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 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/CTP-51-CTNY Check one: [ ] Progress Report [X] Final report

Duration (dates) of entire project, including extensions: From [March 1, 2015] to [Sept. 30, 2018].

Project Title or Topic:

Recent temporal evolution of nitrogen loading and oxygen dynamics in Long Island Sound studied using stable isotope geochemistry

Principal Investigator(s) and Affiliation(s):

1. Mark A. Altabet (U. Massachusetts Dartmouth, School for Marine Science and Technology)

A. <u>COLLABORATORS AND PARTNERS</u>: *(List any additional organizations or partners involved in the project.)*

Jim O'Donnell, U. Connecticut, Avery Pt.
Craig Tobias, , U. Connecticut, Avery Pt.
Wally Fulweiler, U. Boston

B. PROJECT GOALS AND OBJECTIVES:

This project addresses three topic areas specified in the original RFP; 1) Research examining the impact of nutrient reductions on hypoxia in LIS; 3) Synthesis or modeling that contributes directly to our ability to understand and manage anthropogenic perturbations to LIS, and 4.) Research that improves understanding and management of the sources and relative loads of sediments, nutrients, and contaminants into LIS. We address T#1 by developing a 12-yr time series of nitrogen stable isotope ratio ($\delta^{15}N$) in LIS to assess the efficacy of reduced N loading on the LIS N budget. A corresponding oxygen isotope ratio ($\delta^{18}O_2$) and oxygen to argon gas ratio (O_2/Ar) dataset is being used to indicate any corresponding relaxation in hypoxia and the evolution of the relative importance of net production, water column respiration, and benthic respiration. These efforts build on our prior LISS supported work. T#3 will be addressed in the future through box model syntheses of these data to evaluate N and O_2 fluxes. T#4 will be addressed by a $\delta^{15}N$ budget to be developed that will reflect all anthropogenic N sources, point and non-point.

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.)*

Monthly LIS samples continued to be collected through the project period courtesy of the Ct State DEEP LIS Monitoring program. This part of the project has continued to work out very well due to the cooperation and efforts of Matt Lyman and Kay Howard-Strobel. In our synthesis, we have also made extensive use of the other data produced by the DEEP LIS Monitoring program including hydrography and nutrients. Samples for NO_3^- and DON $\delta^{15}N$ analysis are continuing to be collected and archived in order to continue the time series. NO_3^- $\delta^{15}N$ analyses were completed on all samples collected during the project as well as those previously archived. Dissolved gas analysis on collected samples have also been completed. Going forward, dissolved gas samples will only be collected during summer and early fall periods when an observable $\delta^{18}O_2$ signal is present.

Collaboration with Tobias and Fulweiler have involved sample collection from their core incubations to directly assess the isotope signals produced by benthic processes. This involved their collecting aliquots of water overlying cores for DIN isotope as well as dissolved gas analysis and sending to SMAST. At a minimum, water from the beginning and the end of a core incubation was collected for this purpose. All dissolved gas analyses have been completed. DIN isotope analysis is still in progress.

