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## **Environmental Change in Long Island Sound in the Recent Past: Eutrophication and Climate Change**

**P.I. Johan C. Varekamp**, E&ES Wesleyan University, CT - Geochemical proxies and dating of sediment cores, data integration

### **Co-P.I.'s (by 2006)**

- **Ellen Thomas** (Wesleyan University and Yale University, CT) Foraminiferal investigations and stable isotope and trace element studies of foraminifera
- **Mark Altabet** (Univ. of Massachusetts, Dartmouth, MA) Nitrogen isotope studies
- **Sherri Cooper** (Bryn Athyn College, PA) Diatom studies
- **Henk Brinkhuis** with postdoctoral fellows **Francesca Sangiorgi** and **Timme Donders** (Utrecht University, The Netherlands) Dinoflagellate cyst and pollen studies

**Marilyn Buchholtz tenBrink** was a co-PI at the start of the project when she was working at the US Geological Survey at Woods Hole, MA, but she left to work as Branch Chief at the EPA in Rhode Island; Johan Varekamp took over her duties.

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## ABSTRACT

Long Island Sound (LIS) has seen dramatic environmental changes since colonial times, with increased environmental degradation over the last ~200 years (the industrial period), intensifying over the last 50 years with a peak in pollution during the 1950s-1960s. We use core studies to document environmental changes as they occurred during the transitions from the pastoral period to the colonial period (around 1630 AD), from the colonial to the industrial period (around 1800 AD), and within the industrial period.

Our studies show that the influx of sediment into LIS started to increase with the first clear-cutting by European colonists, as documented in our pollen records. Major environmental changes including hypoxia (as indicated by carbon isotope values in benthic foraminiferal tests) started to occur in the early to middle 1800s. At that time, the bottom water salinity of western LIS (as indicated by oxygen isotope values in benthic foraminiferal tests) dropped by several salinity units (psu), probably as the result of enhanced run-off due to changes in land use, in combination with an increased fresh water flux from waste-water treatment plants along the East River into western LIS. Pollen records show increased abundance of marker species indicative of land clearance. A decrease of land-derived organic matter in the late 18<sup>th</sup>-early nineteenth century in some cores suggests that deforestation removed the source for the annual flux of leaves from deciduous trees. The input of sewage-derived Nitrogen increased, as seen in the nitrogen isotope records, which led to an increase in marine primary productivity. The latter is indicated by a strong increase in the mass accumulation rates (MAR) of marine organic Carbon, organic Nitrogen and biogenic silica (diatom frustules). At the same time, the ratio of planktic (centric) to benthic (pennate) diatom species increased, probably as a result of increased water column turbidity, and the abundance of heterotroph relative to autotroph dinocysts increased in parallel. With the increase in planktic productivity came increased productivity of benthic fauna, as indicated by higher benthic foraminiferal accumulation rates (BFAR), and an increase in relative abundance of the diatom-consuming species *Elphidium excavatum*. Both sediment chemical and biotic proxies thus testify to the eutrophication of the Sound over this ~150 year time span.

This pattern started to change in the 1960s-1970s, as indicated by a decrease in the abundance of the most common foraminifer, *Elphidium excavatum*, and its replacement by the omnivorous *Ammonia parkinsoniana*, most notably in western LIS, but progressing eastward into the central Sound. This replacement indicates major changes at the base of the LIS food-chain: a specialist diatom consumer is replaced by an omnivorous form. This replacement may be the result of the decreased availability of diatoms as compared to organic matter produced by other algae, possibly caused by a switch from Nitrogen limitation to silica limitation for primary productivity in western and central sections of the Sound during some periods of the year. Our core data show declining MAR of marine organic carbon and biogenic silica in western LIS as well as declining benthic foraminiferal accumulation rates, supporting this hypothesis of decreased diatom productivity. Such a change in dominant primary producers during at least some times of the year may have major consequences for the LIS ecosystem. The fundamental shifts in the ecosystem together with the persistent freshening, warming, hypoxia and ongoing pollution may all have impacted the lobster populations. We thus provide evidence that multiple stressors impacted the living environment of the LIS lobster population, which weakened them and made them vulnerable to attacks by pathogens.

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### **Introduction to Long Island Sound and this research project**

Long Island Sound (LIS) is an urban estuary that, like many similar highly populated coastal regions, suffers from water quality problems: hypoxia, large inputs from waste water treatment plants (WWTP) as well as a variety of toxins from riverine and atmospheric sources. Changes in the LIS ecosystem over the last decades have been noted, with fish kills due to low oxygen conditions occurring since the 1970's, but the 1998/1999 lobster die-off was sudden and severe. We compare the rates and magnitudes of environmental changes on time scales of 1000s of years, the last 400-200 years and the last 50 years. LIS has undergone dramatic changes over the last centennia, mainly as a result of increased human population pressure, with associated increased human waste flows, changes in landscape, and marine resource extraction (e.g., lobsters, finfish including menhaden, shellfish including oysters). Superimposed on these anthropogenic effects are those of climate change, which have acted over much longer time spans. The effects of anthropogenic CO<sub>2</sub> emissions (including global warming and ocean acidification), however, should be taken into account when assessing regional human influences on this urban estuary. Our direct goal was to establish detailed records of LIS paleo-environments and their biota over the last 100-200 years within the context of environmental changes over the last thousand years, in order to establish an 'environmental baseline', and to assess changes in chemical, physical and biological parameters over the last fifty years against that background. We thus place the lobster die-off of the late 1990's in a context of the last fifty, two hundred and last thousand years.

We used sediment cores from LIS, and established dated records of paleo-temperature, paleo-salinity, and paleo-oxygenation of the water column, using proxies developed for this project and/or adapted from existing approaches. In addition, we established the pollution levels of Mercury and other contaminants in the sediments. The contents of organic carbon, nitrogen, and carbonate carbon, and their isotopic composition as well as the content of biogenic silica were determined and recalculated as "mass accumulation rates" (MAR, g/ cm<sup>2</sup>yr). These parameters serve as indicators for the net organic productivity of the Sound, i.e., marine organic matter that is deposited in the sediments. More refractory organic matter derived from land is also buried, and can be distinguished from its marine counterpart through its characteristic C/N, δ<sup>15</sup>N and δ<sup>13</sup>C signature. The paleo-biological studies of the same sediment samples document the changes in abundance and species composition of assemblages of benthic foraminifera (bottom-dwelling eukaryotic unicellular organisms), diatoms (eukaryotic benthic and planktic primary producers or "micro-algae" with a silica skeleton), dinoflagellates (eukaryote micro-algal primary producers and heterotrophs that build a cyst of organic material) and pollen (indicators of terrestrial vegetation, thus changes in land use). The micro-algae are at the lower end of the food chain, and changes in their abundance and assemblage composition are primary indicators of environmental change and may affect higher trophic levels.

The paleo-environmental core-record approach puts current and recent environmental issues of LIS into a historical perspective. It makes it possible to distinguish long-term trends from fluctuations, and establishes a natural baseline, on which anthropogenic impacts are superimposed. The materials that end up in the sediment are at 'the end of the pipeline': they may have been processed and recycled by biota many times prior to their arrival at, and storage on the LIS bottom. Our data represent the integrated effect of everything that happened to biogenic matter prior to burial, and thus may reflect a sum of bottom-up

ecosystem changes (triggered by changes in micro-algae at the base of the food chain), and top-down ecosystem changes (i.e., removal of biomass by marine resource removal, e.g. fisheries).

### **Studied Materials and Methods**

Samples were collected by the Center for Coastal and Marine Geology (U. S. Geological Survey, Woods Hole, MA), which initiated a comprehensive study of LIS environments in 1996, collecting hundreds of surface samples (green, yellow and blue diamonds labeled SEAX96024, 96017 and JD90701-WLIS, red octagons labeled CONN99056) and 57 short cores (blue squares labeled SEAX 96024, most shorter than 70 cm) in 10 LIS cross sections from 1996-2000 (Figure 1). We organized a cruise (October 2001), during which we collected surface samples and 14 long cores (175-243 cm) along an East-West transect through Long Island Sound (triangles; CONN01066; Table 1). Data were collected on grab samples (surface sediment), twelve of the USGS short cores and on four of the new long cores (Table 2; Figure 1). Details of data collected and interpretations (as listed on p. 5 of the original proposal) are summarized in subsections below. The long cores WLIS75GGC1 and B1GGC1 (also referred to as WLIS75 and B1) are discussed in most detail because of their high time resolution; Cores WLIS75-C1 and B1C2 are short cores from the same locations.

The derivation of the age models for the cores is not treated in great detail in this report. The cores were dated with radiometric methods and chemo-stratigraphy (levels of characteristic pollution, dated on land and by the historical record, mainly Hg), using short-lived radio-isotopes ( $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ ), and radiocarbon data (mainly on shells). The age dates were translated into age models for each core, taking all age evidence into account. Many of the measured parameters are recalculated into mass accumulation rates (MAR), using the linear sedimentation rates (from age-depth relations) and sediment density (derived from measured sediment water contents in each sample and an average sediment grain density). Ages assigned to each sample and, where available, MAR are presented in the data tables.

The total carbon and organic carbon, sulfur and nitrogen analyses were done on an elemental analyzer (combustion, gas-chromatography separation, detection by various techniques), some at Wesleyan University, some at the USGS in Woods Hole. The C and N organic fractions and their isotopic composition were measured in the laboratory of Altabet (UMass, Dartmouth, MA), following techniques developed by him and published in the literature.

The measurement of BSi is a time-intensive, involved technique, because 7-8 silica analyses of high-pH aqueous extracts from a single sample are needed for each single BSi determination (Varekamp et al., 2004, Andersen, 2005). The technique was adapted from literature descriptions, and the Si analyses were carried out on the ICP-AES at Wesleyan University.

For foraminiferal studies (Abramson, 2002), surface samples were stained with Rose Bengal in a 10% buffered formaldehyde solution in order to determine the abundance of living specimens. Core samples were weighed wet, oven dried at 60°C, then weighed dry to determine the water content. Surface samples and core samples were wet-sieved (63  $\mu\text{m}$  sieve size), then dried and weighed. Foraminifera were picked from this size fraction, and at least 100 specimens were picked per sample. At the low diversity of

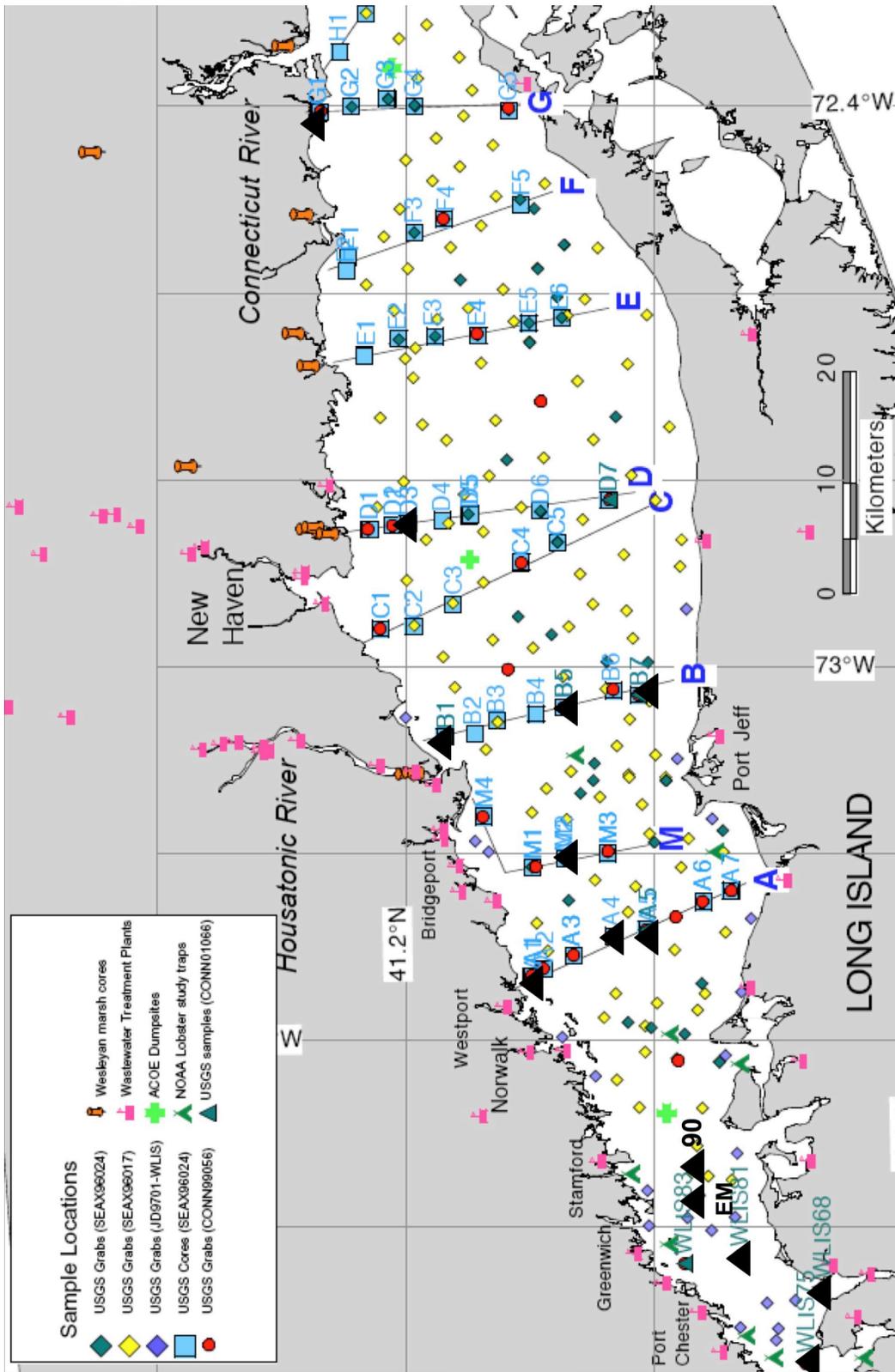
LIS assemblages, this number allows statistically significant conclusions on relative abundance changes in species present at more than 5%. All specimens were mounted in cardboard slides, and placed in an aluminum holder with glass cover. In many samples additional specimens were picked for trace element and stable isotope analyses (Thomas et al., 2000; Lugolobi et al., 2004; Thomas et al., 2004; Thomas and Varekamp, 2006). Care was taken to pick the best-preserved, most glassy specimens for geochemical analyses. For calibration of geochemical proxies only specimens with brightly stained protoplasm in the inner whorls of the test were used, and those with diffuse staining in outer chambers were excluded.

Calcium carbonate tests of the foraminiferal species *Elphidium excavatum* were manually picked in order to measure stable isotope ratios of O and C ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ), and Mg/Ca ratios in some cores. For stable isotope analyses 5-10 specimens are sufficient, so that we could perform these analyses on 12 cores in addition to surface samples (Table 2). For Mg/Ca analyses, a proxy for temperature during calcification, about 40-50 specimens are needed, so that analyses can be performed on samples with abundant foraminifera only. We performed these analyses on 3 cores and surface samples (Table 2).

The stable isotopes of C and O in carbonate (foraminiferal tests) were measured using standard techniques of dissolution in phosphoric acid followed by equilibration with carrier  $\text{CO}_2$  and measurement in a gas inlet mass spectrometer. The data were collected at the stable isotope facility at the University of Santa Cruz (CA) and at Yale University (New Haven, CT). The isotopic ratio of Sulfur was measured at the University of Indiana (Bloomington, IN), using precipitated barite from acid extracts of the samples as material.

In quantitative palynology (Sangiorgi et al., 2005), a weighted amount of sediment is treated with a tablet that contains a specific number of *Lycopodium clavatum* spores followed by sediment dissolution in five subsequent steps in 10% HCl and 38% HF. The residue is then sieved to retain the  $>10\ \mu\text{m}$  fraction, which is mounted on microscope slides and analysed for organic-walled dinocysts, pollen and spores. Between 250 and 300 dinocysts and a minimum of 300 pollen grains were counted from each sample to determine percentages and concentrations.

Data for diatom species (Cooper, in press) were compiled and prepared for principal component analysis, using CANOCO software (2004); the final integration of the diatom data with other proxy data is ongoing.



**Figure 1.** Sample locations in Long Island Sound: surface samples, short cores (USGS) and long cores (Wesleyan University). Studied cores are highlighted as black triangles. Core WLIS90 is labeled as “90” and the Emapact core as “EM”.

### **Subsection 5C1a. Age models (Varekamp)**

Radiocarbon dates were collected on 12 samples in four cores (A1C1, A4C1, WLIS75GGC1, B1GGC2; Table 2) in order to establish age control for the paleo-environmental records. The  $^{14}\text{C}$  determinations were made on carbonate shells instead of organic matter, because we have determined that organic carbon ages tend to be too old, i.e., they reflect the time that the plant died, which is not necessarily the time of deposition of the mud layer in which it is now contained. Ages derived from carbonate-secreting organisms that are living *in situ* approach the age of deposition much better, despite issues of radiocarbon reservoir effects (Varekamp et al., 2005). The upper parts of four cores (A1C1, A4C1, D3C2, B1C1) were analyzed for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ , the first a naturally occurring radioisotope with a dating time span of about 150 years. The presence of  $^{137}\text{Cs}$  derives from atmospheric nuclear tests, which started in the early 1950's and peaked in 1964 (Varekamp et al., 2003; Groner, 2004). Bioturbation blurs the  $^{137}\text{Cs}$  signal, making the resolution less than the five to ten years that is theoretically possible, although we concentrated our efforts on cores with minimum bioturbation, as determined from core X-rays (Table 2).

The  $^{14}\text{C}$  dates on shells were calibrated with the CALIB program on the marine dataset, using the average 400 year reservoir time. Our studies on the radiocarbon reservoir effect in LIS (Groner, 2004) indicate that this value is our best choice. The  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  studies were carried out at the USGS in Woods Hole, and the age models based on these isotopes use the peak of  $^{137}\text{Cs}$  deposition at 1964, the onset of  $^{137}\text{Cs}$  deposition at 1950. The excess  $^{210}\text{Pb}$  profiles are interpreted with the 'constant initial' model, providing in general an average sedimentation rate for the last 100 years of history.

The onset of Mercury pollution in western LIS is related to the hatmaking industry, which started ~ 1820 CE, as indicated by extensive studies of marshes along the Housatonic river as well as the historical industrial record. The peak in Mercury pollution is taken at 1960, as based on extensive earlier marsh studies by us. The onset of land clearing during early colonial times as indicated by the appearance of ragweed pollen (*Ambrosia*) is taken at 1650 CE. The floods of 1955 were caused by two hurricanes striking New York and Connecticut within two weeks of each other, as widely documented in newspapers and historical records. The associated deposits are indicated by a Mercury-rich layer in the outflow of the Housatonic River and a thin layer containing a Mercury anomaly in core A1C1. Core WLIS75GGC1 has a coarse, coal-rich layer with an Hg-enriched top at ~1955, which interrupts the continuous sedimentation.

### **Subsection 5C1b. Carbon Analyses (Varekamp)**

Organic carbon, nitrogen and carbonate contents were determined in samples from 10 cores (Table 2). The organic carbon contents reflect the sum of the supply of organic material from land (leaves, grasses, soil carbon, as well as carbon from WWTPs in more recent times), and the *in situ* produced organic matter ("marine carbon"). The total organic carbon concentration and MAR increased in all cores, most pronouncedly in western LIS (Figure 2). An increase in the MAR of organic matter in all studied cores started around 1800 AD, but was at least in some locations preceded by a smaller increase in the late 1600s. This earlier increase is referred to as the 'beaver peak' (Figure 2), because it may have resulted from destruction of beaver dams during the European fur

trade, with transport of organic matter and nutrients downstream when river morphology changed (Varekamp, 2006). Early colonial changes in land use had an effect as well.

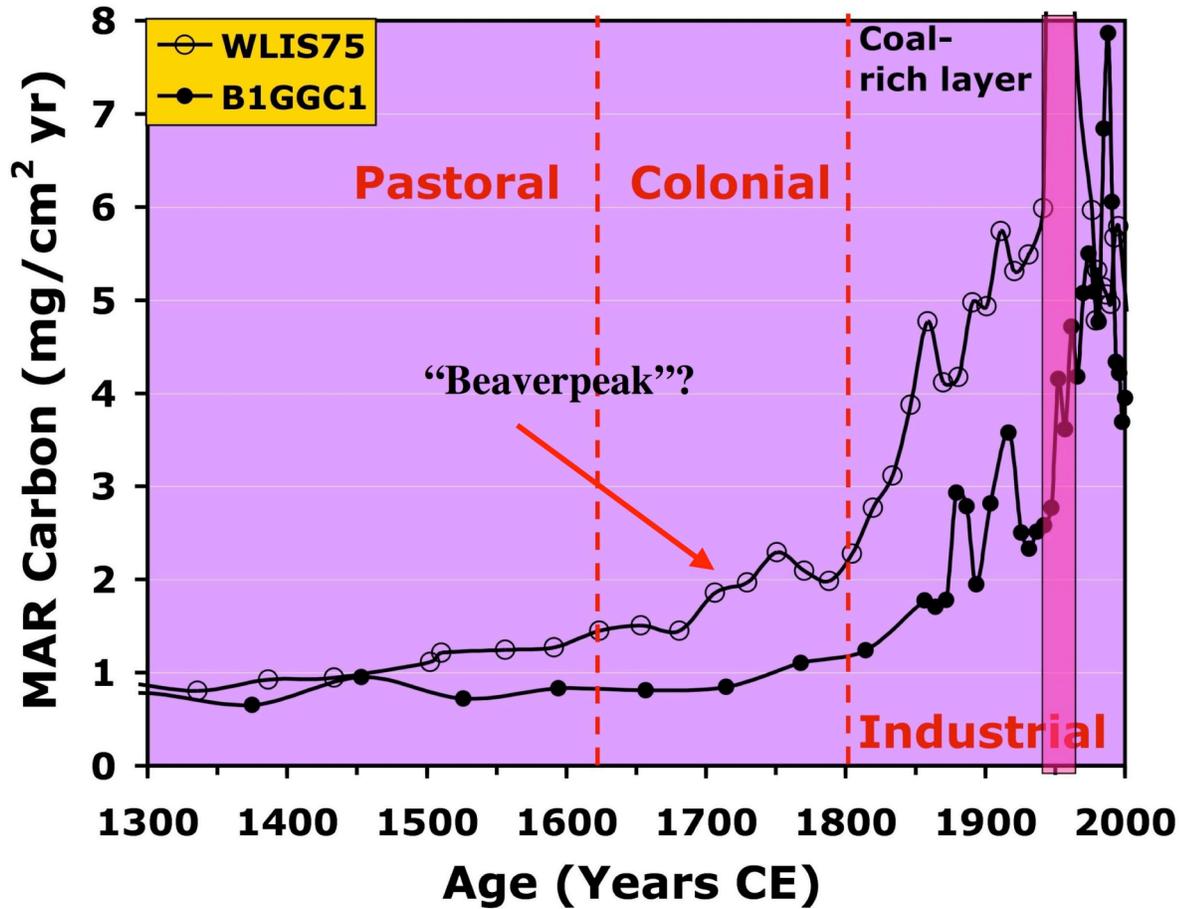
Core WLIS75 (Figure 2) shows a drop in Carbon MAR starting in the early 1900s (somewhat masked by the “coal peak”), whereas core B1 shows a drop later in the 20<sup>th</sup> century. The MAR of organic Carbon and Biogenic Silica (the latter another productivity indicator, see section 5E) from cores A1C1, A4C1 and D3C1 are shown in Figure 3. These records show a minor increase in Carbon burial rate around 1625 CE, with a very steep increase in the mid-1800s. The absolute values of the Carbon burial rates in these three cores are comparable, and the increase over the last 50 years is 10-50 higher than in pre-colonial times. Core A4C1 shows variations in Carbon MAR since the early 1900s, which may be artifacts of effects of the 1950’s hurricanes on the sedimentary record (e.g., occurrence of coarser layer). These records suggest that subtle differences exist between coastal sites and those in central LIS, but all records show strongly increasing organic Carbon burdens, all with large enrichment factors compared to pre-colonial rates.

