig. 1). This tidal basin is fed by the piedmont-derived Cape Fear River, a 6$^{th}$-order stream, and by the Black River and Northeast Cape Fear River, both 5$^{th}$-order coastal blackwater systems (Mallin et al. 1996).

Large quantities of inorganic nutrients enter this system from point sources and nonpoint sources, including urban and suburban land use (lawn fertilizers, golf course runoff, etc.), crop agriculture, and intensive livestock operations, principally swine and poultry (Natural Resources Conservation Service 1995; North Carolina Department of Environment, Health, and Natural Resources 1996; Burkholder et al. 1997; Mallin et al. 1997a; Cahoon et al. 1999). Management of current and future nutrient loads is critical to water quality, especially

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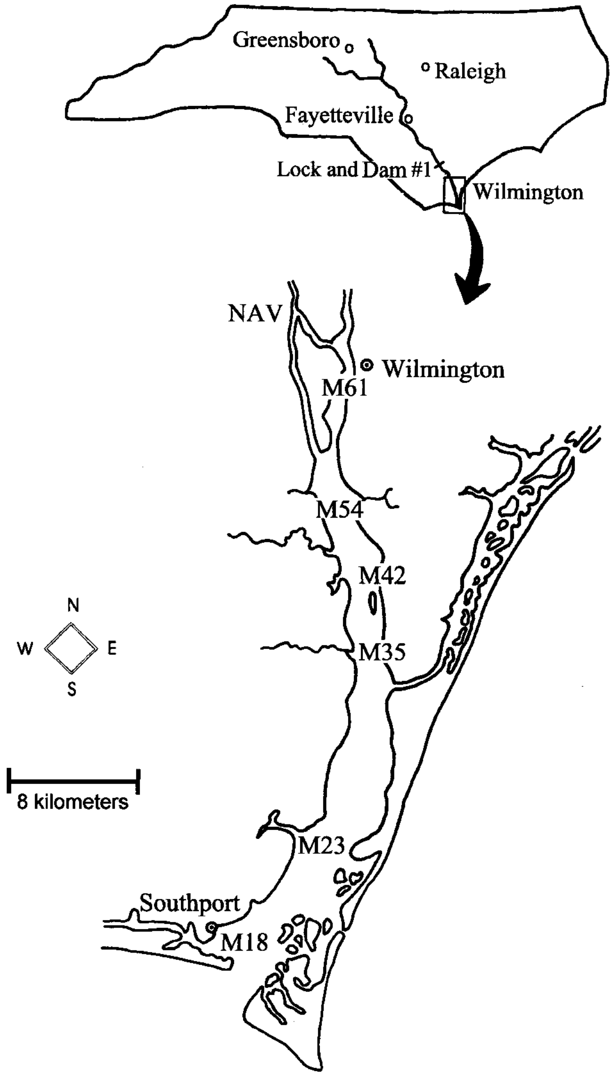


Fig. 1. Sampling stations along the Cape Fear River Estuary, North Carolina, United States. The lower estuary is centered on 33°56′N, 77°58′W.

in nutrient-sensitive estuarine areas. An essential first step for any nutrient management plan is to understand the effects of nutrients and their ratios on the receiving waters. This can be accomplished in part by determining the nutrient, or nutrients, limiting phytoplankton growth in the receiving waters (Howarth 1988).

The principal objective of this research was to determine experimentally the principal nutrients limiting the growth of phytoplankton in three key areas of the Cape Fear River Estuary. Part of this effort was assessing (using bioassay data, in-situ nutrient concentrations, and physical data) the relationship between light and nutrient limitation along the longitudinal axis of the estuary and determining if it remains constant or changes on a seasonal basis. An additional objective was to determine the magnitude and distribution of nutrients, chlorophyll *a* (chl *a*), and various physical water quality parameters seasonally throughout the length of this estuary, and assess how meteorological forcing through rainfall and river flow affects these estuarine parameters.

Previous nutrient limitation studies have indicated N is the primary limiting nutrient in coastal systems, both in North Carolina (reviewed by Mallin 1994) and elsewhere (reviewed by Howarth 1988). Because preliminary data (North Carolina Division of Water Quality unpublished records) indicated inorganic N : P ratios in the Cape Fear system on average well exceeded 16, the Redfield ratio for phytoplankton, we hypothesized that the Cape Fear River Estuary would be primarily P limited.

## Materials and Methods

### Sampling Stations

From July 1994 to June 1995 water for the bioassay experiments was collected at 1–2 mo intervals at two stations, one in the fresh to oligohaline area near Navassa (NAV, 5 km upstream of Wilmington) and the other in the mesohaline area (channel marker 54, or M54, about 5 km downstream of Wilmington) (Fig. 1). After June 1995, experiments at NAV were discontinued and water for bioassays was instead collected at channel marker 23 (M23), a polyhaline station upstream of Southport, North Carolina (Fig. 1). Physical and chemical water quality data were collected monthly at these stations as well as at a series of channel markers distributed along the salinity gradient (Fig. 1). For consistency all stations were sampled on the outgoing tide between 1000 h and 1400 h. Water quality data were collected at NAV, M61, and M54 from July 1994 through June 1996, and for these stations plus M42, M35, M23, and M18 from July 1995 through November 1998.

### Nutrient Limitation Experiments

The hypothesis that P is the principal limiting nutrient in Cape Fear River Estuary (CFRE) water was tested by nutrient limitation bioassays. The basis for these experiments is the addition of the suspected limiting nutrient in excess to replicated estuarine water samples and determination if the phytoplankton community in the samples shows a positive response (i.e., an increase in chlorophyll concentration or carbon uptake). Other possible limiting nutrients (treatments) were tested as well, with a replicated set of control samples incubated to serve as a baseline. The specific design was as follows: water was collected on station in 25-l carboys, returned to the laboratory, and dispensed into 4-l cubitainers (3 liters per cubitainer). Nutrient treatments were added as follows (expressed as final concentration): no additions (controls), phosphate alone (100 μg-P $l^{-1}$ or 3.2 μM), nitrate alone (200 μg-N $l^{-1}$ or 14.3 μM), combination (200 μg-N $l^{-1}$ nitrate and 100 μg-P $l^{-1}$ phosphate), and silicate alone (200 μg-Si $l^{-1}$ or 7.1 μM). All treatments were conducted in triplicate. After nutrient addition, 10 μCi of $^{14}C$-$NaHCO_3$ was added to each cubitainer to allow measurement of photosynthetic $^{14}C$ assimilation as an estimate of algal growth (Paerl et al. 1990; Rudek et al. 1991; Fisher et al. 1992).

