CONNECTICUT SEA GRANT PROJECT REPORT

Please complete this progress or final report form and return by the date indicated in the emailed progress report request from the Connecticut Sea Grant College Program. Fill in the requested information using your word processor (i.e., Microsoft Word), and e-mail the completed form to Dr. Syma Ebbin syma.ebbin@uconn.edu, Research Coordinator, Connecticut Sea Grant College Program. Do NOT mail or fax hard copies. Please try to be address the specific sections below. If applicable, you can attach files of electronic publications when you return the form. If you have questions, please call Syma Ebbin at (860) 405-9278.

Please fill out all of the following that apply to your specific research or development project. Pay particular attention to goals, accomplishments, benefits, impacts and publications, where applicable.

Project #: R/CMC-9-CTNY _ Check one: [ ] Progress Report [X] Final report

Duration (dates) of entire project, including extensions: From [03/01/2009] to [02/28/2011].

Date of Report: April 28, 2011

Project Title or Topic:
Geochemical Budgeting of Dissolved Gases for Understanding Long Island Sound Hypoxia

Principal Investigator(s) and Affiliation(s):

1. Mark A. Altabet , SMAST- U. Massachusetts Dartmouth

A. <u>COLLABORATORS AND PARTNERS</u>: *(List any additional organizations or partners involved in the project.)*
Jim O'Donnell, U. Conn.

B. PROJECT GOALS AND OBJECTIVES:

1. To produce geochemical budgets for O_2 in LIS
2. To separate physical and biological O_2 flux terms and determine their temporal variability
3. To precisely determine the relative contribution to O_2 removal from water column and benthic respiration.
4. To improve O_2 flux representations in predictive numerical models of LIS water quality.
5. To estimate the contribution of benthic denitrification to the LIS nitrogen budget.

C. <u>PROGRESS</u>: (*Summarize progress relative to project goals and objectives. Highlight outstanding accomplishments, outreach and education efforts; describe problems encountered and explain any delays.)*

1) Deployed on LISICOS moorings GTD instruments for in situ N_2 measurement. Sediment denitrification in the summer produces excess N_2 in the lower layer and its flux upward corresponds to ventilation events associated with tidal cycle near Execution Rock.

2) Carried out two field programs with Prof. Jim O'Donnell (UConn) on the RV Connecticut in August 2009 and that overlapped with the GTD deployment. Post-Doc Dr. Laura Bristow, PhD student Santhiska Pather, and REU students Pnina Grossman participated and Sonia Shafner helped prepare for the cruise. Activities included making continuous vertical profiles of gas ratios using an at-sea quadrupole mass spectrometer system developed for this project and collection of discrete samples for shore-based laboratory analyses.

3) Data analysis so far shows good correspondence between in situ GTD, on ship mass spec, and shore based mass spec N_2 concentration analyses. Correspondence is also good between optode (YSI sonde on ship's CTD), on ship mass spec, and shore based mass spec O_2 concentration analyses

4) O_2 isotope determination from cruise samples collected at Execution Rock as well as from the LIS-wide surveys carried out by Ct State DEP continue to show a) photosynthetic O_2 makes a direct contribution to the hypoxic zone and b) a large percentage of the O_2 removal in the hypoxic zone is due to benthic respiration.

D) PROJECT PUBLICATIONS, PRODUCTS AND PATENTS: *(Include published materials with complete references, as well as those which have been submitted but not yet published and those in press. Please attach electronic versions of any journal articles not previously provided.)*

Journal Articles: Not Yet

Conference Papers and Presentations:

1) Bristow, Laura A., Mark A. Altabet and Jim O'Donnell' Toward Geochemical Budgeting of Dissolved Gases in the Hypoxic Western Long Island Sound. LIS Conference 2010

2) Altabet, Mark A., Laura A. Bristow and Jim O'Donnell Remote Continuous Monitoring of N_2 Concentrations in the Hypoxic Western Long Island Sound: a Proxy for Physically Driven Gas Fluxes . LIS Conference 2010

Planned Publications:

1) Comparing in situ and discrete methods for determining dissolved N_2.
2) Time-Series studies of total dissolved gas pressure in Long Island Sound
3) Dissolved O_2 isotope systematics in Long Island Sound - parsing water column and benthic respiration

4) Separating physical and biological components of the western Long Island Sound budget for dissolved O_2.

