MAKING ITS MARK: THE FATE AND TRANSPORT OF NITROGEN AND CARBON IN THE LONG ISLAND SOUND ESTUARY

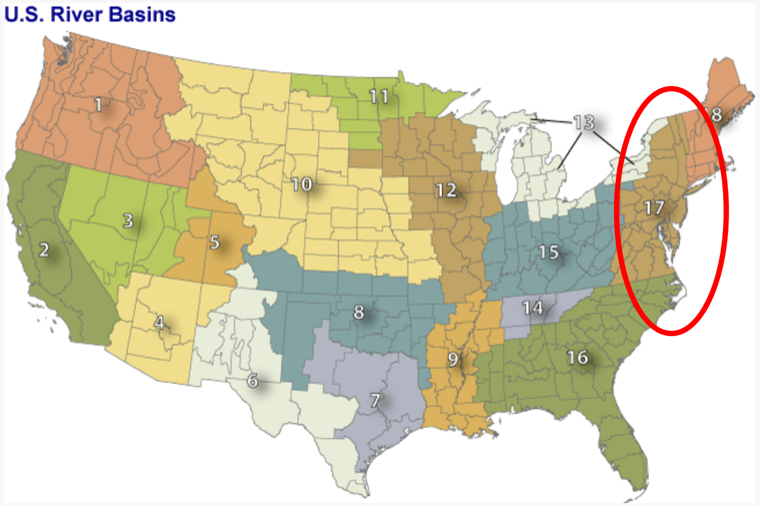
Penny Vlahos[1]

Michael M .Whitney[1], Allison Byrd[1], John R Mullaney[2], Christina Menniti[1], Jamie Vaudrey[1], Lauren Barrett[1], Joseph Warren[1], Jonathan Morrison[2]

[1]University of Connecticut, Department of Marine Sciences

[2]USGS, Connecticut Water Science Center

THE GRAND SCHEME



MID-ATLANTIC DRAINAGE BASIN

Chesapeake Bay watershed

Basin Area: 166,530 km^2
Estuary Area: 11,601 km^2
Avg. Depth 6.4 m (2-53m)

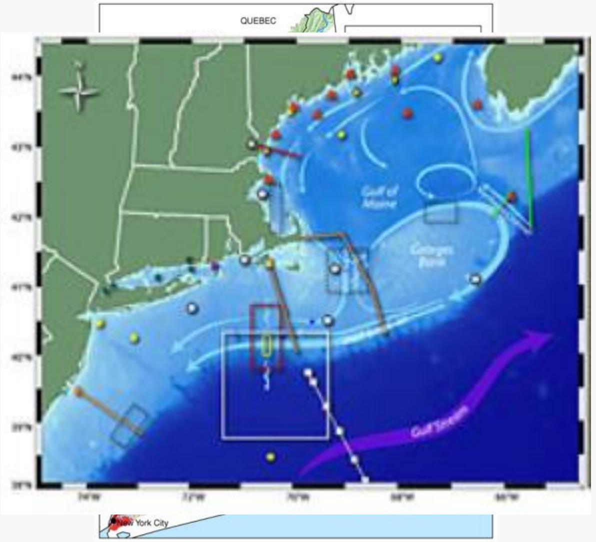
Delaware Bay watershed

Basin Area: 34,965 km^2
Estuary Area: 2,030 km^2
Avg. Depth 8 m (2-45m)

Hudson River watershed

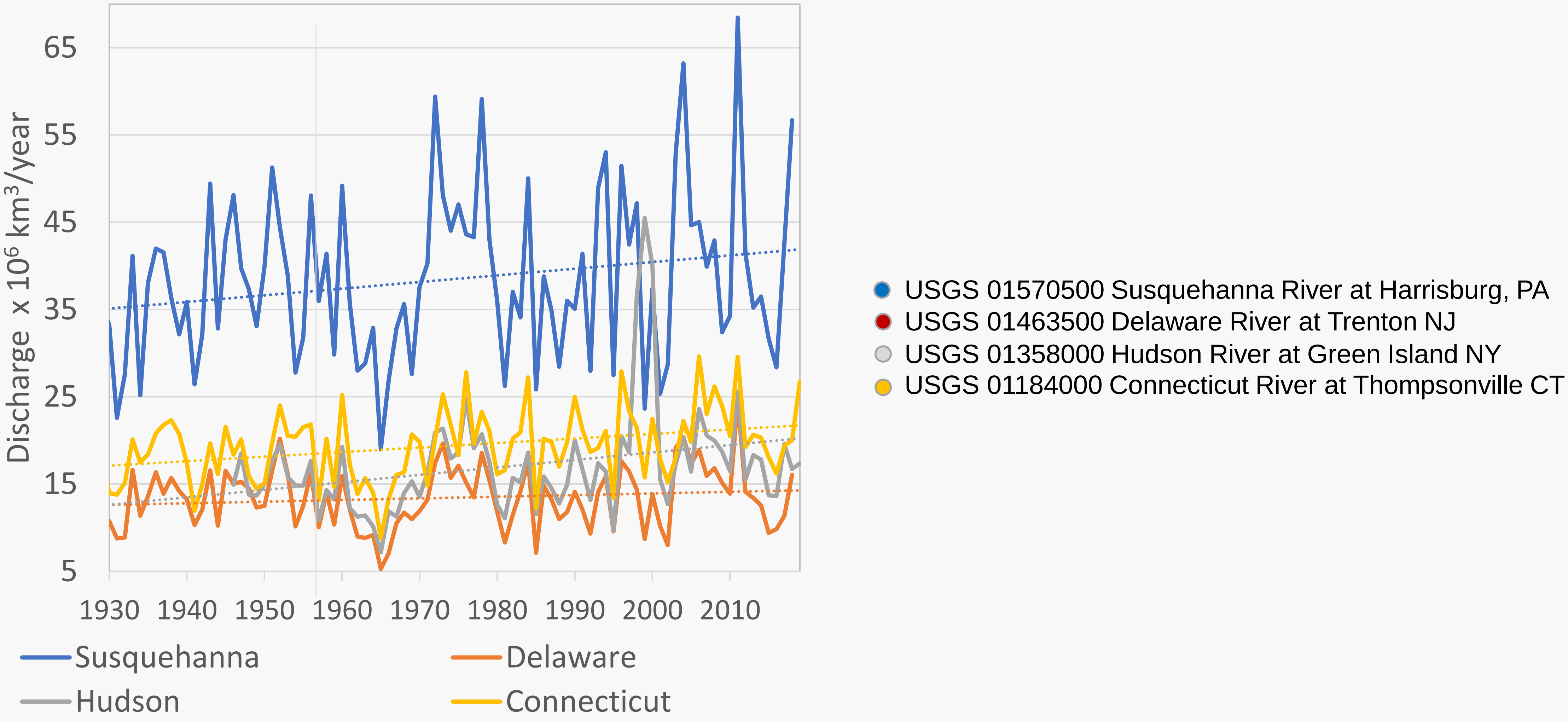
Basin Area: 34,706 km^2
Estuary Area: <2000 km^2
Avg. Depth 30 m (2-60m)

Connecticut River watershed



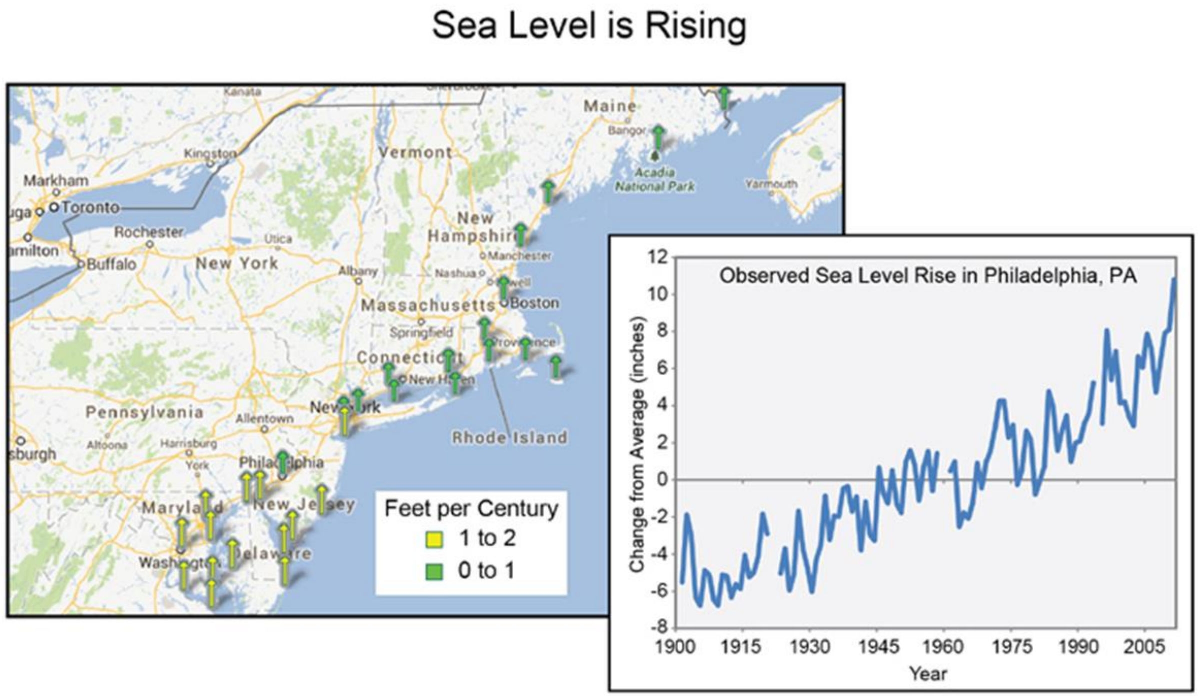
Basin Area: 29,137 km^2
LIS Drainage: 44 030 km^2
Estuary Area: 3,284 km^2
Avg. Depth 19 m (2-70m)

RIVER FLUXES (ANNUAL AVERAGES)



PREDICTED CHANGES IN PRECIPITATION

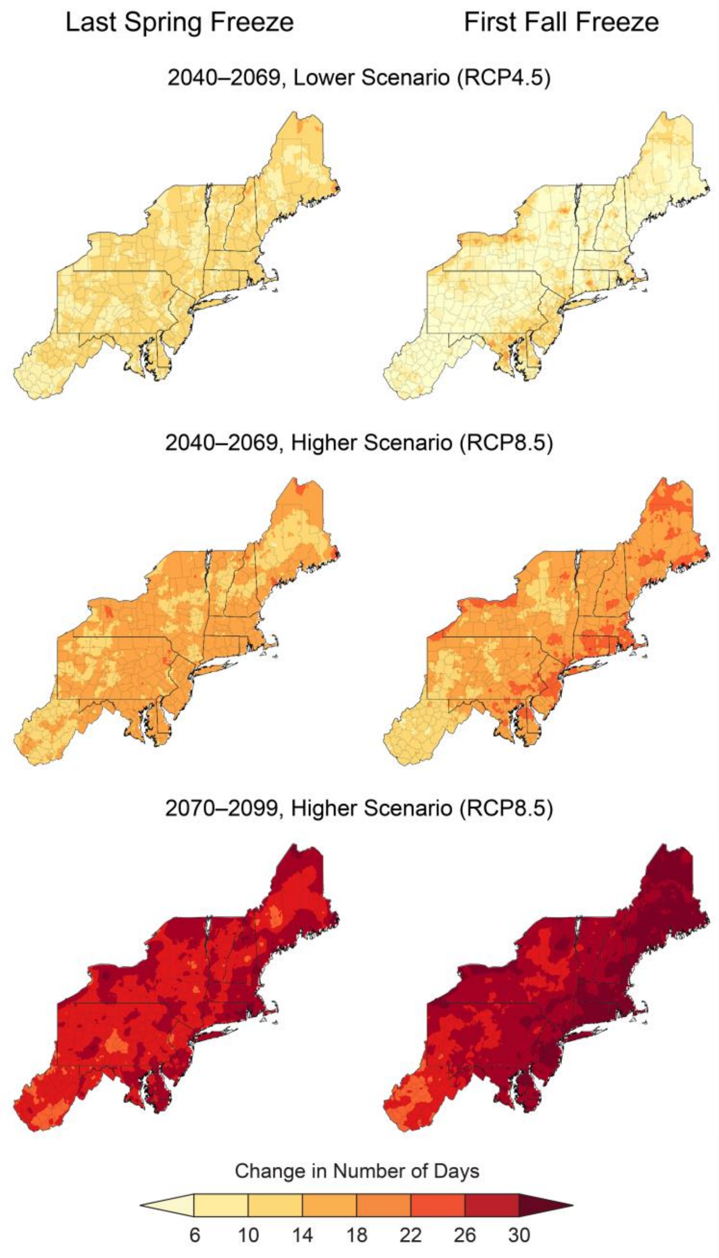
- Increase flooding and coastal erosion, in the Northeast
  - Sea level rise
  - heavy precipitation
  - storm surge



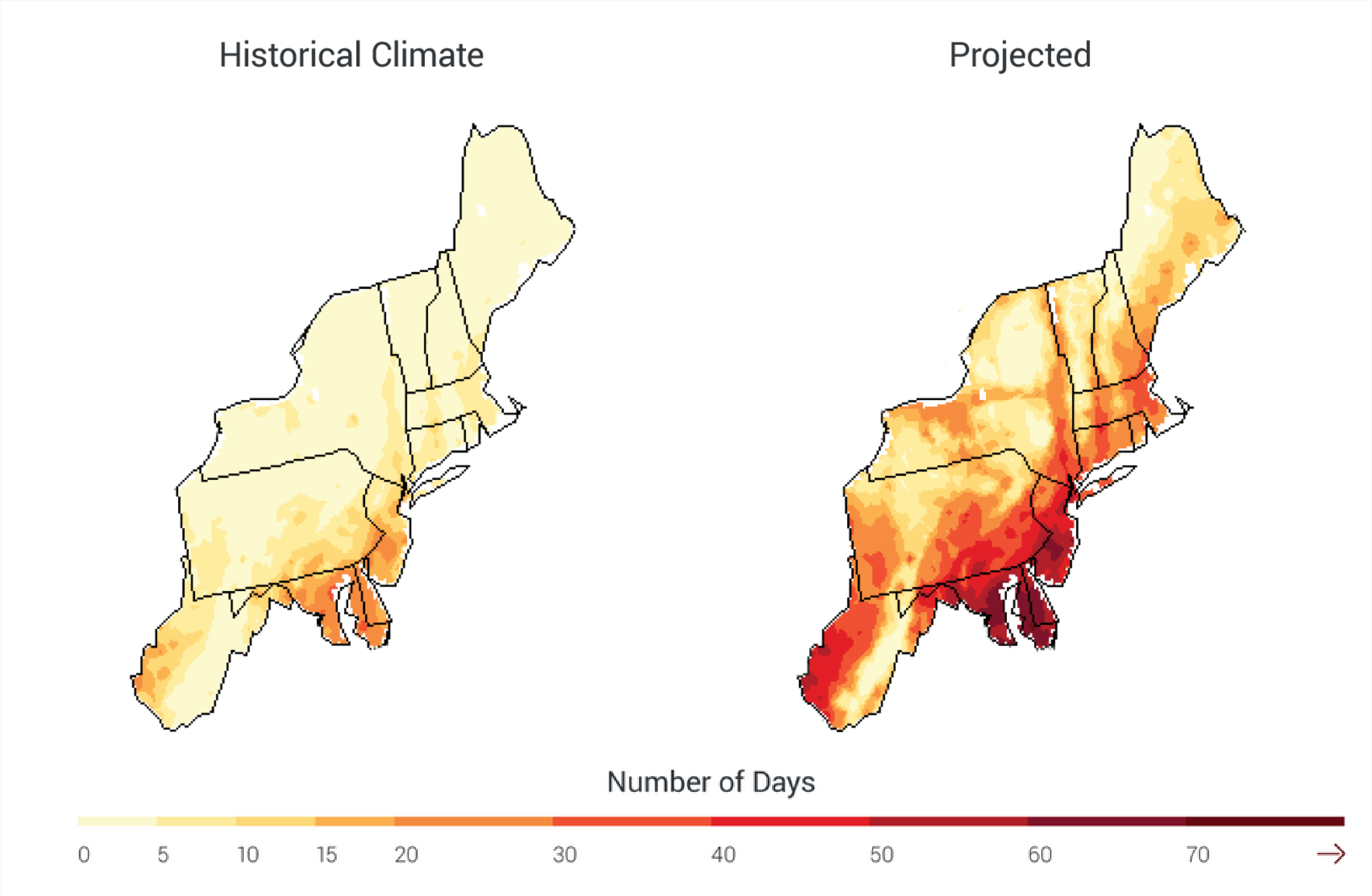
- Source: https://archive.epa.gov/epa/climate-impacts/climate-impacts-northeast.html

INCREASES IN FREEZE FREE PERIOD

- Fourth National Climate Assessment
- https://nca2018.globalchange.gov/chapter/18/