Cubitainers were floated on a flow-through pond near the Department of Biological Sciences at the University of North Carolina at Wilmington. The cubitainers were covered by two layers of neutral density screening to allow about 30% solar irradiance penetration and thus prevent photoinhibition of phytoplankton productivity (Mallin and Paerl 1992). The cubitainers were kept in motion by continuous circular agitation of the pond water using a submerged bilge pump. The cubitainers were sampled daily for 3 d for $^{14}C$ uptake as follows: 50-ml aliquots were filtered through 25-mm Gelman type A/E glass-fiber filters. Filters were fumed with hydrochloric acid vapors for 30 min to remove abiotically precipitated $^{14}C$, then dried and treated with Ecolume scintillation cocktail. Carbon uptake ($^{14}C$ activity) was assayed on a Wallac LKB 1214 Rackbeta liquid scintillation counter. The cubitainers were also sampled daily for chl *a* content; the chl *a* in the 50-ml samples was measured using a Turner Model 10-AU fluorometer and the method of Welschmeyer (1994). We ran each bioassay experiment for 3 d. This length of time was chosen to permit nutrient responses to be demonstrated while minimizing community composition changes and other bottle effects. Nutrient addition experiments were conducted during all months from July 1994 through June 1996, with the exception of October and December of 1994 and 1995.

### Physical Parameters

Water temperature, dissolved oxygen, turbidity, and salinity-conductivity vertical profiles were collected at each station using a Solomat WP803 multiparameter water quality monitor. Secchi depth was also recorded at each station. Solar irradiance was measured at 0.5-m depth intervals using a Li-Cor LI-1000 integrator interfaced with a Li-Cor LI-193S spherical quantum sensor, and the light attenuation coefficient *k* was determined from these data following the procedure in Raymont (1980).

### Nutrients and Chlorophyll *a*

Water samples were collected on-site in amber bottles, stored on ice, and returned to the laboratory for analyses of a suite of nutrient parameters, including total Kjeldahl nitrogen (TKN), nitrate (nitrate + nitrite), ammonium, total phosphorus (TP), orthophosphate (inorganic P), and dissolved silica. Surface and bottom samples were collected until November 1995, after which only surface samples were collected. Statistical analyses demonstrated that, with the exception of TP and sometimes ammonium, there were few significant differences between surface and bottom nutrients and chl *a* (Mallin et al. 1996). Thus, data reported here represent surface samples only. TKN and TP were analyzed from nonfiltered samples using standard methods (American Public Health Association 1995), with total nitrogen (TN) computed as TKN + nitrate. Triplicate water samples were filtered through previously combusted glass-fiber filters (Gelman A/E, nominal pore size = 1 μm). This pore size is a compromise; it permits reasonably rapid filtration of turbid estuarine waters but can pass photosynthetic picoplankton. Chl *a* analyses of the filtered material were conducted in triplicate using the fluorometry method. Filtered samples, standards, and blanks were analyzed for nitrate + nitrite and orthophosphate on an Technicon AutoAnalyzer II at the Center for Marine Science Research, University of North Carolina at Wilmington, using standard techniques (United States Environmental Protection Agency 1992). Ammonium was determined using the phenol-hypochlorite technique (Parsons et al. 1984). Dissolved silica was measured using the molybdenum blue method described in Parsons et al. (1984).

### Statistical Analyses

Nutrient limitation test results were analyzed using the analysis of variance (ANOVA) procedure of SAS (SAS 1987). This test utilizes the mean response data (chlorophyll concentrations and $^{14}C$ uptake) for each cubitainer over the 3-d test for the analysis. If there was a significant difference ($p < 0.05$) among the response means of the various nutrient treatments and controls the ANOVA test was followed by treatment ranking by the LSD procedure (Day and Quinn 1989; Rudek et al. 1991).

In an attempt to understand further the relationship among meteorological and physical forcing, estuarine water quality data, and bioassay results, correlation analyses were conducted on the data from M54 and M23 from July 1994 through June 1996. The degree of nutrient limitation (the enrichment factor) was assessed by determining the percent increase in chl *a* production or $^{14}C$ incorporation over the control values for each treatment in each bioassay, and including these data in the correlation matrix. For example, the August 1994 N treatment yield of 124 μg $l^{-1}$ chl *a*

TABLE 1. Mean (and standard deviation) of selected physical, chemical, and biological parameters for the Cape Fear River Estuary, June 1995–November 1998 (unless otherwise noted).

