The Role of Deep Basins and a Blocking High Pressure Ridge in Incubating Extreme Hypoxia in Western Long Island Sound: Evidence from Isotope Tracers

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Report and Data CD attached

1. Abstract

In 2002, the severe summer hypoxia (less than 1.0 mg O_2/l) in Western Long Island Sound was the worst on record. The suffocation of benthic and pelagic life for the summer months combined with the accumulation of pathogens and heavy metals in the anoxic sediments is an environmental disaster of the first order. The impact on marine life continues to expand and now extends throughout the year. The current regional hypoxia mitigation program centers around nitrogen reduction through wastewater treatment plant discharge regulations. Although a reduction in the total nitrogen input to Long Island Sound has been achieved in the past decade, hypoxia in Western Long Island Sound remains a chronic and growing problem (figure 1). More than two decades of dissolved oxygen surveys show that hypoxia initiates in the Western Long Island Sound and spreads eastward. Hypoxia mitigation plans have generally focused on reducing the nutrient load of East River water entering the Western Long Island Sound.

In this study, we measured isotope tracers of waters entering Long Island Sound from the East River combined with nitrogen and carbon isotope tracers of organic particles to examine the spread of hypoxia from west to east. Isotope tracers yield important additional information that concentration data and standard oceanographic measurements alone can not provide. Oxygen isotope measurements of Long Island Sound waters show that the low dissolved oxygen in the water column is predominantly due to tidal mixing with the relic hypoxic waters found in four small deep basins in the Western Long Island Sound. The small deep basins contain the densest waters and are natural traps for fine grain sediments rich in organic matter that is delivered to the deep basins through tidal and storm resuspension of sediments from the surrounding shallows throughout the year. The tapered shape of Western Long Island Sound combined with the surrounding shallows results in a natural focus of fine grained sediments to deep basins in the Western Sound.

Our isotopic results indicate that four deep basins act as “hypoxia incubators” on the sea floor of Western Long Island Sound and that they are the immediate or proximate causes of hypoxia throughout the water column. During the stratified summer months the denser waters in the deep basins are out of reach of vigorous tidal mixing and only the occasional summer thunder storm ventilates these deeper depths. However, tidal mixing and local currents progressively mix the low oxygen dense waters found in the deep basins with the ventilated surface layer to produce the observed dissolved oxygen gradients in the water column. Our nitrogen isotope tracers demonstrate clearly that the organic particulates sampled in the deep basins derived their nitrogen almost entirely from waste water effluent. Furthermore, oxygen isotope measurements of Western Long Island Sound water combined with salinity and dissolved oxygen data show unambiguously that the eastward spread of low oxygen waters is due directly to mixing with the extremely low oxygen waters of the four deep basins. In other words, the poorly ventilated deep basins loose oxygen to the oxidation of organic matter derived from waste water effluent and these basins reach severe hypoxic conditions early in the summer. Throughout the summer months, these low oxygen waters are slowly mixed vertically and laterally through tidal and current mixing.

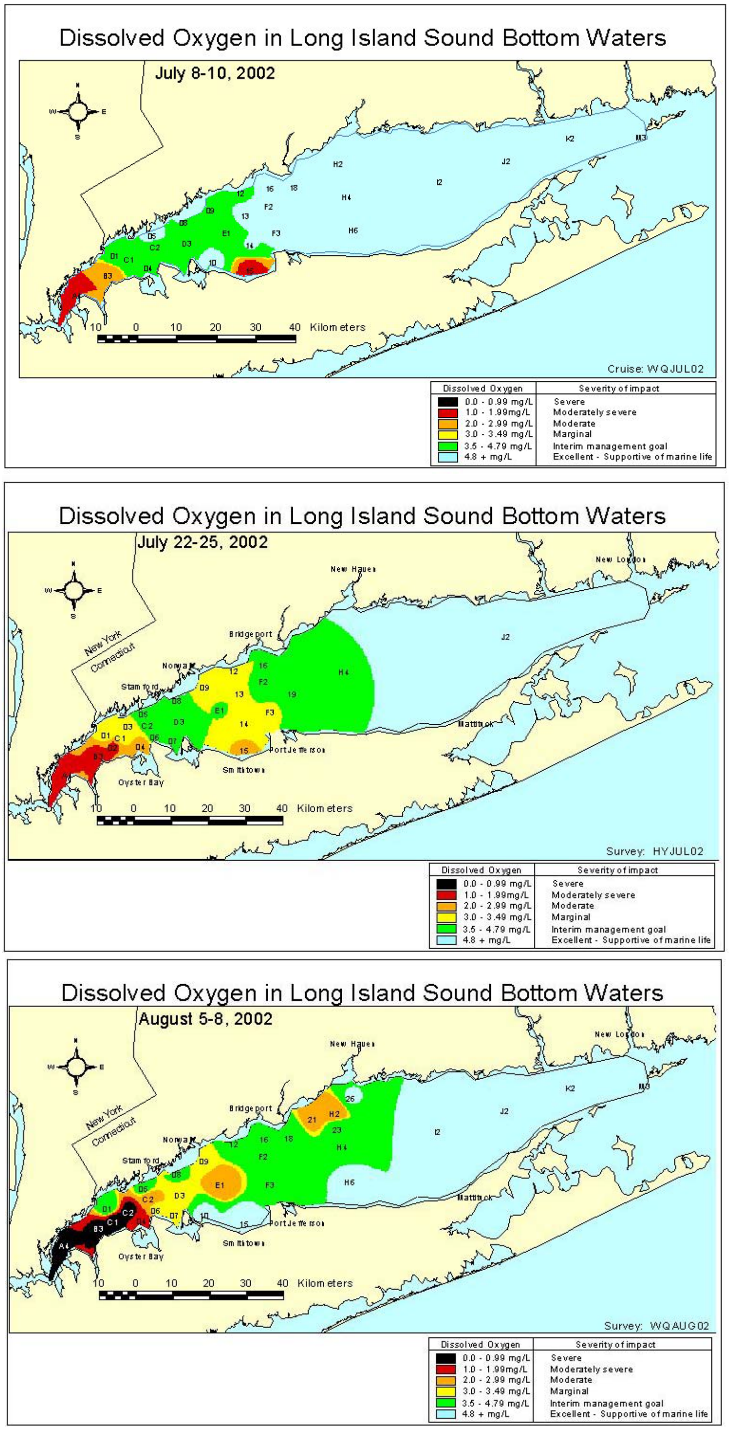

Figure 1. Dissolved oxygen in western Long Island Sound bottom waters (July 8-10 top; July 22-25 middle; August 5-8, 2002 bottom) showing the evolution and eastward propagation of hypoxia during summer months (plots from CTDEP, http://www.dep.state.ct.us/wtr/lis/monitoring/lis_page.htm). Five topographic basins span the long axis of Long Island Sound. The basins are separated from each other by sills and are sequentially affected by hypoxia. Temperature stratification principally controls the summertime vertical density gradient in Long Island Sound. Red is 1.0-1.99mg/l, orange is 2.0-2.99mg/l, yellow is 3.0-3.49mg/l, green is 3.5-4.79mg/l, and light blue is greater than 4.0mg/l.

Based on our isotopic and oceanographic measurements in 2001 and 2002, we conclude that nitrogen loading to Western Long Island Sound is grossly in excess of levels needed for severe summer hypoxia and that the vagaries of summer weather patterns control the severity of hypoxia. The extreme summer hypoxia of 2002 was sustained by a stationary high pressure ridge that blocked the occasional summer thunder storms normally responsible for oxygenation of mid-depth waters. The predictability of this weather phenomenon is poor because it is not associated with a normal mode of climate variability for this region, although there is a very weak correlation of the North Atlantic Oscillation (NAO) and climate in the Long Island Sound region.

Oxygen isotope and salinity measurements show that the four deep basins are directly under the East River mixing zone. Nitrogen and carbon isotopes of the particulate organic matter were measured at select stations to measure the contribution of effluent nitrogen sources in the surface waters and deep basins. Nitrogen and carbon isotope measurements of East River particulate matter indicate little modification by marine organisms in the East River due to the extremely high turbidity leading to very low primary productivity. The carbon and nitrogen isotope results confirm that effluent nitrogen sources are the dominant sources of nitrogen found in the particulate organic matter in the four deep western basins and throughout the water column, and that effluent nitrogen sources are dominantly responsible for the severe hypoxic conditions in the basins. Nitrite is rapidly reduced to background levels as East River Water enters the Western Long Island Sound by Throgs Neck and levels remain low throughout the Western Long Island Sound.

Sediment cores indicate that organic matter has been accumulating at faster rates in the past century than in preanthropognic times and the nitrogen isotopic composition of the organic matter demonstrates the growing contribution of waste water effluent in supplying the nitrogen sources. Only further research can confirm that there is sufficient organic matter in the modern sediments of the four deep basins to support severe hypoxia in the absence of new sources. Dredging or aeration of the contaminated sediments in the four deep basins are undesirable and costly options, however the small geographic extent of these basins makes capping with clean sands or sediments an option worth consideration and further evaluation. There is reason for optimism with respect to mitigating this blight in Western Long Island Sound because the four basins are small in aerial extent, which means that hypoxia abatement strategies can now be targeted more directly at the immediate source of the problem. Lastly, environmental surveys that only sample the deep western basins over-estimate the aerial extent of severe hypoxia in Western Long Island Sound.

