

# Optimizing recovery of eutrophic estuaries: Impact of destratification and re-aeration on nutrient and dissolved oxygen dynamics



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## ABSTRACT

Widespread and global efforts to improve degraded coastal ecosystems, especially those experiencing hypoxia, warrant a renewed focus on understanding and quantifying restoration trajectories. We describe a whole-ecosystem experiment to manipulate dissolved oxygen concentrations using large-scale destratification aeration that was used to document the biogeochemical response of a small estuary to changes in oxygen availability. The experiment was successful in creating oxic and anoxic bottom water conditions at a spatial scale much larger than that encompassed by the aerators. After a period of anoxic conditions, the return of oxygenated bottom water by destratification resulted in rapid decreases in sediment phosphate fluxes, uptake of nitrate and nitrite, and an increase in simulated denitrification rates. Bottom water nutrient concentrations responded near-simultaneously to these changes to benthic–pelagic fluxes. The rapidity with which the ecosystem responded to increases in bottom water oxygen confirms the critical role of dissolved oxygen concentrations in modulating nutrient cycling. This result also provides insight into the likely response of hypoxic and anoxic estuaries to remediation of oxygen deficits at the sediment–water interface.

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## 1. Introduction

Hypoxia and anoxia (defined here as dissolved oxygen concentrations less than 63  $\mu\text{M}$  and 16  $\mu\text{M}$ , respectively) are widespread consequences of eutrophication in coastal areas, and can frequently be linked to nutrient loading from anthropogenic sources (Diaz and Rosenberg, 2008; Zhang et al., 2010). Much of restoration science in these ecosystems has hinged on the paradigm that reduced nutrient loading will decrease the frequency and extent of hypoxic conditions. However, reviews by Duarte et al. (2009) and Kemp et al. (2009) point to more nuanced responses of estuarine biogeochemistry to changed climate and nutrient conditions that may alter restoration trajectories. Whereas reduction of external nutrient loading is an essential prerequisite for remediation of culturally eutrophic basins, such efforts may be insufficient for restoration to a lower trophic state because of internal cycling of nutrients. The eutrophic

state is often a highly stable, self-perpetuating condition once a critical threshold of external nutrient loading has occurred, especially in shallow water bodies (Scheffer, 1998; Søndergaard et al., 2001).

Regulatory frameworks intended to encourage restoration of coastal waters with changed oxygen conditions include the United States' total maximum daily load (TMDL) requirements, set out by the Clean Water Act which establishes target annual loading rates for a pollutant that is responsible for impaired waters. Actions taken within a TMDL context to remediate impaired basins strongly emphasize improvements within the watershed of the water body in question. In the case of coastal waters experiencing hypoxia, these TMDL values are set for N and P loads determined using historical data analysis and/or numerical models that assist in selecting the loading rate that has the highest likelihood of remediating cultural eutrophication. In Europe, stakeholders for estuarine systems like the Baltic Sea have endeavored to improve water quality conditions through multilateral agreements such as the Helsinki Convention, in this case setting “maximum allowable inputs” that are comparable to TMDL targets. This management approach to alleviating the symptoms of eutrophication has

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characteristics of an engineering perspective. Early ecosystem models and approaches (e.g., [Kremer and Nixon, 1978](#)) designed to identify controlling mechanisms and feedbacks were developed using the tenants of H.T. Odum's ecosystem science, one that incorporates thermodynamic constraints borrowed from electrical engineering ([Odum, 1983](#)). An emphasis of these models has been on dynamic simulation and empirically driven formulations.

In contrast, engineers working with wastewater treatment technology have a higher degree of operational control over the variables and configuration of a given wastewater treatment technology intended to reduce concentrations of carbon (C), N, or P in discharge effluent. The wastewater engineer also employs numerical models based on chemical engineering methodologies, to make design and operational decisions in response to a range of wastewater influent and target effluent discharge nutrient concentrations. These numerical exercises are typically reactors in series models employing a variety of biological, chemical, and physical unit process equations, for which design and operation exert a high degree of control over key variables to meet target effluent quality ([Metcalf and Eddy, 2003](#); [Kim et al., 2008](#)). These methods more readily allow the engineer to consider optimization criteria for such processes as nitrification, denitrification, biochemical oxygen demand removal, and phosphorus removal. Although student engineers are commonly told that classic wastewater treatment methods are intensified versions of natural processes, it is also true that processes either unknown or unconfirmed in nature were first characterized in wastewater reactors through application of rigorous mass-balance models and microbiology investigations. Anammox and heterotrophic nitrification are recent notable examples ([Robertson et al., 1988](#); [Van de Graff et al., 1996](#)).

There are parallels between a watershed and process reactor perspective of impaired estuaries. Numerical modeling and empirical work in support of TMDLs identifies controlling rate processes that determine water quality of an estuary. Many processes such as oxygen transfer and water chemistry are common intellectual territory of water quality and wastewater engineering. The differences arise from both practical considerations and approach. A necessary condition to remediate eutrophication in any water body is to reduce the loading responsible for eutrophication in the first place. The watershed TMDL approach is to establish loading reduction targets and means to meet those targets. In contrast, wastewater engineering largely deals with intensive transformation of polluted water in a series of reactors to a quality – often determined in a TMDL process – acceptable for discharge to a water body. In contrast to a TMDL approach, applying engineering methods to impaired basins in situ, with methods and process rationale analogous to wastewater reactors, has a long history of success in water quality and ecological remediation ([Cooke, 2005](#); [Cooke et al., 2005](#)). This engineering method explicitly recognizes that the ecological stability of impaired basin water quality may impede realization of water quality goals set within a TMDL context, at least within the near to intermediate term. Thus, persistent impairments, such as sediment anoxia, may merit in situ remediation in some cases either to force a shift to a desirable alternative stable ecological state, thereafter sustained by an effective TMDL plan, or to maintain acceptable water quality until the long-term benefit of a TMDL plan is realized. However, there are few studies that have evaluated the ecosystem impacts of in situ engineering remediation, such as aeration, in estuaries.

In the summer of 2012, we were presented with a unique opportunity to explore an estuarine system from both a wastewater treatment and ecosystems perspective. Chesapeake Bay the largest estuary in North America, is also under a presidential executive order to implement TMDLs for N and

P. Rock Creek, a sub-tributary of the Patapsco River in the northern portion of Chesapeake Bay is unusual in that its community chose in situ engineering solutions to reduce hypoxia and its negative effects in the early days of Bay management. In 1988, following the recommendation of the engineering company [Dames and Moore \(1988\)](#), an aeration system was installed that currently consists of 830 m of aeration pipes and 138 diffusers. The purpose of aeration is to destroy saline and thermal stratification that isolates bottom water from oxygen-rich surface water. The destratified water column is then responsive to tidal and wind energy that readily mixes oxygen-rich surface water to the bottom, thereby preventing anoxia. The installation cost for the aeration system in Rock Creek was \$253,000 in 1988, with average annual electrical costs of \$11,000 that have ranged from \$6,350 to \$14,000 between 2000 and 2010 ([CH2M HILL, 2011b](#)). Upgrade costs for tertiary treatment and N removal at wastewater treatment plants typically cost millions of dollars, yet impact an area larger than the 353 ha tributary studied here. Although aeration may appear to be a cost-effective solution in Rock Creek, it does nothing to address the other deleterious effects of nutrient loading and larger-scale aeration projects would likely be unsuccessful ([Conley et al., 2009b](#)). This relatively small, tidal estuary is heavily loaded with nutrients, resulting in extreme eutrophic characteristics. After over 20 years of continuous summer use, local government and stakeholders required scientific information to inform their decisions about possible repair, replacement, or removal of the large scale aerators. This place-based question also afforded a serendipitous experimental setting to explore how manipulating dissolved oxygen levels via control of the aerators might affect sediment and water column biogeochemistry.