| | Upper Estuary | | Mid Estuary | | | Lower Estuary | |
|---|---|---|---|---|---|---|---|
| Parameter | NAV | M61 | M54 | M42 | M35 | M23 | M18 |
| Salinity (‰) | 1.0 (2.7) | 3.7 (4.9) | 5.6 (6.0) | 7.8 (7.2) | 11.7 (8.2) | 18.0 (8.2) | 22.7 (7.9) |
| Dissolved oxygen (mg $l^{-1}$) | 6.2 (2.5) | 6.3 (2.4) | 6.5 (2.3) | 7.1 (2.3) | 7.2 (2.2) | 7.5 (1.9) | 7.6 (1.9) |
| Turbidity (NTU) | 32.7 (19.7) | 25.1 (14.6) | 31.9 (16.9) | 25.3 (14.3) | 21.2 (12.4) | 18.6 (13.6) | 17.5 (19.7) |
| Light attenuation ($m^{-1}$) | 3.94 (1.40) | 3.56 (1.15) | 3.84 (1.87) | 3.13 (1.31) | 2.77 (1.12) | 2.15 (0.95) | 1.91 (0.81) |
| Total N (μM)[a] | 96 (32) | 84 (22) | 86 (18) | 75 (21) | 70 (25) | 57 (24) | 44 (23) |
| Nitrate + Nitrite (μM) | 34 (15) | 27 (11) | 27 (10) | 24 (10) | 21 (12) | 14 (8) | 10 (8) |
| Ammonium (μM) | 5.3 (3.4) | 5.7 (3.2) | 6.1 (3.9) | 5.0 (3.6) | 4.4 (3.0) | 3.5 (2.8) | 2.7 (2.0) |
| Total P (μM)[a] | 4.7 (1.9) | 3.6 (1.3) | 4.2 (2.1) | 3.3 (1.2) | 2.7 (1.0) | 2.1 (0.9) | 1.6 (0.7) |
| Orthophosphate (μM) | 1.8 (0.7) | 1.5 (0.5) | 1.4 (0.5) | 1.2 (0.4) | 1.0 (0.4) | 0.7 (0.3) | 0.5 (0.3) |
| Silicate (μM)[b] | 98 (15) | 85 (19) | 82 (25) | 72 (30) | 59 (28) | 53 (30) | 41 (30) |
| Chl *a* (μg $l^{-1}$) | 3.6 (2.4) | 5.4 (4.5) | 6.8 (6.1) | 8.0 (7.8) | 7.3 (6.3) | 6.9 (4.7) | 7.2 (4.4) |

[a] Total N and P data for February 1996–November 1998.
[b] Silicate data for June 1995–July 1996 for all stations except NAV (June 1995–July 1997).

divided by the control yield of 98 μg $l^{-1}$ gives a 27% increase. If the treatment yield was less than the control yield a zero was assigned. Correlations were run using SAS, based on 19 bioassays at M54 and 10 bioassays at M23. Additionally, correlation analyses of rain, river flow, and estuarine physical, chemical, and biological response variables were conducted using the entire dataset from July 1994 through November 1998. Effect of river flow was assessed by using the average daily flow (CFS) for the 7-d period preceding sample collection; flow data were obtained from Lock and Dam #1, about 65 km upstream of the estuary. An appropriate effect of upper watershed rainfall was obtained by determining total rainfall at Greensboro (approximately 300 km upstream of the estuary, Fig. 1) for the 28-d period preceding sample collection. All parameters were tested for normal distribution using the Shapiro-Wilk test. Nonnormally distributed parameters were normalized by log-transformation prior to statistical analysis.

## Results

### Physical Parameters

Water temperatures in the estuary ranged from 5.0°C to 30.0°C. The system was generally well mixed, with little evidence of a thermocline (Mallin et al. 1996, 1997b). Surface salinity at NAV ranged from fresh water to 10‰, with the highest salinities in summer 1997 and fall 1998 (Fig. 2). Stations NAV and M61 can be considered oligohaline, M54, M42, and M35 can be considered mesohaline, and M23 and M18 polyhaline (Table 1). Somewhat higher salinities were detected in bottom samples, demonstrating an occasional salinity wedge in this estuary (Mallin et al. 1996, 1997b). Highest salinities occurred typically during summer, although sharp systemwide decreases were noted in July 1995 following heavy rains, September 1996 following Hurricane Fran (Mallin et al. 1999), and September 1998 following Hurricane Bonnie (Fig. 2).

Dissolved oxygen (DO) concentrations in the upper Cape Fear River Estuary (CFRE) periodically fell below the North Carolina water quality standard of 5.0 mg $l^{-1}$ (Fig. 2). These incidents have occurred anytime from June through September, with particularly severe decreases following animal waste spills and hurricanes (Mallin et al. 1997a, 1999). Samples were collected during mid day, when DO concentrations should be highest. Low DO is not confined to the bottom waters, however. The deep, vertically well-mixed nature of the river and oligohaline estuary maintains hypoxia throughout the water column, with no statistical difference evident between surface and bottom DO levels (Mallin et al. 1996).

Surface water turbidity concentrations were high during periodic elevated flow incidents, and at stations M61 and M54 during winter dredging activities near the Port of Wilmington (Fig. 2). Dredging is permitted near the port from October through March (R. Carpenter, personal communication). While dredging was not ongoing during all of our winter field trips, field notations indicated that when dredging occurred that high turbidity and/or light attenuation also was measured (such as October 1995–February 1996). Bottom-water turbidity was usually higher than surface turbidity (Mallin et al. 1996, 1997b). The highest average turbidity values overall (32 NTU) were observed at M54, possibly due to a salinity-induced turbidity maximum forming in this region of the estuary, coupled with dredging near the port. Turbidity was lowest near the mouth of the estuary at M18 but on occasion still exceeded the state standard of 25 NTU (Fig. 2).

Light attenuation (*k*) was generally high in the

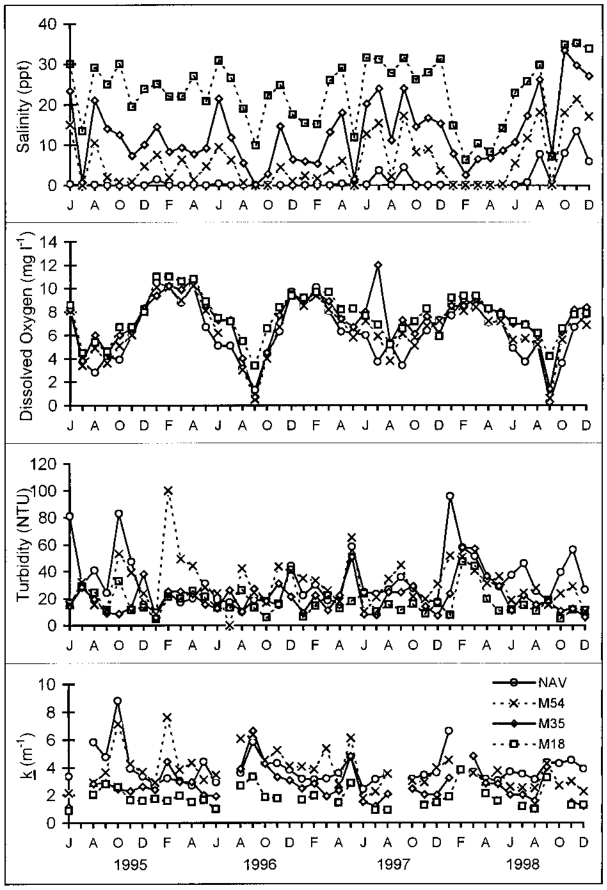


Fig. 2. Physical parameters for selected stations in the Cape Fear River Estuary, June 1995–November 1998.