We used various proxies to distinguish between marine and terrestrial organic matter. In core WLIS75GGC1 we determined the  $\delta^{13}\text{C}$  of the organic matter, a well-defined source indicator (Figure 4; Varekamp et al., 2009) as well as  $\delta^{15}\text{N}$  in 10 cores, which varies slightly between terrestrial and marine organic matter (see Subsection 5C4, Nitrogen). The N/C values indicate the source of the organic matter, because values are generally lower in terrestrial than in marine organic material, although they display a considerable range in each environment (Figure 5).

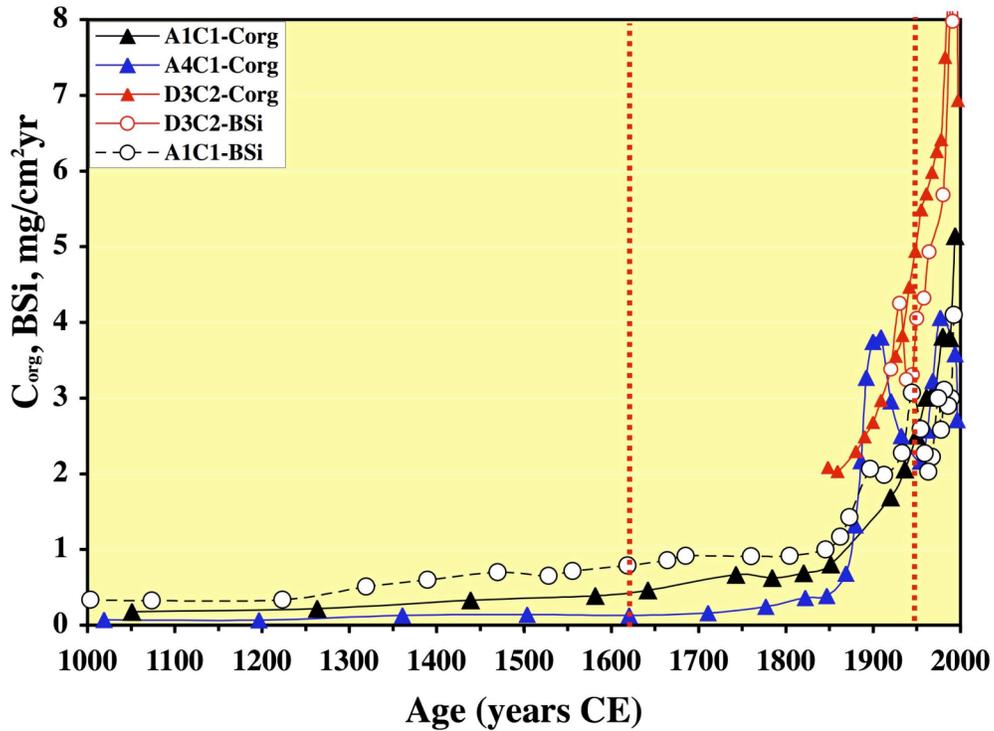
The contributions of the two main sources of organic matter varied strongly throughout each core and between cores (Figure 6). These variations are of direct interest to the origin of the hypoxia in the western Sound, because oxidation of the more labile marine organic carbon is commonly considered the root cause of hypoxia. Our data show, however, that the organic carbon loadings over the last 100 years in Western LIS sediment shifted from dominance by marine carbon (algal matter) to more abundant terrestrial carbon (Figure 6). This seems contradictory to the ‘common wisdom’, i.e., that with on-going eutrophication (nutrient input) the amount of marine organic matter relative to that of terrestrial organic matter should increase. The MAR marine organic matter increased gently over the last 100 years in core B1 (Figure 6), but the MAR of terrestrial organic matter increased more strongly. In the WLIS75 core, the accumulation rate of marine carbon actually decreased over the last 100 years (Figure 6), whereas that of terrestrial carbon increased rapidly. Changes in the ecosystem of western LIS may have led to the loss of marine carbon fluxes to the sediment: increased fishing and harvesting of oysters may have extracted large amounts of marine carbon from Western LIS, some of which was formerly buried in the sediment.

The carbonate content of samples indicates the productivity of hard-shelled organisms (mainly bivalve mollusks and foraminifera, with minor contributions by echinodermata, ostracodes and bryozoans). In most cases the carbonate content co-varies with the organic carbon content. The carbonate data may not always be representative, however, because large shells are randomly recovered in some core samples but not in others, creating a potential bias in the record. Nonetheless, with the increase in primary productivity in the 1700-1800s, the productivity of hard-shelled benthic heterotrophic organisms increased as well (see also below, Subsection 5C6, Benthic foraminifera).

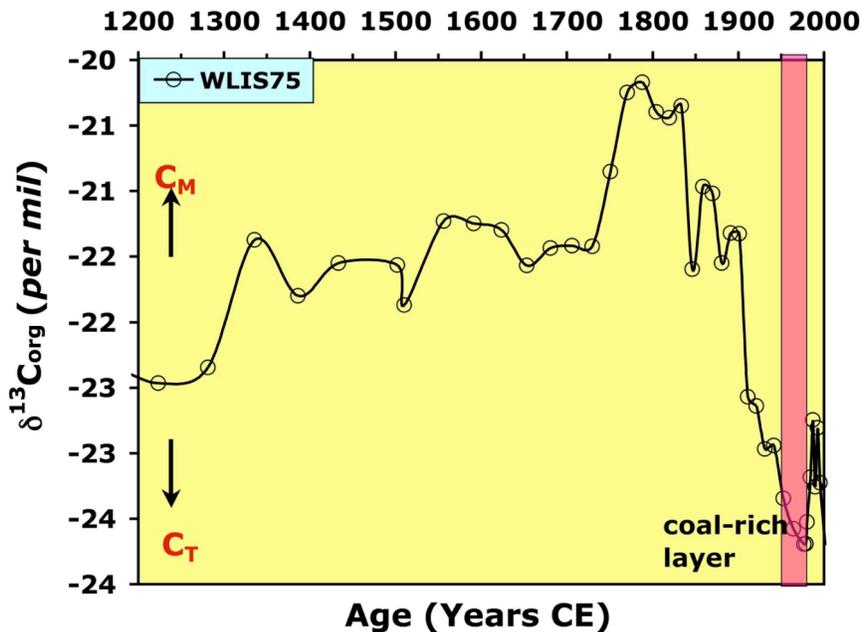
Our data thus show that the western and central sections of LIS became strongly eutrophied over the last ~ 200-300 years as indicated by increasing Carbon MAR. A strong acceleration in Carbon MAR started in the early 1800s in most cores. The contributions of terrestrial carbon increased, and sometimes outweighed the marine contributions, a result of changes in land-use and river character. The decrease in marine organic matter accumulation in western LIS is most striking, and may be related to changes in aquaculture and fishing that removed part of the enhanced Carbon loading from the water column as human food over the last 100 years.



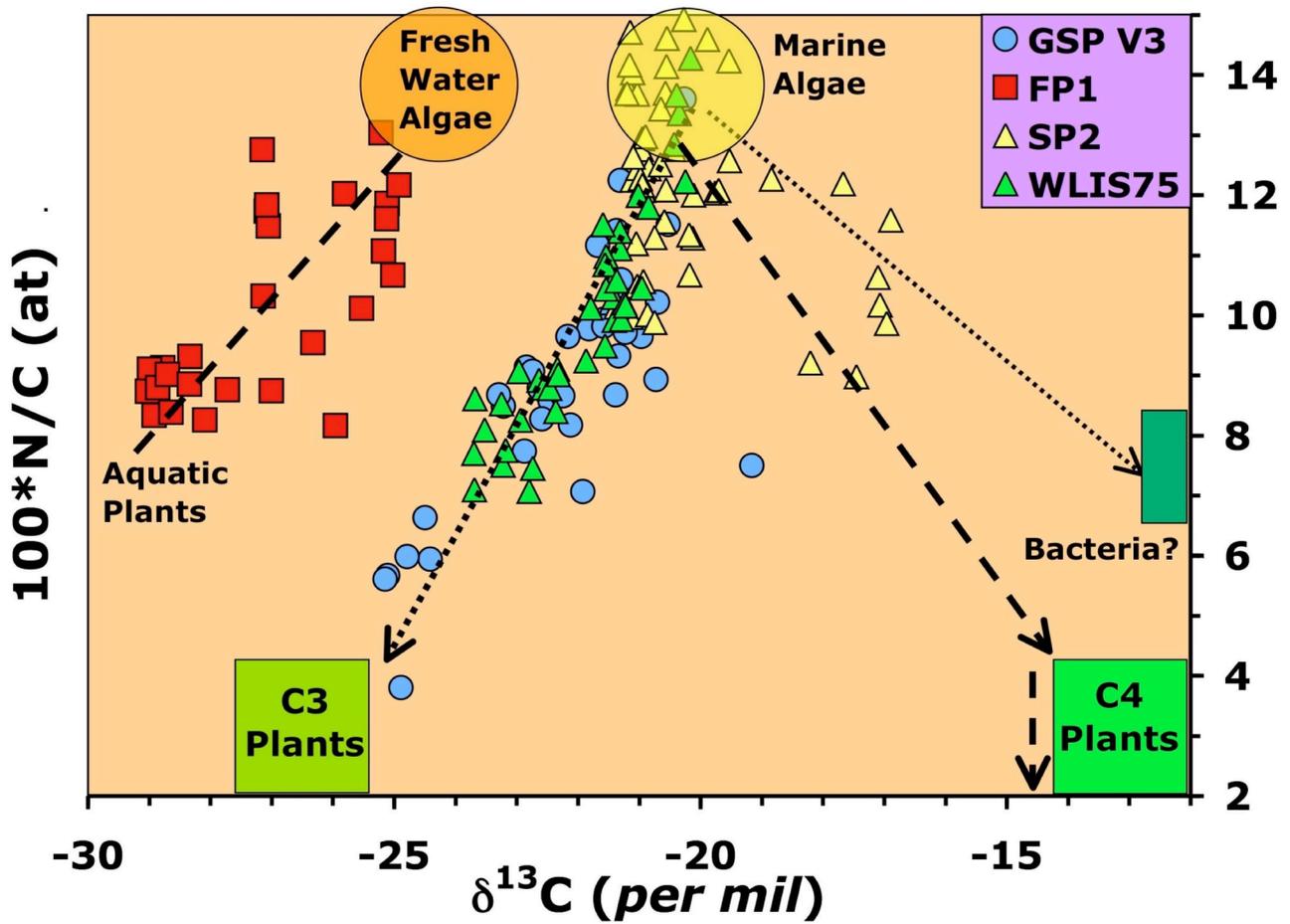
**Figure 2.** Mass accumulation rates of Carbon in cores WLIS75GGC1 and B1GGC1 show an increase since the 1600s, and a strong increase since 1800 AD. Core WLIS75 shows a drop in Carbon accumulation since the mid 1950s, whereas the B1 core shows a drop since the late 1970s.



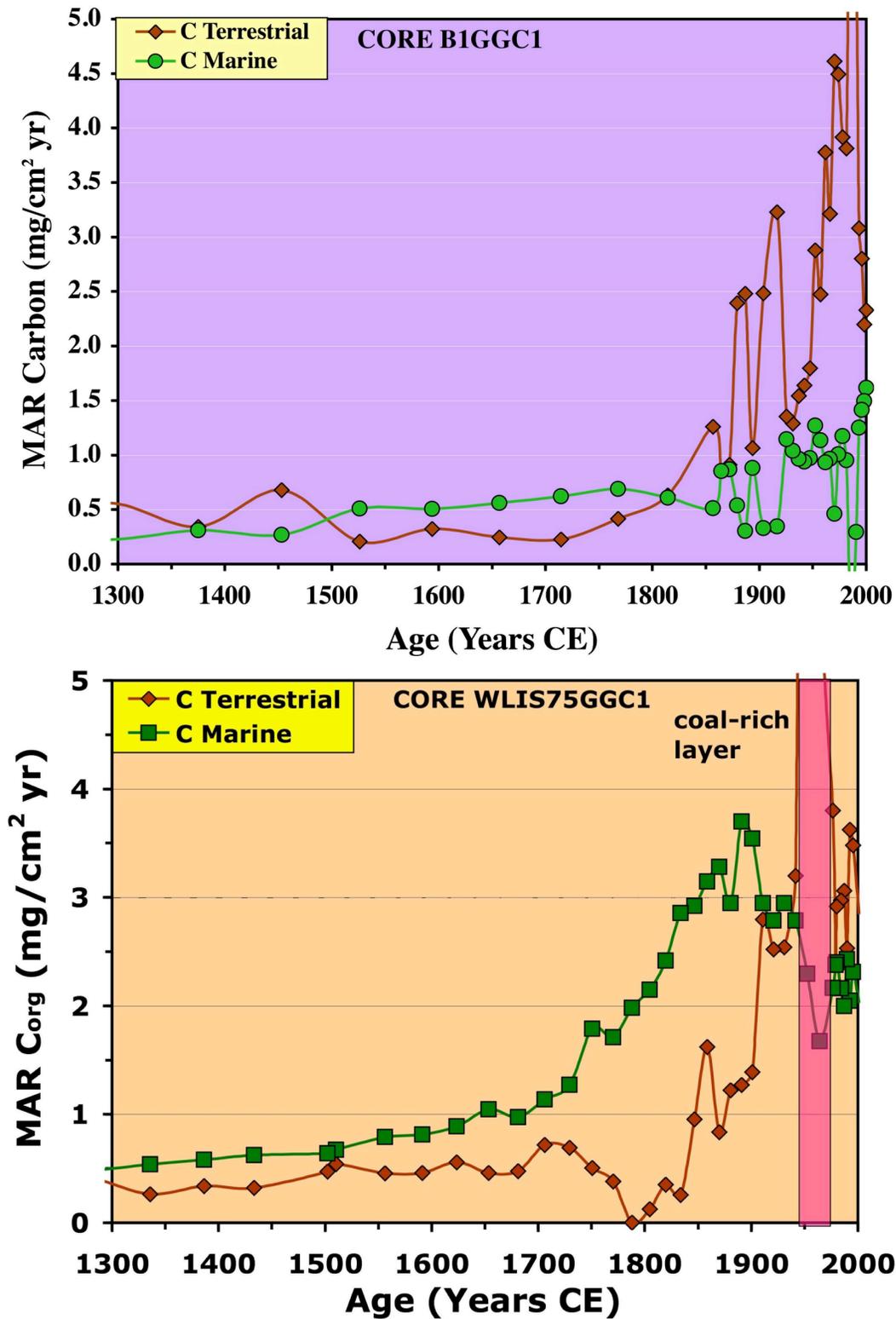
**Figure 3.**  $C_{org}$  and BSi mass accumulation rates in cores A1C1, A4C1, and D3C2. The two productivity parameters in core A1C1 rise between 1600-1700 CE, and show a steep increase from the early 1900s on. Core A4C1 shows a decrease in Carbon burial since the early 1900s similar to core WLIS75GGC1. Core D3C2 shows the Carbon-enriched upper part of the record only.



**Figure 4.** Carbon isotope trends of organic matter in core WLIS75 ( $C_M$  = marine Carbon;  $C_T$  is terrestrial Carbon). Note the strong decrease in  $\delta^{13}C$  since 1800, indicating the increased abundance of terrestrial Carbon. The very low isotope ratios in the mid-1900s are an artifact of the presence of the coal-rich layer (very low  $\delta^{13}C$  in coal).



**Figure 5.** Carbon source tracing with N/C and  $\delta^{13}\text{C}$  in sediment. The WLIS75 samples (located in The Narrows, Figure 1) plot on a mixing array of marine Carbon (algae) and C3 (land) plants. The GSPV3 core samples (Block Island) show mixing between marine Carbon and terrestrial carbon produced by C3 as well as C4 plants (e.g., marsh flora). The other data refer to fresh water environments (FP1, SP2, Block Island).



**Figure 6.** Carbon mass accumulation rates (MAR) for cores B1 (top) and WLIS75 (bottom). The B1 core shows a gentle increase in the  $C_M$  MAR but a much stronger increase in the  $C_T$  MAR, with a sudden decline over the last 20 years. The WLIS75 core shows a decrease to near zero for  $C_T$  around 1800 CE (deforestation??), followed by a strong increase over the last 200 years. The  $C_M$  MAR has decreased since ~1900 CE.

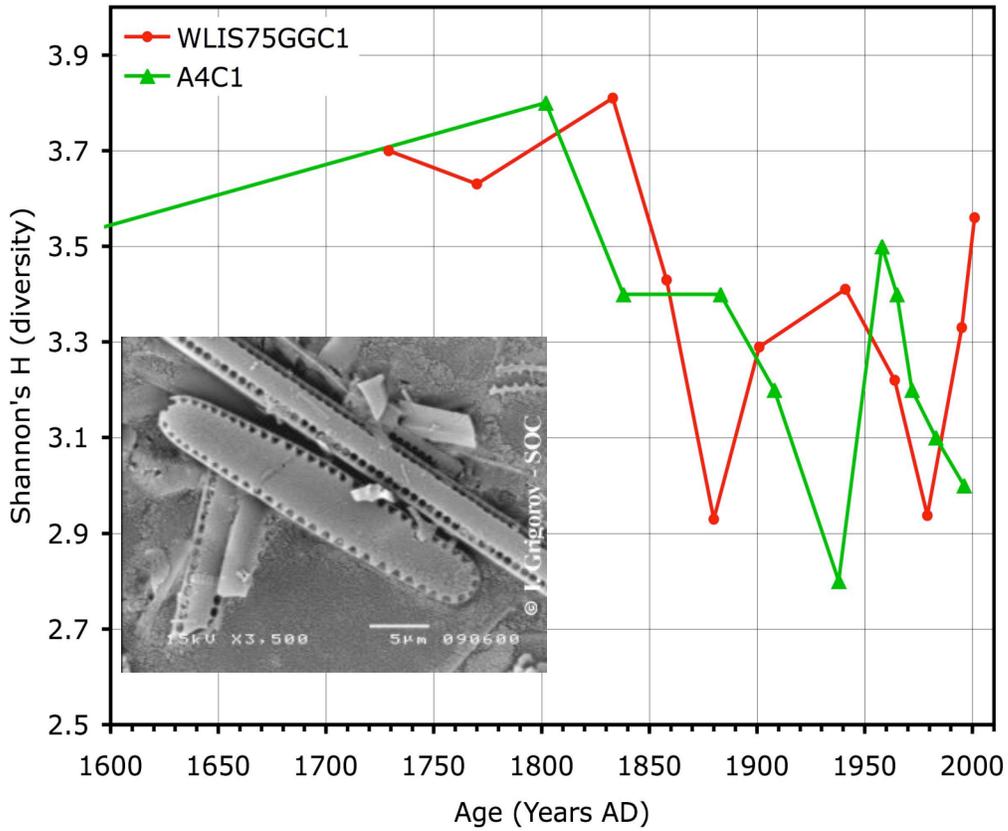
### **Subsection 5C2a. Microfloral composition of diatoms (Cooper)**

Diatoms are photosynthesizing algae that build a 'skeleton' (frustule) from opaline silica, and are an important part of the primary producers in oceanic and coastal ecosystems. They are consumed by many organisms at higher trophic levels, including copepods and some foraminifera. Approximately 800 permanent slides of diatoms were extracted from LIS surface sediments and three sediment cores (Table 1). A total of 34 samples from cores A4C1 and WLIS75GGC1 have been analyzed in detail. Diatom populations in these LIS samples are extremely diverse, with more than 400 morphological species present, including several not yet described species. Dominant species include *Thalassionema nitzschioides*, *Paralia sulcata* and *Cyclotella* species.

The core records show a major increase in diatom centric (planktic) - pennate (benthic) ratios, accompanied by a decrease in diatom diversity (Shannon's H' factor) and species richness since the early 19<sup>th</sup> century (Cooper et al., 2003, 2004; Figures 6A, 6B). Such floral change is an indicator of eutrophication, because the intense blooms of planktic (centric) diatoms strongly increase the turbidity of the water and prohibit light from reaching the benthic diatoms on the seafloor. This is analog to the loss of submerged aquatic vegetation such as sea grasses during eutrophication. The changes in diatom assemblages thus indicate that eutrophication in LIS started in the early 1800s, with eutrophication more pronounced in the westernmost part of LIS.

A major peak in *Pseudonitzschia* species occurred in a WLIS75GGC1 sample dated at ~1935-1940 AD. The occurrence of *Pseudonitzschia* species is of interest because toxic species within this genus can produce domoic acid (DA), a neurotoxin that has been implicated in human poisonings and deaths following the consumption of contaminated shellfish, and the genus is a component of Harmful Algal Blooms (HAB's). Blooms of *Pseudonitzschia* have been associated with large coastal runoff or discharge events, both of which are characterized by pulses of new nutrients. *Pseudonitzschia* has been shown to be more competitive than other diatoms under low Si:N conditions, presumably due to its light state of silicification. We speculate that the relatively high abundance of the species may be related to the impact of the 1938 hurricane on Western LIS, stirring up sediment with nutrients, which may have led to algal blooms.