<u>E)</u> <u>FUNDS LEVERAGED</u>: *(If this Sea Grant funding facilitated the leveraging of additional funding for this or a related project, note the amount and source below.)*
This project was able to share instrumentation and method development/refinement with the following NSF project awarded to the PI:

1) Assessing Coastal Benthic Denitrification using High Precision Water Column N_2/Ar, NSF, $411,601, July 01 2006 to June 30 2010 (1 yr no-cost extension)

2) Nitrogen isotope and N_2/Ar biogeochemistry of the Peru suboxic zone, NSF, $412,000, Feb 01 2009 to Jan 30 2012

<u>F)</u> **<u>STUDENTS</u>:** ***(****Document the number and type of students supported by this project.)*
*Note: **"Supported"** means supported by Sea Grant through financial or other means, such as Sea Grant federal, match, state and other leveraged funds. If a student volunteered time on this project, please note the number of volunteer hours below.*

Total number of **<u>new*</u>** K-12 students who worked with you: 1
Total number of **<u>new</u>** undergraduates who worked with you: 1
Total number of **<u>new</u>** Masters degree candidates who worked with you: 0
Total number of **<u>new</u>** Ph.D. candidates who worked with you: 1

Total number of **<u>continuing**</u>** K-12 students who worked with you: 1
Total number of **<u>continuing</u>** undergraduates who worked with you: 2
Total number of **<u>continuing</u>** Masters degree candidates who worked with you: 0
Total number of **<u>continuing</u>** Ph.D. candidates who worked with you: 0

Total number of volunteer hours: 120

*(Note: ****<u>New</u>*** *students are those who have <u>not</u> worked on this project previously. *****<u>Continuing</u>*** *students are those who have worked on this project previously.)*

In the case of graduate students, please list student names, degree pursued, and thesis or dissertation titles related to this project.

Student Name: Santhiska Pather
Degree Sought: PhD
Thesis or Dissertation Title: Not yet determined
Date of thesis completion: June 2014
Expected date of graduation: same

FOR FINAL REPORTS ONLY, PLEASE COMPLETE THIS SECTION:

G) PROJECT OUTCOMES AND IMPACTS

RELEVANCE OF PROJECT: *(Describe briefly the issue/problem / identified need(s) that led to this work.)*

Hypoxia in western Long Island Sound is a persistent environment problem that has intensified in the last two decades. Recent LISICOS mooring data for continuous O_2 (J. O'Donnell) shows much greater variability than previously identified including cycles associated with the tides and persistent weather patterns. In particular, periods of more extreme summertime hypoxia during periods of poor vertical mixing were identified that were aliased by prior lower frequency surveys indicating a much greater negative impact on biota. However, understanding the causes of these variations is hampered by present inability to distinguish physical and biological terms for a complete O_2 budget. For the biological components alone, the relative contributions from surface productivity, water column respiration, and benthic respiration are poorly know. A key management issue dependent on know these terms and their dependencies is establishing predictive capability for the future course of western LIS O_2 in response on-going and planned remediation efforts as well as climate change.

RESPONSE: *(Describe briefly what key elements were undertaken to address the issue, problem or need, and who is/are the target audience(s) for the work.)*

This project sought to apply several advanced geochemical techniques to quantify the different physical and biological components of the O_2 budget. High precision gas ratio measurements were deployed to identify physical vs biologically driven variations in O_2. Stable isotopes in O_2 were measured to distinguish photosynthetic production, water column respiration, and benthic respiration. The moored GTD component (measures continuously in situ dissolved gas pressure from which N_2 concentrations are derived to trace physical processes) also had the goal of developing infrastructure for future continuous monitoring. The audience for this work is 1) the scientific community seeking to understanding the drivers of LIS hypoxia and 2) the management community needing better data for O_2 relevant processes for developing improved models and thereby predictive capacity.