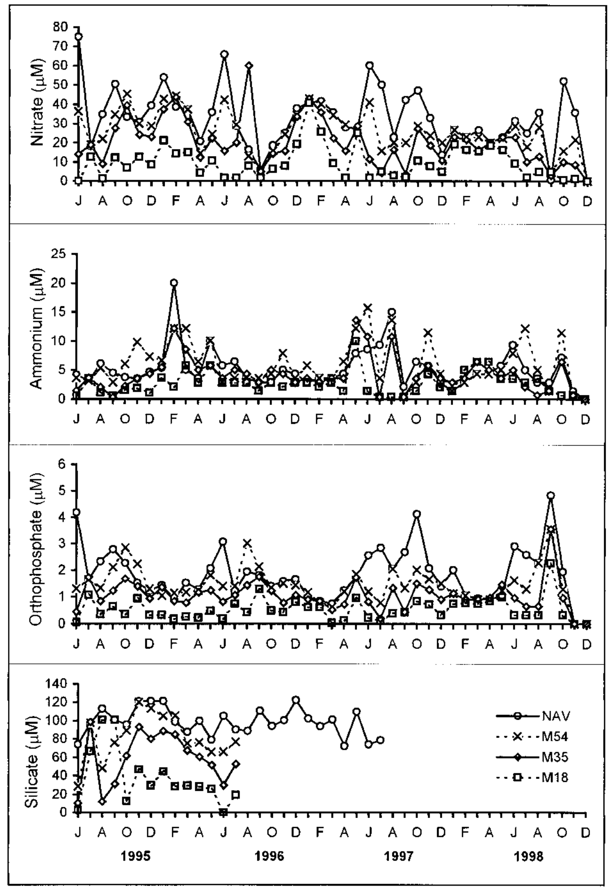


Fig. 3. Inorganic nutrient concentrations for selected stations in the Cape Fear River Estuary, June 1995–November 1998.

CFRE (Table 1). The mean $k$ was nearly 4.0 $m^{-1}$ at NAV, due both to turbidity for the river mainstem and water color from the Black and Northeast Cape Fear Rivers. During fall and winter the turbidity from periodic dredging activities near the Port of Wilmington strongly attenuated light penetration at M61 and M54 ($k > 4.0$ $m^{-1}$). During nondredging periods the $k$ values averaged about 3.0 $m^{-1}$ (Fig. 2). Upper to mid estuary regions such as this are locations where clay-flocculation-based turbidity maxima form (Wells and Kim 1991). Anthropogenic (dredging), physical (high flow), and chemical (water color) sources contribute to high turbidity and strong light attenuation in the upper and middle estuary. Mean light attenuation at M23 and M18 was much less than at the other stations, and with less temporal variability as well (Table 1 and Fig. 2).

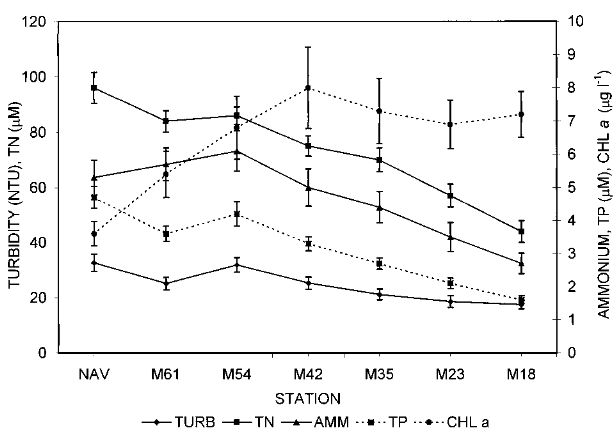


Fig. 4. Mean concentrations (and standard error) of selected parameters by station in the Cape Fear River Estuary, June 1995–November 1998.

## Nutrients

Nitrate concentrations were high in the upper estuary (Table 1). There was a general trend of decreasing nitrate with increasing salinity along the longitudinal axis of the estuary (Table 1 and Figs. 2 and 3). Surface nitrate was elevated estuary-wide during the high river flow months of December through February; occasional peaks of nitrate

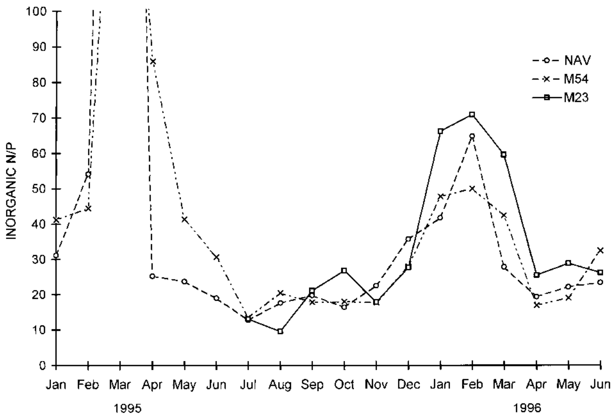


Fig. 5. Inorganic nitrogen to phosphorus ratios for bioassay stations, January 1995–June 1996. In March 1995 ratios at NAV and M54 were 377 and 197, respectively.

