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POSTERS

The ecosystem that is Long Island Sound is the product of a variety of interactions physical, chemical, biological and geological. These factors affect the distribution of properties as well as the processes governing water quality and the health and diversity of the biological community. Close proximity to the New York metropolitan area affects regional climate and the multitude of atmospheric inputs and runoff characteristics introducing a significant anthropogenic supplement to the variety of natural factors. This complexity of interactions, natural and manmade, results in a system characterized by marked spatial and temporal variability. Such variability complicates the establishment of cause and effect relationships and requires especial care in the design of sampling programs. In particular, signal resolution in this system is typically best realized by relatively long sets of high frequency time series data. Although this fact is well known it is only recently with the establishment of the State of Connecticut DEP shipboard surveys in the early 1990's and the subsequent deployment of a network of moored arrays beginning in 1998 sponsored by EPA and NOAA and the associated placement of current profilers on several cross-sound ferries that we have been able to satisfy these criteria. The benefit of these data within a variety of process based studies, first seen in the Proceedings of the 2004 Long Island Sound Research Conference, represents the central theme of this Conference.

Given the value of long term data sets it's appropriate that the Conference starts with a discussion of carbon cycling over the past 1000 years. Using two dated sediment cores obtained in the central and western Sound Varekamp and his co-authors establish an interesting framework for subsequent analyses of the factors governing hypoxia in the western Sound, a subject of continuing interest. This is followed by a review of the DEP shipboard data set by Olsen et.al. and a number of presentations dealing with system dynamics and associated water quality. These are nicely complemented by discussions of the plankton community by Liu and Lin and Dam et.al,, a decadal study of the nearshore fish community of Milton Harbor by McEnroe et.al, several discussions of marsh and wetland dynamics, and an overview of the physical oceanography of the Sound by O'Donnell. In combination these presentations provide essential information on each of the principal components of the Sound ecosystem.

Beyond their individual value the talks presented at this conference show an increasing understanding of the need for and value of interdisciplinary studies if we seek to provide accurate predictions of the role of the variety of factors affecting Sound water quality and the associated biological community and ultimately the resource value of the Sound. It's clear, for example, that physical mixing processes affect a variety of reactions leading to hypoxia which in turn affect and are affected by biological factors. These results indicate that the extent to which we will be able to realize such studies, possibly through the establishment of reference sites that can be routinely monitored by teams of investigators over an extended period of time, will in large part govern future improvements in our understanding of Sound dynamics. This represents a significant challenge to both managers and the scientific community.

W.Frank Bohlen
July, 2009

PAPERS

Carbon Cycling in LIS: Nutrient Fluxes and Landscape Development Over the Last 1000 Years

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ABSTRACT

Long Island Sound sediment carries a record of changing environmental conditions over time, and we present data for organic carbon with its chemical properties $\delta^{15}N$, $\delta^{13}C$ and C/N values from two dated cores in central and western Long Island Sound. The mass accumulation rates of inorganic sediment and total organic carbon increased strongly over the last 200-300 years by factors of 3-8. Between 1700 and 1800 AD, the flux of terrestrial organic carbon almost disappeared from western Long Island Sound, but then became the dominant component of buried organic matter since 1900 AD in both core locations. The $\delta^{15}N$ of buried organic matter increased between 1750 and 1900 AD, indicating enhanced nutrient influxes stemming ultimately from organisms higher up in the food chain (e.g., manure, sewage), and then slowly decreased with the increased percentage of buried terrestrial organic matter over the last 100 years. The amount of buried Biogenic silica (diatom frustules) initially increased but then also started to decrease since the 1920s, indicating that diatoms may no longer have been the dominant primary producer during that period. Overall, the record shows evidence for eutrophication, but in detail, the change-over in dominance from marine organic carbon to sewage carbon and terrestrial carbon in western Long Island Sound over the last 100 years is striking and significant. We cautiously interpret these findings as a result of possible changes in the ecosystem, abundance and transport of marine organic carbon out of Long Island Sound by larger organisms over the last 100 years, together with the gradual shift from diatoms to other primary producers.

INTRODUCTION

Long Island Sound (LIS) has suffered from hypoxia for many decades (Parker and O'Reilly, 1991; Welsh and Eller, 1991; O'Shea and Brosnan, 2000), and probably already since the mid-1800's (Lugolobi et al., 2004; Thomas et al., 2004; Varekamp et al., 2004). The main reason for low bottom-water oxygen is the oxidation of particulate organic carbon (C_{org}), be it suspended in the water column or deposited on the basin floor, in the sediments. This particulate organic carbon may have been produced by organisms in the Sound (marine) or have been transported from land (terrigenous, from soils, plant material) or be anthropogenic, e.g., derived from sewage. The pathways of oxidation are manifold: ingestion of carbon by heterotrophs with respiration and defecation, bacterial decomposition of C_{org} using dissolved O_2, and more complex pathways involving oxidation of C_{org} through the reduction of seawater sulfate.

The more labile carbon is either used by biota (e.g., deposit feeders) or rapidly oxidized, and the more refractory components remain in the sediment as buried organic carbon. Analysis of this remaining carbon provides insight into the C_{org} sources over time, keeping in mind that carbon preserved in the sediment is a somewhat refractory, modified pool. Marine C_{org} (produced by phytoplankton) is probably the most labile, followed by very thin terrestrial carbon fragments, with pieces of lignin-rich C_{org} (wood) the most stable. The sedimentary C_{org} pool thus is probably biased towards terrestrial C_{org}, which is more resistant to re-mineralization than marine C_{org}.

CORE DESCRIPTIONS AND TECHNIQUES

We studied sediment from two core sites in westernmost and central LIS: site WLIS75 site (core WLIS75GGC1) and site B1 (cores B1GGC1 and B1C2; Figure 1). The cores were collected with gravity corers in 1996 and 2001, and sliced into 0.5 cm intervals under clean protocols for metal analyses (Mecray and Buchholtz ten Brink, 2000). Core B1GGC1 was taken in the delta of the Housatonic River and has a strong input from that source. The circulation in LIS brings Connecticut River water and sediment (including Particulate Organic Carbon, POC) along the Connecticut south coast to the western part of the Sound. The sediments in this core are medium silts/clays, with some slightly coarse layers possibly related to storm deposits and shelly layers with bivalves. Core B1C2 is a short core located next to B1GGC1, with similar sediment character. Core WLIS75GGC1 was taken just west of Execution Rock and is strongly impacted by effluents from the East River. The core consists of dark, C_{org}-rich fine sediments, with a coarse layer with large clumps of coal at depth interval 14-24 cm.

The samples were analyzed with a C-N analyzer, both in bulk (Core B1GGC1) and after acid treatment to remove the carbonate component (Cores B1C1, WLIS75GGC1). The $\delta^{15}N$ and $\delta^{13}C$ were analyzed with conventional mass-spectrometric techniques. The biogenic silica content was determined by a sequential extraction analyses technique of DeMaster (1981), with Si detection by ICP-AES (Andersen, 2005). The cores were dated with radiocarbon on handpicked foraminifera and larger shell fragments if available, and the ages were calibrated with Calib5.1 (Stuiver and Reimer, 1993) using their marine data set. The onset of mercury pollution was used as a chemostratigraphic marker at 1820 AD, as dated in the marshes of the Housatonic River with ^{210}Pb techniques (Varekamp et al., 2001). Core B1C2 was dated with ^{210}Pb-^{137}Cs for the last 100 years. Sediment mass accumulation rates (MAR) were determined using the bulk dry density (derived from the sediment H_2O contents and an assumed grain density, cross calibrated with slice density measurements) in combination with age models derived from the ^{14}C dates and other time markers for each core. Carbon accumulation rates were calculated from the sediment MARs and C_{org} data.

To derive the mixing contributions of the various C_{org} components in a sediment we used the conventional binary mixing equation: $R_{mix} = f\,R1 + (1\text{-}f)\,R2$, where f is a weight-based mixing parameter, R1 and R2 are the isotope or elemental ratios in the end-members 1 and 2, and R_{mix} is the ratio in the sediment sample. We can solve the equation above for f when R1, R2 and R_{mix} are known. The three end-members are defined by their $\delta^{13}C$, C/N and $\delta^{15}N$, and through the application of two separate mixing equations the ternary mixture can in theory be resolved (but not all solutions are necessarily unique). Care should be taken with the use of the mixing parameter f: in many earlier studies, authors used the C/N ratios and then applied the f-factors as representative for the proportions of C_{org}. For instance, if $(C/N)_{mix}=0.25\ (C/N)_T + 0.75\ (C/N)_M$, it was usually taken that 25% of the C_{org} was terrestrial (T) and 75 % was marine (M). It is a standard result in the derivation of these equations that the f factors relate to the weight proportions of the denominators in the ratios (e.g., Albarede and Hofmann, 2003), in this case N, and thus represent the proportions of N contributed to the sediment mix (not Carbon). Since the C/N ratios in the two end members are different, the f factors do not represent the contributions of organic carbon to the mixture. To carry out the calculations for carbon contributions correctly, one should use the N/C ratios. When used in combination with $\delta^{13}C$, both denominators equate with approximately total carbon, and this will result in straight mixing lines in N/C versus $\delta^{13}C$ diagrams, whereas C/N versus $\delta^{13}C$ diagrams provide curved mixing arrays. In contrast, plots of $\delta^{15}N$ versus C/N will give straight mixing lines, because ~total N occurs in both denominators. This error occurs in much of the earlier literature, but was been described in an insightful paper by Perdue and Koprivnjak (2007). In the following we describe initially contributions of terrestrial carbon (mainly terrestrial plant material) versus marine carbon as based on N/C and $\delta^{13}C$ mixing calculations. In subsequent graphs we consider the carbon pool in terms of terrestrial plant remains, marine algal matter and sewage particulates, largely based on the $\delta^{15}N$ characteristics.

RESULTS

The age models and other metadata are not all presented here, but can be requested from the authors and will appear in future papers. A dominant parameter in the studies of core sediment is the Mass Accumulation Rate of sediment (MAR), expressed in grams/cm^2.yr. With colonial human settlement in the watersheds of LIS, the sediment flux increased dramatically, and as a result the sediment accretion rates and MARs increased. The MAR of the various elements, compounds and faunal remains are strongly dependent on the sediment MAR, where the mineral fraction of sediment dilutes the other components. The sediment MAR depends strongly on the quality of the age model for the cores and the calculated sample bulk dry densities. The MAR of C_{org} in the two cores shows a strong increase over time (Figure 2), with about a factor of 5-8 between background 700 years ago (1 mg C/cm^2.yr) and peak values over the last 50 years (7-8 mg C/cm^2.yr). The C_{org} weight % in the sediment does not show such a dramatic increase, because the mineral sediment grains dilute the organic carbon component.

The sedimentary C_{org} properties are given by their $\delta^{13}C$, $\delta^{15}N$, $(N/C)_{at}$ (at=atomic ratio). We use binary graphs to derive the properties of the mixing end members C_T (terrestrial organic carbon), C_M (marine organic carbon), and C_S (sewage carbon). A $\delta^{13}C$ versus N/C graph for the samples from core WLIS75GGC1 shows the mixture of the two dominant end members C_T and C_M with two anomalous points from the coal-rich layer (Figure 3). The potential contributions from sewage carbon are difficult to discern in this plot. The $\delta^{15}N$ versus C/N graph (Figure 4) shows a better separation between C_S and C_M, which form a ternary mixture with C_T at the other side of the mixing array. A shortcoming in our current data set from site B1 is the lack of $\delta^{13}C$ data on C_{org} and we have only total carbon data available (C_{org}+$C_{carbonate}$). The carbonate carbon fraction to total carbon at the WLIS site is usually only a few percent, but it is clear from Figure 4 (circled data) that some samples in the B1GGC1 core have substantial carbonate contributions. The end member values (Table 1) are derived both from figures 3 and 4 as well as from compilations by Cravotta (2002) and Meyers (1997). These end member values can be used to partition the sedimentary carbon between C_T, C_S and C_M, which is initially done quantitatively only for C_T and C_M, because most ternary solutions are not unique. The C_S component is combined with C_M, to which it is close in composition.

The MAR for C_T and C_M for the two cores over time are shown as well as the fraction of terrestrial organic carbon (FT) over time, and the carbon isotope values of organic carbon for core WLIS75GGC1 (Figures 5, 6, 7, 8). Terrestrial carbon MAR in WLIS75GGC1 averaged about 0.5 mg C/cm^2.yr until about 1700 AD, then decline steadily during the 18th century to almost 0. From 1800 on, the C_T MAR increased steadily to culminate at 4 mg C/cm^2.yr until the mid 20th century. The C_M MAR gently increased from 1600-1750 AD from about 0.5 to 1.0 mg C/cm^2.yr, followed by a much more rapid increase to about 3.8 mg C/cm^2.yr at about 1900 AD. From 1900 AD on, the C_M MAR decreased steadily from 3.5 mgC/cm^2.yr to ~2 mgC/cm^2.yr. For core WLIS75GGC1, the cross-over point in dominance of C_T versus C_M occurred at about1900 AD (Fig. 5). The fraction of C_T (Figure 7) shows a similar pattern, with a sharp drop in C_T from 1700-1800, followed by a rapid increase between 1800 and 2000 AD. The $\delta^{13}C$ values in the core show a steady rise in C_M from 1700-1800 AD, followed by a long decline to values more typical for C_T (Figure 8).

Core B1GGC1 shows only a minor increase with time of the C_M MAR (from 0.5 mg C/cm^2.yr to 1.5 mg C/cm^2.yr; Fig. 6), whereas the C_T MAR remained steady until about 1800 AD, and then increased strongly to culminate >5 mgC/cm^2.yr in the late 1900s. During the last few decades of the 20th century C_T decreased again to 2.5 mg C/cm2.yr. The fraction of terrestrial organic carbon (FT) decreased generally from 1300 to 1700, then increased to close to 80% in the late 20th century at the B1 site. The N/C values in both cores confirm that C_T contributions increased since 1800 in both cores, and dominated during the last 100 years (Figure 9).

The $\delta^{15}N$ records of the two cores show an increase in $\delta^{15}N$ of 1.0-1.5 ‰, in LIS75GGC1 starting at 1850 AD, whereas in core B1GGC1 values started to increase in the late 1700s (Figure 10). The $\delta^{15}N$ values of all samples from WLIS75GGC1 are 1.0 – 1.5 ‰ heavier than those of B1GGC1. The $\delta^{15}N$ values spiked in the mid to late 1800s, then gently dropped to values even lower than those pre-1800 AD in WLIS75GGC1. Samples from the top of B1GGC1 also show slightly declining values in $\delta^{15}N$, reflecting the dominance of C_T with a $\delta^{15}N$ around 2‰ (Table 1). The heavier $\delta^{15}N$ signature at the WLIS 75 site probably reflects a larger contribution of C_S than at the B1 site (Fig. 10).

The MAR of biogenic silica (BSi) is an independent measure of the burial of primary produced algal carbon, because in LIS much primary productivity is by diatoms which secrete a siliceous frustule (e.g., Capriulo et al., 2002). Values of BSi in samples from core WLIS75GGC1 started to increase from the 1700s, and then decreased strongly between 1900-2000 (Figure 11). The B1GGC1 data do not show strong trends in BSi, with only a tepid increase over the last 50 years (7-8 mg BSi/cm2.yr).

DISCUSSION

The records of carbon deposition at the two sites in westernmost and central LIS show strong similarities as well as pronounced differences. At both sites the total carbon burial rates increased strongly over the last 200-300 years. Both core sites show evidence for major floods during the 1955 hurricane period in the LIS region, with mm-cm sized pieces of coal and flyash at site WLIS75 in westernmost LIS, possibly coarser sediment intervals at site B1 close to the mouth of the Housatonic River. This layer is also present at other sites, e.g. our core site WLIS 81. Both sites have strong spike in Mercury concentration and accumulation rate at levels in the sediment corresponding to ~ 1955 AD, indicating the mobilization of heavily polluted sediment from the uplands (Varekamp et al., 2000, 2003, 2005).

The MARs of Carbon were relatively steady between 1000 and 1600 AD, at low values of 1 mg C/cm2.yr. In both cores, the burial rate of C increased over the last 200-300 years, to reach higher overall values in WLIS75GGC1, followed by a steep drop over the last few decades. Most surprising is the finding that the C_T contributions have varied so strongly over time: the near elimination of C_T between 1700-1800 AD at site WLIS75 is striking. We tentatively explain this as the result of widespread deforestation with loss of the deciduous leaf cover at that time in the Manhattan-Long Island region, and a dramatic decline in the flux of C_T. At the same time, the flux of nutrients started to increase, leading to enhanced primary productivity and burial of algal matter. The cores at site B1 (at the mouth of the Housatonic River) do not show this drop in C_T during the 18th century, but both cores show a strong dominance of C_T over the last 100 years. All C_{org} parameters indicate the same pattern, whether based on MARs (thus dependent on the age model) or not ($\delta^{13}C$ or organic matter, N/C, FT). The BSi and $\delta^{15}N$ values are also independent indicators, suggesting a strong decrease in diatom burial since the 1920s. Both core records show slightly declining $\delta^{15}N$ over that same period. Both the relative contents and the absolute flux of C_T increased between 1800 and 2000 AD, and it appears that it was the largest organic carbon flux entering LIS.

CONCLUSIONS

The MAR and composition of LIS sediment are strongly affected by changes in landscape and land use as well as the fluxes of nutrients into the Sound over time. Reconstruction of such changes is possible by determining the sediment proxy indicators. As expected, sediment at the more westerly site WLIS75 is enriched in sewage carbon compared to the more easterly-central B1 site. The main features of the two core records are increased sedimentation rates and sedimentary carbon burden, overall isotopically heavier nitrogen (derived from wastes higher up in the food chain, such as manure and sewage), enhanced primary productivity, but also and most surprisingly, strongly enhanced input of terrestrial carbon over the last 200 years. The initial deforestation with early colonization in the 18th century led to an almost complete elimination of the flux of organic carbon from the land. The subsequent reforestation and renewed presence of deciduous forest led to a strong flux of terrestrial carbon into the Sound. The carbon buried in sediment possibly represents a refractory residue relative to the primary productivity, and the strong decrease in C_M in both core locations may not necessarily reflect strictly a decrease in primary productivity. The fact remains that the C_M MAR decreased over the last 100 years in the western site. Explanations may invoke that part of the primary productivity carbon may be cycled during the last century differently from before through the food chain: the C_M may be exported to a larger degree with higher organisms from the Sound, or captured more efficiently by humans (fishing). The decrease in BSi burial rates, however, suggests that diatom productivity (as contrasted to overall productivity) has been declining over the last 50 to 100 years, as also indicated by an assemblage change in benthic foraminifera (diatom consumers decrease in abundance relative to omnivorous species; Thomas et al., 2004). The data presented here do not support a simple model that explains the severe hypoxia in western Long Island Sound in the 20th century as a direct result of increased primary productivity caused by nutrient pollution from sewage treatment plants only. The hypoxia probably already existed in the mid 1800s (Lugolobi et al., 2004; Varekamp et al., 2004), but the make-up of carbon in the sediment and the fluxes and the processing of carbon in the Sound has changed in a profound way over the last 100 years. At least part of these complex changes in the LIS carbon cycle may have been brought about by both top-down (removal of top-predators as well as filter feeders such as oysters) and bottom-up (eutrophication) changes in the ecosystem (Jackson et al., 2002).

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TABLE 1. End member compositions of organic carbon. as derived from our mixing plots and literature data

END MEMBERS	C/N	100* N/C	δ13C	δ15N
C(terrestrial) - C_T	**33**	**3**	**-26**	**+2.5**
C(marine) – C_M	**7**	**14.3**	**-20**	**+7.5**
C(sewage) - C_S	**9.5**	**10.5**	**-21.5**	**+9.8**

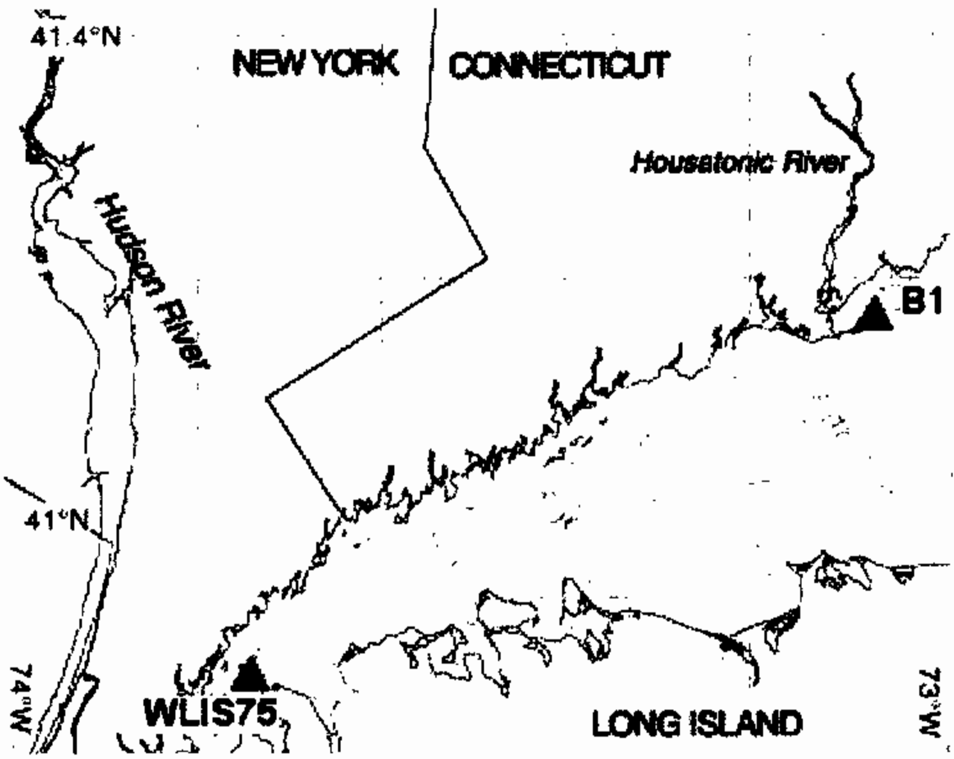

FIGURE 1. Core locations in LIS: WLIS75 just west of Execution Rock in western Long Island Sound and cores B1C2 and B1GGC1 near the mouth of the Housatonic River in central Long Island Sound.

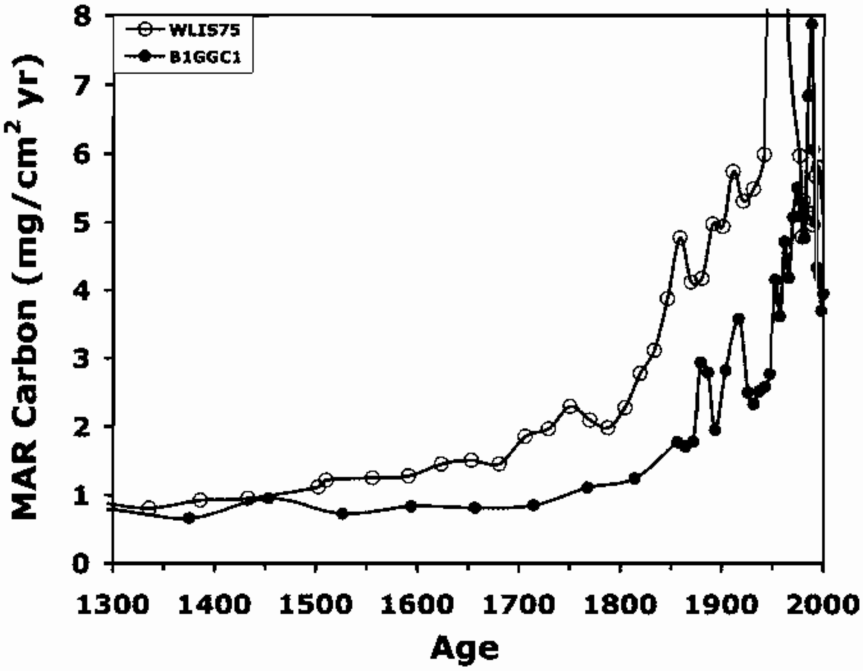

FIGURE 2. Carbon mass accumulation rates in cores WLIS75GGC1 (organic Carbon) and B1GGC1 (total Carbon). Note the rate increase starting in the mid 1700s and the exponential increase over the last 100 years. The modern Carbon accumulation rate is close to five times larger than the pre-colonial accumulation rate.

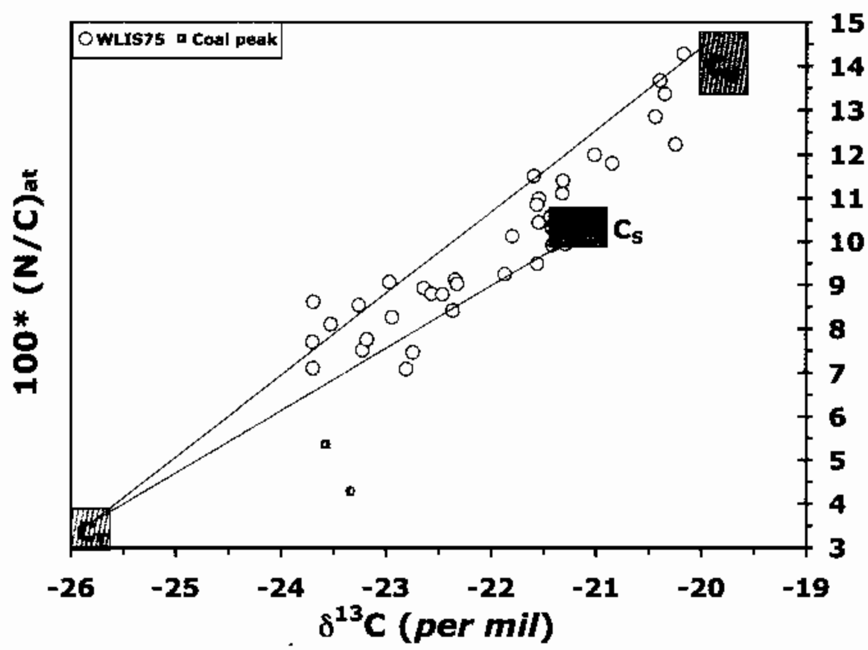

FIGURE 3. Characteristics of organic carbon in LIS sediment of core WLIS75GGC1. The sediment contains a mixture of organic carbon made up of largely C3 landplants (C_T), marine algae (C_M) and sewage carbon (C_S). The endmembers were taken after Cravotta, 1997 and Lamb et al. (2006). We use $\delta^{13}C$ versus 100*N/C because straight mixing lines can be drawn to the various endmembers (instead of curved arrays in C/N versus $\delta^{13}C$ plots). The two outlying samples are sediment rich in detrital coal fragments. The C_S and C_M sources are not well distinguished in this plotting space. $(N/C)_{at}$ represents the atomic ratio of Nitrogen and Carbon.

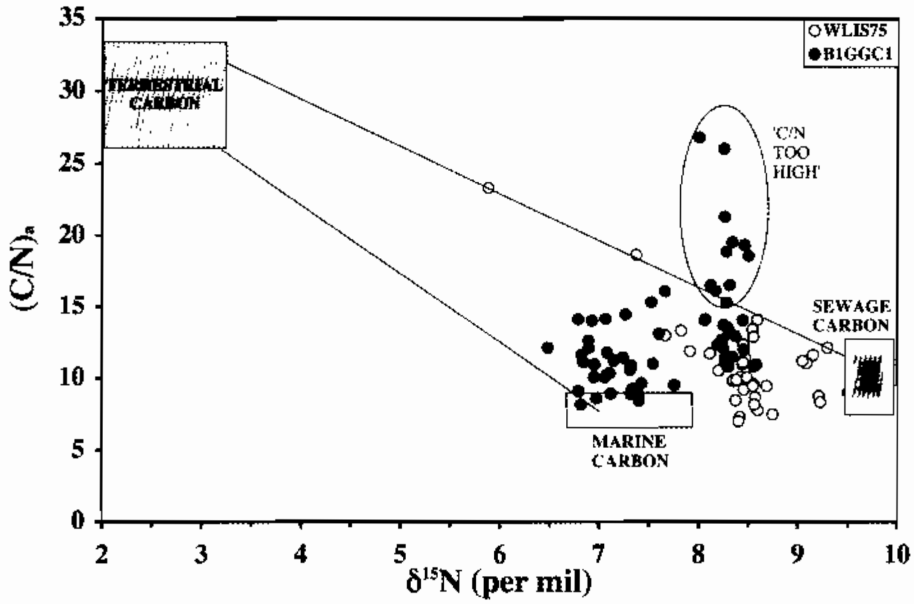

FIGURE 4. End members of C_{org} as defined in $\delta^{15}N$ versus C/N. The separation between C_S and C_M is better than in figure 3.

