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Environmental Change in Long Island Sound over the last 400 years

P.I.'s

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Introduction

Long Island Sound (LIS) suffers from seasonal anoxia which has been argued to be anthropogenic and to result from nutrient pollution (eutrophication), possibly impacted by global warming leading to enhanced water stratification. The goal of our research has been to use sediment samples to develop indicators for water quality in the past (eutrophication proxies; retrospective analyses). Initially, we collected and studied surface sediment samples and measured their associated water column parameters to develop and calibrate these proxies. Subsequently, we applied the proxies to samples from sediment cores collected along transects through LIS. Surface samples and cores were collected with an emphasis on East-West transects, because in modern-time LIS hypoxia predominates in the West. The cores were dated using radioisotope techniques and pollen records to reconstruct water quality in LIS over the last 1000 years. We studied a few samples that go back in time up to 10,000 years to establish a benchmark of pastoral (pre-colonization) conditions.

The approach has two aspects: I. Reconstruction of water column parameters over time, and II. Documentation of changes in benthic foraminiferal faunal assemblages over time. We consider the changes in water quality as derived for the past (aspect I) to be potential drivers for ecological changes, and studied benthic foraminifera which are low in the food chain to characterize coeval ecological changes in the LIS bottom environment (aspect II).

Samples and Techniques

Surface sediment samples were collected on a grid in the Sound during sampling cruises in 1960-1961 (archived samples from the Peabody Museum, Yale University), June 1996, June 1997, August 1999, June 2000, November/December 2000, and November 2001. Water samples and bottom sediment samples with living (i.e. Rose-Bengal stained) foraminifera were collected during all EPA funded cruises (post 1997). Sample lists are given in appendices IA and IB. Water samples from the two largest rivers draining into LIS (Connecticut and Housatonic River) were collected in 2000 and 2001 (Appendix IIA). Cores were collected during the 1996-1997 USGS cruises; in 2000 additional gravity cores were taken in westernmost LIS in Hempstead Harbor (WLIS68) and near Execution Rock (WLIS75). Archived cores from an earlier cruise (Atlantic Twin cruise, LISAT cores, USGS; 1984) were sampled in the core repository of the Woods Hole Oceanographic Institution to obtain information on the early sedimentary record.

Water temperature, dissolved oxygen and salinity were determined on board ship using a YSI meter, which was calibrated in the laboratory (zero oxygen and air saturated water) and on-board (air saturated water). The temperature measurements were calibrated with mercury laboratory thermometers. The salinity was measured on board ship with a salinity meter, which was calibrated in the laboratory using conductivity standard solutions. Water depth and location were registered on board from the captain's instrument readings (Figure 1).

The sediment grab samples were collected with a Van Veen grab sampler equipped with downward looking video and still cameras in order to verify the integrity of the grab sample. The overlying water was removed and the upper 2 cm of sediment was collected with a Teflon-coated, flat-bottomed scoop. During cruises after 1997, the

upper 2 cm of the mud was split into a sample that was placed in a standard formaldehyde-Rose Bengal solution to stain living foraminifera, a split for trace metal analyses, and a bulk split for other chemical and physical analyses. The 1996-1997 USGS grab samples were not stained for the presence of living foraminifera.

The cores collected during the 1996-1997 USGS cruises were taken using the USGS's hydrostatically dampened gravity corer, which collected 11-cm diameter cores of up to 70 cm long in clear, polycarbonate tubing. The cores were extruded and sliced into 0.5 cm slices; samples were archived at the USGS in Woods Hole. Water contents were measured for each sample by measuring the sample weight before and after drying. The water contents were used to calculate dry bulk densities of the sediment using a dry rock density of 2.6.

The LIS and river water samples were analyzed for salinity with an 'in house' developed conductivity method. An 'Amber' high sensitivity conductivity meter with a probe for high conductivity measurements was calibrated with a series of standard seawater solutions diluted with distilled water. Measurements were done in a thermal bath at 25 °C. The samples were analyzed after calibration, with regular runs of standards to detect any drift, which was then corrected for where needed. The water samples were also analyzed for Ca, Mg, Sr, alkalinity, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. The samples were filtered (0.45 micrometer) directly upon retrieval, except for some samples from the 1999 cruise. The water samples were not poisoned, so that some of the 1999 samples may have suffered from minor oxidation of organic carbon in the bottles after collection. The Ca, Mg, Sr analyses were done on the ICP-AES at Wesleyan University, using commercially available standard solutions with Ca-Mg-Sr in seawater proportions. Standard seawater solutions were used for validation. Matrices of the commercial standard solution were matched with NaCl for LIS waters and were prepared in distilled water for river water samples. Most core samples were analyzed for ^{137}Cs and ^{210}Pb by gamma ray counting (at the USGS) for dating purposes.

The organic carbon and inorganic carbon contents of the sediment samples were analyzed at the USGS in Woods Hole. Biogenic Silica was measured at Wesleyan University in timed extraction sequences in several cores. Recovery from local standard samples reproduced well compared to literature data. Major and trace element analyses were carried out on all samples by ICP-AES at Boston University and for Hg by AAS at Wesleyan University. The isotope data on water and calcite were collected at Yale University, University of Maryland, and the University of California at Santa Cruz, each with their own precision and accuracy protocols. The precision of carbonate carbon and oxygen isotope analyses is <0.1 ‰.

The Mg-Ca-Sr data on foraminiferal shells were first collected at Cambridge University (UK) and later at Rutgers University (NJ, USA) where the same UK scientist (Dr. C. Lear) was a postdoctoral fellow at the time. The ^{14}C data were collected at NOSAMS Woods Hole Oceanographic Institution using their standard precision and accuracy calibrations.

Foraminifera were picked from a split of the >63 μm sediment fraction and at least 100 specimen were picked per sample. All specimens were mounted in cardboard slides, and placed in an aluminum holder with glass cover. In many samples additional specimens were picked for trace element and stable isotope analyses. Care was taken to pick the best preserved, most glassy specimens for geochemical analyses. For calibration

of geochemical proxies only specimens in which brightly stained protoplasm was present in the inner whorls of the test were used, and specimens with diffuse staining in outer chambers were excluded.

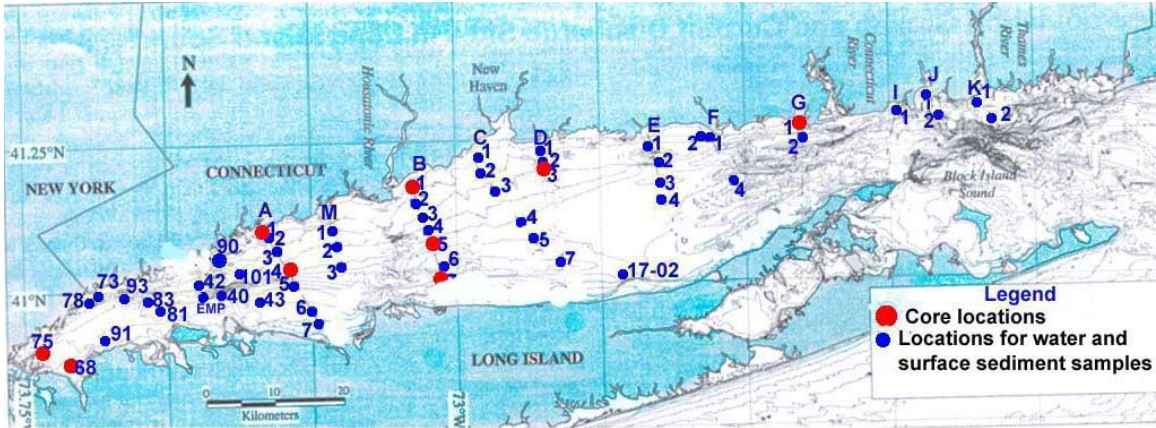


Figure 1. Sampling locations for cores, surface sediment samples and water samples.

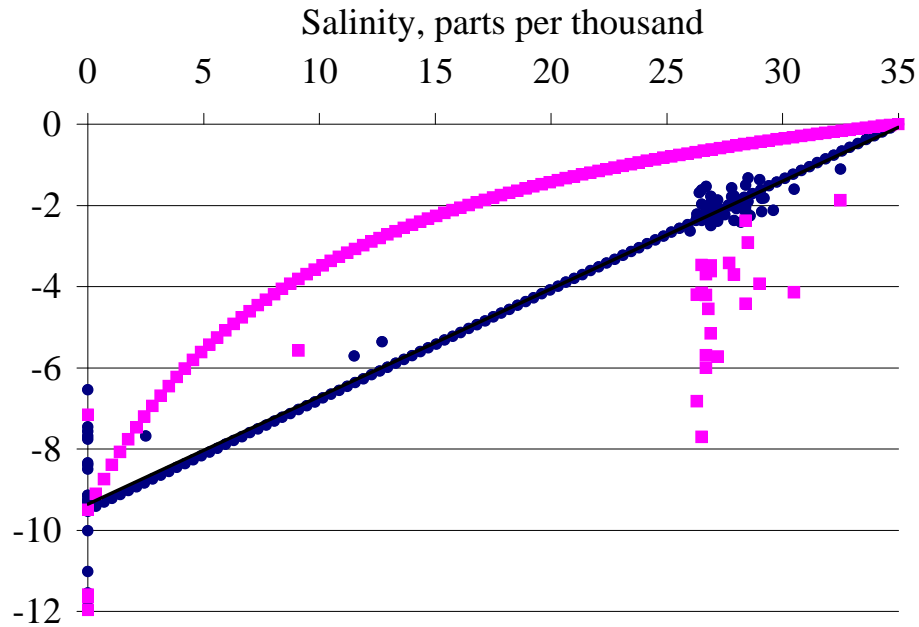


Figure 2. Mixing model for modern LIS for stable isotopes in the water column. The dark blue straight line is the mixing line between ocean and river water for $\delta^{18}\text{O}$; most data points plot close to this line. The curved purple line is the $\delta^{13}\text{C}$ mixing curve; all data points plot well below this mixing curve. The latter is explained as a result of the addition of isotopically light carbon from oxidation of organic matter in the bottom waters.

Results

We calibrated several proxies from our modern LIS studies, largely based on an average mixing model between sea water and river water (Figure 2), using the measured parameters. We obtained relations between salinity and $\delta^{13}\text{C}$ (DIC), $\delta^{18}\text{O}(w)$ (w =water)

and Ca, Mg, Sr and bicarbonate. We also obtained relations between $\delta^{18}\text{O}(\text{cc})$ (cc=calcite from foraminifera), $\delta^{18}\text{O}(\text{w})$ and Mg/Ca(cc) and water temperature. The $\delta^{18}\text{O}(\text{cc})$ in live foraminifera and $\delta^{18}\text{O}(\text{w})$ were out of equilibrium by -1.1‰, which we recorded as an *in vivo* effect for the species of foraminifera that we used for the isotope study (*Elphidium excavatum*).

