10TH BIENNIAL

Long Island Sound Research Conference *Proceedings* 2010

October 29-30, 2010
University of Connecticut
Stamford, CT

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Proceedings of the Long Island Sound Research Conference held
October 29-30, 2010 at University of Connecticut, Stamford, CT

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Since 1992, the Long Island Sound Foundation has sponsored ten Long Island Sound Research biennial conferences, in cooperation with the Connecticut and New York Sea Grant programs.

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INTRODUCTION

Estuarine ecosystems are complex due to the diversity of governing factors terrestrial, atmospheric and oceanic all leavened by the effects of man and the associated industrial, social and political factors. This complexity is particularly evident in the Long Island Sound system due to the regional high population density and the extent of the watershed affecting the magnitude and quality of freshwater supplies. Given this complexity, understanding sufficient to permit the development and implementation of discharge standards and resource management plans requires interdisciplinary study sensitive to a wide range of spatial and temporal scales. Review of the past ten years of Research Conferences shows progressive and continuing appreciation of this fact with increasing emphasis on long term time series studies and development of multi-disciplinary predictive models. Global climate change has recently added another component to this already rich mix.

The 2010 Long Island Sound Research Conference had as its theme “Regional Perspectives”. The call resulted in the submission of a variety of talks and posters, summarized in this volume, dealing with regional characteristics which together contribute perspective while individually often dealing with very local issues such as site specific studies of water quality. Studies presented deal with a variety of spatial and temporal scales using a multiplicity of tools. High resolution remote sensing is represented as well as a several new and improved laboratory and field analytical chemical techniques. The prodigious efforts in the tagging of 53,000 horseshoe crabs *(Limulus polyphemus)* presented by Kasinak and co-workers and conservation implications together with the results of the eel grass inventory discussed by MacLachlan and Tiner and O’Donnell’s analysis of long term trends in wind forcing all have the potential to contribute to ongoing analyses of the effects of global climate change on the Sound. They also complement analyses of the “health of the Sound” and associated indicators such as those presented by Rose, Burg and Tedesco.

Beyond the range of subjects covered, the 2010 Conference attracted participants from Massachusetts, Rhode Island, Connecticut and New York consistent with the regional theme. In addition, the talks presented provided clear indication of the increasing sophistication of estuarine science as it is being applied to Long Island Sound. Although there remains the perennial concerns regarding funding overall there is clear reason for optimism given the talents of the young investigators present at the Conference and the quality and breadth of the studies presently underway.

W. Frank Bohlen
University of Connecticut
September, 2011

PAPERS

Hyperspectral Imager for the Coastal Ocean(HICO): Long Island Sound

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Long Island Sound is an unusual estuary because river input is lengthwise and most of the summer stratification is the outcome of solar irradiance as opposed to horizontal advection of river effluent that is found in most estuaries. Thus, effluent reaching the Sound and solar heating lead to horizontal stratification that build a separate zone along the Connecticut coast with high bulk stratification (O'Donnel 1993). Seasonal changes in discharge of rivers and fast tidal currents are typical for the Long Island Estuary and require quasi-synoptic techniques for coverage of environmental parameters. Therefore, remote sensing can be useful to derive information that is related to hydrographical factors and processes.

In response to the need of remote sensing data for the coastal zone, a new sensor was designed by the Naval Research Laboratory. The instrument, the hyperspectral imager for the coastal ocean (HICO™), is now space-borne and is presently flown on the International Space Station (Lucke et al. 2010; Davis et al., 2010). The spectral range of this instrument is from 0.4 μm to 0.9 μm and has a spectral resolution of about 6 nm, allowing detailed spectral analysis of marine features that cannot be resolved with other color imagers presently flown at spacecraft altitude. In the following, HICO™ concepts are briefly described and some preliminary results based on selected HICO™ bands are presented. Various band ratios and resulting color composites, as well as supervised classification with the Spectral Angle Mapper (SAM), were applied to HICO™ data showing the retrieval of information on plume structure and patchiness along the coasts of Long Island Sound.

HICO™'s performance requirements take into account the specific environment of coastal regions. Taking into account major performance parameters, and with a ground resolution of about 90 m at nadir, it is possible to identify fine color gradients and frontogenesis. HICO™ images cover all water-penetrating wavelengths, with spectral binning of 5.7 μm which is adequate to capture the shape of coastal ocean spectral features (Corson et al., 2010). An advantage is the very high signal-to-noise-ratio that is greater than 200 in the spectral range of 0.45 μm to 0.7 μm.

One image over Long Island Sound was acquired, close to low slack water on January 18, 2010 (Figure 1), and its analysis and interpretation will be described in the following by using radiance measurements. The analysis showed that during the time of overflight of the International Space Station on that date, the Connecticut coast was dominated by discharge of suspended sediments whereas the inner part of the Sound had lower radiance values that indicated lower sediment concentrations. A spectral partition was also noted in MODIS data (not shown here) that were recorded about two hours apart from the HICO™ overflight and showed a lower attenuation coefficient at the center axis of Long Island Sound. The major river effluents along the Connecticut coast with high sediment load were recognized by strong color fronts that separate the shore water from the inner part of the Sound. This is shown with a color composite that was based on color annotations with red 0.638 μm, green 0.552 μm and blue 0.460 μm.

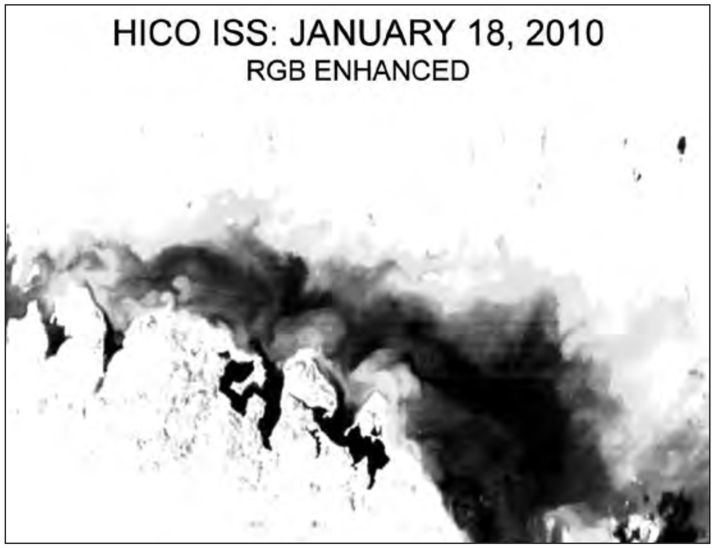

FIGURE 1: Coverage of Long Island Sound on January 18, 2010 with HICO™ at slack tide at the Race, 13:25 local time. Enhanced RGB color composite of three HICO™ channels: Red: 0.638 µm Green: 0.552 µm Blue: 0.460 µm.

Two images that are based on spectral regions at 0.460 µm and 0.552 µm, respectively, are shown in Figure 2. The enhanced RGB HICO™ image also showed in the southern part of the Sound alongshore sediments transport with local plankton blooming indicated as light green.

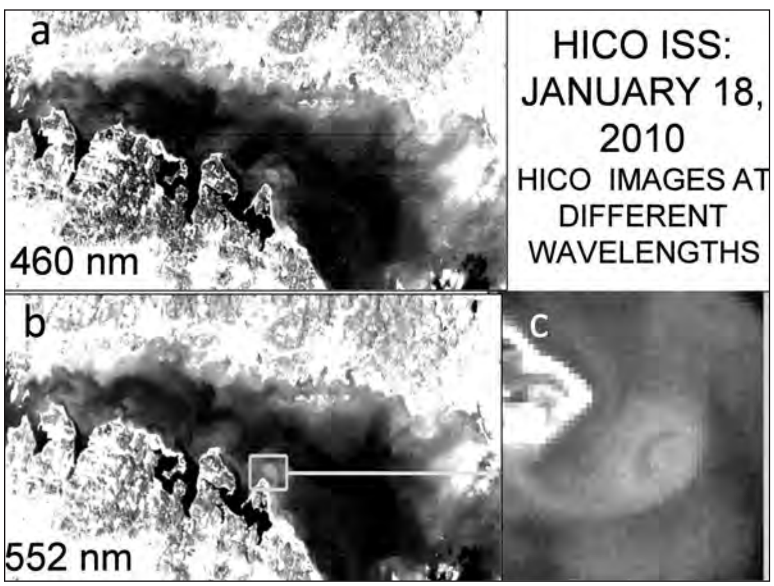

FIGURE 2: HICO™ images for wavelengths at 460 nm (a) and 552 nm (b). The insert in b is enlarged in Figure c.

Ratio techniques aid to enhance boundaries and gradients, and for the study of Long Island Sound, the building of ratios was used in the construction of an RGB image that was based on a reference band at 0.552 µm. The ratio 0.460/0.552 µm was displayed in red, the ratio 0.552 µm/0.638 µm in green and 0.460 µm/0.638 µm in blue. The corresponding image is shown in Figure 3 (left side). The HICO™ image was further analyzed with supervised classification as shown in Figure 3 (right side). This image was generated by using the ENVI spectral angle mapper (SAM) which matches image spectra to reference spectra using a physically-based spectral classification method, whereby the required reference endmember spectra can be extracted directly from the image. SAM compares the angle between the endmember spectra that are considered as n-dimensional vectors where n is the number of bands and each pixel vector in n-dimensional space. Smaller angles represent closer matches to the reference spectrum. This technique, when used on calibrated data, is relatively insensitive to illumination and albedo effects. The analysis with SAM detected more patchiness in the distribution of suspended sediment load in the coastal regime of Connecticut compared to observations along the Long Island coast.

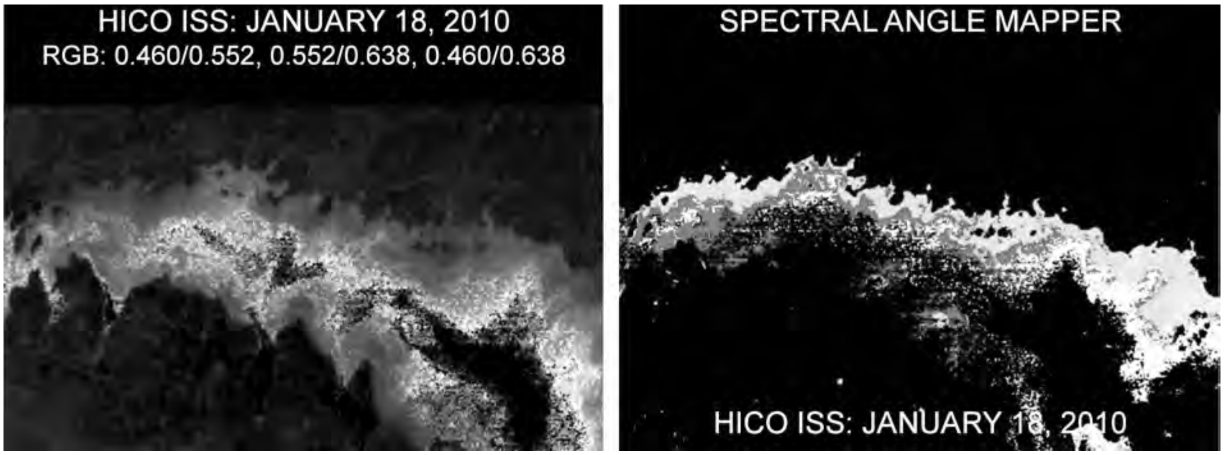

FIGURE 3: a: Image based on three different ratios: 0.460/0.552 μm displayed in red, 0.552 μm/0.638 μm displayed in green and 0.460 μm/0.638 μm displayed in blue. b: Supervised classification with the Spectral Angle Mapper.

In conclusion, it can be stated that ratio building and supervised classification with three channels of HICO™ data can identify loads of suspended matter and water masses through their gradients and frontogenesis in the Sound. The data presented here show the advantages of high spectral and spatial resolutions that are generated by HICO; however, further analysis is in progress to determine spectrally frontogenesis and eutrophication in Long Island Sound.

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Assessing the Health of Long Island Sound: The LISS Environmental Indicators Program

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ABSTRACT

The Long Island Sound Study (LISS) Environmental Indicators program is a key tool that was first developed in the late 1990's and is used by managers, scientists and educators to assess and report on the health of Long Island Sound. The current program compiles available data from LISS-funded monitoring, partner agencies and individual research studies in a series of presentations available online. Indicators are synthesized from physical, chemical and biological data from land, water and the benthos, as well as management and land use information. As new information has become available over time, the indicators program has expanded, with approximately 60 indicators currently in use. This presentation will highlight efforts underway to revisit, update and improve the environmental indicators program. These efforts include implementation of recommendations from a 2008 review, improved web presentation, increased data availability and transparency, and a gap analysis, with a major science-based re-evaluation planned for spring 2011.

BACKGROUND

Environmental indicators track changes to the quality and condition of the air, water, land, and ecosystems on various geographic scales, and related human health and economic conditions. Whereas definitions of "environmental indicator" vary, most of them emphasize that an environmental indicator is a selected quantifiable variable that describes, analyzes, and presents scientific information and its significance. Environmental indicator programs often serve multiple purposes, including assessing environmental conditions and trends, raising public awareness, communicating complex issues, and tracking progress toward goals.

The LISS formally began to collect, organize, and assess environmental indicators in the late 1990s, following approaches taken by management programs for other coastal water bodies, such as the Chesapeake Bay and Puget Sound. The driver, in common with other environmental management programs, is the need for information to gauge the condition of the ecosystem in response to stressors. The indicators were first organized around the Pressure, State, Response model, where pressures, such as increased pollutants loads or the loss of habitat, change the state of the ecosystem, such as dissolved oxygen levels or fish abundance, then leading to a response to manage the pressures. This organization of indicators was later expanded to the Driver, Pressure, State, Impact, Response model. The LISS began by assessing data available from federal, state, and other databases. Indicators identified in the LISS Monitoring Plan provided a starting point for evaluation. This list was expanded and altered through discussion by various LISS workgroups and through LISS workshops. Data were summarized from a Sound wide perspective and organized using the PSR model and used to develop a *State of the Sound* report in 2001. Indicators were updated annually with a *State of the Sound* report prepared approximately every two years.

CURRENT EFFORTS (http://longislandsoundstudy.net/category/status-and-trends/)

Currently, the Long Island Sound Study Environmental Indicators program consists of approximately 60 indicators, drawing on existing monitoring data sets of water quality, habitat, marine and coastal animals and land use. The program uses data sets available from federal, state and non-profit monitoring efforts in the Sound region. In 2006, the Long Island Sound Study commissioned Shimon Anisfeld of Yale University to review the program and make recommendations for improvement. His report was delivered in 2008, and has provided the program with a framework for moving forward.

The Long Island Sound Study Environmental Indicators program has recently undergone a major update, revision and transition to a more interactive website format. Whenever possible, updated data through 2010 from state, federal and non-profit agencies have been obtained and incorporated into existing indicators. An EPA Quality Assurance Project Plan (QAPP) was developed and approved for the Indicators Program and the Long Island Sound Study Sound Health report. The focus of the new web design has been to create a consistent format that could be applied to all indicators (see example, Figure 1). Each indicator now has its own webpage that is housed within the Indicators Program microsite, which itself is hosted on the Long Island Sound Study website. All of the indicator webpages are linked, with navigational bars on the top and sides of each page to allow simple transitions from one indicator to another. The graphical design has been improved and data is now available in both table and chart format. The transition from a PowerPoint to a webpage format has also greatly increased the space available for each indicator, and as such, much more detail has been provided about how indicator data is collected, processed and analyzed before presentation. If primary data sources are available on the web (e.g. state agency reports, federal data warehouses), links have been created to these data sources on an indicator's webpage.

FUTURE WORK

A gap analysis was performed as part of the recent program update and revision. We identified spatial and temporal data gaps, procedural problems and the need for a scientific review of the program as part of this gap analysis.

Gaps in spatial resolution identified were as follows: 1) Information on Long Island Sound embayments is currently being collected by a variety of non-profit and volunteer monitoring programs but has not been incorporated into any of the existing indicators. Recent Management Committee and Scientific and Technical Advisory Committee discussions have highlighted the need for an improved understanding of LIS embayments, so this should be considered a priority moving forward. 2) Most of the chemical, physical and biological data available for Long Island Sound are collected from the water column, and information on benthic communities and sediment quality is (relatively) sparse. While the EPA is working with Connecticut Department of Environmental Protection to update the LIS Sediment Quality Index based on samples collected during summer 2010, this still remains a major gap in the Indicators Program. 3) The existing indicator on tidal wetland loss at major tidal wetland complexes in Long Island and southwestern Connecticut needs to updated, and consideration should be given to develop an indicator tracking tidal wetland abundance for the entire Sound. 4) Currently we have indicators for three coastal habitats, but the habitat restoration initiative has identified 12 coastal habitats in need of protection. Ideally we would be able to create indicators for all 12 habitats in the future.

Opportunities to address gaps in temporal resolution were also identified. One criticism that has been voiced regarding the LIS Water Quality Monitoring Program is that it samples monthly throughout the year and bi-weekly in summer months. The limited ability to sample at high temporal frequency means that short-term fluctuations in physical, chemical and biological parameters are not captured in the monitoring datasets. Fortunately, there are datasets available that have higher temporal (if limited spatial) resolution. These include the LISICOS buoy monitoring network, the LIS ferry monitoring programs and the USGS gaging stations. Future efforts to incorporate these datasets into new indicators are a promising way to leverage existing data to meet an identified need. Additionally, there are sizeable gaps in the Indicator Program with regard to several CCMP topic areas. 1)

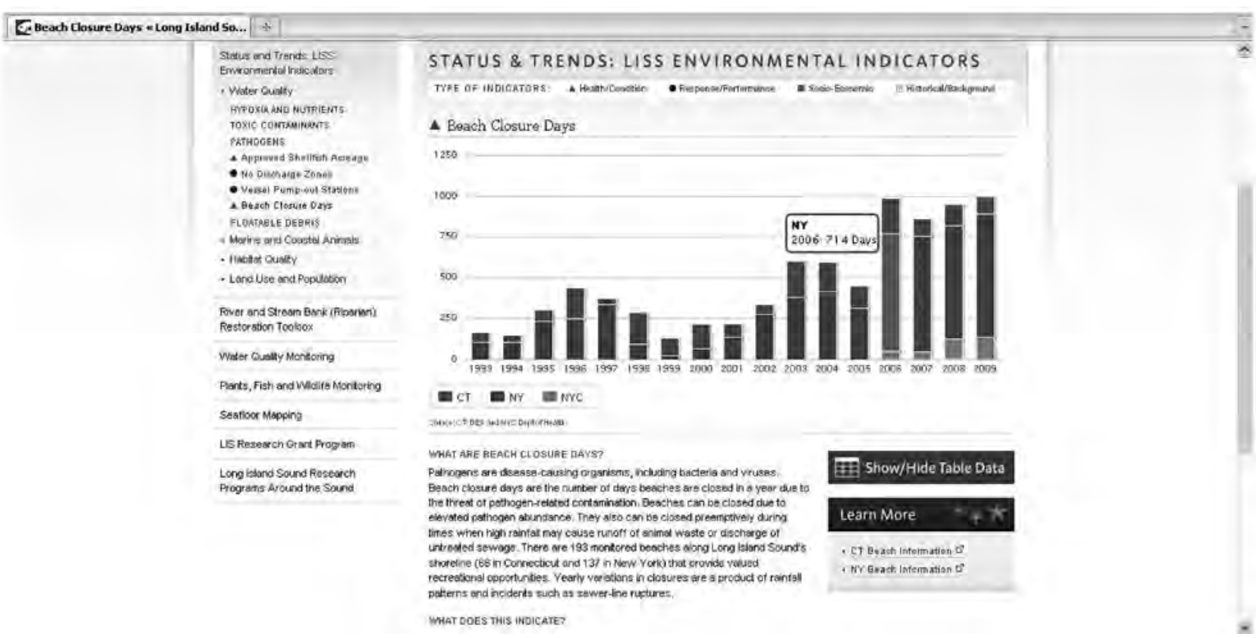
New York City has an active program to collect and remove floatable debris from its waterways, which has been incorporated into a new indicator as part of the revision. However, information on floatable debris for the majority of Long Island Sound is currently limited to data collected on volunteer beach cleanup days. 2) The pathogens indicators currently in use do not provide information on pathogen abundance in Long Island Sound. Numbers of beach closure days can be significantly affected by patterns in precipitation, since beaches are routinely automatically closed (without pathogen testing) following periods of heavy rainfall. Vessel no discharge zones are designed to reduce pathogen inputs into the Sound, but to our knowledge, local measurements of pathogen reduction in no discharge zones are not currently available. This is an area that could be targeted for improvement.

The Long Island Sound Environmental Indicators Program faces ongoing challenges in obtaining datasets specific to the Sound. Virtually the entire state of Connecticut is located within the Long Island Sound watershed, so data collected at the state level can be used by the program. However, only a small portion of the state of New York is in the Long Island Sound watershed, so data reported for the entire state of New York (e.g. fisheries landings) cannot be attributed entirely to Long Island Sound. Finding an efficient, reliable way to obtain Long Island Sound specific data will allow many of the indicators to be updated more frequently as we move forward.

Finally, a protocol needs to be established for what to do with indicators that are no longer being updated. For example, data on osprey nesting adults goes back to 1984, but monitoring programs were discontinued when the populations were deemed recovered. Harvest data for oysters in Connecticut goes back to 1983, but in 2008 and 2009, Connecticut shellfish harvesters did not report their harvest to the state because of a dispute over a possible tax on their harvest. Currently these data sets are being moved into 'historical' section of the indicators program, but a discussion of how to deal with this type of situation is warranted.

A scientific review of the indicators program is planned for 2011. The goals of this review are to 1) assess health/condition indicators and recommend additions, deletions and improvements; 2) create socioeconomic indicators and 3) recommend appropriate methods for trend analysis. The review team will be drawn primarily from the local scientific community, including members of the Long Island Sound Scientific and Technical Advisory Committee.