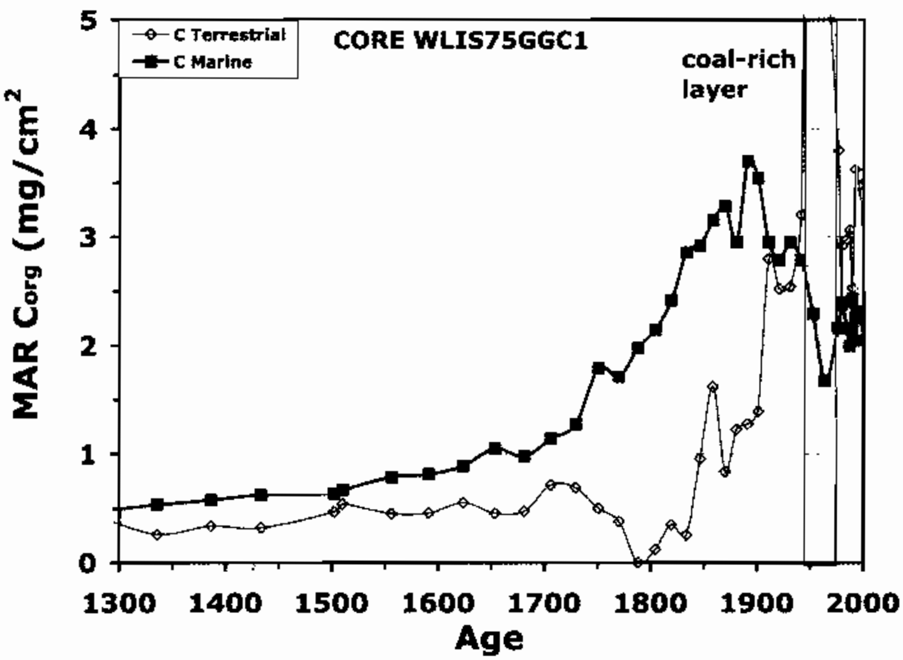

FIGURE 5. MAR of C_T and C_M in WLIS75GGC1. Note the strong decrease in C_T during the period 1700-1800 and the strong increase since 1800. The 'coal layer' is the debris layer related to the 1955 floods.

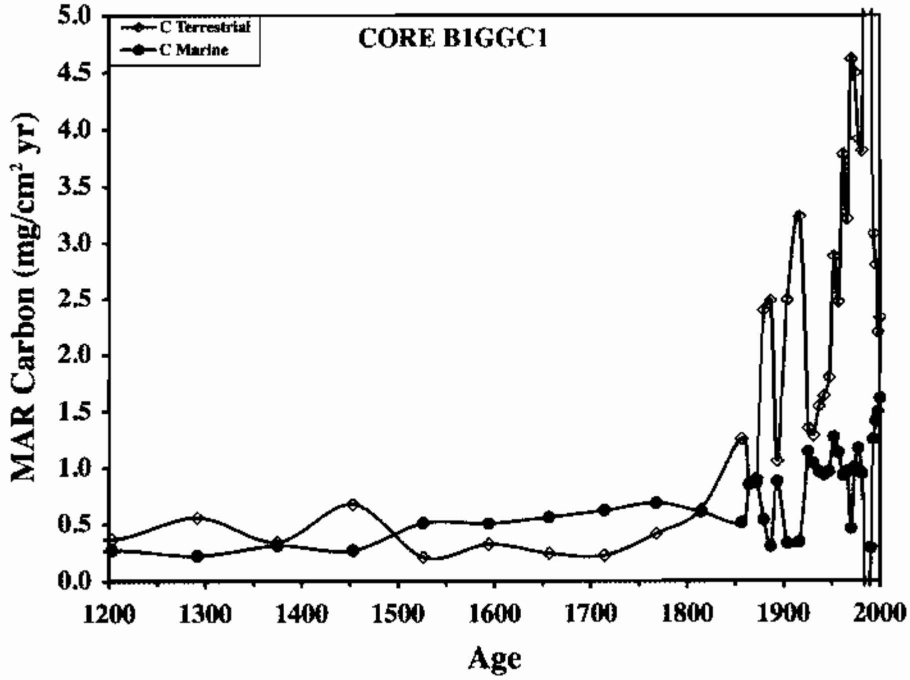

FIGURE 6. MAR of C_T and C_M in core B1GGC1. Note the dominance of C_T over the last 100 years.

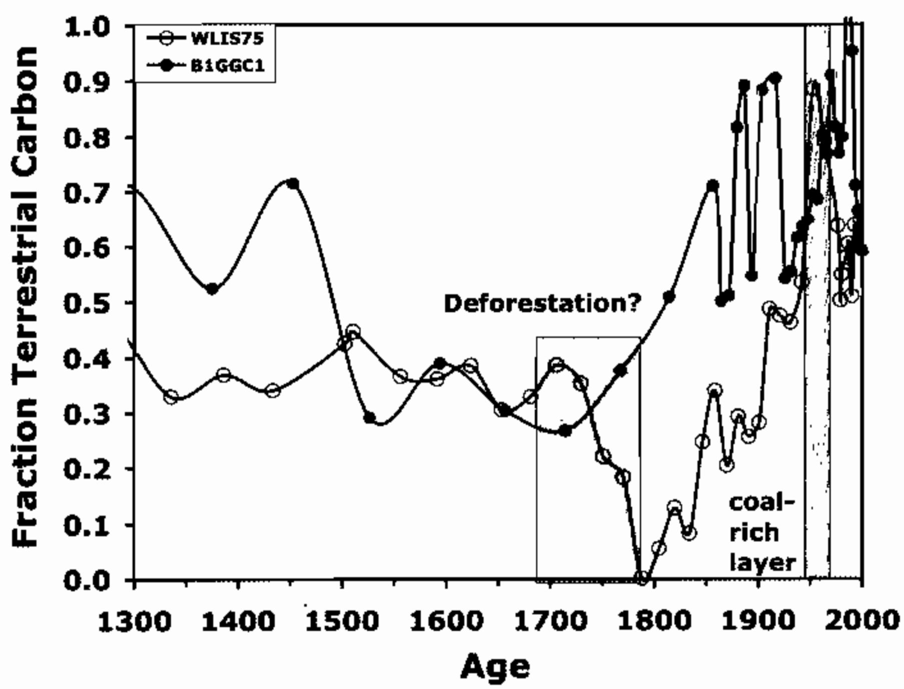

FIGURE 7. The fraction of C_T (FT) versus time for both cores. The decrease in C_T contributions between 1700-1800 in WLIS75GGC1 is shown with the 'deforestation box'. The dominance of C_T in both cores over the last 100 years is evident.

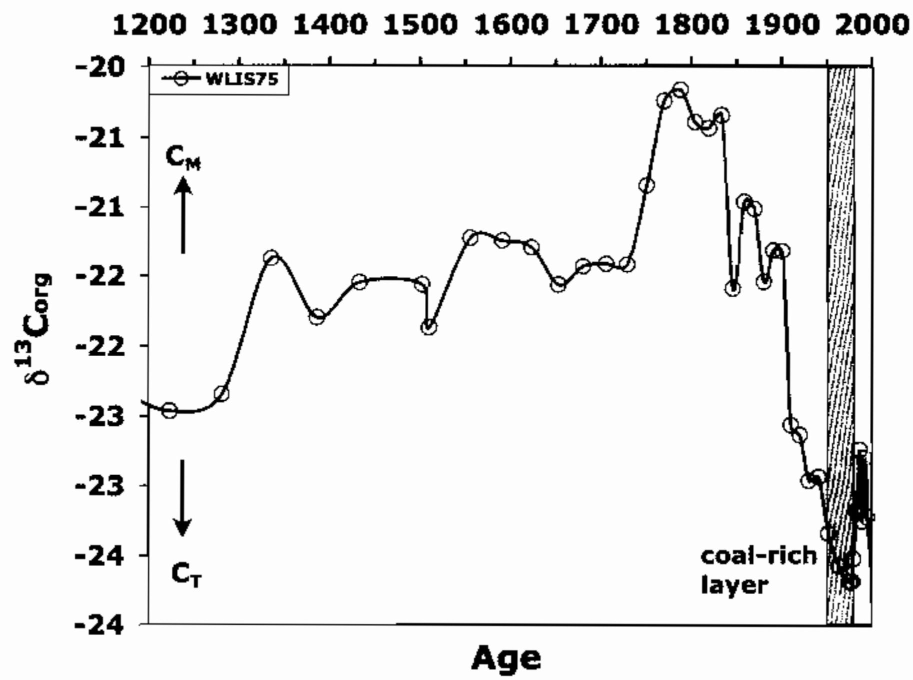

FIGURE 8. The record of $\delta^{13}C$ of organic matter in core WLIS75GGC1, showing the lower values (C_T) over the last 100 years.

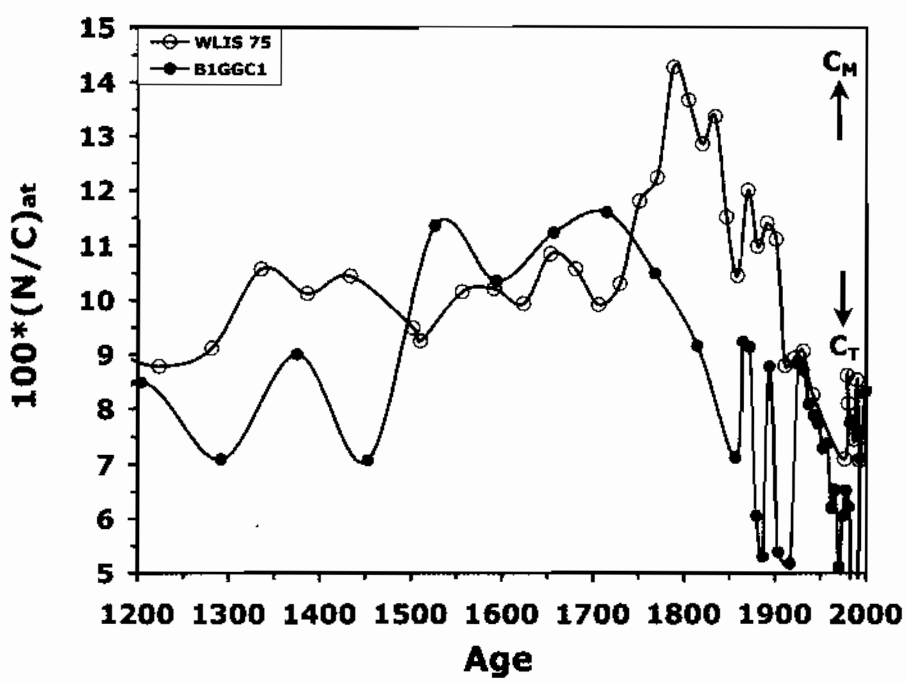

FIGURE 9. N/C record over time for both cores, showing the increase in C_T in recent times.

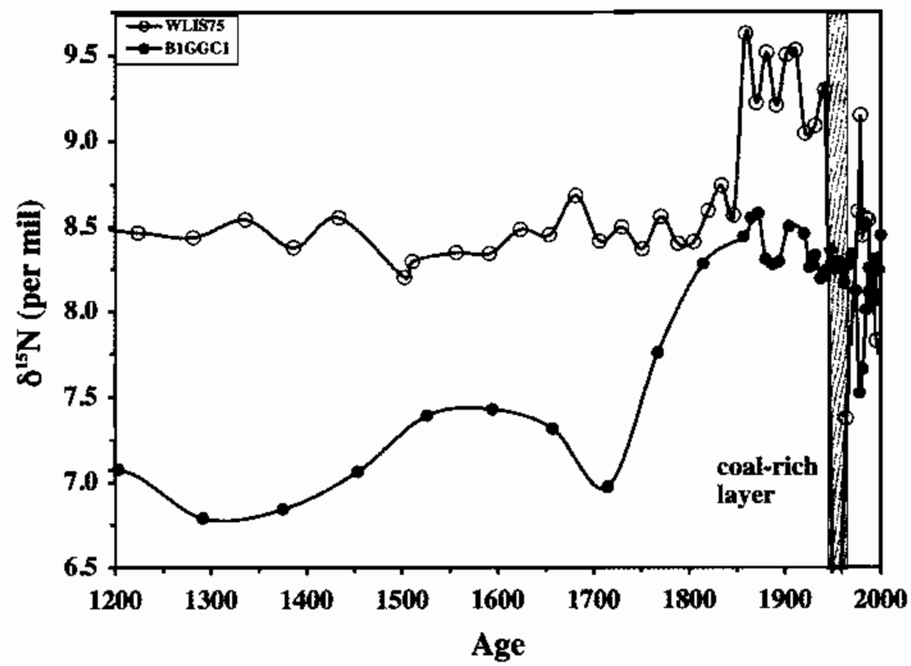

FIGURE 10. The δ15N record for both cores, showing the strong increase from around 1800 on with a slight decrease since 1900.

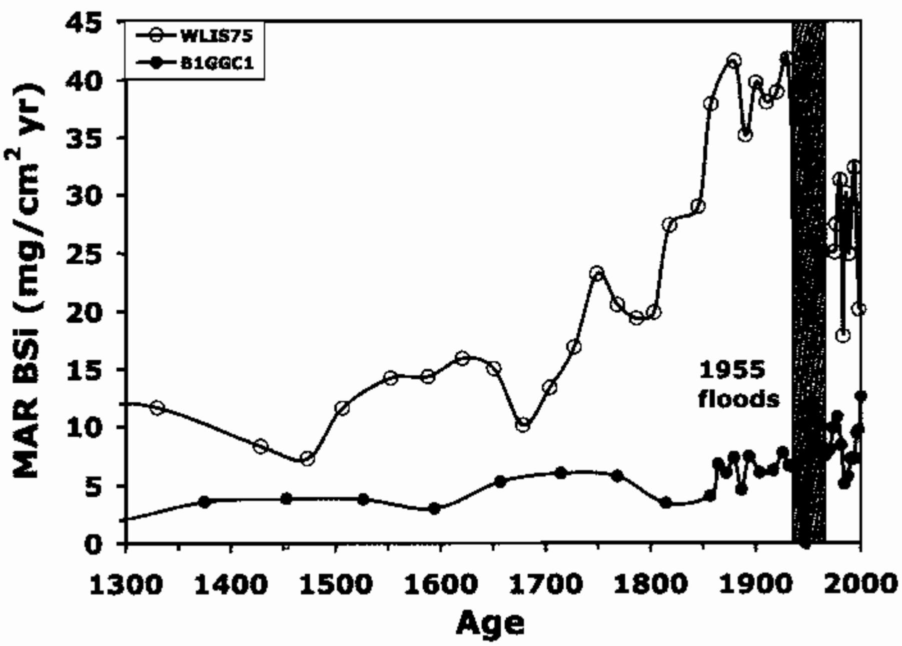

FIGURE 11. Record of BSi MAR in both cores, showing the increase in BSi accumulation since the 1800s followed by a decrease since the early 1900s in core WLIS75GGC1. The BSi MAR in core B1GGC1 increased slightly over the last century.

Connecticut Department of Environmental Protection Long Island Sound Ambient Water Quality Monitoring Program: Overview and Analysis of Program Data

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ABSTRACT

Since 1991, the Connecticut Department of Environmental Protection (CTDEP) has been monitoring the water quality of Long Island Sound (LIS). Year-round monthly sampling includes monitoring for nutrients, chlorophyll a, biological oxygen demand, and water column profiles of temperature, salinity, irradiance and dissolved oxygen. Additional biweekly summer sampling at 25-35 stations provides data on the recurrent low dissolved oxygen condition known as hypoxia. The program has been expanded in recent years to include monthly phytopigment, phytoplankton and zooplankton monitoring. An extensive long-term data base exists and is available by request. The CTDEP encourages the research community to make use of the monitoring program and the resultant data base as an aid to complementary research and assessment efforts in Long Island Sound and elsewhere.

INTRODUCTION

In January of 1991 the Connecticut Department of Environmental Protection (CTDEP) initiated a water quality and hydrographic survey to provide continuity to the LISS data set and to ensure that data would be available as the LISS progressed into the implementation phase. This survey continues in an expanded form with EPA support as the Department's Long Island Sound Ambient Water Quality Monitoring Program (the "Program"). Over the long-term, the data from this Program are essential to assess trends in water quality, especially responses to implementation of the LISS *Comprehensive Conservation and Management Plan* (CCMP) recommendations (LISS 1994). Nitrogen enrichment in particular has been determined to be a primary cause of low dissolved oxygen conditions in the Sound. Reducing the loading of this nutrient is a major goal in the management actions being taken by the LISS and participating jurisdictions to improve the health of the Sound. In particular, the data will allow the Department and the LISS to assess the effectiveness of management actions taken to reduce nutrient inputs to the Sound.

METHODS

CTDEP began intensive summer dissolved oxygen monitoring in June of 1991. During the summers of 1991-1993 most of the summer dissolved oxygen sampling was conducted as part of a cooperative intra-agency effort between the Bureau of Natural Resources and the Bureau of Water Management. In 1994 the Program increased the number of summertime monitoring stations to 48 permanent sampling stations. Eighteen of these permanent stations were also sampled as part of the monthly water quality monitoring program. In 2002, with increasing interest in ecosystem based monitoring, the DEP expanded the scope of the Long Island Sound Monitoring Program. Thanks to a grant from the EPA, through the National Coastal Assessment, surveys included sampling for Meso and Micro Zooplankton, Phytoplankton and phytopigment analysis using the HPLC method. The plankton sampling is now included as part of the programs regular survey thanks to increased funding from the EPA through the Long Island Sound Study.

EQUIPMENT

Water sampling is conducted with the cooperation of CTDEP's Bureau of Natural Resources' Fisheries Division aboard the 50-ft R/V *John Dempsey*. Water column profiles are taken with a Sea-Bird model SBE-19 SeaCat Profiler (CTD), equipped with dissolved oxygen (YSI model 5739), photosynthetically-active radiation (PAR) (Licor spherical underwater model 193SA), and fluorometer (Wet Labs WETStar mini fluorometer) sensors. The CTD collects temperature, conductivity, pressure, dissolved oxygen, PAR, and fluorometer (chlorophyll a) data at a rate of twice per second as the unit is lowered through the water column. The instrument calculates secondary parameters of salinity, depth, and density. The data can be viewed in real-time with the onboard computer and uploaded to the computer during or after cast completion. Generally, the CTD unit is mounted on a rosette water sampling device (General Oceanics model 1015 Rosette Multi-Bottle Array) which also holds up to ten, 5-liter Niskin water sampling bottles. To maintain a continuous profile during the downcast all sampling is done during the upcast.

MEASUREMENTS

Water samples for nutrient analysis are collected at two depths. Surface water samples are collected approximately two meters below the surface; bottom water samples are collected at five meters off the bottom. Near-bottom samples for Winkler titration are collected at one meter off the bottom. Surface and bottom water samples are filtered in the onboard laboratory and the filters and filtrate delivered to the analytical laboratory for analyses of nutrients and other relevant parameters. Whole (unfiltered) water samples are delivered to the analytical laboratory for 30-day biological oxygen demand.

DISCUSSION

The Long Island Sound Study has defined hypoxia as low concentrations of dissolved oxygen; specifically "hypoxia" refers to the low dissolved oxygen condition that develops each summer in the bottom waters of Long Island Sound (LISS 1994). In the Long Island Sound region waters are considered hypoxic if the dissolved oxygen level drops below 3.0 mg/L, however, in 2002 CT DEP adopted a more protective water quality criteria setting the acute value to 3.5 mg/L. In Long Island Sound hypoxia occurs annually, starting late June to early July with a maximum typically in August and subsiding in September (Figure 1). Hypoxia has affected from 5% to nearly 50% of LIS study area with 65% of the stations we survey having been hypoxic at least once during the past 18 years. In general, the key factor that promotes the development of hypoxia in the Sound is the presence of excess nutrients, especially nitrogen. Excess nitrogen contributes to the excessive growth of phytoplankton. When the phytoplankton die, they sink to the bottom where natural decomposition of this organic matter takes place, consuming oxygen in the process. Excess nitrogen and the abundant phytoplankton blooms it supports are important to the development of low dissolved oxygen conditions in LIS. However, the characteristics of each year's occurrence, including annual variability in the timing, duration, spatial extent, and severity of the hypoxic event, are largely driven by weather conditions. The timing and strength of summer stratification, which is important to the development of hypoxia, depend on winter, spring, and summer weather patterns and conditions. Stratification in Long Island Sound is primarily a function of temperature, with salinity differences contributing only slightly. The stratification of the water column sets up in the late spring to early summer and restricts exchange between highly oxygenated surface waters and oxygen depleted bottom waters. The larger the temperature differences between surface and bottom waters, the stronger the barrier to oxygen movement.

The maximum area of hypoxia had been decreasing year to year from 1994 through 2002. However, since the summer of 2002 the area of hypoxia has been increasing with large areas affected by severe hypoxia, dissolved oxygen values less than 1 mg/L (Figure 2). Some of the factors that could be contributing to the increase in hypoxic area are large algal blooms with large volumes of brown algae in the western Sound in 2003 and 2004 as well as summer weather patterns. During 4 of the past 6 summers the northeast has experienced near record precipitation and when the precipitation was at or below averag, the summers saw near record heat (Figure 3). The summers of 2003, 2004, 2006, and 2008 were ranked in the top 15 wettest summers with 2006 being the wettest summer recorded since 1895. Temperatures during the summers of 2002 and 2005 ranked them in the top 15 hottest summers with 2005 being the second hottest summer recorded since 1895 (NOAA). Higher than average temperatures during the summer can strengthen the stratification in LIS and lead to a longer and more severe hypoxic event. Increased precipitation in the region can bring in more nutrients which in turn fuel the growth of phytoplankton in the sound which can also lead to increases in hypoxic area and severity.

The temperature structure of the water column in Long Island Sound over the summer plays an important role in the development and extent of hypoxia. A correlation between the intensity of the thermal stratification and the maximum area of hypoxia was observed and the relationship was surprisingly consistent. Years with warmer overlying waters and a tight thermal gradient had larger areas of hypoxia and years with less stratification had smaller areas. Further, years with temperature changes occurring over a small depth interval had the largest areas affected by low DO. In fact the three years with the largest areas 1994, 2003, 1995 all had nearly a 4 degree C temperature change within the top 10 to 12 meters and up to a 6 degree difference from surface to bottom. These temperature differences were observed during the survey representing the maximum area of hypoxia. Years with smaller areas such as 1997 and 1992 had temperature differences of only 1-2 degrees C from surface to bottom. The temperature structure within LIS could be a good indicator for the development of hypoxia and could be used to help determine when and where we focus our monitoring over the summer.

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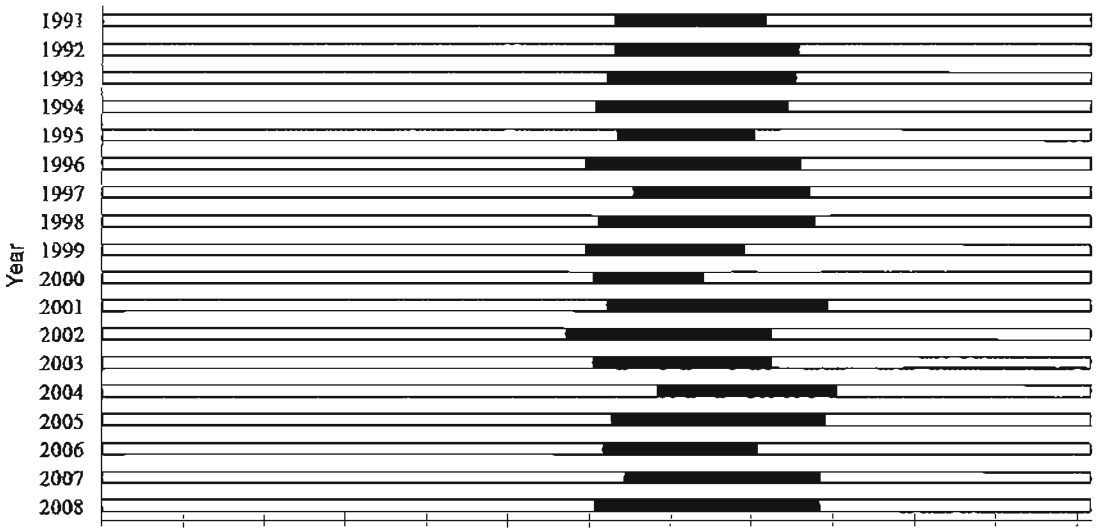

FIGURE 1. Timing and duration of Hypoxia in Long Island Sound, earliest start date June 20th summer 2002 and the latest end date was September 26th summer 2004.

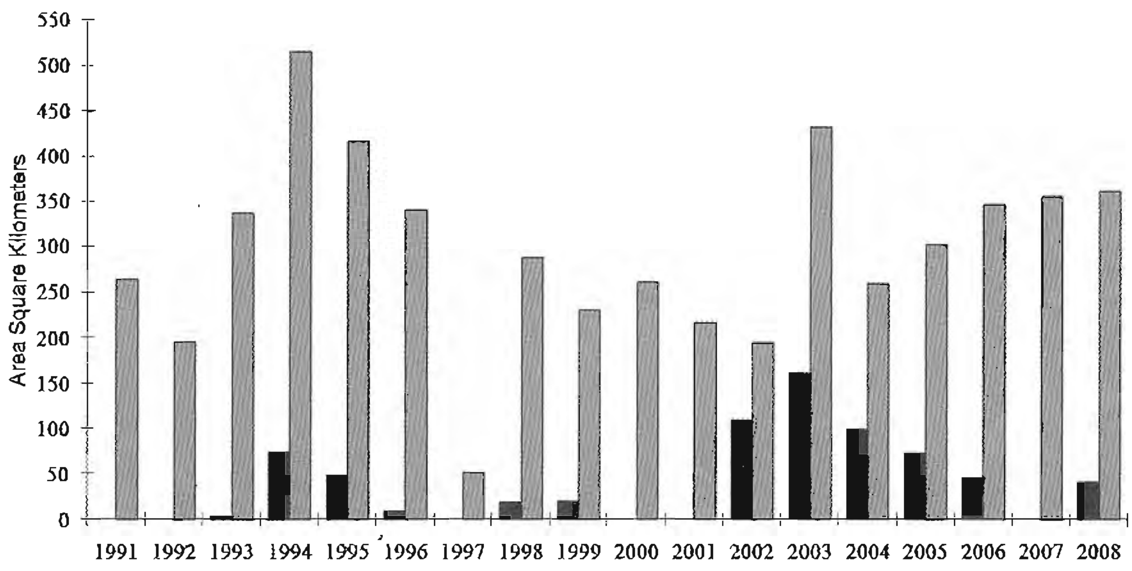

FIGURE 2. Maximum area in square kilometers with dissolved oxygen values below 3.5 mg/L (gray bars) and below 1 mg/L (black bars).

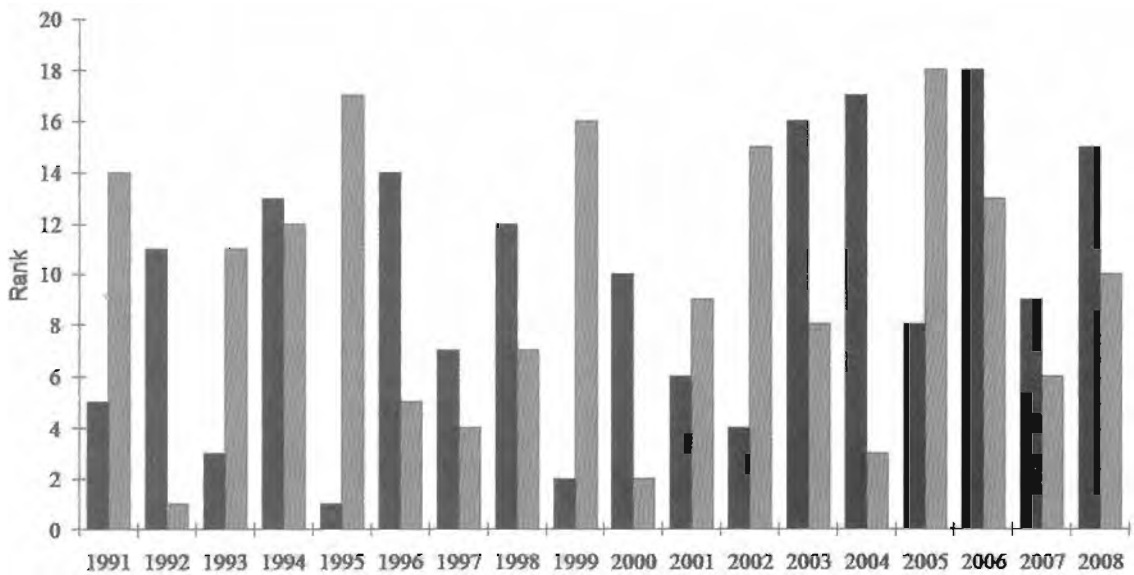

FIGURE 3. Rank, over the 18 years of the program, of temperature (gray bars) and precipitation (black bars). Higher numbers indicate hotter / wetter summers

Correlation of Temperature Lags and Hypoxia in Long Island Sound

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ABSTRACT

We present new evidence suggesting that variability in physical mixing processes is the primary causative factor driving interannual variability of the extent of hypoxia in Long Island Sound (LIS) over the last two decades. Surface waters in Long Island Sound reach maximum temperatures in early August. Bottom waters, however, are slower to warm and reach their annual temperature maxima from a few days to several weeks later. Using 17 years of CTDEP monitoring data at 14 stations, we examine the interannual variability and spatial structure of these surface to bottom temperature lags. We observe that the interannual variability in these temperature lags is highly correlated (r >70%) with the extent of summertime hypoxia and the lags also show a strong spatial structure. We propose that these temperature lags are a measurable proxy for vertical mixing rates and that longer lags are the result of reduced vertical mixing.

DATA AND METHODOLOGY

The Connecticut Department of Environmental Protection (CTDEP) has conducted an ongoing water quality (WQ) sampling program in Long Island Sound (LIS) since 1991. Among other WQ parameters, the CTDEP surveys measure near surface and near bottom water temperatures at a number of stations in LIS at a sampling rate of once to twice per month, making these records suitable for the estimation by station and year of when maximum water temperatures occur at the surface and the bottom. Our analysis includes data through 2007. Figure 1 shows the locations of the 14 stations used in our analysis. Of these, B3, D3, H6, I2, and M3 have been sampled regularly since 1991; A4, C1, C2, E1, H2, H4, and J2 since 1995; and F2 and K2 since 1996.