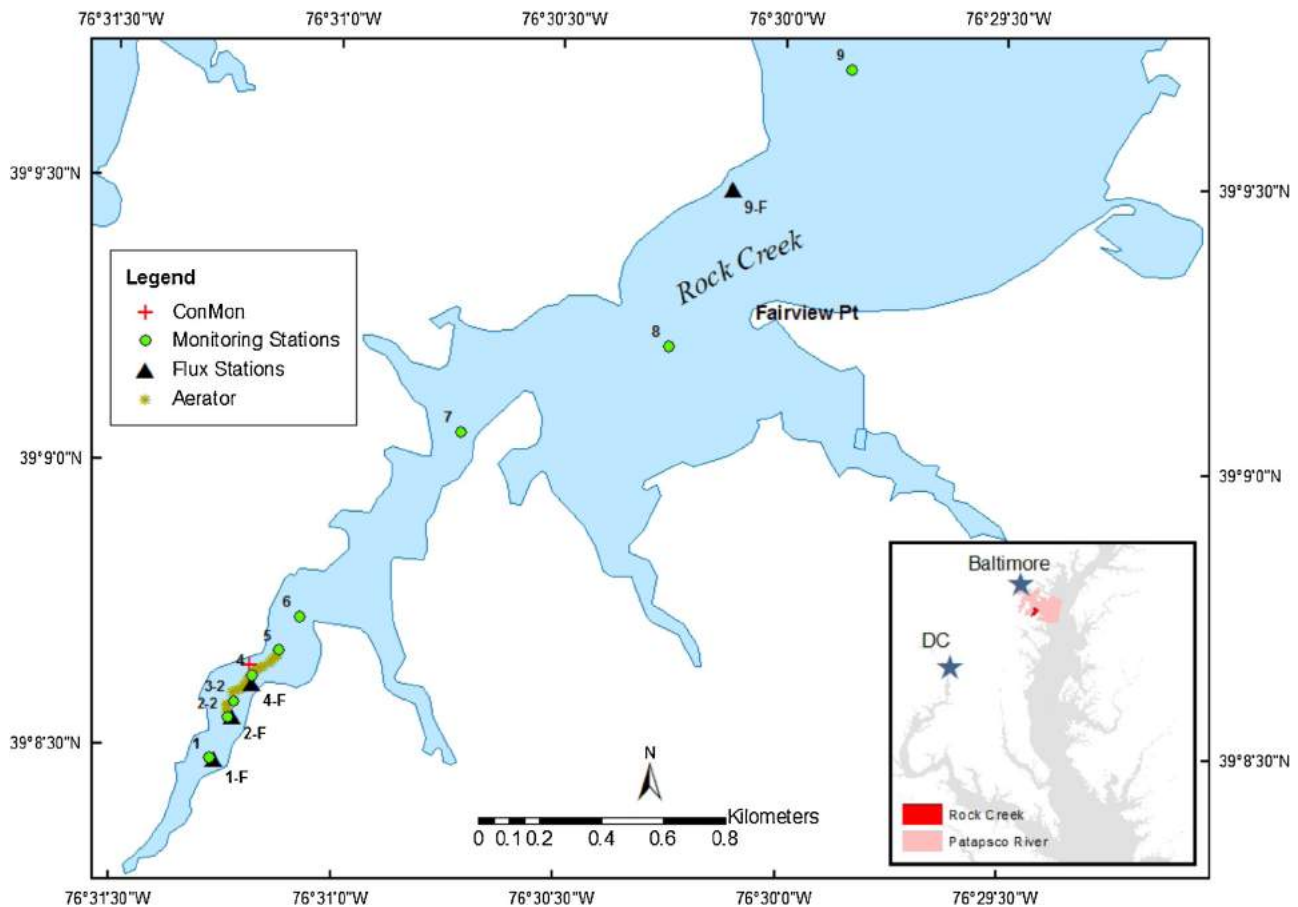
The majority of studies describing the impact of depleted oxygen on nutrient biogeochemistry rely on time series, or datasets of sediment nutrient fluxes that use the natural gradient of water column conditions often characteristic of estuarine systems, where salinity, oxygen, and temperatures vary in space. Important questions have remained regarding the effects of destratification. In particular, the effect of sediment oxygen demand (SOD) on water quality and on nutrient dynamics with and without destratification needs detailed investigation. Here we present our effort to take advantage of a tributary scale experiment to evaluate whether aeration (a) impacts water column SOD and water quality and (b) affects nutrient fluxes and benthic–pelagic coupling processes. Borrowing from the engineering perspective, we consider how rate processes may act to optimize response of estuaries to changed oxygen or nutrient conditions using a combination of direct measurement and modeling techniques.

This study neither promotes nor denigrates destratification as a remediation measure in tidal estuaries. Instead, the aeration system here was leveraged as a whole ecosystem experiment, enabling manipulation of bottom water oxygen and providing an opportunity to measure system response to a simulated recovery that was designed to provide insights into the biogeochemistry that affects larger scale restoration efforts for hypoxic estuaries.

## 2. Methods

### 2.1. Study site

In order to evaluate the biogeochemical response of an impacted, hypoxic estuarine system to changes in bottom water oxygen concentrations, we experimentally manipulated the aeration system of Rock Creek. Rock Creek is a 353-ha tidal creek tributary to the Patapsco River in Anne Arundel County, Maryland ([Fig. 1](#)). The creek has experienced poor water quality for about 35 years. A large scale aeration system was installed in the creek by the Anne Arundel County Department of Public Works in October



**Fig. 1.** Map of Rock Creek estuary and location within the larger Chesapeake Bay USA. Sample locations are noted for continuous monitoring site (ConMon), grab and vertical profile samples (monitoring stations), and sediment core collection sites (flux stations). Aeration zone is indicated by overlapping yellow asterisk symbols. Fairview Point, labeled, is the boundary used for estimating residence time and tidal exchange with the Patapsco River. Note that Station 9 was sampled during grab sample events only.

1988 to mitigate low dissolved oxygen and resident complaints of hydrogen sulfide odors and fish kills. At optimal working condition, the system aerates the water column using air transmitted by on-land compressors via diffusers at a rate of  $15,574 \text{ L-atmosphere air min}^{-1}$ .

Situated in the northern reaches of Chesapeake Bay nutrient loadings to Rock Creek enter from both the land and tidal exchange. The Chesapeake Bay Program provided modeled output for watershed loadings using the Chesapeake Bay Watershed Model (CBWM) version 5.3.2, a complex simulation platform covering a  $166,000 \text{ km}^2$  drainage basin adapting the formulations and framework of HSPF (USEPA, 2010). This model simulates nutrient loads for the entire Chesapeake Bay watershed based on 1194 river segments. Modeled watershed loadings of N and P normalized to the boundaries of the Rock Creek watershed are  $13,430 \text{ kg N year}^{-1}$  and  $1500 \text{ kg P year}^{-1}$ . Land use in the Rock Creek watershed is dominated by residential and urban development (80%). Forested land accounts for 20%, and 0.2% of land use is identified as agricultural use (Maryland Department of Planning, 2010). The residences located on the southeast shoreline of Rock Creek use septic wastewater treatment, while those on the northeast shoreline has city water and public sewers. This watershed covers  $1041 \text{ ha}$ , resulting in a land to water area ratio of 2.9:1. Normalizing the nitrogen loading from the watershed to the area of the tidal receiving waters in Rock Creek results in a relatively low loading rate ( $3.8 \text{ g N m}^{-2} \text{ year}^{-1}$ ). In this system, tidal influx of nutrients from the larger Patapsco tributary are much larger and have been estimated to fall between  $139,000$  and  $218,000 \text{ kg N year}^{-1}$  (this

study; Dames and Moore, 1988). This type of “upside down” nutrient budget, where the largest source of nutrients is from an adjacent estuarine ecosystem rather than freshwater inputs from the surrounding local watershed, has also been identified in Greenwich Bay a tributary of Narragansett Bay in Rhode Island, USA (DiMilla et al., 2011). The tidal portion of the tributary has an average depth of 2.9 m, a tidal range of 0.3 m, and a maximum depth of 5.7 m. Cronin and Pritchard (1975) report a water volume of  $9.60 \times 10^6 \text{ m}^3$ . Salinity in Rock Creek ranged from 5 to 10.2 during the course of this study.

A two-dimensional, finite element, depth-averaged hydrodynamic model was applied by CH2M HILL (2011a) to quantify the tidal exchange between Rock Creek and the Patapsco River as part of their efforts to determine engineering requirements for the aeration system. This work took advantage of the surface water modeling system (SMS; Froehlich, 1989), parameterizing the RMA-2 hydrodynamic model to characterize tidal exchange and storm water inflow, and the RMA-4 model to simulate flushing (USACE, 2004). Simulated dye studies were carried out to compute a residence time, estimated at the boundary of Fairview Point (Fig. 1) to be 32 days, with stormwater simulations resulting in lower residence times of about 13 days (CH2M HILL, 2011a).

## 2.2. Study design

Because dissolved oxygen saturation is lower during the hot summer months, the study was designed to occur during the warmest weeks of the year (July and August, 2012) to maximize the

potential of capturing anoxic and hypoxic oxygen concentrations. Baseline conditions for biological, chemical, and physical variables were established while the aerators were operational, and these were monitored again during a two week experimental period when the aeration system was turned off. These same variables were measured during a recovery period of two weeks with aeration. The two-week schedule of baseline-experiment-recovery sampling was selected to range over the biweekly spring-neap tidal cycle typical of these waters. Monitoring of baseline conditions occurred from July 2 through the 10th, at which time the aerators were shut down until the recovery phase of monitoring beginning July 20th. The field campaign to document system response consisted of near-continuous monitoring of bottom water conditions of basic parameters at one location, vertical profiles and grab samples for water chemistry along a transect spanning the aeration zone out to the Patapsco River, and limited sediment core collection and incubations to quantify sediment metabolic processes and fluxes of N and P (Fig. 1). While the study was focused on oxygen concentrations within the area directly influenced by the aeration systems, stations were chosen along the axis of Rock Creek longitudinally from the upstream (southern) end in the aeration zone, but also extended into the mouth of Rock Creek, and beyond into the Patapsco River. Two locations along the aeration zone were selected for additional sampling perpendicular to the main sampling transect.

