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.

Name of Submitter: Craig Tobias

Date of Report submission: 1/12/19

Project #: (R/CTP-52-CTNY) RFA 15098 Check one: [ ] Progress Report [X] Final report

Duration (dates) of entire project, including extensions: From [02/2016] to [09/2018].

Project Title or Topic: Biogeochemical Nitrogen Loss vs. Recycling in Long Island Sound: Connecting Sediments to Overlying Water

Principal Investigator(s) and Affiliation(s):

1. Craig Tobias, University of Connecticut
2.
3.
4.

A. COLLABORATORS AND PARTNERS: Wally Fulweiler - Boston U., Mark Altabet - U Mass Dartmouth, Patrick Plummer – USCG Academy

B. PROJECT GOALS AND OBJECTIVES: Measure the seasonal N removal rates via denitrification and anammox and the N recycling rates of ammonification, nitrification, and DNRA in LIS.

C. PROGRESS: 1) Coordination with the Fulweiler and Altabet projects.

Standardization of sampling equipment was completed between the Tobias and Fulweiler groups. Coordination of field sampling is complete. The Fulweiler group supplied split samples to the Altabet group with the exception of Nov 2017 sampling when the Tobias group supplied splits to the Altabet group

2) Field Sampling

Field operations are done. Field sampling was conducted June 2016, Dec/Jan 2016-2017, June 2017 (pre-bloom), August 2017 (bloom + hypoxia), and November 2017 (post-bloom). Five LIS stations along the east-west axis of Long Island Sound (LIS) were targeted in summer and winter of year one. Three stations in the western Sound were targeted in year two. All of the campaigns cored five stations. Both campaigns used UCONN vessels and marine ops personnel.

3) Incubations and Analysis

Cores collected from each field campaign were used for 1) isotope pairing measurements of direct and coupled denitrification; 2) isotope dilution experiments to determine gross sediment mineralization; 3) characterization of sediment geochemistry; 4) measurement of net respiration and fluxes of inorganic nitrogen and carbon 5) Denitrification / DNRA / Anammox partitioning experiments All incubations from all field collections have been completed. Chemical and isotopic analyses is complete from all experiments.

4) Delays

None

D. PROJECT PUBLICATIONS, PRODUCTS, PRESENTATIONS AND PATENTS

Journal Articles (List URLs): See planned publications below.

Conference Papers: None

Proceedings or book chapters: None

Web sites, Software, etc.: None

Technical Reports/Other Publications: This report and attached Summary of Findings

Other Products (including popular articles): None

Publications planned / in progress: Two papers are in preparation for submission to Limnology and Oceanography, and Estuaries and Coasts - Spring 2019. Tobias will be the lead author on one and PhD student Patrick Plummer will be the lead author on the other

Patents: None

Presentations and Posters:

Tobias, C. 2018. Biogeochemical Nitrogen Loss vs. Recycling in Long Island Sound: Connecting Sediments to Overlying Water. Presentation to Long Island Sound STAC, Groton, CT.

Tobias, C. 2017. Biogeochemical Nitrogen Loss vs. Recycling in Long Island Sound: Connecting Sediments to Overlying Water. Presentation to Long Island Sound STAC, Groton, CT.

Twarz, S., Rollinson, V., Schlink, C., Tobias, C., 2018. Sediment N-Cycling in Long Island Sound: Spatial and Temporal Patterns of Denitrification, DNRA, and Gross Mineralization. AGU Ocean Sciences Meeting, Portland, OR

E. FUNDS LEVERAGED: *Not yet*

F. STUDENTS:

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

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

Total number of volunteer hours: High school science teacher – 100 hrs

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

Student Name: Patrick Plummer
Degree Sought: PhD
Thesis or Dissertation Title: Geochemical controls on nitrate reduction pathways in marine sediments
Date of thesis completion: Expected Spring 2020
Expected date of graduation: Expected Spring 2020

G. VOLUNTEER HOURS:

100 volunteer hours from a high school science teacher conducting lab analyses.

H. PICTORIAL: Please find attached after the data summary.

I. HONORS AND AWARDS: None to date.

J. DATA MANAGEMENT PLANS: Data is being archived according to the QAPP. It will be made publicly available within the proscribed timeframe.

FOR FINAL DEVELOPMENT AND RESEARCH GRANT REPORTS, PLEASE COMPLETE THIS SECTION:

K. PROJECT OUTCOMES AND IMPACTS

RELEVANCE OF PROJECT:
Considerable effort has been spent to address nitrogen (N)- fueled eutrophication and extant hypoxia in Long Island Sound (LIS). The residence time of N depends on the input fluxes, which have received well-deserved attention in LIS, but also the recycling and loss rates, which have received less attention in LIS. In many estuarine systems, the recycling and flux of dissolved inorganic nitrogen (DIN) from sediments back to overlying water is an important N supply that supports water column primary productivity when external inputs are small. It can further contribute to a hysteresis in the recovery of eutrophied systems following nutrient reduction. For LIS, Altabet and Varekamp (2010) documented **"**significant anthropogenic N reserves in LIS sediments which may continue to be released back into the water column for some time to come". Several sediment N-cycling reactions (ammonification, nitrification, and dissimilatory nitrate reduction to ammonium - DNRA) act to recycle N and ultimately support the DIN flux to overlying water. Only two reactions however, denitrification (nitrate conversion to N_2) and anammox (ammonium conversion to N_2) remove N from the estuarine landscape. As point and nonpoint N sources are reduced, the relative importance of these N_2-exporting boundary fluxes assumes a more central role for characterizing N retention in LIS. A better understanding of the balance of, mechanisms behind, and controls on sediment N recycling vs removal reactions is necessary for gauging the rsponse of LIS hypoxia to changes in N loading, and/or predicting a realistic eutrophication recovery trajectory in response to decreased N loading. The work performed in this project was designed to fill the data gap that currently exists for LIS with respect to sediment nitrogen recycling vs. loss.