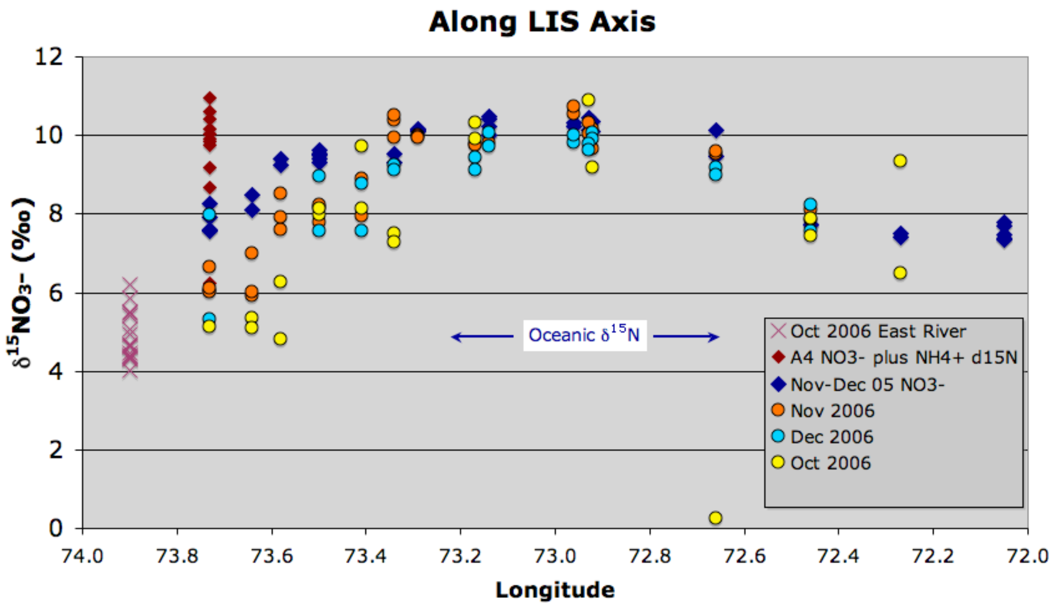
A MS student (see below) has completed her thesis on a previously overlooked aspect of the LIS N isotope budget – the role of dissolved organic nitrogen (DON). She examined both archived samples and samples collected in the course of this project. While DON concentration and isotope composition is not being determined on samples being collected at present, as they are preserved by freezing, this remains a possibility into the future.

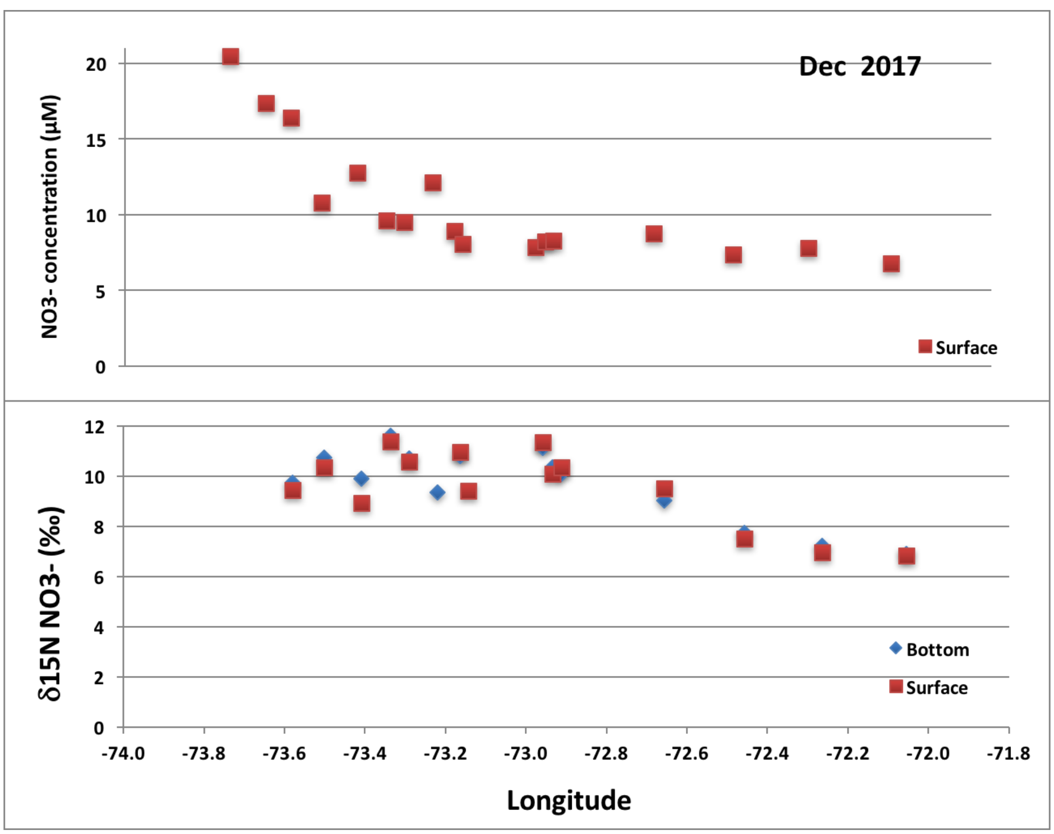
To date, the modeling component of the project described in the original proposal has not been carried out. Unfortunately, the collaborative partner needed for this effort was not able to bring adequate resources to bear on this problem. This remains a goal for future projects.

