Final Report

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Trace Metals, Organic Carbon, and Inorganic Nutrients in Surface Waters of the Long Island Sound: Sources, Cycling and Effects on Phytoplankton Growth.

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Summary

This study provides an extensive dataset of dissolved trace metals (silver, cadmium, copper, nickel, lead, iron, and zinc), inorganic (ammonia, nitrate, phosphate and silicates), and organic (urea, dissolved organic nitrogen, carbon and phosphorous, as well as particulate carbon and nitrogen) constituents during high and low riverine flow conditions in surface waters of the Long Island Sound. Analysis of the data showed that the mechanisms influencing the biogeochemistry of the Sound are very complex. However, a few preliminary conclusions could be drawn:

- There are two distinct biogeochemical regimes within the Long Island Sound: an area of relatively high metal levels in the East River/Narrows and an area in the eastern region of the Sound that had comparatively lower levels.

- During low flow conditions, the East River was the most dominant external source of most trace metals, while during high flow conditions; the most important external source was the Connecticut River.

- Large internal sources of copper, nickel and zinc were detected under low flow conditions implicating the importance of internal processes such as remobilization from contaminated sediments within the Sound.

- The mechanisms controlling the biogeochemistry of the Long Island Sound were different under different river flow. During high flow conditions, the system was most influenced by biological activity. During low flow conditions, the Long Island Sound was influenced by the remobilization of metals from contaminated sediments. Future work (such as the actual measurement of diffusive benthic fluxes) is needed to substantiate these preliminary findings.

Objectives:

Objective 1:

Establish levels of metals, organic carbon and nutrients in surface waters of the Long Island Sound. Establish the relative importance of natural and

anthropogenic sources of dissolved constituents to the Long Island Sound. Water samples were collected at 40 stations beginning at the Battery of the East River, progressing east to the Race in the Long Island Sound, in July 2000 and in April 2001. Additional samples were collected at stations along the salinity gradients of the Thames, Connecticut, Quinnipiac and Housatonic rivers. All of the samples collected in both cruises have been analyzed for salinity, POC, PON, DOC, inorganic nutrients (NO_4, NH_4, PO_4, SiO_4), organic nutrients (urea, DON, DOP) and size-fractionated chlorophyll *a* (whole, > 20 µm, 5-20 µm, & < 5 µm), as well as for trace metals. Additional parameters measured at each location were salinity, pH, temperature, and dissolved oxygen. Consistent with the location of the anthropogenic sources in the NYC region, the levels of inorganic nutrients were about 2-3 times higher in the East river and western Long Island Sound compared to the Race in the eastern part of the Sound. Our trace metal results were consistent with the nutrient distributions; the highest levels of metals were also detected in the East River-Western LIS.

Objective 2:

Evaluate the ability of nutrients and copper to control the intensity of the phytoplankton blooms in the Long Island Sound. Nutrient addition experiments were conducted at three stations in the western Long Island Sound, and at single locations in the East River and eastern Long Island Sound. Our preliminary results indicated that Western Long Island Sound and East River phytoplankton communities appeared to be nutrient replete, and did not respond to additions of phosphate, nitrate, ammonium, silicate, copper or EDTA. This contrasts starkly with the phytoplankton communities in Central and Eastern Long Island Sound, which displayed a strong growth response to nitrogen additions (nitrate and ammonium). Moreover, we observed species-specific differences to the additions of nitrogenous nutrients in Central and Eastern Long Island Sound. For example, while the growth of smaller picoplankton, such as *Synechococcus sp.*, was not affected by N-additions, larger diatoms species increased in biomass. Since larger cells are more likely to sink to the bottom of Long Island Sound, and contribute to hypoxia, these experimental results imply that increased N-loading to Long Island Sound could spread the hypoxia problem from Western Long Island Sound to central and eastern Long Island Sound waters.

During our April 2001 cruise, we found only the Central Long Island Sound phytoplankton to be nutrient-depleted (N-limited). The absence of nutrient limitation of phytoplankton in Eastern Long Island Sound in spring contrasts with our summer experiments. This difference suggests that during the spring freshet, the Connecticut River, which supplies Long Island Sound with 70% of its freshwater, provides phytoplankton in Eastern Long Island Sound with a copious supply of nutrients. When flow rates diminish during summer months, Eastern Long Island Sound phytoplankton communities transition to a nutrient limited state.

Presentations:

1. Gobler, C.J., S.A. Sañudo-Wilhelmy, N.J. Buck and M.E. Sieracki. Effects of nutrient inputs on phytoplankton growth rates in Long Island Sound. Long Island Sound/ New England Estuarine Research Society. October 24-26, 2002. University of Connecticut. Groton, Connecticut.
2. Buck, N.J., S.A. Sañudo-Wilhelmy, and C.J. Gobler. Dissolved trace metal cycles in the Long Island Sound: Temporal and Spatial Trends. Long Island Sound/ New England Estuarine Research Society. October 24-26, 2002. University of Connecticut. Groton, Connecticut.
3. Gobler, C.J., S.A. Sañudo-Wilhelmy, N.J. Buck and M.E. Sieracki. Impacts of nutrient loading on phytoplankton communities across Long Island Sound", Contributed oral presentation at the 2003 ASLO meeting Aquatic Science Meeting, Salt Lake City, UT, Feb 13, 2003).

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Mr. Nathaniel Buck was supported by this grant. He has participated in the design, sampling and analysis of samples and this work is part of his thesis project at the Marine Sciences Research Center. He completed his Master of Science in Marine Environmental Sciences on December 2002.

Carbon and Trace Metal Cycling in Long Island Sound Surface Waters

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Dissolved trace metal (Ag, Cd, Cu, Fe, Pb, Ni, Pb, Zn), inorganic nutrient (NH_4, NO_3, PO_4, H_4SiO_4), DOC, DON and DOP concentrations were measured at 43 stations in the surface waters of Long Island Sound (LIS) during low (July 2000) and high (April 2001) flow conditions. Trace metal distributions defined two geographical regimes: an area of relatively high metal and nutrient levels in The East River/Narrows and another in the eastern region of the sound which had comparatively lower levels. Mass Balance calculations showed that the East River is the most influential external source of most inorganic nutrients (NH_4, NO_3, PO_4), and sewage-derived Ag during summer conditions. Additional internal fluxes of dissolved Cu (73%), Ni (77%), and Zn (78%) relative to fluvial inputs were also found during the same period. In contrast, during high flow, the main source of metals and nutrients to the LIS appears to be the Connecticut River and small sinks relative to ideal dilution of river water and seawater along the estuary were found for Zn (32%) and Fe (82%). Principal component analysis indicated that biological activity associated with primary productivity and the remobilization of metals from contaminated sediments could be the main processes influencing the chemical composition of LIS.

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INTRODUCTION

Situated along the northwest Atlantic coast, Long Island Sound (LIS) is surrounded by some of the most densely populated areas in the United States including coastal Connecticut, New York City, and Westchester, Suffolk and Nassau counties. More than 8 million people reside within the Sound's watershed and millions more utilize its shores on a seasonal basis for recreation (Andersen 2002). Long Island Sound has for many years supported robust shellfish and finfish populations of commercial importance and provided feeding, breeding, nesting and nursery areas for numerous plant and animal species (Andersen 2002). After the enactment of the amended Clean Water Act of 1987, LIS was designated an Estuary of National Significance and in 1988 the Long Island Sound Study (LISS) was initiated (Andersen 2002). Due to its highly urbanized nature, the LIS estuary system is effected by a number of anthropogenic activities. The LISS identified a number of priority areas of environmental concern within the Sound including hypoxia, toxic contamination, pathogen contamination, habitat destruction and alteration, and excessive amounts of floatable debris (EPA 1994). In 1991, LIS ranked 10th in the most contaminated sites among 200 coastal locations around the United States (Robertson *et al.* 1991). As a result, a Comprehensive Conservation and Management Plan (EPA 1994) was developed to enhance water quality and to protect habitat and living resources while ensuring compatible human uses.

In 1994, the Long Island Sound Study identified hypoxia as the most significant water quality problem affecting LIS (EPA 1994), and increases in the inorganic nitrogen supply have been implicated in creating hypoxic conditions within the bottom waters of western LIS (NYSDEC 1999, O'Shea and Brosnan 2000). As a result, most management decisions have focused on the dynamics of N input. However there are other constituents besides N which are important in creating hypoxic conditions. Recent calculations found that organic carbon inputs account for at least 25 percent of oxygen consumption within LIS (NYSDEC 1999). Carbon inputs can originate from sewage overflow events and phytoplankton growth. However, the form in which carbon is produced by these events can have varying effects on hypoxia. Much of the carbon formed during phytoplankton blooms is in the dissolved form. (Brenner et al 1993; Kirchman *et al.*; KepKay *et al.* 1993). Unlike particulate organic carbon which sinks through the water column,

dissolved organic carbon might not contribute to bottom water hypoxia, especially when the water column is stratified. Thus, inputs and fluxes of organic compounds such as dissolved organic carbon, nitrogen, and phosphate are an important components when understanding estuarine dynamics.

Loadings of toxic metals were also a concern of the EPA. LIS receives inputs of effluent from 86 wastewater treatment plants, 225 industrial facilities, and 16 power plants (Wolfe *et. al.* 1991). The effects of these discharges are reflected in the high levels of toxic metals being reported in sediments, mussels, and bottom dwelling fish (Brownawell *et al.* 1991; Robertson *et al.* 1991; Turgeon and O'Conner 1991). For example, Cu levels in many species of bivalves collected in LIS approach or exceed toxic levels (Grieg *et al.* 1977; Arimoto and Feng 1982; Brownawell *et al.* 1991) and sediments throughout LIS contain levels of Cu, Pb, Ag, Cd, and Zn which are in the upper 10% of national inventories (Robertson *et al.* 1991) and may be exerting toxic effect on indigenous benthic species (Brownawell *et al* 1991). While extensive research has been done in sediment and bioindicator species regarding metal contamination by anthropogenic inputs, the biogeochemical cycles of these elements in the water column of the estuary are still unknown. In fact, the LISS Study reported (EPA 1994) that "there are virtually no reliable data on dissolved metal concentrations in the LIS." The only exception to this qualification is a recent study conducted by Rolfhus and Fitzgerald (2001) which examined the spatial and temporal distributions of mercury within the sound.

This study was designed to enhance the understanding of dissolved trace metals (Ag, Cd, Cu, Fe, Ni, Pb, Zn), and inorganic (NH_4, NO_3, PO_4, H_4SiO_4) and organic constituents (DON, DOP, DOC, PON, POC, Urea) in the surface waters of the estuary under high (April 2001) and low (August 2000) runoff conditions. Mass balance calculations were used to establish the relative importance of various allochthonous and internal sources (e.g. riverine, sewage inputs, benthic flux) into the Sound. Elevated levels of Ag, accompanied by high levels of the inorganic nutrients NO_3, and PO_4 identified areas affected by sewage inputs (Sanudo-Wilhelmy and Flegal 1992; Ravizza and Bothner 1996), while DOC and Fe were used to identify geochemical carrier phases. Distributions of H_4SiO_4 and Ni were used as indicators of diagenetic fluxes (Flegal *et al.*

1991, Aller and Benninger 1981). Principal component analysis and trace metal – nutrient relationships were used to determine the factors influencing their biogeochemical cycles and trends and how they changed temporally and spatially. The comparison of metal and nutrient distributions in LIS with other urban and pristine estuaries permitted the assessment of the impacts of riverine and anthropogenic inputs on dissolved constituents in estuaries.

Study Site

Long Island Sound is roughly 93 km long and 34 km at its widest point. It extends from Hell Gate in the East River at New York City to The Race which is marked by Plum and Fishers Islands (Figure 1). Long Island Sound is the sixth largest estuary in the United States with a surface area of 3284 km^2 and ranks third in the U.S. in terms of volume holding 6.2×10^{10} m^3 of water. The Sound has a mean depth of 20 m and a maximum depth of 90 m (EPA 1994; Wolfe *et al.* 1991).

Lacking a freshwater input at its head, LIS is not a classic estuary. Fresh water flow enters into the embayment from runoff and drainage along the coast of Long Island, New York and Connecticut. The discharge of four major tributaries (Thames, Housatonic, Quinnipiac, and Connecticut rivers) comprise most of the freshwater input with the Connecticut River, which empties into the central basin, being responsible for ~ 70% of total inflow. The land drainage area of LIS covers 45,100 km^2 and extends as far north as Canada. It includes the highly urbanized areas of coastal Connecticut, New York City, and Westchester, Suffolk, and Nassau Counties (EPA 1994). More than 70% of this area lies within the drainage basin of the Connecticut river which includes the entire state of Connecticut and portions of Vermont, New Hampshire, Massachusetts and New York.

Saline waters enter from both the western and eastern ends of the Sound. The East River, located on the western end of the sound, is a 26 km long tidal straight which connects New York Harbor to the adjoining LIS (Jay and Bowman 1975). Surface water exchange from the East River to western LIS has been estimated at 5×10^4 L d^{-1} (Blumberg and Pritchard 1997). Inflow of deeper oceanic water occurs on the eastern margin through The Race. The eastern sill rises to a depth of 21 m which controls the volume of oceanic seawater(1.68×10^{12} L d^{-1}). Deeper, more saline ocean water exhibits

a net westerly flow, while fresher surface waters generally moves eastward through The Race at an estimated 7.9×10^{11} L day^{-1} (Riley 1967, Valle-Levinson and Wilson 1998, Gay 2002).

METHODS

Sampling Scheme

Forty nine stations were sampled during peak (April 2001) and low (July 2000) tributary flow conditions to examine the impact of riverine and sewage inputs on various water column constituents. A 20 station east/west transect beginning at The Battery in the East River and progressing eastward to The Race in Eastern LIS (ELIS) was sampled (Figure 1). Since there was a steep spatial gradient for several constituents of interest in Western LIS (WLIS), stations were closer together at the western end while in Central LIS (CLIS) and ELIS stations were sampled further apart. To establish the impact of fluvial input on chemical constituents within the water column, additional three to five station, north/south transects in each of LIS's largest rivers (the Thames, Connecticut, Quinnapiac, and Housatonic) were sampled. River transects began at the mouth of each river and extended to the freshwater end-member. The importance of each tributary as a source for trace metals, organic carbon and nutrients were established by mass balance estimates (see below). Additional sampling sites included the five LIS National Status and Trends sites at Manhassett Bay, Huntington Harbor, Oyster Bay, Hempstead Harbor and Port Jefferson Harbor. Based on shoreline and bathymetry attributes LIS was divided into five geological regions; The East River, The Narrows, The Western Basin, The Central Basin, and The Eastern Basin. The boundaries for each region are denoted in Figure 1.

Sample Collection

Cruises were conducted aboard the R/V PAUMANOK of Southampton College. At each sampling station automated probes were used to measure conductivity, temperature, light penetration, pH, and dissolved oxygen. Seawater samples were collected using a peristaltic pump equipped with trace metal clean Teflon tubing attached to a 7m trace metal clean boom (Flegal *et al.* 1991). The boom was submerged to a depth of 1 m and directed into approaching currents and prevailing winds. Whole unfiltered seawater samples were collected for the analysis of

chlorophyll *a*, POC and PON. Dissolved samples were obtained by filtration through trace metal clean, polypropylene capsule filters (<0.2 μm) and analyzed for inorganic nutrients (NO_3, NH_4, H_4SiO_4, PO_4), DOC, DON, Urea and dissolved trace metals (Ag, Cd, Cu, Fe, Ni, Pb, Zn).

Sample Analysis

DOC samples were analyzed in duplicate by high temperature catalytic oxidation using a Shimadzu TOC-5000 Total Organic Carbon Analyzer(Sugimura and Suzuki 1988, Benner and Strom 1993). Duplicate POC and PON samples were dried at 60° C before analysis on a Carlo Erba NA 1500 NCS system (Sharp 1974). Salinity was measured on a Beckman induction salinometer. Chlorophyll was analyzed in triplicate by standard fluorometeric methods (Parsons *et al.* 1984). Standard spectrophotometric methods were used to analyze nitrate (Jones 1984), urea (Newell *et al.* 1967), ammonium, phosphate and silicate (Parsons *et al.* 1984) in duplicate. Total dissolved nitrogen and total dissolved phosphate concentrations were determined in duplicate using persulfate oxidation methods (Valderrama 1981). DON was calculated as the difference between TDN and dissolved inorganic nitrogen (nitrate, nitrite, ammonium), while DOP was calculated as the difference of TDP and ortho-phosphate.

Measurements of intercalibration DOC samples (provided by J. Sharp of U. Delaware) were within 5% of the consensus value. Standards for all samples were prepared by weight using certified standards available from Fisher Scientific. Calibration curves used for the determination of inorganic nutrients, DOC, DON, and POC/PON yielded linear regressions with coefficients of 0.9975 or greater. Recoveries of SPEX Certi-Prep inorganic nutrient standard reference material at environmentally representative concentrations were $97 \pm 8\%$ for nitrate, $106 \pm 8\%$ for ammonium, and $101 \pm 4\%$ for phosphate. Recoveries of SPEX Certi-prep organic nutrient standard reference material at environmentally representative levels were $94 \pm 12\%$ for total nitrogen and $109 \pm 8\%$ for total phosphorous. Precombustion of glassware and acid-washed plasticware provided adequately low blanks for DOC, DON and DOP (<10% of lowest sample).