2. Introduction

Nitrogen loading from wastewater treatment plants along the East River tripled between the 1950s and 1980s (Wolf et al., 1991) creating the dominant source of nitrogen and phosphorous to Long Island Sound (figure 2). During the 1990's, New York made reductions in total nutrients released to the Western Long Island Sound, but the record-breaking hypoxia of 2002 show that these efforts were clearly not enough to mitigate catastrophic hypoxia. Currently, New York discharges approximately 100,000lbs/day nitrogen to Long Island Sound, which is more than twice the nitrogen input from the entire State of Connecticut. However, the net amount of nitrogen discharged from the East River into the Western Long Island Sound is uncertain due to the strong tidal flow in the East River (Blumberg and Prichard, 1997) and the previous lack of a suitable East River Water tracer. Recent estimates of the role of East River Water on Long Island Sound hypoxia are entirely model based (Blumberg and Prichard, 1997).

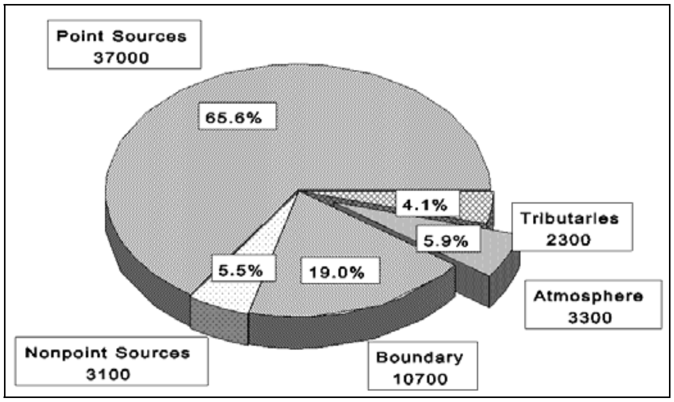

Figure 2. Nitrogen flux to Long Island Sound in tons per year (source is Conn. Dept. Environ. Protection at http://dep.state.ct.us/). Currently, New York discharges approximately 100,000lbs/day nitrogen to Long Island Sound, the majority of it from the East River. Approximately one third of the nitrogen flux to Long Island Sound enters via the East River.

Not only is the East River the dominant source of nitrogen, pathogens, and dissolved contaminates to the Western Long Island Sound, but its close proximity to the chronic hypoxic zone exacerbates its deleterious effects. High on any list of engineering solutions to mitigate hypoxia in Western Long Island Sound is the diversion of East River effluents to the Hudson or beyond. Aeration of bottom waters has been successful in mitigating hypoxia in lakes and this approach has been raised as a possible solution for hypoxic harbors in Western Long Island Sound. Less practical proposals, such as tidal damming of the East River, have their proponents and critics but pressure is mounting for a solution, particularly after the record hypoxia of 2002.

In order to estimate the cost versus benefits of engineering proposals to mitigate East River contribution to Long Island Sound hypoxia, it is imperative to document the seasonal evolution of hypoxia on a fine scale to better understand the mechanisms responsible for the development of severe hypoxia in some years and not in others. There is debate whether oxygen consumption in the Western Long Island Sound occurs primarily at the sediment-water interface on the broad shallows and embayments, in the deep basins, or in the water column. It is not known whether there are isolated regions of intense oxygen consumption, and if so, the extent of lateral and vertical mixing of these low oxygen waters.

To help resolve these fundamental questions, we first mapped the concentrations of dissolved oxygen both vertically and geographically during the evolution of summer hypoxia in 2002. Next we determined the nitrogen source of the particulate organic matter in water filtered from the water column using the nitrogen and carbon isotopes which differentiate between effluent sources versus natural marine sources of nitrogen. Lastly, we measured the conservative mixing tracers, oxygen isotopes of the water molecule and salinity, to quantify the role of physical mixing versus *in situ* oxygen consumption in maintaining the dissolved oxygen gradients in the water column and geographically. To quantify the mixing of East River water and Long Island Sound water, we use oxygen isotope measurements of East River water and western Long Island Sound water. East River water has a unique concentration of heavy water ($H_2^{18}O$) that allows a precise measure of the concentration of East River water as it mixes into Western Long Island Sound. The East River water acquires its unique $H_2^{18}O$, $H_2^{17}O$, $H_2^{16}O$, $HD^{16}O$, $HD^{17}O$, and $HD^{18}O$ abundances from mixtures of Hudson River water, originating high in the Adirondacks (figure 3). Using less than a droplet of water, the mass spectrometer can determine the precise fraction of East River water in any sample of Long Island Sound water, as well as measure mixing of intermediate water masses within Long Island Sound.

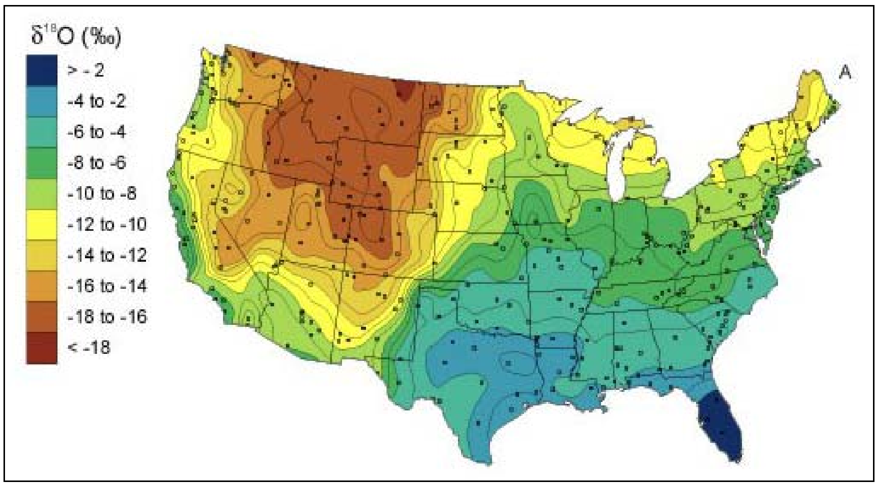

Figure 3. Generalized map of North America with contours showing how the mean annual $H_2^{18}O/H_2^{16}O$ ratios of meteoric lake, river, and spring water vary over the land surface. The isopleths (lines of equal values) intersect the East Coast, and as a result, each bight, sound, or gulf has a unique meteoric $H_2^{18}O/H_2^{16}O$ ratio. Isopleths are contoured in conventional δ-notation referenced to Vienna SMOW standard. The oxygen isotope isopleths shift seasonally principally due to temperature-dependent fractionation. Figure from (from Kendall and Coplen (2001). The Hudson River and Connecticut watersheds span nearly 6 per mil on the $\delta^{18}O$ scale due to their north-south orientations and nearly 300-mile distance.

3. Purpose

This research has three primary objectives: *First*, map in detail the dissolved oxygen concentration in Western Long Island Sound during the development of summer hypoxia. *Second*, determine the role of physical mixing versus *in situ* consumption of dissolved oxygen in controlling the low oxygen values and the dissolved oxygen gradients in Western Long Island Sound. The oxygen isotope concentrations combined with salinity are conservative water molecule tracers used to estimate mixing. *Third,* nitrogen and carbon isotope measurements on particulate matter collected in the extreme hypoxic zones are used to document the contribution of nitrogen from waste water effluent versus natural marine nitrogen.

4. Hypothesis

Tidal mixing of East River water into the Western Long Island Sound acts as a nutrient “pump” to the Western Long Island Sound surface waters, where phytoplankton rapidly sequester the excess macronutrients and settling particles deliver the organic matter to the deep western basins. It is probably no coincidence that the evolution of Western Long Island Sound hypoxia begins in the waters underlying the mixing zone of East River water and Long Island Sound waters. The deep western basins underlying the East River Mixing Zone fill up with low oxygen bottom waters to the level of the barrier sills and eventually mix eastward over the barrier sills. Export of this bottom water may be a prerequisite for wide spread hypoxia in Long Island Sound.

5. Materials and Method

A water droplet of Long Island Sound water is made up of millions of H_2O molecules that contain a variety of isotopic combinations: $^1H^1H^{16}O$, $^1H^2H^{16}O$, $^2H^2H^{16}O$, $^1H^1H^{17}O$, $^1H^2H^{17}O$, $^2H^2H^{17}O$, $^1H^1H^{18}O$, $^1H^2H^{18}O$, $^2H\ ^2H^{18}O$, where ^1H is the common hydrogen and ^2H is a hydrogen atom containing 2 neutrons, also known as deuterium. Torgersen (1979) was the first to recognize the power of the water molecule isotope tracer for coastal work and applied this technique to a study of the New England shelf waters. Subsequently, numerous researchers monitored the H_2O isotope chemistry all major rivers in North America on a monthly basis (figure 3) and monitored the isotope chemistry of coastal waters and their sources (Bauch et al., 1995, Weppernig et al., 1996; Smith et al, 1998; Houghton et al., 2000; Khatiwala et al., 2000; Ekwurzel et al., 2001.) In a modeling study, Chapman et al., 1986 used the oxygen isotope tracer and a coastal flow model to estimate the along shore flow and cross shelf mixing rates for the entire Middle Atlantic Bight, including source waters for Long Island Sound.

In coastal waters the $H_2{}^{18}O$ concentration depends on the fresh water sources. This results from the fact that the $H_2{}^{18}O$ / $H_2{}^{16}O$ ratio of precipitation is primarily regulated by the vapor pressure difference between these two molecules and the temperature difference between the source region (region of evaporation) and the region of precipitation. As a result, the rare $H_2{}^{18}O$ molecule is progressively depleted in precipitation at higher latitudes and colder seasons (figure 3). The isotope tracer method has several advantages in Long Island Sound coastal studies: (i) The isotope tracer is a conservative property of seawater. We gain a degree of freedom in coastal oceanography when we combine the $H_2{}^{18}O$ measurements with salinity data to "type" different water masses. (ii) The $H_2{}^{18}O$/ $H_2{}^{16}O$ ratio is a physical property of seawater, and therefore it is an ideal oceanographic tracer. (iii) The isotopic measurement can be made precisely and accurately on one droplet of seawater.