FIGURE 1. Sample indicator page from the newly redesigned web presentation.



Changes in Eelgrass, *Zostera marina,* Distribution Through Surveys in Eastern Long Island Sound, Connecticut and New York

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The U.S. Fish and Wildlife Service conducted eelgrass inventories in the eastern end of Long Island Sound in 2002, 2006, and 2009. Using aerial photography, GIS tools, and field inspections these inventories examined the distribution and temporal changes in this habitat important for many coastal marine animals. Eelgrass is a rooted vascular sea grass living fully submerged in shallow coastal marine waters in patches ranging from individual plants to beds covering many acres. The plant provides numerous ecological services including altering water flow and nutrient cycling, is an important food source for some birds, fish, marine turtles, invertebrates, and provides critical habitat and nursery grounds for many animals including commercially, recreationally and ecologically important fish species. The 2009 work surveyed 172 eelgrass beds covering 1,980 acres.

The work supports the interest of many stakeholders in Long Island Sound including the State of Connecticut's Office of Long Island Sound Programs and U.S. Environmental Protection Agency.

This presentation outlines the methods used in the surveys, summarizes inventory results, and compares the findings over time.

LIS Sub-basin changes in eelgrass acreage

Sub-basin	**2006-2009**	**2002-2009**
Little Narragansett Bay	60	58
Stonington Harbor	-15	13
Quimbog Cove	**-21**	50
Mystic Harbor	21	83
Palmer-West Cove	**-12**	**-12**
Mumford Cove	7	-4
Paquonock River	-3	-6
New London Harbor	-2	2
Goshen Cove	**-28**	**-33**
Jordan Cove	1	-5
Niantic Bay	**-57**	73
Rocky Neck State Park	-8	0
Duck Island Roads	2	5
Fishers Island, NY	145	152
North Shore, NY	-14	-5
Plum Island, NY	-2	8
Total	+74	+381

Water Quality of Brackish Water in Jamaica Bay: Monitoring of Fecal Indicator (FIB)

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ABSTRACT

Increase of both organic material and nutrients in estuaries due to urban anthropogenic activities, poses serious threats. The impact is manifested in enrichment of bacterial activity, and increase in BOD leading to potential oxygen depletion, both in the water column and in the sediment. This is particularly relevant in coastal areas of New York City (NYC) such as the Jamaica Bay, ~73 sq. km wetland estuary environment bordered by Kings County and Queens County of NYC, receives large inputs of the nutrients in terms of nitrogen and phosphorous from several point sources. This study attempts to capture the broad spectrum of nutrients and microbial contamination, by periodically collecting samples from various mixing zones (high to low) and locations close to point sources in Jamaica Bay area. EPA approved IDEXX method has been used for water microbiology analysis. Preliminary scanning of microbe levels in the near shore surface water showed high frequency range of concentrations. Fecal coliform, Escherichia coli and Enterococci were consistently higher than previously reported. Fecal coliform concentrations were well above the 200 counts/100 ml state bathing standard, with a geometric mean of 1200 counts/100 ml. Enterococci concentrations were found to be an order of magnitude higher than previous concentrations at 3 counts/100 ml. Based on these preliminary results, the water quality of this estuarine environment requires further investigation to understand the extent of nutrients loading and bacterial contamination both temporally and spatially.

INTRODUCTION

Jamaica Bay is located in the southwestern end of Long Island. It is an estuarine embayment that consists of tidal wetlands and open waters (NYCDEP, 2006). Open waters of the bay are classified for recreational use including bathing, fishing and boating (NYCDEP, 2009). It has been characterized as a temperate, eutrophic estuary, with open water salinities ranging from about 20-26 ppt, temperatures from 1°C to 26°C, and pH from 6.9-9 (USFWS, 1997). The bay receives large inputs of nutrients from several point sources including wastewater-treatment plants (WWTPs), combined sewer overflows/storm water (CSOs) during heavy precipitation, and subway dewatering practices. Non-point sources including leachate from landfills lining the shores, atmospheric deposition, and subsurface discharge of groundwater also deliver nutrients (Benotti et al., 2007). Recent improvements in storm water retention infrastructure by the NYC Department of Environmental Protection (NYCDEP) are expected to reduce the loading of pathogenic bacteria such as fecal coliforms and enterococci.

In 2009, sanitary water quality was superior for Jamaica Bay with summer fecal coliform and enterococcus concentrations below the New York State Standard for bathing at all monitoring sites, except Bergin Basin (NYCDEP, 2009). Average fecal levels have been in compliance with the bathing standard since 1985, with the exception of 1990 (NYCDEP, 2006) however, recent research has showed that average fecal levels have significantly risen above the bathing standard during the months of August, September and October.

Research conducted nearby in the Hudson River estuary from September 2006 to September 2007 has yielded similar results to Jamaica Bay. Twenty six percent of the samples collected in the Hudson River Estuary showed enterococci concentrations greater than the single sample exceedance of the suggested federal guideline for water quality at marine swimming beaches (Michaels, 2008). Enterococci concentrations in the Hudson River varied significantly depending on location and time sampled (Michaels, 2008). In an attempt to fill up the knowledge gaps on the temporal and spatial variations and inter-relation of nutrients and microbial communities in this urbanized estuary of Jamaica Bay, this study reports the preliminary results on the occurrences of fecal indicative bacteria (FIB) in the moderate mixing zone of Canarsie Pier, Brooklyn.

STUDY AREA

All samples were collected from Canarsie Pier (N40^{o} 37.800', W073^{o} 53.028') between August and October, 2010 at five sites along the shoreline. Canarsie Pier is located in the north-western part of the bay and can be classified as having a relatively moderate mixing zone (Figure 1). It is located just to the west of the 26th Ward WWTP, as well as the Pennsylvania, and Fountain Avenue landfills. The pier is situated in between two combined sewer overflow outfall areas just to the north. The main use of the pier is for recreational purposes such as fishing and boating and is the only recreational area for many nearby residents. Although this study began at Canarsie pier, sampling will be conducted at several other locations around the bay at both high and low mixing zones.

SAMPLE COLLECTION

The sampling involves the weekly collection of surface water samples from five locations at the Canarsie Pier, Brooklyn. Five pairs of near shore water samples were collected from the shoreline, as well as twenty feet offshore of each site. They were collected in IDEXX 100 ml sterile vessels containing sodium sulfate. The samples were diluted with 90 ml for Fecal coliforms including Escherichia coli and 50 ml of sterile water for Enterococci. IDEXX media Colilert-18 (pt# 5,610,029) was added for growing the Fecal coliforms and Escherichia coli, while Enterolert (pt# 5,620,865) was added for culturing Entorococci. The samples were immediately stored in a cooler and brought back to the lab for incubation within four hours of collection.

ON SITE MEASUREMENT

Physical parameters of water were measured on site by YSI multiprobe instrument prior to collection of water for microbiology. Temperature (^{o}C), conductivity (mS/cm), salinity (ppt), pH, ORP (mV), and dissolved oxygen (mg/L) in three replicates.

LABORATORY MEASUREMENT

Once in the lab, each sample is transferred from the 100 ml recyclable sterile vessels into IDEXX quanti-trays; with each tray containing 51 wells. The trays were then run through the quanti-tray sealer. As the tray passes through the sealer, the 100 ml sample/media mix is evenly dispersed throughout the 51 wells and then incubated at optimal conditions for microbial growth. Fecal coliform and Escherichia coli are incubated for 18 hours at 35^{o}C and Enterococci are incubated for 24 hours at 41^{o}C. Upon completion of incubation the quanti-trays were observed in visible light and UV light for Fecal coliforms and E. coli/Enterococci respectively.

In order to positively identify fecal coliforms in each sample the color of the wells in the trays were observed carefully. For positive detection of fecal coliforms in the samples containing colilert-18, the color of well in the tray must be yellow; equal to or greater than the comparator. Each yellow well is counted and converted into the most probable number (MPN) as per IDEXX conversion chart. For positive detection of Escherichia coli, the trays are placed under ultra violet light; fluorescent wells are counted as positive E. coli and converted into an MPN. For positive detection of Enterococcus the trays are placed under ultra violet light and the fluorescent wells are counted and converted into an MPN.

RESULTS

Weekly monitoring results of physical parameters of Jamaica Bay waters at Canarsie Pier (Table 1) from August 27 to October 17, 2010 were consistent with previous measurements taken and meet the criteria of an estuarine environment. However, microbial occurrence was not agreeable with previous concentrations. The geometric mean taken of each of the fecal indicative bacteria in the three months period was consistently higher than previously reported, with some concentrations as much as orders of magnitude higher than New York State Standards for Bathing (Table 2). Temporal variability was not significant for fecal coliform, however both E. coli and Enterococci concentrations showed significant temporal variability and concentrations fluctuated from <5 counts/100 ml to > 400 counts/ 100 ml (Figure 2). Sampling was also done after two major wet weather events. After both events, it was found that all bacteria concentrations increased with the exception of E. coli after the first event. After the first event there were no E. coli concentrations detected; this may be due to some technical problem in incubating temperature. There is a distinct variation in different FIB concentration with tidal fluctuation. Fecal coliforms and E. coli concentrations at high tides were higher than at low tide. Enteroccoci concentrations were slightly higher at low tide than at high and moderate tide (Figure 4).

DISCUSSION

Occurrences of fecal indicative bacteria in Jamaica Bay at Canarsie Pier proved to be higher than previously reported by the New York City Department of Environmental Protection. Fecal coliform concentrations exceeded the 200 counts/100 ml New York State Standards for Bathing. Escherichia coli counts, although not previously reported, were in compliance with the bathing standards at 71 counts/100 ml. Enterococcus concentrations also were in compliance with the 35 cells/100 ml bathing standard at 29 counts/100 ml however, the concentrations were almost one order of magnitude higher than previously reported average concentration ~3 counts/100 ml. The variation in microbial occurrence after rainfall events may be facilitated by the nutrients inflow to the bay as a result of surface runoff, as well as increased CSO outfalls during times of heavy precipitation. Higher enterococci concentrations after the rainfall events also may be a result of natural or environmental sources of contamination to overlying water (Ferguson et al., 2005). Research conducted at several beaches in California has showed that E. coli and enterococci are able to survive and regrow in such an environment. Depending on the organic content of the sediment, the bacteria may be provided the necessary nutrients to aid in their survival and regrowth. In addition, the rewetting and drying of the sediment at different tidal conditions may also facilitate microbial growth in the sediment. As water is brought onshore, nutrients may be provided to the microbes living in situ.

Further investigation is required to understand the temporal and spatial variability of microbial occurrence in Jamaica Bay. To understand the occurrences and distribution of fecal indicative bacteria, weekly monitoring of both surface water samples and sediments will be continued at Canarsie Pier and conducted at other locations near point sources in Jamaica Bay with various mixing zones.

In conclusion, this study clearly demonstrated the fact that water quality of Jamaica Bay can be varied to great extent to show elevated high level of FIB including Fecal coliforms, Escherichia coli and Enterococci in post summer months despite their annual average counts within the limit of bathing standard, reported elsewhere (NYCDEP, 2009). Further investigation is necessary to understand the microbial occurrence of these bacteria in Jamaica Bay.

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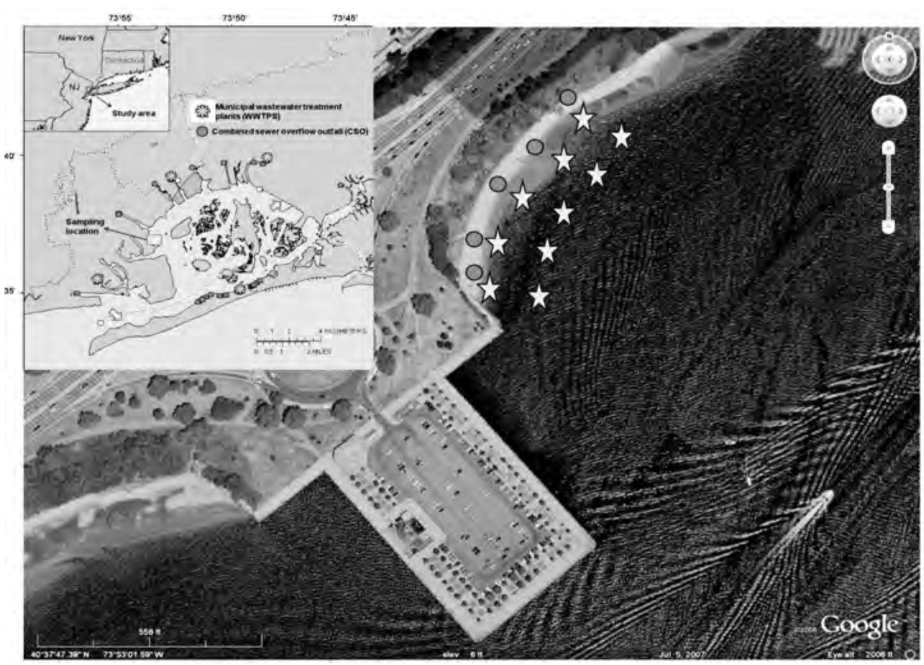

FIGURE 1. Image of study area with selected sampling sites.

Parameter/Analyte	Average	Range
Temperature (^oC)	23.1	18.8-23.4
Conductivity (mS/cm)	44.9	36.0-47.9
Salinity (ppt)	26.9	21.6-28.7
pH	7.87	7.35-7.96
ORP (m V)	233.5	162.8-309.6
Dissolved Oxygen (mg/L)	11.1	7.3-12.6

TABLE 1. Physical water parameter measurements taken by YSI multiprobe instrument.

Fecal Indicator Bacteria (FIB)	Current Research Aug-Sep 2010	NYC-DEP Summer 2009	NYC-DEP Summer 2004-2006
Fecal Coliform Counts/100mL	1124 (>200.5->4010)	64 (n/a)	n/a (23.5-51.4)
Escherichia coli Counts/100mL	71 (<1.0-542)	n/a	n/a
Enterococcus Counts/100mL	29 (38.9->401)	3 (n/a)	3 (n/a-740)

TABLE 2. Geometric mean of FIB concentrations.

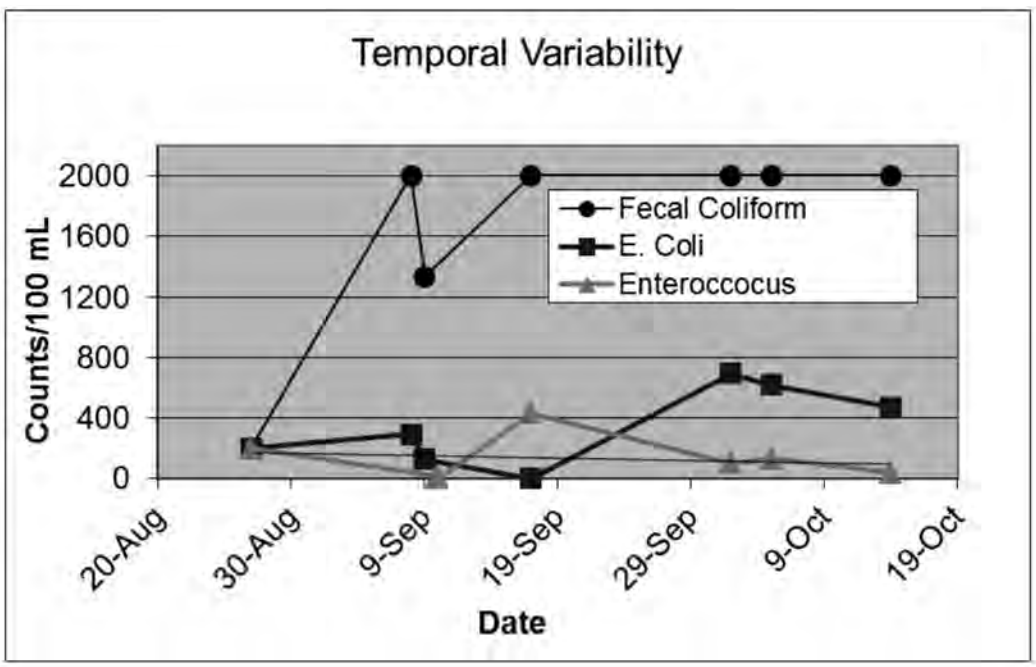

FIGURE 2. Temporal variability of FIB from August to October, 2010.

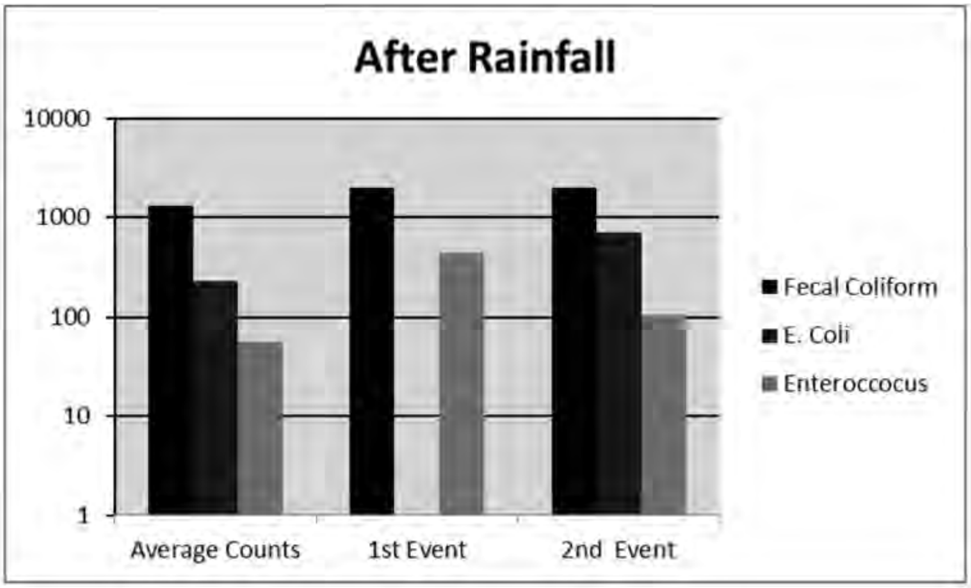

FIGURE 3. Comparison of average bacteria concentrations with concentrations post wet weather events.

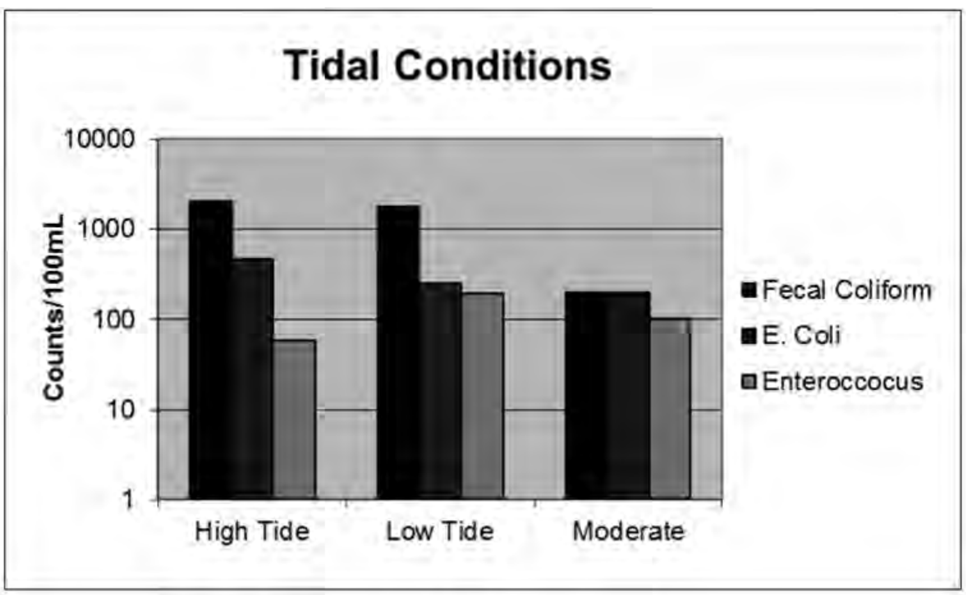

FIGURE 4. Variability of microbes with various tidal conditions.

Comparison of Solid Phases for the Detection of Phthalate Esters

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ABSTRACT

Phthalic acid esters (PAEs) are organic contaminants that are ubiquitous in the environment. Efficient methods for environmental extractions of PAEs are necessary, especially in order to maximize sample recoveries. Binding studies were conducted to compare activated carbon (AC), carbon nanotubes (CNTs) and C-18 resin affinities for PAEs. Results showed that though AC is an efficient and cost effective adsorbent material for AC was a less favorable SPE adsorbent, as all eluted samples resulted in compromised chromatogram baseline and decreasing LODs. C-18 resulted in higher recoveries of all six PAEs, therefore was a more efficient extraction material for this group of target compounds, with K_{OW}'s ranging from 1.6 to 8.1. DEHP was found to be a contaminant in laboratory ultra-pure water and the major PAE contaminant in waste water effluent. Based on an outflow estimate of $6.5x10^9$ L of treated effluent entering LIS each day total DEPH entering LIS could be in the order of 670 kg day^{-1} (1730 moles day^{-1}). DEHP will associate strongly with particulates and therefore the estuary will likely become a trap for this contaminant resulting in high exposures to LIS biota.

INTRODUCTION

Emerging contaminants are chemicals found to be ubiquitous in our environment, due to high production volumes, persistence and a tendency to bioaccumulate; the consequences of which are a matter of much study. Many compounds have been found to be biologically active, triggering hormone-like actions in physiological systems. Known as endocrine disrupters (EDs), these chemicals may exert harmful effects in wildlife and humans. For example, compounds eliciting estrogen-like responses released in waste water have resulted in feminization of over 82-100% of the male smallmouth bass observed in the Potomac (Iwanowicz *et al.* 2009). This severely reduces the reproductive capacity of this species. Similar negative effects could be contributing to the decline of aquatic species, such as lobsters, in the Long Island Sound (LIS).