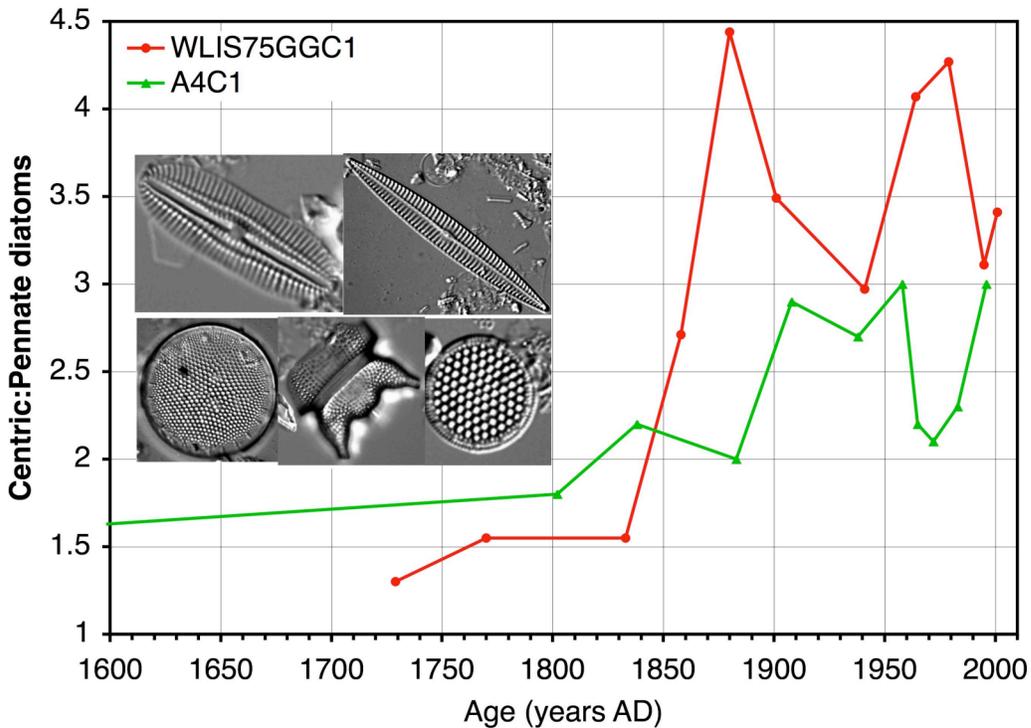
### Diatom diversity (Shannon's H)

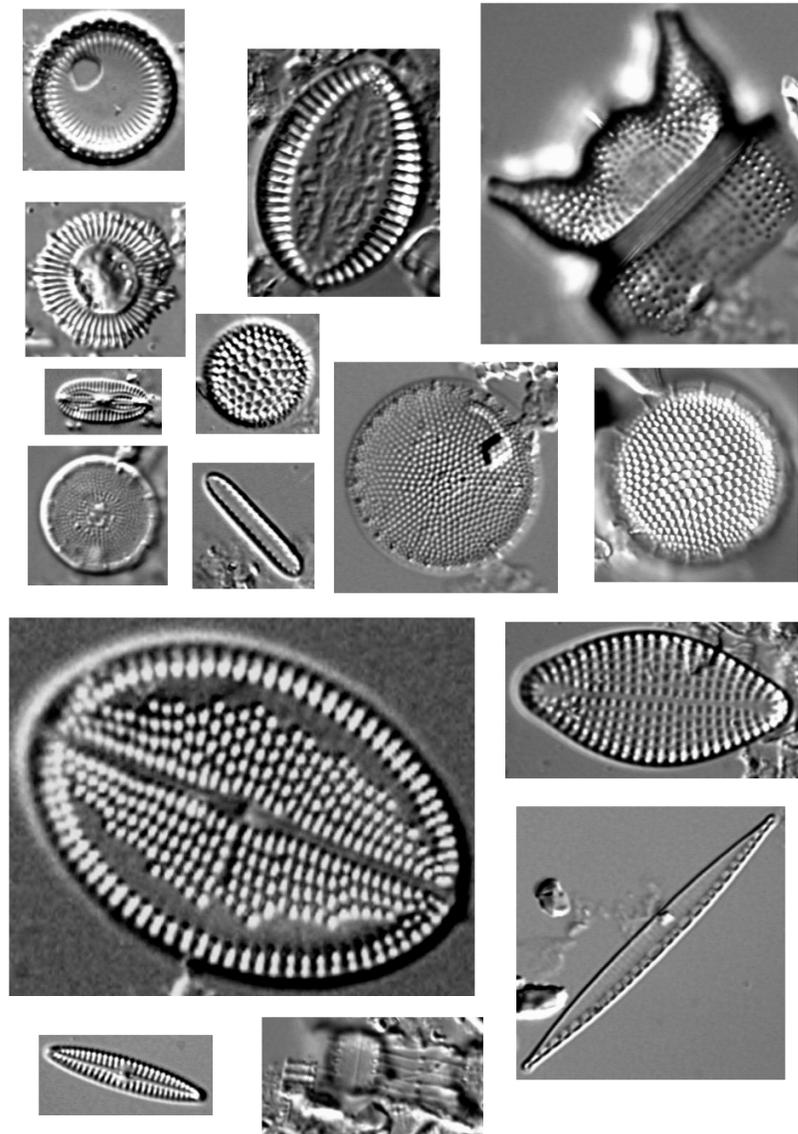


Centric:



Pennate Diatoms in 2 cores





**Figure 7.** Change in diatom floral assemblages over time in cores WLIS 75GGC1 and A4C1, with photographs of diatoms as identified in our samples. **Figure 7A** (Upper): decline in diversity of diatom floras starting in the early 1800s, strong variability since 1850 AD until the present. Inset in the upper figure: the common species *Thalassionema nitzschioides*. **Figure 7B** (middle): Increase in the ratio of centric (planktic) to pennate (benthic) species. Centric diatoms are generally round or triangular, pennate diatoms oval to very elongate oval. The ‘dip’ around 1950 in the WLIS75GGC1 record coincides with the coal-rich layer. **Figure 7C** (lower): Images of diatom species identified from sediment samples in Long Island Sound, captured from the microscope via video camera and Snappy™ hardware. All images are at the same scale.

### **Subsection 5C2b. Floral composition of dinocysts and pollen (Brinkhuis, Sangiorgio, Donders)**

Hundred and eleven samples were processed and analyzed for organic carbon-walled dinoflagellate cysts, pollen, and spores. One core (WLIS75GGC1: 43 samples) was analyzed for dinoflagellate cysts (dinocysts) only. The other three cores (WLIS81GGC2: 21 samples; A1C1: 25 samples; A4C1: 22 samples) were analyzed for both dinocysts and pollen (Table 2).

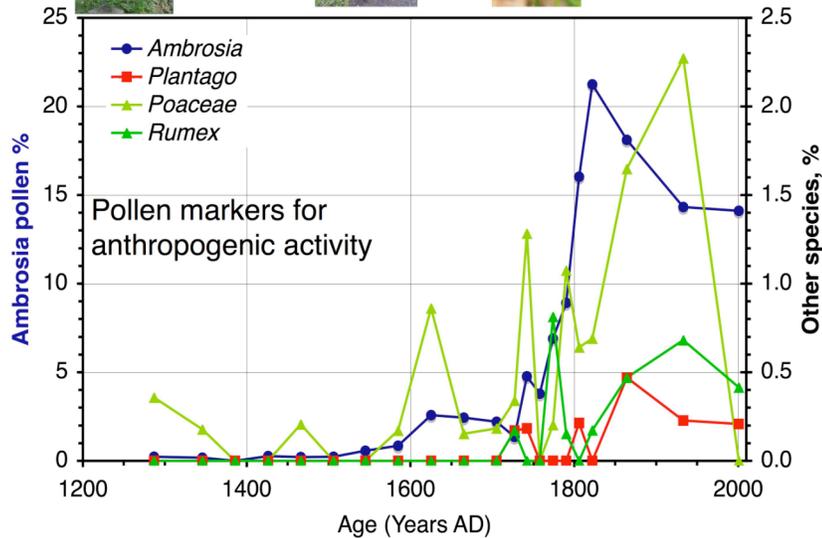
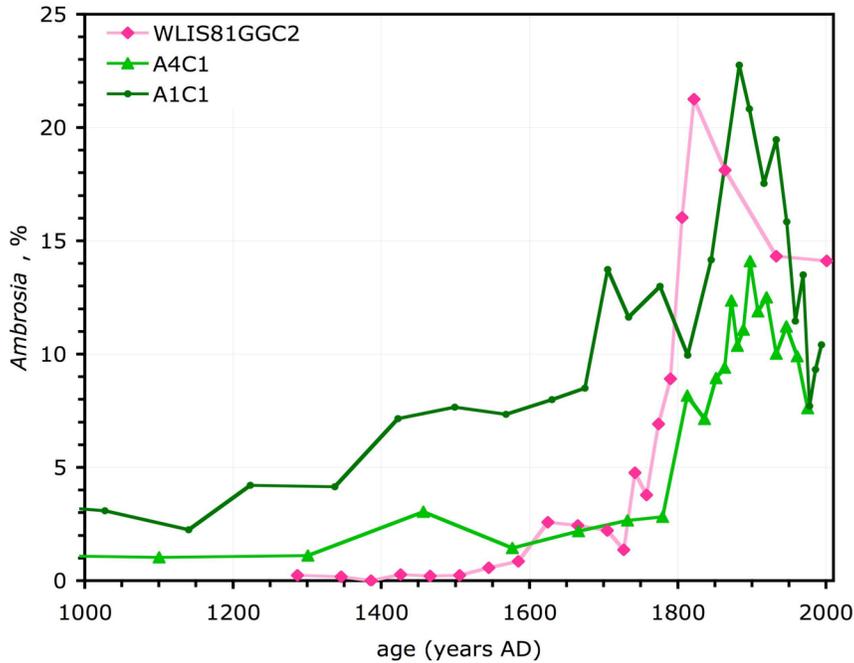
The pollen analyses are indicative of a typical thermophilous mixed forest. Pollen records indicate vegetation changes in the uplands surrounding the Sound, which may be caused by humans (deforestation and agricultural development) and climate change (Figure 8). The most important pollen type used to date postcolonial events is *Ambrosia* (ragweed), an early successional plant that rapidly occupies cleared sites. In all the studied cores, pollen indicative of human influence are found, including *Ambrosia*, *Plantago* (plantains), *Rumex* (docks and sorrels), and Poaceae (various grasses). The plantains were likely imported from Europe. *Ambrosia* pollen abundance increased in two phases. An initial increase around 1600 AD (most clearly seen in coastal core A1C1) is related to early colonial land clearance in the 17<sup>th</sup> century. A much more extensive period of replacement of forests by grasses and forbs (probably as the result of increasing agriculture) occurred in the early 1800s, and is documented in all three studied cores (Figure 8). This pollen core records also show a decrease in these “landclearing” pollen relative to tree pollen from around 1900 on, when agricultural activity started to decline and forests began regrowth.

The Poaceae pollen show a pattern similar to that of *Ambrosia*, and *Plantago* and *Rumex*, with increases from the late 18<sup>th</sup> century on. The pollen records document without any doubt the occurrence and severity of land-clearing during colonial and industrial times, which also impacted the carbon export from land (see section 5C2).

Dinocysts abundances are used to trace changes of the marine ecosystem in response to human impact or climate change. Dinoflagellates populations consist of both primary producers (autotrophs) and heterotrophs. Shifts towards heterotrophic dinocyst abundances are commonly interpreted as a signal of eutrophication, reflecting the high availability of food and thus allowing for increased abundance of heterotrophs. Dinocysts also provide climate information, because the distribution of autotrophic dinocyst species is linked to sea surface water temperatures.

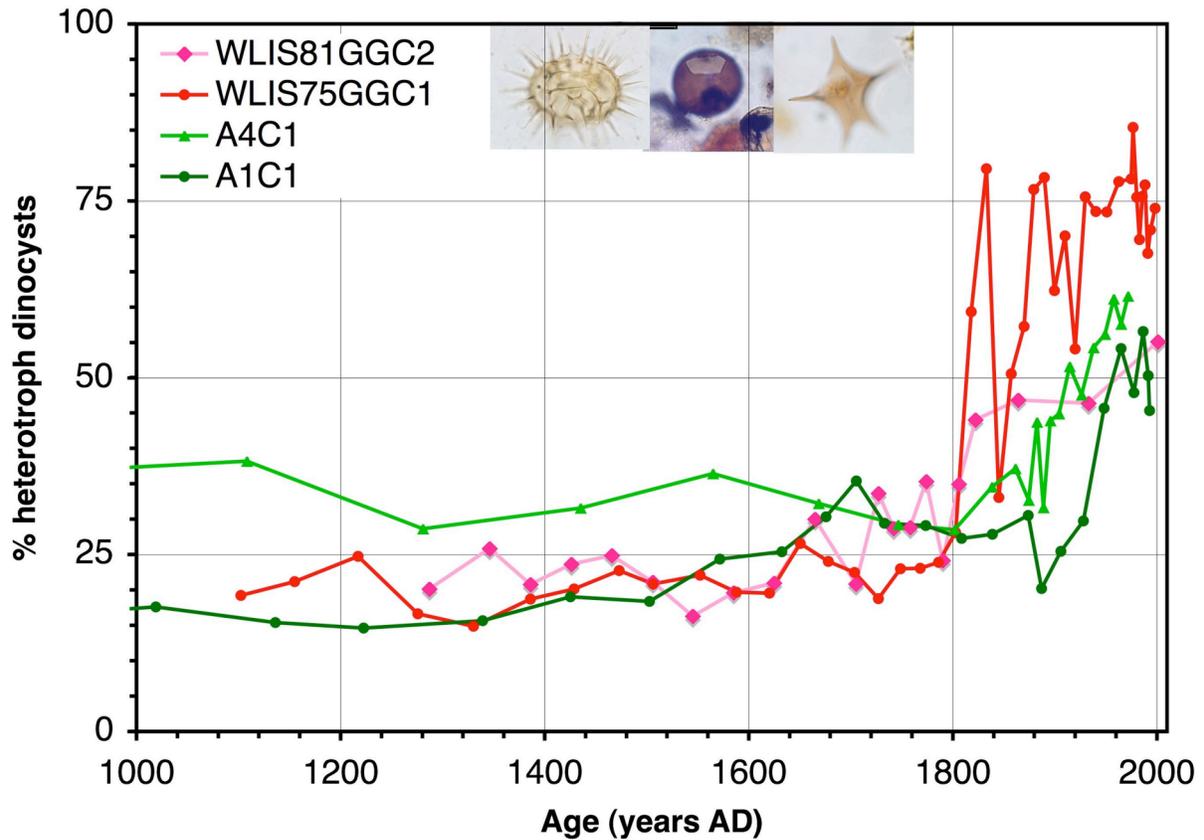
Dinocyst data suggest that eutrophication started in late 18<sup>th</sup> -early 19<sup>th</sup> century, with a strong increase in relative abundance of heterotrophic taxa. The signal is strongest in the Narrows (westernmost LIS, core WLIS75, Figure 9). The eutrophication may have started later at the location of core A4C1, in deeper water than core A1C1 and further to the East than cores WLIS81GGC2, WLIS75GGC1. Cold water dinocyst species (e.g. *Spiniferites elongatus*) show peak abundances in some intervals (e.g., 1400-1500 AD, 1665-1806 AD), probably related to the cooler temperatures of the Little Ice Age.

Ragweed pollen abundance, 3 cores



**Figure 8.** Relative abundance of pollen indicative of land-clearing. **Figure 8A** (upper): abundance of ragweed (*Ambrosia*) pollen in 3 cores. The shallowest core (A1C1) shows an increase in ragweed pollen at the time of European colonization (middle 1600's). All three cores show a strong increase in relative abundance of ragweed pollen around 1800, followed by a decline from about 1900 on. **Figure 8B** (Lower): Pollen records from core WLIS81, in western Long Island Sound. An increase of pollen indicative of land-clearing, including *Ambrosia* (ragweed), *Plantago* (plantains), *Rumex* (docks and sorrels) and Poaceae (grasses) started in the 17<sup>th</sup> century in colonial times, but strongly increased in the early 19<sup>th</sup> century.

## Heterotroph dinocyst % in 4 cores

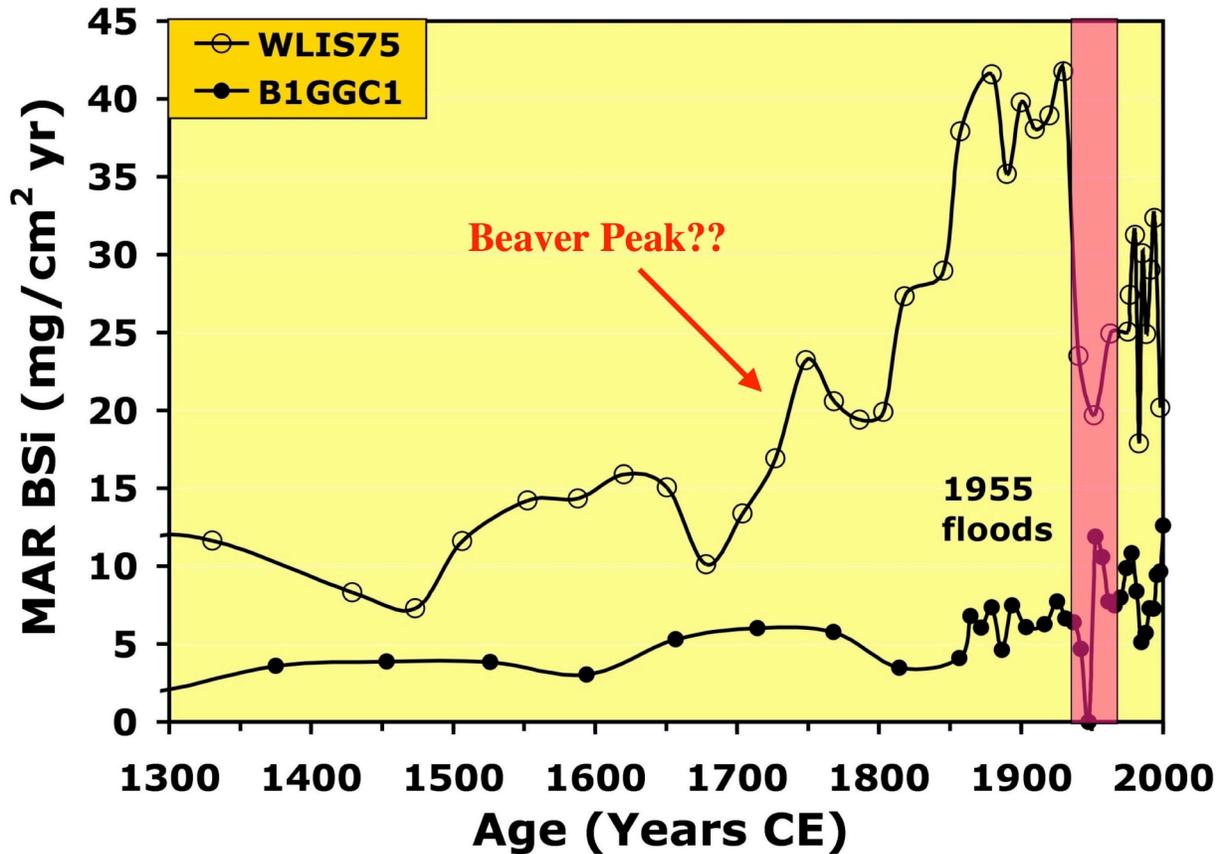


**Figure 9.** Relative abundances of heterotroph dinocysts in cores WLIS75, WLIS 81 and A4C1. Pictures show photographs of the LIS heterotrophic dinocysts species *Selenopempix quanta*, *Brigantedinium cariacense*, and *Stelladinium stellatum*.

**Subsection 5C3. Mass abundance of diatom valves (biogenic silica) Varekamp**

Diatom remains consist of the organic remains as well as diatom skeletons (frustules) made of biogenic silica (BSi). The BSi content of sediment samples was measured in eight cores (Table 2). The BSi accumulation rates are direct indicators of the paleo-productivity (by diatoms) of the Sound, and are expected to correlate with the calculated marine organic carbon MAR. Our data show that the cores in Western LIS have substantially higher BSi contents than central and east LIS sites, both in pre-colonial samples and during the eutrophication period (Figure 10).

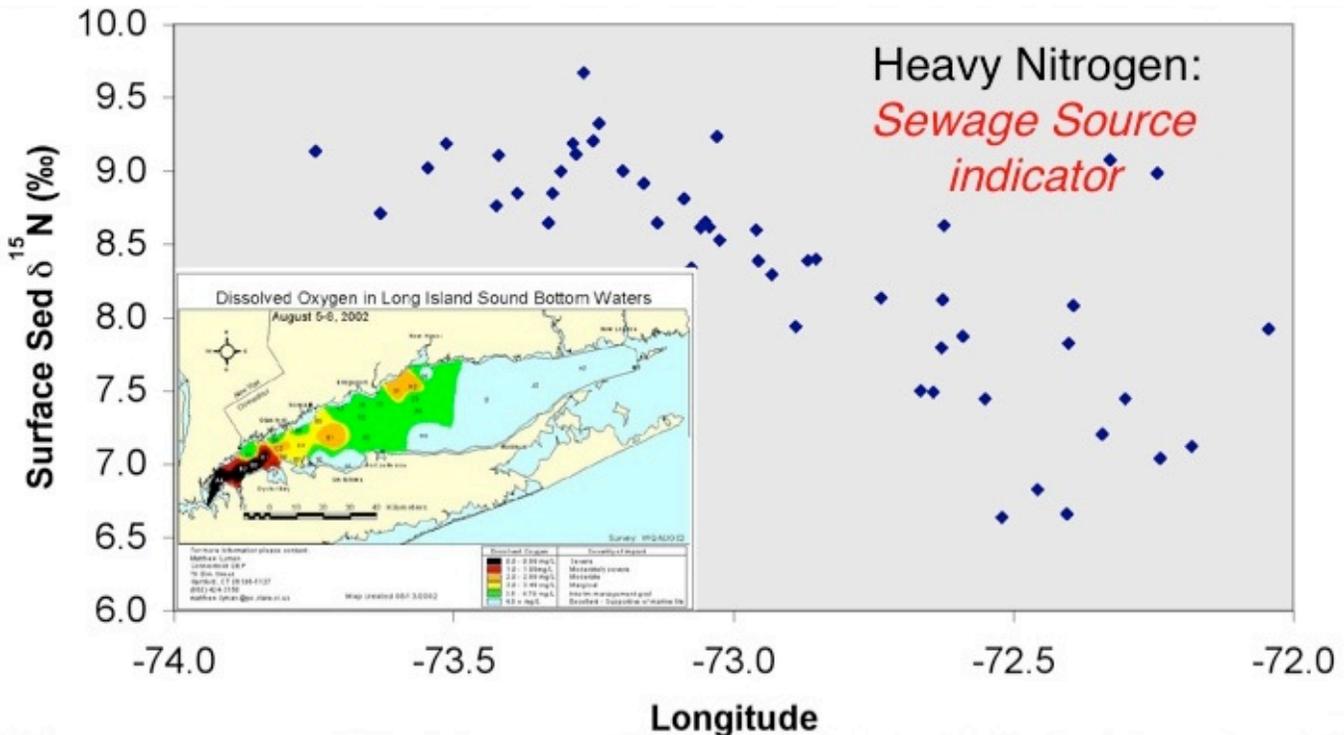
The BSi data generally show gentle increases since ~1600 CE, with much higher values in more recent sediments. This increase in BSi indicates an increase in diatom productivity of the Sound over the last ~ 300 years. When expressed as MAR of BSi (mg BSi/cm<sup>2</sup> yr), we observe an exponential increase in several cores (e.g., A1C1, D3C2, Figure 3). Core WLIS75 shows a decline in BSi accumulation rates over the last 100-50 years, which parallels the decrease in burial of marine organic matter (Figure 6). This strongly suggests that the diatom productivity has become less intense during that period (Figure 10), especially in the deeper waters of western LIS.