We reconstructed the LIS bottom water temperature, salinity and oxygen concentration in the past 1000 years as follows:

1. The Mg/Ca readings in calcite were translated into bottom water temperatures, using a salinity-independent calibration between measured Mg/Ca in living (i.e., Rose-Bengal stained) foraminifera from surface sediment and measured bottom water temperatures. The water temperatures are instantaneous measurements, whereas the Mg/Ca in the foraminifera reflects the water conditions over the life span of the organism (1-6 months). The seasonal bottom water temperature variation is about 20 °C, so the main uncertainty is related to the ‘life span parameter’, which creates inherent noise in the calibration curve (Figure 3).

The obtained bottom water temperature record from core A1C1 shows a good qualitative correlation with the GISP2 ice core isotope record, which is a qualitative proxy for paleo-temperatures. In this record, we recognize the Medieval Warm Period (Figure 4) and the Little Ice Age, as well as signals of the Modern Global Warming over the last 100 years. The absolute magnitude of our calibration may be slightly offset because of the effects mentioned above, but the observed trends are compatible with the known paleoclimate record. These paleo-temperature records were then used to calculate the paleosalinity and the dissolved oxygen record for several cores (shown are data for core A1C1).

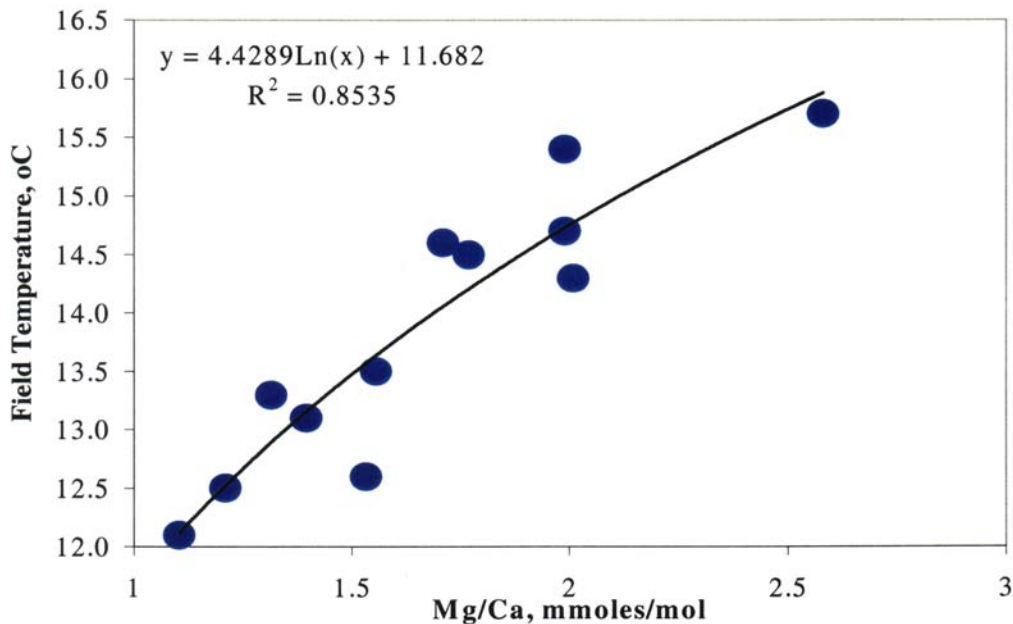


Figure 3. Calibration of Mg/Ca in foraminiferal calcite from living (Rose-Bengal stained) foraminifera in surface sediment samples versus measured bottom water temperatures.

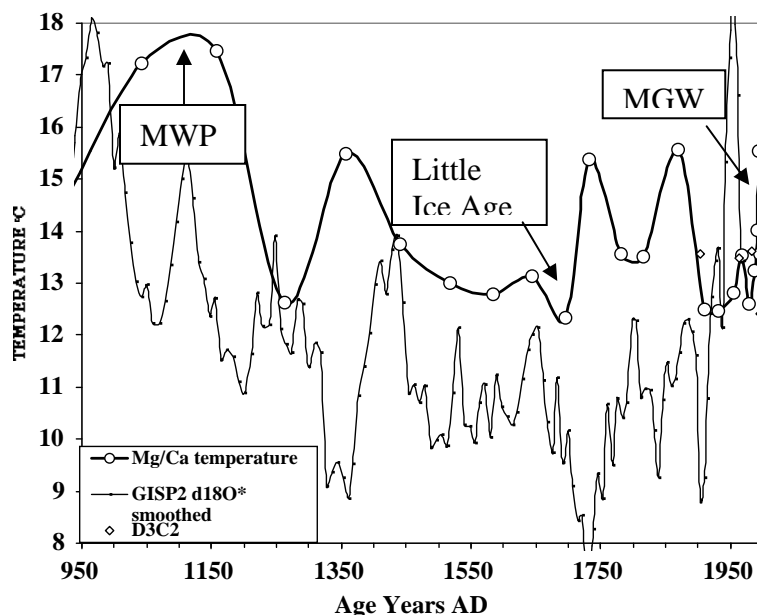


Figure 4. Paleo-temperature record from core A1C1 based on Mg/Ca thermometry. The Medieval Warm Period (MWP), the Little Ice Age and Modern Global Warming (MGW) are evident. The thin line is a smoothed and scaled record of the GISP2 ice core isotopic record, showing similar trends in paleo temperatures. Offsets between the A1C1 and GISP2 record result both from age errors and the lower time-resolution in A1C1.

2. In the next step, we used the measured $\delta^{18}\text{O}(\text{cc})$ and the estimated Mg/Ca bottom water temperatures to calculate the $\delta^{18}\text{O}(\text{w})$, taking the *in vivo* effect into account. The $\delta^{18}\text{O}(\text{w})$ was then related to paleo salinity using the modern mixing model of Figure 2. This derivation is sensitive to the Mg/Ca temperature errors, but the temporal trends should remain the same. The paleo-salinity record (Figure 5) shows fluctuations over the pastoral period, with high salinities during the Medieval Warm Period and lower salinities during the Little Ice Age. The 20th century has on average slightly lower salinities, and the main features are the two sharp low-salinity pulses that occurred around 1900 and 1975. All cores show more ‘extreme low-salinity events’ during the last 200 years. The western LIS cores show a consistent decrease in overall salinity over the last 200 years.

3. The paleo-salinity record was then used to estimate the bicarbonate content and $\delta^{13}\text{C}(\text{DIC})$ of the LIS bottom waters in the past, using the modern mixing model. The difference between measured and calculated $\delta^{13}\text{C}$ values was labeled ‘excess $\delta^{13}\text{C}$ ’ or $\delta^{13}\text{C}^*$ (Thomas et al., 2000). Excess $\delta^{13}\text{C}$ values were all negative, indicating addition of ‘light carbon’ (i.e., derived from oxidation of organic material) to the mix of seawater and river water. The $\delta^{13}\text{C}^*$ is thus a prime indicator of disturbances in the local carbon cycle. The observed light values indicate that organic carbon (isotopically light carbon)

has been oxidized and added to the dissolved inorganic carbon reservoir in the LIS bottom waters. A record of excess $\delta^{13}\text{C}$ values for core A1C1 is given in Figure 6.

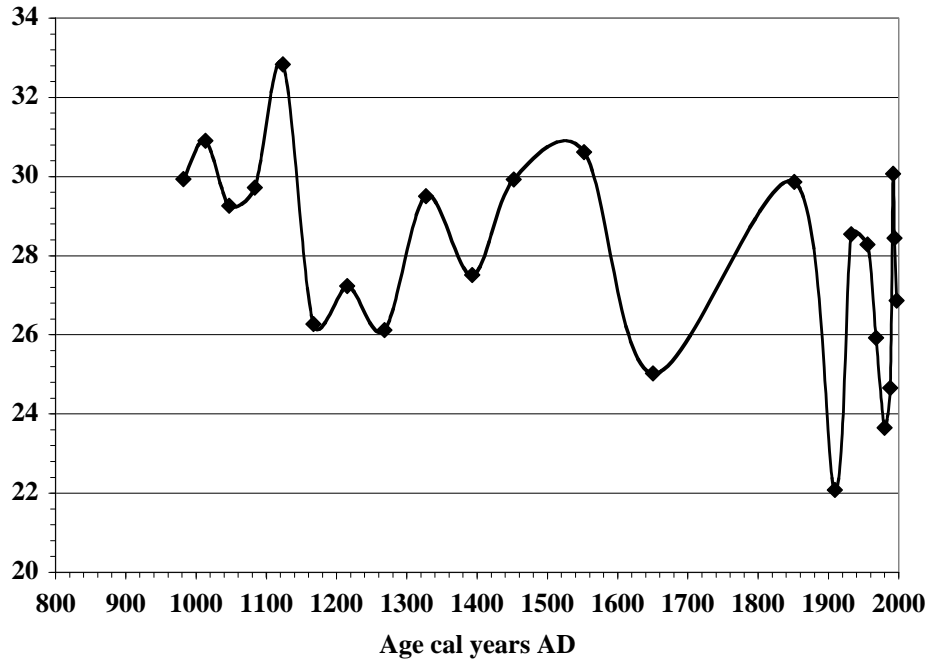


Figure 5. Paleo-salinity record of core A1C1, showing the high salinities during the Medieval Warm Period and the short-lived low-salinity events of the 20th century around 1900 and 1975.



Figure 6. Excess carbon isotope record for core A1C1, showing an overall decline in values since 1800 AD and an extreme low around 1975.

