Metabolism in central Long Island Sound, minute by minute: Estimates from in situ oxygen and nitrate measurements

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Introduction

Nitrate and ecosystem metabolism in Long Island Sound

Terrestrial export of anthropogenic nitrogen, particularly as nitrate, a by-product of wastewater de-ammonification, continues to pose a threat to coastal estuaries. In Long Island Sound, eutrophication

Figure 1. Location of the Central Sound Buoy along the major east-west axis of Long Island Sound (41° 8.25' N, 072° 39.30' W; 27 m depth). Also shown are relevant CTDEP water quality monitoring stations. Station I2 is coincident with the study site.

has been implicated as a cause of harmful algal blooms and recurring patterns of benthic hypoxia. Using an array of automated sensors, including the SUNA, an *in situ* UV spectrophotometer, we investigated controls on ecosystem metabolism and nutrient uptake in central LIS over daily, monthly, and seasonal time scales.

We present daily estimates of ecosystem metabolism (NEM), gross primary production (GPP), and new production for a three month period during the summer of 2010. On daily time scales, variability in nitrate concentration was governed primarily by diel uptake and recharge, which are coupled directly to the photosynthetic cycle. Physical forcings such as wind stress both enhanced & masked this central biogeochemical signal.

We derive estimates of GPP and NEM from free-water measurements of dissolved oxygen and nitrate. To isolate daily fluxes in the variables, we applied a series of high-pass Fourier transformations before correcting our estimates for air-sea gas exchange.

Methods & data analysis

Building a biogeochemical time series: Collection & validation of high-frequency *in situ* data