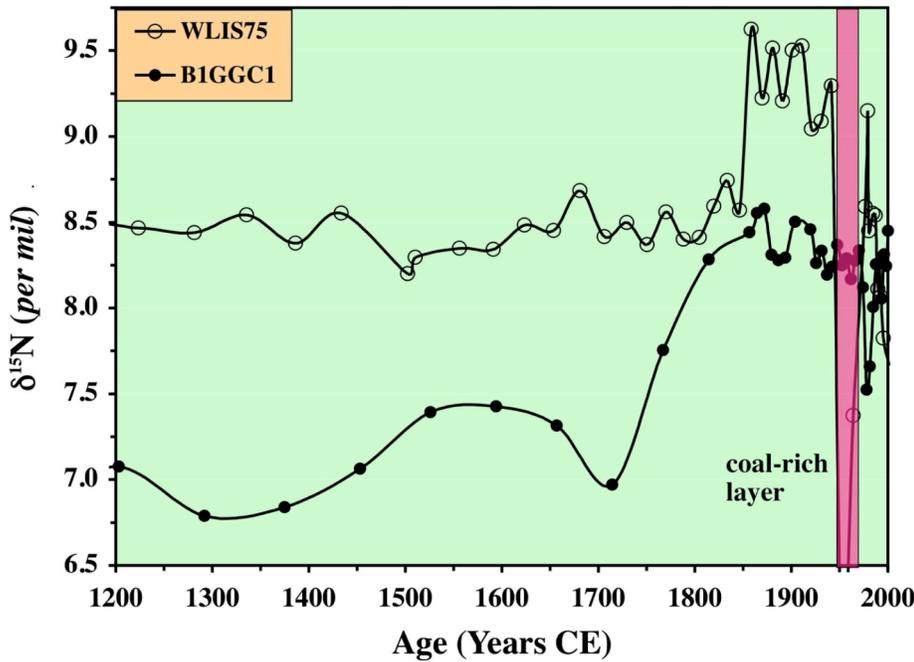
**Figure 10.** Mass accumulation rate of Biogenic Silica for cores WLIS75 and B1. Core WLIS75 shows a first increase in diatom productivity ~1650 CE (beaver eradication?), strong increases between 1800 and 1950 CE, followed by a strong decrease in the second half of the 20<sup>th</sup> century. Core B1 shows a gentle increase over the last 150 years. Note the difference in MAR values for the full period between the Central LIS site (B1) and Western LIS site (WLIS75).

**Subsection 5C4. Nitrogen abundance and isotopic composition (Altabet, Varekamp)**

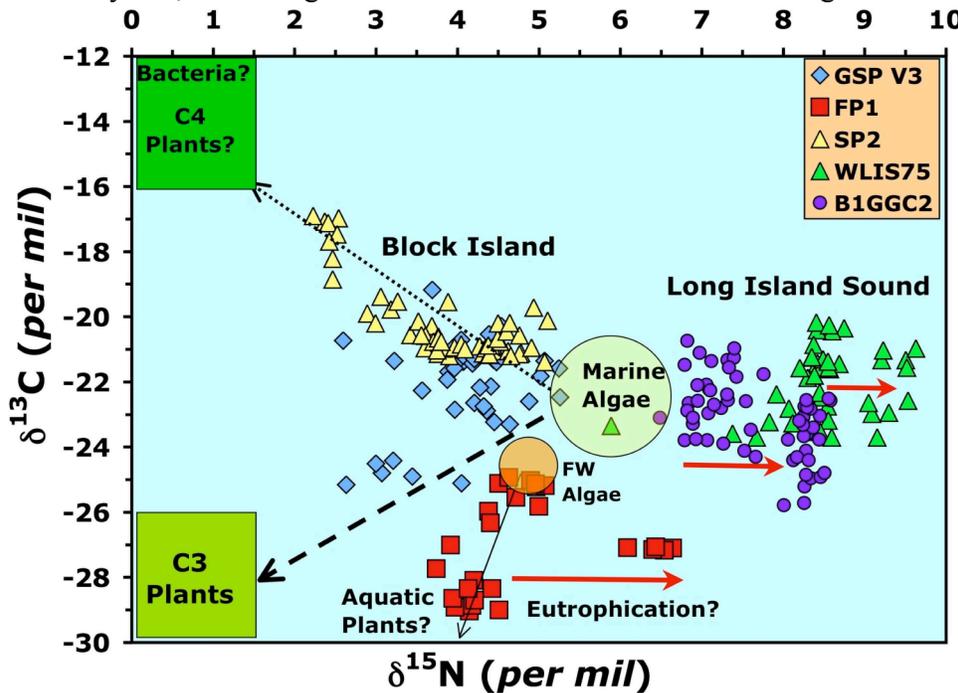
Samples from ten cores and a broad array of sediment surface samples were studied in detail for their N contents and the  $\delta^{15}\text{N}$  of the bulk organic matter (Altabet and Varekamp, 2004, 2007; Andersen, 2005; Varekamp et al., 2006; Boon et al., 2006). Relatively heavy Nitrogen isotope values (more positive  $\delta^{15}\text{N}$  values) are indicative of addition of sewage Nitrogen from WWTPs, or of denitrification occurring under hypoxic to anoxic conditions in the water column or sediment pore waters. In addition, organic debris that stems from mammals and other organisms higher up the food chain has isotopically heavier Nitrogen than that from organisms lower on the food chain. In surface samples and in samples from the water column, heavier  $\delta^{15}\text{N}$  values occur towards the more western parts of LIS, where also the most massive WWTP inputs occur. This isotopically heavy Nitrogen correlates with increased Nitrogen concentrations in the sediment as well as seasonal hypoxia/anoxia in the water column (Figure 11). This spatial correlation between “heavy Nitrogen” and hypoxia in the modern Sound (Figure 11) suggests that hypoxia occur largely in areas where the  $\delta^{15}\text{N}$  is high, stemming from *in situ* denitrification and/or from an isotopically heavy WWTP Nitrogen source. The correlation between increased Nitrogen contents and heavier isotope ratios suggest that enhanced input of WWTP nitrogen is the main driver for these signals. Our current data from EPA-funded work on the water column also suggests that *in situ* denitrification probably plays a much smaller role than WWTP inputs.



**Figure 11.** Nitrogen isotope values in surface sediment from LIS, showing a trend of isotopically heavier Nitrogen to West-LIS, where WWTPs have the greatest input and where water circulation may be the most impaired. These data indicate that WWTP inputs, hypoxia, and heavy Nitrogen are spatially associated in western LIS.



**Figure 12.** Nitrogen isotope records for cores WLIS75 and B1. The strong increases in N isotope values around 1800 CE are indicative of input of heavy N, most likely from human waste (sewage and sewage treatment plants). Note that the B1 location has lighter N isotopes even during the pre-industrial period. The WLIS75 values decrease over the last 50 years, indicating the decrease in burial rate of marine organic carbon.

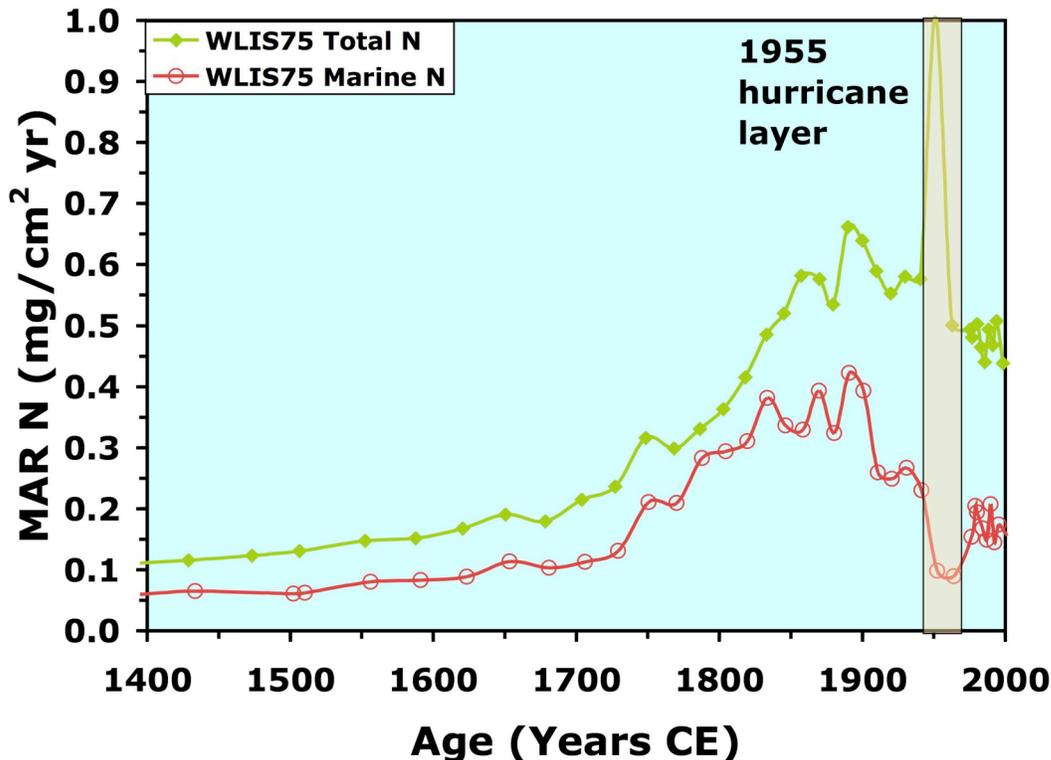


**Figure 13.** C-N isotope relations in cores WLIS75, B1 and cores from Block Island, RI (GSPV3, Great Salt Pond; FP1 and SP2, fresh water ponds). The LIS samples increase in  $\delta^{15}\text{N}$  to the west, from GSPV3 in Block Island to core B1 close to the Housatonic River mouth, to WLIS75, with superposed “jumps” (red arrows) from samples in the top of the cores as a result of eutrophication.

Our core records all show increases in  $\delta^{15}\text{N}$  towards the core tops, in most cases by 1-3 ‰. Core WLIS75 is unusual with relatively high  $\delta^{15}\text{N}$  values through most of the core (Figures 12, 13) and only a small increase in the core top. This heavy Nitrogen isotope signal goes back to the bottom of the core dated at about 1200 CE, indicating that the western end of LIS (the Narrows) may have had a nitrogen source with heavy  $\delta^{15}\text{N}$  long before European colonization, or that denitrification processes have been active in this part of LIS for a long period.

A spatial trend of increasing  $\delta^{15}\text{N}$  values in sediment grab samples from East to West in the Sound (Figures 11, 13) was further investigated by our later studies on Block Island, located in Block Island Sound, the eastern extension of LIS. Pre-colonial era samples show marine algae in BI's Great Salt Pond with  $\delta^{15}\text{N}$  values ~ 5‰, whereas higher values of 7‰ are found in the central Sound (core B1). The highest  $\delta^{15}\text{N}$  values occur in WLIS75 in the west at 8‰ (Figure 13). Eutrophication  $\delta^{15}\text{N}$  jumps occur throughout the region superposed on that spatial “background” trend.

Nitrogen concentration profiles follow largely the trends for organic carbon, although some of the variation in the records is related to the difference in N/C values in terrestrial versus marine carbon. A record of the burial rate of ‘marine Nitrogen’ for core WLIS75, using the partition into marine and terrestrial carbon in combination with the N/C value of marine algae, shows the eutrophication effects as well as the decrease in fixation/burial of ‘marine nitrogen’ over the last 100 years (Figure 14).



**Figure 14.** Burial rate of marine Nitrogen in core WLIS75GGC1, showing the fixation of ‘marine nitrogen’ and the probable effects of ongoing Nitrogen inputs from 1750 CE on. Note the decrease in marine nitrogen burial rate over the last 100 years, in agreement with the BSi,  $C_{\text{org}}$ , and foraminiferal data (see below).

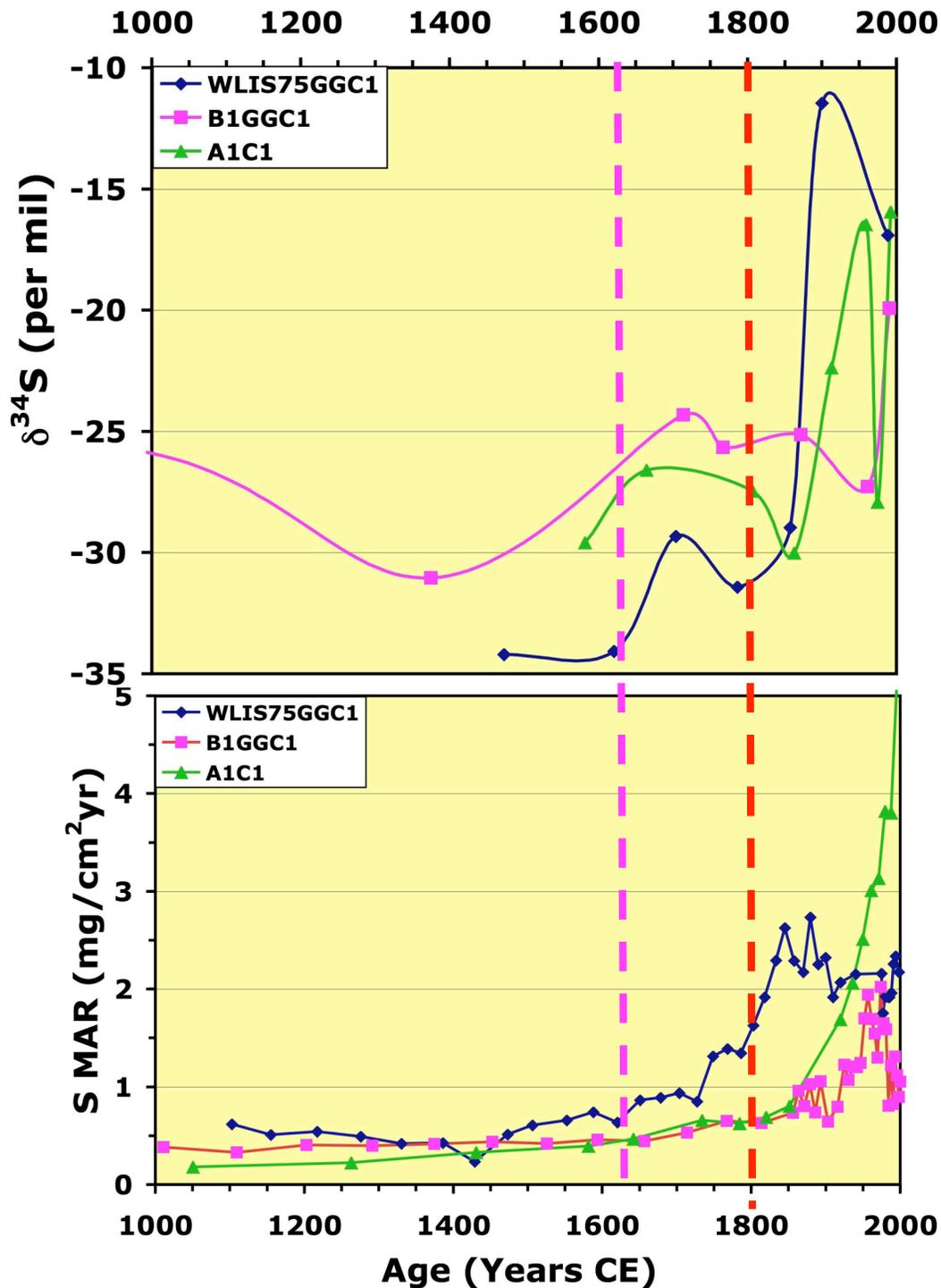
### **Subsection 5C5. Diagenetic sulfur abundance (Varekamp)**

The marine organic carbon in LIS sediments consists of that part of the primary produced organic matter in LIS that has not been consumed or exported from the Sound by mobile heterotrophic organisms or oxidized by various means. Terrestrial organic carbon is also partially preserved during sediment accumulation (see discussion in section 5C1), but is probably less directly involved in the LIS food chain because of its more refractory character. Organic carbon may have been removed from the sediment or water column through oxidation by dissolved O<sub>2</sub> in seawater, which ultimately may lead to hypoxia. The return of the isotopically (δ<sup>13</sup>C) light photosynthate to the water as dissolved inorganic carbon (DIC) leaves a signal in the carbon isotopic composition of carbonate, as discussed in the section below. Part of the organic carbon is oxidized through the marine sulfate reduction pathway, according to



This loop also adds light carbon to the DIC pool, but does not directly consume dissolved O<sub>2</sub>. The reduced sulfur compounds (mainly HS<sup>-</sup> and minor H<sub>2</sub>S) may diffuse back into the water column, where re-oxidation to sulfate will take place. The latter process is using up additional dissolved O<sub>2</sub>, thus contributing to the severity of hypoxia. Alternatively, the reduced sulfur species may be fixed in the sediment as pyrite (FeS<sub>2</sub>) through a complex pathway with several intermediate mineral phases. The amount of pyrite in the sediment thus serves as an indicator for the fraction of organic matter that was oxidized without involvement of dissolved O<sub>2</sub>. The sulfur isotopic composition of the pyrite provides insights into the rates of the reduction and diffusion processes.

The reduced sulfur contents of samples from three cores were determined together with the δ<sup>34</sup>S values of the sulfur (Table 2, data tables). The sulfur contents of the sediment samples are 1-5 % S (weight), increasing towards the core tops (Figure 15, bottom). The sulfur isotope data indicate complex processes of sulfur reduction and mobility, and suggest that the rate of sulfur reduction has increased over the last 150 years, leading to “isotopically heavier” sulfide minerals (Figure 15, top). The pre-colonial sediments contain clean, well crystallized pyrite crystals (commonly in framboids), with low δ<sup>34</sup>S (-35 to -25 ‰), whereas the younger sediments have higher reduced sulfur contents, less well-defined crystal shapes, with isotopically heavier sulfur (up to -12 ‰). Models of sulfate diffusion and cycling of reduced Sulfur species indicate that reduction rates, fueled by the abundance of labile organic matter, were much higher over the last 150 years than before (discussed in detail by Andersen, 2005). Over the last 150 years more H<sub>2</sub>S and HS<sup>-</sup> escaped back to the bottom waters, enhancing the hypoxia and possibly causing harmful sulfide concentrations close to the sediment-water interface. The δ<sup>13</sup>C values of carbonates (Subsection 5C7) are a proxy for the total amount of mineralization of organic carbon prior to, during, or after deposition, independent of the chemical pathway. The calculated O<sub>2</sub> depletion (Figure in Subsection 5C7) is based on the δ<sup>13</sup>C data, assuming that all C<sub>org</sub> oxidation used O<sub>2</sub>. The buried sulfide component can thus be used to correct for the fraction of C<sub>org</sub> that was mineralized by the sulfate reduction loop. This work is in preparation, together with estimates on the O<sub>2</sub> re-supply rate to the bottom waters.



**Figure 15.** Sulfur mass accumulation rates (MAR) in cores WLIS75GGC1, B1GGC1 and A1C1 show an increase ~ 1640 CE (purple line), with an acceleration ~ 1800 CE (red line). Sulfur MAR values in modern times are ~ 3-10 times pre-colonial values. The increases in Sulfur MAR are accompanied by shifts of 5-25 ‰ in  $\delta^{34}\text{S}$  of the sulfides towards heavier values, although the records show substantial variability.

### **Subsection 5C6. Assemblages of benthic foraminifera (Thomas)**

Benthic foraminiferal assemblages were studied in 40 surface samples (collected in 2001, 2002 and 2005), and in 360 core samples in 16 cores (Table 2). Data were also available from our earlier work (Thomas et al., 2001) on 110 grab samples collected in 1996/1996, 1999 and 2000, and literature data on foraminiferal abundances in surface samples collected in 1948 and 1961 (Thomas et al., 2000).

The most common species are *Elphidium excavatum*, *Elphidium incertum*, *Buccella frigida*, *Eggerella advena*, *Trochammina squamata*, and *Ammonia parkinsoniana* (formerly described as *A. beccarii*, or *A. beccarii* s.l.). Rare species (< 5%) include *Rheophax scopiurus*, *Textularia earlandi*, *Lagena* spp., *Buliminella elegantissima*, *Fursenkoina fusiformis*, *Bolivina* spp., *Hopkinsina* sp., *Quinqueloculina* spp., and *Polymorphina novangliae*. These rare species are more common in eastern LIS, and in the sections deposited before the 20<sup>th</sup> century (Thomas et al., 2000). Species characteristic for coastal salt marsh environments (e.g., *Trochammina macrescens*, *Trochammina inflata*, *Ammotium salsum*) are found in surface samples and cores close to the shore. These species have not been found as living specimens in surface samples and are probably transported from the marshes, together with the commonly present fragments of marsh cord grasses.

*Elphidium excavatum* is a specialist which consumes living or at least fresh diatoms. It is the most abundant species in LIS surface and core samples, and commonly constitutes >90% of the assemblage in samples with water depths of less than 10-12 m. At such shallow depths, the species takes up diatoms, but does not digest the chloroplasts, which keep functioning within the foraminifera (klepto-chloroplastidy). These foraminifera thus become functionally photosynthesizers, which gives them a competitive advantage over pure heterotrophs in sunlit waters. *Elphidium excavatum* was absent in the deepest locations (e.g., Core A5GGC1) before the mid-1900s, but became common at these depths afterwards. The species increased in relative abundance at all locations and water depths, starting in the early to mid 19<sup>th</sup> century, but decreased strongly in relative abundance in western Long Island Sound after the early 1970s. Another fairly common species is *Elphidium incertum*. The ecology of this species is not well known, except that it flourishes in quiet water conditions (no strong current activity).

In deeper waters, at depths below light penetration, *Buccella frigida* is common in most surface samples and cores, reaching up to 60% of the assemblage. Little is known about the ecology of this species, but it is most common in fine-grained sediments rich in organic matter. In some cores the species declines slightly in relative abundance towards the present day, but in many cores there are no clear trends in abundance.

The two most common agglutinated species are *Eggerella advena* (up to 65%) and *Trochammina squamata* (up to 30%). These species were common to dominant in samples collected at water depths > 20 m in central and eastern LIS before the 1960s, but declined rapidly afterwards. The former species is well known to survive under low oxygen and severely polluted conditions, but is more sensitive to low salinity conditions than the other common LIS foraminiferal species, and probably therefore absent in westernmost LIS (the Narrows).

In cores collected in deeper water (e.g., A5GGC1), calcareous foraminifera (including *E. excavatum*) were absent before the 1800s, with only agglutinated taxa

present (*E. advena*, *T. squamata*, various species of *Rheophax*). At some deep-water locations (~35 m) even today calcareous taxa are absent.

*Ammonia parkinsoniana* was a rare species (never >10%) in surface samples collected in 1948 and 1961, and in almost all core samples, but abundant (up to 85%) in surface samples collected in 1996/1997 in western LIS and the Narrows, as well as in one sample close to the mouth of the Connecticut River (Thomas et al., 2000; Abramson, 2002). *Ammonia parkinsoniana* is a cosmopolitan species, which survives wide swings in temperature and salinity, and is very common in highly polluted regions. It is known to be omnivorous and consumes refractory carbon as well as living phytoplankton.

The abundance of *Ammonia* species relative to *Elphidium* species is commonly expressed as the *Ammonia-Elphidium* index (A-E index, Figure 16), observed to have high values in eutrophied waters, including Chesapeake Bay and the Gulf of Mexico. The increase in relative abundance of *Ammonia parkinsoniana* (thus the A-E index) has become more pervasive (i.e., reached further east) over the last 10 years, as shown by our observations on grab samples (Figure 16).