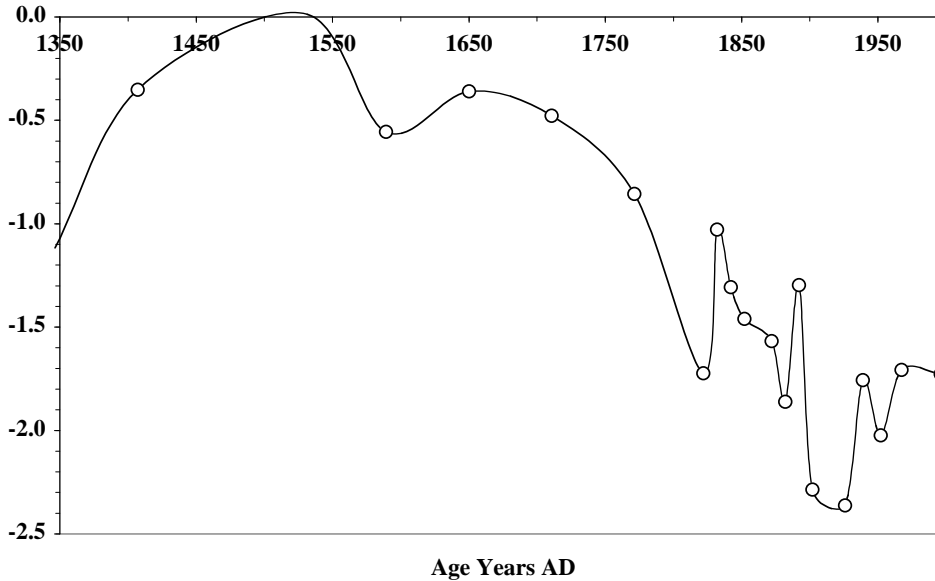


Figure 7. Excess carbon isotope record for core A4C1, showing a strong drop in values since 1800 AD and lows around 1900 and 1950 AD.

The sharp negative peak around 1975 correlates in time with the low salinity peak, suggesting that nutrient input into the Sound was enhanced during this period of excess river discharge. The record for core A4C1 (Figure 7) shows a more pronounced decline from 1800 to recent, with extreme lows around 1900 and 1950, both well-documented wet periods with extensive floods in Connecticut.

4. The $\delta^{13}\text{C}^*$ values obtained in the above procedure can be used to model the oxygen demand in LIS bottom waters over time. We calculated the O_2 saturation levels in bottom waters for the reconstructed temperature (T_w) and salinity (S). We then calculated how much light carbon must have been added (as bicarbonate from oxidized organic carbon) to obtain the $\delta^{13}\text{C}^*$ values. From the stoichiometry of the reaction: $\text{C}_{\text{org}} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+$, we calculated the O_2 consumption from that carbon oxidation process. We plot this as the oxygen consumption index (OCI), which is the absolute oxygen demand divided by the available oxygen at saturation at that temperature. The OCI record for core A1C1 is shown in Figure 8. Values in excess of 100% indicate that oxygen was supplied through mixing of the water column, or that large amounts of organic carbon were oxidized through the sulfate reduction cycle. This oxygen consumption record is not necessarily a true “hypoxia” record, because the oxygen levels in bottom waters are a function of both oxygen consumption and oxygen re-supply through mixing. The highs in oxygen consumption correlate with high temperatures, indicating that the rate of oxygen demand increases with increasing bottom water temperature. The high temperatures of the Medieval Warm period did not generate excessively high oxygen demands, probably because there was not as much organic carbon available for oxidation as during the last 200 years.

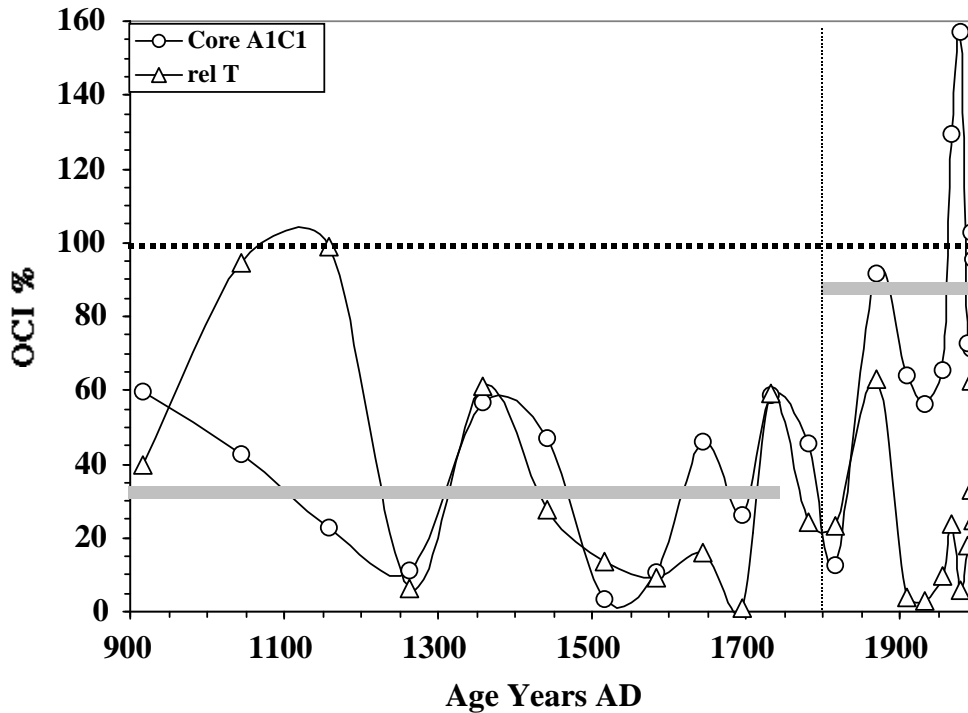


Figure 8. Oxygen consumption index (OCI) versus time for core A1C1 (open circles). The grey lines show the average value for the pastoral and colonial stages (pre-1800) and the higher average rates of oxygen demand after 1800. The temperature (expressed as relative temperature, i.e., % of maximum temperature, open triangles) correlates with the OCI, indicating that oxygen demand was larger when it was warm both in the past and in modern times (except at the core bottom).

5. The organic carbon (Corg) and biogenic silica (BSi) data were recalculated as Corg and BSi accumulation rates, parameters that express the deposition rate of these two substances per cm^2 per year in different areas of the Sound. They are direct proxies for the sum of organic productivity and organic carbon import into LIS (Corg) and organic productivity by diatoms (BSi). We have contracted for C/N ratios and $\delta^{13}\text{C}$ in bulk organic matter to be determined in the core samples but these analyses are still outstanding. The latter data will enable us to distinguish between changes in carbon import from the watershed (terrestrial organic carbon) and *in situ* (i.e., in LIS) produced marine organic carbon in the sedimentary records. In the records of all cores, the accumulation rates of carbon and biogenic silica increased exponentially, starting very gradually around 1650, increasing around the early 1800's and showing exponential growth in the 20th century. Records for BSi and Corg accumulation in core A1C1 are given in Figure 9.

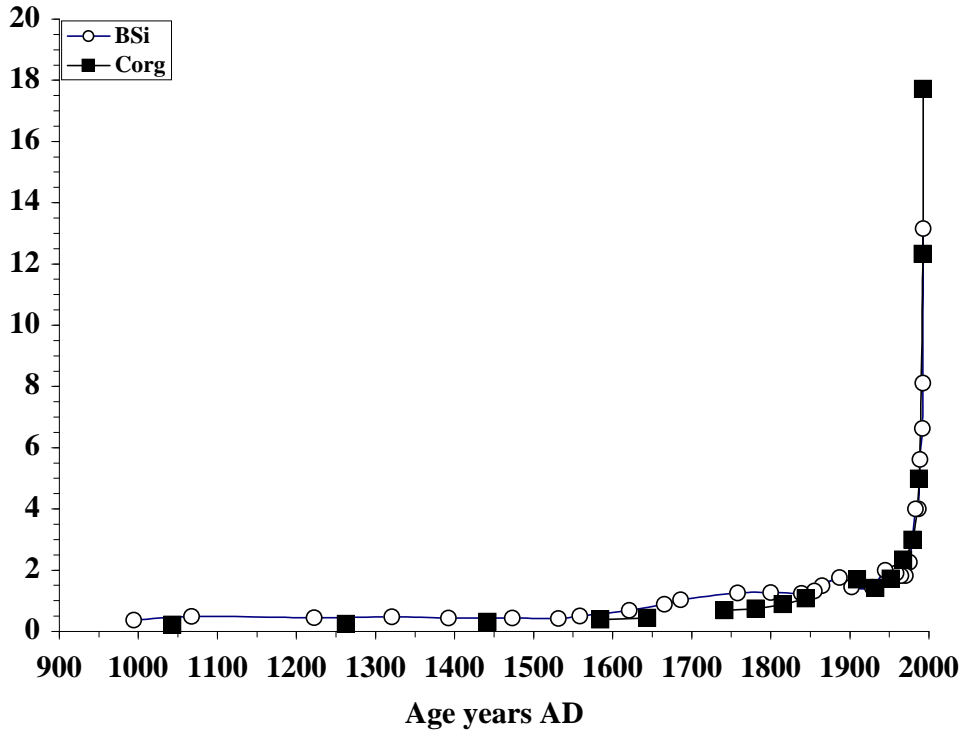


Figure 9. Accumulation rates of Bsi and Corg in core A1C1. Note the increase in accumulation rates starting around 1650, accelerating around 1850 and sharply rising in the mid 20th century.

8. Contaminant studies show strongly increased contaminant burdens, with the delivery of increased metal loads to LIS starting around 1850 AD for most metals. The increase in Hg loadings, however, which we relate to the onset of the hatting industry in Connecticut, started around 1820. The counts of *C. perfringens*, a bacterial spore and sewage indicator, show a similar pattern, and are also a crude indicator for population density around LIS.

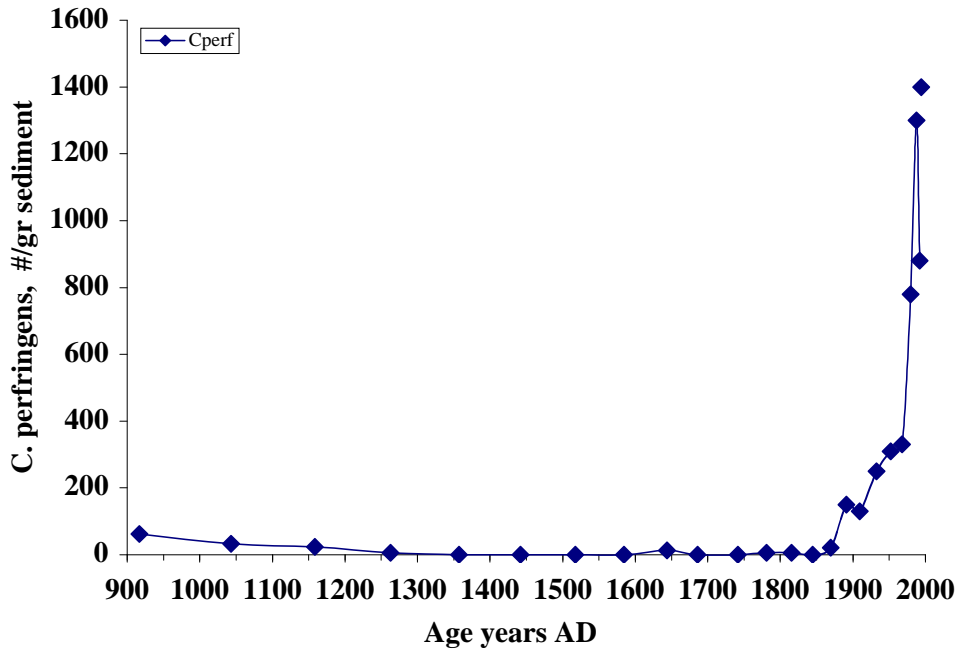


Figure 10. Abundances of *C. perfringens*, a sewage indicator, in core A1C1. This is a direct indicator of sewage input into the Sound as well a population density proxy.