### 2.3. Continuous monitoring station

Near continuous measurements of bottom water dissolved oxygen, pH, conductivity and salinity, oxidation–reduction potential, turbidity and temperature were recorded during the course of the experiment using a YSI Model 6920 deployed within the aeration zone (Fig. 1). The instrument was installed 0.5 m from the bottom sediments, within a 3 in. diameter standpipe attached to a pier and experienced an average water depth of 3 m over the course of the study. Maintenance was performed regularly to calibrate and reduce biofouling on the sensor system.

### 2.4. Vertical profiles

Water column vertical profiles were measured using a YSI 6920 multi-probe sonde at sunrise and sunset throughout the study (15 total days), with special attention paid to include sampling dates that marked the start and end of each phase of the study and daily sampling during the experimental aeration shut off period. Sampling at dawn and dusk captured the likely minimum and maximum dissolved oxygen conditions within the system. The sonde sensors, calibrated daily and used to perform vertical profiles (0.5 m increments) at each station, were used to measure dissolved oxygen, pH, conductivity and salinity, oxidation reduction potential, turbidity and temperature at dusk and dawn during scheduled sampling days. Secchi disk depth, total depth and GPS coordinates were noted at each sampling station along with meteorological conditions. To determine whether manipulation of the aeration system impacted the Rock Creek tributary, we tested the relationship between distance from aerators and dissolved oxygen using linear regression (Ellis and Schneider, 1997) for each phase of the baseline-experiment-recovery periods of the study using the R-statistical package (R Core Team, 2013).

### 2.5. Grab samples for water chemistry

Water was collected at the surface and bottom of the water column at four stations on four days during the baseline-experiment-recovery periods; 1 day each for the baseline (aeration) and experiment (no aeration) phase, and on two

occasions in the recovery (aeration) period. These samples were analyzed for dissolved and particulate nutrients including ammonium ( $\text{NH}_4$ ), nitrate–nitrite ( $\text{NO}_3\text{--NO}_2$ ), nitrite ( $\text{NO}_2$ ), total dissolved nitrogen (TDN), particulate nitrogen (PN), ortho-phosphate ( $\text{PO}_4$ ), total dissolved phosphorus (TDP), particulate phosphorus (PP), and particulate carbon (PC) following standard techniques (Grasshoff, 1976; D'Elia et al., 1977). Whole-water analyses of 5-day biochemical oxygen demand (BOD), and fluorometrically determined active chlorophyll-a and phaeophytin concentrations were also completed following EPA method 445.0, SM 10200H.3. To determine the impact of aeration on these measurements, we applied a modified before-after-control-impact analysis of variance (BACI ANOVA), with variation attributable to treatment (aeration, no aeration) and time period (before, during, after) accounted for in the ANOVA model. An interaction term between temporal variability and treatment effects was also included. If this interaction term was assessed as statistically significant, post-hoc testing was applied with the least squares means approach to determine which treatment had an effect (Underwood, 1993).

### 2.6. Sediment coring

To determine sediment biogeochemistry, we collected intact sediment cores on July 17, 2012 under no aeration (experimental phase) and on August 1, 2012 with aeration (recovery period) conditions from four stations both adjacent and distant to the aerator system (Fig. 1). All sampling containers were acid-washed. At each station, a plexiglass cylinder 10 cm in diameter was used to extract an intact sediment core of the bottom sediments. Only a single core was used rather than replicates. Boynton and Rohland (1998) demonstrated that variability associated with triplicate cores collected in the Chesapeake Bay was 5–20% (Coefficient of variation; CV) for SOD and  $\text{NH}_4$ , and 20–25% CV for  $\text{PO}_4$  flux. This contrasts with sediment flux differences measured between habitats that varied by factors of 20 $\times$  ( $\text{NH}_4$  and SOD) and 50 $\times$  ( $\text{PO}_4$ ). This larger variability with changes in habitat emphasizes the need for investing measurement efforts across spatial scales rather than replication, as also demonstrated by Cowan and Boynton (1996). In much of the impacted Chesapeake Bay ecosystem, fluxes are dependent on microbial activity as there is minimal benthic infauna activity (especially in Rock Creek) that might lead to greater variability and a need for core replication in other systems (Cowan and Boynton, 1996). Sediment core samples were taken at depths ranging from 1.9 to 3.0 m, a depth range that represented most depths in the tributary. The YSI model 6920 multi-probe instrument was used to record surface and bottom water column readings for water temperature, salinity and conductivity, dissolved oxygen and pH at each station. At each station two collapsible, air-tight containers were filled with water pumped from approximately 0.5 m above the sediment surface for use with laboratory incubations. Cores were transported in the dark and under site water to maintain field conditions prior to the incubations.

Photic zone depths estimated from Secchi disk measurements using Chesapeake Bay specific conversions (Keefe et al., 1976) indicated light would not penetrate to bottom sediments at these stations. Additional surficial sediment samples (1 cm depth) were collected to measure chlorophyll-a, phaeophytin, plus particulate phosphorus, carbon, and nitrogen concentrations.

### 2.7. Benthic-pelagic flux measurements

Experiments to measure exchanges of N, P, and sediment oxygen demand (SOD) were performed under controlled laboratory conditions. Sediment cores were placed in darkness in a



temperature-controlled holding tank that was set to temperature values recorded from the field. The overlying water in the sediment cores was slowly replaced with fresh ambient bottom water without disturbing the sediments, and capped with a gas-tight lid fitted with a stir bar and dissolved oxygen probe (WTW StirrOx® G probe with Oxi197i meter). The incubation of each sediment core microcosm lasted 4 h with water samples extracted every hour for  $\text{NH}_4$ ,  $\text{NO}_2$ ,  $\text{NO}_3\text{--NO}_2$ , and  $\text{PO}_4$ . At the time of water extractions for analysis, the displaced water volume was replaced with collected bottom water. Dissolved oxygen concentrations and water temperature values were also recorded following each nutrient sample. Data collected in incubations were used to determine fluxes between sediment and water column for  $\text{NH}_4$ ,  $\text{NO}_2$ ,  $\text{NO}_3\text{--NO}_2$ ,  $\text{PO}_4$  and SOD by plotting a time course of changing nutrient or dissolved oxygen concentrations and estimating a slope using linear regression techniques. Linear regression was also used to evaluate the relationship between bottom water concentrations and flux values using the R-statistical package (R Core Team, 2013).

## 2.8. Modeling to estimate denitrification and nitrification

Denitrification was not measured directly in this study and as an alternative we employed a novel sediment flux modeling approach to estimate these values. We also used the model to estimate rates of sediment–water  $\text{NH}_4$ ,  $\text{NO}_2\text{--NO}_3$ , and  $\text{PO}_4$  fluxes, which we validated with observed fluxes to improve our confidence in modeled nitrification and denitrification rates. We applied a two-layer sediment flux model (SFM; Di Toro, 2001; Brady et al., 2013; Testa et al., 2013) to examine the biogeochemical response of the sediments to the deoxygenation of the water-column after the aerators were turned off during the experimental phase. SFM has successfully reproduced sediment–water fluxes of ammonium ( $\text{NH}_4$ ), nitrate ( $\text{NO}_3$ ), phosphate ( $\text{PO}_4$ ), and dissolved silica ( $\text{Si}(\text{OH})_4$  or  $\text{DSi}$ ) for diverse chemical and physical environments throughout Chesapeake Bay.

The model structure for SFM involves four general processes: (1) the sediment receives depositional fluxes of particulate organic carbon and nitrogen, as well as biogenic and inorganic phosphorus and silica, from the overlying water, (2) the decomposition of particulate matter produces soluble intermediates that are quantified as diagenetic fluxes, (3) solutes react, transfer between solid and dissolved phases, are transported between the aerobic and anaerobic layers of the sediment, or are released as gases ( $\text{CH}_4$ ,  $\text{N}_2$ ), and (4) solutes are returned to the overlying water. SFM numerically integrates mass-balance equations for chemical constituents in two functional layers: an aerobic layer near the sediment–water interface of variable depth ( $H_1$ ) and an anaerobic layer below that is equal to the total sediment depth (10 cm) minus the depth of  $H_1$ .