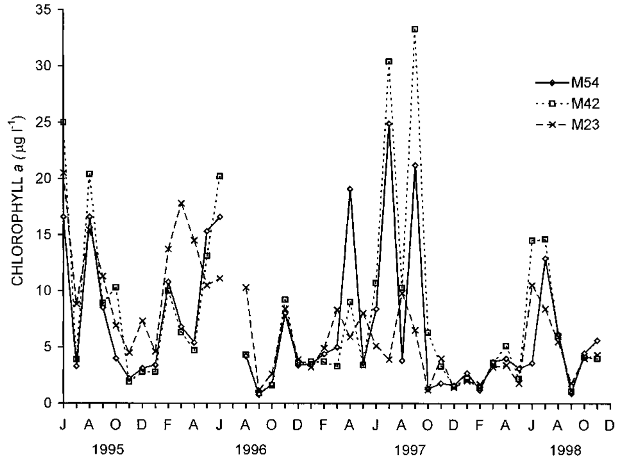


Fig. 6. Chlorophyll *a* concentrations for selected stations in the Cape Fear River Estuary, June 1995–November 1998.

also occurred in the upper estuary during summer (Fig. 3). Ammonium concentrations peaked at M54 and decreased toward the ocean (Table 1 and Fig. 4). There was no discernible seasonal trend in ammonium (Fig. 3). The nitrate fraction of total dissolved inorganic nitrogen was much larger than the ammonium fraction, suggesting considerable anthropogenic loading. TN concentrations showed a slight decrease from NAV to M54, and a sharper decline to M18 (Table 1 and Fig. 4). TN values were generally lower in the fall and increased during late winter–early spring and other months of high river flow.

Orthophosphate concentrations ranged from 5 μM to below the 0.3 μM detection limit (Fig. 3). Concentrations declined downstream concurrently with salinity increases (Table 1). An evident seasonal pattern was a summer–early fall increase (Fig. 3), common among North Carolina estuaries (Mallin 1994), and low values in early spring. TP concentrations showed a peak at M54 followed by declining levels concurrent with increasing salinities (Table 1 and Fig. 4). The only seasonal pattern evident was lowest values in late winter–early spring (Mallin et al. 1997b). Orthophosphate generally comprised between 30% and 40% of the total P in the CFRE (Table 1).

Silicate concentrations were generally high in river water entering the CFRE, with a pronounced spatial pattern of decreasing concentrations with increasing salinity (Table 1 and Fig. 3). Si concentrations entering the estuary at NAV were highest during the late fall–early winter and silicate decreased to minimum values in late spring of 1996 and 1997 (Fig. 3). Average values were generally similar to those found in an earlier study of silicate in the Cape Fear system (Willey and Atkinson 1982).

Molar ratios of inorganic N (nitrate + ammonium) to orthophosphate can prove useful in determining potential limiting nutrients (Howarth 1988). There is some variability in the relative N and P requirements of different classes of algae and some physiological flexibility in their needs as well. However, N : P values well above or below the Redfield ratio of 16:1 can reasonably be interpreted as probable limitation by the scarcer nutrient. Inorganic N : P molar ratio data corresponding to the bioassays were computed for the period January 1995 through June 1996 (Fig. 5). Spring N : P ratios at NAV were well above 16, suggesting P limitation. At M54, N : P ratios were well above 16 January–June 1995 and January–March 1996 (Fig. 5), again suggesting spring P limitation. The other months appear to be borderline for nutrient limitation. At M23 molar ratios suggest P limitation from January to March 1996, with borderline ratios the other months (Fig. 5). The median molar ratios for NAV, M54, and M23 during the bioassay months were 23.5, 31.5, and 27.2, respectively, indicating that P was likely an important limiting nutrient in this estuary.

## CHLOROPHYLL *A*

Phytoplankton biomass, indexed as chl *a,* displayed a longitudinal spatial pattern (Table 1 and Fig. 4) and two temporal patterns (Fig. 6). Concentrations were lowest in the oligohaline estuary, increased to a peak at M42 (just below the turbidity maximum), and decreased slightly at the three most seaward stations (Table 1 and Fig. 4). Estuarine chlorophyll maxima often occur downstream of turbidity maxima, where both light and nutrients are readily available (Harding et al. 1986; Cloern 1987). Highest concentrations were ob-

TABLE 2. Results of nutrient limitation bioassays showing nutrient treatments yielding chlorophyll *a* and $^{14}C$ responses significantly ($\alpha$ = 0.05) greater than control. NAV experiments run July 1994–June 1995; M23 experiments run July 1995–June 1996.

| | | Station | | | | | |
|---|---|---|---|---|---|---|---|
| | | NAV | | M54 | | M23 | |
| Year | Month | Chl *a* | $^{14}C$ | Chl *a* | $^{14}C$ | Chl *a* | $^{14}C$ |
| 1994 | July | | | [a] | | | |
| | August | | | N, N+P | | | |
| | September | | | N, N+P | | | |
| | November | | | | | | |
| 1995 | January | | | | N | | |
| | February | | | | Si | | |
| | March | | N, P | N, P, Si | P, N+P | | |
| | April | | N | N | N, P | | |
| | May | | | | | | |
| | June | | | | | | |
| | July | | | | | N, N+P | |
| | August | | | N, N+P | N, P, N+P | N, N+P | N, P |
| | September | | | N+P | | N, N+P | |
| | November | | | | N, P, N+P | N+P | N, N+P, Si |
| 1996 | January | | | | | P, N+P | |
| | February | | | | | P, N+P | P, N+P, Si |
| | March | | | | | N+P | |
| | April | | | | | N+P | |
| | May | | | | | N+P | N+P |
| | June | | | N, N+P | | N, N+P | N, N+P |

[a] Experiment not run.

served during summer and lowest concentrations in late fall or winter (Fig. 6). There also appeared to be an overlying meteorologically-induced pattern controlling chlorophyll concentration. During the dry summer of 1997 peak concentrations reached between 30 $\mu g\ l^{-1}$ and 35 $\mu g\ l^{-1}$, while heavy flushing and strong light attenuation associated with hurricanes and heavy rain events in the summer–early fall periods of 1995, 1996, and 1998 led to lower chlorophyll concentrations (Fig. 6). The CFRE occasionally exhibited abundant phytoplankton biomass when physical conditions appropriate for growth and retention were present; otherwise chl *a* remained at moderate levels (Table 1 and Fig. 6).

## Nutrient Addition Experiment Results

The fresh to oligohaline Cape Fear River upstream of Wilmington, near Navassa, is deep (10 m), both highly colored and turbid, and contains abundant organic and inorganic nutrients. Bioassays conducted at NAV during 1994 and 1995 showed little stimulation of phytoplankton productivity from nutrient additions (Table 2). Only during March (P and N) and April (N) 1995 was significant stimulation of phytoplankton growth found via the $^{14}C$-uptake bioassay.