RESPONSE:
The work was be conducted in a way that represents an advancement over past flux studies through the use of isotope tracer and follows an experimental design that yields kinetic information about N processing and loss that dovetails into functional representations of biogeochemical reactions in LIS hypoxia modeling efforts. The work: 1) assessed sediment-water DIN exchanges; 2) quantified N removal via denitrification and anammox; 3) quantified N recycling/retention via ammonification (mineralization), nitrification, and dissimilatory nitrate reduction to ammonium (DNRA); 4)characterized kinetic functions of O_2, NO_3^- and temperature on N removal in a way that is suitable for incorporation into the LIS modeling framework; 5) assess the magnitudes of sediment N removal and return to overlying water in the broader context of LIS N inputs an export to offshore waters. . All measurements occurred seasonally, along the east-west eutrophication gradient in LIS. The target audience includes all stakeholders involved in nutrient and hypoxia management of LIS.

RESULTS: Please see the attached Summary of Findings document.

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

  The work provides constraints on rates of sediment N turnover, release to the overlying water, and removal of reactive N via conversion to N2 gas. Such information guides appropriate model parameterization and/or validation. Representing these processes in model space is essential for building a reasonable predicative capacity for how LIS hypoxia might respond to future N loading scenarios.

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

  Evaluating the source/sink strength of N with respect to the water column helps establish appropriate expectations of the 'recovery' trajectory of LIS water quality. The importance of appropriately managed expectations in process of forming policies should not be underestimated.

- 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?

  See response above.

- 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?

  Costs associated with nutrient management that results in achieving target LIS hypoxia goals over a time period acceptable to a consensus of stakeholders.

J. Stakeholder Summary

Low oxygen (hypoxia) in the waters of Long Island Sound (LIS) is ultimately caused by nitrogen (N) fueling an overproduction of algae that sink to the bottom, decay, and consume oxygen. High amounts of N loading to LIS has occurred for more than a century. Recent reductions in present day loading may be offset by a large reservoir of N in LIS sediments that is potentially available for return back to overlying water. Conversely, there are reactions in the sediment that have the capacity to convert biologically reactive N into N_2 gas which vents back to the atmosphere. In short these reactions help to remove N from LIS. Presently the balance between the N recycling reactions and the N removal reactions in LIS sediments is not known. Nor is it known if these reactions are large or small relative to N inputs and the rate at which N is flushed out of LIS.

Our results show that the amount of N contained in each 2cm of the sediments is about equivalent to 1 year's worth of external N inputs. Within this reservoir, there is a smaller fraction of N that is actively cycling on timescales of days to weeks. During the cycling, oxygen is consumed by the sediments but this is likely smaller, probably no more than 20-25%, of the oxygen consumption rate in the overlying water. The amount of biologically available N that gets leaked from the sediments back to the overlying water during sediment N cycling is approximately 17% of the amount of N that is loaded to LIS each year. This amount is on the order of 1/3 of WWTP inputs and roughly equivalent to the total riverine inputs of N.

The sediments also remove N from LIS. The conversion of biologically reactive N to N_2 occurs at a rate that is about 10% of the external N inputs. It is approximately the same amount as that flushed out of LIS by the tides. This removal is temperature dependent (higher rates at higher temperatures) but independent of the amount of N in the bottom water. Nearly all the N removed originates from N previously deposited into the sediments as particulates from the overlying water.

Currently the N dynamics in LIS sediments are tipped towards supplying more N towards overlying water. In that sense they should be considered net source of N when building contemporaneous annual N loading budgets. The N removal benefits of sediments should not be discounted however. It could be argued that they are attenuating about half of that N return to overlying water and equally important as flushing for N removal.

In summary, sediments are not primarily important for the actual magnitude of hypoxia in any given year. But, via release of N back to the overlying water, could be important for prolonging the persistence of hypoxia on decadal scales by contributing to the overall nutrient delivery to the water column that ultimately fuels hypoxia.

Summary of Findings LISS Project (R/CTP-52-CTNY) RFA 15098

Title: Biogeochemical Nitrogen Loss vs. Recycling in Long Island Sound: Connecting Sediments to Overlying Water

Investigator: Craig Tobias, University of Connecticut

1.0 Introduction

The findings presented here encapsulate the results from five sampling cruises in Long Island Sound (LIS), outcomes from several different types of incubation experiments, and associated chemical/isotopic analyses. These data serve as the basis for a manuscript in preparation for submittal to Limnology and Oceanography. Submission is planned for the early spring of 2019.

The findings are organized around fundamental questions regarding nitrogen cycling in the sediments of Long Island Sound (LIS), connectivity of those processes to the overlying water, and assessment of the relative magnitude of sediment processes within the broader nitrogen budget of LIS. The following questions are addressed:

-How much N resides in the shallow sediments of LIS?

-How much of that N is actively cycling?

-What is the sediment oxygen demand associated with mineralization and nutrient cycling generally?

-What fraction of the N turnover in the sediments results in a net flux of N back into the water column?

-What is the rate of removal of N via denitrification?

-How large are all of these N cycling reactions relative to N loading into and tidal N export out of LIS?

2.0 Findings

2.1 Setting and Sampling

The five sampling cruises occurred in July 2016, Jan2017, July 2017, August 2017, and November 2017. Timing of the sampling was designed to capture the spatial gradient of processes throughout all of LIS under summer and winter conditions (July 2016 and Jan 2017), and then focused on western LIS under pre-, during-, and post- hypoxia conditions in the summer/fall of 2017. Based on monitoring data from CT Department of Energy and the Environment and from moored instrumentation maintained by the LISICOS program, 2017 was not a severe hypoxia year either in terms of minimum dissolved oxygen concentration or extent of hypoxia.

Sampling stations were located near LISICOS buoys and revisited within a radius of 300m. In order to scale measurements for comparison to LIS N loading magnitudes, each of the stations was assumed to be representative of an area of LIS that extended approximately half way to the next station in the east-west direction and to the 5m isobath along the north and south shorelines Fig 1).