The transport and fate of several phthalic acid esters (PAEs) has received widespread attention in recent years due to the discovery that several PAEs are endocrine disrupting compounds and may exert harmful effects to animals and humans. During the past 40 years, the high production volume of PAEs (mainly in the production of PVC and the numerous commercial uses of) has led to their ubiquitous presence as environmental pollutants, even in marine environments as remote as the Enewetak Atoll in the South Pacific, in concentrations greater than those of well-known persistent organic pollutants such as DDT and PCBs (Atlas, Giam 1981). Although classical organic pollutants are routinely monitored for in the LIS, there are few studies on the presence and distributions of emerging EDs in the LIS.

Solid-phase extraction is a method employed for the adsorptive removal of and detection of phthalates. More recently, several reports have indicated that carbon nanotubes (CNTs) are a far superior adsorbent than traditionally used extraction resins for several organic pollutants, including PAEs (Cai *et al*. 2003). Yet there are growing concerns regarding the potential environmental, health and safety of nanomaterials, which have also become regarded as emerging contaminants. Therefore the use of CNTs for environmental remediation or as disposable laboratory products must be carefully evaluated in order to ascertain the benefits versus the potential risks. The purpose of this study was to compare the extraction efficiency of CNTs with C-18 resin and activated charcoal (AC) for the detection of several PAE compounds. The most effective extraction method was then applied to the detection of PAEs in waste water effluent, in order to evaluate the potential impact that these contaminants may have in the Long Island Sound.

METHODS

Solid-Phase Extraction: PAE standards were purchased from Accustandard containing dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), butylbenzyl phthalate (BBP), di-ethylhexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP), (d4) dibenzyl phthtalate was used as recovery standard for water extracts. All solvents were pesticide grade. Carbon nanotubes were purchased from Cheap-Tubes Inc., (multiwalled, 50-80nm outer diameter, 10-20µm length. C18 was obtained from UCT Clean-Up extraction columns; granular activated carbon (AC) (20-40 mesh) was manufactured by EMD (Darco) and crushed to powder using a motar and pestle. Empty 6mL glass solid phase extraction (SPE) cartridges were thoroughly cleaned and triple solvent rinsed before addition of 0.5g of solid phase sandwiched between two PFTE frits. PAEs samples were spiked directly to the SPE cartridge containing 5ml of MilliQ water resulting in a final concentration of 100ng/ml. Acetonitrile (AcN) and ethyl acetate (EA) were compared as elution solvents. Benzyl benzoate (500ng) was added as an internal standard. Samples were analyzed by GC (Agilent 7890A) with µECD detector, using nitrogen as the carrier gas and DB-5 column (30m x 0.53mm x 0.25µm). All other GC analytical parameters were as described by EPA method 8061. *Binding Kinetics:* To determine the static adsorption capacity, DMP was used as the target analyte due to greater water solubility compared to the other PAEs. A standard curve for DMP was obtained using concentrations of 1, 5, 10, 25 and 50µg mL^{-1} in milliQ water. Emission was measured at 350nm using a Hitachi F-2500 fluorescence spectrophotometer, excitation wavelength 275nm. A linear regression slope was obtained (R^2=0.994). Samples were prepared as follows; 50mg of CNT, C18 or AC was shaken for 1 hour with 50ml aliquots of aqueous solution containing a series of concentrations of DMP (0-50ug ml^{-1}). Equilibrium was assumed after 1 hour.

Waste-water Analysis: 1L samples of wastewater effluent were obtained from the Town of Groton Water Pollution Control Facility. Half of the samples were GFF filtered prior to C18 solid phase extraction. Samples were analyzed by GC-MS (Agilent 5975C MS) using PCI, with methane as the reagent gas, in SIM mode.

RESULTS AND DISCUSSION

Solid Phase Extraction: Recoveries of the six target PAE compounds from CNT as the solid phase, and using AcN as the elution solvent, were poor. The smallest and least hydrophobic PAE (DMP) gave highest recovery (72%) however the recoveries of the larger PAEs were low (0-42%). These results are in disagreement to those previously published (Cai *et al*. 2003) where 90-110% elution (AcN) was obtained from CNTs for the four PAEs (K_{OW} range 2.42-6.2) studied. Recoveries from CNTs were enhanced by elution with a less polar solvent (EA), yet recoveries of PAEs in this study, with K_{OW}'s comparable to those investigated by Cai *et al*. remained unfavorable (8-70% Figure 1a). Recoveries of PAEs from C-18 sorbent (AcN) improved compared to CNTs yet recovery of larger PAEs were also low (85% DMP; 64% DEP; 0-28% larger PAEs). AcN (EPA method 8061 PAE extraction solvent) was found to be a poor choice for the elution of this compound group due to the large range of K_{OW}'s. Percentage recoveries of target compounds from C-18 using EA resulted in maximal recovery of all six PAEs with a minimal volume (3ml) of solvent (Figure 1b). The poor recoveries of PAEs from CNTs were suspected to be due to reported enhanced binding capacities CNT compared to C-18. Comparison of CNT sorbent masses found that recoveries for five PAEs were increased by using a reduced amount of sorbent (Figure 2). This indicates a strong sorption capacity of CNTs PAEs thus requiring greater extraction solvent volumes to recover sorbed PAEs. Decreased CNT sorbent mass also enhanced recoveries of chlorobenzenes (Lui *et al.* 2004). Results for AC as a solid phase adsorbent were inconclusive due to matrix effects which produced unanalyzable chromatograms.

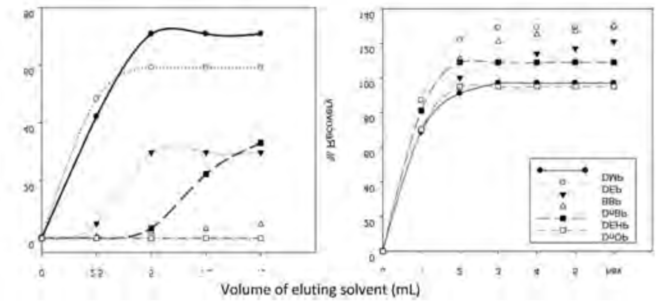


FIGURE 1

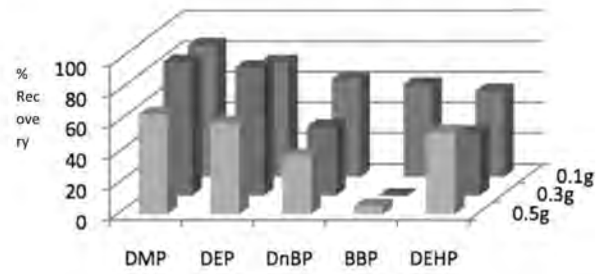


FIGURE 2

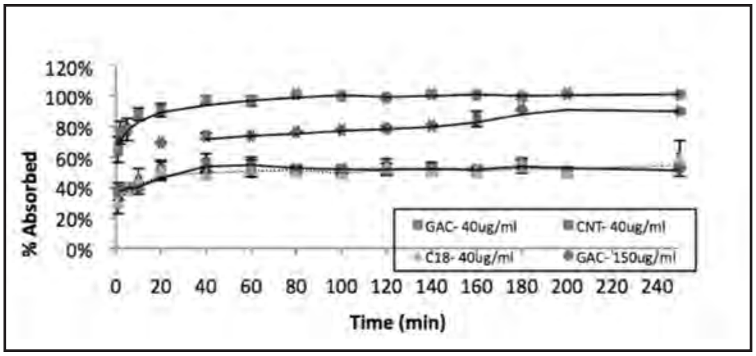
FIGURE 1: % recovery of target phthalates from a) CNTs and b) C-18 adsorbents using ethyl acetate as the eluting solvent

FIGURE 2: % recovery of target phthalates from CNTs of different sorbent bed masses

Binding Studies: Time to equilibrium studies using DMP found C-18 and CNTs reach equilibrium by 40 min with 40ug/ml DMP, attaining 52-53% absorption maximum (Figure 3). AC absorbed 97% of DMP by 60 min, with 100% absorption by 80 min. Initial uptake rate of AC (0.65min-1) is double that of C-18 and CNTs (0.31 and 0.37 min^{-1}). Experiment was repeated for AC with a higher DMP concentration in order to obtain equilibrium distribution coefficients (K_{eq}); C18 and CNTs= 1080 L Kg^{-1}, AC= 9000 L Kg^{-1}. Sorption isotherms indicate binding capacities AC>CNT>C18. The linear shape of the GAC isotherm suggested partitioning into the sorbent and/or adsorption sites of the AC far from being saturated. The Freundlich isotherm model provided a good fit for the data (Figure 4). The Freundlich constants (K_f) which give a measure of adsorption capacity, were 108 (C-18) <184 (CNT) <217 (AC) L Kg^{-1}.

Detection of Phthalates in Water Samples: 1L amber glass bottles were filled with MilliQ water and spiked with 100ng each PAEs, and extracted using C-18. Recoveries (Figure 5) were between 95% - 112% however results also indicated a DEHP contamination (0.34 – 0.49 µg mL-1) in the MilliQ water obtained from the point of use (POU) dispenser (Figure 5). These results confirm those previously published where DEHP concentrations in Ultra High Purity water ranged from 1.89 µg mL^{-1} (RO permeate) to 0.20µg L^{-1} POU (Lui *et al.* 2008). DEHP was also determined to be the most prevalent PAE in waste water effluent (Table 1). The results obtained in this study are consistent with literature values (1.74 – 182 µg L^{-1}) reported for DEHP in waste water effluent (Fromme *et al*. 2002). The organic carbon partitioning co-efficient (K_{OC}) was determined from the observed K_{OC} (using the formula proposed by Schrap *et al.* 1995) where;

$$K_{oc}^{obs} = \frac{C_s([DEHP_{POM}]=[DEHP_{unfiltered}]-[DEHP_{filtered}])}{C_w([DEHP_{filtered}])} \quad \text{and} \quad K_{oc}^{true} = \frac{K_{oc}^{obs}}{1-K_{oc}^{obs}\cdot[DOC]}$$



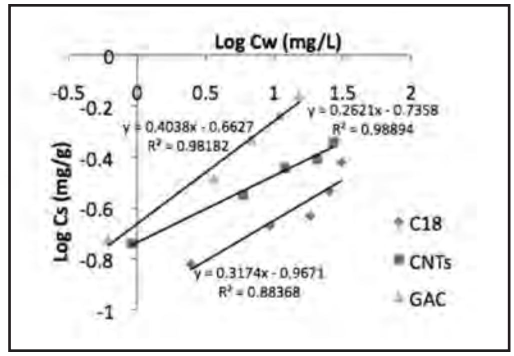
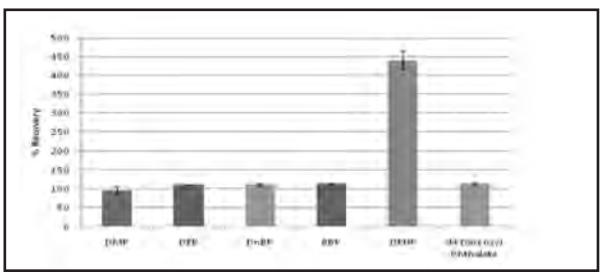


FIGURE 3: Time to equilibrium studies with DMP (40ug/mL) and C-18, AC and CNTs; Due to 100% DMP absorption by activate charcoal, time to equilibrium was reinvestigated with AC using a greater DMP concentration.

FIGURE 4: Freundlich isotherm model fit of the binding isotherm data.

The K_{OC} value for DEHP obtained for this effluent data is 449,460 L Kg^{-1} (literature values 87,420-510,000).When normalized for organic carbon, the partitioning of DEHP between both particulate (POC) and colloidal/dissolved organic carbon (DOC) fractions was found to be equal, therefore both POC and DOC play a significant role in the transport of DEHP in waste water effluent.



Phthalate Ester	Conc. detected in waste water effluent ($\mu g\ L^{-1}$): Filtered:	Unfiltered:
DMP	3.4 (N.D. – 13.5)	N.D.
DEP	N.D.	N.D.
DnBP	N.D.	N.D.
BBP	N.D.	N.D.
DEHP	30 (21 – 39)	104 (26 – 223)
DnOP	Inc.	Inc.
Organic carbon ($mg\ L^{-1}$)	*8.3 (7.13 - 10.10)*	*34.2 (31.92 – 36.07)*

FIGURE 5: Recovery experiment using C18 and 1L MilliQ water spiked with PAEs showing DEHP contamination

TABLE 1: Concentrations of phthalate esters in waste water effluent.

A good SPE material gives highest recoveries with minimal elution solvent volume. AC was found to be a less favorable SPE adsorbent, as all eluted samples resulted in chromatograms that appeared to be highly contaminated, requiring more cleanup procedures to lower LODs. Although sample recoveries increased with less CNT mass, C-18 resulted in higher recoveries of all six PAEs, therefore was a more efficient extraction material for this group of target compounds, with K_{OW}'s ranging from 1.6 to 8.1. DEHP was found to be a contaminant in laboratory ultra-pure water and the major PAE contaminant in waste water effluent. An estimated $6.5x10^9$ L of treated effluent enters LIS each day (NY-2000**).** Assuming Groton WPCF represents all effluent data, amount of DEPH entering LIS could be in the order of 670 kg day^{-1} (1730 moles day^{-1}). Entering LIS, DEHP will associate strongly with particulates as solubility of DEHP decreases and partitioning to organic carbon increases with salinity, therefore the estuary will likely become a trap for this contaminant. DEHP is known to bioconcentrate therefore the sediments may be a significant source of DEHP to benthic dwelling organisms.

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ACKNOWLEDGEMENTS

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Movement Patterns and Population Genetics of the American Horseshoe Crab in Relation to Long Island Sound Conservation Strategies.

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ABSTRACT

The Connecticut Department of Environmental Protection (CTDEP) established three no-harvest zones for the horseshoe crab (*Limulus polyphemus*) population as part of a conservation plan for the species. Data from a long-term mark/recapture study of horseshoe crabs in conjunction with a microsatellite-based genetic survey of the population were analyzed to determine if this plan was appropriate to conserve genetic diversity and broaden our knowledge of movement patterns of *Limulus* in Long Island Sound (LIS). To date, ~53,000 crabs have been tagged over a 10 year period through the Project *Limulus* program with an annual average recapture rate of 12 to 15%. In addition to the ongoing tagging study, 187 horseshoe crabs collected from 5 distinct sites spanning the geographic extent of Long Island Sound (Rye and Mt. Sinai, NY; Milford, New Haven, and Groton, CT) were genotyped for 11 microsatellite loci to determine the overall genetic health of the LIS population and determine if regional genetic differentiation was sufficient to identify sub-populations within this region. The genetic data indicates that the LIS *Limulus* population is genetically homogenous with no signs of inbreeding and substantially similar to other Mid-Atlantic populations. Data from the mark-recapture study indicate significant migration east and west along the north shore of LIS relative to the original tag site and in addition cross LIS migrations have also been observed. Therefore, the locations of the established no-harvest zones are appropriate to conserve genetic diversity. However, based on their tri-state migration patterns, a multi-state management strategy is needed for the LIS horseshoe crab population.

INTRODUCTION

The American Horseshoe Crab, *Limulus polyphemus*, lives along the Atlantic coast of the United States from Maine to the Yucatan Peninsula (Anderson and Shuster, 2003). *L. polyphemuss* is an economically and ecologically important species. Economically, *L. polyphemus* hemolymph is harvested for the multi-million dollar biomedical industry that uses the blood-clotting compound *Limulus* Amoebocyte Lysate (LAL). This product is mainly used to detect pathenogenic endotoxins in vaccines (Berkson and Shuster 1999). Adult horseshoe crabs are commercially harvested for use as bait in the eel and whelk fisheries (Manion et al., 2000; Ferari and Targett, 2003). Ecologically, horseshoe crabs are important members of food webs up and down the coast of the eastern United States and are biologically linked to many different species. They provide habitat for more than 20 epibiont species, one is only found on horseshoe crabs (Turner et al., 1988; Dietl et al., 2000; Grant, 2001). Of particular importance is their tight ecological link to shorebirds. *Limulus* eggs are a major food source for migrating shorebirds (Castro and Myers, 1993; Clark et al., 1993; Botton et al., 1994). While there have been extensive studies conducted on the populations of horseshoe crabs which live along the mid-Atlantic coast, there has been a lack of research conducted on the horseshoe crabs which inhabit the New England region, and specifically the crabs which live in the Long Island Sound.

Project *Limulus* is a broad scale research initiative which is focused on the horseshoe crabs which inhabit Long Island Sound. The overall goals of Project *Limulus* are to understand the basic population dynamics and genetics of the crabs, to understand their links to other species, and to develop management plans for the conservation of *Limulus* (Beekey et al., 2008). Project Lim-molecular is a sub-branch that focuses on the molecular analysis of the population, with goals to establish the structure of the population genetics of the horseshoe crabs as well as to determine the effectiveness of the established conservation plans in place.

The harvest of horseshoe crabs is permitted within Long Island Sound by New York and Connecticut state laws. However, in 2006, the Connecticut Department of Environmental Protection (CTDEP) established three no-harvest zones within LIS in an attempt to provide horseshoe crabs with the opportunity to increase their population size. These no-harvest zones are located at Milford Point Beach in Milford, Sandy Point Beach in New Haven, and Menunketesuck Island in Westbrook, CT. The Connecticut shoreline is a total of 110 miles long, not including near-shore islands. Milford Point and Sandy Point are located 11 miles apart, and Menunketesuck Island is another 25 miles from Sandy Point. Due to the proximity of the no-harvest zones, we investigated whether they would be effective in maintaining the genetic diversity of the horseshoe crabs in LIS.

METHODS

Mark Recapture study:

Project *Limulus* researchers and volunteers have been tagging horseshoe crabs in LIS since 2000. From 2000–2007 yellow Floy Cinch-tags (model FT-4, 8”: http://www.floytag.com) and from 2008-2010, U.S. Fish and Wildlife Service issued white disc tag were attached to crabs using a #2 Yellow scratch awl to make a hole in the lower rear of either the right or left posterior side of the prosoma. The tag number, sex (based on the morphology of the pedipalps), and mating behavior were recorded (Mattei et al., 2010). Recapture data were obtained by researchers and volunteers who reported organisms to the USFW.

Microsatellite genotype determination:

Tissue samples were collected from Rye (39) and Mt. Sinai (37), NY; Milford (38), New Haven (35), and Groton (38), CT. The distal segment of the 3rd walking leg of each individual was excised, stored on ice in the field and subsequently frozen at -80 degrees C until further processing. Frozen muscle tissue dissected from stored samples was ground in liquid nitrogen without thawing, and stored at -80 degrees C. DNA was isolated from ground tissue with the Gentra Puregene Cell Kit (Quiagen, Valencia, CA) following the manufacturers protocols.. Microsatellite Loci (D60, A315, A37, A67, D3, A42, A40, A5, A64, A52, A38) were genotyped by fluorescent primer PCR using primer pairs and amplification conditions previously described in King and Eackles (2004). Amplified Microsatellite Loci were sized by capillary electrophoresis at the DNA Analysis Facility on Science Hill (Yale University) using an Applied Biosystems 3730xl 96-Capillary Genetic Analyzer (DS31 5 Color Dye Family, Liz-500 size standard). Electrophoretogram output was analyzed for determination of fragment size and allele assignment using GeneMarker (Softgenetics, State College, PA). Allele Identity and Frequency Statistics and Analysis of Molecular Variance (AMOVA) between populations were calculated using GENEALEX (Peakall and Smouse, 2006). Fixation indices and Hardy-Weinberg Equilibrium analyses were calculated with GenePop (Rousset, 2008).

RESULTS

The tagging effort has increased throughout the past 10 years (Figure 1). From 1997-2000 a few hundred crabs were tagged, and in 2000 the first 6 recaptures were found. In 2010, with the help of hundreds of volunteers, over 14,000 crabs were tagged and 3295 were recaptured. According to the mark recapture data 95% of horseshoe crabs tagged in LIS are recaptured within LIS. Horseshoe crabs migrate all over the Sound; this includes crossing state boundaries and moving from Connecticut to New York and Rhode Island. 87% of the horseshoe crabs recaptured within 30 days of their tag date are found at the site that they were tagged at. With increasing time after tagging there is an increase in the number of crabs that are found further away from their original tag site. Around 33% of the crabs recaptured after 200 days after tagging were found at the same location (Figure 2).

To date a total of 187 individuals from 5 different beach locations have been amplified across 11 different microsatellite loci. There is no evidence showing any regional genetic differences within the Long Island Sound population. A pairwise population comparison test was performed in order to detect any subpopulation division. There was no significant differentiation between any of the beach locations we tested, significance defined by $P > 0.05$ (Table 1). The populations of horseshoe crabs within the LIS also are in a state of good relative genetic health. The population is in Hardy-Weinberg equilibrium, and there is no evidence of inbreeding (F_{is} -0.015 value is close to zero). Thirdly, the population is comparable to other Mid-Atlantic populations of horseshoe crabs. The number of effective alleles and heterozygosity of the populations are not significantly different from published data of populations in the Greater Delaware Bay Region (King, 2005).

DISCUSSION

The mark/recapture data shows that 95% of the horseshoe crabs tagged within the Long Island Sound stay there, although they migrate all through the Sound. The horseshoe crabs show site affinity within a breeding season, although as time goes on more crabs are found further away from their original tagging site.

The genetic data show that the horseshoe crabs are one population and can be managed as a unit. It also suggests that the established no harvest zones are appropriately located to conserve the genetic diversity of the horseshoe crabs in the LIS. Due to the observed movement patterns of the crabs a multi-state management plan should be developed to further conserve the LIS horseshoe crab population.