Compared to NAV, the station at channel M54 (Fig. 1) is shallower (3.5 m), the estuary broader, and the water less highly colored by dissolved organic material. Although color decreased, turbidity can be high (Table 1 and Fig. 4). This area is well mixed by wind, tide, and river current. Chl *a* was higher and most nutrient concentrations were lower relative to NAV (Table 1 and Fig. 4). Chl *a* bioassay results showed significant N stimulation in August and September 1994 at M54 (Table 2). In March and April significant P and N limitation occurred (Tables 2 and 3). There was also significant Si stimulation in February and March 1995 as indicated by $^{14}C$ (Table 2). Chl *a* bioassays demonstrated significant N stimulation during August, September, and November 1995, with P stimulation shown also in the August and November $^{14}C$ bioassays (Table 2). Nutrient additions failed to stimulate significant algal growth at M54 in the January through May 1996 bioassays, but N and N + P additions provided significant stimulation in June 1996 (Table 2).

Overall, nutrient additions caused significant stimulation of algal growth in 10 of 19 bioassay experiments at M54. Seasonally, N was the major limiting nutrient in summer. According to correlation analyses, the degree of N stimulation (enrichment factor) was significantly related to water temperature ($r = 0.513$; $p = 0.025$), and the N + P enrichment factor was likewise related to water temperature ($r = 0.655$; $p = 0.002$). P stimulation occurred principally in late winter–spring; however, P additions did show stimulation periodically during other months.

In contrast to M54, water from M23 showed significant responses to nutrient additions during all bioassays from July 1995 to June 1996 (Table 2). N

TABLE 3. Significant (α = 0.05) correlation coefficients between physical and meteorological factors and estuarine response variables for station M42 in the Cape Fear River Estuary.[a] Pearson correlation coefficient (r)/probability (p).

| Variable | Water Temp | Salinity | Turbidity | Flow | Rain |
|---|---|---|---|---|---|
| Turbidity | −0.336<br>0.032 | −0.644<br>0.001 | | 0.509<br>0.001 | 0.398<br>0.012 |
| Light Attenuation | −0.470<br>0.003 | −0.865<br>0.001 | 0.812<br>0.001 | 0.678<br>0.001 | 0.496<br>0.002 |
| TN | −0.395<br>0.012 | −0.409<br>0.009 | | 0.442<br>0.006 | |
| Nitrate | −0.542<br>0.001 | | | | |
| TP | | −0.547<br>0.001 | 0.553<br>0.001 | 0.352<br>0.030 | 0.355<br>0.029 |
| Phosphate | | −0.399<br>0.001 | | | 0.455<br>0.004 |
| Silicate | −0.636<br>0.019 | −0.703<br>0.007 | | 0.836<br>0.001 | |
| Chl *a* | 0.540<br>0.001 | 0.600<br>0.001 | | −0.503<br>0.001 | −0.463<br>0.003 |
| Flow | −0.517<br>0.001 | −0.855<br>0.001 | 0.509<br>0.001 | | 0.602<br>0.001 |
| Rain | | −0.669<br>0.001 | | | |

[a] FLOW = average river flow (CFS) at Lock and Dam #1 for 7-d period preceding estuarine sample collection; RAIN = total rainfall at Greensboro airport for 28-d period preceding sample collection.

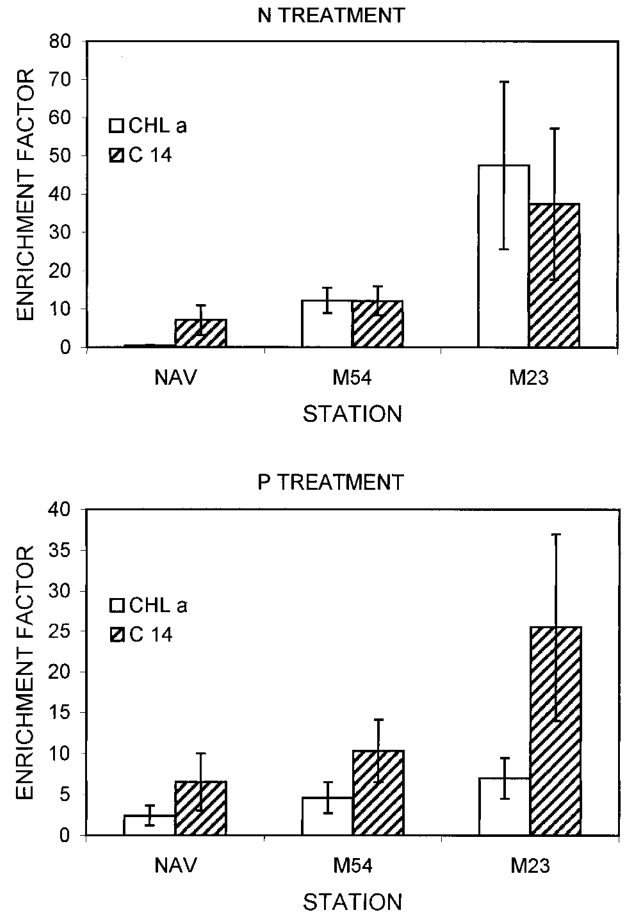


Fig. 7. Nutrient treatment enrichment factors for response variables (percent increase over control) by station for nutrient limitation experiments in the Cape Fear River Estuary.

and N + P stimulation was evident during July, August, September, and November 1995; P or N + P stimulation occurred January through May 1996; and N and N + P stimulation occurred in June 1996 (Table 2). As at M54, the N-enrichment factor was significantly correlated with water temperature ($r = 0.715$; $p = 0.020$) and inversely correlated with light attenuation ($r = -0.685$; $p = 0.042$), indicating the increased susceptibility to N stimulation caused by increased water clarity (Fig. 7). The P-enrichment factor for chl *a* response displayed a strong inverse relationship with TP concentration at M23 ($r = -0.743$, $p = 0.018$). Station M23 thus exhibited strong seasonality, or switching, between N and P stimulation of phytoplankton productivity. For both N and P additions, the enrichment factor demonstrated an increasing down-estuary trend (Fig. 7). Silicate additions significantly stimulated $^{14}C$ uptake at M23 on two occasions, November 1995 and February 1996 (Table 2).