Major findings of this project include:

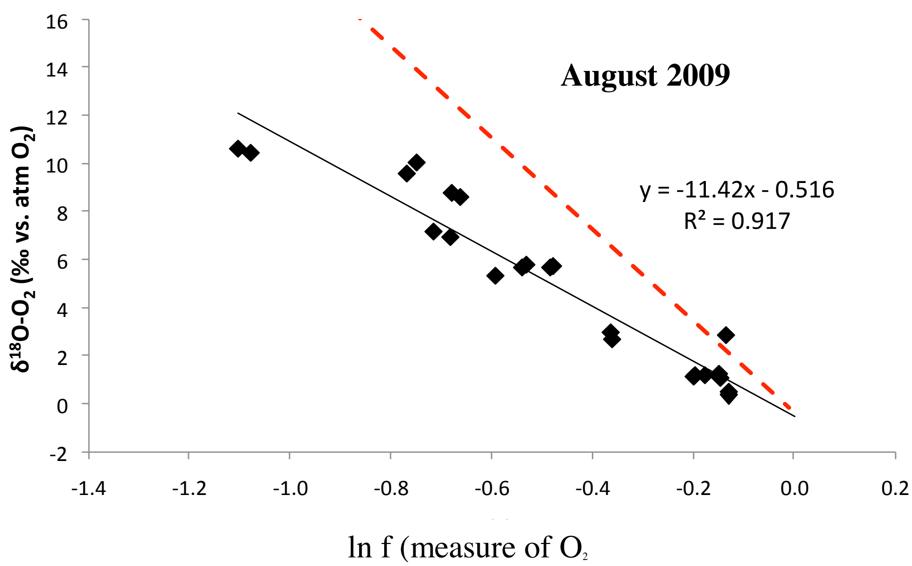
1) While exceptions have been observed, the $\delta^{15}N$ of NO_3^- accumulating in LIS during winter has not significantly changed (compare next 2 figures). In 2006 and 2017, NO_3^- in central LIS had $\delta^{15}N$ values near 10‰, significantly higher than the marine average of 5 ‰ and indicative of anthropogenic inputs. The most recent analyses of samples from Dec 2018 and Jan 2019 also show $\delta^{15}N$ NO_3^- even higher than in 2006 with values as high as 12‰. A likely explanation is that despite dramatically lower of N inputs over this time period, high $\delta^{15}N$ N stored in sediments remains an important source of wintertime NO_3^- through remineralization and nitrification. Planned analyses of the $\delta^{15}N$ of DIN released from sediment cores (samples provided by Fulweiler) will help confirm or reject this hypothesis. If confirmed, a major