ACKNOWLEDGEMENTS

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<table>
<tr><th></th><th>Rye</th><th>Milford</th><th>New Haven</th><th>Groton</th></tr>
<tr><td>Rye</td><td></td><td></td><td colspan="2" rowspan="3">No Significant Differentiation P > 0.05</td></tr>
<tr><td>Milford</td><td>0.012</td><td></td></tr>
<tr><td>New Haven</td><td>0</td><td>0.019</td></tr>
<tr><td>Groton</td><td>0.011</td><td>0.001</td><td>0.011</td><td></td></tr>
<tr><td>Mt Sinai</td><td>0.002</td><td>0.008</td><td>0 0</td><td></td></tr>
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TABLE 1. Estimates of genetic differentiation between populations (Amova-Rst). Probability values based on 99 permu.

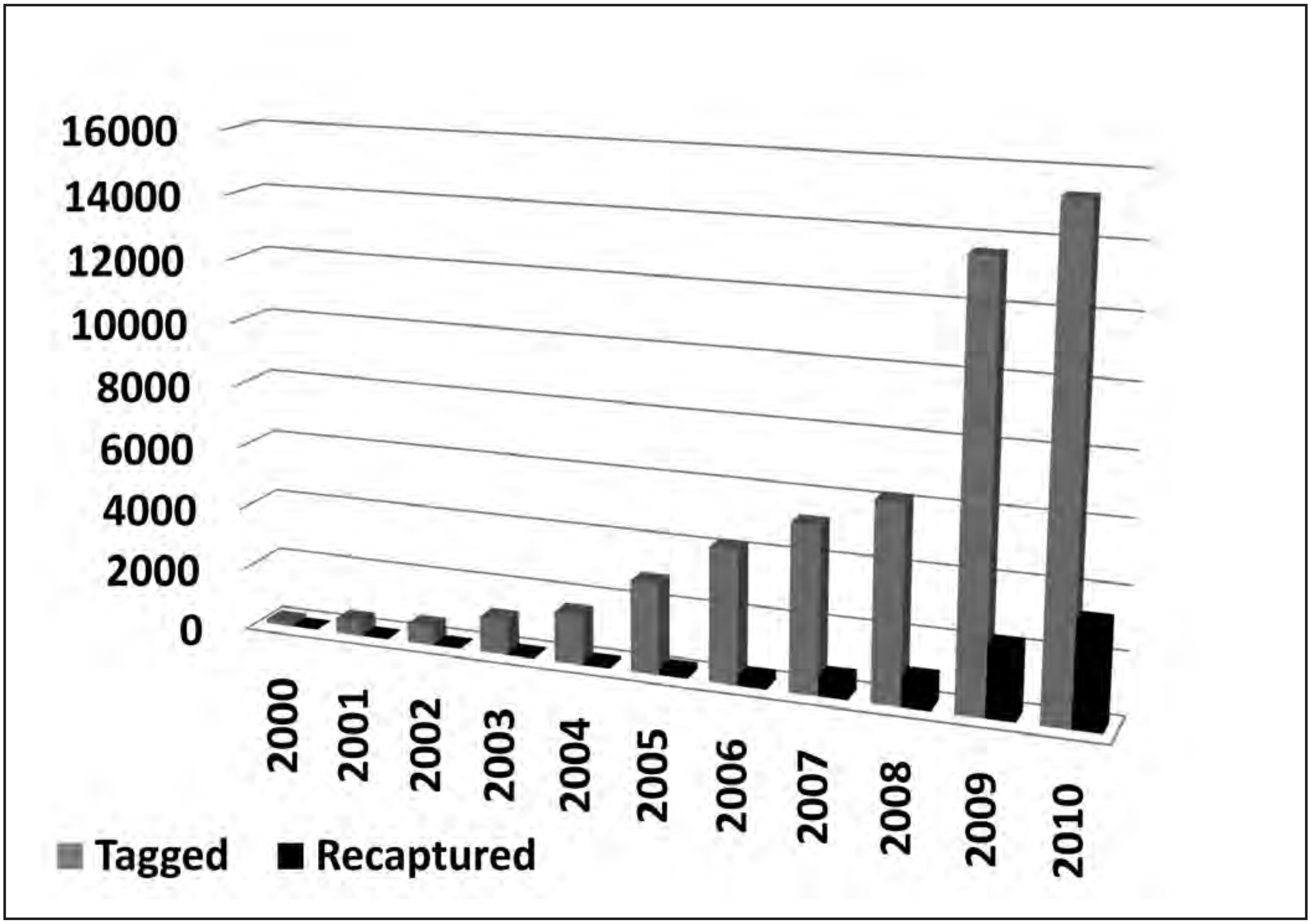

FIGURE 1. Number of tagged and recaptured horseshoe crabs per year across spawning beaches throughout Long Island Sound.

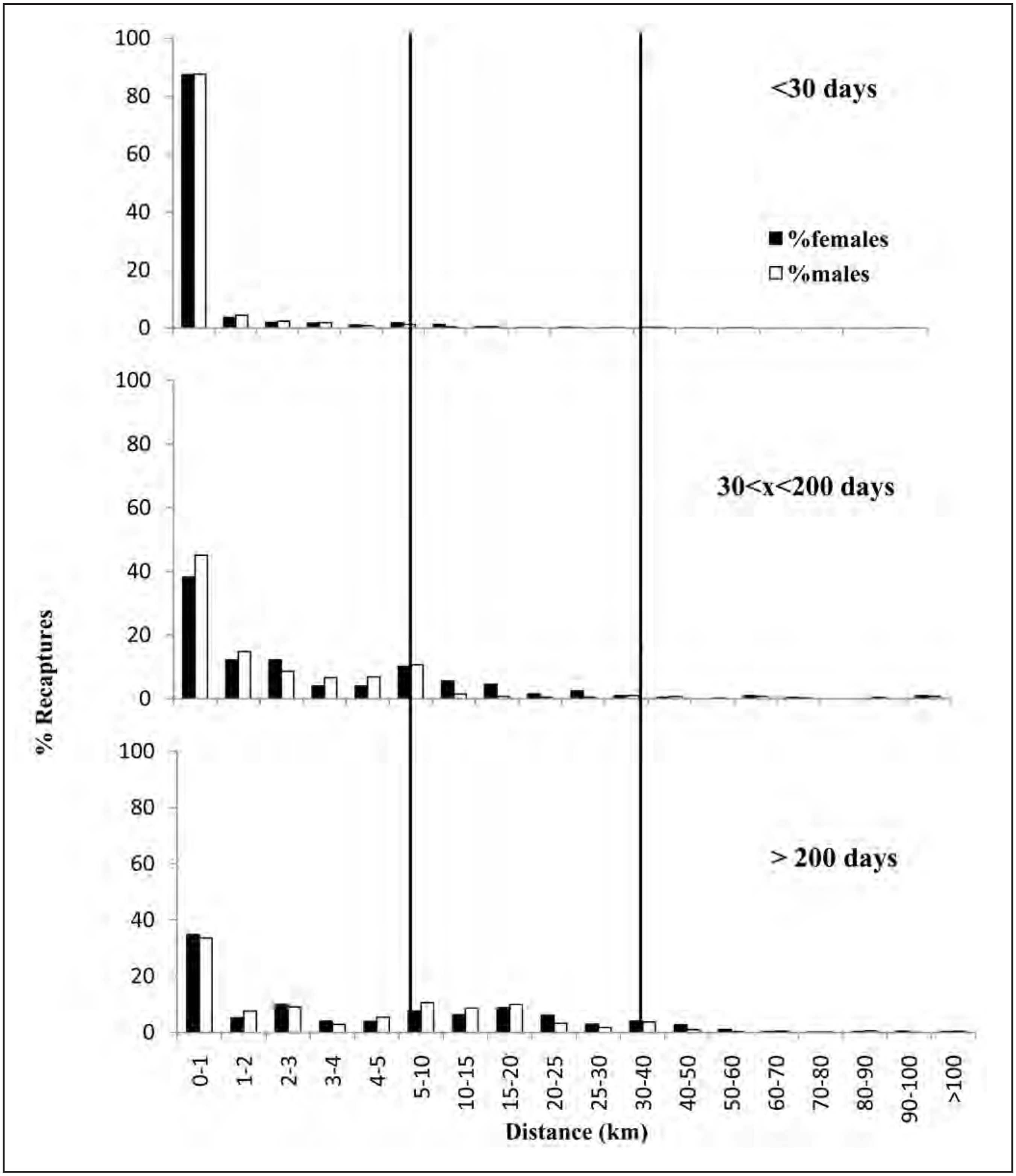

FIGURE 2. Number of recaptured female and male horseshoe crabs plotted by distance and time (less than 30 days, between 30 and 200 days, and greater than 200 days) from when they were originally tagged.

Detection of Hydroxyl Radicals in Marine Sediments Using Disodium Terephthalate

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ABSTRACT

It has been suggested that hydroxyl radicals (OH•) form at the oxic-anoxic interface in marine sediments, but their existence in marine sediments has never been shown. We developed a method to detect OH• in marine sediments using disodium terephthalate (TPA) and confirmed the TPA results using benzoic acid (BA), which has been used previously to detect OH• in marine waters. TPA reacts with OH• to form the fluorescent hydroxylated product hydroxyterephthalate (OHTPA), while BA forms UV-active hydroxylated products (OHBA).

We confirmed OH• formation at the oxic-anoxic interface by injecting TPA and BA into intact sediment cores and determining oxygen concentrations with microelectrodes. We suggest using TPA rather than BA for OH• detection in sediments, since OH• detection using TPA has a lower detection limit than OH• detection using BA. Inter-calibration experiments using BA and TPA in samples with marine salinities gave a conversion factor of 2.82 ± 0.09 moles OH• reacted per moles OHTPA produced between OHTPA concentrations and cumulative concentrations of OH•.

The fluorescence spectrum of humic material in natural waters overlaps partially with the fluorescence spectrum of OHTPA. Consequently, the humic fluorescence signal from a control must be subtracted from the OHTPA fluorescence signal. Additionally, sediment cores incubated with TPA should be sliced under nitrogen atmosphere to prevent oxidation of reduced iron, and propanol should be added as a reaction quencher immediately after slicing.

Using appropriate care, TPA can be used to detect OH• in natural marine sediments with a better detection limit than BA.

Keywords: hydroxyl radical, terephthalic acid, benzoic acid, Fenton reaction, sediment chemistry, redox reaction

1. INTRODUCTION

Investigations of hydroxyl radical (OH•) formation rates in the marine environment have mainly focused on water column processes. However, King et al. (1995) proposed that OH• form in natural marine sediments when both Fe(II) and oxygen are present, which occurs close to the interface between the oxic and anoxic sections of the sediment. Past investigations have shown that oxidation of Fe(II) to Fe(III) does occur at the oxic-anoxic interface in sediments and could be a significant source of $O_2$2- and H_2O_2 (King et al., 1995). H_2Ov is formed in the Fe-catalyzed disproportionation of O_2-, and OH• are then formed stoichiometrically from H_2O_2 at the oxic-anoxic interface in the Fenton reaction (Southworth and Voelker, 2003):

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

OH• life times are on the order of nanoseconds and their concentrations cannot be determined directly. Therefore, we estimated OH• formation rates using their specific and selective reactions with disodium terephthalate (TPA) and benzoic acid (BA). The fluorescent compound hydroxy terephthalate (OHTPA) is formed when TPA reacts with OH• (Didenko and Suslick, 2002). BA has been previously used in marine environments and reacts with OH• to form the stable product hydroxybenzoic acid (OHBA) at constant ratios of the ortho (o) - meta (m) - and para (p) - configurations (Zhou and Mopper, 1990).

This study aimed to establish a procedure for determining OH• formation rates in marine sediments using TPA. We found that TPA reacts with OH• in marine sediments resulting in concentration profiles similar to OHBA. The ionic strength of seawater competes with the reaction between both probes and OH•, but both probes give detectable signals in seawater. By intercalibrating TPA with BA, we arrived at a conversion factor of 2.82 ± 0.09 moles OH• reacted per moles OHTPA produced between OHTPA concentrations and cumulative concentrations of OH•. Since TPA has a lower detection limit than BA, TPA is the preferred probe. In addition, the method works best when using a TPA concentration of 5 mM, slicing cores under nitrogen atmosphere, deducting the fluorescence signal from a control, and using propanol to quench the reaction between TPA and OH• at the end of an incubation.

2. MATERIALS AND PROCEDURES

2.1 Concentration determinations of OHTPA and OHBA

OHTPA is not commercially available and was synthesized from 2-bromoterephthalic acid (95%, Aldrich) according to a reported (Field and Engelhardt, 1970; Miura et al., 1988) and modified method (Qu et al., 2000; Yan et al., 2005) using hydrochloric acid (certified ACS Fisher), anhydrous sodium acetate (enzyme grade Fisher), phenolphthalein (certified ACS Fisher), potassium hydroxide (50% w/w Labchem), sodium hydroxide (extra pure Across) and copper powder (99% Across). OHTPA fluorescence was determined in 1 cm quartz cuvettes using a Hitachi F-2500 fluorescence spectrophotometer at λ_{ex}=315, λ_{em}=425 nm (Qu et al., 2000). An OHTPA standard solution (0.1 to 100 $\mu molL^{-1}$, prepared by diluting a 100 $\mu molL^{-1}$ solution) was used to calibrate fluorescence determinations.

OHBA standard solutions were prepared with p-OHBA (99+% Across) using Milli-Q water. OHBA was quantified by HPLC using a Hewlett-Packard 1100 liquid chromatography system. A hypersil ODS-2 column (5μm particle size, 25 cm length, 4.6 mm i.d.) was used for all separations (Lindsey and Tarr, 2000; Zhou and Mopper, 1990). Samples were brought to pH 2-3 using H_2SO_4 then loaded into a 1.5 mL loop. The analytes were pre-concentrated on-column during the initial 3 min, and were then eluted by increasing the solvent strength. The elution gradient was: water at pH ~2.5 (A) and acetonitrile (HPLC grade Fisher) (B); 0-3 min 15% B, 3-13 min linear to 75% B, 13-15 min linear to 100% B. The flow rate was 1.0 $mLmin^{-1}$. Analytes were detected by absorbance at 254 nm.

2.2 Determination of the effect of ionic strength on the reaction between OH• radicals and TPA or BA

A set of probe solutions with Fenton reagent additions was used to investigate the effect of ionic strength on apparent OH• formation rates and the optimal probe concentration to evaluate OH• formation rates. The Fenton reaction was produced by mixing hydrogen peroxide (30% Fisher) and ferrous sulfate (certified by the American Chemical Society (ACS) Fisher). Milli-Q water was used in the preparation of chemicals, standards, and artificial seawater (ASW) solutions.

2.3 Sediment-core collection and incubation procedures

Sediment cores were collected by SCUBA divers at four meters depth, the cores were sealed with rubber caps and duct tape immediately after collection, and were stored in a cooler until incubation. Cores were collected using polycarbonate tubes, 25.6 cm tall and 8.9 cm in diameter with holes every 5 mm along the sides. A black PVC sleeve covered the tube to seal the holes during collection. Incubations were started within one hour of sediment core collection. All experimental incubations were carried out in triplicate. Controls were used for both TPA and BA incubations, since humic acid fluorescence overlaps with OHTPA fluorescence and OHBA can be derived from lignin degradation (Lobbes et al., 1999).

Before the start of the incubation, oxygen-concentration profiles were determined using a needle oxygen electrode (Unisense OX-N) connected to a picoammeter (Unisense PA 2000). The oxygen electrode was mounted in a micromanipulator to obtain one reading every 0.5 mm according to previously established procedures (Clesceri et al., 2005). At the start of the incubation, 500 µL of TPA (approximate final pore water concentration 4.4 mM) or BA (approximate final pore water concentration 0.2 mM) solutions were injected into the intact cores through the core-tube holes by puncturing the PVC sleeve with a syringe. Sediment porosity determined from previous samples collected at the same site was used to estimate pore water concentrations. Finally, all core tubes were resealed, with rubber caps and duct tape, and incubated in the dark for 24 hrs at 16ºC.

At the end of the incubation, oxygen concentration profiles were determined again. The top 50 mm of the sediment cores were sliced every 5 mm for the first 10 mm and then every 10 mm for the remainder of the isolated 50 mm section. Each sediment slice was delivered to a muffled (500ºC, 6 hours) glass 50-mL centrifuge tube and the sediment samples were centrifuged at 2500 rpm for 20 minutes to separate the sediment pore water from the sediment. The sediment pore water was removed using a glass pipette and filtered using muffled (450ºC, 3 hours) GF/F filters. Filtered samples were delivered to in muffled glass scintillation vials and stored at 4ºC in the dark. All concentration determinations were carried out within 12 hours of sample collection.

2.4 Sediment core experiments
A series of core incubation experiments were designed to evaluate the possible application of both molecular probes to detect OH• concentrations in sediment pore water. Anoxic sediment core slices exposed to oxygen are likely to undergo redox reactions that could affect apparent OH• formation rates. Thus, we tested the effect of slicing sediment samples in pure nitrogen versus air. Probe solutions were quenched with propanol in previous experiments but the performance of TPA and BA in sediments using this reaction quencher needed to be evaluated to test the potential inhibitory effect of propanol on the OH• and probe reaction. Probe solutions were injected into nine sediment cores collected in June 2009 to compare OH• detection in marine sediments using TPA and BA as molecular probes. Cores were collected according to procedures previously described.

3. RESULTS AND DISCUSSION

3.1 Intercalibration of TPA and BA response
A conversion factor was calculated to estimate OH• detected by TPA. The number of OH• moles reacted per mole of formed OHBA has been found to be 5.87 ± 0.18 moles (Armstrong et al., 1960; Lindsey and Tarr, 2000; Zhou and Mopper, 1990). In order to estimate a factor for OH•/TPA, we used the ASW data from the previous experiment and the average concentration for OHBA and OHTPA. A linear fit for OHBA (0.0026) and OHTPA (0.0054) were used to calculate a conversion factor by dividing the OHBA slope by the OHTPA slope (0.48) (Fig. 3). This factor was multiplied by 5.87 ± 0.18 OH• moles and the number of OH• moles reacted by moles of OHTPA corresponded to 2.82 ± 0.09 OH• moles. This value can be used in seawater experiments to calculate OH• concentration using TPA as a molecular probe.

3.2 Sediment-core-incubation experiments
3.2.1 TPA response to different atmosphere conditions during core slicing

Our results showed that OHTPA concentration profiles resulted in higher OH• concentrations in the first 10 mm of sediment (Fig 2A). OH• concentration decreased with depth in sediment cores sliced under a nitrogen atmosphere. In contrast, an air atmosphere resulted in OHTPA concentration profiles that showed a subsurface maxima of OH• concentration at 10 mm then decreasing with depth and increasing again at 50 mm. While these results appeared to exhibit a difference between the OHTPA profiles obtained under nitrogen and air atmosphere, the difference was not statistically significant (p□0.05, two tailed paired *t*-test). Despite the fact that we did not find a difference directly relevant to OHTPA, we decided to use a nitrogen atmosphere for the following experiments. This decision was supported by the evidence of changes in the distribution of reduced iron in sediment cores which may point out possible changes in the redox conditions of marine sediments during slicing under regular atmospheric conditions (Burdige et al., 2004; Burdige and Zheng, 1998). The oxic-anoxic interface in the sediment cores was defined by an average oxygen profile obtained for each experimental condition (Fig.2B).

3.2.2 TPA response to the use of propanol as OH•-probe reaction quencher

Our OHTPA profiles results indicate that higher OH• concentrations occur in the first 10 mm of sediment with a decreasing OH• concentration with depth in sediment cores amended with propanol (Fig. 3A). In contrast, cores amended with ASW resulted in higher OHTPA concentrations with an increasing OH• concentration with depth in sediment core samples over the surface 30 mm, then decreasing slightly down to 50 mm. Results indicated a significant difference between the OHTPA profiles from cores with and without using propanol (p□0.05, two tailed paired *t*-test). Based on these results and the fact that the difference was clear between treatments we decided to use propanol as a reaction quencher after slicing samples under a nitrogen atmosphere. This decision was supported by the smaller variability between triplicates of the propanol experiment represented by the error bars (Fig. 3A). The oxic-anoxic interface in the sediment cores was defined by an average oxygen profile obtained for each experimental condition (Fig.3B).

3.2.3 Evaluation of OH• detection by TPA and BA

OHBA and OHTPA control profiles showed lower concentrations than OHBA and OHTPA experimental profiles (Fig. 4A). An average oxygen profile was obtained for each experimental condition (Fig.4B). OHBA and OHTPA experimental profiles showed higher OH• concentrations over the first 10 mm of sediment with a decreasing OH• concentration with depth. No significant difference was found between the OH• profiles obtained by the BA and the TPA approaches (p□0.05, two tailed paired *t*-test). These results support that both analytical approaches were in good agreement with each other.

Some studies have pointed out the higher selectivity of TPA over BA to capture OH• (Buxton et al., 1988; Saran and Summer, 1999). Another important aspect to consider is the difference in pH dependence of each molecular probe. The TPA hydroxylation reaction is almost independent of pH in the pH 5-8 range (Li et al., 2004), which makes it suitable for OH• detection in the pH range of seawater and sediment pore water samples. In contrast, the BA hydroxylation occurs faster under acidic conditions only (Lindsey and Tarr, 2000; Saran and Summer, 1999).

4. CONCLUSIONS

A procedure for determining OH• formation rates in marine sediments using TPA was established. OHTPA and OHBA were determined in Milli-Q water, ASW, and sediment pore water samples. The optimal TPA and BA concentrations to detect OH• formation were 5 mM and 0.2 mM respectively, agreeing with previous reports (Lindsey and Tarr, 2000; Saran and Summer, 1999). OHTPA and OHBA detection limit determinations were 0.04 nM and 0.07 nM, respectively.

The ionic strength of seawater competes with the reaction between OH• and both probes. TPA and BA performance to detect OH• clearly showed that OH• formation rates were quenched by the presence of anions in seawater but both probes give detectable signals in seawater.