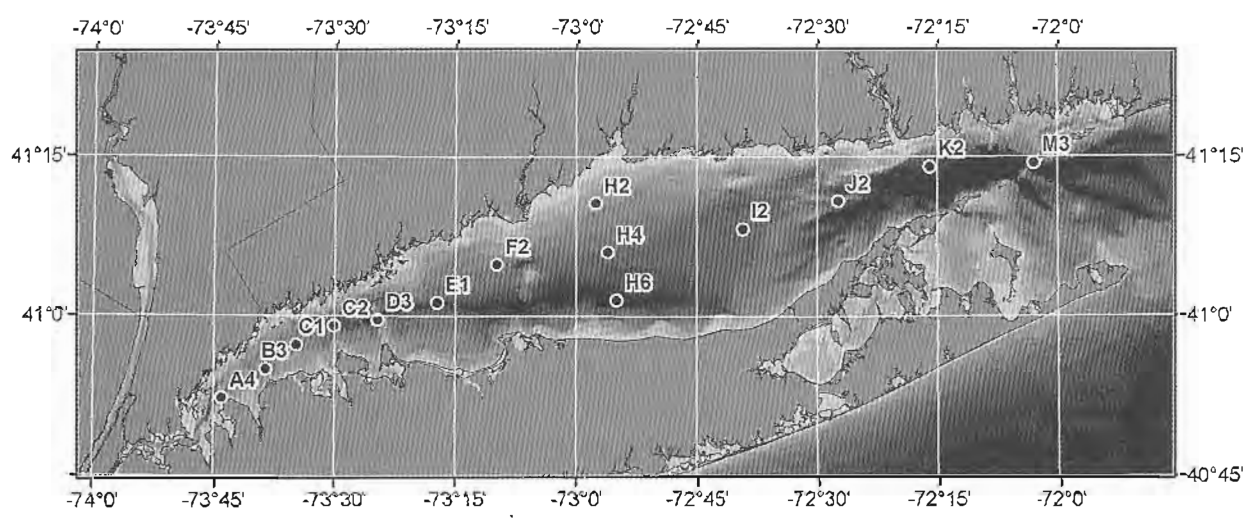

FIGURE 1. CTDEP stations. Bathymetry is contoured at 5 m intervals.

Because the CTDEP surveys are only conducted every two weeks, the CTDEP data must be interpolated in order to estimate when the temperature maxima occur. In addition, spatial temperature gradients in conjunction with semidiurnal tides create the possibility of aliasing. Gauss-Markov smoothing and filtering (Wunsch, 2006) was used for the interpolation. Also referred to as Objective Interpolation (OI), this method is able to incorporate estimates of the aliasing error into the interpolation. The OI parameters used were 8.0°C for the expected data variance due to the annual cycle, 0.35°C for the expected uncertainty in the measurements due to tidal aliasing, and 100 days for the timescale over which to weight the data for the interpolation. Figure 2 shows an example of the CTDEP temperature data for station H6 for 1997 and 1998 and the OI interpolation of this data. Note that the maximum bottom temperature occurs latter than the maximum surface temperature for both years, and that the amount by which it lags is measurably greater in 1998 than in 1997.

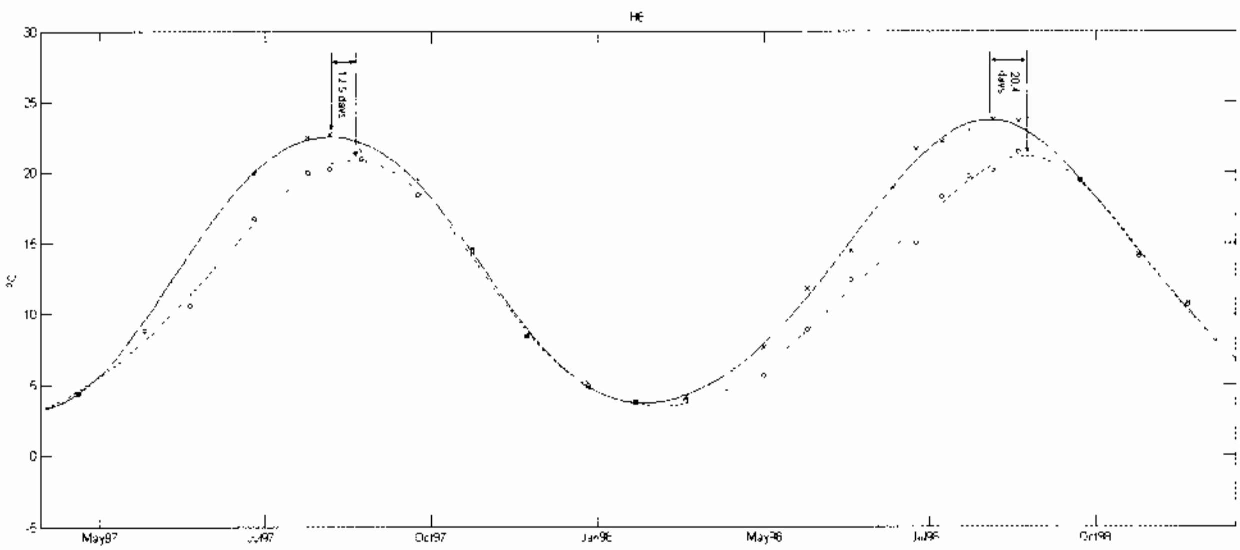

FIGURE 2. CTDEP data at station H6 from 1997 and 1998 for surface (x) and near bottom (o) temperatures along with OI results for surface (solid line) and near bottom (dashed line) temperatures. As indicated by the arrows, the maximum water temperatures at the surface occur earlier than those at the bottom. The OI methodology provides an estimate of these lags at H6 of 12.5 ± 7.3 days for 1987 and 20.4 ± 6.1 days for 1998.

RESULTS

For the 14 stations and 17 years, data was available for the calculation of 200 lags. These represent our best estimate of the time difference between when each year's surface temperature maxima and bottom temperature maxima occurred. In addition to the interpolated values which were used to determine the times of maximum temperatures, the OI method provides the uncertainties associated with each interpolated value. These were used in conjunction with Monte Carlo methods (Press, et al, 1992) in order to determine the uncertainties in the time estimations. Our lag estimates and their associated uncertainties are shown in Table 1. Of the 200 lag estimations, only four are negative, and none of these is significantly different from zero: bottom waters in LIS warm up more slowly than surface waters.

	A4	B3	C1	C2	D3	E1	F2	H2	H4	H6	I2	J2	K2	M3	A [Km²]
1991		12.8 ± 7.9			12.7 ± 7.8					15.8 ± 7.3	13.3 ± 7.9			3.6 ±27.1	319
1992		15.6 ± 9.5			7.8 ±26.4					7.5 ±10.2	11.6 ± 9.9			2.8 ± 8.0	223
1993		17.0 ± 6.2			22.3 ± 6.5					22.8 ± 5.9	11.6 ± 6.3			7.2 ± 22.8	518
1994		24.4 ± 7.3			31.8 ± 6.8					32.6 ± 6.9	16.2 ± 6.0			3.0 ± 6.8	1023
1995	10.6 ± 6.5	17.3 ± 8.2	16.1 ±11.7	26.7 ± 8.5	29.3 ±10.4	30.4 ±12.7		18.0 ± 9.5	27.6 ± 9.2	25.1 ± 9.0	21 ± 9.2	-1.3 ± 9.3		10.9 ±43.3	790
1996	12.3 ± 5.5	11.2 ± 6.3	12.2 ± 6.2	8.4 ± 5.9	10.5 ± 6.0	4.2 ± 9.7	20.5 ± 8.1	14.8 ± 6.6	21.9 ± 6.9	15.8 ± 6.5	10.9 ± 6.7	3.2 ± 8.7	8.3 ± 8.3	3.7 ± 8.0	570
1997	7.0 ± 5.5	10.7 ± 6.1	16.2 ± 7.4	16.8 ± 6.9	11.6 ± 6.8	18.7 ± 7.7	8.8 ± 7.9	4.8 ± 6.9	23.3 ±10.8	12.5 ± 7.3	15.2 ± 6.6	-1.5 ± 7.0	8.8 ± 8.1	8.4 ± 8.7	78
1998	10.1 ± 5.4	18.0 ± 7.1	12.7 ± 6.5	13.3 ± 7.3	15.4 ± 6.7	21.1 ± 6.6	13.8 ± 6.4	14.3 ± 6.6	21.9 ± 6.4	20.4 ± 6.1	18.9 ± 7.0	9.5 ± 6.5	5.4 ± 7.5	8.1 ± 6.7	435
1999	16.6 ± 5.8	21.2 ± 6.3	20.7 ± 6.3	19.8 ± 6.5	19.6 ± 6.6	15.6 ± 6.9	12.8 ± 6.9	15.7 ± 5.8	15.0 ± 6.4	21.4 ± 6.6	17.8 ± 6.2	4.6 ± 7.7	17.9 ± 7.8	6.2 ± 7.3	313
2000	15.4 ± 6.0	19.1 ± 6.7	16.7 ± 7.4	19.7 ± 8.0	21.5 ± 7.4	19.9 ± 7.7	11.9 ± 7.4	8.1 ± 7.3	14.2 ± 7.6	12.8 ± 8.4	11.3 ± 8.5	5.4 ± 7.3	0.0 ± 8.5	0.5 ± 8.5	448
2001	13.8 ± 5.8	13.3 ± 6.4	11.1 ± 7.5	16.7 ± 6.6	13.0 ± 6.4	13.0 ± 7.0	11.3 ± 6.4	10.4 ± 5.8	12.6 ± 6.4	13.0 ± 6.2	6.6 ± 6.5	6.7 ± 6.9	14.0 ± 8.1	15.3 ± 7.6	344
2002	11.5 ± 6.4	20.3 ± 7.6	19.8 ± 8.5	16.6 ± 7.1	19.4 ± 8.2	32.1 ± 7.9	7.6 ± 8.7	18.2 ± 6.5	25.2 ± 8.8	20.1 ± 7.7	21.8 ± 7.0	12.5 ± 7.5	10.6 ± 7.2	6.7 ± 6.1	337
2003	22.5 ± 7.8	23.9 ± 7.9	37.3 ± 7.4	31.7 ± 7.8	11.6 ± 6.9	25.1 ± 7.3	20.9 ± 7.2	22.9 ± 6.7	29.6 ± 6.9	13.1 ± 7.3	19.3 ± 7.1	8.5 ± 7.3	15.1 ± 8.9	4.2 ± 12.0	894
2004	7.3 ± 6.3	19.5 ± 7.4	19.1 ± 7.3	12.2 ± 7.2	13.3 ± 6.7	19.3 ± 8.3	9.1 ± 7.4	14.4 ± 6.9	9.0 ± 7.4	12.9 ± 6.7	10.0 ± 6.5	-0.1 ± 8.6	4.9 ± 7.9	2.2 ± 7.6	523
2005	15.1 ± 8.9	24.3 ± 9.0	35.0 ± 7.6	31.2 ±10.9	28.1 ± 8.5	34.0 ± 7.0	22.2 ± 7.7	11.9 ± 9.0	21.3 ± 7.4	23.6 ± 6.8	-2.5 ± 7.5	3.1 ± 7.7	3.2 ± 9.7	1.8 ± 8.0	466
2006	17.2 ± 6.5	26.6 ± 7.3	24.2 ± 7.9	26.9 ± 6.1	26.1 ± 6.5	25.5 ± 5.9	12.6 ± 6.4	13.3 ± 7.6	11.9 ± 6.3	24.4 ± 6.0	19.1 ± 6.6	12.1 ± 6.7	17.9 ± 7.2	8.9 ± 6.9	518
2007	7.6 ± 5.6	10.5 ± 6.0	14.4 ± 7.3	12.2 ± 6.4	7.1 ± 6.7	22.0 ± 6.5	13.0 ± 6.8	12.3 ± 6.7	21.5 ± 6.9	18.7 ± 7.1	3.2 ± 7.5	0.9 ± 7.7	4.5 ± 8.8	2.5 ± 8.2	420
r	47%	51%	42%	46%	50%	22%	64%	75%	34%	55%	22%	7%	10%	-13%	

TABLE 1. Main panel: lags [days] and uncertainties of LIS bottom temperature maxima from surface temperature maxima by year (rows) and station (columns) as determined by OI analysis of CTDEP survey data. A blank cell indicates that the station was not sampled that year. Right-hand column: area [Km²] of maximum hypoxia reported by CTDEP for each year. Bottom row: correlation of each station's lag times with hypoxia areas.

ANALYSIS

Based on their survey results, the CTDEP also calculates an estimate of the area of maximum hypoxia extent for any given year. (CTDEP, 2004; O'Brien-Clayton, 2008) We compared these areas with the lags shown in Table 1 and found these were consistently positively correlated for all the stations in the central and western Sound: i.e., years when there was a greater hypoxic extent are years when there was also a greater lag in when the maximum temperature at the bottom occurs compared to that at the surface. The stations in the eastern Sound (I2, J2, K2, and M3) are not significantly correlated. Table 1 shows the values for the correlations of each individual station in the bottom row.

The lags shown in Table 1 also exhibit a strong along-Sound spatial structure. Lags are generally shorter in the east and longer in the west. If this spatial structure in the lags were due to the concurrent bathymetry structure, lags would increase in deeper waters to the east. That the lags in the east are instead much shorter than those in the west is consistent with the notion that the lags are representative of the degree of vertical mixing occurring: less mixing results in less vertical heat transport resulting in a longer time for the bottom waters to reach their maxima. LIS hypoxia also shows a strong along-Sound structure with greater hypoxia to the west and so the spatial structure of the lags also correlates with that of hypoxia.

The left-hand panel of Figure 3 summarizes the correlation between the temperature lag estimates and the annual hypoxic extents published by the CTDEP. When all stations are included as is shown in this plot, the correlation is 71% for the 17 years. This is significant at well above the 99% level. (Emery and Thomson, 2001) If the four eastern stations – which show short lags and presumably represent areas of LIS that are well-mixed – are excluded, the correlation between the mean annual lags and the annual hypoxia extent is 76%. Linear regressions (including an intercept) for the 17 years yield r^2=53% for the spatial means of all 14 stations, and r^2=60% when the four easternmost stations are excluded from the means.

The right-hand panel of Figure 3 shows the spatial correlation of the temporal means of the temperature lags with along-Sound distances. The spatial correlation of these is also significant at well above the 99% level with $r = -73\%$ and $r^2 = 56\%$. Note, however, that station A4 shows significantly less lag than a simple linear relationship would predict which may indicate that there is more mixing occurring at this station than elsewhere in the western Sound. This could be due to A4's proximity to the East River.

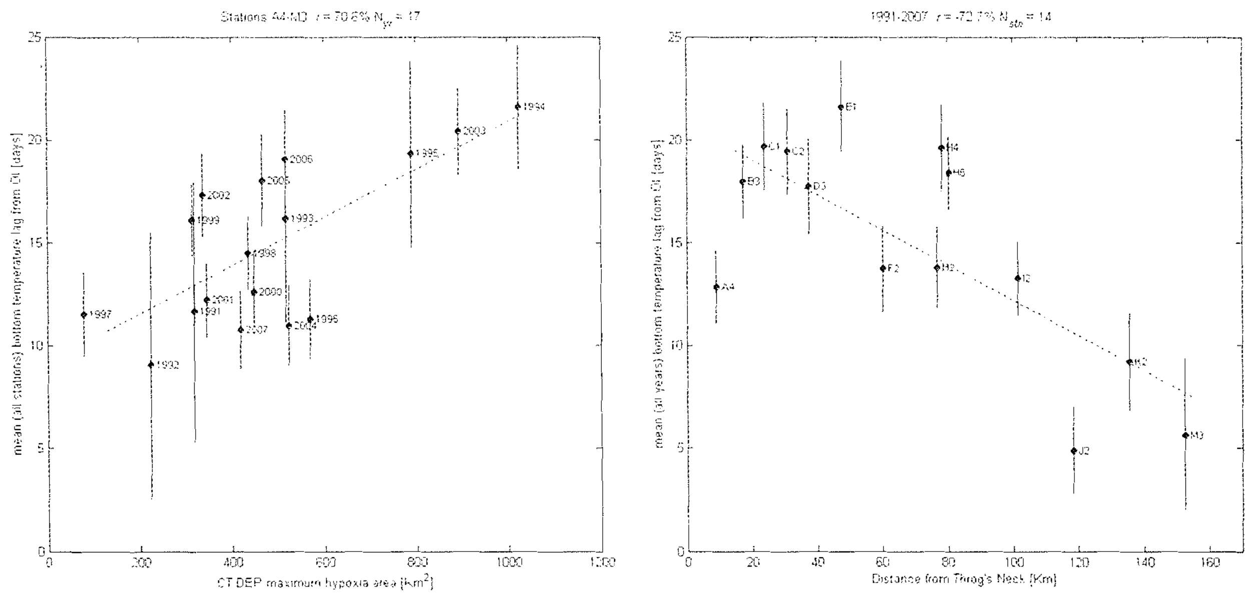

FIGURE 3. Correlation of lags by year at all stations with maximal hypoxia areas (left panel, $r = 71\%$) and correlation of lags by station for all years with along-Sound distance (right panel, $r = -73\%$). The lags shown in both panels are means, and the error bars indicate the uncertainties in the means.

DISCUSSION

McCardell and O'Donnell (2008) used the solution of Lamb (1932) to show that measurements of the amplitude attenuation or phase lag of a periodic scalar signal generated at or near the surface of the water column could be used to compute vertical eddy diffusivities. McCardell and O'Donnell used the per day frequency generated by the diurnal solar cycle; our OI results indicate that a similar calculation might be done using the per year frequency. There are, however, some assumptions that were made by McCardell and O'Donnell that cannot be made when doing a per year calculation. The first of these assumptions is that the water column is deep compared to the diffusive length scale, $\sqrt{2K_V/\omega}$ where K_V is a vertical eddy diffusivity and ω is the forcing frequency. This depth is on the order of a few meters for the per day signal, but on the order of a hundred meters for the annual signal. Another assumption made is that the eddy diffusivity coefficient does not vary at the forcing frequency. This is certainly not the case for the annual frequency, as there is a strong annual cycle of reduced summertime eddy diffusivities due to stratification as well as increased fall and wintertime diffusivities due to both the loss of density stratification and increased surface wind stress. We believe that it would be premature to report our results as diffusivity coefficients until we better understand the effects of these assumptions. Numerical simulation does, however, indicate that the relationship between the temperature lags and the eddy diffusivities remains monotonic: i.e. longer lags indicate lower eddy diffusivities and shorter lags higher diffusivities. We therefore do believe the temperature lags are a valid proxy for eddy diffusivity coefficients, and that longer lags are the result of reduced vertical mixing.

CONCLUSIONS

We have shown that the bottom waters in LIS warm more slowly than the surface waters and have quantified 200 of these lags at 14 locations for up to 17 individual years. There is a highly significant correlation between the interannual variability of these lags and that of the extent of summertime hypoxia in LIS. The correlation we observe is perhaps the most compelling yet reported between the interannual variation in LIS summertime bottom hypoxia and any environmental factor. Moreover, this correlation is with a physical parameter that is independent of biological factors. While our proposition that these temperature lags are representative of vertical mixing rates is suppositional, these lags are undoubtedly representative of physical processes and cannot be due to biological activity. This would seem to indicate that a reduction in nitrogen loads into LIS, while undoubtedly beneficial, may not result in observable improvements in oxygen levels for any particular year.

Although our results indicate that variability in vertical mixing rates appears to drive the severity of bottom hypoxia, what causes the interannual variability in vertical mixing rates in LIS is unknown and should be investigated. Furthermore, because vertical mixing is a physical process that is driven by physical parameters, LIS may be particularly sensitive to variation in climatic forcing and the effects of global warming may have a strong impact upon this region.

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Impact of Anthropogenic Nitrogen Input on Long Island Sound Water Quality

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Point source and non-point source (NPS) nitrogen loads in the past 15 years from 11 areas (Figure 1 and Table 1) along the coast of Long Island Sound (LIS) were obtained from Connecticut Department of Environmental Protection. Of the 11 areas, Areas 2, 4, 8, and 9 supply more than 80% of the total nitrogen to the Sound (Table 1). Nitrogen input from Areas 2 and 4 is dominated by non-point sources (riverine and coastal NPS); whereas nitrogen input from Areas 8 and 9 is dominated by point sources (sewage treatment plants, STPs, Table 1). It is worth noting the different nitrogen sources because nitrogen loads from STPs are more manageable than those from non-point sources.

Area #	Major rivers/cities/STPs	Tributaries	Coastal NPS	STPs	Sum	% of total N-load
Area 1	Shetucket River, Quinebaug River, Groton-New London	2013973 (64%)	699617 (22%)	410957 (13%)	3124547	5.6
Area 2	Connecticut River, Farmington River, Hartford-Middletown	16510687 (81%)	1632814 (8%)	2129740 (11%)	20273241	**36.2**
Area 3	Quinnipiac River, New Haven area	917356 (38%)	708862 (29%)	816093 (33%)	2442311	4.4
Area 4	Housatonic River, Milford-Stratford	4608681 (87%)	242379 (5%)	423691 (8%)	5274751	**9.4**
Area 5	Bridgeport-Westport		411399 (40%)	628492 (60%)	1039891	1.9
Area 6	Stamford-Greenwich		472222 (44%)	598597 (56%)	1070819	1.9
Area 7	Port Chester-New Rochelle		164226 (19%)	687960 (81%)	852186	1.5
Area 8	Wards Island, Hunts Point, Bowery Bay, Tallman Island		501432 (4%)	13204671 (96%)	13706102	**24.5**
Area 9	Newtown Creek, Red Hook		272252 (4%)	6858602 (96%)	7130854	**12.7**
Area 10	Great Neck-Glen Cove		238090 (38%)	392327 (62%)	630416	1.1
Area 11	Kings Park-Port Jefferson		369967 (77%)	111931 (23%)	481898	0.9

TABLE 1. Nitrogen loads (kg/yr) from 11 areas along the coast of LIS. Numbers are averages from 1991 to 2005. Values in parentheses are percentages of different nitrogen sources for a particular area. The 4 areas in bold supply the most nitrogen.

Time series data were deseasonalized (yearly cycles removed) so that the long-term trends and cyclical variations around the trend line (the so called Trend-Cycle Component) can be assessed. The trend-cycle component is estimated by smoothing the time series data using a simple moving average with span k equal to the length of seasonality s (12 mo in this case). Seasonal indices representing the effect of each season were also calculated.

Time series data of total nitrogen loads for Areas 2, 4, 8, and 9 are presented in Figure 2. There is no clear trend for the total nitrogen loads from the two major riverine (non-point) sources (Areas 2 and 4) except for some long-term cyclical variations (Figures 2a and 2b). Seasonal indices show that the nitrogen loads from these places peak around March-April and dip around July-August. In contrast, the total nitrogen loads from Area 8 (dominated by STPs) showed a slight decrease trend between 1991 and 1996, a significant drop from 1997 to 1999 likely as a result of much improved nitrogen removal efficiencies, and a rebound after 2003 probably due to the relaxation of regulations for further facility upgrade (Figure 2c). Total nitrogen loads from Area 9 dropped significantly from 1994 to 1995 and slightly from 1995 to 1999, and leveled off thereafter (Figure 2d). As expected, nitrogen loads from these two STP-dominated areas did not show any significant seasonal variations.

Long-term trends of individual water quality parameters (chlorophyll a (Chl-a), total dissolved nitrogen (TDN), total dissolved phosphate (TDP), and dissolved oxygen (DO)) at 18 sampling stations within LIS were also analyzed. Time series data for two sites, A4 (located at the west tip of LIS with very poor water quality) and M3 (located at the east tip of LIS with good water quality) are presented in Figure 3 for illustration purposes. Chl-a levels at all stations decreased gradually from 1991 to 1999, rebounded quickly around 2000-2002, and then leveled off thereafter (see Figures 3a and 3b for example). TDN concentrations showed a similar long-term trend (see Figures 3c and 3d for example). These long-term trends for Chl-a and TDN appeared to reflect the trend of the total nitrogen loads from areas 8 and 9, indicating that the reduction of nitrogen at STPs indeed had a positive impact on LIS water quality. Interestingly, TDP concentrations increased steadily from 1991 to about 2002, dropped in the following year, and then leveled off thereafter (see Figures 3e and 3f for example). This different trend suggests that the sources for phosphorus and nitrogen might be different. DO levels did not show any long-term trends (see Figures 3g and 3f for example). Minimum annual DO did not improve over the past 15 years either. This lack of improvement in DO levels is intriguing considering the fact that N-loads from major STPs have been reduced significantly. The exact reasons for the lack of DO improvement may be quite complicated and a couple of possible explanations are proposed. First, there might be other important sources of N-loads to LIS (e.g., nitrogen input through groundwater discharge into LIS, or recycling of organic nitrogen from LIS sediment) that are not included in current nitrogen budget. If these uncounted terms are large, then the total nitrogen load may not decrease significantly even though the point source loads are reduced. Second, it is possible that a threshold nitrogen level exists for the DO level to improve, and the reduction in the total nitrogen load has not reached the threshold yet.

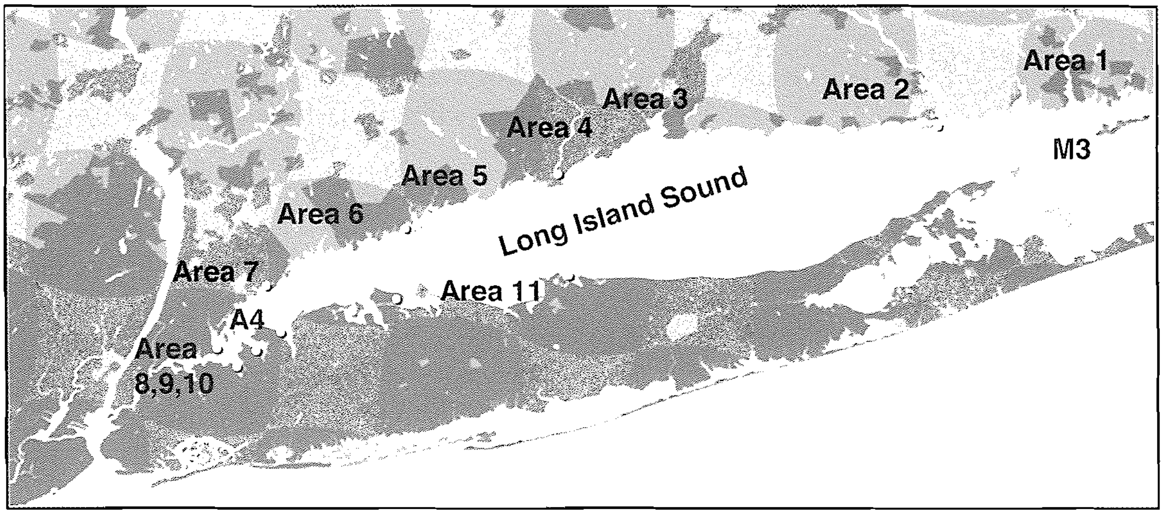

FIGURE 1. Map showing areas where total nitrogen loads are available, and locations of two sampling stations A4 and M3.

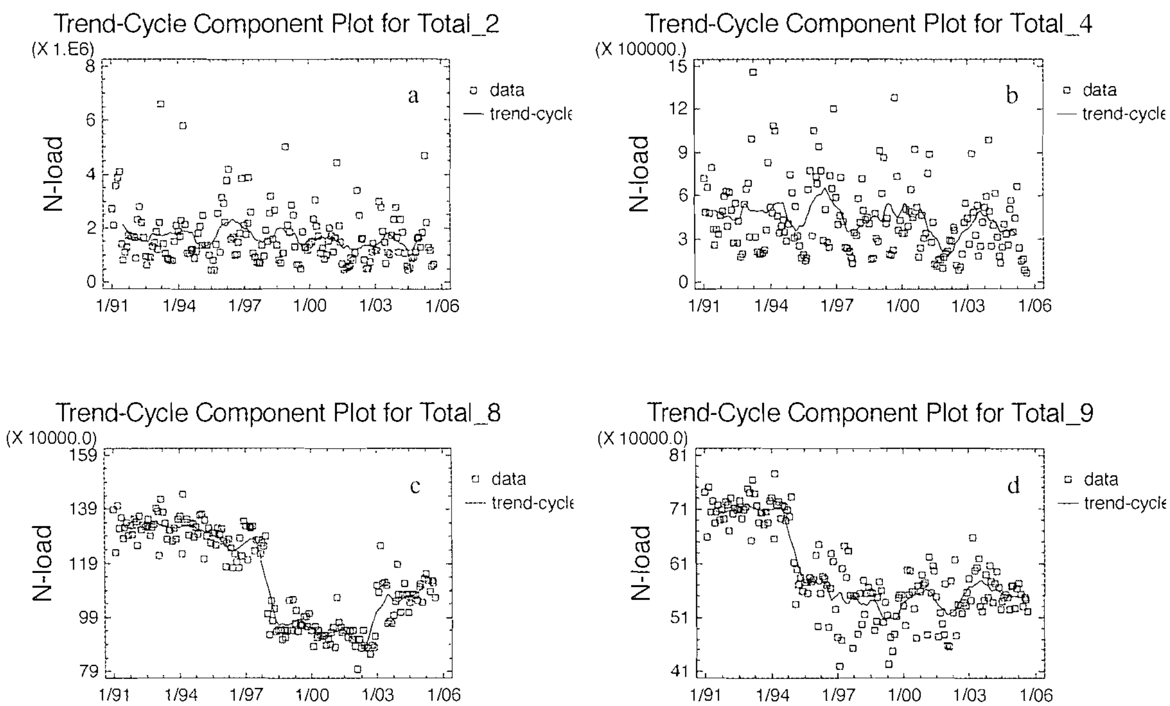

FIGURE 2. Trend-cycle component plots of total nitrogen loads for Areas 2, 4, 8, and 9.

