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Nitrogen and silicon limitation of phytoplankton communities across an urban estuary: The East River-Long Island Sound system

Christopher J. Gobler [a,*], Nathan J. Buck [a], Michael E. Sieracki [b], Sergio A. Sañudo-Wilhelmy [a]

[a] *Marine Sciences Research Center, SUNY at Stony Brook, Stony Brook, NY 11794-5000, USA*
[b] *Bigelow Laboratory for Ocean Sciences, PO Box 475, West Boothbay Harbor, ME 04575-0475, USA*

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Abstract

To understand how nutrient loading may impact phytoplankton community growth, structure, and photosynthetic efficiency in Long Island Sound (LIS), nutrient enrichment (N, P, or Si) experiments were conducted at stations along the longitudinal gradient of the East River-Long Island Sound system during high and low river flow conditions (spring and summer). During summer, East River (ER) phytoplankton showed no response to N, P, or Si additions. In contrast, N enrichment significantly increased growth rates of all algal size classes (pico- (<3 μm), nano- (3–20 μm) and microphytoplankton (>20 μm)) and most major groups (dinoflagellates, diatoms) beyond control treatments in all regions of LIS (western, WLIS, central, CLIS and eastern, ELIS). Nitrogen enrichment also increased particulate organic carbon production and the photosynthetic efficiency of the phytoplankton community. During spring, ER phytoplankton remained nutrient replete, while larger phytoplankton (nano- and microphytoplankton; diatoms, dinoflagellates) within WLIS and CLIS algal communities were stimulated by N and/or Si additions (1.5- to 7-fold increased growth rates). An absence of response in ELIS phytoplankton following nutrient enrichment during spring together with elevated dissolved inorganic nutrients concentrations and river discharge rates suggests that seasonal variation in river flow can impact the degree to which ELIS phytoplankton are nutrient-limited. A 14-year record of nutrient concentrations and ratios in LIS suggested that our experimental results were representative of long-term seasonal trends, with N-limitation most likely to occur during the spring, summer, and fall in CLIS, during summer and fall in ELIS, and during late spring and summer in WLIS. The existence of low silicate levels relative to inorganic nitrogen in WLIS during spring months suggested that anthropogenic nutrient loading in this region may promote the seasonal Si-limitation of diatoms at this time.

Keywords: phytoplankton; nutrients; nutrient ratios; nutrient limitation; eutrophication

1. Introduction

Estuaries are experiencing increased environmental pressure as expansion of coastal population centers progresses across the globe. Mobilization of nitrogen (N) and phosphorus (P) to surface waters associated with human population growth can have a multitude of adverse impacts on coastal ecosystems, including nuisance algal blooms, hypoxia, and the subsequent loss of marine life, biodiversity, and habitats (reviewed by Richardson and Jorgensen, 1996; de Jonge et al., 2002). As such, significant efforts are currently underway to restrict the flux of nutrients to many coastal regions to mitigate their potentially negative environmental impacts. To properly assess the impact of nutrient overenrichment and the efficiency of subsequent nutrient reduction strategies in estuaries, a comprehensive understanding of how nutrients affect phytoplankton community growth, biomass, production, and diversity is required.

Situated along the northwest Atlantic coast, Long Island Sound (LIS) is one of the most urbanized estuaries on earth, as it is surrounded by some of the most densely populated

* Corresponding author.
E-mail address: cgobler@notes.cc.sunysb.edu (C.J. Gobler).

areas in the United States, including the nation's largest metropolis, New York City. The Sound's watershed extends north to Canada and receives effluent from hundreds of waste water treatment plants, industrial facilities, and power plants (Wolfe et al., 1991; Anderson and Taylor, 2001). The urbanized nature of LIS has contributed to the onset of hypoxic conditions within the bottom waters of western and central LIS, which have recurred annually for the past half century (Parker and O'Reilly, 1991). Since increases in nitrogen supply to LIS are perceived as being primarily responsible for these hypoxic events, the bulk of management decisions regarding LIS to date have focused on limiting discharge of N to the estuary (EPA, 1994; NYSDEC, 2000; O'Shea and Brosnan, 2000).

The premise that N loading contributes to hypoxia in LIS is largely predicated upon the assumption that the accumulation of phytoplankton biomass in this system is proportional to, and hence limited by, nitrogen supply. There is an abundance of literature to support such a hypothesis, as phytoplankton communities in many coastal marine environments have been shown to be N-limited (Ryther and Dunstan, 1971; Howarth, 1988; Fisher et al., 1992), likely due to high denitrification rates, slow nitrogen fixation rates and substantial releases of P from sediments (Boynton and Kemp, 1985; Howarth, 1988). However, unlike most major estuaries, there has been a dearth of peer reviewed research published on phytoplankton and nutrients dynamics in LIS. Research conducted fifty years ago demonstrated that levels of chlorophyll and nutrients are elevated in western LIS relative to the rest of the estuary and suggested N might influence phytoplankton biomass in LIS (Riley and Conover, 1956; Conover, 1956; Harris, 1959). However the input of sewage derived nutrients discharged into LIS has increased substantially since these early studies as population in the NY metropolitan region has increased by 40% (Sweeny and Sañudo-Wilhelmy, 2004). While two recent studies have confirmed the persistence of the east-west gradient in nutrient concentrations in LIS (Capriulo et al., 2002; Sweeny and Sañudo-Wilhelmy, 2004), a comprehensive study of how nutrients affect phytoplankton growth, biomass, or community structure across this gradient has yet to be conducted.

The aim of this study, therefore, was to determine which nutrients (N, P, and Si) limit the net growth rates of phytoplankton communities across the longitudinal eutrophication gradient which exists from the East River to eastern Long Island Sound. Cruises were conducted across the LIS-East River system during high and low freshwater flow conditions to contrast the input of fluvial discharge on nutrient–algal interactions. By evaluating algal community biomass, size structure, speciation, and photosynthetic efficiency, in concert with levels of particulate organic matter and dissolved nutrients during field experiments, a description of phytoplankton-nutrient interactions in LIS was established. Finally, our experimental results are placed in the perspective of a 14-year record of nutrient concentrations and ratios across LIS.

2. Materials and methods

Long Island Sound is roughly 93 km long and 34 km at its widest point, and extends from the East River at New York City to The Race, which is marked by Plum and Fishers Islands (Fig. 1). LIS is the third-largest estuary in the United States with a volume of 6.2×10^{10} m^3. The Sound has a mean depth of 20 m and a maximum depth of 90 m (Wolfe et al., 1991; EPA, 1994). LIS is not a traditional estuary, as it lacks a freshwater source at its head. Instead, the western headwaters of LIS exchange with the lower salinity waters of New York Harbor through the East and Harlem Rivers (Fig. 1). To the east, LIS connects with the Atlantic Ocean and receives 70% of its freshwater from its largest tributary, the Connecticut River (Fig. 1), whose watershed extends as far north as Canada. Deeper, more saline ocean water exhibits a net westerly flow, while fresher surface water generally moves eastward through The Race (Riley, 1967). This array of geographic and nautical features makes the hydrodynamics of LIS both unique and complex.

We conducted cruises across the East River and LIS during July of 2000 and April of 2001. Such an approach allowed for the experimental examination of the response of phytoplankton to nutrient additions under low (July) and high (April) river discharge periods. River water fluxes were obtained from the United States Geological Survey. The average freshwater flow from the four Connecticut rivers with the largest discharge into LIS (Connecticut, Thames, Quinnipiac,

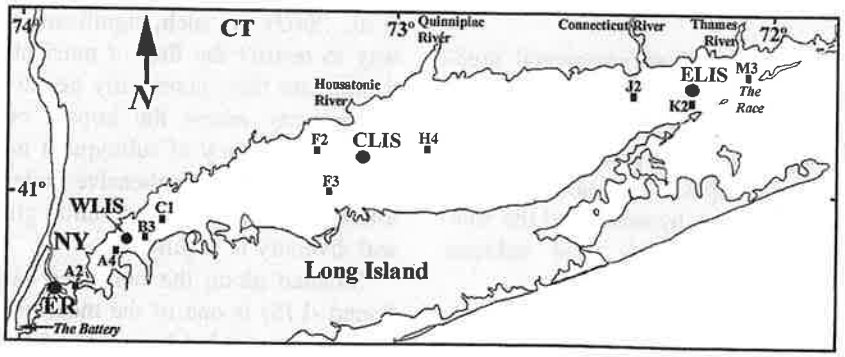


Fig. 1. Long Island Sound, USA, with experimental sites in the East River (ER), western Long Island Sound (WLIS), central Long Island Sound (CLIS), and eastern Long Island Sound (ELIS) as noted with black circles. CTDEP monitoring stations from which nutrient data were used are noted as black squares. Major CT rivers are also shown.