A working range for TPA and BA concentrations for use in seawater samples was clearly defined with very small differences in performance for different concentrations of TPA and BA. After an intercalibration between TPA and BA response, a conversion factor of 2.82 ± 0.09 moles OH• reacted per moles OHTPA was obtained. This conversion factor could be used in future determinations in seawater and sediment pore water samples.

Our results showed not only that OH• were formed in marine sediments, but also that the higher OH• concentrations were linked to the oxic-anoxic sediment interface. The higher OH• concentration found at the region of the sediment oxic-anoxic interface correspond to the idea that this region is where the Fenton reaction in sediments would take place under intermittent redox oscillations in sediments with the subsequent limited presence of Fe^{2+} and H^2O^2 (Burdige, 2006; Canfield, 1994; Mayer, 2004).

This finding is of great importance to the knowledge of OM preservation and remineralization in sediments, where intermittent oscillation in redox conditions has been linked to degradation of recalcitrant OM by oxygen-containing reactive species such as H^2O^2 and OH• (Paciolla et al., 1999; Voelker et al., 1997).

ACKNOWLEDGEMENTS

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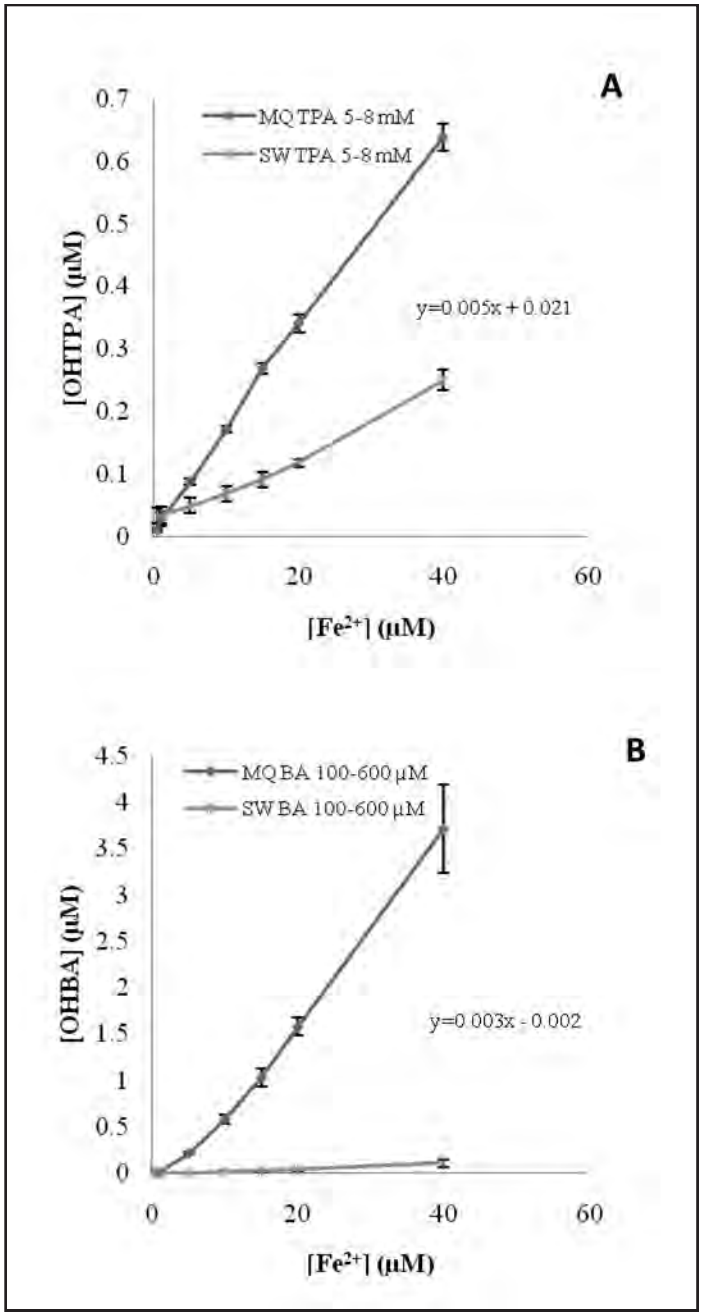

FIGURE 1. Evaluation of the ionic strength effect on the performance of (A) TPA (5-8mM) and (B) BA (100-600 μM) as molecular probes to capture OH•. Fenton reagents at increasing concentration were used to estimate each probe response. The resulting OHTPA and OHBA concentrations were higher in Milli-Q probe solutions. A ratio for the SW OHBA/OHTPA resulted in the number of OH• moles that react by number of OHTPA moles in this case 2.82 ± 0.09 OH• moles.

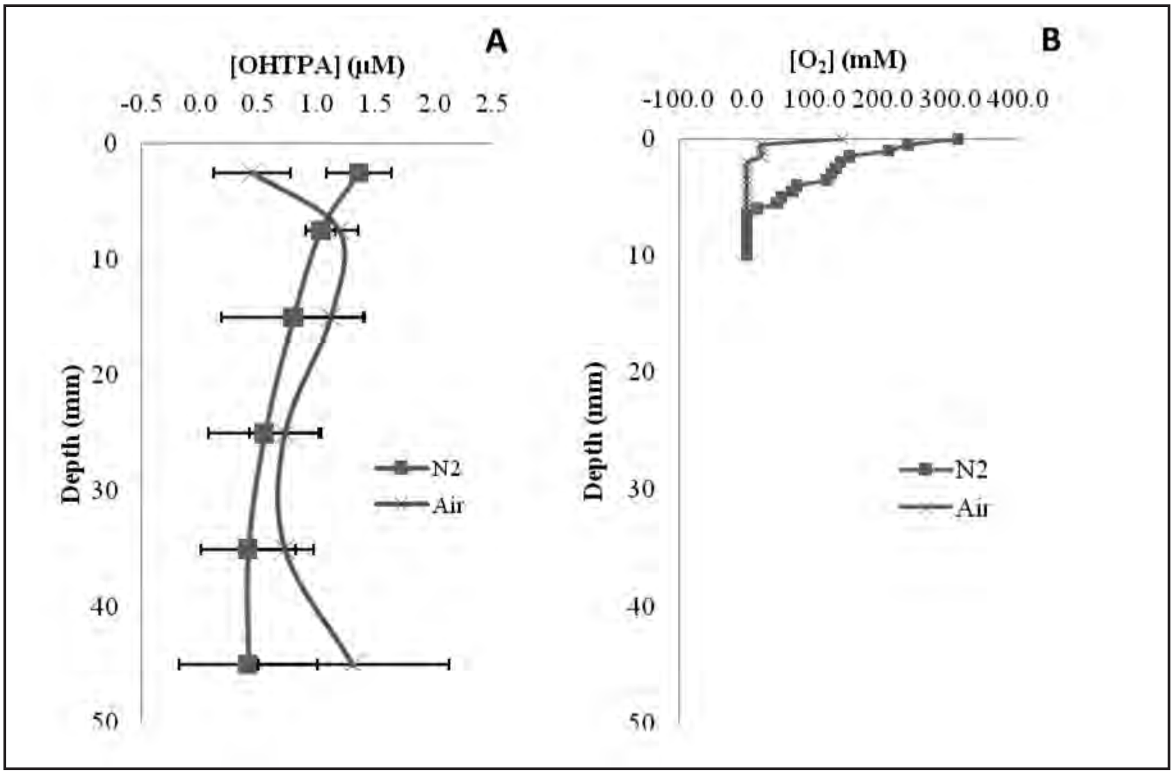

FIGURE 2. Sediment-core incubation experiment results. (A) OHTPA profiles for sediment cores sliced under nitrogen and oxygen atmosphere, and (B) oxygen concentration profile for each experimental condition. Oxygen decreased with sediment depth. Control core OHTPA concentrations were subtracted from experimental cores.

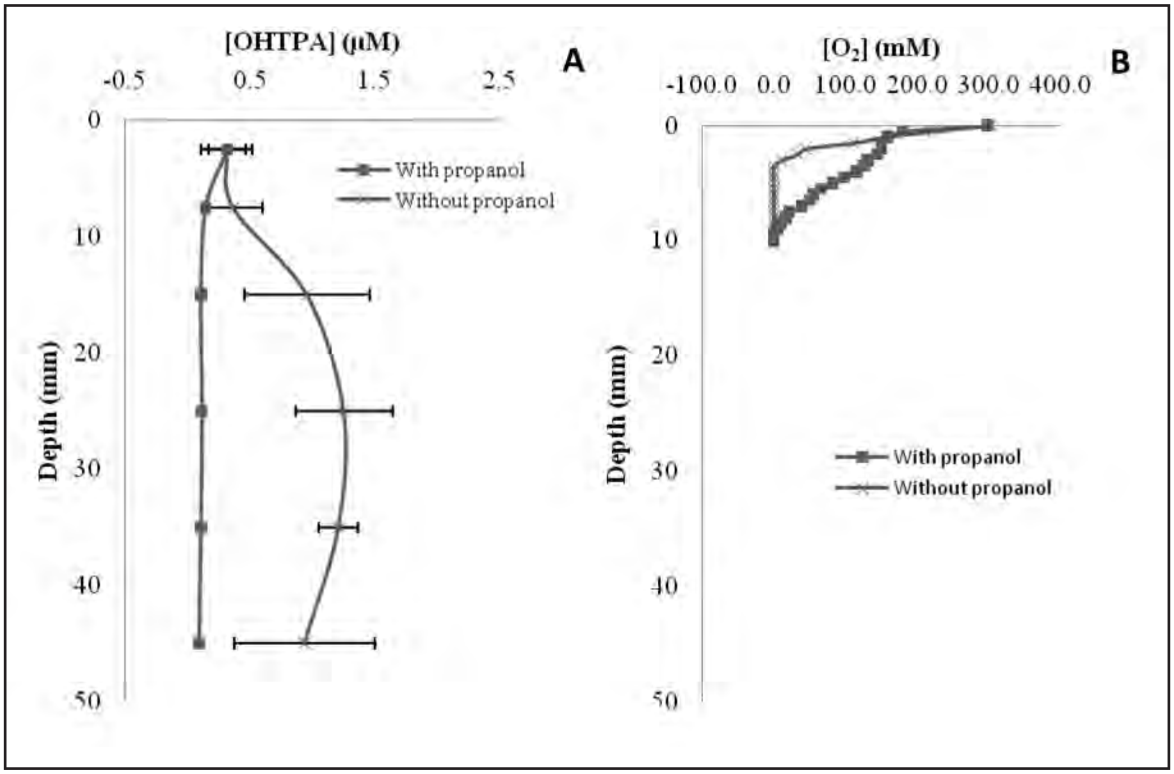

FIGURE 3. Sediment-core incubation experiment results. (A) OHTPA profiles for sediment cores sliced under nitrogen amended with propanol and non propanol, and (B) oxygen concentration profile for each experimental condition. Oxygen decreased with sediment depth. Control core OHTPA concentrations were subtracted from experimental cores.

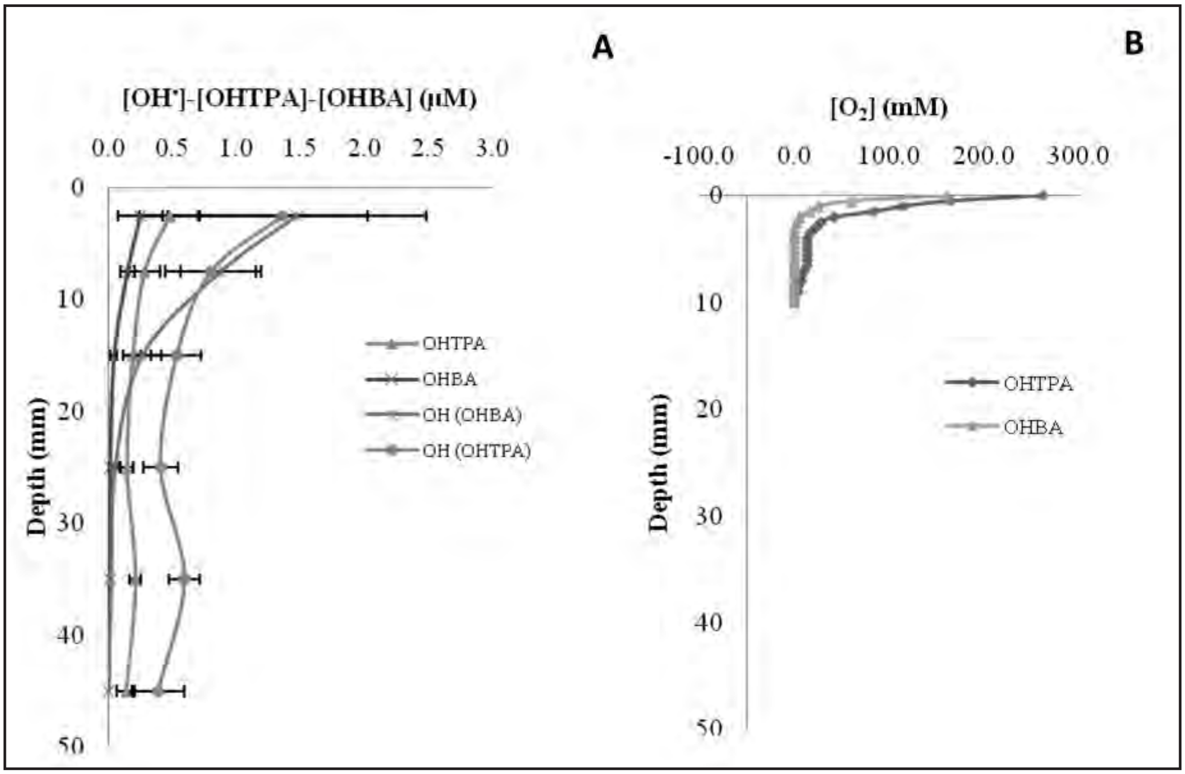

FIGURE 4. Sediment-core incubation experiment results. (A) OHTPA, OHBA, OH•, and (B) oxygen concentration profile for each experimental condition. Oxygen decreased with sediment depth. Control core OHBA and OHTPA concentrations were subtracted from experimental cores. OH• concentration profiles were calculated using BA (5.87±0.18) and TPA (2.82±.08) factors. OH• concentration obtained from both analytical approaches agreed and both indicated that higher OH• concentrations were found at oxic-anoxic sediment interface where Fenton reaction in sediments takes place.

A Change in the Wind: Long Term Trends in the Forcing of Long Island Sound

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ABSTRACT

The distribution of materials in Long Island Sound is sensitive to the pattern of the circulation which is strongly influenced by the wind directly and through its effect on sea level variations at the boundaries. Long term changes in the characteristics of the wind field have been noted at Providence, RI, and Bridgeport, CT. We present an analysis of all the existing long term wind records in New England and demonstrate that there has been a 20% decline in the summer and winter mean wind speed over the last 50 years throughout the region. We also note that both the summer mean vector velocity components have declined as has the winter mean eastward velocity component . The evolution of the North Atlantic Oscillation index leads us to suggest that the reductions we observe are a consequence of changes to the characteristics of synoptic scale systems.

1. INTRODUCTION

Long Island Sound (LIS) is a shallow embayment in southern New England that is separated from the ocean by Long Island, NY. Figure 1 shows a map of the coastline of the region together with locations to which we refer. The central axis of LIS lies almost parallel to the orientation of the adjacent continental shelf (approximately 70°) making it particularly sensitive to the east component of the wind stress. It has an average depth of 21 m and is 160 km in length. To the east, LIS is bordered by Block Island Sound (BIS) and the southern New England shelf. To the west, it is connected to the estuary of the Hudson River by the East River, a tidal strait.

Both tidal and meteorologically forced variations in sea level on the adjacent shelf propagate into LIS through The Race and the East River. However, Wong (1990) demonstrated that the East River effectively filters out the energetic high frequency (diurnal and semidiurnal) sea level variations from the lower Hudson though it does allow the low frequency disturbances to propagate in to western LIS. The high frequency variability of the circulation in the Sound is, therefore, dominated by the tides forced at the Race. Wong (1990) showed that low frequency sea level differences along the Sound are controlled by the difference in the response of the shelf to wind at Sandy Hook, in the apex of the New York Bight (see Figure 1), and at Montauk Point, which lies at the ocean boundary of BIS. Presumably, the meteorologically forced along Sound pressure gradients described by Wong (1990) modulate the density driven exchange through the East River and, consequently, the transport of dissolved materials.

O'Donnell et al. (2007 and 2008) showed that stratification in western LIS was sensitive to winds from the northeast and that the frequency of occurrence of winds from that direction exhibited decadal scale fluctuations. Between 1947 and 2003, hourly wind observations at Bridgeport during July and August fell in the range 15°− 75° true 12% of the time. This fraction varied ± 3% with positive anomalies in the 1950s and 1997-2003 and several periods of negative anomalies between 1960 and 1997. Pilson (2008) examined record of wind speed at Providence, RI, between 1964 and 2006 and showed that the mean monthly wind speed had decreased from 17.5 to *14.5 km/hr* during that period. There is, therefore, substantial evidence of long term trends and cycles in the magnitude and direction of an important forcing agent of the circulation in LIS and that this is likely to influence the variability of the ecosystem.

In this paper we examine the wind data archive maintained by the National Climatic Data Center to assess whether the variations in the characteristics of the wind discovered by O'Donnell et al. (2007) and Pilson (2008) are local phenomena or whether they are representative of the entire New England region. Since the circulation is sensitive to the wind stress, a vector which is usually parameterized with a quadratic dependence on the velocity components, we also report the long-term variations in the monthly mean velocity components. In section 2, we summarize the data sources and the characteristics of the data record. We then describe the data analysis procedures. In Section 3 we present the results. In the final section we discuss the implications of our findings.

2. DATA AND ANALYSES

The National Climatic Data Center (NCDC) maintains an archive of hourly meteorological observations at a global array of locations. We extracted all the records obtained in New England between 1940 and 2005 for analysis. These station extend from Caribou, ME, to Lakehurst, NJ, and Bangor, ME, to Buffalo, NY. Note that the station histories are all different. Some stations were moved or had the altitude of the sensors moved. In others the records were interrupted. We discuss these issues when they effect the analyses. Since we are interested in trends at each station, we did not adjust measurements to a standard elevation above the ground.

The data were converted from the WD16 (1948-1964), WIND (1964-1995) and WND2 (1995-2005) formats to vector velocity components in *m/s*. The difference in these formats is mainly a consequence of the directional resolution of the anemometers. Monthly mean vector components and speeds were then computed for each station, as were the standard deviations of these quantities.

The annual cycle of the wind speed throughout the northeast is remarkably consistent. For all 33 stations, the annual cycle of the mean monthly speed are almost co-linear when the annual mean at the stations are subtracted. The maximum speeds occur in the winter during the February-April interval and that minimum speeds occur in late summer, July-September. The amplitude of the variations range from 0.5 to 1*m/s*. To examine the long term evolution of the wind field we also computed the seasonal means by averaging over these three -month intervals.

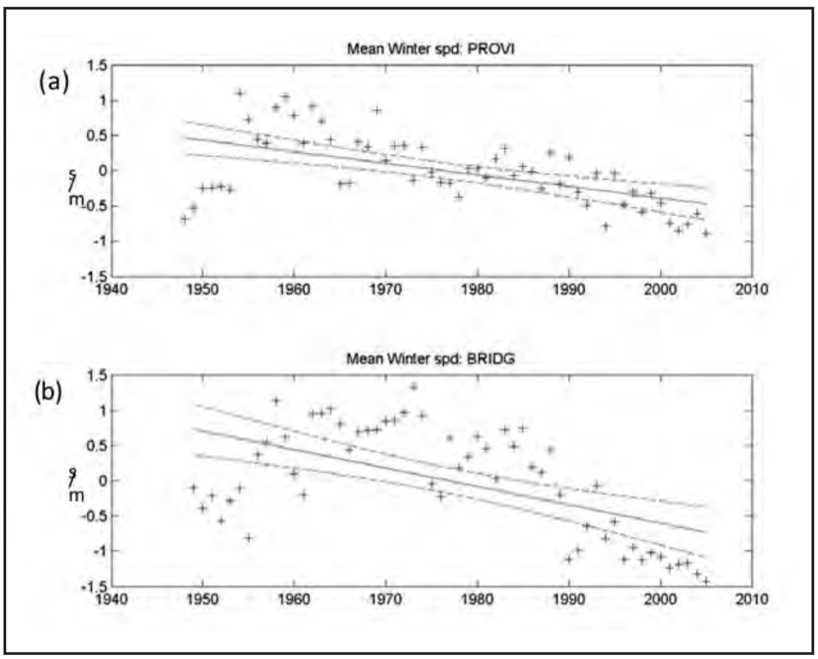

Figure 1.
Time dependence of the winter average wind speed at (a) Providence and (b) Bridgeport. The solid lines show the least squares regression of a linear trend through all the data and the dashed lines show the 95% confidence interval.

