James River Sediment Oxygen and Nutrient Exchange (SONE) Study

DRAFT
Final Report
Version 1
May 12, 2014

Submitted to
Virginia Department of Environmental Quality

Performing Organization:
Virginia Institute of Marine Science
College of William & Mary
P.O. Box 1346
Gloucester Point, VA 23062

Principal Investigator: Dr. Iris C. Anderson

Authors: Iris C. Anderson and Jennifer W. Stanhope

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Purpose/Objectives

The purpose of this project was to perform measurements of sediment : water nutrient fluxes, metabolic rates and sediment characteristics at six sites along the James River. Data will be used to calibrate the James River water quality model. The data collected during August 2012 and April 2013 included:

1. Sediment : water fluxes of dissolved oxygen (DO), dissolved inorganic nitrogen and phosphorus (DIN, DIP), dissolved inorganic carbon (DIC), dissolved organic nitrogen and carbon (DON, DOC), and dissolved silica (Si).
2. Metabolic rates (gross primary production, respiration, net community production, sediment oxygen demand)
3. Sediment characteristics: grain size, bulk density, organic content, benthic chlorophyll *a*, extractable nutrients (DIN), organic carbon content, total nitrogen content, total phosphorus content

Background

Virginia Department of Environmental Quality (VaDEQ) is undertaking a comprehensive review of the existing Site-Specific Numeric Chlorophyll-*a* (chl *a*) criteria for the tidal James River system. As part of this review, the James River water quality model is being revised and requires additional empirical data to develop relationships between environmental drivers and chl *a* concentrations. In particular, benthic fluxes of oxygen and nutrients are critical for the model calibration and verification; however, there are very limited data for the James River estuary. The limited data that are available were collected more than 18 years ago, in the early 1980's (Cerco, 1985) and 1994 (Meyers, 1995), and likely do not represent today's benthic conditions. This effort will provide empirical data for the James River water quality model and the scientific basis for the potential water quality standards rulemaking process, which may result in revisions to nutrient allocations contained in the Chesapeake Bay TMDL.

Methods

Site selection: Six sites were selected based on modeling requirements (consultation with Jian Shen, Jim Fitzpatrick) and to leverage data collections by Paul Bukaveckas, Ken Moore, and Kim Reece in the James River and Margie Mulholland in the Lafayette River. We identified five sites near the Chesapeake Bay Program (CBP) long term monitoring stations, as listed in Table 1 and shown in Figure 1. One additional site was selected in the Lafayette River. Three of the sites (TB_1m, CH_1m, LA_1m) were located on the shoals of the James River, Chickahominy River, or Lafayette River at approximately 1-m water depth (MSL) and the three other sites in the James River (TB_2m, 4H_2m, CC_2m) were located in deeper water at approximately 2-m water depth.

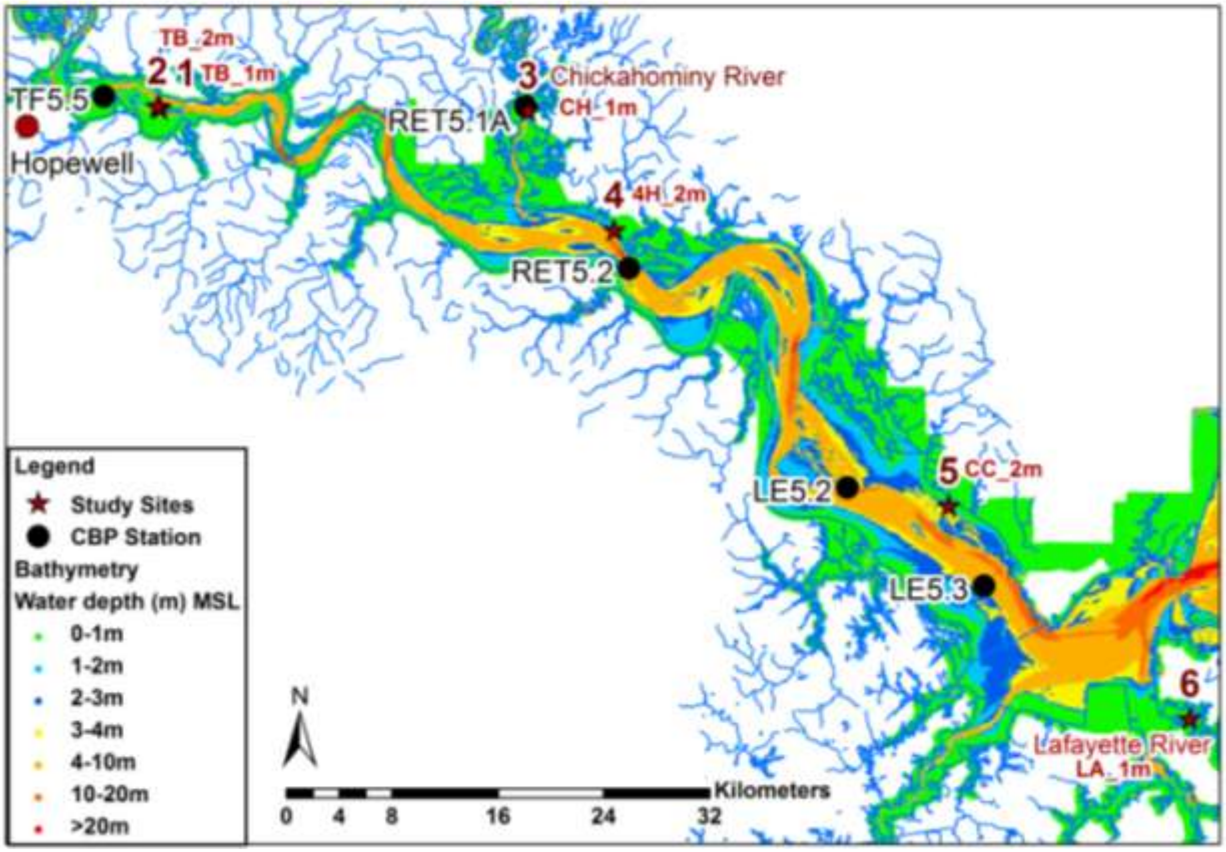

Figure 1. Map of the James River, Chesapeake Bay Program (CBP) stations, and study sites.

Table 1. Study Sites and Chesapeake Bay Program (CBP) station information

Site #	Location (abbreviation)	Water Depth (m; MSL)	Latitude	Longitude	CBH Segment Description	Nearest CBP station	Other WQ Station
1	Tar Bay **(TB_1m)**	1	37.3058	-77.1847	James River - Tidal Fresh region	TF5.5	VIMS SAV (Moore); 1999-2009
2	Tar Bay **(TB_2m)**	2	37.3069	-77.1871	James River - Tidal Fresh region	TF5.5	VIMS SAV (Moore); 1999-2009
3	Chickahominy River near Simpson Island **(CH_1m)**	1	37.3095	-76.8707	Chickahominy River - Tidal Fresh region	RET5.1A	
4	Near 4-H Club above Jamestown Island and Jamestown-Scotland Ferry pier **(4H_2m)**	2	37.2291	-76.7953	James River - Oligohaline region	RET5.2	JMS043.78 (CONMON); 2006-2008
5	Near James River Country Club **(CC_2m)**	2	37.0448	-76.5066	James River - Mesohaline region	between LE5.2 and LE5.3	JMS018.23 (CONMON); 2006-2008; JMS017.96 (CONMON); 2012-present
6	Lafayette River, east of Hampton Road Bridge **(LA_1m)**	1	36.9021	-76.2988	Lafeyette River - Mesohaline region		

Site characterization: Sediment and water samples were collected concurrently with metabolism/nutrient flux sediment cores (described below) during 13-20 August 2012 and 1-8 April 2013 at three randomly selected stations within each of the six sites (Figure 1). Due to logistical constraints, we collected cores and conducted experiments from two sites at a time (see Table 2 for dates of field sediment and water samples collections). Parameters, measured in sediments in the 0-1cm and 1-5cm depth horizons, included: bulk density, organic content, grain size, DIN (NH_4^+, NO_x [NO_3^- + NO_2^-]), organic carbon content, total nitrogen content, total and inorganic phosphorus content. In addition, benthic chl *a* and phaeophytin concentrations were determined in the 0-1cm depth horizon. Water column characteristics measured at the time of core collection at each site included: profiles of temperature, salinity, turbidity, *in vivo* chl *a*, and DO (using a YSI model 6600); underwater photosynthetically active radiation (PAR) at multiple depths, and vertical light attenuation coefficient [K_d]. Grab samples from mid-water column depth using a submersible pump were taken for determinations of DIN, DIP (PO_4^{3-}), DON, DOC, silica (Si), and extractable chl *a* and phaeophytin. Table 3 provides a summary of analytical methods used for each parameter. Detection limits for NO_3^-, NH_4^-, PO_4^{3-}, and Si were 0.20, 0.36, 0.15, and 0.05 μM, respectively.

Determinations of shallow water benthic and pelagic metabolism and nutrient fluxes: Sediment mesocosm cores (clear acrylic, 13.3 cm inner diameter x 40 cm tall, approximately 20 cm depth of sediment with average surface area to water volume ratio of 4.82 m^{-1}[standard error=0.07] and sediment volume to water column volume ratio of 0.93 [standard error=0.03]) were collected at three randomly selected stations at approximately the same water depth within each of the six sites (Figure 1) and used for concurrent determinations of sediment oxygen demand (SOD), gross primary production (GPP), respiration (R), net community production (NCP), and nutrient fluxes (DIN, DIP), DON, DOC, and Si. The mesocosm cores were incubated in fiberglass chambers filled with site water in an environmental growth chamber (VIMS) at in-situ temperatures and light. For comparative purposes, the temperature of the incubations was set based on the first site visited in the season, thus all sites in a season had approximately similar temperature. After returning from the field and prior to starting the incubations, cores were uncapped and immersed overnight in the dark. Metabolism and nutrient flux experiments were initiated the next morning by capping the cores with clear acrylic lids. Water within the cores was constantly mixed with a magnetic stirrer. Additionally, three cores with water only from each site were incubated to distinguish water column from sediment processes. To simulate *in situ* light at the sediment surface during midday sunny conditions (estimated as 1600 μE m^{-2} s^{-1}) we multiplied the mean % of incident light reaching the sediment surface in the field (underwater PAR at sediment surface/incident PAR above water surface) by 1600 μE m^{-2} s^{-1} to determine the target underwater PAR levels for each set of cores. Light at the sediment surface inside the fiberglass incubation chambers (filled with site water and the cores) was adjusted with shade cloth to attain the target PAR levels and measured with a Li-Cor underwater PAR sensor (model 192A, Li-Cor, Inc., Lincoln, NE) at three locations inside of the chambers under the shade cloth. These PAR values were adjusted for additional attenuation due to the core lids (6.5% reduction). The mean PAR measured at the sediment surface during the light incubations are provided in Figure 2. A linear regression between experiment PAR levels versus % of incident light measured in the field at the sediment surface at the time of core collection showed a strong relationship (r^2=0.959, p<0.001) verifying that we successfully simulated in situ field conditions in laboratory incubations.

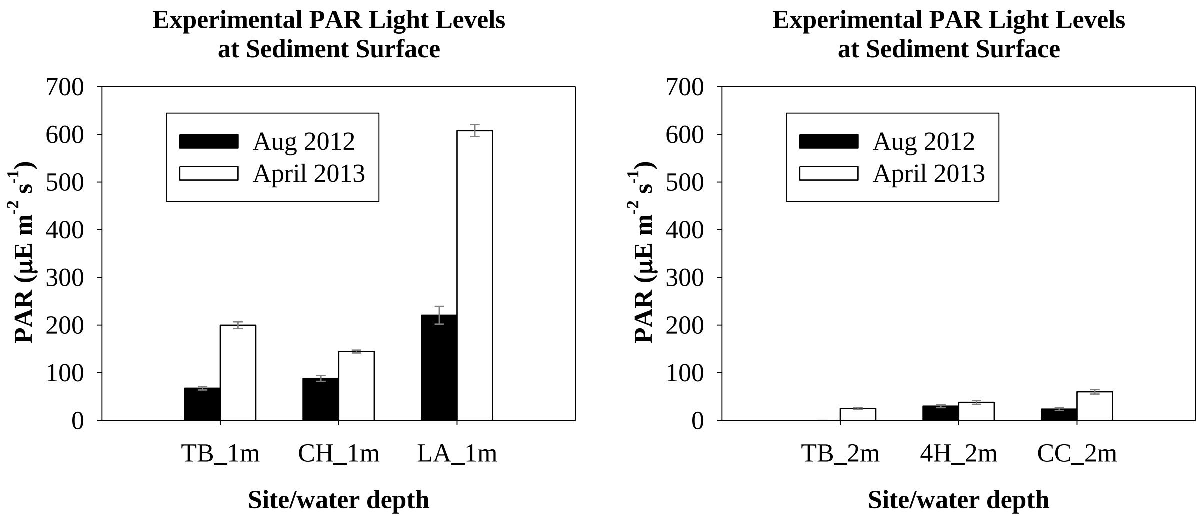

Figure 2. Measured underwater PAR at the sediment surface (mean ± standard error) during the light incubations of the experiments for the 1m and 2m sites in August 2012 and April 2013.

To determine the net exchange of nutrients, dissolved inorganic carbon (DIC), and DO between the sediment and overlying water, water samples were collected during a 24-hour period at dawn, mid-day, dusk, and dawn (simulated by turning lights on and off in the chamber). The cores were connected to a reservoir system so that water removed during sampling was replaced with water from the respective site. Dissolved oxygen concentrations in the sampled water were measured using a Hach Luminescence DO sensor. Samples for DIC were collected in 8mL hungate tubes (pre-spiked with 15 µL saturated mercuric chloride) and kept cold under water until analysis. Samples were also collected from the water reservoirs to correct for dilution in the cores. Changes in DIC in the light and dark were used for determining rates of benthic and pelagic metabolism, including R, GPP, and NCP. Changes in DO were used for determining SOD. Water samples taken concurrently with the DO and DIC measurements were filtered (Gelman Supor, 0.45 µm) and frozen until analyzed for Si, DIN, DIP, DOC, and DON (Table 3). Net uptake or release of nutrients from sediment was determined by changes in nutrient concentrations in the light or dark.

Table 2. Field sediment and water samples collection dates

Sites	Dates
TB_1m, TB_2m	13 August 2012; 8 April 2013
CH_1m, 4H_2m	20 August 2012; 1 April 2013
CC_2m, LA_1m	15 August 2012; 3 April 2013

Table 3. Summary of analytical methods

Analyses	Methods/Instrument	References
Nutrient		
Nitrate, Nitrite	Cadmium reduction/diazotization; Lachat[1]	Smith and Bogren, 2001
Ammonium	Phenol Hypochlorite method; Lachat[1]	Liao, 2001
Dissolved inorganic phosphorus (phosphate)	Molybdate method; Lachat[1]	Knepel and Bogren, 2001
Total dissolved nitrogen (TDN) / dissolved organic nitrogen (DON)	Alkaline persulfate digestion; Lachat[1]	Koroleff, 1983
Dissolved inorganic carbon (DIC)	Acidification to CO_2; LI-6252 CO_2 analyzer	Neubauer and Anderson, 2003
Dissolved organic carbon (DOC)	680ºC catalytically-aided combustion oxidation/non-dispersive infrared detection; Shimadzu TOC-V analyzer	
Silica	Molybdate in acidic solution method; Lachat[1]	Wolters, 2002
Temperature, salinity, dissolved oxygen, turbidity, chlorophyll a (in vivo) (field measurements)	YSI 6600 multiparameter sonde	
Dissolved oxygen (metabolism experiments)	Hach Luminescence DO sensor	Hach Method 10360
Chlorophyll *a* (extracted; phytoplankton biomass)	Chla – Acetone – DMSO Extract/ fluorometry; Turner Designs Flurometer, Model 10-AU	Shoaf and Lium, 1976, Arar and Collins, 1997.
Photosynthetically active radiation (PAR)	LiCor LI-192SA Underwater and LI-190SA quantum sensors	
Sediment characterization		
Sediment organic content	Loss on ignition (500°C)	
Benthic chlorophyll *a* and phaeophytin (microalgae biomass)	Chl *a* –Acetone Extract/ spectrophotometry; Beckman Coulter DU800 Spectrophotometer	Neubauer et al., 2000; Lorenzen, 1967
Sediment nutrients (dissolved inorganic N and P)	Potassium chloride-extraction	Kenney and Nelson, 1982
Sediment grain size	sieving method (>63µ); pipette method (<63µ)	Plumb, 1981
Total N and organic C content	Fision Model EA 1108 Elemental Analyzer	
Organic and inorganic P content	HCl extraction; Molybdate method; Lachat[1]	Aspila et al., 1976

[1] The Lachat auto analyzer (QuikChem 8000 Automated Ion Analyzer, Lachat Instruments, Loveland, CO) is a continuous flow automated analytical system that complies with US Environmental Protection Agency (EPA) standards.

Benthic hourly DIC, DO, and nutrients fluxes were corrected for DIC, DO, and nutrient uptake or release measured in the water blanks and calculated as follows:

$$\text{Benthic F } (\mu\text{mol m}^{-2}\text{ h}^{-1}) = (\text{Slope}_{\text{sed+water}} - \text{Slope}_{\text{water}}) * \frac{V}{SA} \qquad \text{Eq. 1}$$

F is hourly flux in either the dark or light.
$\text{Slope}_{\text{sed+water}}$ is the slope of the linear regression of DIC, DO, or nutrient concentrations in the sediment+water core versus hours elapsed (mmol L^{-1} hr^{-1} for DIC and DO; umol L^{-1} hr^{-1} for nutrients).
$\text{Slope}_{\text{water}}$ is the slope of the linear regression of DIC, DO, or nutrient concentrations in the water-only core versus hours elapsed (mmol L^{-1} hr^{-1} for DIC and DO; umol L^{-1} hr^{-1} for nutrients).
V represents water volume inside the core (L).
SA represents the surface area of the sediment inside the core (m^2).

Daily benthic nutrient fluxes were calculated as follows:

$$\text{Daily nutrient flux } (\mu\text{mol m}^{-2}\text{ d}^{-1}) = (F_l * h_l) + (F_d * h_d) \qquad \text{Eq. 2}$$

F_d represents hourly flux in the dark (μmol m^{-2} h^{-1}).
F_l represents hourly flux in the light (μmol m^{-2} h^{-1}).
h_l represents hours of light.
h_d represent hours of dark.

Benthic metabolism (based on DIC) was calculated as follows:

$$\text{R (mmol C m}^{-2}\text{ d}^{-1}) = F_d * 24 \text{ hrs} \qquad \text{Eq. 3}$$

$$\text{GPP (mmol C m}^{-2}\text{ d}^{-1}) = h_l * (F_d - F_l) \qquad \text{Eq. 4}$$

$$\text{NCP (mmol C m}^{-2}\text{ d}^{-1}) = -(\text{GPP} - \text{R}) \qquad \text{Eq. 5}$$

F_d represents hourly DIC flux in the dark (mmol C m^{-2} h^{-1}).
F_l represents hourly DIC flux in the light (mmol C m^{-2} h^{-1}).

Sediment oxygen demand (SOD) was based on DO measurements and calculated as follows:

$$\text{SOD (mmol O}_2\text{ m}^{-2}\text{ d}^{-1}) = F_d * 24 \text{ hrs} \qquad \text{Eq. 6}$$

F_d represents hourly O_2 flux in the dark (mmol O_2 m^{-2} h^{-1}).

NCP (Eq. 4) is represented as a negative number when GPP exceeds R since it was measured as uptake of C. When NCP is negative it represents net autotrophy and net uptake of C; when positive it represents net heterotrophy and net release of C. Negative nutrient flux indicates uptake of nutrient into the sediment and conversely, positive nutrient flux represents release of nutrients from the sediment.

Pelagic metabolism (R, GPP, NCP) and nutrient fluxes were also calculated using the equations above (Eq. 2-5), except hourly pelagic light and dark fluxes were scaled to expected total water depth (1m or 2m) and calculated as follows:

$$\text{Pelagic F } (\mu\text{mol m}^{-2}\text{ h}^{-1}) = (\text{Slope}_{water}) * \frac{1000\text{L}}{\text{m}^3} * D_t \qquad \text{Eq. 7}$$

F is hourly flux in either the dark or light
Slope_{water} is the slope of the linear regression of DIC, DO, or nutrient concentrations in the water-only core versus hours elapsed (mmol L^{-1} hr^{-1} for DIC and DO; umol L^{-1} hr^{-1} for nutrients)
D_t is total water depth (m)

Statistical analysis: Preliminary analyses of all data (means, standard errors) were completed using Microsoft Excel. Minitab 16 (Minitab, Inc., State College, PA) was used to perform linear regressions and analysis of variance (ANOVA) on metabolism and nutrient flux data to determine differences by site and season. Interactions between all variables were tested. Levene's test of homogeneity of variance was conducted to determine if means had similar variances. If the test was found to be significant ($p<0.05$), data were natural log transformed. Tukey's test was used to evaluate pair-wise comparisons after a significant ANOVA; differences were considered significant at $p<0.05$. When significant interactions were found, one-way ANOVAs were conducted on 1) each site to determine seasonal differences and 2) each season to determine site differences. Principal Components Analysis (PCA) was conducted using PRIMER 6 (Primer-E, Inc., Plymouth, UK) (Clarke, 1993; Clarke and Warwick, 2001) after data were transformed and normalized.