There have been no benthic foraminiferal studies of LIS between the early 1960s and the middle 1990s, so that we did not have information when the increase in the A-E index started. Our studies of core samples document that the *Ammonia* species began its unprecedented increase in abundance in the late 1960s to early 1970s in westernmost LIS, spreading eastward from there with time (Figure 17).

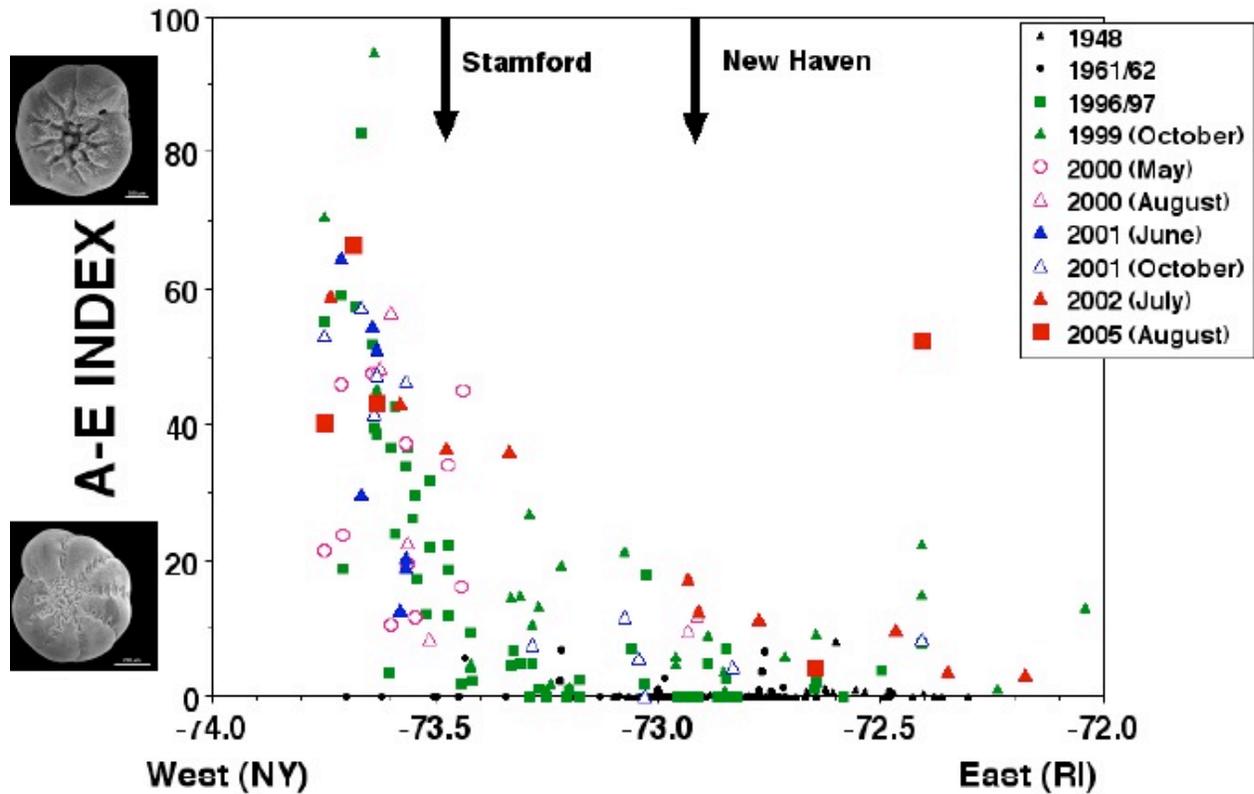
Our core studies also document that benthic foraminiferal accumulation rates increased in most cores but most pronouncedly in western LIS, starting in the early to middle 1800s (Figure 18). The absolute abundance of the species *E. excavatum* and its accumulation rate thus increased at many locations, followed by a decline (especially in western LIS) over the last few decades.

We interpret the faunal changes as caused by an increase in diatom productivity in the early to middle 1800s (in agreement with the diatom data shown in subsection 5C2a), leading to overall increased relative as well as absolute abundance of *E. excavatum*, and the penetration of this species to depths at which it could not survive formerly. At these greater depths, the abundant planktic (centric) diatoms reached the bottom when the overall productivity increased: the increase in diatom productivity took place at the same time that the centric:pennate diatom values increased (Figure 7), and that the relative abundance of heterotrophic dinoflagellates increased (Figure 9), indicating that the eutrophication of the LIS ecosystem started to impact the benthic as well as planktic ecosystem. In addition, the relative abundance of the agglutinated species *Eggerella advena* in deep-water cores such as A4C1 may have declined as the result of decreasing salinity of the bottom waters (Subsection 5C7).

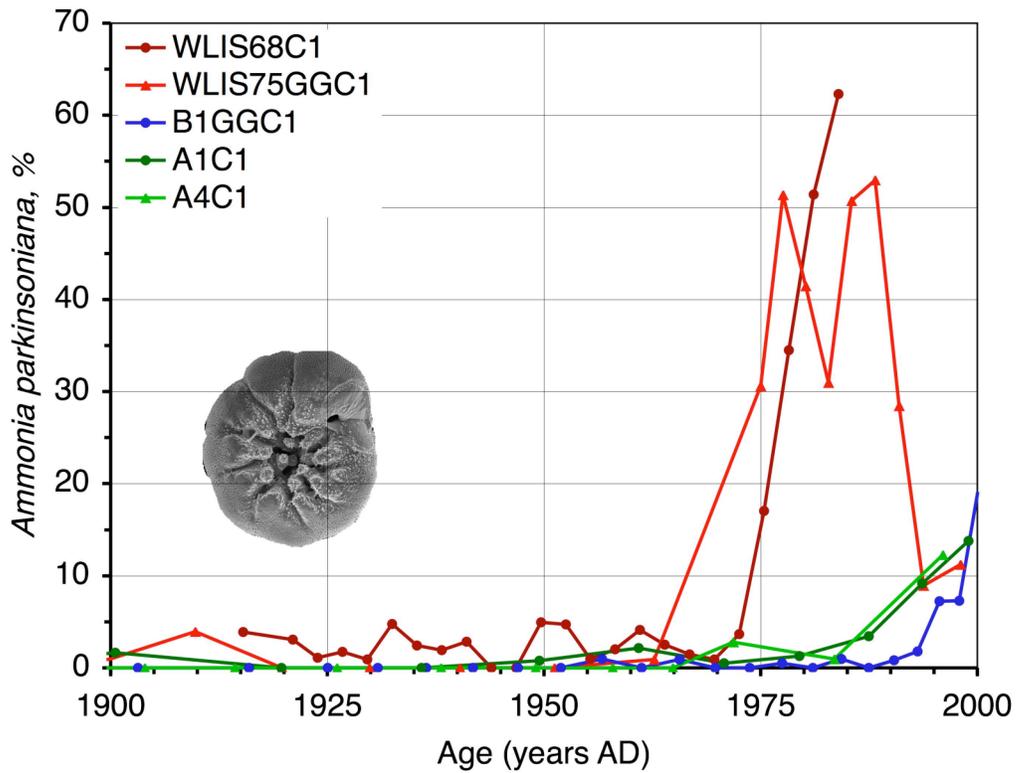
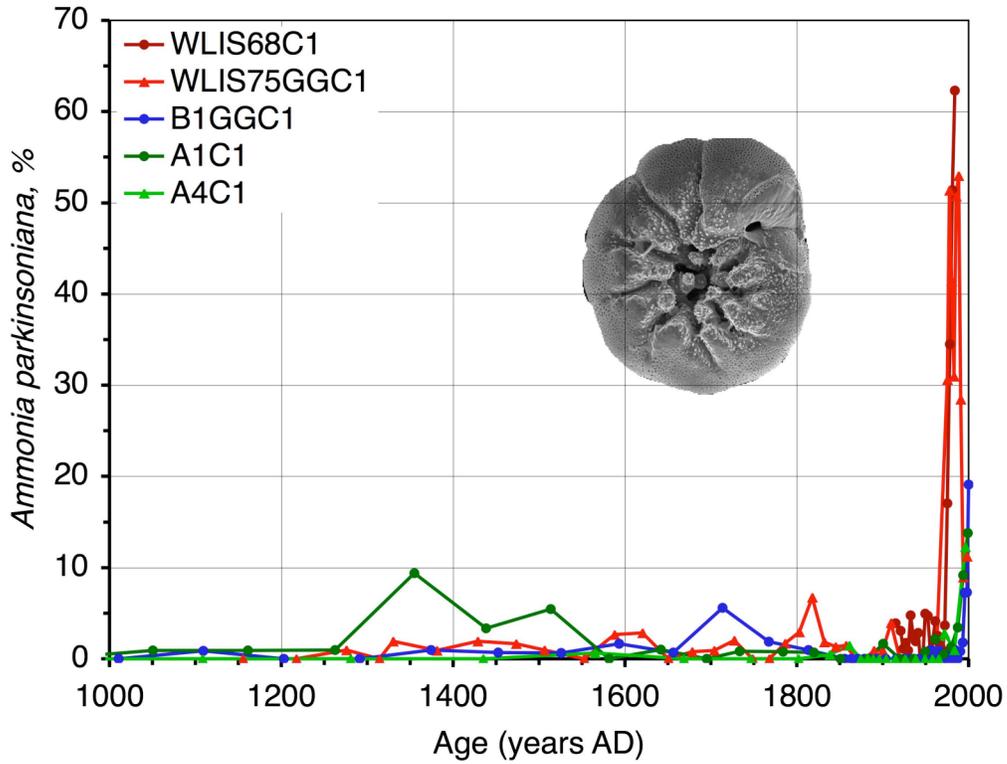
The eutrophication reached a new phase in the late 1960s to early 1970s, continuing until today, with the decrease in relative and absolute abundance of *E. excavatum* due to an increased relative abundance of *Ammonia* species, and an overall decline in foraminiferal absolute abundance (Figures 17, 18). This is a major, qualitative change, indicating that bottom faunas of unicellular eukaryotes underwent severe faunal turnover. A similar faunal change has been observed in other eutrophied waters (e.g., Gulf of Mexico), and has been tentatively explained by hypoxic conditions. In our opinion this explanation is not highly probable for LIS, because both *Elphidium excavatum* and *Ammonia parkinsoniana* are extremely resistant to low oxygen

conditions, and able to survive even full anoxia for several days in mesocosm experiments. The regional rise in water temperatures could be a contributing factor, because in general, *Ammonia* species are more common in warm waters than *Elphidium* species. It is, however, improbable that the rise in temperatures is the main factor causing the rise in abundance of *A. parkinsoniana* and the strong decline in abundance of *E. excavatum* (Fig. 17), because temperatures are not very different in the Narrows, Western and Eastern LIS.

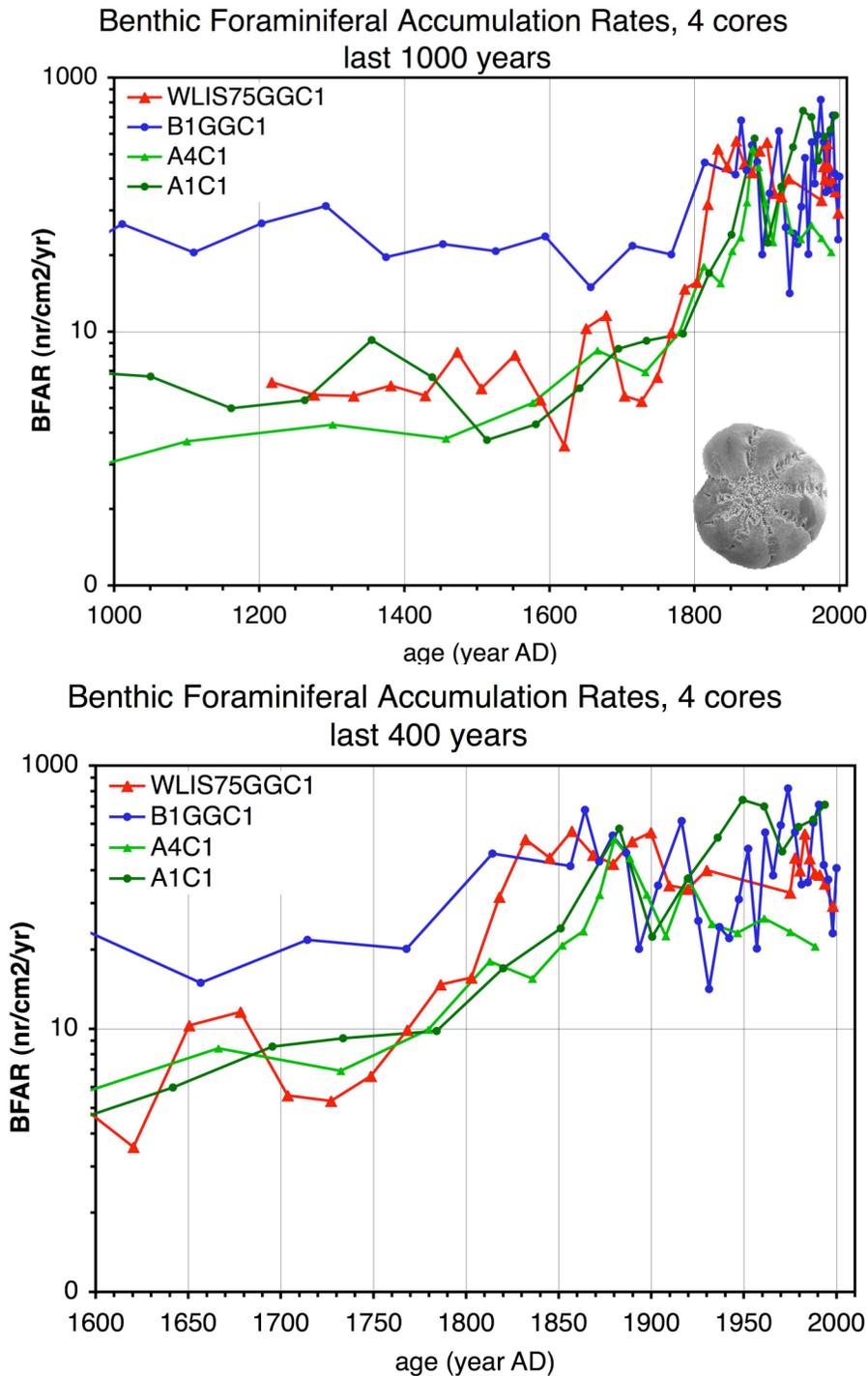
A more probable cause for the decrease in abundance of *E. excavatum* may be a decrease in diatom productivity as seen in the biogenic silica records (subsection 5C3, Figure 10). This decline may be the result of the low N/Si values that are reached during stages of severe eutrophication. This may have led to declining abundances of the specialized diatom consumer *E. excavatum*, which was the most abundant foraminifer in LIS since its establishment as a salt-water estuary about 10,000 years ago (Varekamp et al., 2005). Limited genetic evidence on the genus *Ammonia* in LIS, however, allows the possibility that the recent increase in relative abundance was caused by an invasive cryptospecies, but more research is needed to further explore this hypothesis.



**Figure 16.** The A-E Index, i.e., the abundance of *Ammonia* species relative to that of *Elphidium* species as a function of longitude in LIS over time (1948-2005) from grab sample data. The data for 1948 and 1961 (in black) are from the published literature as referenced in Thomas et al., 2000, with values of the A-E index consistently below 10%. Note the very strong dominance of *Ammonia* species over *Elphidium* species in western LIS in samples from the 1990s and later; no grab samples were collected between the 1960s and the 1990s.



**Figure 16.** The relative abundance of the generalist feeder *Ammonia parkinsoniana* in cores in west to central LIS. **Figure 16 A** (upper): last 1000 years; **Figure 16B** (lower): last 100 years.



**Figure 17.** Benthic foraminiferal accumulation rates (BFAR) expressed as number of foraminifera per square cm per year for 4 cores. Note the logarithmic scale. **Figure 17A** (upper): record for the last 1000 years; **Figure 17B** (lower): record for the last 400 years. The relative abundance of *Elphidium excavatum* (shown in inset in 17A) and the overall benthic foraminiferal accumulation rate increased in the 1800s, probably due to the consumption of the abundant centric (planktic) diatoms. Note the recent decrease in benthic foraminiferal productivity, at the time when the omnivorous *Ammonia parkinsoniana* became dominant, while overall BFAR decreased (Figure 16).

### **Subsection 5C7. Isotopic and trace element composition of foraminiferal tests (Thomas/Varekamp)**

Our earlier work (Thomas et al., 2001) had shown that the common species *Elphidium excavatum* can be used for isotope studies, with  $\delta^{18}\text{O}$  as a combined proxy for water temperature and salinity (vital effect  $\sim 1.1\text{‰}$ ), and  $\delta^{13}\text{C}$  as a proxy for the  $\delta^{13}\text{C}$  value of dissolved inorganic carbon (DIC) in the bottom waters at the time that the foraminifer secreted its test. Stable isotopes of O and C are routinely used in deep-sea paleoceanography, but they have not been widely used in coastal and estuarine studies where proxy calibration is more challenging. Benthic foraminifera have an unknown lifespan (between a few months to a few years), and potentially calcify during this full time, during which environmental variables such as temperature and salinity vary strongly on a seasonal time scale. Foraminifera do not calcify during the coldest months of the year; we derived an average temperature of foraminiferal calcite of  $\sim 13^\circ\text{C}$ .

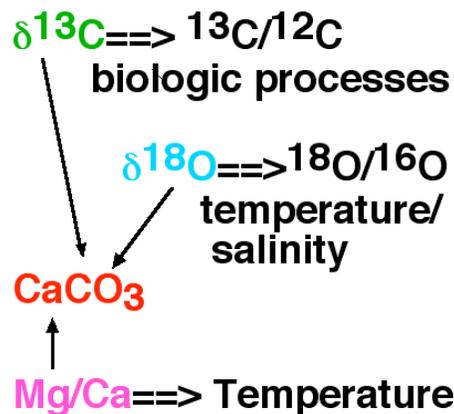
We used the following approach (Figure 18): the temperature of calcification of foraminiferal tests can be derived from Mg/Ca values. This method was calibrated with modern samples (living foraminifera and measured water temperatures) during an earlier study (Figure 19). Samples collected during a sudden 'hot spell' in early spring/summer 2003 were excluded from that data set. The scatter in the data derives from the seasonal variations in water temperature, and the variable life span of the foraminifera. The calibration precision is not great, but trends towards 'warmer and cooler' are reflected in the Ca/Mg values. The  $\delta^{18}\text{O}$  value of benthic foraminiferal tests is influenced by temperature and salinity, thus the salinity can be derived from the  $\delta^{18}\text{O}$  value once the temperature is known. The  $\delta^{13}\text{C}$  value of the tests gives information on the  $\delta^{13}\text{C}$  of DIC in the waters, but is also influenced by salinity. Once the salinity is known, we can correct the  $\delta^{13}\text{C}$  value of the foraminiferal calcite for salinity, using a mixing model for LIS (Figure 20). The salinity-corrected  $\delta^{13}\text{C}$  is labeled the 'excess  $\delta^{13}\text{C}$ ' or ' $\delta^{13}\text{C}^*$ '. Lower  $\delta^{13}\text{C}^*$  values in calcite indicate contributions from the oxidation of organic matter in the water column to the DIC pool, and are thus a proxy for hypoxic conditions. In modern LIS, we observe a clear correlation between the East-West location in the Sound and the value of  $\delta^{13}\text{C}^*$ , with more negative values closer to New York City, where hypoxic conditions are more common and more extreme (Figure 21).

Our core data show (Figures 22, 23) that salinities in LIS waters have decreased markedly, especially in westernmost LIS (The Narrows) and in cores in western and Central LIS close to river mouths, in shallow waters. Such a drop in salinity was also indicated by the declining abundance of the benthic foraminifer *E. advena* (Subsection 5C6). In these regions we see relatively large natural variability, but the drop in salinity by several psu units starting in the early 19<sup>th</sup> century is unprecedented, and was accompanied by an increased amplitude in variability. The overall drop in salinity is most likely caused by changes in land use (higher runoff with more impervious surfaces), and enhanced fresh water inputs from the WWTP in more recent times. The latter may represent a substantial volume of water, comparable in magnitude to the water flux of the Housatonic River. This WWTP fresh water flux is largely discharged into the western part of LIS, mainly through the East River and direct discharge of WWTP along the Sound. The freshening trend may have strengthened the degree of stratification during the summer, which may have enhanced hypoxia by cutting off the  $\text{O}_2$  re-supply to bottom waters..

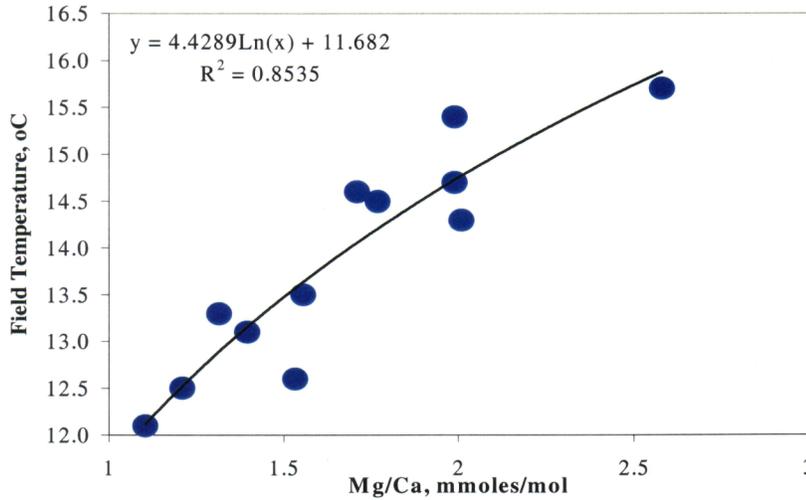
The excess  $\delta^{13}\text{C}$  values for the same 11 cores show a very notable decrease in the early to middle 19<sup>th</sup> century, at the same time as the lowered salinity (Figure 22). We interpret this strong decrease over the last 150 years as a result of the addition of isotopically light carbon to the DIC pool through the oxidation of organic matter (be it carbon from land or from locally produced algae). This signal is very robust and appears in all cores, and does not diminish markedly over the last few decades. The excess  $\delta^{13}\text{C}$  values also show a higher amplitude of variability after the strong decline in values in the early 19<sup>th</sup> century, and show a stronger decline in westernmost LIS and in shallower locations. The excess  $\delta^{13}\text{C}$  values were then used to estimate oxygen saturation levels of the bottom waters: the excess  $\delta^{13}\text{C}$  values allow us to calculate the amount of organic matter that must have been oxidized, and through simple equivalence, the amount of oxygen needed for this oxidation (1 mole of  $\text{O}_2$  per 1 mole of C-organic). The paleo temperature provides the amount of  $\text{O}_2$  that the waters could hold at saturation, and from the excess  $\delta^{13}\text{C}$  values we calculate how much of that  $\text{O}_2$  was left (Figure 22). This method assumes no resupply of  $\text{O}_2$  through mixing and the sulfate reduction loop has not yet been incorporated in the calculations. The final data show that hypoxia did not occur at most locations in the Sound until about 150 years ago.