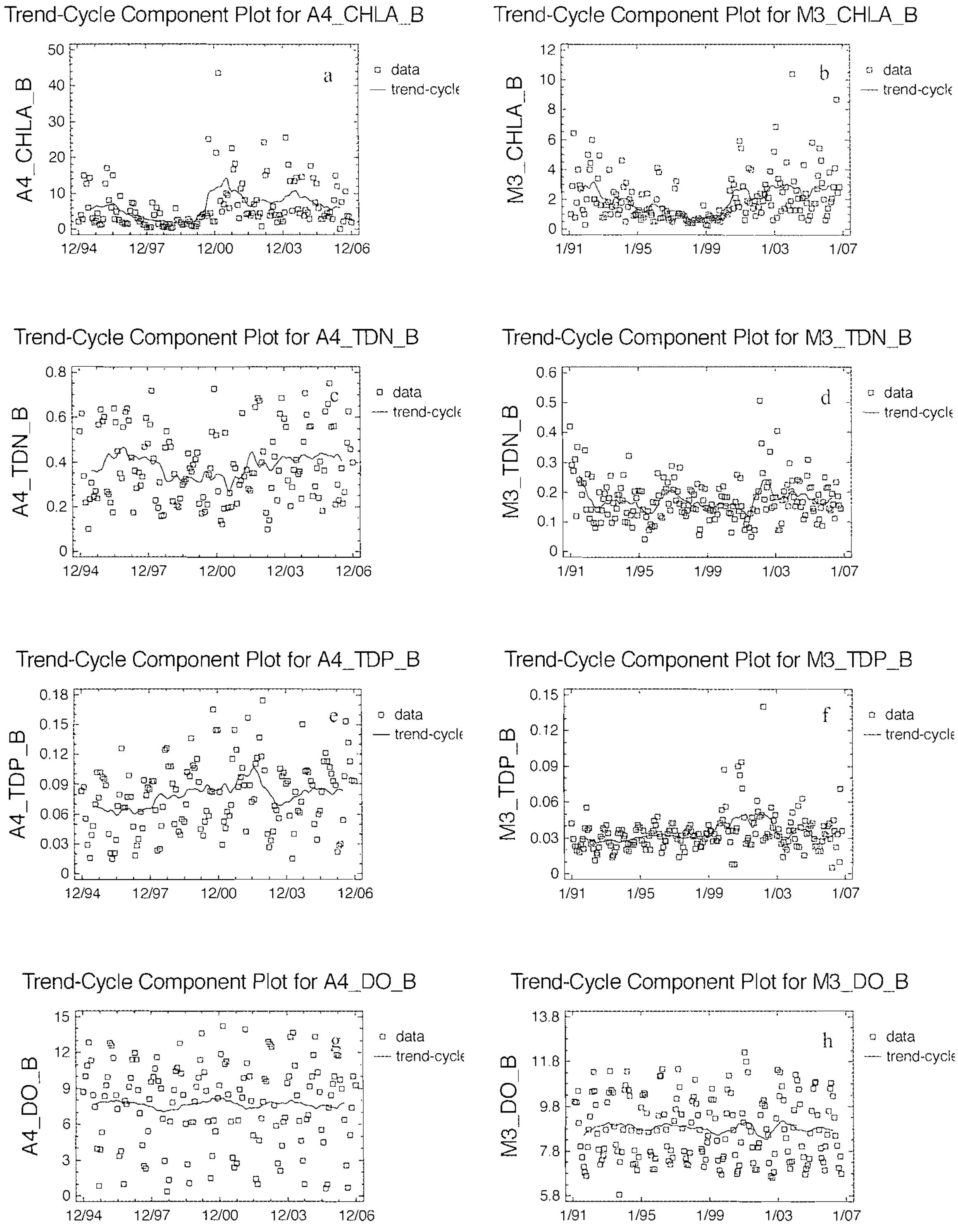

FIGURE 3. Trend-cycle component plots of Chl-a, TDN, TDP, and DO for stations A4 and M3

Temporal and Spatial Variation of Phytoplankton Community in Long Island Sound

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ABSTRACT

From January 2007 to June 2008, 162 phytoplankton samples collected from 12 stations throughout Long Island Sound were analyzed. Overall, 106 species were identified, bacillariophyceae (71 species) were the dominant species, followed by dinophyceae (29), euglenophyceae (3), chlorophyceae (2) and cryptophyceae (1). In terms of cell density, diatom contributed 62.00% of the total biomass, while dinoflagellate 14.18%. Diatoms were present throughout the whole year, dominated by *Thalassiosira* spp., but overall phytoplankton community structure varied by season. Total phytoplankton cell concentrations were highest in March (9,718 cells·mL^{-1}) and lowest in February (63 cells·mL^{-1}). Phytoplankton abundance and chlorophyll *a* concentration were higher in the western sound than the eastern. Average cell concentrations were 2,559-2,667 cells·mL^{-1} at the western stations A4 and B3, 791-853 cells·mL^{-1} in the central sound stations H4 and I2, and 392-1,152 cells·mL^{-1} in the eastern sound J2 and K2. Both the Shannon-Wiener species diversity index (H') and Evenness were higher in the central Sound (F2 to J2) than other sections. A negative correlation was found between total phytoplankton abundance (and chlorophyll *a* concentration) and dissolved oxygen with a 3-month time lag.

INTRODUCTION

Long Island Sound is an urban estuary with strong anthropogenic influence. Within 50 miles of the shoreline there lives a 20-million population. Through three major rivers, the Thames, the Connecticut, and the Housatonic River, and many non-point sources, LIS receives inputs of nutrients, especially in the western section of the Sound. Tens of thousand tons of nitrogen is loaded into the Sound each year (Goebel et al., 2006). Such eutrophication condition likely causes alteration in phytoplankton community structure and primary productivity. It has been shown that the high nitrogen loads promoted the high rates of phytoplankton production and standing stock in the western Sound (Goebel et al., 2006; Goebel and Kremer, 2007), similar to Chesapeake Bay (Smith and Kemp 1995), creating an estuarine gradient as seen in various systems (Nixon, 1992). As a temperate estuary, LIS experiences seasonal variations in physical, chemical, and biological conditions. It has long been observed that phytoplankton abundance is high during late winter-early spring and low during late fall and early winter (Conover, 1956; Harris and Riley, 1956). Long-term monitoring of phytoplankton abundance and species composition is crucial for us to understand how the nitrogen reduction program, which began in 1994, is impacting the phytoplankton community and primary production, and hence structure and function of other trophic levels along the food chain.

High production and standing stock in the western Sound coincides with episodic hypoxia in the bottom water particularly from mid-July through September. It occurs annually and extends over 50 square miles (Long Island Sound Study, 1994) and usually last 1-2 months. Hypoxia has been observed in the deep water of cwLIS every summer since 1987 although anecdotal reports on mild episodes dated back in the early 1900's. It is believed that hypoxia is the consequence of high nutrient inputs, stratification and stagnant conditions. In Chesapeake Bay, NO_3^- loading led to hypoxia (Hagy et al., 2004). In Long Island Sound, high rates of phytoplankton production fueled by excessive nutrients might be the major source of organic matter, which is consumed by bacteria resulting in hypoxia (HydroQual 1996, 1999).

Although tremendous effort has been made to understand the structure and function of the ecosystem and the mechanism of hypoxia, many basic issues still remain. In this study, we analyzed the temporal and spatial variation of phytoplankton community in LIS, and investigated whether surface phytoplankton standing stock is related to hypoxia in the bottom water.

MATERIALS AND METHODS

Samples were collected by the personnel of the Long Island Sound Water Quality Monitoring Program from Connecticut Department of Environmental Protection from January 2007 to June 2008, from ten stations (A4, B3, C1, D3, E1, F2, H4, I2, J2, and K2) (Fig. 1). For each sample a 50-mL subsample was concentrated to 1 mL using Utermohl Settling Chamber for at least 24 hours. The concentrated sample was examined under an Olympus BX51 microscope at 400 x magnification. Phytoplankton taxa were identified following standard keys (Tomas, 1993, 1997) and related references (Griffith, 1961; Wood and Lutes, 1968; Schnitzer, 1979; Capriulo et al., 2002). Cells were enumerated under the microscope following Hasle (1981).

RESULTS AND DISCUSSION

General phytoplankton community structure

Based on the cruises in Long Island Sound from January 2007 to June 2008, a total of 162 phytoplankton samples were analyzed. A total of 106 species were identified, with bacillariophyceae (71 species) being the dominant species, followed by dinophyceae (29), euglenophyceae (3), chlorophyceae (2) and cryptophyceae (1). In terms of cell concentration, diatom contributed 62.00% of the total biomass, while dinoflagellate accounted for 14.18%, cryptomonads 0.38%, green algae 5.80%, and euglenoids 0.03%. Dinoflagellate proportion out of total phytoplankton cell concentration increased in 2008 relative to 2007. In addition, there was a substantial proportion (17.62%) of an unrecognized group of phytoplankton, which was a round in shape, brown in color, and very small in size (<5 μm) and could not be identified under the light microscope. *Thalassiosira* sp., which was found in 98.15% of all the 162 samples analyzed, was abundant and dominant throughout the whole year, followed by round brown unidentified species (68.52%), *D. fragilissimus* (62.35%), *Navicula* sp (59.88%), *P. triestinum* (51.85%) and *S. costatum* (51.23%).

Temporal and spatial change of phytoplankton

The phytoplankton community changed with season. There were two peaks of phytoplankton abundance in one year, one in March of 2007 and the other in July-August of 2007, with cell concentrations of 3,343±2,440 and 3,618±2,865 cells·mL^{-1}, respectively. Cell concentration was lowest in winter time (161±62 cells·mL^{-1}) (Fig. 2). Maximum primary production and chl *a* concentration have previously been reported in late winter-early spring in LIS (Conover, 1956; Sun et al, 1994). Species number of phytoplankton also changed with season, with more species in Autumn and Winter than in Spring and Summer (Fig 2). The lowest (7) was found at Station D in March of 2007, the highest (30) at station E and F in October of 2007. The dominant species were diatoms, followed by dinoflagellates. Shannon-Wiener species diversity index (H') and evenness (J) showed the same tend, with the highest level appearing in late autumn and early winter (Nov and Dec 2007) and the lowest in late spring (May 2007). The species diversity index fluctuated between 1.32-3.74, their Evenness between 0.20-0.55, respectively.

Dominant phytoplankton species also changed seasonally: spring was dominated by, in the order of decreasing abundance, round brown unidentified species, *Leptocylindrus minius*, *Scenedesmus* sp., *Thalassiosira* sp., *S. costatum*, *T. nordenskioldii*, *T. gravida*, *P. micans*; summer was dominated by round brown unidentified species, *T. nordenskioldii*, *D. fragilissimus*, *Thalassiosira* sp., *P. triestinum*, *T. gravida*; autumn was dominated by *S. costatum*, *P. triestinum*, *Thalassiosira* sp., *P. minium*, *D. fragilissimus*; and winter was dominated by

Asterionellopsis glacialis, L. minius, T. nordenskioldii, H. circularisquama, T. gravida, T. nitzschiodes, S. turris, and the round brown unidentified species.

Spatially, phytoplankton abundance was generally higher in the western Sound than the eastern Sound. Average cell concentrations for stations A4 and B3 were 2,259-2,677 cells·mL^{-1} throughout the year, and those in the central Sound (H4, I2) 791-853 cells·mL^{-1}, and 392-1,152 cells·mL^{-1} in the eastern sound (J2, K2). Capriulo et al. (2002) reported that both the <10 and >20 μm fractions were more abundant in the western Sound and 10-20 μm size fraction was fairly uniform in the Sound. Similar western-eastern trend in phytoplankton abundance has been reported over half a century ago (Riley and Conover, 1956; Harris and Riley, 1956). In contrast, Shannon-Wiener species diversity index (H') and evenness (J) were higher in the central sound (F2 and H4). The Sound-wide diversity index varied from 2.79-3.12 and evenness from 0.41-0.46 (Table 1). Neither species number nor dominant species showed remarkable variation between different stations in the Sound.

Previous studies implied that higher phytoplankton biomass in cwLIS was due to higher nutrient loading and benthic nutrient regeneration in the relatively shallow western region (Bowman, 1977; Aller and Benninger, 1981; Wolfe et al., 1991). During our study period, it is a surprise to observe that phytoplankton abundance, both in cell concentration and chl *a*, was unrelated to nutrient concentrations when Sound-wide data were considered together ($p>0.05$). The lack of relation might reflect a more complex growth dynamics of phytoplankton than the abundance indicates. Nutrient utilization supports growth of phytoplankton, which can be grazed, die, or sink to bottom water. Accordingly, measured nutrient concentration may not represent the amount of nutrients utilized by phytoplankton. Information on phytoplankton growth dynamics and nutrient flux in the water column is needed to gain a better understanding on how phytoplankton dynamics is regulated by nutrient availability.

Hypoxia and correlation with phytoplankton abundance

Hypoxia (DO<3 mg·L^{-1}) was detected in cwLIS bottom water (A4, B3, C1, D3, E1 and F2) in July and August of 2007 during our study period. The lowest DO was 1.91 mg·L^{-1}, found in A4 with. Severity of hypoxia decreased from western to eastern sound. When regression analysis was performed for phytoplankton abundance (and Chl *a*) against concomitant dissolved oxygen, no significant correlation was found ($p>0.05$). However, when a three-month time lag was inserted, a significant negative correlation was found. For instance, dissolved oxygen in July was negatively correlated with phytoplankton abundance (and Chl *a*) in April ($p<0.05$). A similar pattern was noted in August. When averaging phytoplankton abundance (and Chl *a*) over three months preceding the time when DO was concerned, there was a strong correlation between them for July and August (Fig. 3). The correlation was not significant for earlier months, apparently because stronger mixing and resultant replenishment of DO by sinking surface water disrupted the correlation.

It has been hypothesized that high phytoplankton production is the major source of organic matter leading to hypoxia (HydroQual 1996, 1999). Anderson and Taylor (2001) also suggest that autochthonous carbon from phytoplankton bloom, rather than allochthonous carbon input, is the main cause of hypoxia in bottom water. In spring, phytoplankton grows rapidly when nitrogen is abundant. As they sink to the bottom, labile organic matter may temporarily store in bottom water or sediment due to low temperature at the time repressing bacterial metabolism. This may explain why no correlation was found between chlorophyll *a* concentration and concurrent dissolved oxygen. With temperature increases in the summer, decomposition and mineralization of organic carbon accelerates. This process depletes the oxygen in the water column, and the oxygen replenishment from surface waters is barred by the pycnocline when water column is stratified as a result of surface temperature rise (Rudnick and Oviatt, 1986). Therefore, when a time lag of three months was inserted, a significant negative correlation appeared. This time offset might reflect the process that link activities in the water column and that at the seafloor (Sun et al., 1994). However, as our observation of the negative correlation has been obtained only for

2007, whether it is a general trend remains to be investigated. Furthermore, hypoxia is extremely complex, involving physical, chemical and biological factors. The mechanistic understanding of this phenomenon needs to be determined with more comprehensive analysis including hydrographic data.

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TABLE 1. Shannon-Wiener species diversity index (H') and evenness (J) of each station in LIS between Jan/2007 and Jun/2008. Average ± Stdev, n=162

Station	Diversity index	Evenness
A4	2.82±0.71	0.42±0.11
B3	2.90±0.67	0.43±0.10
C1	2.98±0.60	0.44±0.09
D3	2.99±0.71	0.44±0.11
E1	2.81±0.84	0.42±0.12
F2	3.12±0.89	0.46±0.13
H4	3.06±0.57	0.45±0.09
I2	2.98±0.85	0.44±0.13
J2	3.02±0.87	0.45±0.13
K2	2.79±1.14	0.41±0.17

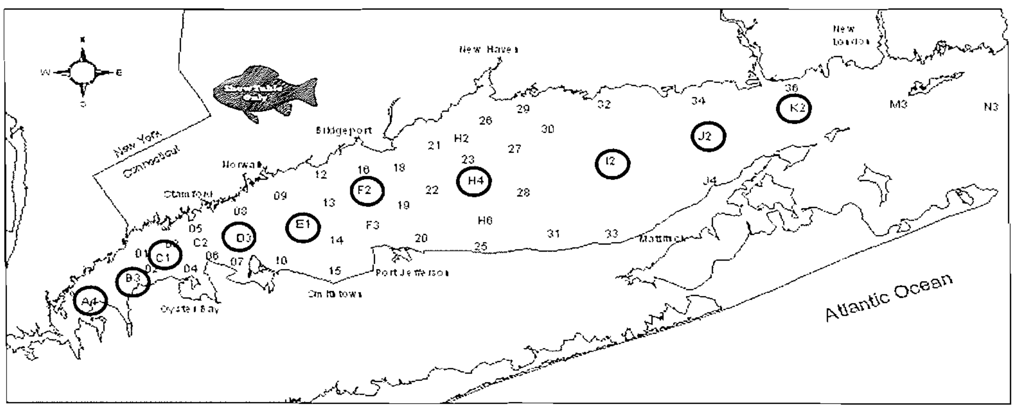

FIGURE 1. Sampling stations in LIS.

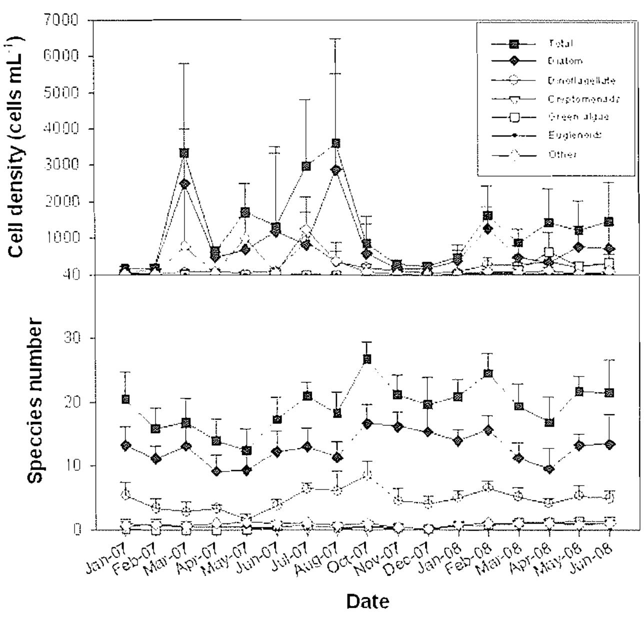

FIGURE 2. Temporal variation of phytoplankton abundance and species number.

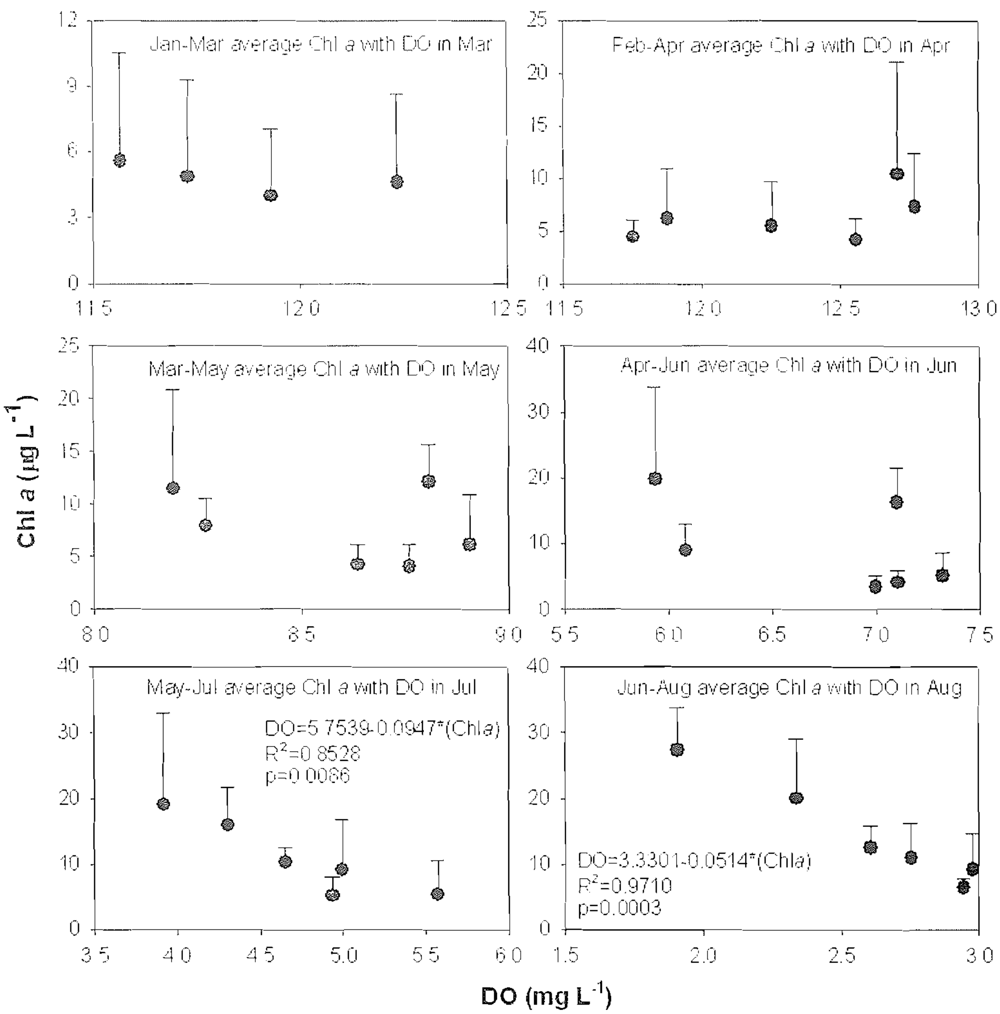

FIGURE 3. Relationship of surface average Chl a and DO at bottom waters with 3-month time lag in 2007.

Bloom Observations With Satellites in the Peconic Bay

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As plankton distribution appear at various spatial and temporal scales, the satellite study had the objective to estimate the requirements for monitoring patterns and trends in the distribution of parameters in the Peconic Bay that can be derived from remote sensing systems. Spatial and temporal changes in plankton distribution are complex in nature and are super-imposed by human-induced signals. The following contribution presents a short extract of a three-year study with satellites over the Peconic Bay. The actual research project includes observations not only over the Peconic Bay but also coverage for Long Island Sound.

Changes and cycles of plankton distribution were investigated with the satellite sensors SeaWiFS, MODIS, Landsat ETM and ALI. Observations demonstrate fast fluctuations in spatial and temporal distribution of plankton, its associated pigments, and other spectrally active material that cannot be readily detected with conventional ship operations. Data further indicated that observations of plankton blooming may go undetected if spatial and temporal resolutions are not in sync with the timeframe of bloom occurrence.

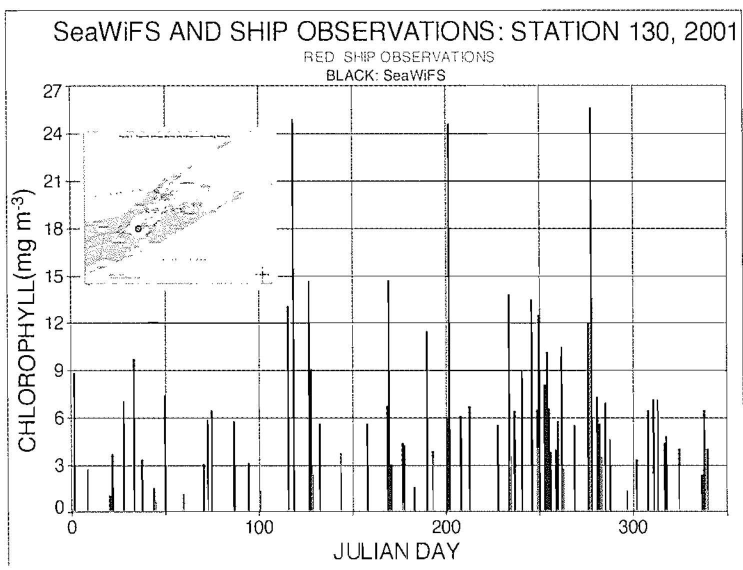

FIGURE 1. Chlorophyll observations in the Peconic Bay with conventional ship observations (red) and SeaWiFS (black) for station indicated in the insert

As an example, all avalable SeaWiFS chlorophyll data for the year 2001 were geometrically corrected with the corresponding values for the Peconic Bay shown in Figure 1. In that time frame, aside from the higher frequency of observations with SeaWiFS, it is evident that ship observations had no indication of significant bloom events while the satellite observations showed at several occasions elevated chlorophyll concentrations.

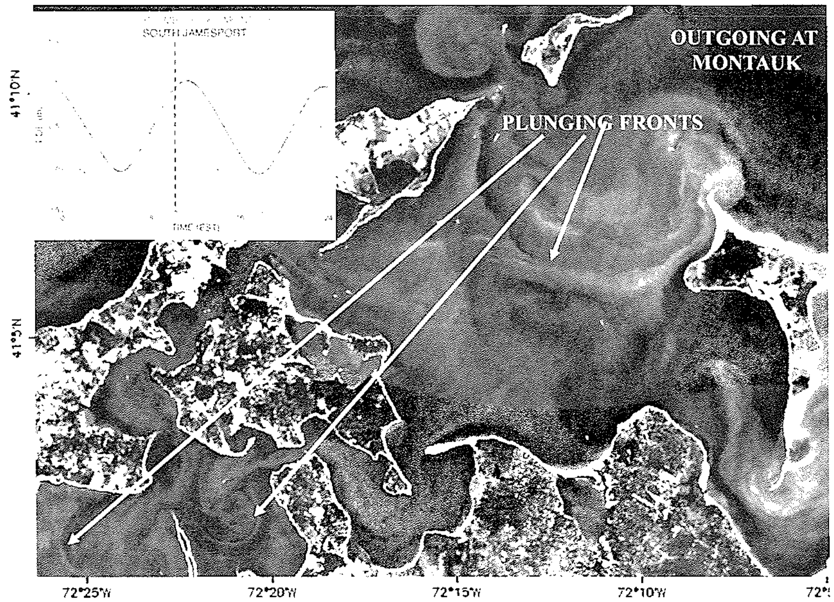

FIGURE 2. Landsat image recorded on September 27, 2000

Tidal flow and wind conditions create a complicated distribution of plankton/particle distribution in the Peconic Bay and also the fact that the hydrography of the Peconic Estuary is highly related to dynamics of the eastern Long Island Sound. An example of the hydrography in the inlet towards the Peconic Bay Estuary, Figure 2 shows the Landsat overpass on September 27, 2000 and the corresponding tidal range for Montauk and South Jamesport. During data acquisition of Landsat, tides at South Jamesport were incoming whereas the station at Montauk registered outflowing tide. The image emphasizes the surface manifestation between Orient Point and Gardiner Island. This structure was not reported elsewhere and seems to be a result of frontogenesis that results in an inflow jet and a plunge front at the region between Orient Point and Gardiners Island. The strong flow over the bottom makes the flow turbulent and a front line is formed through tidal intrusion of water from Long Island and Block Island Sound. It is assumed that dense fluid entering the sound leads to the plunging front and the formation of a leading internal wave.

The study illustrates the need for high spectral and temporal resolutions in observing the spatial distribution of plankton and for understanding the response to physical forcing. Therefore, it would be beneficial to integrate frequent satellite observations of plankton distribution with conventional observations aboard ships. This is of importance in the Peconic Bay where in the last 23 years bay scallop populations have drastically declined.

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Detection of Hydroxyl Radicals in Marine Sediments

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INTRODUCTION

Organic carbon in the form of sedimentary organic matter (SOM) may be preserved from enzymatic degradation. In marine sediments SOM may be protected by inorganic matrices, such as small mesopores on mineral surfaces or between mineral grains. These mesopores are too small and avoid the interaction between organic molecules and microbial enzymes (Mayer, 2004; Zang et al., 2001).

It has been shown that OM preservation and remineralization in sediments is significantly impacted by oxygen (Burdige, 2006; Burdige et al., 1992; Warnken et al., 2001). In addition to oxygen acting as an electron acceptor, enzymes such as oxygenases or peroxidases can use oxygen as a cofactor in degrading nonhydrolyzable compounds such as lignin, hydrocarbons, and other more refractory organic compounds. It has been proposed that remineralization of refractory OM occurs through the production of strong oxidants such as peroxide (H_2O_2) and other reactive oxygen-containing radicals (Canfield, 1994; Hedges and Keil, 1995).

The hydroxyl radical ($OH^•$) is a highly reactive transient which oxidant activity is capable of degrade a wide array of organic compounds ($E^{•\prime}$= 2.7 V), playing an important role as an oxidant in the environment. However, it is unknown whether this highly reactive transient also plays a role in degradation of organic material in marine sediments.

The $OH^•$ activity has been evaluated in seawater with different degradation effects on dissolved organic matter (DOM) cycling (Goldstone et al., 2002; Jank et al., 1998; Kwan and Voelker, 2003; Lindsey and Tarr, 2000a; Lindsey and Tarr, 2000b; Molot et al., 2003; Mopper K., 1990; Southworth and Voelker, 2003; Vaughan and Blough, 1998), but studies regarding the possible role of $OH^•$ in DOM degradation in marine sediments are absent. In this study, we propose that $OH^•$ is present in marine sediments at the oxic-anoxic interface and disodium terephthalate can be used as a molecular probe to detect $OH^•$ in marine sediments.