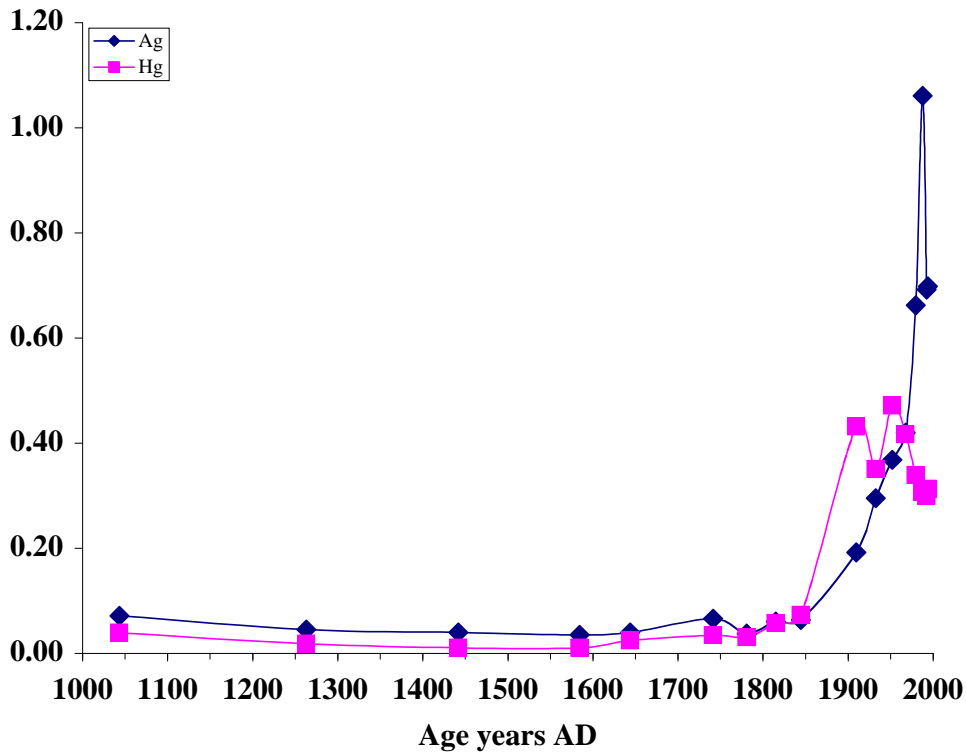


Figure 11. Concentrations of Silver (Ag) and Mercury (Hg) in core A1C1. Silver is enriched in sewage and the pattern shows strong similarities with that of *C. perfringens*.

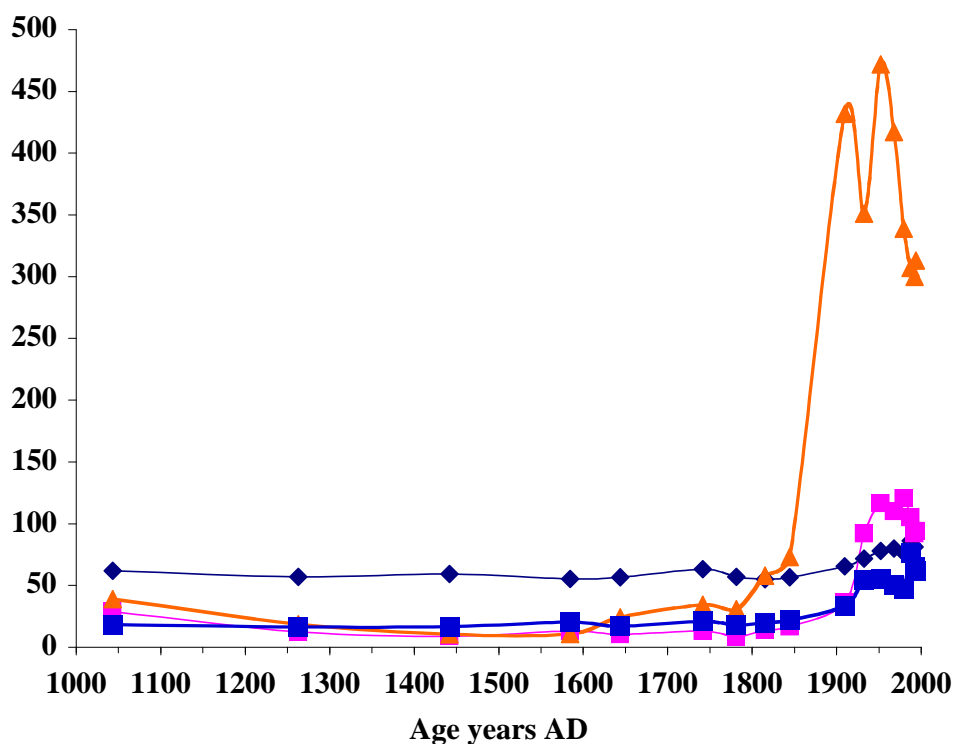


Figure 12. The concentrations of Cr, Cu, Pb and Hg (in ppb) in core A1C1. All these metals increase towards the top of the core section, but the increases start at different times: Hg around 1820, Pb and Cu in the mid-1800's and Cr in the 1900's. The two peaks in Hg concentration are related to floods at around 1900 and 1955 AD.

9. The surface sediment studies show a strong east west gradient in $\delta^{13}\text{C}^*$, contaminant burdens and Corg-BSi, indicating that the western Sound is more heavily impacted by anthropogenic inputs than the east. In addition, fine grained sediment transport from east to west may exacerbate this effect.

10. The sediment accumulation rates vary over the Sound but in general, sediment accretion increased dramatically over the last 100-150 years, most likely the result of changes in land use in the watersheds. A sediment mass accumulation rate plot for core A1C1 is given in Figure 13.

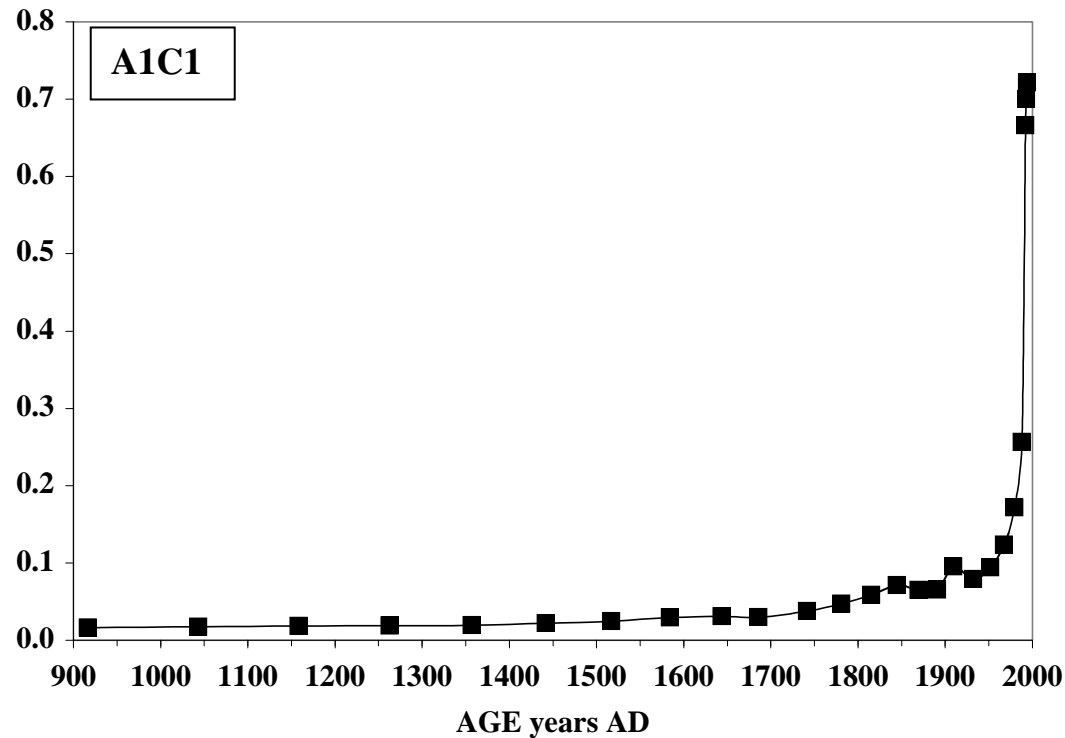


Figure 13. Sediment accumulation rates expressed as mass/cm² yr show an increase from 1650 to 1800 and then a rapid increase over the 20th century.

11. The foraminiferal studies of surface samples collected in 1948, 1961, 1996/1997, 1999, 2000, and 2001 show that a major assemblage change occurred between the sample collection in 1961 and that in 1996. In 1948 and 1961 the species *Elphidium excavatum* was the most abundant species, and in samples from depths of less than 10-12 m it commonly comprised >90% of the total population. Probably, the species is most abundant at depths where light penetrates to the bottom because under these conditions, diatoms, the main food source of *E. excavatum*, occur abundantly even as benthos. At greater depths *Buccella frigida* was more common, and below about 30 m the agglutinated species *Eggerella advena*. The species *Ammonia beccarii* was rare (<5% in a few samples, absent in most). During the pre-1960 period, the major faunal zonation thus was by water depth. In samples collected in 1996/1997 and later *E. excavatum* is still common in central to eastern Long Island Sound, especially at water depths <12 m, and the relative abundance of *B. frigida* had not changed significantly from 1961 values. *E. advena*, however, had become rare or absent in all samples in 1996 and later, in contrast to the deep-water samples collected in 1961 and before. In addition, there was a strong East-West faunal gradient in samples collected in 1996 and later: the relative abundance of the species *Ammonia beccarii* s.l. (more specifically probably *A. beccarii tepida*) increased strongly in western Long Island Sound. The species was present in many more samples than in 1961 and 1948 in the central and eastern basins, while it dominated samples (>75%) in westernmost LIS. The relative abundance of *A. beccarii* can be expressed in the so-called *Ammonia-Elphidium* index:

$A-E = \# Ammonia / (\# Ammonia + \# Elphidium) * 100$. Values for this index for several years are shown in Figure 14. There is a negative correlation between the A-E index and the absolute abundance of benthic foraminifera (number of foraminifera per gram of dry sediment) in the grab samples: samples with abundant *E. excavatum* usually have more foraminifera per gram of sediment than samples with abundant *A. beccarii*.