The $H_2{}^{18}O$/ $H_2{}^{16}O$ ratio is usually expressed as the fractional difference between the ratio measured in the sample to the ratio in Vienna Standard Mean Ocean Water (VSMOW) (Craig, 1961) according to the following notation:

$$\delta^{18}O(^{o}/_{oo}) = \frac{{}^{18}O/{}^{16}O_{sample} - {}^{18}O/{}^{16}O_{VSMOW}}{{}^{18}O/{}^{16}O_{VSMOW}} \times 1000$$

Water molecules sampled in the Central and Eastern Long Island Sound fall on a single $H_2{}^{18}O$-salinity mixing line indicating a simple mixture of Connecticut River Water and Continental Shelf Water (figure 4). In the Western Long Island Sound the primary $H_2{}^{18}O$-salinity mixing line is intersected by another $H_2{}^{18}O$-salinity mixing line indicating

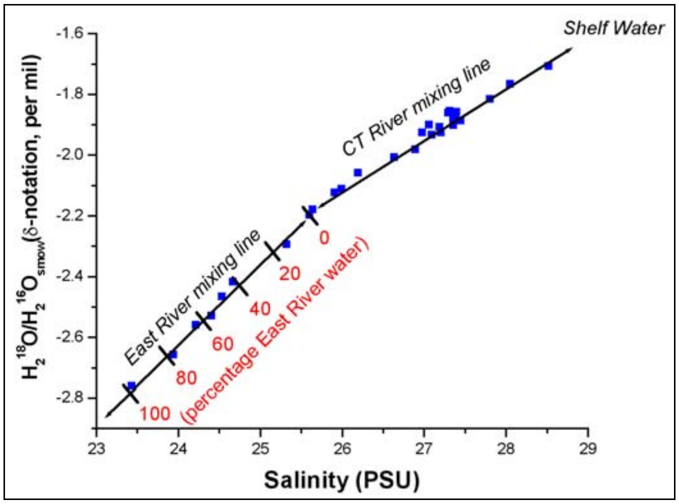

Figure 4. Oxygen isotope and salinity (in standard practical salinity units, per mil) measurements from Long Island Sound transect between the Throgs Neck and the Connecticut River. The percentage of East River water that is mixed into the Western Long Island Sound is illustrated graphically and can be quantified by standard isotope mixing equations. The East River to Connecticut River transect was sampled in September 2001 and the data are contoured in map view in figure 5. The dominant mixing line is between Connecticut River water and Shelf Water. The East River water mixes into Western Long Island Sound and intersects the Connecticut River water-Shelf Water mixing line at approximately –2.2 $\delta^{18}O$ and 25.7 per mil salinity. The East River mixing line extends geographically from Throgs Neck to Rye, New York. The CT River mixing line extends from Rye New York to The Race.

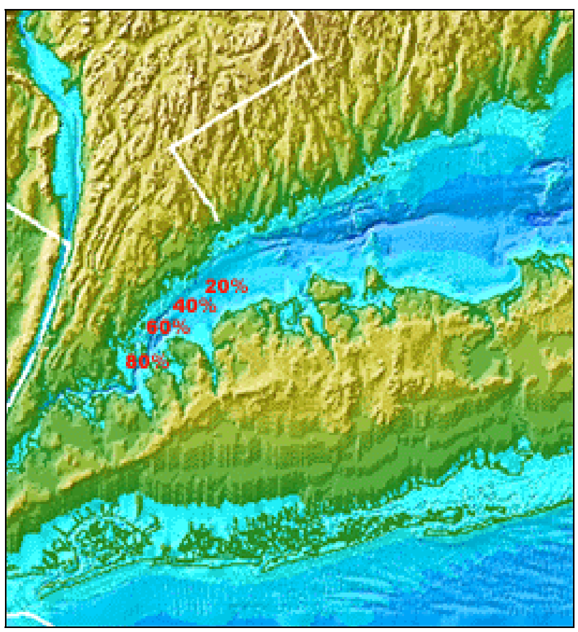

Figure 5. Map of percentage of East River water measured in the Western Long Island Sound using the $H_2{}^{18}O$ tracer during September 2001.

mixtures of East River Water (figures 4 & 5). The exact mixture of East River Water in a sample of Western Long Island Sound water can be computed graphically as illustrated in figures 4 and 5. The intrusion of the salty continental shelf water up the axis of the Long Island Sound contains a more complex mixture of water molecules with water molecule isotope combinations indicating an origin in the Labrador Sea, with mixtures of

St Lawrence River Water, sea ice melt water, and Gulf Stream Water. The relative combination of these upstream sources changes seasonally. Using an automated gas source mass spectrometer optimized and dedicated for water isotope measurements, it is possible to "type the origins" of any droplet of Long Island Sound water.

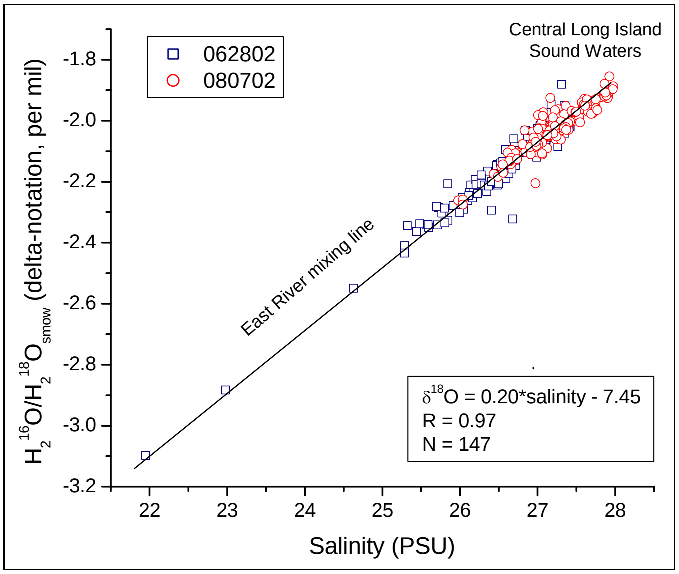

Figure 6. Oxygen isotope and salinity (in standard practical salinity units, per mil) measurements from Long Island Sound transects between the Throgs Neck and Greenwich, CT. The percentage of East River water that is mixed into the Western Long Island Sound can be quantified by standard isotope mixing equations. The East River to Greenwich, CT transects were sampled in late June (06/28/02) and early August of 2002 (08/07/02). The 2-component mixing line is between East River Water and central Long Island Sound Water. The East River mixing line extends geographically from Throgs Neck to Rye in our Sept. 2001 cruise (figure 4) and beyond Greenwich in the dry summer of 2002 illustrated in this figure. East River water is the dominant source of fresh water in Western Long Island during the summer of 2002 compared to its more restricted contribution in 2001 (see Figure 4). The high concentration of East River water in Western Long Island Sound during the summer of 2002 may have further contributed to the record-breaking extreme hypoxia of 2002.

In this study, the oxygen isotope composition of water molecules sampled from the Western Long Island Sound were analyzed along with salinity, temperature, dissolved oxygen, nitrite, phosphate, and the nitrogen and carbon isotopic composition of particulate matter at a subset of 28 stations approximately evenly spaced between Greenwich and the East River (figure 7). We sampled the Western Long Island Sound stations during the weeks of June 28, 2002, July 15, 2002, August 7, 2002, August 26, 2002, and September 14, 2002. A pilot sampling, equipment test, and instrument calibration cruise was done on June 21, 2002.

All twenty-eight hydrographic stations (table 1) were not occupied on each cruise due to time and funding constraints, weather constraints, and occasional equipment failure constraints. The important role of the deep basins in spreading hypoxia (figure 8) was recognized early in our program so cruises normally began in the East River and sampling progressed eastward until time restrictions forced us to focus our efforts on laboratory analyses of archived samples in time for the next scheduled cruise. Each station was sampled at 3 meter intervals from the bottom to the surface. Samples were collected aboard our 28 foot Boston Whaler survey boat (R/V Isotope) equipped with underway and vertical water profiling pumping system, conductivity, temperature, dissolved oxygen. For this study, all water samples were collected on the deck using a pump system and reinforced tygon tubing spooled on an electric winch. In addition, the R/V Isotope is equipped with 600 KHz. side scan sonar, and a variety of depth sounders. Navigation equipment includes several GPS systems. Nitrite, phosphate, conductivity, oxygen isotopes of seawater and carbon and nitrogen isotopes of particulate matter were analyzed at the Lamont-Doherty Earth Observatory laboratory, and all other measurements were measured *in situ*. Oxygen isotopes were measured to a precision of ±0.03 per mil determined by daily analyses of laboratory standard NADW-1. Salinity measurements in the range of 3 to 34 per mil (PSU) were made using Portasal 8410 (Guildline).

Table 1. Station locations.