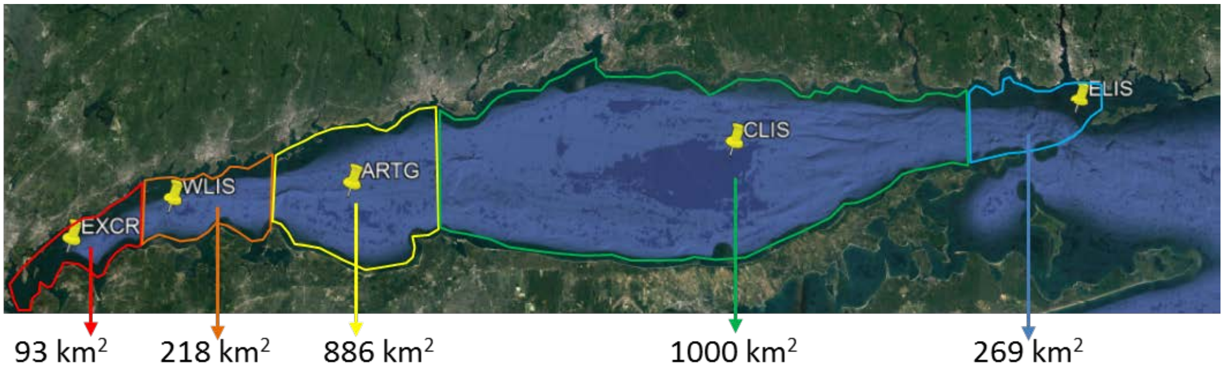

Figure 1. Station locations and polygon areas assigned to each station. Moderate to severe hypoxia was restricted to EXCR and WLIS polygons in 2017 with an area of ~ 200 km^2

2.2 Sediment Nitrogen Inventory

At 2 cm intervals,sediment to a depth of 6 cm was analyzed at all stations for particulate organic nitrogen (PON), porewater dissolved inorganic nitrogen (DIN), and ion exchangeable (bound) NH_4^+. The 6 cm sediment depth was chosen as a standardized sampling depth that was easily obtainable at all stations, including the coarse-grained ELIS station. It is a depth that can be reached by common infauna and therefore potentially participate in oxygen and nutrient exchanges with the overlying water. There were no consistent differences in the vertical distribution in sediment DIN or PON and all depths were aggregated at each station for each sampling time.

PON was the largest reservoir of N in sediment. Sediment % N was maximal in the western sound in excess of 0.3% N and declined in an eastward direction by almost a factor of 10 toward the mouth of LIS (Fig 2). The higher δ^{15}N-PON values in western sound are consistent with higher anthropogenic N loading in that region (Fig 2). After bulk density is considered, each cm of sediment in the western sound contained 10-30 gN m^{-2} while the sediments of central and eastern LIS contained 3-6 gN m^{-2} per cm of depth (Fig 3). When scaled to station specific areas (Fig 1), each 1 cm interval of sediment in LIS contained on the order of 24 million kg of N. Two thirds of that is contained in the western sound (EXRC, WLIS, and ARTG). This total per cm inventory of sediment PON is equivalent to about half of the annual load to LIS (44 E^6 kgN y^{-1};

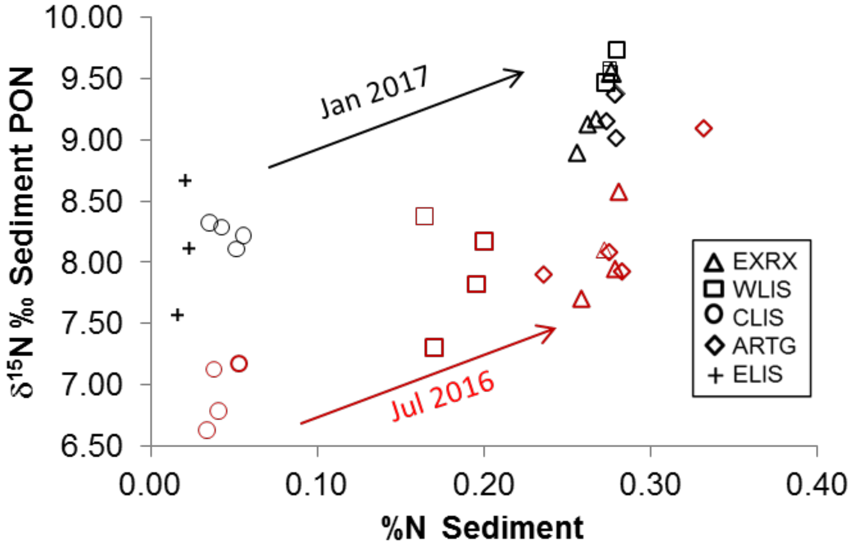

Figure. 2 Nitrogen stable isotope composition of sediment PON

Mullaney and Schwarz, 2013). The rate of N burial in LIS sediments was estimated from two scenarios: First, LIS sediment (at the measured %N) was assumed to be accreting at a rate equivalent to the historical local rate of sea level rise (2.5 mm yr^{-1}). Second, nitrogen and carbon burial rates in western LIS and Block Island Sound reported in Varekamp (2010) were extrapolated for each region of LIS. These two approaches yielded a PON burial rate in LIS on decadal scales of 6-10 million kg N y^{-1}. This magnitude suggests that on the order of 14-24% of N inputs to LIS are retained in the sediment PON pool on long (decadal +) timescales.