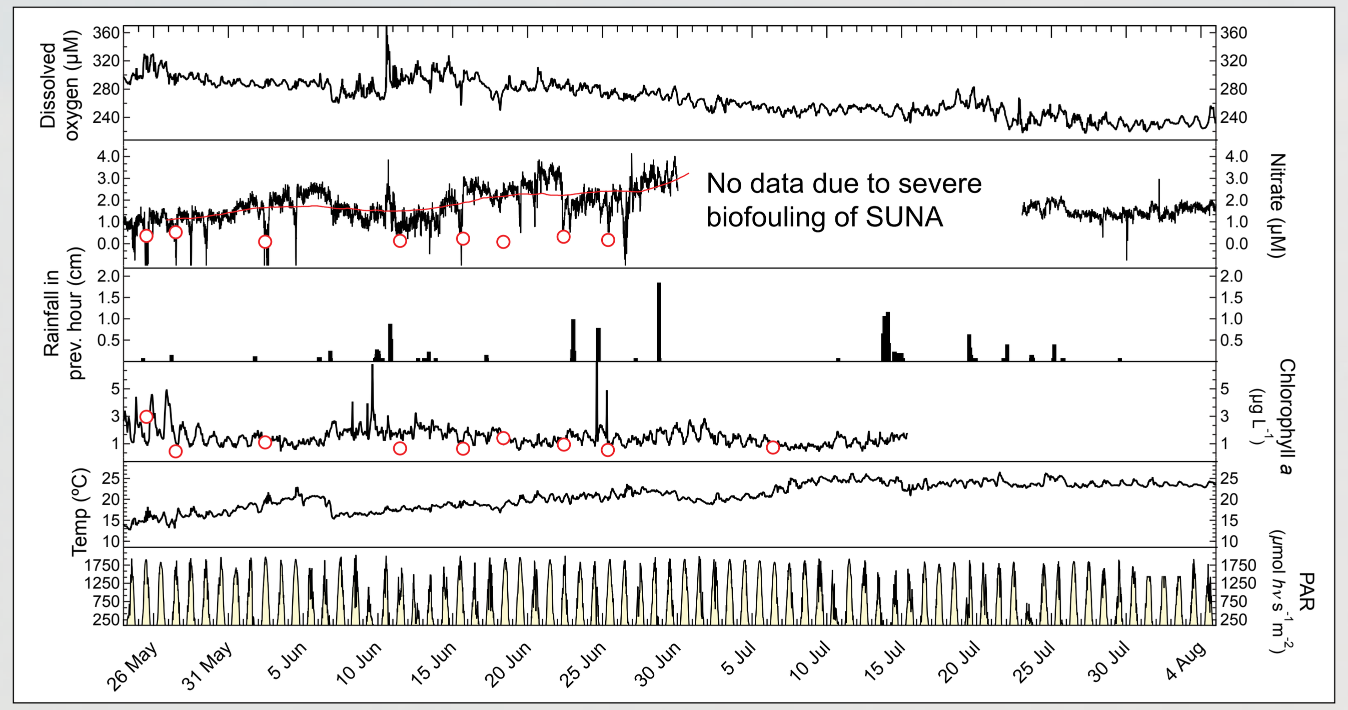

Figure 2. Open red circles are concentrations of nitrate and chlorophyll *a* in discrete samples. With the exception of the period lost to fouling, the SUNA proved capable of detecting relative changes in nitrate concentration on the order of 0.1 μmol L^{-1} on time scales > 12 hours. Low turbidity enabled us to detect these small relative changes despite absolute concentrations that never exceeded 3.87 μmol L^{-1} NO_3^-.

Daily oscillations in NO_3^- and dissolved oxygen data yield estimates of ecosystem metabolism

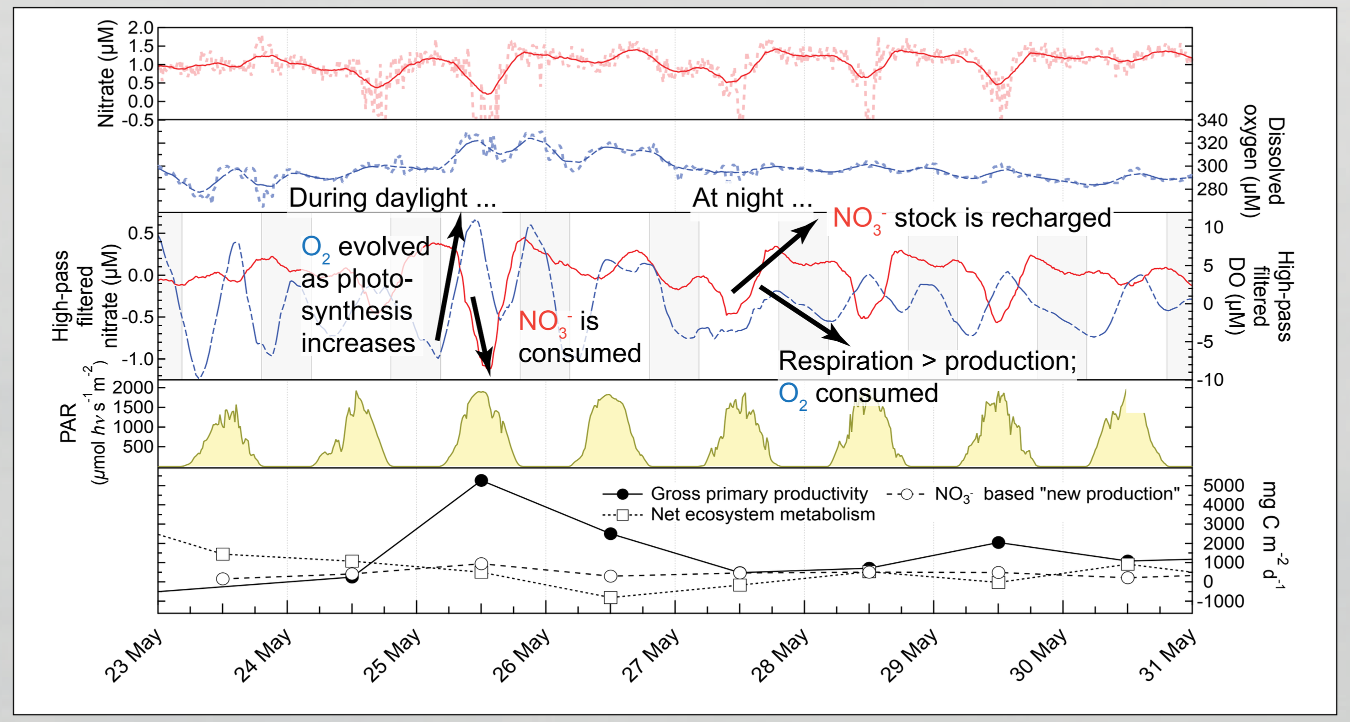

Figure 3. High-pass Fourier transformations of the nitrate and DO datasets emphasize the inverse daytime relationship between nitrate assimilation and DO production. We exploited the magnitudes of these complementary signals to estimate rates of ecosystem metabolism & new production (last panel & **Fig. 6**).