Station #	Longitude	Latitude
1	73 52' 18"	40 47' 42"
2	73 50' 30"	40 48' 0"
3	73 48' 48"	40 48' 12"
4	73 47' 12"	40 47' 48"
5	73 47' 8"	40 48' 22"
6	73 47' 4"	40 48' 56"
7	73 47' 0"	40 49' 30"
8	73 46' 34"	40 49' 52"
9	73 46' 8"	40 50' 14"
10	73 45' 42"	40 50' 36"
11	73 45' 21"	40 51' 29"
12	73 45' 0"	40 52' 21"
13	73 44' 39"	40 53' 14"
14	73 44' 18"	40 54' 6"
15	73 44' 0"	40 53' 45"
16	73 43' 42"	40 53' 24"
17	73 43' 24"	40 53' 3"
18	73 43' 6"	40 52' 42"
19	73 40' 18"	40 56' 48"
20	73 39' 47"	40 56' 17"
21	73 39' 15"	40 55' 45"
22	73 38' 44"	40 55' 14"
23	73 38' 12"	40 54' 42"
24	73 34' 24"	40 55' 36"
25	73 34' 38"	40 56' 32"
26	73 35' 3"	40 57' 33"
27	73 35' 29"	40 58' 35"
28	73 35' 54"	40 59' 36"

Salinity calibration was made using standard seawater (IAPSO). Precision is routinely better than 0.002 per mil. Water samples were collected for dissolved nutrients (nitrite and phosphate). We also filtered seawater from several stations (0.4 micron) and refrigerated and stored the filters in the dark in cleaned poly bottles. Nutrient concentrations were analyzed by standard spectrophotometric techniques using an autoanalyzer (LACHAT). Precision is routinely better than 1%. Dissolved oxygen was measured using a Jenway 9200 meter with an accuracy of $\pm$2%. Pump sample temperature was measured with an Omega CDH-420 meter and a Jenway 9200 temperature instrument. Conductivity was measured with a precision of 0.002 per mil PSU in the laboratory and temperature was measured to a precision of $\pm 0.1^{o}$C at sea.

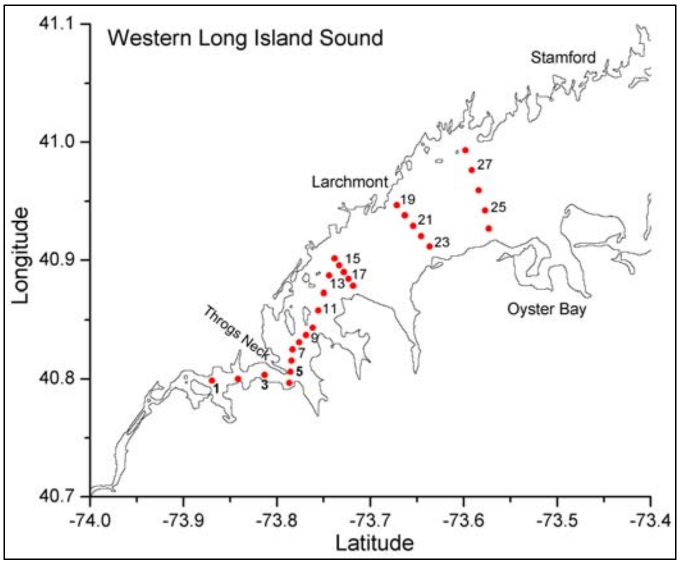

Figure 7. Map of sampling station locations.

6. Discussion

The Western Long Island Sound is divided into a series of deep basins averaging between 30 and 33 meters water depth (figure 9). Sills averaging between 20 and 15 meters separate these basins and there appears to be little or no communication between the basins during summer months. Temperature and salinity measurements indicate "relict" winter water residing in the deep basins, left over from late winter when the region was vertically mixed top to bottom and generally homogeneous (figure 10). The dissolved oxygen plots show the development of hypoxia in these deep basins beginning with dissolved oxygen values greater than 3.0ml/l in late June dropping to values below 1.0 in late August (figure 8). It is important to note that our data show that the low oxygen values are generally restricted to the deep basins and are not as widespread as the CTDEP maps indicate in figure 1. CTDEP maps are based on single bottom water measurements made at 5 stations in the Western Long Island Sound. It is significant that CTDEP sampled in the deep basins where our measurements show the bottom waters to be anomalously low compared to bottom waters in the shallower surrounding area. Sampling the deep basins lead CTDEP to over estimate the geographic extent of extreme hypoxic conditions in Western Long Island Sound. It appears that CTDEP's coarse sampling may have also masked the key role of the deep basins in spreading hypoxia in the region.

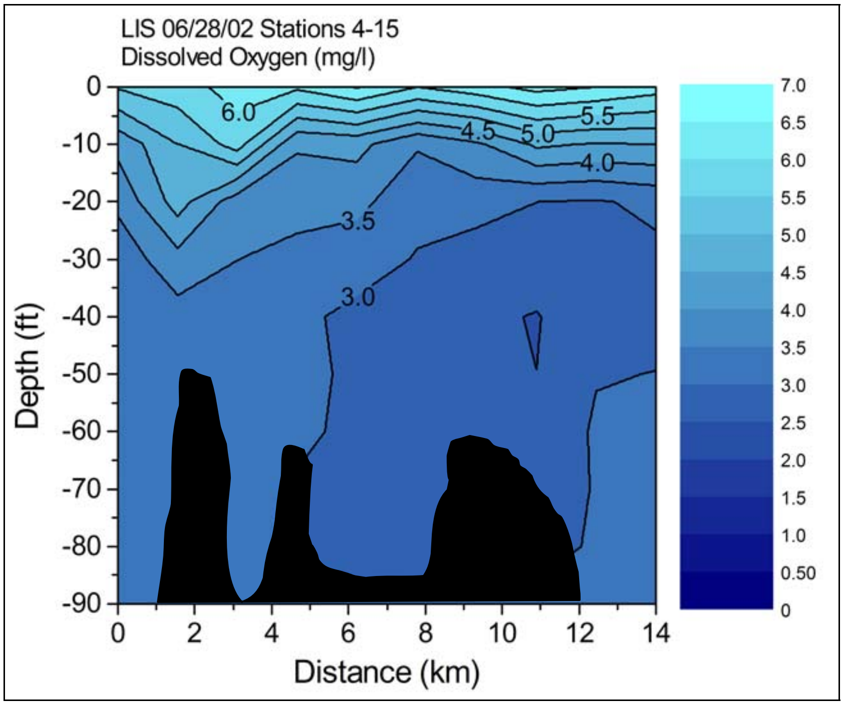

Figure 8a. Dissolved oxygen along transect 4-15 between 0 and 90 feet on June 28, 2002.

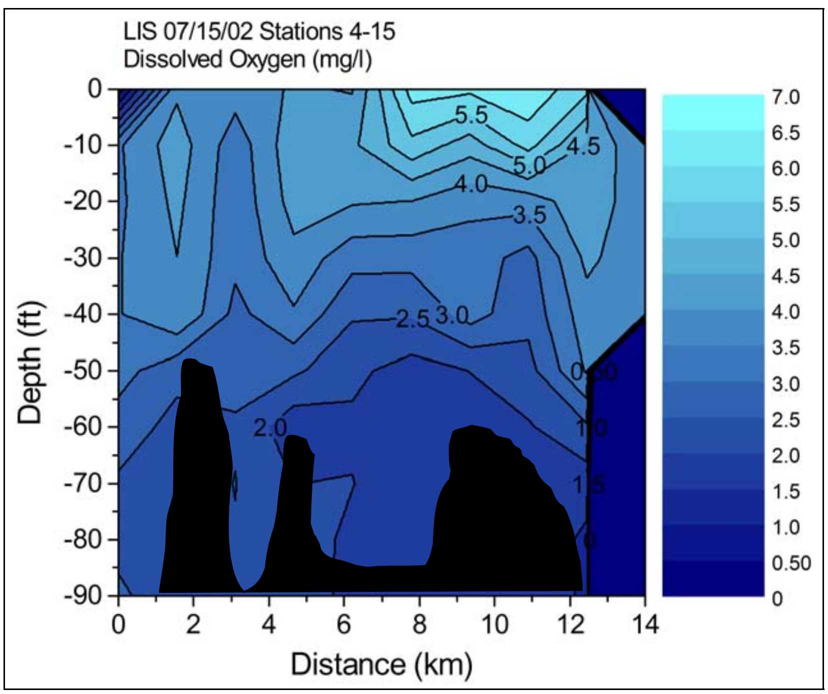

Figure 8b. Dissolved oxygen along transect 4-15 between 0 and 90 feet on July 15, 2002.

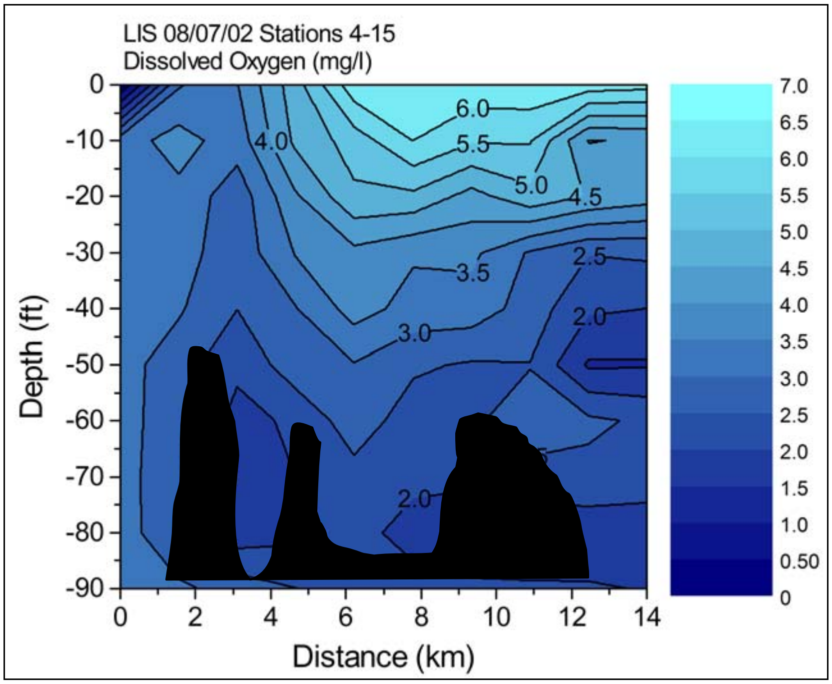

Figure 8c. Dissolved oxygen along transect 4-15 between 0 and 90 feet on August 7, 2002. Note that our dissolved oxygen values in the deep basins never go below 2.0 ml/l which is twice as high as the values reported by the CTDEP and plotted in Figure 1 (lower panel). Our sampling period overlapped exactly with the CTDEP. Our dissolved oxygen instrument calibration was checked during every station and we are confident in our data accuracy and precision. We measured dissolved oxygen values below 1.0 ml/l in late August (see Figure 8d).