The difference in benthic foraminiferal faunal composition in grab samples taken in or before 1961 and in grab samples taken in or after 1996 constitutes a major, qualitative change in faunas, indicating that bottom faunas of unicellular eukaryotes underwent severe faunal turnover between these years.

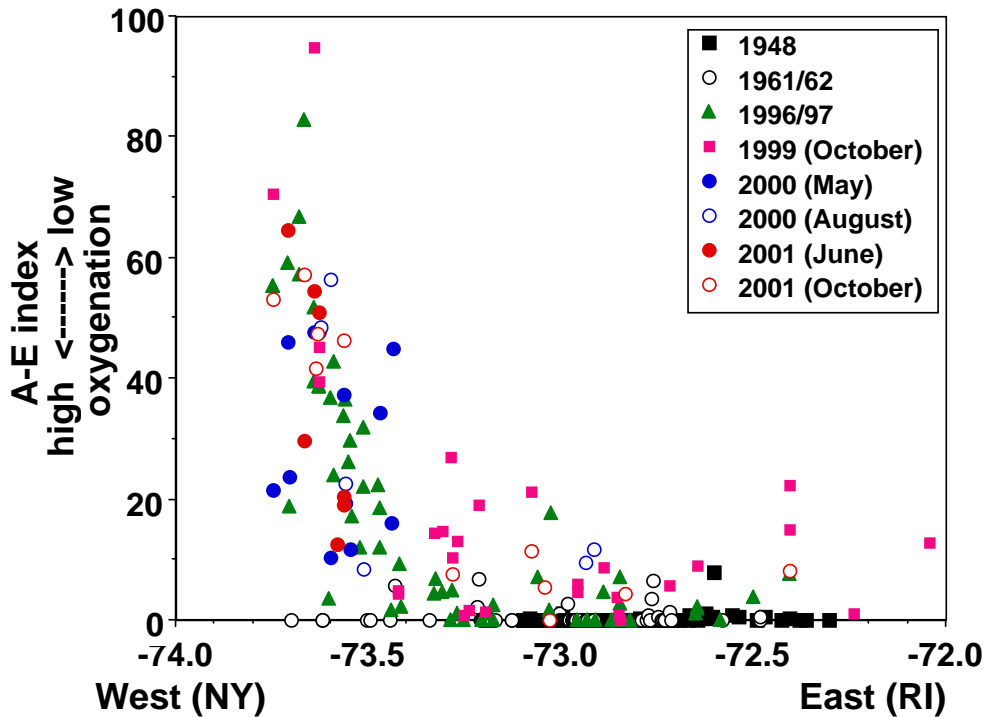


Figure 14. *Ammonia-Elphidium* (A-E) index in surface samples taken at various years, plotted against longitude. Note the very low values throughout the Sound in samples taken in 1948 and 1961 (black symbols).

12. Foraminiferal studies of core samples place the observations of grab samples representing only a few time intervals within a longer-term framework. Cores collected at water depths <10 m (e.g., A1C1) show high relative abundances of *E. excavatum* (~80%) throughout, with an increase in abundance after 1800 AD (to ~90%). In cores from deeper water (e.g., core A4C1), the *E. excavatum* abundance increased from <30% to >40% at the same time (Figure 15). This deeper water core A4C1 contained abundant *Eggerella advena* in the lower layers, but that species almost disappeared in the younger layers. At the same time of the increase in relative abundance of *E. excavatum*, the absolute abundance of foraminifera increased strongly at all depths (figure 16).

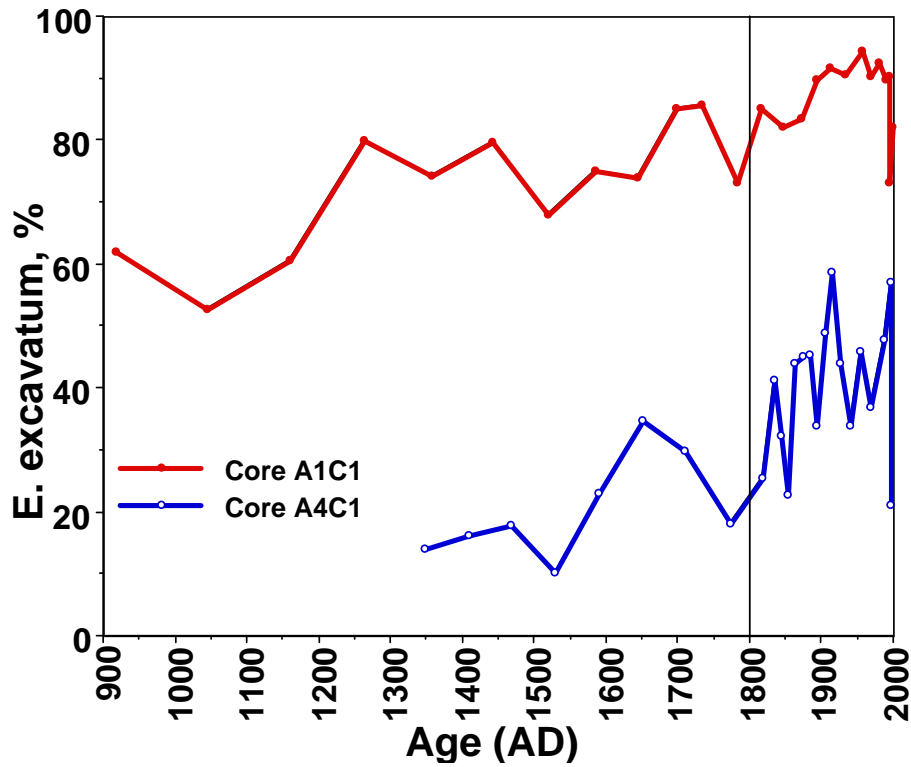


Figure 15. Relative abundance of the diatom-consuming *E. excavatum* in a shallow (A1C1) and deep (A4C1) water cores on the A-transect in the western basin of LIS.

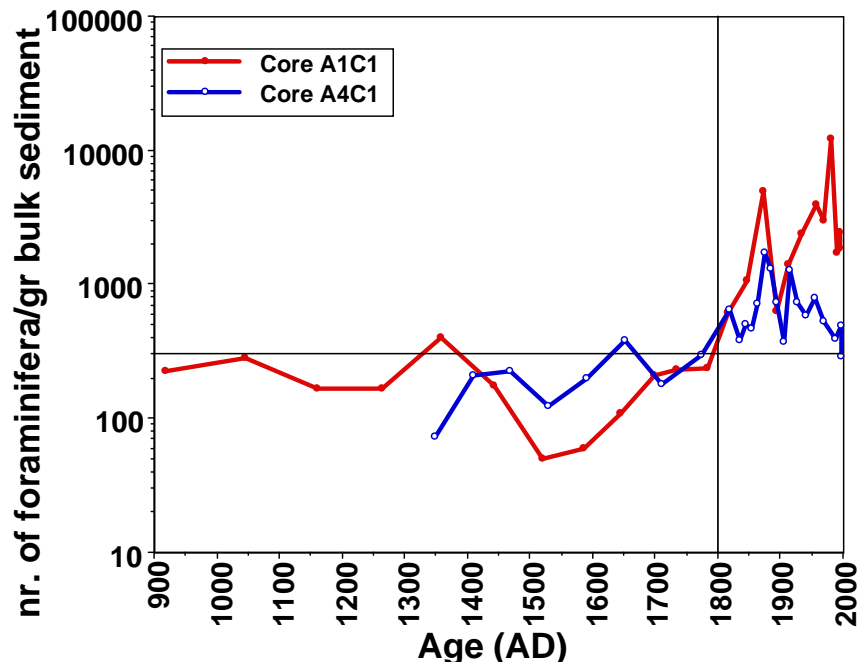


Figure 16. Absolute abundances of benthic foraminifera in a shallow water (A1C1) and deep water (A4C1) core on the A-transect in western LIS; note logarithmic scale.

The studies of the younger core samples enabled us to confirm the timing of the change in faunal composition documented from the grab sample studies. Starting in the early 1970s in westernmost LIS (The Narrows, cores WLIS68 and WLIS75), the absolute abundance of foraminifera and the relative abundance of *E. excavatum* decreased sharply, while the relative abundance of *A. beccarii* (figure 17) increased rapidly. This increase in relative abundance of *A. beccarii* occurred later (in the 1980s) in western LIS basin (cores A1C1 and A4C1) than in The Narrows (figure 17). Further east, the late increase in *A. beccarii* (since 1980) was documented only in cores collected in shallow waters that were taken close to the mouths of rivers in the central and eastern basin of LIS (B1C1 close to the Housatonic River, G1C1 close to the Connecticut River). Deeper locations in the central basin (e.g., locations B5, B7) do not show any *A. beccarii*.

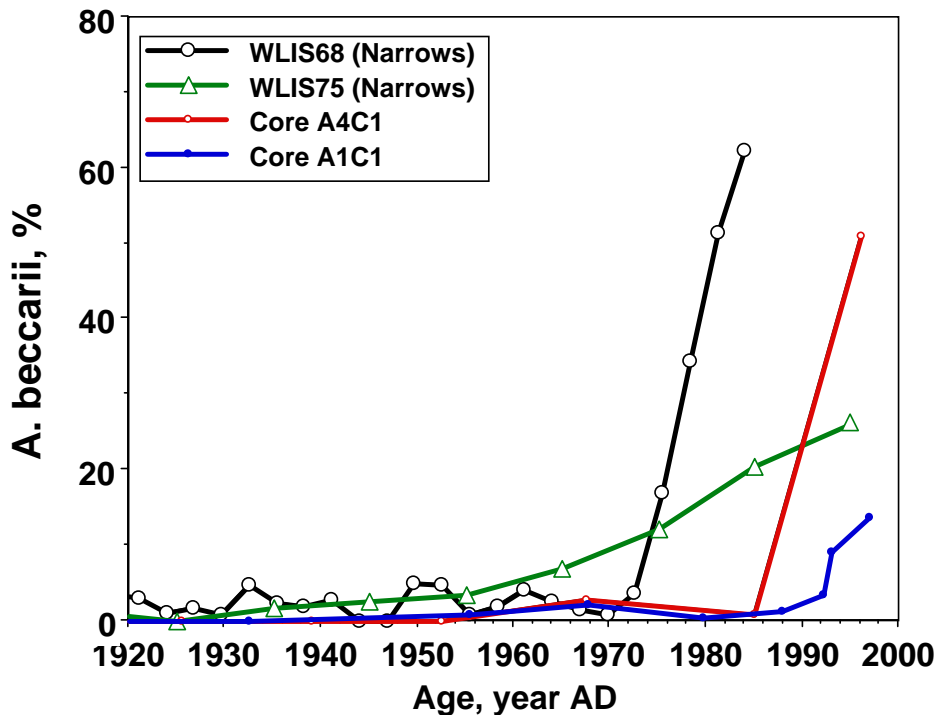


Figure 17. Relative abundance of *Ammonia beccarii* in a deep water (A4C1) and a shallow water core (A1C1) in the western basin of LIS, and in a deep water (WLIS 75; close to Execution Rock) and shallow water (WLIS68, Hempstead Harbor) core taken in the Narrows.