Results & discussion

Surface NO_3^- inventory explained by both recurring daily production cycle & physical forcings

Most of the variation in daily nitrate concentration (~59%) was explained by the quantity of dissolved oxygen evolved during photosynthesis, used here as a proxy for the strength of the photosynthetic cycle (Fig. 4a).

A smaller proportion of the variability was explained by wind stress (~19%) and significant wave height (~18%; Fig. 4b and 4c).

Daytime nitrate minima and dissolved oxygen maxima occurred nearly simultaneously on the majority (> 70%) of days during the study period; both were strongly correlated with the daily peak in photosynthetically active radiation.

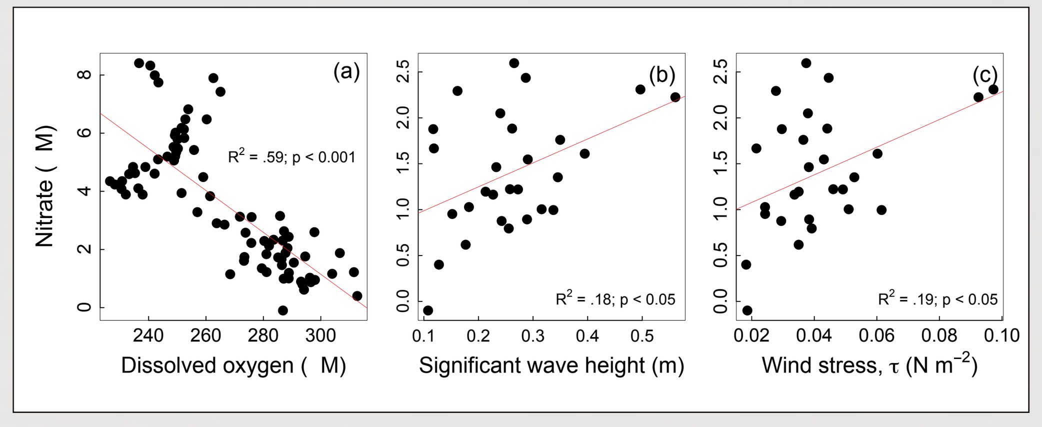

Figure 4. Nitrate concentrations on a given day were determined primarily by the amount of photosynthesis that occured; wind and wave height determined lesser fractions of the variation. Daily average nitrate concentrations are plotted here versus daily averages of dissolved oxygen concentration, wave height and wind stress.

Case study: A wind event alters the baseline photosynthetic signal on multiple time scales