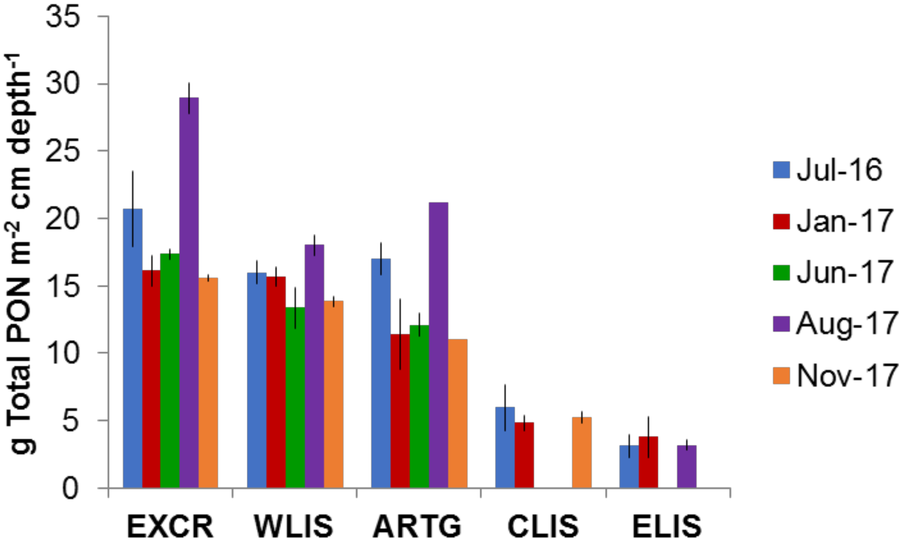

Figure. 3 Total sediment organic nitrogen inventory attributable to each cm of sediment depth based on 0-6 cm measurements.

2.2 How Much N is Cycling?

A small fraction of the sediment N reservoir is actively/rapidly cycling. The porewater plus extractable NH_4^+ fraction constitutes 0.1% of the total sediment N pool at each station (Fig 4). The extractable NH_4^+ was 2-5 times more abundant than the free porewater NH_4^+.

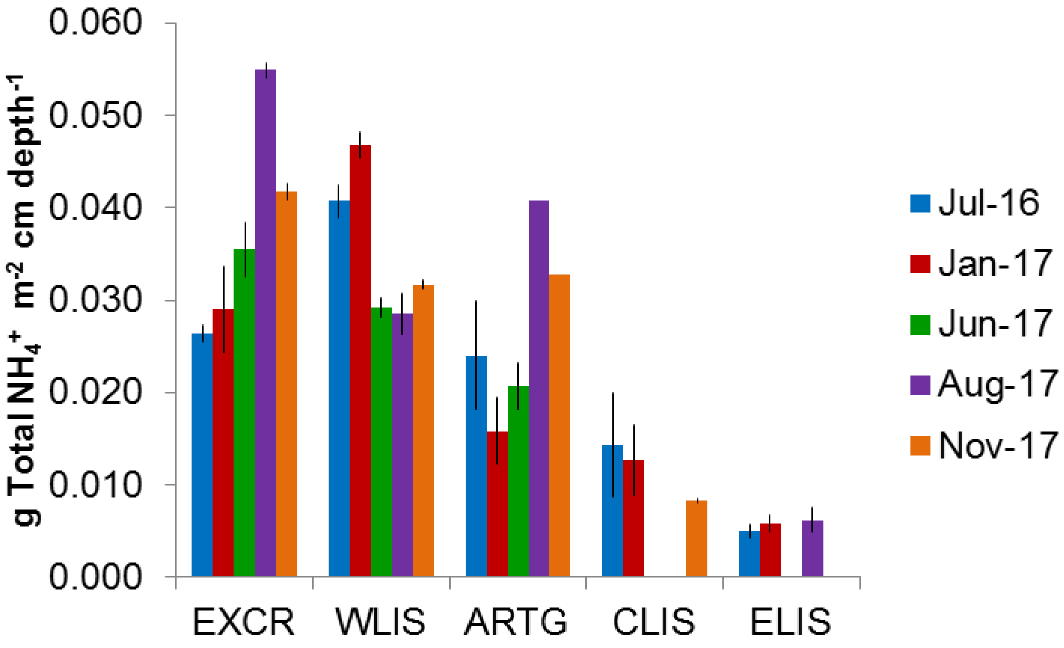

Figure. 4 KCL-extractable NH_4^+ inventory attributable to each cm of sediment depth based on 0-6 cm measurements.

Gross N mineralization measured by isotope dilution yielded rates of 0.002 to 0.020 gN m-^{2} per cm of sediment depth. Rates were higher by a factor of 1.5 – 2 in the summer as would be expected with warmer temperatures (Fig 5). High variance in rates observed periodically were due to heterogeneous contributions from infauna respiration to the mineralization rate. The range of daily mineralization rates were of similar magnitude to the extractable NH_4^+ inventories suggesting that the sediment NH_4^+ pool is turned over rapidly – on the scale of days to weeks even in the winter when rates were lower. If viewed from the perspective to the total sediment N inventory (Fig 3), the mineralization rate would take a minimum of 3-5 years to turnover this reservoir even if all PON was readily labile; which it is not. The magnitude of the mean gross N mineralization in each cm of sediment depth, when scaled to all of LIS, is 12.4 million kgN y^{-1} with an estimated error of 50%. Relative to the annual N load, each cm of sediment is turning over a mass of N equivalent to about 1/3 of the N inputs.