Housatonic) between the years 1990 and 2000 was 5.0×10^7 m^3 d^{-1}. The summer (July 2000) cruise was characterized by low river discharge conditions with the flow of the Connecticut rivers being measured at 2.0×10^7 m^3 d^{-1}, which is 40% of the decadal average. In contrast, the spring cruise (April 2001) was characterized by high discharge conditions, with the flow of the Connecticut rivers (2.4×10^8 m^3 d^{-1}) being nearly five times the decadal average.

Cruises were conducted aboard the R/V Paumanok of Southampton College, Long Island University. We collected water from four stations across the East River-Long Island Sound system: Hell Gate within the East River (ER), Execution Rock in western Long Island Sound (WLIS), Stratford Shoals in central Long Island Sound (CLIS), and a station north of Plum Island and between the mouths of the Connecticut and Thames River in eastern Long Island Sound (ELIS; Fig. 1). Station locations were specifically chosen to represent a spectrum of conditions ranging from high to low levels of anthropogenic influence moving eastward across LIS (Riley, 1967; Sweeny and Sañudo-Wilhelmy, 2004).

On station, surface water was collected using a peristaltic pump equipped with acid-washed Teflon tubing attached to a 7 m trace-metal-clean-boom (Gobler and Sañudo-Wilhelmy, 2001). The boom was submerged to a depth of 1 m and directed into approaching currents and prevailing winds. Whole unfiltered seawater samples were collected and transferred with minimal bubbling to triplicate, 20 l, polyethylene carboys. Dissolved phase (<0.2 μm) samples were obtained by filtration of Sound water through acid-washed, polypropylene capsule filters. Duplicate filtered samples were stored frozen and analyzed for inorganic nutrients (analytical methods described below). All materials associated with the sampling, handling, and storage of seawater during this project were submerged in 10% HCl for 1 month before cruises, and rinsed liberally with distilled-deionized water and sample water before use. Ancillary measurements made at each station included surface temperature and salinity (measured with a Hydrolab© Quanta CTD), as well as Secchi disk depth. Field salinity measurements were confirmed by analysis of a single filtered sample from each station on a Beckman© induction salinometer (model # RS 7B). Using whole water from the triplicate carboys, triplicate chlorophyll *a* and POC/PON samples were collected using precombusted GF/F glass fiber filters (nominal pore size 0.7 μm) and stored frozen. Triplicate whole water samples were also preserved in Lugol's iodine (5% final concentration), glutaraldehyde (2% final concentration), and paraformaldehyde (0.5% final concentration) for later characterization of the phytoplankton community. Preserved samples were immediately stored at 4 °C, and paraformaldehyde-preserved samples were transferred to liquid nitrogen after 1 h.

Plankton community bioassays were conducted to assess nutrient limitation of phytoplankton communities in the LISER system. One liter of seawater was transferred to acid clean 1.2 l polycarbonate flasks. Triplicate flasks were singularly amended with either nitrate (20 μM), ammonium (20 μM), silicate (20 μM), or phosphate (1.25 μM), or were left unamended as a control treatment. The concentrations of these additions were similar to previously observed increases of these nutrients in the water column of Long Island Sound (Sweeny and Sañudo-Wilhelmy, 2004; Buck et al., 2005), and ratios of additions were consistent with Redfield stoichiometry. Since ambient levels of ammonium can be sporadically high in some regions of LIS throughout the year (Anderson and Taylor, 2001) and since nitrate is often the primary form of dissolved nitrogen in many Connecticut rivers (Buck et al., 2005), we contrasted the impacts of ammonium additions with those of nitrate. Nutrient stocks were filter-sterilized (0.2 μm) and stored frozen. Experimental bottles were incubated in a flow-through incubation chamber aboard the research vessel, which received a constant flow of surface water from Long Island Sound and thus maintained in situ temperature. The incubation chamber was also covered with neutral-density screening which reduced ambient light penetration by 33% to prevent photoinhibition (Govindjee, 1975). Since the extinction coefficient at various stations during experiments ranged from 0.3 to 0.9 (based on Secchi disc readings), the light levels used in our experiments were similar light levels present between at 1.5 and 4 m in the water column, which was within the mixed layer and euphotic zone of all experimental stations. After 48 h, samples were removed from experimental flasks for chlorophyll *a* and POC/PON analysis. Whole water samples were also preserved as described above for later characterization of the phytoplankton community.

Chlorophyll *a* (chl *a*) was analyzed by standard fluorometric methods with acidification (Parsons et al., 1984). Duplicate POC and PON samples were dried at 60 °C before analysis on a Carlo Erba NA 1500 NCS system (Sharp, 1974). Standard spectrophotometric methods were used to analyze nitrate/nitrite (Jones, 1984), ammonium, phosphate, and silicate (Parsons et al., 1984) in duplicate. Measurements of standard reference material for POC, PON, nitrate, nitrite, ammonium, and phosphate were all within 10% of certified values.

The total number of suspended chlorophyll *a*-containing and phycoerythrin-containing cells were quantified at Bigelow Laboratory for Ocean Sciences using flow cytometric fluorescence and light scatter patterns (Olson et al., 1991). Paraformaldehyde-preserved samples were analyzed on a Becton Dickinson FACScan flow cytometer, providing abundance, size (calculated from forward light scatter), and cell fluorescence for all identifiable cell populations. Data were grouped by size and fluorescence: we separated picoplankton (<3 μm) into phycoerythrin-containing cyanobacteria (presumed to be *Synechococcus* sp.) and non-phycoerythrin-containing picoeukaryotes, and we grouped chlorophyll *a* containing particles in the 3–20 μm range into a group broadly defined as 'nanoplankton'. Lugol's- and glutaraldehyde-preserved plankton samples were settled in counting chambers and enumerated on an inverted light microscope (Hasle, 1978). Settled microphytoplankton (>20 μm) were identified to the genus or species level and were generally grouped as diatoms or dinoflagellates, as these two classes represented the large majority (>90%) of the microphytoplankton observed.

Maximum quantum efficiency of photosystem II was estimated from in vivo (F_o) and DCMU (3,4-dichlorophenyl-1,1-dimethylurea)-enhanced in vivo fluorescence (F_{DCMU}) of field and experimental samples (Parkhill et al., 2001). To avoid diel variations in these estimates, both of these fluorescence characteristics were measured at or close to the same time each day. For this procedure, sub-samples of whole seawater from stations or experimental bottles were stored in the dark for 30 min, mixed, and measured on a Turner Designs model-10AU fluorometer once the reading stabilized (approximately 30 s; Kolber et al., 1988; Parkhill et al., 2001). DCMU (in ethanol) was added (final concentration 10 μM) to samples which were then mixed and measured again fluorometrically once this reading stabilized (approximately 30 s). Maximum quantum efficiency of photosystem II (F_v/F_m) was calculated using the formula: $F_v/F_m = (F_{DCMU} - F_o)/F_{DCMU}$. All readings were blank corrected using 0.2 μm filtered seawater from stations or experimental bottles. DCMU blocks electron transfer between PSII and PSI and yields maximal fluorescence. Previous studies have demonstrated that F_v/F_m can be a sensitive diagnostic of nutrient limitation, reaching a maximal value of ~0.7 under nutrient replete conditions, and decreasing to less than half of that under nutrient limitation (Kobler et al., 1988; Parkhill et al., 2001).

The response of the phytoplankton communities to nutrients was evaluated via the determination of mass or cell specific growth rates using the formula: $\mu = \ln(B_f/B_o)/t$, where μ is the net growth rates, B_f is the final amount of biomass (cell density, chlorophyll *a*, or POC) in a given treatment, B_o is the initial amount of biomass in the water column, and t is the duration of the experimental incubation (generally 48 h). Growth rates and changes in parameters associated with phytoplankton communities (POC:PON, F_v/F_m) during experimental incubations were statistically evaluated via one-way ANOVAs, followed by Tukey multiple comparisons tests of treatments, controls, and initial in situ conditions at each station (Sokal and Rolf, 1994). Non-normally distributed data sets were log transformed.

To place our experimental results in the perspective of annual cycles and long term nutrient trends in LIS, we complied the record of inorganic nutrient concentrations in LIS generated by the Connecticut Department of Environmental Protection (CTDEP), 1991–2004. To be consistent with our experimental design, we synthesized data from CTDEP stations surrounding each of our experimental stations: A4, B3, and C1 in western LIS, F2, F3, and H4 in central LIS, J2, K2, and M3 in eastern LIS and A2 in the East River (Fig. 1). Monthly averages were calculated for DIN, DIP, and DSi (dissolved silicon) for each region based on over 400 individual data points per station per nutrient. Ratios of DIN:DIP and of DIN:DSi were generated for each individual sampling date and monthly means of nutrient ratios were also calculated. CTDEP nutrient concentrations were determined using standard techniques (Parsons et al., 1984) coupled with a flow-injection auto analyzer. Detection limits for ammonium, nitrate, silicate, and orthophosphate were 0.21, 0.14, 0.23, and 0.04 μM, respectively.