Rate coefficients for aerobic-layer reactions (e.g., nitrification) are relatively similar. These reactions are modeled to be dependent on the depth of the aerobic layer,  $H_1$ . For example, the nitrification rate expression in the mass balance equations for  $\text{NH}_4^+$  is a product of the aerobic layer nitrification rate constant ( $k_{\text{NH}_4^+,1}$ ) and the depth of the aerobic layer:

$$k_{\text{NH}_4^+,1}H_1 = \frac{D_{\text{NH}_4^+}k_{\text{NH}_4^+,1}}{K_{\text{LO1}}} \quad (1)$$

$K_{\text{LO1}}$  is the sediment–water mass transfer coefficient. The product  $D_{\text{NH}_4^+}k_{\text{NH}_4^+,1}$  is made up of two coefficients, neither of which is readily measured. The diffusion coefficient ( $D_{\text{NH}_4^+}$ ) in a millimeter thick layer of sediment at the sediment water interface may be

larger than the diffusion coefficient in the bulk of the sediment due to the effects of overlying water shear. It is therefore convenient to subsume two relatively unknown parameters into one parameter that is calibrated to data, called  $\kappa_{\text{NH}_4^+,1}$ :

$$\kappa_{\text{NH}_4^+,1} = \sqrt{D_{\text{NH}_4^+}k_{\text{NH}_4^+,1}} \quad (2)$$

$\kappa_{\text{NH}_4^+,1}$  is termed the reaction velocity, since its dimensions are length per time. Squared reaction velocities are then incorporated in the reaction term of the following mass balance equations for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the aerobic layer,  $H_1$ :

$$\kappa_1^2 = \kappa_{\text{NH}_4^+,1}^2 \theta_{\text{NH}_4^+}^{(T-20)} \left( \frac{K_{M,\text{NH}_4^+} \theta_{K_{M,\text{NH}_4^+}}^{(T-20)}}{K_{M,\text{NH}_4^+} \theta_{K_{M,\text{NH}_4^+}}^{(T-20)} + [\text{NH}_4^+(1)]} \right) \left( \frac{[\text{O}_2(0)]/2}{K_{M,\text{NH}_4^+,\text{O}_2} + [\text{O}_2(0)]/2} \right) \quad (3)$$

$$\text{Nitrification rate} = \frac{\kappa_1^2}{K_{\text{LO1}}} \times \text{NH}_4^+(1) \quad (4)$$

and denitrification in each layer:

$$dk_i = k_{\text{NO}_3^-,i} \theta_{\text{NO}_3^-}^{(T-20)} \quad (5)$$

where  $dk_i$  is denitrification and the  $k_{\text{NO}_3^-}$  is the denitrification rate constant for each layer.

$$\text{Denitrification rate} = dk_i \times \text{NO}_3^-(i)$$

Note that denitrification in  $H_1$  represents that which occurs at the oxic/anoxic interface. Complete details of the model structure can be found in Di Toro (2001) and Testa et al. (2013).

Organic matter deposition rates (including particulate biogenic C, N, P, and Si) for each year and station were estimated using a Hooke–Jeeves pattern search algorithm (Hooke and Jeeves, 1961) to minimize the root mean square error (RMSE) between modeled and observed  $\text{NH}_4$  flux (Brady et al., 2013). We use this method because deposition may be episodic, and resuspension may disperse previously deposited material from a given location. Deposition is also notoriously difficult to estimate. The modeled  $\text{NH}_4$  flux integrates the accumulation of particulate organic N that was actually processed in the sediments over a given period while accounting for burial and nitrification losses. Prior attempts to use overlying water chlorophyll as an index of deposition across many stations in Chesapeake Bay had limited success, while applications of this approach to estimate deposition has matched observations favorably (Brady et al., 2013).

For Rock Creek, we initialized model runs by simulating SFM from 1994–2011 at a nearby station in the Patapsco River (using  $\text{NH}_4$  to compute deposition as described above) with sediment–water flux observations (39.178°N, –76.498°W). We then simulated the year 2012 (including the experiment) at the four flux stations in Rock Creek (Stations 1-F, 2-F, 4-F, and 9-F), where observations of overlying-water salinity, temperature, DO, and dissolved nutrients ( $\text{NH}_4$ ,  $\text{NO}_3\text{--NO}_2$ ,  $\text{PO}_4$ ) made 6 days before, during, and after the experiment were interpolated linearly to represent daily values. These interpolated values were used to represent boundary conditions and contribute to the calculation of sediment–water nutrient and oxygen fluxes. Please refer to Di Toro (2001), Brady et al. (2013), and Testa et al. (2013) for more details on the model structure, formulation, and calibration.

### 3. Results

#### 3.1. Continuous monitoring station

Conditions in Rock Creek were ideal for the experimental manipulation of the aerators because high summer temperatures ( $>25^{\circ}\text{C}$ ) insured a rapid response of water column dissolved oxygen concentrations. Water temperature ranged between 26 and  $30^{\circ}\text{C}$ , and the bottom water DO concentrations alternated between oxic, anoxic/hypoxic, and oxic conditions during the course of the change in aeration (Fig. 2). In addition to the experimental manipulation of the aerators (no aeration) from noon on July 10 to noon on July 19, the public reported aerator malfunctions on July 5th, 6th and 8th. The continuous monitoring data agree with these reported, unplanned outages (Fig. 2), although vertical profile data were not collected on these dates. The change in aeration yielded near-immediate effects on oxygen conditions in the water column. For example, sonde measurements at the continuous monitoring station plummeted from 125 to  $6\mu\text{M}$  within 11 h of the aerator shutoff (Fig. 2). The YSI sonde was removed from the system overnight on July 12th due to a battery issue, resulting in a brief break in the data collection that can be seen in Fig. 2.

The degree to which the aeration, or lack of aeration, affected the dissolved oxygen of the estuary is remarkable in that a relatively small area of engineered aeration resulted in impacts to dissolved oxygen up to 2 km away at Station 8. To visualize these effects, we computed DO isopleths (DPlot Graph Software, 2012) by interpolating the results of vertical profile measurements taken at 8 Stations along the longitudinal axis of the estuary extending from the landward station to the Patapsco River (Fig. 3). Sampling frequency for these stations includes more frequent profiles during the experimental/no aeration time period, which may result in a greater bias in the degree of detail visible in these figures. However, by design, the aerators create a less variable environment. Bottom waters were anoxic across the estuary during the time period when the aerators were turned off (recall that dates when outages were reported by the public were not sampled). The aerators had an impact on DO concentrations

for some distance ( $\sim 2$  km) seaward towards the Patapsco, with a relatively rapid response of the water column. Dissolved oxygen concentrations sampled in the morning at Station 4 had increased from  $42.2\mu\text{M}$  (aerators off for another 4 h) to  $89.7\mu\text{M}$  20 h after aerators were turned back on. The linear regression relationship between DO concentrations and distance from aeration was only significant when the aerators were turned off during the experimental phase ( $\text{DO} = 0.0016 \times \text{DISTANCE} + 0.45$ ;  $p < 0.01$ ,  $F = 44.85$ ), and no significant difference could be detected across the vertical profile data between the Patapsco and the aeration zone when they were operational during the recovery/baseline periods. Bottom waters continued to experience hypoxic conditions, but overall hypoxic volume was much reduced. These graphs also show how well mixed the water column was in the vicinity of the aerators.

#### 3.2. Water column nutrients and chlorophyll-a

At Stations 2-2 and 4, both of which are close to the aerators, rates of BOD decreased during the experimental period (aerators turned off; samples collected on July 11th), even as surface concentrations of chlorophyll-a increased to bloom conditions (Fig. 4,  $>450\mu\text{g L}^{-1}$ ). Dissolved inorganic phosphate concentration increased slightly under low oxygen conditions, ammonium values increased, nitrate–nitrite concentrations decreased, and dissolved organic N and P concentrations remained relatively stable. BACI ANOVA results identified statistically significant responses of bottom water concentrations for  $\text{NO}_3\text{--NO}_2$  ( $F = 15.16$ ,  $p = 0.008$ ) and surface concentrations of chlorophyll-a ( $F = 4.53$ ,  $p = 0.032$ ).

Stoichiometric ratios of dissolved inorganic N and P remained above 16 at all stations and sampling times except at Station 4, the site situated closest to an aerator, where surface and bottom N:P ratio decreased to 5 and 9, respectively, as a result of increased DIP concentrations on the July 20th sampling date. Dissolved inorganic N and P concentrations were typically well above half saturation constants describing phytoplankton uptake ( $\sim 0.5\mu\text{M NL}^{-1}$  and  $0.1\mu\text{M PL}^{-1}$ ; Malone et al., 1996). The exceptions to this were