Trace metal clean techniques were used for handling and analyzing all samples within the trace metal clean facility of SUNY-Stony Brook (Sanudo-Wilhelmy and Gill 1999). Samples designated for dissolved trace metal analysis were first acidified with quartz distilled hydrochloric acid (Q-HCl) to final pH of <1.5). After two months storage to ensure the release of all the metals absorbed to the sides of the sample bottle, dissolved trace metal samples were pre-concentrated by organic solvent extraction using ammonium 1-pyrrolidine-dithiocarbamate /diethylammonium diethyldithiocarbamate (APDC/DDDC), as described by Bruland *et al.* (1985). Concentrates and digests were quantified on a Hitachi Zeeman-8100 graphite furnace atomic absorption spectrophotometer (GFAAS) employing standard addition techniques. Calibration curves for analysis of trace metals yielded linear regressions with coefficients of 0.9995 or greater. Recoveries of Canadian reference seawater (CASS-3) ranged from 95-105% for all metals. Procedural blanks and detection limits (3 * standard deviation of mean blank) for metal analysis are listed in Table 1 and are consistent with quality analysis found in contemporary peer reviewed literature (Bruland *et al.* 1985).

	Ag (pM)	Cu (nM)	Cd (pM)	Ni (nM)	Zn (nM)	Fe (nM)	Pb (pM)
n	19	28	28	28	28	28	6
Average Blank	1.69	0.12	6.10	0.16	0.34	0.85	43.95
Stdev	0.90	0.06	3.07	0.10	0.19	0.37	15.07
Detection limits	2.71	0.17	9.21	0.31	0.56	1.11	45.21

Table 1. Procedural blanks and Instrumental Detection Limits. n = number of blanks analyzed.

Principal Component Analysis

Principal component analysis was used to extract composite variables from the original data to assess the underlying patterns in the distribution of the measured parameters (Boyer *et al.* 1997). Multivariate analysis was performed using Statistica 5.1 (1997). Raw data were transformed using logrithmic transformation, a practice used to

scale down high scores among variables (Sokal and Rohlf 1995). The PCA solution was rotated   (using Varimax normalized) to optimize statistical results and the composition of each principal component. The factor scores were saved for each sampling period and plotted to identify which stations clustered with respect to one another and whether or not associations were consistent between the two sampling periods.

Principal component analysis was applied to metal and nutrient data for 38 LIS stations sampled to identify significant relationships among the data. Measurements obtained from the enclosed bays of the five National Status and Trends were excluded from analysis due to the long residence times of these systems and the restricted exchange within LIS. NO_3, PO_4, silicate, Chl a, DOC, Ag, Cu, Cd, Ni, Zn, Fe, salinity and temperature were the constituents used to identify the principal mechanisms influencing the biogeochemical behavior of LIS. Only principal components whose eigenvalues were greater than one were retained.

RESULTS

River water fluxes were obtained from the United States Geological Survey (www.usgs.gov). The average freshwater flux into LIS from the Connecticut rivers between the years 1990 and 2000 was on the order of 5.0×10^{10} L d^{-1}. The Summer (July 2000) cruise was characterized by low river flow conditions with the flux of the Connecticut rivers being measured at 2.0×10^{10} L d^{-1} which is 40% of the decadal average. In contrast, the Spring cruise (April 2001) was characterized by high discharge conditions with the flux of the Connecticut rivers (2.4×10^{11} L d^{-1}) being 485% of the decadal average.

Mean values of duplicate measurements of dissolved trace metals (Ag, Cd, Cu, Fe, Ni, Pb, Zn) from filtered (<0.45 μm) seawater collected in July 2000 and April 2001 are listed in Tables 2 and 3, respectively. The relative standard deviation of duplicate analyses was never greater than $\pm$ 15% and was characteristically around $\pm$ 5%. Nutrient concentrations (NH$_4$, NO$_3$, PO$_4$, H$_4$SiO$_4$, Urea, DON, DOP, DOC) for low flow and high flow conditions are listed in Tables 4 and 5. Ancillary data (salinity, temperature, O$_2$, secchi depth, Chl a, POC, PON) collected during high flow conditions (April 2001) for LIS stations are listed in Tables 6 while ancillary data collected during low flow conditions (July 2000) are listed in Table 7. Table 8 and 9 displays data for the freshwater tributaries (Housatonic, Quinnipiac, Connecticut and Thames Rivers) for low and high flow, respectively.

Temporal and spatial variability in nutrients and metal levels within LIS

Temporal differences in nutrients and metal levels within the area of study were determined by comparing the mean concentrations measured under low and high flow conditions. Within LIS, average dissolved NO$_3$ (mean 4.90 μM) and H$_4$SiO$_4$ (10.5 μM) were higher during the April sampling period than the mean measured under low flow conditions (3.73 μM and 5.42 μM, respectively). In contrast, the average PO$_4$ concentrations were higher under low flow conditions (1.37 μM vs. 0.70 μM under high flow). As observed for dissolved PO$_4$, dissolved Ag concentrations were also higher during low flow conditions (90.0 pM) when compared to high flow conditions (76.3 pM). However, unlike Ag, mean concentrations of Cd and Fe displayed the reverse trend, with

higher mean concentrations being measured during the April sampling period (Cd-229 pM; Fe- of 33.4 nM) versus the July sampling period (Cd-196 pM; Fe-25.0 nM). In contrast to Ag, Cd, and Fe mean concentrations of Cu (21.6 nM and 21.5 nM), Ni (32.5 nM and 29.1 nM) and Zn (29.3 nM and 29.6 nM) remained relatively constant. Statistical t-tests (Sokal and Rohlf 1995) for the difference between two means in July and April indicated temporal differences were only significant for PO_4 (p = 0.00042), H_4SiO_4 (p =0.039619) and Cd (p = 0.035068).

Spatial differences in nutrients and metal levels within the area of study were determined by comparing the mean concentrations measured within the East River, Narrows, Western Basin, Central Basin, and Eastern Basin of LIS (Figures 2, 3, 4). Concentrations of PO_4, and NO_3, and Ag showed strong west to east gradients with all three constituents showing at least an order of magnitude decrease from the East River to the Eastern Basin. Within the East River region, average levels of PO_4 during the July sampling period, were 3.32 ± 1.10 μM while mean NO_3 levels were 14.0 ± 7.45 μM. Eastern basin concentrations were markedly lower for both constituents with mean PO_4 levels of 0.64 ± 0.11 μM and mean NO_3 levels of 0.96 ± 0.93 μM. Ag showed strikingly similar west to east gradients with concentrations decreasing from the East River (248 ± 88.2 pM) to the eastern basin (38.5 ± 14.1 pM) by an order of magnitude.

Distributions of the dissolved trace metals Cu, Ni, and Zn (Figure 4) were also found to decrease from west to east but to a lesser degree than Ag, PO_4, and NO_3. For example, during low flow conditions, average Zn concentrations were 46.5 ± 2.56 nM in the East River and 13.9 ± 13.9 nM in the eastern basin. Dissolved Ni and Cu decreased by about half from the East River to the Eastern Basin with average concentration ranging from 39.6 ± 11.5 nM and 28.6 ± 4.33 nM to 18.9 ± 4.73 nM to11.3 ± 2.12 nM, respectively. In contrast to constituents with decreasing west to east gradients, levels of Cd, Fe, and DOC (Figures 2, 3, 4) showed uniform distributions throughout LIS. For example, the highest average concentration of Cd (0.23 ± 0.05 nM) was located in the East river and the lowest mean concentration (0.18 ± 0.07 nM) was found within the Narrows region while the Eastern Basin contained an intermediate level (0.21 ± 0.074 nM) . Likewise, the highest average value for DOC (191 ± 6.67 μM) was found within

the Narrows while the lowest mean concentration (148 ± 42.8 μM) was located in the Eastern Basin.

Temporal and spatial variability in nutrients and metals within the National Status and Trends Sites

Contrasting concentrations of nutrients and trace metals were also observed among the five National Status and Trends sites sampled (Manhasset Bay, Hempstead Harbor, Oyster Bay, Huntington Bay, Port Jefferson Harbor; Tables 2, 3, 4, 5, 6, 7). Inorganic nutrient concentrations measured in Port Jefferson Harbor contained the highest levels of NO_3 (2.41 ± 0.26 μM) and PO_4 (1.55 ± 0.32 μM) during low flow conditions, while Hempstead Harbor contained the highest levels of H_4SiO_4 (4.73 ± 0.07 μM) during the same sampling period. The highest levels of Ag (170 pM), Ni (50.8 nM), and Fe (53.6 nM) were detected in Manhasset Bay during high flow conditions while Port Jefferson Harbor had the highest concentrations of Cd (164 pM), Cu (33.3 nM), and Zn (48.1 nM) during the same sampling period. Hempstead Harbor had the lowest measured concentrations of Cd (73.3 pM), Ni (26.2 nM), Zn (11.0 nM) and Fe (5.73 nM) during the April sampling period. The lowest Ag (27.8 pM) concentration was detected in Oyster Bay during low flow while the lowest Cu (18.9 nM) concentration was found in Huntington Bay during high flow.

Temporal and spatial variability in nutrients and metal levels measured in the Connecticut Rivers

Concentrations of dissolved metals measured in the Quinnipiac (Q), Housatonic (H), Connecticut (C), and Thames (T) River stations were extremely variable and did not follow a consistent trend (Tables 8 and 9). For example, within the Thames River, negligible changes in concentrations were found when comparing high flow conditions with low flow conditions for Ag (22.3 pM vs. 25.5 pM), Cd (69.2 pM vs. 64.2 pM), Cu (26.7 nM vs. 22.2 nM), Fe (2580 nM vs. 2100 nM), Ni (22.2 vs. 26.2 nM) and Zn (33.2 nM vs. 36.9 nM). Similarly, in the Housatonic River similar values of Fe were found for high and low conditions (1300 nM vs 1180 nM). In contrast however, dissolved Cd and Ag in the Housatonic River were markedly higher during the April sampling period (Cd-315 pM vs 63.1 pM in July; Ag-53.3 pM vs. 12.1 pM in July) and Cu, Ni, and Zn showed markedly higher values during the July sampling period (Zn-75.6 nM vs 40.5 nM in April; Ni-88.2 nM vs. 52.7 nM in April; Zn-75.6 nM vs. 40.5 nM in April). In the

Connecticut River, levels of Fe were almost two times higher during low flow conditions (773 nM) when compared to high flow conditions (313 nM), while levels of Cd, Cu, Zn were higher during high flow conditions(Cd-67.4 pM; Cu-32.3 nM; Zn-34.1 nM) when compared to low flow conditions (Cd-35.4 pM; Cu-16.0 nM; Zn-18.5 nM). Levels of Ni and Ag, in the Connecticut River were relatively similar when comparing low to high flow conditions (Ni-22.5 nM vs. 23.8 nM; Ag-6.14 pM vs. 6.87 pM, under low and high flow conditions, respectively). Concentrations of Fe and Cd in the Quinnipiac River were higher during the Summer sampling period (Fe-791 nM; Cd-348 pM) compared to the Spring sampling period (Fe-131 nM; Cd-94.6 pM), while concentrations of Ni and Ag were higher during the July sampling period (Ni-116 nM; Ag-313 pM) when compared to the April sampling period(Ni-20.9 nM; Ag-791 pM). Concentrations of Cu and Zn showed little seasonal change between low and high discharge conditions (Cu-47.5 nM vs 36.1 nM, respectively; Zn-20.9 nM vs. 23.1 nM, respectively).

Mean concentrations of dissolved nutrients measured at the zero salinity end member in the Housatonic, Quinnipiac, Connecticut and Thames River stations were extremely variable and did not follow a consistent temporal or spatial trend (Tables 8 and 9). For example, while levels of H_4SiO_4 were an-order of magnitude higher during high flow in all of the rivers (H-108 ± 5.01 μM; Q-146 ± 6.70 μM; C-135 ± 7.51 μM; T-146 ± 6.70 μM) when compared to low flow (H-12.13 ± 1.81 μM; Q-9.82 ± 0.22 μM; C-30.2 ± 0.43 μM; T-14.6 ± 0.22 μM), levels of dissolved PO_4 and NO_3 varied with season and location. Levels of PO_4 in the Housatonic River were higher in April (4.42 ± 0.01 μM vs. 1.28 ± 0.10 μM in August) while PO_4 levels in the Quinnipiac and Thames Rivers were higher in July (Q- 1.19 ± 0.08 μM vs. 0.20 ± 0.01 μM in April;T-0.97 ± 0.00 μM vs. 0.63 ± 0.04 μM in April). The levels of PO_4 in the Connecticut River seems to be independent of flow conditions (0.51 ± 0.06 μM and0.61 ± 0.02 μM under low and high flow respectively). Similar to levels of PO_4, levels of NO_3 in the Housatonic River were higher in April (22.3 ± 8.73 μM vs. 80.2 ± 2.13 μM in August) while NO_3 levels in the Quinnipiac, Thames, and Connecticut Rivers were higher in July (Q- 20.3 ± 5.59 vs.17.6 ± 6.56 μM in April; T- 22.7 ± 0.02 μM vs.13.1 ± 9.60 μM in April; C-22.1 ± 7.69 μM vs. 14.9 ± 2.35 μM in April).

Principal component analysis

The results of principal component analysis for the high flow period identified four composite variables which represents 79.0 % of variance within the data (Table 10). The factor loadings, or correlations between the original variables and the principal components, indicate four modes of variation in the data The first component is characterized by high loadings (> 0.70) of NO_3, PO_4, H_4SiO_4, Fe and their inverse relationship to Chlorophyll *a* and accounts for 33.8% of the variance within the system. Principal component two contains high factor loading values for Cu, Ni, and temperature and explains 19.1% of the total variance. Representing 17.3% of the variance of the data, component three is most strongly influenced by Ag and Cd. Finally, component four explained 8.81% of the variability in the data and it is exclusively influenced by the variance of dissolved organic carbon.

For the low flow period, multivariate statistical analyses resulted in a rotated factor matrix with a three component solution responsible for 73.4% of the variance (Table 10). The first, and most significant, component explains 38.0% of variance in the data and was distinguished by the significant positive factor loading of DOC and Fe associated with the negative loading of Cd and salinity. The second component, accounting for 24.81% of the total variance is influenced by the high loading of Cu, Ni, and Zn. Component three, with 10.63% of the variance, is characterized by the inverse association of Chl *a* with NO_3, PO_4, and Ag.

Anthropogenic perturbations of trace metals and nutrients in LIS

Comparisons of metal and nutrient concentrations measured in LIS with those reported for other estuaries with different levels of urbanization are useful in assessing the impact of anthropogenic and fluvial inputs on several chemical constituents within LIS. Box plots of metal and nutrient levels for the five regions of LIS and the five National Status and Trends sites sampled, as well as the levels reported for samples within the Peconic Bay (PB; Breuer *et al.* 1999), Great South Bay (GSB; Clark 1999), San Francisco Bay (SFB; Flegal *et al.* 1991), and the Hudson River (HR; Sanudo-Wilhelmy and Gill 1999) with similar salinities (>19), are shown in Figures 2, 3 and 4.

During this study, there was a very strong anthropogenic signal of inorganic nutrients (PO_4 and NO_3) within the East River and Narrows area (Figure 2). Elevated levels of inorganic nutrients in the East River/Narrows region parallel the high levels of dissolved Ag (Figure 3) which is a well documented tracer of sewage (Sanudo-Wilhelmy and Flegal 1991). The significant correlation between NO_3 ($r^2 = 0.95$, p< 0.05) and PO_4 ($r^2 = 0.79$, p< 0.05) with dissolved Ag within the western end of LIS (Figure 5), further confirms that sewage is the likely source of these constituents. Comparisons of Ag, PO_4, and NO_3 concentrations, with those reported for other urban estuaries showed that their concentrations within this region of LIS were similar to those reported in SFB and the HR estuary. However, concentrations of Ag within the East River are some of the highest values ever reported in the United States (Figure 3) and are greater than the levels reported for SFB and the HR. Levels of Ag found in the Narrows, were slightly lower than East River concentrations, but were similar to those reported for SFB and the HR. As with Ag, dissolved PO_4 and NO_3 within the western extent of LIS were comparable to estuaries whose water quality is substantially affected by anthropogenic inputs. For example PO_4 and NO_3 levels in the East River and Narrows were both comparable to the levels reported in SFB but markedly higher than the levels reported in less urbanized estuaries such as PB and GSB (Figure 2).

The high levels of Ag, PO_4, and NO_3 measured in the western part of LIS is consistent with the high volume of sewage discharged into that area. Though significant improvements have been made in sewage treatment and sewage input loads have

decreased in the New York City watershed over the past several decades (O'shea and Brosnan 1997), the negative impact of these discharges on the water quality of this area is not surprising. For example, O'Shea and Brosnan (2000) reported that six water pollution control plants discharge effluent into the East River at a rate of 36.75 $m^3 s^{-1}$. Additional inputs are supplied by numerous combined sewage overflows and storm sewers. The volume of sewage which enters the East River each day ($3.18 \times 10^9 \, l \, d^{-1}$) is higher than the volume of fresh water entering eastern LIS through the Thames river during low flow conditions ($1.25 \times 10^9 \, l \, d^{-1}$).

In contrast to the western extent of LIS, concentrations of anthropogenic tracers within the eastern region were comparable to levels measured in estuaries with less urbanization (i.e. PB and GSB). For example, concentrations of Ag within the Western, Central, and Eastern Basins were markedly lower than those reported for SFB and the HR and similar to the values reported for PB and GSB (Figure 3). Dissolved NO_3 concentrations were an order of magnitude lower in eastern LIS with respect to SFB but similar to concentrations found in GSB (Figure 2). Dissolved PO_4 concentrations within eastern LIS were markedly lower for not only the highly urbanized SFB but also the PB and GSB systems (Figure 2).