METHODS

Disodium terephthalate (TPA) has been used to detect $OH^•$ in solutions of different ionic strength (Barreto et al., 1994; Linxiang et al., 2004; Qu et al., 2000). TPA reacts with $OH^•$ to produce a single orto-hydroxylated compound, 2-hydroxy terephthalate acid (HTPA), which is a highly fluorescent (Manfred and Karl, 1999). HTPA fluorescence was measured using a Hitachi F-2500 fluorescence spectrophotometer at $\lambda_{e\lambda}$=315, λ_{em}=425 nm (Qu *et al.*, 2000).

The ortho-hydroxyterephthalate acid standard is not commercially available, so it was synthesized based on previous references with minor modifications (Field and Engelhardt, 1970; Miura et al., 1988; Yan et al., 2005). Once the HTPA have been prepared, a stock solution and a set of HTPA standard solutions (10mL) were prepared. A stock solution and a set of TPA solutions (10mL) were prepared for kinetic experiments.

The linear range of fluorescence response and the detection limit was determined with a set of HTPA standard solutions. The Fenton reaction was used to generate $OH^•$, the concentration of TPA solution, hydrogen peroxide (H_2O_2) and Fe^{2+} solution were in agreement with previous information (Lindsey and Tarr, 2000b; Linxiang et al., 2004; Yan et al., 2005). The reaction order was estimated based on the response of a set of TPA solution with different concentrations of TPA (5, 6, 7, 8 mM). The effect of the ionic strength was evaluated by preparing TPA solutions in freshwater and artificial seawater samples.

Sampling of sediment cores

Six sediment core samples were obtained at the Avery Point dock. Samples were divided in three control and three experimental treatments. Treatment cores were injected with a TPA probe solution every 5 mm down to 50 mm sediment depth, a final concentration of 5 mM in sediment pore water was achieved, and both untreated and treated cores were incubated in darkness for 24 hrs. Oxygen profiles were obtained using an oxygen sensor just at the end of incubation. Sediment cores were sliced, and sediment samples were centrifuged to obtain sediment pore water. The sediment pore water was filtrated through GFF (0.4-μm pore size), and fluorescence was measured. The incubation experiments were performed at three different dates, november 2007, may and september 2008.

RESULTS AND DISCUSSION

The linear range of fluorescence response of HTPA concentration corresponded to 0.1 μM to 50 μM (Fig. 1). The detection limit was 0.27 nM. The reaction order for TPA and $OH^{\bullet}$ was estimated as a second order reaction for both freshwater and seawater solutions (Fig. 2). TPA response to $OH^{\bullet}$ in solutions of different ionic strength was evaluated. A dramatic difference was observed between freshwater and seawater solution, but this effect although it minimizes TPA capacity to outcompete major cations as bromine to trap $OH^{\bullet}$ is not enough to hinder $OH^{\bullet}$ detection (Fig. 3).

In this study, we proposed that $OH^{\bullet}$ are formed at the oxic-anoxic interface in marine sediments through the Fenton reaction:

$$Fe(II) + H_2O_2 + H^+ \rightarrow Fe(III) + OH^{\bullet} + H_2O$$

The source of H_2O_2 would be the oxidation of Fe^{2+} to Fe^{3+} that occurs at oxic-anoxic interfaces (King *et al.*, 1995). H_2O_2 is formed in the Fe-catalyzed disproportionation of O_2^-. A pH of seawater (~8-8.4) and concentrations of Fe(II) in the range 1-10 μM result in an estimated steady state concentration of H_2O_2 in the range of 100-500 nM (Aksnes and Wassmann, 1993). Fe(II) concentrations occur in the ~5-150 μM-range at the oxic-anoxic interface in sediment pore waters of Long Island Sound (Aller, 1980) and could be representative of other marine sediment pore waters (Skoog et al., 1996; Thamdrup and Canfield, 1996). H_2O_2 has a relatively long half life and has been shown to stoichiometrically form $OH^{\bullet}$ in natural waters containing DOM (Southworth and Voelker, 2003).

TPA was used to detect $OH^{\bullet}$ in marine sediments. HTPA concentration profile for the three different sampling and incubation dates showed a maxima in $OH^{\bullet}$ concentration at the depth where oxygen concentrations became undetectable (Fig. 4). These findings indicated conclusively the presence of $OH^{\bullet}$ in sediments and a correlation between oxygen concentration and $OH^{\bullet}$ formation.

The difference in HTPA profile between treatment and control samples corresponds to the presence of humic substances (HS) in marine sediments which appear to increase with depth as a result of humification processes in anoxic conditions. Nevertheless, the signal of HS in the control cores is low there is a possibility of humic substances release in deeper portions of the sediment which may explain an apparent second HTPA increase at depth. These findings may indicate not only that TPA has the potential to detect $OH^{\bullet}$ presence in marine sediments, but also the possible $OH^{\bullet}$ effect on degradation of refractory DOM or the possible release of HS as a consequence of dissolution of the physical protection or degradation of the chemical protection of OM in sediments.

CONCLUSION

The concentration profile of HTPA showed a maxima in $OH^{\bullet}$ concentration at the depth where oxygen concentrations became undetectable. These findings indicated conclusively the presence of $OH^{\bullet}$ in sediments and a correlation between oxygen concentration and $OH^{\bullet}$ formation. The aggressive nature of the $OH^{\bullet}$ makes it likely that $OH^{\bullet}$ plays an active role in modification of sedimentary OM. Burial of sedimentary OM removes reduced carbon from degradation over long time periods and is therefore a key step in the global carbon cycle. The possibility that $OH^{\bullet}$ plays a role in this key step opens up some very interesting research possibilities that would add significant knowledge to our understanding of the global carbon cycle.

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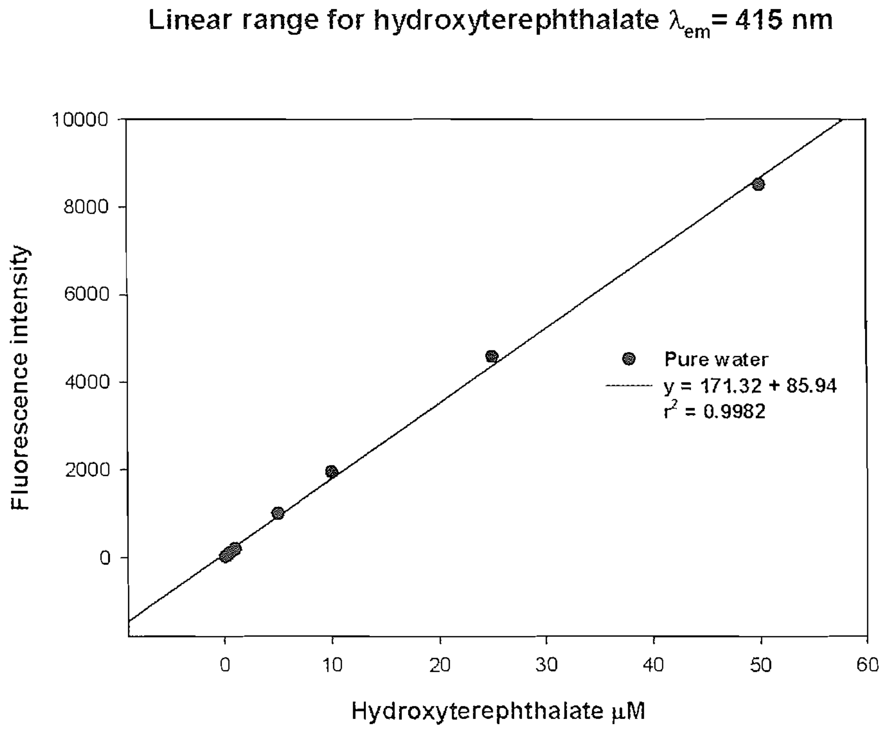

FIGURE 1. Hydroxyterephthalate (HTPA) calibration curve and determination of linear range of detection 0.1 to 50 µM.

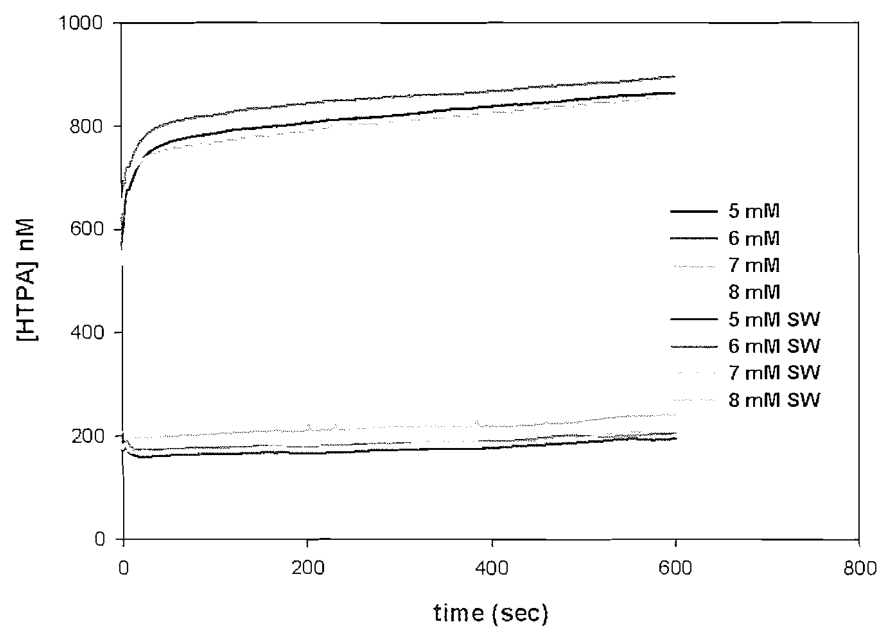

FIGURE 2.Terephthalate (TPA) solutions of increasing concentration (5-8 mM) in freshwater and seawater were used to determine a second order reaction of HTPA response to the presence of hydroxyl radicals (OH•).

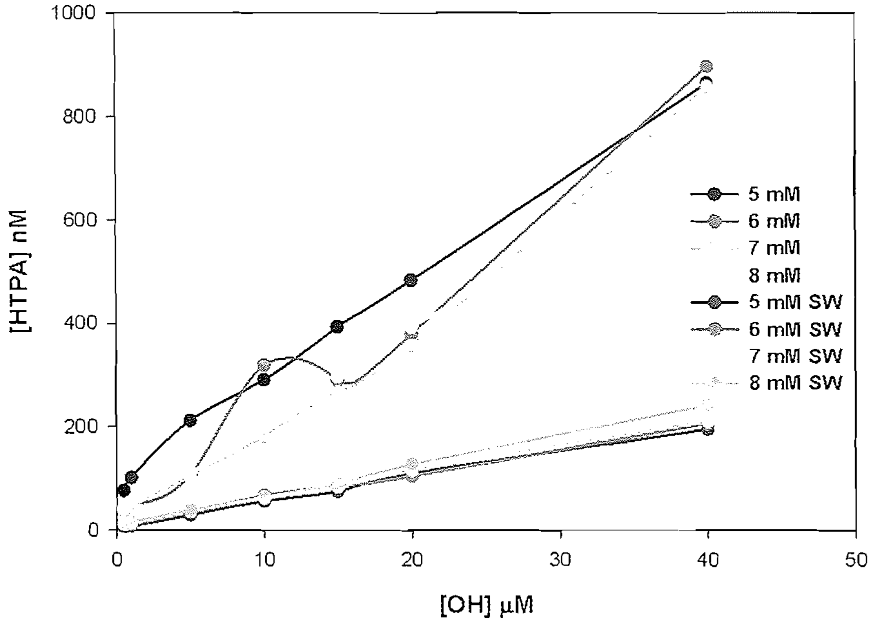

FIGURE 3. Evaluation of the ionic strength effect on hydroxyl radical detection using different concentration of TPA in freshwater and seawater solutions. Lower yields of HTPA concentration were obtained in seawater solutions but OH• are detectable.

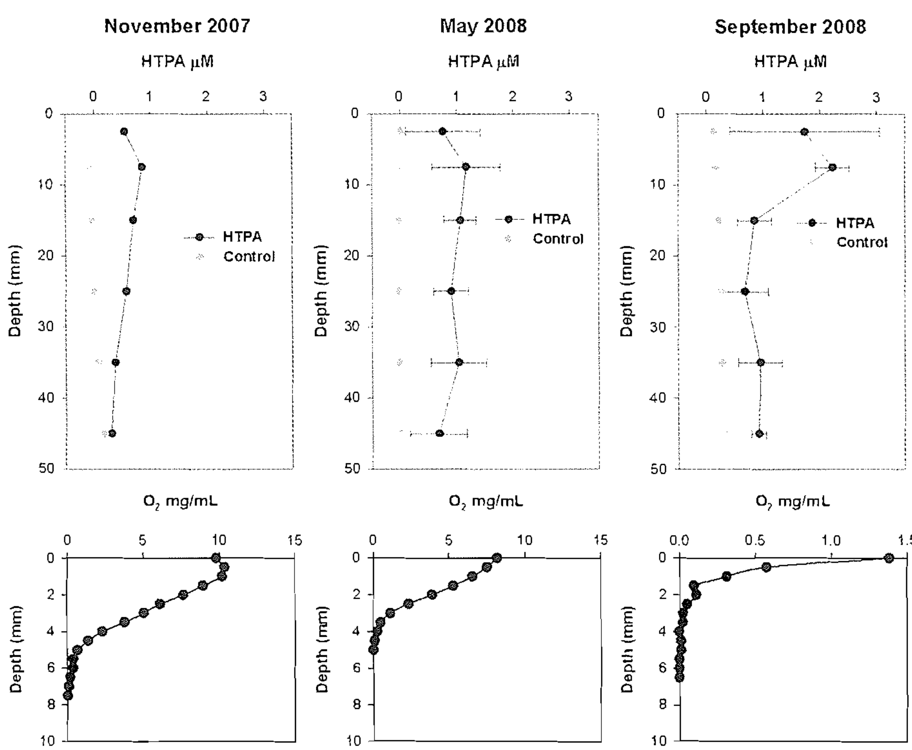

FIGURE 4. Detection of hydroxyl radicals in marine sediments. OH• profiles are presented for control and treatment sediment core incubations during three different sampling dates. The correspondent oxygen profile is presented. Different oxygen penetration depths are evident for each sampling date.

Alkylphenols and Lobsters in Long Island Sound: Patterns, Mechanisms, and Consequences

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INTRODUCTION

Alkylphenols are used in industrial and household detergents, paints, wetting agents, wood pulping, textile manufacture, plastic manufacture, petroleum recovery, phenolic resins, as antioxidants, polymer stabilizers, and curing agents, and in many other ways (Naylor et al. 1992, Naylor 1995, Ying et al. 2002). An estimated 500 million pounds of alkylphenols are used annually (Naylor et al. 1992, Ying et al. 2002), and approximately 60% of these end up in the aquatic environment via discharge from inefficient wastewater treatment plants or other release points (Warhurst 1995, Renner 1997, Ying et al. 2002). Contamination by alkylphenols and their breakdown products in rivers, oceans, and sediments is well known and widespread (Hale et al. 2000). Levels of alkylphenols in sediments have been reported as high as 70,000 mg/kg in the United States (Ying 2006). Certain alkylphenols were found in the urine of 95% of a human test population and have been implicated in a number of health problems such as reduction in fertility and meiotic disruptions (Calafat et al. 2005, Crain et al. 2007, vom Saal et al. 2007).

Juvenile hormone regulates metamorphosis and molting in insects (Riddiford 1994), and methyl farnesoate plays a similar role for crustaceans (Laufer et al. 1987). We isolated bioactive compounds from the hemolymph of lobsters from Long Island Sound and used a sensitive invertebrate bioassay (Biggers & Laufer 1996, 1999, Biggers & Laufer 2004) to identify four compounds with juvenile hormone activity. We identified the compounds using gas chromatography/mass spectroscopy (GC/MS) as 2-t-butyl-4-(dimethylbenzyl)phenol (Compound 1), 2,6-bis-(t-butyl)-4-(dimethylbenzyl)phenol (Compound 2), 2,4-bis-(dimethylbenzyl)phenol (Compound 3), and 2,4-bis-(dimethylbenzyl)-6-t-butylphenol (Compound 4).

We hypothesize that alkylphenols might negatively affect lobsters in LIS lobsters in two separate ways: through disruption of tanning and sclerotization during molting (e.g., Sacher 1971, Zomer & Lipke 1981, Sugumaran et al. 1992), and through endocrine disruption (e.g., Sumpter 1995, Hayes et al. 2006, Johnson et al. 2008, Ostrach et al. 2008, Planello et al. 2008, Ramakrishnan & Wayne 2008, Zhang et al. 2008). We have evidence that alkylphenols are incorporated into lobster cuticles during molting and that this weakens cuticular structure (Chen et al. 2009; Chen et al. unpublished data). We hypothesize that lobsters with weaker cuticles may be more susceptible to microbial invasions such as the bacterial infection associated with epizootic shell disease (SD) (Smolowitz et al. 2005).

The purpose of the current study was to assess the magnitude of the threat posed to lobsters by alkylphenol pollution by monitoring spatial and temporal patterns of contamination in Long Island Sound. We used GC/MS to monitor alkylphenol contamination levels in the hemolymph of lobsters from a broad geographic area in Long Island Sound (LIS) between 2002 and 2008. We also looked for correlations between the incidence and level of alkylphenol contamination and lobster sex and SD status. We expected that lobsters would be able to rid themselves of contaminants during molting and predicted that female lobsters should be more susceptible to contamination than male lobsters because they molt less often. Because we hypothesized that alkylphenols may play a role in SD, we also predicted that SDd lobsters would have higher contamination levels than unaffected lobsters.

METHODS

We sampled the hemolymph of lobsters caught in commercial traps by fishermen, the Connecticut Department of Environmental Protection, or Millstone Environmental Laboratory during 2001-2008. Hemolymph samples (2mL) were taken with 5-cc plastic syringes and 23-gauge needles, then transferred to 15 mL pyrex test tubes containing an ice-cold mixture of acetonitrile (2 mL) and 4% NaCl (2 mL). Samples were mixed and stored at -20°C before preparation for analysis. Samples were prepared for GC/MS as described by Laufer et al (2005). Mass spectrometric detection and quantification were also performed as described by Laufer et al (2005), but with phenanthrene (M.S. 178) as the internal standard.

The area we sampled (Figure 1) could be broadly divided into three distinct regions: western Long Island Sound (LIS West), central Long Island Sound (LIS Central), and eastern Long Island Sound (LIS East). We used a three factor nested ANOVA to compare variation in alkylphenol concentrations recovered from hemolymph between years, regions, and collecting trips, with year and area as fixed factors and collecting trip nested within both year and region. 2002, 2006, and 2008 were excluded from this analysis because we did not obtain lobsters from all three regions in those years. We were only able to obtain SD lobsters from LIS East, so we tested the effect of SD on alkylphenol hemolymph concentration using a reduced version of the analysis described above using LIS East data only, with year, collecting trip, and SD status as fixed factors and collecting trip nested within year. 2008 data were excluded because we did not obtain SD negative lobsters in LIS East in that year. 2004 was the only year for which we were able to obtain both male and female lobsters from multiple collecting trips in all three regions. For this reason, we tested the effect of lobster sex on alkylphenol hemolymph concentration using only 2004 data with region and lobster sex as fixed factors and collecting trip nested within region. We compared incidence of alkylphenol contamination between regions using a chi square test. All statistical tests were performed using JMP 6.0 (SAS Institute, Inc) and include only years or regions containing at least two collecting trips.

RESULTS

We found alkylphenols in the hemolymph of 160 (32%) of 500 lobsters from LIS. Of the 160 contaminated lobsters, 76 (48%) were contaminated with one alkylphenol, 50 (31%) were contaminated with two alkylphenols, 22 (14%) were contaminated with three alkylphenols, and 12 (8%) were contaminated with four alkylphenols. Incidence of alkylphenol contamination varied significantly between regions, ranging from 76 of 157 (48%) in LIS West to 68 of 246 (28%) in LIS East and 17 of 97 (18%) in LIS Central (Figure 1; Chi Square test: df=2, c^2=25.06, $p<0.0001$). Among contaminated lobsters, contamination patterns were similar between regions (Figure 2). Compound 3 was the most pervasive overall (71% of all contaminated lobsters), followed by compound 1 (47%), compound 4 (43%), and compound 2 (21%).

Levels of alkylphenol contamination in lobster hemolymph were extremely variable and ranged from our detection limit of 1 ng/mL to 5000 ng/mL, with an extreme outlier that contained 24600 ng/mL. Mean contamination levels varied significantly as a function of LIS region, year, and collecting trip, but not lobster sex or SD status (Table 1). Tukey's HSD post-hoc tests (Zar 1999) revealed that contamination levels were highest in LIS West, intermediate in LIS East, and lowest in LIS Central (Figure 3). Contamination levels were also significantly higher overall in 2003 and 2004 compared to 2005 and 2007, although this pattern varied with geographic region (Figure 3).

Contamination levels varied widely as a function of location and year of capture. In LIS West, mean contamination levels declined steadily between 2003 and 2007. We did not detect any alkylphenols in LIS Central in 2003, but observed a decline between 2004 and 2007. In LIS East, alkylphenol levels fluctuated between 2002 and 2008. In all locations, both the incidence and level of contamination varied strongly with collecting trip (Figure 1, Figure 3).

DISCUSSION

We detected all four alkylphenolic compounds in every region and in every year sampled, although both incidence and level of contamination were extremely variable. Our collecting trip data show that contamination is extremely patchy: collecting trips conducted in the same location and the same year often yielded dramatically different contamination rates (e.g., 0% vs. 100% for the two 2008 trips in LIS East – see figure 3). We did not detect any monthly pattern in incidence or level of alkylphenol contamination (data not shown), although our sampling was not designed to test for this effect, and we cannot eliminate the possibility that monthly patterns are masked by spatial and annual variation in our dataset. Overall, our dataset suggests that alkylphenol contamination is a persistent but environmentally heterogeneous problem in LIS lobster populations, particularly in LIS West and LIS East.

Male and female lobsters were equally likely to be contaminated with alkylphenols, suggesting that alkylphenols are not more likely to accumulate during the longer molt cycle of females. Lobsters may be able to clear contaminants during intermolt periods by excretion or sequestration in tissues such as the hepatopancreas or epidermis, although these potential pathways for the metabolism and excretion of alkylphenols remain untested. Consistent with this hypothesis, Laufer et al (2005) observed female lobsters with uncontaminated hemolymph carrying contaminated embryos. Egg bearing female lobsters do not molt, so assuming the alkylphenols passed to the ovaries from the hemolymph, this observation suggests that the lobsters were able to clear the contaminants from their hemolymph (but not their eggs) during intermolt.

We also failed to find any correlation between SD status and hemolymph alkylphenol content. However, SD can take many months to develop into visible lesions (Smolowitz et al. 2005). Our expectation that SD lobsters should have higher contamination levels was based on the assumption that alkylphenol content of hemolymph would remain relatively constant over a period of months. If lobsters are able to clear alkylphenols from their hemolymph through excretion, sequestration, and molting, then it will be necessary either to measure alkylphenol concentration in hemolymph immediately before the molt that precedes development of SD lesions, or to directly measure the alkylphenol content of SD and unaffected cuticles.

CONCLUSIONS

Alkylphenol contamination levels in hemolymph are spatially and temporally patchy and do not correlate with lobster sex or SD. Based on these findings, we propose that lobsters exposed to alkylphenols carry them in their hemolymph initially but soon clear them either through excretion, metabolism, or sequestration in tissues. Thus, alkylphenol content of hemolymph represents the recent rather than the long-term environmental history of lobsters, and shows promise as an environmental indicator. We predict that hemolymph alkylphenol content should correlate well with temporal and spatial patterns of environmental contamination.

Our results suggest that lobsters in LIS are repeatedly exposed to endocrine disrupting alkylphenols across a broad geographic area. We do not fully understand the ways in which these compounds affect the biology of lobsters, but have good reason for concern: earlier work on other crustaceans (Borst et al. 1987, Abdu et al.

1998) and mosquitos (Sacher 1971) suggests that alkylphenols may disrupt both the metamorphosis of larval lobsters and the sclerotization and tanning of adult lobster cuticle. Additional work is urgently required in Long Island Sound and elsewhere to assess the environmental distribution of these and other endocrine disrupting compounds, and to understand their biological consequences for lobsters and other organisms.

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TABLE 1. Analysis of variance (ANOVA) in alkylphenol contamination levels as a function of geographic region, year of capture, collecting trip, sex, and SD status. Collecting trip nested within region, year, or both as appropriate. Significant p-values (α=.05) are in bold.

Test	Source of Variation	Degrees of Freedom	Mean Square	F	p
Shell Disease (CT East only)	Year	5	9.686	28.923	**<.0001**
	Collecting Trip	8	5.730	17.110	**<.0001**
	SD	1	0.076	0.228	0.6337
	Year * SD	5	0.457	1.364	0.2417
	Collecting Trip * SD	8	0.209	0.624	0.7566
	Error	*137*	*0.335*		
Sex (2004 only)	Region	2	2.708	3.988	**0.0232**
	Sex	1	0.382	0.563	0.4558
	Collecting Trip	5	3.474	5.116	**0.0005**
	Region * Sex	2	0.135	0.199	0.8201
	Collecting Trip * Sex	5	0.427	0.629	0.6786
	Error	*65*	*0.679*		
Region, Year, Collecting Trip (2003, 2004, 2005, 2007)	Region	2	5.921	15.028	**<.0001**
	Year	3	6.250	15.862	**<.0001**
	Region * Year	6	5.336	13.542	**<.0001**
	Collecting Trip	26	3.810	9.669	**<.0001**
	Error	*357*	*0.394*		

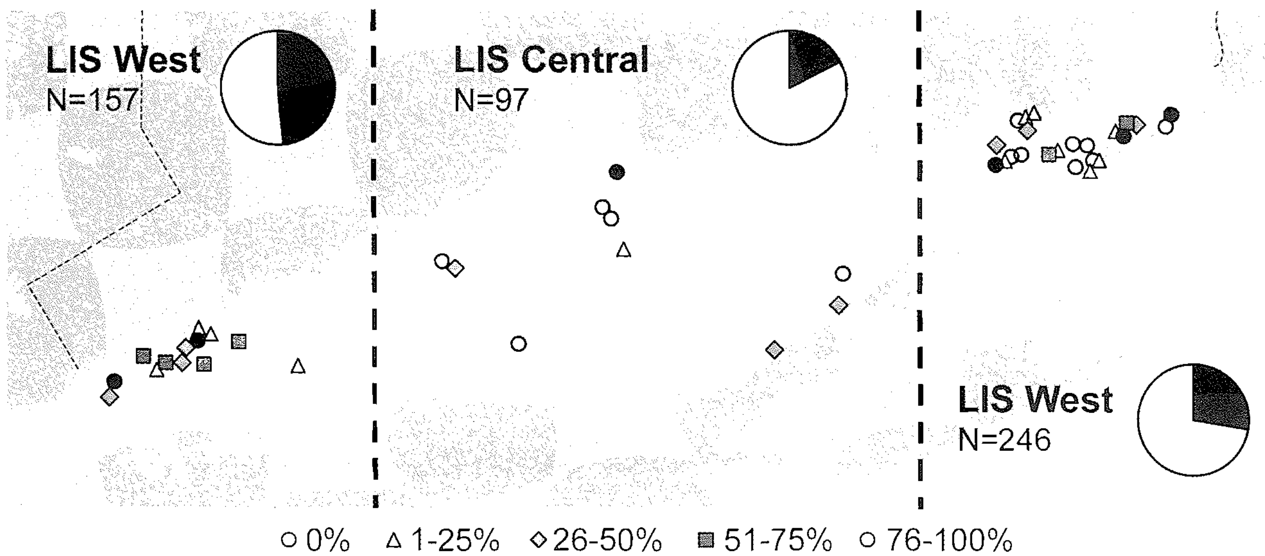

FIGURE 1. Map of LIS showing widespread alkylphenol contamination. Each point represents a single collecting trip, and the shape and shade of that point (see legend) indicate the percent of lobsters from that trip contaminated with at least one alkylphenol. Black portions of large pie charts show the total proportion of contaminated lobsters collected from each major region (regions separated by dashed lines). N=total sample size from each region. Figure created using GPS visualizer (www.gpsvisualizer.com).

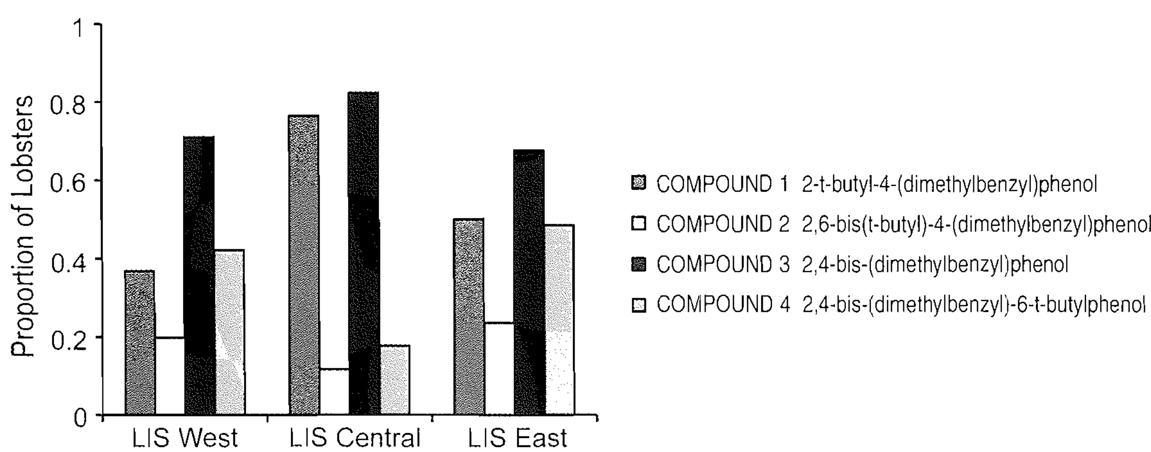

FIGURE 2. Proportion of lobsters contaminated with each of four alkylphenols in LIS West, LIS Central, and LIS East.