3. Results

3.1. Summer

During the summer, there was a strong spatial gradient in dissolved nutrients among the experimental stations in Long Island Sound, with generally high levels in ER, and progressively lower levels present moving east through the LIS stations toward the Atlantic Ocean (Table 1). Specifically, the ER contained 58.5 ± 10.2 μM DIN (ammonium, nitrate, nitrite), 4.57 ± 0.23 μM DIP, and 7.51 ± 1.04 μM DSi (Table 1). In contrast, all LIS stations had <2 μM DIN and DIP, and only slightly higher levels of DSi (~ 2–5 μM; Table 1). Chl *a* and abundances of nano-phytoplankton in LIS displayed a trend similar to dissolved nutrients during the summer cruise, with ER being the notable exception (Table 1). Moderate concentrations of chl *a* were found across the LIS, with WLIS hosting levels (6.06 ± 1.62 μg l^{-1}) more than double those found at other stations (Table 1). Consistent with observed chl *a* concentrations, nano- and microphytoplankton cell densities in WLIS (1.51 ± 0.32 × 10^4 ml^{-1} and 1.26 ± 0.15 × 10^3 ml^{-1}; Table 1) were an order of magnitude and two-times, respectively, the densities found at all other stations (Table 1). In contrast, picophytoplankton densities were high in ELIS and CLIS (2.76 ± 0.91 × 10^5 ml^{-1} and 2.11 ± 0.27 × 10^5 ml^{-1}, respectively; Table 1), but were lower in WLIS and ER (3.08 ± 0.15 × 10^4 ml^{-1} and 4.03 ± 0.19 × 10^3 ml^{-1}, respectively; Table 1). Diatoms and dinoflagellates represented 81 ± 3.3% and 18 ± 4.1% of microphytoplankton at all stations (Table 1). *Synechococcus* sp. made up a similar portion of the picophytoplankton in CLIS and ELIS (80% and 54%), was a minor component in ER (17%), and was scarce in WLIS (<1%; Table 1). While temperatures at each station during summer were similar (20.6–22.0 °C), salinities steadily increased from 23.4 PSU in ER to 28.4 PSU in ELIS (Table 1).

There were no statistically significant changes in chlorophyll *a*, POC, or any of the phytoplankton populations monitored during the summer ER experiment following the addition of nutrients (Fig. 2, Table 2). In contrast, the addition of nitrogenous nutrients yielded substantial increases in the carbon and chlorophyll *a* specific growth rates of phytoplankton at each LIS station during summer experiments (WLIS, CLIS, and ELIS). In WLIS, only nitrate enrichment yielded growth rates significantly greater than control treatments ($p < 0.05$; Fig. 2). With the exception of *Synechococcus* sp., this response was observed across the full spectrum of phytoplankton, as growth rates of eukaryotic picophytoplankton, nanophytoplankton, diatoms and dinoflagellates were all significantly higher in the nitrate treatment relative to control treatments ($p < 0.05$ for all; Table 2). Among the microphytoplankton, *Chaetoceros* sp., *Coscinodiscus* sp., and *Prorocentrum* sp. were the three most abundant species following the nitrate addition, representing 47 ± 15% of cells in this size class (data not shown). Although the POC:PON ratio was lowest in the nitrate treatment after the 48-h experiment (12.2 ± 3.1), it did not differ significantly from other

Table 1
Water quality and phytoplankton community structure in the Long Island Sound-East River system during summer (July 2000) and spring (April 2001) cruises. WLIS, CLIS, and ELIS are western, central and eastern Long Island Sound. T is temperature in °C, S is salinity in PSU, DIN is dissolved inorganic nitrogen, DIP is dissolved inorganic phosphorus, DSi is dissolved inorganic silicon, all in μM. Chla is chlorophyll *a* in μg l^{-1}, Pico is the picophytoplankton ($\times 10^3$ cells ml^{-1}), Syn is *Synechococcus* sp. ($\times 10^3$ cells ml^{-1}), PEUKS is picoeukaryotic phytoplankton ($\times 10^3$ cells ml^{-1}), Nano is nanophytoplankton ($\times 10^4$ cells ml^{-1}), Micro is microphytoplankton ($\times 10^3$ cells ml^{-1}), Diatoms are in 10^3 cells ml^{-1} and Dinos are dinoflagellates in 10^3 cells ml^{-1}. Values are means with standard deviation in parentheses

	T	S	DIN	DIP	DSi	DIN:DIP	DIN:DSi	POC	POC:PON
Summer									
ER	21.6	23.4 (0.01)	58.5 (10.2)	4.57 (0.23)	7.51 (1.04)	12.8 (2.00)	7.89 (1.23)	19.9 (1.21)	5.95 (0.46)
WLIS	22.0	25.4 (0.00)	1.05 (0.07)	1.20 (0.13)	5.21 (0.69)	0.88 (0.09)	0.20 (12)	71.1 (0.11)	10.4 (1.08)
CLIS	20.6	26.7 (0.02)	1.87 (0.82)	0.48 (0.09)	4.12 (0.36)	3.89 (1.02)	0.45 (0.12)	25.5 (5.54)	7.86 (1.99)
ELIS	20.7	28.4 (0.01)	0.58 (0.30)	0.54 (0.07)	1.89 (0.04)	1.07 (0.29)	0.31 (0.08)	35.2 (3.67)	10.12 (1.53)
Spring									
ER	8.9	19.8 (0.00)	35.3 (1.06)	1.75 (0.18)	25.5 (2.12)	20.2 (1.14)	1.38 (0.08)	25.0 (2.69)	10.65 (1.59)
WLIS	9.8	24.8 (0.01)	4.84 (0.48)	0.26 (0.18)	2.87 (0.04)	18.6 (1.71)	1.69 (0.01)	63.9 (12.9)	7.77 (0.02)
CLIS	10.4	25.3 (0.01)	0.89 (0.18)	0.34 (0.05)	1.95 (0.04)	2.62 (0.29)	0.50 (0.06)	29.7 (8.17)	10.4 (0.60)
ELIS	7.1	26.0 (0.02)	8.79 (1.42)	0.44 (0.03)	1.66 (0.16)	20.0 (2.58)	5.30 (0.68)	12.2 (0.47)	8.79 (0.59)

	Chla	Pico	Syn	PEUKS	Nano	Micro	Diatoms	Dinos
Summer								
ER	0.20 (0.018)	4.03 (0.19)	0.67 (0.09)	3.36 (1.64)	1.0 (0.05)	0.50 (0.04)	0.41 (0.07)	0.09 (0.02)
WLIS	6.06 (1.62)	30.8 (1.46)	0.21 (0.05)	30.7 (1.37)	15 (0.32)	1.26 (0.15)	1.06 (0.21)	0.20 (0.04)
CLIS	0.52 (0.08)	211 (26.6)	114 (1.53)	97.3 (14.6)	1.8 (0.31)	0.28 (0.03)	0.23 (0.02)	0.06 (0.01)
ELIS	0.48 (0.07)	276 (90.9)	222 (6.02)	54.5 (3.11)	1.27 (0.09)	0.55 (0.1)	0.42 (0.03)	0.14 (0.03)
Spring								
ER	1.16 (0.49)	1.79 (0.28)	0.16 (0.08)	1.61 (0.28)	0.41 (0.02)	0.16 (0.07)	0.14 (0.03)	0.02 (0.00)
WLIS	7.03 (1.13)	2.58 (3.35)	0.02 (0.01)	2.56 (0.34)	9.28 (0.52)	1.09 (0.19)	1.09 (0.09)	0.03 (0.01)
CLIS	3.05 (0.05)	38.5 (1.74)	0.07 (0.02)	38.4 (1.73)	10.8 (1.60)	0.40 (0.06)	0.36 (0.40)	0.04 (0.01)
ELIS	1.36 (0.02)	3.99 (4.16)	0.35 (0.08)	3.70 (0.35)	0.90 (0.08)	0.23 (0.01)	0.16 (0.08)	0.08 (0.02)

treatments (all other treatments 14.7 ± 0.5; Table 3). The nitrate addition did, however, significantly enhance the photosynthetic efficiency ($F_v/F_m = 0.69 \pm 0.02$) of the algal community relative to unamended control treatments ($F_v/F_m = 0.57 \pm 0.04$; $p < 0.05$; Table 3).