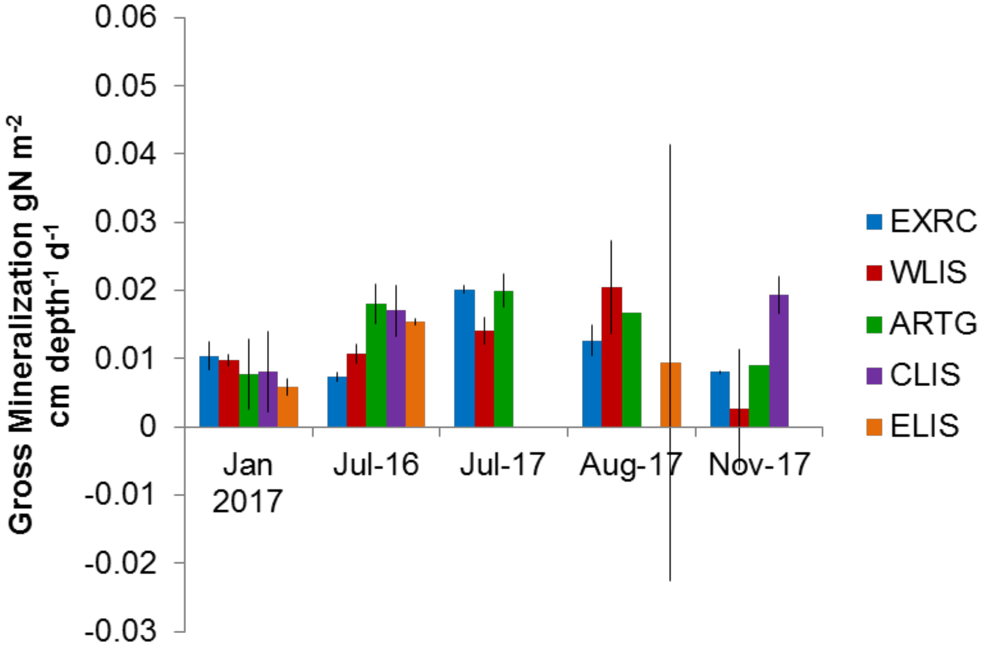

Fig. 5 Gross N mineralization measured over a 0-6 cm interval and normalized per cm sediment depth.

2.3 What is the Sediment Oxygen Demand

Mineralization in the sediment generated an oxygen demand (sediment oxygen demand – SOD) from the water column. The net flux of O_2 from overlying water into the sediment showed high v variance at some times/stations attributable to infaunal respiration. The SOD across sites and times ranged from 0.15 to 0.9 mmol O_2 m^{-2} hr^{-1} which, when converted to N mineralization using Redfield O_2:N stoichiometry was on par with the measured gross N mineralization rate attributable to 1-2 cm of sediment depth. This parity suggests, that the processes in the top 1-2 cm of sediment are actively participating in exchanges of with the overlying water. The SOD most commonly followed first order kinetics with respect to O_2 concentration with a first order rate coefficient of 0.003 – 0.004 hr^{-1}, although there were some sites and times when O_2 loss was independent of dissolved O_2 concentration. Relative to the most recent reported ranges of water column respiration in LIS (Goebel and Kremer 2007), the measured SOD is equivalent to 3 – 10 meters of depth integrated water column respiration on a per square meter basis. Given the thickness of the water column below the pycnocline in the hypoxic zone in LIS (15-20 m), the fractional contribution of sediments to total O_2 demand in the western sound would be on the order of 10-35%. Although there are some lower water column respiration rates reported for LIS (Eller 1991) that would suggest that SOD might be more important.

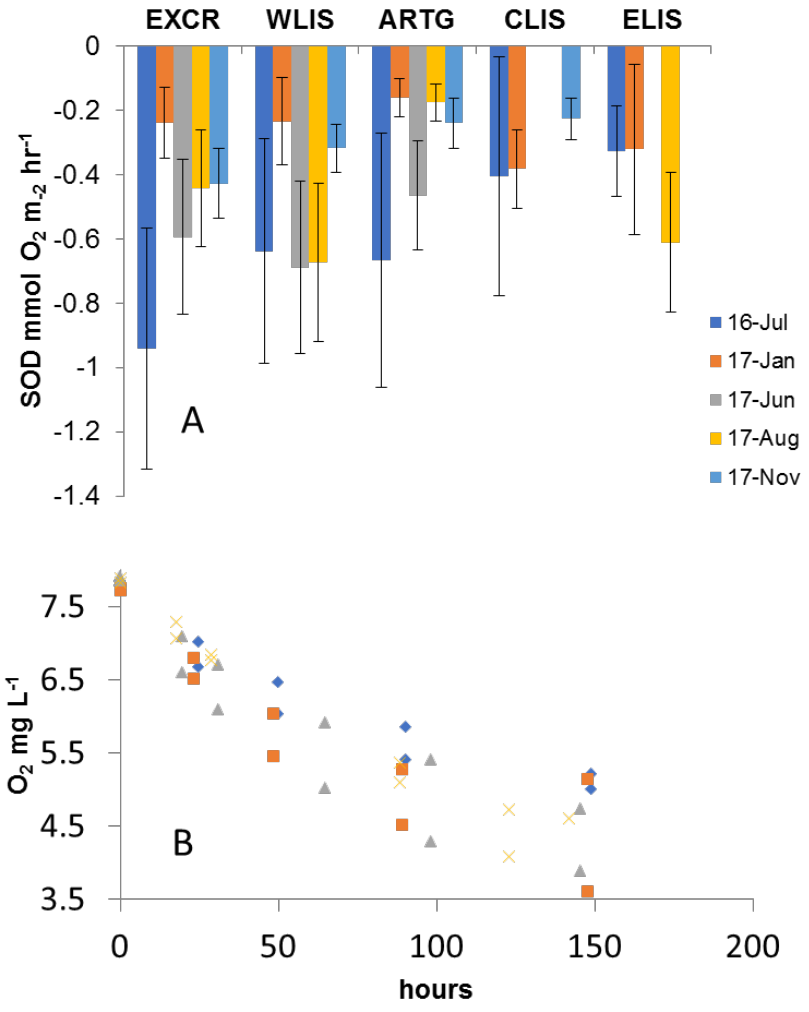

Fig. 6 Sediment oxygen demand (SOD) – panel A. Time series dissolved O_2 concentrations measured during sediment-water core incubations –panel B.

2.4. What Fraction of N Turnover Returns to the Water Column

Some fraction of the N turnover is released to the water column. With only a couple exceptions, there was a net flux of both NH_4^+ and NO_3^- from sediments to overlying water (Fig 7 a,b,c). NH_4^+ fluxes were 2-3 times NO_3^- fluxes and especially large in the presence of macroinfauna. On average the total DIN flux ($NH_4^+ + NO_3^-$; ~ 20 – 30 µmoles N m^{-2} hr^{-1}) was similar in magnitude to 1-2 cm worth of gross mineralization and a stoichiometrically equivalent SOD over a similar depth. The measured NO_3^- flux added to the coupled denitrification rate (see below) provided an estimate of gross nitrification of 25 µmoles N m^{-2} hr^{-1} which was similar in magnitude to the average total DIN flux. Nitrification represented a 1/3 of the gross mineralization rate ascribed to a 1 cm sediment interval and served as a small oxygen sink that was ~ 2 % of SOD. When scaled to the whole of LIS, the magnitude of the annual DIN flux from the sediment to the overlying water was approximately 17% as large as total N loading from external sources. This amount is on the order of 1/3 of WWTP inputs and roughly equivalent to the total riverine inputs of N.