The paleo-temperature data (Figure 23) suggest that over the long term, LIS had relatively high water temperatures about 1000 years ago (during the Mediaeval Warm period), much colder water temperatures in the early 1600s (Little Ice Age), and that modern global warming was starting to have its effects over the last 100 years. We are presently working with Dr. Pagani at Yale University and one of his graduate students to apply a recently developed organic geochemical proxy (Tex86, based on lipids from crenarcheotes) to provide a more detailed paleo-temperature record, and compare it with the Mg/Ca record.

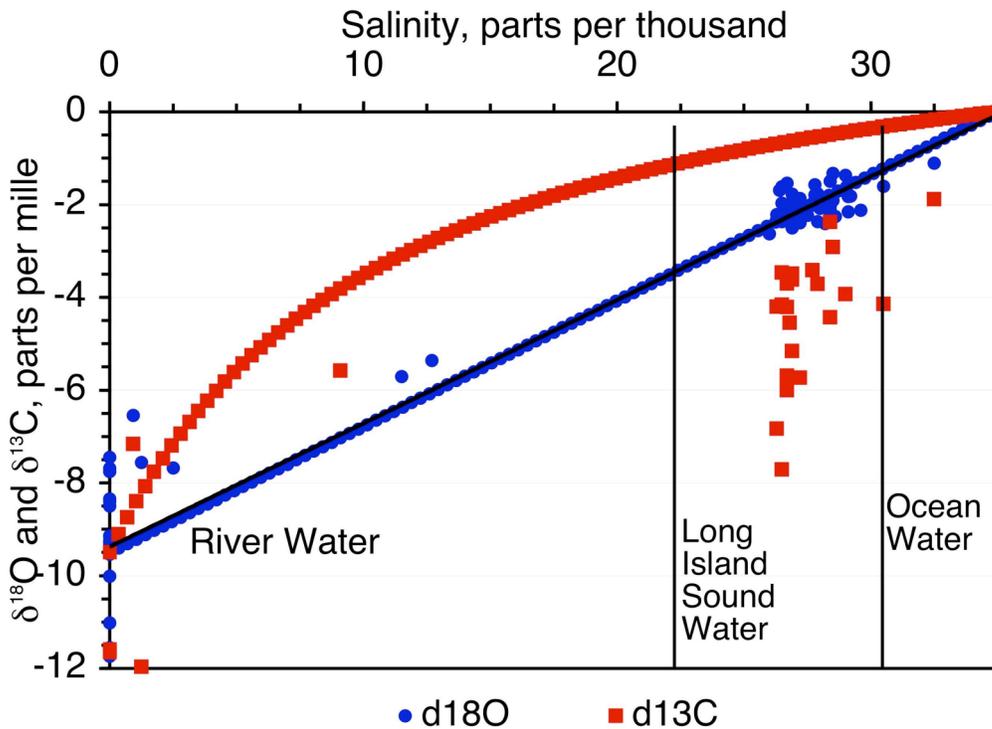
There is no evidence in the excess  $\delta^{13}\text{C}$  values that hypoxia occurred during the warm period 1000 years ago, indicating that the main driver for the hypoxia remains the eutrophication and associated high rate of algal productivity and/or supply of terrestrial organic matter in the Sound. Both climate and water freshening modulate the intensity and/or duration of hypoxia, but our data document that the ultimate driver for the process is the ‘overabundance’ of organic matter.



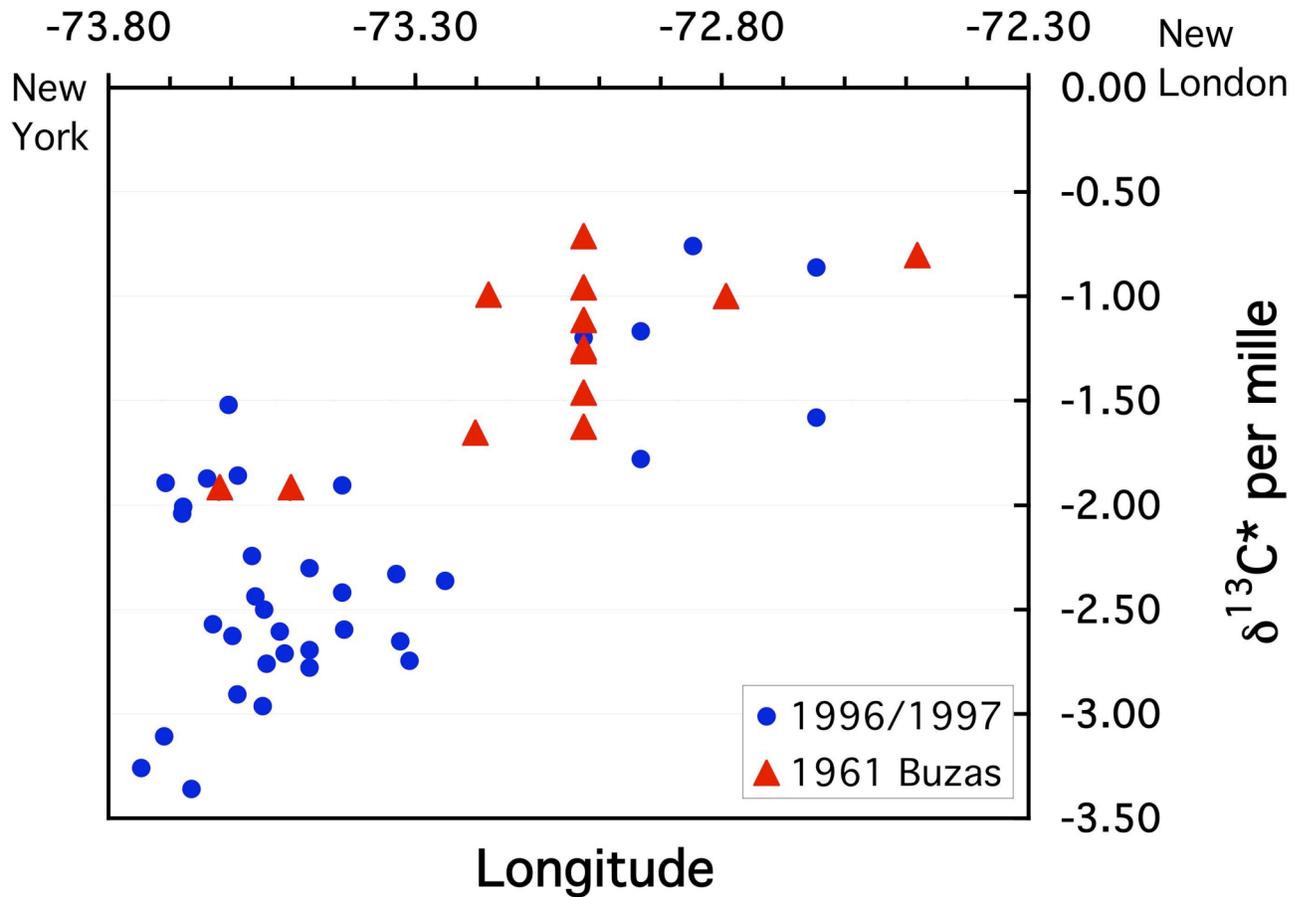
**Figure 18.** Proxies measured in the tests of *Elphidium excavatum* from LIS in order to trace past environments.



**Figure 19.** Calibration of the Mg/Ca thermometer in modern LIS with *Elphidium excavatum*. Living foraminifera were collected with bottom water temperature.

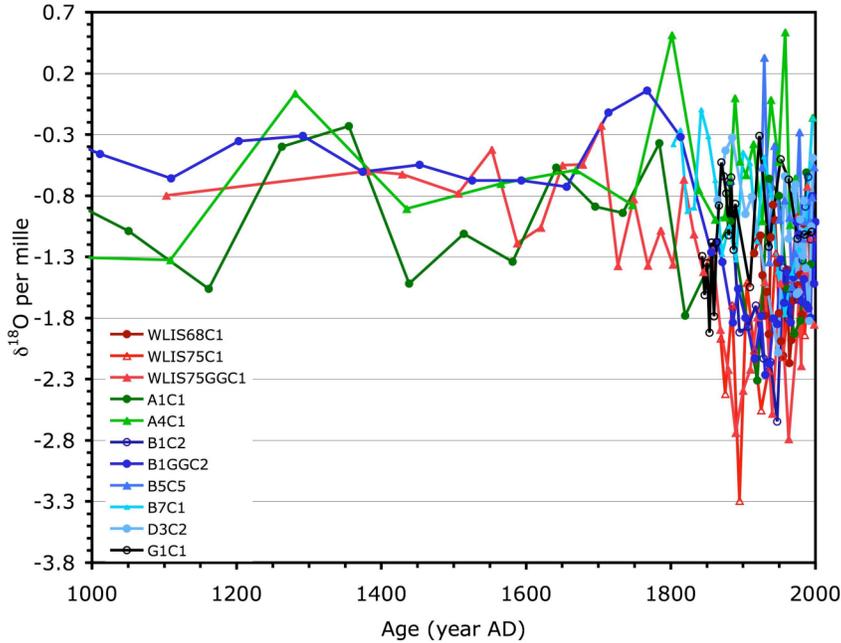


**Figure 20.** Mixing model for LIS waters, with LIS salinities indicated;  $\delta^{18}O$  in water and  $\delta^{13}C$  in Dissolved Inorganic Carbon (DIC) were measured in ocean and river waters. The DIC concentrations differ in river and ocean water, creating a mixing curve between salinity and  $\delta^{13}C$ . The  $\delta^{18}O$  values in LIS waters (blue dots) plot along the mixing line, whereas DIC  $\delta^{13}C$  values (red squares) plot below the mixing curve, indicating that isotopically light carbon has been added to the DIC pool after mixing of river and ocean waters. We assume that the oxidation of organic matter provides this additional source of light carbon.

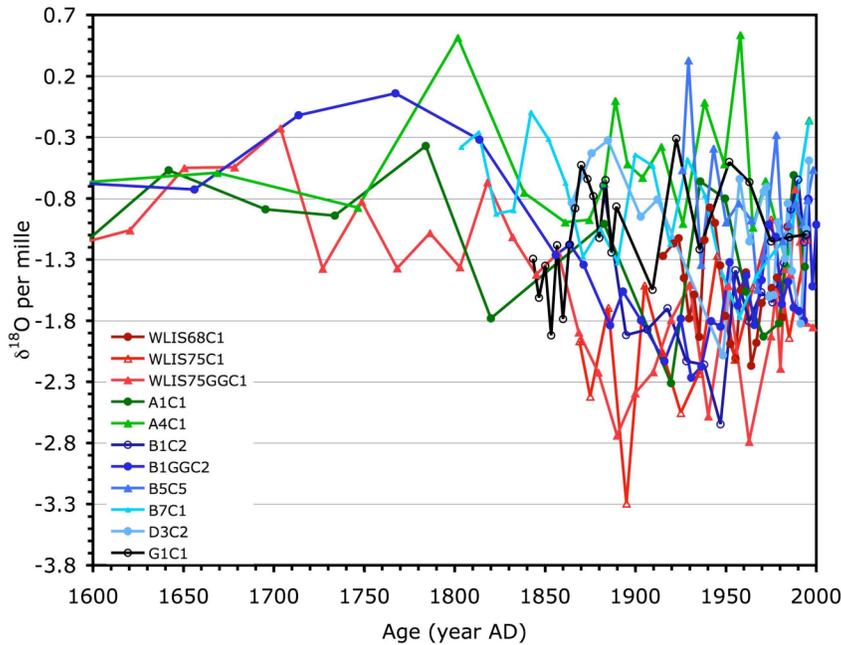


**Figure 21.** The excess  $\delta^{13}\text{C}$  values ( $\delta^{13}\text{C}^*$ ) in carbonate from living foraminifera in surface sediment samples plotted here against longitude. The Western section of the Sound shows very low values, which are lower in the 1996/97 data set than in the data obtained on specimens in the collection of Buzas (obtained from the Peabody Museum, Yale University), which were sampled in 1961 and 1962. The  $\delta^{13}\text{C}$  in carbonate is a proxy for the  $\delta^{13}\text{C}$  of DIC, which is impacted by the oxidation of organic matter in the water column or sediment bed. The correlation between seasonal anoxia and the  $\delta^{13}\text{C}^*$  parameter in the modern environment is used to retrodict hypoxic conditions of the past from core data, under the assumption that oxidation of organic matter used dissolved oxygen (but see subsection 5C5, Figure 14).

Oxygen isotope values, 11 cores, last 1000 years

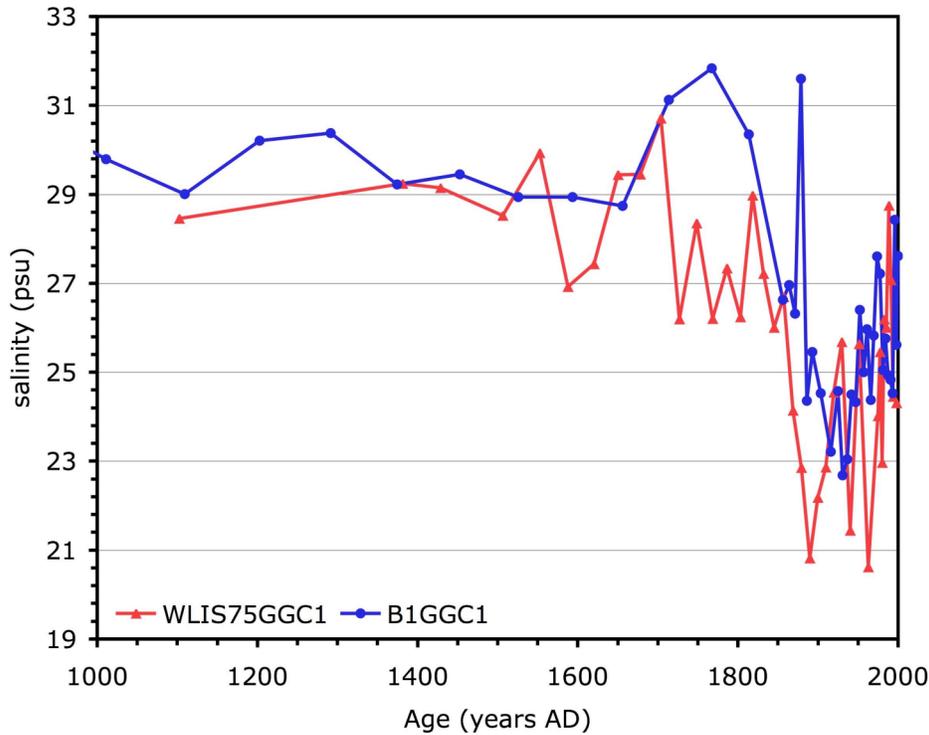


Oxygen isotope values, 11 cores, last 400 years

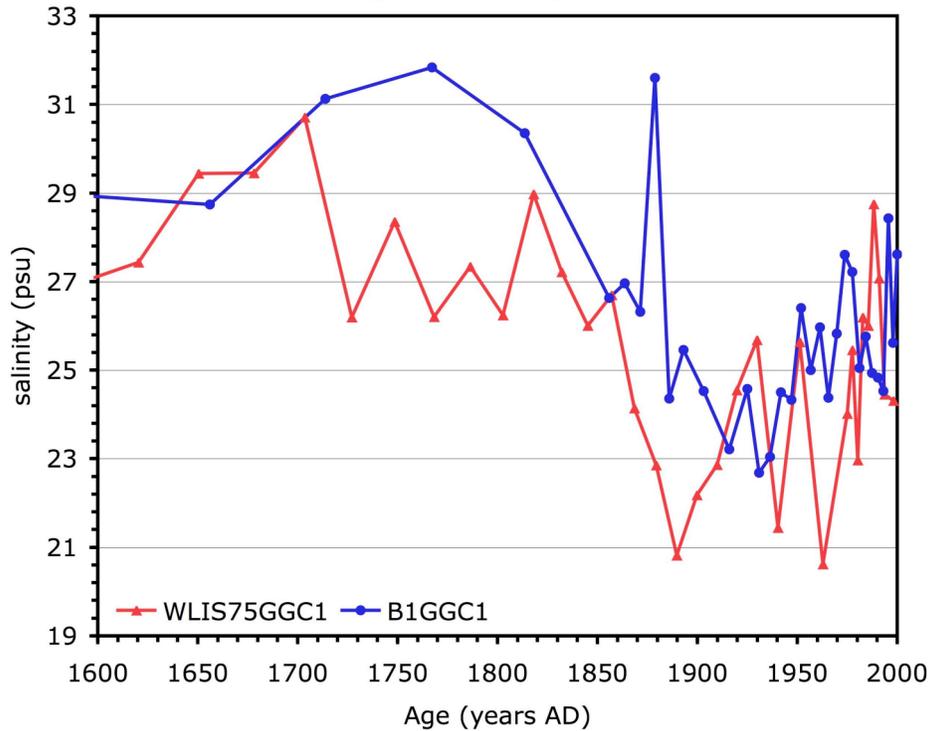


**Figure 22.** Values of  $\delta^{18}\text{O}$  in calcite of tests of *Elphidium excavatum* from 11 LIS cores versus age. Red/pink: cores in The Narrows; green: cores in the Western LIS basin; blue: cores in Central LIS basin; black: cores in Eastern LIS basin. Round symbols: cores taken in waters < 10m; triangles: cores taken in waters > 10 m. Open symbols: data on short cores B1C2, WLIS75-C1 taken close to long cores B1GGC2 and WLIS75GGC1 (closed symbols). More negative values indicate lowered salinities during calcification, because the effects of temperature variation are too small to explain the observed changes (see text). Top: record over the last millennium; Bottom: record over the last 400 years.

### Salinity, last 1000 years

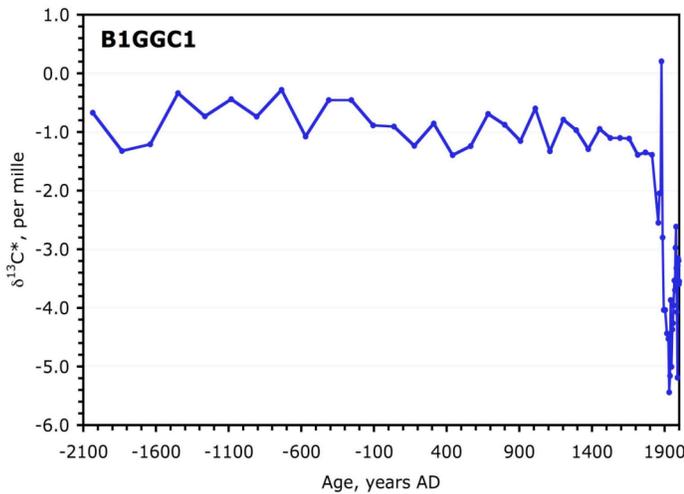


### Salinity, last 400 years

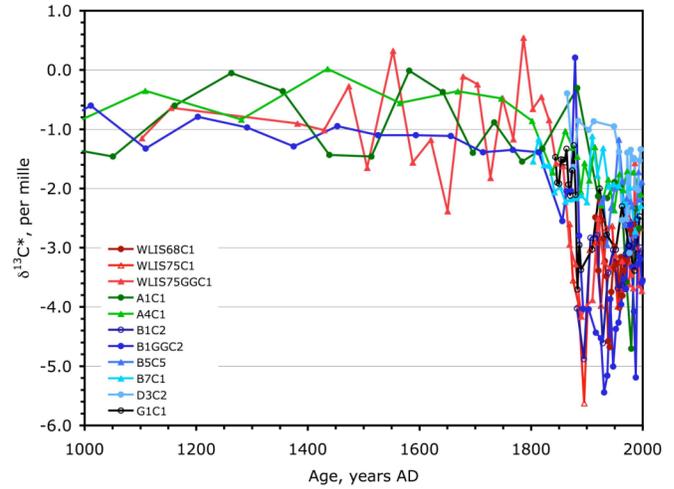


**Figure 23.** Changes in calculated salinity (using the  $\delta^{18}\text{O}$  values from Figure 22, but incorporating temperature effects) in LIS bottom waters, based on data from cores WLIS75 and B1. Note the strong drop over the last 150 years by more than 6 psu. **Top:** record over the last millennium; **Bottom:** record over the last 400 years.