RESULTS: *(Summarize findings and significant achievements in terms of the research and any related education or outreach component; cite benefits, applications, and uses stemming from this project, including those expected in the future. Include qualitative and quantitative results.)*

We have several major findings so far;

1) N_2 and O_2 concentration data allow for separating physical and biological terms in the O_2 budget since in the water column N_2 acts as an inert gas. Data analysis so far shows excellent correspondence between in situ GTD, on ship mass spec, and shore based

mass spec N_2 concentration analyses. This is encouraging finding for establishing continuous N_2 monitoring into the future along with O_2 and other parameters measured on the LISICOS moorings. However, the manufacturer-provided GTD instruments have not proved to be as robust as anticipated and we have been spending the last part of the project improving their ability to survive extended deployment in LIS and reducing the cost of these improvements to permit routine use. We are planning a third cruise this summer with Jim O'Donnell to continue to evaluate the next generation of GTD's. This is beyond the project period and will be funded from other sources, but we see this as necessary to optimize the impact of this project's results. We will also attempt to bootleg continue deployment of the GTD's as well as seek support in the future to build longer data time-series.

2) GTD data shows time-scales of variability similar to O_2. Particularly for tidal cycles, inverse relationship with O_2 confirms that enhanced vertical mixing produced by vertical sheer causes downward O_2 transport and ventilation of the lower layer. Downward transport of O_2 co-occurs with upward transport of N_2 in excess of equilibrium with the atmosphere. This development of N_2 excess in the lower layer during summer is likely from N_2 production by benthic denitrification and this technique may prove a novel approach for evaluation this term in the LIS nitrogen budget.
3) Large signals are observed in dissolved O_2 stable isotope composition. These variations are observed both across the axis of LIS during Conn. DEP surveys as well in highly resolved vertical profiles during our two cruise. Our qualitative interpretations are that a) photosynthetic O_2 makes a direct contribution to the hypoxic zone in western LIS via downward missing and ameliorates low O_2 and b) a large percentage of the O_2 removal in the hypoxic zone is due to benthic respiration (larger than previously reported). One implication of the latter finding is that LIS management must take into account organic production that may be initially stored in sediments but respired at a later time. In this way, production during the winter/spring bloom may contribute to summertime hypoxia. Another is that accurate models must represent the full seasonal cycle for nutrient input and productivity as well as simulate transient organic matter storage/respiration in the sediments.

We are now working closely with Jim O'Donnell's group on quantitative analysis and interpretation of these data through modeling and synthesis with physical data (in addition to mooring-based O_2 data). We view this as a necessary precursor to high-quality publication of the results of this project.

Update - March 14, 2012

We participated in a cruise with Jim O'Donnell's group to western LIS in August 2011. We focused on time series studies at Execution Rock (ExRk) and along a transect between this station and station E1 to capture possible tidal influence. Samples were collected for dissolved gas analysis and returned to the lab. A GTD system was in place at ExRk and we will be comparing its continuous output to these discrete observations.

N_2/Ar was examined as an indicator of biogenic inputs of N_2 gas from sediment denitrification. As expected the lower, hypoxic layer at ExRk had elevated biogenic N_2, but the signal was much less than predicted – only 1 to 2 umol/kg. Similar observations were made along the transect. Either sediment denitrification during the late summer is much less than anticipated or the signal is rapidly lost by exchange to the atmosphere. Constraining the LIS dissolved gas exchange with atmosphere will therefore ultimately constrain the magnitude of denitrification a potentially important term in the LIS N budget

O_2/Ar was measured to isolate the biological changes to O_2. At ExRk, the hypoxic zone was clearly caused by biological drawdown, but surprisingly no surface signal expected from high primary productivity was observed in the surface layer. As before, tidal flushing appeared to be associated with enhanced transport of O_2 into the subsurface hypoxic zone. Along the transect, near surface observations were similar but the progressive subsurface biological depletion of O_2 toward the west was obvious.

$\delta^{18}O_2$ was measured to isolate further the individual biological influences on O_2. The relationship between $\delta^{18}O_2$ and [O_2] is indicative of the relative importance of benthic respiration, water column respiration, and photosynthesis. At ExRk and along the transect, the sediments appear to account for about 40% of the O_2 drawdown, suggesting its much greater importance than considered at present for LIS hypoxia. However, $\delta^{18}O_2$ vs [O_2] relationships become offset to lower $\delta^{18}O_2$ values from east to west, which may be accounted for by progressive downward mixing of photosynthetically produced O_2 suggest that this too is an important term for understanding hypoxia. Full interpretation requires merging with physical data and simple model simulation. We are currently work with Jim O'Donnell's group in this respect and plan on having results to present at the June 2012 STAC meeting.