The impact of nitrogen on the phytoplankton community was more pronounced in CLIS. Both nitrate and ammonium treatments yielded chl *a*-specific growth rates which were $\sim 1.0\ d^{-1}$, a rate significantly greater than the control treatment which had a slightly negative net growth rate ($p < 0.001$; Fig. 2). Similarly, carbon specific growth rates in both N treatments were significantly (5–6-fold) higher than control treatments ($p < 0.001$ for all; Fig. 2). This growth response was also observed among most phytoplankton size classes, as densities of picoeukaryotic phytoplankton, nanophytoplankton, diatoms and dinoflagellates were all significantly higher in the nitrogen treatments relative to initial densities and controls ($p < 0.05$; Table 2). In a manner similar to WLIS, *Synechococcus* sp. densities were unaffected by nitrogen (Table 2). *Chaetoceros* sp., *Nitzchia* sp., and *Prorocentrum* sp. became the three most abundant microphytoplankton species during the nitrate and ammonium incubations, representing $51 \pm 12\%$ of microplankton cells present. Like the WLIS experiment, nitrogen additions yielded the lowest POC:PON ratio (9.1 ± 0.40), although this ratio was not significantly different from control treatments (11 ± 1.4; Table 3). However, community photosynthetic efficiencies following both nitrogen additions (nitrate treatment $F_v/F_m = 0.65 \pm 0.05$; ammonium treatment $F_v/F_m = 0.64 \pm 0.01$) were significantly higher than the unamended control treatments ($F_v/F_m = 0.56 \pm 0.01$; $p < 0.05$; Table 3).

The most dramatic response to experimental nitrogen loading among the algal community during the summer was in ELIS. Chlorophyll-specific growth rates in nitrate and ammonium treatments ($>1.25\ d^{-1}$) were nearly an order of magnitude greater than all other treatments ($p < 0.001$ for all; Fig. 2). Carbon specific growth rates ($\sim 0.4\ d^{-1}$) were lower than chlorophyll-specific growth rates in the N-treatments, but were significantly greater than all other treatments ($p < 0.001$ for all; Fig. 2). For the only time during this study, every component of the phytoplankton community which was quantified yielded a statistically significant increase in growth rates during both nitrogen treatments relative to all other treatments (Table 2; $p < 0.05$ for all). The largest response in the nitrate and ammonium treatments was displayed by nanophytoplankton, whose growth rates was $\sim 1.4\ d^{-1}$ (Table 2). The most abundant diatom following these additions was *Thalassiosira* sp. ($20 \pm 5.1\%$ of microplankton), while *Prorocentrum* sp. was the most common dinoflagellate ($22 \pm 7.2\%$ of microplankton). The impact of nitrogen loading was also seen in POC:PON ratios and the photosynthetic efficiency of the phytoplankton community, which were significantly lower and higher, respectively, in the nitrogen treatments relative to unamended controls ($p < 0.05$ for all; Table 3). Moreover, neither phosphorus nor silicon yielded enhanced growth of any algal group during any of the summer experiments.

Table 2
Net growth rates of phytoplankton during nutrient enrichment experiments at the four stations (ER, WLIS, CLIS, ELIS) during summer and spring. Control (C), nitrate (N), ammonium (A), orthophosphate (P), and silicon (S) refer to the experimental treatments. Phytoplankton groups evaluated during experiments were picoeukaryotes (PEUK; <3 μm), *Synechococcus* sp. (SYN), nanophytoplankton (Nano: 3–20 μm), diatoms (>20 μm) and dinoflagellates (Dinos; >20 μm). Numbers represent mean net growth rates of triplicate incubations, with standard deviations appearing in parentheses. Numbers in bold type denote mean net growth rates which were significantly greater than the control treatments ($p < 0.05$; ANOVA; Tukey)

	Summer					Spring				
	PEUK	SYN	Nano	Diatoms	Dinos	PEUK	SYN	Nano	Diatoms	Dinos
ER										
C	0.54 (0.02)	0.23 (0.08)	0.30 (0.02)	0.39 (0.08)	−0.86 (0.28)	**0.21 (0.02)**	−0.58 (0.16)	**0.32 (0.02)**	**0.62 (0.34)**	**0.33 (0.30)**
N	0.57 (0.03)	0.65 (0.14)	0.32 (0.03)	0.42 (0.16)	−0.35 (0.23)	**0.18 (0.03)**	−0.59 (0.10)	**0.39 (0.02)**	**0.72 (0.19)**	**0.00 (0.07)**
A	0.60 (0.01)	0.36 (0.09)	0.31 (0.01)	0.53 (0.10)	−1.18 (0.75)	**0.13 (0.12)**	−0.71 (0.31)	**0.41 (0.07)**	**0.70 (0.23)**	**0.28 (0.28)**
P	0.60 (0.04)	0.32 (0.17)	0.33 (0.03)	0.34 (0.08)	−1.15 (0.59)	**0.24 (0.01)**	−0.66 (0.22)	**0.37 (0.03)**	**0.73 (0.52)**	**0.09 (0.06)**
S	0.58 (0.07)	0.10 (0.10)	0.31 (0.02)	0.50 (0.14)	−0.82 (0.34)	**0.20 (0.01)**	−0.85 (0.40)	**0.42 (0.05)**	**0.79 (0.26)**	**0.15 (0.13)**
WLIS										
C	0.52 (0.04)	0.20 (0.17)	0.56 (0.03)	0.89 (0.07)	0.30 (0.10)	0.59 (0.05)	0.13 (0.11)	0.24 (0.01)	−0.17 (0.03)	−0.21 (0.07)
N	**0.70 (0.03)**	0.53 (0.14)	**0.72 (0.04)**	**1.16 (0.20)**	**0.96 (0.26)**	0.53 (0.07)	0.02 (0.09)	0.25 (0.02)	**0.35 (0.02)**	**1.16 (0.13)**
A	0.58 (0.07)	0.35 (0.26)	0.60 (0.01)	0.91 (0.31)	0.75 (0.39)	0.53 (0.08)	0.28 (0.17)	0.30 (0.01)	**0.43 (0.04)**	**0.95 (0.26)**
P	0.52 (0.03)	0.51 (0.25)	0.54 (0.09)	0.88 (0.20)	0.15 (0.06)	0.59 (0.07)	0.15 (0.08)	0.24 (0.02)	−0.04 (0.01)	0.22 (0.10)
S	0.59 (0.01)	0.09 (0.01)	0.59 (0.01)	0.97 (0.21)	0.34 (0.14)	0.72 (0.10)	−0.17 (0.40)	**0.46 (0.01)**	**0.64 (0.08)**	−0.20 (0.18)
CLIS										
C	−0.11 (0.04)	0.13 (0.01)	0.21 (0.14)	−0.30 (0.17)	−0.20 (0.09)	0.07 (0.04)	−0.52 (0.19)	−0.15 (0.02)	0.16 (0.02)	−0.09 (0.03)
N	**0.34 (0.05)**	0.13 (0.01)	**1.28 (0.10)**	**0.56 (0.11)**	**0.87 (0.24)**	0.01 (0.04)	−0.27 (0.05)	**0.61 (0.15)**	**0.66 (0.09)**	**0.45 (0.19)**
A	**0.47 (0.04)**	0.07 (0.01)	**1.52 (0.11)**	**0.64 (0.13)**	**0.89 (0.11)**	0.04 (0.01)	−0.07 (0.20)	**0.70 (0.07)**	**0.76 (0.21)**	**0.82 (0.20)**
P	−0.13 (0.02)	−0.15 (0.10)	0.49 (0.04)	−0.38 (0.06)	−0.48 (0.34)	0.11 (0.07)	−0.58 (0.17)	−0.34 (0.02)	0.24 (0.08)	−0.36 (0.09)
S	−0.11 (0.01)	−0.08 (0.06)	0.43 (0.18)	−0.09 (0.09)	−0.57 (0.57)	0.07 (0.04)	−0.67 (0.22)	−0.19 (0.04)	**0.79 (0.13)**	−0.33 (0.22)
ELIS										
C	0.02 (0.01)	0.21 (0.04)	0.23 (0.02)	0.11 (0.05)	0.21 (0.05)	0.50 (0.07)	−0.05 (0.08)	0.33 (0.03)	0.44 (0.14)	−0.12 (0.11)
N	**0.52 (0.26)**	**0.50 (0.06)**	**1.39 (0.24)**	**1.24 (0.39)**	**1.04 (0.16)**	0.58 (0.03)	0.07 (0.07)	0.40 (0.03)	0.48 (0.22)	0.00 (0.00)
A	**0.77 (0.04)**	**0.54 (0.04)**	**1.39 (0.43)**	**1.23 (0.37)**	**1.13 (0.22)**	0.56 (0.03)	0.02 (0.09)	0.37 (0.03)	0.47 (0.16)	−0.26 (0.17)
P	0.07 (0.01)	0.34 (0.05)	0.27 (0.04)	0.10 (0.05)	0.21 (0.11)	0.56 (0.05)	−0.06 (0.07)	0.37 (0.04)	0.37 (0.21)	−0.02 (0.01)
S	0.07 (0.02)	0.36 (0.01)	0.27 (0.02)	0.20 (0.04)	−0.5 (0.01)	0.52 (0.07)	0.04 (0.19)	0.42 (0.02)	0.57 (0.20)	0.05 (0.02)

3.2. Spring

During the spring experiments, a pattern somewhat similar to summer conditions was apparent in the distribution of dissolved nutrients across LIS. Levels of all dissolved nutrients were again highest at ER (DIN = 35.3 ± 1.06 μM; DIP = 1.75 ± 0.18 μM; DSi = 25.5 ± 2.12 μM) and decreased through WLIS and CLIS (Table 1). However, ELIS displayed elevated levels of DIN (8.79 ± 1.42) and DIP (0.44 ± 0.03 μM) relative to other LIS stations (Table 1). In