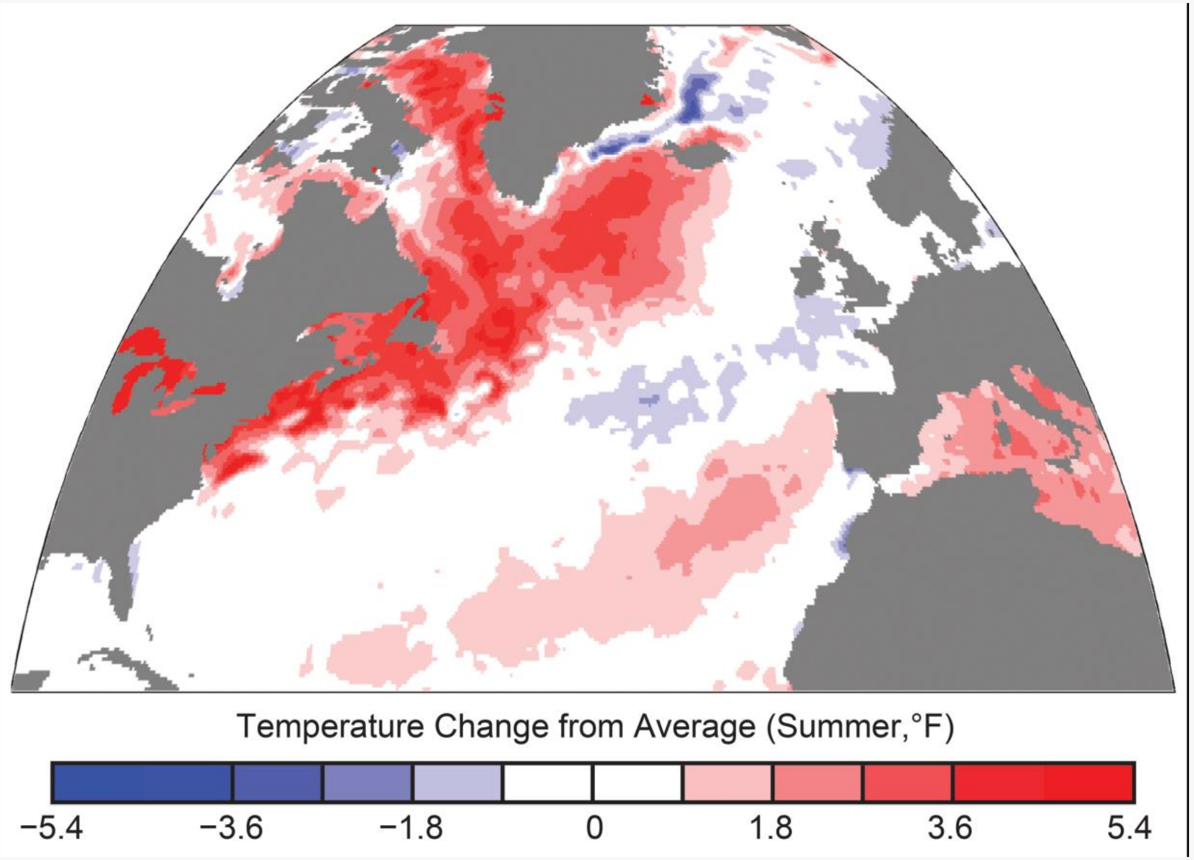


INCREASES IN DAYS >90°F



Fourth National Climate Assessment https://nca2018.globalchange.gov/chapter/18/

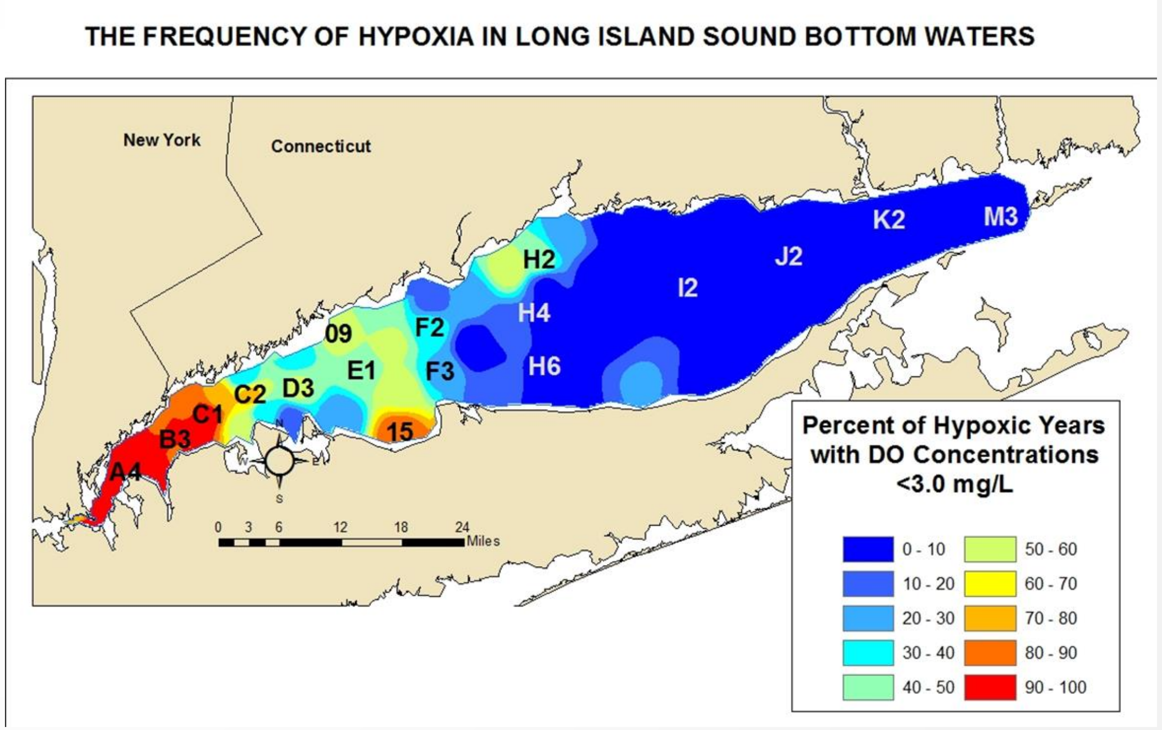
2012 HEAT WAVE – NCA 2018



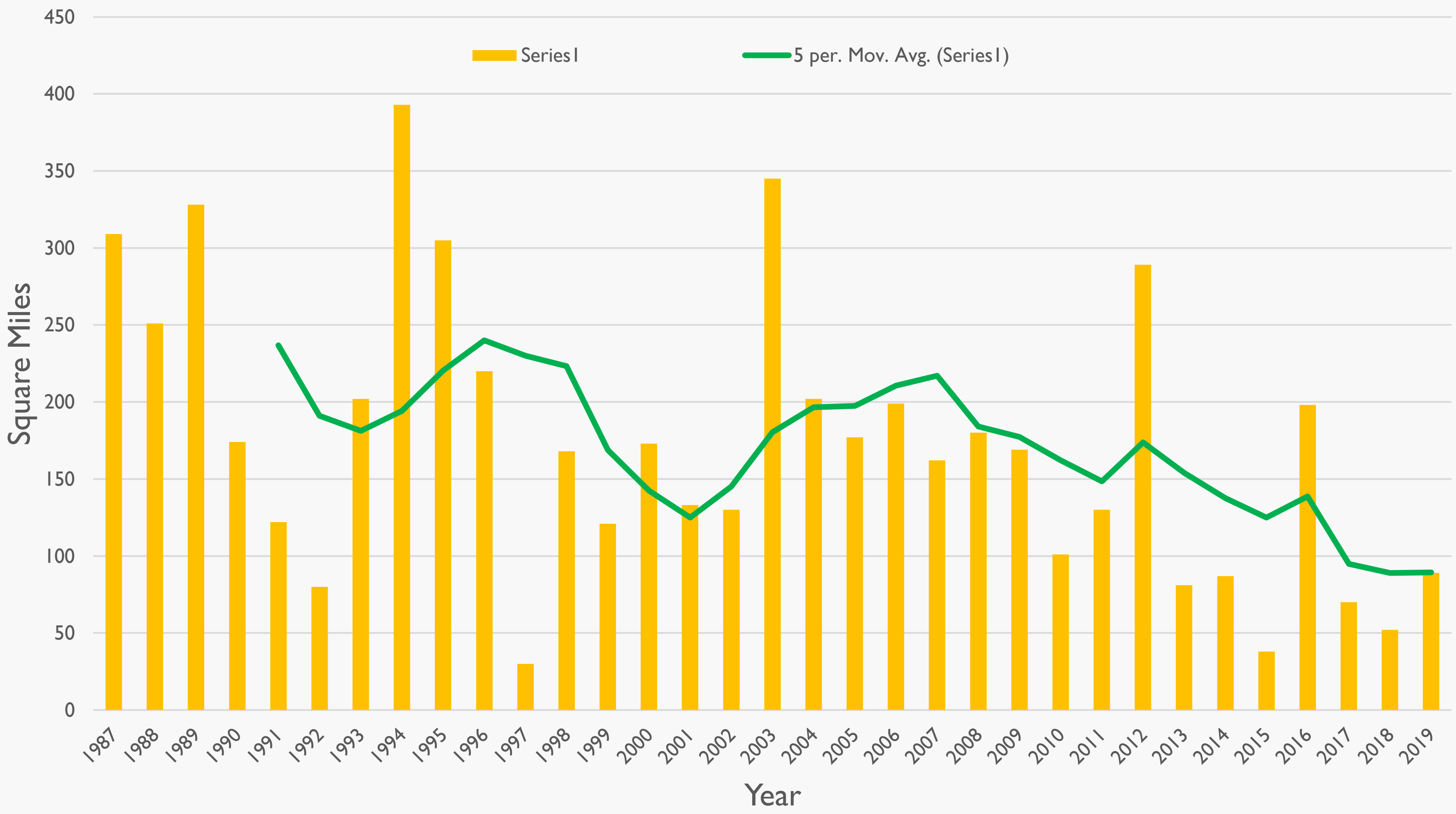
THE CONCERN

HYPOXIA

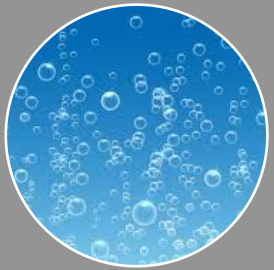
- Low dissolved oxygen
  - Hypoxia in Long Island Sound occurs annually **starting late June to early July** with a maximum typically in August and subsiding in September
  - Has affected from **5% to nearly 50%** of LIS study area
  - **65% of the stations CT-DEEP stations** have been hypoxic at least once over the duration of the Program.



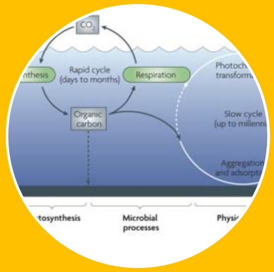
LONG ISLAND SOUND AREA OF HYPOXIA



UNDERSTANDING LONG ISLAND SOUND (LIS) (THE CHEMICAL)

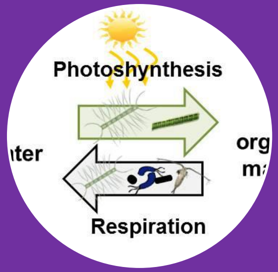


DO Trends

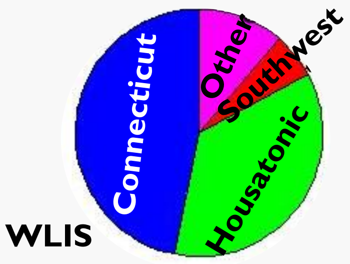


OC Budgets

N Budgets

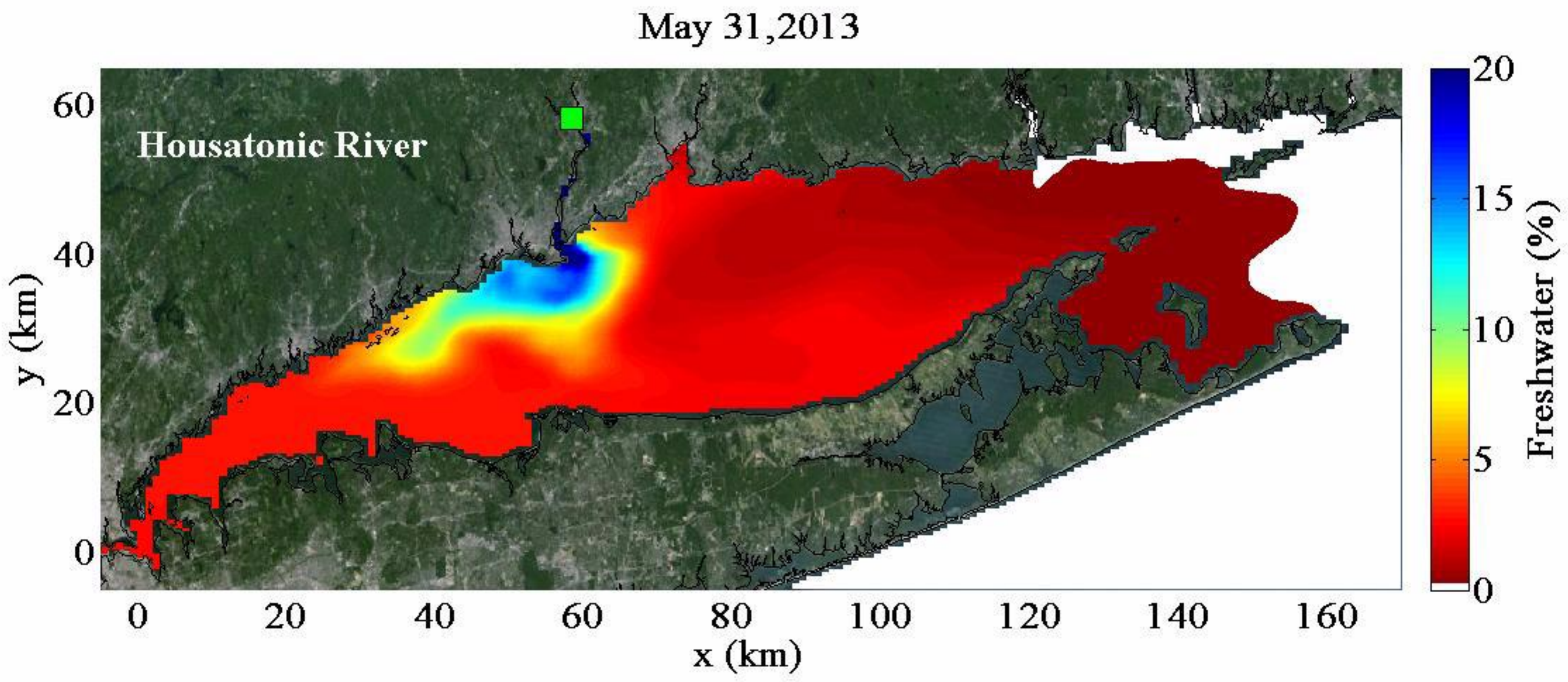


Respiration & DIC



UNDERSTANDING LONG ISLAND SOUND (LIS) (THE PHYSICAL)

- Models water currents, temperatures, and salinities
- Passive tracers added to each river to track their plumes
- CT and Housatonic are largest freshwater sources in WLIS



PART I: DISSOLVE OXYGEN TRENDS IN LIS

- Specific Aims
  - Examine DO, T, and S Trends from 1994-2014
  - stations were chosen along the west-east axis of LIS

Continental Shelf Research 151 (2017) 1–7

Contents lists available at ScienceDirect

Continental Shelf Research

journal homepage: www.elsevier.com/locate/csr

ELSEVIER

Timescales for determining temperature and dissolved oxygen trends in the Long Island Sound (LIS) estuary

Allison Staniec*, Penny Vlahos

University of Connecticut, Department of Marine Sciences, 1080 Shennecossett Road, Groton, CT, 06442, United States

ARTICLE INFO

Keywords:
Time Series
Long Island Sound
Dissolved Oxygen
Temperature Trends
Hypoxia
Climate

ABSTRACT

Long-term time series represent a critical part of the oceanographic community's efforts to discern natural and anthropogenically forced variations in the environment. They provide regular measurements of climate relevant indicators including temperature, oxygen concentrations, and salinity. When evaluating time series, it is essential to isolate long-term trends from autocorrelation in data and noise due to natural variability. Herein we apply a statistical approach, well-established in atmospheric time series, to key parameters in the U.S. east coast's Long Island Sound estuary (LIS). Analysis shows that the LIS time series (established in the early 1990s) is sufficiently long to detect significant trends in physical-chemical parameters including temperature (T) and dissolved oxygen (DO). Over the last two decades, overall (combined surface and deep) LIS T has increased at an average rate of 0.08 ± 0.03 °C yr^{-1} while overall DO has dropped at an average rate of 0.03 ± 0.01 mg $L^{-1} yr^{-1}$ since 1994 at the 95% confidence level. This trend is notably faster than the global open ocean T trend (0.01 °C yr^{-1}), as might be expected for a shallower estuarine system. T and DO trends were always significant for the existing time series using four month data increments. Rates of change of DO and T in LIS are strongly correlated and the rate of decrease of DO concentrations is consistent with the expected reduced solubility of DO at these higher temperatures. Thus, changes in T alone, across decadal timescales can account for between 33 and 100% of the observed decrease in DO. This has significant implications for other dissolved gases and the long-term management of LIS hypoxia.