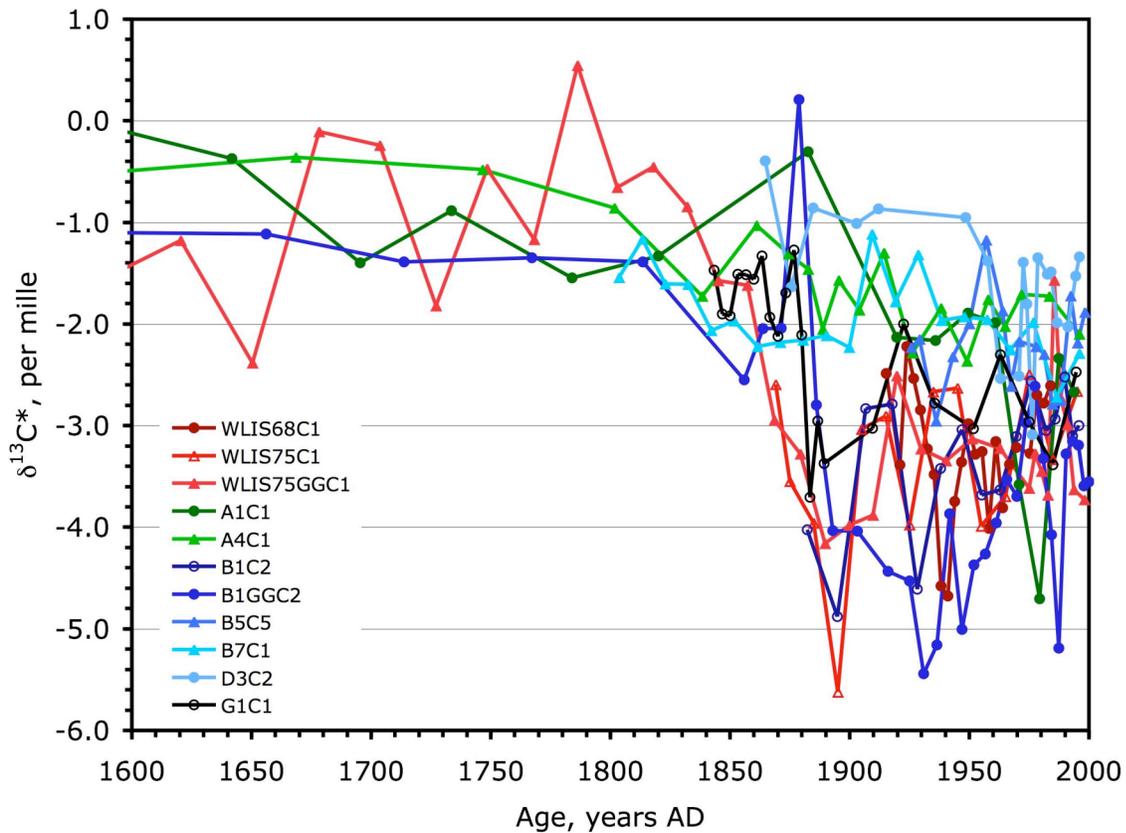
'Excess' Carbon isotope values, last 4000 years



'Excess' Carbon isotope values, 11 cores, last 1000 years



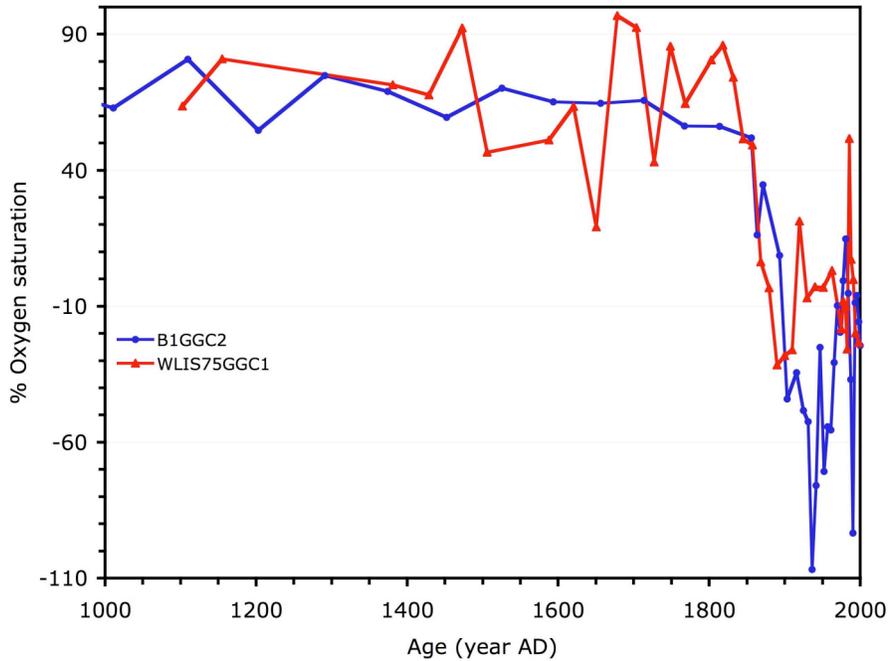
'Excess' Carbon isotope values, 11 cores, last 400 years



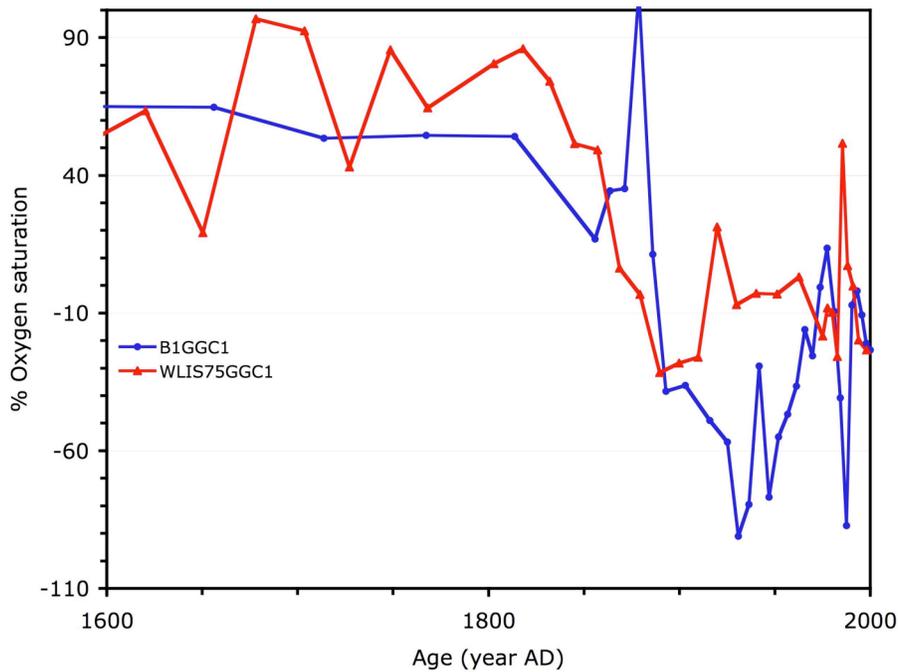
**Figure 24.** Excess  $\delta^{13}\text{C}$  values in calcite of tests of *Elphidium excavatum* from 11 LIS cores versus age. Red/pink: cores located in The Narrows; green: cores located in the Western LIS basin; blue: cores located in Central LIS basin; black: cores located in Eastern LIS basin (see Figure 1 for exact locations). Round symbols: cores taken in waters < 10m; triangles: cores taken in waters > 10 m. Open symbols: data on short cores B1C2, WLISC1 taken close to the long cores (closed symbols) at these sites.

**Top:** records over the last 4000 and 1000 years; **Bottom:** record over the last 400 years.

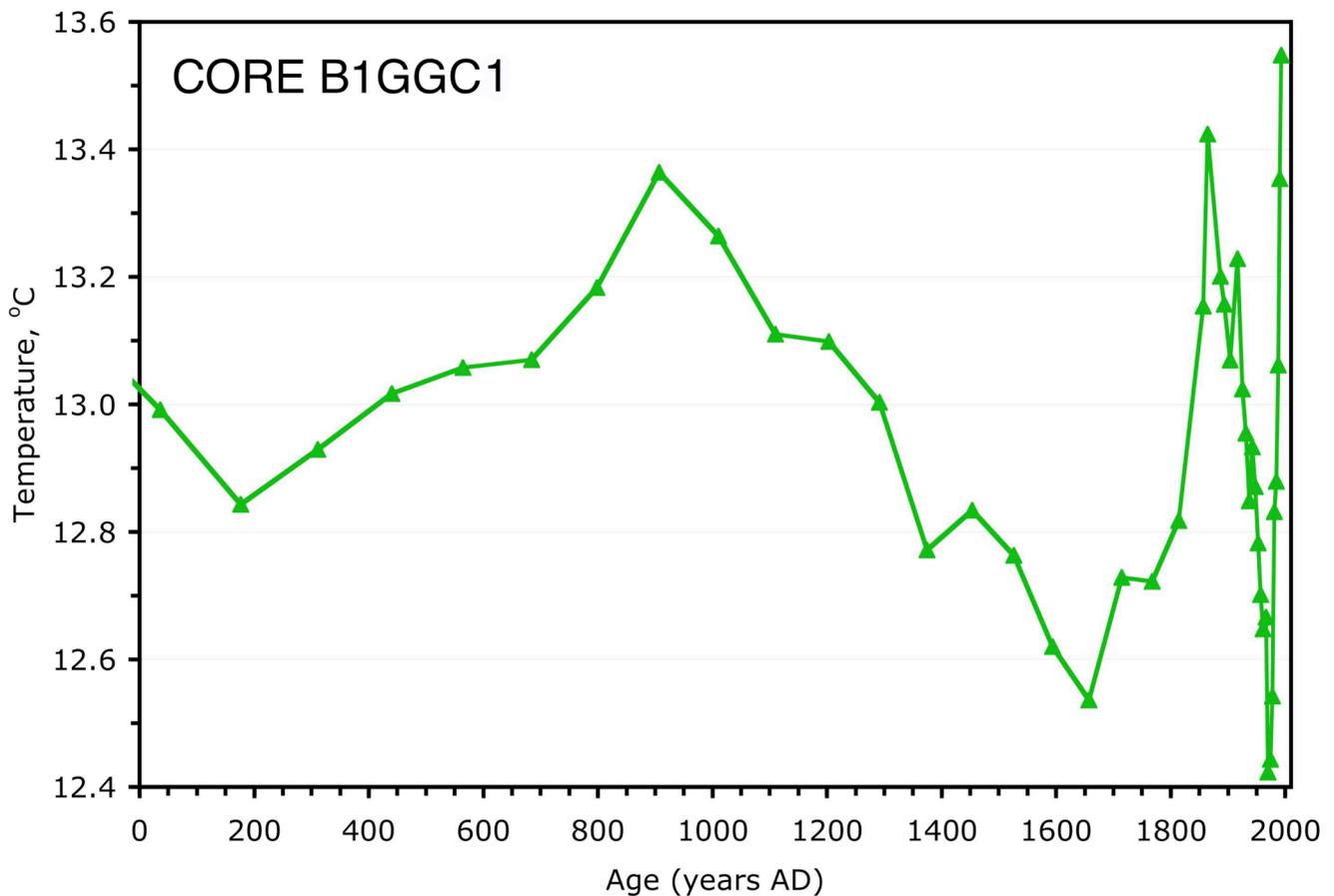
### Oxygen saturation, last 1000 years



### Oxygen saturation, last 400 years



**Figure 25.** Virtual oxygen saturation of LIS waters over time, estimated with data from cores WLIS75 and B1. The negative saturation levels are an artifact of the assumptions that no oxygen re-supply took place (zero mixing during stratification), and there is no correction for the sulfate reduction loop when calculating the  $O_2$  loss from the oxidation of C-organic. **Top:** record over the last millennium; **Bottom:** record over the last 400 years.



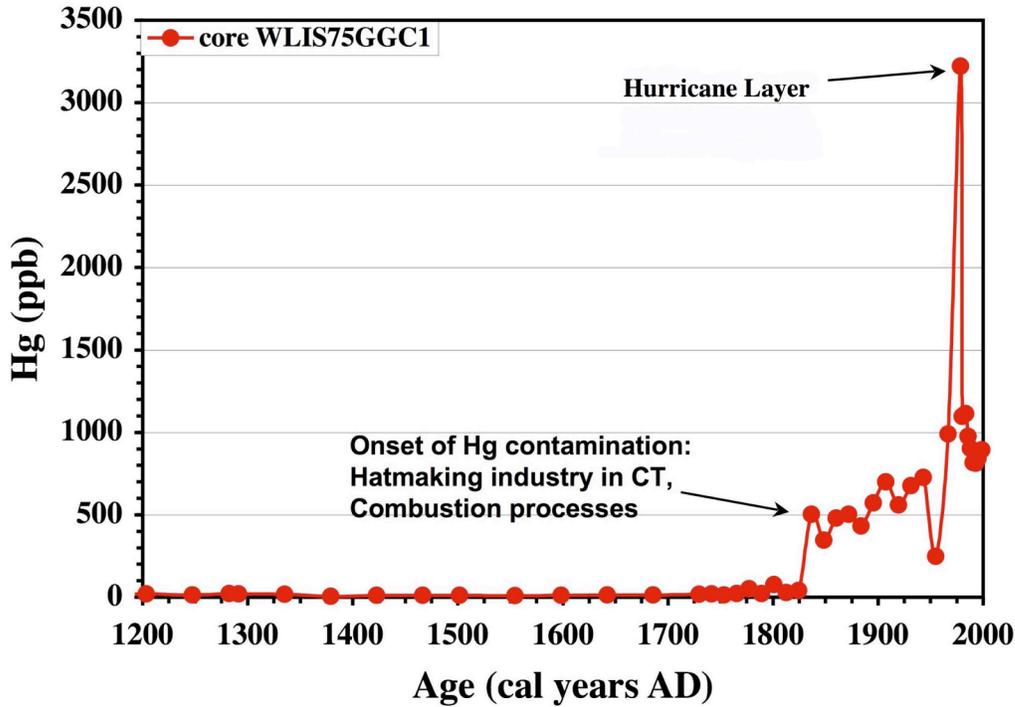
**Figure 26.** Five-point moving averages of annually averaged temperature of LIS bottom waters as calculated from Mg/Ca values of benthic foraminifera from core B1GGC1 (water depth 8m). The temperature peak around 1000 AD correlates with the Medieval Warm Period, whereas the large dip ~1600 AD is the bottom of the Little Ice Age. The temperature high around 1850 AD is puzzling, but shows up in all our core temperature records. The warming trend since 1950 is probably reflecting Modern Global Warming.

### **Section 5C8. Trace metal contamination in Long Island Sound (Varekamp)**

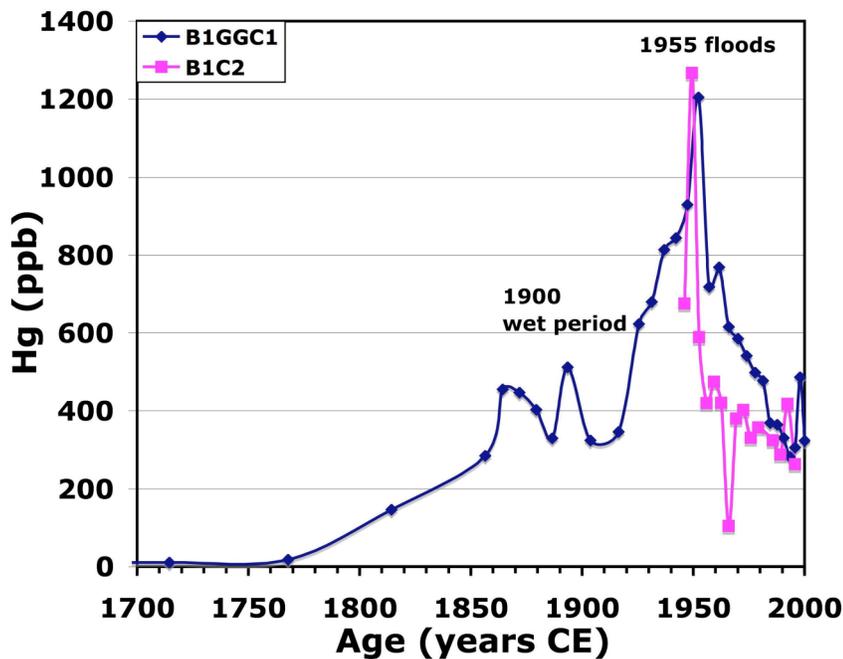
The Mercury (Hg) concentrations in LIS sediment are somewhat reflective of overall metal pollution in the Sound (Varekamp et al., 2003). The Hg profiles provide also isochronous horizons related to the sudden deposition of thin layers of highly contaminated sediment during major hurricanes, e.g., the two hurricanes that struck CT in 1955 within two weeks of each other. Mercury in LIS sediment derives from several sources: the generic atmospheric Hg deposition that provides it directly to Sound waters, the wash-out of the atmospheric deposition in the watersheds, the small point sources along the rivers that provide a continuous flux of Hg, the WWTPs that have particulates enriched in Hg, and last but not least, the large upland areas contaminated with Hg from a single industrial source (hat making in Danbury, Bethel and Norwalk). The riverine sediments near these cities are severely polluted, with Hg concentrations up to 100 ppm, while 0.5 ppm Hg is considered notable Hg peak pollution from atmospheric deposition.

The contaminated sediments are moved during floods (e.g., associated with hurricanes) and flushed as fine, suspended debris into LIS, creating thin Hg-rich layers (Figures 27, 28). Western LIS has the higher concentrations of Hg in the Sound, with close to 1 ppm Hg in areas with fine-grained sediment in West-LIS. Most core profiles show the overall pollution trends (starting in the early 1800s, peaking in the 1960-1970s, with decreasing concentrations to modern times), with superimposed “sudden event” layers that are rich in Hg. A typical example is the coal-rich layer in core WLIS75GGC1 (Figure 27), which has up to 3.3 ppm Hg. The Housatonic River is the main outflow for “hat-making Hg”, and Hg concentrations in core B1GGC1 at its mouth reach up to 1.2 ppm Hg (Figure 28). The latter layer is associated with the 1955 hurricanes, and that signal can be followed from the Housatonic delta to the A1C1 and A4C1 coring sites. The 1900 Hg peak in core B1 is associated with a longer, relatively wet period, which also shows up in the salinity records as a salinity ‘low’ (section 5C7).

The Hg levels in LIS sediments are relatively high, but it is unlikely that Hg pollution would be the main driver for the lobster die-off, because the Hg concentrations had already decreased from their peak values in the 1960-1970 period when the die-off took place. Nonetheless, the permanently high levels of such toxins may weaken the biological system of the lobsters over time, so they become more vulnerable to other stressors. Other trace metals such as Cu, Zn and Cr are also relatively abundant in LIS sediment, with the Housatonic as an important source (the ‘Brass Valley’). The sedimentary Pb concentrations are not directly impacted by industrial Pb releases from the Housatonic River watershed, but are largely a result of sediment focusing of Pb-enriched soils, with Pb ultimately derived from the combustion of leaded gasoline. The introduction of unleaded gasoline saw a dramatic decrease in Pb concentrations of sediment, so once more, the toxicity of LIS surface sediment had already decreased strongly over the period 1970 to 1990, and the presence of a particular trace metal as the main driver behind the lobster die-off is unlikely.



**Figure 27.** Mercury contamination record for core WLIS75GGC1, showing the onset of pollution associated with the hatting industry and the spike from the 1955 floods with the “coal-rich” layer. Part of the Hg pollution presumably also stems from sewage inputs.



**Figure 28.** Mercury profiles in cores B1 and B1C2. The overall contamination level increases since the late 1700s, probably associated with the onset of the hatting industry in Danbury; large scale Hg pollution of the atmosphere associated with coal-burning and industrialization started in the mid to late 1800s. The two spikes at 1900 and 1955 are associated with ‘wet periods’ and watershed ‘flush-out events’.

## Conclusions

Long Island Sound has seen three levels of anthropogenic impact over the last 400 years: during the colonial era, the industrial period from 1850 to early 1900s, and the last 50 years. Physical, chemical and biological changes have occurred, and many of those were unprecedented, having no parallels in the pre-colonial period, for which our records go back to almost 4000 years. The impacts can be distinguished by their root causes: land use changes, contaminant inputs, nutrient inputs, aquatic food extraction, and climate change.

The sediment flux into LIS has increased in two phases since the arrival of European colonists: 1). an early colonial phase (1600-1750) of enhanced sediment generation and transport, possibly partly related to changes in landscape associated with the fur trade (removal of beavers with subsequent loss of beaver dams, organic rich sediment transport to LIS) and 2). the last 200 years, in which increased sediment fluxes were related to large-scale modification of the landscape by humans (forest to agricultural land, urban development of paved surfaces). Our pollen records indicate initial land clearing in the 17<sup>th</sup> century, followed by a rapid increase in forest removal during the 18<sup>th</sup> and early 19<sup>th</sup> century, followed by regrowth of forests during the 20<sup>th</sup> century. The net result is a tripling to five-fold increase in sediment accumulation rates in The Narrows and the Western LIS basin, and at least a doubling or tripling in the Central LIS basin. The eastern Sound is mostly a non-depositional area, where sediment moves in sand-waves due to the vigorous tidal currents, but no net deposition occurs with the exception of some near-shore locations (e.g., core G1C1).

The loading of the sediments with organic carbon and nitrogen as well as diatom remains (biogenic Silica) also increased in two pulses: an early phase associated with the beaver-dam removal, sending extra nutrients into the Sound, whereas a much larger change occurred starting ~200 years ago and continuing at least to some extent until today: the rate of organic carbon accumulation in cores from western LIS increased by a factor of up to 5. The  $\delta^{13}\text{C}$  and N/C values of organic matter documents, however, that a large part of the organic matter preserved in the sediments was not locally produced but derived from land. The late 1700s early 1800s saw a low flux of carbon from land, because the landscape was largely deforested at the time. We also documented that in western LIS the burial of marine carbon actually decreased over the last 100 years. Our studies on N-isotopes and sewage indicators document the strongly enhanced input of sewage-derived materials in the Sound over the last 150 years, leading to Nitrogen enrichment and eutrophication, going back up to 200 years.

The presence of metallic pollutants also has increased over the last 150 years, and we documented that the Hg loading of the Sound is conditioned both by the strength of the overall atmosphere-derived Hg pollution, as well as periodic inputs of heavily Hg-contaminated sediment during hurricanes and wet periods.

The data on assemblages of diatoms, dinocysts and foraminifera confirm that marine organic productivity increased strongly during these 200 years, with a first episode of severe eutrophication starting in the early 1800s, as indicated by changes in species composition in all three microfossil groups.

The water temperature in LIS estimated from Mg/Ca in benthic foraminiferal tests varied conform the northern hemispheric climate trends, with relatively warm waters during the Medieval Warm period (~1000 AD), colder waters during the Little Ice Age (1300-1700 AD) and evidence for modern global warming during the last 150 years. The exact

calibration of the water temperature records needs more work, but the trends towards 'warmer' and 'cooler' are well defined, with the cool temperature estimates supported by independent dinocyst data.

The paleo-salinity records depend on the quality of the paleo-temperature records, but the observed changes are so large that we are confident that 'more saline' and 'less saline' trends are robust, although the exact values in psu may be uncertain estimates. The paleosalinity trends are also supported by foraminiferal census data and the only conclusion is that there was a striking overall freshening of western and coastal LIS over the last 150 years. Water input by WWTP is one possible reason, but changes in land use leading to the presence of more impervious surfaces may have enhanced run off, and overall changes in climate may have contributed as well. Whatever the combination of drivers is, we consider this freshening trend of the western Sound, with superimposed steep freshening events during very wet periods, as a highly significant environmental shift over the last 150 years.

The degree of water oxygenation is a function of the strength of stratification during the summer (influenced by water temperatures, salinity and wind - current patterns), and of the availability of O<sub>2</sub> consuming organisms and oxidation of organic carbon. We developed a parameter that indicates the amount of oxidation of organic matter in the past, and found that the western and central Sound have suffered from hypoxia for more than 150 years. Earlier warm periods (Mediaeval Warming) were not characterized by such hypoxia. We conclude that the main driver of hypoxia in LIS is the eutrophication of the Sound, resulting from enhanced N-inputs, leading to enhanced productivity of organic matter, where oxidation of that organic carbon depletes the bottom waters in oxygen during times of stratification (summer).

The environmental evolution of LIS over the last thousand years can thus be outlined as follows: 1000 years ago, the environmental changes were largely driven by natural fluctuations in climate and gradual changes in the terrestrial biosphere and landscape. By 1600 AD, we see the first signs of disturbance, at least in part the result of the initial land clearing by the early colonists, followed by the impact of the watershed disturbances associated with beaver eradication. The last 200 years show the most profound changes, unprecedented over thousands of years, and dominantly caused by human activities: enhanced sewage-derived input, with associated increases in organic productivity, larger carbon fluxes from the land into LIS, freshening of the Sound and more extreme events in salinity, and pollution with a variety of contaminants, including toxic metals. Broad changes in micro-flora and -fauna during this period can be attributed to increases in turbidity as a result of enhanced organic productivity as well as the enhanced productivity itself. These changes are reflected in the ratios of heterotrophic to autotrophic dinocysts, centric to pennate diatoms, and overall increased abundances of heterotrophic benthic organisms (foraminifera) as well as changes in species dominance in all three groups.

The last few decades stand out from the centennial to millennial developments through a set of profound shifts: the dominant foraminifer *Elphidium excavatum*, a specialized diatom consumer, started to decrease in relative and absolute abundance in the late 1960s - early 1970s, especially in western LIS. This organism was replaced by an omnivorous foraminifer, *Ammonia parkinsoniana*, and at the same time, diatom productivity may have decreased, as shown by the burial rates of biogenic silica in the western Sound. We interpret this set of data with the broad observation that some parts of the Sound may have switched from nitrogen-limited productivity to silica-limited productivity, at least

during parts of the year. The fertilization with nitrogen compounds led to enhanced diatom productivity (especially of planktic forms) about 200 years ago, but the supply of silica to LIS has remained constant or even decreased over time. As a result, dissolved silica has become a limiting nutrient for diatoms, and the ecological niche of diatoms (especially late in the spring bloom) is taken over by other micro-algae that do not need silica (e.g., dinoflagellates, cyanobacteria). This shift in primary productivity may reverberate through the food chain, because many organisms (such as copepods, shell fish) preferably consume diatoms. We are not yet ready to state that this shift is dominating the LIS ecosystem today, but we propose that there are many locations especially in western LIS where this shift in nutrient limitation occurs. Similar arguments have been made in other strongly human-impacted coastal regions, e.g., the Gulf of Mexico.