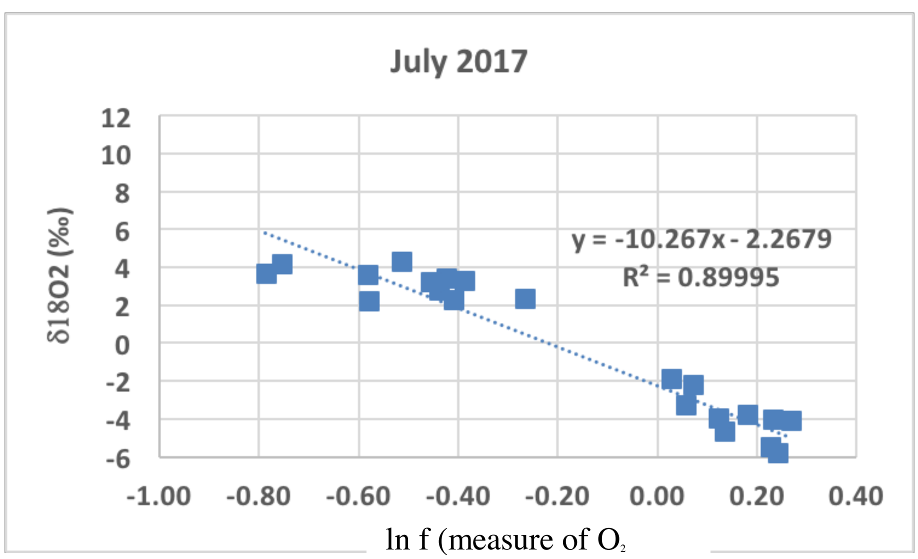
implication would be that the benefits of reduction in nitrogen loading to LIS may take many years to be apparent.