Concentrations of Cu, Ni and Zn within LIS were consistent with levels reported in PB, GSB, SFB and HR (Figure 4). Cu and Ni levels within LIS were comparable to the levels reported for both the highly urbanized estuaries SFB and HR and for less urbanized estuaries such as, PB and GSB. Dissolved Zn, on the other hand, was found to have slightly increased levels when compared to PB and SFB. However, when compared to the HR, Zn levels measured within the entire LIS were markedly lower.

Levels of constituents that displayed uniform distributions throughout LIS, such as Cd, Fe, and DOC (Figure 2, 3, 4) also showed contrasting variations with levels reported in other estuaries. First, Cd was markedly lower when compared to levels reported in SFB and the HR. In contrast, Cd levels in LIS were similar to those reported in the less urbanized PB and GSB. Dissolved Fe levels throughout LIS resembled the concentrations reported in PB, GSB and the HR. DOC concentrations within LIS were similar to the levels reported in PB but lower than those of GSB.

Internal and external sources of dissolved trace metals, inorganic nutrients and organic carbon to LIS

Mass balance estimates were used to quantify the impacts of fluvial, oceanic and internal inputs of dissolved constituents to LIS. The relative contributions of the four freshwater tributaries, the East River, and oceanic flux were determined by using the expression:

$$\Sigma \, (C_{river} \times Q_{river}) + C_{East\ River} \times Q_{avg\ East\ River} + C_{ocean} \times Q_{ocean\ in} + X$$
$$= C_{median\ LIS} \times Q_{ocean\ out}$$

where C represents concentrations of dissolved constituents, and Q represents water fluxes. Any additional "source" needed to balance the inputs and outputs within the estuary is represented by X. The level measured in the freshwater end member for each river was used for river concentrations. For ocean concentrations, NO_3, DOC, Ag and Fe measured in the east end high salinity end member were used. For PO_4, H_4SiO_4, Ni, Cu, Zn, and Cd concentrations reported in shelf waters off eastern LIS by Bruland and Franks (1983) were used. Values of Q for the rivers were obtained from the United States Geological Survey. The East River flux into LIS was taken to be 9.50×10^{10} L d^{-1} as reported by Blumberg and Pritchard. (1997) was used. The oceanic volume exchange in (1.68×10^{12} L d^{-1}) and out (2.12×10^{12} L d^{-1}) of the estuary were reported by Riley (1967).

The mass balance calculations showed strong temporal changes in the external sources of dissolved inorganic nutrients and metals into LIS (Table 11). The Connecticut River, which is responsible for ~70% of the freshwater input into LIS had a volume flux slightly less than that of the East River (9.50×10^{10} L d^{-1}) which has markedly higher concentrations of inorganic nutrients and metals (with the exception of Fe; Table 8). As a result, the East River is the most important fluvial source of NO_3 (70.1%), PO_4 (94.2%), and sewage derived Ag (99.0%) as well as dissolved Cu (84.4%), Ni (76.3%) and Zn (84.8%) when compared with other fluvial sources (Table 11). In contrast, because levels of Fe were an order of magnitude higher within the Connecticut River when compared to the East River, the Connecticut River was responsible for 51.2% of the Fe input during low flow. While the East River was found to be the most influential allochthonous source

of metals into LIS, during low flow it was less important relative to the total flux out of the estuary (Table 12). Percentages of Cu, Ni and Zn within the East River relative to the concentrations leaving the estuary amounted to only 1.54%, 5.28%, and 7.46%, respectively.

During high flow conditions, the main fluvial source of metals and nutrients to LIS appears to shift from the East River to the Connecticut River with the exception of Ag (Table 11). Compared to the East River, the Connecticut River supplies LIS with a much greater volume of water (an order of magnitude greater) during high discharge conditions. As a result, the Connecticut River is the most influential fluvial source of Cu (68.5%), Ni (55.9%), Zn (62.8%) and Fe (70.0%) as well as NO_3 (61.6%) and H_4SiO_4 (76.9%; Table 12).   However, the Connecticut River, supplied only 4.39% of Cu, 9.98% of Ni, and 20.6 % of Zn in the water exiting to the ocean (Table 12). This suggests dissolved levels of these metals are strongly influenced by *in situ* processes as opposed to external inputs during both low and high flow.

Mass balance estimates also showed a large imbalance between fluvial and oceanic supply of Cu, Ni and Zn to LIS and export to the ocean (Tables 13 and 14). For example, additional inputs of Cu (73%), Ni (77%), and Zn (78%) are needed in order to account for the export of these metals from LIS to the ocean (Table 13). These large imbalances suggest that internal processes control the concentrations of Cu, Ni, and Zn within LIS.   As stated earlier, LIS has received significant inputs of contaminants (O'Shea and Brosnan 2000) which are reflected by the high levels of metals found within the sediments of LIS (Wolfe *et al.* 1992). Sediment bound metals could represent a large reservoir which can reenter the water column in the dissolved form via a number of processes, including diffusion and sediment resuspension (Aller 1984). A large sedimentary input into LIS by diagenetic remobilization is consistent with the elevated levels observed for Cu, Ni and Zn throughout the system away from point sources located within the East River/Narrows region.

Biogeochemical behavior of LIS as interpreted by principal component analysis

Principal component analysis (PCA) was used to identify the processes responsible for the cycling of metals observed in LIS. Analysis allowed for the formation of a few (3-4) new correlating variables which represent linear composites of the data without substantial loss of information. PCA explained 73.4% of the variance during the Summer sampling period and 79.0% during the Spring sampling period and were interpretable, reflecting processes reported within LIS by past studies. Primarily, principal component analysis indicated that the sources, transports and processes affecting the biogeochemical properties of LIS were very different between the spring and summer sampling periods, which will be discussed below.

During the high flow sampling period (Table 10), the first component represents the uptake of nutrients and Fe by phytoplankton (chlorophyll *a*) and accounted for 33.8% of the total variance. The relatively high contribution for factor one indicates that primary productivity is an important factor influencing the distributions of NO_3, PO_4, H_4SiO_4 and Fe during high discharge conditions. This is consistent with the fact that during spring conditions there is an increase in nutrient inputs from runoff and light intensity creating optimal conditions for spring blooms of phytoplankton (Riley 1956). The populations of these blooms are dominated by diatoms (Riley 1956), species that have exhausted the surface waters of nutrients within LIS in a matter of weeks (Riley and Conover 1956). This intense primary productivity is likely the process represented by the first factor extracted by PCA.

The second high flow component is identified by the association of Cu, Ni and temperature which, could be attributed to the influence of inputs via benthic flux. Increased temperature is known to exert a significant influence on the magnitude of Mn flux (Aller 1980, Hunt 1983) an element whose behavior is strongly coupled to the benthos and strongly covaries with Ni (Sanudo-Wilhelmy and Gill 1999). Thus, the second component reflects the importance of internal processes, such as benthic remobilization from contaminated sediments.

The third high flow component is influenced by high loading of Ag and Cd, constituents attributed to anthropogenic inputs within the East River/Narrows region. It is worth observing that PCA is a hierarchical analysis, and the principal components

associated with benthic flux were found to have a greater influence on the system than components associated with sewage effluent. This suggests that the benthos is the major contributor of contaminants to the whole LIS as opposed to point sources.

During the low flow sampling period, principal component one was characterized by high loading of DOC and Fe which were inversely related to salinity and Cd (Table 10). Principal component two was characterized by high loading of Cu, Ni, and Zn. As discussed earlier, the concentrations of these three metals within LIS are believed to have originated from benthic flux.

Factor scores (Tables 15 and 16) were plotted for each sampling period to identify any chemically distinct areas of LIS. Distributions of factor scores in relation to one another can indicate how the average water quality varies over the study area (Boyer *et al.* 1997). During high flow, the score plots for the first two principal components displayed marked differences between the samples collected within the five geographic regions of LIS (Figure 6). For this period, the sample separations shown by the two components reflect spatial changes in influences of primary productivity and benthic flux and resemble patterns reported in the past (Riley 1952, Aller and Yingst 1980, Aller and Benninger 1981, Hunt 1983, Aller 1994). The East River was found to have high nutrient stocks and low Chl *a* while the western end of the sound displayed reverse trends. Principal component two denotes increased influence in the narrows and western end of the sound which agrees with observations of benthic flux in this region despite lower water temperatures (Aller 1994). The clustering of factor scores for principal component one with principal component three (Ag and Cd; Figure 6) also reflected the geographic regions of LIS. Principal component three had the largest effects at stations 1-8 (East River), and decreasing influence with stations in western LIS, a trend consistent with earlier observations. Factor score plots of principal component one with principal component two and principal component three demonstrates that biogeochemical variations are relatively distinct within the geographic regions of LIS and behave differently relative to each other.

During low flow, the clustering of score plots for the first two components resemble the geographic areas of LIS and displays marked differences between the samples collected within these areas.   Principal component one show stark separation of

the freshwater end member stations from the stations within LIS (Figure 7). However, principal component one makes little contribution to the differences within the Sound and suggests spatial homogeneity of LIS during low discharge conditions with respect to Fe, DOC, Cd and salinity. Factor score plots for principal component two agree nicely with observations of a decreasing west to east gradient of benthic flux within LIS as a result of increased water temperatures during Summer conditions (Aller 1994). It is noteworthy that, while the processes effecting the biogeochemistry of LIS changed temporally, the chemical dissimilar regions remained the same. This observation could indicate the long term influence of sedimentary metals in LIS.

Identification of trace metal sources and biogeochemical behavior using metal-nutrient relationships

The impact of anthropogenic and natural processes controlling the distributions of trace metals in LIS was established by investigating nutrient:metal relationships. Some trace metals (Cd, Cu, Ni, and Zn) have positive relationships with limiting nutrients (PO_4 and H_4SiO_4) in the open ocean waters of the Atlantic Ocean (Bruland 1983). Deviations from a linear metal -- nutrient relationship may be indicative of additional inputs not observed in open ocean environments (Martin *et al.* 1980).

Cd and PO_4 concentrations measured in LIS were different from the Cd:PO_4 relationship established for the North Western Atlantic (Figure 8). This suggests that primary control of Cd concentrations within LIS is not associated with biogenic production and remineralization which is characteristic of oceanic waters. Within the East River, PO_4 was enriched with respect to Cd which is consistent with the anthropogenic inputs of PO_4 from sewage in this region. In contrast, the eastern area of LIS had excesses of Cd relative to Cd:PO_4 relationships suggesting a) an alternative source of Cd into the LIS system or; b) that PO_4 is removed from the water column faster from the water column than Cd (biologically preferential uptake of PO_4 over Cd; Boyle *et al.* 1981).

Dissolved Cu, Ni, and Zn in LIS all displayed large excesses when compared to oceanic ratios of Cu: H_4SiO_4, Ni: H_4SiO_4 and Zn: H_4SiO_4 (Figure 9). The different ratios and slopes found between the different sampling periods and geographic areas display the

complexity of the processes controlling the distributions of nutrient and metals within LIS. During low flow, significant correlations were found for Cu and H_4SiO_4 ($r^2 = 0.61$, $p<0.05$) and Zn and H_4SiO_4 ($r^2 = 0.729$, $p<0.05$). This suggests Cu, Zn and H_4SiO_4 may have a similar source, possibly inputs from the sediments, as suggested from mass balance analysis. Aller and Benninger (1981) reported fluxes of H_4SiO_4 from sediments within LIS that increased with temperature and thus had the highest flux rates in the summer. Diagenetic remobilization of H_4SiO_4 has also been reported in San Francisco Bay (Flegal *et al.* 1991). Flegal *et al* (1991) suggested that the existence of simultaneous sources and sinks can result in small net changes in bulk concentrations of H_4SiO_4 despite large benthic fluxes. During high flow conditions, Cu: H_4SiO_4 and Ni: H_4SiO_4 relations begin to weaken. This can be explained by the seasonal variation in flow rates of the Connecticut river which increases inputs of Cu, Ni, and Zn into the eastern basin and by changes in rates of diagenetic remobilization due to seasonal changes in bottom water conditions.

Characterization of organic matter within the LIS

Sources of organic matter were assessed by using carbon to nitrogen ratios (C/N) measured in the particulate and dissolved phases within LIS and comparing them to other natural materials (e.g. soil, phytoplankton biomass). There are several sources of organic carbon into an estuarine system such as LIS which include allochthonous (i.e. fluvial dissolution of soil catchment or organic matter derived from industrial or agricultural wastes; Maybeck 1993), and autochthonous (primary productivity) sources. Unfortunately, the cycling of organic carbon in marine environments is complex, and accurate and precise measurements are difficult to obtain (Williams and Bauer 1993). As a result, relative contributions of various sources of carbon to the total flux are difficult to determined for most estuarine systems (Abril *et al.* 2002). The situation is further complicated by mounting evidence suggesting the conservative behavior of DOC is often due to simultaneous sources and sinks which result in small net changes in overall concentrations (Raymond and Bauer 2000, Abril *et al.* 2002).

Distributions of DOC were uniform throughout LIS during low and high flow conditions with levels within the East River and Narrows being comparable to concentrations in the eastern region of LIS. However, average C/N ratios for dissolved organic matter were significantly higher during the April sampling period (range 7.81-24.14) when compared to the July sampling period (range 6.23 – 15.38; t-test, p = 0.000317; Figure 10). Dissolved C/N ratios during high flow were closer to C/N ratios observed for terrestrial humic (21-28) or fulvic acids (20-22) and lignin (78). During low flow conditions C/N ratios were more similar to that in marine humic acids (8-12) and phytoplankton biomass (6.6; Rostad *et al.* 1997). Thus, these increased C/N ratios during high flow conditions are likely to be the result of increased runoff and higher terrestrial inputs.

For the particulate phase, C/N ratios also showed temporal variabilty between the Spring and Summer sampling periods. During low flow, concentrations of POC did not display any definitive spatial patterns. However, POC concentrations were found to increase with increasing Chl *a* concentrations (Figure 11), and a positive correlation ($r^2 =$ 0.73, p<0.05) was found between POC and Chl *a*. The correlation between the two had a y intercept of 0.28 mg/l suggesting photosynthetic activity is not the only source of POC but plays an important role regarding its concentrations in the surface waters. Further evidence of this qualification can be seen by observing particulate C/N ratios during high flow conditions and comparing them to Chl *a* measurements (Figure 10). Observations of spatial distributions found that in areas of increased Chl *a* concentrations, C/N ratios approach Redfield values (6.6). However, elevated C/N ratios were found in the East River (~ 12) and Eastern Basin region (12-15) of LIS where Chl *a* levels were relatively low. This suggests external sources (i.e. sewage or fluvial inputs) as the mechanism controlling particulate C and N levels within these latter regions.

Inputs of organic matter, whether internal or external, can be a contributing component in creating hypoxic conditions within the bottom waters of LIS. Thus, sources and sinks of carbon within LIS should be identified.   While this study does not directly implicate anthropogenic activity as an important source of carbon into LIS, it cannot be completely ruled out. In a recent study concerning the behavior of organic carbon in nine European estuaries, Abril *et al.* (2002) found that increased carbon loads

due to pollution might be efficiently removed by mineralization in estuaries with long residence times such as LIS (63-166 days; Turekian *et al* 1996). As a result, these estuaries behaved as efficient filters and never became saturated with carbon. To obtain a more accurate assessment of the sources and sinks of DOC and POC within LIS, a number of addition parameters (i.e. bioassays, isotopic tracers) will need to measured in addition to simple distributions of bulk organic carbon.

CONCLUSIONS

This study provides an extensive database of dissolved trace metals (Ag, Cd, Cu, Ni, Pb, Ni Zn,), inorganic (NO_3, NH_4, PO_4, H_4SiO_4) and organic (Urea, DON, DOP, DOC, PON, POC) constituents during low and high discharge conditions in the surface waters of Long Island Sound. Analysis suggest that the mechanisms controlling the biogeochemistry of the system are very complex. However, a few preliminary conclusions can be drawn. First, there are two biogeochemical regimes: an area of relatively high metal levels in the East River/Narrows and an area in the eastern region of the Sound which had comparatively lower metal levels. Second, during low flow conditions, the East River was the dominant external source of most trace metals (Ag, Cd, Cu, Ni, Zn) while during high flow conditions, the most influential external source of trace metals was the Connecticut river with the exception of sewage derived Ag. Third, large internal sources of Cu, Ni, and Zn were detected during low flow conditions implicating the importance of internal processes, such as benthic remobilization, to the biogeochemistry of LIS. Principal component analysis suggested the mechanisms controlling the biogeochemistry of LIS were different under high and low flow. During high flow conditions, the system was most influenced by the uptake of inorganic nutrients and iron by phytoplankton, benthic flux, and anthropogenic inputs. During low flow conditions the system was influenced heavily by processes associated with heterotrophic activity and, to a lesser extent, by concentrations of Ni, Zn, and Cu supplied by increased benthic flux due to increased water temperature.