3. RESULTS

Following Pilson (2008), the deviation from the long term winter average wind speed at Providence is shown in Figure 1a. The variation of the same property at Bridgeport is shown in Figure 1b. The straight solid lines in these figures is the result of a linear regression through the data and the dashed lines show the 95% confidence intervals (Emery and Thompson, 2001) . The decline of the average summer wind speed at Providence is approximately 1 *m/s* over the last half century. At Bridgeport, a station approximately 100 km to the west, the decline is almost 2 *m/s.*

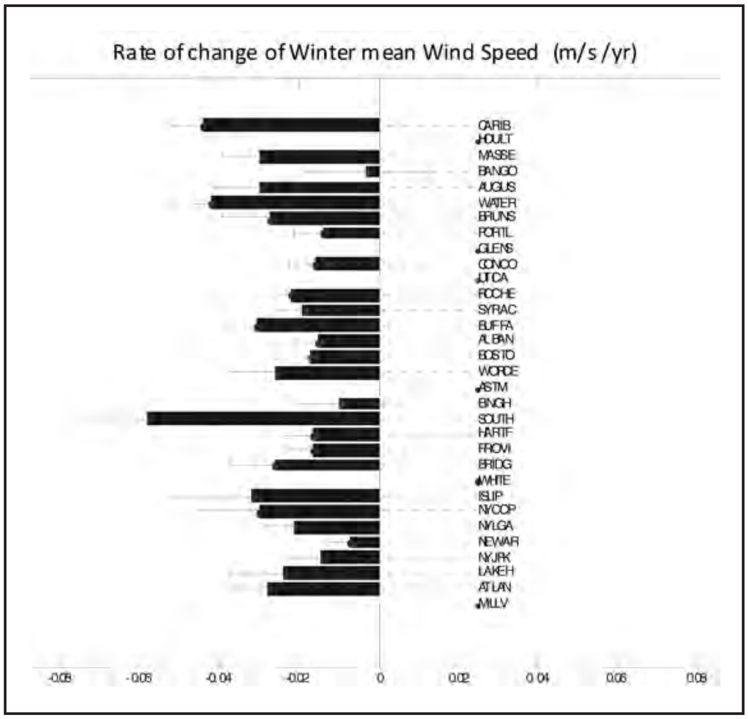

FIGURE 2. Variation of the rate of change of the winter mean wind speed (m/s /yr) among the stations with more than 20 years for which estimates could be made.

Note that a large fraction of the data shown in Figure 2 lie outside the confidence interval and that there is serial correlation in the residuals, a clear indication that the assumption of a linear decline is overly simplistic. This long term trend is superimposed on decadal-scale variations which are much more complex. However, for the purposes of describing the very long term changes in this large data set, the slope of the linear regression line is a helpful summary statistic. Of course, other possibilities include comparing the average seasonal mean between, for example, 1950-1960 and 1995-2005.

We applied this regression procedure to all the 26 stations for which more than 20 years of seasonal means could be estimated and Figure 2 summarizes the results for the rate of change of the winter mean wind speed. The solid bars show the rate of change and the error bars indicate the 95% confidence interval (assuming the residuals are independent). All stations show a decline and only Bangor, ME, and Binghamton, NY, have confidence intervals that include zero. Applying this approach to the summer means yields similar results: all stations except Bangor exhibit a decline and only Binghamton, NY, Bridgeport, CT, Newark, NJ, and Lakehurst, NJ, have confidence intervals that include zero.

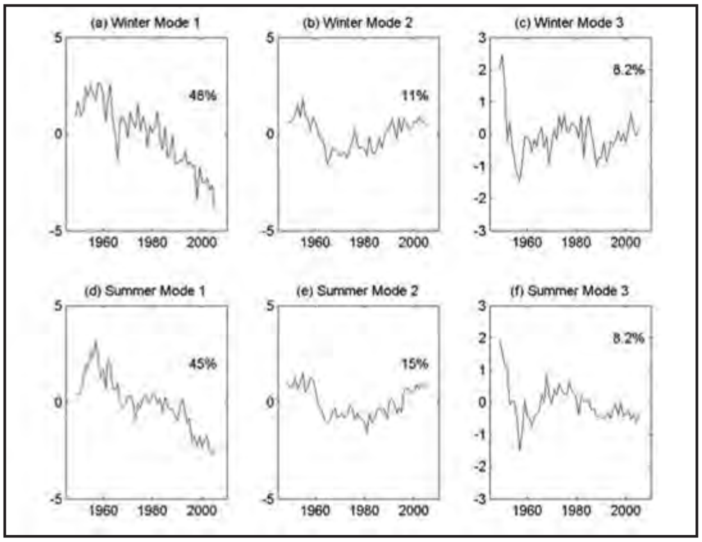

FIGURE 3. Amplitude of the first three empirical orthogonal functions for 17 stations (see Table 1) with continuous records of mean winter (a-c) and summer (d-f) wind speeds.

An empirical orthogonal function (EOF) analysis (see Emery and Thompson, 2001) seeks to find patterns that are common to several time series. It is a non-parametric approach and therefore avoids the limitations imposed by regression which requires an *a priori* hypothesis about the structure of the pattern. The difficulty is that the time series must be continuous and over a common time interval. Fortunately, the seasonal mean speed series at 17 stations were continuous for the interval 1947-2005 and we subjected these series to EOF analyses. Figure 3 shows the time evolution of the amplitudes of the first three modes of for the winter (a-c) and the summer (d-f). In both the seasons the first mode explains almost 48% of the variance in the observations and the amplitude shows a temporal decline. The second mode explains and additional 10% of the variance and describes an decrease from the 50s to the 70s and then an increase from 1980 to 2005.

4. SUMMARY AND DISCUSSION

It has been noted by Pilson (2008) that the mean summer wind speed at Providence has declined over the last half century. Our analysis of all of the records in the NCDC Surface Airways data archives for stations in New England has revealed that this is not the result of a local anomaly or flaw in the meteorological instruments at the site. It is clearly a manifestation of a regional scale change in the wind climatology. Estimates of the rates of decline are uncertain since the slopes obtained by regression are sensitive to the data distribution and decadal-scale variations. The average over all stations during winter is -0.024 *m/s/yr* and during summer we obtained -0.018 *m/s/yr.* There are suggestions of decadal-scale variations in the data records but these are not clearly revealed in the time series or the EOF analyses.

Though we do not present the details here, we also explored the long term variation in the velocity components and found similar results. Both the east and north summer mean velocity components exhibited a long term decline at all but 2 stations. The winter mean east components were also all negative. The winter mean northward components were less consistent and only three stations showed trends that were significantly different from zero as determined by the 95% confidence interval.

The leading model of atmospheric variability at seasonal time scales is known as the North Atlantic Oscillation (NAO). Hurrell (1995) defined an index of the NAO cycle that is based on the difference in departures of sea level pressure variations from the long term mean between Iceland and Portugal. The index is, therefore, a measure of the meridional pressure gradient and it is highly correlated with the strength of the westerly winds over the North Atlantic. The decadal-scale variations in the NAO index are well known and have been shown to influence rainfall and temperature throughout Europe and, to a lesser extent, the eastern seaboard of the United States. Curiously, the index has been increasing since 1960, when it was at the lowest value for over a century, which correspond to the time the mean winds in the northeast begin to decline. That declining seasonal mean westerly wind components should correlate with the increasing NAO is surprising, the reverse is expected. However, as Hurrell et al. (2003) point out, the changes to the seasonal mean pressure fields that the NAO describes also modify the tracks of synoptic scale storms. A shift to the northeast is associated with positive NAO periods as is a modest reduction in the intensity of storms in the southern range. This suggests that the explanation for the decline in the mean velocity components and speed we report may require an analysis of the high frequency fluctuations.

The data we present clearly reveals that mean surface wind speed and the velocity components in New England have significantly fallen in magnitude over the last five decades. However, this analysis raises more questions than it answers. It will likely be necessary to examine a more extensive data set and global models to understand how this phenomena is linked to the northern hemisphere atmospheric circulation. Further, since the wind forces the shelf circulation and exchange between estuaries and the inner shelf, these changes may translate to long term modifications to coastal ecosystems. The potential magnitude of these effects deserve urgent attention if the impacts of management action and human activities are to be detected.

ACKNOWLEDGEMENTS

I am grateful to Prof. S. Nixon of the University of Rhode Island for drawing my attention to the observations that show the long term decline in the monthly mean wind speed at Providence, and to J. Edson and W.F. Bohlen for helpful suggestions. This work was supported by the EPA Long Island Sound Program.

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ABSTRACTS

Generation and Propagation of M6 Overtides in Long Island Sound

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Nonlinear mechanisms give rise to overtide frequencies that are integer multiples of the principle tidal frequency. The M6 is an overtide with a frequency three times that of the primary M2 semidiurnal tide. Overtides are of interest because they modulate or distort the shape and timing of the fundamental tide. Because their generation and propagation is sensitive to a combination of physical factors, they can also serve as a means by which to evaluate hydrodynamic model performance.

Observations in Long Island Sound (LIS) indicate that the M6 overtide shows a notable increase in amplitude in the Western Sound compared to the East. M6 generation, however, should be greatest in the East, where the primary M2 current is strongest. We examine the generation and propagation of the M6 in simple channels using numeric and analytic methods and show that, despite its higher frequency, attenuation at the M6 frequency is less than that at the M2. The observed spatial distribution of M6 amplitudes can therefore be explained as a consequence of non-local generation and propagation.

These results imply that those portions of an estuary which are strongly dissipative at the M2 frequency may nevertheless be weakly dissipative at the M6 frequency. This effect would be particularly important in shallow and shoaling areas of an estuary and the distribution of M6 amplitudes is a sensitive indicator for the tuning of hydrodynamic models in shallow regions. We conclude by comparing the observed distribution of M6 amplitudes in LIS with those from hydrodynamic models of the region.

Observations of Wind Response in Central and Western Long Island Sound

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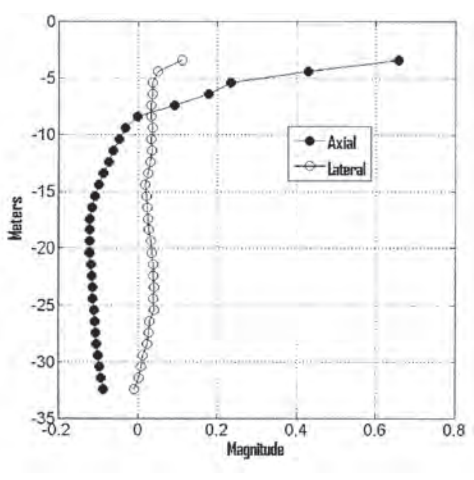
Current observations available from multiple adcp moorings in central and western Long Island Sound are analyzed to describe the characteristics of the response to variable wind forcing. Current response has a distinct vertical structure as indicated by that from an NOS mooring at 73^{o} 45.96'; 40^{o} 50.41' (Figure 1). Directional sensitivity and implications for both vertical mixing and exchange flows are discussed. Companion model results provide a description of detailed spatial patterns in response.



Vertical Structure of Mode 1 Subtidal Current Fluctuations at 73^{O} 45.96; 40^{O} 50.41

An Inverse Approach to Modeling Residual Circulation in Western Long Island Sound

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The occurrence of seasonal hypoxia in western Long Island Sound is well established. This has prompted intense seasonal surveys to determine more precisely the circulation and density conditions that persist in this region on a seasonal timescale. I will demonstrate how the use of harmonic analysis and spatial smoothing of data collected during ship surveys can reveal the state of the estuary over the duration of the survey, and further how this relates to steady-state conditions. Using weighted total least squares, it is also possible to test whether the traditionally assumed dynamics of estuarine circulation are consistent with these measurements in western Long Island Sound.

Estuary-Shelf Exchange Pathways for the Long Island Sound

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Buoyant waters exiting the Long Island Sound and denser waters entering from the shelf tend to flow along preferred pathways. The physical and chemical characteristics of the waters exchanged depend on these paths. These pathways can vary with forcing conditions. Under density-driven conditions, near-surface buoyant waters flow with the coast on the right (in the northern hemisphere) and the incoming saltwater is offset both vertically and horizontally. Tidal residual circulation and wind-driven flow can create other exchange pathways. This numerical modeling study investigates exchange for the Long Island and Block Island Sounds, with connections to the shelf via several passes between islands, to determine where incoming shelf waters come from under different forcing conditions. Simulation results indicate that the tidal residual circulation creates indirect routes into and out of the estuary. Wind-driven currents during storms, in contrast, lead to more direct pathways that can advect shelf waters from different areas than usual. Passive tracers are used to track waters entering the estuary from different shelf regions and waters exiting from the Connecticut River, the largest freshwater source. Variations of pathways and corresponding freshwater and saltwater fluxes are analyzed for spring and neap tides, high and low discharge, and eastward and westward wind conditions.

Characterization of Solar Radiation Energy Input to Long Island Sound – With Application Toward Understanding the Variability in the Severity of Hypoxia

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Hypoxia, extremely low levels of dissolved oxygen, occurs primarily in the bottom waters of western Long Island Sound (LIS) during the summer months. A critical factor affecting the duration and extent of this hypoxic condition is that atmospheric oxygen is inhibited from penetrating downward into the bottom waters because a stable density stratification in the water column develops during summer. This density stratification is caused by large energy inputs through the surface combined with a reduction in wind-induced mixing. Solar radiation is the dominant mechanism of energy transfer into LIS surface waters during the onset and development of hypoxia.

This presentation will discuss efforts to characterize the spatial and temporal variability of solar energy input into LIS with emphasis on a correlation to the severity of hypoxia. Results presented will include surface measurements from shore stations, moored buoys and the R/V Connecticut as well as estimates of surface solar radiation derived from numerical radiative transfer model predictions based on satellite data.

Observed Tidal Cycles of Stratification, Shear & Turbulent Overturns in Eastern Long Island Sound

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Moored CTD profiler records from a site in eastern Long Island Sound near the estuary axis are used, together with multiple years of several-times daily ferry-based current profile observations made on a nearby transect, to characterize tidal cycles of stratification, shear, and turbulent overturns. The moored profilers collected free-ascending casts ~hourly for periods of several weeks, and are used to examine tidal cycles in stratification, and in turbulent overturns based on Thorpe sorting. During a 9-week fall 2002 deployment, stratification peaked during late ebb and was minimal during peak flood, as expected due to tidal straining of the along-estuary density gradient. Thorpe sorting identified about 260 turbulent overturns, each of which passed stringent tests to remove false overturns due to sensor noise. Overturns occurred at all depths, with typical heights ~0.75 to 2.5 m, and slightly larger values in the upper water column. Thorpe scales were typically 0.5 to 1.5 m and related linearly to overturn heights, with the ratio near the maximum theoretical value, implying the overturns were at most several hours old, as expected given the timescales of tidal- and wind-related processes driving turbulence. Based on standard scaling relationships for dissipation and eddy viscosity in terms of Thorpe scale and buoyancy frequency across the overturn, dissipation rates ranged from about 2×10^{-8} to 6×10^{-7} W/kg and eddy viscosities ranged from about 10^{-4} to 10^{-3} m2/s. In the upper water column, overturns were significantly more common during the early/peak ebb current than the rest of the cycle, but at deeper depths there was a bimodal distribution with overturns most common during late flood as well as during early/peak ebb. The implication is that bed friction controls the tidal cycle of turbulence in the deeper part of the water column, but in contrast, the tidal cycles of shear and stratification set upper water column turbulence. Significantly, during spring 2003 and fall 2003 deployments at the same site, not only did stratification and overturn characteristics differ from the fall 2002 conditions, but the phasing of tidal cycles in overturns also did not follow similar patterns. This suggests the phasing of overturns is sensitive to week-to-week and seasonal changes in the background conditions. Based on harmonic fits to the ferry-based current measurements, shear takes slightly higher magnitudes in the upper water column, peaks with opposite senses during late ebb and peak flood, and is minimal during early and late flood. A leading-order term in the tidal-average momentum equations is determined by the relative phasing of the tidal cycles of shear and eddy viscosity, making these findings relevant for their role in shaping how tidal processes influence the low-frequency non-tidal (residual or subtidal) circulation that determines the fate of waterborne materials.

The Role of Habitat Complexity and Heterogeneity in Structuring Benthic Communities of New Haven Harbor, Long Island Sound

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Understanding and distinguishing the physical and biological features structuring marine habitats is critical for managing coastal and estuarine resources. Habitat structure affects communities and diversity over varying temporal and spatial scales. However, how habitat structural components interact across spatial scales to shape the ecology of the benthos is poorly understood. The relationship between benthic community structure and variation in habitat complexity and variation in habitat form (heterogeneity) was examined at eight stations in New Haven Harbor. Underwater video surveys and associated sediment sampling were carried out to identify the abiotic and biotic features associated with different habitat forms. Quantitative measures of complexity, such as shell particulate length and cover, were considered in relation to species composition and diversity. In this system, shell hash contributed the most to habitat complexity, although this finding may be mediated by a seasonal influx in macroalgae. This study highlights the need for coastal and marine studies to take habitat complexity and heterogeneity into account.

Identification and Screening of Potential Upland, Beneficial Use, and Dewatering Sites for Dredged Material From Long Island Sound Region

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In preparation of the development of a regional Dredged Material Management Plan for Long Island Sound, a site inventory was performed to identify and characterize potential alternative disposal sites for dredged material within the Long Island Sound region, including 1) upland and alongshore disposal sites (including beneficial use alternatives), and 2) sediment de-watering and re-handling sites. The study area included Washington County in Rhode Island, the entire State of Connecticut, and Westchester, Bronx, Queens, Suffolk, and Nassau counties in New York, as well as the Boroughs of Brooklyn and Manhattan. Potential sites were identified and characterized for their existing uses, size, location, potential to accept dredged material, special conditions, and costs for use. Data was compiled from several sources, including the Environmental Impact Statement for the Designation of Dredged Material Disposal Sites in Central and Western Long Island Sound, phone interviews with site owners, aerial photos, municipal land records, local planning and zoning officials, and State and Federal GIS data layers. Sites were then screened against criteria set forth by the Project Delivery Team. Those sites that did not meet these requirements and sites where owners had no interest or regulatory ability to accept material were then removed from the inventory. Ultimately, an inventory of about 157 potential upland and beneficial use material placement sites, and 22 potential dewatering sites was developed. This inventory will provide the U.S. Corps of

Engineers and other dredging proponents a list of environmentally acceptable, practicable management alternatives that can be considered in their analysis of options to manage their dredging projects. These upland and beneficial use sites provide an alternative to open-water disposal of dredged material in Long Island Sound.

First Observations Over Long Island Sound with the Hyperspectral Imager for the Ocean (HICOTM)

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The Hyperspectral Imager for the Coastal Ocean (HICOTM) was designed by the Naval Research Laboratory and is a space-borne instrument presently flown on the International Space Station (ISS) [1]. The spectral range of HICO is from 0.4µm to 0.9µm, with a spectral resolution of about 6 nm, allowing detailed spectral analysis of marine features that cannot be resolved with other color imagers presently flown at spacecraft altitude.

The presentation will introduce techniques that were applied in interpreting HICO data over Long Island Sound. Based on three HICO-RGBs, various band ratios and resulting color composites, as well as supervised classification with the Spectral Angle Mapper (SAM), provided information about plume structure along the northern coast of the Long Island Sound but showed different spectral response along the Long Island coast. The ground resolution of about 90 m at nadir makes it possible to identify fine color gradients and frontogenesis. The interpretation of HICO-RGB imagery will be compared with auxiliary data.

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Distributions of Organic Contaminants and Metals in Western Long Island Sound: Insights from Novel Sewage Source-specific Tracers

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Organic and metal contaminants in Long Island Sound are derived from a combination of sources, including, but not limited to, sewage discharges which are most intense in the metropolitan region in the western Sound and atmospheric deposition. Redox sensitive elements that are generally less particle reactive may become enriched in sediments under suboxic or anoxic conditions existing in overlying waters or sediments (e.g., Mo, Re, U, and even Cd), or preferentially mobilized (e.g., Mo). Our study aimed to compare and contrast the distribution of selected classes of wastewater-derived organic contaminants with different particle reactivities and expected degrees of persistence and anthropogenically mobilized trace metals that are likely to have multiple sources to LIS. Redox sensitive elements were also analyzed to explore the possibility that their distributions in surficial sediments and dated sediment cores may be indicative of spatial and temporal variations in hypoxia or eutrophication. Sampling of surficial sediments was conducted in 2008 along a 45 mile transect between more sewage impacted sites near the Throgs Neck Bridge and a site north of Mt. Sinai Harbor; to allow better comparisons, surficial grab samples and two sediment cores were collected in primarily muddy, suboxic sediment regimes.

A unique and notable aspect of this study was the measurement of a suite of waste-water derived quaternary ammonium compounds (QACs). QACs were easily detected in all sediments, and there was a consistent west to east gradient in their concentrations. Very small changes in the composition of QACs with widely varying hydrophobicities are consistent with very strong association with sediments of sorbed QACs, such that they are essentially particle tracers of sewage affected sediments. The relationships between QACs and selected trace metals suggests contribution of these metals from sewage or other WLIS sources, especially for Ag, which has often been suggested as a sewage tracer. Other trace metals do not increase as greatly towards the west, and the relationships between QACs suggest more important additional sources to WLIS. Results from the analysis of redox-sensitive metals indicates Mo is enriched in muddy suboxic WLIS sediments, but to a lesser extent than that observed in very highly eutrophied sediments from Jamaica Bay.

Mercury Contamination in Long Island Sound: Local Sources Versus Atmospheric Deposition

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Mercury (Hg) contamination in sediment from Long Island Sound and its coastal marshes shows a strong increase over the last 100-200 years. The Hg contamination sources were both local (e.g., the hat-making industries of Danbury and Norwalk, CT) and regional (e.g., coal and garbage combustion, various industries). Most sediment Hg profiles from the western Sound show a steep increase in Hg concentration and Hg accumulation rates in the early to mid 1800s. New Hg profiles from the Jarvis Creek salt marsh (Branford, CT) and from two Block Island freshwater ponds (RI; Fresh Pond and West Beach marsh) show very different time - concentration profiles. The Jarvis Creek Hg profiles are very similar to those from central and western Long Island Sound marshes, but the Block Island Hg profiles are very different. The two ^{210}Pb-^{137}Cs dated profiles from Block Island show a gentle increase since the mid to late 1800s, followed by a very steep increase starting in the late 1930s-early 1940s. The West Beach marsh core shows a gentle decline over the last 40-50 years, whereas in the Fresh Pond core the top sediment became mixed during coring. The excess Hg (Hg*) inventories at Block Island are smaller than most of the Hg* inventories of Long Island Sound sediment. The only Hg sediment profiles from Connecticut that look like those from Block Island are from cores collected at Lake Louise on top of Talcott Mountain, CT, and in Chapman Pond along the Connecticut River, CT. Both of these records are not yet precisely dated, but have small Hg* inventories, gentle increases at the bottom of the contaminated section, and steep Hg increases in the upper part of the profiles. These two locations are not affected by the local Connecticut hat-making Hg sources, and the freshwater environments of Block Island also have not been impacted by that Hg source. We therefore hypothesize that most Hg profiles from Long Island Sound sediment and coastal marshes have been impacted by Hg-rich sediment discharges from the Housatonic and Norwalk rivers, which both carried strongly Hg-contaminated sediment to the Sound from the areas with hat-making factories in Connecticut. The mixing of sediment in the Sound must have been efficient enough to carry this Hg-contaminated mud from western to central Long Island Sound with tidal flushing and storms. Long Island Sound Hg profiles thus show the impact of local and regional Hg contamination sources, whereas the mountain-top lakes such as Lake Louise and remote freshwater ponds such as those on Block Island provide insight in variations of Hg contamination through atmospheric deposition only over time.