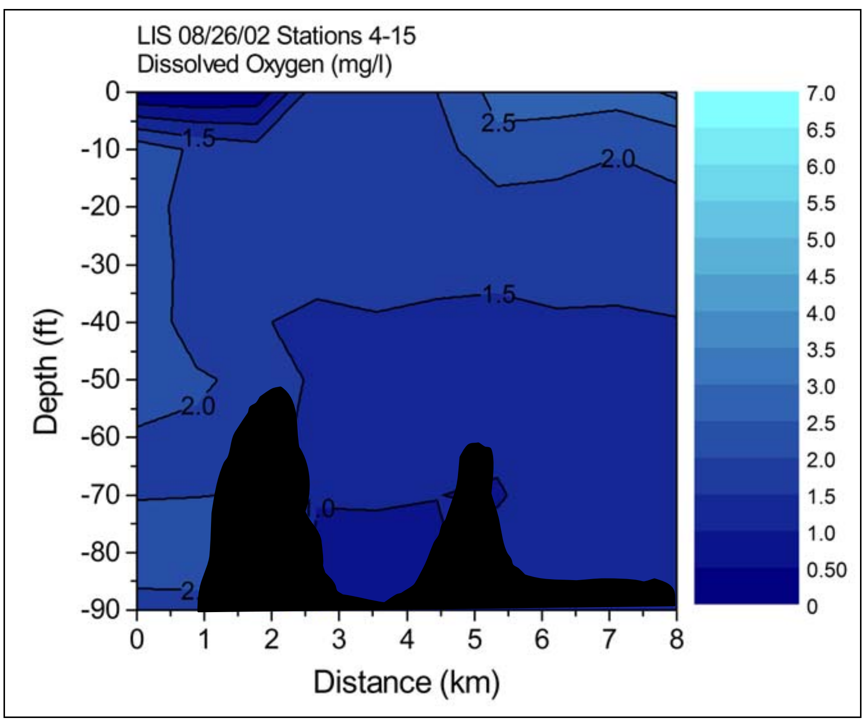

Figure 8d. Dissolved oxygen along transect 4-8 between 0 and 90 feet on August 26, 2002.

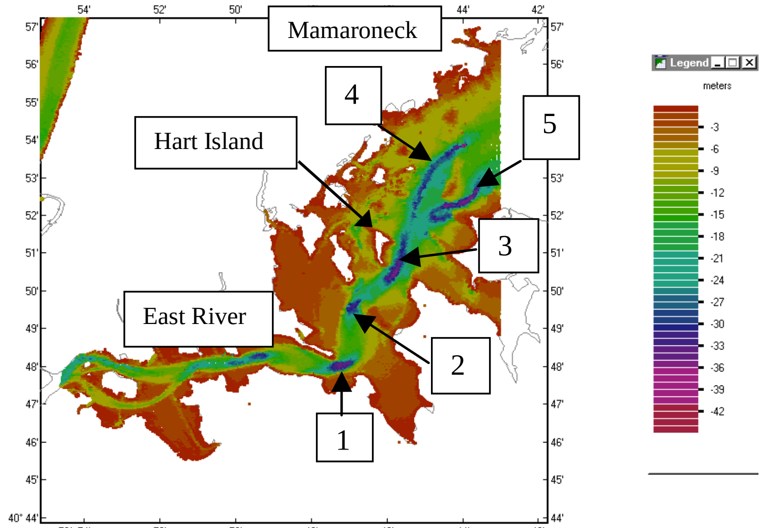

Figure 9. A detailed bathymetry of East River and Western Long Island Sound illustrates the locations of the five (5) deep basins that have an average water depth between 28 and 33 meters. There is one deep basin within the East River (not numbered) and another at the confluence of the East River and the Long Island Sound marked as 1. Within the eastern Long Island Sound there are four more deep basins marked 2, 3, 4, and 5. The deep basins, marked by dark blue, are located where headlands narrow the East River and Long Island Sound. The deep basins are filled with relict water produced during the preceding winter months when vertical mixing extended to the depths of these basins. The extremely low dissolved oxygen values are restricted to the bottom of these basins. The basins are separated from each other by sills and do not directly exchange waters. Basin one is an exception because it is ventilated daily due to intense tidal mixing in the Throgs Neck that reaches down to the bottom of the basin with each tidal cycle.

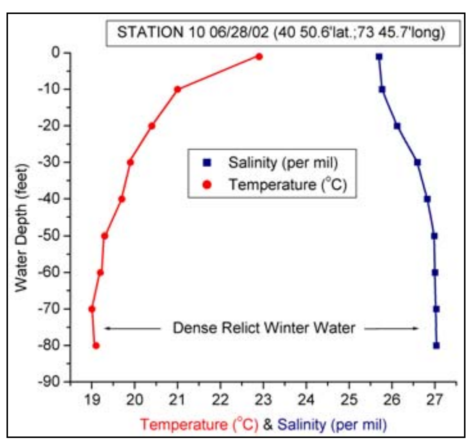

Figure 10. Temperature and salinity plot for station 10 (06/28/02) located in basin number 3 east of Hart Island (see Figure 10) showing the dense relict winter water in the deep basin between 70' and 80'. Winter seawater temperatures are near freezing and vertical mixing from winter storms homogenizes the water column in the western Long Island Sound. Spring warming stratifies the water column and tidal mixing slowly erodes the winter water where it pools in the deep basins. By late June the deep basins have warmed to 19^{o}C and have salinities around 27 per mil, however this is the densest water found in the western Long Island Sound at this time of year.

In this section we use the oxygen isotope tracer measured in the water molecule to determine if the low dissolved oxygen values in the mid-water column are simply due to mixing of these waters with the deep basin waters versus *in situ* oxygen consumption. If the mid water column hypoxia is due to mixing with the deep basins, then the role of the deep basins in hypoxia development is significantly enhanced. More importantly, engineering solutions to mitigate hypoxia would be very different if the condition originates in isolated basins. This scenario is in contrast with the impression gained from CTDEP maps (figure 1) that indicate a broad and pervasive hypoxia throughout the western Long Island Sound. The dissolved oxygen plots in figures 8a-d clearly show the low oxygen bottom water in the deep basins and the aerated surface water that is exchanging with the atmosphere.

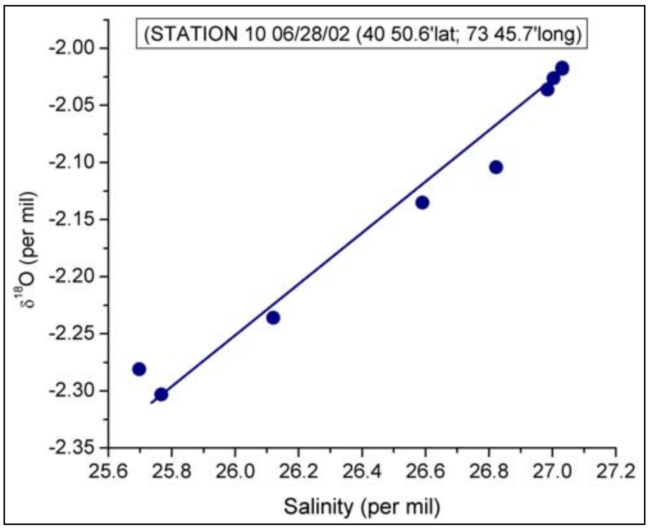

Figure 11. Oxygen isotope ratio in seawater versus salinity for station 10 (06/28/02). The $\delta^{18}O$ ($H_2{}^{18}O/H_2{}^{16}O$) and salinity pair are a conservative water tracer. The linear relationship between $\delta^{18}O$ ($H_2{}^{18}O/H_2{}^{16}O$) and salinity data for station 10 indicate mixing between the "relict" winter water and the overlying water column.

The oxygen isotope and salinity data in figure 11 demonstrates the 2-component mixing between the relict winter water in the deep basins and East River water at the surface. If dissolved oxygen values in the mid water depths is also controlled by mixing with the low oxygen deep basins then there should be a linear relationship between dissolved oxygen and salinity or $\delta^{18}O$. Figure 12 shows that the mid-depth dissolved oxygen is due to physical mixing with the low oxygen in the deep basins. The oxygen must be consumed through oxidation of organic rich sediments found in the deep basins. The high organic content of the basin sediments stems from the excessive supply of nitrite and nitrate from the East River and the algal blooms supplied by these nutrients.