SIGNAL TO NOISE

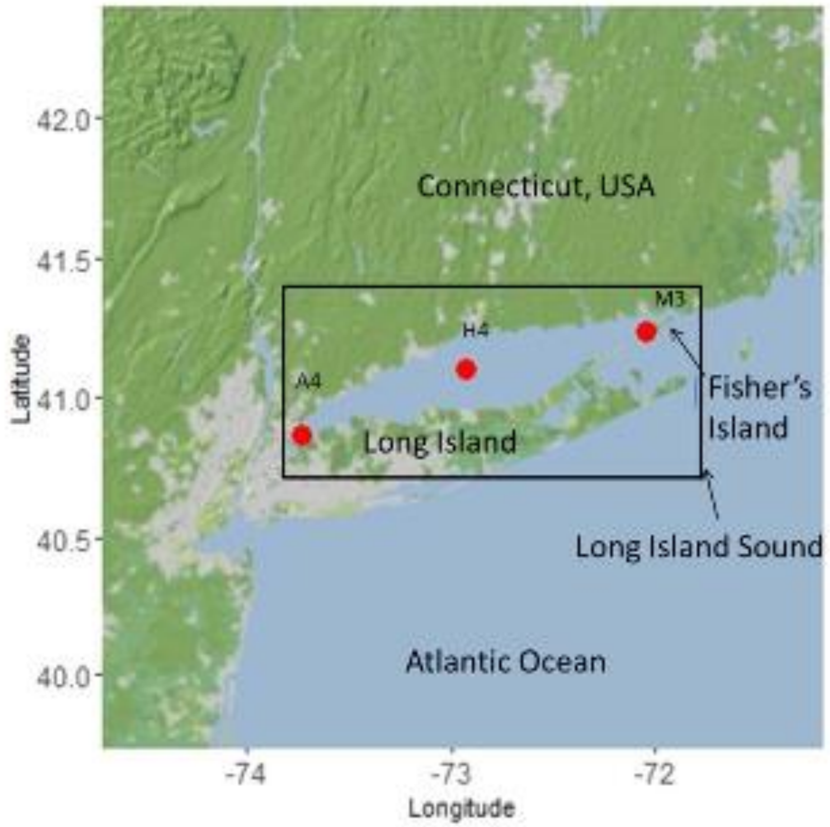
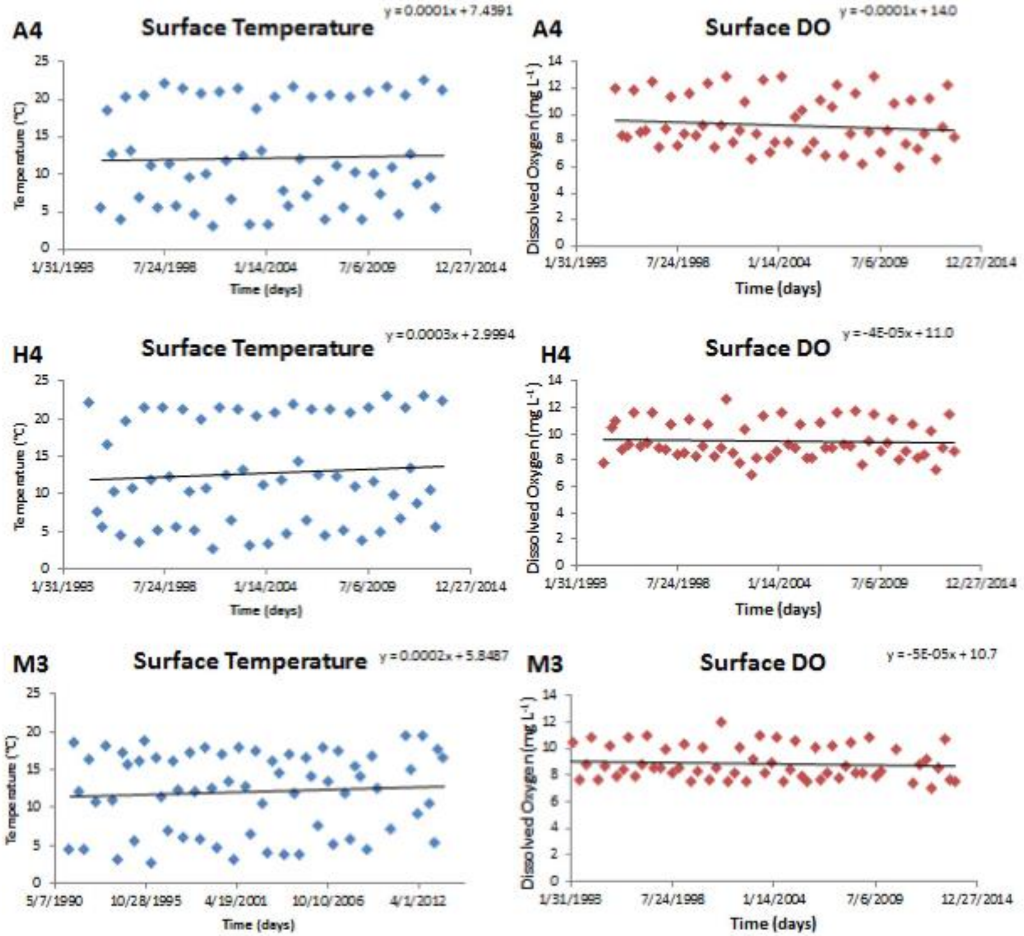


Fig. 1. Selected stations monitored (approximately monthly) year-round by DEEP in the Long Island Sound.



APPROACH

- Tiao et al. (1990) and Weatherhead et al. (1998) adapted by Henson et al. (2016).
- Evaluates the magnitude of a linear trend and the noise in a time series to determine n*
- The data is fit to a linear trend plus noise:

$$Y_t = \mu + \omega X_t + N_t$$

Data y-intercept slope noise

$$n^* = \left(\frac{3.3\sigma_n}{|\omega|} \sqrt{\frac{1+\phi}{1-\phi}} \right)^{2/3}$$

SOURCES OF BIAS

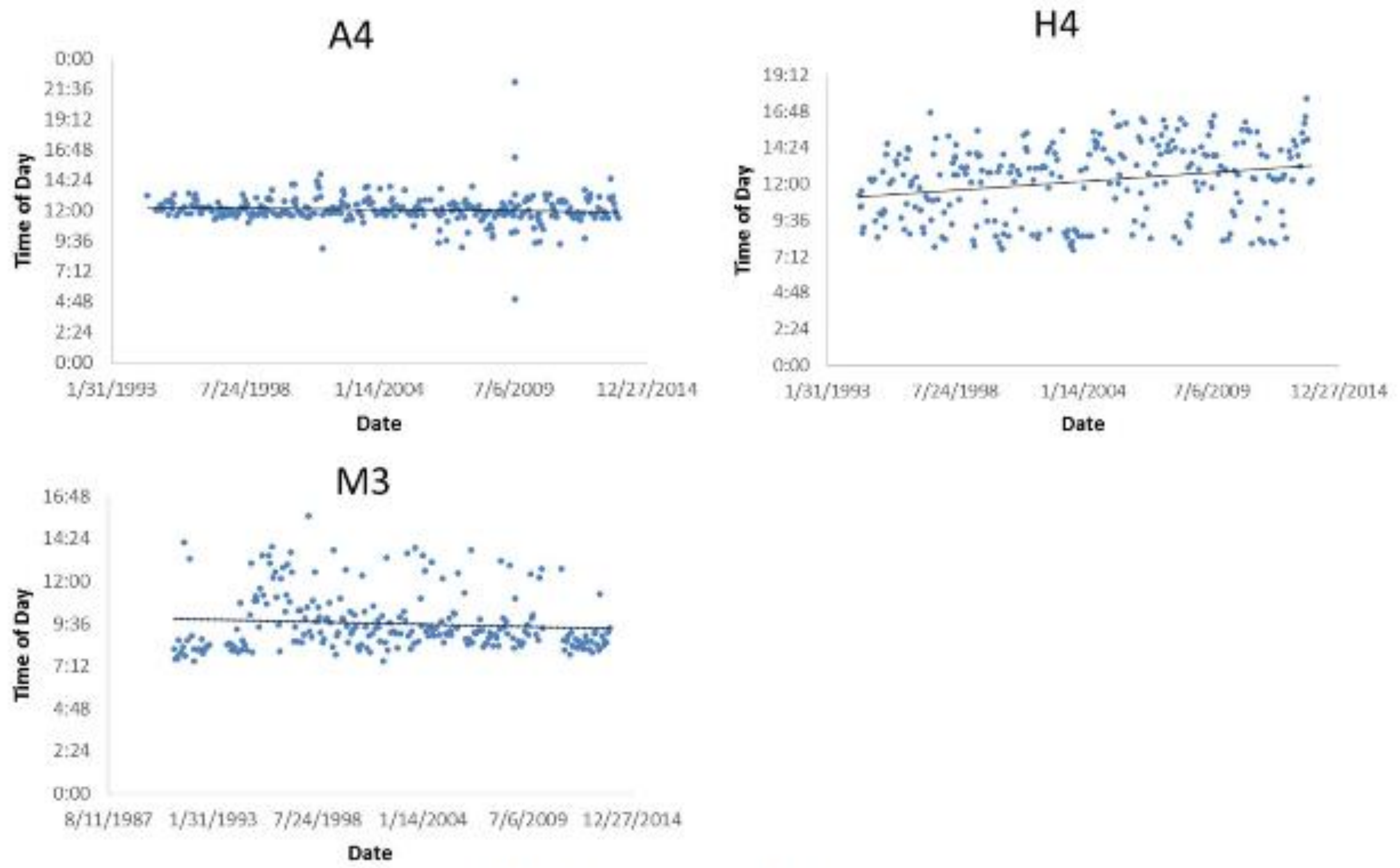
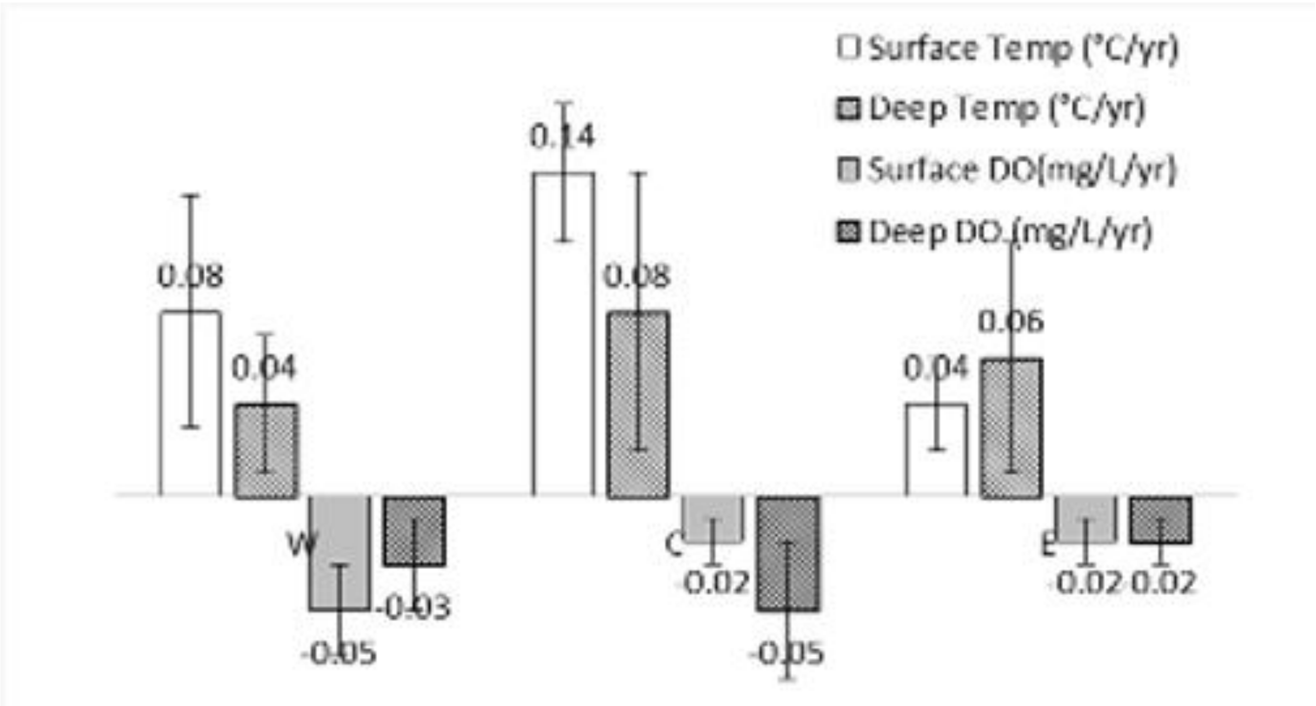


Fig. 4. Time of day of sampling at each station.

SIGNIFICANT TRENDS (1994-2014)



A4 H4 M3

MAJOR RESULTS

- Study confirms a warming trend of **0.08 ± 0.03 °C yr^{-1}** across LIS and a decrease in DO of **−0.03 ± 0.01 mg $L^{-1}yr^{-1}$** over the 1994–2014 period.
- The correlation between the rate of change in T and the rate of change in DO implies that long-term processes operating on decadal timescales control these trends that the **decrease in LIS DO can be accounted for solely through increases in T on these timescales**
- An additional important implication of this work is the influence of this warming on other dissolved gas solubilities in semi-enclosed estuaries for **gases such as CO_2, CH_4, and N_2** that are highly sensitive to temperature and may follow similar reductions in standing stock.

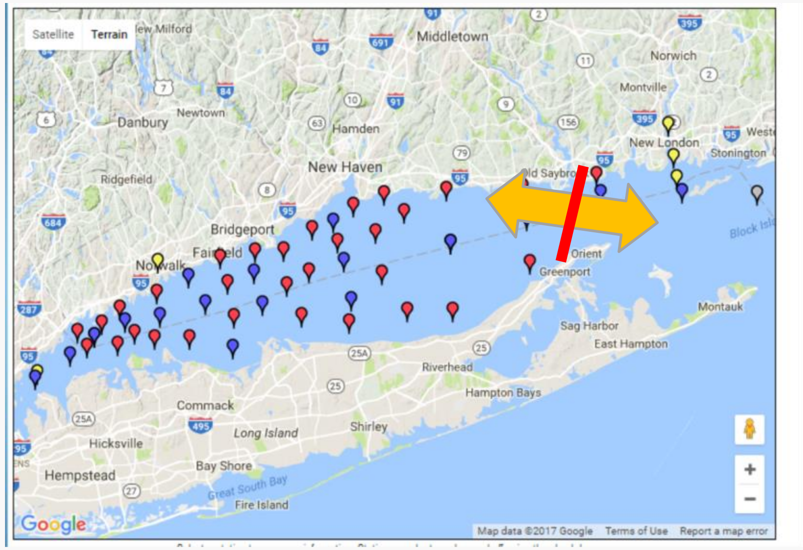
PART II: VARIATIONS IN ORGANIC CARBON FLUXES FROM LONG ISLAND SOUND TO THE CONTINENTAL SHELF

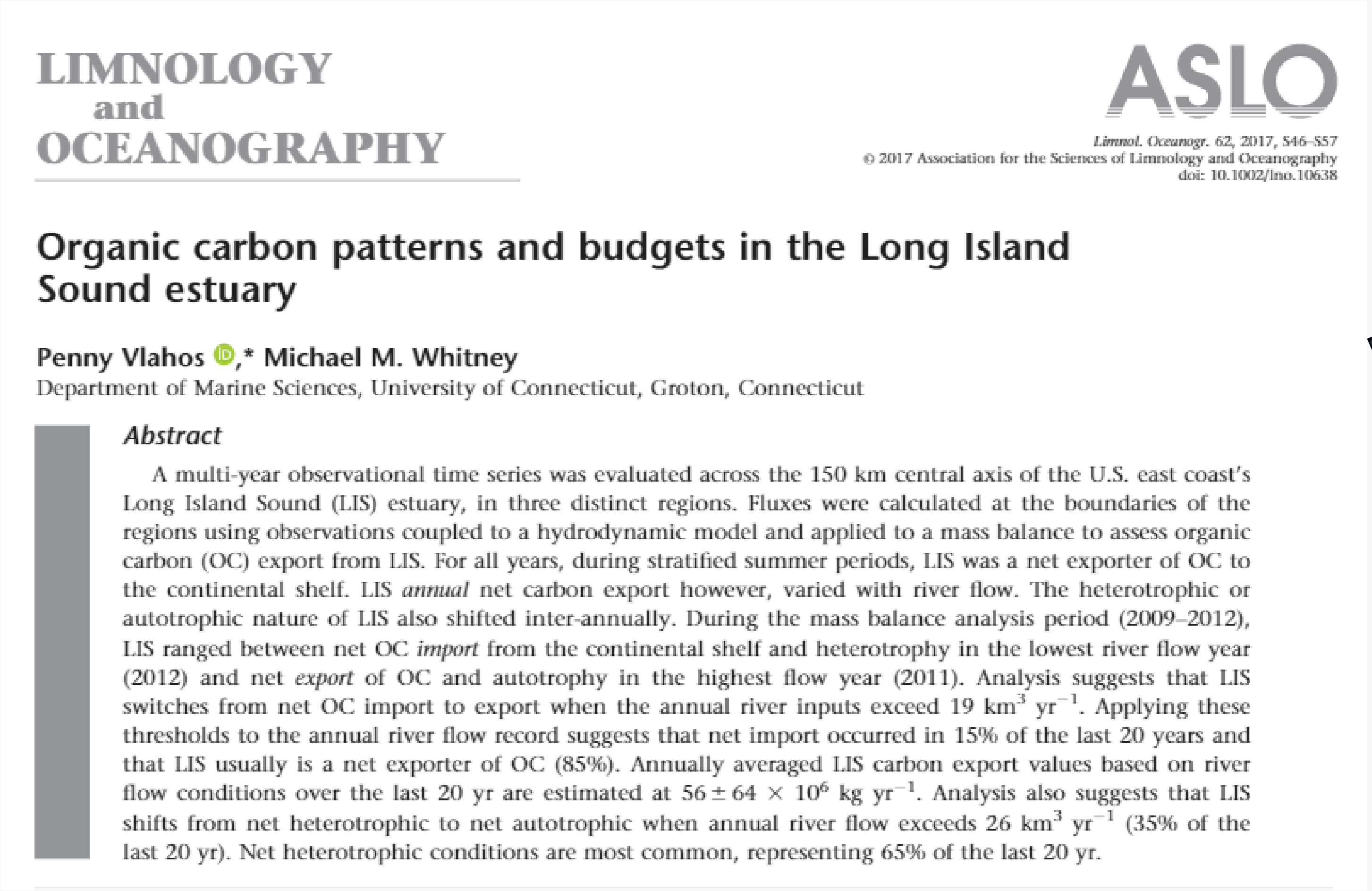
Penny Vlahos & Michael Whitney

Department of Marine Sciences, University of Connecticut

OBJECTIVES: CT SEA GRANT R/ER-28

- This study provides the basic chemical and physical measurements required to determine the net export of organic C and N by conducting focused studies at the outer boundary of LIS (the Race) to close the C and N balance of LIS.