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TABLES

Station #	Ag (pM)	Cd (pM)	Pb (pM)	Cu (nM)	Ni (nM)	Zn (nM)	Fe (nM)
1	324	180	500	27.0	30.4	45.8	60.4
2	295	273	497	32.0	43.5	46.6	88.3
3	353	316	684	35.6	54.8	47.6	57.5
4	208	218	345	27.0	49.6	51.0	47.7
5	159	201	716	26.1	33.6	45.0	32.6
6	147	223	298	23.9	25.6	44.0	29.4
7	103	208	180	21.3	47.0	50.9	31.6
8	77.6	172	154	24.9	45.1	42.9	29.3
9	170	109	261	27.6	50.8	44.9	53.6
10	26.6	86.1	94.4	21.0	33.6	35.2	18.7
11	85.7	264	20.4	24.6	37.6	35.5	13.4
12	40.7	148	---	26.4	50.3	28.9	21.2
13	76.8	73.3	234.4	24.3	26.2	11.0	5.73
14	14.1	141	---	29.1	20.8	18.0	8.96
15	14.8	185	---	19.8	26.7	30.4	7.01
16	27.8	159	29.5	20.0	29.5	25.7	11.9
17	6.17	216	---	23.1	28.8	24.9	8.96
18	35.8	158	54.2	18.9	32.8	25.4	19.3
19	54.4	165	---	21.9	37.0	23.2	33.5
20	39.2	184	---	17.7	32.9	22.7	11.4
21	54.4	195	---	17.6	39.2	23.9	6.80
22	87.7	164	38.4	33.3	36.4	48.1	32.0
23	44.3	185	---	27.6	31.6	27.7	11.0
24	33.5	216	---	33.4	43.8	36.8	32.3
25	***	***	***	***		***	***
26	34.2	244	---	26.6	41.4	19.2	***
27	60.5	212	---	29.0	35.5	26.3	8.69
29	113	227	---	32.4	43.5	52.5	48.1
31	54.9	181	---	21.7	25.0	13.0	7.56
32	53.5	169	---	12.6	18.0	***	39.00
33	26.6	255	---	13.8	26.9	7.62	6.09
35	62.3	172	---	10.9	21.7	8.69	14.3
37		167	---	12.4	14.9	7.9	43.8
37A	14.4	135	---	21.9	23.3	14.9	213
37B	15.2	82.9	---	25.8	30.8	27.8	509
39	41.0	98.5	---	13.7	18.0	***	1.42
40	32.2	186	---	10.2	16.0	9.73	6.60
41	44.6	191	---	8.35	13.4	7.22	16.9
42	57.1	191	---	15.8	27.8	3.82	51.0
43	73.4	200	---	23.9	32.0	42.6	45.5
44	24.3	200	---	10.9	17.5	10.0	38.5

Table 2: Dissolved trace metals in Long Island Sound, July 2000. --- Below detection limits, *** missing values.

Station #	Ag (pM)	Cd (pM)	Pb (pM)	Cu (nM)	Ni (nM)	Zn (nM)	Fe (nM)
1	93.9	296	88.3	19.2	31.3	40.9	58.8
2	108	175	41.2	22.3	22.3	37.1	58.0
3	132	221	89.1	23.9	28.7	40.8	44.3
4	191	214	49.1	27.7	35.0	51.2	34.4
5	242	236	110	30.5	45.2	44.8	56.0
6	164	311	40.9	29.1	38.9	43.8	25.6
7	159	325	10.2	32.2	36.4	43.9	14.0
8	97.7	173	96.9	29.5	30.5	36.2	14.3
9	223	175	22.4	32.9	38.3	30.5	34.6
10	165	353	5.00	33.8	49.7	41.4	11.8
11	137	272	4.96	27.6	32.9	25.6	8.58
12	43.2	284	---	30.8	37.8	24.9	11.8
13	26.8	93.2	107	31.8	44.4	10.5	4.08
14	76.3	170	---	16.2	36.2	24.9	10.5
15	51.2	220	---	31.2	37.6	42.1	12.1
16	21.5	222	207	18.8	25.6	4.91	3.00
17	6.05	210	---	26.8	36.8	22.8	39.3
18	33.8	197	105	22.8	32.1	25.0	84.2
19	42.8	200	---	21.4	22.1	21.1	46.8
20	24.7	223	---	23.5	35.5	20.4	23.0
21	37.7	240	---	17.6	30.3	19.4	7.50
22	85.0	381	65.1	31.2	42.2	41.7	120
23	14.3	220	---	19.2	33.0	16.0	11.0
24	28.9	222	---	31.5	38.1	41.1	82.0
25	44.9	161	---	31.6	42.5	45.5	162
26	21.4	177	---	20.3	26.6	11.5	***
27	33.6	243	---	20.6	26.1	16.8	14.9
29	54.8	162	---	20.2	33.9	41.6	28.9
31	21.9	225	---	20.5	37.5	25.2	33.7
32	55.3	173	---	11.8	20.5	11.7	14.4
33	22.9	217	---	13.9	13.7	6.20	271
35	34.9	334	---	9.59	23.2	51.7	19.2
37C	3.52	57.1	---	12.3	11.5	89.8	***
39	29.1	118	---	12.0	13.0	4.49	2.46
40	31.3	187	---	8.6	20.1	9.43	27.2
41	28.9	156	---	8.9	12.9	7.92	23.6
42	48.0	146	---	12.3	27.7	25.7	167
43	78.2	198	---	21.0	27.7	29.6	***
44	17.2	232	---	11.4	9.56	39.3	6.33

Table 3: Dissolved trace metals in Long Island Sound, April 2001. --- Below detection limits, *** missing values

Station #	DOC (uM)	STDEV	NH4 (uM)	STDEV	NO3 (uM)	STDEV	DON (uM)	STDEV	Urea (uM)	STDEV	PO4 (uM)	STDEV	DOP (uM)	STDEV	Silicate (uM)	STDEV
1	199	20.9	22.9	3.18	19.0	1.72	18.9	2.35	1.32	0.09	3.49	0.32	1.39	0.34	6.03	0.53
2	196	17.7	30.2	5.42	21.3	1.57	21.9	3.27	1.08	0.11	4.48	0.64	1.40	0.16	6.51	0.89
3	195	7.87	27.0	2.45	21.6	0.70	25.7	0.26	1.08	0.08	4.58	0.23	1.22	0.18	7.51	1.04
4	173	17.7	29.0	0.76	10.0	1.59	13.0	2.87	0.83	0.04	3.09	0.00	1.47	0.50	6.48	0.84
5	179	1.69	13.8	1.92	5.59	1.48	17.7	2.83	0.79	0.01	1.77	0.10	1.17	0.57	4.10	0.51
6	161	30.9	12.7	0.38	6.55	0.17	18.9	0.02	0.67	0.02	2.49	0.10	0.98	0.13	6.48	0.20
7	196	12.10	16.4	2.26	5.40	0.39	25.5	1.49	0.45	0.03	3.52	0.28	0.44	0.21	5.70	0.26
8	189	16.2	3.48	0.52	2.52	0.01	13.4	4.28	0.41	0.06	2.24	0.65	1.00	0.76	5.90	0.17
9	213	13.1	0.16	0.05	0.20	0.09	16.6	2.49	0.30	0.00	0.39	0.05	1.69	0.08	0.48	0.03
10	186	4.71	0.34	0.01	0.71	0.08	19.2	4.69	0.10	0.07	1.20	0.13	2.00	0.32	5.21	0.69
11	199	7.51	0.59	0.06	0.61	0.41	21.7	4.66	0.64	0.03	0.72	0.13	3.09	0.04	4.41	0.46
12	184	36.7	3.07	4.15	0.20	0.05	16.5	3.48	0.64	0.00	0.60	0.14	2.19	0.22	2.60	0.20
13	211	1.65	0.65	0.15	0.18	0.12	31.3	7.50	0.73	0.05	0.65	0.18	3.59	1.16	4.73	0.07
14	166	33.7	0.76	0.05	0.21	0.05	24.2	0.35	0.77	0.00	0.37	0.04	2.12	0.07	5.03	0.22
15	174	0.11	0.53	0.30	0.48	0.23	21.0	2.38	0.87	0.00	0.30	0.01	2.38	0.95	4.81	2.21
16	222	33.4	0.81	0.51	0.23	0.10	21.8	0.71	0.71	0.06	0.40	0.11	0.69	0.08	4.62	0.21
17	143	21.0	0.68	0.03	0.22	0.07	20.9	3.82	0.88	0.28	0.47	0.18	2.04	0.57	4.36	0.34
18	188	4.20	0.33	0.28	0.35	0.12	15.8	0.19	0.77	0.05	0.53	0.04	1.74	0.17	4.55	0.14
19	162	2.90	0.41	0.24	0.28	0.04	14.1	1.05	0.57	0.06	0.43	0.15	1.80	0.26	4.42	0.58
20	173	23.2	0.21	0.29	0.31	0.01	15.1	1.25	0.51	0.02	0.28	0.00	1.69	0.17	4.21	0.23
21	146	1.68	1.74	1.42	0.13	0.01	11.7	0.78	0.64	0.07	0.47	0.01	1.79	0.42	4.12	0.36
22	168	4.22	3.51	0.00	2.41	0.26	9.54	3.22	0.65	0.28	1.55	0.32	0.88	0.03	2.32	0.12
23	153	***	0.34	0.31	0.23	0.11	13.5	0.79	0.55	0.11	1.11	0.12	1.68	0.45	5.78	0.14
24	189	17.6	0.88	0.32	0.87	0.07	13.9	0.79	0.95	0.65	1.13	0.40	1.60	0.70	6.32	0.67
25	207	10.5	0.70	0.25	2.41	0.08	13.0	0.29	0.44	0.07	0.77	0.05	1.67	0.25	6.52	0.22
26	167	5.07	2.97	3.45	0.18	0.02	8.29	1.63	0.39	0.04	0.28	0.06	1.43	0.19	2.80	0.47
27	179	***	0.32	0.33	0.07	0.01	21.0	4.64	0.29	0.01	0.90	0.05	1.16	0.37	15.63	2.79
28	201	3.86	0.48	0.04	5.28	1.85	21.1	1.43	0.76	0.42	1.73	0.55	0.22	0.00	20.15	17.00
29	229	32.9	0.31	0.18	0.24	0.02	17.3	3.73	0.15	0.10	0.66	0.01	1.13	0.64	9.75	3.30
32	156	29.0	0.49	0.17	1.53	1.48	10.8	4.46	0.04	0.05	0.60	0.01	0.47	0.19	21.17	24.43
33	233	58.6	0.29	0.17	0.43	0.28	14.1	3.38	0.41	0.02	0.48	0.01	0.93	0.22	2.38	0.33
35	128	2.33	0.43	0.07	1.28	0.14	10.6	0.32	0.47	0.00	0.62	0.07	0.71	0.10	2.55	0.09
36	139	18.2	0.62	0.21	2.92	0.30	12.1	0.86	0.51	0.07	0.80	0.10	0.59	0.18	3.57	0.08
37	244	1.30	1.83	0.80	4.07	0.36	26.4	0.49	0.50	0.26	0.96	0.06	1.03	0.60	10.72	0.04
37A	256	19.5	3.07	0.23	21.7	3.65	16.3	0.13	0.50	0.07	1.18	0.15	1.69	0.27	12.59	0.41
37B	***	***	2.70	1.01	28.0	7.75	13.9	3.67	0.41	0.17	1.32	0.19	0.64	0.18	0.60	0.28
39	143	2.56	0.15	0.12	0.42	0.12	17.1	6.39	0.45	0.04	0.54	0.07	1.04	0.21	1.89	0.04
40	125	***	0.54	0.23	0.64	0.17	15.1	0.49	0.43	0.09	0.75	0.00	0.95	0.14	2.22	0.08
41	117	8.33	0.43	0.12	0.67	0.17	12.3	1.98	0.47	0.02	0.70	0.03	0.69	0.33	2.01	0.00
42	196	27.2	0.13	0.19	0.32	0.09	17.6	4.27	0.44	0.00	0.36	0.02	0.55	0.00	4.66	0.04
43	179	5.12	0.56	0.03	0.57	0.06	17.1	0.94	0.46	0.00	0.59	0.04	0.77	0.21	4.83	0.11
44	140	8.75	0.51	0.05	0.24	0.15	13.5	1.65	0.32	0.00	0.56	0.11	0.44	0.05	1.91	0.28

Table 4: Dissolved Nutrients in Long Island Sound, July 2000. *** missing values

Station #	Station Name	Lat (N)	Long (W)	Salinity (ppt)	Temp (C)	DO (mg/l)	Secchi (m)	Chl a (ug/l)	STDEV	POC (mg/l)	STDEV	PON (mg/l)	STDEV
1	Battery Park	40 41.963	74 00.279	23.49	21.14	5.98	2	0.36	0.08	0.25	0.13	0.00	0.02
2	East River	40 43.744	73 58.027	23.17	21.56	4.84	2	0.35	0.02	0.25	***	0.05	0.00
3	Hell Gate	40 46.974	73 56.202	23.39	21.61	6.57	2.1	0.20	0.02	***	***	***	***
4	N. Brother Is.	40 47.949	73 54.175	24.46	20.72	4.98	2.3	0.39	0.07	***	***	***	***
5	College Point	40 48.046	73 50.840	24.95	20.33	5.19	1.4	0.95	0.23	***	***	***	***
6	Throgs Neck	40 48.249	73 48.725	25.15	20.72	6.38	2.2	1.80	0.61	***	***	***	***
7	Narrows	40 48.245	73 46.258	24.94	19.92	6.75	1.8	5.29	0.52	***	***	***	***
8	Narrows	40 50.282	73 45.894	25.67	20.19	7.06	1.8	9.45	0.41	0.63	0.01	0.19	0.00
9	Manhasset Bay	40 49.355	73 42.854	25.11	21.95	11.92	1.1	12.00	0.28	2.38	1.08	0.29	0.00
10	Execution Rock	40 52.279	73 43.972	25.40	22	8.54	2	0.85	0.06	0.05	0.01	0.01	0.00
11	Mamaroneck	40 55.581	73 42.238	25.59	21.82	9.61	1.6	1.96	0.81	***	***	0.10	0.00
12	Scotch Caps	40 54.952	73 40.915	25.70	23.55	11.85	1.8	2.95	0.22	1.24	0.02	0.16	0.01
13	Hempstead Harbor	40 52.469	73 41.156	25.52	24.53	9.7	2	1.87	0.09	1.24	0.07	0.14	0.07
14	Matinecock Point	40 56.156	73 36.591	25.81	22.86	11.37	2.2	2.92	0.21	1.20	0.07	0.15	0.07
15	Oak Neck Point	40 57.276	73 32.427	25.92	24.26	9.6	2.2	2.03	0.15	0.82	0.13	0.08	0.00
16	Oyster Bay	40 55.741	73 30.153	25.75	24.74	10.96	1.8	1.66	0.24	***	***	0.11	0.00
17	Loyd Point	40 58.260	73 30.153	26.07	23.36	10.5	2.2	1.13	0.08	0.79	0.01	0.08	0.00
18	Huntington Bay	40 55.392	73 25.368	25.97	21.07	7.78	2.2	1.86	0.30	0.54	0.01	0.07	0.01
19	N. of Huntington Bay	40 59.619	73 24.114	26.37	19.94	8.23	2.5	0.92	0.09	0.33	0.03	0.06	0.03
20	N. of Smithin Bay	41 02.024	73 13.951	26.26	19.99	9.28	2.8	1.32	0.23	0.38	0.08	0.07	0.01
21	Stratford Shoal	41 04.291	73 05.058	26.69	20.63	8.2	3	0.56	0.05	0.34	0.07	0.05	0.07
22	Port Jeff Harbor	40 56.961	73 04.316	25.69	21.83	7.21	1.9	2.77	0.00	0.55	0.04	0.08	0.04
23	S. of Housatonic	41 08.683	73 05.478	26.80	19.69	6.23	1.9	1.45	0.13	0.44	0.02	0.05	0.02
24	Mouth of Housatonic	41 11.241	73 07.257	23.27	21.7	7.96	***	3.34	0.01	0.79	0.03	0.10	0.03
25	Nells Island	41 11.804	73 06.749	17.98	22.46	9.45	***	8.90	0.49	1.21	0.12	0.18	0.12
26	Mid Sound	41 06.638	72 55.224	26.47	21.78	9.23	3.5	1.08	0.05	0.46	0.05	0.07	0.05
27	S. of Westhaven	41 12.543	72 55.974	27.07	21.07	8.33	3	0.75	0.13	0.38	0.08	0.05	0.08
29	New Haven	41 17.792	72 54.435	24.38	22.84	8.86	1.1	10.65	0.49	1.89	0.19	0.21	0.19
31	Northville	41 07.590	72 39.084	27.19	20.65	8.26	4.8	2.15	0.34	0.30	0.02	0.04	0.02
32	6 mile Shoals	41 10.024	72 29.067	29.22	18.84	7.62	5.25	1.21	0.22	0.13	0.02	0.02	0.02
33	Dumping Ground	41 12.476	72 21.924	28.56	20.26	8.09	5.25	0.70	0.08	0.27	0.23	0.02	0.23
35	Long Island Shoal	41 14.650	72 18.771	28.85	19.1	8	5	0.38	0.11	0.21	0.06	0.04	0.06
36	Mouth of Conn.	41 15.303	72 19.81	25.91	20.92	7.94	2.5	1.04	0.04	0.36	0.01	0.06	0.00
37	Conn. River	41 15.818	72 20.467	10.61	24.46	8.87	***	2.53	0.11	0.62	0.05	0.11	0.05
37A	South Cove	41 16.830	72 20.654	6.11	25	8.54	***	3.78	0.11	0.88	0.03	0.15	0.03
37B	Old Lyme	41 19.211	72 20.92	1.55	25.18	9.21	***	4.43	0.32	0.27	0.01	0.04	0.01
39	Plum Island	41 14.249	72 11.765	28.38	20.72	8.11	5	0.53	0.00	0.29	0.01	0.03	0.00
40	S. of New London	41 15.788	72 04.77	29.92	18.42	8.07	5	0.50	0.13	0.14	0.04	0.01	0.00
41	GE plant	41 16.784	72 06.063	29.99	19.46	8.08	***	0.46	0.00	***	***	***	***
42	New London Bridge	41 20.627	72 05.148	25.63	22.01	9.17	1.5	3.07	0.41	0.79	0.03	0.11	0.00
43	New London	41 21.706	72 05.253	24.89	22.74	8.11	1.5	1.90	0.28	1.30	0.21	0.17	0.04
44	The Race	41 09.251	72 05.253	29.81	19.03	7.97	5	0.49	0.18	***	***	***	***