<u>Results</u>

Site Characteristics

Mean column characteristics for the six sites in the James, Chickahominy, and Lafayette Rivers are provided in Table 4. We conducted sampling in August 2012 to represent high temperature conditions during the summer, which ranged from 26.4 to 29.3°C. Sampling in April 2013 was conducted to represent cooler temperatures, which ranged from 10.2 to 14.8 °C, and to assess benthic conditions prior to or during the spring phytoplankton bloom. Salinity was lower in April (0.1-15.6) than August (0.2-22.6), due to greater freshwater discharge in the spring. Daily mean USGS discharge at station#2037500 (James River near Richmond, VA) during the sampling dates had a range of 1490 to 2340 ft^3 s^{-1} in August and 6450 to 9250 ft^3 s^{-1} in April. Salinity was also lower at the 3 upper James River sites (TB_1m, TB_2m, 4H_2m) and the Chickahominy River sites (CH_1m) than CC_2m and LA_1m during both seasons. Water column chlorophyll *a* (chl *a*) concentrations were generally higher in August at most sites, except at CC_2m in April where a phytoplankton bloom was observed with mean chl *a* concentration of 151.2 µg L^{-1} (Figure 3). As a result, DIN and DIP concentrations decreased to below detection limits at this site (Table 4). NO_x and Si concentrations were higher in April at the four lower salinity sites, while DIP concentrations were higher in August at all sites. Both DIP and Si increased with salinity in August, most likely due to desorption of DIP from particulates and remineralization. DIN:DIP ratio was above 16 at all sites in April and at TB_1m and TB_2m in August, indicating potential P limitation for phytoplankton. DIN:DIP ratio was below 16 in August at the other four downriver sites, suggesting potential N limitation. All sites had Si:DIP ratios above 16, indicating no potential Si limitations for diatoms; 4H_2m in August was the exception with a Si:DIP ratio of 11.6 and a mean chl *a* concentration lower than other sites. In August, chl *a* and Si appear to be negatively correlated, suggesting that production of phytoplankton was likely dominated by diatoms. DON and DOC concentrations were higher in August at TB_1m, TB_2m, CC_2m, and LA_1m. They were also the dominant form of nutrients in August at all sites, indicating high remineralization of organic matter. Bottom water DO was lower in August, consistent with the high summer temperatures. The percent of incident light that reached the sediment surface (i.e., available light) was higher for the 1-m sites and in April, when light attenuation was lower (Figure 4, Table 4).

Principal Component Analysis was performed on mean water column characteristics by site and season; principal components 1 and 2 (PC1, PC2) together explain 56.2% of the variance of the means (Figure 5). PC1 clearly differentiated the site means by season, where positive scores were associated with August data and higher temperature, light attenuation, phaeophytin, DON, and DOC concentrations and lower % incident light at the sediment surface, Si, and bottom DO concentrations. PC2 differentiated the sites by their position along the estuarine gradient, in which positive scores were associated with lower salinity and DIP concentrations and higher NOx and NH_4^+ concentrations.

Mean sediment characteristics for the six sites in the James, Chickahominy, and Lafayette Rivers are provided in Table 5. Benthic chl *a* concentrations were higher in April at the upriver sites of TB_1m and TB_2m and in the Lafayette River, LA_1m (Figure 6). Most sites were sandy with fairly low organic and %N, C, PIP, and TPP content, except CH_1m (Figure 6, Table 5). The % PIP and TPP content were also lower in April at most sites. There was no clear seasonal trend for %N and C content. Sediment extractable NH_4^+ was generally higher at TB_2m, while extractable NO_x was low at all sites (Figure 7).

Principal Component Analysis was performed on mean sediment characteristics by site and season and principal components 1 and 2 (PC1, PC2) together explain 78.6% of the variance of the means (Figure 8). PC1 differentiated sites by nutrient content and grain size; negative scores were associated with greater organic matter, %N, %C, and %PIP content and silt and clay fraction. PC2 arranged sites based on benthic chl *a* and phaeophytin concentrations and sediment extractable NH_4^+, in which negative scores had greater concentrations of these parameters. Unlike the PCA analysis of the water column characteristics, the PCA analysis of sediment did not indicate a clear seasonal pattern.

Hourly benthic fluxes for 1 meter sites

The effect of light on hourly benthic fluxes could be assessed for the 1-m sites because the sediment cores were exposed to greater PAR levels during the light incubations than for the 2-m site cores, in particular during April (Figure 2). The differences between light and dark DO and DIC fluxes were most apparent in April at TB_1m and LA_1m where light availability was higher, in which positive DO fluxes (release of DO from the sediment) and negative DIC fluxes (DIC uptake into the sediment) in the light indicated autotrophy and were in the opposite direction of the dark fluxes (Figure 9). In August, all sites displayed heterotrophy with positive DIC fluxes and negative DO fluxes in both the light and dark. There appears to be a slight light effect for CH_1m in August where DIC and DO fluxes in the light were reduced, compared to the dark fluxes. Hourly NH_4^+ fluxes also responded to light for TB_1m and CH_1m in August and TB_1m in April, in which effluxes were decreased or fluxes into the sediment occurred (Figure 10), likely due to benthic microalgal (BMA) primary production as indicated by both the high DIC uptake and DO release (Figure 9). Dark NH_4^+ and Si fluxes were out of the sediment for all three sites in August, suggesting remineralization of benthic and pelagic diatoms. NO_x uptake in the light and dark was highest at TB_1m in April, likely due to BMA assimilation during the daytime and possibly denitrification (DNF) and dissimilatory nitrate reduction to ammonium (DNRA) at night (Figure 10). The assumption of benthic diatom production at TB_1m in April was also supported by Si uptake in the light (Figure 10). PO_4^{3-} release was observed only at LA_1m in August (Figure 11). DON fluxes in the light and dark for most sites were negligible (Figure 11). DOC fluxes in August were also negligible due to the large replicate variability, except for dark uptake at LA_1m (Figure 11). In April, dark DOC uptake was observed at TB_1m, possibly providing carbon for DNF or DNRA.

Benthic metabolism and daily nutrient fluxes

Sediment oxygen demand (SOD), based on DO uptake into the sediment in the dark scaled to 24 hours, was generally higher at TB_2m in August, although a significant difference was only observed with 4H_2m (Table 6, Figure 12). SOD in April was lowest at 4H_2m, which was the site with the lowest %OM and highest %sand (Table 5, 6). Benthic respiration, measured as DIC release in the dark scaled to 24 hours, was higher at CH_1m in August; only TB_1m and CH_1m demonstrated significantly higher respiration in August than in April (Table 6, Figure 12). In August, all sites demonstrated positive net community production (NCP), thus were net heterotrophic (Figure 13). NCP was significantly higher in August than in April for the two upper James River sites (TB_1m, TB_2m) and CH_1m (Table 6). In April, TB_1m demonstrated net autotrophy (negative NCP) and CH_1m, LA_1m, and 4H_2m were in balance (NCP close to zero). Similarly, GPP was highest at TB_1m and LA_1m in April, when more light reached the benthos (Figure 13, Table 6). There was no significant difference by site for GPP in August, likely due to the reduced light availability and PAR across all sites (Figure 2, 4; Table 6).

Daily NH_4^+ fluxes in August were out of sediments at all the net heterotrophic sites, except 4H_2m, likely due to the low %OM and high sand content (Figure 14). NH_4^+ fluxes were higher in August than in April for the two upper James River sites (TB_1m, TB_2m) and the lower James site, CC_2m (Figure 14, Table 7). NO_x uptake was highest at TB_1m in April, which was the net autotrophic site, indicating BMA assimilation (Figure 14, Table 7). In August NOx uptake was highest at the heterotrophic TB_2m site (Figure 14, Table 7), likely due to reduction of NO_x by a combination of DNF and DNRA; concurrent release of NH_4^+ suggests reduction of NO_3^- by DNRA.. During the 24 hour incubation period, which was continuously dark due to the very low % incident light measured at the sediment surface at TB_2m (Figures 2, 4), DO concentrations in the overlying water of the sediment cores decreased rapidly to zero, while NH_4^+ increased and NO_x decreased (Figure 15). High remineralization rates also likely contributed to the large NH_4^+ flux out of the sediment. Daily Si fluxes were also released from the sediment in August at all sites, suggesting benthic and pelagic diatom decomposition (Figure 14). Si fluxes were significantly higher in August than in April for the upper James River sites (TB_1m, TB_2m) and CH_1m, similar to NCP patterns (Figures 13, 16, Table 7). Si fluxes in April generally were negligible at CH_1m, LA_1m, TB_2m, and 4H_2m or into the sediment at the net autotrophic TB_1m, except for CC_2m which had a phytoplankton bloom and was a net heterotrophic site. PO_4^{3-} fluxes were out of the sediment in August at LA_1m, TB_1m, and CC_2m, and were negligible in April due to PO_4^{3-} concentrations being below detection limits in the overlying water (Figure 16).

The patterns for daily DON and DOC fluxes were less clear due to the large variability of the sediment core replicates in August and April (Figure 17). There were no significant differences by date or site for both nutrients (Table 7). In August DON were taken up at TB_1m and LA_1m, while DON was released at CC_2m in August and at CH_1m and LA_1m in April. DOC was released at CH_1m in both seasons and at 4H_2m in August.

Drivers of benthic metabolism and daily nutrient fluxes

To further assess the patterns of benthic metabolism and nutrient flux rates, PCA was conducted on the mean rates by site and season. Principal components 1 and 2 (PC1, PC2) together explain 60.7% of the variance of the means (Figure 18). PC1 clearly differentiated the site means by season, where negative scores were associated with August data and higher NCP (net heterotrophy) and daily Si and NH_4^+ fluxes. 4H_2m in August was more similar to the April sites. PC2 differentiated the sites by water depth, for which the 1m sites mostly had positive scores and were associated with greater GPP and R and generally lower DON and DOC fluxes.

Step-wise multiple regressions were conducted to determine relationships between benthic R and GPP and water column and sediment characteristics. Benthic R was positively related to sediment %OM content (r^2=0.41, p=0.006) in August, while R was positively related to benthic phaeophytin in April (r^2=0.26, p=0.033) (Figure 19). Benthic GPP was positively related to experiment PAR levels during the light incubation in April, accounting for 56.0% of the variability (p=0.001) (Figure 20). The linear regression in August was not significant but similar to that in April. GPP was not related to benthic chlorophyll in either season. Benthic GPP in April was positively related to water column NH_4^+ concentrations in a multiple regression with experiment PAR, together explaining 86.0% of the variability (p<0.001), with the following equation:

$$\text{Benthic GPP (mmol C m}^{-2}\text{ d}^{-1}) = 0.0576*\text{Expt PAR (uE m}^{-2}\text{ s}^{-1}) + 4.85*NH_4^+ (\mu M) - 5.96 \quad \text{Eq. 8}$$

Benthic NCP is based on the balance of benthic GPP and R and we found that NCP was strongly affected by respiration in August (r^2=0.77, p<0.001; Figure 21), when there was higher water column temperature. In April, with lower water temperatures and K_d values and higher NO_x concentrations, NCP was driven primarily by GPP, accounting for 57.5% of the variability (p<0.001; Figure 21).

Daily NH_4^+, NO_x, Si, and PO_4^{3-} fluxes generally corresponded to the sites' trophic status, in which sediment cores with positive NCP (net heterotrophy) tended to have NH_4^+, NO_x, Si, and PO_4^{3-} released from the sediment (Figure 22). NH_4^+, NO_x, Si, and PO_4^{3-} uptake or no net release occurred for sediment cores with negative NCP (net autotrophy) and sometimes low NCP (e.g., for NH_4^+ and PO_4^{3-} fluxes). The main exception to this pattern was for the TB_2m cores in August when there was high NO_x uptake with high NCP, which was likely due to anoxic conditions, as described above. In April, NO_x flux was positively related to NCP, accounting for 73% of the variability ($p<0.001$, Figure 16). For both seasons, Si fluxes were also positively related to NCP ($r^2=0.65$, $p<0.001$, Figure 16). Plots of daily DON and DOC flux data versus NCP suggested that NCP played a smaller role in determining their fluxes (Figure 23).

Pelagic metabolism and daily nutrient fluxes

This experiment was optimized to determine benthic metabolism and nutrient fluxes, therefore PAR levels were set to match *in situ* light levels at the sediment surface. The water-only cores were exposed to light levels similar to the sediment+water cores in order to remove the pelagic effect and calculate benthic rates. A 1m water column is most likely well-mixed and the cores were approximately 0.4m tall, thus the pelagic rates provided in this report may be close to *in situ* light conditions; however we were not able to simulate the light regime over a 2 meter water column. The results are still presented in this report for comparison purposes.

Pelagic R and GPP were highest at CC_2m in April even with the low PAR level (24.9 $\mu E\ m^{-2}\ s^{-1}$), likely due to the large phytoplankton bloom (Figure 24, Table 8). Respiration had no significant differences by site in August (Table 8). GPP was higher in August than April for all the 1m sites (TB_1m, CH_1m, LA_1m) when water column chlorophyll *a* concentrations were also higher (Figure 24; Tables 4, 8). All the 1m sites were also net autotrophic (negative NCP) in August and April, whereas the 2m sites were predominantly net heterotrophic, as expected due to the lower light levels, except for CC_2m that had the large phytoplankton bloom (Figure 24).

Pelagic daily NH_4^+, NO_x, and PO_4^{3-} fluxes at the 1m sites were taken up or negligible due to the water column being net autotrophic in both seasons, except for LA_1m in August when it released PO_4^{3-}, possibly due to high respiration rates (Figure 25). There was net NO_x uptake or no release at all the 2m sites in August and April (Figure 25), possibly due to some phytoplankton assimilation in the low light. TB_2m and CC_2m had the largest NH_4^+ release in August, possibly due to high mineralization rates (Figure 25, Table 9). Pelagic Si was generally removed from the water column or had no net change in August, but released in April for most sites except CC_2m (Figure 26). DON fluxes were greater in August for CH_1m and LA_1m and released, possibly due to higher temperatures, while the DON fluxes generally decreased in April (Figure 26, Table 9). At TB_2m in August, which had high NH_4^+ release, DON and DOC were removed from the water column (Figure 26). 4H_2m had high NH_4^+, PO_4^{3-}, and DOC uptake from the water column in August (Figures 25, 26; Table 9).

Drivers of pelagic metabolism and daily nutrient fluxes for 1-m sites

Step-wise multiple regressions were conducted to determine relationships between pelagic R and GPP with water column characteristics for the 1m sites only. GPP was positively related to water column chl *a* concentrations in August and April (r^2=0.71, p<0.001), with a clear separation of points by season (Figure 27). Pelagic GPP was also positively related to salinity in a multiple regression with water column chl *a*, together explaining 82.0% of the variability (p<0.001), with the following equation:

$$\text{Pelagic GPP (mmol C m}^{-2}\text{ d}^{-1}) = 80.5*\ln(\text{chl } a)\ (\mu\text{g L}^{-1}) + 2.42*\text{salinity} - 131 \qquad \text{Eq. 9}$$

In April, pelagic R was positively related with water column chl *a* concentration (r^2=0.68, p=0.006). Similar to the benthic NCP regression, pelagic NCP was positively related to R in August, but not in April (r^2=0.51, p=0.030, Figure 28). Pelagic GPP only accounted for 25% of the variability of NCP for both August and April (p=0.034, Figure 28). When plotting the pelagic daily nutrient fluxes versus NCP, NH_4^+, NO_x, PO_4^{3-}, and DON fluxes generally corresponded to the sites' trophic status, in which net autotrophic water only cores removed these nutrients or had minimal release and the slightly net heterotrophic cores demonstrated release of PO_4^{3-} and DON (Figure 29). NO_x uptake increased with greater net autotrophy for the August cores (r^2=0.55, p=0.023). There were no clearcut patterns in April.

Discussion

Comparison to 1994 James River SONE Study

A SONE study was conducted in May and August 1994 in the James and York River; however, sediment cores were collected at different sites and water depths, 2m for their shoal sites and 4 to 7m for channel sites (Meyers, 1995). In addition, in the Meyers' study cores and water blanks were incubated on the ship deck for 4 hours using separate cores for light and dark flux measurements. Although the sites were not in the same locations (Figure 30), graphs of benthic hourly light and dark DO, NO_x, NH_4^+, PO_4^{3-}, and Si fluxes are plotted for the 2m sites from both this study and the 1994 study for comparative purposes. In August 1994, the magnitude of benthic DO, NH_4^+, PO_4^{3-}, and Si effluxes was lower although the field water temperatures in August 1994 (24.7-29.6°C) were similar to August 2012 (27.2-29.3°C) (Figures 31, 32). There was some variation in responses to light in 1994 compared to 2012; however, light attenuation and % available light at the sediment surface were not provided in the Meyers' report (1995). NO_x fluxes were generally out of the sediment in 1994 and of greater magnitude than in 2012 when fluxes were either insignificant or into the sediment, suggesting denitrification. At the TB site the water column became anoxic during incubation likely increasing denitrification.. RET5, which was located at the confluence of the Chickahominy and James Rivers (Figure 30), appeared to be the most heterotrophic site with the largest DO uptake and NO_x, NH_4^+, PO_4^{3-}, and Si release; this is likely due to the high sediment organic C content of approximately 2.7-2.8%, compared to 4H_2m, which was 0.2%. For the spring comparison, the 1994 experiment occurred in May, instead of April and water temperatures were higher (17.3-19.0°C) than in April 2013 (10.8-14.8°C), which may explain the greater NO_x, NH_4^+, PO_4^{3-}, and Si fluxes (positive and negative) in 1994 for the two upper James River sites in particular, TF5 and RET5 (note the change in TF5 location to farther upriver) (Figures 33, 34). Dark DO fluxes were relatively similar.

Important factors affecting benthic metabolism and nutrient fluxes

Seasonally-influenced factors of water temperature, light attenuation, and water column NH_4^+ concentration were important drivers of benthic GPP in study sites in the James River, while sediment %OM and phaeophytin were important drivers of benthic R. Benthic GPP and R determined benthic NCP, which in turn regulated nutrient fluxes out of or into the sediment. We observed a clear separation of metabolic status and nutrient response by season; in August, the sites were all net heterotrophic and released NH_4^+, NO_x, Si, and PO_4^{3-} due to greater water temperatures and reduced light reaching the sediment surface. Respiration played a greater role than GPP in determining trophic status. The exception for nutrient release was at TB_2m, when the water column became anoxic and NO_x was taken up by DNRA and DNF. In April, the 1m sites were net autotrophic or close to being in balance. Nutrients were either taken up by sediments or efflux was reduced due to increased BMA primary production when light availability was greater. Water column NH_4^+ concentrations were another important factor supporting benthic GPP in April, but not in August when sediment remineralization rather than the water column likely provided the nitrogen to support benthic GPP. In other shallow estuarine systems sediment remineralization was similarly observed to be highest during summer (Anderson *et al.*, 2013). The 2m sites were either net heterotrophic or close to being in balance due to less light available at the greater water depth. In April GPP was more important in determining NCP.

In many studies of shallow estuarine systems, where the benthos are in the photic zone, similar relationships have been observed (Anderson *et al.*, 2013; Alsterberg *et al.*, 2011, 2012; Sundbäck *et al.*, 2000, 2004; Eyre and Ferguson, 2005; Ferguson *et al.*, 2007). For example in the New River Estuary (NRE), NC, a shallow system with more than 50% of the estuary at less than 2m water depth (mean sea level), Anderson *et al.* (2013) found that light attenuation, water temperature, benthic chl *a*, and sediment %OM were important drivers of benthic GPP, R, NH_4^+ fluxes, and DNF. The shallow sites (0.5m and 1.5m MLW) tended to be net autotrophic and NCP was a predictor of NH_4^+ fluxes. In this study BMA biomass (chl *a*) was not an important predictor for metabolism and nutrient flux rates, which was likely due to the NRE having generally lower light attenuation (1.5-3.5 m^{-1}) and greater benthic chl *a* concentrations (mean: 48.1-108.8 mg L^{-1} in the 0-3mm depth horizon) than in the James River (Tables 4, 5).

<u>Conclusions</u>

In conclusion, studies of nutrient and metabolic fluxes conducted in the James River during August 2012 and April 2013 suggest that:

- Light matters. When sufficient light reaches the benthos, sediments tend to become net autotrophic and either remove or reduce the flux of mineralized NH_4^+ to the water column.
- The benthos matters, at least at 1m MSL. Benthic respiration can contribute as much or more DIC or DO to the water column as pelagic respiration (scaled to water column depth).
- Net community production was driven by GPP in April and R in August. NCP indicates the direction of nutrient fluxes between sediments and water column.

- During summer the benthos at all sites was net heterotrophic. Fluxes of NH_4^+, PO_4^{3-}, and silicate from sediments to water column were proportional to the degree of benthic net heterotrophy.