LIMNOLOGY and OCEANOGRAPHY

ASLO

Limnol. Oceanogr. 62, 2017, S46–S57

doi: 10.1002/lno.10638

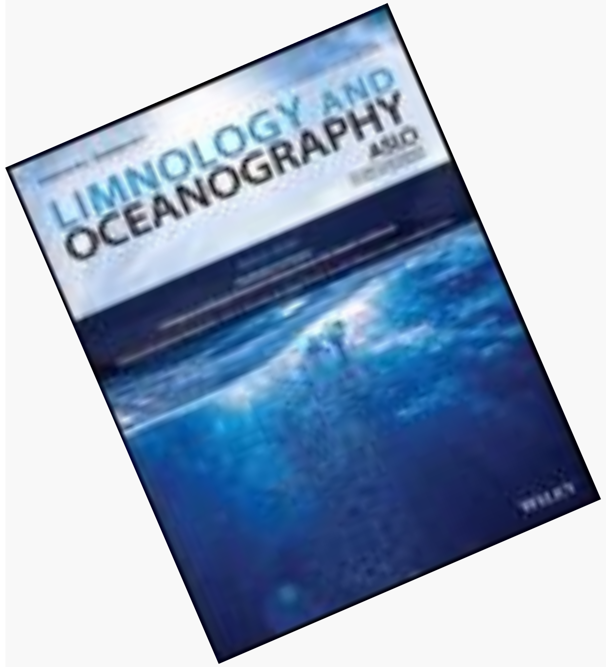
Organic carbon patterns and budgets in the Long Island Sound estuary

Penny Vlahos,* **Michael M. Whitney**

Department of Marine Sciences, University of Connecticut, Groton, Connecticut

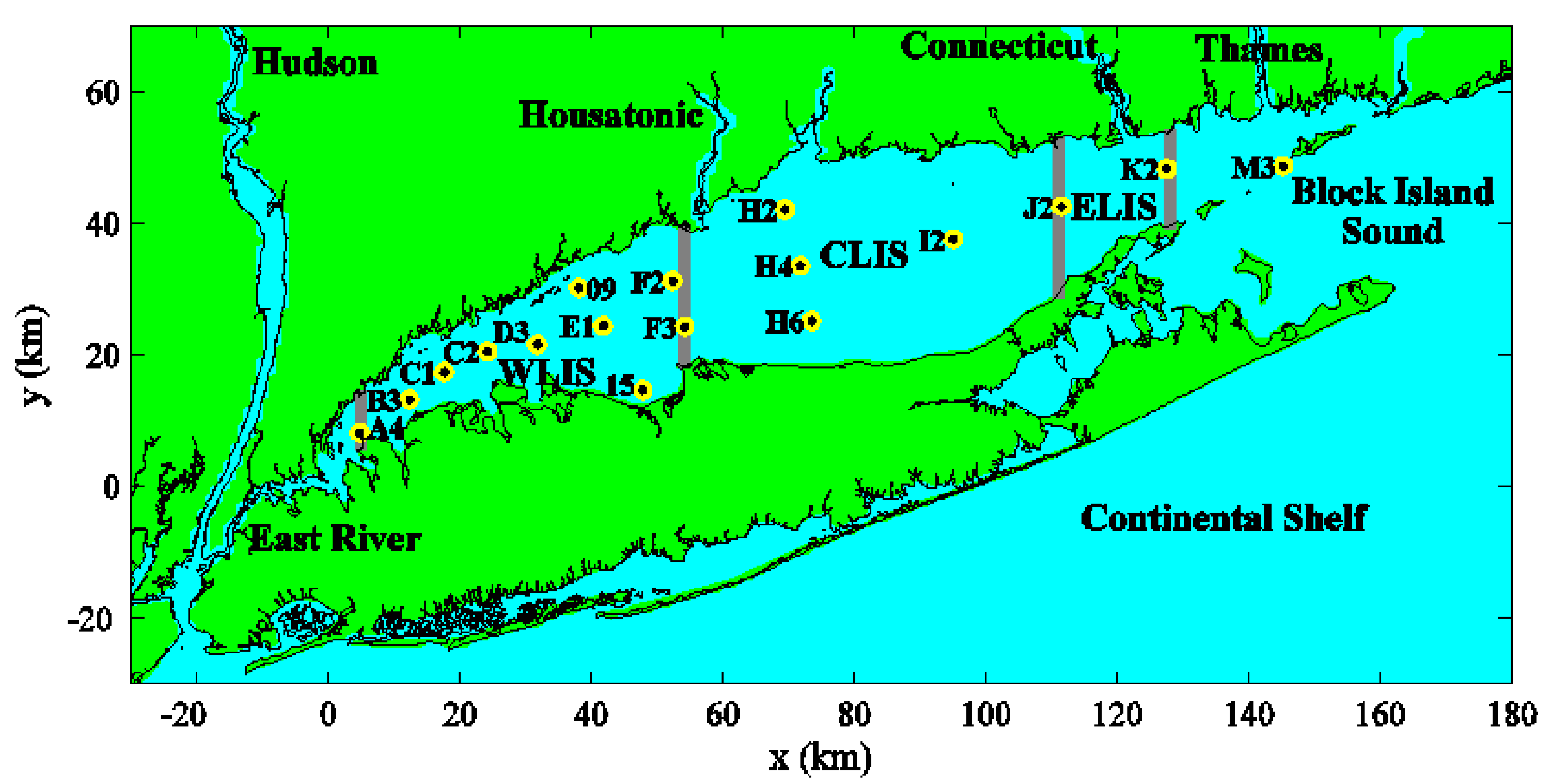
Abstract

A multi-year observational time series was evaluated across the 150 km central axis of the U.S. east coast's Long Island Sound (LIS) estuary, in three distinct regions. Fluxes were calculated at the boundaries of the regions using observations coupled to a hydrodynamic model and applied to a mass balance to assess organic carbon (OC) export from LIS. For all years, during stratified summer periods, LIS was a net exporter of OC to the continental shelf. LIS *annual* net carbon export however, varied with river flow. The heterotrophic or autotrophic nature of LIS also shifted inter-annually. During the mass balance analysis period (2009–2012), LIS ranged between net OC *import* from the continental shelf and heterotrophy in the lowest river flow year (2012) and net *export* of OC and autotrophy in the highest flow year (2011). Analysis suggests that LIS switches from net OC import to export when the annual river inputs exceed 19 km^3 yr^{-1}. Applying these thresholds to the annual river flow record suggests that net import occurred in 15% of the last 20 years and that LIS usually is a net exporter of OC (85%). Annually averaged LIS carbon export values based on river flow conditions over the last 20 yr are estimated at $56 \pm 64 \times 10^6$ kg yr^{-1}. Analysis also suggests that LIS shifts from net heterotrophic to net autotrophic when annual river flow exceeds 26 km^3 yr^{-1} (35% of the last 20 yr). Net heterotrophic conditions are most common, representing 65% of the last 20 yr.

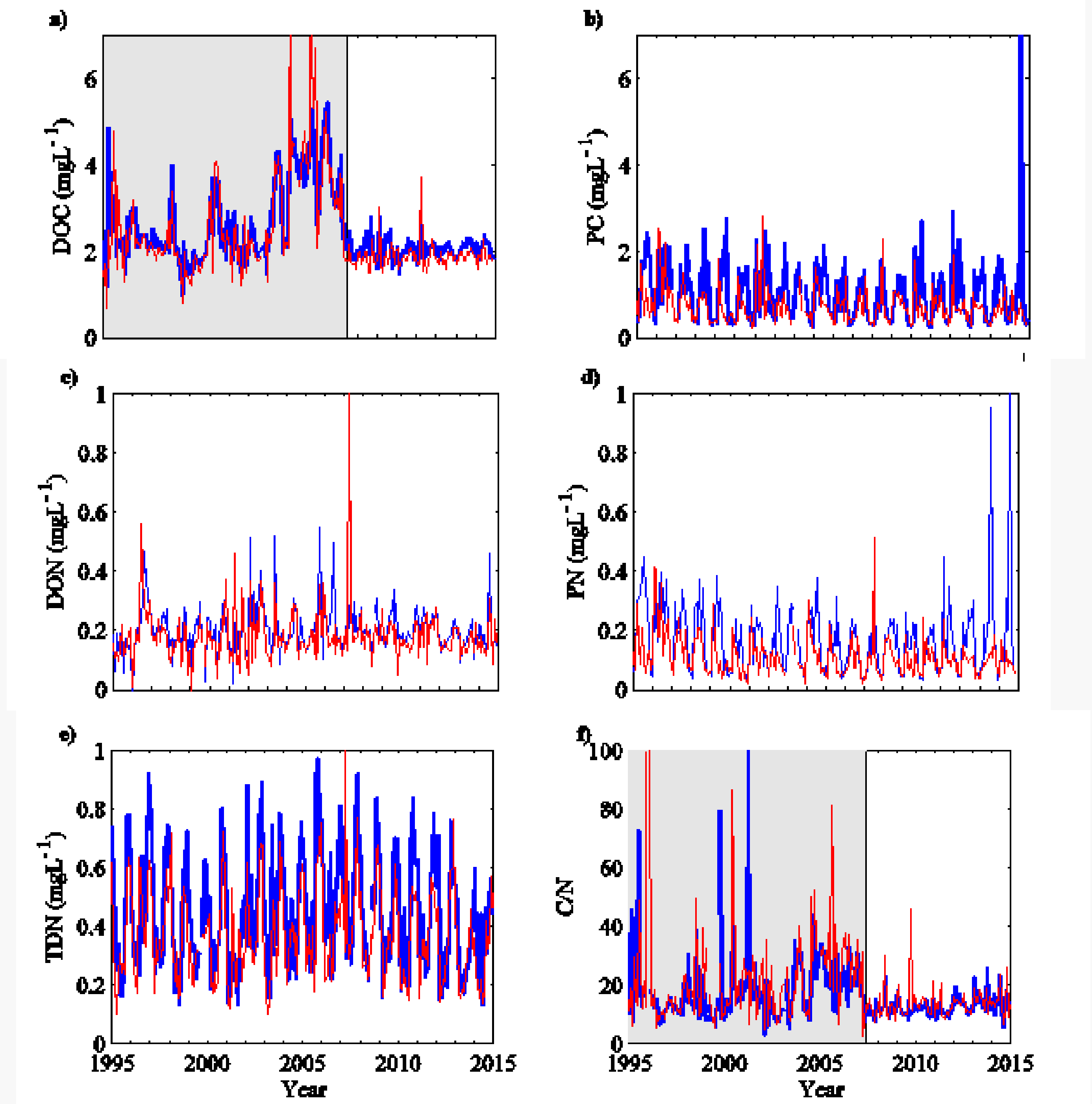


L&O Special Issue: "**Headwaters to oceans: ecological and biogeochemical contrasts across the aquatic continuum**" 2017

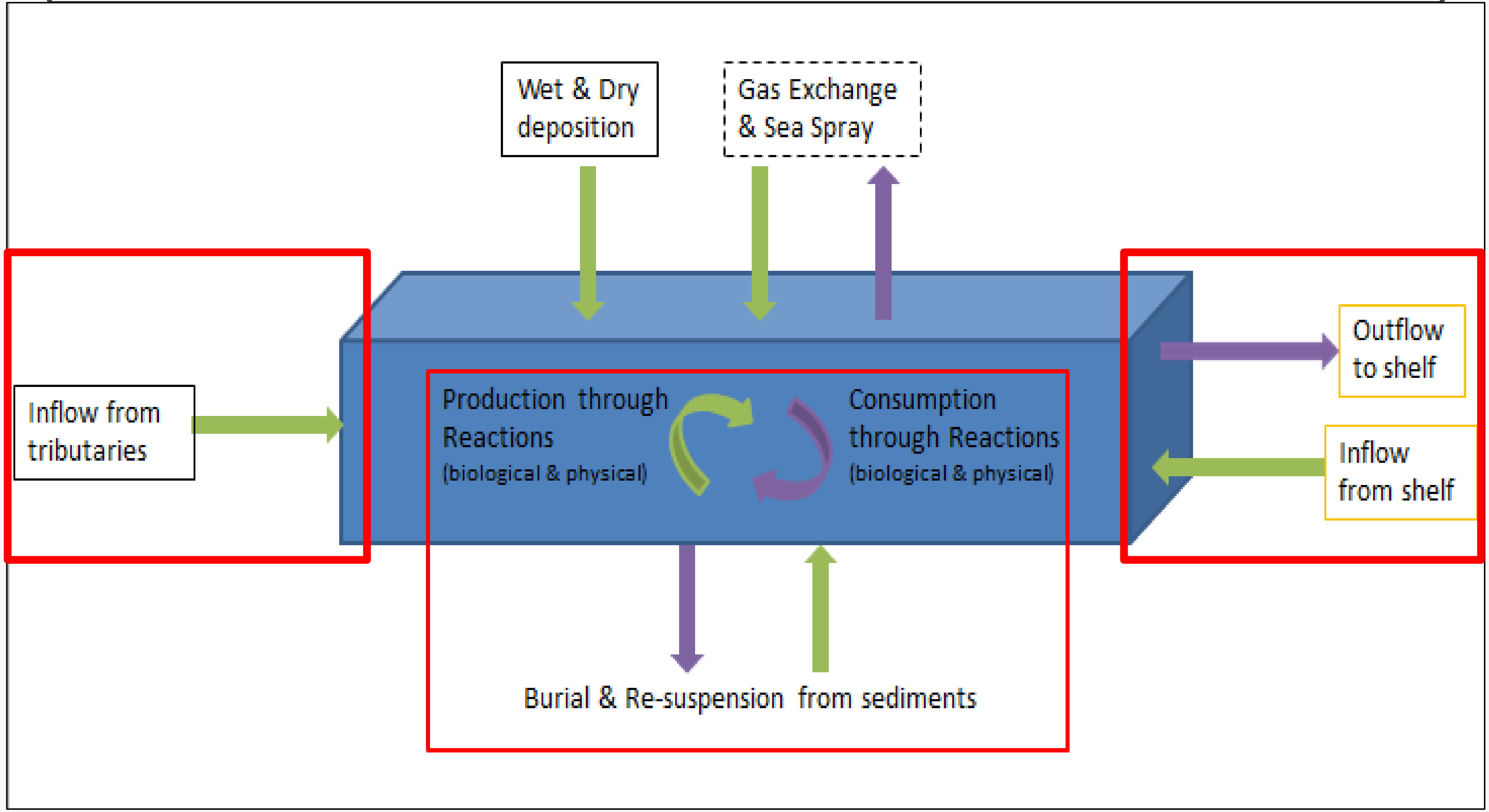
APPROACH


Hudson
Housatonic
Connecticut
Thames
Block Island Sound
CLIS
ELIS
WLIS
East River
Continental Shelf
A4
B3
C1
C2
D3
09
E1
F2
F3
15
H2
H4
H6
I2
J2
K2
M3
y (km)
x (km)
60
40
20
0
-20
-20
0
20
40
60
80
100
120
140
160
180

CT-DEEP STATION **A4** IN WLIS (1995-2015)



FIRST ORDER LIS ORGANIC CARBON BALANCE



HYPOTHESES

- LIS is an exporter of OC to the continental shelf and is therefore "autotrophic" on an annual basis
- The autotrophic/heterotrophic nature of LIS varies seasonally

NET ECOSYSTEM PRODUCTION (NEP)

"THE RATE OF ORGANIC CARBON (OC) ACCUMULATION IN AN ECOSYSTEM"

$OC_{in} > OC_{out}$ = heterotrophic ecosystem

$OC_{in} < OC_{out}$ = autotrophic ecosystem

RIVER OC INPUTS TO LIS MULLANEY (2016)