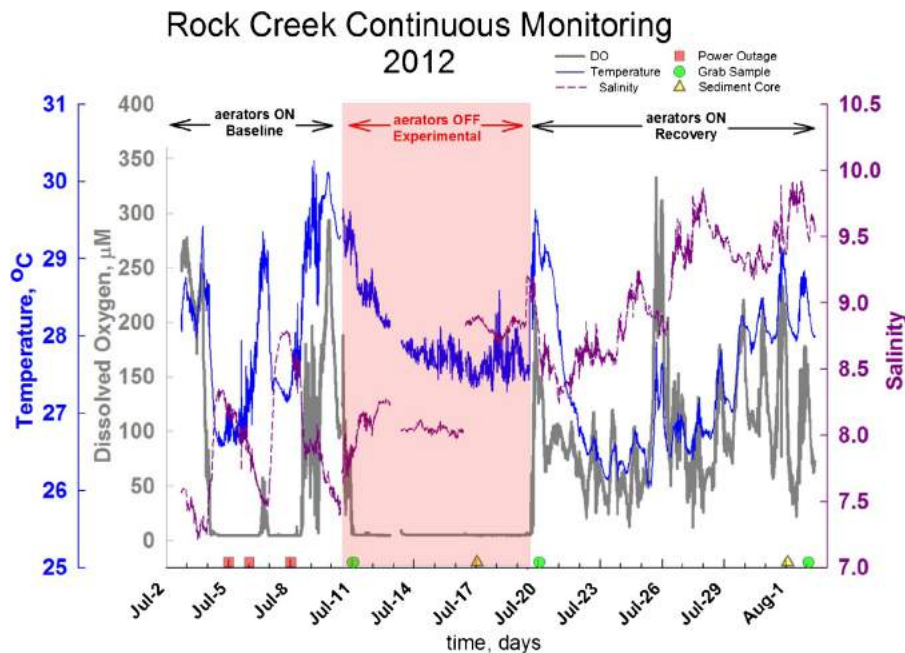
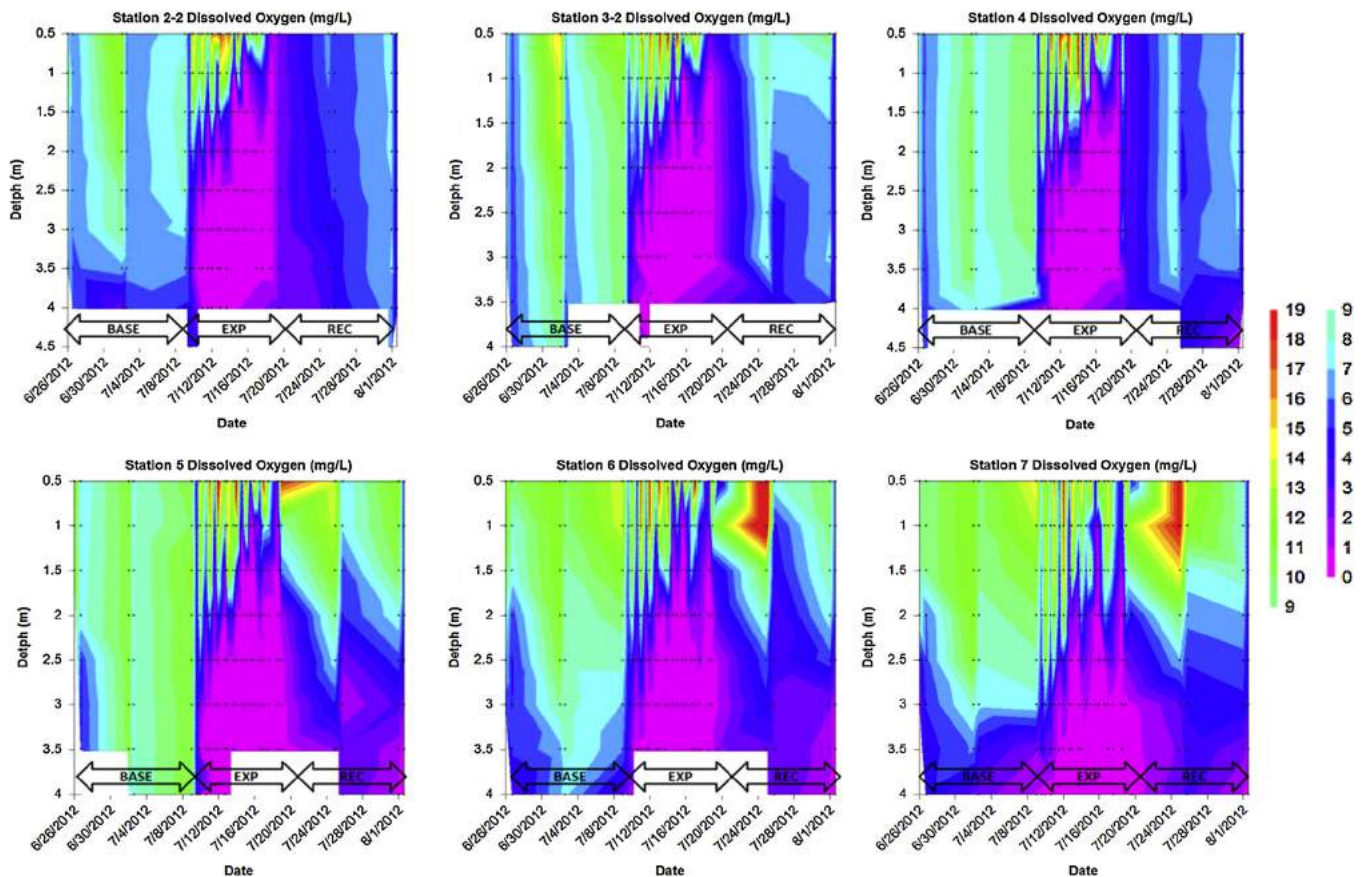


Fig. 2. Temperature, salinity, and DO concentrations at the continuous monitoring station over the course of the study. The baseline-experimental-recovery time periods of the study are labeled with appropriate text and arrows. Sampling dates and reported aerator power outages are indicated by symbols along the x-axis. An initial grab sample was taken June 26, 2012 prior to ConMon deployment.



**Fig. 3.** Isopleths of water column dissolved oxygen ( $\mu\text{M}$ ) concentrations developed from vertical profile data. Stations are organized from the landward most location (1) to a station  $\sim 2$  Km from the aeration system (8). Public reported power outages of the aerators occurred on July 5th, 6th, and 8th.

surface DIN concentrations at Stations 4 and 8 on July 20th, and  $\text{PO}_4$  concentrations at Station 9 in surface waters on June 27th and July 11th. Chlorophyll-*a* concentrations at Station 9 were relatively low throughout the study period, while concentrations measured at Stations 4 and 8 peaked on July 11th, followed by steady declines through the August 2nd recovery period.

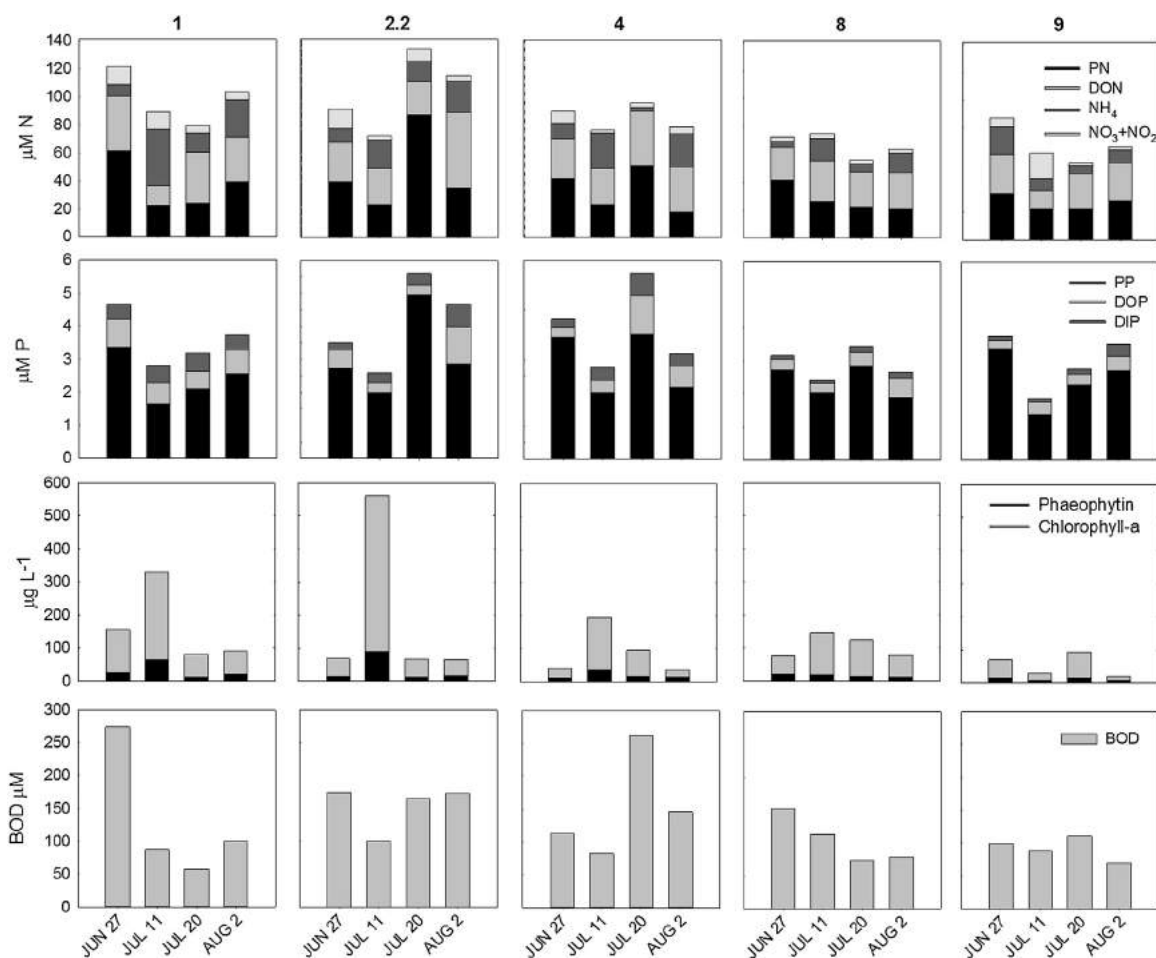
### 3.3. Sediment nutrient flux experiments