Table 3
The particulate organic carbon to nitrogen ratios and the photosynthetic efficiencies of photosystem II in phytoplankton communities across Long Island Sound during summer and spring cruises. Values are shown for measurements in the field (initial) and measurements in various experimental treatments after 48 h experiments (control, nitrate, ammonium, phosphate, and silicon). WLIS, CLIS, and ELIS are western, central and eastern Long Island Sound. Values are means with standard deviations in parentheses. Numbers in bold type denote POC:PON ratios and photosynthetic efficiencies which were significantly greater than the control treatments ($p < 0.05$; ANOVA; Tukey)

			Initial	Control	Nitrate	Ammonium	Phosphate	Silicon
Summer	East River	POC:PON	5.95 (0.46)	7.82 (0.23)	7.65 (0.67)	7.70 (0.69)	7.06 (0.86)	7.62 (1.41)
		F_v/F_m	0.59 (0.02)	0.68 (0.01)	0.66 (0.03)	0.70 (0.02)	0.69 (0.02)	0.69 (0.01)
	WLIS	POC:PON	10.4 (1.08)	13.9 (1.20)	12.2 (3.09)	14.2 (4.72)	15.2 (1.00)	14.6 (2.86)
		F_v/F_m	0.63 (0.01)	0.57 (0.04)	**0.69 (0.02)**	0.62 (0.07)	0.58 (0.01)	0.60 (0.02)
	CLIS	POC:PON	9.85 (0.36)	11.4 (1.38)	9.14 (0.40)	8.31 (1.12)	12.7 (1.66)	11.9 (2.21)
		F_v/F_m	0.58 (0.01)	0.56 (0.01)	**0.65 (0.05)**	**0.64 (0.01)**	0.57 (0.02)	0.58 (0.02)
	ELIS	POC:PON	10.1 (1.53)	12.9 (1.24)	**9.01 (0.71)**	**8.22 (0.49)**	11.6 (1.16)	11.2 (1.73)
		F_v/F_m	0.59 (0.03)	0.55 (0.04)	**0.65 (0.02)**	**0.64 (0.01)**	0.62 (0.04)	0.63 (0.01)
Spring	East River	POC:PON	10.6 (1.59)	11.8 (3.31)	11.1 (1.81)	10.1 (1.03)	10.7 (0.46)	9.52 (0.37)
		F_v/F_m	0.37 (0.02)	0.56 (0.06)	0.61 (0.03)	0.59 (0.03)	0.59 (0.02)	0.57 (0.08)
	WLIS	POC:PON	7.78 (0.02)	9.03 (0.86)	10.2 (1.01)	7.78 (0.77)	8.00 (1.49)	13.5 (1.76)
		F_v/F_m	0.59 (0.04)	0.68 (0.02)	0.69 (0.03)	0.68 (0.03)	0.75 (0.04)	0.76 (0.01)
	CLIS	POC:PON	10.4 (0.06)	12.9 (0.64)	**9.60 (0.11)**	**9.44 (1.59)**	15.0 (1.09)	15.4 (1.50)
		F_v/F_m	0.36 (0.03)	0.30 (0.06)	**0.49 (0.02)**	**0.50 (0.01)**	0.30 (0.02)	0.33 (0.04)
	ELIS	POC:PON	8.80 (0.60)	11.0 (2.60)	11.3 (2.07)	11.0 (1.82)	8.81 (2.21)	9.13 (1.27)
		F_v/F_m	0.59 (0.11)	0.57 (0.12)	0.55 (0.04)	0.53 (0.02)	0.57 (0.11)	0.54 (0.12)

a manner consistent with the summer pattern, the greatest levels of chl *a* (7.03 ± 1.13 μg l^{-1}), and microphytoplankton ($1.09 \pm 0.19 \times 10^3$ ml^{-1}; Table 1) were observed in WLIS. Although CLIS had lower levels of chl *a* (3.05 ± 0.05 μg l^{-1}), it had the greatest densities of pico- and nanophytoplankton ($3.85 \pm 1.74 \times 10^4$ ml^{-1} and $1.08 \pm 1.60 \times 10^4$ ml^{-1}, respectively; Table 1). *Synechococcus* sp. densities were substantially lower at all stations during the spring (range $0.2–3.5 \times 10^3$ ml^{-1}; ~5% of picoplankton; Table 1), while diatoms were again the dominant class of microphytoplankton ($87 \pm 13\%$; Table 1). While temperatures at each station during spring were similar (7.1–10 °C), salinities steadily increased from 19.8 PSU in ER to 26.0 PSU in ELIS (Table 1).

The response of the phytoplankton community of LIS during the spring cruise differed from that of the summer experiments. At both the ER and ELIS stations, nutrient additions did not significantly enhance the growth rates of most phytoplankton populations relative to unamended controls (Fig. 3; Table 2). In contrast, in WLIS, both nitrogen and silicon additions yielded significant changes in the algal community there. Chl *a*-specific growth rates during nitrate, ammonium, and silicon incubations were all significantly greater than unamended control treatments ($p < 0.05$ for each; Fig. 3). While these treatments also yielded significantly higher carbon-specific growth rates ($p < 0.05$ for all; Fig. 3), the most substantial response was in the silicon treatment which had carbon-based growth rates that were more than twice the control treatment (Fig. 3). The algal response within the WLIS silicon treatment was due to the growth of both small and large diatoms. Silicon loading yielded significantly higher growth rates of nanophytoplankton and larger diatoms (such as *Thalassionema* sp. and *Thalassiosira* sp.) relative to all treatments with the exception of the nitrate and ammonium addition ($p < 0.001$; Table 2). Diatoms and dinoflagellates were the only group which experienced significantly higher growth rates in the nitrate and ammonium additions relative to control treatments (Table 2; $p < 0.001$). *Amphidinium* sp. was the numerically dominant dinoflagellate ($10 \pm 4.9\%$ of microplankton) in the nitrogen treatments, while *Leptocylindrus* sp. was the most abundant diatom in these treatments ($32 \pm 6.5\%$ of microplankton). POC:PON ratios and photosynthetic efficiencies were not significantly altered by nutrient additions in WLIS (Table 3).

Nitrogen and silicon also had discernible impacts on the CLIS phytoplankton community during the spring. Nitrate and ammonium additions yielded growth rates which were significantly greater than all other treatments ($p < 0.001$ for all; Fig. 3). Although silicon additions did not significantly alter chl *a*-specific growth rates, they yielded carbon-specific growth rates that were significantly greater than control treatments ($p < 0.05$ for all; Table 2). Differential analysis of the total phytoplankton community indicated that the nanophytoplankton, diatoms, and dinoflagellates were responsible for the noted increase in biomass in experimental treatments, as growth rates of these groups during the enrichment of nitrate and ammonium were approximately five times greater than control treatments (Fig. 3; $p < 0.001$ for all). Diatom growth rates were also significantly greater than controls following the addition of silicate (Fig. 3; $p < 0.05$). *Coscinodiscus* sp. and *Leptocylindrus* sp. were two microphytoplankton that became numerically dominant in the nitrogen treatments ($48 \pm 19\%$ of microplankton), whereas *Thalassionema* sp. and *Navicula* sp. achieved the highest densities within silicon treatment ($61 \pm 16\%$ of microplankton). Finally, POC:PON (9.60 ± 0.011 and 9.44 ± 1.59) and photosynthetic efficiency of the algal communities (F_v/F_m: 0.49 ± 0.02 and 0.50 ± 0.01) in the nitrate and ammonium treatments were significantly lower and greater, respectively, than unamended control treatments (POC:PON $= 12.9 \pm 0.64$, $F_v/F_m = 0.30 \pm 0.06$; $p < 0.05$ for all; Table 3). The silicon treatment did not impact these parameters (Table 3). Moreover, phosphorus did not alter the growth of any algal group during any of the spring experiments.

4. Discussion

During this study, we experimentally demonstrated that nitrogen is the element which most frequently limits the accumulation of phytoplankton biomass in LIS. Our research additionally demonstrated that there was a spatial gradient in the degree of nitrogen limitation moving west to east across LIS and that the response to nitrogen loading among phytoplankton was heterogeneous, with only particular species and size classes experiencing enhanced growth during each experiment. Moreover, our spring experiments demonstrated that silicon can also limit the net accumulation of diatoms in LIS and that ELIS can become a nutrient-replete environment when Connecticut river flow rates are elevated. Together, these results lead to a new understanding of nutrient-phytoplankton dynamics in this urban estuary.