Table 4. Mean mid-water column characteristics

Site/ depth	Kd	% light at sed surface	Sal	Turb	Temp	Chl *a*[1]	Phae[1]	bottom DO	NO_x	NH_4^+	PO_4^{3-}	DON	Si	DOC	DIN/ DIP ratio[2]	Si/ DIP ratio[2]
	m^{-1}			NTU	°C	µg L^{-1}	µg L^{-1}	mg L^{-1}	- µM -							
August 2012																
TB_1m	3.26 (0.04)	4.3 (0.1)	0.2 (0)	17.4 (1.1)	29.3 (0)	61.6 (0.4)	20.13 (0.38)	7.62 (0.15)	4.28 (0.09)	4.73 (0.24)	0.16 (0.01)	23.82 (0.2)	3.85 (0.54)	414.5 (10.6)	57.3	24.4
TB_2m	4.81 (0.05)	0 (0)	0.2 (0)	30.5 (0.3)	29.2 (0)	69.2 (0.9)	19.53 (0.73)	8.42 (0.07)	5.59 (0.72)	1.79 (0.37)	0.19 (0.02)	26.01 (2.23)	6.22 (0.75)	388.7 (9.9)	39.9	33.6
CH_1m	2.63 (0.05)	5.5 (0.3)	2 (0)	13 (0.8)	26.4 (0.1)	24.4 (0.9)	7.82 (0.48)	5.63 (0.04)	0.2 (0.01)	0.29 (0.03)	0.35 (0.01)	20.38 (0.32)	7.35 (0.52)	334.9 (9.6)	1.4	21.0
4H_2m	2.17 (0.01)	1.9 (0)	5.4 (0)	15.4 (0.3)	27.2 (0)	9.5 (0.3)	3.61 (0.19)	5.86 (0.01)	6.98 (0.1)	1.32 (0.02)	1.13 (0.01)	19.37 (0.39)	13.13 (0.18)	258.6 (5.9)	7.3	11.6
CC_2m	1.52 (0.05)	1.6 (0.3)	18 (0)	6.3 (0.2)	28 (0)	20.2 (0.4)	4.1 (0.08)	5.88 (0.02)	BD[3]	0.37 (0.08)	0.84 (0.01)	24.9 (0.62)	32.1 (0.44)	279.1 (9.4)	0.6	38.3
LA_1m	2.37 (0.04)	14 (0.8)	22.6 (0)	16.2 (0.5)	29.2 (0.1)	22.2 (5.1)	6.53 (1.09)	6.15 (0.04)	0.22 (0.08)	0.46 (0.02)	1.72 (0.02)	27.97 (0.79)	53.42 (1.34)	389.8 (17)	0.4	31.0
April 2013																
TB_1m	2.04 (0.06)	11.2 (0.5)	0.1 (0)	16.7 (3.2)	14.6 (0)	13.8 (0.8)	4.39 (0.35)	11 (0.02)	12.9 (0.02)	4.14 (0.02)	BD	14.83 (2.28)	100.75 (0.5)	248.1 (NA)	114	672
TB_2m	2.09 (0.03)	4.1 (0.2)	0.1 (0)	20.8 (2.6)	14.8 (0)	15.9 (0.4)	3.55 (0.66)	10.86 (0.12)	12.49 (0.19)	2.48 (0.04)	BD	16.01 (1.95)	98.04 (0.15)	262.6 (23.2)	99.8	654
CH_1m	2.87 (0.11)	9.8 (1.6)	0.2 (0)	21.9 (1.9)	11.1 (0)	12.3 (0.6)	5.63 (0.14)	10.31 (0.08)	4.64 (0.08)	0.79 (0.01)	BD	23.94 (1.32)	41.78 (1.96)	498.3 (1.2)	36.2	279
4H_2m	2.41 (0.01)	2.1 (0)	0.1 (0)	20.2 (0.1)	10.2 (0)	15.1 (0.6)	4.84 (0.48)	11.75 (0.03)	17.56 (0.03)	1.09 (0.06)	BD	18.66 (1.2)	82.67 (1.4)	341.7 (19.1)	124	551
CC_2m	1.09 (0.08)	3.1 (0.3)	11.6 (0.1)	8 (0.9)	11 (0)	151.2 (12.9)	2.81 (0.33)	17.07 (0.03)	BD	BD	0.17 (0)	23.2 (1.4)	38.98 (1.99)	275.8 (12.4)	3.1	260
LA_1m	0.94 (0.04)	46.9 (1.2)	15.6 (0)	12.9 (7.4)	10.8 (0.1)	5.8 (0.4)	1.04 (0.13)	10.92 (0.02)	BD	BD	BD	19.87 (0.29)	13.54 (0.07)	311.2 (5)	2.9	90.3

Standard error given in parentheses, n=3, except for TB_1m in April 2013 for DOC (n=1). Kd=light attenuation; %light at sed surface= % incident light measured at sediment surface; Sal=salinity; Turb= turbidity; Temp=temperature; chl a=chlorophyll a; phae=phaeophytin; DON=dissolved organic nitrogen; DOC=dissolved organic carbon.

[1] extracted chlorophyll *a* and phaeophytin.

2 If PO_4^{3-} (DIP) was below detection, the detection limit was used to calculate the molar ratio.

[3]BD=below detection. Detection limits for NO_x, NH_4^-, PO_4^{3-}, and Si were 0.20, 0.36, 0.15, 0.05 µM, respectively.

Table 5. Mean sediment characteristics. All sediment properties are for 0-5cm depth horizon except for chl *a* and phaeophytin, which is 0-1cm.

Site	chl *a*	phaeo	bulk density	Water content	OM	Sand	Silt	Clay	PIP	TPP	Total N	Total Organic C	C/N molar ratio	N/P molar ratio
	mg m^{-2}		g DW mL^{-1}	% by mass										
August 2012														
TB_1m	34.2 (4.1)	78.2 (7.4)	1.37 (0.04)	25.48 (0.35)	1.3 (0.04)	92.4 (1.3)	3.6 (0.8)	3.9 (0.5)	0.009 (0.002)	0.014 (0.005)	0.03 (0.01)	0.23 (0.06)	8.4 (0.7)	5.5 (0.8)
TB_2m	41.2 (8)	148.6 (42.8)	0.94 (0.11)	44.91 (7.17)	5.45 (1.16)	39.6 (15.8)	34.6 (9.9)	25.8 (6)	0.04 (0.001)	0.05 (0.002)	0.17 (0.03)	2.29 (0.55)	15.8 (0.7)	7.3 (1.2)
CH_1m	44 (10.4)	155.9 (13.6)	0.24 (0.01)	77.8 (2.12)	15.39 (1.2)	11.2 (1)	41 (1.4)	47.9 (1.1)	0.061 (0.003)	0.078 (0.004)	0.47 (0.02)	5.44 (0.33)	13.4 (0.2)	13.5 (1.1)
4H_2m	25.3 (2.8)	83.5 (16)	1.62 (0.01)	24.46 (1.05)	0.96 (0.25)	93.6 (1.5)	2.1 (0.6)	4.2 (0.9)	0.01 (0.002)	0.017 (0.003)	0.03 (0.01)	0.20 (0.05)	8.4 (0.9)	3.4 (0.3)
CC_2m	37.5 (8.9)	180.2 (40.4)	1.02 (0.05)	40.83 (3.06)	3.36 (0.48)	64.8 (4.4)	14.9 (1.9)	20.3 (2.5)	0.019 (0.004)	0.032 (0.007)	0.09 (0.02)	0.78 (0.13)	9.8 (0)	7 (0.4)
LA_1m	26.2 (4.1)	180.3 (27.7)	0.86 (0.28)	45.16 (10)	4.76 (1.73)	36.9 (23.8)	36.1 (14)	27 (9.9)	0.028 (0.008)	0.033 (0.012)	0.14 (0.04)	1.62 (0.53)	12.7 (0.8)	13 (3.6)
April 2013														
TB_1m	104.4 (30.4)	186 (43)	1.08 (0.24)	40.36 (7.71)	3.42 (1.39)	71.9 (11.7)	17 (8.4)	11.1 (3.6)	0.02 (0.029)	0.008 (0.005)	0.1 (0.05)	0.91 (0.56)	8.6 (1.7)	6.7 (1.6)
TB_2m	89.4 (29.3)	168.9 (30.6)	1.23 (0.07)	35.84 (1.56)	3.44 (0.73)	59.1 (15.3)	22.4 (8.8)	18.5 (6.5)	0.02 (0.032)	0.006 (0.001)	0.09 (0.03)	2.13 (0.42)	39.7 (18.2)	5.7 (0.7)
CH_1m	27.6 (0.9)	123.8 (25.9)	0.34 (0.03)	73.29 (1.25)	14.95 (0.58)	8.8 (1.9)	36.6 (5.3)	54.6 (7.2)	0.036 (0.062)	0.011 (0.01)	0.68 (0.08)	6.61 (0.12)	11.6 (1.1)	26.5 (7)
4H_2m	23.9 (6.5)	62 (19.4)	1.48 (0.05)	26.13 (1.02)	1.19 (0.27)	91.0 (3.1)	3.0 (1.0)	6.1 (2.0)	0.007 (0.011)	0.001 (0.001)	0.06 (0.01)	0.48 (0.13)	9.6 (0.3)	8.4 (0.8)
CC_2m	41.7 (12.1)	130.7 (13)	1.26 (0.13)	32.95 (2.7)	1.94 (0.28)	78.7 (4.3)	8.9 (1.8)	12.4 (2.6)	0.01 (0.015)	0.004 (0.002)	0.06 (0.01)	0.48 (0.13)	9.6 (0.3)	8.4 (0.8)
LA_1m	45.4 (5.2)	213.9 (41.9)	1.32 (0.3)	34.14 (9.17)	2.6 (1.34)	60.7 (27)	23.5 (17.5)	15.8 (9.5)	0.016 (0.021)	0.011 (0.009)	0.09 (0.05)	1.02 (0.61)	12.8 (0.5)	9.4 (0.7)

Standard error given in parentheses, n=3, except for TB_1m in August 2012 for OM (n=2). Chl *a*= benthic chlorophyll *a*; phae=benthic phaeophytin; OM= organic matter, PIP=particulate inorganic phosphorus (P); TPP=total particulate P.

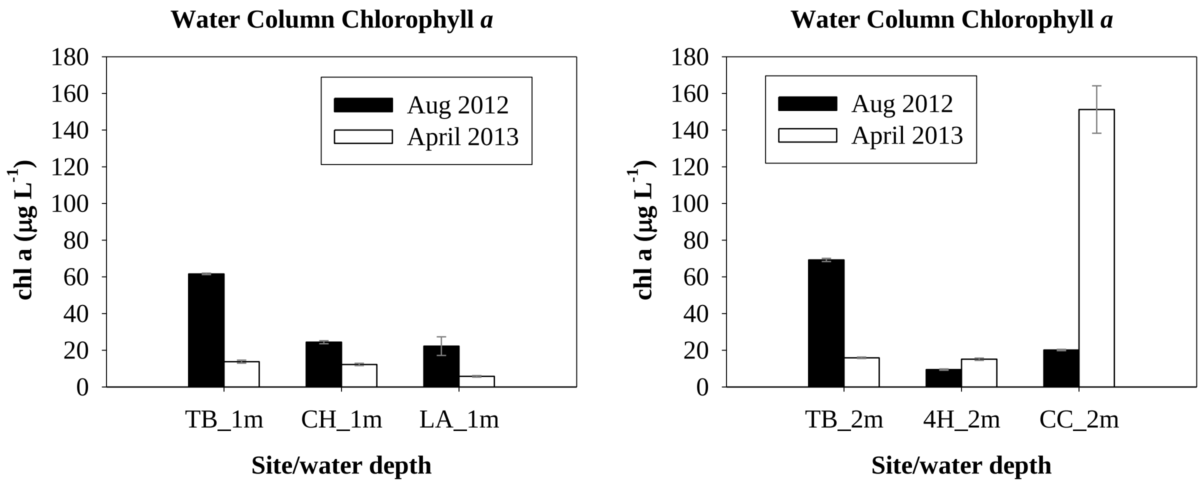

Figure 3. Water column chlorophyll a concentrations (mean ± standard error) at 1m (left) and 2m (right) sites in August 2012 and April 2013.

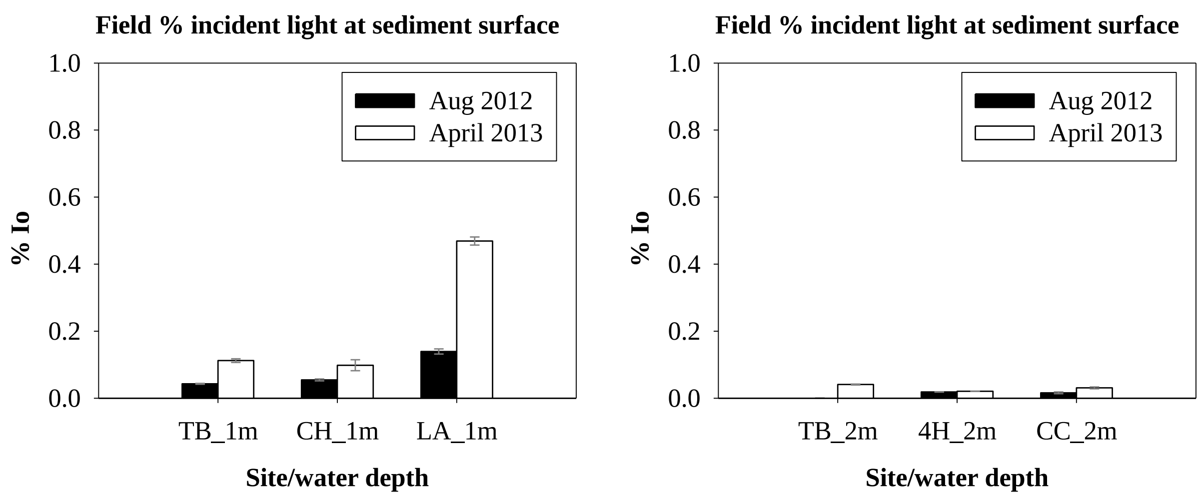

Figure 4. Percent incident light that reaches the sediment surface (mean ± standard error) at 1m (left) and 2m (right) sites in August 2012 and April 2013.

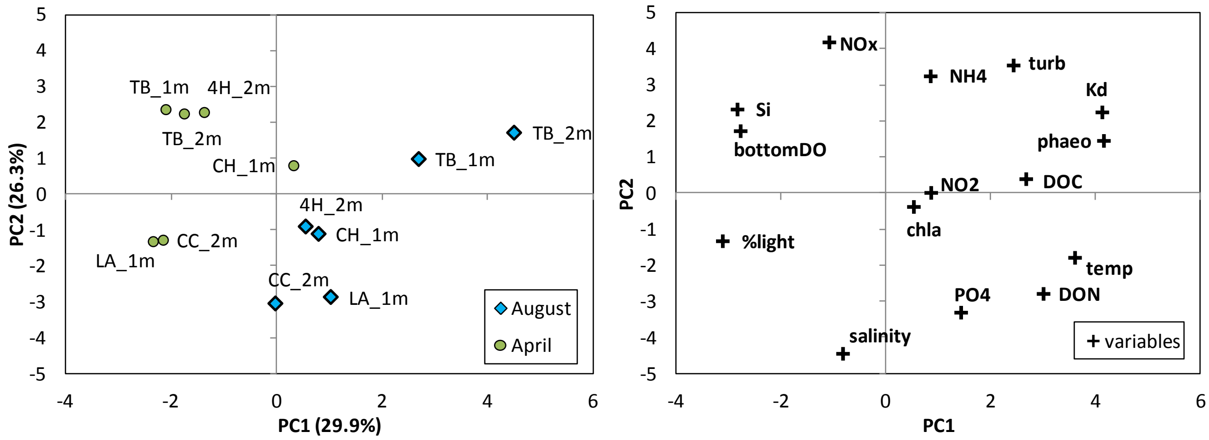

Figure 5. PCA ordination of mean water column characteristics by site and season (left) and of the coefficients for the variables (right). The coefficients for the variables are multiplied by 10 in order to plot them on a similar scale of the PC scores. Temperature, PO_4^{3-}, and field % incident light at sediment surface were transformed as ln(x).

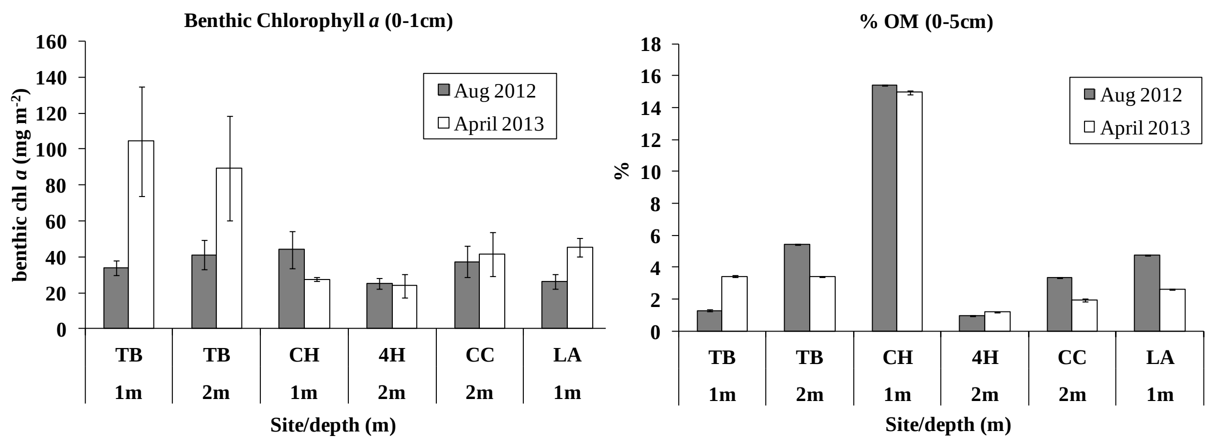

Figure 6. Benthic chlorophyll *a* (left) and sediment percent organic matter content (right) (mean ± standard error) at 1m and 2m sites in August 2012 and April 2013.

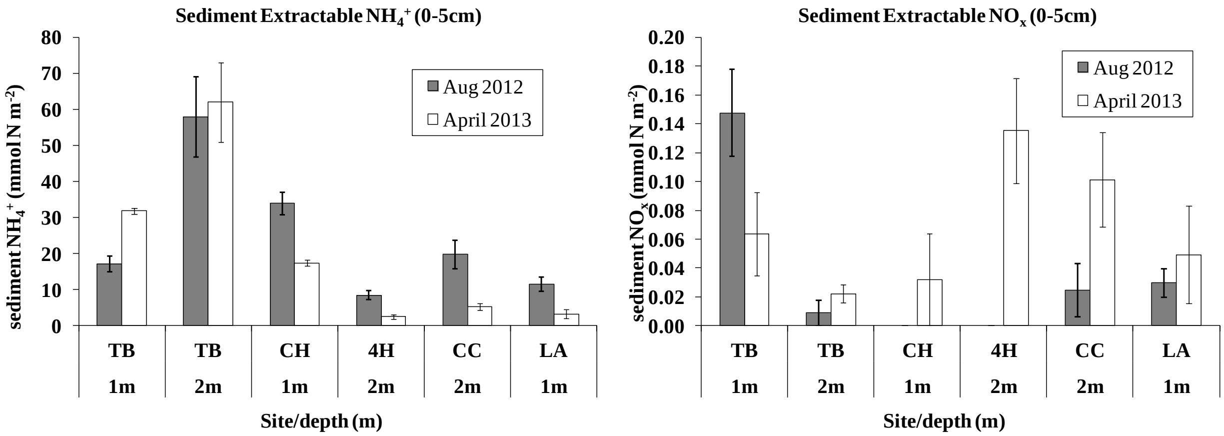

Figure 7. Sediment extractable NH_4^+ and NO_x (mean ± standard error) at 1m and 2m sites in August 2012 and April 2013.

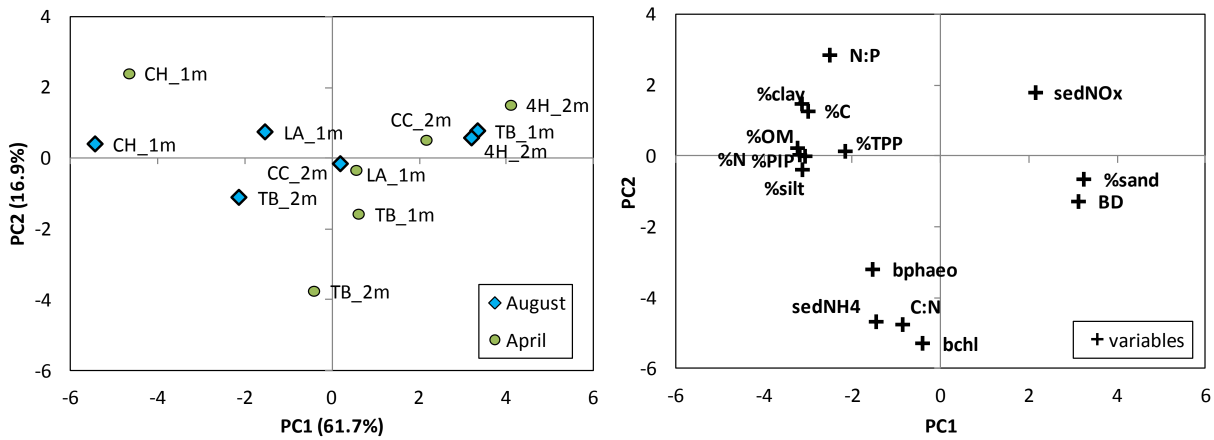

Figure 8. PCA ordination of mean sediment characteristics by site and season (left) and of the coefficients for the variables (right). The coefficients for the variables are multiplied by 10 in order to plot them on a similar scale of the PC scores. % organic matter (OM), %N content, benthic chlorophyll a (bchl) were transformed as ln(x).