The results of the sediment core incubations inform our understanding of observed water column water quality patterns (Fig. 5). Under anoxic conditions, Stations 1-F, 2-F, and 4-F nitrate–nitrite fluxes from the sediments to the water column were zero, or were directed into sediments. At these same stations, SOD rates were so low and measured under such low dissolved oxygen conditions that zero SOD flux was measured, yet these rates increased dramatically when the aerators were turned back on. Depth-normalized BOD measurements were used to compute integrated water column respiration for comparison to these sediment oxygen demand values (Fig. 5). Measured ammonium fluxes were similar in magnitude at Stations 1-F, 2-F, and 9-F during the experimental phase of the study (no aeration), however measurements of these fluxes varied by station when aerated conditions returned, with extremely high fluxes during the recovery period ( $>1000 \mu\text{M N-NH}_4 \text{m}^{-2} \text{h}^{-1}$ ) computed at Station 2-F and low rates documented at Station 4-F. Phosphate fluxes represented a stark contrast, with high rates of sediment P release ( $19.1\text{--}70.5 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) observed under anoxic conditions and an immediate return to very low fluxes ( $0\text{--}25.3 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) once aeration returned. Station 9-F, which is located nearest the Patapsco, displayed different patterns from

those cores collected closer to the aerators. The bottom water oxygen and nitrate fluxes measured at this site during the experimental aeration shut-off period were actually higher than that documented during the recovery period, when DO concentrations fell below  $63 \mu\text{M}$ .

To examine these flux measurements relative to bottom water conditions, we developed a series of sediment flux versus concentration plots. Linear regression analyses indicated that sediment fluxes and bottom water concentrations were significantly correlated for SOD,  $\text{NO}_2$ , and  $\text{PO}_4$ , but not for  $\text{NH}_4$  or  $\text{NO}_3\text{--NO}_2$  (Fig. 6). To put the relative magnitude of these rates in context, measurements collected as part of a Chesapeake Bay wide sediment flux monitoring program were also included on the plots, using data selected from estuarine locations with similar salinity, temperature, and water depth conditions (Boynton and Bailey, 2008). Rock Creek SOD and nitrite fluxes exhibited a pattern of declining values with decreased bottom water concentrations of DO or nitrite as previously reported (Cowan and Boynton, 1996). However, the picture for phosphate, ammonium, and nitrate–nitrite is more complex. Rock Creek has particularly high DIP fluxes compared to all other Chesapeake Bay systems apart from the Corsica River estuary, and DIP fluxes increase with increasing bottom water  $\text{PO}_4$  concentrations. Compared to other systems, bottom water nitrate concentrations were particularly low in Rock Creek in relation to the measured fluxes, regardless of whether the samples represented aerated or non-aerated conditions (Fig. 6). The rates of net uptake of nitrate–nitrite make these measurements stand out from other systems. Ammonium fluxes and bottom water concentrations of this analyte were also especially high and were not significantly correlated with one another. Basic characteristics of the four stations sampled are provided in Table 1.





**Fig. 4.** Water column dissolved and particulate N and P, phaeophytin, chlorophyll-a, and rates of biological oxygen demand (BOD) at the five stations where these grab samples were collected. All measurements are for bottom water apart from pigments, which represent surface samples. The aerators were shut-off for a period inclusive of the July 11th sampling date.

Of note is the lower sediment particulate nutrients measured at Station 4-F, the closest sampling location to the aerators.

### 3.4. Model predicted denitrification and nitrification

The application of a sediment biogeochemical model to simulate sediment responses to deoxygenation allowed for computations of nitrification and denitrification, as well as interpretation of the observed sediment–water nutrient and DO fluxes (Table 2). Estimated rates of denitrification varied with station, with higher rates estimated for the more upstream reaches of Rock Creek (Station 1-F and 2-F, Table 2). With the exception of Station 2-F, denitrification was reduced under anoxic conditions, which was associated with declines in nitrification (Table 2). In the case of Station 2-F, denitrification was enhanced under anoxic conditions, but this increase was driven by model-predicted sediment uptake of bottom water  $\text{NO}_3$ ; the observations do not support such high rates of sediment  $\text{NO}_3$  uptake at this station. Across all stations, model-simulated denitrification was highly correlated with overlying-water  $\text{NO}_3$  and was consistent with rates measured in other regions of Chesapeake Bay (Testa et al., 2013; Kana et al., 2006).

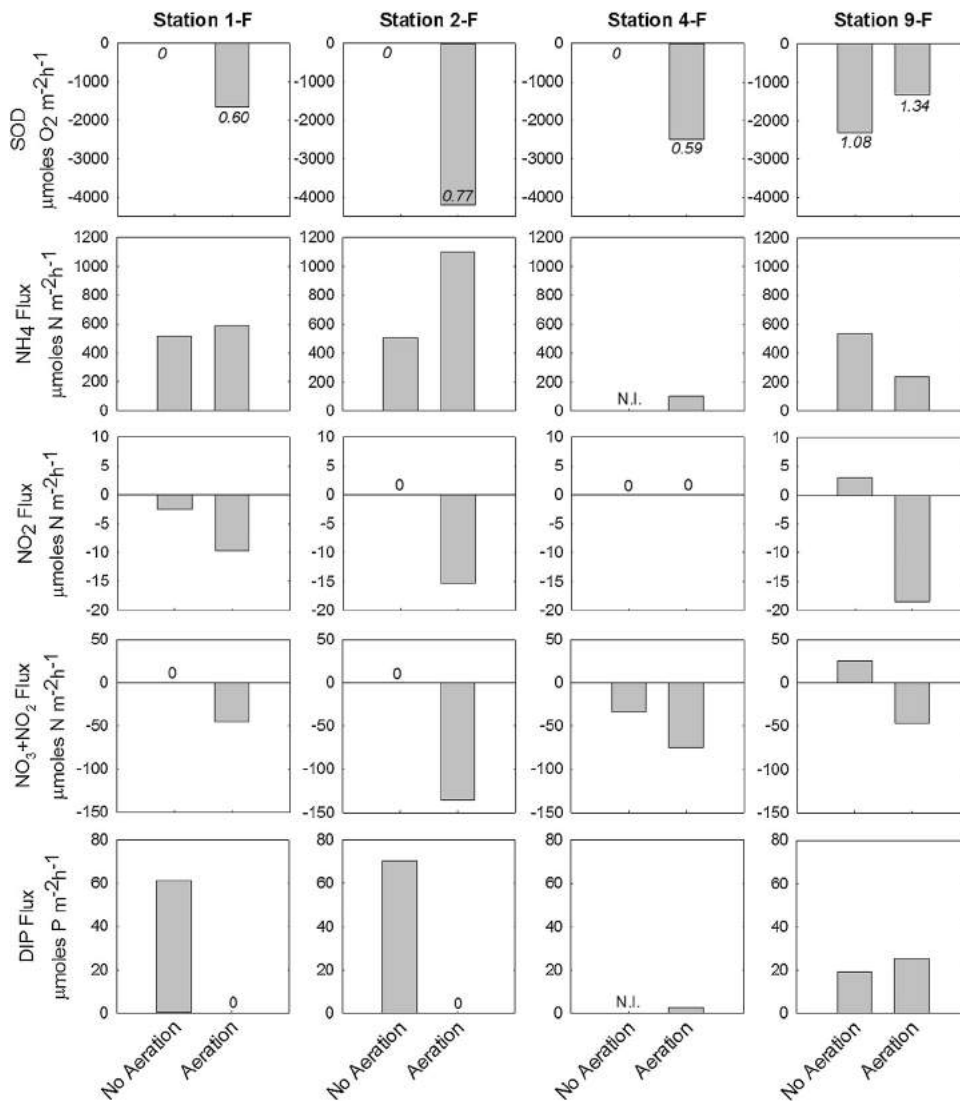
SFM was validated against, and reasonably reproduced the observed patterns of sediment–water fluxes of  $\text{NH}_4$ ,  $\text{NO}_3\text{--NO}_2$ ,  $\text{PO}_4$ , and DO on July 17th and August 1st, 2012, respectively, but with several key model–data misfits. SFM captured the magnitude of sediment–water  $\text{NH}_4$  fluxes across stations (Table 2), but the

model was unable to capture the large rates of sediment  $\text{NO}_3$  uptake observed during the recovery period. SFM did not represent sediment–water exchanges well at Station 2-F, including the extremely large sediment water  $\text{NH}_4$  releases and  $\text{NO}_3\text{--NO}_2$  and DO uptake recorded during the recovery period. However, SFM captured the reduction in sediment DO uptake and elevation of  $\text{PO}_4$  release during the experimental period (no aeration) at Stations 1-F, 2-F, and 3-F (Table 2).