As has been commonly observed in other temperate, coastal marine ecosystems, N was the element which most commonly limited the production of phytoplankton biomass in LIS during this study (Figs. 2 and 3; Ryther and Dunstan, 1971; Howarth, 1988; Fisher et al., 1992). There was, however, significant temporal and spatial variability in the manner in which N loading impacted the LIS phytoplankton at the community level. During our summer cruise, we observed a strong spatial gradient in N limitation of phytoplankton communities moving eastward through the ER-LIS system. Although ER phytoplankton were unaffected by N enrichment, this treatment yielded an increasingly larger growth response with increasing distance from New York City (Fig. 2). This gradient is consistent with the observed changes in DIN levels in LIS across the longitudinal gradient of the estuary (Buck et al., 2005), which transitions from extremely high concentrations in ER and WLIS stations (32.2 ± 19.9 μM; $n = 9$; Fig. 4) to low levels in CLIS and ELIS (1.23 ± 1.22 μM; $n = 15$; Fig. 4) during summer months. These observations are also in agreement with mass balance estimates for the estuary which indicate that during low freshwater flow periods (summer), the brackish, tidal East River is the dominant source of N to the LIS ecosystem (Buck et al., 2005).

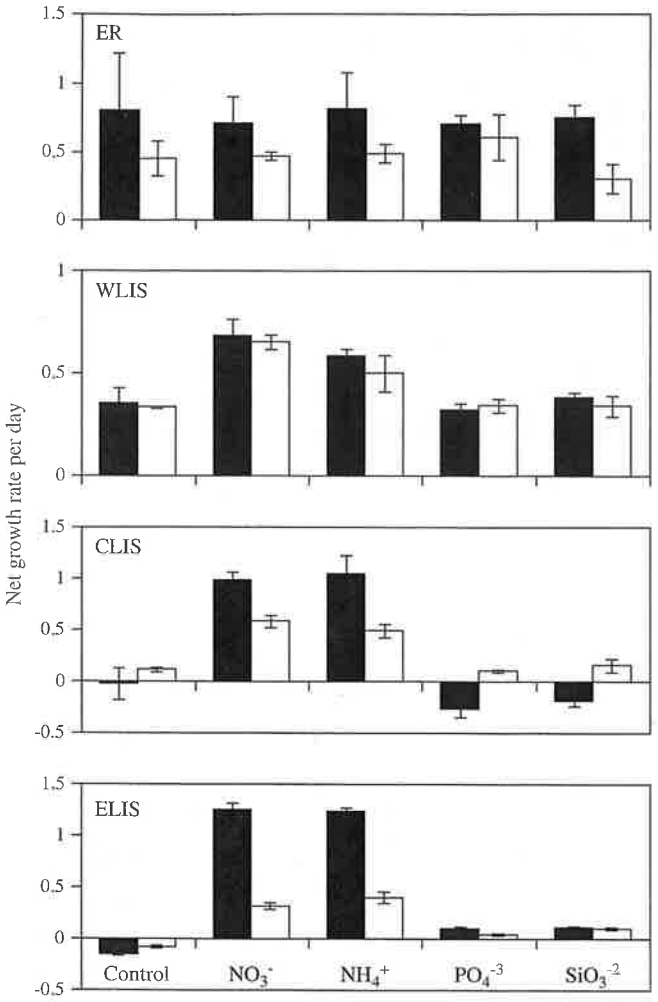


Fig. 2. Net growth rates of plankton communities at experimental stations (ER, WLIS, CLIS, ELIS) during summer, based on changes in levels of chlorophyll *a* (black bars) and POC (white bars). NO_3^- is nitrate, NH_4^+ is ammonium, PO_4^{-3} is orthophosphate, SiO_3^{-2} is silicon. Error bars represent ± 1SD of triplicate measurements.

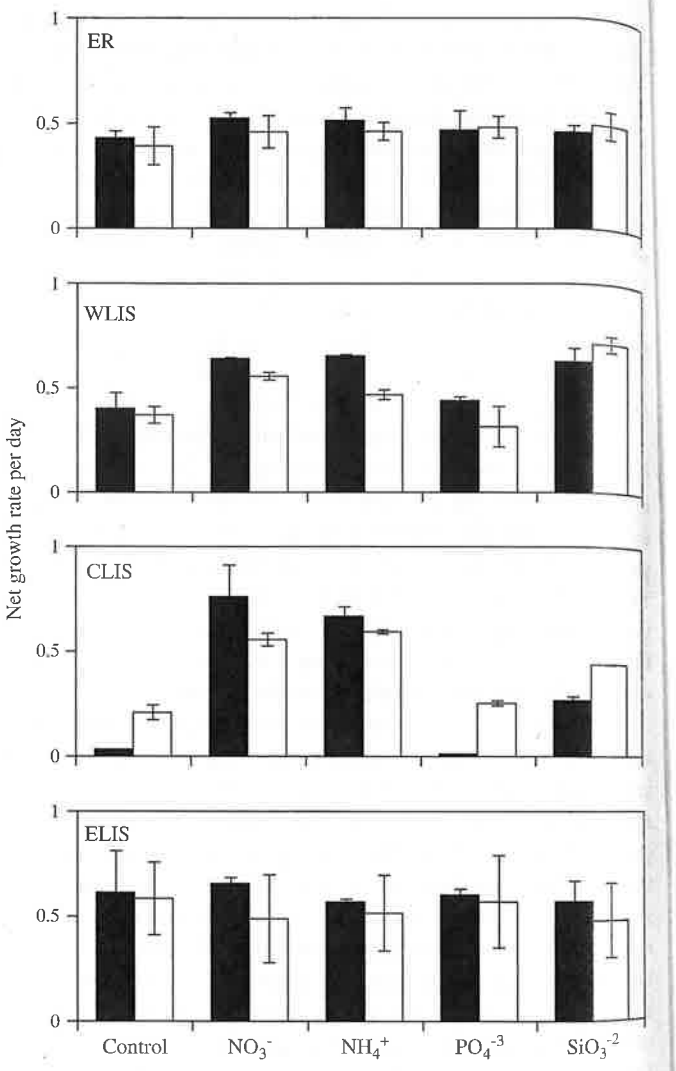
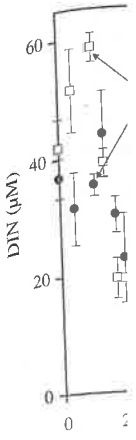


Fig. 3. Net growth rates of plankton communities at experimental stations (ER, WLIS, CLIS, ELIS) during spring, based on changes in levels of chlorophyll *a* (black bars) and POC (white bars). NO_3^- is nitrate, NH_4^+ is ammonium, PO_4^{-3} is orthophosphate, SiO_3^{-2} is silicon. Error bars represent ± 1SD of triplicate measurements.

During our spring experiments, the responses of the algal community to N additions were similar to the summer results at all stations except ELIS, where phytoplankton were unaffected by nutrient additions. There are multiple lines of evidence suggesting that changes in the discharge rates of rivers in Connecticut (Connecticut River, Thames River) influenced the dramatic transition of this station from the most N-limited during the summer to N-replete during the spring. For instance, DIN levels (8.79 ± 1.42 μM; Table 1) and the DIN:DIP ratio (20.0 ± 2.58; Table 1) at the ELIS experimental station during spring experiments were significantly greater than levels and ratios found during the summer (0.58 ± 0.30 μM DIN; 1.07 ± 0.29 DIN:DIP; $p < 0.05$ for both; Student's *t*-test; Table 1). Similarly, Buck et al. (2005) reported that among eight eastern LIS stations situated between the mouths of the Connecticut and Thames Rivers (including the ELIS experimental station; Fig. 1), DIN concentrations during the spring (5.03 ± 2.38 μM; Fig. 4) were ~5-fold greater than the levels present at the same stations during the summer (1.08 ± 0.29 μM; $p < 0.001$; Student's *t*-test; Fig. 4). Concurrently, flow rates of Connecticut rivers during the spring experiments were 5-fold higher than the long term mean discharge rates, and mean salinities in eastern LIS were, on average, 3.8 ± 1.2 PSU lower than levels observed during the summer (Buck et al., 2005). Combined with the relatively high photosynthetic efficiencies observed in ELIS during the spring (0.59 ± 0.02; Table 3), these results suggest that seasonally elevated Connecticut river flow rates are capable of delivering nutrients to ELIS which may alleviate nutrient limitation of primary producers there. The ephemeral nature of Connecticut river discharge as a nutrient source contrasts with the sewage-impacted East River which flows tidally into LIS and, hence, represents a more chronic source of nutrients to the estuary. As such, it would seem consistent nitrogen reductions would most effectively reduce algal biomass along the East River area, while reductions along the Connecticut River watershed would be most effective during spring months.