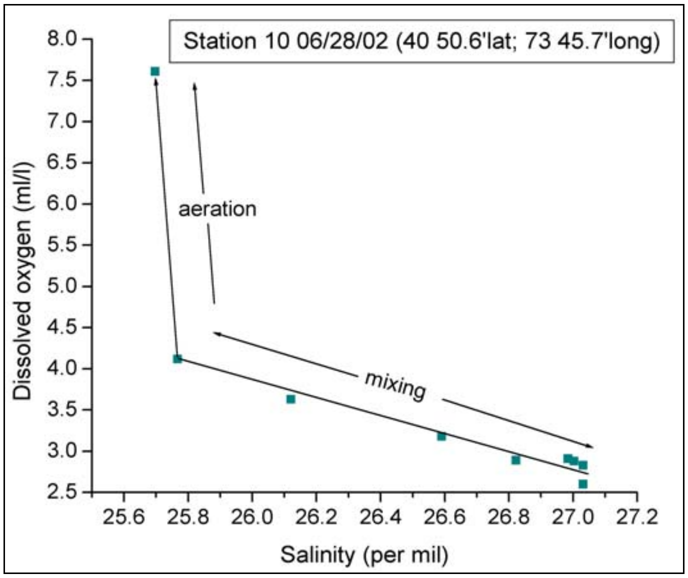

Figure 12. Dissolved oxygen versus salinity for station 10 (06/28/02) showing the mixing of low oxygen bottom water with the overlying water column. The sample taken from 1' below the surface shows that the sample is nearly equilibrated with the atmosphere.

Carbon and nitrogen isotopes of organic matter are widely used tracers in estuaries, particularly polluted environments. Nitrogen isotopes are especially diagnostic of effluent sources of nitrogen versus marine sources (e.g. Crago, 2002) and this tracers have been more recently been applied to Long Island Sound hypoxia studies. Marine sources average between 4 and 5 per mil while particles with wastewater nitrogen sources average between 10 and 11 per mil (figure 13). There has been some speculation in estuary research that early spring phytoplankton blooms, use a predominantly marine source of nitrogen, and supply an important fraction of the organic matter found in surface sediments. In light of the focusing of the fine fraction sediments into the deep basins of the Western Long Island Sound, we measured the $\delta^{15}N$ of particulate matter filtered from the water column at select stations and depths, with an emphasis on the deep basins and the East River (figure 14). Figure 14 shows the particulate organic matter found in the deep basins has $\delta^{15}N$ values between 10 and 12, diagnostic of nearly 100% wastewater effluent. These results validate the long-standing emphasis by EPA and other regulatory agencies on nitrogen reduction programs to mitigate hypoxia in Western Long Island Sound.

Carbon isotope measurements are also a measure of particle origin but with a strong influence by biochemical kinetic processes that fractionate the carbon isotopes as a function of primary production rates and CO_2 limitations, among many other variables. The lowest $\delta^{15}N$ values marked by highly variable $\delta^{13}C$ values are founding the East River (figure 14). The low $\delta^{15}N$ values for the East River particle samples (figure 14) may seem contradictory to the findings of Crago (2002) illustrated in figure 13, which shows the highest $\delta^{15}N$ values are associated with the highest fraction of wastewater in a Massachusetts estuary. The East River is so well mixed by tidal currents and the water is so turbid that primary production is extremely limited.

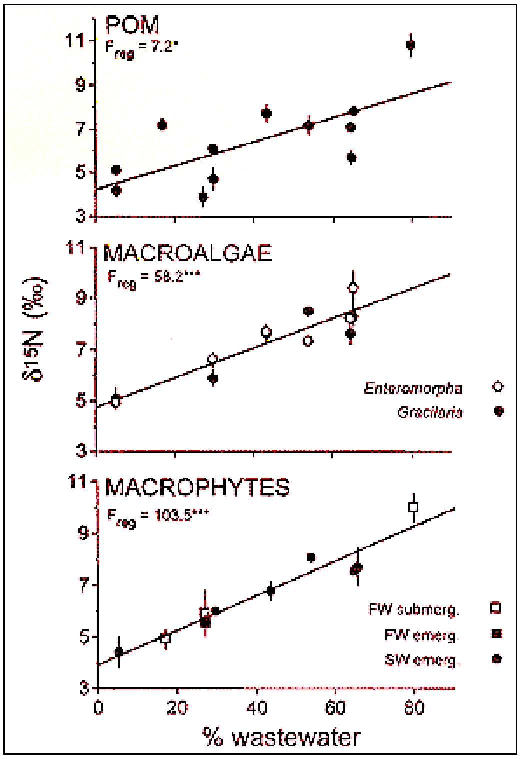

Figure 13. Plots of nitrogen isotope values of particulate organic matter (POM) top panel, macroalgae middle panel, and macrophytes bottom panel versus percentage of wastewater in a Massachusetts estuary from the Ph.D. thesis of Marci Cole's of Boston University. Figure is from Crago (2002). This figure shows the typically strong correlation between nitrogen isotopes and wastewater concentration as measured in organic particles.

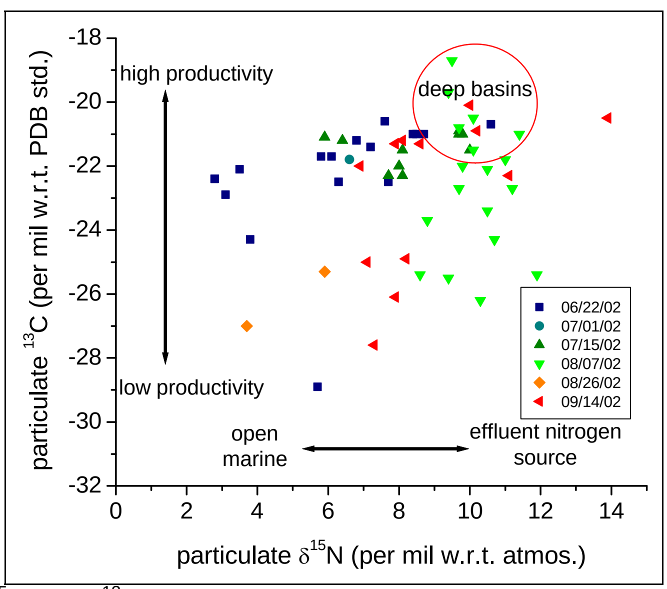

Figure 14. Particulate $\delta^{15}N$ and $\delta^{13}C$ analyses of filtered water samples collected during all of the cruises in 2002. $\delta^{15}N$ values above seven are dominantly derived from waste water nitrogen sources (see figure 13a) and includes the particulate matter sampled from the deep basins. This figure demonstrates that the particulate matter in the deep basins, which are primarily responsible for incubating and spreading the hypoxia in Western Long Island Sound, have wastewater nitrogen sources.

Therefore, the $\delta^{15}N$ and $\delta^{13}C$ values of particles collected in the East River simply represent the isotopically unaltered wastewater discharge particles. In an elegant study by Varekamp et al., (2003), they showed that $\delta^{15}N$ from sediment cores in Long Island Sound shifted from marine values in preanthropogenic times to high values in recent times along with an increase in the total organic carbon content in sediments deposited in the past century.

7. Predictability

Speculation about El Nino (ENSO) or the North Atlantic Oscillation's (NAO) role in the timing and magnitude of Long Island Sound hypoxia has crept into the scientific and popular press with little documentation. These are two of the better known large scale climate dipole patterns that explain much of the interannual climate variability around the world. Evans et al., (1998) first mapped the correlation between ENSO and global precipitation and temperature station data and showed the very weak correlation between mean annual temperature and precipitation anomalies for the Long Island Sound region. NAO has a moderate influence on winter climate conditions for the Long Island Sound region but a very weak correlation with summer climate indices.

Our isotope tracer results are largely in agreement with previous studies that emphasize the importance of calm summer sea state for the development of extreme hypoxia, such as occurred in 2002 and 1999. There is an abundance of high quality meteorological stations in the Long Island Sound region with instrumental records that span the last 130 years. Observations show that summer thunder storms are the principal ventilator of mid-depth oxygen in Western Long Island Sound. Wind gust data could provide a proxy for the frequency of thunder storms but the data are not compiled in a user friendly summary. An alternative is to use the mean monthly rainfall data since thunder storms are the primary source of mid-summer precipitation in this region. Rainfall data are more readily available in great detail and in useful summaries. Rainfall data quality is reasonably high for the past century and the data are coherent over multiple meteorological stations in the region. We selected the 140 year long monthly rainfall time series from Central Park (NY) as our Long Island Sound vertical mixing proxy for the summer months June, July, and August. Figure 15 shows the July rainfall record for the past 140 years. There were five years that were dryer than 2002, including the record-breaking low precipitation in 1999 (0.44"). The year 2002 was the most severe hypoxia on record while 1999 was the most extensive and also extremely severe. If we use 2" as the July drought cut off, we see a recurrence interval ranging between 15 and 20 years.

In order to assess the predictability between rainfall, our proxy for summer ventilation of Western Long Island Sound, and the North Atlantic Oscillation (NAO) indices for June/July/August (figure 16), we plotted July rainfall versus NAO and computed the correlation between July rainfall and NAO (figure 17). We also compared the correlation between the rainfall in the neighboring months (June and August) as well as other NAO time intervals, specifically May/June/July and July/August/September were also analyzed. Figure 17 is typical of all the combinations and permutations and clearly shows that NAO indices are not correlated with summer precipitation in general or with "drought" years specifically. These results stress the importance of "now casting" hypoxia in Long Island Sound based on real time weather analysis and monitoring the water column, rather than spending more time speculating on the role of large scale climate dipole patterns and false hopes for some degree of predictability. Analysis of figure 15 indicates that chaotic nature of weather rules the fate of Long Island Sound hypoxia.