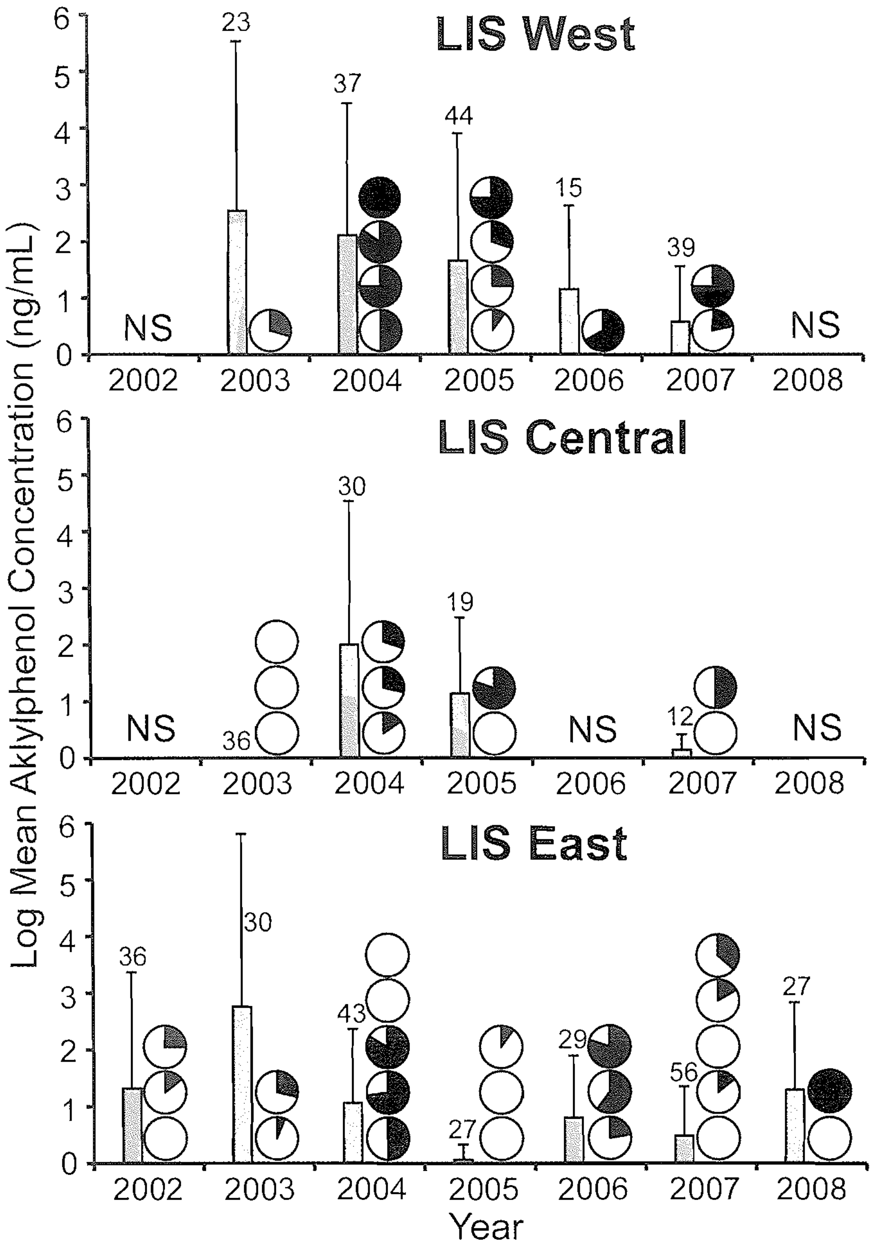

Figure 3. Columns: mean alkylphenol concentration over time for LIS West, LIS Central, LIS East. Error bars are standard deviations. Circles: each circle represents one collecting trip. Dark portions indicate the proportion of lobsters from that collecting trip contaminated with at least one alkylphenol. Numbers above columns are sample sizes. NS: not sampled in that year.

Management for *Liatris scariosa* var. *novae-angliae* in a Coastal Meadow in Southeastern Connecticut

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Liatris scariosa var. *novae-angliae*, New England Blazing Star, is a state-listed plant occurring in sand plains and coastal habitats. This "Species-of-Special-Concern" in Connecticut occurs in a 1.62 ha (4 ac.) coastal meadow in Old Saybrook, CT managed by the Lynde Point Land Trust (LPLT). The meadow was rapidly filling in with shrubs in spite of annual mowing. The population in 2005 was 460 plants. The goal of this management project is to restore and maintain this coastal meadow and its relatively large population of New England Blazing Star. With cost-share funding from the Natural Resources Conservation Service (NRCS), and further conservation assistance from CT Sea Grant, NRCS, UConn Cooperative Extension, and other contractors, the LPLT has undertaken a new management regime focused on conserving the New England Blazing Star chiefly through shrub removal and late fall mowing.

SITE DESCRIPTION

This small (1.62 hectarea) coastal meadow is located in Old Saybrook, CT within 1 km of Long Island Sound. The soils of the site are mapped as Agawam fine sandy loam with 0 – 3% slopes (well-drained glacial outwash). The area has an agricultural past chronicled historically and in 1934 aerial photographs. Currently, the areameadow is flanked by residential development, a utility right-of-way, and a roadway. A cart path bisected the meadow, and deer paths could be foundcrisscross throughout the site. The meadow is managed under easement by the Lynde Point Land Trust, and was mown annually in early July. The site is dominated by grasses, herbaceous perennials, transgressive shrubs, as well as a patch of conifers. Species include little blue stem (*Schizachyrium scoparium*), Indian grass (*Sorghastrum nutans*), butterfly weed (*Asclepias tuberosa*), roundhead lespedeza (*Lespedeza capitata*), wild indigo (*Baptisia tinctoria*) and numerous goldenrods and asters (*Solidago* spp. and *Aster* spp. *{(sSensu lato]*) such as stiff aster (*Ionactis linariifolius*). Shrubs include winged sumac (*Rhus copallina*) and choke cherry (*Prunus virginiana*). Conifers include blue spruce (*Picea pungens*) and white pine (*Pinus strobus*).

SITE MANAGEMENT

The population of New England Blazing Star was identified in the late summer of 2005. A plan of conservation was agreed upon by the LPLT after consultation with several conservation partners. This included a suite of management actions undertaken in 2006, including:

- organized greater community interest in the Old Saybrook site and speciesand communications, ;
- established partnerships and commitments with LPLT, CT Sea Grant, NRCS, UConn Cooperative Extension and other contractors;
- conducted an initial botanical inventory;
- determinefocused on primary threats to bei.e., inappropriate timing of out-of-time mowing, incursive woody plants,;
- checked for unfettered pedestrian access, and deer browse;
- selectively applied herbicide treatment after seed set; and
- delay mowing until fall (prescribed burning was not an option due to adjacent roadway and homes).

Further management actions were taken during 2007 to better secure the populations of New England Blazing Star:

- erected a fence erected to limit access;
- applied deer repellant to discourage browsing throughout the summer;
- conducted a second inventory in late summer to monitor progress:
- mowed late in year after seed set;
- selectively treated the meadow with an herbicide treatment to decrease shrub growth and invasive plants; and
- cut and removed ornamental conifers to increase meadow habitat.

Continuing management actions were undertaken as warranted in 2008:

- applied deer repellant applied in early summer;;
- applied herbicide selectively in late winter/early spring; and
- conducted a third inventory .

RESULTS

Anecdotal accounts report the population size of New England Blazing Star within the meadow has declined steadily over the past 10 years, prompting conservation actions to be taken. In 2006, prior to active management, there were 460 New England Blazing Star plants with 95 % of the plants occurring in more open sites and within 1 meter of cart path or deer trail. In 2007, after one year of active management, there were 3,399 plants with the majority of plants located along a cart path. In 2008, there were 837 plants with 349 recently clipped stems due to eastern cottontail rabbit browse. The amount of goldenrods (*Solidago* spp.) and deer tongue (*Dichanthelium clandestinum*) is rapidly increasing.

Future plans for the site include better coordination of management actions to ensure that herbicide applications take place prior to mowing and include goldenrods and deer tongue will be included in herbicide applications, along with shrubs. We plan to Rresearch rabbit control measures; and continue monitoring the number and locations of New England Blazing Star in fall of each year.

Detection of Antibiotics in the Thames and Mystic Rivers

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ABSTRACT

Urbanized rivers and estuaries can receive anthropogenic materials from a variety of sources. Concern over the release of antibiotics, for example, has grown because wastewater facilities have few methods for removing these compounds from effluents prior to their release into aquatic ecosystems (Alvarez 2004). The Thames River (New London County, CT) has several potential point sources of antibiotics including two water-treatment facilities. To investigate the presence of antibiotics in the Thames, samples of water, aggregates, and sediments were obtained from four sites along this river. For comparison, samples of water and aggregates from one site on the less urbanized Mystic River (New London County, CT) were also evaluated. Results of ELISA tests revealed the presence of fluoroquinolone in the upstream aggregates and all of the sediment fractions of the Thames, as well as in surface aggregates of the Mystic River. Sulfamethoxazole was detected in some water, aggregate, and sediment fractions of the Thames, but was absent in Mystic River samples. The presence of antibiotics in estuarine waters increases the likelihood that bacteria will come into contact with these drugs and develop resistance. In fact, low concentrations of antibiotics have been found to increase expression of bacterial plasmids containing antibiotic resistance genes (Beaber 2004). Future research will focus on how chronic, low-level antibiotic exposure affects the microbial community and physiology of bivalves, and its potential impact on human health and disease.

INTRODUCTION

Antibiotics have significantly reduced morbidity and mortality caused by bacterial disease since the first therapeutic use of penicillin in 1942. Within three years, however, 20% of the *Staphylococcus aureus* in hospitals were penicillin-resistant (Champoux et al. 1994, Taubes 2008). For nearly seven decades, antibiotics have infiltrated aquatic environments through sewage treatment effluents and agricultural runoff. Wastewater treatment plants and private septic systems are principal sources of antibiotics in the aquatic environment as unused or unfinished prescriptions are flushed down the toilet (Heberer 2002). Most municipal wastewater facilities have few, if any, methods for the removal of antibiotics or their secondary metabolites from effluents prior to their release into open aquatic systems (Alvarez et al. 2004). In eastern Connecticut, the Thames River is an industrialized waterway with several potential point sources of antibiotics including two water-treatment facilities. The purpose of this study was to investigate whether two antibiotics, fluoroquinolone and sulfamethoxazole, were present in the Thames River, and to compare the results with those obtained from a less urbanized river (Mystic River), and to those in the published literature.

Treated wastewater can contain antibiotic concentrations as high as micrograms per liter, subjecting aquatic organisms to chronic, low levels of these drugs (Hirsch et al. 1999, Kolpin et al. 2002, Glassmeyer et al. 2005). Chronic, low-level antibiotic exposure has been found to induce beneficial effects in bacteria, which may be intermediary steps on the path to antibiotic resistance. For example, antibiotic concentrations on the order of parts per million catalyze transcriptional pathways in bacteria independent of the traditional stress response (Goh et al. 2002). In addition, intermicrobial signaling molecules have demonstrated antibiotic properties at higher concentrations; a process known as hormesis (see Davies et al. 2006), and certain species of bacteria have shown a propensity to use a host of antibiotic compounds as a source of nutrition (Martinez 2008). Beaber et al. (2004) demonstrated that exposure to chronic environmental stressors such as ultraviolet light or low concentrations of antibiotics on the order of 1 part per billion activate the SOS response in bacteria, which increases the transcription of antibiotic resistance genes that reduce DNA degradation. Alarmingly little is known about the physiological impact of these compounds on human health and disease (Kolpin et al. 2002).

Sulfamethoxazole and fluoroquinolone are recalcitrant antibiotics, known for their stability in marine and estuarine waters and sediments (Hirsch et al. 1999, Kummerer 2001, Heberer 2002, Kummerer 2003). Sulfamethoxazole is normally prescribed in combination with trimethoprim to combat urinary and respiratory tract infections. The two chemicals create a synergistic effect that prevents microbes from producing tetrahydrofolic acid, a cofactor in bacterial DNA synthesis (Masters et al. 2003). Fluoroquinolones work by inhibiting the action of DNA gyrase and topoisomerase IV, which allow DNA to uncoil so replication can commence. The quinolones are commonly prescribed for infections of the sinuses, skin, joints, and bones (Drlica 1999). Both sulfamethoxazole and fluoroquinolone-resistant bacteria have been identified and isolated in clinical settings (Smilack 1999, Linder et al. 2005).

METHODS

Samples were taken just south of the Pfizer, New London, and Groton sewer lines (Pfizer: 41° 19'54.88" N, 72° 04'49.21" W; New London: 41° 20'29.63" N, 72° 05'18.64" W; Groton: 41° 21'15.45"N, 72° 05'04.90" W), and at a fourth site located upstream, just north of the U.S. Naval Submarine Base (41° 24'39.59" N, 72° 05'54.40" W). Collections were made during an ebbing tide to make certain that effluents were carried toward the sampling gear. At each site, five fractions were collected in duplicate: surface water and aggregates, mid-depth water and aggregates, and bottom sediments. In addition, samples of surface water and aggregates from one site on the Mystic River (41° 23'06.59" N, 71° 57'27.91" W) were collected. This river has no obvious point source for antibiotic release. Surface samples were collected with a Niskin bottle at approximately 1.0 m depth. Mid-water samples were collected at 2-3 m below the surface depending on the water depth at the particular site. The collected water was transferred via a peristaltic hand pump into a 1-L Imhoff settling cone with a 15-ml Falcon tube attached to the bottom (Lyons et al. 2005). The cone was allowed to stand, undisturbed for 20 minutes in order to separate aggregates from the water. This period of time was sufficient to allow aggregates larger than approximately 400 μm to settle (Hill 1998). A 500-ml sub-sample of the supernatant was then collected and placed in a plastic bottle. The Falcon tube with aggregates was removed and capped. Sediment samples were collected at all four sites using a Ponar grab. Sub-samples were taken from the top layer of the sediment sample and placed in 15-ml Falcon tubes. All samples were then placed on ice and transported to the laboratory.

In the laboratory, water samples were transferred to 15-ml Falcon tubes and subjected to centrifugation at 3220 x g for 15 minutes to remove humic material that could interfere with the analysis. After spinning, the supernatant from each tube was decanted into a clean Falcon tube and placed in a freezer (-20° C) until analyzed. For the analysis, 50 μl of the water sample was placed into one well of an ELISA microtiter plate. In a competitive ELISA, the microtiter plate is composed of 96 wells that are coated with the compound of interest. A sample is then introduced to the wells in combination with a primary antibody designed to bind the compound of interest. If the sample contains a high concentration of the molecule of interest, then the primary antibody will be prevented from binding to the chemical coating the well. After the sample is introduced, a secondary antibody containing a peroxidase tag is added, and will bind to the primary antibody. The substrate tetramethylbenzidine (TMB) is then added, and is oxidized by the peroxidase producing a colorimetric reaction with an intensity that is inversely proportional to the concentration of the chemical of interest present in the sample. In other words, a high colorimetric signal means very little of the molecule of interest is present and vice versa. Other variations of ELISA detection exist, most notably the sandwich ELISA, which begins with the primary antibody lining the microtiter wells instead of the compound of interest. In this study, the microtiter plate utilized to detect the presence of fluoroquinolone was a competitive ELISA, whereas the plate used to detect the presence of sulfamethoxazole was a sandwich ELISA.

Aggregate samples were allowed to settle in a refrigerator (4° C) for 24 hours before the overlying water was removed. The amount of aggregated material obtained for most samples was low, thus precluding drying and weighing of Falcon tubes with and without aggregates to determine mass. Therefore, the volume of settled material in each Falcon tube was estimated, and an equal volume of methanol was used in the extraction procedures (volume-to-volume). Aggregates for the fluoroquinolone test were subjected to an "Animal Feed" extraction protocol (Bioo-Scientific), whereas aggregates for the sulfamethoxazole test went through a "PCB-Soil" extraction protocol (Abraxis). Samples of the extract were then loaded into wells of the appropriate ELISA microtiter plate and analyzed as above. After extraction, aggregate masses were washed three times by re-suspending in Milli-Q water and pelleting by centrifugation. The aggregates were then vacuum filtered onto pre-ashed, pre-weighed GF/C (nominal pore size = 1.2 μm) filters. The filters with collected aggregates were dried to a constant weight at 70° C, and aggregate mass determined by difference.

Sediments were massed wet (i.e. still containing pore water) and divided into 10 g samples in separate weigh boats. Sediments for the fluoroquinolone test were subjected to an "Animal Feed" extraction protocol (Bioo-Scientific), whereas aggregates for the sulfamethoxazole test went through a "PCB-Soil" extraction protocol (Abraxis). A sample of the sediment extract was then loaded into wells of the appropriate ELISA microtiter plate and analyzed as above. Following analysis, sediments were removed from their Falcon tubes and transferred to individually labeled, pre-massed weigh boats, which were then placed in a fume hood so that excess water could evaporate. After evaporation, sediments were pulverized and pans placed in an oven at 70° C. Weigh boats and sediments were dried to a constant weight, and sediment mass determined by difference.

RESULTS

Fluoroquinolone was below detection limits in the surface and mid-depth waters sampled from the Pfizer, New London, Groton, and Sub-base (upstream) sites of the Thames River. Similarly, fluoroquinolone was below the limits of detection in the surface waters of the Mystic River (Fig. 1). Surface and mid-depth waters sampled at the Pfizer site contained sulfamethoxazole at average concentrations of 0.039 μg/L, whereas surface waters from the New London site averaged 0.024 μg/L. Sulfamethoxazole concentrations were below the limits of detection in the mid-depth water at the New London site, the surface and mid-depth waters at the Groton and Sub-base sites, and the surface water at the Mystic River site (Fig. 1).

Surface and mid-depth aggregates at the Sub-base site contained fluoroquinolone at average concentrations of 1.9 μg/kg and 29.4 μg/kg, respectively. Surface aggregates at the Mystic River site contained fluoroquinolone at an average concentration of 799.9 μg/kg. Fluoroquinolone was below the limits of detection in the surface and mid-depth aggregates of the Pfizer, New London, and Groton sites (Figure 2). Surface and mid-depth aggregates sampled from the Pfizer site contained sulfamethoxazole at average concentrations of 3074.0 μg/kg and 2111.0 μg/kg, respectively. Surface aggregates sampled at the New London site and mid-depth aggregates sampled at the Sub-base location contained sulfamethoxazole at average concentrations of 1573.0 μg/kg and 670.4 μg/kg, respectively. Sulfamethoxazole concentrations were below the limits of detection in the mid-depth aggregates sampled at New London, the surface and mid-depth aggregates sampled at Groton, and the surface aggregates sampled at the Sub-base and Mystic River sites (Figure 2).

Sediment fractions contained fluoroquinolone in the following average concentrations: 4.4 μg/kg at Pfizer, 2.2 μg/kg at New London, 2.3 μg/kg at Groton, and 7.4 μg/kg at the Sub-base sites (Figure 3). Sediments sampled at the Pfizer and New London sites contained sulfamethoxazole at average concentrations of 33.8 µg/kg and 9.8 µg/kg, respectively. Sulfamethoxazole concentrations were below the limits of detection for sediments sampled from the Groton and Sub-base sites (Figure 3).

DISCUSSION

The purpose of this study was to investigate whether recalcitrant antibiotics are present in the Thames River, and compare the results to other rivers. Sulfamethoxazole concentrations in the surface and mid-depth water fractions ranged from 0.024 µg/L to 0.039 µg/L, which are similar to the values being reported in the relevant literature. For example, Hirsch et al. (1999) found median surface water sulfamethoxazole concentrations of 0.030 µg/L in the surface waters of six streams and rivers in Germany. Maximum concentrations of sulfamethoxazole in the German rivers were on the order of 0.480 µg/L (Hirsch et al. 1999). In the United States, Glassmeyer et al. (2005) reported median sulfamethoxazole concentrations of 0.069 µg/L in the surface water of ten sites downstream of wastewater treatment plants. Maximum sulfamethoxazole concentrations in U.S. rivers were on the order of 0.542 µg/L (Glassmeyer et al. 2005). Additionally, neither antibiotic was detectable in water samples from the Mystic River, which is less industrialized than the Thames. Low or undetectable concentrations of antibiotics in water fractions are not unreasonable as sewage effluents will be immediately diluted by river water upon exiting the outfall pipe. Other factors such as tides, vertical mixing due to differences in estuarine salinity and temperature, and recent rainfall could further affect the concentration of antibiotics in water samples taken at any given time. Additionally, although water fractions were centrifuged at 3220 x g for 15 minutes to remove humic matter, it is possible that a fraction of low molecular weight dissolved humics did not precipitate. If this was the case, then the reactive phenol and carboxyl groups could have bound to the antibiotics resulting in false negatives or unusually low concentrations.

To our knowledge, this manuscript represents the first work reporting antibiotic concentrations in marine aggregates. Fluoroquinolone concentrations ranged from 1.9 µg/kg to 799.9 µg/kg, and sulfamethoxazole ranged from 670.4 µg/kg to 3074.0 µg/kg in collected aggregates. These values are considerably higher than the concentrations detected in both the water fractions and the sediments, and could be the result of the scavenging of dissolved and particulate organic matter as flocculant material forms. As a result, marine aggregates could serve as an import mechanism for the bioaccumulation of antibiotics and other potentially harmful substances in suspension and deposit-feeding marine animals. Aggregates can be a pathway that allows suspension-feeding bivalves to ingest dissolved and microparticulate material (0.5-1.0 µm) that they would otherwise not be able to capture efficiently (Alber and Valiela 1996, Ward and Kach 2008). Ingestion of antibiotic-laden aggregates by bivalves could hold negative health implications for organisms higher up in the food chain, including humans.

Thames River sediments contained fluoroquinolone concentrations ranging from 2.2 µg/kg to 7.4 µg/kg, and sulfamethoxazole concentrations ranging from 9.8 µg/kg to 33.8 µg/kg. According to Kim and Carlson (2007), sulfamethoxazole was found in the sediments of the Cache la Poudre River in northern Colorado at a mean concentration of 1.2 µg/kg. The concentrations of antibiotics detected in the Thames River sediments are lower than those in aggregates, which is counterintuitive since recalcitrant drugs like sulfamethoxazole and fluoroquinolone should accumulate in sediments. It is possible the drugs are being diluted and carried away in the surface waters when the effluents first enter the river. Alternatively, aggregates that settle out of the water could be re-suspended by storm events. When the aggregates re-enter the water column, more antibiotics are scavenged, resulting in higher antibiotic concentrations than in the sediments. A final possibility could be the presence of other chemicals that are binding to or breaking down the antibiotics, so the drugs are not detected by the ELISA assay.

Beaber et al. (2004) utilized antibiotic concentrations ranging from 1 part per billion to 200 parts per million to induce the SOS response in *Vibrio cholera* and *Escherichia coli*, which are representative of concentrations used in a number of other studies (Goh et al. 2002, Miller et al. 2004, Maiques et al. 2006). In this study, the antibiotic concentrations in the water fractions were below those utilized by Beaber et al. (2004) to produce the SOS response in bacteria, however the concentrations detected in the aggregate and sediment fractions do fall within the requisite values to induce the SOS response. This indicates that bacteria in the Thames River may be exposed to antibiotic concentrations significant enough to induce transcription of antibiotic resistance genes.

The sampling protocol employed in this study provided only a 'snapshot' of the antibiotic concentrations in the Thames River, and may not be indicative of concentrations that could be present at different tidal periods or seasons. For example, antibiotic concentrations may be considerably higher when effluents are actively being released by the sewage treatment plants or during the winter months when the number of prescriptions of antibiotics may be higher. Therefore, a far more extensive sampling regime would have to be implemented in order to accurately describe the concentrations of antibiotics in the Thames River. Furthermore, other classes of antibiotics aside from the quinolones and sulfonamides may be present, and more sensitive screening assays may need to be utilized in order to measure the presence of antibiotics more precisely. Additionally, future studies should focus on whether antibiotic-resistant bacteria have evolved in the Thames River due to the low-level antibiotic concentrations detected.

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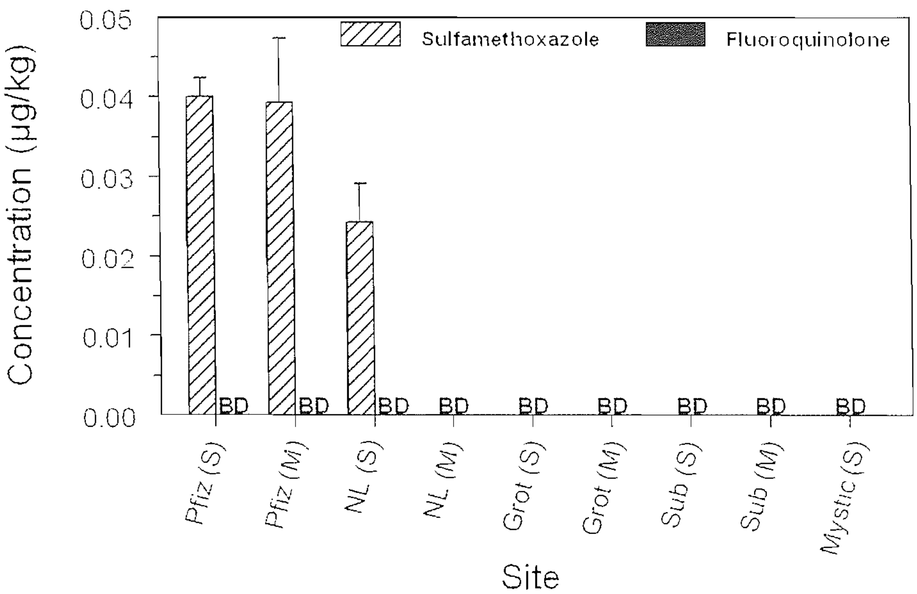

FIGURE 1. Antibiotic concentrations in surface (S) and mid-depth (M) water fractions of the Thames (Pfiz, NL, Grot, Sub) and Mystic Rivers (Mystic). Data are presented as means and range of 2 replicate samples. Site designations are: Pfiz = Pfizer, NL = New London, Grot = Groton, Sub = Sub-base (see text for details). BD = Below Limits of Detection.

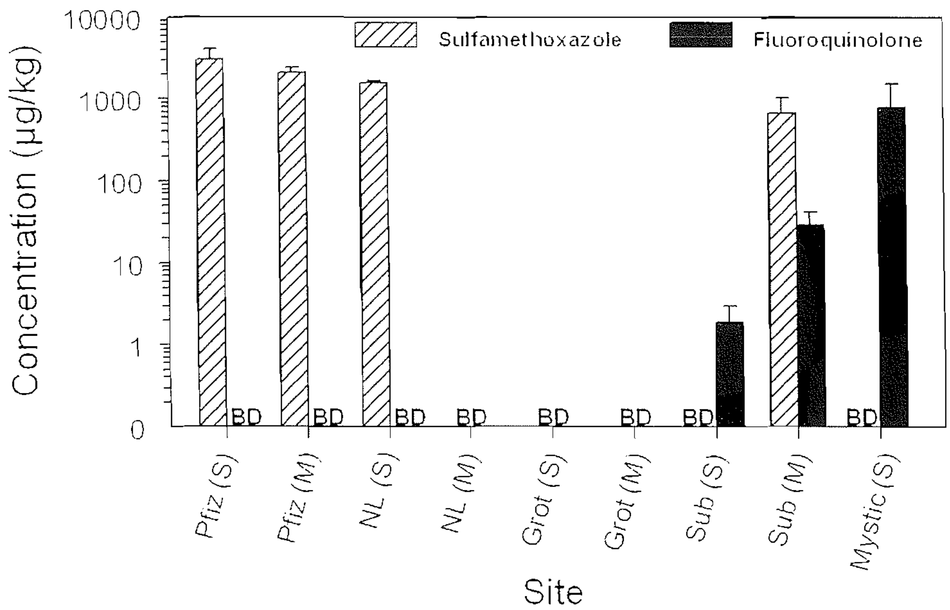

FIGURE 2. Antibiotic concentrations in extracts of aggregates collected in the surface (S) and mid-depth (M) waters of the Thames (Pfiz, NL, Grot, Sub) and Mystic Rivers (Mystic). Data are presented as means and range of 2 replicate samples. Site designations are: Pfiz = Pfizer, NL = New London, Grot = Groton, Sub = Sub-base (see text for details). BD = Below Limits of Detection.