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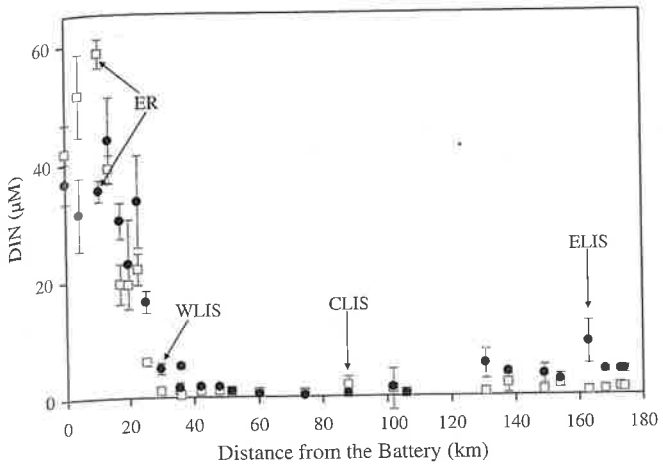

Fig. 4. Concentrations of dissolved inorganic nitrogen (DIN) across the East River and Long Island Sound during summer (open squares) and spring (black circles). Values on the *x*-axis are represented as distance from the Battery, which is the southern extent of the East River. Location of experimental stations are noted. Error bars represent ± 1SD of duplicate measurements.

The LIS phytoplankton community displayed a diversity of responses to nutrient loading during our study. For example, although N enhanced levels of algal growth rates relative to control treatments during the majority of experiments we conducted in LIS (five of six), it was only during the summer experiment in ELIS that N additions significantly enhanced densities of *Synechococcus* sp. beyond control treatments (Table 2). In contrast, in four of the six experiments conducted in LIS, nanophytoplankton experienced significantly increased cell densities relative to control treatments, while in five of the six LIS experiments, microphytoplankton significantly increased in cell density relative to control treatments (Table 2). The contrasting responses of these groups suggest that larger phytoplankton are the most likely to be nutrient limited and to take advantage of N pulses is LIS, particularly during spring months. This may be due to nutrient uptake velocities in larger cells which exceed those found in smaller cells (Raven and Kubler, 2002). Additionally, these results suggest that sudden increases in nutrient loading, such as those which occur during combined sewage overflows in LIS (Anderson and Taylor, 2001) could have a direct and negative impact on hypoxia in the estuary, since larger phytoplankton, such as diatoms, are more likely than picoplankton to create a substantial flux of organic carbon to the benthos (Smetacek, 1985; Ducklow et al., 1986; Kiorboe et al., 1996), and, in turn, increase sediment oxygen demand (EPA, 1994; Justic et al., 2002).

In contrast to the LIS stations, the ER station displayed high levels of inorganic nutrients and low levels of chlorophyll and never responded to the addition of inorganic nutrients during this study (Figs. 2 and 3). While our results are certainly consistent with the previous conclusion that the ER is not a nutrient-limited system (Garside et al., 1976; Malone, 1977; Samuels et al., 1983), the presence of low algal biomass in ER, despite high nutrient levels, remains an anomaly. It is notable that during both ER experiments, the algal community grew at substantial rates in all treatments (Figs. 2 and 3), suggesting that a factor which previously limited the accumulation of biomass in the field was removed by a bottle effect. There were also increases in the photosynthetic efficiency (F_v/F_m) during both experiments in all treatments (Table 3), suggesting there was a physiological basis for the increase in algal biomass. Since ER has extremely high tidal flushing rates (Blumberg and Pritchard, 1997), it is possible that the abatement of this physical removal factor by bottling experimental seawater simply allowed phytoplankton to utilize the high levels of nutrients in the ER without being physically advected. In this estuary, significantly lower tidal flushing in the WLIS, which receives a substantial flux of nutrients from ER, typically results in this region experiencing the accumulation of high standing crops of algal biomass (O'Shea and Brosnan, 2000). Furthermore, if the low light levels in the East River (1% light level = 3.1 ± 1.2 m) keep the algal community there light limited, the light levels during our incubations may have increased photosynthetic rates. Intense zooplankton grazing could also keep phytoplankton stocks low in this region (Gobler et al., 2002), although this would likely not account for the observed changes in photosynthetic efficiency. Finally, it is possible that a toxic substance was rendered inert during experiments, due to binding on bottle walls or by organic matter, allowing the previously inhibited algal community to bloom (Samuels et al., 1983; Sweeny and Sañudo-Wilhelmy, 2004).

The enhancement of diatom growth and biomass by silicon additions in WLIS and CLIS during our spring cruise marks the first documentation of Si limitation in this ecosystem. Eutrophication can contribute to declines in diatom abundances and commensurate increases in populations of non-silicon requiring algae, as N loading increases DIN:DSi ratios (Doering et al., 1989; Turner et al., 1998; Gobler and Boneillo, 2003). Healthy diatom cells typically contain one mole of silicon for every mole of cellular nitrogen (Brzezinski, 1985). The ratios of DIN:DSi at all LIS stations during our summer cruise were low before these incubations (<0.5; Table 1), suggesting that nitrogen would have limited diatom growth rates, a conclusion consistent with our experimental results (Fig. 2). By contrast, the lower DSi concentrations during our spring cruise yielded elevated DIN:DSi ratios in WLIS (1.7; Table 1), which could have led to Si limitation of diatoms (Fig. 3; Table 2). In CLIS, where the response to Si was less pronounced (Fig. 3; Table 2), the DIN:DSi ratio was correspondingly lower than in WLIS, but was also higher than levels found at all stations in summer (Table 1). In addition to slightly elevated levels of N in spring, the seasonal cycle of Si may have also contributed to the Si limitation of diatom growth. Dissolved Si levels are often at a minimum during spring months when benthic fluxes of Si are low in LIS (Aller and Benninger, 1981) and the spring diatom bloom has recently subsided and likely depleted Si pools (Sieracki et al., 1993; Townsend and Thomas, 2002). Moreover, our findings suggest that continual managerial reductions in N loads to LIS (EPA, 1994) may favor a greater abundance of diatoms during spring months, as the DIN:DSi decrease to ratios which may cease to limit diatoms. Such an alteration in phytoplankton species composition may

Table 4
Mean monthly concentrations and ratios of dissolved inorganic nitrogen (DIN; nitrate, nitrite, and ammonium), dissolved inorganic phosphorus (DIP; orthophosphate), and dissolved silicon (DSi) found in the East River (ER), western, central, and eastern Long Island Sound (WLIS, CLIS, ELIS) as measured by the Connecticut Department of Environmental Protection. Numbers represent mean levels, with standard errors appearing in parentheses