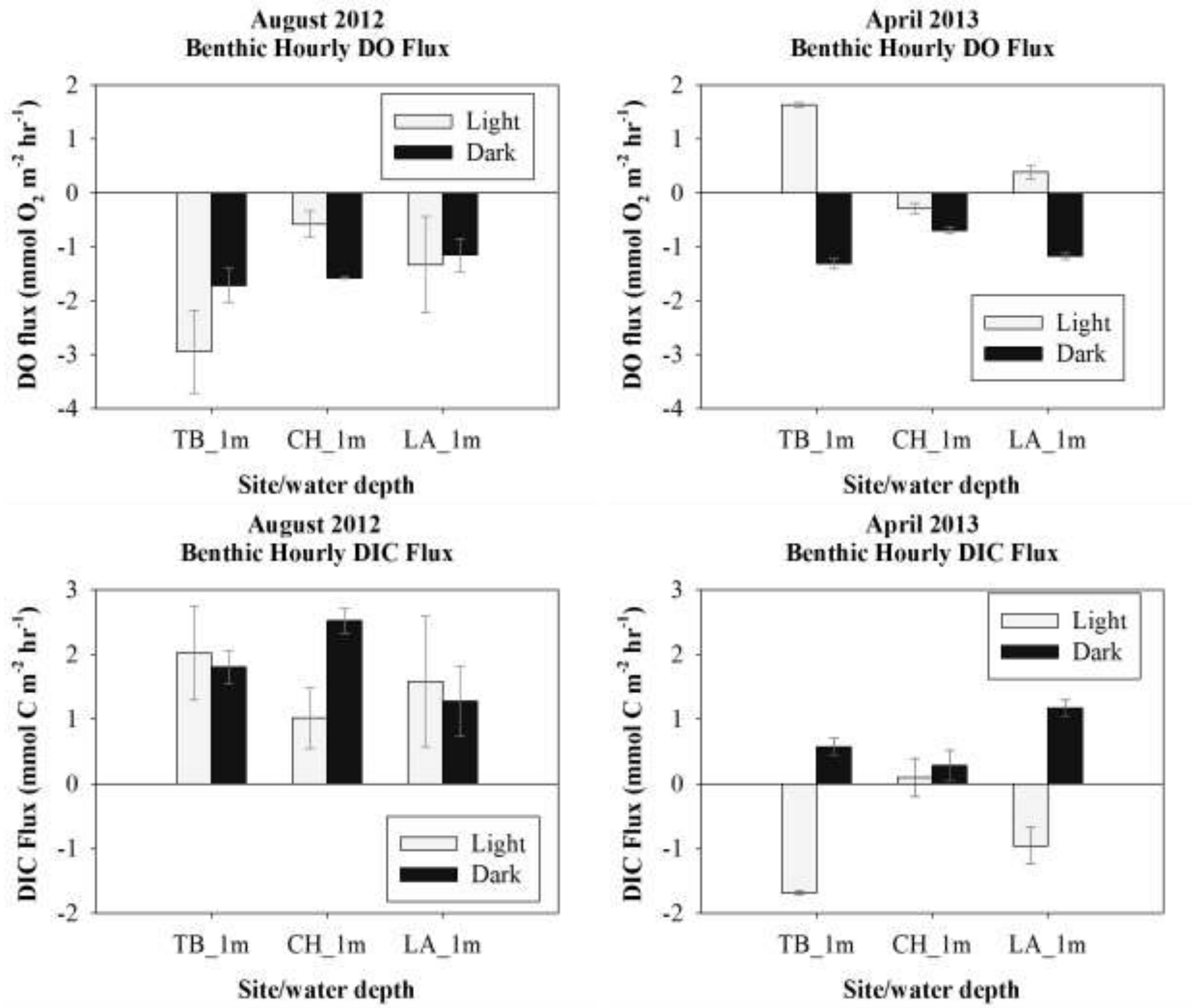

Figure 9. Benthic hourly DO and DIC fluxes (mean ± standard error) at 1m sites in August 2012 (left) and April 2013 (right).

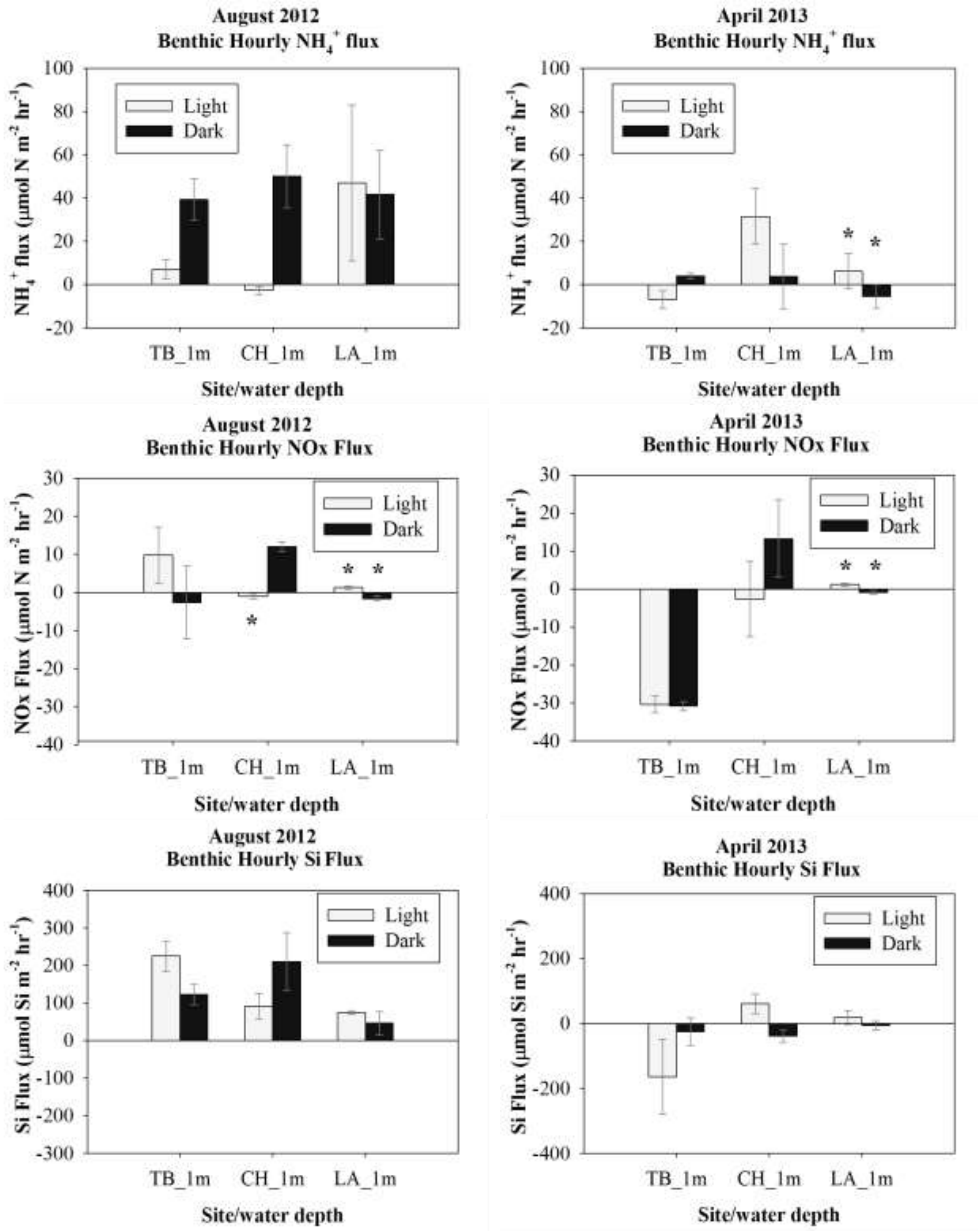

Figure 10. Benthic hourly light and dark NH_4^+, NO_x, and Si fluxes (mean ± standard error) at 1m sites in August 2012 (left) and April 2013 (right). *denote nutrient concentrations were below detection.

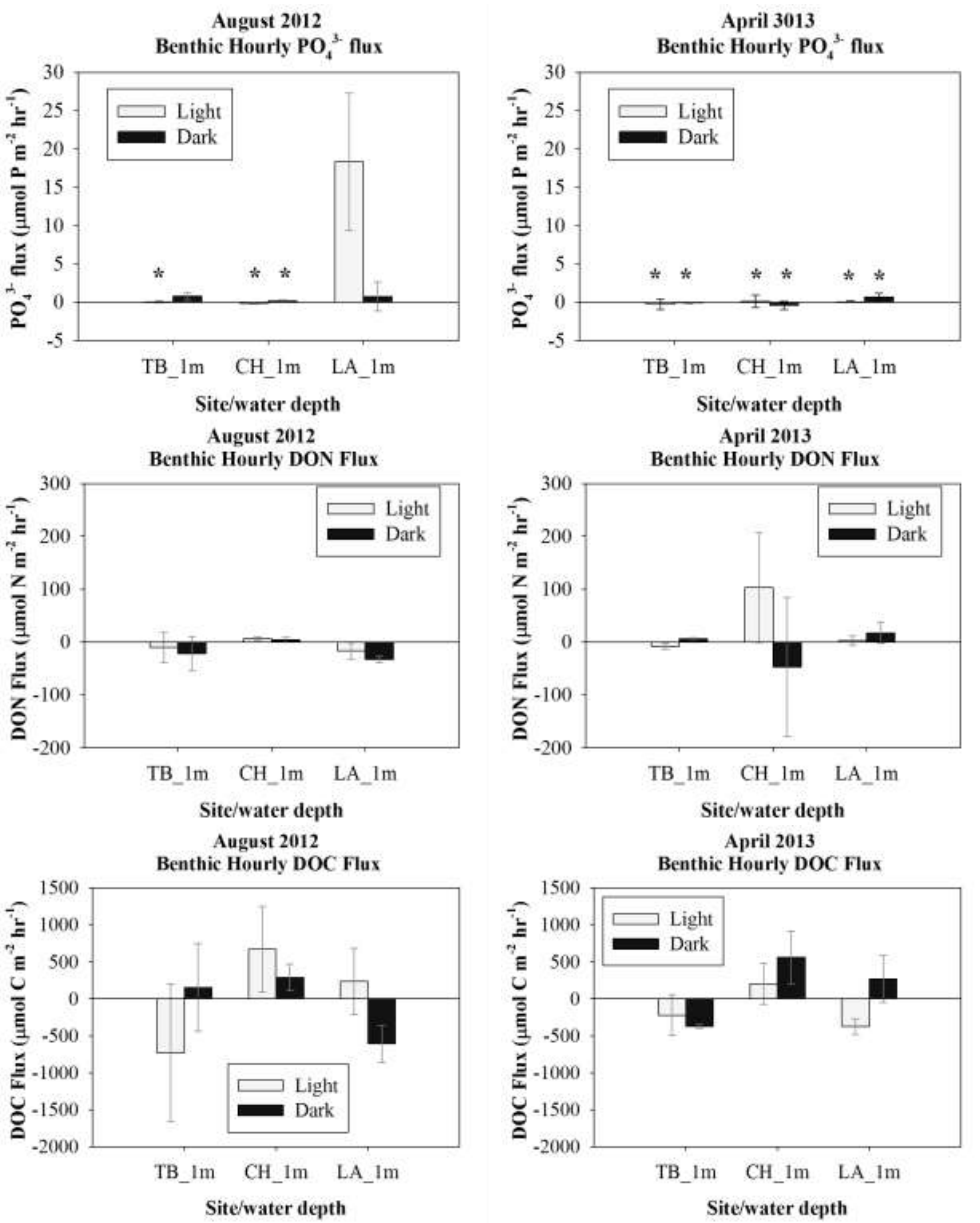

Figure 11. Benthic hourly light and dark PO_4^{3-}, DON, and DOC fluxes (mean ± standard error) at 1m sites in August 2012 (left) and April 2013 (right). *denote nutrient concentrations were below detection.

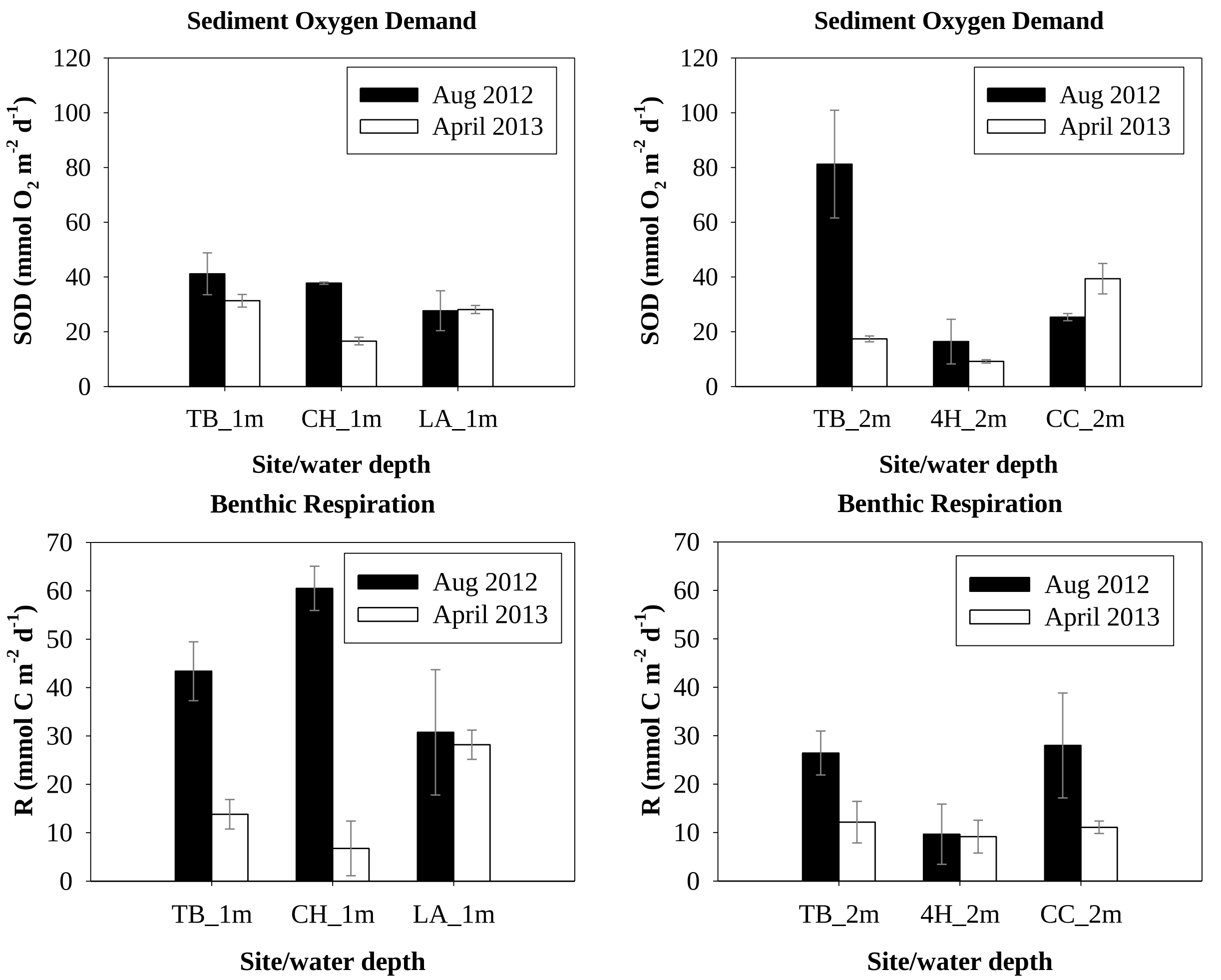

Figure 12. Benthic sediment oxygen demand (SOD) and respiration (R) (mean ± standard error) at 1m (left) and 2m (right) sites in August 2012 and April 2013.

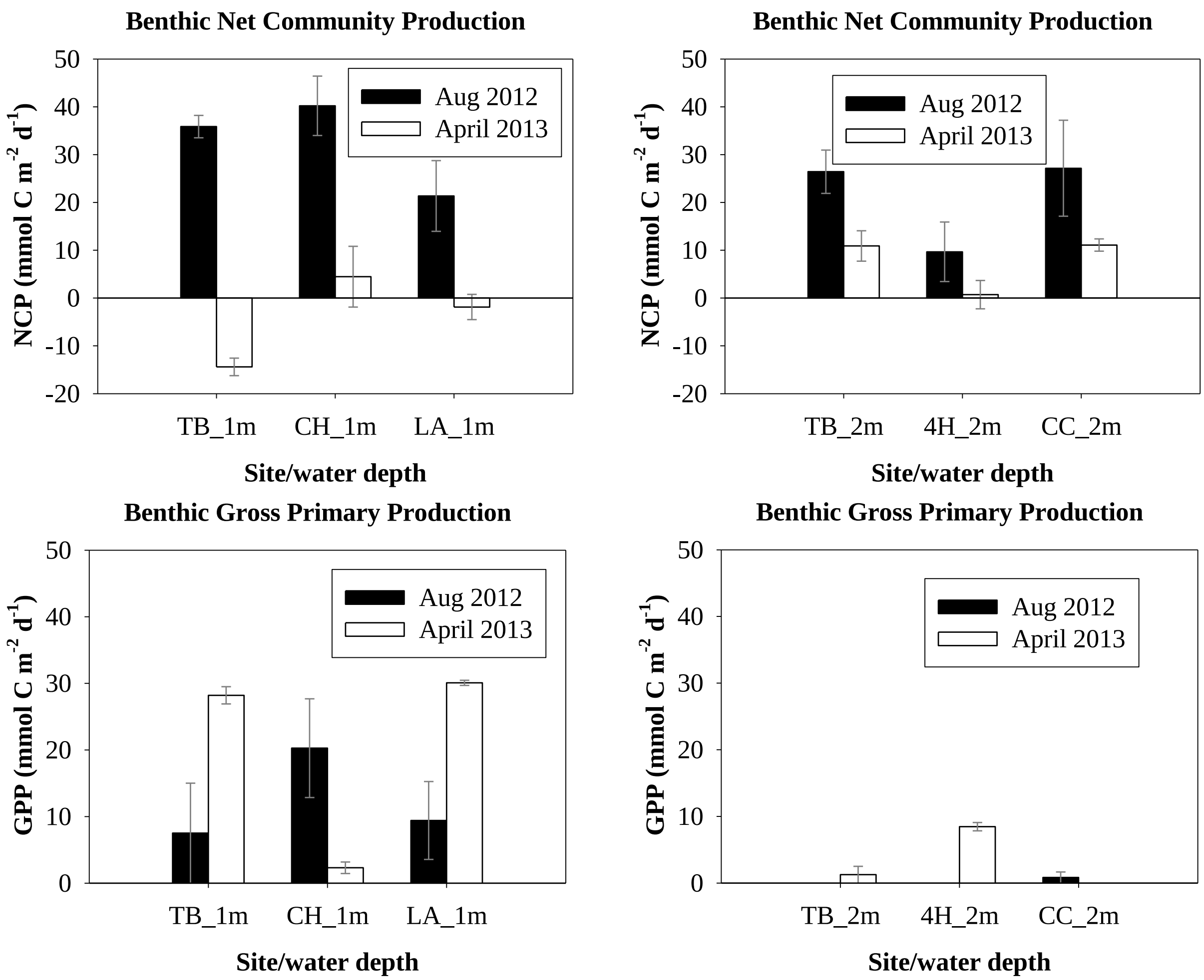

Figure 13. Benthic net community production (NCP) and gross primary production (GPP) (mean ± standard error) at 1m (left) and 2m (right) sites in August 2012 and April 2013.

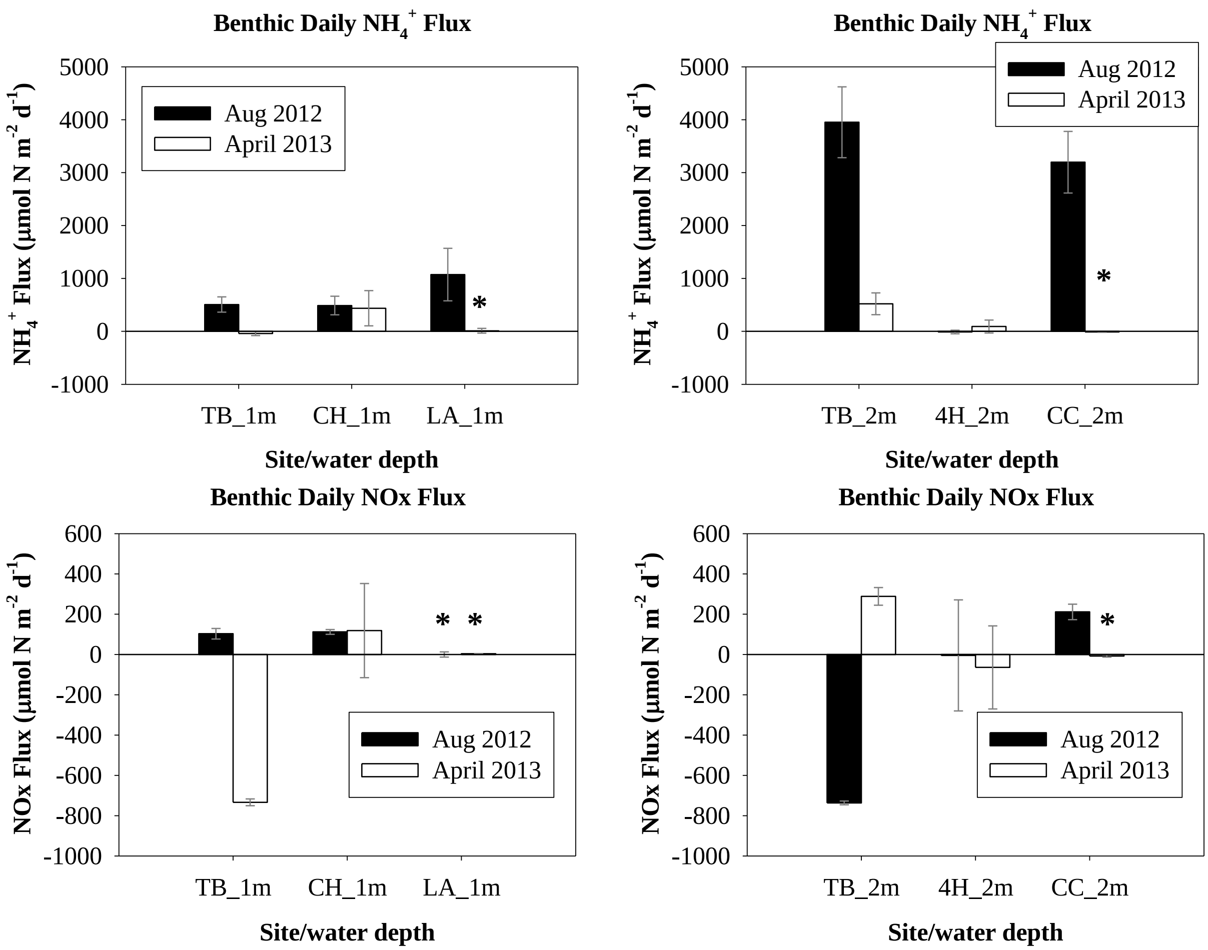

Figure 14. Benthic daily NH_4^+ and NO_x fluxes (mean ± standard error) at 1m (left) and 2m (right) sites in August 2012 and April 2013. *denote nutrient concentrations were below detection.