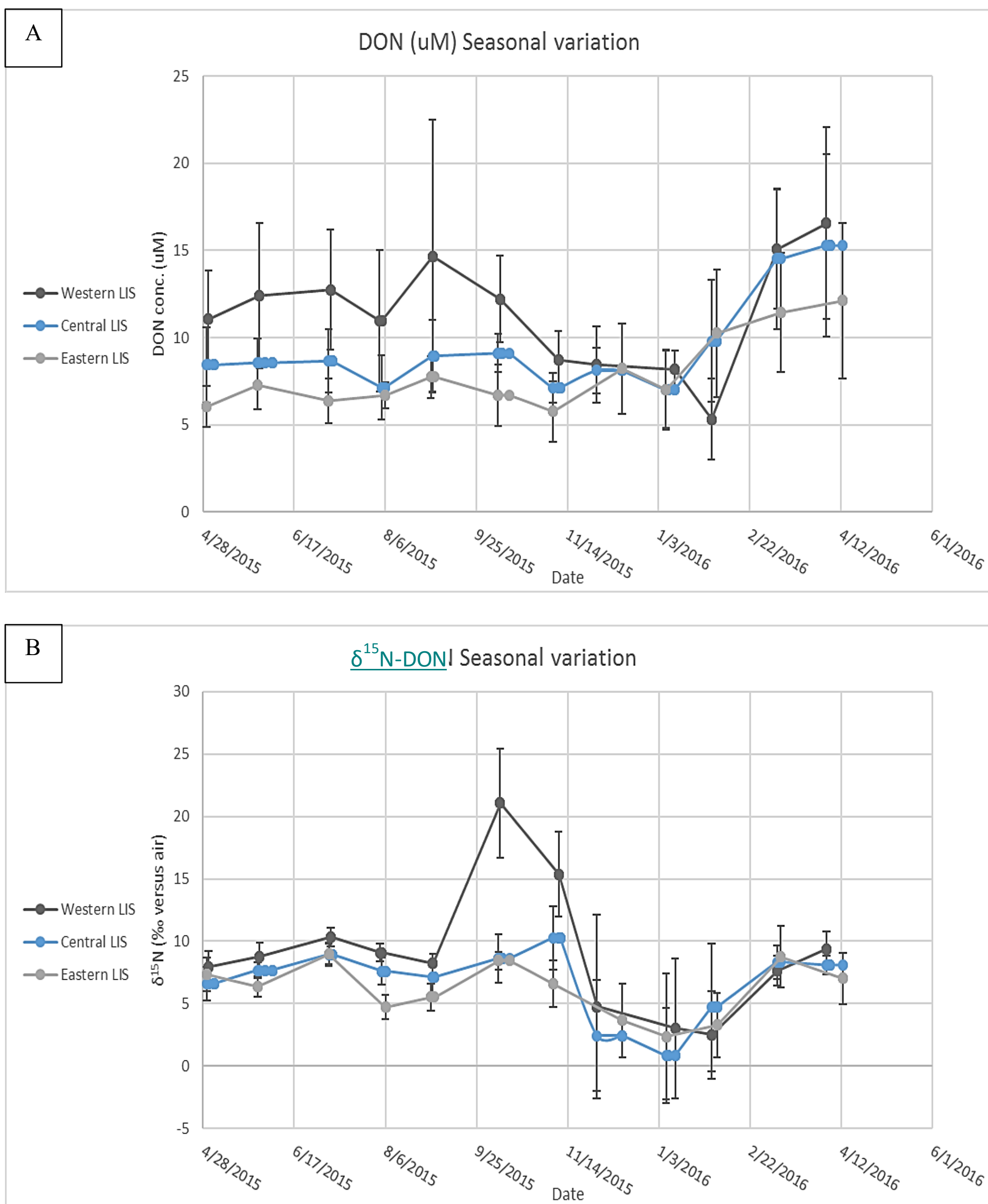


2) In August 2009, the relationship between the removal of O_2 and the $\delta^{18}O_2$ suggested that half of the hypoxic conditions experienced in LIS were due to respiration in the water column and the other half due to respiration in the sediments (see next two figs.) In July 2017, similar observations were made suggesting no long term change in this situation. An important assumption was that benthic column respiration conveyed little change in $\delta^{18}O_2$ as compared to the water column. This was confirmed by analysis of core incubation samples collected by Wally Fulweiler. This result is consistent with the $\delta^{15}N$ NO_3^- observation indicating continued importance of LIS sediments as both a sink for O_2 and a source of DIN.





3) Dissolved organic nitrogen was observed to be seasonally and geographically dynamic suggesting that this overlooked N reservoir could be important to supporting productivity in the spring and summer (see next figure). During spring and summer when DIN is depleted, a clear W to E concentration and $\delta^{15}N$ gradient is observed suggesting the East River as a source of DON produced from anthropogenic N that is consumed (or diluted) to the E. However, DON concentration increased more uniformly across LIS with the late winter bloom and through this period DON $\delta^{15}N$ rose over time. At this time, DON appears to be a by-product of the phytoplankton bloom.



D. <u>PROJECT PUBLICATIONS, PRODUCTS AND PATENTS</u>: *(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.)*

MS Thesis;

Prajapati, S. (2017) *Temporal evolution of nitrogen loading in Long Island Sound using stable isotope geochemistry: A role for dissolved organic nitrogen (DON)* University of Massachusetts Dartmouth, 98 pp.

Paper in Preparation;

"*Nitrogen isotope composition in Long Island Sound: Impact of anthropogenic loading*"

E. <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.)*

None

F. <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.*

A MS student has completed her thesis by working on this project

Student Name: Sheel Prajapati
Degree Sought: MS
Thesis or Dissertation Title: *see products*
Date of thesis completion: November, 2017
Date of graduation: January, 2018

G. <u>VOLUNTEER HOURS:</u>
(List the number of hours provided to the project by volunteers, i.e., individuals who were not compensated in any way or for whom involvement is not part of their paid occupation. This could be students or citizens. What was their contribution?)

None

H. <u>PICTORIAL</u>: Please provide high resolution images/photos of personnel at work, in the field or laboratory, equipment being used, field sites, organism(s) of study. Attach images as separate files (do not embed). Include links to websites associated with the research project. Please include proper photo credits and a caption with date, location, names of people, and activity. These images are useful to document your project in future CTSG publications, websites and presentations.

Mass spectrometer system at SMAST used to measure NO_3^- isotope composition. Lab Manager Rupsa Roy is show here fixing the autosampler
Photo Credit – Mark A. Altabet
Feb. 16, 2018

I. <u>HONORS AND AWARDS</u>: *(List any honors or awards received during the reporting period, for anyone working on the project. This can be for best paper or poster, university awards, etc.*) Specify:

None Yet

J. **<u>DATA MANAGEMENT PLANS:</u>** Proposals funded in 2014-2016 and later cycles are required to have a data management plan in place. All environmental data and information collected and/or created must be made visible, accessible, and independently understandable to general users, free of charge or at minimal cost, in a timely manner (typically no later than two years after the data are collected or created). This is a reminder that your CTSG funded research data needs to be archived and accessible as outlined in the data management plan you submitted with your proposal. If there have been any modifications, adjustments or new information available regarding the location, timing, type, formatting and metadata standards, content, sharing, stewardship, archiving, accessibility, publication or security of the data produced please elaborate here.