Table 5: Ancillary parameters in Long Island Sound, July 2000. *** missing values

Station #	DOC (uM)	STDEV	NH4 (uM)	STDEV	NO3 (uM)	STDEV	DON (uM)	STDEV	UREA (uM)	STDEV	PO4 (uM)	STDEV	DOP (uM)	STDEV	Silicate (uM)	STDEV
1	188	6.50	21.3	1.38	15.5	2.00	19.6	3.28	0.63	0.04	1.56	0.11	0.19	0.05	38.6	3.54
2	208	4.45	18.0	2.41	13.4	3.79	14.1	0.71	0.73	0.38	1.54	0.64	0.00	0.85	29.8	3.30
3	203	2.99	26.3	0.10	9.08	1.72	8.75	1.66	0.18	0.14	1.75	0.19	0.00	0.36	25.5	2.13
4	216	5.84	29.6	3.16	14.2	4.12	25.7	2.85	0.84	0.22	2.37	0.61	0.34	0.11	43.1	10.1
5	190	6.27	22.3	2.73	7.88	0.32	17.9	2.18	0.50	0.25	1.78	0.22	0.22	0.02	16.3	1.22
6	175	0.83	13.4	3.88	9.29	3.72	12.2	***	0.50	0.05	1.25	0.05	0.25	0.13	18.0	7.45
7	186	3.27	18.0	0.10	15.3	7.74	11.8	1.77	0.43	0.06	1.43	0.27	0.49	0.23	16.9	1.43
8	199	18.0	7.19	0.79	8.96	1.07	20.5	2.32	0.84	0.49	1.21	0.46	0.06	0.28	16.5	0.00
9	204	2.73	0.26	0.01	1.13	0.10	14.2	0.19	0.22	0.00	0.46	0.46	0.30	0.29	0.51	0.04
10	174	0.05	1.77	0.40	3.08	0.54	9.10	1.82	0.11	0.02	0.16	0.18	0.50	0.26	2.89	0.04
11	165	13.0	0.49	0.42	1.07	0.45	17.3	2.20	0.13	0.04	0.28	0.18	0.44	0.04	2.01	0.69
12	198	37.5	0.89	0.04	4.42	0.45	17.6	0.00	0.20	0.21	0.18	0.12	0.60	0.04	0.37	0.00
13	175	5.65	0.13	0.04	3.25	1.38	17.3	2.07	0.09	0.07	0.11	0.01	0.38	0.10	1.44	1.46
14	191	1.21	0.15	0.03	1.60	0.18	16.4	0.50	0.11	0.04	0.20	0.00	0.54	0.03	0.80	0.63
15	197	1.55	0.25	0.13	1.46	0.14	12.5	1.25	0.06	0.01	0.08	0.05	0.64	0.00	1.01	1.01
16	191	7.45	0.09	0.04	0.16	0.09	12.6	0.00	0.09	0.04	0.06	0.03	0.61	0.06	1.93	0.72
17	186	22.1	0.25	0.11	0.66	0.09	18.4	2.34	0.19	0.18	0.03	0.01	0.69	0.03	0.74	0.04
18	184	6.82	0.17	0.03	0.38	0.02	16.9	3.10	0.11	0.09	0.15	0.03	0.50	0.02	0.32	0.26
19	184	1.34	0.24	0.10	0.19	0.05	13.7	0.14	0.09	0.06	0.30	0.05	0.37	0.11	2.99	0.69
20	171	1.32	0.03	0.01	0.13	0.01	12.0	1.89	0.12	0.02	0.30	0.13	0.32	0.11	2.97	0.62
21	157	3.75	0.16	0.00	0.73	0.07	9.91	0.64	0.06	0.02	0.35	0.05	0.34	0.12	3.96	0.04
22	162	5.02	0.92	0.05	0.58	0.08	16.1	1.15	0.19	0.02	0.45	0.02	0.46	0.01	3.43	1.41
23	150	10.8	***	***	1.12	0.61	9.66	0.24	***	***	0.09	0.02	0.50	0.05	3.90	1.39
24	177	0.96	3.86	0.36	8.16	1.27	10.6	3.34	0.07	0.00	0.56	0.03	0.62	0.19	30.8	0.14
25	172	34.0	3.86	0.36	15.3	3.18	11.8	2.69	0.12	0.11	1.06	0.03	0.37	0.10	86.1	18.5
26	184	41.6	0.38	0.10	1.05	0.36	7.79	0.75	0.00	0.03	0.54	0.21	0.40	0.10	4.04	0.45
27	145	2.13	0.10	0.04	0.21	0.06	8.46	0.09	0.04	0.03	0.26	0.06	0.59	0.10	9.24	5.18
29	182	5.83	0.72	0.11	8.53	0.09	15.2	0.50	0.61	0.12	0.82	0.22	0.79	0.16	10.1	0.64
31	170	8.96	0.47	0.26	4.85	2.25	9.82	0.00	0.11	0.03	0.60	0.29	0.32	0.28	6.88	0.55
32	187	7.47	0.88	0.34	3.02	0.20	10.2	2.01	0.21	0.10	0.47	0.01	0.45	0.11	6.74	0.21
33	149	4.28	1.35	0.08	2.12	1.54	9.49	0.51	0.17	0.04	0.65	0.28	0.29	0.39	21.0	0.21
35	122	1.34	1.19	0.22	1.23	0.77	11.3	0.73	0.15	0.04	0.48	0.00	0.25	0.08	2.45	0.55
37 C	242	13.4	2.26	0.03	9.23	0.14	13.5	0.80	0.11	0.01	0.40	0.06	0.67	0.16	73.4	3.56
39	143	26.6	0.83	0.10	7.97	3.55	7.06	1.41	0.21	0.08	0.44	0.03	0.34	0.02	0.66	0.17
40	122	8.62	1.21	0.07	2.80	0.00	7.40	2.35	0.00	0.21	0.47	0.04	0.33	0.06	3.50	0.69
41	119	3.59	1.41	0.38	2.65	0.27	10.9	2.11	0.61	0.20	0.40	0.03	0.61	0.29	1.33	0.17
42	185	21.4	3.63	0.47	9.59	4.49	16.0	1.78	0.41	0.46	0.43	0.05	0.32	0.18	45.5	16.5
43	235	32.3	4.31	0.27	10.3	5.19	19.0	2.78	0.18	0.03	0.50	0.03	0.10	0.10	58.4	0.07
44	149	0.53	0.91	0.17	3.15	0.27	9.79	0.71	0.19	0.04	0.41	0.07	0.77	0.07	7.18	1.70

Table 6: Dissolved Nutrients in Long Island Sound, April 2001. *** missing values

Station #	Station Name	Lat (N)	Long (W)	Salinity (ppt)	Temp (C)	DO (mg/l)	Secchi (m)	Chl a (ug/l)	STDEV	POC (mg/l)	STDEV	PON (mg/l)	STDEV
1	Battery Park	40 41.963	74 00.279	19.96	8.89	8.13	1.5	0.45	0.06	0.44	0.05	0.04	0.01
2	East River	40 43.744	73 58.027	19.41	8.75	8.35	1.0	0.47	0.01	0.39	0.02	0.03	0.00
3	Hell Gate	40 46.974	73 56.202	19.76	8.97	7.18	1.5	0.66	0.28	0.47	0.07	0.04	0.01
4	N. Brother Is.	40 47.949	73 54.175	20.44	9.49	33.8	1.8	0.43	0.01	0.44	0.01	0.04	0.00
5	College Point	40 48.046	73 50.840	23.60	8.72	7.18	2.6	0.80	0.05	0.51	0.02	0.05	0.01
6	Throgs Neck	40 48.249	73 48.725	24.37	8.79	7.24	2.8	2.27	0.24	0.58	0.04	0.07	0.06
7	Narrows	40 48.245	73 46.258	24.08	10.55	8.89	2.8	3.51	1.76	0.49	0.03	0.05	0.01
8	Narrows	40 50.282	73 45.894	24.52	10.64	8.99	2.3	5.47	0.87	1.06	0.13	0.13	0.01
9	Manhasset Bay	40 49.355	73 42.854	23.86	10.66	8.75	1.5	14.93	0.59	1.47	0.17	0.24	0.00
10	Execution Rock	40 52.279	73 43.972	24.83	9.76	8.92	2.3	3.95	0.63	0.65	0.09	0.08	0.01
11	Mamaroneck	40 55.581	73 42.238	25.19	10.9	7.65	2.0	6.38	0.32	0.92	0.01	0.14	0.04
12	Scotch Caps	40 54.952	73 40.915	24.72	11.03	8.2	1.8	7.42	1.12	1.10	0.08	0.14	0.04
13	Hempstead Harbor	40 52.469	73 41.156	24.58	11.61	7.32	1.8	6.43	1.45	1.22	0.10	0.17	0.04
14	Matinecock Point	40 56.156	73 36.591	24.81	11	14.18	2.0	7.97	1.07	1.13	0.03	0.14	0.01
15	Oak Neck Point	40 57.276	73 32.427	24.68	10.73	9.99	1.8	9.22	0.31	1.13	0.02	0.17	0.03
16	Oyster Bay	40 55.741	73 30.153	25.06	11.28	7.85	1.5	12.23	0.70	1.33	0.04	0.20	0.00
17	Loyd Point	40 58.260	73 30.153	24.81	11.3	14.35	2.0	8.99	0.42	1.04	0.20	0.15	0.04
18	Huntington Bay	40 55.392	73 25.368	25.60	9.63	***	2.0	6.63	0.77	0.31	0.03	0.04	0.03
19	N. of Huntington Bay	40 59.619	73 24.114	25.95	7.96	***	2.5	3.97	0.32	0.65	0.10	0.07	0.10
20	N. of Smithin Bay	41 02.024	73 13.951	25.94	9.2	***	3.5	0.50	0.03	0.29	0.01	0.05	0.01
21	Stratford Shoal	41 04.291	73 05.058	26.26	12.61	12.36	2.5	1.71	0.03	0.39	0.06	0.03	0.06
22	Port Jeff Harbor	40 56.961	73 04.316	25.90	10.06	11.57	2.3	1.17	0.08	0.43	0.01	0.06	0.01
23	S. of Housatonic	41 08.683	73 05.478	25.96	10.81	12.36	3.0	1.71	0.11	0.45	0.08	0.05	0.08
24	Mouth of Housatonic	41 11.241	73 07.257	18.30	13.36	10.56	***	0.95	0.03	0.35	0.02	0.04	0.02
25	Nells Island	41 11.804	73 06.749	8.82	13.44	11.11	***	1.18	0.06	0.35	0.06	0.04	0.06
26	Mid Sound	41 06.638	72 55.224	27.00	***	12.36	3.0	1.46	0.06	0.44	0.03	0.04	0.03
27	S. of Westhaven	41 12.543	72 55.974	26.28	13.99	13.26	3.0	3.51	0.79	0.41	0.06	0.04	0.06
29	New Haven	41 17.792	72 54.435	23.19	11.37	***	2.0	2.46	0.15	0.70	0.04	0.09	0.04
31	Northville	41 07.590	72 39.084	26.77	7.6	11.4	4.0	2.66	0.28	0.42	0.10	0.05	0.02
32	6 mile Shoals	41 10.024	72 29.067	27.50	6.7	11.52	5.0	1.99	0.58	0.27	0.04	0.03	0.01
33	Dumping Ground	41 12.476	72 21.924	23.70	7	11.57	2.2	0.80	0.08	0.23	0.04	0.02	0.00
35	Long Island Shoal	41 14.650	72 18.771	28.42	6.9	10.1	2.5	0.74	0.19	0.31	0.06	0.03	0.01
37 C	Mouth of Conn.	41 14.910	72 19.897	8.37	8.9	12.18	3.0	1.50	0.18	0.97	0.03	0.07	0.00
39	Plum Island	41 14.249	72 11.765	28.01	7	10.12	5.5	0.77	0.01	0.20	0.00	0.02	0.00
40	S. of New London	41 15.788	72 04.77	28.87	7.5	12.25	5.5	0.73	0.08	0.12	0.04	0.01	0.04
41	GE plant	41 16.784	72 06.063	28.99	7.3	10.22	6.0	0.77	0.09	0.30	0.09	0.02	0.09
42	New London Bridge	41 20.627	72 05.148	22.33	10.6	10.7	5.5	1.19	0.15	0.33	0.03	0.03	0.03
43	New London	41 21.706	72 05.253	14.95	11.9	9.76	5.5	2.54	0.33	0.38	0.09	0.03	0.09
44	The Race	41 09.251	72 05.253	27.38	6.8	10.11	4.0	0.85	0.06	0.28	0.06	0.02	0.06

Table 7: Ancillary parameters in Long Island Sound, April 2001. *** missing values

Station #	DOC (uM)	STDEV	NH4 (uM)	STDEV	NO3 (uM)	STDEV	DON (uM)	STDEV	Urea (uM)	STDEV	PO4 (uM)	STDEV	DOP (uM)	STDEV	Silicate (uM)	STDEV
T.R.	344	***	4.77	0.65	22.7	0.02	9.34	1.63	0.93	0.04	0.97	0.00	2.94	0.19	14.6	0.22
Q.R.	314	***	7.33	0.33	20.3	5.59	25.3	3.31	1.51	0.91	1.19	0.08	2.26	0.07	9.82	0.22
H.R.	460	21.0	7.07	0.40	22.3	8.73	80.1	5.13	0.67	0.01	1.28	0.10	9.04	0.03	12.1	1.81
C.R.	323	10.4	17.1	0.88	22.1	7.69	18.4	10.4	0.76	0.02	0.61	0.02	1.68	0.17	30.2	0.43

Station #	Station Name	Salinity (ppt)	Temp (C)	DO (mg/l)	Secchi (m)	Chl a (ug/l)	STDEV	POC (mg/l)	STDEV	PON (mg/l)	STDEV
T.R.	Thames River	2.53	23.78	7.16	***	2.8	0.13	0.78	0.15	***	***
Q.R.	Quinnipiac River	0.15	19.98	7.86	***	1.44	0.09	0.43	0.13	***	***
H.R.	Housatonic River	0.13	22.22	7.44	***	3.32	0.43	0.71	0.09	***	***
C.R.	Connecticut River	0.11	23.21	7.56	***	10.23	0.39	1.10	0.06	***	***

Station #	Ag (pM)	Cd (pM)	Pb (pM)	Cu (nM)	Ni (nM)	Zn (nM)	Fe (nM)
T.R.	25.5	64.2	83.1	22.1	26.2	36.9	2100
Q.R.	13.2	348	184.1	47.5	36.7	20.9	790
H.R.	12.1	63.1	139.3	30.1	88.2	75.6	1300
C.R.	6.14	35.4	---	16.0	22.5	18.5	774

Table 8: Fresh water end member data in Long Island Sound, July 2000. *** missing values

Station #	DOC (uM)	STDEV	NH4 (uM)	STDEV	NO3 (uM)	STDEV	DON (uM)	STDEV	UREA (uM)	STDEV	PO4 (uM)	STDEV	DOP (uM)	STDEV	Silicate (uM)	STDEV
T.R.	277	8.11	0.83	0.09	13.1	9.60	10.9	4.51	0.05	0.08	0.63	0.04	0.59	0.05	146	6.70
Q.R.	243	3.47	12.4	9.44	17.6	6.56	17.4	7.83	0.23	0.03	0.20	0.01	0.50	0.01	245	1.40
H.R.	199	9.27	15.2	0.51	80.2	2.13	96.1	6.15	0.51	0.00	4.42	0.01	0.38	0.04	108	5.01
C.R.	228	***	3.86	0.34	15.0	2.35	14.0	0.81	0.06	***	0.51	0.06	0.85	0.17	135	7.51

Station #	Station Name	Salinity (ppt)	Temp (C)	DO (mg/l)	Secchi (m)	Chl a (ug/l)	STDEV	POC (mg/l)	STDEV	PON (mg/l)	STDEV
T.R.	Thames River	0.56	16.7	9.28	2.0	***	***	0.97	0.01	0.05	0.01
Q.R.	Quinnipiac River	0.19	16.29	9.21	***	***	***	0.10	***	0.08	0.12
H.R.	Housatonic River	0.12	13.7	10.19	1.5	***	***	0.97	0.04	0.11	0.15
C.R.	Connecticut River	0.08	8.3	17.31	***	0.94	0.03	1.21	0.10	0.10	0.01

Station #	Ag (pM)	Cd (pM)	Pb (pM)	Cu (nM)	Ni (nM)	Zn (nM)	Fe (nM)
T.R.	22.3	69.1	160	26.7	22.2	33.2	2580
Q.R.	31.9	94.6	86.0	36.1	116	23.1	131
H.R.	53.3	315	412	65.8	52.7	40.5	1180
C.R.	6.87	67.0	65.1	32.0	23.8	34.2	313

Table 9: Fresh water end member data in Long Island Sound, April 2001. *** missing values

Low Flow

	1	2	3
NO$_3$	0.650	0.401	-0.536
PO$_4$	0.106	0.682	-0.605
SILICATE	0.662	0.448	0.147
CHL *a*	0.408	0.178	0.650
DOC	0.838	0.289	0.148
Ag	-0.405	0.502	-0.605
Cu	0.143	0.872	0.101
Cd	-0.723	0.281	-0.194
Ni	0.135	0.812	0.011
Zn	0.164	0.840	-0.087
Fe	0.883	0.184	-0.189
SALINITY	-0.919	-0.031	-0.099
TEMP	0.021	-0.020	0.638
% of total variance	37.972	24.809	10.631
cumulative %	37.972	62.781	73.411

High Flow

	1	2	3	4
NO$_3$	0.774	0.118	0.037	0.382
PO$_4$	0.810	-0.079	0.440	0.161
SILICATE	0.883	0.213	-0.129	-0.018
CHL *a*	-0.788	0.405	-0.012	0.158
DOC	0.111	0.216	0.010	0.899
Ag	0.140	0.113	0.818	0.290
Cu	0.126	0.887	0.133	0.278
Cd	-0.203	0.000	0.801	-0.202
Ni	0.031	0.810	0.221	0.022
Zn	0.393	0.528	0.508	-0.034
Fe	0.712	0.382	-0.236	-0.275
SALINITY	-0.564	-0.468	0.500	-0.204
TEMP	0.015	0.769	-0.305	-0.047
% total variance	33.765	19.117	17.327	8.805
cumulative %	33.765	52.882	70.209	79.014

Table 10: Results of principal component analysis shown as factor loadings of the extracted principal components. Each solution was quartimax normalized to optimize statistical results.