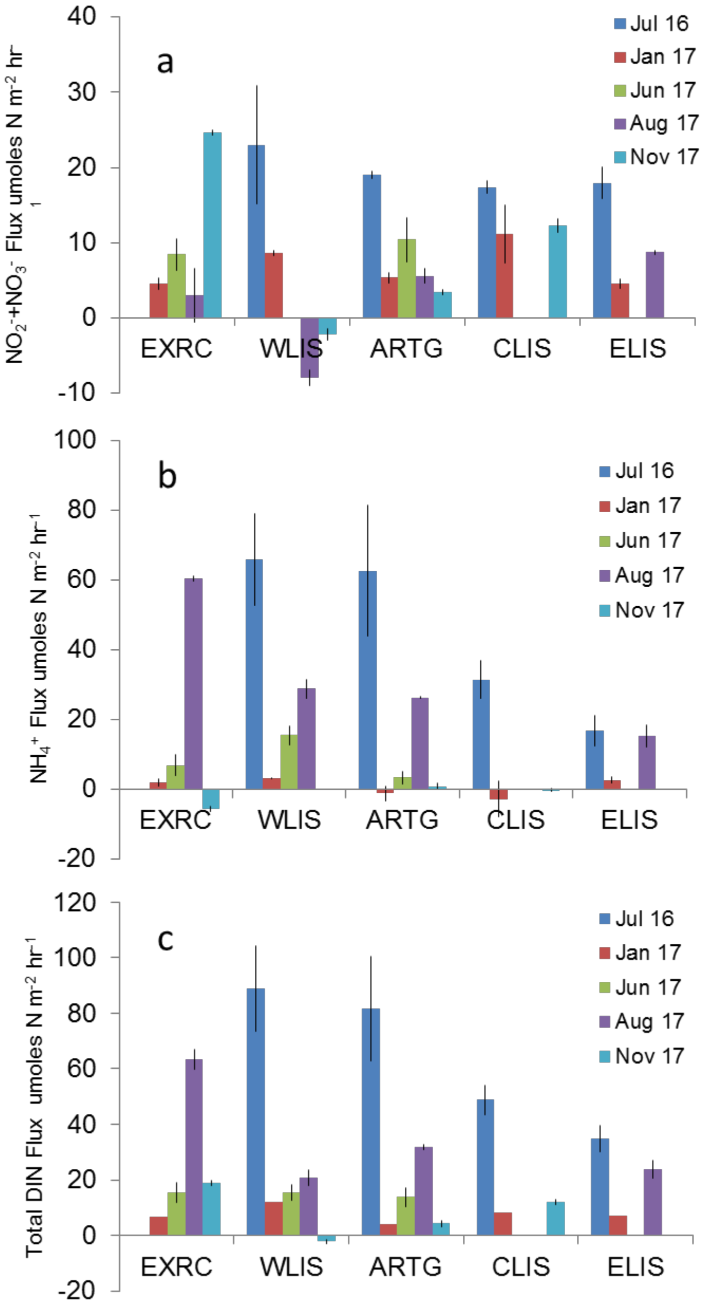

Figure 7. Sediment-water DIN flux summary. Positive values denote mass transfer from sediments to overlying water. Values derived from linear regressions from duplicate core incubations. Error bars are the RMSE of all linear fits to the time series core data.

2.5. How Much is Removed from the System; Denitrified?

Denitrification was overwhelmingly coupled to sediment nitrification and ranged 100 to 600 µmoles N m^{-2} d^{-1} across sites and times (Fig 8). Rates were positively correlated to water temperature and independent of bottom water nitrate concentration (Fig 9 a,b). The magnitude