## Physical Forcing and Estuarine Responses

Correlation analyses were used to assess the impact of physical forcing on estuarine response parameters. Data in Table 3 are from station M42, a mid-estuary site chosen for presentation because this station is below the anthropogenic impact zone from seasonal dredging but upstream of major ocean dilution (Fig. 1). Rainfall in the upper watershed was strongly correlated with average flow rates in the river proper. Salinity was inversely correlated with average river flow at Lock and Dam #1 for the week previous to estuarine sample collection, as well as with total rainfall at Greensboro for the preceding month. River flow was significantly correlated with turbidity in the estuary, indicating long-distance transport from upper coastal plain and piedmont regions. Flow was also strongly correlated with increases in light attenuation in the estuary. Both turbidity and light attenuation were inversely related to salinity as well. It is thus evident that watershed rainfall and river flow can be potentially important physical forcing mechanisms in this estuary by increasing light attenuation through delivery of turbidity particles downstream.

River flow was significantly correlated with TN, TP, and silicate concentrations at M42. Farther downstream at M35 the flow was also significantly correlated with TN concentrations ($r = 0.522$; $p = 0.001$), nitrate ($r = 0.417$; $p = 0.007$), and orthophosphate ($r = 0.462$; $p = 0.003$). In the lower estuary at M23 the flow was correlated with TN ($r = 0.593$; $p = 0.001$), nitrate ($r = 0.598$; $p = 0.001$), TP ($r = 0.375$; $p = 0.020$), and orthophosphate ($r = 0.559$; 0.001). Nitrate, TN, and silicate concentrations showed significant inverse correlations with water temperature (Table 3), possibly indicating increased delivery to the estuary during winter, and/or less utilization of these nutrients by phytoplankton and riparian wetland plants during winter.

A significant positive relationship between chl *a* and water temperature corroborated the seasonal pattern of estuarine chl *a* concentrations alluded to earlier. Chlorophyll was positively correlated with salinity but inversely related to river flow and rainfall in the piedmont. Strong currents likely inhibit chl *a* increases while reduced river discharge enhances production and retention of chl *a*.

## Discussion

Turbidity is known to be an important factor influencing phytoplankton productivity in riverine estuaries (Cloern 1987). The Cape Fear River originates well into the piedmont, and carries a significant load of sediment and other turbidity-producing materials downstream to estuarine waters (Table 3 and Fig. 4). Dredging in the Port of Wilmington also contributes turbidity-producing materials directly to the estuary. High turbidity caused by estuarine dredging and upstream rainfall and runoff may reduce nutrient limitation of phytoplankton in at least two ways. An obvious factor is the creation of physical conditions in which light, rather than nutrients, becomes limiting. Another likely effect of turbidity is that dredging and runoff activities may increase delivery of nutrients to phytoplankton. Clay particles adsorb P, organic N, ammonium, and other materials, which are then carried into streams during runoff events (Froelich 1988; Balogh and Watson 1992; Burkholder 1992; Natural Resources Conservation Service 1995). Our data show significant correlations between turbidity and TP (Table 3). In the CFRE, TP concentrations were highest at the turbidity maximum (M54, Fig. 4), as has been found in other estuaries (Lebo and Sharp 1993). Particle-bound P may be desorbed in estuarine waters either because there is a concentration gradient in the less phosphate-rich mesohaline waters or because other more abundant anions outcompete P for surface sites as salinity increases (Froelich 1988). This desorption would then help relieve P limitation in the water column. Ammonium and organic N are also bound to sediments and ammonium and TN displayed peaks at M54, the turbidity maximum (Fig. 4). Concentrations of N are also often significantly higher in the bottom waters than surface waters (Mallin et al. 1996); turbidity pulses, dredging activities, and benthic fluxes (Rizzo and Christian 1996) may have the effect of delivering ammonium to the upper water column to relieve N limitation.

Factors controlling phytoplankton production demonstrate two distinct patterns in the CFRE (Table 2). Longitudinally, the estuary shows a strong trend of increasing sensitivity to nutrient additions with increasing salinity (Fig. 7). Because of turbidity and reduced light penetration, phytoplankton production at the oligohaline station NAV appears to be limited principally by light availability. There is no generally accepted bioassay procedure to confirm light limitation. Rather, light limitation is assumed from high ambient nutrient levels, lack of phytoplankton stimulation by nutrient addition bioassays, and/or by mathematical modeling procedures (Wofsy 1983; Pennock and Sharpe 1994). Light is constrained at NAV due to the inputs from blackwater tributaries as well as particulate turbidity. The river at NAV is deep and well mixed, likely keeping phytoplankton cells under aphotic conditions for extended periods. It appears that the area near channel marker 54 is a transition zone between light and nutrient limitation in this estuary. Meteorology plays an important role in the regulation of phytoplankton productivity in mid estuary. Upstream rainfall and consequent watershed runoff increase loading of nutrients, mineral turbidity, and other light attenuating materials, leading to light limitation. Winter dredging also increases turbidity and contributes to light limitation. Dry, low river flow conditions lead to decreased nutrients, turbidity, and light attenuation, and increased phytoplankton biomass, with phytoplankton production becoming nutrient limited. The estuary near M23 was nutrient limited most of the year. Light limitation was apparently not as important a limiting factor at M23 compared with M54, although the N enrichment factor for the bioassays was inversely related to light attenuation (i.e., clearer water meant stronger stimulation or limitation).

In the CFRE there is a second (temporal) pattern of factors limiting phytoplankton production, which is the seasonal switching of controls on phytoplankton production. In summer, N limitation prevails, and in our bioassay experiments water temperature was significantly correlated with N stimulation. Following the classification scheme of Fisher et al. (1992) summer responses at M54 and M23 would fall under the category of exclusive N limitation. Late summer is typically the period of highest phosphate concentrations in North Carolina estuaries (Rudek et al. 1991; Mallin 1994). Low DO conditions prevalent during that period can allow sediment-bound P to enter the water column, which would tend to drive the N:P ratio downward (Fig. 5). As mentioned, summer N:P ratios in the Cape Fear River were near the Redfield ratio.