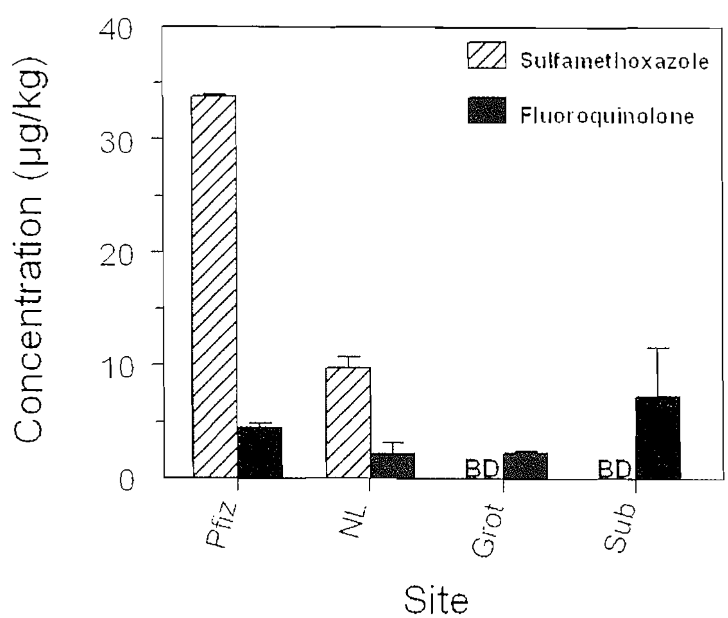

FIGURE 3. Antibiotic concentrations in extracts of sediments collected in the Thames River. Data are presented as means and range of 2 replicate samples. Site designations are: Pfiz = Pfizer, NL = New London, Grot = Groton, Sub = Sub-base (see text for details). BD = Below Limits of Detection.

Project *Limulus*: What Long Term Mark/Recapture Studies Reveal About Horseshoe Crab Population Dynamics in Long Island Sound

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ABSTRACT

Project *Limulus* is a long-term study of the population dynamics of the horseshoe crab population in Long Island Sound (LIS). We have tagged over 20,000 spawning adults from >20 beaches ranging from Greenwich to Stonington, CT since 1997. Cumulative recapture rates have reached 9%. On average 90% of the crabs are recaptured within a few miles of their original tag site within the first season. Between seasons, on average, 45% of crabs are recaptured within the same locality of where they were tagged. Of all recaptures, 99% of recaptured individuals are found within LIS. This past year we expanded the study into RI, NY, and MA collaborating with many groups for a regional horseshoe crab census. Preliminary findings reveal low spawning numbers compared to Delaware Bay across the region.

INTRODUCTION

The Atlantic horseshoe crab, *Limulus polyphemus*, inhabits the eastern coast of the United States ranging from the Yucatan Peninsula northward to Maine with spawning populations distributed intermittently along the coast (Anderson and Shuster 2003). The highest abundance and frequency of horseshoe crabs exists between New Jersey and Virginia centered on the Delaware Bay (Botton and Ropes 1987). Extensive research has been conducted on horseshoe crab populations residing around the Delaware Bay and the Southeastern United States (Rudloe 1980, Shuster and Botton 1985, Botton et al. 1988, Wenner and Thompson 2000, Smith et al. 2002) but no comprehensive regional work has been done for spawning populations in New England. In fact, until recently most data on existing horseshoe crab populations in New England were outdated (Shuster 1950, 1957, 1982, Baptist et al. 1957). While presenting important historical information on size distributions, spawning sex ratios and movement patterns within New England, these studies do not provide data relevant to spawning densities, survivorship, or recruitment.

The status of the Long Island Sound (LIS) horseshoe crab population is relatively unknown. Based on limited harvest data, the Atlantic States Marine Fisheries Commission (ASMFC) concluded that the western portion of LIS showed significant or marginally significant positive trends in population size while no trend was detected in eastern LIS (ASMFC 2006). However, the ASMFC also stated that overall indices for LIS have trended downward since their peak in the early to mid – 1990's and are at levels near or below those encountered in the mid-1980's. The only scientific evidence to support historic population levels in LIS are based on data collected from 1957-1962, and published by Sokoloff (1978) who estimated the population of horseshoe crabs in Cold Spring Harbor, NY to be ~30,000. More recent studies have focused on mating behavior (Mattei *et al.* 2007) and preliminary studies of population dynamics (Mattei, 2006).

Project *Limulus* is a community research endeavor whose participants tag and collect data on the population of horseshoe crabs that inhabit LIS. Participants learn the economic and ecological importance of horseshoe crabs to human health and the LIS ecosystem. Nonprofit environmental educational organizations, K-12 School groups, and undergraduate research assistants participate with the goal of promoting science literacy and monitoring the majority of LIS spawning beaches in Connecticut and New York. The goal of Project *Limulus* is to determine the population dynamics, migration patterns, and ecological links to other species in LIS. Started in 2003 and based at Sacred Heart University, Project *Limulus* participants have tagged horseshoe crabs that spawn on beaches along the Long Island Sound coastline during the spawning season. We also have some participants that utilize trawling to capture horseshoe crabs who then tag and release them (e.g. The Maritime Aquarium, SoundWaters). In 2008, Project *Limulus* started surveying spawning beaches to monitor spawning density. Here we present results from the long term mark recapture study and the initial data from the 2008 spawning surveys.

METHODS

Each year during the first full and new moon of May and June (+/- two days for weather), Connecticut beaches were surveyed for horseshoe crab activity on receding tides. Prior to 2007, encountered animals were tagged with a yellow Floy Cinch-up fish tag. Since 2007, encountered animals were tagged with a US Fish and Wildlife disc tag. Both tags did not harm the animals in any way and similar tagging methods have been used by researchers in New Jersey, Delaware, and Florida (Swan 2005). Data collected included prosoma width (PW) (straight-line measure in cm) and sex. Breeding individuals were noted, as were their mate's tag number. If more than one male was present, additional males were recorded as satellite males. Recaptured individuals were noted as to date, locality, and mate tag number if applicable. Each tag carries a unique specimen ID number, a contact phone number, and an email address. Therefore, some recaptures are called in by the public.

Spawning density was examined beginning with the first full moon of April and every full and new moon thereafter until mid July two hours after the highest high tide. Spawning surveys were conducted on multiple beaches by researchers and volunteers using a sampling protocol developed by James-Pirri et al. (2005). At each site, a coin flip determined the starting point of the survey (north vs. south end of site). The location of the first quadrat ($9m^2$)was randomly determined within the initial 10m of beach. All subsequent quadrats were systematically placed 10m apart (40 quadrats per site per survey). Each quadrat was located adjacent to the water's edge with the quadrat extending into the water. The number of horseshoe crabs with respect to mated pairs, mated pairs with satellite males, and solitary crabs (females and males) was counted within each quadrat. Previously tagged animals encountered within any quadrat were immediately recorded. Environmental conditions (weather, wave height, air/water temperature, and light levels) were recorded prior to the start of each survey.

RESULTS

Over 20,000 spawning adults from more than 20 beaches ranging from Greenwich to Stonington, CT have been tagged since 1997 (Figure 1). This past summer alone, project participants deployed 6, 272 federal disc tags. Our cumulative recapture rate is 9%. Cumulative recapture rates have reached 9%. The sex ratio of tagged crabs has remained fairly constant over the past ten years (Figure 2). Of all recaptures within one month, 75% of the crabs are found within a mile of their original tagging location (Figure 3). The percentage of crabs recaptured at their original tagging site declines over time. Of the crabs recaptured 5 months after tagging, 40% of crabs are found within a mile of where they were originally tagged. In addition, male and female horseshoe crabs appear to move east and west of the tag site with equal frequency. Of all recaptured individuals 99% are found within LIS.
Over 223 surveys were conducted across the Connecticut coastline during the 2008 spawning season covering 26 beaches. The seasonal spawning density of horseshoe crabs in Long Island Sound (measured as the number of mated females per meter squared) was on average 0.008 females/m^2. The highest seasonal spawning density (0.02 females/ m^2), averaged across 24 surveys, was found on Sandy Point in New Haven, CT. Notable spawning densities were recorded at Esker Point in Groton, Jordon Cove Beach in Waterford, Short Beach in Branford, and isolated beaches along Greenwich Point compared to other beaches (range 0.05-2.9females/m2) although these were restricted to one or two surveys. Spawning densities were typically higher during nighttime rather than daytime high tides. In general, the CT spawning density is three orders of magnitude lower than spawning populations reported from DE Bay although CT remains higher than Rhode Island or Massachusetts (Table 1).

TABLE 1. Median and range of spawning indices from Massachusetts, Rhode Island, Connecticut, and Delaware Bay (*Unpublished data from Alison Leschen and Mary-Jane James-Pirri; **Data from Smith *et al.* 2002)

	MA*	RI	CT	DE Bay**
Median Spawning Index (# mated females/m^2)	0.002	0.006	0.008	~1.0
Range	0-0.018	0-0.01	0-0.29	0.7-3.0

DISCUSSION

In general, horseshoe crabs tagged in LIS tend to remain in LIS supporting the idea of a LIS sound subpopulation. There is evidence from other studies indicating relatively closed populations in large embayment areas such as the Delaware and Chesapeake Bays (Swan, 2005). Site fidelity is rather strong within the spawning season. Three quarters of all crabs recaptured within 30 days of the original tag date were located at or near their original spawning beach. However, between spawning seasons, site fidelity decreases. Of the 40 percent of crabs that were recaptured at their original tag location, the majority were recaptured over non-consecutive years suggesting that horseshoe crabs may not spawn annually. Horseshoe crabs do cross LIS to the northern shore of Long Island and vice versa. Interestingly, the majority (> 95%) of crabs that were recaptured on the opposite side of LIS from where they were tagged were female. Sex ratios appear relatively constant although there has been a slight increasing trend in the number of males to females since 2003. However, sex ratios in LIS are on average 1 female to 1.7 males, far lower than DE's sex ratio of 1 female to 4.9 males (Swan, Hall, and Shuster, 2007).

Spawning densities in LIS are nearly three orders of magnitude lower than Delaware Bay. Surveys conducted across the CT coastline in 2008 reveal that horseshoe crabs tend to spawn in higher densities at night than during the day. However, there were a few exceptions for some beaches where night time surveys recorded lower densities than daytime surveys throughout the season. The surveys also indicated that horseshoe crabs in LIS tend to spawn on almost any type of beach including sand, mud, cobble, and in some cases reinforced seawalls. For example, spawning surveys in Bridgeport documented horseshoe crabs attempting to deposit eggs in extremely shallow depressions among concrete and asphalt pieces at the end of a street. Furthermore, surveyors watched as a few horseshoe crabs attempted to excavate a nest in grass at the top of a cobble seawall. Spawning success in poor quality beaches is likely to be low. Why horseshoe crabs spawn on these poor quality beaches is a mystery.

In conclusion, the tag data support the notion that horseshoe crabs in LIS remain in LIS with few exceptions. Sex ratios are skewed towards males but there is a lower ratio of males to females in LIS compared to DE Bay. Horseshoe crabs exhibit moderate site fidelity within a spawning season but site fidelity decreases over time. Spawning indices are significantly lower in LIS than in DE Bay.

ACKNOWLEDGEMENTS

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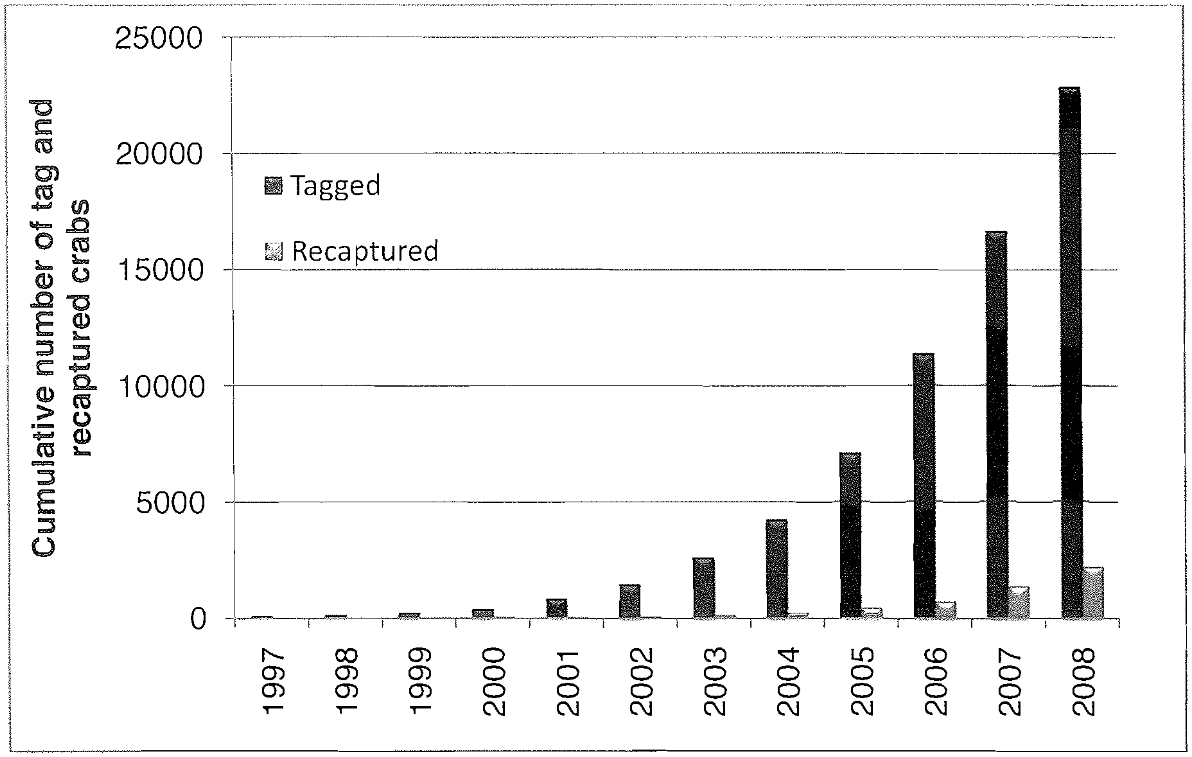

FIGURE 1. Cumulative number of crabs tagged and recaptured by Project *Limulus* Participants since 1997.

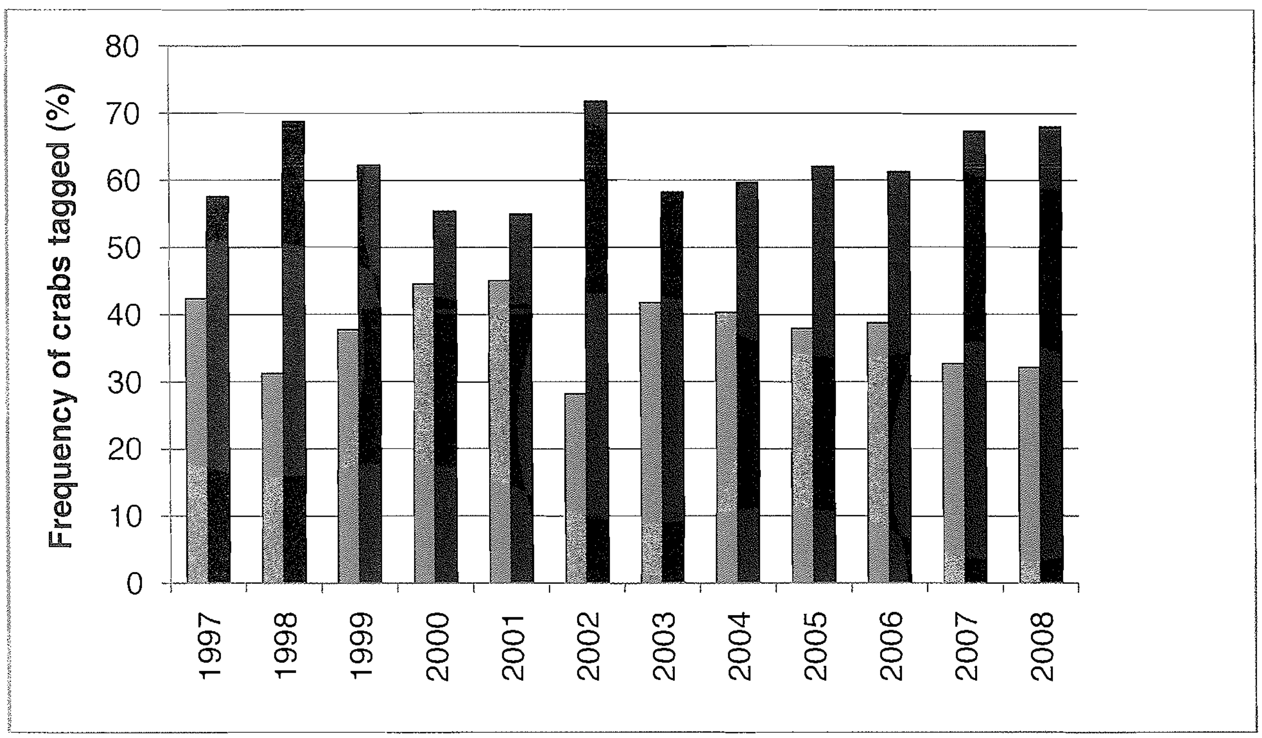

FIGURE 2. Number of crabs tagged by sex from 1997-2008. Gray indicates the percentage of females and black indicates the percentage of males.

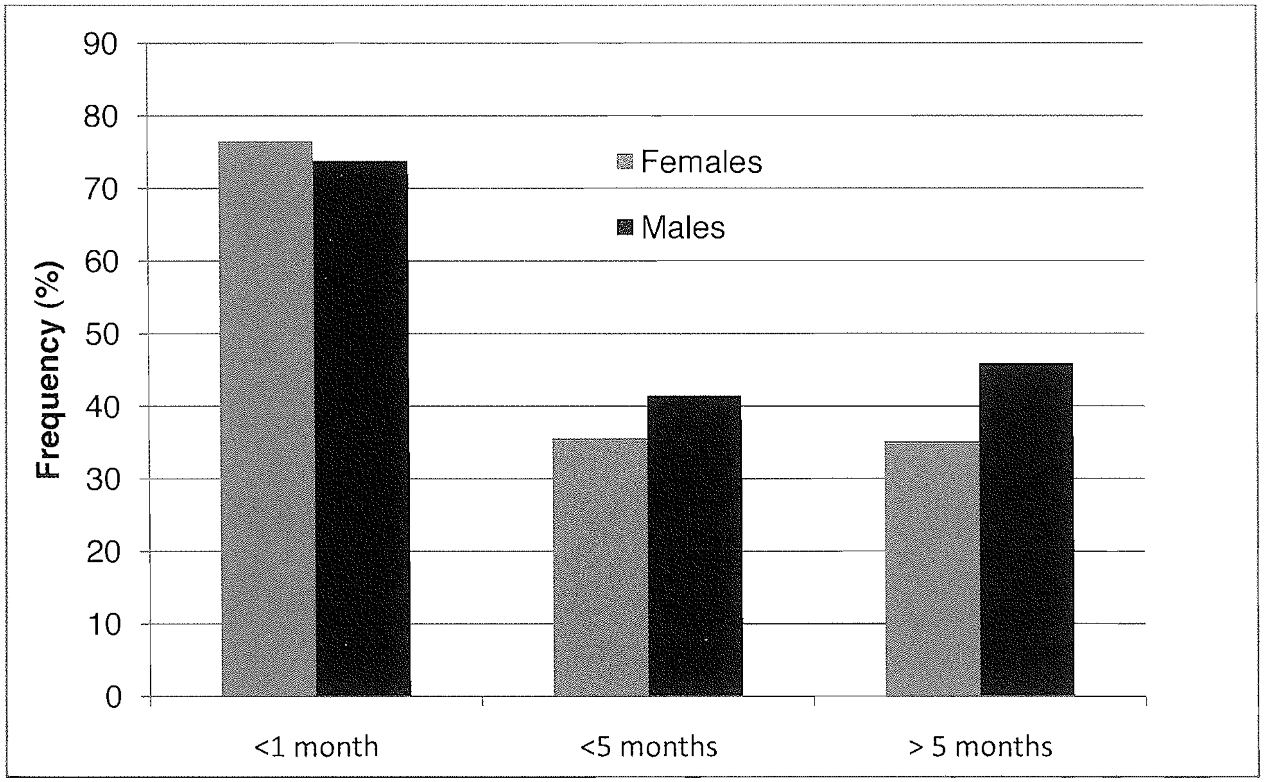

FIGURE 3. Frequency of crabs by sex that were recaptured at the same location they were tagged less than 1 month after tagging, less than 5 months after tagging, and greater than 5 months after tagging.

ABSTRACTS

The Sedimentary Record of Sulfur Cycling in Long Island Sound: Implications for Future Remediation Efforts

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Since the late 1700's, human activities have increased the delivery of nutrients to Long Island Sound causing increased rates of primary productivity and seasonal hypoxia. Increases in organic matter deposition rates can increase sulfate reduction rates and sediment sulfur burial rates, which in turn effects the pathways and rates of oxygen depletion, metal cycling, and pH. To document these changes in Long Island Sound, we present sediment geochemistry (organic C, total S, $\delta^{34}S$-pyrite) results from cores covering the last ~1200 years. From pre-colonial times to the late-1900s, sediment sulfur accumulation rates increased by a factor of 3-12 and pyrite $\delta^{34}S$ shifted towards more positive values by 11-23‰. In general, sulfur burial rates correlate linearly with organic carbon accumulation rates demonstrating that sulfur burial is limited by the availability of organic matter. These results illustrate that future remediation models should consider changes in sulfate reduction and sulfur burial rates.

Long Island Sound N Isotope Biogeochemistry

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Dated sediment cores show that the onset of eutrophication and increasing $\delta^{15}N$ began with urbanization of the LIS watershed in the mid-1800's. This ^{15}N enrichment can be caused by 1) higher $\delta^{15}N$ in sewage sources, 2) biological N removal in rivers, and/or 3) denitrification removal of nitrate in LIS proper. The isotopic composition of N sources to LIS as well as a seasonal study of the LIS water column has been carried out to distinguish between them. Summertime subsurface O_2 does not appear to become low enough and nitrate concentration not high enough to fuel significant denitrification. Instead high $\delta^{15}N$ values for WWTP effluent appears to be the primary source. The fall/winter increase in nitrate and its isotopic composition is presented as a case study. High $\delta^{15}N$ values confirm an ultimate source from WWTP plants but $\delta^{18}O$ of 2 to 3 ‰ shows production by nitrification occurring in LIS proper.

Inter-Annual Variations in Summertime Bottom Temperature and Bottom Dissolved Oxygen in Western Long Island Sound Over Six Decades

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Both long term trends and inter-annual variations in the seasonal evolution of bottom temperature and bottom dissolved oxygen is western Long Island Sound are described in light of a data set spanning the six decades 1946-2006. Variations in summertime thermal and haline stratification contribute to variations in vertical mixing which influences the vertical eddy flux of both heat and dissolved oxygen. Analyses point directly to the importance of meteorological forcing in controlling stratification and vertical mixing.

Numerical simulations support this result. They provide insight into the response of the water column structure in western Long Island to the combined effects of wind forcing and heating and cooling, and they provide estimates in the associated variations in vertical mixing.

State of the Sound: Water Quality Parameters and Planktonic Resources from 1988 to 2005

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Water quality parameters have been systematically monitored in Long Island Sound since 1988, starting with the Long Island Sound Study (1988-89) and later with the CT DEP Water quality Monitoring Program (1991-present). In these monitoring programs, data have been collected monthly or biweekly throughout the year at numerous stations through the Sound. In this presentation, we synthesize information from these monitoring programs to provide a view of the State of the Sound for the last two decades. We will highlight temporal and spatial trends for the period 1988-2005 on water quality parameters (temperature, salinity, nutrients and their stoichiometric ratios, dissolved oxygen, and chlorophyll) in the Sound. In addition, we will also examine changes in some water quality parameters, zooplankton and primary production in the central Sound from the 1950's to the present decade. We interpret the information in the context of the Comprehensive Management Program for the Sound.

What Controls Summertime Hypoxia in Long Island Sound?

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Hypoxia (dissolved oxygen concentration < 3 mg 02 L'I) is a pervasive summertime feature in bottom waters of western Long Island Sound, LIS. Using data from the water quality monitoring programs in the Sound (1988-2005), we examined the relative importance of temperature, nutrients and vertical stratification in determining both the concentrations and rates of change of dissolved oxygen in western LIS. Multiple regression analysis indicates that temperature is the dominant factor for oxygen concentration. Similarly, the temporal oxygen depletion rate is significantly correlated to the temporal rate of change of the vertical density gradient and temperature. In addition, high frequency studies as part of the Long Island Sound Integrated Coastal Observing System (LISICOS) reveal short-term (3-7 days) ventilation events driven by vertical mixing. Hence, hypoxia appears to be mostly controlled by physical factors. An implication is that despite aggressive efforts to reduce nutrient loadings, future climatic scenarios must be considered in the management of hypoxia the Sound.

Controls on the Formation of Bottom Water Hypoxia in WLIS: A Laboratory Experiment

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The goal of this research was to investigate how the interaction of various environmental factors influences the release of ammonia and/or sulfides from WLIS sediments. It is critical to understand these factors, as both ammonia and sulfide have been implicated in hypoxic water formation and fisheries deaths. Proper management of the fisheries resources of Long Island Sound cannot occur without such information.

A series of controlled laboratory experiments was conducted utilizing sediments collected from three stations located in WLIS . Sediments were subjected to a combination of temperature, dissolved oxygen. plankton, and bioturbation. Triplicate samples were taken every 6-8 hours throughout the week-long experimental run. The results of the analyses were analyzed using NCSS software.

The results of this work demonstrate that temperature, dissolved oxygen, and the addition of plankton are driving factors behind sulfide and ammonia release from WLIS sediments. The study also suggests that sediment organic content further influences such release.

This work is the first to clearly demonstrate the relationship between these factors and the formation of hypoxic bottom waters in Long Island Sound.

Subtidal Variability of Dissolved Oxygen in Western Long Island Sound

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A simple model of the subtidal budget of dissolved oxygen in estuaries is developed and applied to observations in western Long Island Sound. The goal is to analyze the causes of hypoxia and develop a predictive capability for its onset and duration by estimating mixing coefficients and comparing simple models of their temporal variability. A single-segment lower-layer box-model for western Long Island Sound is developed. The lower layer oxygen budget is influenced by a mean advection toward the west, horizontal dispersion, vertical mixing, and pelagic and benthic respiration. Inverse methods and eight years of fortnightly ship surveys of salinity, temperature and dissolved oxygen throughout the water column at seven stations along the axis of western Long Island Sound are used to estimate parameters and evaluate the model performance. We find a subsurface respiration rate of 3.6 ± 0.6 mM/m^3/day and a vertical mixing rate of 0.23 ± 0.04 cm^2/s. A forward model is used to test whether the estimated mixing and respiration can be used to predict temporal variation of mean lower layer DO using DO data at one boundary station and temperature data elsewhere. This approach can assist efficient monitoring of estuarine DO levels.

Anoxia in the Thames River: Observations in Norwich Harbor

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Norwich Harbor is located at the head of the Thames River, the third largest drainage basin to the Long Island Sound. Anoxic bottom-water conditions in Norwich Harbor is a phenomenon that has been documented during previous summers, but the evolution and variability of the low-oxygen levels have not been effectively shown through observations. Developing a further understanding of these conditions may help explain seasonal ecosystem shifts in the Thames River and Long Island Sound. An observational program was initiated in June 2008 to study the stratification and oxygen levels in Norwich Harbor. Daily vertical profiles of temperature, salinity, and dissolved oxygen paired with monthly tidal cycle monitoring provide new insight to the pattern of the anoxic and hypoxic conditions that are present in the harbor during the summer months. One observed pattern is the sudden recovery of dissolved oxygen once every month which may be related to tidal cycle variations.

The Physical Oceanography of Long Island Sound

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In Long Island Sound the freshwater from the rivers of Connecticut mix with the ocean water that enters through The Race and the brackish water that is transported through the East River. Most mixing is accomplished by the interaction of the tidal currents and the topography and this largely determines the distribution of heat and salt in the Sound. The resultant density distribution also drives the circulation which is difficult to resolve in observations. A Significant motion is a consequence of wind. There is a direct effect of the wind over the Sound but it also causes sealevel changes at the ocean boundaries. We summarize the results of recent analyses of observations and models that describe the hydrographic structure of the Sound and the structure and variability of the circulation.

Modeling Overtides in Long Island Sound

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Long Island Sound is a complex estuary with a bathymetry that leads to nonlinear interactions. These nonlinearities generate tidal velocity oscillations at frequencies that are higher than, and multiples of, the main semidiurnal forcing frequency. Known as overtides, these higher frequency interactions can create a time-averaged transport and are not very well understood due to the complex mechanism of their generation. Using a numerical evaluation of an analytic model, the unique overtides in western Long Island Sound are evaluated and it is shown that a one dimensional model with time invariant eddy viscosity cannot accurately reproduce these overtides.

Tidal and Residual Circulation in Long Island Sound

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A three-dimensional numerical hydrodynamic model for Long Island Sound is applied to examine the spatial structure of the tidal and residual circulation in the basin, and the dynamics controlling the longitudinal and lateral circulation. At tidal periods, the longitudinal momentum balance involves local acceleration, barotropic pressure gradient, and stress divergence; the lateral momentum balance involves local acceleration, barotropic pressure gradient, and Coriolis acceleration, with some contribution from the baroclinic pressure gradient at depth. Tidal period lateral circulation is driven primarily by the imbalance between barotropic pressure gradient and Coriolis acceleration. The residual longitudinal momentum balance involves primarily longitudinal advection and the total longitudinal pressure gradient. Results indicated that residual longitudinal advection arises from the interaction of tidal period lateral motion and lateral gradients in longitudinal tidal currents. The residual lateral momentum balance is essentially geostrophic. Features of the simulated tidal period and residual current structure compare favorably with those features derived from available ADCP current observations in the central Long Island Sound.