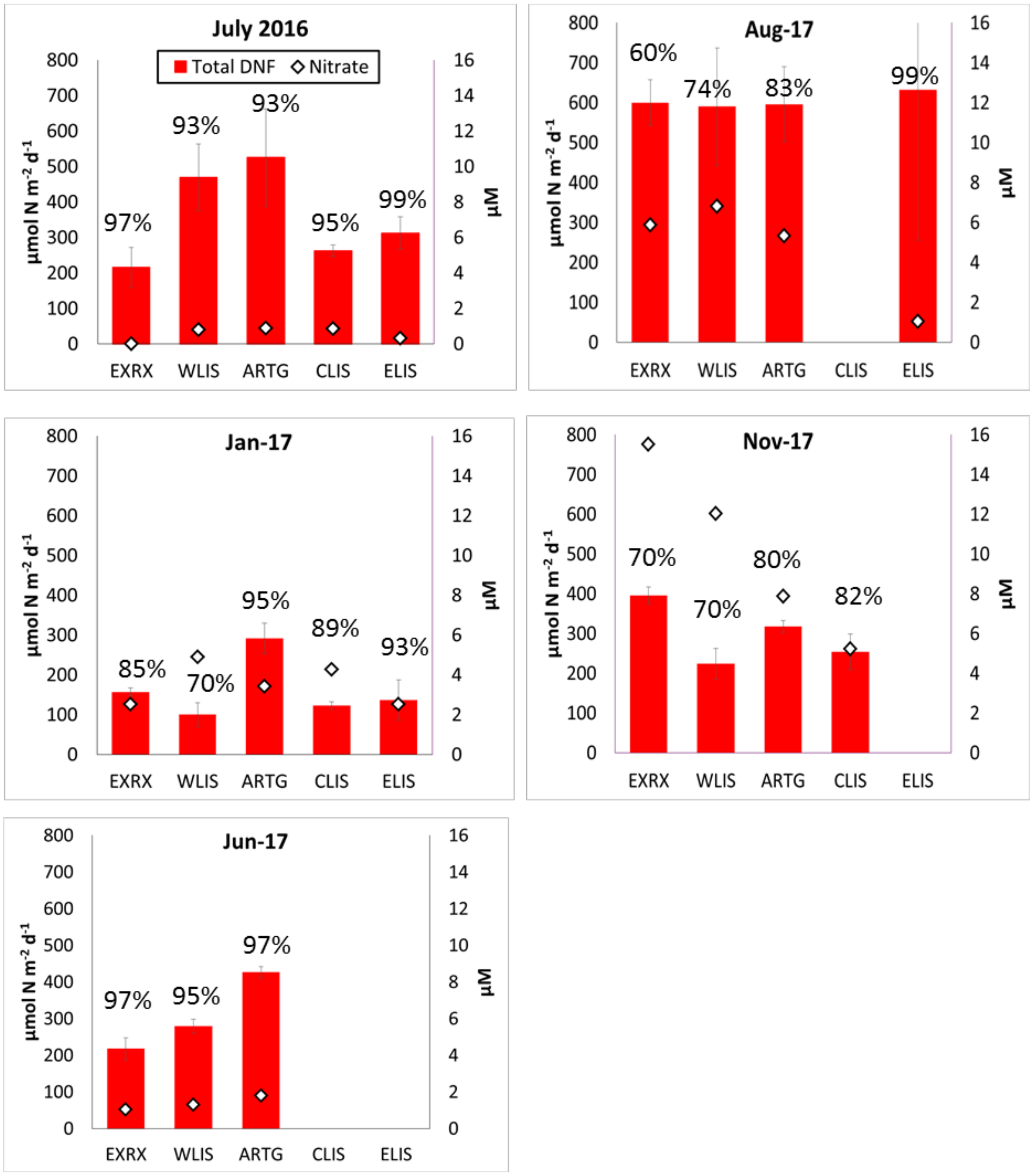

Figure 8. Dentrification rate (red bars and left axis) and bottom water nitrate concentration (symbols and right axis). Percentages are the fraction of total denitrification that is coupled to nitrification in the sediments as opposed to denitrification of bottom water nitrate.

of denitrification was similar to that of the net DIN ($NH_4^+ + NO_3^-$) flux from the sediment to the overlying water. The denitrification efficiency, calculated as the denitrification rate divided by the sum of denitrification + DIN flux, was 32-42% across the sound with the highest efficiency in the eastern sound. When the denitrification rates were scaled annually and to the LIS areas assigned to each station (Fig 1), the total mass of N denitrified was ~ 4 million kgN y^{-1}; or approximately 10% of the annual N load.

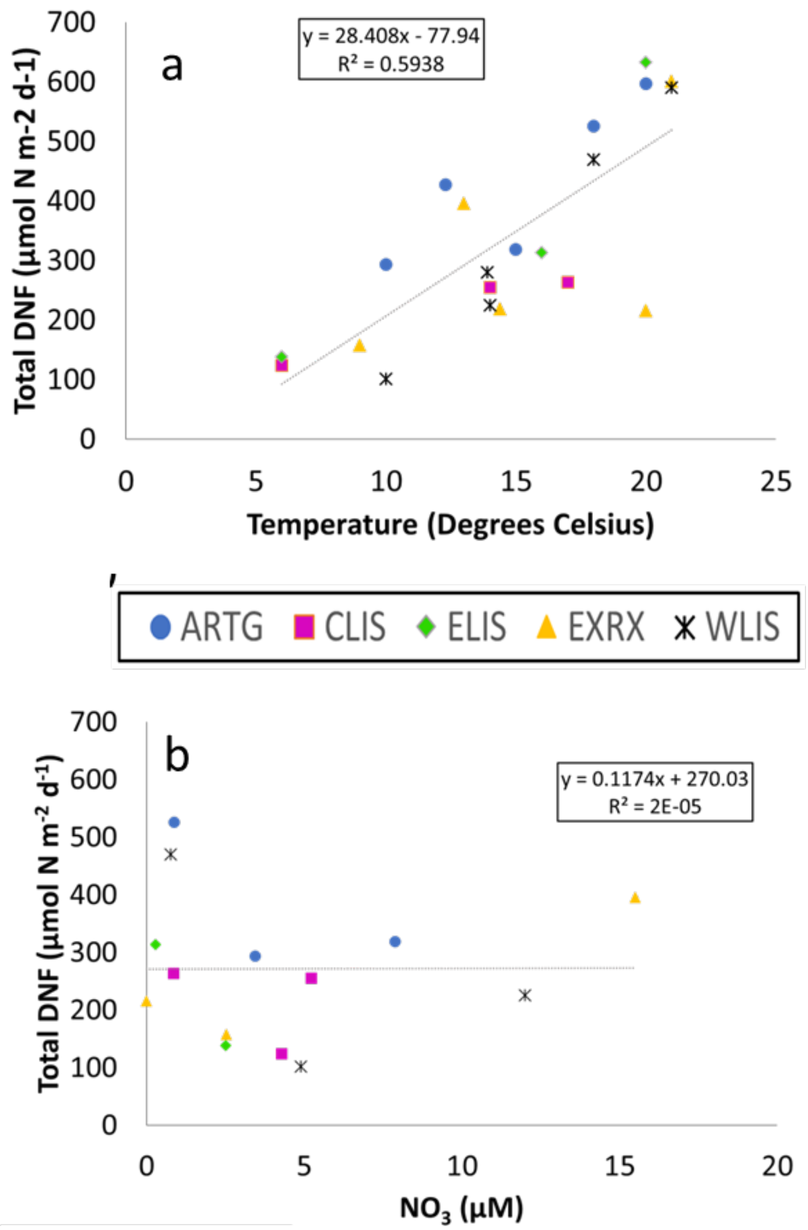

Figure 9. Dentrification rates as a function of temperature (a) and bottom water nitrate concentration (b). Rates include contributions from both coupled and direct denitrification.