## 4. Discussion

Anoxia is strongly linked with benthic nutrient remineralization in estuarine sediments because in the absence of oxygen sediment bacteria use alternative terminal electron acceptors to oxygen (Middelburg and Levin, 2009). In particular, Fe-reduction releases Fe-bound phosphorus and sulfide production (via sulfate reduction) dissolves Fe(III) and Mn(IV). Both of these processes release ferric-bound phosphate from sediments to the water column (Rozan et al., 2002). It also directly depletes dissolved oxygen from water through sulfide oxidation and through oxidation of soluble Fe(II) and Mn(II). Observational studies of estuarine biogeochemistry have confirmed patterns of enhanced sediment phosphorus (P) release under hypoxic conditions (e.g., Jordan et al., 2008), as well as in response to elevated pH driven by phytoplankton blooms (Gao et al., 2012). Kemp et al. (1990) were among the early estuarine ecologists to describe the effects of depleted bottom water oxygen on nitrification of ammonium to





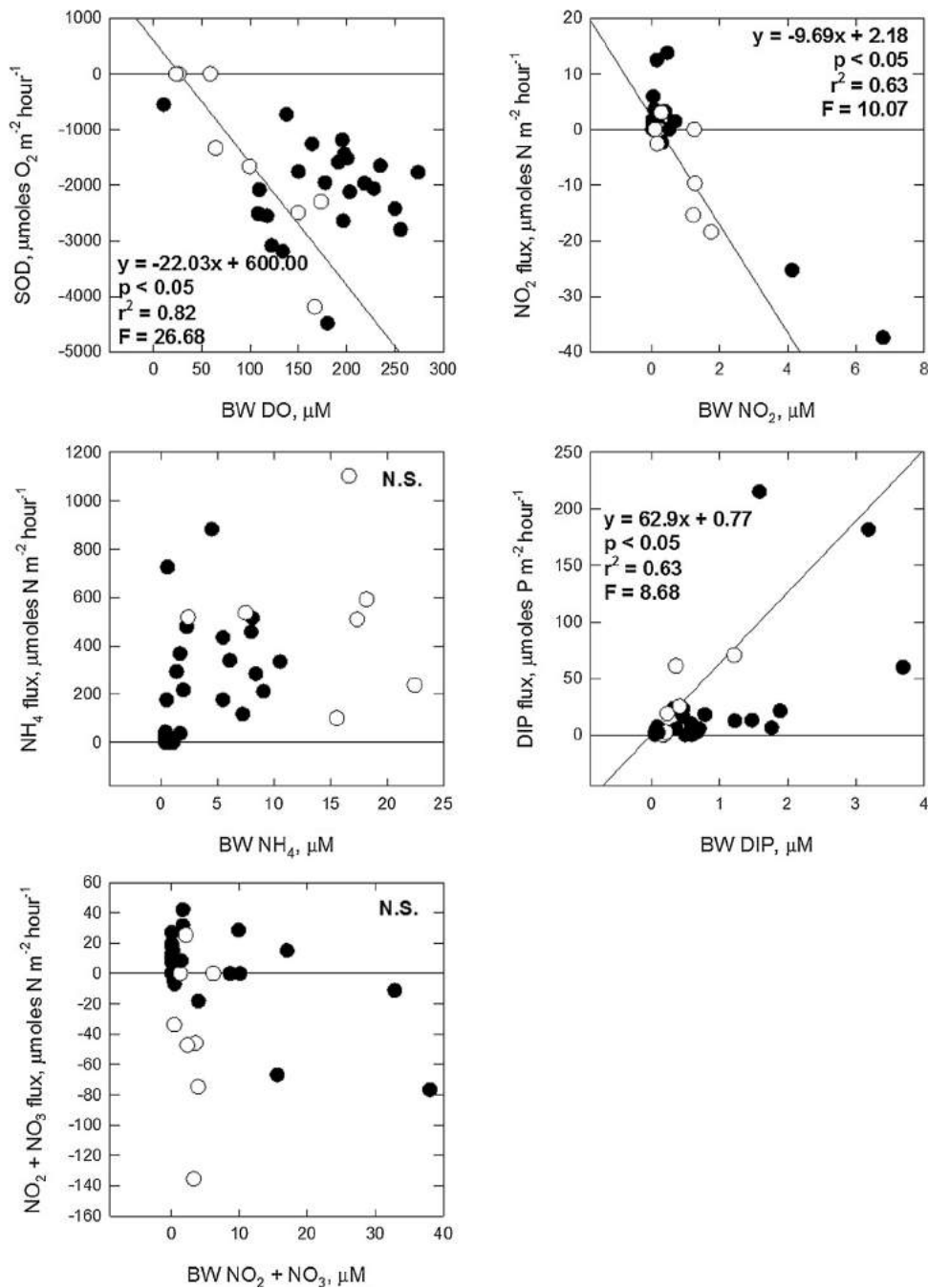
**Fig. 5.** Flux measurements computed from sediment core incubation experiments under no aeration (experimental phase) and aeration (recovery phase) conditions. Incubations where flux rates could not be determined are identified as not interpretable (N.I.). The ratio of BOD values (integrated for the water column;  $\mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$ ) to SOD measurements are reported under the bars for all SOD graphs. Zeroes represent both fluxes and depth-integrated BOD values.

nitrate–nitrite, thus reducing denitrification to dinitrogen gas, increasing ammonia flux to the surface water, and creating a feedback that helps sustain eutrophication. This mechanism was later used to explain non-linear restoration trajectories of estuaries where nutrient management had occurred, indicating possible hysteresis and regime shifts to a new system state where nutrients are more efficiently recycled (Kemp et al., 2005). Moreover, anoxia is known to substantially increase ammonium desorption from marine sediments (Morse and Morin, 2005). Hypoxia and anoxia thus contribute significantly to how efficiently enriched coastal waters recycle and retain nutrients (Fisher et al., 1982).

In shallow water, sediment biogeochemical processes are a major contributor to the ecosystem response to changes in dissolved oxygen concentrations. For example, at Station 1-F the ratio of sediment oxygen demand to integrated water column respiration ranged from 0 to 0.68. Under oxygen-depleted conditions, the accumulation of sulfidic minerals and other highly reduced compounds occurs at an accelerating pace (Katsev et al., 2007), while the absence of benthic communities eliminates biotic irrigation of sediments, preventing deep penetration of oxygen which is otherwise restricted by diffusion to the top few millimeters (Diaz and Rosenberg, 1995). The net effect of these

changes is the emergence of a highly reactive sediment surface with a high oxygen demand, some of which is biotic in nature, but also substantially driven by abiotic oxidation (Wang, 1980; Adams et al., 1982). These patterns are consistent with our observations in Rock Creek, where sediment oxygen demand was high during the recovery period when DO in the overlying water was again available for uptake.

There are profound consequences of these processes for nutrient cycling. Oxygen is required for ammonium oxidation, but hydrolysis of organic nitrogen that produces ammonium occurs in both oxic and anoxic conditions, allowing remineralization of organic matter in the absence of oxygen (Soetaert and Middelburg, 2009) and accumulation of ammonium loosely bound to sediment organic material or in porewater (Seitzinger et al., 1991). Under nitrate-poor and/or oxygen-limited conditions, the oxidation step ultimately controls removal of excess N from the system as  $\text{N}_2$  gas (i.e., nitrification; e.g. Kemp et al., 1990). Based on the results of our measurements of sediment fluxes and bottom water nutrient concentrations, hypoxia created in Rock Creek during this experiment appears to have caused a sudden lack of availability of nitrate and nitrite to fuel denitrification in the sediments at stations closest to the aerators, even as ammonium



**Fig. 6.** Flux measurements plotted with bottom water nutrient concentrations for the Rock Creek study (open circles) as well as seven other estuaries with comparable depth, temperature, and salinity conditions (Boynton and Bailey, 2008; <http://www.gonzo.cbl.umces.edu/data.htm>). Rock Creek measurements are from experimental (no aeration) and recovery (aeration) phase sampling. Significant linear regressions are included for oxygen,  $\text{NO}_2$ , and DIP for Rock Creek data. N.S. in upper right indicates "not significant".

fluxes to the water column were measured under hypoxic conditions suggesting that nitrification was oxygen-limited. Theoretically, denitrification and nitrate fluxes should be close to zero. Under more permanent anoxic conditions, we would expect to have measured this response, but in the case of the simulated values the availability of nitrate from the overlying water persisted for enough time when the aerators were turned off to permit continued nitrate influx and associated direct denitrification. Dissimilatory nitrate reduction to ammonium (DNRA), which we did not directly measure or model, would also enhance  $\text{NH}_4$  production and  $\text{NO}_3$  uptake under low-oxygen/sulfidic

conditions (An and Gardner, 2002; Brunet and Garcia-Gil, 1996). Modeled output for Station 2-F produced patterns that were in conflict with our flux measurements. In this instance, interpolated bottom water chemistry used for simulation purposes may not have replicated the rapid response of the system to de-oxygenation, and the model-derived estimates of organic matter deposition may not have been representative for this site. These results emphasize the often-complex interactions between temperature, nitrate and organic matter availability, and oxygen levels in regulating denitrification (Nowicki, 1994; Cornwell et al., 1999), and provide insight to how future experimental designs could be

**Table 1**  
Characteristics of coring stations including depth, light, salinity, dissolved oxygen and sediment nutrient and chlorophyll (total, phaeophytin, & active chl-a) to highlight conditions where net sediment–water nutrient fluxes were measured.