- Watershed size
- Land use patterns
- River flowrates

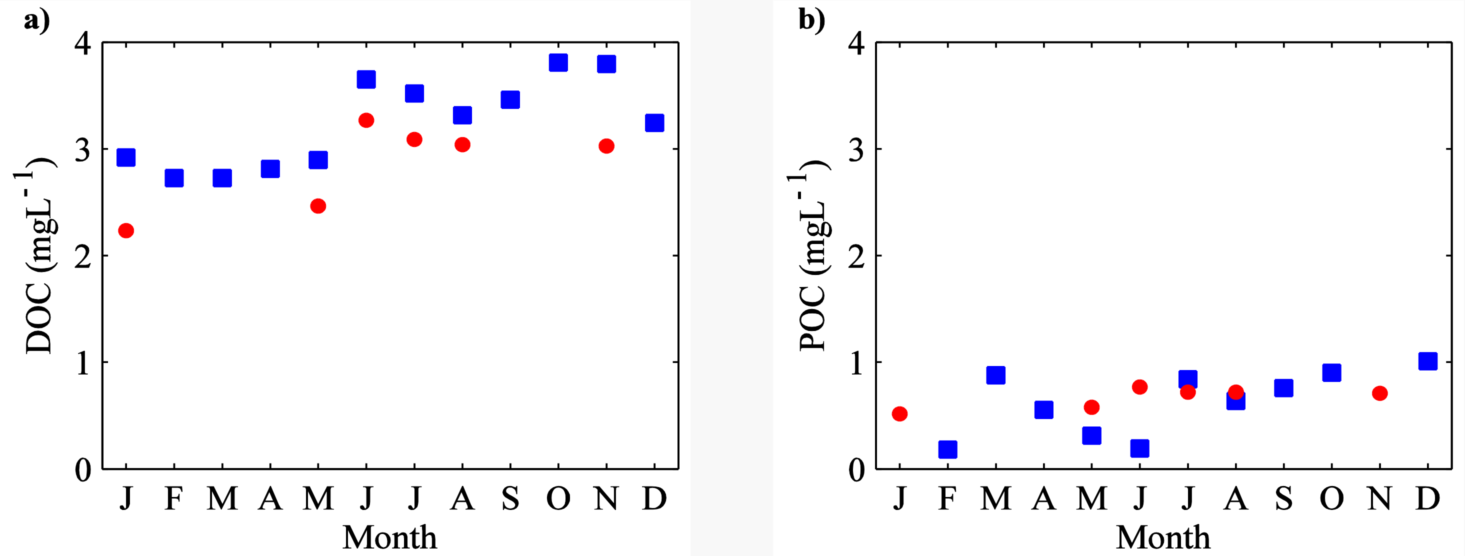
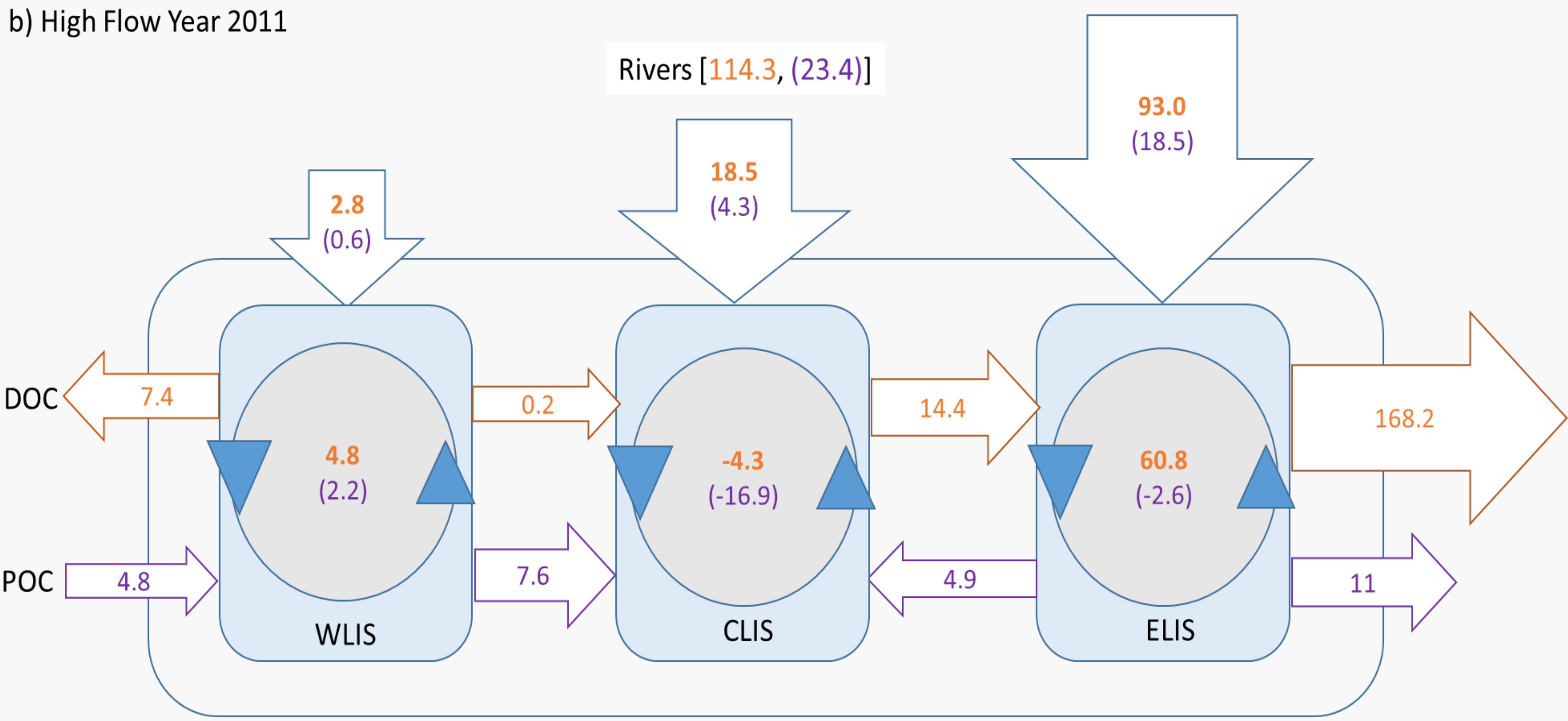


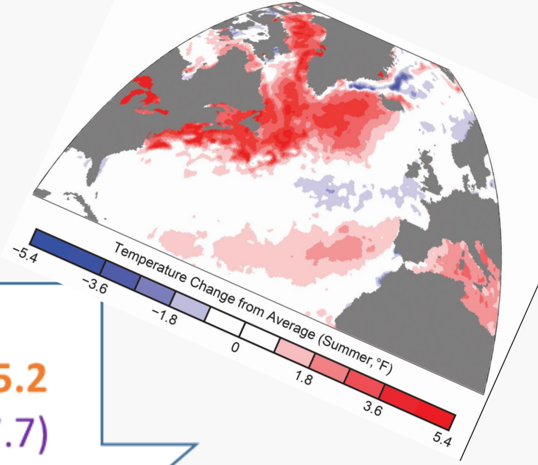
Figure S1 Seasonal cycle for river concentrations of a) DOC and b) POC based on Mullaney (2016). Connecticut River cycle (squares) and Housatonic River cycle (circles) are shown. The Housatonic River cycle is applied to all other rivers.

RESULTS: LIS OC BALANCE - HIGH FLOW YEAR (2011)

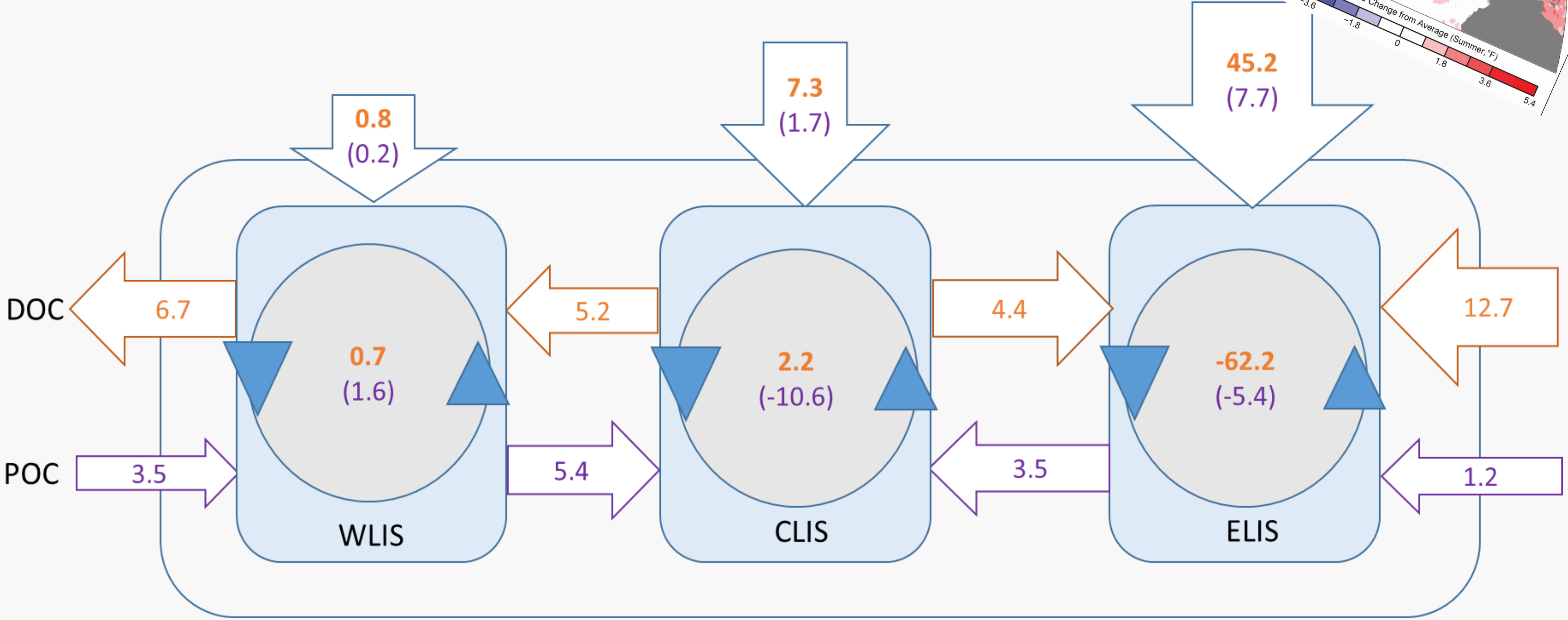


DOC, POC

Results: LIS OC Balance - Low Flow Year (2012)

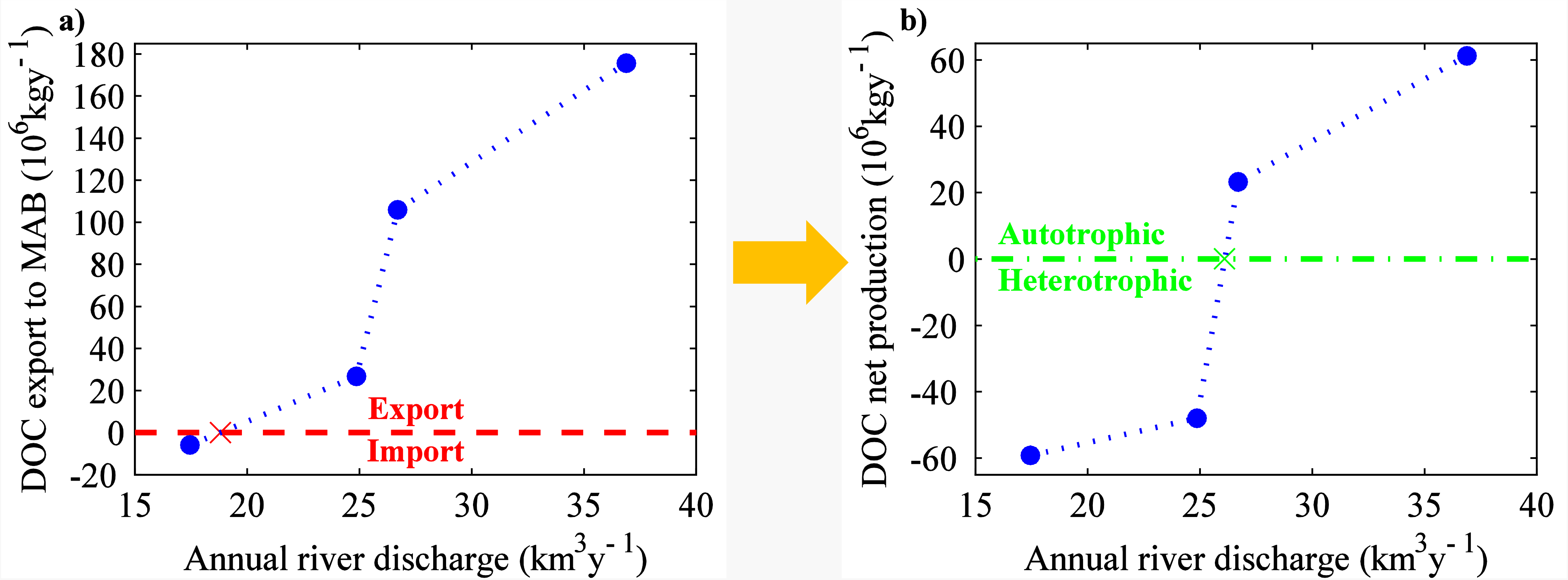


a) Low Flow Year 2012



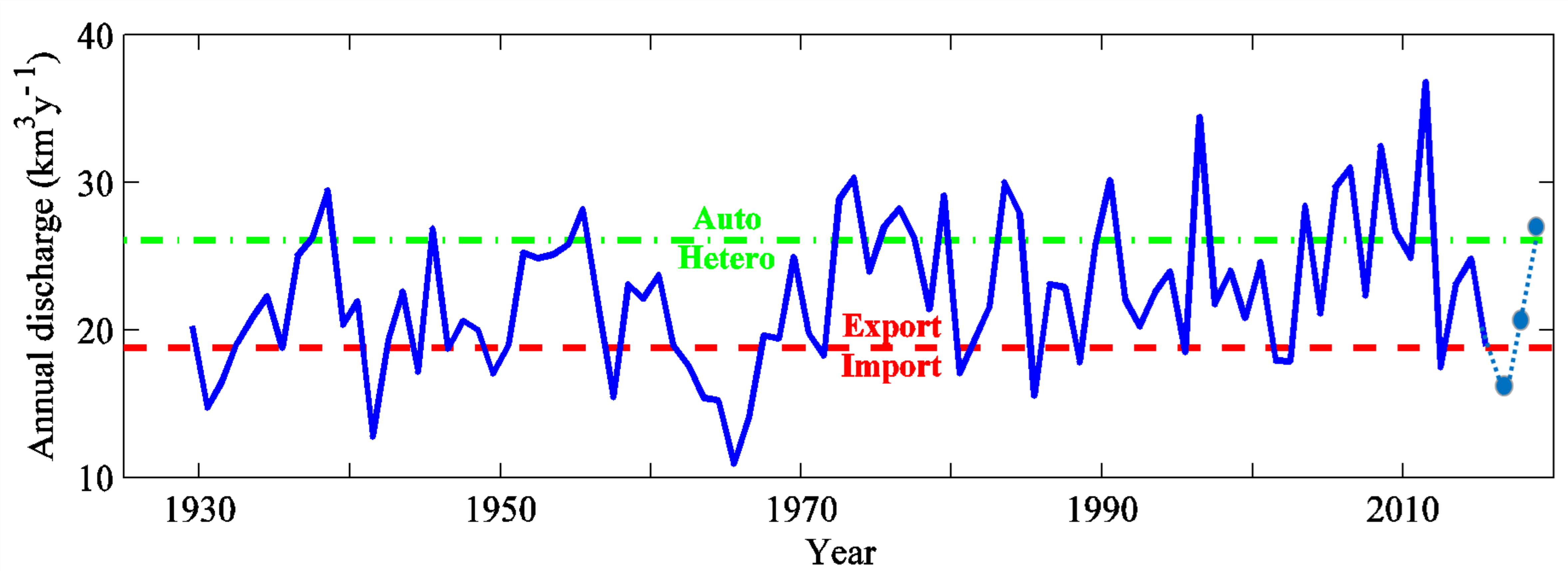
DOC, POC

LIS-OC EXPORT RESULTS 2009-2012



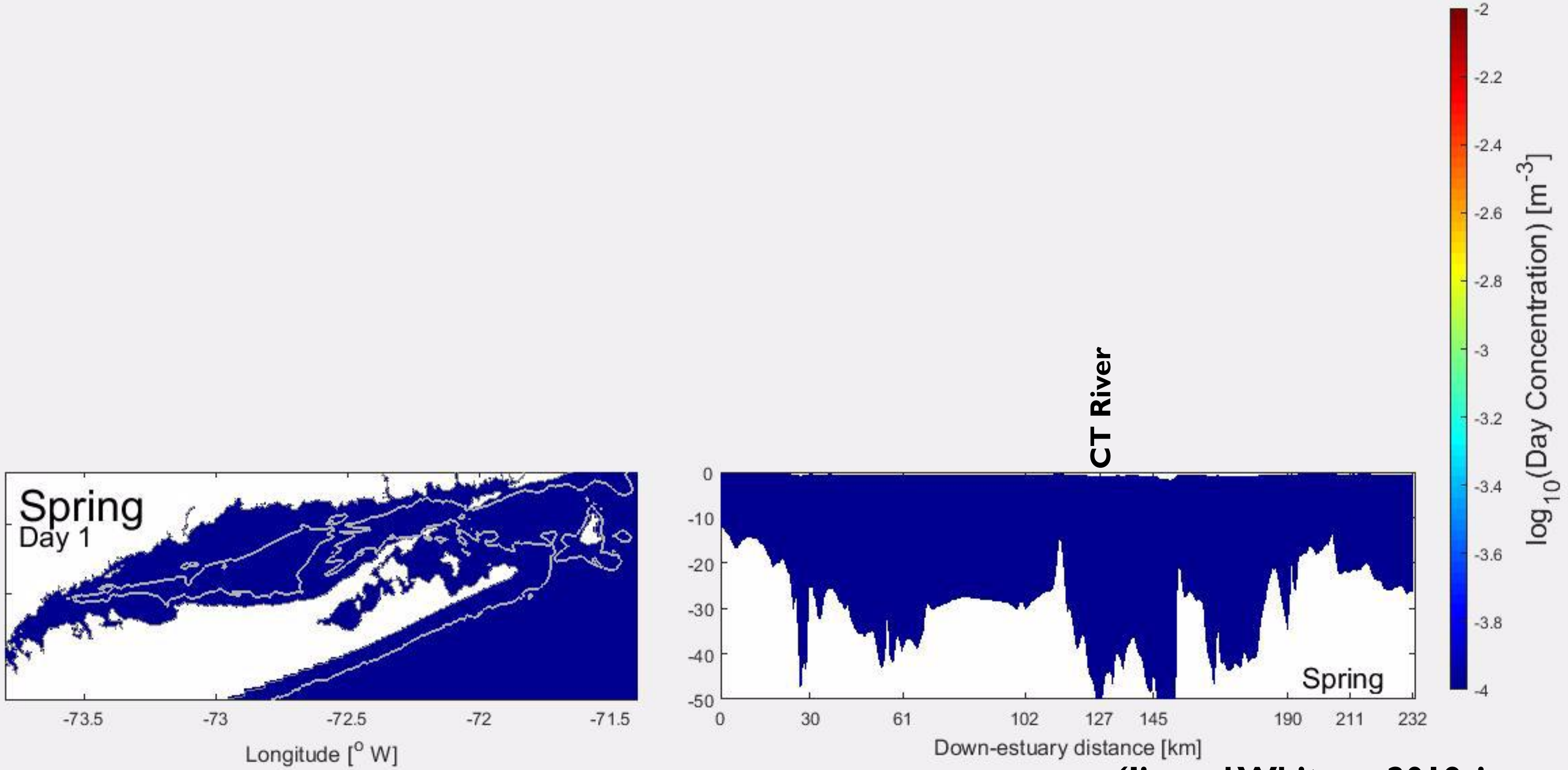
1) OC import <19 km^{3}yr^{-1}
2) OC Export, heterotrophic between 19 to 26 km^{3}yr^{-1}
3) OC Export, autotrophic > 26 km^{3}yr^{-1}

LIS RIVER INPUTS 1930-2015



CONNECTICUT RIVER DYE PULSES

- CT River tracer (in ROMS model) reaches WLIS in spring and summer by different routes
- Model indicates 6-16% of seasonal load reaches WLIS



(Jia and Whitney, 2019, in prep)

OC EXPORT

- The heterotrophic or autotrophic nature of LIS is related to low or high river flow conditions respectively and shifts inter-annually.
- Annually averaged LIS carbon export values to the adjacent Mid Atlantic Bight continental shelf based on flow conditions over the last 20 years are estimated at **$56 \pm 64 \times 10^6$ kg y^{-1}.**
- Export rages are a minimum of **-6×10^6 kg y^{-1} and maximum of $+175 \times 10^6$ kg y^{-1}**

OC EXPORT

- OC is delivered to the LIS *from* the MAB during low flow years where freshwater inputs average **below 19 km^3yr^{-1}** which represent **15% of the last 20 years**.
- OC **flux reverses** and delivers DOC to the MAB when freshwater flowrates exceed this threshold.
- The years in which river flow averages between **19 to 26 km^3yr^{-1}** represent years when the LIS both exports DOC to the MAB and is **net heterotrophic**. These are the most common conditions for LIS **representing 50%** of the time period.
- When river inputs **exceed 26 kg^3y^{-1},** LIS is both and exporter of DOC to the MAB and **net autotrophic**, This latter case applies to **35% of the last 20 years.**

HYPOTHESES

- LIS is a exporter of OC to the continental shelf and is therefore "autotrophic" on an annual basis
- Its not so simple: LIS is heterotrophic and GAINS OC from the shelf during relatively low flow years **(15%)**
- LIS is autotrophic and exports OC to the shelf during relatively high flow years **(35%)**
- LIS is heterotrophic and a net exporter of OC during mid flow years **(50%)**
- The autotrophic/heterotrophic nature of LIS varies seasonally
- LIS trophic status varies seasonally though the patterns shift interannually

PART III: NITROGEN BUDGETS OF THE LONG ISLAND SOUND ESTUARY

Penny Vlahos[1], Michael M Whitney[1], John R Mullaney[2], Jonathan Morrison[2], Christina Menniti[1]

[1]University of Connecticut Departments of Marine Sciences & Environmental Engineering

[2]USGS Connecticut Water Science Center

GOALS

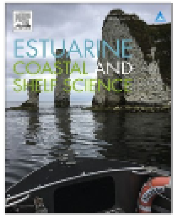
- to quantify nitrogen exports to the adjacent continental shelf
- to understand the relative importance of the nitrogen sources and sinks in a broader geochemical context
- to understand temporal trends in LIS nitrogen budgets
- to deduce the extent of denitrification and burial in the LIS system across these decadal timescales.
- It is anticipated that this study may serve as a baseline for the region and comparison for other regions globally.