Lateral Structure and Daily to Seasonal Variability of Eastern Long Island Sound Near-Surface Temperature, Salinity, and Chlorophyll

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Lateral (across-estuary) structure of temperature and salinity at an estuary mouth are important to estimates estuary-ocean heat and salt exchange; the same applies for primary producers and other suspended materials. In Eastern Long Island Sound lateral structure may be pronounced due to complex geometry, yet remains poorly known. From mid-June 2005 through August 2006, across-estuary (New London to Orient Point) transects of temperature, salinity, and Chlorophyll fluorescence a few meters deep were collected nominally 8 times daily from the ferry M/V John H (www.gso.uri.edu/foster) and mapped to 18 fixed sites 1 km apart. Transect-wide, the temperature progressed regularly between 3-5 C and 20-25 C in winter and summer; salinities were typically between 22 and 30 PSU, with minima in Oct-Nov 2005 due to an unusually wet autumn, and marked responses to river runoff on several-day timescales; Chlorophyll varied strongly on day-to-week timescales centered on the range of 0.5-3 □g/l in non-winter months and 0.3-1.0 □g/l from about Oct 2005 to Jan 2006, suggesting an annual cycle of irregular population growth as opposed to a spring bloom. Relative to northern sites, at southern sites temperatures were 3-5 C warmer in summer and 1-2 C cooler in winter; salinities were 2-4 PSS fresher year-round; and Chlorophyll was typically 1-3 □g/l higher. Each observed lateral (north-south) gradient parallels a large-scale gradient along the estuary axis (east-west) and implies water at southern sites originates farther to the west, as consistent with the observed peak in the south of the eastward residual flow out of the estuary. Implications of the lateral structure will be discussed, for example field sampling design to estimate suspended material flux, and siting of monitoring buoys.

The Seasonal Cycle of Thermohaline Circulation in Long Island Sound

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Simulations involving the assimilation of CTDEP hydrographic data are used to describe the seasonal evolution of the temperature, salinity, the associated density stratification, and residual Eulerian current fields throughout the basin. The model results highlight a pool of cold, dense water residing in the deep area of the central Sound which persists through the spring, until it is replaced by an intrusion of warm, saline water over Mattituck Sill in early summer.

The model results are also used to quantify the seasonal variations in the transport of volume, salt and heat through Long Island Sound, and the exchange with both Block Island Sound and New York Harbor. Analysis of the eastward and westward directed volume transports show that exchange increases during the stratified summer months. The net transports of salt and heat are decomposed to determine the relative contributions of different physical mechanisms.

A Study on River Discharge and Salinity Variability in the Long Island Sound and Middle Atlantic Bight

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This study investigates the seasonal to decadal variability of Long Island Sound (LIS) river discharges, LIS surface salinities, and Middle Atlantic Bight shelf surface salinities. Wavelet analysis is used to obtain power estimates at each period. Correlations among river discharges and salinities are calculated for high-pass (T :s 1.5 years), band-pass (1.5 years < T < 10 years), and low-pass (T ~ 10 years) time series. Correlations with standard climate indices also are examined. River discharges and surface salinities have strong annual cycles that are statistically distinguishable from background noise. Interannual peaks in the discharge and salinity power spectra are evident. Some rivers exhibit significant decadal variability. There are strong correlations among discharge records at all frequencies. Annual and interannual variability of estuarine and shelf salinities have significant positive correlation with each other and negative correlation with river flow. There is little evidence of significant correlation with climate indices.

Establishing the Dynamics and Causes of *Alexandrium fundyense* Blooms, Cysts, and Saxitoxins in Long Island Sound

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Paralytic shellfish poisoning (PSP) caused by dinoflagellates in the genus *Alexandrium* is a serious environmental and health issue in coastal waters around the world. Saxitoxin-producing *Alexandrium fundyense* cells have been detected within Long Island Sound (LIS) for nearly three decades. We compared the densities and dynamics of *Alexandrium fundyense* and PSP events in LIS during the 1980s to events which occurred during 2007 and 2008, focusing on harbors along the north shore of Long Island. Densities of *Alexandrium fundyense* during the 1980s and 2007 were similar. However, an unprecedented PSP event in the Northport–Huntington Harbor system lead to the closure of more than 7,000 acres of shellfish beds in 2008. The PSP event was caused by an *Alexandrium fundyense* bloom which persisted for more than two months and achieved densities of more than one million cells per liter. Saxitoxin concentrations and bloom causes will also be discussed.

Detection of Organic Contaminants in the Thames River Estuary Using Passive Sampling Methods

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Measuring contaminants in marine systems is a challenge due to the nature of discrete sampling and the large water volumes that typically need to be extracted. Currently our ability to detect organic contaminants in coastal systems is limited by these laborious techniques and limits chemical monitoring in observing networks. Passive sampling requires no external energy and allows the determination of accurate time weighted average or equilibrium concentrations. Passive sampling devices often mirror bioaccumulation rates in marine biota and can be a useful tool when determining toxicological effects on the local ecosystem. As passive samplers are fairly inexpensive, easy to use, and small in size, they provide a cost effective alternative to conventional grab sampling methods or large volume water extractions currently in use in most long term water quality monitoring programs. Polymer Coated Glass Fiber Filters (POGs) and Organic Rapid Equilibrating (ORE) samplers were deployed in the bottom waters of the Thames River Estuary in Connecticut. Here we present data derived from the Thames River Estuary in August 2006 and October 2007 using rapid equilibrating passive sampling methods.

Impacts of Physiography and Anthropogenic Activity on Accumulation of Organics and Heavy Metals in Western Long Island Sound Sediments

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The western end of the Long Island Sound estuary borders metropolitan New York, and is severely impacted by anthropogenic activities. To understand the temporal and spatial distributions of pollutants and organic matter, we surveyed the area from the R/V Hugh Sharp in the summer of 2006. We collected high-resolution subbottom seismic profiles, multibeam bathymetric data and 25 gravity cores. The acoustic images revealed a narrow and sinuous channel partly flanked by bedrock, and areas of sediment deposition. The total organic matter and heavy metal contents measured in the sediments confirm that their concentrations increase towards New York City and that they are greatest in post-industrial times. The data also reveals that sediment accumulation is episodic and that there are only a few areas of continuous sedimentation. The overall funnel shape, bedrock constrictions, and the limited connection to the East River due to the narrow, shallow sill of Hell Gate have most likely influenced the effects of physical processes (storms, waves, tidal currents) and the regions from where sediment is eroded and deposited.

Integrating Multi-Temporal Spectral and Structural Information to Map Wetland Vegetation in a Lower Connecticut River Tidal Marsh

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This study examines the effectiveness of using multi-temporal satellite imagery, field spectral data, and LiDAR top of canopy data to classify and map the common plant communities of the Ragged Rock Creek marsh, located near the mouth of the Connecticut River. Visible to near-infrared (VNIR) reflectance spectra were measured in the field over the 2004–2006 growing seasons to assess the phenological variability of the dominant marsh plant species, Spartina patens, Phragmites australis and Typha spp. Phragmites was best distinguished from other species by its high NIR response late in the growing season. Typha spp. had a high red/green ratio and S. patens had a unique green/blue ratio relative to other species throughout the bulk of the growing season. The field spectra and single date (2004) LiDAR canopy height data were used to define an object-oriented classification methodology for the three plant communities in multi-temporal QuickBird multispectral imagery collected over the same time interval. The classification was validated using an extensive field inventory of marsh species. Overall maximum fuzzy accuracy for the classification was 97% for Phragmites, 63% for Typha spp. and 80% for S. patens meadows and improved to 97%, 76%, and 92%, respectively, using a fuzzy acceptable match measure. This study demonstrated the importance of the timing of image acquisition for the identification of targeted plant species in a heterogeneous marsh. These datasets and protocols may provide coastal resource managers, municipal officials and researchers a set of recommended guidelines for remote sensing data collection for marsh inventory and monitoring. See also doi:10.1016/j.rse.2008.05.020

Nutrient Effects and Marsh Drowning in Long Island Sound

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In an effort to understand possible linkages between nutrient loading and marsh drowning, we have been fertilizing salt marsh plots at Hoadley Creek in Guilford, CT for the past 4 years. Results so far indicate that while N fertilization leads to higher aboveground productivity, the effects of nutrients on belowground productivity at our site are not significant. Soil respiration appears to be positively affected by both N and P addition. However, sediment elevation table (SET) data give no indication that fertilization has led to relative elevation loss. Our results to date suggest that nutrients are unlikely to play an important role in marsh drowning in Long Island Sound. Comparison of Hoadley Creek to two other marshes (a restoring marsh at Jarvis Creek and a drowning marsh at Sherwood Island) support this conclusion and suggest that sediment starvation may play a role in drowning at Sherwood Island.

Changes in the Charles E. Wheeler Wildlife Refuge Salt Marsh in Milford, Connecticut

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The Charles E. Wheeler Wildlife Refuge, located at the mouth of the Housatonic River in Milford, CT, is a dynamic coastal marsh. The marsh, divided by a spit, is eroding in the back while the front marsh is accreting. Jonas and Cuomo (2003) determined the factors responsible for the marsh accretion. This study builds upon their work by documenting rates of change in both marsh areas. Marsh patches in both areas were demarcated using a Trimble GPS and then compared to previous maps and aerial photographs using ArcGIS software. Ongoing sediment trap experiments will further characterize the erosion patterns in the back marsh. Work completed thus far demonstrates substantial increase in marsh coverage in the front marsh since 2003, while the back marsh shows evidence of erosion relative to historical extent. Such information is needed if managers are to effectively predict the effects of climate change on coastal areas

Benthic Habitat Mapping in Long Island Harbors and Bays

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We are conducting benthic habitat surveys and related benthic biotope characterization studies in Port Jefferson Harbor, Huntington and Northport Bays, and Cold Spring Harbor - Oyster Bay along the south shore of Long Island Sound. Information on the character and distribution of benthic habitats in these coastal environments is necessary for understanding the biological importance of different habitats, an essential component of ecosystems-based management. In these studies we are characterizing the sediment surface using high-resolution acoustic mapping techniques (multibeam bathymetry and backscatter along with side-scan sonar imaging) and then sampling for sediments and benthic fauna based on the observed acoustic patterns. The acoustic, grain-size, and faunal patterns are then analyzed statistically to characterize benthic biotopes. Pronounced changes in acoustic backscatter were found throughout these areas, and grain-size and faunal assemblages corresponded well with observed backscatter patterns. All three areas studied had moderately diverse faunal assemblages, but both species richness measures and the dominance of opportunists suggested that stressors were present.

An Ecopath Food Web Model for Long Island Sound

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Understanding food web structure and dynamics of ecological systems is a key element in developing more effective environmental assessment and management procedures. Although various components of the Long Island Sound (LIS) ecosystem have been studied in detail, a framework for food web research has been lacking. In this study, we a) collected and reviewed data available in the scientific literature and technical reports on food web components and interactions in LIS; b) using this and other data, constructed an Ecopath, mass balance food web model for LIS; and c) assessed food web and ecosystem properties based on the model and implications for future work and management. We reviewed over 2,200 journal articles and reports and found a significant lack of LIS-specific data that can be used for food web model development (i.e. biomass, production, consumption, diet composition), particularly for inshore waters, bays and rivers, and also for many taxonomic groups. The Ecopath model developed focused on the offshore, deeper water habitats of LIS and was comprised of 32 trophic functional groups / taxa. Analyses of the food web indicate that there is a high diversity of interactions among the functional groups, however there are generally two to three links among successive trophic levels within the web which is common to other systems. Efficiencies in trophic transfers from one level to the next were low at low trophic levels but increased with increasing trophic level. Comparison of network flow metrics to other estuarine systems suggests that food web dynamics in Long Island Sound may differ on several accounts from these other systems. However other aspects of network dynamics were similar. Examples of applications of the model and suggestions for future work are presented.

Marine Aggregates Facilitate Ingestion of Nanoparticles by Suspension-Feeding Bivalves

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The promise of nanomaterials for science and technology is great, but the ecotoxicological risks may be equally large. Recent studies on a few fish and invertebrate species have provided some data which suggest that harmful effects are possible. The way in which nanoparticles are taken up by aquatic organisms, however, has been little studied. We examined uptake of nanoparticles by two species of suspension-feeding bivalves, the mussel (*Mytilus edulis*) and the oyster (*Crassostrea virginica*).

Most suspension-feeding bivalves capture particles < 1 µm with a retention efficiency of < 15%, leading to the assumption that nanoparticles can not be ingested in large numbers. During certain times of the year, however, > 70% of suspended particles are incorporated within aggregates that are > 100 µm in size. Therefore, we delivered bivalves fluorescently labeled, 100-nm polystyrene beads that were either (1) dispersed, or (2) embedded within laboratory-generated aggregates. Results indicate that aggregates significantly enhance the uptake of 100-nm particles. Nanoparticles had a longer gut retention time (> 72 hours) than 10-µm polystyrene beads, and accumulated in the gut and digestive gland. Our data suggest a mechanism for significant nanoparticle ingestion, and have implications for toxicological effects and transfer of nanomaterials to higher trophic levels.

The Nearshore Fish Community of Milton Harbor, NY Over the Last Decade

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The finfish community of a tidal marsh in Milton Harbor, NY was sampled by beach-seine in 1991 and 1992 (McEnroe et al., 1995) and environmental parameters (water temperature, DO, salinity, tide level) monitored. We repeated the study in 2002 and 2004. Eleven species were collected in 1991, 12 in 1992, 16 in 2002, and 14 in 2004. Both the number of species and fish abundance peaks in Aug.-Sept. and correlates with increased seasonal water temperature. The killifishes and silversides were dominant in all years. Five species were collected in the 1990's but not 2004. Conversely, five others were found in 2004 but not in the 1990's. While both adult and juvenile killifish and silversides were present, most fish collected (75-100%) in each seine were juveniles illustrating the importance of this habitat as a nursery area. Further data on fish abundance and changes between the 1990's and 2004 will be discussed.

Project *Limulus*: What Long Term Mark/Recapture Studies Reveal About Horseshoe Crab Population Dynamics in Long Island Sound

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Project *Limulus* is a long-term study of the population dynamics of the Horseshoe Crab population in Long Island Sound (LIS). We have tagged over 20,000 spawning adults from >20 beaches ranging from Greenwich to Stonington, CT since 1997. Cumulative recapture rates have reached 9%. On average 90% of the crabs are recaptured within a few miles of their original tag site within the first season. Between seasons, on average 45% of crabs are recaptured within the same locality of where they were tagged. Male and female horseshoe crabs appear to move east and west of the tag site with equal frequency. Of all recaptures 99% of recaptured individuals are found within LIS. This past year we expanded the study into RI, NY, and MA collaborating with many groups for a regional horseshoe crab census. Preliminary findings reveal low spawning numbers compared to Delaware Bay across the region.

Assessing Bait Worm Packaging as a Potential Vector of Invasive Species to Long Island Sound

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The ecological and economic health of Long Island Sound (LIS) currently is being threatened by introductions of invasive species. This project is researching the potential for the seaweed packaged with bait worms to be a vector of invasive algae to LIS. Oftentimes, this seaweed is discarded into the Sound and any spores of non-native species included may then be introduced into the water. Bait is purchased from several commercial vendors in Connecticut and New York. Subsamples of the seaweed are placed in culture, and growth of associated macro- and micro-algae is monitored. Microscopic analyses on general algal composition and molecular analyses for specific micro-algal species sequences are conducted. Data collected thus far indicate that no non-native seaweeds are likely being introduced through this method. Two species of toxic micro-algae have been found with molecular techniques. Findings are expected to guide future management control of bait worms and appropriate disposal methods.

Population Dynamics and Reproductive Phenology of the Invasive Rhodophyte *Grateloupia turturu* in the Long Island Sound

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Grateloupia turuturu is a large, non-native rhodophycean alga first discovered in Narragansett Bay, and now spreading into Long Island Sound. We report population dynamics from three distinct sites; a thermally impacted, unstable cobble beach, a thermally impacted, stable rock platform (both at Millstone Point, CT), and a rocky shore population at Avery Point, CT. At the unstable cobble site, neither *G. turuturu* nor *Chondrus crispus* showed any periodicity in cover. At the stable substrate site *C. crispus* has dominated through 2008, occupying up to 75% of the substrate, compared with a maximum of 5% cover of *G. turuturu*. At the thermally unimpacted site, *C. crispus* is also dominant. *G. turuturu* tetrasporophyte densities show clear phenology, with maxima (450 mm^{-2}) during February and March. Cystocarp densities are aperiodic (ca. 3 mm^{-2}), though carpospore release appears to occur between June and October. *G. turuturu* populations may expand; reproduction ensures steady propagule pressure.

POSTERS

Temporal and Spatial Distributions of Benthic Forminifers in Western Long Island Sound

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Benthic foraminiferal assemblages were studied in western Long Island Sound from two cores recovered by the R/V *Hugh Sharp* in 2006. The goal was to understand their spatial and temporal distributions to assess the impact of anthropogenic activities such as pollutants and organic matter loading on their ecosystem. Benthic foraminifers *Elphidium spp.*, *Buccella frigida,* and *Ammonia beccarii* were identified and counted. *Elphidium spp.* dominated the assemblages but is most abundant to the west. B. *frigida* occurs at similar intervals as *Elphidium spp.* In both cores, *A. beccarii* appears in the upper 50 cm where the abundance of *Elphidium spp.* and *B. firgida* decreased. These patterns are correlated to an increase in organic matter contest, lead (Pb) concentrations, and a peak in the magnetic susceptibility signal indicating that the temporal changes in formininferal distribution resulted from environmental stresses. The low diversity in the foraminiferal assemblages is not related to anthropogenic activities but to normal estuaruine conditions.

Optical Characterization of Long Island Sound and Implications for Remote Sensing

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Water column optical properties are proxies to significant biogeochemical water quality parameters such as phytoplankton biomass, suspended sediments, particle size distribution and dissolved carbon. Remotely sensing optical properties from space would provide regular synoptic estimates of these parameters in surface waters of Long Island Sound (LIS) at spatial resolution of <1 km^2. In optically complex waters like LIS, standard methods for retrieving chlorophyll concentrations are inaccurate due to the influence of colored terrigenous material (e.g., sediments and chromophoric dissolved material, CDM). We are engaged in developing and parameterizing more complex semi-analytical approaches to account for the heterogeneity of optical properties in these waters. As part of that effort, we have collected bio-optical field data throughout LIS from various seasons. Long Island Sound is characterized by moderately high phytoplankton concentrations (Chl 1-45 μg/L) increasing toward to the west, and exhibits strong localized influence by riverine delivery of CDM and suspended sediments, however winds, tides, and subtidal estuarine circulation redistribute optical constituents in ways which are still poorly understood. Nevertheless, optical remote sensing algorithm parameters such as backscattering ratio (0.9% ± 0.16%), exponential CDM absorption spectral slope (0.0146 ± 0.0014), and powerlaw particulate attenuation spectral slope (0.475 ± 0.061) exhibit low variability outside of immediate riverine influence. Consistency in these parameters minimizes the necessity for sub-regional "tuning" of retrieval algorithms, thereby enhancing algorithm robustness and retrieval accuracy.

Promoting Best Management Practices for Marine Anglers Using Baitworms

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Marine polychaetes (e.g., *Nereis virens, Glycera dibranchiata)* are used by marine anglers as live bait. The worms are packed in flats with seaweed (usually the brown macroalgae *Ascophyllum nodosum*), and shipped over the U.S. Researchers examining the contents of baitworm boxes determined that other living algae, fungi, invertebrates, and microalgae are present. Anglers, disposing of the seaweed in the water, may introduce species that could become invasive and harmful. A 2008 public outreach campaign initiated by the Northeast Sea Grant Programs involved the posting of multi-lingual signs at boat ramps, bait shops, and coastal town halls asking marine anglers to dispose of unused worms, seaweed, and cartons in the trash, not in the water. Connecticut Sea Grant and Connecticut Department of Environmental Protection are collaborating on a complementary pilot with volunteer bait shops to place similar stickers on bait boxes at point-of-sale. A post-season follow-up evaluation is planned.

Management for *Liatris scariosa* var *novae-angliae* in a Coastal Meadow

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Liatris scariosa var. *novae-angliae* (New England Blazing Star) is a state-listed plant occurring in sand plains and coastal habitats. The species occurs in a 4 acre coastal meadow in Old Saybrook , CT managed by the Lynde Point Land Trust (LPLT). The meadow was rapidly filling in with shrubs in spite of annual mowing. The population in 2005 was 460 plants. With funding from the Natural Resources Conservation Service, the LPLT has undertaken a management regime focused on shrub removal and late fall mowing. For the past two years, shrubs were sprayed with an herbicide in the late fall with mowing in early winter. In the fall of 2007, there were 3, 399 plants indicating at least the short term effectiveness of this management regime. *Liatris* plants will be counted and density determined in the fall of 2008 and shrub regrowth assessed to determine if further herbicide treatment is necessary

Benthic Ecological Investigations in Western Long Island Sound: Benthic Invertebrate and Shellfish Population Assessments in and Around Sheffield Harbor, Norwalk, CT

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From January 2007 to the present, benthic biological and shellfish sampling surveys have been conducted in and around the Sheffield Harbor area as part of a larger study designed to not only assess the environmental and biological characteristics of the area, but also assess potential environmental impacts that may result from the removal and replacement of several underground power cables running from Norwalk, CT to Long Island, NY. The seven power cables to be replaced occupy an area about 1500 feet wide. The primary objectives of this investigation are to: (1) document the benthic biological characteristics of the cable corridor before, during and after the construction activity, (2) monitor the health and viability of the shellfish population by using calibrated oysters, and (3) to conduct shellfish resource surveys in the cable corridor before and after the construction activities. We will present preliminary findings of data collected prior to the construction activities.

Detection of Antibiotics in the Thames and Mystic Rivers

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Wastewater facilities have few methods for removing antibiotics from effluents prior to their release into aquatic ecosystems (Alvarez 2004). The Thames River has several point sources of antibiotics including two water treatment facilities. Water, aggregates, and sediments were obtained from four sites along the Thames, in addition to water and aggregates from one site on the Mystic River. ELISA tests revealed the presence of fluoroquinolone in the aggregates and sediments ofall Thames sites, as well as surface water and aggregates from the Mystic River. Sulfamethoxazole was detected in some water, aggregate, and sediment fractions of the Thames, but was absent in Mystic River samples. Low-level antibiotic concentrations have been found to increase expression ofbacterial plasmids containing antibiotic resistance genes (Beaber 2004). Future tests will focus on how chronic, low-level antibiotic exposure affects the microbial community and physiology of bivalves, and its potential impact on human health and disease.

The Residual Current Flow in Western Fishers Island Sound

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The exchange flow between Long Island Sound and Fishers Island Sound is not well documented and no long-term current measurements exist. To this end, current data have been collected for the first time in western Fishers Island Sound over a 6-month period from March to September 2008, using a bottom-mounted, upward-looking ADCP. This platform also included an acoustic telemetry system to relay the in-situ current measurements to a nearby surface buoy, and subsequently to shore via cellular modem in real-time. These data reveal a mean northwest flow of approximately 6 cm s^{-1}. The near-surface measurements deviate significantly from the mean, and may be primarily wind-driven. This strong residual flow suggests Fishers Island Sound may significantly influence Long Island Sound waters.

Tidal Currents and Friction over Large Marine Sand Waves in Eastern Long Island Sound

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Sand wave fields are unique bathymetric structures. Marine sand waves form on sand bottoms that are exposed to strong tidal currents. Sand waves in the eastern Long Island Sound study area range from 7 to 17 m in height and from 77 m to 164 m in wavelength. This research investigates how tidal currents, bottom friction, and mixing are modified over this large marine sand wave field. Observations were collected with shipboard and moored Acoustic Doppler Current Profilers (ADCP) and Conductivity Temperature Depth (CTD) profilers during spring of 2008. Preliminary results have revealed several interesting findings. Near-bottom tidal currents tend to channel water in the troughs; these currents are skewed to the surface tidal current direction. The tidal shear stress is strong over the sand wave field and the shear reaches the water surface. This indicates strong mixing. The CTD data show there is strong stratification despite the strong mixing.

Factors Controlling Bottom Dissolved Oxygen in Long Island Sound

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The primary factor controlling the bottom DO changes spatially and temporally. For non-summer seasons, bottom DO is strongly associated with water temperature. During summer, for the westernmost and shallow stations, density stratification controls bottom DO. In deep stations stratification does not seem to control bottom oxygen availability. West of the Central Basin, bottom DO continues to decrease during summer until it reaches its minimum when bottom temperature is around 19~20 °C. The recovery of bottom DO at the beginning of fall is fast, but surprisingly not necessarily associated with increase in the wind speed. This leads us to hypothesize that the DO recovery may be a manifestation of either reduced microbial activity combined with the depletion of organic matter. Spring bloom seems to be an important source of organic carbon pool and biological uptake of oxygen may is more important in the seasonal evolution of bottom DO than previously thought.

Enhanced Sidescan-Sonar Imagery, North-Central Long Island Sound

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The U.S. Geological Survey, National Oceanic and Atmospheric Administration (NOAA), and Connecticut Department of Environmental Protection have been working cooperatively to map sea-floor geology within Long Island Sound. Sidescan-sonar imagery collected during three NOAA surveys (H11043, H11044, and H11045) has been used to interpret surficial sediment distribution and sedimentary environments within the Sound. The original sidescan-sonar imagery generated by NOAA was used to evaluate navigational hazards, which does not necessarily require consistent tone matching throughout the survey. To fully utilize these data for geologic interpretation, artifacts within the imagery, primarily due to sidescan-system settings, processing techniques, and environmental noise, need to be minimized. Sidescan-sonar imagery from surveys H11043, H11044, and H11045 in north-central Long Island Sound was enhanced by matching the grayscale tones between adjacent sidescan-sonar lines to decrease the patchwork effect caused by numerous artifacts and provide more coherent sidescan-sonar imagery for use in geologic interpretation.

Long Term Trends in the Temperature of Long Island Sound

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We have aggregated almost two decades of observations of temperature from moored instruments and ship surveys in a publically accessible data system at LISICOS.UCONN.EDU. Since the observations are at irregular intervals in space and time, analysis of trends is complicated. We use the moored observations to estimate the temporal autocorrelation function of temperature. We find that the zero-lag values vary seasonally and with axial location in the Sound. We estimate the spatial autocorrelation function using near synoptic ship surveys and find no evidence that it is not homogeneous. To develop maps of the near bottom temperature distribution, a quantity of interest to environmental managers, we use objective analysis. We show that there are 5-10 year cycles in the area of the Sound where the bottom water exceeds 20.5 C

Down-Slope Gravity-Driven Movement of the Nepheloid Layer: Implications for Estuarine Environmental Health

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Sidescan-sonar imagery provides evidence that down-slope gravity-driven movement of the nepheloid layer constitutes an important mode of transporting sediment into the deeper basins of Long Island Sound. In the Western Basin, these currents have formed dendritic patterns of low backscatter on the seafloor that exceed 7.4 km in length, combine and widen down-slope, and reach widths of over 0.6 km at their southern distal ends. Similar patterns are also present in the Central Basin, but are much smaller. We hypothesize that the density contrast between the heavier nepheloid layer and lighter ambient seawater creates an instability that causes the layer to flow down-slope across the seafloor. Because many contaminants preferentially adsorb onto fine-grained organic-rich sediments and because the Sound is affected by seasonal hypoxia, mechanisms and pathways of fine-grained sediment transport are important factors determining the eventual fate of contaminants and their potential impact on estuarine environmental health.

A Comparison of Particle Selection in the Eastern Oyster *(Crassostrea virginica)* and Blue Mussel *(Mytilus edulis)*

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Suspension-feeding bivalve molluscs have long been recognized as an integral part of benthic ecosystems, playing a major role in nutrient cycling and seston composition. The eastern oyster *(Crassostrea virginica)and* blue mussel *(Mytilus edulis),* are commercially important bivalves and major players in the benthic ecosystem o fthe Sound. Yet little is known about the mechanisms upon which they rely to determine which particles are ingested and which are cycled back into the environment.

The effects of particle surface properties on selection in these suspension-feeding bivalves were examined. Mussels and oysters were fed combinations of particles with different surface characteristics and all biodeposits collected. Flow cytometry was used to analyze the proportion of particles rejected as pseudofeces and egested as feces. Our data will help elucidate the mechanisms used by bivalves to differentiate among food and other particles in the natural environment.

Monitoring Tidal Water Elevation and Quality in Wetland Embayments of Long Island Sound

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Recent tidal wetlands trends analysis by the N.Y.S. Department of Environmental Conservation (NYSDEC) revealed that low marshes were disappearing. To investigate the cause(s), the U.S. Geological Survey (USGS), in cooperation with NYSDEC, has begun monitoring four wetland embayments of Long Island Sound (LIS). The USGS is establishing and operating a station that monitors water elevation at each embayment. Water temperature, specific conductance, and salinity also are recorded at two embayments; a water-quality monitor is operated at a third. Provisional results indicate that mean lower low water elevation differs greatly among embayments and LIS. These differences, coupled with variations in freshwater input, strongly affect embayment water chemistry and marsh habitat.

High Resolution Geophysical Survey of Western Long Island Sound Offshore New York: An Estuary Floor Shaped by Bottom Currents and Human Activity

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In June 2006, we surveyed the western most section of Long Island Sound onboard the R/V HUGH SHARP (http://www.explore-the-sound.org). Analysis of high-resolution multibeam bathymetric data collected reveals sedimentary features consistent with a net westward direction of bottom currents. These features include: (1) Large sedimentary waves spaced about 100m west of two km-scale features outcropping through sediments; (2) Prominent sediment drifts or scour marks west of shipwrecks and bouldry outcrops; (3) Series of subtle, sub-parallel sedimentary furrows aligned in general EW direction along the north slope of surveyed area. Lack of short wavelength sedimentary waves is consistent with muddy substrate and weak bottom currents (<10cm/s) documented in western Long Island Sound. Fields of pockmarks of gas-charged sediments may indicate localized, active venting of fluids and/or gas. High-resolution bathymetry also highlights numerous anthropogenic disturbances such as pipelines, cables, shipwrecks, anchor drag marks, and dredge spoils.