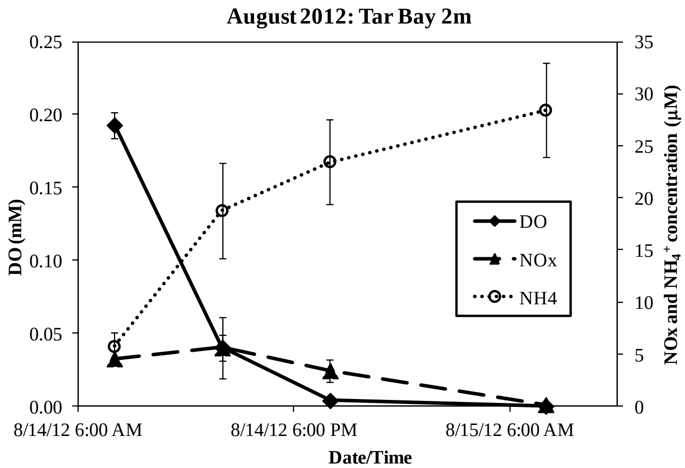

Figure 15. DO, NO_x, and NH_4^+ concentrations (mean ± standard error) in the overlying water of the sediment cores collected from Tar Bay 2m (TB_2m) during the 24-hour incubation period in August 2012.

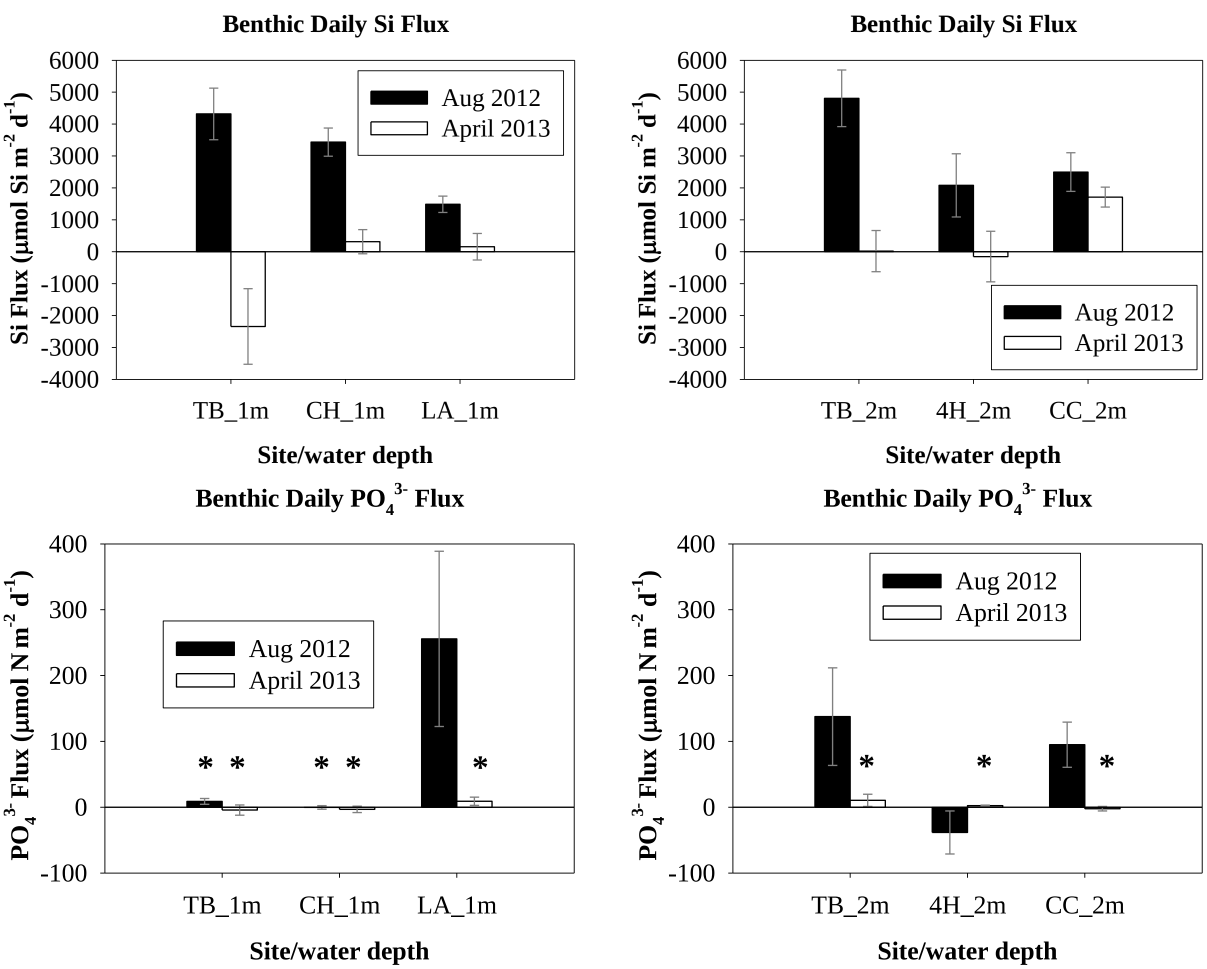

Figure 16. Benthic daily Si and PO_4^{3-} fluxes (mean ± standard error) at 1m sites in August 2012 (left) and April 2013 (right). *denote nutrient concentrations were below detection.

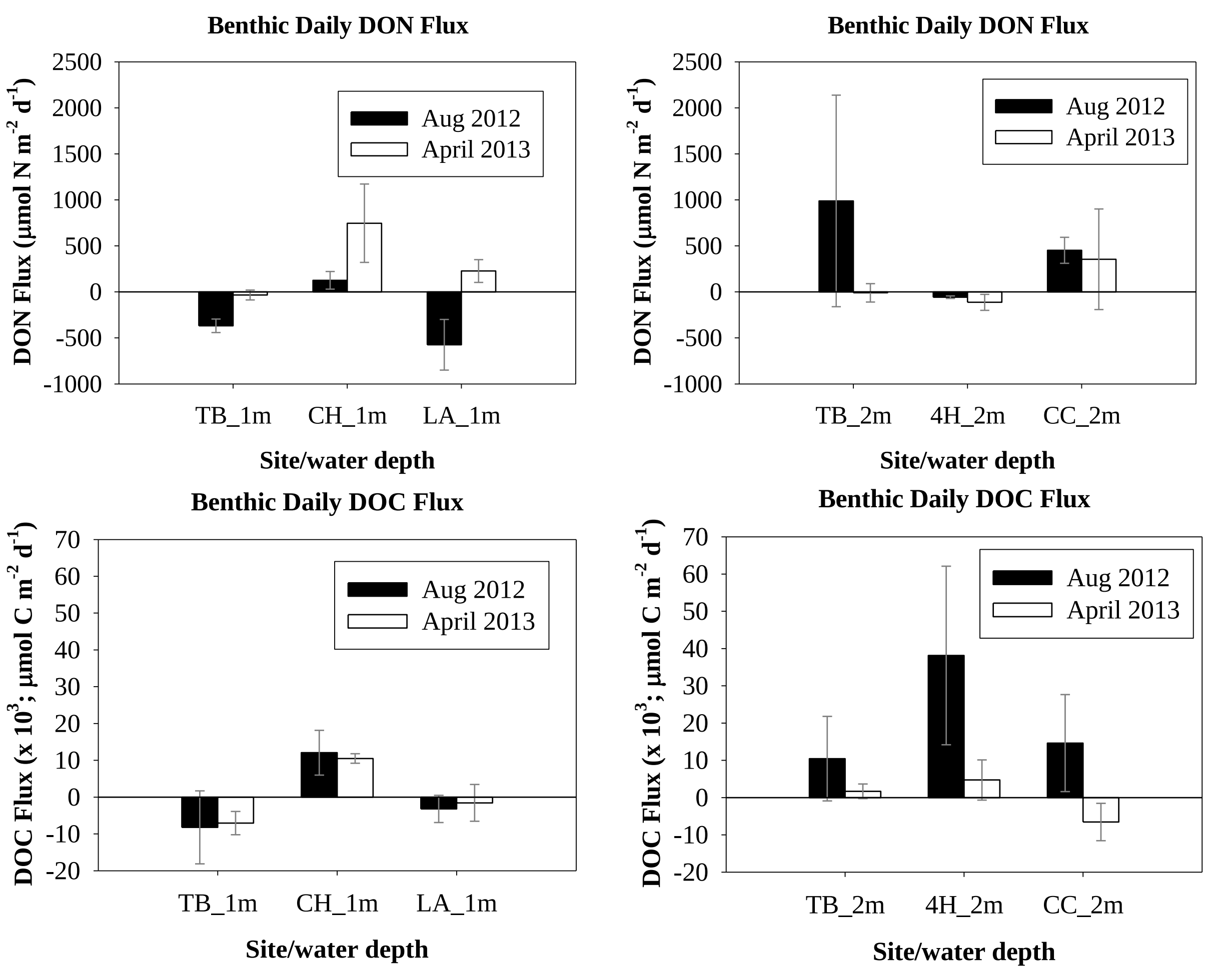

Figure 17. Benthic daily DON, and DOC fluxes (mean ± standard error) at 1m sites in August 2012 (left) and April 2013 (right). *denote nutrient concentrations were below detection.

Table 6. Summary of the two-way ANOVAs of all sites during August 2012 and April 2013 for sediment oxygen demand (SOD), benthic respiration (R), benthic gross primary production (GPP), and benthic net community production (NCP).

Parameter	n	F	df	Date p value	Site p value	Interaction p value	Date Effect	Site Effect
SOD*	36	12.05, 10.17, 5.96	1, 5, 5, 24	0.002	<0.001	0.001	TB_1m: NS	Aug: TB_2m > 4H_2m
							TB_2m: Aug > April	
							CH_1m: Aug > April	
							4H_2m: NS	April: (TB_1m, CC_2m, & LA_1m) > (TB_2m & CH_1m) > 4H_2m
							CC_2m: April > Aug	
							LA_1m: NS	
Respiration*	35	11.09, 2.25, 3.08	1, 5, 5, 23	0.003	0.084	0.029	TB_1m: Aug > April	Aug: CH_1m > 4H_2m
							TB_2m: NS	
							CH_1m: Aug > April	
							4H_2m: NS	April: NS
							CC_2m: NS	
							LA_1m: NS	
GPP*	35	6.99, 9.03, 6.15	1, 5, 5, 23	0.015	<0.001	0.001	TB_1m: NS	Aug: NS
							TB_2m: NS	
							CH_1m: Aug > April	
							4H_2m: April > Aug	April: (TB_1m, LA_1m) > 4H_2m > (TB_2m, CH_1m, & CC_2m)
							CC_2m: NS	
							LA_1m: NS	
NCP	35	63.55, 3.10, 4.19	1, 5, 5, 23	<0.001	0.028	0.008	TB_1m: Aug > April	Aug: NS
							TB_2m: Aug > April	
							CH_1m: Aug > April	
							4H_2m: NS	April: (TB_2m, CH_1m, & CC_2m) > TB_1m
							CC_2m: NS	
							LA_1m: NS	

Note: Table provides the parameter evaluated, number of samples (n), the F-statistic (date, site, interaction) and degrees of freedom (date, site, interaction, error), the probability for each of the main effects (date, site) and interactions term, the significant Tukey's pair-wise comparisons (p<0.05) for the main effects. If the interaction term is significant, one-way ANOVAs were conducted separately by: 1) site to assess seasonal differences and 2) date to assess site differences (shaded boxes) and the significant Tukey's pair-wise comparisons for the one-way ANOVAs are provided. See appendix for detailed one-way ANOVA results. *SOD was transformed as ln(x); R was transformed as ln(x+1); GPP was transformed as ln(x+2). Higher NCP indicates more heterotrophy; greater GPP indicates more autotrophy.

Table 7. Summary of the two-way ANOVAs of all sites during August 2012 and April 2013 for benthic daily fluxes of NOx, NH_4^+, PO_4^{3-}, DON (dissolved organic N), DOC (dissolved organic carbon), and Si.

Parameter	n	F	df	Date p value	Site p value	Interaction p value	Date Effect	Site Effect
Daily NOx	36	0.04, 4.14, 12.16	1, 5, 5, 24	0.851	0.007	<0.001	TB_1m: Aug > April	Aug: all sites > TB_2m
							TB_2m: April > Aug	
							CH_1m: NS	
							4H_2m: NS	April: all sites > TB_1m
							CC_2m: Aug > April	
							LA_1m: NS	
Daily NH_4^+*	36	46.44, 9.73, 6.06	1, 5, 5, 24	<0.001	<0.001	0.001	TB_1m: Aug > April	Aug: (TB_2m & CC_2m) > (TB_1m & CH_1m) > 4H_2m; LA_1m > 4H_2m
							TB_2m: Aug > April	
							CH_1m: NS	
							4H_2m: NS	April: TB_2m > TB_1m
							CC_2m: Aug > April	
							LA_1m: NS	
Daily PO_4^{3-}	36	7.76, 3.04, 2.57	1, 5, 5, 24	0.01	0.029	0.053	Aug > April	LA_1m > 4H_2m
Daily DON	36	0.19, 1.34, 1.29	1, 5, 5, 24	0.668	0.281	0.302	NS	NS
Daily DOC	34	3.17, 2.21, 1.06	1, 5, 5, 22	0.089	0.089	0.41	NS	NS
Daily Si	36	60.50, 1.90, 5.02	1, 5, 5, 24	<0.001	0.131	0.003	TB_1m: Aug > April	Aug: NS
							TB_2m: Aug > April	
							CH_1m: Aug > April	
							4H_2m: NS	April: CC_2m > TB_1m
							CC_2m: NS	
							LA_1m: NS	

Note: Table provides the parameter evaluated, number of samples (n), the F-statistic (date, site, interaction) and degrees of freedom (date, site, interaction, error), the probability for each of the main effects (date, site) and interactions term, the significant Tukey's pair-wise comparisons ($p<0.05$) for the main effects. If the interaction term is significant, one-way ANOVAs were conducted separately by: 1) site to assess seasonal differences and 2) date to assess site differences (shaded boxes) and the significant Tukey's pair-wise comparisons for the one-way ANOVAs are provided. See appendix for detailed one-way ANOVA results. *NH_4^+ flux was transformed as ln(x+150). Larger flux for pairwise comparisons indicates either greater efflux from sediment into the water column or lesser influx to sediment from the water column.

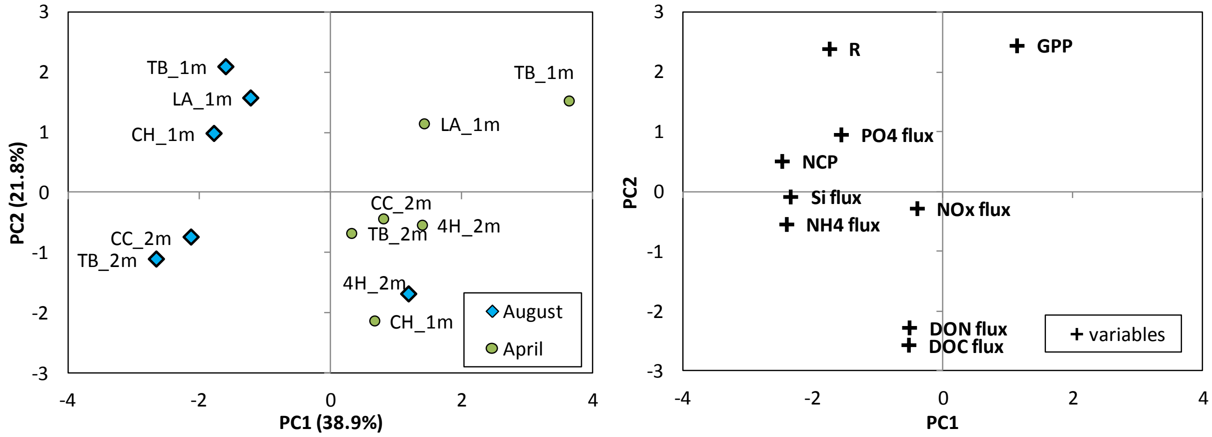

Figure 18. PCA ordination of mean benthic metabolism and daily nutrient flux rates by site and season (left) and of the coefficients for the variables (right). The coefficients for the variables are multiplied by 5 in order to plot them on a similar scale of the PC scores. The following variables were transformed as: ln(R+1), ln(NOx+800), ln(NH_4^++50), ln(PO_4^{3-}+50), and ln(DOC+900).

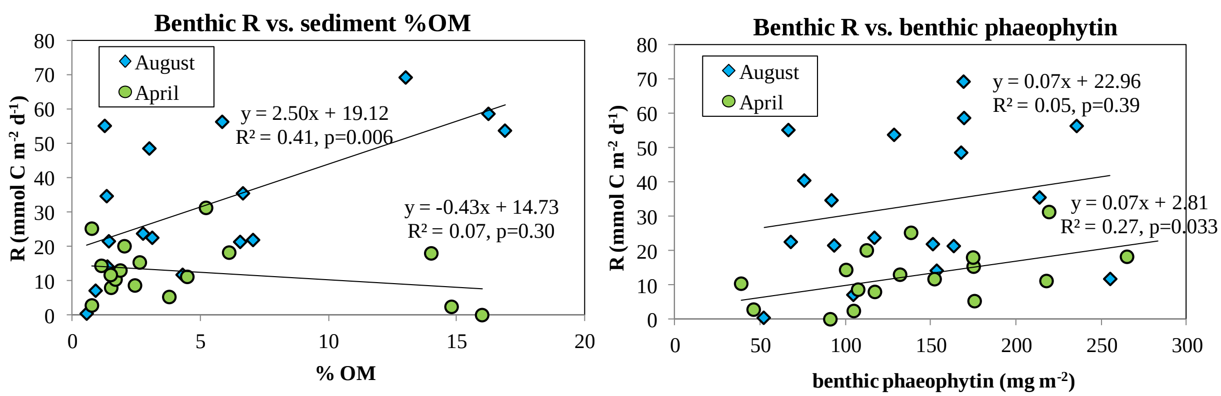

Figure 19. Benthic respiration (R) versus sediment % organic matter content (left) and benthic phaeophytin (right) for replicates of all sites in August 2012 and April 2013.

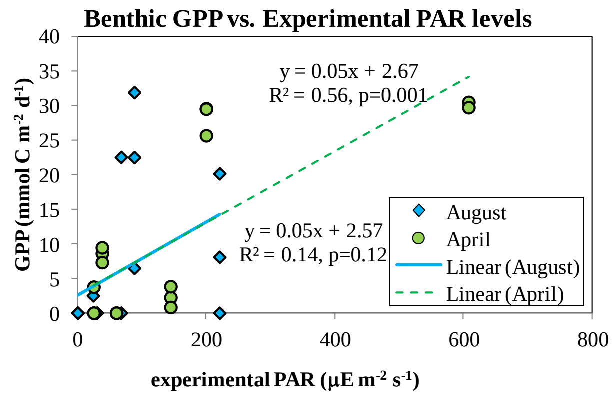

Figure 20. Benthic gross primary production (GPP) versus experimental PAR levels at the sediment surface during the light incubations for replicates of sites in August 2012 and April 2013.