Estuarine, Coastal and Shelf Science 232 (2020) 106493

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: http://www.elsevier.com/locate/ecss



Nitrogen budgets of the Long Island Sound estuary

Penny Vlahos [a,b,*], Michael M. Whitney [a], Christina Menniti [a], John R. Mullaney [c], Jonathan Morrison [c], Yan Jia [a]

[a] University of Connecticut, Department of Marine Sciences, United States
[b] University of Connecticut, Departments Chemistry and Environmental Engineering, United States
[c] U.S. Geological Survey, New England Water Science Center, United States

A B S T R A C T

Nitrogen (N) inputs to coastal ecosystems have significant impacts on coastal community structure. In N limited systems, increases in N inputs may lead to excess productivity and hypoxia. Like many temperate estuaries, Long Island Sound (LIS), a major eastern U.S. estuary, is a N limited system which has experienced seasonal hypoxia since the 1800s. This study is the first effort to constrain the total N cycle in this estuary. The approach utilizes data collected over the last two decades in the LIS time series with hydrodynamic model results to generate both monthly and annual N budgets between 1995 and 2016. Of the total N that is delivered to LIS through rivers and atmospheric inputs, 40% is exported to the adjacent continental shelf on the order of $10.8 \pm 8.9 \times 10^6$ kg N/year. Of this export, 41% is dissolved organic N, 29% is particulate organic N, 32% is nitrate + nitrite, and −3% is ammonium. The remaining 60% of the N delivered to LIS is either buried in sediments or lost through denitrification. This inferred internal loss rate is equivalent to 5.4 g N/(m^2year). This study serves as an example of the significant inter-annual variations that estuarine budgets undergo as efforts to understand coastal biogeochemical cycles move forward.

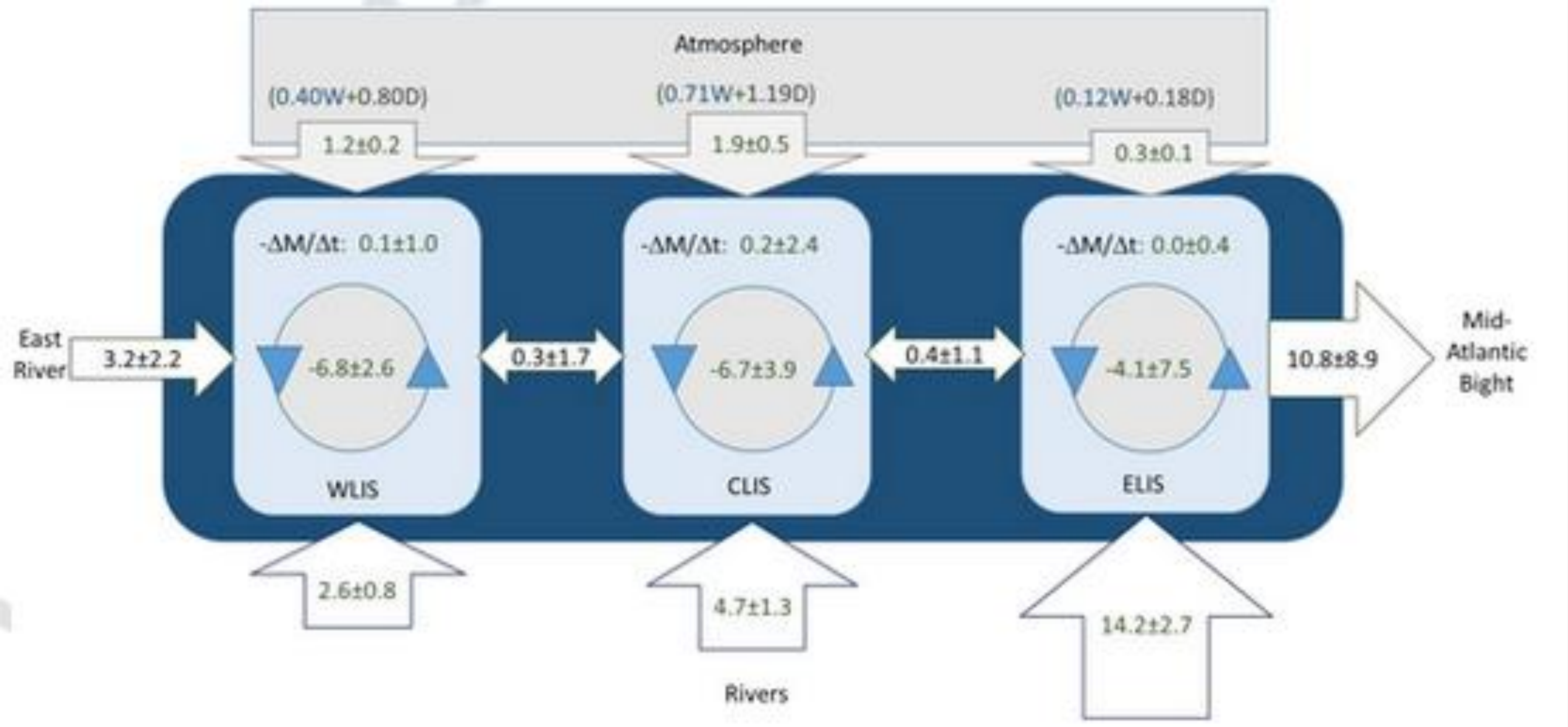
- Combination of:
    - ROMs, CT DEEP, USGS and National Atmospheric Deposition Program (NADP)

- For the overall nitrogen budget in LIS, TN requires 5 sub budgets of individual species in order to account for changes between these pools using ROMs (a total of 5 mass balances x (annual+4 seasonal = 5) = 25 mass balances).

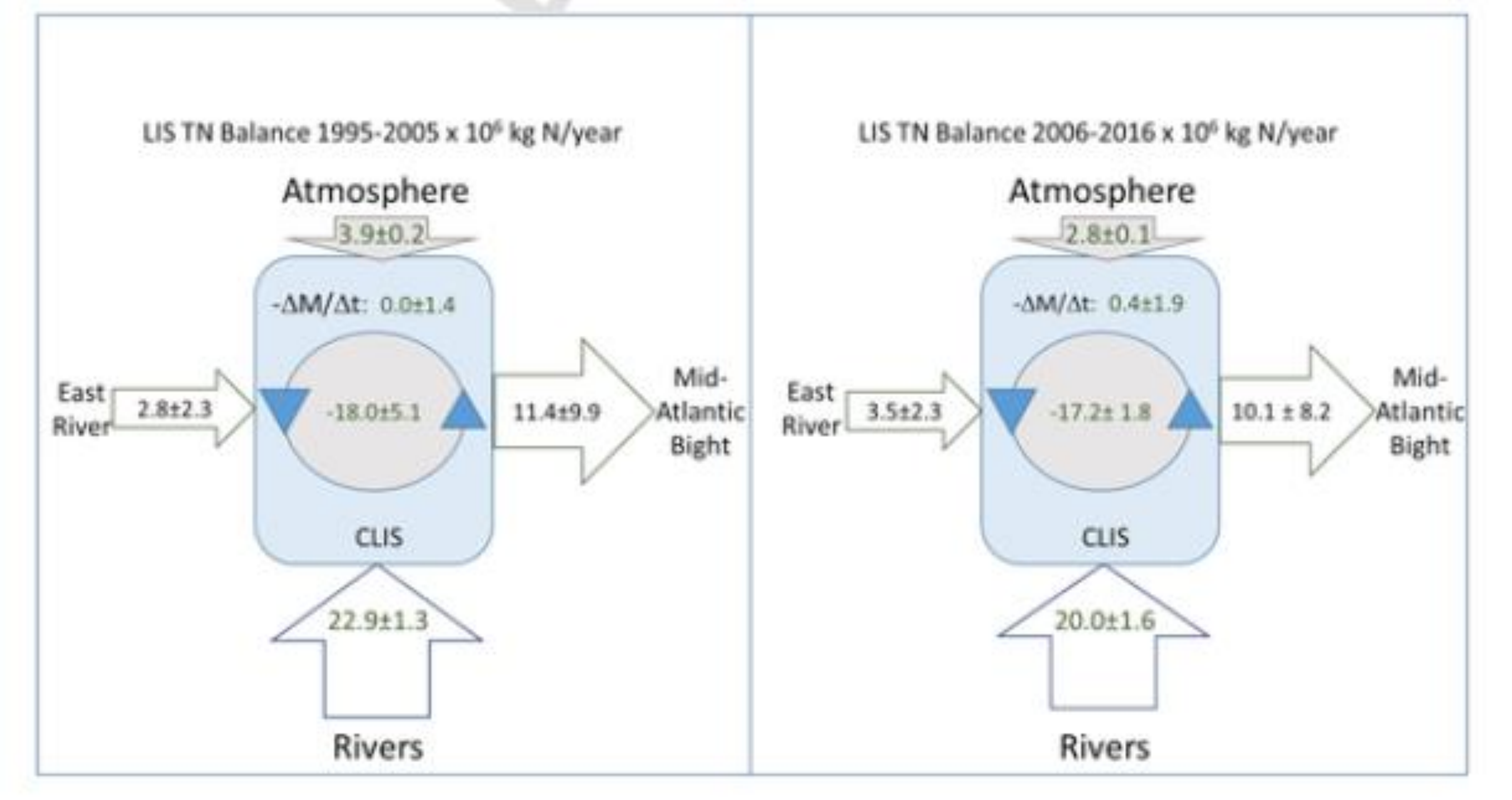
$$\text{TN} = \sum DON + PN + NH_4^+ + \underbrace{NO_2^- + NO_3^-}_{NO_x^-}$$

- The exciting part ☺ will be this internal conversion and should yield net burial + nitrification - denitrification - groundwater inputs etc. in each region and should shift seasonally and inter-annually.