Low Flow

	NO3	PO4	Silicate	DOC	Ag	Cd	Cu	Ni	Zn	Fe
Thames	1.5	0.36	1.46	1.62	0.14	2.37	0.86	0.84	0.89	8.95
Quinnipiac	0.25	0.08	0.18	0.27	0.01	2.38	0.34	0.22	0.09	0.63
Housatonic	5.88	1.91	4.86	8.66	0.26	9.33	4.7	11.3	7.27	22.2
Connecticut	22.6	3.54	46.9	23.6	0.51	20.2	9.63	11.2	6.9	51.2
East River	70.1	94.2	46.9	65.8	99.0	65.7	84.4	76.3	84.8	17.0

High Flow

	NO3	PO4	Silicate	DOC	Ag	Cd	Cu	Ni	Zn	Fe
Thames	1.19	0.96	1.51	1.64	0.69	0.84	1.26	1.15	1.34	12.3
Quinnipiac	1.48	0.28	0.29	1.72	1.36	1.06	1.57	5.56	0.86	0.59
Housatonic	16.9	15.8	2.62	3.11	2.17	8.82	7.2	6.32	3.79	13.4
Connecticut	61.6	35.9	76.9	69.8	9.67	36.8	68.5	55.9	62.8	69.7
East River	18.8	47.1	18.7	23.7	86.1	52.5	21.5	31.1	31.2	4.05

Table 11: Total contribution of the ($Q_{river} \times C_{river}$) Thames, Quinnipiac, Housatonic, Connecticut, and East River ($Q_{ER} \times C_{ER}$) with respect to all fluvial inputs during low and high flow. Values are in percentages.

Low Flow

	NO$_3$	PO$_4$	Silicate	DOC	Ag	Cd	Cu	Ni	Zn	Fe
Thames	2.39	0.06	0.21	0.14	0.07	0.08	0.06	0.06	0.08	8.35
Quinnipiac	0.40	0.01	0.03	0.02	0.01	0.03	0.06	0.02	0.01	0.58
Housatonic	9.39	0.32	0.69	0.74	0.14	0.43	0.22	0.78	0.64	20.8
Connecticut	36.1	0.59	6.70	2.01	0.27	0.88	0.47	0.77	0.61	47.8
East River	111.8	15.7	6.71	5.61	52.1	7.72	1.54	5.28	7.46	15.9

High Flow

	NO$_3$	PO$_4$	Silicate	DOC	Ag	Cd	Cu	Ni	Zn	Fe
Thames	2.23	0.61	15.4	0.44	0.18	0.40	0.10	0.21	0.44	65.13
Quinnipiac	2.76	0.18	23.9	0.46	0.34	0.50	0.13	0.99	0.28	3.16
Housatonic	31.6	9.92	26.6	0.83	0.55	2.30	1.05	1.13	1.24	71.3
Connecticut	115	22.6	649	18.7	2.45	21.9	4.39	9.98	20.6	370
East River	35.2	29.6	51.0	6.36	21.8	6.86	6.26	5.56	10.2	21.5

Table 12: Total contribution of the Thames, Quinnipiac, Housatonic, Connecticut, and East River with respect to total oceanic output ($C_{median\ LIS} \times Q_{ocean\ out}$). Values are in percentages.

|	Friver	Focean	FLUXin	FLUXout	Imbalance (X)
NO3	1.90×10^6	7.80×10^5	2.68×10^6	6.13×10^5	3.45×10^5(56%)
PO4	3.35×10^5	3.77×10^5	7.12×10^5	8.57×10^5	1.45×10^5(17%)
Silicate	1.25×10^6	3.90×10^6	5.15×10^6	6.99×10^6	1.84×10^6(26%)
DOC	2.66×10^7	1.82×10^8	2.08×10^8	2.76×10^8	6.80×10^7(25%)
Ag	23.5	15.9	39.4	61.7	22.3 (36%)
Cd	339	259	598	312	-286
Cu	3220	5270	8490	3.15×10^4	2.3×10^4 (73%)
Ni	3390	7670	1.10×10^4	4.76×10^4	3.66×10^4 (77%)
Zn	5210	5210	8330	3.86×10^4	3.03×10^4 (78%)
Fe	2.93×10^4	5.01×10^4	7.94×10^4	1.92×10^4	-6.02×10^4

Table 13: Mass balance equations for Long Island Sound during the low flow sampling period. The Summer cruise was characterized by low river flow condtions (Quinnipiac 2.32×10^8 L d^{-1}, Housatonic 5.01×10^9 L d^{-1}, Connecticut 1.94×10^{10} L d^{-1}, Thames 1.25×10^9 L d^{-1}) Fluxes are reported in moles d^{-1}. The imbalance column shows the necessary input needed to balance the total output. Negative numbers indicate the estuary is a trap for those measured constituents. F_{river} = river input; F_{ocean} = oceanic input; $FLUX_{in}$ = total flux in; $FLUX_{out}$ = total flux out; Imbalance = $FLUX_{out}$ - $FLUX_{in}$. Parentheses represent the percent of the imbalance relative to the total output

	Friver	Focean	FLUXin	FLUXout	Imbalance (X)
NO3	5.83×10^6	7.80×10^5	6.61×10^6	3.12×10^6	-3.49×10^6
PO4	3.45×10^5	3.77×10^5	7.22×10^5	5.48×10^5	-1.74×10^5
Silicate	3.84×10^7	3.90×10^6	4.23×10^7	5.01×10^6	-3.73×10^7
DOC	7.87×10^7	1.82×10^8	2.61×10^8	2.94×10^8	3.3×10^7 (11%)
Ag	17.1	22.3	39.4	67.6	28.2 (41%)
Cd	43.9	261	304	368	64 (14%)
Cu	1.13×10^4	527	1.65×10^4	3.52×10^4	1.87×10^4
Ni	1.03×10^4	4.37×10^4	5.39×10^4	5.74×10^4	3500 (6%)
Zn	1.31×10^4	4.58×10^4	5.89×10^4	4.00×10^4	-1.89×10^4
Fe	1.08×10^5	8220	1.17×10^5	2.04×10^4	-9.66×10^4

Table 14: Mass balance equations for Long Island Sound during the high flow sampling period. The Spring cruise wass characterized by high dishcharge conditions (Quinnipiac 4.90×10^9 L d^{-1}, Housatonic 1.23×10^{10} L d^{-1}, Connecticut 2.41×10^{11} L d^{-1}, Thames 5.31×10^9 L d^{-1}). Fluxes are reported in moles d^{-1}. The imbalance column shows the necessary input needed to balance the total output. Negative numbers indicate the estuary is a trap for those measured constituents. F_{river} = river input; F_{ocean} = oceanic input; $FLUX_{in}$ = total flux in; $FLUX_{out}$ = total flux out; Imbalance = $FLUX_{out}$ - $FLUX_{in}$. Parentheses represent the percent of the imbalance relative to the total output.

Station #	PC 1	PC 2	PC 3
1	0.025	0.627	-1.598
2	-0.173	1.252	-1.470
3	-0.371	1.589	-1.497
4	0.028	0.539	-3.206
5	-0.322	0.580	-0.694
6	-0.257	0.507	-0.647
7	-0.129	1.068	-0.109
8	-0.131	1.023	0.504
10	0.068	-0.193	0.155
11	-0.666	0.568	0.546
12	-0.562	0.427	1.141
14	-0.365	-0.485	1.352
15	-0.442	-0.394	1.160
17	-0.648	-0.379	1.108
19	-0.442	-0.193	0.323
20	-0.522	-0.482	0.615
21	-0.923	-0.267	0.331
23	-0.659	0.280	0.497
24	-0.311	0.960	0.908
27	-0.673	0.603	0.778
29	0.066	1.656	0.831
31	-0.237	-0.287	0.687
33	-0.487	-1.281	-0.033
35	-0.464	-1.792	-1.149
36	0.059	-0.749	-0.547
40	-0.606	-2.039	-0.953
42	-0.054	-1.250	0.401
43	-0.371	0.299	0.480
44	-0.420	-2.024	-0.729
T.R.	2.351	-0.398	-0.303
Q.R.	1.584	0.593	0.054
H.R.	2.678	1.034	0.656
C.R.	3.377	-1.392	0.409

Table 15: Values of factor scores for each station for the low flow sampling period. Factor scores were plotted relative to one another to indicate how average water quality varies over the study area.

Station #	PC 1	PC 2	PC 3	PC 4
1	1.200	-0.453	1.076	-0.049
2	1.183	-0.697	0.535	0.777
3	0.973	-0.355	0.961	0.564
4	1.224	-0.150	1.235	0.866
5	0.829	0.170	1.482	0.307
6	0.406	0.238	1.517	0.096
7	0.241	0.472	1.472	0.528
8	0.062	0.290	0.520	1.029
9	-1.072	0.863	0.710	0.988
10	-0.759	0.890	1.354	-0.035
11	-0.972	0.504	0.831	-0.047
12	-1.221	0.676	0.329	0.660
13	-1.283	0.497	-1.207	0.854
14	-1.111	0.208	0.025	0.590
15	-1.358	0.943	0.184	0.422
16	-2.065	-0.127	-1.061	0.501
17	-1.660	0.958	-1.192	-0.502
18	-1.181	0.431	-0.205	-0.281
19	-0.688	-0.312	-0.037	-0.168
20	-0.394	-0.153	-0.030	-0.946
21	-0.578	0.004	0.029	-0.751
22	-0.092	0.733	1.201	-1.353
23	-0.794	0.033	-0.651	-1.038
24	0.587	0.797	0.011	-0.625
25	1.084	0.958	-0.116	-0.502
27	-0.804	0.390	-0.236	-1.351
29	0.251	0.199	0.168	0.169
31	0.014	-0.242	0.162	-0.268
32	-0.066	-1.525	-0.126	0.721
33	0.695	-1.642	-0.678	-1.016
35	0.178	-1.109	0.975	-2.080
39	-0.378	-2.514	-1.100	2.617
40	0.194	-1.735	-0.377	-0.782
41	0.066	-2.073	-0.676	-1.095
42	0.875	-0.302	-0.354	-1.914
44	0.157	-1.952	-0.098	1.176
T.R.	1.713	1.169	-2.663	-1.388
Q.R.	1.163	0.811	-2.553	1.379
H.R.	1.985	1.805	-0.007	1.399
C.R.	1.396	1.302	-1.410	0.550

Table 16: Values of factor scores for each station for the low flow sampling period. Factor scores were plotted relative to one another to indicate how average water quality varies over the study are
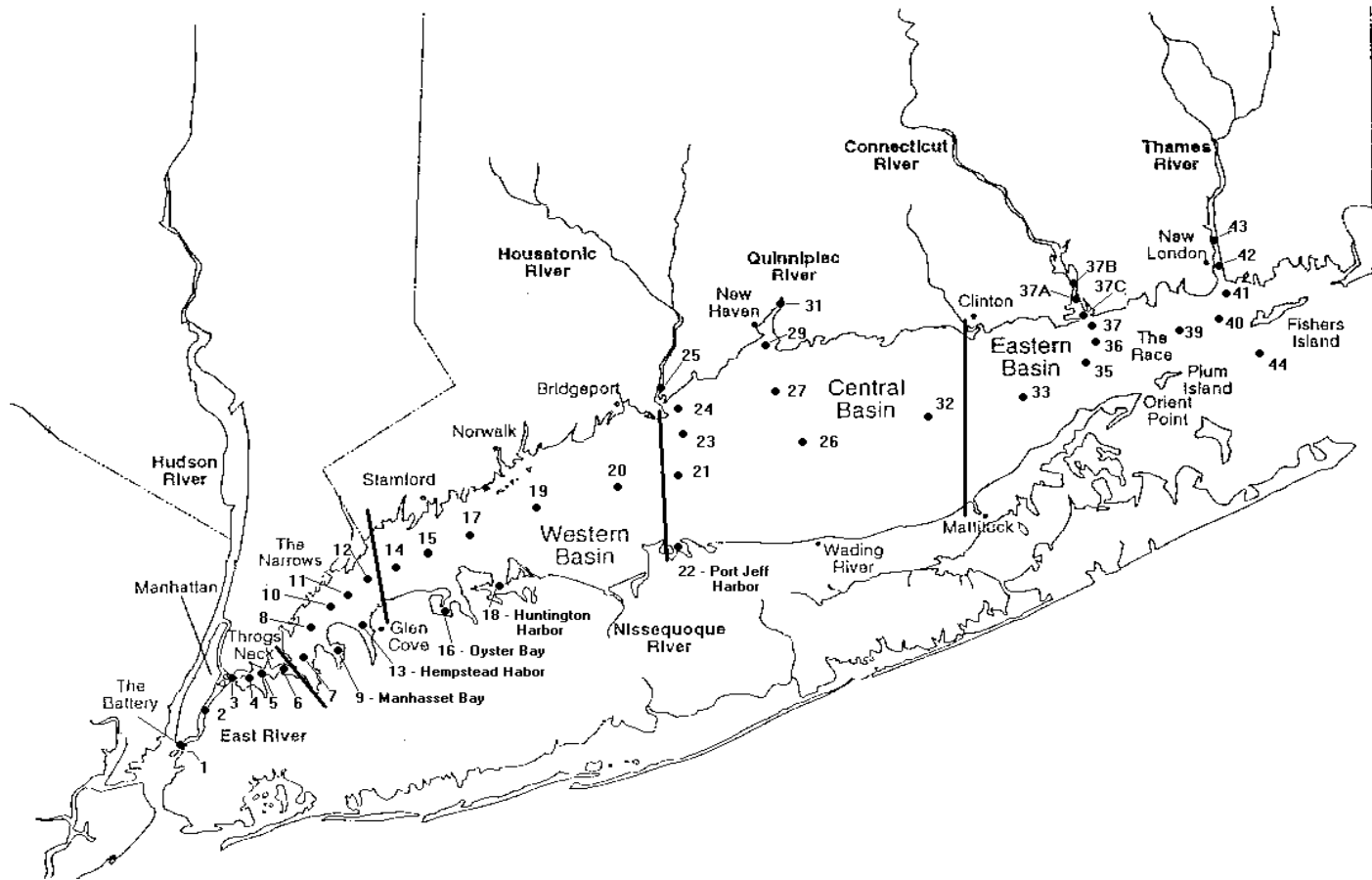
FIGURES