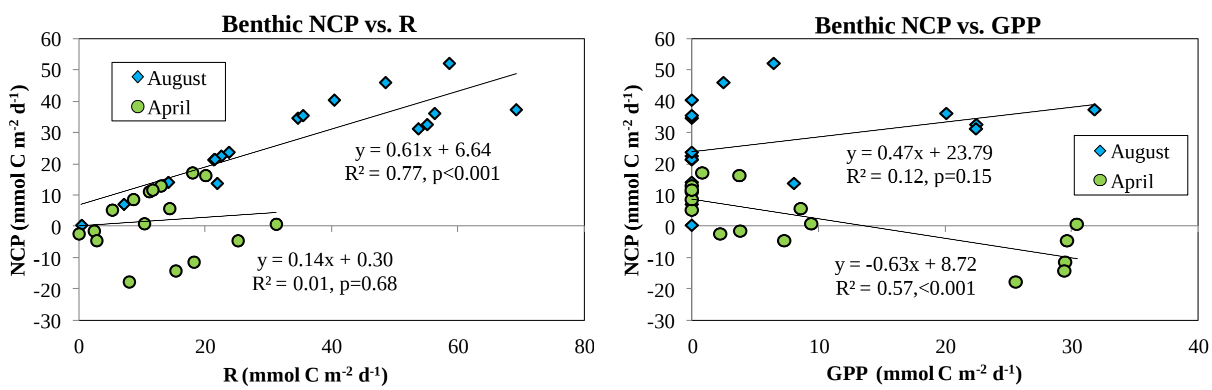

Figure 21. Benthic net community production versus respiration (R) (left) and gross primary production (right) for replicates of all sites in August 2012 and April 2013

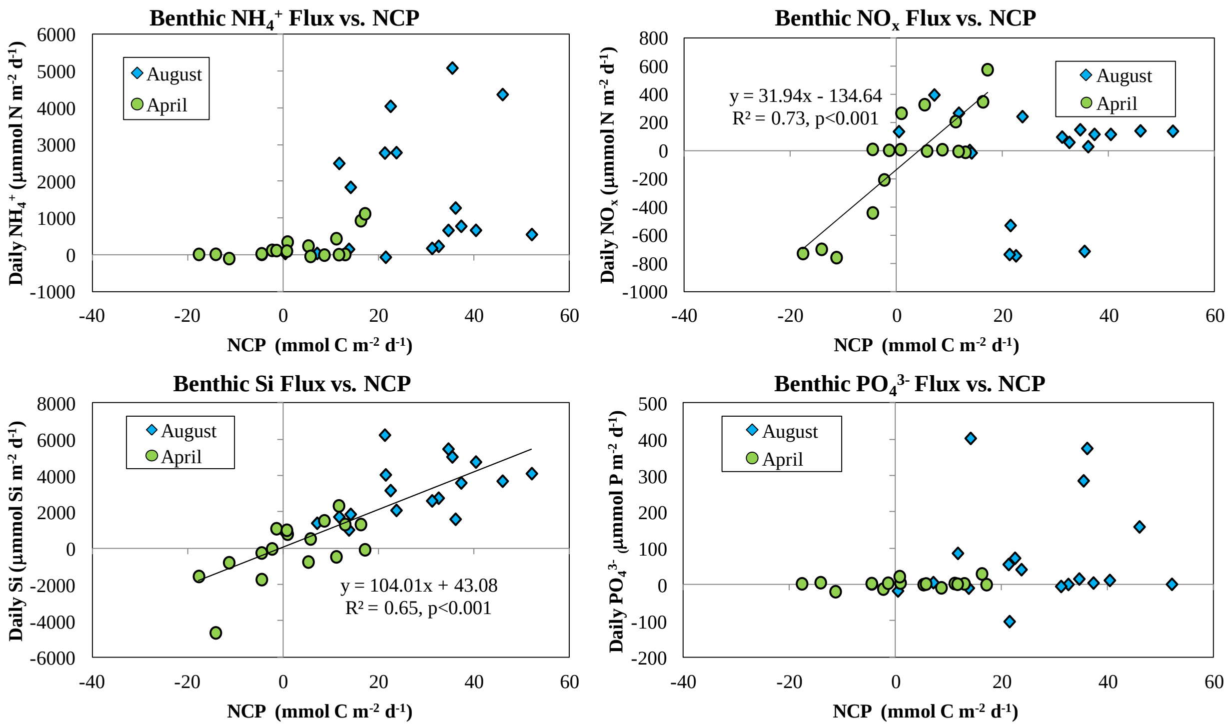

Figure 22. Benthic daily NH_4^+, NO_x, Si, and PO_4^{3-} fluxes versus and net community production (NCP) for replicates of all sites in August 2012 and April 2013. The linear regression result for daily for NOx vs. NCP includes only the April data. The linear regression for Si vs. NCP includes August and April data together.

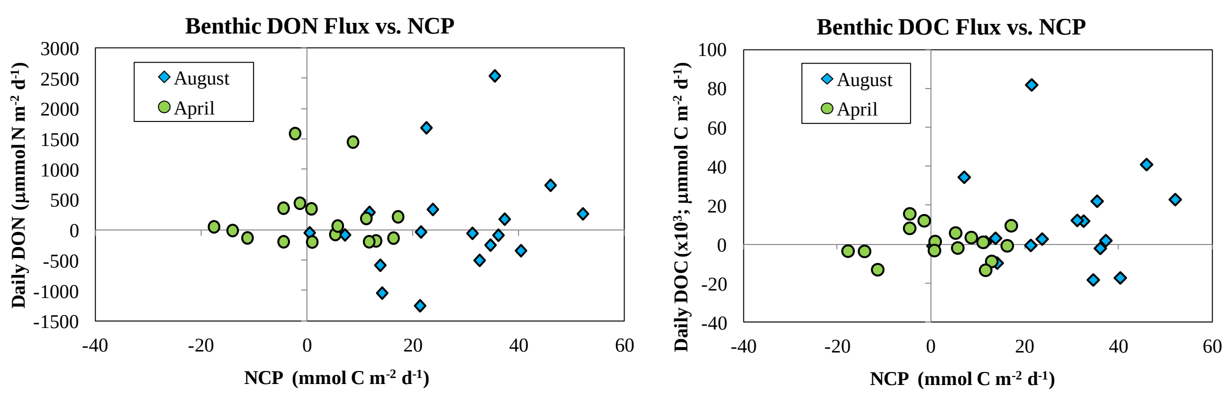

Figure 23. Benthic daily DON and DOC fluxes versus and net community production (NCP) for replicates of all sites in August 2012 and April 2013

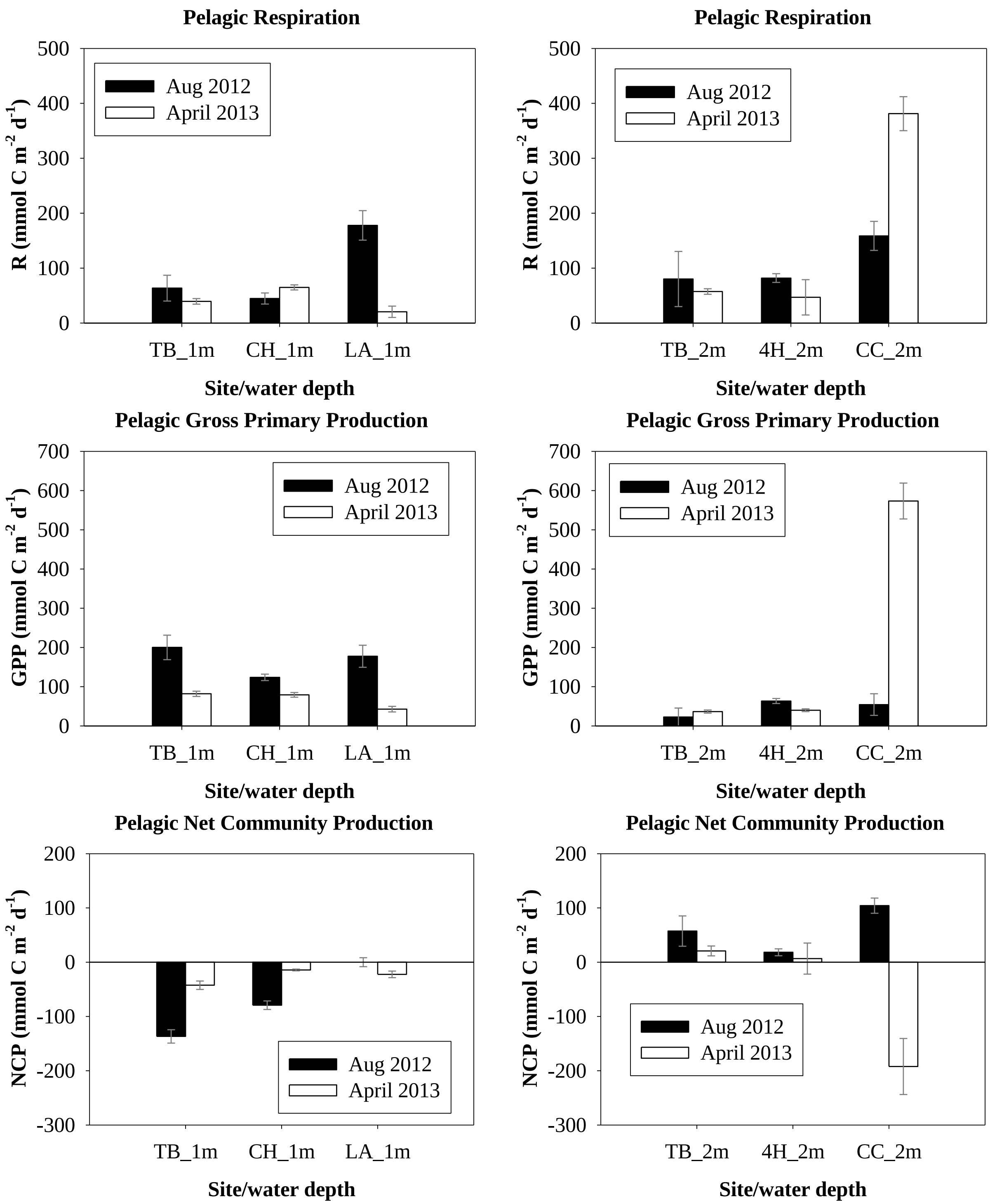

Figure 24. Pelagic respiration (R), gross primary production, and net community production (mean ± standard error) at 1m (left) and 2m (right) sites in August 2012 and April 2013.

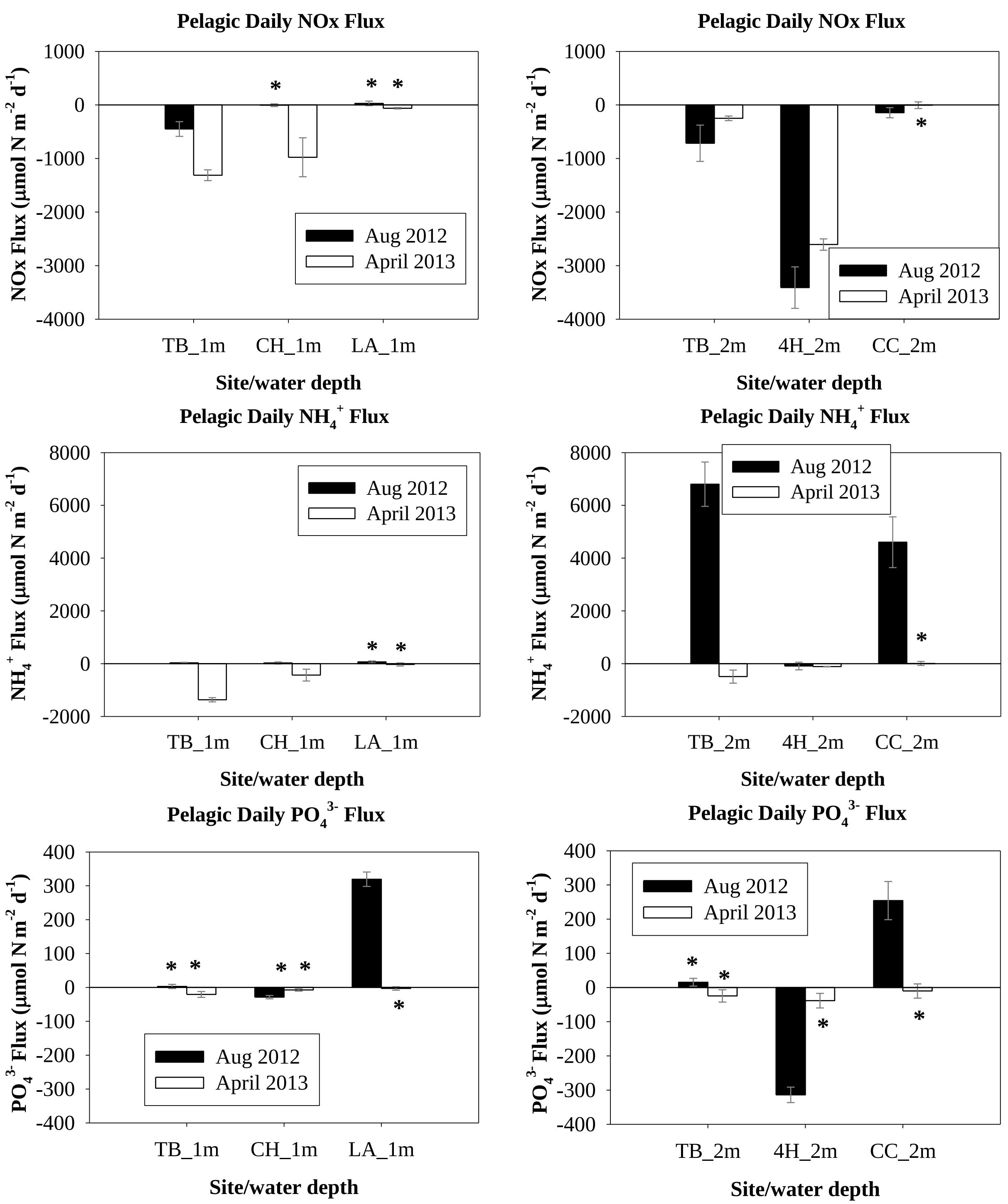

Figure 25. Pelagic daily NH_4^+, NO_x, and PO_4^{3-} fluxes (mean ± standard error) at 1m (left) and 2m (right) sites in August 2012 and April 2013. *denote nutrient concentrations were below detection.

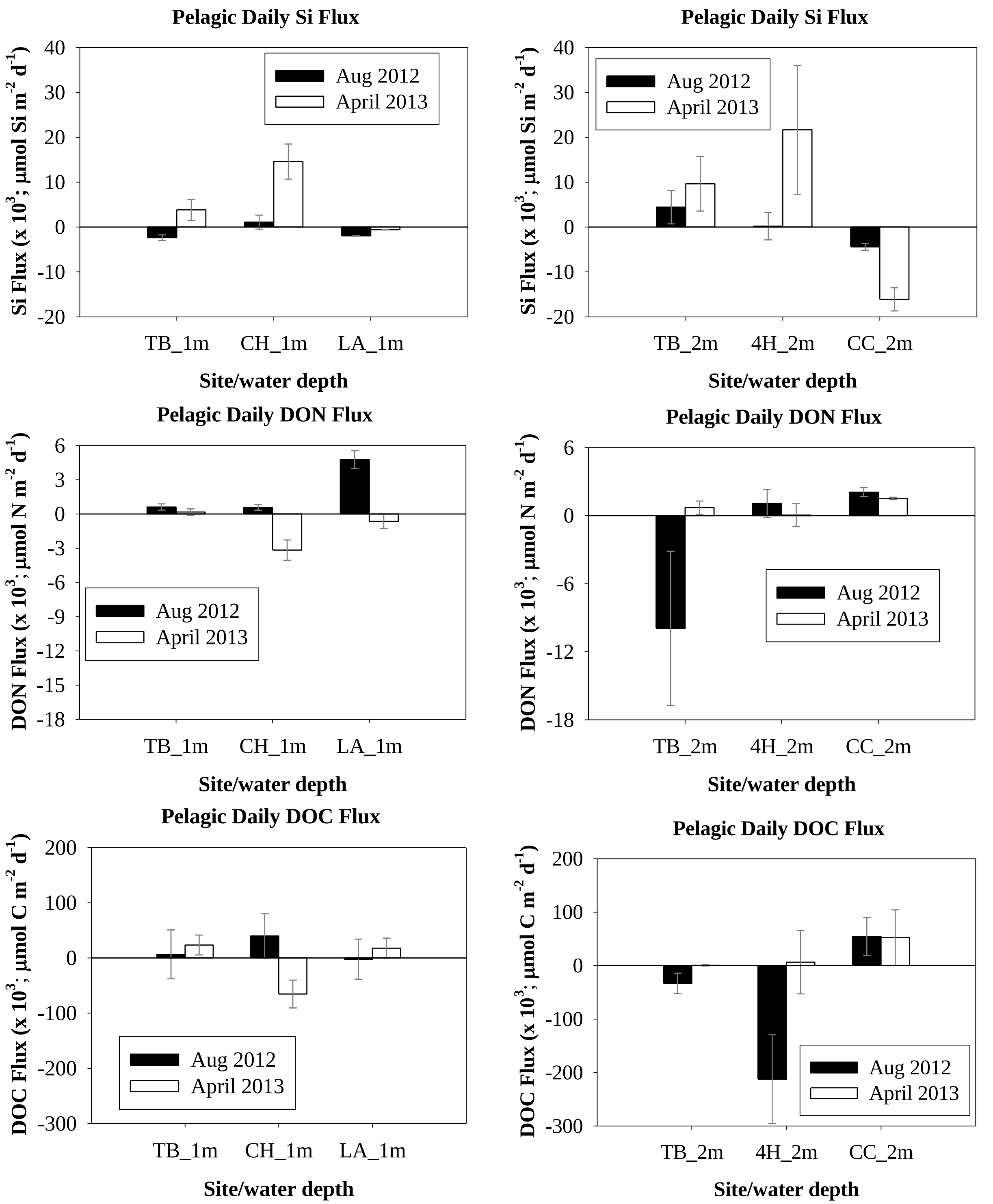

Figure 26. Pelagic daily Si, DON, and DOC fluxes (mean ± standard error) at 1m (left) and 2m (right) sites in August 2012 and April 2013. *denote nutrient concentrations were below detection.

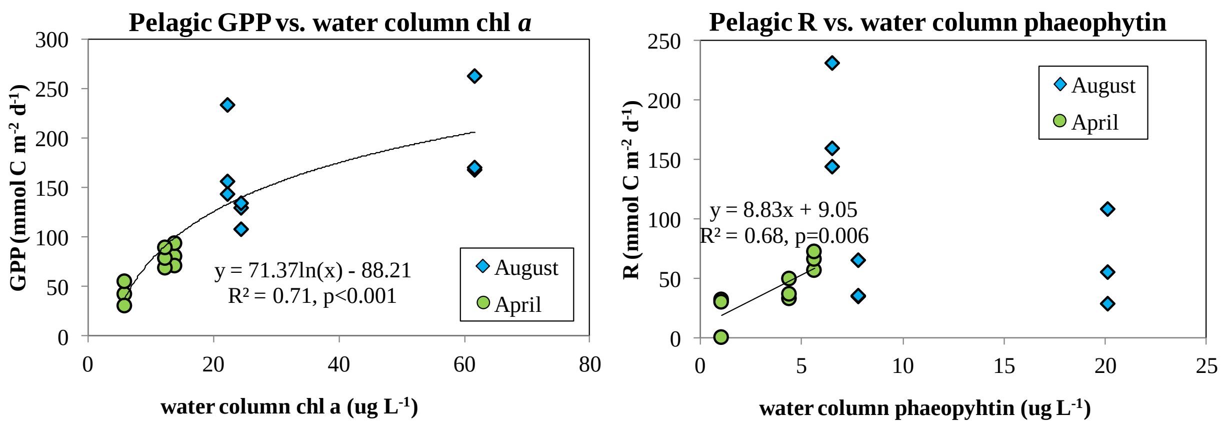

Figure 27. Pelagic gross primary production (GPP) versus water column chlorophyll *a* (left) and respiration (R) versus water column phaeophytin (right) for replicates of 1-m sites in August 2012 and April 2013. The natural log-linear regression result for GPP vs. water column chl a includes August and April data together, while the regression for R vs. water column phaeophytin includes only the April data.

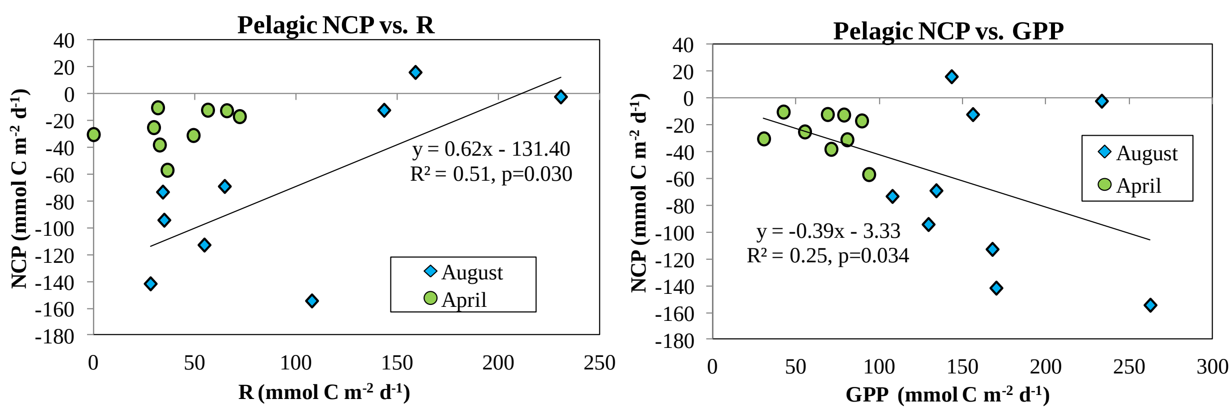

Figure 28. Pelagic net community production versus respiration (R) (left) and gross primary production (GPP) (right) for replicates for 1-m sites in August 2012 and April 2013. The linear regression result for NCP vs. R includes only the August data. The linear regression for NCP vs. GPP includes August and April data together.