Conclusions and Main Findings

Our data indicate that the eutrophication of LIS started around 1800 AD, as indicated by increased burial rates of Corganic, BSi, sewage indicators (*C. perfringens*) and benthic foram abundances. Data from Dr. M. Altabet on the same cores show that the nitrogen concentrations and nitrogen isotope signatures changed at the same time (ongoing studies), indicating that the nutrient sources displayed a dramatic change during this period. The salinity and water temperature have oscillated over time within a narrow range, but showed more extreme events over the last 200 years. The low salinity peaks in the 20th century suggest that wet periods now translate more directly into, low salinity

events of several years, possibly with related water stratification and hypoxia events. The low salinity events of the early 1900's and 1950's and 1970's correlate well with the regional precipitation records (Figure 18). Climatic trends are conform northern hemispheric temperature patterns, with good evidence for modern global warming which may have enhanced water stratification over the last 50 years. The oxygen demand record shows a strong increase from 1800 on, and correlates reasonably well with the paleo temperature record. The strong hypoxia-anoxia of the last decades may be the result of the combined effects of high bottom water temperature (high rates of Corganic mineralisation and enhanced water column stratification) as well as high organic productivity (availability of labile organic carbon). Most parameters in the modern Sound show decreasing water quality to the west.

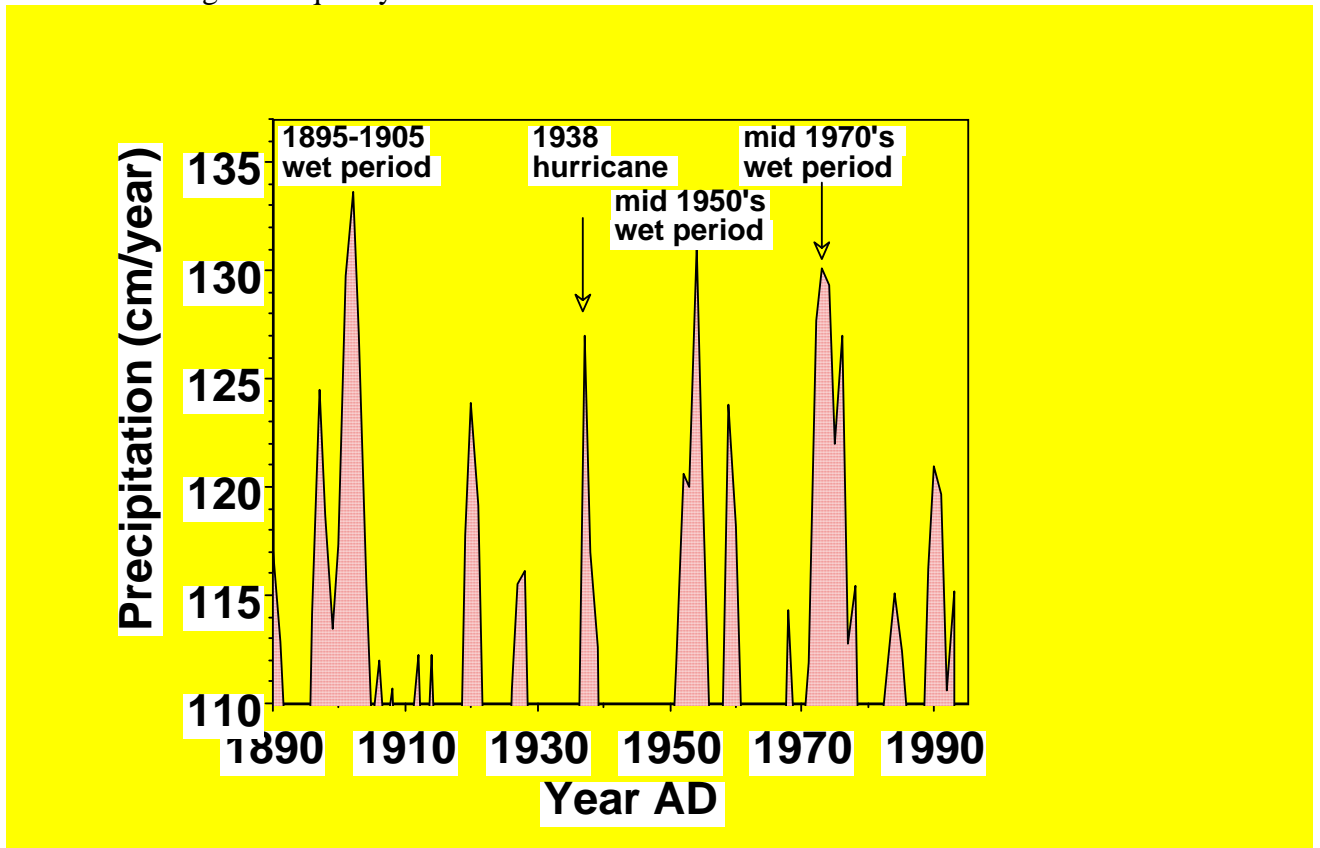


Figure 18. Precipitation record for southern New England.

The changes in benthic foraminiferal faunas can be separated into two separate events:

I. overall foraminifera abundance increased since about 1800, which was coupled with an increase in relative abundance of *E. excavatum* at all water depths. The increase in abundance of this diatom-consuming species *E. excavatum* at depths below the photic zone suggests that the higher productivity of pelagic diatoms since 1800 could now be delivered to the sea floor in greater numbers. The decrease in relative abundance of *E. advena* in the deeper water cores is likely coupled to this increase of *E. excavatum* abundance.

II. The second major event was heralded with the increase in relative abundance of *A. beccarii*, which started in the early 1970s in western LIS. This appearance of *A. beccarii* rapidly spread to the east, starting at the mouths of the main rivers. This increase in *A. beccarii* abundance was accompanied by a decrease in *E. excavatum* abundance, suggesting a major shift in the food chain or environmental parameters at this time.

Similar increases in relative abundance of *Ammonia* species relative to *Elphidium* species have been observed in the Gulf of Mexico and in Chesapeake Bay, and were explained as a result of hypoxia. Laboratory studies of both *Ammonia* and *Elphidium* species indicate that they are highly resistant to hypoxia and even anoxia, and show no difference in susceptibility. Another possible cause of the increasing relative abundance of *A. beccarii* might be the increase in LIS water temperatures with modern global warming. Laboratory and field studies indicate that *Ammonia* species need temperatures in excess of 20 °C for about 30 days to reproduce successfully and prolifically. It is only during the last few decades that LIS bottom waters were that warm for that long.

The high nitrogen influx of the last few decades (as indicated by the *C. perfringes* records in cores) may have played a major role as well. The biogenic silica data indicate that recently diatom productivity may have decreased. Such a change in primary producers away from diatoms has been observed in modern phytoplankton studies in LIS as well as in other eutrophied waters (e.g., Gulf of Mexico). The newly emerging species are dinoflagellates and cyanobacteria, which may be better adapted to use the high nutrient influxes. At high nutrients levels, diatoms become Si-limited and can no longer sustain blooms because they become Si-limited. A decrease in availability of diatoms would explain why the diatom-consuming species *E. excavatum* could no longer compete successfully with the more omnivorous *A. beccarii*.

If high N/Si ratios have indeed led to a decreasing availability of diatoms in LIS, the consequences for the overall ecosystem may be severe. Diatoms as primary producers form one of the basic elements of the LIS food chain, and are the preferred food of many organisms at higher levels (e.g., copepods). Dinoflagellates and cyanobacteria are much less used as a food source, and such a change in the base of the food chain may have led to changes in the overall ecosystem, including the documented higher abundance of jellyfish and lowered abundances of fish and shell fish.

In conclusion, the eutrophication has been an ongoing process for close to two hundred years, possibly with the associated low oxygen conditions of the LIS bottom waters. With the eutrophication came the associated changes in benthic ecosystem, with higher productivity and enhanced levels of diatom consuming foraminifera. The occurrence of hypoxia may have been exacerbated by higher temperatures and increased water stratification. A second major ecosystem shift occurred over the last 30-40 years, possibly a result of the change in population dynamics of diatoms which became silica-limited and the take over of dinoflagellates as primary producers and *A. beccarii* species as benthic foraminifera. Again, a combined effect of eutrophication and increased water temperatures may have played a role.

APPENDIX IA

List of surface sediment samples of each cruise and their geographical locations including samples collected by Buzas in 1961.