A Four-Thousand Year TEX_{86} Record of Long Island Sound Surface Water Temperature

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Long Island Sound (LIS) has seen dramatic environmental changes since colonial times, with increased environmental degradation over the last ~ 200 years during the industrial period. In recent history LIS ecosystems have been impacted by land use changes, contaminant input, changes in nutrient input, aquatic food extraction, and climate change. In the late 1990s the LIS lobster populations collapsed, possibly caused by a combination of anthropogenic and natural environmental stressors. Ecosystem problems such as the lobster die-off are generally studied in hindsight, without detailed information on environmental conditions prior to their occurrence, and without records of similar past events and their association with specific environmental parameters, such as temperature. Core studies may offer insight into past ecosystem events and baseline environmental conditions through the use of biogeochemical proxies, including isotope and trace element studies of carbonate fossils and organic biomarker molecules. The application of oxygen isotope values from carbonate microfossils as a temperature proxy is difficult in estuarine environments because of the strong influence of salinity fluctuations. Mg/Ca values in carbonates of LIS benthic foraminifera provide a bottom water temperature proxy that may also be influenced by the carbonate saturation state of the water. The recently developed tetraether index (TEX_{86}) temperature proxy is based on the number of cyclopentane rings in the glycerol dialkyl glycerol tetraethers (GDGTs) of the membrane lipids of marine Crenarchaeota, which changes in response to temperature, probably for the purpose of regulating membrane fluidity. Crenarchaeota are one of the three major groups of non-thermophilic Archaea, a widely distributed, abundant, and ecologically diverse group that have been found over a large depth range in the photic and aphotic zones of the water column. This proxy can therefore be used in organic-rich sediments deposited in many different settings. We sampled three cores from western and central LIS, dated using Hg-pollution profiles, ^{210}Pb - ^{137}Cs, and ^{14}C, and analyzed samples for Tex_{86} for the purpose of generating a 4,000 year temperature reconstruction of Long Island Sound surface waters. We compare the TEX_{86} paleotemperature record data with a Mg/Ca record based on benthic foraminifera. Preliminary data indicate that temperatures of LIS waters, as averaged over the part of the year that the proxy organisms are biologically active, generally fluctuated between 12-14^{o}C and probably represent an average of surface water temperature over the growing season.

Estimating Sediment Metal in Norwalk Harbor Using Sediment Mean Grain Size and Loss on Ignition Data

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The presence of elevated levels of anthropogenically-derived metals in shallow-water marine sediments poses a recognized hazard to bottom-dwelling marine organisms and, under certain circumstances, to benthic (seafloor) marine ecosystems (N.O.A.A., 1994). Infaunal organisms such as worms ingest marine sediments in order to extract food in the form of organic debris. Mollusks such as oysters are filter feeders and will bioaccumulate toxins from near-bottom suspended sediments, for example, sediments remobilized by harbor dredging or the laying of cable or pipeline.

Previous studies show that there are three sedimentary factors that influence metal contaminant concentration: 1) small grains have a larger surface area/volume ratio than large grains so that a unit volume of fine grained sediment contains more attachment sites for scavenged metals than does an equal volume of coarse grained sediment, 2) fine grained sediments may contain large numbers of clay minerals which bear electrostatic charges making clays very efficient at scavenging metals from the water column, and 3) organic material, which is typically deposited in the same low-energy environments as fine grained sediments, is also effective at scavenging metals.

A multivariate regression model that relates metal concentration to grain size and loss on ignition was tested for sediments in Norwalk Harbor by comparing model results to observed sediment metal concentration values. The model recreated observed concentration patterns well. Residuals were also mapped. Large positive or negative residuals occur where the observed and predicted concentrations were not well matched. Such locations, depending on whether observed concentrations were higher or lower than predicted concentrations, were described as *hot spots and cold spots*. One such hot spot was associated with the presence of a power plant and deep-water dock. A cold spot at the west end of the outer harbor was associated with a more exposed area assumed to have more vigorous circulation.

Sediment Characteristics in Relation to Hypoxic Events in Smithtown Bay

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The purpose of this study was to obtain an integrated understanding of the physical and chemical aspects of bottom sediments in Smithtown Bay in LIS and their relationship to hypoxic bottom water formation. This project incorporated sediment, chemical, and water parameters into an ArcGIS framework. It is part of a larger study whose goal is to better understand the dynamic nature of Smithtown Bay's benthic infaunal communities and their relation to hypoxia. The study utilized data from monthly research cruises in Smithtown Bay between May and September of 2009 and 2010. A total of 10 sampling cruises took place, during each of which sediment, water, and benthic infaunal samples were taken from 13 sites within the bay.

Geospatial analysis was performed on the sediment data gathered from the cruises. A base map focusing on Smithtown Bay was constructed using ArcGIS 9.3 software and layers showing sediment type, sediment grain size, sediment temperature, and TOC were overlain onto it. Qualitative analysis and spatial statistics were performed on both the data and constructed maps in order to identify spatiotemporal patterns in sediment characteristics throughout the sampling period.

To date, detailed maps showing sediment type, grain size, temperature, and TOC of Smithtown Bay have been constructed for all cruises during the summers of 2009 and 2010. These are fine-scaled maps that have allowed for identification of relatively small spatial patterns and temporal changes in sediment characteristics that occurred during the sampling period. Qualitative analysis that has been performed has attempted to explain these spatial and temporal trends. Ultimately, data and analysis from this project will play an important role in the aforementioned comprehensive study. The spatiotemporal sediment findings from this research, along with water chemistry and benthic infaunal data, will provide crucial insight into the specific physical and chemical characteristics leading to hypoxia in Smithtown Bay and their subsequent effects on local benthic communities.

Interactions Between Hypoxia and Sewage-derived Contaminants on Gene Expression in Fish Embryos

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Contaminated environments often present multiple stressors to wildlife. In coastal systems receiving both urban runoff and sewage effluents, aquatic species may be faced with sewage-derived chemical contaminants as well as hypoxic conditions due to excess nutrients and organic carbon loads. Estrogen and estrogen mimics, hypoxia, and other contaminants can all potentially act as endocrine disruptors, making it important to understand their interactive effects. At particular risk to the effects of these stressors are immature organisms undergoing rapid development and sexual differentiation in shallow coastal ecosystems. We chose to evaluate the interactive effects of hypoxia and sewage-derived contaminants in embryos of a model test species, the zebrafish *Danio rerio*, and a common indigenous species, the mummichog *Fundulus heteroclitus*. To this end we measured expression of estrogen receptor alpha (ERα, aromatase B (AromB), cytochrome P4501a (Cyp1a), and hypoxia inducible factor 1α (Hif1α) by quantitative real time polymerase chain reaction (q-RT-PCR) under normoxic and hypoxic conditions in embryos exposed estrogen or beta-naphthoflavone, a model P4501a inducer, and in embryos exposed to surface sediments collected from around Jamaica Bay and along a transect in Western Long Island Sound, representing a wide range of exposures differing in degree of sewage inputs and degree of hypoxia. CYP1a was found to be most responsive to environmental conditions among the genes evaluated, with ER and AromB demonstrating limited response in embryos of both species. Hif1α showed good expression levels, but less environmental modulation than Cyp1a. Hypoxia tended to enhance gene expression. These results demonstrate that fish embryos respond to sediment associated contaminants and that hypoxia influences the magnitude of these responses. Levels of sewage tracer compounds and redox sensitive metals were also determined in the sediments tested to quantify the influence of sewage inputs and to try to discern degree of hypoxia. This aspect of the study will be discussed in a companion presentation by Brownawell et al. Supported by the Dissolved Oxygen Benefit Fund through a grant from the National Fish and Wildlife Fund.

Growth and Survival of Nereis sp. in Anoxic and Sulfidic Systems: A Possible new Nutritional Pathway

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Nereis virens and *Nereis diversicolor* are polychaete worms frequently found in shallow estuarine sand and mud bottoms in the northern hemisphere. Both are tube dwellers and omnivorous. They are also both generally found in sediment prone to hypoxia or anoxia due to high levels of organic matter. High sulfide concentrations are often correlated with hypoxic and/or anoxic conditions (Vismann, 1990).The ability of some organisms to thrive in sulfide-rich environments has been shown to be due to metabolic associations with sulfide-oxidizing endosymbiotic bacteria (Cavanaugh et al., 1981, Cavanaugh, 1983). These symbionts provide their host with all the fixed carbon and energy needed to thrive in environments with high concentrations (>1 millimolar) of hydrogen sulfide (Markert et. al., 2007). These bacteria have been found in shallow water hosts as well as in hydrothermal vent fauna (Giere, 1982).

The objectives of this study were to explore correlations between controlled environmental parameters (D.O., sulfides, temperature) and the bacterial communities found in the mid and hindgut of the Nereid worms exposed to these conditions. Nereid behaviors, (e.g. amount of time spent on the surface, tube location, tube density etc,) under the different ecological conditions of each experimental habitat, were noted. In addition, the mid-gut and hindguts of the Nereids were examined for the presence of endosymbiotic bacteria similar to that found in the surfclam *Spisula subtruncata* (Thiriot-Quievreux and Soyer, 1986).

Preliminary analysis reveals a higher number of burrows closer to the sulfidic zones in the experimental habitats compared to the controls. The burrow density is also greater in the more sulfidic habitats. Analyses also reveal the apparent presence of bacteria within the mid-gut and hindgut region of the Nereids. It is hypothesized that these bacteria may be endosymbionts that are at least partly responsible for the survival of Nereis sp. under anoxic, sulfidic conditions.

Remote Continuous Monitoring of N2 Concentrations in the Hypoxic Western Long Island Sound: a Proxy for Physically Driven Gas Fluxes

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Subsurface hypoxia has occurred annually in the western Long Island Sound since the 1970s. Its development reflects the interplay between the physical supply of atmospheric O_2 via vertical mixing, near-surface biological production and removal by water-column and sedimentary respiration. However, there remains significant uncertainty as to the time-varying magnitudes of the factors determining high frequency variations in O_2 concentrations during these periods of minimal O_2, particularly the relative contributions of the biological and physical terms.

A gas tension device (GTD) measures in situ total dissolved gas pressure, and can be used for continuous monitoring of dissolved gas dynamics. The partial pressure of N_2 gas is estimated by subtracting O_2 (measured) and H^2O (calculated) partial pressures. Since N_2 is largely inert, variations in the partial pressure of N_2 traces variations in physical gas transport. An exception is the production of N_2 by microbial denitrification, which can occur in LIS sediments. Benthic denitrification is the predominant removal term for N from LIS particularly during the summer, it thus has a critical role in ameliorating LIS eutrophication and being able to constrain this term is important for the overall LIS N budget. Our goal is to use a combination of continuous N_2 and O_2 records to parse physical and biological O_2 fluxes with adjustment for denitrification.

Two GTD's were deployed on the LISICOS mooring at Execution Rocks in May 2010 in combination with O_2 sensors and CTD's and will be kept in position till the fall overturn allowing for a continuous, highly temporally resolved N_2 concentration record to be derived. These data will be used to monitor the development of hypoxic conditions and variability associated with tidal and diel cycles as well as meteorological conditions. Moored GTD's are likely to prove to be an important permanent addition to the complement of continuous remote data gathering for monitoring dissolved gas transport and exchange processes.

Toward Geochemical Budgeting of Dissolved Gases in the Hypoxic Western Long Island Sound

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Summertime subsurface hypoxia in the western Long Island Sound continues to have strong negative environmental impacts. The development of summertime hypoxia must reflect an insufficiency in the physical supply of atmospheric O_2 via vertical mixing and photosynthetic production relative to removal by water-column and sedimentary respiration. However, there remains significant uncertainty as to the magnitudes of the factors determining O_2 concentrations particularly during the short summertime periods of minimal O_2 and their variability over diel and tidal cycles. We have employed geochemical budgeting using high precision dissolved gas ratio and isotope analysis to separate biological and physical fluxes, which naturally integrate over inherent scales of variability.

A cruise was undertaken in August 2010 during the period of most intense hypoxia in the western Long Island Sound. Dissolved gas analyses were made on board using a quadrupole mass spectrometer modified to obtain high resolution, real-time, gas ratio profiles from a submersible pump attached to the CTD rosette. The ratio of non-conservative species to an inert species was measured to separate biological and physical influences. Discrete samples were also collected and analyzed back in the laboratory for the full complement of high precision gas ratio and isotope analysis (□$^{15}N_2$ and □$^{18}O_2$).

A geochemical budget for the western Long Island Sound will be presented focussing on the summertime period of hypoxia to parse physical and biological processes. This budget will ultimately be used to improve predictive numerical models of Long Island Sound water quality, which is critical for future management decisions.

Benthic Communities of New Haven Harbor: Spatial and Temporal Trends in Relation to Selected Environmental Factors and Habitat Structure

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The coastal bays and inlets of Long Island Sound have a long history of chronic physical and chemical disturbances. Yet we have little quantitative information on how they have changed over time and the directions of those changes, save for a few sites. New Haven Harbor is perhaps the busiest and one of the most impacted coastal systems in Long Island Sound. However, information on the ecological condition of the harbor is fragmentary. In order to assess historic and current ecological conditions, a review of previous studies and a more recent survey of the harbor were carried out. Benthic grab samples and underwater video was collected at 11 sites in the harbor to characterize the habitats and macrobenthic community structure. Our initial analysis suggests surprisingly diverse communities in some portions of the harbor, and some significant long-term (since 1983) changes. The utility of long term monitoring relative to management issues and marine spatial planning is discussed.

Long-Term Changes in Copepod Diversity in Long Island Sound.

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In Long Island Sound (LIS), sea surface temperatures have increased 1□ C over the past 30 years, much faster than the regional and global average (Rosenszeig, 2008). The ecology of LIS in the context of global warming provides insight into the future response of other urban estuaries of the Northeast and Mid-Atlantic to regional warming trends. These processes have already been documented for coastal Rhode Island as well as Narragansett Bay in Massachusetts (Nixon et al. 2009, Oviatt, 2004, Sullivan et al. 2007), but have not been studied in detail in LIS. However, two historical year-long, large-scale surveys, Riley (1956) and Capriulo et al. (2002), have been conducted in the center of LIS and along its Connecticut shore. These provide a baseline for comparison with current surveys I am conducting in LIS. Preliminary results of my surveys indicate that diversity of the most important zooplankton organism (copepods) has increased. Furthermore, the increase is similar to the latitudinal gradient observed by Turner (1981), suggesting LIS is coming to resemble a more southern ecosystem. This shift has coincided with potentially increased gelatinous zooplankton abundance as well. The interaction of these two trends can potentially cause additional stress to an urban estuary already stressed by eutrophication and habitat loss.

Thermal Tolerance of the Invasive Tunicate Styela Clava Larvae

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Styela clava, commonly known as the club tunicate, is an invasive species and a marine fouling organism found in Long Island Sound. *Styela clava* are ascidians that are able to out-compete native filter feeders, build dense fowling colonies, and are very resistant to environmental changes. Wood (2009) demonstrated that adult *Styela* taken from Long Island Sound were able to tolerate temperatures up to 30^{o}C. This high tolerance of adult *Styela* to elevated temperatures means that the geographic range of *Styela* could potentially expand to the Tropics. The likelihood of this occurring, however, is increased if the thermal tolerance of *Styela* larvae equals or exceeds that of the adults. The purpose of this experiment was to determine the thermal tolerance limits for *Styela* larvae.

Gametes were stripped from adult pre-conditioned *Styela* and mixed in sterile containers filled with seawater. These containers were kept at constant temperatures of 16^{o}C and 24^{o}C. Containers were checked on a weekly basis and the number of settled and surviving Styela juveniles were counted. Results demonstrate that the larvae of *Styela clava* can survive and settle at temperatures of 24^{o}C. Experiments are underway to determine whether *Styela* larvae can survive at 30^{o}C. This experiment has shown that the larvae of this invasive species can survive at temperatures commonly found south of Long Island Sound and suggests that *Styela* may be able to spread to these areas.

Impacts of Climate Change on the Spring Bloom in Long Island Sound

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It has been hypothesized that during warm winters, the winter-spring bloom in temperate coastal waters is suppressed due to increased zooplankton grazing. However, this has not yet been tested in LIS. This project is examining the role of temperature-enhanced, zooplankton grazing in mitigating the development of the LIS spring bloom. We are conducting field studies of the physical and chemical characteristics, phytoplankton and zooplankton species composition and abundance, and primary productivity and grazer-induced mortality rates of phytoplankton in LIS during winter and spring. In addition, primary productivity and zooplankton grazing rates at elevated, ambient, and reduced winter seawater temperatures using bottle incubations (48-hours) are being measured. Mesocosm experiments with manipulated seawater temperatures are also being conducted to further investigate the impacts of elevated and reduced seawater temperatures on the magnitude and composition of the spring bloom. The ambient seawater temperatures ranged between 1-6^{o}C between January and April and the experimental warmer and colder temperatures were, in general, +3^{o}C and -3^{o}C ambient.

The 2010 spring phytoplankton bloom occurred during early February during which chlorophyll a concentrations in central LIS exceeded 10 ug L^{-1}. The bloom consisted of > 1,000 diatoms ml^{-1} but was also comprised of a significant proportion of smaller phytoplankton (nano- and picophytoplankton; > 50% of chlorophyll *a*). Experimental manipulations of seawater temperature had mixed effects on microzooplankton grazing rates during 48-hour incubation periods. In a two-week mesocosm experiment, however, conducted during late winter, higher temperatures yielded lower chlorophyll and diatom levels and higher abundances of ciliates and other microzooplankton grazers. Microzooplankton community grazing rates were significantly higher in the elevated-temperature mesocosms compared to the ambient-temperature mesocosms ($p<0.05$). Such a suppression of the spring bloom would alter benthic-pelagic coupling and have implications for coastal fisheries.

Factors Promoting Blooms of the PSP- and DSP-producing Dinoflagellates, *Alexandrium fundyense* and *Dinophysis acuminata*, in Long Island Sound

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Globally, the phytoplankton communities of many coastal ecosystems have undergone phase shifts in recent decades, becoming increasingly dominated by harmful algal blooms (HABs). The duration, intensity, and distribution of HABs have all increased, with growing negative impacts on human health, fisheries, and economies. Long Island Sound (LIS) is a prime example of an estuary undergoing such changes. Prior to 2006, algal blooms in LIS were viewed as nuisances and contributors to hypoxia. Since then, blooms of the saxitoxin-producing dinoflagellate *Alexandrium fundyense* have lead to paralytic shellfish poisoning (PSP)-induced closures of nearly 10,000 acres of shellfish beds in Northport and Huntington Bays during four of the past five years. In 2008, a second dinoflagellate, *Dinophysis acuminata*, began forming large, annual blooms (>100,000 cells L-1) in this same system and NOAA's biotoxin laboratory in Charleston, SC, has recently confirmed these blooms are generating the toxins okadaic acid and DTX-1, both of which are the causative agents of diarrhetic shellfish poisoning (DSP) syndrome. This represents only the third report of DSP-producing blooms in the US. This presentation will review the dynamics of A. *fundyense* and D. *acuminata* blooms during 2008, 2009, and 2010 and explore the collective role that nutrient loading, organic matter loading, and trophic interactions, including allelopathy, play in promoting blooms of these toxic dinoflagellates.

Gill Morphology and Oxygen Diffusion Distance in Juvenile Striped Killifish, *Fundulus majalis*

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Killifishes (*Fundulus* spp.) are important forage fishes in the Sound. Larval and juvenile striped Killifish (*Fundulus majalis*) inhabit shallow marsh pools which become warm and oxygen-limited in summer. To investigate potential physiological and morphological adaptations of killifish to this environment we studied gill morphology. Gill surface area (GSA) and oxygen diffusion distance are important parameters for oxygen uptake at the gills. To measure these parameters fish were collected from marsh pools in late summer, weighed, measured and the gills were fixed in Karnovsky's solution. For scanning electron microscopy (SEM) they were rinsed, dehydrated in a graded ETOH series, and critically point dried, sputter-coated and were observed with ISR-SR-50 SEM. Gill morphology (number of filaments, filament length, lamellar density, and lamellar size) were quantified using SEM. To measure oxygen diffusion distance from water to blood, samples were embedded in Araldite 502/Embed 812 ™ plastic medium for transmission electron microscopy (TEM). Stained (uranyl acetate and calcinated lead citrate) thin sections were examined using a FEI/Philips Morgagni 268 transmission electron microscope (TEM). Gill lamellar diffusion distance was measured using the technique of Matey et al., 2008. Gill structure and oxygen diffusion distance will be compared to other fishes.

Fiddler in the Marsh- Spatial Distribution and Abundance of Uca spp. in Salt Marshes of Central Long Island Sound

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As sea level rise (SLR) becomes a greater concern to the management and conservation of our coastlines, salt marshes are starting to experience significant changes in their character and ecology. Recent studies have documented changes in vegetation distribution and pattern in salt marshes due to SLR in the Northeast. However, there has been little to no examination of potential changes in marsh fauna. Fiddler crabs, *Uca spp*., are ubiquitous members of salt marsh communities and their burrowing activity is intimately tied to salt marsh dynamics. As such, fiddler crabs may be good sentinel species to illuminate the effects of SLR on salt marsh ecology.