The reduction of oxidized N to N_2 gas via denitrification was likely marginally supplemented by a small amount of anaerobic ammonium oxidation (Anammox; Table 1). An alternate fate for nitrate/nitrite in sediments was Dissimilatory Nitrate Reduction to Ammonium (DNRA) which effectively competed with denitrification for nitrate particularly in the summer (Table 1). Based on the DNRA : Denitrification ratio (Table 1), about one third of the $NO_{2,3}^-$ produced during gross nitrification was returned back to the sediment NH_4^+ inventory by DNRA. This amount was approximately equivalent to amount of $NO_{2,3}^-$ released to the water column across the sediment-water interface.

Table 1. Fate of nitrate in western LIS sediments. Percentages are derived from ratios of potential rates measured in anaerobic slurry experiments. Winter data are ranges of July and August experiments.

	% Denitrification	% Anammox	% DNRA
Summer 2017			
EXCR	45-57	19-24	19-36
WLIS	21-27	1-4	72-75
ARTG	32-52	3-9	39-65
Winter 2017			
EXCR	60	12	28
WLIS	64	13	23
ARTG	58	12	30

2.6 Summary of Sediment N Processes in a LIS Nitrogen Budget Context

The following comparison is currently in need of a more rigorous error assessment. This will be done prior to publication. Nevertheless, it provides some sense of the relative importance of various sediment processes relative to total N throughput in LIS. The usual cautions about mass balances assuming steady state as well as potential timescale mismatches apply. The sum of losses via denitrification + tidal export + burial account for 35 to 44% of annual N loads. If the DIN flux from sediment to overlying water is considered an additional N ‘load’ to the water column, the sum total losses account for 30-37 % of N inputs.

The purpose of this budget is not to create a mass balance that exhibits closure. Its function is to indicate which processes are of a magnitude that might influence/inform construction of a more robust budget. Despite the ongoing error assessment of the fluxes in Fig. 10, it seems evident that our current understanding of the loss terms is both advancing, and could use some additional improvement. Assessments of scaling approaches, and spatial resolution are good places to start.

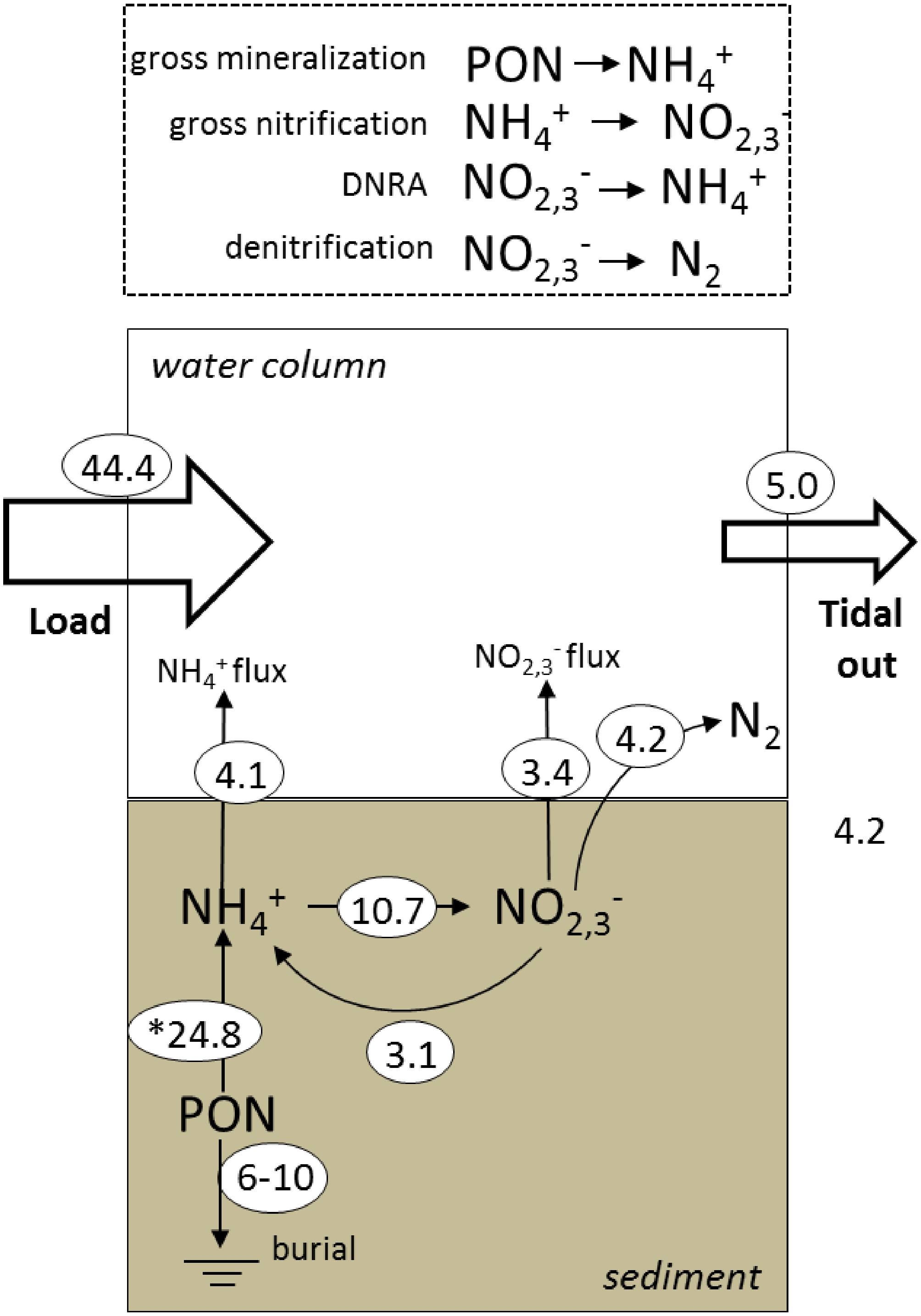

Figure 10. Annual whole LIS N process fluxes (millions kgN y^{-1}). Asterisk denotes gross mineralization ascribed to a 2 cm thick interval of sediment. The tidal export flux was supplied by M. Whitney pers. comm. 2018.


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