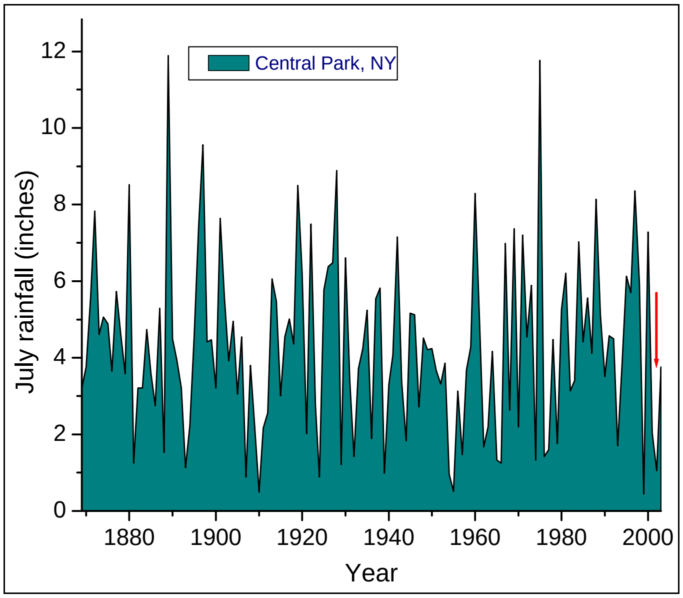

Figure 15. Plot of July monthly precipitation data from Central Park, N.Y. In the last 136 years only four years were as dry or dryer then 2002: 1907 (0.89"), 1924 (0.89"), 1939 (0.99"), 1955 (0.51"), and 1999 (0.44"). Since most of the July precipitation comes in the form of thunder storms, Central Park precipitation record is a good proxy of wind events capable of ventilating the mid depths in Western Long Island Sound. Red arrow marks July 2002 value of 1.05 inches.

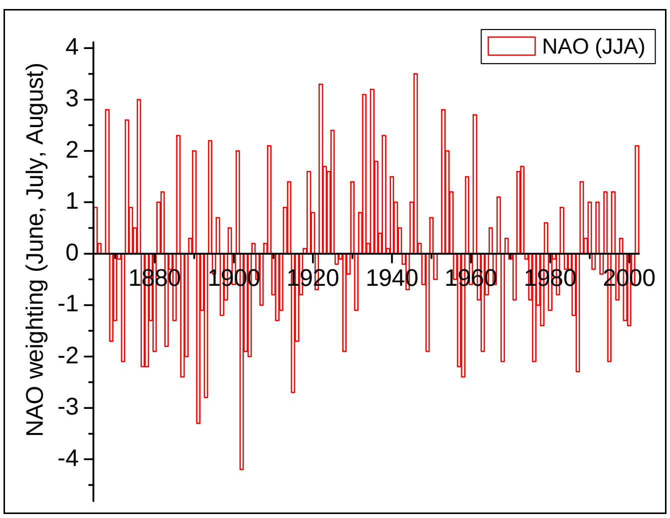

Figure 16. North Atlantic Oscillation weighting for June, July, August average.

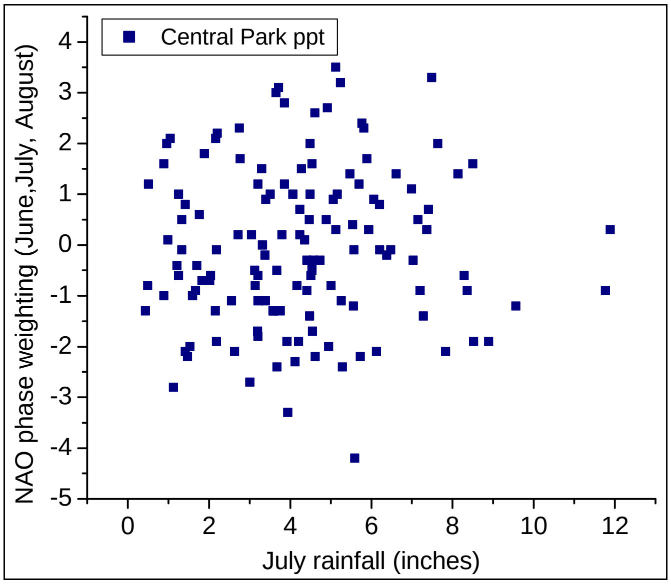

Figure 17. Plot of July rainfall for Central Park, NY versus the North Atlantic Oscillation (NAO) weightings for June, July, August. The plot shows that there is no correlation between very low rainfall, our proxy for calm July conditions conducive to hypoxia in Western Long Island Sound, and the North Atlantic Oscillation phase or weightings. The North Atlantic Oscillation (NAO) is the only large-scale climate pattern that is correlated to weather in the Long Island region, although the correlation is highest in winter months. Unfortunately, this plot indicates that it is highly unlikely that extreme hypoxia, such as occurred in 2002, can be predicted by climatological data or indices.

8. Conclusions

In the summer of 2002, the hypoxia in Western Long Island Sound was the worst in recorded history (figures 1). A series of four cruises from late June to late August document the steady decline of dissolved oxygen in the Western Long Island Sound reaching anoxic conditions (<1mg/l) by late August (figures 10a – 10d). The lowest dissolved oxygen values are found in a string of four narrow deep basins averaging 30 meters water depth that are connected by sills of varying heights (figure 8). During the stratified summer months these small basins are not directly aerated by tidal mixing and apparently only partially ventilate during summer storms. Stable oxygen isotopes and salinity measurements of seawater provide a powerful conservative water mixing tracer especially useful in Western Long Island Sound. Application of this mixing tracer shows unequivocally that the low dissolved oxygen in the water column is due to mixing with the extremely low oxygen waters of the deep basins (figure 12). In other words, the deep basins act as incubators of hypoxia that spreads vertically and laterally from these five sources. Nitrogen and carbon isotope tracers of the organic matter in these deep basins demonstrate a pure wastewater source of the nitrogen in the particulates (figures 13 & 14). Although these results confirm the role of excess nitrogen from wastewater treatment plants as the source of the organic matter responsible for oxygen consumption, the importance of the five deep basins in incubating and spreading the extremely low dissolved oxygen values is a primary contribution of this study. These basins average 30 meters water depth but they are narrow and of small geographic extent (figure 12). Hypoxia mitigation programs are directed toward reduction in nitrogen flux to the region, although the present flux is massively in excess necessary to induce extreme hypoxia. It is recommended that future mitigation plans recognize the critical importance of the deep basins in generating and spreading hypoxia and consider engineering solutions directed at these immediate and proximate sources of hypoxia. Lastly, it is clear that the blocking high pressure system that resided over the region for much of the summer of 2002 blocked the canonical storm tracks (figure 15) and thereby prevented episodic storm aeration of the intermediate depth waters, which ultimately lead to the record-breaking hypoxic conditions. It therefore appears that conditions are set for a repeat of the catastrophic hypoxia of 2002 whenever the vagaries of climate lead to a prolonged stationary high pressure system resident in July and August (figure 15). The North Atlantic Oscillation (NAO) is the only large scale climatology that correlates with the Long Island Sound region, albeit most strongly in winter months. Statistical analysis of the 140 year long weather record from nearby meteorological stations (figure 15) and the phase and weighting of the North Atlantic Oscillation (NAO) index (figure 16) show that there is no correlation of NAO and low precipitation anomalies in mid summer (figure 17) which we use as a proxy for thunder storm frequency and ventilation of Long Island Sound waters.

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Smith P.C, R.W. Houghton and R.G. Fairbanks. 2001. Interannual variability of boundary fluxes and water mass properties in the Gulf of Maine and on Georges Bank:1993-1997; *Deep-Sea Res*. II, vol. 48, no. 1-3, 37-70.

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APPENDIX I

A1. PROJECT ORGANIZATION AND TASK RESPONSIBILITIES

The PI (principal investigator) is Prof. Richard G. Fairbanks from the Lamont-Doherty Earth Observatory of Columbia University (tel: 845-365-8499). Richard Mortlock (Senior Staff Associate tel: 845-365-8489), also at the Lamont-Doherty Earth Observatory, assisted Prof. Fairbanks. Prof. Fairbanks was responsible for all sampling, sample logging, and stable isotope quality assurance. Prof. Fairbanks was responsible for approving and accepting final product/deliverables. Mr. Mortlock was responsible for generating stable isotope data and for quality assurance of the salinity and nutrient measurements. Ms. Anna Claudia Dragonovic was responsible for the salinity and nutrient measurements.

Personnel Organization Table

Investigator	Organizational responsibilities	Analytical responsibilities
Fairbanks	- sampling coordination - experimental design - approving and accepting final product/deliverables	
Mortlock	- macronutrient quality assurance - salinity quality assurance - sample logging assurance - instrument maintenance - ordering supplies - field measurements calib. - sample archive and preservation - data archiving	- stable isotopes of O - field Measurements (T, dissolved O_2) - carbon and nitrogen isotopes of particulate filters - T, S, dissolved O_2
Dragonovic	- salinty measurements - macronutrient measurements	- S - NO_2, PO_4

A2. Data Responsibilities

All data are archived in Microsoft Excel 2000 format. The column header format includes the following headings: station number, station water depth, latitude, longitude, sampling date, sampling time, sample water depth, temperature, salinity, O_2, NO_2, oxygen isotope value, nitrogen isotope value, comments. A readme file will include instruments used and instrument calibration, precision and accuracy data. Each cruise will contain data files that are approximately 60KB each. Data analysis computations will be done in EXCEL spreadsheets and all equations accessible. For example, the percent East River Water will be computed using the standard isotope mass balance equations (Tan and Strain, 1980). For simple 2-component mixing of the East River and Long Island Sound water such as illustrated in figure 2:

$f_{er} + f_{lis} = 1$

$f_{er}S_{er} + f_{lis}S_{lis} = S_m$

$f_{er}\delta^{18}O_{er} + f_{lis}\delta^{18}O_{lis} = \delta^{18}O_m$

$f_{er}PO_{4\ er} + f_{lis}PO_{4\ lis} = PO_{4\ m}$

where $f_{er,}$ f_{lis} are the corresponding fractions of East River water and Central Long Island Sound Water and S, $\delta^{18}O$ and PO_4 are the corresponding salinity, $\delta^{18}O$ and PO_4 water mass concentrations. Three and four-component mixing can be computed by adding additional terms.