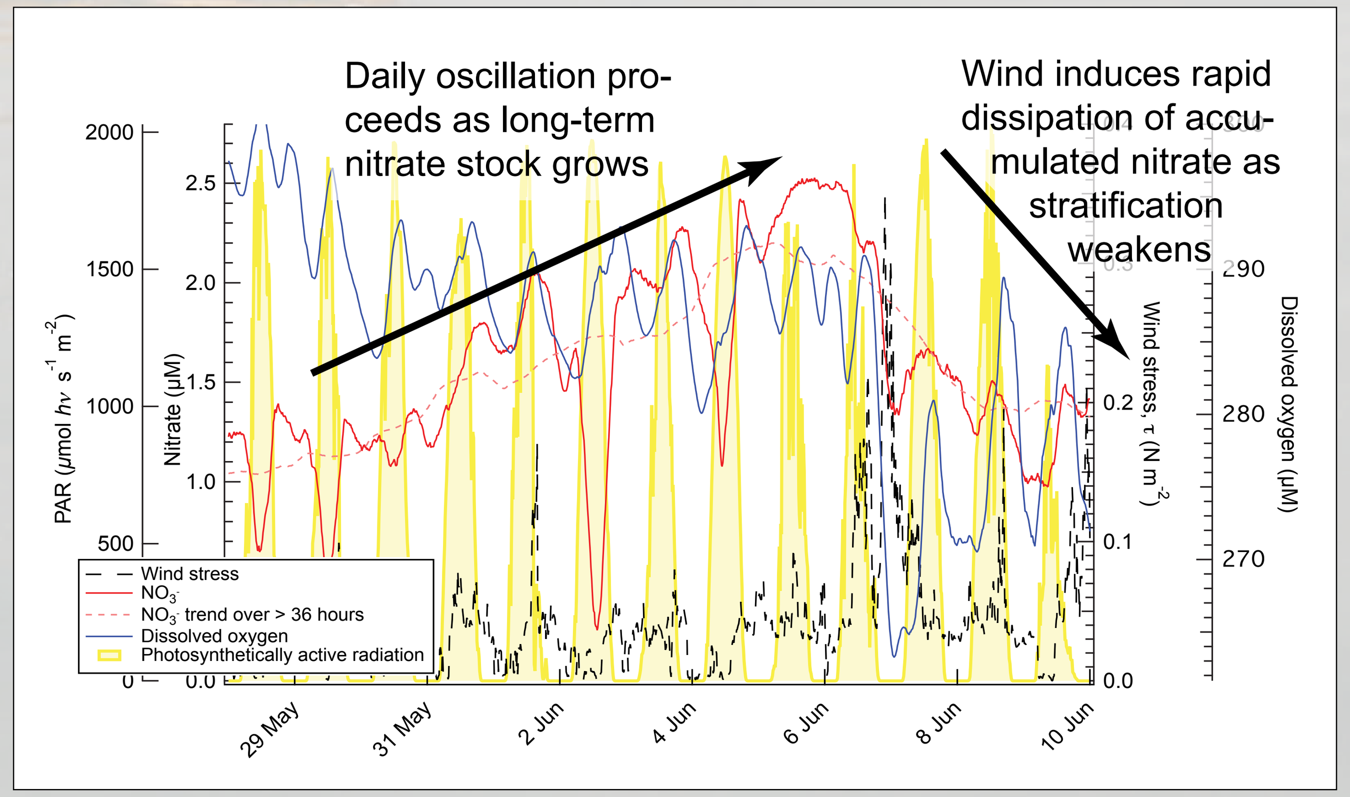

Figure 5. Dissipation of accumulated nitrate stock through deepening of mixed layer, immediately following the onset of a wind event during the night of 8 June 2010. The broken red line shows the long-term trend in nitrate concentration. A similar drop in surface DO concentration is also evident during the event, as oxygen in the well-ventilated surface water is exchanged with the oxygen-depleted bottom layer.

Central Long Island Sound exhibits significant daily variation in rates of primary production and net ecosystem metabolism

Our estimates of ecosystem metabolism agree generally with published values for central Long Island Sound. The central Sound remained weakly autotrophic over the course of the study period, though daily estimates (Fig. 6) suggest the system experiences a high degree of interdaily variability encompassing both net heterotrophy and net autotrophy. Peak productivity at the station was significantly lower than summertime maxima which have been observed at the western end of the Sound, where inputs of anthropogenic nitrogen are larger and water depths are shallower.

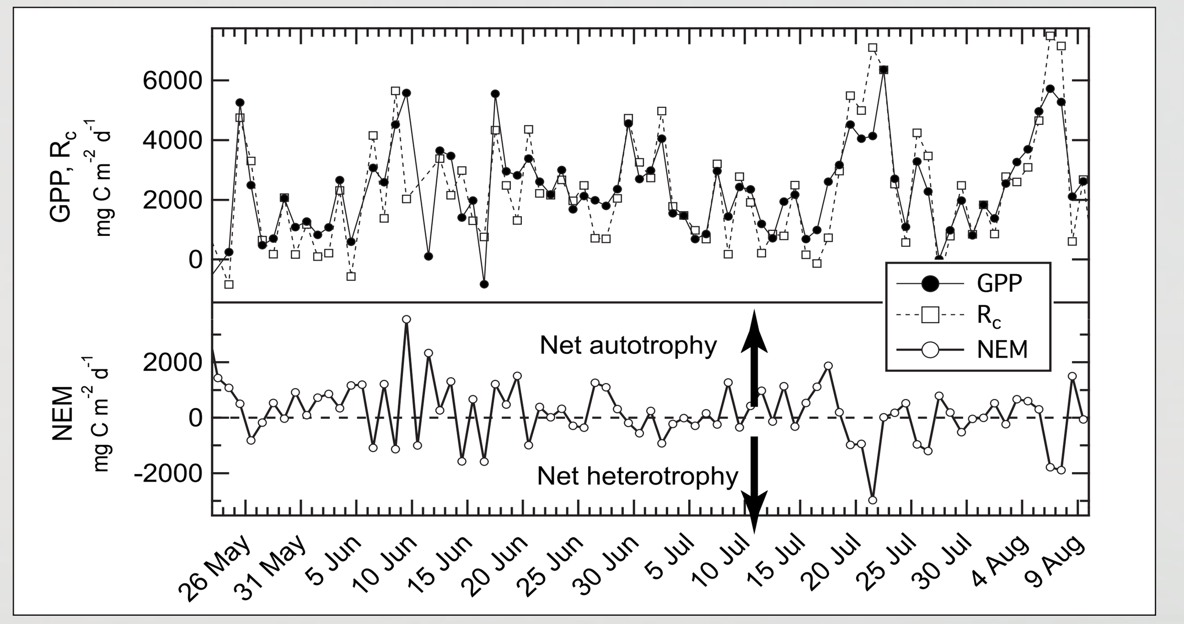

Figure 6. Variation in daily rates of (a) gross primary productivity and community respiration and (b) net ecosystem metabolism. NEM is the balance between the two other variables.