	DIN	DIP	DSi	DIN:DIP	DIN:DSi	DIN	DIP	DSi	DIN:DIP	DIN:DSi
ER						*CLIS*				
Jan	31.3 (3.65)	1.49 (0.32)	25.8 (8.87)	20.1 (1.67)	2.49 (1.13)	13.4 (0.75)	1.96 (0.07)	71.5 (4.52)	6.77 (0.43)	0.30 (0.11)
Feb	28.8 (3.11)	1.95 (0.28)	34.5 (6.31)	16.7 (1.78)	1.21 (0.76)	12.0 (1.00)	1.70 (0.04)	59.4 (4.22)	6.63 (0.56)	0.21 (0.03)
Mar	37.2 (3.15)	3.23 (0.29)	58.9 (9.66)	12.9 (2.11)	1.11 (0.37)	8.60 (1.57)	0.90 (0.10)	29.0 (6.72)	6.72 (0.81)	0.36 (0.08)
Apr	29.0 (4.79)	1.99 (0.31)	43.0 (7.22)	28.5 (15.6)	1.02 (0.36)	2.90 (0.51)	0.56 (0.06)	13.0 (2.60)	3.39 (0.48)	0.35 (0.17)
May	33.0 (3.10)	2.52 (0.25)	64.1 (8.62)	13.6 (0.90)	0.63 (0.09)	1.96 (0.31)	0.52 (0.05)	14.9 (1.86)	3.53 (0.54)	0.17 (0.04)
Jun	28.2 (2.25)	2.33 (0.40)	37.7 (6.83)	17.0 (3.89)	1.94 (0.87)	1.34 (0.29)	0.49 (0.04)	18.3 (1.76)	2.06 (0.47)	0.08 (0.03)
Jul	47.0 (5.51)	3.78 (0.24)	65.7 (6.67)	12.2 (1.04)	0.72 (0.05)	1.37 (0.35)	0.41 (0.03)	25.9 (3.31)	3.22 (0.80)	0.07 (0.02)
Aug	41.4 (3.00)	2.58 (0.17)	52.6 (7.12)	16.3 (0.86)	1.79 (0.90)	2.88 (1.04)	0.73 (0.06)	41.5 (4.80)	3.77 (1.45)	0.08 (0.03)
Sep	41.7 (3.19)	4.43 (0.42)	78.3 (9.95)	9.85 (0.62)	0.79 (0.15)	4.84 (1.03)	1.35 (0.07)	47.6 (5.09)	3.12 (0.56)	0.09 (0.02)
Oct	42.9 (4.32)	2.03 (0.44)	53.9 (12.8)	26.0 (4.75)	1.07 (0.18)	5.90 (0.95)	1.91 (0.08)	50.5 (4.51)	2.77 (0.50)	0.22 (0.05)
Nov	30.9 (2.10)	2.50 (0.31)	33.6 (4.71)	13.6 (1.55)	1.69 (0.72)	9.47 (1.09)	2.07 (0.08)	66.3 (5.38)	4.24 (0.36)	0.16 (0.01)
Dec	24.8 (3.58)	2.08 (0.21)	37.5 (2.54)	12.1 (1.28)	0.67 (0.10)	12.2 (0.83)	2.10 (0.06)	78.1 (6.34)	6.04 (0.47)	0.19 (0.02)
WLIS						*ELIS*				
Jan	23.4 (3.40)	2.43 (0.15)	76.5 (5.30)	9.28 (1.01)	0.31 (0.04)	9.55 (0.59)	1.21 (0.05)	38.0 (2.29)	7.99 (0.52)	0.28 (0.04)
Feb	21.5 (2.21)	1.69 (0.12)	50.9 (7.10)	11.7 (0.78)	0.89 (0.29)	8.28 (0.63)	0.98 (0.03)	30.7 (2.33)	8.36 (0.61)	0.29 (0.03)
Mar	8.27 (1.16)	0.68 (0.06)	10.1 (2.39)	15.2 (2.99)	3.33 (0.76)	4.91 (0.74)	0.66 (0.06)	16.0 (2.18)	6.61 (0.74)	0.36 (0.03)
Apr	5.64 (0.89)	0.57 (0.07)	6.89 (0.80)	8.77 (1.92)	1.94 (0.68)	3.87 (0.40)	0.60 (0.04)	23.4 (3.66)	6.36 (0.61)	0.17 (0.02)
May	8.34 (1.14)	0.65 (0.10)	12.9 (1.58)	10.5 (1.76)	1.01 (0.27)	3.23 (0.29)	0.46 (0.04)	21.0 (1.54)	7.96 (1.65)	0.14 (0.01)
Jun	5.79 (0.96)	0.68 (0.08)	12.0 (2.18)	6.67 (0.82)	0.43 (0.06)	2.38 (0.29)	0.56 (0.04)	18.2 (0.77)	4.40 (0.66)	0.13 (0.01)
Jul	2.64 (0.52)	0.57 (0.06)	27.8 (5.19)	3.93 (0.64)	0.52 (0.21)	1.06 (0.13)	0.50 (0.03)	15.1 (1.22)	2.54 (0.36)	0.09 (0.02)
Aug	4.80 (0.95)	1.28 (0.11)	44.2 (5.37)	2.81 (0.55)	0.09 (0.02)	2.17 (0.33)	0.63 (0.04)	26.5 (2.39)	2.78 (0.36)	0.08 (0.01)
Sep	8.36 (1.57)	1.97 (0.15)	52.2 (6.33)	3.03 (0.50)	0.12 (0.01)	3.54 (0.46)	0.87 (0.04)	21.7 (1.81)	4.02 (0.50)	0.18 (0.02)
Oct	19.2 (2.10)	2.65 (0.14)	64.5 (6.92)	6.81 (0.60)	0.63 (0.18)	3.89 (0.47)	1.01 (0.02)	23.4 (1.71)	3.84 (0.48)	0.17 (0.02)
Nov	25.3 (2.00)	2.75 (0.12)	85.4 (6.59)	9.06 (0.59)	0.33 (0.03)	6.40 (0.58)	1.24 (0.05)	30.5 (1.71)	5.06 (0.36)	0.23 (0.03)
Dec	27.3 (2.35)	2.79 (0.09)	79.6 (4.95)	9.85 (0.75)	0.40 (0.04)	8.11 (0.58)	1.42 (0.07)	41.2 (2.93)	5.44 (0.36)	0.21 (0.01)

benefit higher trophic levels of the food web (Irigoien et al., 2002). However, a greater abundance of diatoms could have a less favorable impact on hypoxia in LIS. As noted previously, a greater abundance of larger diatoms could increase C-fluxes to bottom waters (Smetacek, 1985; Ducklow et al., 1986; Kiorboe et al., 1996) and thus exacerbate bottom hypoxia in LIS, particularly if increased diatom abundance was accompanied by enhanced copepod grazing and fecal pellet production (Turner et al., 1998). However, the degree to which these potentially enhanced fluxes due to diatom dominance may be off set by potentially lower levels of total algal biomass associated with reductions in N loads is not known.

4.1. Long term trends in nutrients and nutrient ratios in the Long Island Sound-East River system

An evaluation of the changes in mean monthly nutrient concentrations and ratios in LIS from 1991 to 2004 assists in placing our field experiments in the perspective of longer term trends and annual cycles. During this time, dissolved inorganic nitrogen levels in LIS were generally highest during cooler months (Nov–Mar) and lowest during the summer (Table 4). We observed modest, but non-significant, decreases in mean levels of DIN at each station during the 14-year period (2.5, 2.4, 1.0, and 0.7 μM lower from 1998 to 2004 compared to 1991–1997 at ER, WLIS, CLIS, and ELIS, respectively), likely due to the ongoing effort to reduce nitrogen loads to this estuary (EPA, 1994). As expected, the East River displayed chronically high levels of all dissolved nutrients (Table 4), confirming that inorganic nutrient limitation is not likely to occur there (Figs. 2 and 3; Table 2). Within LIS, WLIS had relatively high mean monthly DIN levels (>5 μM) except during summer (Jul–Aug). Consideration of these data in conjunction with our experimental results, suggests WLIS is likely to be consistently N limited during summer, and only ephemerally N-limited at other times (e.g. our spring experiments; Fig. 3; Table 2). CLIS generally had lower nitrogen levels and lower DIN:DIP and DIN:DSi ratios than eastern regions of LIS during spring months (Mar–Jun; Table 4). This trend reversed during later summer and fall, when DIN levels in ELIS became lower than CLIS, likely reflecting the seasonal decline in fluvial discharge of the Connecticut River during this period. Together with our experimental results (Figs. 2 and 3, Table 2), these data suggest N-limitation persists in CLIS during spring, summer, and fall, and in ELIS during summer and fall only due to the strong influence of the Connecticut River as a nutrient source to ELIS in spring.

An examination of observed nutrient ratios compared to the Redfield ratio (16 N: 16 Si: 1 P) supports the idea that N is the most commonly limiting element in central and eastern LIS. The mean monthly DIN:DIP ratios in these regions were ~7 during winter months, as low as 2 during summer and always below the Redfield ratio (16). Extending nutrient stoichiometry to silicon, mean monthly DIN:DSi ratios never exceeded 0.4, and were <0.1 during summer months. How-

CLIS during spring (Table 2; Fig. 3C), the highest mean monthly DIN:DSi ratios and lowest DSi concentrations were found during the month of April (Table 4). Moreover, there was a mean annual decrease of DSi in CLIS of nearly 60 μM between January and April, evidence of a substantial silicon demand during this period likely due to the occurrence of the spring diatom bloom (data not shown).

The western region of LIS was the most dynamic portion of the estuary with regard to nutrients as very high mean levels of DIN (23 μM), DIP (2.4 μM), and DSi (77 μM) in January were very rapidly drawn down to substantially lower levels during February and March (Table 4), coincident with the spring bloom (data not shown). This drawdown occurred in a non-Redfieldian manner, as mean DIN:DIP ratios increased from ~9 in January to a balanced 15 in March. Concurrently, mean DIN:DSi ratios rose from ~0.3 in January to ≥1 during February through May, a ratio which may limit diatom growth (see discussion above). Although mean monthly DSi levels were never undetectable (Table 4), many observations during spring were ≤2 μM, a level at which diatom growth is restricted (Egge and Aksnes, 1992). This long term data suggests the Si-limitation of diatoms we observed during our spring experiments (Fig. 3; Table 2) may be representative of seasonal phenomenon in this region of LIS.

Finally, the chronically high levels of DIP (>0.5 μM; Table 4) and low DIN:DIP ratios relative to the Redfield ratio at all LIS stations (2–15; Table 4), and the inability of P to affect phytoplankton growth rates anywhere in LIS during our experiments (Figs. 2 and 3; Table 1) suggests P rarely limits the production of phytoplankton biomass in LIS. This contrasts with some other temperate estuaries, where P-limitation is annually observed during spring months (Malone et al., 1996; Mallin et al., 1999). This is likely due, in part, to excessive anthropogenic phosphorus loading associated with sewage discharge in LIS (Sweeny and Sañudo-Wilhelmy, 2004). Since anoxic sediments overlain by hypoxic waters are a rich source of P to estuaries (Ingall and Janke, 1994), and since nearly half of LIS bottom waters can be hypoxic during summer (Parker and O'Reilly, 1991), it is likely that benthic fluxes are also a strong source of P to this system. Finally, absence of P-limitation may also be a function of the relatively high salinity (>20 ppt) throughout the entire estuary, since systems which are not substantially influenced by freshwater are generally less likely to be P-limited (Hecky and Kilham, 1988).

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