The files are archived on CD's with copies in the isotope laboratory data archive cabinet. CD copies of the data will be provided to all relevant agency officials. All data calibration corrections and calculations will be done in Excel format and these "working" files will be archived in the same manner as the final data. All original field notebooks and notes will be archived in the office of Richard Mortlock with photocopies in the office of Richard Fairbanks. Data plots, contouring, and graphs will be done with the Origin version 6.1 plotting and graphing software package where possible. Bathymetry will be plotted using the NGDC Coastal Relief Model and data files, vol. 01, US NE Atlantic Coast. Regional images of the greater Long Island Sound region may include ArcGIS formated files produced with ArcView 8.1.

A3. Field Sampling Specifics

Sample collection and QC activities- Cruises were conducted aboard the R/V Isotope, a 28' Boston Whaler survey boat operated by Fairbanks' laboratory. The survey boat is equipped with a Garmin model 2800 GPS, on board computer, generators, winch, water pumps, and davit boom. Water is sampled at 10-foot depth intervals via a peristaltic pump and measured inline entirely through nylon reinforced Tygon-brand tubing. At each sampling station temperature and dissolved oxygen were measured. Temperature was measured via a PT100 sensors built into a digital thermometer and dissolved O_2 meter. An Omega CDH-420 digital thermometer was used for temperature analyses on station and a Jenway 9200 DO_2 meter was used for dissolved O_2 and temperature measurements.

The Jenway 9200 and Omega CDH-420 were calibrated according to manufacturer's recommendations on a daily basis. Dissolved oxygen was calibrated using saturated air at the ambient barometric pressure and dry nitrogen for a zero point at the beginning of each station.

A sampling event consists of the following: At each station and depth a single 125 ml glass bottle was rinsed three times and filled with seawater to capacity, capped with a poly seal cap, sealed with electrical tape, and stored for laboratory analyses of both salinity and oxygen isotopes. Nutrient samples were filtered (0.45 micron) using a 50ml polypropylene syringe and disposable filters. Filtered water was collected in a polypropylene 60 ml bottle, wrapped with electrical tape (previously rinsed three times with the same filtered water) and acidified with 3 drops of 6N HCl (to pH less than 2). All samples were collected using the peristaltic pump with a polypropylene collection line. The collection line was purged with water for no less than 60 seconds prior to each sampling, sufficient to replace the water in the line 7 times. The holding time for all lab based parameters (excluding N-isotopes) will be less than 2 months. The holding time for N-isotopes will be less than 6 months. The following quality control activities were performed:

1. Replicates: A minimum of 4 replicate nutrient, salinity-isotope samples were collected during each sampling trip. Duplicate values did not differ by more than 0.005 aborbance units for phosphate and nitrite, 0.01 per mil for salinity and 0.06 per mil for $\delta^{18}O$.

2. Blanks: At Lamont, nutrient bottles were filled with filtered double deionized water and acidified with 3 drops of 6N HCL (as per samples), stored and analyzed as "processed sample blanks. Processed blanks that measure above the stated detection limits and above the reagent blank were used to correct sample concentrations. There are no processing blanks for salinity and oxygen and nitrogen isotopes.

A4. Sampling Handling and Custody Requirements

All samples were stored at the Lamont Doherty Earth Observatory (LDEO) at Palisades, NY. Salinity and O18 samples were stored in bottles and permanently labeled LIS-# etc. Nutrient bottles are permanently labeled N-# etc. After all laboratory based measurements were made and the quality assurance of the measurements verified, the bottles were recycled for subsequent sampling trips. The sample identification (ID) is LIS/mo/da/yr/sta. X/depth and assigned to each sampling event. LIS refers to Long Island Sound, followed by the sample date, station number, sample depth. Sample bottles and all measured properties (field and laboratory) were logged with the corresponding sample ID. Samples which were stored refrigerated (nutrients, filters) were placed in Ziploc bags submerged in ice immediately after collection and placed in a freezer at the end of the sampling day (boat docked in Greenwich Connecticut port each night). The samples were stored frozen overnight and driven back to the isotope lab at Lamont-Doherty the next day where they remained frozen until analysis.

A5. Analytical Method Requirements

Sample Analyses – Oxygen isotopes will be measured on a VG PRISM III Mass Spectrometer by standard methods (Craig 1961) to a precision of $\pm$0.03 per mil determined by daily analyses of laboratory standard DDW-2 (Instrument linearity and accuracy is measured by comparison of DDW-2 to NBS standard water VSMOW, GISP, and SLAP. Our accuracy is estimated to be within 0.03 per mil by comparison of measurements of North Atlantic Bottom Water with VSMOW. We are not detection or size sample limited. Atmospheric nitrogen is used for our reference gas for nitrogen isotopes and measurements were made on a Europa Mass Spectrometer following standard methods (Craig 1961) to a precision of 0.20 per mil. Salinity measurements in the range of 3 to 34 per mil (PSU) were made using a Portasal 8410 (Guildline). Standardization was made using standard seawater (IAPSO). Precision is better than or equal to 0.002per mil. Subsequent analyses of IAPSO water after standardization suggest that measurements are accurate to within 0.004 per mil. The limits of detection are 3 per mil. Nutrient concentrations were analyzed by standard spectrophotometric techniques (Parsons et al, 1984) using Perkin Elmer Model Lambda 3B (UV-V) or Spectronic 21 Spectrophometers. Detection limits (based on 3 times the standard deviation of the blank) for phosphate and nitrite were 0.1 uM and 0.03 uM, respectively. Precision for phosphate and nitrite was 0.1 uM and 0.05 uM respectively. Accuracy is estimated to be < 5%.

A6. Other Data Quality Indicators

Representativeness: The objective of the research is to: 1) measure the dissolved oxygen in the hypoxic regions of Western Long Island Sound through the summer months, 2) establish the role of the deep basins in the Western Long Island Sound basins as incubators of hypoxia, 3) measure the nitrogen and carbon isotopes of particulate matter in the hypoxic region to determine if waste water effluent is the source of particulate organic matter nitrogen. These objectives will be accomplished by collecting samples in the hypoxic regions in the Western Long Island Sound in a relatively dense array (Table 1). This type of sampling scheme will establish the temporal 3-dimensional variability of the system.

Comparability: This research provides the first measurements of oxygen isotopes combined with dissolved oxygen and carbon and nitrogen isotope measurements of particulate matter in the Western Long Island Sound. Therefore, there are no local data with which to compare our results. However, the data generated in this research will be comparable with our oxygen isotope shelf water studies and river isotopic analyses. All of those studies have used the same sampling and analysis protocols. The temperature, salinity and dissolved oxygen data are complimentary to the Connecticut Department of Environmental Protection (DEP) broad-scale survey and historical data sets. York Harbor Study includes East River and a few hydrographic stations in the Western Long Island Sound that can be compared to our measurements, particularly for dissolved oxygen. The dissolved oxygen, temperature, and salinity time series data from the University of Connecticut's mooring located at 40 57.35 N 73 34.80W (also Connecticut DEP's station C2), which is located between our stations 25 and 26, are a great benefit to placing our results in time. The coordinates of the "University of Connecticut's Western Long Island Sound" mooring are incorrectly listed as 41 57.35 N 73 34.80W, which is somewhere near the city of Danbury Connecticut.

Completeness: The role of the deep basins in spreading hypoxia can be determined with a limited set of stations. The contribution of waste water nitrogen to the particulate organic matter in the hypoxic zone can be done with a limited subset of the stations.

A7. Peer Review

The final products of this research are enclosed in this report and submitted to EPA for approval and comments and then will be submitted to peer-reviewed journals.

A8. Instrument, Equipment, and Supplies testing and Maintenance Requirement

All of the instruments used in this research such as the VG Prism III gas source mass spectrometer, the spectrophotometer, and Guildline Portasal 8410, are maintained to manufacturers specifications and calibrated daily with laboratory standards.

A9. Assessments/Oversight

All of the field and laboratory activities was overseen by the Richard Fairbanks and Richard Mortlock.

A10. Data Review, Validation and Usability

Fairbanks and Mortlock have reviewed all of the data. All data are reported in Tables attached. In the primary data files, no data were eliminated from the database. When pertinent, a Q-test for outlying results were applied. The blank values are submitted along with the sample data and QC data. Detection limits are defined as 3 times the standard deviation of the blanks. Notebooks and instrument printouts are saved for future inspections. At the request of EPA, Fairbanks will provide a separate file that includes a set of data that Fairbanks judges to be suitable for their intended use, namely the evaluation of the impact of deep basins on the Western Long Island Sound hypoxia. It was not necessary to exclude any data due to poor data quality or poor sample quality or due to marginal value to the stated goals. Such data might include outliers that make no scientific sense with respect to the surrounding data field.

A11. Documentation and Records

This final report was prepared by Richard Fairbanks and Richard Mortlock and includes a background section, methodology, results and discussion, as well as complete data tables and figures.