LIS TN BUDGETS (1995-2016) X 10^6KGN/YEAR

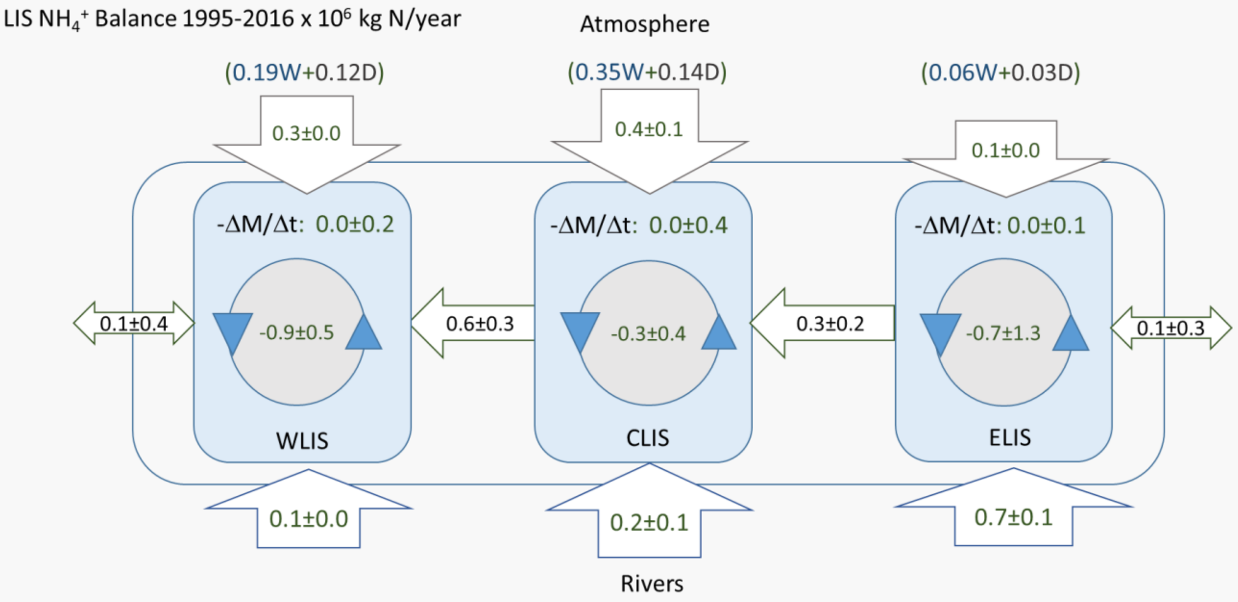


DECADAL TRENDS

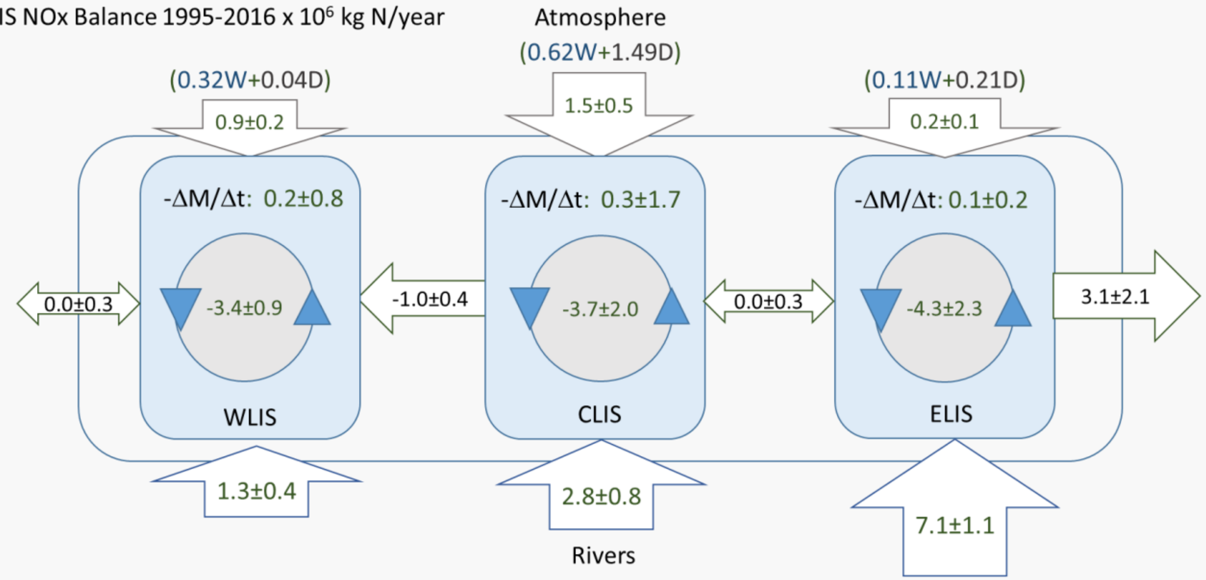


$$TN = \sum DON + PN + NH_4^+ + NO_2^- + NO_3^-$$

NH_4^+



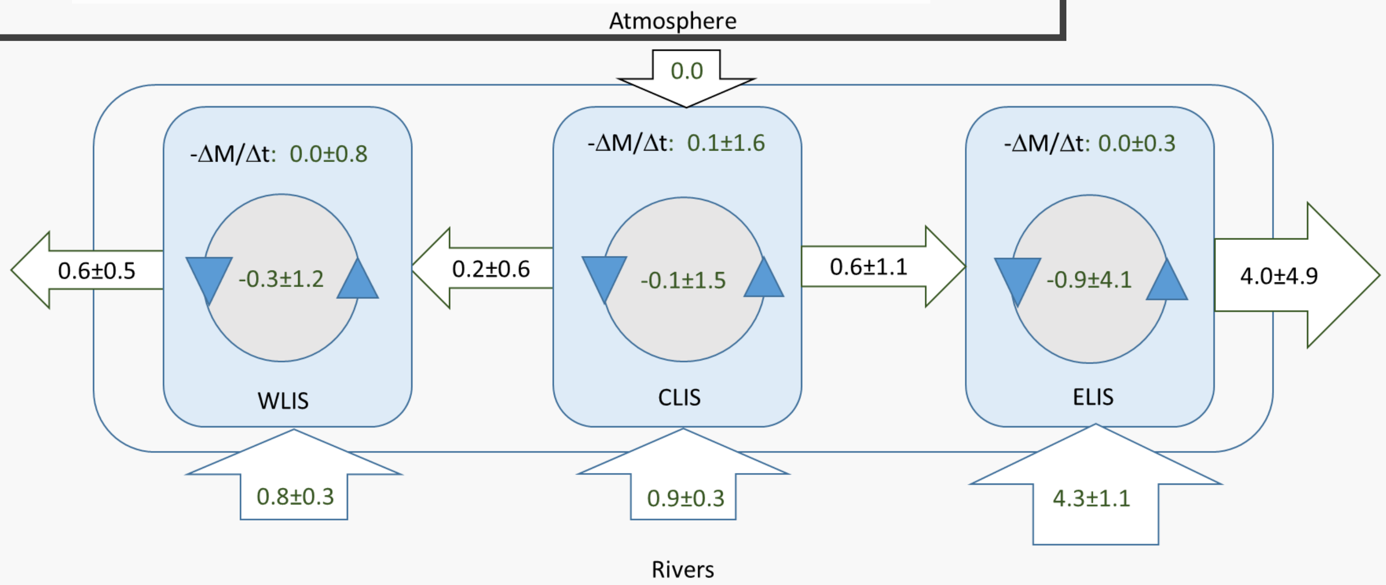
$NO_2^- + NO_3^-$



$$TN = \sum DON + PN + NH_4^+ + NO_2^- + NO_3^-$$

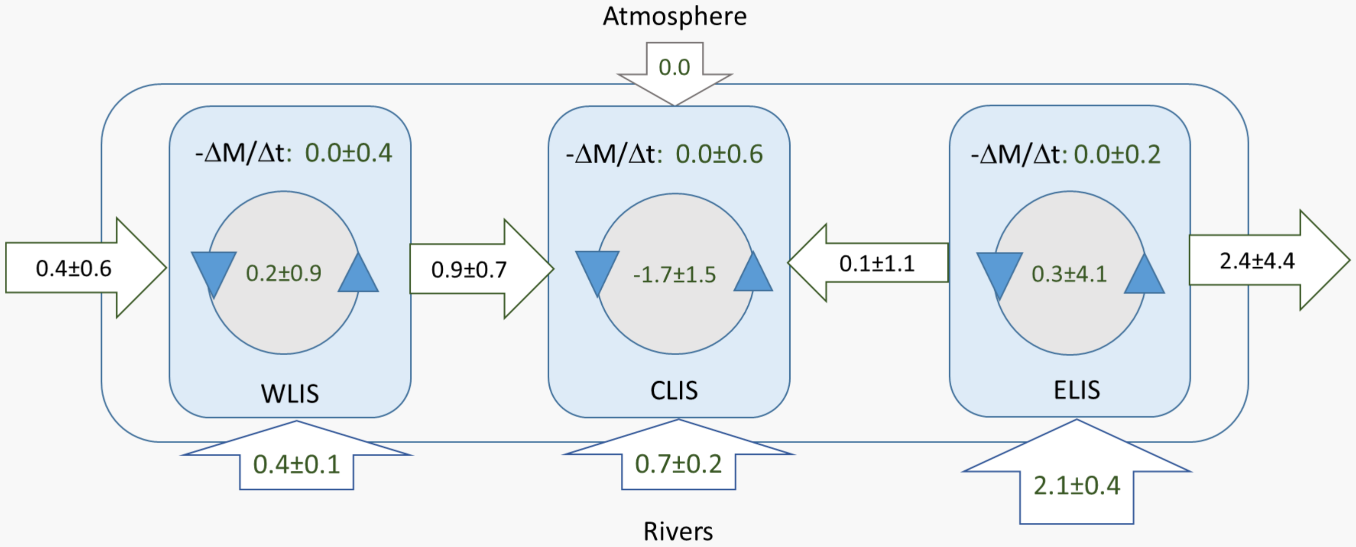
LIS DON Balance 1995-2016 x 10^6 kg N/year

DON

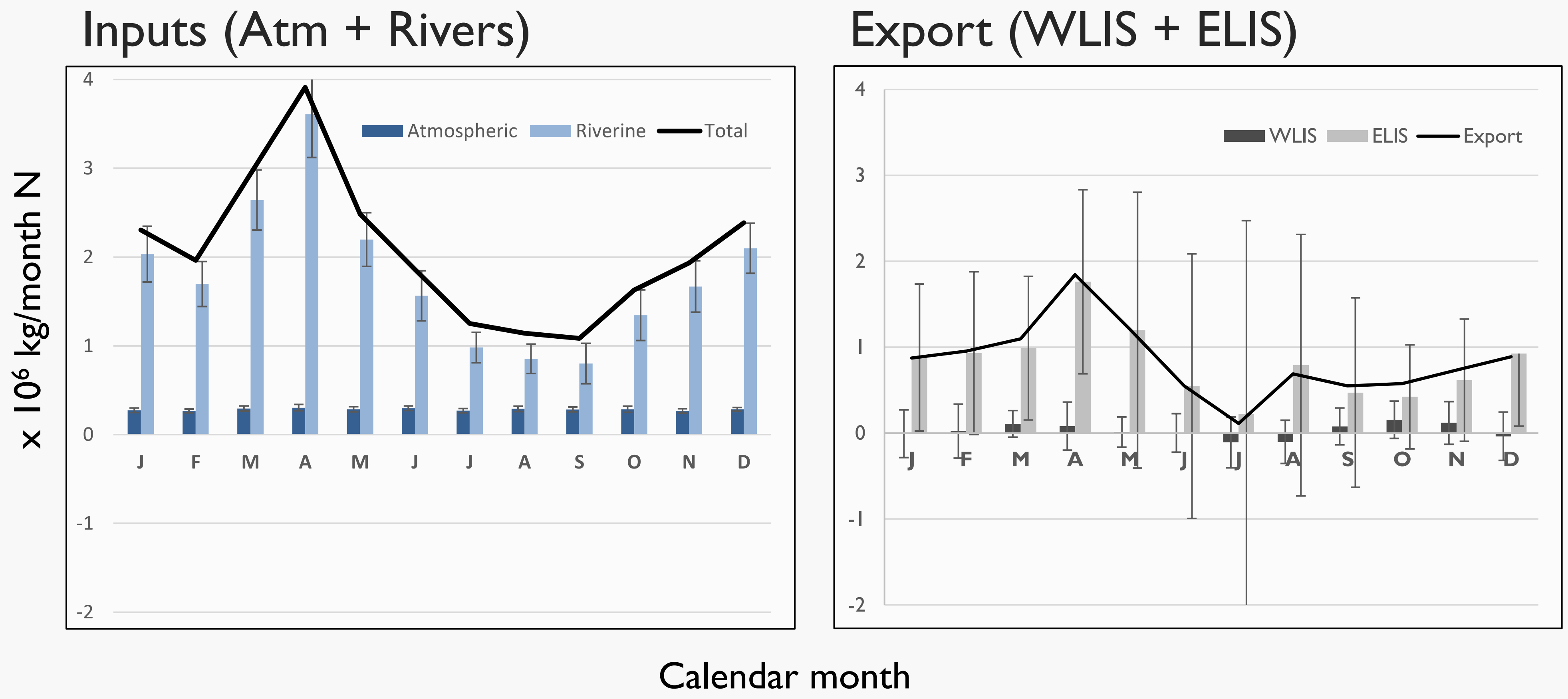


LIS PN Balance 1995-2016 x 10^6 kg N/year

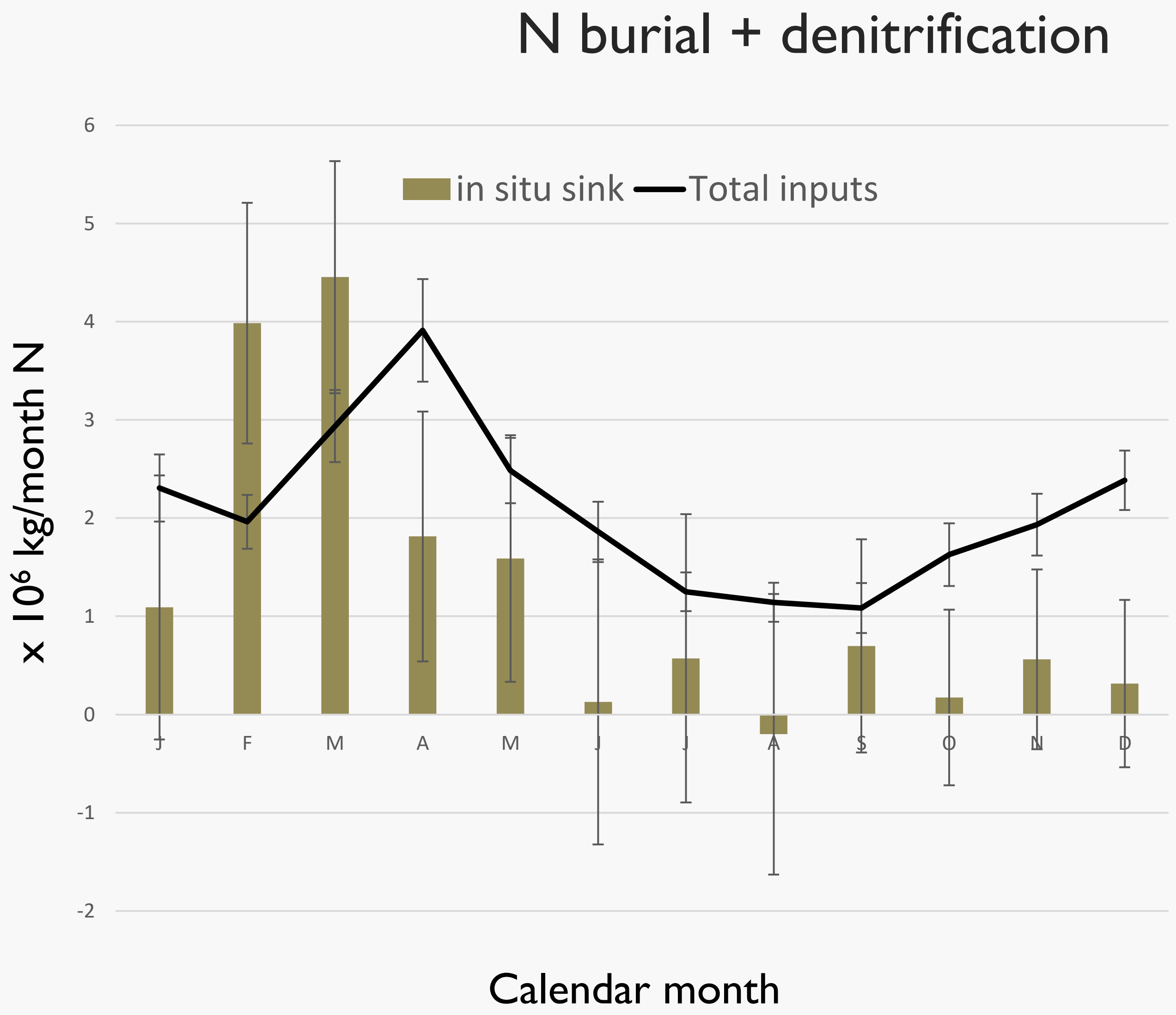
PN



LIS SEASONAL TRENDS (1995-2016)



LIS SEASONAL TRENDS (1995-2016)



- 60% of inputs consumed
- 40% of inputs exported

SUMMARY OF N BALANCE RESULTS

- 10.8 ± 8.9 x 10^6 kg N exported to the MAB (0 to 22 x 10^6 Kg N/year)
- Of this:
  - 43% exported as dissolved organic N,
  - 25% exported as particulate organic N,
  - 32% exported as nitrate + nitrite and
  - <1% exported as ammonium
- 60% of the N delivered to LIS is either buried in sediments or lost through denitrification.
- This internal loss rate is equivalent to 5.4 g N/m^2y^1

PREDICTED CLIMATE SHIFTS IN LIS IMPLY:

- More ppt? → OC export and a shift to more frequent net autotrophy

BUT

- Higher T's → more heterotrophy over T extreme periods (coupled to low ppt and >bacteria)
- Intensification of the N cycle
  - More N burial
  - More denitrification
  - More TN export primarily as organic N
- Inter-annual variations are significant!!!!!

***Future work will further address impact on warming for respiration rates and DIC budgets

Part IV: The Long Island Sound Respire Program

R/CMC-15-CTNY

LIS Respire

Sea Grant Connecticut

Long Island Sound Study
A Partnership to Restore and Protect the Sound

Sea Grant New York

RESEARCH TEAM

Penny Vlahos
Chemical Oc.
UConn

Jamie Vaudrey
Biological Oc.
UConn

Michael Whitney
Physical Oc.
UConn

Lauren Barrett
Doctoral candidate
UConn

Matthew Lyman
All Oc.
CT DEEP - LISS

LIS Respire

OBJECTIVES

1) To **measure respiration rates** and biological oxygen demand (BOD) at 10 Long Island Sound (LIS) water quality stations over the project period.

2) To measure **key biogeochemical parameters** at these stations (pCO_2 and total alkalinity (TA)), in addition to those already measured in the LIS surveys (pH, nutrients, dissolved oxygen (DO), chlorophyll a and organic carbon).

3) To conduct incubations on dissolved and particulate organic carbon (DOC, POC) that measure **degradation rates** at 10 sites across LIS to complement respiration studies.

OBJECTIVES

4) To evaluate the above values across LIS spatially and temporally to begin the foundational work for a **combined LIS biogeochemical model** that considers respiration in terms of season (i.e. temperature (T), salinity (S), stratification), location, depth, DOC and POC lability and important biogeochemical parameters.

5) To conduct a LIS **DO balance for LIS from 1991 to present**.

6) To ascertain the utility of adding respiration and/or inorganic carbon components to the Long Island Sound Water Quality Monitoring Program.

LIS Respire

LIS RESPIRATION RATES

- Goebel et al., (2006, 2007) (dark and light incubations)
  - -50 and 1660 mmol O_2 $m^{-2} day^{-1}$.

- 2018 - Respiration rates (dark incubations) varied as much as 40% from peak productivity in the afternoon to minimum productivity before sunrise.
  - For example the first order respiration constant of 7 AM samples ranged from 0.0058-0.0259 h^{-1} (average: 0.015 ± 0.010 h^{-1}) and 5 PM samples ranged between 0.0189 to 0.0306 h^{-1} (average: 0.023 ± 0.007 h^{-1}).

LIS Respire

Approach – The Basics

$$C_{106}H_{263}O_{110}N_{16}P + \mathbf{106}\ O_2 \Leftrightarrow \mathbf{106}\ CO_2 + \mathbf{106}\ H_2O + \mathbf{16}\ NH_3 + H_3PO_4$$

APPROACH

$$\frac{1}{106}\frac{dO_2}{dt} = -\frac{1}{106}\frac{dCO_2}{dt} = -\frac{1}{16}\frac{dNH_3}{dt} = -\frac{dH_3PO_3}{dt}$$

LIS Respire

HYPOTHESES

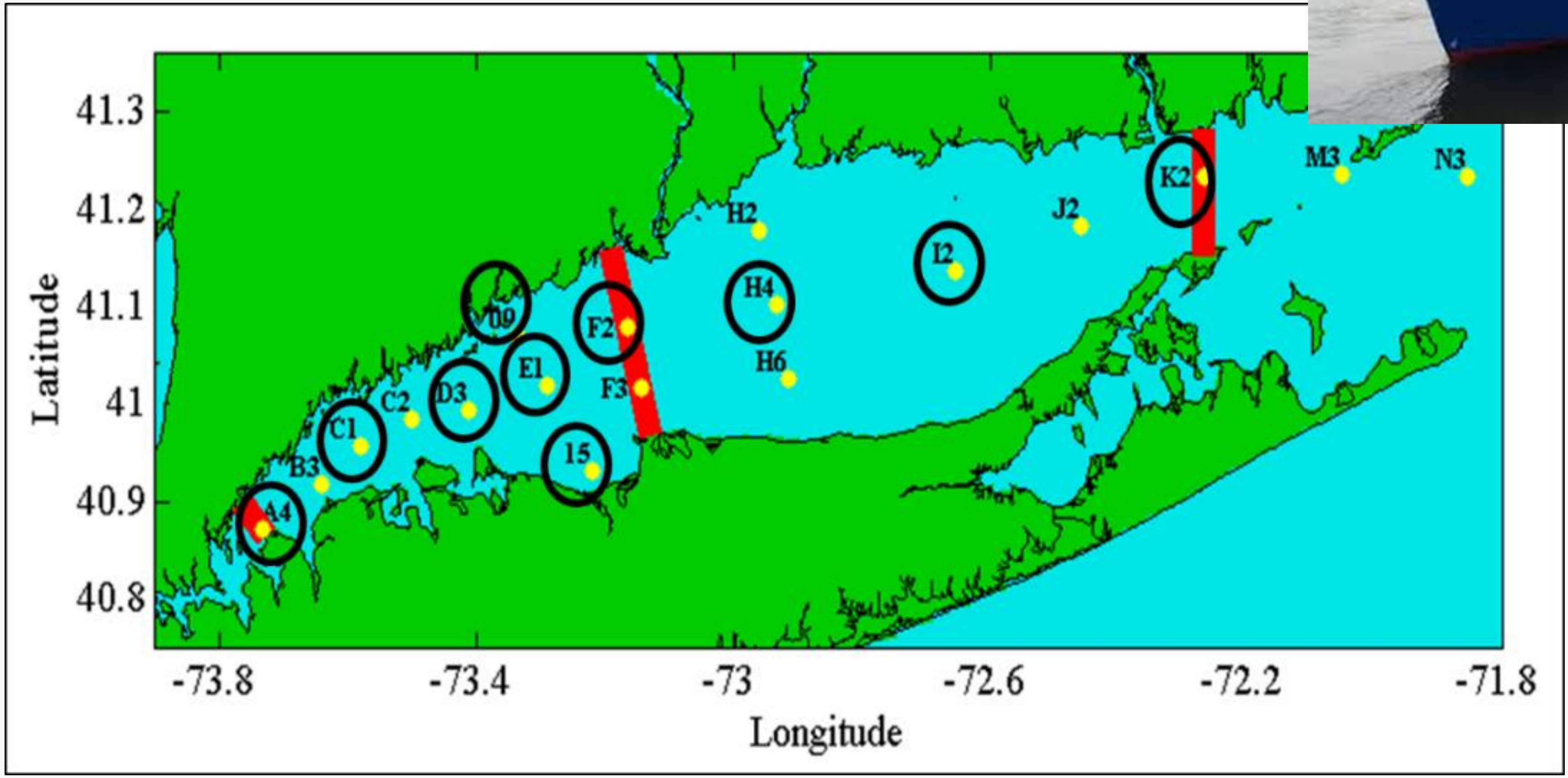
I) Respiration rates in LIS vary spatially and temporally in regular patterns from west to east and seasonally.