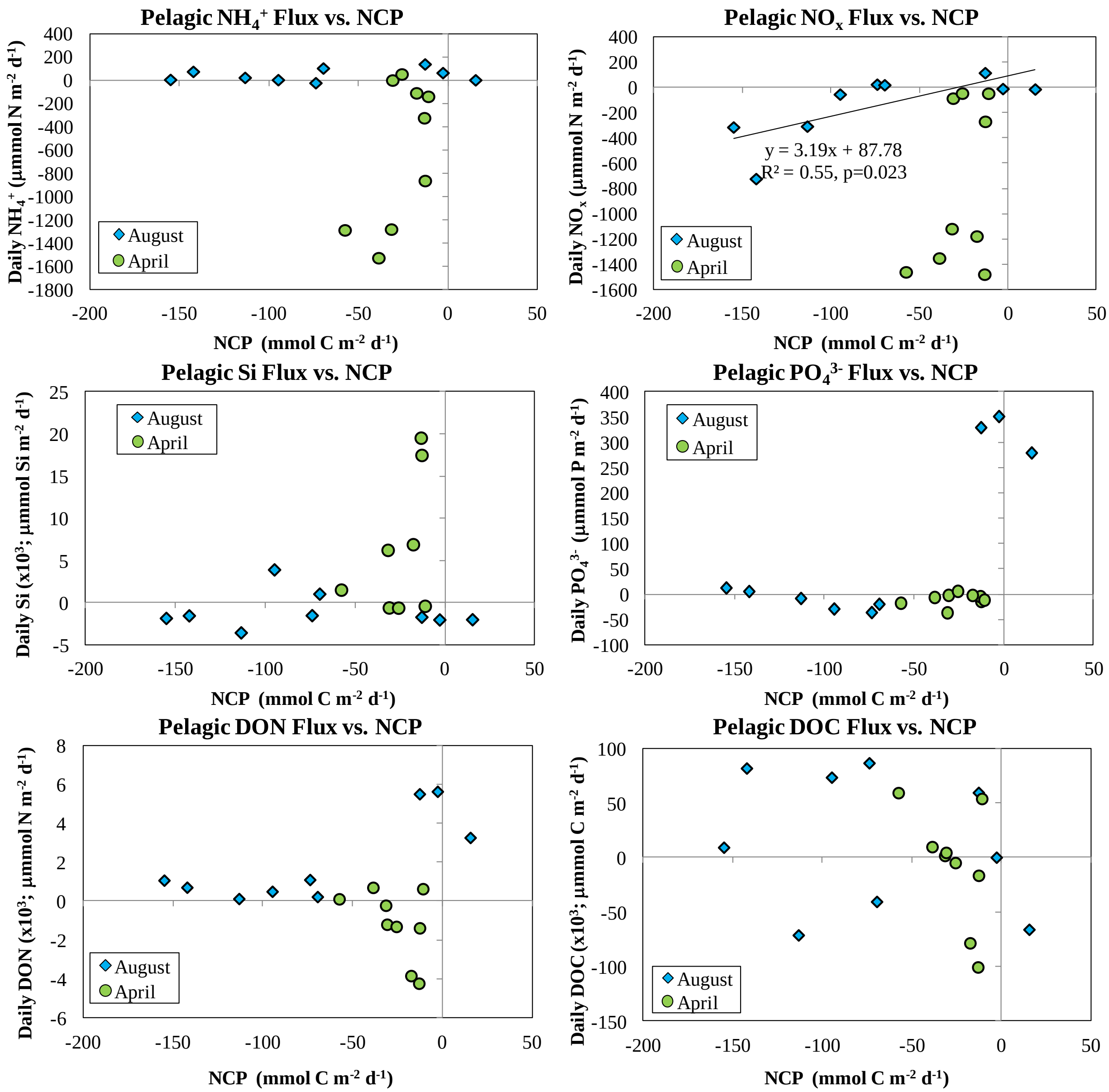

Figure 29. Pelagic daily NH_4^+, NO_x, Si, PO_4^{3-}, DON, and DOC fluxes versus pelagic net community production (NCP) for replicates for 1-m sites in August 2012 and April 2013. The linear regression result for daily for NOx vs. NCP includes only the August data.

Table 8. Summary of the two-way ANOVAs of all sites during August 2012 and April 2013 for pelagic respiration (R), gross primary production (GPP), and net community production (NCP).

Parameter	n	F	df	Date p value	Site p value	Interaction p value	Date Effect	Site Effect
Respiration*	34	2.66, 4.13, 4.27	1, 5, 5, 22	0.117	0.008	0.007	TB_1m: NS TB_2m: NS CH_1m: NS	Aug: NS
							4H_2m: NS CC_2m: Apr > Aug LA_1m: NS	April: CC_2m > LA_1m
GPP	34	7.02, 39.26, 60.40	1, 5, 5, 22	0.015	<0.001	<0.001	TB_1m: Aug > Apr TB_2m: NS CH_1m: Aug > Apr	Aug: (TB_1m & LA_1m) > (TB_2m, 4H_2m, & CC_2m)
							4H_2m: NS CC_2m: Apr > Aug LA_1m: Aug > Apr	April: CC_2m > all sites
NCP	34	8.38, 9.67, 24.08	1, 5, 5, 22	0.008	<0.001	<0.001	TB_1m: Apr > Aug TB_2m: NS CH_1m: Apr > Aug	Aug: CC_2m > (4H_2m & LA_1m) > (TB_1m & CH_1m); TB_2m > (TB_1m & CH_1m)
							4H_2m: NS CC_2m: Aug > Apr LA_1m: NS	April: all sites > CC_2m

Note: Table provides the parameter evaluated, number of samples (n), the F-statistic (date, site, interaction) and degrees of freedom (date, site, interaction, error), the probability for each of the main effects (date, site) and interactions term, the significant Tukey's pair-wise comparisons ($p<0.05$) for the main effects. If the interaction term is significant, one-way ANOVAs were conducted separately by: 1) site to assess seasonal differences and 2) date to assess site differences (shaded boxes) and the significant Tukey's pair-wise comparisons for the one-way ANOVAs are provided. See appendix for detailed one-way ANOVA results. R was transformed as ln(x+1). Higher NCP indicates more heterotrophy; greater GPP indicates more autotrophy.

Table 9. Summary of the two-way ANOVAs of all sites during August 2012 and April 2013 for pelagic daily fluxes of NOx, NH_4^+, PO_4^{3-}, DON (dissolved organic N), DOC (dissolved organic carbon), and Si.

Parameter	n	F	df	Date p value	Site p value	Interaction p value	Date Effect	Site Effect
Daily NOx	36	0.59, 65.66, 6.69	1, 5, 5, 24	0.452	<0.001	<0.001	TB_1m: Aug > Apr	Aug: all sites > 4H_2m
							Rest of sites: NS	April: all sites > 4H_2m; (CC_2m & LA_1m) > (CH_1m & TB_1); TB_2m > TB_1m
Daily NH_4^+	36	107.86, 33.35, 29.91	1, 5, 5, 24	<0.001	<0.001	<0.001	TB_1m: Aug > Apr	Aug: (TB_2m & CC_2m) > (TB_1m, CH_1m, 4H_2m, & LA_1m)
							TB_2m: Aug > Apr	
							CH_1m: NS	
							4H_2m: NS	April: all sites > TB_1m
							CC_2m: Aug > Apr	
							LA_1m: NS	
Daily PO_4^{3-}	36	22.39, 60.67, 49.78	1, 5, 5, 24	<0.001	<0.001	<0.001	TB_1m: NS	Aug: (CC_2m & LA_1m) > (TB_1m, TB_2m, & CH_1m) > 4H_2m
							TB_2m: NS	
							CH_1m: Apr > Aug	
							4H_2m: Apr > Aug	April: NS
							CC_2m: Aug > Apr	
							LA_1m: Aug > Apr	
Daily DON	36	0.01, 2.88, 3.70	1, 5, 5, 24	0.939	0.36	0.013	TB_1m: NS	Aug: LA_1m > TB_2m
							TB_2m: NS	
							CH_1m: Aug > Apr	
							4H_2m: NS	April: (TB_1m, TB_2m, 4H_2m, CC_2m) > CH_1m
							CC_2m: NS	
							LA_1m: Aug > Apr	
Daily DOC	36	1.58, 3.13, 3.17	1, 5, 5, 24	0.22	0.026	0.025	All sites: NS	Aug: (CH_1m & CC_2m) > 4H_2m
								April: NS
Daily Si	35	4.07, 4.70, 2.47	1, 5, 5, 23	0.055	0.004	0.063	NS	(CH_1m, 4H_2m, & TB_2m) > CC_2m

Note: Table provides the parameter evaluated, number of samples (n), the F-statistic (date, site, interaction) and degrees of freedom (date, site, interaction, error), the probability for each of the main effects (date, site) and interactions term, the significant Tukey's pair-wise comparisons ($p<0.05$) for the main effects. If the interaction term is significant, one-way ANOVAs were conducted separately by: 1) site to assess seasonal differences and 2) date to assess site differences (shaded boxes) and the significant Tukey's pair-wise comparisons for the one-way ANOVAs are provided. See appendix for detailed one-way ANOVA results. Larger flux for pairwise comparisons indicates either greater efflux from sediment into the water column or lesser influx to sediment from the water column.

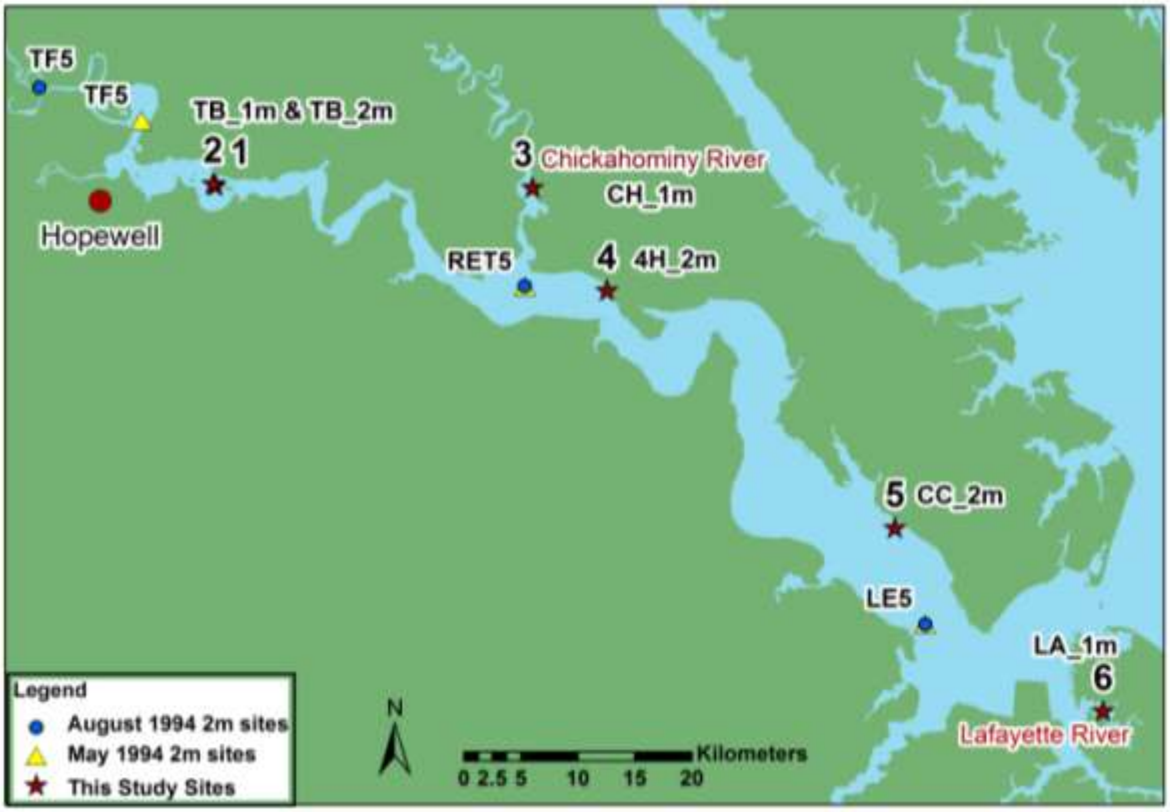

Figure 30. Locations of the August and May 1994 2m study sties (Meyers, 1995) relative to this study's sites.

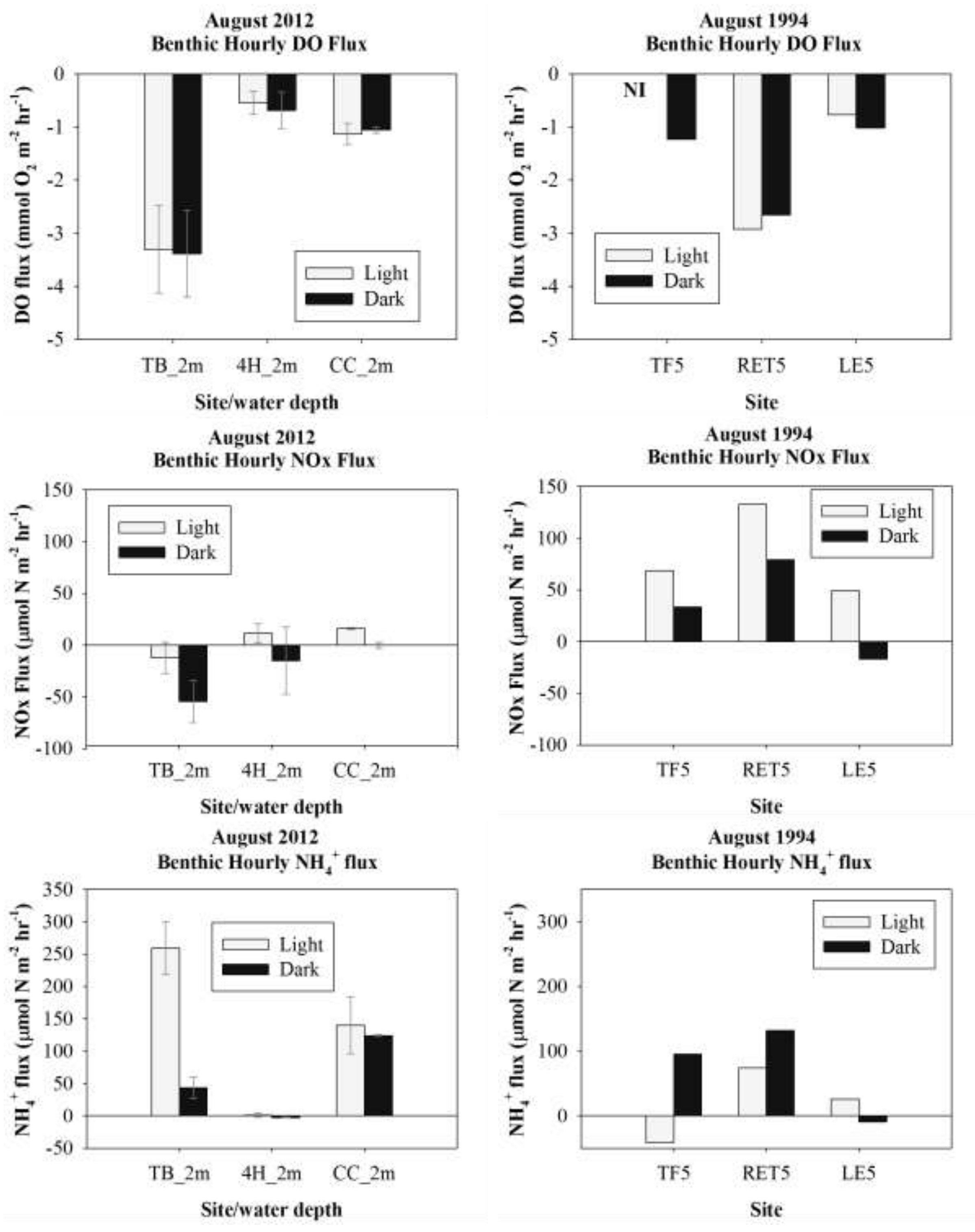

Figure 31. Benthic hourly light and dark DO, NO_x, and NH_4^+ fluxes (mean ± standard error; SE data not available for 1994) at 2m sites in August 2012 (left) and August 1994 (right; data from Meyer, 1995). NI=not-interpretable.

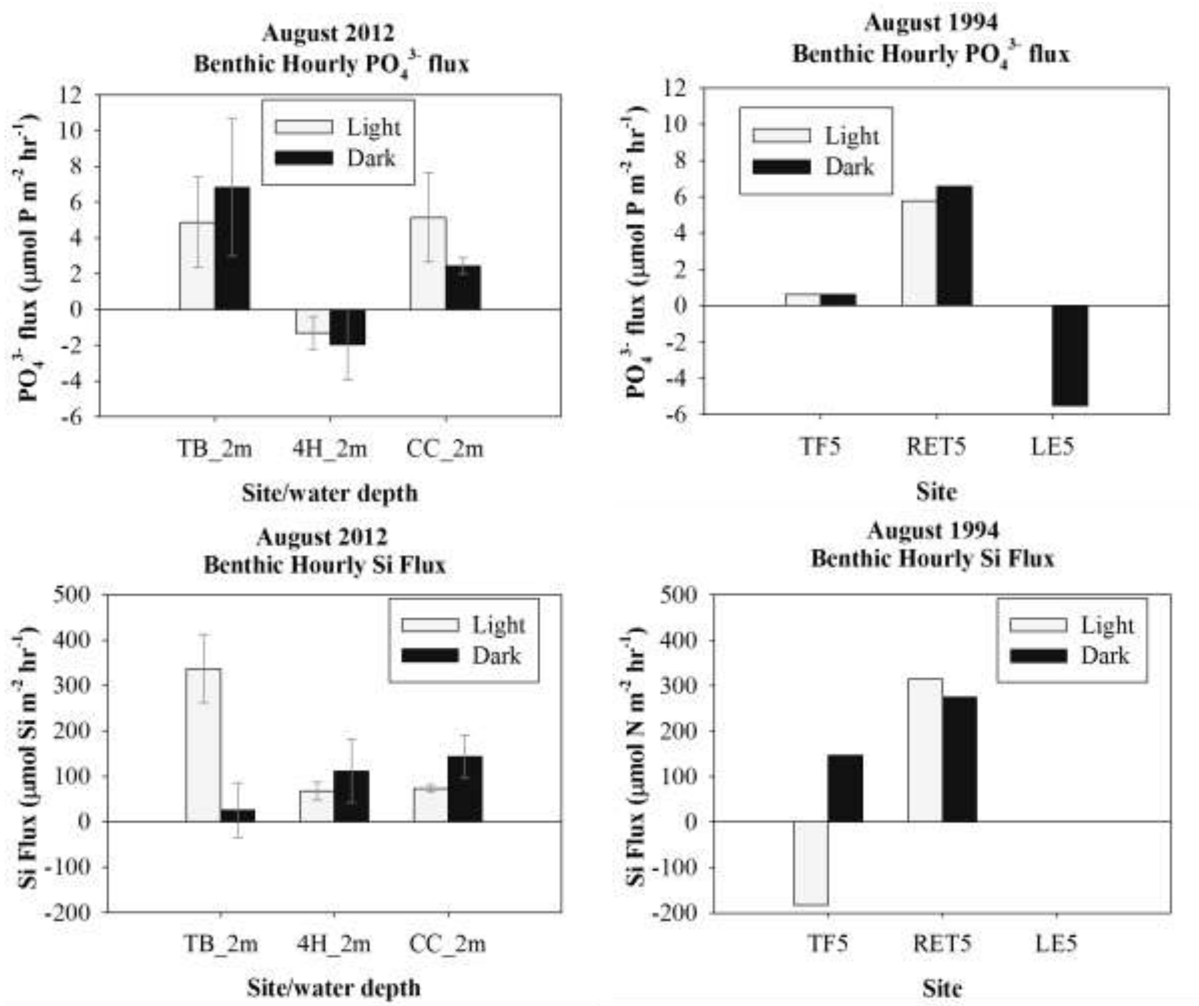

Figure 32. Benthic hourly light and dark PO_4^{3-} and Si fluxes (mean ± standard error; SE data not available for 1994) at 2m sites in August 2012 (left) and August 1994 (right; data from Meyer, 1995).