In late fall and winter, particularly in mid estuary, light availability apparently becomes the limiting factor and experimental nutrient additions have little or no effect on phytoplankton growth. In the upper-to-middle estuary, winter nutrient levels are high, light penetration is poor in the turbid, highly colored waters, and chl *a* levels are low. River flow, normally high in winter, is inversely correlated with chl *a* concentration in the estuary. This is in contrast to other estuaries such as the Neuse, Pamlico, and Patuxent where winter dinoflagellate blooms occur as a response to winter nutrient pulses (Kuenzler et al. 1979; Sellner et al. 1991; Mallin et al. 1993; Mallin 1994). Dredging and periodic rainfall and runoff episodes add turbidity to the CFRE, driving the system to periodic light limitation. This is most prevalent in winter, with permitted channel dredging activity and increased flow to the lower estuary because of reduced evapotranspiration in cold weather. Light attenuation was determined to be the major limiting factor during winter in the Delaware estuary, subsequently switching to P limitation in late spring (Pennock and Sharp 1994). Light limitation is thus important on a temporal scale, particularly in the upper estuary and near the turbidity maximum.

During spring in the CFRE significant P limitation occurs, demonstrated by both bioassays and high inorganic N:P molar ratios. Most of the spring experiments indicated primary P limitation, according to the classification of Fisher et al. (1992). Spring P limitation may be a result of high winter-spring flow bringing inorganic N to the lower estuary (Table 3), and possibly the remineralization of organic N compounds formed during the previous year's biological activity. Agricultural runoff has been described as a cause of spring N + P co-limitation in other North Carolina estuaries, while elevated summer primary productivity, increased P availability, and reduced runoff lead to strong summer N limitation (Rudek et al. 1991; Paerl et al. 1995).

Research in other estuaries has also shown nutrient loading, and nutrient ratios and limitation dynamics, may vary seasonally. In the Patuxent River, Maryland, N was the limiting nutrient during summer and P during spring (D'Elia et al. 1986). A similar pattern has been described for the Chesapeake Bay (Fisher et al. 1992; Malone et al. 1996), while in the Rhode River there was strong summer N limitation and weak spring P limitation (Gallegos and Jordan 1997). The spring freshet (with the high N:P ratio from agricultural runoff) contributes to P limitation in the spring, whereas minimum discharge, coupled with increased relative importance of wastewater effluent with its lower N:P ratio, contributes to summer N limitation. P availability varies seasonally in estuaries: in spring, P is rapidly taken up by estuarine biota (Lebo and Sharp 1993) but regenerated during summer months (Lebo and Sharp 1992).

Our studies utilized two experimental measures of nutrient limitation ($^{14}C$ incorporation and chl *a* production). They often showed similar results, but at times one method showed significant effects of a nutrient input while the other method showed no statistical effect. There may be a number of reasons for this difference, including differential $^{14}C$ uptake and biomass of individual phytoplankton species (Coleman and Burkholder 1994), and/or timing of effects. Some species may have little chl *a* biomass per cell but may display rapid uptake of labeled carbon. The converse may also apply at times, with some cells accumulating significant chl *a* biomass over 3 d, with slow uptake of labeled carbon. Averaging the results over 3 d for statistical comparisons may have an effect as well. Chl *a* may peak within a day or two and then decline due to zooplankton grazing, while $^{14}C$ uptake continues (see also Paerl et al. 1990). Combined with the molar ratios of nutrient concentrations, significant stimulation of one or more biological indicators by nutrient addition experiments is needed to provide a good assessment of factors limiting phytoplankton.

It is evident that the CFRE is strongly linked to the middle and upper watershed, including the distant piedmont. Correlation analysis has demonstrated rainfall at Greensboro in the upper watershed (after a lag time) is strongly related to flow in the lower river. Furthermore, this analysis has shown rainfall and river flow are both correlated significantly with nutrient concentrations in the estuary. Combined with the large amount of turbidity-producing substances entering the system from upstream, this is evidence that nonpoint source runoff is an important source of nutrients (and probably other pollutants) to the estuary.

The Cape Fear is the largest river in North Carolina with an open connection to the sea, allowing for generally high flushing and flow velocities. Periods of low flow lead to increased water clarity, reduced nutrient loading, and the increased likelihood of nutrient limitation rather than light limitation. Watershed rainfall and increased river flow suppresses chl *a* accumulation in this system, in contrast to other large estuaries that are less heavily flushed. In the Neuse Estuary, watershed rainfall and river flow are correlated significantly with increases in N loading and phytoplankton productivity (Mallin et al. 1993). In tributaries of the Chesapeake Bay, river flow has been related to increases in nitrate delivery and chl *a* biomass (Malone et al. 1988; Jordan et al. 1991; Gallegos 1992).

All North Carolina estuaries are N limited to various degrees (see Mallin 1994 and references within), but the CFRE is N limited mainly in summer and early fall. There appears to be a continuum with respect to limiting nutrients among the large riverine estuaries in North Carolina studied. Orthophosphate concentrations in the CFRE are much lower than in either the Pamlico River Estuary or the Neuse River Estuary, while inorganic N concentrations are as high or higher (Stanley 1987; Christian et al. 1991; Rudek et al. 1991; Paerl et al. 1995; Mallin et al. 1996). The New River Estuary (with excess P from wastewater treatment plant inputs) and the Pamlico River Estuary (phosphate mining inputs) are mostly N limited (Kuenzler et al. 1979; Mallin et al. 1997b). The Neuse River Estuary (wastewater treatment plant inputs and nonpoint agricultural runoff) is N limited most of the year and co-limited by N + P in spring in the lower estuary, but equally N limited and P limited in the oligohaline area (Rudek et al. 1991; Paerl et al. 1995). The lower CFRE is seasonally divided by N and P limitation, with P limitation stronger and more persistent than in any of the North Carolina riverine estuaries previously studied. In this respect the CFRE is more similar to Chesapeake Bay than it is to its neighbors to the immediate north.

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