No changes

K. PROJECT OUTCOMES AND IMPACTS

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

The decline of the environmental quality of LIS in the latter half of the 20th century is associated with anthropogenic nitrogen loading leading to eutrophication and summertime hypoxia. To remediate this problem the first part of the 21th century has seen dramatic reductions in that loading. This project examined indicators of the positive impact of N loading reduction.

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.)*

Nitrogen isotope composition on archived and newly collected samples for LIS was determined to look for evidence of reduction in anthropogenic N contribution. Oxygen isotope composition in dissolved oxygen gas was gas was examined to determine the contribution of sediment vs water column respiration to summertime hypoxia and whether there have been any changes over the last decade. The audience for this work are other scientists working in LIS as well as policy makers.

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.)*

For details see the "Progress" section above

Consider the following as they apply to your research and any related outreach/education.

- What new tools, technologies, methods or information services were developed from this work? Have any been adopted / implemented for use and by whom?

  Nitrogen isotopes were developed as a tool for long-term monitoring of LIS with respect to the system-wide influence of anthropogenic nitrogen. These are highly-precise measurements regarding specialized instrumentation and to our knowledge, we are on the only group involved in long-term studies of this kind in LIS. Similarly, oxygen isotopes of dissolved oxygen were developed to understand the system wide contributors to respiration and hence summertime hypoxia.

- What are the environmental benefits of this work? Have policies been changed? How has conservation (of ecosystems, habitats or species) been improved?

  The lack of response in measured parameters to reduction in nitrogen loading underscores that patience is needed to realize the environmental benefits from the huge expense made in WWTP upgrades. Our results underscore that as it took many decades for eutrophication to reach critical levels, it will take time post-loading reduction for anthropogenic nitrogen to be released from storage (like the sediments) in LIS. Not yet obvious if this perspective has influence policies and conservation.

- What are the social payoffs of this work? Who has benefited from this work? Have attitudes / behaviors of target audience changed? Elaborate. Have policies been changed?

None yet identified

- What are the economic implications / impacts of this work? (Where possible, please quantify.) Have new businesses been created /or existing businesses retained as a result of this research? Have new jobs been created or retained? Are new businesses or jobs anticipated?

None yet identified

J. Stakeholder Summary (This is an abstract of your research and findings written for a lay audience)

It is well recognized that anthropogenic nitrogen loading is the primary cause of eutrophication and summertime hypoxia in LIS. Accordingly, regulatory efforts and large expenditures have focused on reducing N loading (TDML), mainly from sewage and wastewater treatment plants (SWTP). In parallel, on-going monitoring is intended to detect improvement from these efforts and computer models have been developed to predict and inform these regulations. In this project, we have used natural variations in stable isotope ratio as a powerful geochemical approach to identify and quantify N and O_2 sources and sinks that integrates over inherent spatial and temporal variability. In particular for nitrogen, we focused on the contributions from anthropogenic sources. For oxygen, we focused on the relative roles of sediments and the water column for respiration during summertime hypoxic conditions.

We have shown that that over the last 12 years, no observable change on the contribution of anthropogenic N to LIS, despite dramatic changes in anthropogenic N loading over this period. This observation is consistent with large amounts of stored N in LIS sediments that will likely take many years to remove from the system. This perspective is also consistent with our observation of no apparent change in a large contribution of the sediments to LIS respiration over a similar time period. Our results underscore that as it took many decades for eutrophication to reach critical levels, it will take time post-loading reduction for anthropogenic nitrogen to be released from storage in LIS sediments.