II) Respiration rates are related to the “quality” of organic matter characteristic of that time and location.

III) Respiration rates in LIS can be predicted from some combination of T, S, DOC, POC, nutrients, pH, pCO_2 and TA when used in conjunction with DO.

LIS Respire

SAMPLING APPROACH



LIS Respire

METHODS

- CONTROS HydrosFIA for continuous TA measurements

- Eureka Manta+ 40 probe (measuring DO, pH, T and S) fitted with a Turner C-sense for continuous pCO_2

- Community respiration will be determined from the oxygen rate of change in dark experimental bottles (3 L)

- OM degradation rates in LIS using 6 h dark

- BOD after Jouanneaua et al., (2014)

- Nutrients (N and P species)

Long Island Sound Respire Project

To Date:

- 10 cruises complete (carbonate system)
  - 6 respiration complete

Next Steps:

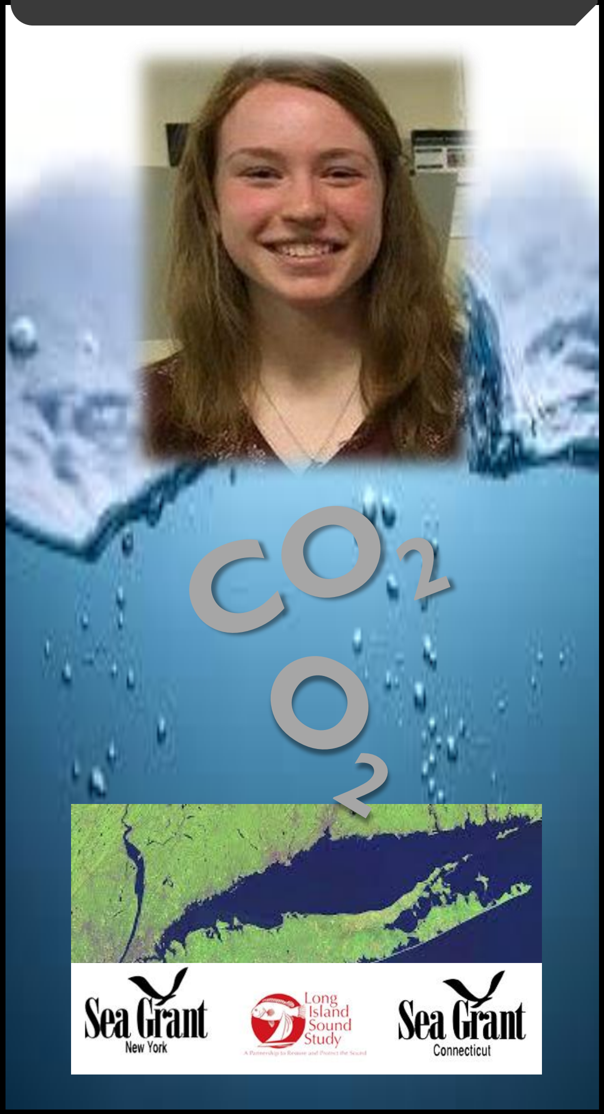
- Alkalinty of LIS Embayments (ALISE)
- Shell Day

THANK YOU

Our Group: https://env.chem.uconn.edu/

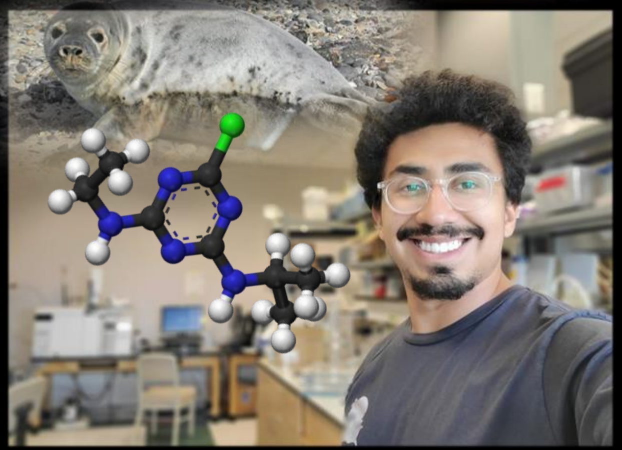
Sea Spray

Biogeochemistry



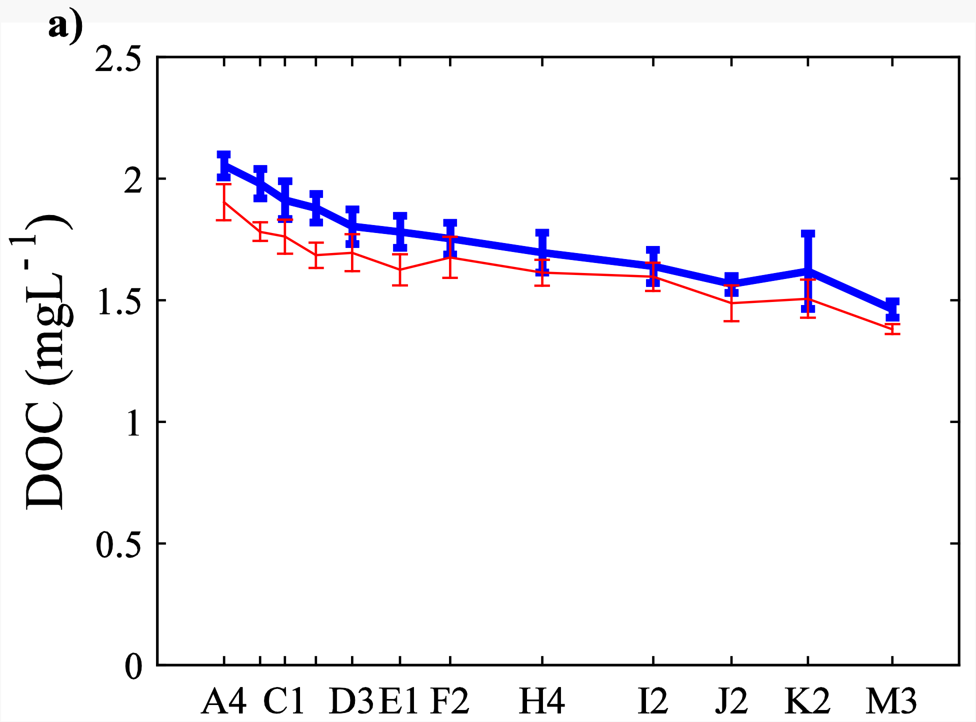
Passive Sampling

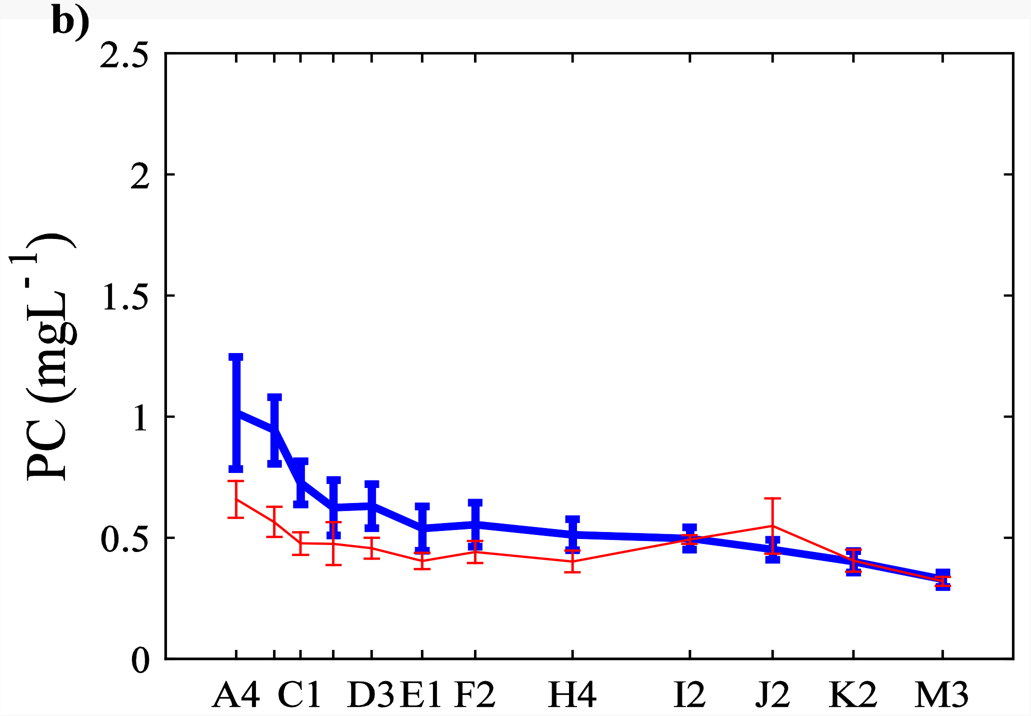
Fulbright & REU



EXTRA SLIDES

ACROSS LIS TRENDS ORGANIC CARBON
(JANUARY 2008 TO DECEMBER 2014)

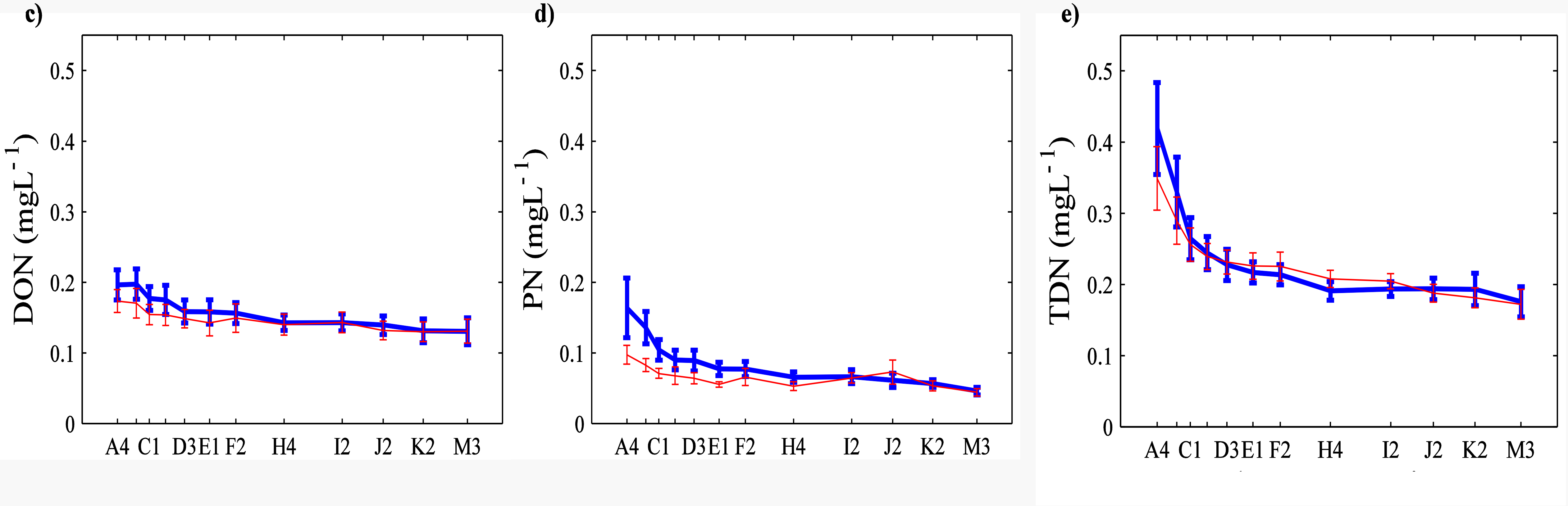




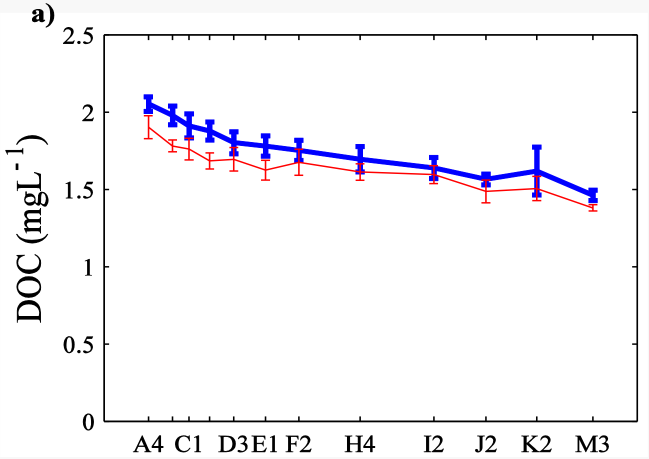
- 0.003 $mgL^{-1}km^{-1}$ (r^2= 0.90)

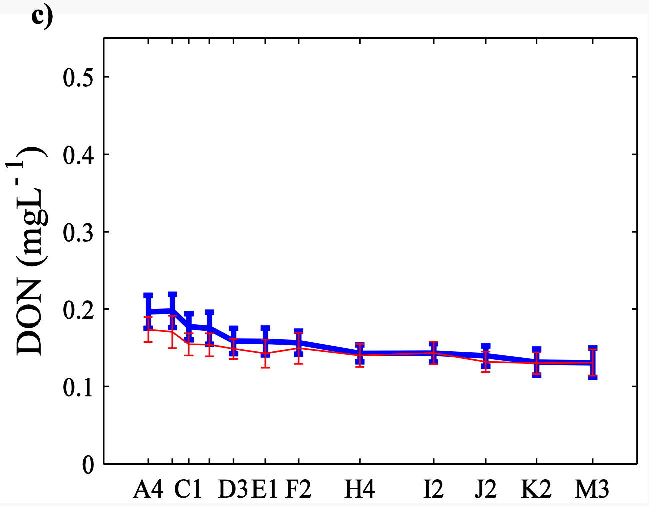
-0.004 $mgL^{-1}km^{-1}$ (r^2= 0.78) surface
-0.001 $mgL^{-1}km^{-1}$ (r^2= 0.32) deep

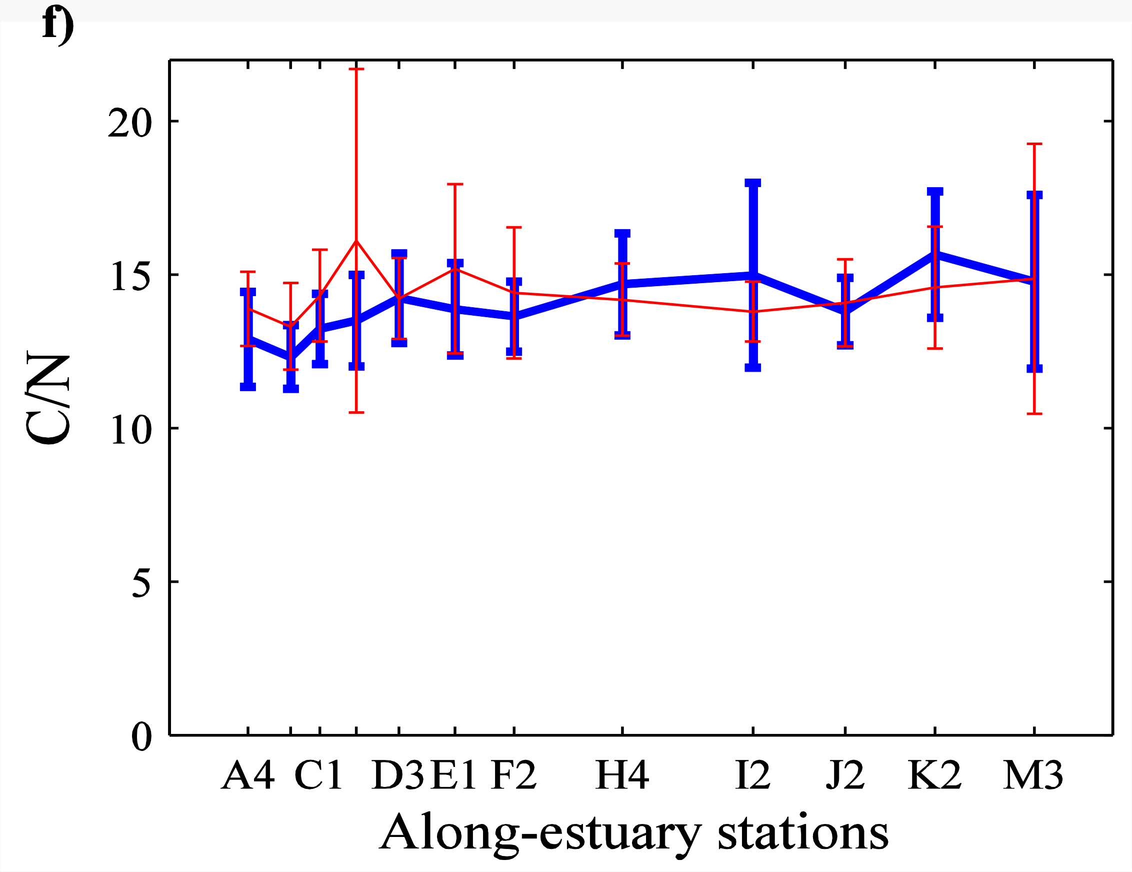
ACROSS LIS TRENDS NITROGEN
(JANUARY 2008 TO DECEMBER 2014)



ACROSS LIS TRENDS C/N (JANUARY 2008 TO DECEMBER 2014)







west (13 ± 3) to east (16 ± 8)