In how far the lobster community was directly impacted by these shifts is currently unknown. The combination of changes in water temperature, salinity, presence of toxins, switch in primary producers, and changes in the lower part of the food chain may have had an impact on lobster populations. Our data show that a combination of many stressors occurred, and this was probably more damaging to the lobster ecology than one specific factor. Ultimately, the lobsters may have been weakened through all these environmental shifts and as a result became more vulnerable to a variety of pathogens that led to the strong die off in lobsters in the mid to late 1990s.

## References

- Abramson, I., 2002, Benthic foraminifera as environmental proxies in Long Island Sound. Undergraduate Thesis, Wesleyan University, p. 276.
- Altabet, M. and Varekamp, J.C. 2004, Nitrogen Isotopic Ratio Records The Eutrophication History of Long Island Sound. *EOS Trans. AGU*, 85 (17), *Jt. Assem. Suppl.*, Abstract GC41B-02
- Altabet, M.A., and Varekamp, J.C. , 2007. The nitrogen isotope biogeochemistry of Long Island Sound; insights into mechanism(s) of <sup>15</sup>N enrichment in eutrophication-impacted estuaries ASLO 2007 Aquatic Sciences Meeting, Santa Fe, NM
- Andersen, N., 2005, The eutrophication history of Long Island Sound. Undergraduate Thesis, Wesleyan University, Middletown CT.
- Boon, N., Altabet, M., Varekamp, J.C., Nutrient dynamics in LIS. . *Eighth Biennial Long Island Sound Research Conference*, United States Coast Guard Academy, New London, CT, Program and Abstracts Volume, 37.
- Cooper, S. R., Thomas, E., and Varekamp, J. C., 2003. Environmental Change in Long Island Sound: Diatoms from Sediment Cores. *17<sup>th</sup> North American Diatom Symposium*, October 21-26, Islamorada, FL
- Cooper, S. R., Thomas, E., and Varekamp, J. C., 2004. Long Island Sound: diatoms from sediment cores as part of environmental and ecological change studies. Mid- Atlantic Ecology Conference: Sustainable Landscapes, March 27-28, Franklin & Marshall College, Lancaster, PA, Abstracts p. 6
- Groner, M., 2004, The carbon cycle in Long Island Sound: radiocarbon studies of carbonates. Undergraduate Thesis, Wesleyan University p. 123
- Lugolobi, F., Varekamp, J. C., Thomas, E., and Buchholtz ten Brink, M. R., 2004. The use of stable carbon isotopes in foraminiferal calcite to trace changes in biological oxygen demand in Long Island Sound. *6<sup>th</sup> Biennial LIS Res. Conf. Proc.*: 47-51
- Sangiorgi, F., Brinkhuis, H., Thomas, E., Varekamp, J. C., and Cooper, S., 2005. Eutrophication trends and human impact in Long Island Sound (USA): organic walled dinoflagellate cyst and pollen records as part of a multidisciplinary study, *Workshop on Dinoflagellates and their Cysts: Their Ecology and Databases for Palaeoceanographic Reconstructions*. Liverpool (UK), 31 august-2 September 2005.
- Thomas, E., Gapotchenko, T., Varekamp, J. C., Mecray, E. L., and Buchholtz ten Brink, M. R., 2000, Benthic foraminifera and environmental changes in Long Island Sound, *Journal of Coastal Research*, 16: 641-655.

Thomas, E., Abramson, I., Varekamp, J. C., and Buchholtz ten Brink, M. R., 2004. Eutrophication of Long Island Sound as traced by Benthic Foraminifera. *Sixth Biennial LIS Research Conference Proc.:* 87-91

Thomas, E., and Varekamp, J. C., 2006. Benthic Foraminifera: Ecosystem Monitors of Eutrophication in Long Island Sound. *Eighth Biennial Long Island Sound Research Conference*, United States Coast Guard Academy, New London. CT, Program and Abstracts Volume, 37.

Varekamp, J. C., 2006. The historic fur trade and climate change. *EOS Transactions AGU*, 87 (52), 26 December. doi:10.1029/2006EO520002, 2006

Varekamp, J.C., Kreulen, B., and Buchholtz ten Brink, M.F, and Mecray, E., 2003, Mercury contamination chronologies from Connecticut wetlands and Long Island Sound sediments. *Environmental Geology*, 43, 268-282

Varekamp, J. C., Thomas, E., Lugolobi, F., and Buchholtz ten Brink, M. R., 2004. The paleo-environmental history of Long Island Sound as traced by organic carbon, biogenic silica and stable isotope/trace element studies in sediment cores. *Sixth Biennial LIS Research Conference Proc.:* 109-113

Varekamp, J. C., Thomas, E., and Groner, M., 2005. The late Pleistocene – Holocene History of Long island Sound, *Seventh Biennial LIS Research Conference Proceedings*, 2004, p. 27-32

Varekamp, J. C., Altabet, M. Thomas, E., Ten Brink, M., Andersen, N., and Mecray, E., 2009. Carbon cycling in LIS: nutrient fluxes and landscape development over the last 1000 years. *Ninth Biennial LIS Research Conference Proceedings*, 2008, p. 2-13.

### **LIS PUBLICATIONS funded by the 'Lobster Grant'**

1. Varekamp, J.C., Kreulen\*, B., and Buchholtz ten Brink, M.F, and Mecray, E., 2003, Mercury contamination chronologies from Connecticut wetlands and Long Island Sound sediments. *Environmental Geology*, 43, 268-282.
2. Thomas, E., Abramson\*, I., Varekamp, J. C., and Buchholtz ten Brink, M. R., 2004. Eutrophication of Long Island Sound as traced by Benthic Foraminifera. *Sixth Biennial LIS Research Conference Proc.:* 87-91
3. Lugolobi\*, F., Varekamp, J. C., Thomas, E., and Buchholtz ten Brink, M. R., 2004. The use of stable carbon isotopes in foraminiferal calcite to trace changes in biological oxygen demand in Long Island Sound. *6<sup>th</sup> Biennial LIS Res. Conf. Proc.:* 47-51
4. Varekamp, J. C., Thomas, E., Lugolobi,\* F., and Buchholtz ten Brink, M. R., 2004. The paleo-environmental history of Long Island Sound as traced by organic carbon, biogenic silica and stable isotope/trace element studies in sediment cores. *Sixth Biennial LIS Research Conference Proc.:* 109-113
5. Varekamp, J.C., 2005, Meeting volume, conference Living on the Edge, Bologna, Italy.
6. Varekamp, J.C., Mecray, E.L., and Zierzow, T., 2005, Once spilled, still found: Metal contamination in Connecticut wetlands and Long Island Sound sediment from historic industries. Chapter in book on 'Our Changing Coasts', editors Whitelaw and Visiglione, E.Elgar Publishers, Chapter 9, p. 122-147.
7. Varekamp, J.C. 2006, The historical fur trade and climate change. *Eos magazine*, v.87, # 52, p. 593, 596-597.
8. Cooper, S.R., E. Gaiser and A. Wachnika, in press. Chapter 18: Estuarine paleoenvironmental reconstructions using diatoms. Pages 352-373 In: E. Stoermer & J. Smol (eds.), *The Diatoms: Application for the Environmental and Earth Sciences*, Volume 2, Cambridge University Press, Cambridge.

### **LIS ABSTRACTS**

#### **2001**

- 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.
- 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.
- 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.
- 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.
- 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**

- 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,
- 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.
- 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.
- 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.
- Varekamp, J.C., and Buchholtz ten Brink, M.R.. Mercury in Connecticut and Long Island Sound sediment. Long Island Sound /NEERS Research Conf, Oct. 24-26, Groton, CT.
- 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.
- 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.
- Varekamp, J. C., Thomas, E., Lugolobi\*, F. and Buchholtz ten Brink, M. R. Paleoenvironmental History of Long Island Sound, CT, USA. AGU Fall meeting,
- 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.

## **2003**

- 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 "LIS Lobster Research" meeting, January 17, Groton, CT
- 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
- Cooper, S. R., Thomas, E., and Varekamp, J. C., 2003. Environmental Change in Long Island Sound: Diatoms from Sediment Cores. 17<sup>th</sup> North American Diatom Symposium, October 21-26, Islamorada, FL

## **2004**

- Altabet, M. and Varekamp, J.C. Nitrogen Isotopic Ratio Records The Eutrophication History of Long Island Sound. *EOS Trans. AGU*, 85 (17), *Jt. Assem. Suppl.*, Abstract GC41B-02
- Andersen\*, N. and Varekamp, J.C. Paleoproductivity indicators in Long Island Sound. *AGU EOS Trans. AGU*, 85 (17), *Jt. Assem. Suppl.*, Abstract GC43A-02
- Bronsther, \* R., Welsh\*, P. and Varekamp, J.C., Mercury in Connecticut and Long Island Sound: Impact of historic hatting industries. *EOS Trans. AGU*, 85 (17), *Jt. Assem. Suppl.*, Abstract B21A-02

- Carey, D. A., and Varekamp, J.C., Evidence of historical wet period deposits in central Long Island Sound: Source and transport processes based on mercury profiles and sedimentology. 7<sup>th</sup> Biennial Long Island Sound Research Conference, Program and Abstracts. November 4-5.
- Cooper, S. R., Thomas, E., and Varekamp, J. C., 2004. Long Island Sound: diatoms from sediment cores as part of environmental and ecological change studies. Mid-Atlantic Ecology Conference: Sustainable Landscapes, March 27-28, Franklin & Marshall College, Lancaster, PA, Abstracts p. 6
- Cooper, S. R., Thomas, E., Varekamp, J. C., and Sangiorgio, F., 2004. Anthropogenic Eutrophication of Long Island Sound: effects on diatom communities through time. 7<sup>th</sup> Biennial Long Island Sound Research Conference Proceedings, November 4-5.
- Cooper, S. R., Thomas, E., Varekamp, J. C., and Sangiorgio, F., 2004. Western Long Island Sound: Evidence from Diatom Studies of Eutrophication and Environmental Change in the 19th Century; AERS Fall Meeting, October 14-16, 2004, New Jersey Meadowlands Commission, Lyndhurst, NJ, USA
- Groner\*, M., Thomas, E., and Varekamp, J.C., Radiocarbon studies of Long Island Sound sediments. *EOS Trans. AGU*, 85 (17), *Jt. Assem. Suppl.*, GC43A-04
- Thaler\*, B., Thomas, E., and Varekamp, J. C., Benthic foraminifera in the changing ecosystem of Long Island Sound. *EOS Trans. AGU*, 85 (17), *Jt. Assem. Suppl.*, Abstract GC43A-05
- Thomas, E., Varekamp, J. C., Thaler\*, B., and Groner\*, M., The urban sea: anthropogenic influences on benthic foraminifera in Long Island Sound (USA). IGC 32, Florence, Italy, August 2004
- Thomas, E., Varekamp, J. C., Acosta\*, Z., Thaler\*, B., Cooper, S., and Sangiorgio, F., 2004. Eutrophication of western Long Island Sound, GSA Annual Meeting, Abstracts 36(6): 212-17.
- Thomas, E., Varekamp, J.C., Thaler\*, B., and Acosta\*, Z., Anthropogenic influences on benthic foraminiferal faunas in Long Island Sound. 7<sup>th</sup> Biennial Long Island Sound Research Conference, Program and Abstracts. November 4-5.
- Varekamp, J.C., Lugolobi\*, F., Thomas, E., Mecray, E. and Buchholtz ten Brink, M.R.L., The eutrophication of Long Island Sound. *EOS Trans. AGU*, 85 (17), *Jt. Assem. Suppl.*, Abstract GC41B-01

## 2005

- Varekamp, J.C. and Thomas, E., The environmental history of Long Island Sound with evidence for human impacts. Symposium, Living on the Edge, abstract vol. p.12-13.
- Thomas, E., Varekamp, J.C., Thaler\*, B. and Sangiorgio, F. The American Mediterranean: the influence of human populations on the ecosystem of Long Island Sound. Symposium, Living on the Edge, abstract vol. p.10-11.
- Sangiorgio, F., Brinkhuis, H., Thomas, E., Varekamp, J. C., and Cooper, S., 2005. Eutrophication trends and human impact in Long Island Sound (USA): organic walled dinoflagellate cyst and pollen records as part of a multidisciplinary study, *Workshop on Dinoflagellates and their Cysts: Their Ecology and Databases for Palaeoceanographic Reconstructions*. Liverpool (UK), 31 august-2 September 2005.

## 2006

- Varekamp, J.C., Altabet, M.A., and Thomas\*, C.R. Mechanism of  $^{15}\text{N}$  enrichment in eutrophication-impacted estuaries. ASLO Ocean Sciences meeting, Honolulu, HI, 2006.
- Varekamp, J. C., Thomas, E., Long Island Sound - a human dominated estuary. AGU spring meeting, Baltimore. *Eos Trans. AGU*, 87 (36), Jt. Assem. Suppl., Abstract B24A-07
- Thomas, E., and Varekamp, J. C., Benthic foraminifera in a human-dominated environment: Long Island Sound. FORAMS 2006 (Invited), *Anuário do Instituto de Geociências*, 29 (1), 573-574.
- Varekamp, J. C., Mercury contamination in Long Island Sound, USA, from the historic hat-making industry. ISEG7 meeting, Beijing, China, September 2006
- Goldoff\*, B, Varekamp, J. C., and Neupane\*, A., Mercury Contamination In W-Connecticut and Long Island Sound from historic hat-making sources. GSA annual meeting, Philadelphia, October 2006
- Thomas, E., Varekamp, J. C. Avener\*, E., Multiproxy records of eutrophication in Long Island Sound. *Annual Meeting, Abstracts with Programs*, 38 (7), 323
- Best, M. M.R., Bibeau, K., Spitzberg, D., Thomas, E., Varekamp, J.C., Bernatis J., Shell fragmentation as an indicator of benthic conditions. GSA annual meeting, Philadelphia, October 2006
- Thomas, E., and Varekamp, J. C., Benthic Foraminifera: Ecosystem Monitors of Eutrophication in Long Island Sound. *Eighth Biennial Long Island Sound Research Conference*, United States Coast Guard Academy, New London. CT, Program and Abstracts Volume, 37.
- Varekamp, J. C., Thomas, E., Buchholtz ten Brink, M. , and Mecray, E., 2006. The Environmental Impact of Early Western Colonization on Long Island Sound: Beavers meet Climate Change, *Eighth Biennial Long Island Sound Research Conference*, United States Coast Guard Academy, New London. CT. Program and Abstracts Volume, 39-40.
- Boon\*, N., Altabet, M., Varekamp, J.C., Nutrient dynamics in LIS. . *Eighth Biennial Long Island Sound Research Conference*, United States Coast Guard Academy, New London. CT, Program and Abstracts Volume, 37.

## 2007

- Altabet, M.A., and Varekamp, J.C. The nitrogen isotope biogeochemistry of Long Island Sound; insights into mechanism(s) of  $^{15}\text{N}$  enrichment in eutrophication-impacted estuaries ASLO 2007 Aquatic Sciences Meeting, Santa FE, NM
- Varekamp, J. C., Thomas, E., and Lewis, R. S., 2007. Early Long Island Sound: the American Black Sea? . *ICP9*, Shanghai, China, September 3-7, 2007, p. 99
- Thomas, E., and Varekamp, J. C., 2007. The Flooding of Long Island Sound. *AGU*, 88 (52), Fall Meet. Suppl., Abstract PP13B-1277

## 2008

- Varekamp, J. C., Thomas, E., and Lewis, R. S., 2008. The Formation and Evolution of Long Island Sound – the ‘American Black Sea’. Invited, American Quaternary Association Biennial Meeting, June 5-7, Pennsylvania State University, State College, PA.

Varekamp, J. C., Thomas, E., and Lewis, R. S., 2008. The Formation and Evolution of Long Island Sound. *GSA Annual Meeting*, 282-3.

Varekamp, J. C., and Thomas, E., 2008. Paleo-environmental records from Long Island Sound: a thousand year perspective. Long Island Sound Ninth Biennial Research Conference, October 30-31, New London, CT

Altabet, M. A., and Varekamp, J. C., 2008. Long Island Sound N Isotope Biogeochemistry, Long Island Sound Ninth Biennial Research Conference, October 30-31, New London, CT

## **2009**

Thomas, E., Varekamp, J. C., Cooper, S., Sangiorgi, F., Donders, T., 2009. Proxies for Eutrophication in Long Island Sound. '*Coasts and Estuaries in a Changing World*', CERF 2009, Portland, OR (Nov. 1-5, 2009).

Varekamp, J. C., Altabet, M. Thomas, E., Ten Brink, M., Andersen\*, N., and Mecray, E., 2009. Hypoxia in Long Island Sound; since When and Why. '*Coasts and Estuaries in a Changing World*', CERF 2009, Portland, OR (Nov. 1-5, 2009).

## **2010**

Thomas, E., Varekamp, J. C., Cooper, S., Sangiorgi, F., Donders, T., 2010. Microfossil proxies for anthropogenic environmental changes in Long Island Sound. Geol. Soc. America, Regional Meeting, Baltimore, 13-16 March 2010

• student author

## **Undergraduate Senior Research Theses**

**Abramson, I.**, 2002, Benthic foraminifera as environmental proxies in Long Island Sound. p. 276. Credit.

**Goldoff, B.**, 2002, The Danbury hatting industry: a source of Mercury for the Still River Basin and Long Island Sound. p. 198. Honors.

**Groner\*, M.**, 2004, The carbon cycle in Long Island Sound: radiocarbon studies of carbonates. p. 123. Credit.

**Andersen, N.**, 2005, The eutrophication history of Long Island Sound. High Honors.

## **MA Thesis**

**Lugolobi, F.** 2003, Water quality trends in Long Island Sound over the last 400 years: isotope studies on carbonates p. 273.

## **Popular Press Coverage LIS**

- August 24, 2003 – New York Times “A History Told by Real Muckrakers; Digging Clues From the Slime of Long Island Sound”, <http://www.nytimes.com/2003/08/24/nyregion/history-told-real-muckrakers-digging-clues-slime-long-island-sound.html?pagewanted=1>)
- March 15, 2004 - Newsday – Fate of mercury in Long Island Sound
- March 19, CPTV, short interview about health of LIS (CPTV – a delicate balance)
- April 25, 2004, New Haven Register, article about Health of LIS.
- April 2006 – Interview on NPR, climate change and LIS
- April 8, 2006: Varekamp was invited speakers at the Long Island Sound Citizens

Summit, Bridgeport, CT

- June 2006 – interview in Hartford Courant on careers of JCV and ET
- April 22, Earthday 2007 – Hartford Courant Front page article on our LIS work – ‘The “Canaries” under the Sound’
- May 2007: “Attack of the Jellyfish--Is nitrogen pollution changing the food chain in the Long Island Sound?”, Soundkeeper, [http://www.soundkeeper.org/update\\_detail.asp?ContentID=299](http://www.soundkeeper.org/update_detail.asp?ContentID=299)
- July 2009: Radio interview with Ellen Thomas, Crossroads Magazine, Diocese Hartford

Core site	Core #	Core length (cm)	X-rays	longitude	latitude	Water Depth (m)
WLIS81	GGC1	209.0	x	-73.63132	40.93122	19.0
WLIS81	GGC2	186.0	x	-73.63087	40.93082	19.0
WLIS68	GGC1	179.5	x	-73.66463	40.86605	10.0
WLIS68	GGC2	175.5		-73.66493	40.86628	10.0
WLIS75	GGC1	177.0	x	-73.74622	40.87792	19.0
WLIS75	GGC2	168.2	x	-73.74625	40.87792	19.0
A5	GGC1	197.0	x	-73.28140	41.00715	27.0
B1	GGC1	201.0	x	-73.07512	41.16875	8.0
B1	GGC2	187.5	x	-73.07563	41.16882	8.2
B5	GGC1	243.0		-73.04333	41.07287	29.0
B7	GGC1	201.0	x	-73.02968	41.01298	33.0
B7	GGC2	215.0	x	-73.03015	41.01317	33.6
D7	GGC2	230.5	x	-72.82157	41.03570	38.6
D7	GGC3	237.5	x	-72.82122	41.03657	38.4

**Table 1.** Location of long cores taken during the joint USGS-Wesleyan University cruise CONN01066 in October 2001. Cores WLIS75 and B1 have been studied in detail for this grant, with ongoing work on core WLIS81.

**Table 2.** Data collected on the 1996-1997 cores, the 2000 'Empact' core, the 2001 cores and surface samples collected between 1997 and 2004. Latitude and Longitude are given in decimal degrees.

	longitude	latitude	water depth (m)	Age, depth	MAR	grain size	Corg	d13C Corg	N %, N isotopes	S%, S isotopes	C perfringens	B Si	Hg	Dinoflagellates	Pollen	Foraminifera	Foram stable isotopes	Mg/Ca	Diatoms	NOTE
<b>Cores 96-97</b>																				
WLIS68	40.86602	-73.66458	7.4	X		X						X	X			X	X		(X)	Narrows
WLIS75C1	40.87808	-73.74664	18.8	X		X						X	X			X	X	X		Narrows
EMPACT	40.94830	-73.56700	18.3			X						X				X				Narrows, 12/12/2000. Diver
WLIS90C	40.96390	-73.56598	19.5			X										X				Narrows
A1C1	41.09888	-73.33173	8.6	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	West
A4C1	41.03305	-73.28798	25.0	X	X	X	X		X	X	X	X	X	X	X	X	X	X	(X)	West
B1C2	41.16876	-73.07495	6.5	X		X	X		X	X	X					X	X			Central
B5C5	41.07358	-73.04298	26.0	X		X	X		X	X	X					X	X			Central
B7C1	41.01275	-73.03023	31.0	X		X	X		X	X	X					X	X			Central
M2C2	41.07215	-73.20511	20.0													X				West, CaCO3 dissolution
D3C2	41.19841	-72.84716	5.0	X	X	X	X		X	X	X	X	X			X	X	(X)		Central
G1C1	41.27000	-72.40717	5.0	X		X	X		X	X	X					X	X			East
<b>Cores 2001</b>																				
WLIS 75 GGC1	40.87792	-73.74622	19.0	X	X	X	X	X	X	X		X	X	X		X	X		(X)	Narrows
WLIS 81 GGC2	40.93082	-73.63087	19.0	X		X							X	X	X	(X)				Narrows
A5 GGC1	41.00715	-73.28140	27.0	X		X							X			(X)				West, no forams >10cm
B1 GGC1	41.16875	-73.07512	8.0	X	X	X	X		X	X	X	X	X			X	X	X		Central
<b>SURFACE</b>						X	X		X	X	X	X	X	X	X	X	X	X	(X)	ALL