Rates of productivity in Long Island Sound & some other estuaries

Study location	Productivity (mg C m^{-2} d^{-1} ± 95% CI)			Community respiration (mg C m^{-2} d^{-1} ± 95% CI)	Reference
	Gross	Net community	Net ecosys. metabolism		
Central LIS, spring-summer 2010	2080 ± 244	1150 ± 223	180 ± 245	1260 ± 320	This study
Central-west LIS, approx. 14 km south of New Haven, spring-summer, 2002-2003	2620 ± 900	–	–	–	Goebel et al. 2006
Western LIS, monthly rates at 8 stations to west of longitude 72° 40' W, 2002-2003	40 (± 110) to 17300 (± 6100)	–12500 (± 2700) to 11600 (±11000)	–	–500 (± 300) to 16600 (±2700)	Goebel et al. 2006
Narragansett Bay, RI, at T-Wharf, S end Prudence Island, annual mean, 1995-2000	2500 ± 310	–	–410 ± 130	2900 ± 380	Caffrey 2004
Waquoit Bay, MA, at Central Basin, annual mean, 1995-2000	2100 ± 94	–	94 ± 63	2800 ± 130	Caffrey 2004
Chesapeake Bay, lower section (polyhaline; to south of latitude 38° N), annual mean, 1990-1992	1670	–	210	1460	Kemp et al. 1997

Evaluating the *f*-ratio: At low concentrations, nitrate still drives significant production in Long Island Sound

Daily values of the *f*-ratio (i.e., the amount of new production based on nitrate or other allochthonous forms of nitrogen expressed as a fraction of productivity based on all forms of N) ranged from 0.03 to 0.87.

The average ratio of 0.51 suggests a signficant fraction of summertime production in the central Sound is driven by nitrate inputs, even though nitrate consistently comprises a small fraction of the total dissolved nitrogen inventory at the site (Fig 7). A large fraction of these nitrate inputs are anthropogenic (Anisfeld et al. 2007). Ammonium can come from both autochthonous and allochthonous sources in estuaries, complicating calculation of the *f*-ratio from nitrate uptake. In central LIS, however, anthropogenic ammonium did not comprise a significant fraction of TDN; this suggests nitrate drives much of the production.

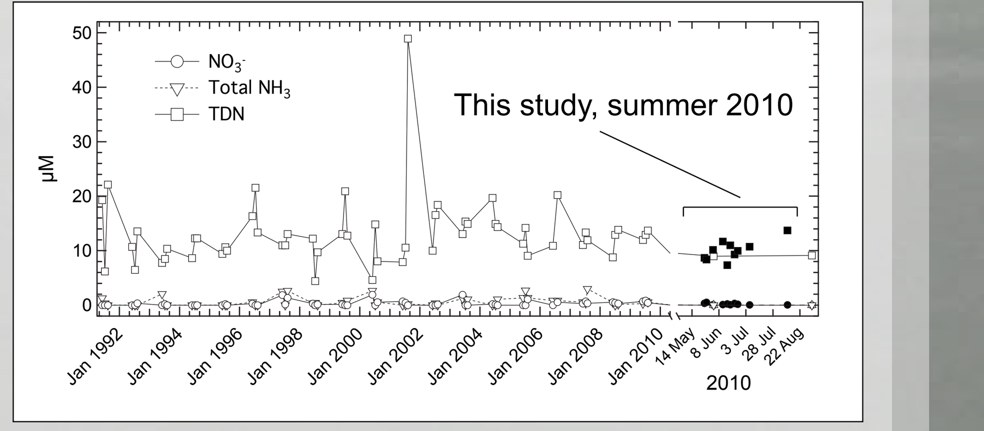

Figure 7. Bioavailable nitrogen speciation as a fraction of total dissolved nitrogen (TDN) in central LIS. Historical data (open markers) are from CTDEP monthly sampling program (M. Lyman, unpub. data)

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