Cruise	Sample I. D	Latitude (degrees N)	Longitude (degrees W)	Water Depth (m)
Buzas 1960	B14	40.900	-73.620	10.0
	110a	41.020	-73.500	28.0
	13/1	41.230	-73.030	10.0
	13/10	41.230	-73.030	11.0
	13/11	41.230	-73.030	10.0
	13/13	41.230	-73.030	10.0
	13/15	41.230	-73.030	11.0
	13/5	41.230	-73.030	11.0
	13/7	41.230	-73.030	10.0
	59/6	41.250	-72.480	3.0
	B116	41.020	-73.180	28.0
	B120	41.120	-73.200	25.0
	B34	41.270	-72.790	16.0
	June 1996	A1G	41.100	-73.330
A2G		40.960	-73.250	16.0
A3G		41.100	-73.310	15.0
A4G		41.030	-73.290	24.0
A5G		41.000	-73.168	29.0
A6G		41.160	-72.930	19.3
A8G		40.940	-73.268	22.3
B6G		41.160	-73.030	18.0
C3G		41.170	-72.850	20.0
C4G		41.110	-72.890	28.0
D1G		41.230	-72.850	10.0
D2G		41.210	-72.849	14.4
D3G		41.200	-72.847	16.6
D4G		41.180	-72.650	27.0
D5G		41.150	-72.837	29.0
D7G	41.040	-72.820	37.0	
G1G	41.270	-72.410	5.0	

Cruise	Sample I. D	Latitude (degrees N)	Longitude (degrees W)	Water Depth (m)	
June 1997	WLIS-97-60G	40.930	-73.520	11.4	
	WLIS-97-64G	40.940	-73.590	14.9	
	WLIS-97-68G	40.870	-73.670	7.4	
	WLIS-97-72G	40.890	-73.680	10.0	
	WLIS-97-73G	40.900	-73.710	12.3	
	WLIS-97-74G	40.910	-73.680	12.8	
	WLIS-97-78G	40.930	-73.710	8.3	
	WLIS-97-83G	40.970	-73.640	11.7	
	WLIS-97-88G	40.950	-73.600	17.7	
	WLIS-97-89G	40.970	-73.590	19.2	
	WLIS-97-90G	40.960	-73.570	19.5	
	WLIS-97-91G	41.000	-73.600	5.1	
	WLIS-97-93G	41.010	-73.560	8.7	
	WLIS97-75G	40.880	-73.750	20.0	
	WLIS97-81G	40.930	-73.630	15.0	
	40-02G	40.980	-73.420	30.0	
	40-02G	40.980	-73.420	30.0	
	42-01G	41.010	-73.470	24.0	
	42-01G	41.010	-73.470	24.0	
	42-02G	40.960	-73.470	17.0	
	43-01G	40.970	-73.510	22.0	
	44-01G	40.970	-73.540	15.0	
	44-02G	40.960	-73.550	21.0	
	44-03G	40.940	-73.550	14.0	
	CONN99056	A1G	41.100	-73.330	12.0
		A3G	41.100	-73.310	15.0
		A4G	41.030	-73.290	24.0
		A6G	41.160	-72.930	19.3
		A7G	40.940	-73.240	16.3
		A8G	40.940	-73.268	22.3
		B1G	41.170	-73.075	7.6
		C4G	41.110	-72.890	28.0
D1G		41.230	-72.850	10.0	
D2G		41.210	-72.849	14.4	
D3G		41.200	-72.847	16.6	
D7G		41.040	-72.820	37.0	
E4G		41.140	-72.650	26.0	
G1G		41.270	-72.410	5.0	
G2G		41.270	-72.406	5.0	
I1G		41.290	-72.240	6.4	
K2G		41.280	-72.043	15.0	
WLIS9775G	40.880	-73.750	20.0		
WLIS9781G	40.930	-73.630	15.0		
40-02G	40.980	-73.420	28.0		

Cruise	Sample I. D	Latitude (degrees N)	Longitude (degrees W)	Water Depth (m)
0C063000	41-01G		-73.440	7.4
	42-01G	41.280	-73.470	24.0
	44-02G	40.910	-73.540	17.0
	WLIS101G	41.160	-73.430	6.0
	WLIS73G	40.960	-73.710	21.0
	WLIS75G	40.940	-73.750	11.1
	WLIS78G	40.930	-73.710	11.4
	WLIS81G	40.980	-73.630	14.0
	WLIS83G	40.980	-73.640	18.8
	WLIS90G	40.010	-73.570	18.0
	WLIS91G	40.010	-73.600	6.0
	WLIS93G	40.980	-73.560	10.0
0C0110500	101G	41.160	-73.430	6.0
12/9/00	Empact G	41.574	-73.348	18.3
0C062901	4101G		-73.440	21.0
	WLIS68G	40.940	-73.590	14.9
	WLIS73G	40.960	-73.710	21.0
	WLIS81G	40.980	-73.630	14.0
	WLIS83G	40.980	-73.640	18.8
	WLIS90G	40.010	-73.570	18.0
8/01/01	Empact G	41.574	-73.348	18.3
ST083101	WLIS90G	40.578	-73.346	18.0
CONN01066	A5G	41.000	-73.168	29.0
	B1G	41.100	-73.045	9.0
	B5G	41.040	-73.020	31.0
	B7G	41.010	-73.020	36.0
	D7G	41.020	-72.490	42.0
	WLIS68G	40.520	-73.398	10.0
	WLIS75G	40.530	-73.450	20.0
	WLIS81G	40.558	-73.379	20.0
	WLIS83G	40.585	-73.380	11.0
	WLIS90G	40.578	-73.339	19.0

APPENDIX IB

List of all water samples from each cruise and their geographical locations.

Cruise	Sample I. D	Latitude (degrees N)	Longitude (degrees W)	Depth (m)	
CONN99056	A1W	41.100	-73.330	12.0	
	A3W	41.100	-73.310	15.0	
	A4W	41.030	-73.290	24.0	
	A7W	40.940	-73.240	16.3	
	B6W	41.160	-73.030	18.0	
	C4W	41.110	-72.890	28.0	
	D1W	41.230	-72.850	10.0	
	D7W	41.040	-72.820	37.0	
	E4W	41.140	-72.650	26.0	
	F4W	41.170	-72.520	23.0	
	G1W	41.270	-72.410	5.0	
	I1W	41.290	-72.240	6.4	
	J1W	41.309	-72.182	7.0	
	M3W	41.040	-73.200	28.0	
	WLIS97-81W	40.930	-73.630	15.0	
	WHW2				
	17-02W	41.150	-72.720	20.0	
	40-02W	40.980	-73.420	28.0	
	0C063000	41-01W		-73.440	7.4
		42-01W	41.280	-73.470	24.0
44-02W		40.910	-73.540	17.0	
43-01W		40.870	-73.510	18.0	
WLIS-73W		40.960	-73.710	21.0	
WLIS-75W		40.940	-73.750	11.1	
WLIS-78W		40.930	-73.710	11.4	
WLIS-81W		40.980	-73.630	14.0	
WLIS-83W		40.980	-73.640	18.8	
WLIS-90W		40.010	-73.570	18.0	
WLIS-91W		40.010	-73.600	6.0	
WLIS-93W	40.980	-73.560	10.0		
	41-01W		-73.440	7.4	

Cruise	Sample I. D	Latitude (degrees N)	Longitude (degrees W)	Depth (m)
0C0110500	4101W		-73.440	21.0
	101W	41.160	-73.430	6.0
0C026901	41-01W		-73.440	7.4
	WLIS-101W	41.160	-73.430	6.0
	WLIS68W	40.940	-73.590	14.9
	WLIS-73W	40.960	-73.710	21.0
	WLIS-81W	40.980	-73.630	14.0
	WLIS-83W	40.980	-73.640	18.8
	WLIS-90W	40.010	-73.570	18.0
ST083101	WLIS-90W	40.578	-73.346	18.0
CONN01066	A5W	41.000	-73.168	29.0
	B1W	41.100	-73.045	9.0
	B5W	41.040	-73.020	31.0
	B7W	41.010	-73.020	36.0
	D7W	41.020	-72.490	42.0
	WLIS68W	40.520	-73.398	10.0
	WLIS75W	40.530	-73.450	20.0
	WLIS81W	40.558	-73.379	20.0
	WLIS83W	40.585	-73.380	11.0
	WLIS90W	40.578	-73.339	19.0
DEP(8/2000)	ST01			
	ST02			
	ST03			
	ST05			
	ST06			
	H6			

Appendix IIA

List of samples collected from the Connecticut River (CR) and Housatonic River (HR).

Sample name	Date Collected	Sample name	Date Collected
CR1	5/13/2000	CR16	8/1/01
CR2	6/12/2000	CR17	8/9/01
CR3	2/9/01	HR-A	
CR4	2/9/01	HR-B	
CR5	3/20/01	HR1	6/15/00
CR6	4/2/01	HR2	6/15/00
CR7	4/12/01	HR3	6/15/00
CR8	4/13/01	HR4	5/4/01
CR9	4/16/01	HR5	7/4/01
CR10	4/29/01	HR11	3/8/01
CR11	5/6/01	HR12	3/8/01
CR12	5/9/01	HR13	3/8/01
CR13	5/17/01	HR14	3/8/01
CR14	5/26/01(HD)		
CR15	6/9/01		

APPENDIX IIB

List of studied cores and their geographical locations.

Cruise	Core name	Latitude (degrees N)	Longitude (degrees W)	Depth (m)
June 1996	A1C1	41.100	-73.330	9.0
	A4C1	41.030	-73.290	25.0
	B1C2	41.170	-73.075	6.5
	B5C5	41.074	-73.044	26.0
	B7C1	41.013	-73.030	31.0
	D3C2	41.198	-72.847	5.0
	G1C1	41.270	-72.407	5.0
	0C26901	WLIS-68	40.940	-73.590
0C063000	WLIS-75	40.878	-73.747	18.4

Results from this Grant

Publications

1. Varekamp, J.C., Buchholtz ten Brink, M.R., Mccray, E.L., and Kreulen, B., 2000, Mercury in Long Island Sound sediments. *J. Coastal Research. Spec. issue*, vol. 16, 613-626.
2. Thomas, E., Gapotchenko, T., Varekamp, J.C., Buchholtz ten Brink, M.F., and Mccray, E., 2000, Foraminifera in Long Island Sound surface sediments in 1999: evidence for recent environmental change, *J. Coastal Research. Spec. issue*, vol. 16, 641-655.
3. Thomas, E., Gapotchenko, T., Varekamp, J.C., Buchholtz ten Brink, M.F., and Mccray, E., 2000, Foraminifera in Long Island Sound surface sediments in 1999: Evidence for recent environmental change, CD USGS, open file report 00-304.
4. Thomas, E., Abramson I., Varekamp, J. C., and Buchholtz ten Brink M. R., 2003, Eutrophication of Long Island Sound as traced by benthic foraminifera. In: LIS Research Conference Proceedings.
5. Lugolobi*, F., Varekamp, J. C., Thomas, E., and Buchholtz ten Brink, M.R., 2003, The use of stable Carbon isotopes in foraminiferal calcite to trace changes in biological oxygen demand in Long Island Sound. LIS Research Conference Proceedings.
6. Varekamp, J. C., Thomas, E., Lugolobi, F., and Buchholtz ten Brink, M. R., 2003, The paleo-environmental history of Long Island Sound as traced by organic carbon, biogenic silica and stable isotope / trace element studies in sediment cores. In: Long Island Sound. LIS Research Conference Proceedings.
7. Varekamp, J.C., Zierzow, T., Mccray, E.L and Buchholtz ten Brink, M. Once spilled, still found: Metal contamination in Connecticut wetlands and Long Island Sound sediment from historic industries. Chapter in book on "Our Changing Coasts", Connecticut College (in press).
8. Varekamp, J.C., Lugolobi, F., Thomas, Altabet, M. E., Mccray, E., and Buchholtz ten Brink, M.L.: The history of eutrophication in Long Island Sound: I. chemical indicators. *Limnology and Oceanography*, Special issue on Eutrophication of estuaries (in prep).
9. Thomas, E., Varekamp, J.C., Abramson, I., Mccray, E., and Buchholtz ten Brink, M.L.: The history of eutrophication in Long Island Sound. II. Biological indicators. *Limnology and Oceanography*, Special issue on Eutrophication of estuaries (in prep).
10. Lugolobi, F., Varekamp, J.C. and Thomas, E., 2004, The modern environment of Long Island Sound. *Marine Chemistry* (in prep).