Figure 1: Index map of Long Island Sound including stations locations for this study. The dark lines denote the boundaries for each geographic region. From west to east – The East River, The Narrows, The Western Basin, The Central Basin and The Eastern Basin.
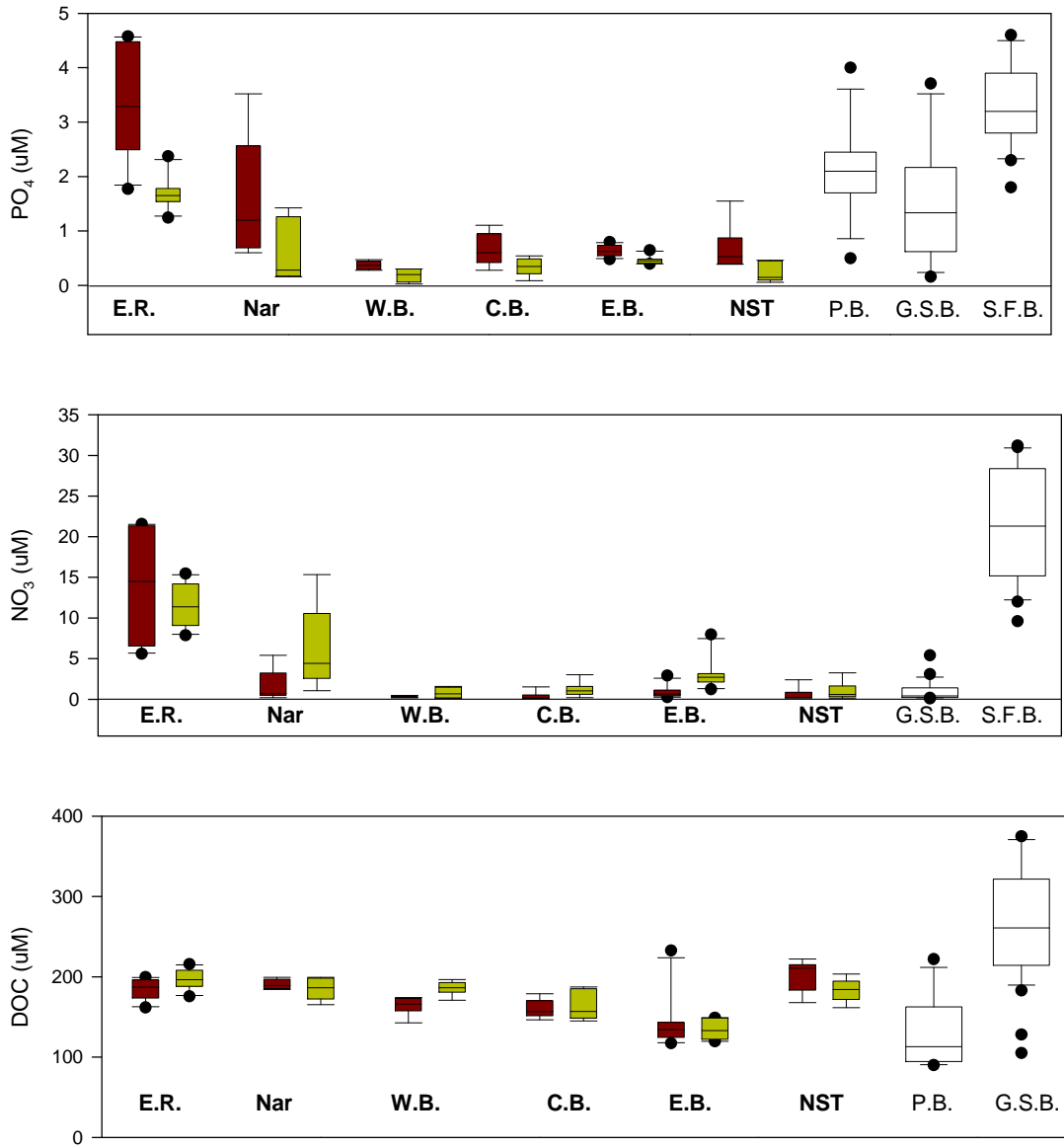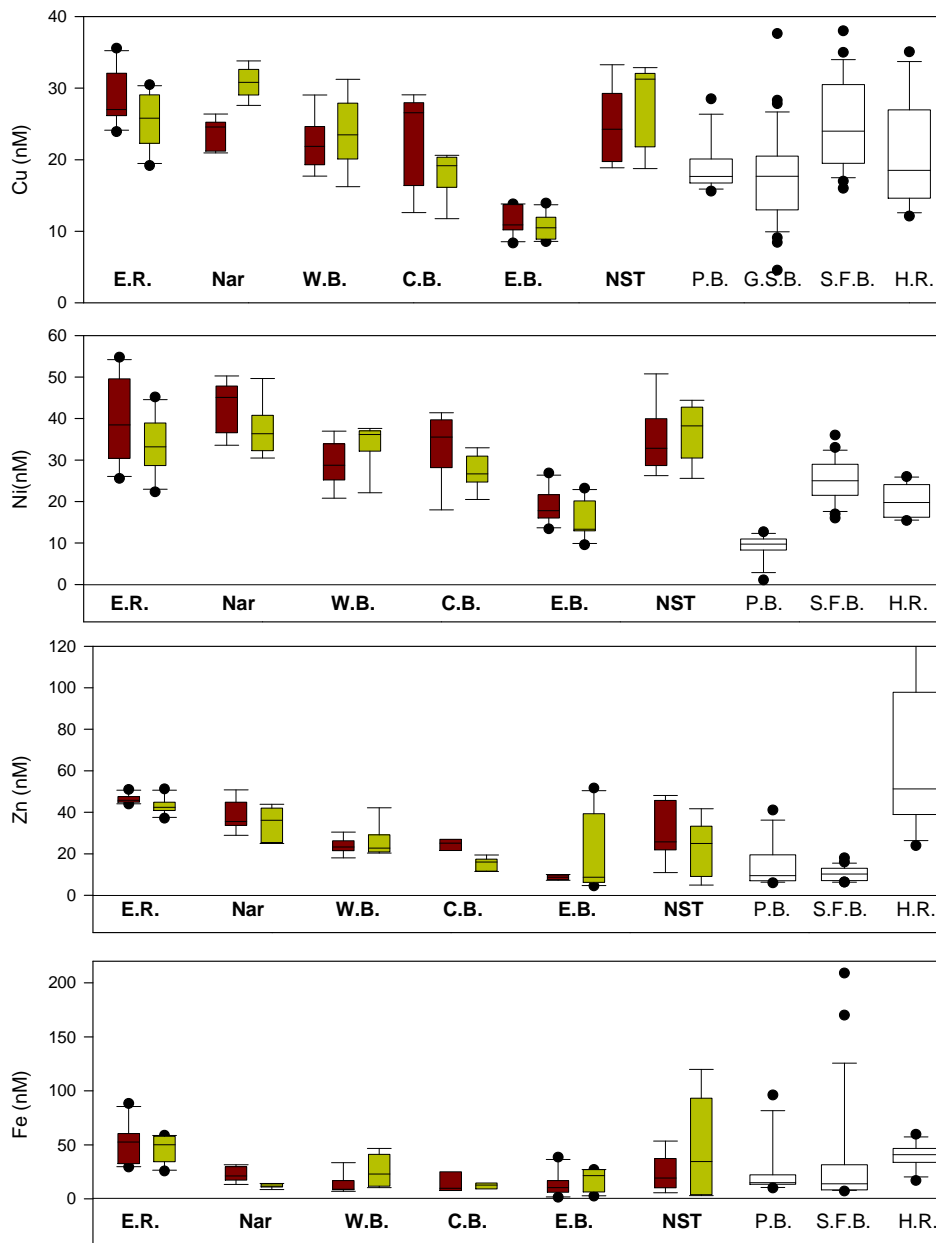
Figure 2: Surface concentrations of nutrients in Long Island Sound (E.R., East River; Nar, Narrows; W.B., Western Basin; C.B., Central Basin; E.B. Eastern Basin; NST, National Status and Trend sites sampled) as compared to levels in The Peconic Estuary System (PB; Breuer *et al*. 2000), Great South Bay (GSB; Clark 2000), and Southern San Francisco Bay (SFB; Flegal et al. 1991). Dark Boxes represent low flow conditions while lighter boxes, high flow.
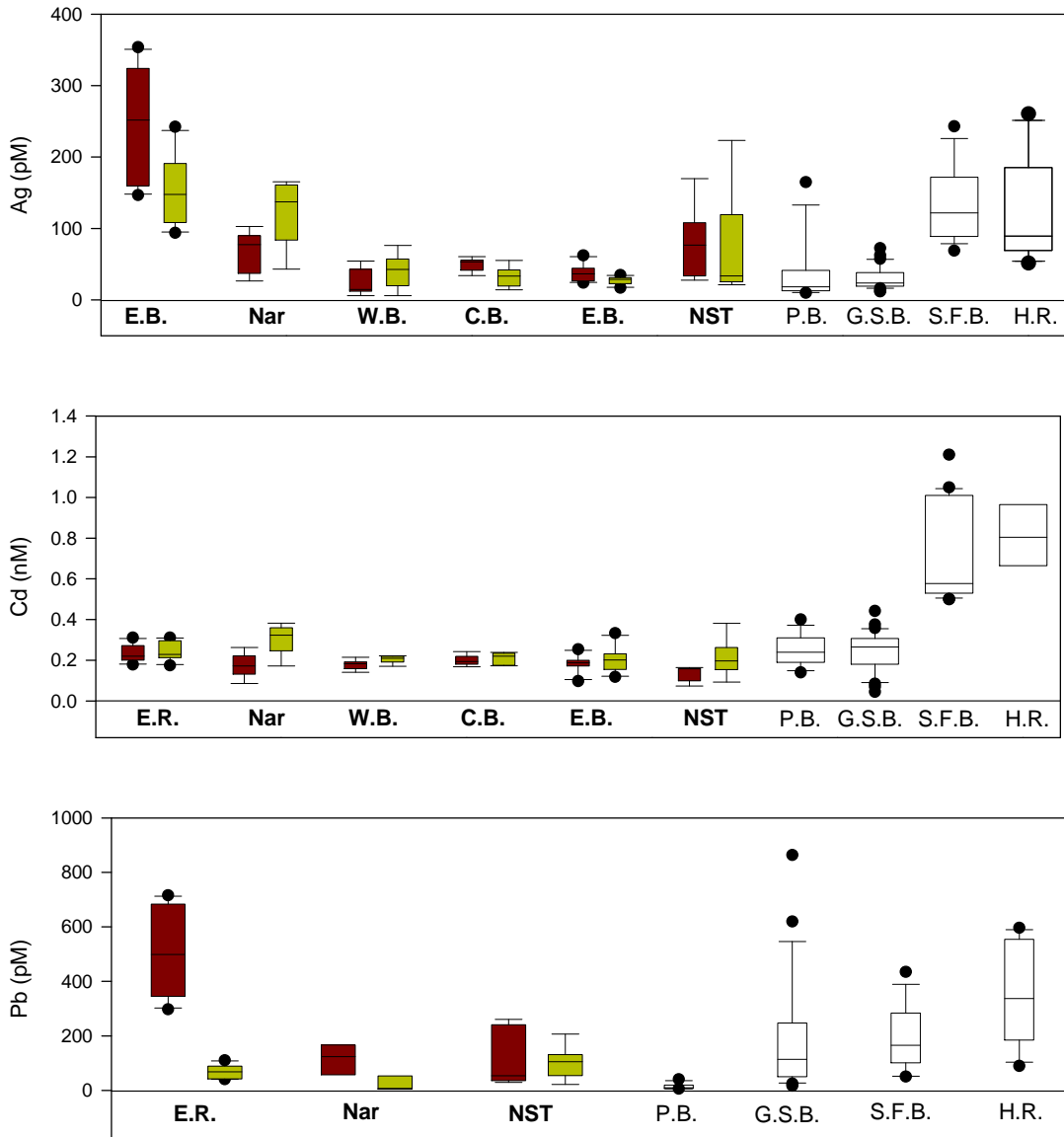
Figure 3: Surface concentrations of silver, cadmium, and lead in Long Island Sound (E.R., East River; Nar, Narrows; W.B., Western Basin; C.B., Central Basin; E.B. Eastern Basin; NST, National Status and Trend sites sampled) as compared to levels in The Peconic Estuary System (PB; Breuer *et al*. 2000), Great South Bay (GSB; Clark 2000), Southern San Francisco Bay (SFB; Flegal et al. 1991) and The Hudson River (HR; Sanudo-Wilhelmy and Gill, 1999). Dark Boxes represent low flow conditions while lighter boxes, high flow.

Figure 4: Surface concentrations of copper, nickel, zinc, and iron in Long Island Sound (E.R., East River; Nar, Narrows; W.B., Western Basin; C.B., Central Basin; E.B. Eastern Basin; NST, National Status and Trend sites sampled) as compared to levels in The Peconic Estuary System (PB; Breuer *et al.* 2000), Great South Bay (GSB; Clark 2000), Southern San Francisco Bay (SFB; Flegal et al. 1991) and The Hudson River (HR; Sanudo-Wilhelmy and Gill, 1999). Dark Boxes represent low flow conditions while lighter boxes, high flow.