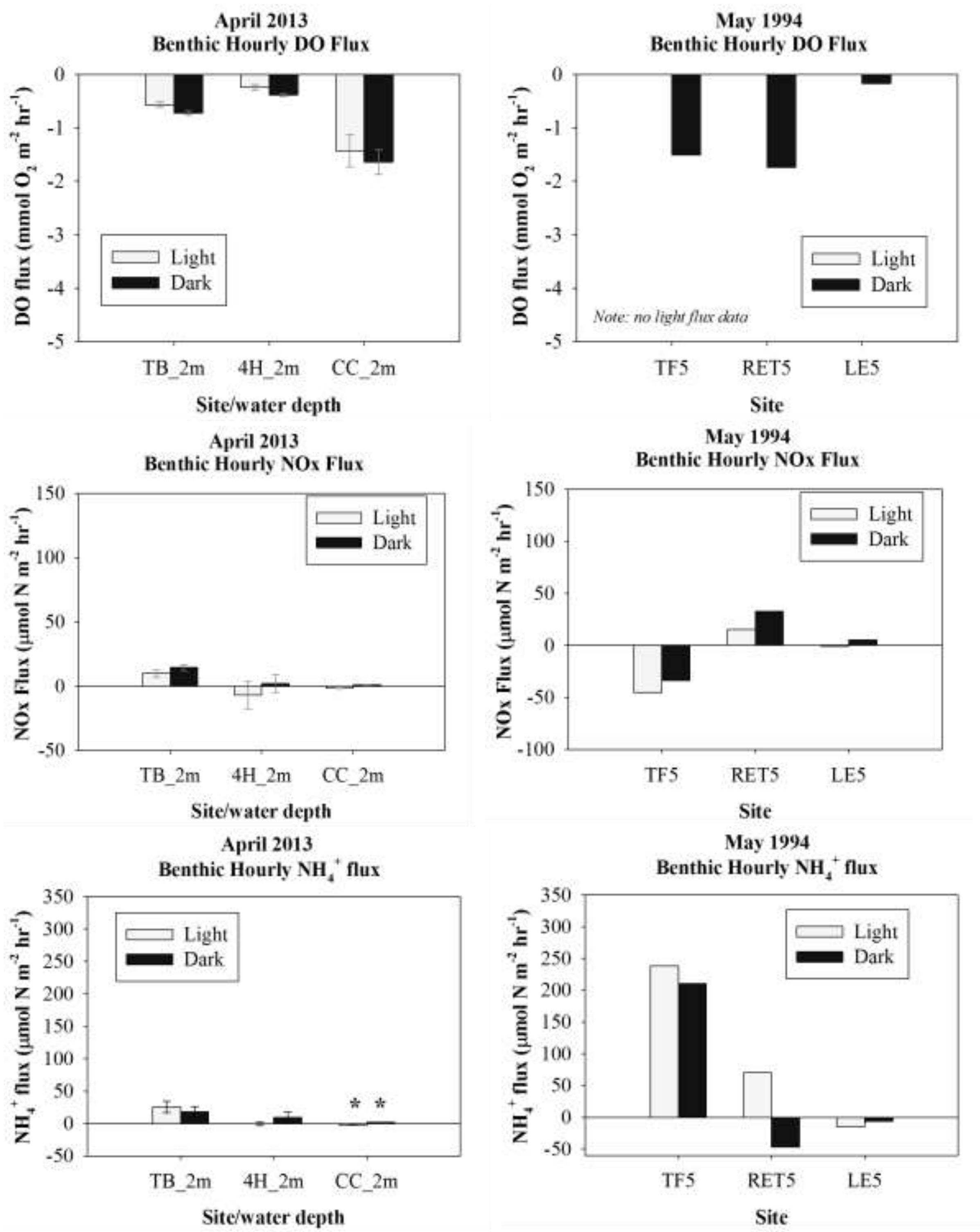

Figure 33. Benthic hourly light and dark DO, NO_x, and NH_4^+ fluxes (mean ± standard error; SE data not available for 1994) at 2m sites in April 2012 (left) and May 1994 (right; data from Meyer, 1995). *denote nutrient concentrations were below detection.

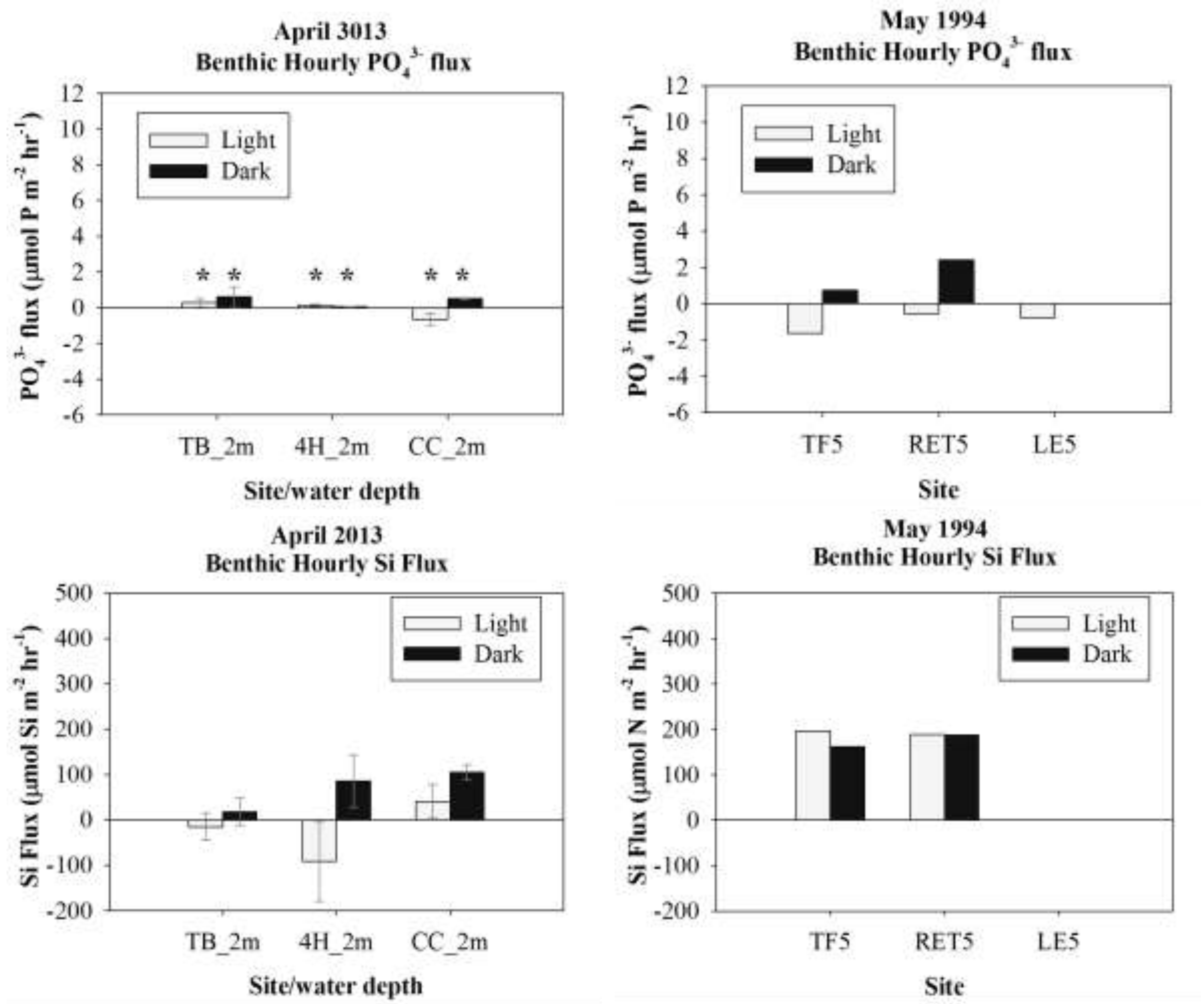

Figure 34. Benthic hourly light and dark PO_4^{3-} and Si fluxes (mean ± standard error; SE data not available for 1994) at 2m sites in April 2012 (left) and May 1994 (right; data from Meyer, 1995). *denote nutrient concentrations were below detection.

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Appendix

Table A1. Date and location of each replicate sediment core collected for each site

Site#-replicate#	Site abbreviation	Date collected	Latitude (DD)	Longitude (DD)
1-1	TB_1m	8/13/2012	37.30583	-77.18508
1-2	TB_1m	8/13/2012	37.30575	-77.18472
1-3	TB_1m	8/13/2012	37.30572	-77.18444
2-1	TB_2m	8/13/2012	37.30733	-77.18828
2-2	TB_2m	8/13/2012	37.30692	-77.18706
2-3	TB_2m	8/13/2012	37.30625	-77.18492
3-1	CH_1m	8/20/2012	37.31061	-76.86958
3-2	CH_1m	8/20/2012	37.30950	-76.87067
3-3	CH_1m	8/20/2012	37.30883	-76.87089
4-1	4H_2m	8/20/2012	37.22906	-76.79528
4-2	4H_2m	8/20/2012	37.22694	-76.79175
4-3	4H_2m	8/20/2012	37.22547	-76.79117
5-1	CC_2m	8/15/2012	not reported	not reported
5-2	CC_2m	8/15/2012	37.04481	-76.50661
5-3	CC_2m	8/15/2012	37.04481	-76.50661
6-1	LA_1m	8/15/2012	36.90308	-76.30008
6-2	LA_1m	8/15/2012	36.90214	-76.29883
6-3	LA_1m	8/15/2012	36.90214	-76.29886
1-1	TB_1m	4/9/2013	37.30650	-77.18656
1-2	TB_1m	4/9/2013	37.30581	-77.18456
1-3	TB_1m	4/9/2013	37.30556	-77.18403
2-1	TB_2m	4/9/2013	37.30578	-77.18300
2-2	TB_2m	4/9/2013	37.30558	-77.18258
2-3	TB_2m	4/9/2013	37.30519	-77.18017
3-1	CH_1m	4/1/2013	37.31097	-76.86956
3-2	CH_1m	4/1/2013	37.31200	-76.86744
3-3	CH_1m	4/1/2013	37.30867	-76.86883
4-1	4H_2m	4/1/2013	37.22894	-76.79536
4-2	4H_2m	4/1/2013	37.22728	-76.79372
4-3	4H_2m	4/1/2013	37.22550	-76.79133
5-1	CC_2m	4/3/2013	37.04506	-76.50694
5-2	CC_2m	4/3/2013	37.04461	-76.50539
5-3	CC_2m	4/3/2013	37.04458	-76.50533
6-1	LA_1m	4/3/2013	36.90192	-76.29864
6-2	LA_1m	4/3/2013	36.90194	-76.29750
6-3	LA_1m	4/3/2013	36.90181	-76.29697

Table A2. Mean (standard error [SE]) benthic light and dark dissolved oxygen (DO) fluxes and sediment oxygen demand (SOD) by site and date.

Site abbreviation	Date	light DO flux	SE	dark DO flux	SE	SOD	SE
		mmol O_2 m^{-2} h^{-1}				mmol O_2 m^{-2} d^{-1}	
TB_1m	August 2012	-2.95	0.77	-1.72	0.32	41.17	7.65
TB_2m	August 2012	-3.30	0.82	-3.38	0.82	81.22	19.69
CH_1m	August 2012	-0.57	0.24	-1.57	0.02	37.76	0.40
4H_2m	August 2012	-0.54	0.22	-0.68	0.34	16.42	8.16
CC_2m	August 2012	-1.13	0.20	-1.06	0.05	25.34	1.31
LA_1m	August 2012	-1.33	0.89	-1.15	0.30	27.68	7.27
TB_1m	April 2013	1.63	0.04	-1.31	0.10	31.33	2.29
TB_2m	April 2013	-0.57	0.05	-0.72	0.04	17.40	1.05
CH_1m	April 2013	-0.29	0.10	-0.69	0.06	16.60	1.37
4H_2m	April 2013	-0.24	0.05	-0.38	0.03	9.19	0.64
CC_2m	April 2013	-1.43	0.30	-1.64	0.23	39.40	5.56
LA_1m	April 2013	0.38	0.13	-1.17	0.06	28.11	1.46

Table A3. Mean (standard error [SE]) benthic light and dark dissolved inorganic carbon (DIC) fluxes, respiration, net community production (NCP), and gross primary production (GPP) by site and date.

Site abbreviation	Date	light DIC flux	SE	dark DIC flux	SE	Respiration	SE	NCP	SE	GPP	SE
		mmol C m^{-2} h^{-1}				mmol O_2 m^{-2} d^{-1}					
TB_1m	August 2012	2.03	0.73	1.81	0.25	43.37	6.09	35.87	2.34	7.51	7.51
TB_2m	August 2012	2.52	0.19	1.10	0.19	26.43	4.53	26.43	4.53	0.00	0.00
CH_1m	August 2012	1.02	0.47	2.52	0.19	60.49	4.57	40.22	6.21	20.28	7.41
4H_2m	August 2012	0.77	0.19	0.40	0.26	9.68	6.21	9.68	6.21	0.00	0.00
CC_2m	August 2012	1.77	0.43	1.17	0.45	27.99	10.83	27.16	10.04	0.84	0.84
LA_1m	August 2012	1.59	1.01	1.28	0.54	30.76	12.95	21.35	7.39	9.41	5.85
TB_1m	April 2013	-1.68	0.04	0.58	0.13	13.82	3.05	-14.39	1.83	28.21	1.29
TB_2m	April 2013	0.69	0.08	0.51	0.18	12.15	4.30	10.90	3.18	1.26	1.26
CH_1m	April 2013	0.10	0.29	0.28	0.24	6.76	5.65	4.46	6.35	2.30	0.87
4H_2m	April 2013	-0.29	0.11	0.38	0.14	9.17	3.38	0.71	2.96	8.46	0.62
CC_2m	April 2013	1.76	0.22	0.46	0.05	11.09	1.29	11.09	1.29	0.00	0.00
LA_1m	April 2013	-0.95	0.28	1.17	0.13	28.19	3.03	-1.88	2.64	30.07	0.39

Table A3. Mean (standard error [SE]) benthic light and dark NOx fluxes and daily NOx flux by site and date.

Site abbreviation	Date	light NOx flux	SE	dark NOx flux	SE	Daily NOx flux	SE
		μmol N m^{-2} h^{-1}				μmol N m^{-2} d^{-1}	
TB_1m	August 2012	9.73	7.45	-2.67	9.59	103.30	26.13
TB_2m	August 2012	-12.34	15.21	-54.31	20.19	-736.75	9.32
CH_1m	August 2012	BD		12.01	1.24	112.31	11.99
4H_2m	August 2012	11.39	9.40	-15.07	32.60	-4.51	275.74
CC_2m	August 2012	15.78	1.15	-0.14	2.89	211.51	38.45
LA_1m	August 2012	BD		BD		BD	
TB_1m	April 2013	-30.34	2.23	-30.82	1.16	-733.76	16.97
TB_2m	April 2013	9.79	2.58	14.46	2.21	288.68	43.80
CH_1m	April 2013	-2.65	9.86	13.20	10.17	118.72	233.62
4H_2m	April 2013	-7.04	10.50	2.09	6.77	-63.98	206.12
CC_2m	April 2013	-1.66	0.25	1.14	0.32	BD	
LA_1m	April 2013	BD		BD		BD	

BD=below detection.

Table A4. Mean (standard error [SE]) benthic light and dark NH_4^+ fluxes and daily NH_4^+ flux by site and date.

Site abbreviation	Date	light NH_4^+ flux	SE	dark NH_4^+ flux	SE	Daily NH_4^+ flux	SE
		μmol N m^{-2} h^{-1}				μmol N m^{-2} d^{-1}	
TB_1m	August 2012	7.00	4.33	39.29	9.65	507.10	144.40
TB_2m	August 2012	259.23	40.77	43.18	16.17	3952.96	669.21
CH_1m	August 2012	-2.74	1.84	49.96	14.72	487.56	175.47
4H_2m	August 2012	1.07	2.96	-2.50	0.53	-11.78	34.37
CC_2m	August 2012	140.27	43.99	124.17	1.79	3197.53	582.49
LA_1m	August 2012	47.06	36.00	41.73	20.54	1073.43	496.24
TB_1m	April 2013	-6.90	4.13	4.04	1.33	-39.78	38.41
TB_2m	April 2013	25.30	8.89	17.82	8.15	521.25	204.85
CH_1m	April 2013	31.47	12.87	3.80	14.94	437.09	332.73
4H_2m	April 2013	-0.72	2.54	8.78	8.34	91.94	121.69
CC_2m	April 2013	BD		BD		BD	
LA_1m	April 2013	BD		BD		BD	

BD=below detection.

Table A5. Mean (standard error [SE]) benthic light and dark PO_4^{3-} fluxes and daily PO_4^{3-} flux by site and date.

Site abbreviation	Date	light PO_4^{3-} flux	SE	dark PO_4^{3-} flux	SE	Daily PO_4^{3-} flux	SE
		µmol P m^{-2} h^{-1}				µmol P m^{-2} d^{-1}	
TB_1m	August 2012	BD		0.78	0.45	8.77	4.48
TB_2m	August 2012	4.89	2.52	6.82	3.84	137.60	74.11
CH_1m	August 2012	BD		BD		BD	
4H_2m	August 2012	-1.31	0.90	-1.97	1.96	-38.31	32.65
CC_2m	August 2012	5.15	2.49	2.43	0.45	95.01	34.30
LA_1m	August 2012	18.34	8.95	0.76	1.87	255.64	133.09
TB_1m	April 2013	BD		BD		BD	
TB_2m	April 2013	BD		BD		BD	
CH_1m	April 2013	BD		BD		BD	
4H_2m	April 2013	BD		BD		BD	
CC_2m	April 2013	BD		BD		BD	
LA_1m	April 2013	BD		BD		BD	

BD=below detection.

Table A6. Mean (standard error [SE]) benthic light and dark dissolved organic nitrogen (DON) fluxes and daily DON flux by site and date.

Site abbreviation	Date	light DON flux	SE	dark DON flux	SE	Daily DON flux	SE
		µmol N m^{-2} h^{-1}				µmol N m^{-2} d^{-1}	
TB_1m	August 2012	-10.23	28.06	-21.94	31.59	-368.51	73.51
TB_2m	August 2012	15.30	74.36	74.52	19.54	989.00	1149.28
CH_1m	August 2012	6.15	3.42	4.07	4.77	125.68	95.90
4H_2m	August 2012	3.27	5.85	-9.71	7.55	-57.79	14.38
CC_2m	August 2012	22.40	9.58	14.24	5.87	451.99	141.61
LA_1m	August 2012	-16.97	16.23	-32.88	6.58	-574.36	275.76
TB_1m	April 2013	-8.55	5.53	6.39	1.39	-33.41	53.75
TB_2m	April 2013	-5.98	5.67	5.65	2.70	-9.85	99.69
CH_1m	April 2013	102.90	103.64	-46.98	131.16	745.98	425.66
4H_2m	April 2013	-17.38	6.98	9.05	7.43	-113.21	87.29
CC_2m	April 2013	3.47	2.87	27.11	50.63	355.08	546.32
LA_1m	April 2013	2.45	8.91	17.09	20.42	227.20	123.40

Table A7. Mean (standard error [SE]) benthic light and dark dissolved organic carbon (DOC) fluxes and daily DOC flux by site and date.

Site abbreviation	Date	light DOC flux	SE	dark DOC flux	SE	Daily DOC flux	SE
		μmol C m^{-2} h^{-1}				μmol C m^{-2} d^{-1}	
TB_1m	August 2012	-728.38	928.74	154.01	593.67	-8216.07	9897.49
TB_2m	August 2012	1163.63	1791.18	1736.18	130.64	10454.03	11348.53
CH_1m	August 2012	668.82	581.24	288.76	176.47	12060.95	6082.41
4H_2m	August 2012	1840.99	1669.82	1266.53	359.13	38151.90	23969.23
CC_2m	August 2012	481.89	675.17	773.27	402.05	14624.91	13017.26
LA_1m	August 2012	235.48	445.89	-608.04	249.77	-3205.43	3700.84
TB_1m	April 2013	-221.43	274.38	-372.86	24.34	-7055.78	3160.26
TB_2m	April 2013	17.18	55.22	128.60	208.28	1693.63	1955.19
CH_1m	April 2013	202.87	275.80	561.24	356.32	10492.66	1276.73
4H_2m	April 2013	2882.06	897.99	-2721.70	711.37	4726.21	5377.25
CC_2m	April 2013	123.55	187.96	-703.03	304.73	-6540.44	5017.33
LA_1m	April 2013	-374.22	107.72	270.19	318.34	-1570.60	4987.36

Table A7. Mean (standard error [SE]) benthic light and dark Si fluxes and daily Si flux by site and date.

Site abbreviation	Date	light SI flux	SE	dark SI flux	SE	Daily SI flux	SE
		μmol Si m^{-2} h^{-1}				μmol Si m^{-2} d^{-1}	
TB_1m	August 2012	224.42	39.70	122.71	26.25	4318.09	809.02
TB_2m	August 2012	336.78	74.38	24.87	60.22	4807.67	888.45
CH_1m	August 2012	90.68	33.86	210.52	76.06	3434.63	440.95
4H_2m	August 2012	67.27	19.52	111.59	69.84	2079.81	990.90
CC_2m	August 2012	73.32	8.62	143.45	47.85	2496.08	605.97
LA_1m	August 2012	74.34	4.99	45.96	30.61	1486.15	254.27
TB_1m	April 2013	-164.33	115.11	-25.05	42.72	-2342.20	1182.56
TB_2m	April 2013	-15.20	29.91	18.24	30.16	19.74	646.70
CH_1m	April 2013	60.45	29.99	-38.51	18.46	312.82	378.82
4H_2m	April 2013	-91.32	88.19	86.06	57.73	-151.83	794.16
CC_2m	April 2013	40.80	37.26	104.49	17.01	1711.65	313.73
LA_1m	April 2013	18.04	21.76	-6.08	12.63	155.61	415.79

Table A7. Mean (standard error [SE]) sediment extractable NH_4^+ and NO_x from 0-5cm depth horizon by site and date.

Site abbreviation	Date	NH_4^+	SE	NO_x	SE
		mmol N m^{-2}			
TB_1m	August 2012	17.16	2.17	0.15	0.03
TB_2m	August 2012	57.93	11.11	0.01	0.01
CH_1m	August 2012	33.97	3.13	0.00	0.00
4H_2m	August 2012	8.50	1.32	0.00	0.00
CC_2m	August 2012	19.77	3.88	0.02	0.02
LA_1m	August 2012	11.517	1.88	0.030	0.01
TB_1m	April 2013	31.82	0.83	0.06	0.03
TB_2m	April 2013	62.00	10.99	0.02	0.01
CH_1m	April 2013	17.41	0.84	0.03	0.03
4H_2m	April 2013	2.52	0.65	0.14	0.04
CC_2m	April 2013	5.28	1.01	0.10	0.03
LA_1m	April 2013	3.260	1.28	0.049	0.03