Student theses

- Abramson, I.** , 2002. Benthic foraminifera as environmental proxies in Long Island Sound (BA). pp. 276
- Groner, M.**, 2004, The carbon cycle in Long Island Sound: radiocarbon studies of carbonates (BA). pp 169.
- Zierzow, T.** , 2002, Metal contamination in sediments from the Housatonic River watershed, CT. (MA) pp. 262, Environmental consultant, MA.
- Lugolobi, F.** 2003, Environmental Issues in Long Island Sound (MA)., pp 258. Now a PhD candidate in marine geochemistry at Boston University, Boston, MA.

Presentations with published abstracts

2000

1. Thomas, E., Gapotchenko, T., Varekamp, Buchholtz ten Brink, M.R., and Mecray, M.L., 2000, Environmental change in Long Island Sound over the last 35 years. AGU spring meeting, Washington DC.
2. Buchholtz ten Brink, Mecray, E.L., and Varekamp, J.C., 2000, Mercury in sediments from Long Island Sound. AGU spring meeting, Washington DC.
3. Varekamp, J.C., Buchholtz ten Brink, Mecray, E.L., and Kreulen, B., 2000, Mercury in sediments from Long Island Sound. GSA meeting, Reno NV.
4. Thomas, E., Gapotchenko, T., Varekamp, Buchholtz ten Brink, M.R., and Mecray, M.L., 2000, Environmental change in Long Island Sound over the last 35 years. GSA meeting, Reno NV
5. Thomas, E., Gapotchenko, T., Varekamp, Buchholtz ten Brink, M.R., and Mecray, M.L., 2000, Environmental change in Long Island Sound over the last 35 years. LIS research conference, biennial meeting
6. Varekamp, J.C., Buchholtz ten Brink, Mecray, E.L., and Kreulen, B., 2000, Mercury in sediments from Long Island Sound. LIS research conference, biennial meeting

2001

7. Varekamp, J.C., Lauriat, K., Buchholtz ten Brink, M.R. and Mecray, M.L. Historical records of Mercury contamination in sediment cores in Connecticut and Long Island Sound. GSA Northeastern meeting
8. Thomas, E. Shackeroff, J., Varekamp, J.C., Buchholtz ten Brink M.R., and Mecray, M.L. Foraminiferal records of environmental change in Long Island Sound. GSA Northeastern meeting
9. Varekamp, J.C., Lauriat, K., Zierzow, T., Buchholtz ten Brink, M.R.L. and Mecray, E.L., Mercury in sediments from the Long Island Sound Region. AGU spring meeting
10. Varekamp, J.C., Hg in the Housatonic River Basin AGU spring meeting
11. Zierzow, T. R. Varekamp, J. C., Buchholtz Ten Brink, M. R., and Mecray, E. L. Metal contamination in sediments from the Housatonic River watershed. GSA, annual meeting, Boston.
12. Abramson, I., Bowman, S., Thomas, E., Varekamp, J. C., Mecray, E. L., Moore, J., and Buchholtz Ten Brink, M., Benthic foraminifera in Long Island Sound: indicators of environmental changes. GSA, annual meeting, Boston.
13. Lugolobi, F., Varekamp, J.C., Thomas, E., and Buchholtz Ten Brink, M., Historical changes in water chemistry and summer hypoxia in Long Island Sound, GSA, annual meeting, Boston.
14. Thomas, E., Lugolobi, F., Abramson, I., and Varekamp, J.C., Changing environments in Long Island Sound over the last 400 years. AGU fall meeting, SF, December.
15. Varekamp, J. C., 2001, Environmental Change in Long Island Sound: climate change and eutrophication. Second Long Island Sound Lobster Health Symposium, November 29-30 2001, Ronkonkoma, NY.

2002

16. Varekamp, J. C., Thomas, E., Mecray, E. L. and Buchholtz Ten Brink, M., The historical record of water quality in LIS. Long Island Sound workshop, Batelle laboratories, March 6-7, Groton CT,
17. Thomas, E., Lugolobi, F., Varekamp, J.C., Paleoceanographic proxies in Long Island Sound, CT USA. Goldschmidt Conference, Davos, Switzerland, *Geochimica Cosmochimica Acta* 66, # 15A, p. A772.
18. Thomas, E., Abramson, I., Varekamp, J.C., Buchholtz ten Brink, M.R., Eutrophication of Long Island Sound as traced by benthic foraminifera. Long Island Sound /NEERS Research Conference, Oct. 24-26, Groton, CT.
19. Varekamp, J.C., Thomas, E., Lugolobi, F., and Buchholtz ten Brink, M.R., Paleoenvironmental history of Long Island Sound. Long Island Sound /NEERS Research Conference, Oct. 24-26, Groton, CT.
20. Varekamp, J.C., and Buchholtz ten Brink, M.R.. Mercury in Connecticut and Long Island Sound sediment. Long Island Sound /NEERS Research Conference, Oct. 24-26, Groton, CT.
21. Lugolobi, F., Varekamp, J.C., and Thomas, E., The use of carbon isotopes to trace changes in biological oxygen demand in Long Island Sound. Long Island Sound /NEERS Research Conference, Oct. 24-26, Groton, CT.
22. Abramson, I., Thomas, E., Varekamp, J.C., and Buchholtz ten Brink, M.R., Benthic foraminifera in Long Island Sound as indicators of eutrophication. GSA Annual meeting, Denver, October. p.384.
23. Varekamp, J. C., Thomas, E., Lugolobi, F. and Buchholtz ten Brink, M. R. Paleoenvironmental History of Long Island Sound, CT, USA. AGU Fall meeting, San Francisco, December.
24. Buchholtz ten Brink, M., Butman, B., Bothner, M., Poppe, L., Murray, R., Varekamp, J. C., Thomas, Mecray, E., Harris, C., Signell, R., Fate and Impact of Contaminants in Sediments of the NE United States. AGU Fall meeting, San Francisco, December.

2003

25. Varekamp, J.C., Thomas, E., Buchholtz ten Brink, M., Altabet, M., and Cooper, S., The paleo environmental history of Long Island Sound. Abstract volume of the Internal Working Meeting of the LIS Lobster Initiative, Thursday, January 16-Saturday, 2003, University of Connecticut at Avery Point, Groton, CT
26. Lugolobi, F., Varekamp, J.C., Thomas, E., M.L. Buchholtz ten Brink, and Mecray, E., Carbon Cycling in Long Island Sound Over the Last 1000 Years, Fall meeting AGU

2004

27. Varekamp, J. C., Thomas, E., Buchholtz ten Brink, M., Altabet, M., Cooper, S., and Sangiorgi, F., 2004. Environmental Change in Long Island Sound in the Recent Past: Eutrophication and Climate Change. Abstract volume of the Lobster Research Initiative Working Meeting, May 3-4, 2004, Marine Science Building, University of Connecticut at Avery Point, Groton

28. Bronsther, R., Welsh, P. and Varekamp, J.C., Mercury in Connecticut and Long Island Sound: Impact of historic hatting industries. Spring AGU meeting
29. Groner, M., Thomas, E., and Varekamp, J.C., Radiocarbon studies of Long Island Sound sediments. AGU spring meeting
30. Varekamp, J.C., Lugolobi, F., Thomas, E., Mecray, E. and Buchholtz ten Brink, M.R.L., The eutrophication of Long Island Sound. AGU spring meeting.
31. Andersen, N. and Varekamp, J.C. Paleoproductivity indicators in Long Island Sound. AGU spring meeting.
32. Altabet, M. and Varekamp, J.C. Nitrogen Isotopic Ratio Records The Eutrophication History of Long Island Sound. AGU spring meeting
33. Thaler, B., Thomas, E., and Varekamp, J.C., Benthic Foraminifera in the Changing Ecosystem of Long Island Sound. AGU spring meeting

Invited Talks

2000. Environmental Change in Long island Sound over the last 40 years. Peabody Museum Associates, Yale University, New Haven CT; September 2000.
2000. Environmental change in Long Island Sound over the last 35 years. GSA meeting, Reno NV
2001. The State of the Sound, EPA/ Save the Sound meeting, NY Botanical Garden, NY, March 2001
2001. Environmental Change in Long Island Sound: climate change and eutrophication. Second Long Island Sound Lobster Health Symposium, November 29-30, Ronkonkoma, NY.
2001. Long Island Sound Environments over the last 400 years, Woods Hole Oceanographic Institution, Departmental Colloquium in Geology, October 2001.
2002. The historical record of water quality in LIS. Long Island Sound workshop, Batelle laboratories, March 6-7, Groton CT,
2002. Changes in the Long Island Ecosystem over the last Millennium. Department of Geology & Geophysics, Global Change Presentations, Yale University, October 2002
2003. Paleoenvironmental history of Long Island Sound. SMAST, University of Massachusetts, New Bedford MA, 26 March
2003. Once Spilled – Still Found – metal pollution in sediments from Long Island Sound and its coastal wetlands. Connecticut College, Groton CT, Conference on “Our Changing Coast, 29 March.

Outreach and Popular Press

- April 16, 2004, Southern CT State University, New Haven: **Global warming or sewage input: why is Long Island Sound running out of breath?** Endowed lecture series in coastal science at SCSU.
- May 24, 2004, Mystic SeaPort Public Lecture Series, **Global Warming and the Rising Tides in Long Island Sound**, University of Connecticut, Stamford Campus, CT.
- August 24, 2003, 2003 – *New York Times*, Metrosection on Sunday “ **Muckrakers discover history in Long Island Sound**”
- March 15, 2004, *NewsDay*, Article on **Mercury in Long Island Sound**.
- March 25, 2004, *CPTV*, Program on Energy – **A Delicate Balance**, tv appearance discussing environmental issues of LIS.
- April 25, 2004, *New Haven Register*, article on **Long Island Sound** health.