Three marsh systems along the central Connecticut coast were studied using a landscape approach in order to determine the spatial distribution and abundance of fiddler crabs in relation to vegetation patch structure and tidal zonation. Data on the abundance of burrows and presence/ absence of live fiddler crabs were analyzed over multiple spatial scales. Burrows of fiddler crabs are concentrated in patch types associated with the low marsh habitat (i.e. bare ground, tall *Spartina alterniflora*) as commonly known, except in highly eroded low marsh. However, we also found live fiddler crabs in the high marsh, especially in patches of short *Spartina alterniflora* and *Disticulus spicata*. In addition, burrows are also found in hummocky *Spartina patens* and *Disticulus spicata* and *Spartina patens* mixed patches on the high marsh. These results suggest a significant expansion of the area that is occupied by fiddler crabs.

The presence of fiddler crabs in high marsh habitats may be triggered by physical changes related to SLR and other factors. High to low marsh transformation, and the creation, coalescence of salt pannes, and small waterways may create corridors and refugia which allow fiddler crabs to move into previously unfavorable habitats. Future studies should address the exact details of their expansion and experimentally test if they are contributing to salt marsh changes. The correlation between the spatial distribution of fiddler crabs and physical changes in salt marshes may provide important information in assessing and predicting the health of these valuable and vulnerable ecosystems in the future.

Salt Marsh Recovery in Jarvis Creek Marsh, Branford, CT: Tides Rule

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Coastal salt marsh ecosystems are affected by tidal flushing, which can be expressed as marsh inundation frequency. Sediment accretion is determined by accumulation of below-ground biomass, supply of terrestrial and marine sediments, and the efficiency of trapping such particulates. We took surface samples and cores in Jarvis Creek Marsh (Branford, CT) to study salt marsh accumulation rates under different conditions. In Jarvis Creek Marsh, a tide gate restricted tidal flow to the landward part of the marsh, and vegetation became dominated by *Phragmites australis*. The tide gate was removed around 1979, tidal flow was largely restored, and *Phragmites* became replaced by *Spartina alterniflora*. We studied agglutinated benthic foraminiferal assemblages in marsh surface samples to establish a relationship between inundation frequency (determined by tide stick data) and species abundances. We studied peat core samples from within and outside the old tide gate and reconstructed past inundation frequencies. Cores are dated using Hg-pollution profiles, ^{210}Pb-^{137}Cs and ^{14}C. Inner Jarvis Creek Marsh had a stable, high marsh environment before the installation of the tide gate (core section below ~ 40 cm), with vegetation dominated by *Spartina patens*, and benthic foraminiferal assemblages dominated by high marsh species (e.g., *Trochammina macrescens*, *Trochammina inflata* and *Tiphotrocha comprimata*). A core section with *Phragmites* roots (~40-20 cm) reflects the period of tidal flow restriction, and has high marsh foraminiferal assemblages. *Spartina alterniflora* roots dominate in the upper 20 cm of the core, reflecting the removal of the tide gate. The relative abundance of high marsh species decreased abruptly, and low marsh species *Ammotium salsum* and *Miliammina fusca* became dominant. Towards the recent, *M. fusca* increased relative to *A. salsum*, indicating decreasing inundation frequency. The early high marsh environment kept up with the rate of sea-level rise, but could do so no longer during tidal restriction: *Phragmites* could not produce and/or trap enough material for high enough accretion rates. When tidal flow was restored, a low marsh was established with high accretion rates. The inner Jarvis Creek Marsh is now accreting faster than the rate of sea-level rise, changing from low-low marsh to high-low marsh environments. It has not yet recovered to its former high-marsh environments, but with ongoing fast accretion can be predicted to do so in several more decades, unless increasing rates of sea level rise in the future outpace these high sediment accretion rates.

Characterizing the Biofuel Potential of Long Island Sound Macroalgae

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The purpose of this study was to evaluate the biofuel potential of four locally-occurring macroalgal species from Long Island Sound. In order to be considered a feasible candidate, algae needed to demonstrate significant growth rates in cultivation systems, as well as chemical profiles that are suitable for the production of biodiesel and other biofuels. A novel indoor cultivation system was designed and tested on three different macroalgae: *Ulva lactuca*, *Codium fragile*, and *Fucus vesiculous*. A fourth algae, *Chondrus crispus*, was grown using established methods. Chemical suitability was evaluated based on overall lipid content and FAME content upon trans-esterification.

Results demonstrate that all four species of macroalgae can successfully be grown in culture although growth rates varied among the different macroalgal species as well as with different growth media. Overall lipid content, as well as FAME content, varied among the four macroalgae as well; FAME content for at least one of the species studied was able to be enhanced by altering the growth media.

The data support the idea that at least two of the locally-occurring macroalgal species examined in this study have significant potential as biofuel feedstock species. Further study is needed in order to determine the ideal light and growth media dosing regimes for these candidate species. This work was supported by a grant from the Connecticut Center for Advanced Technology.

POSTERS

A Comparison of CODAR and ADCP Surface Current Records in Western LIS

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ABSTRACT
Knowledge of currents and circulation patterns are essential for predicting the transport and fate of particles and dissolved materials in the water column. An analysis of surface currents and related dynamical properties in western LIS has been done using radial velocities derived from CODAR (Coastal Ocean Dynamics Application Radar),which measures surface currents from the Doppler shifts of radar sea scattered echo, and ADCP (Acoustic Doppler Current Profiler) data.

The former yields a spatially and temporally averaged surface current measurement whereas the latter produces a subsurface profile measurement.

Differences between estimates of currents from the two instruments can be explained in terms of random errors and vertical shear in the surface layer.

To evaluate the differences of two measurements, the correlation coefficients were computed. Errors in radar bearing determination were found corresponding to the geometrical CODAR-ADCP station differences.

Biogeochemical Factors Affecting Mercury Speciation in Long Island Sound

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Sulfur, organic matter quality and quantity; sediment structure and composition can all affect the conversion of inorganic mercury to methylmercury, a process mostly mediated by bacteria. The relative importance of these factors with regard to mercury methylation in an economically and environmentally important estuary, Long Island Sound (LIS), was investigated during summer 2009 and fall 2009 at two stations, in the western and central LIS.

Preliminary results show that sulfur, not organic matter, explains methylmercury variability in the western station sediment. In the central station sediment, total mercury is related to both organic matter and total sulfur content, but methylation is related to neither. We also show that bottom water hypoxia indirectly affects mercury methylation in sediments, as it changes the ratio of acid volatile sulfur-AVS (=FeS) to chromium reducible sulfur-CRS (=pyrite and elemental S), which is proxy for bottom water oxygenation (higher AVS/CRS ratios indicate hypoxia/anoxia). And AVS has been shown to reduce mercury methylation by limiting mercury partitioning into porewater thus reducing its bioavailability.

Concentration of Heavy Metals in the Fauna of Meadow Lake

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ABSTRACT
Meadow Lake is an urban water body located in Flushing, Queens, New York City between two major highways, the Van Wyck Expressway and the Grand Central Parkway. The lake is connected via tidal gate to Flushing Bay of the Long Island Sound. The lake's history and location have tarnished the lake sediment in metal contaminants; preliminary investigation has found anomalously high concentrations of potentially toxic metals such as copper, lead and zinc in the sediments. The goal of this study in to quantify the concentration of various metals assimilated by the fauna of Meadow Lake and to assess the extent of the bioaccumulation of these metals within the Meadow Lake food web. The metals of interest were selected from the EPA Primary Pollutants list and include arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver and zinc. The concentration of the natural radioactive element polonium 210 will also be quantified. This study will include representatives several species such as snakeheads, American eel, white perch, gizzard shad, Menidia, blue crabs and grass shrimp.

Continuous Offshore to Shoreline Sea-Floor Mapping - Combined Multibeam and LIDAR Bathymetry from off New London and Niantic, Connecticut

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The USGS, in cooperation with NOAA and the Connecticut DEP, is producing detailed maps of the sea floor in Long Island Sound. The current phase of this cooperative research program is directed toward studies of sea-floor topography and its effects on the distribution of sedimentary environments and benthic communities. Anthropogenic wastes, toxic chemicals, and changes in land-use patterns resulting from residential, commercial, and recreational development have stressed the environment of the Sound, causing degradation and potential loss of benthic habitats. Detailed maps and interpretations of the sea floor are needed to evaluate the extent of adverse impacts and to manage resources wisely in the future. As part of this overall effort a 4-m resolution bathymetric grid was created by merging NOAA data from multibeam surveys H11441 and H11442, conducted in deeper waters off New London and Niantic, Connecticut, with those from hydrographic LIDAR surveys H11224 and H11225, conducted in adjacent shallower nearshore waters. The resultant datasets are provided in UTM Zone 18 NAD83 and geographic WGS84 projections and are adjusted to mean lower low water. Together these merged data reveal a larger, more continuous perspective of sea-floor topography than previously available, providing a fundamental framework for research and resource management activities along this part of the Connecticut coastline.

Surveyed depths within the study area range from sea level at mean lower low water to more than 65 m. The shallowest areas occur along shorelines and on isolated bathymetric highs, such as Bartlett Reef and Twotree Island. Exposed bedrock outcrops, boulder lag deposits of the Fishers Island and Clumps moraines, sand-wave fields, and scour depressions reflect the strength of the oscillating tidal currents; bedform asymmetry allows interpretations of net sediment transport. Anthropogenic artifacts visible in the bathymetric data include a dredged channel, shipwrecks, dredge spoils, mooring anchors, prop-scour depressions, buried cables, and bridge footings. To facilitate access, compatibility, and utility, these datasets are provided online in ESRI ArcRaster-grid and GeoTIFF formats at: http://pubs.usgs.gov/of/2009/1231/

Digital Seismic-Reflection Data From Rhode Island Sound, 1975-1980

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In 1975 and 1980, the U.S. Geological Survey (USGS) conducted three seismic-reflection surveys in Rhode Island Sound (RIS) aboard the research vessels Asterias and Neecho: cruise ASTR75–June surveyed eastern RIS in 1975, cruise AST–80–6B surveyed southern RIS in 1980 and NECH80-1 surveyed western RIS in 1980. Over 1,400 km of seismic data from these surveys were recorded in analog form and archived at the USGS Woods Hole Coastal and Marine Science Center's Data Library. In response to recent interest in the geology of RIS for industrial applications and academic research, and in an effort to make the data more readily accessible while preserving the original paper records, the seismic data from these cruises were scanned and converted to 300-dpi black and white TIFF and 200-dpi grayscale PNG images and SEG-Y data files. Navigation data were converted from U.S. Coast Guard LORAN time delays to latitudes and longitudes that are available in ESRI shapefile format and as eastings and northings in space-delimited text format. These data complement and extend previous work to convert analog seismic-reflection data in Long Island and Block Island Sounds to digital form (http://woodshole.er.usgs.gov/openfile/of02-002/). The RIS seismic data are available online at http://pubs.usgs.gov/of/2009/1002/ and http://pubs.usgs.gov/of/2009/1003/.

Pathological Changes, Disease, and Tissue Metals in Eastern Oysters From Five Sites Along the Connecticut Coast

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This study examined trends in the incidence of heavy metal contamination in sediments and tissues of the eastern oyster (Crassostrea virginica) from five sites in LIS and the corresponding prevalence of pathological changes such as inflammatory responses, mucus production in gill regions, parasitic burden, degeneration of digestive cells neoplasia and infectious agents (MSX, Dermo, Turbellaria, SSO, etc.) in oysters from those sites. Oysters were collected during November-December 2008 from three locations in the lower Housatonic River estuary, one location in New Haven harbor and one location in the lower Menunketesuck River in Westbrook. Sediment metal concentrations at these sites were correlated with sediment grain-size and sediment LOI. Oyster tissue copper contents varied across the sites and ranged from 1510 ± 549 mg/kg (dry weight) at Housatonic River site 1 to 250 ± 90 mg/kg in New Haven harbor. Differences in oyster tissue metal contents were not attributed solely to differences in sediment composition (grain-size and metal contents). However, an inverse relationship between oyster tissue copper and zinc contents and ambient salinity was noted. Observations of total pathological changes by site demonstrated no clear relationship with tissue metal concentrations but demonstrated a similar trend when compared to sediment copper and zinc concentrations from their respective sampling locations. The 'background' pathology of previously observed infectious agents common to LIS oysters was observed, however no trends could be associated with tissue or sediment metals measured in this study.

Potential Effects of Phytoplankton Abundance and Diversity on the Eastern Oyster, *Crassostrea virginica*, in Long Island Sound

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Little is known about the effects of fluctuating physical factors on the trophic relationship between phytoplankton and the eastern oyster, *Crassostrea virginica*, in Long Island Sound. The purpose of this research was to examine factors that influence plankton abundance and diversity including site, season, temperature, turbidity and salinity, and to investigate the effect on oysters. Abundance and diversity was determined from plankton tow samples collected once per season from 2008 through 2009, which was examined via microscopy and compared to past studies. Additional plankton samples were collected through the use of a Niskin bottle during Fall 2009 and Spring 2010 blooms. These samples were examined via flow cytometry at the National Marine Fisheries Lab in Milford, Connecticut. Glycogen analysis of oyster tissue was carried out to determine the available stored energy and use during the period of Fall 2009 and Winter 2010. The examination of oyster glycogen in relation to the plankton studies will provide insight to the relationship between phytoplankton abundance and diversity and oyster productivity.

Phytoremediation by *Eichhornia Crassipes* to Remove Contaminants from Water

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This study was conducted to determine if the use of *Eichhornia crassipes* is an effective method of phytoremediation to remove common contaminants from freshwater. Tanks containing local lake water and water hyacinth with and without samples of coal ash and ash from local incinerators were tested weekly for pH, dissolved oxygen and hardness for monitoring purposes. Nitrate, phosphate, iron, and copper levels were tested to determine if the plant was effectively removed pollutants from the water for twelve weeks. Data analysis using mathematical models was utilized to further determine the effects of water hyacinth.

The presence of *E. crassipes* did not significantly reduce contaminant levels to the capacity it had the potential to. Pollutants in the water fluctuated. Nutrient concentrations reached two distinct equilibrium points during Weeks 5 and 10 of the study. However, the heavy metals did not reach equilibrium.

Copper levels did not show significant changes and remained within a small range of values which suggests that the presence of the water hyacinth had a minimal effect. Concentrations of iron varied during the first four weeks of the study but then continued to reach more consistent values. Nutrient concentrations fluctuated throughout the study, showing both increasing and decreasing levels which provides conflicting evidence of the effectiveness of water hyacinth as a viable phytoremediation method. Changes in concentrations were assumed to be due to the presence of *E. crassipes*.

The comparison between the calculated phytoremediation potential and observed concentrations of the contaminants showed a wide variation. Beyond the approximate sixty three day time interval in which water hyacinth actively affected contaminant level, equilibrium was reached.

Chemical tests indicated that this phytoremediation method is not harmful to the environment. Overall, this possible water management technology using water hyacinth was not an effective method of phytoremediation for nutrients but can be considered effective for metal removal.

Strong Claws May Help Explain Population Growth of Non-Native *Hemigrapsus sanguineus* and Decline of Resident Crabs in Western Long Island Sound

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Purchase College (SUNY)x
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Hemigrapsus sanguineus, is an invasive crab that has become overwhelmingly dominant in western Long Island Sound. Densities of *H. sanguineus* have fluctuated since 2001 between 70-160 m^{-2} in the mid-intertidal, the zone of maximum abundance at the Rye, NY site. June population densities decreased by 56% from 2009-2010, apparently due to a recruitment shortfall; the young-of-the-year (4-10 mm) were mostly absent from samples. However, *H. sanguineus* still dominates, comprising >99% of crabs captured across the intertidal zone. Claw morphology and crushing force determine the outcome of agonistic encounters between crabs. The crushing force of *H. sanguineus* was determined by measuring the force required to open claws. Crushing force increased with carapace width, though not linearly. Males were stronger than females, and the disparity increased with crab size. Although the sample size of green crabs *(Carcinus maenus)* was small (n = 5), these resident non-natives had a smaller crushing force per mm carapace width than *H. sanguineus*. The large crushing force of *H. sanguineus* relative to body size may provide it access to a greater range of prey, and may have helped the non-native out-compete other crab species.

The Distribution of the Scleractinian Coral Astrangia Poculata in Long Island Sound

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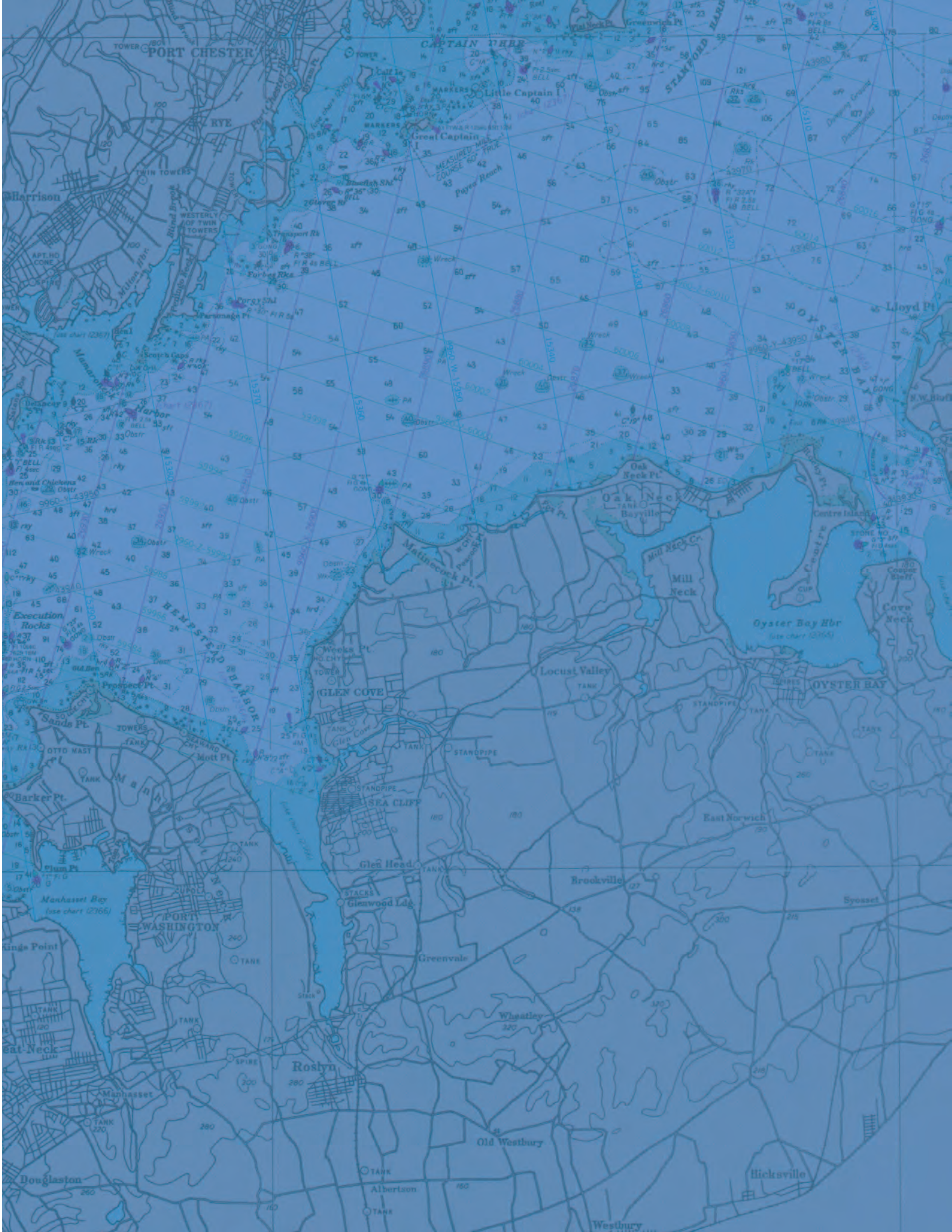
Astrangia poculata is the only scleractinian coral found in shallow water along the northeast coast of the United States in areas such as Long Island Sound (LIS). Though observed in this area, little knowledge on the extent of its distribution in local waters is known. Estuaries, like LIS, are constantly changing, as such; organisms that inhabit these dynamic waters need to be readily adaptable to changes in factors including temperature, salinity, dissolved oxygen, and eutrophication. Research was completed during the summer of 2008 and 2009 on three breakwaters across LIS to determine the distribution of *A. poculata*. Breakwaters have been shown as a suitable habitat for temperate corals because they are not a reef building species of coral. Results demonstrate that coral abundance was highest in the East, at the Stonington Harbor breakwater, and lowest in the West, at the Milford Point breakwater perhaps indicating an East to West gradient in distribution that may be dependent on salinity, hypoxia or other factors. Results also illustrate a significant difference (P<0.01) in abundance at 2 depths, where as abundance at 6 meters was approximately 10 times higher than at 2 meters.

NOTES



PORT CHESTER
RYE
Harrison
TWIN TOWERS
CAPTAIN HBR
Little Captain I
Great Captain I
STAMFORD HARBOR
MEASURED MILE COURSE 60° TRUE
Lloyd Pt
OYSTER BAY
Oak Neck Pt
Oak Neck
Bayville
Mill Neck Cr
Mill Neck
Centre Island
Cove Neck
Oyster Bay Hbr
Matinecock Pt
Locust Valley
OYSTER BAY
HEMPSTEAD HARBOR
Execution Rocks
Prospect Pt
Sands Pt
Mott Pt
Barker Pt
Plum Pt
Weeks Pt
GLEN COVE
SEA CLIFF
East Norwich
Glen Head
Brookville
Glenwood Ldg
Syosset
Manhasset Bay
PORT WASHINGTON
Kings Point
Greenvale
Wheatley
Roslyn
Manhasset
Old Westbury
Hicksville
Albertson
Douglaston
Westbury