Low Flow (July 2000)
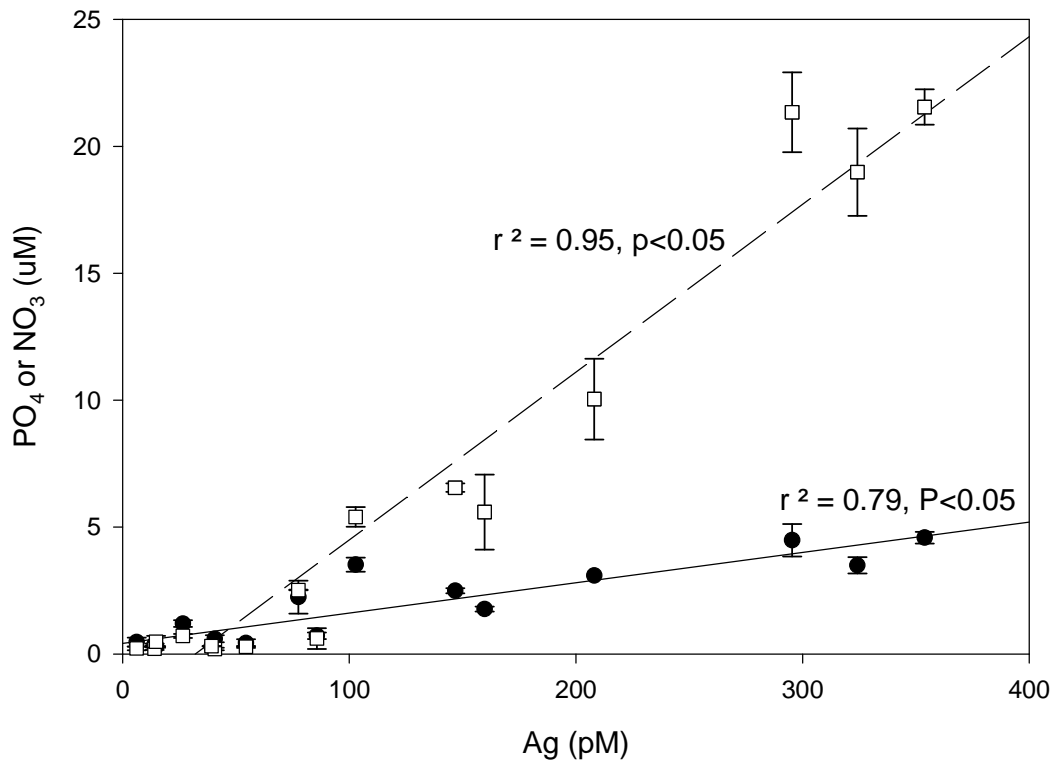
Figure 5: Dissolved silver, nitrate (squares) and phosphate (circles) in the East River and Narrows of Long Island Sound during the low flow sampling period.
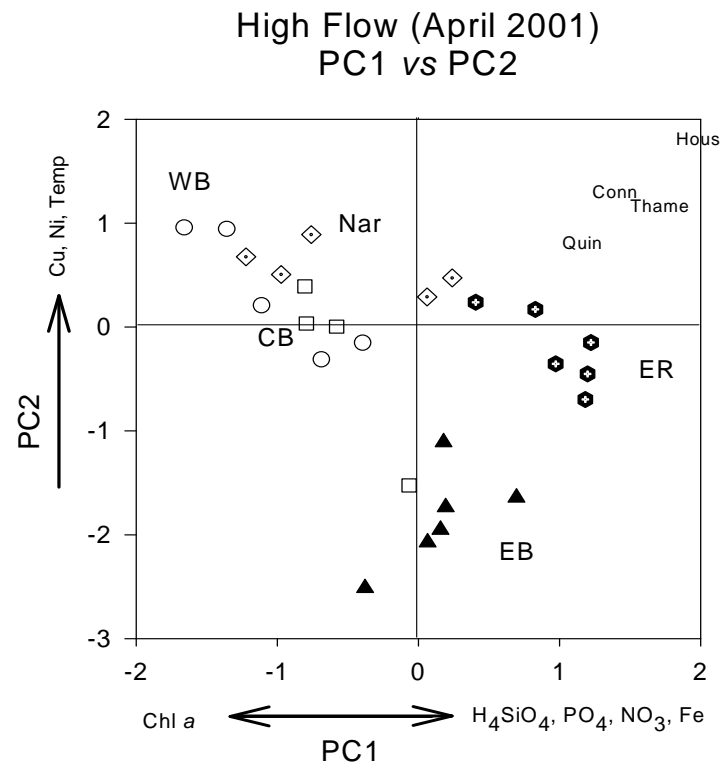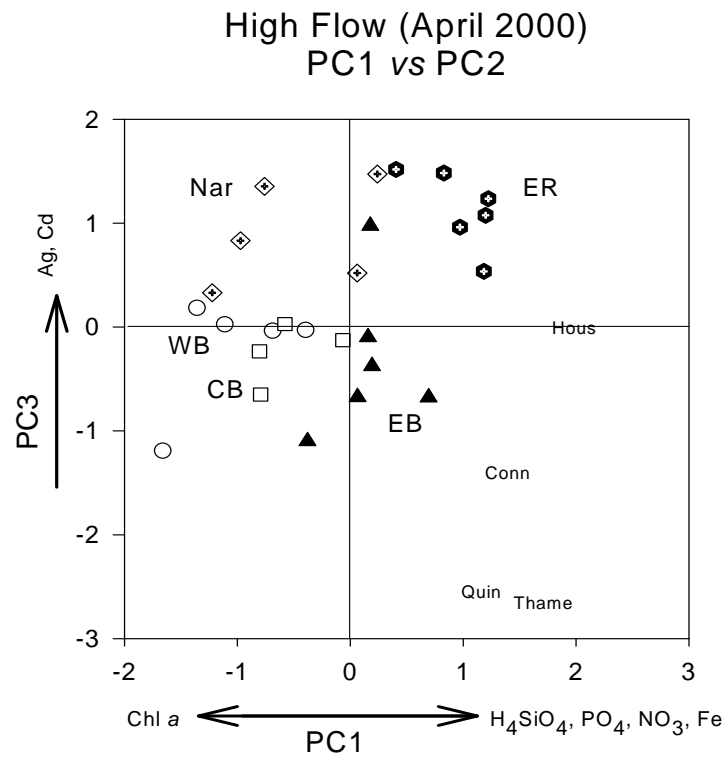
Figure 6: Long Island Sound sample data set. Principal component model projections for the first and second principal components during the Summer sampling period. ER, East river; Nar, Narrows; WB, Western Basin; CB, Central Basin; EB, Eastern Basin
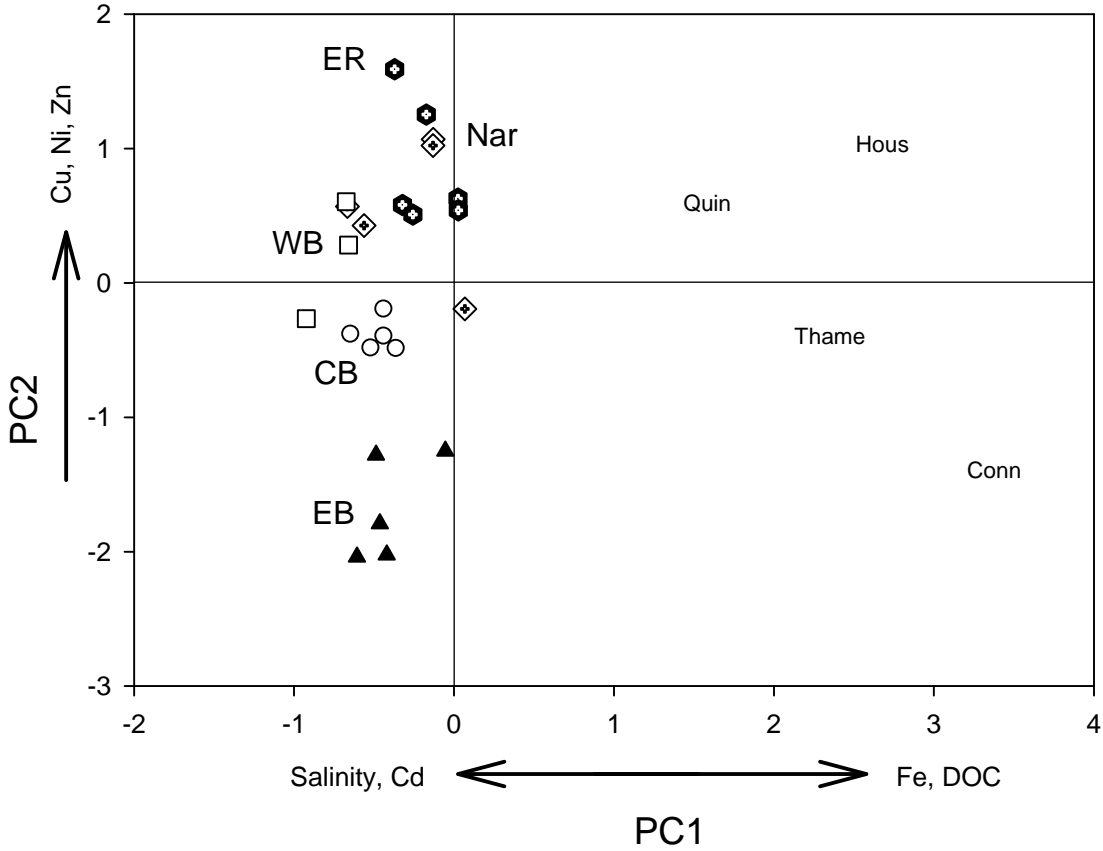
Figure 7: Long Island Sound sample data set. Principal component model projections for the first and second principal components during the Summer sampling period.
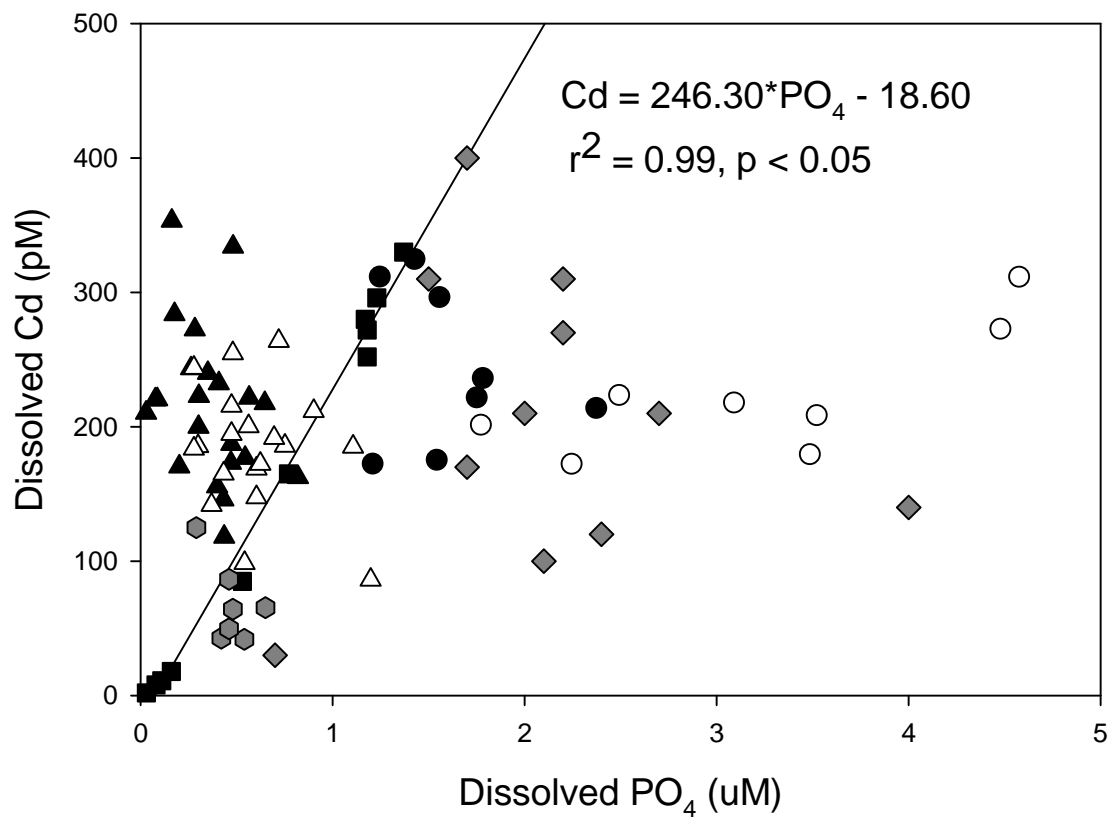
Figure 8: Dissolved cadmium – Dissolved phosphate relationships. . Filled squares with solid regression line represent Northwest Atlantic (Bruland 1983). Open circles represent stations 1-8 during low flow, while filled circles represent stations 1-8 during high flow. The Triangles represent the remainder of the sound stations with open triangles denoting low flow and filled triangles denoting high flow.
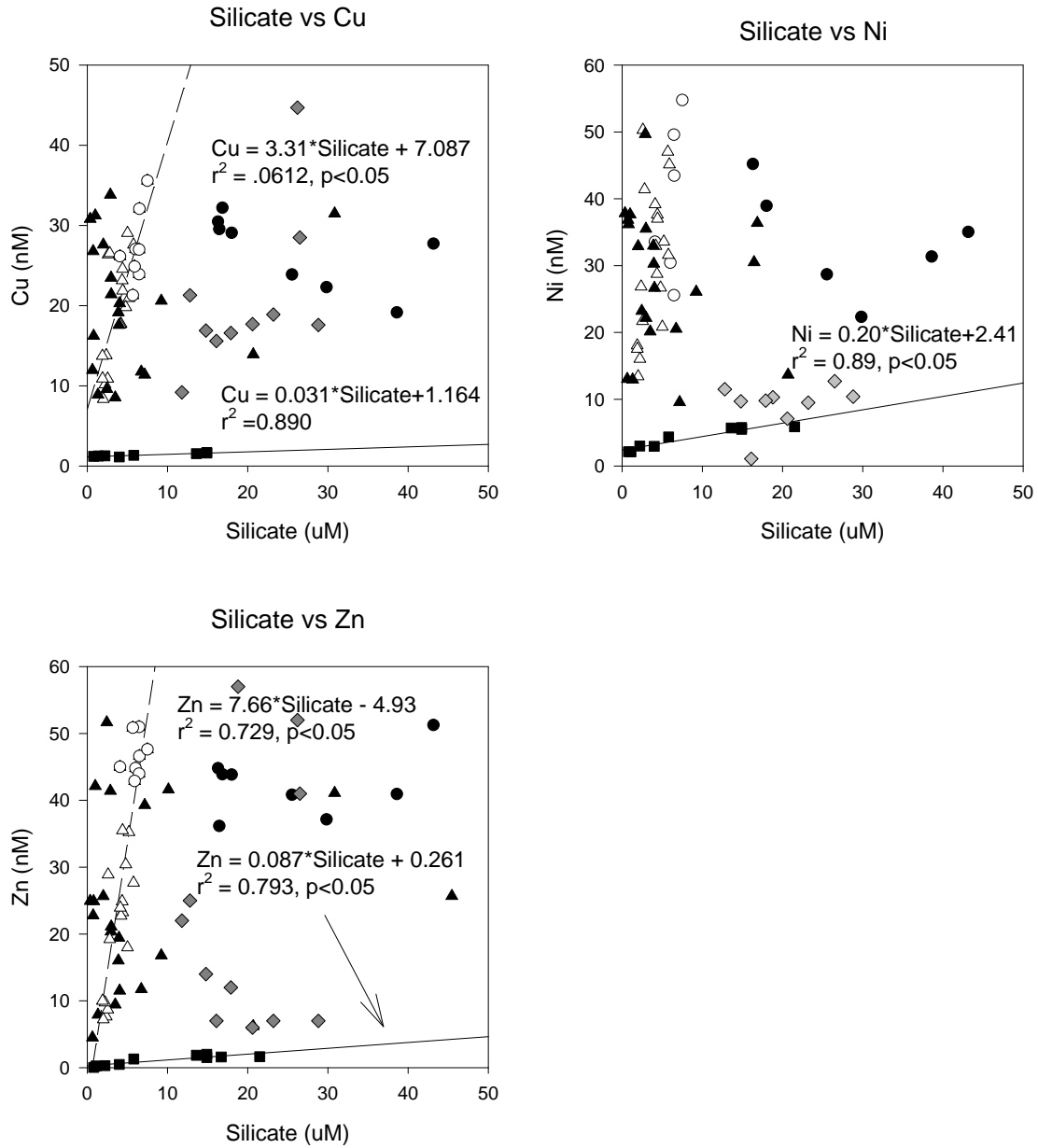
Figure 9: Dissolved copper, nickel, and zinc vs. dissolved silicate relationships. Filled squares with solid regression line represent Northwest Atlantic (Bruland 1983). Open circles represent stations 1-8 during low flow, while filled circles represent stations 1-8 during high flow. The Triangles represent the remainder of the sound stations with open triangles denoting low flow and filled triangles denoting high flow. Dashed lines represent regression relationships during the low flow sampling period
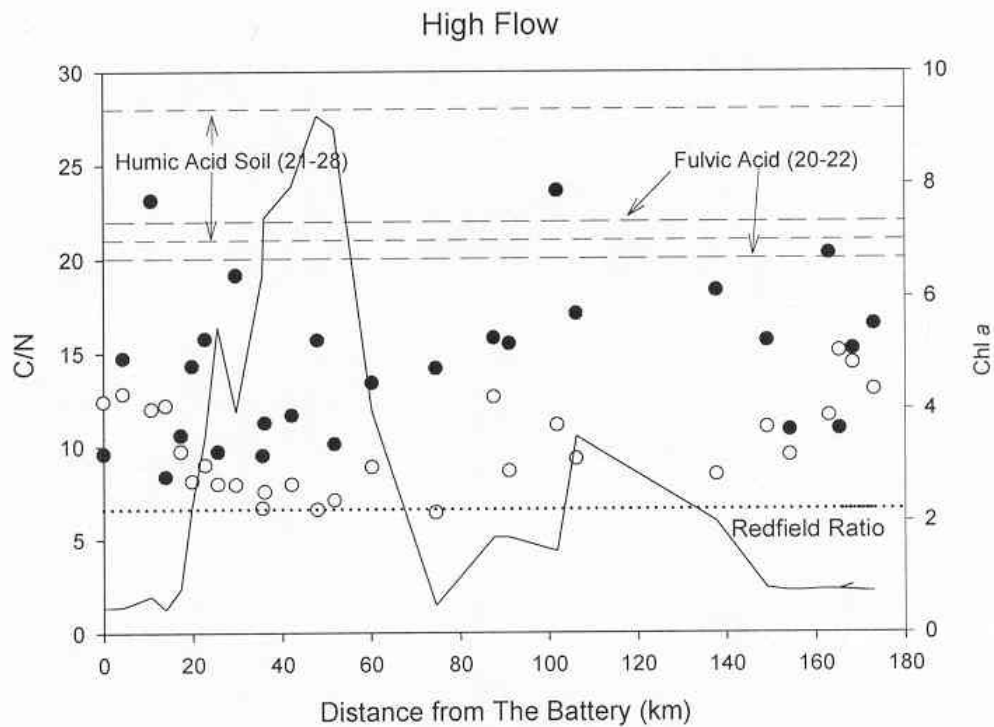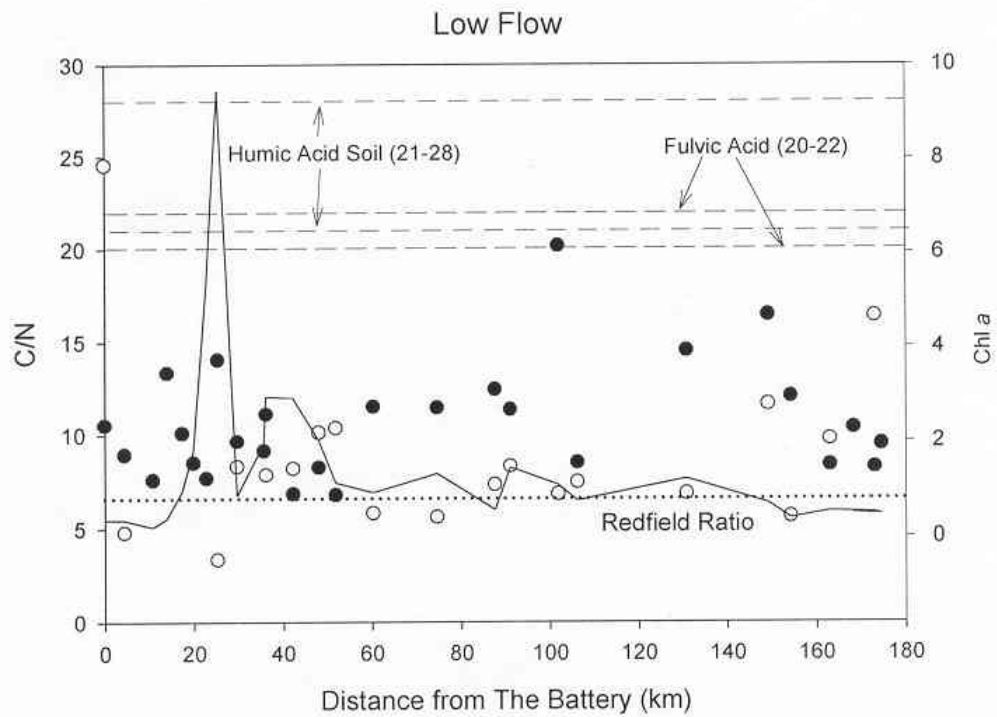
Figure 10: C/N ratios for particulate (open circles) and dissolved phases (closed circles), and Chl *a* measurements (solid line). Dotted line represents Redfield C/N ratio while dashed line represents C/N fulvic acid ratio within soils and dash-dot-dash line represents C/N
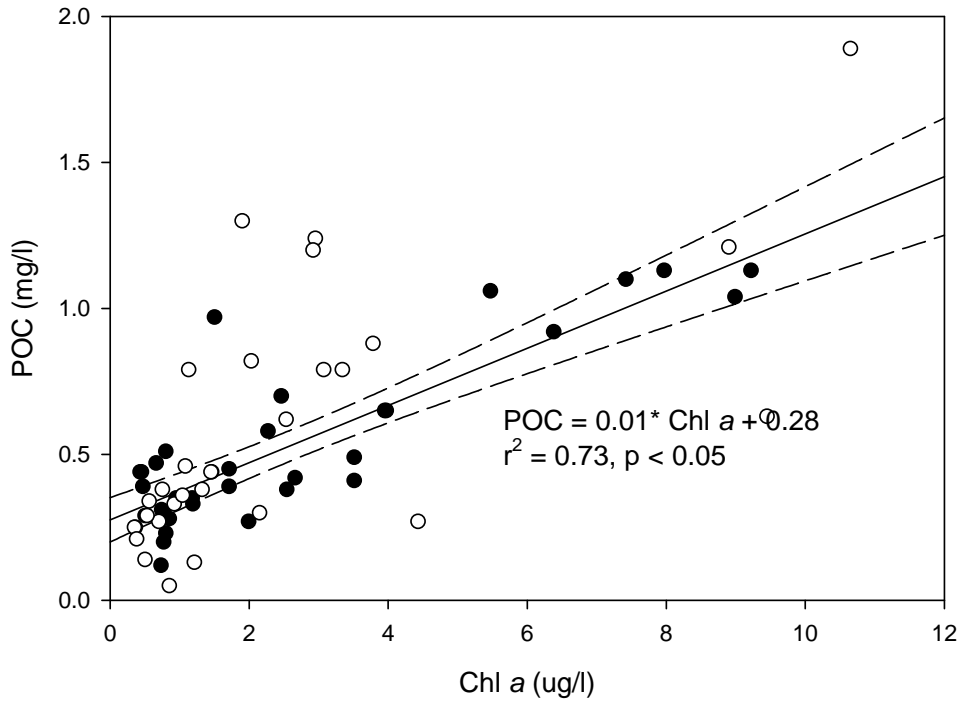
Figure 11: Chl *a* – particulate organic carbon relationships, filled circles represent high flow conditions while open circles represent low flow conditions. The dark solid line represents the correlation for high flow with long dashed lines denoted 95% confidence limits.