Station	Total depth (m)	Secchi (m)	Depth at 1% light (m)	Bottom salinity	Bottom DO ( $\mu\text{M}$ )	PN (%)	PC (%)	PP (%)	Total chl-a ( $\text{mg m}^{-2}$ )	Phaeophytin ( $\text{mg m}^{-2}$ )	Active chl-a ( $\text{mg m}^{-2}$ )
7/17/2012; Experimental phase (no aeration)											
1-F	2.3	0.6	1.63	8.48	58.8	0.440	4.330	0.083	169.04	201.73	56.97
2-F	2.4	0.8	2.16	8.59	26.3	0.350	3.840	0.059	119.41	159.15	30.99
4-F	3.0	0.5	1.36	8.61	23.4	0.030	0.260	0.004	102.66	119.25	36.41
9-F	2.1	0.7	1.89	8.71	173.1	0.190	1.760	0.062	201.89	235.85	70.86
8/01/2012; Recovery phase (aeration)											
1-F	2.0	0.6	1.63	9.02	99.4	0.510	4.750	0.096	164.62	197.68	54.80
2-F	2.3	0.5	1.36	9.13	166.9	0.510	4.660	0.092	167.53	202.93	54.79
4-F	1.7	0.4	1.08	9.12	149.7	0.030	0.290	0.004	101.03	104.41	43.02
9-F	1.9	0.6	1.63	9.68	64.4	0.150	1.720	0.050	185.41	222.12	62.01

optimized to meet the model input and validation data needs of the numerical modeling efforts.

Release of phosphate was rapid and particularly noticeable at those stations adjacent to the aeration system. Increased sediment fluxes of P under anoxic conditions is a widely acknowledged phenomenon that is largely a result of the release of P sorbed to ferric iron (e.g., Sundby et al., 1992), when ferric iron is reduced and then bound in ferrous sulfide as a consequence of the activity of iron-reducing and sulfate-reducing bacteria ubiquitous in organic sediments (e.g., Cornwell and Sampou, 1995). The continued supply of ammonium and increase in P fluxes under oxygen-depleted conditions support a more parsimonious estuarine nutrient budget in the sense that inputs of N and P are recycled with high efficiency from the sediments to the water column. At the short time scale evaluated in this study, this phenomenon was clearly present at several stations in Rock Creek during our manipulations.

During the no-aeration phase of this study, water-column concentrations and sediment–water nutrient and oxygen fluxes responded rapidly to altered oxygen concentrations at sites near the aerators. In fact, it was clear that bottom water column nutrients responded almost simultaneously to those changes observed from sediment core incubation measurements. Many of these responses were expected, such as elevated bottom water ammonium and phosphate concentrations accompanied by increased sediment–water fluxes under anoxic conditions (Testa and Kemp, 2012), reduced nitrate–nitrite concentrations via (presumably)  $\text{NO}_x$  reduction and nitrification inhibition (Kemp et al., 1990), and reduced sediment and water column biological oxygen demand as aerobic respiration of organic material was

inhibited by a lack of dissolved oxygen in the bottom waters (Sampou and Kemp, 1994). These tight relationships between sediment and water column processes describe a close coupling between metabolic activity in the two habitats, which is in some part due to the shallow nature of Rock Creek, as well as its relatively long residence time.

Surface chlorophyll-a concentrations measured at a station in the vicinity of the aerators were at levels indicative of a phytoplankton bloom ( $>450 \mu\text{g L}^{-1}$ ) during the experiment with aeration off (Fig. 4, Station 2-2). We speculate that this is likely a function of the changed hydrodynamic conditions around the aerators, although a lack of replication of the experiment limits our confidence in this interpretation. Where surface water was once subducted to light limited depths under aerated conditions (only 1% of surface light available at 1–2 m, Table 1), the lack of water column mixing during the experiment likely allowed the plankton community to remain closer to the surface light source to maximize growth rates and the accumulation of phytoplankton biomass, especially considering that inorganic nutrient levels are high in Rock Creek (e.g., DIN  $>14 \mu\text{M}$ ). The role of mixing in inhibiting phytoplankton growth and blooms has been well documented in the Delaware estuary, where the surface mixed layer extends deeper than the light compensation depth (Pennock, 1985; Harding et al., 1986). Huisman et al. (2004) provide strong evidence in the laboratory and in field studies that vertical mixing in the water column can favor green algae and diatoms over cyanobacteria. Controlling factors are turbulent diffusivity as a function of water depth and species-specific cyanobacteria buoyancy. Although the physical effects of engineered destratification on the water column are well understood, ecosystem effects

**Table 2**  
Modeling results performed to estimate rates of denitrification and nitrification not measured in the sediment core incubations. For comparison, modeled estimates and measured values of  $\text{NH}_4$ ,  $\text{NO}_3\text{--NO}_2$ ,  $\text{PO}_4$  and DO fluxes are also provided. Measured flux values are italicized. Negative values indicate fluxes into the sediment; positive values indicate flux out of the sediment. N.I. indicates flux results were not interpretable. All rates are in  $\mu\text{M m}^{-2} \text{h}^{-1}$ . Denitrification rates are measured as  $\text{N}_2\text{--N}$ .

Station	Date	$\text{NH}_4$ flux	$\text{NO}_3\text{--NO}_2$ Flux	Denitrification	Nitrification	$\text{PO}_4$ flux	DO flux
1-F							
No aeration	7/17/2012	562	<i>517</i>	–19.4	<i>0</i>	21.4	1.1
Aeration	8/1/2012	413	<i>592</i>	–30.6	<i>–46.0</i>	65.7	34.9
2-F							
No aeration	7/17/2012	535	<i>509</i>	–85.7	<i>0</i>	87.2	1.7
Aeration	8/1/2012	428	<i>1102</i>	–4.9	<i>–135.5</i>	50.9	46.0
4-F							
No aeration	7/17/2012	252	<i>N.I.</i>	–5.6	<i>–33.9</i>	7.4	1.7
Aeration	8/1/2012	205	<i>100</i>	–25.5	<i>–74.8</i>	41.7	16.3
9-F							
No aeration	7/17/2012	535	<i>535</i>	–9.7	<i>25.2</i>	32.1	22.4
Aeration	8/1/2012	390	<i>237</i>	–3.1	<i>–47.2</i>	39.9	36.7

and nutrient impacts are less well characterized (e.g., Conley, 2012). In lakes and reservoirs where destratification has been practiced for over 70 years, water quality improvements have been mixed. Cooke et al. (2005), in a review of destratification performance, report inconsistent improvements to chlorophyll-*a* concentrations and Secchi disk depth even when minimum mixing criteria are met. Hanson and Austin (2012) analyzed 35 years of water quality data from a lake near Minneapolis, Minnesota that had undergone destratification, including a two-year period where aeration had been turned off. Although destratification clearly prevented anoxia at the lake bottom and reduced internal phosphorus loading, heavy external nutrient-loading from storm-water prevented improvements in surface water quality. In a global sense, therefore, site-specific context constrains destratification as a tool for water quality improvement. Better understanding of these ecological and hydrological constraints would help to inform the large-scale effect destratification could have on ecosystem function.

As the history of this destratification system demonstrates, there are site-specific circumstances that may merit use of this technology. However, widespread applicability of destratification to remediate cultural eutrophication at large scales in estuarine environments should not be inferred from the findings of this study. Managing the symptoms of eutrophication, in this case hypoxia, by relying solely on destratification leaves impacted aquatic systems vulnerable and dependent on long term support of communities; reliant on engineered infrastructure to maintain a desired water quality goal. Discussion of the application of large-scale geo-engineering aeration and destratification projects to mitigate estuarine hypoxia has occurred elsewhere in the literature (Conley et al., 2009b; Conley, 2012; Stigebrandt and Gustafsson, 2007), and has highlighted the need to treat underlying causes of impaired coastal water quality. We hope the findings presented here of how one ecosystem responds to alternating oxic and hypoxic bottom waters will provoke a shift in research to the study of processes and mechanisms that control recovery of ecosystems following restoration and management actions. Nixon (2009) provided a definition of “oligotrophication” as a decrease in the rate of supply of organic matter to a system, calling on the community to recognize that an emphasis on water column nutrient and chlorophyll-*a* concentrations focuses attention on the symptoms of this process rather than the mechanisms that must be reversed to encourage restoration. The results of this study suggest the same. We must determine what factors control the processes that have an impact on both eutrophication and oligotrophication. Indeed, many of the modeling efforts done to date have focused on reproducing the eutrophication process, while fewer have examined the dynamics of oligotrophication (Soetaert and Middelburg, 2009; Boynton et al., 2014). Describing and quantifying the relationships between carbon production, heterotrophic respiration, sediment metabolism, nutrient cycling, and bottom water DO concentrations are critical to these new studies.

This study's ecosystem scale manipulation of oxygen and subsequent documentation of the biogeochemical response in the water column and sediments represents an early attempt to carry out the type of experiments that are critical to better understand the way that coastal waters respond to changes in oxygen. Admittedly, this study does not encompass the spatial or temporal scales that are of concern to large scale TMDL restoration efforts. However, our initial findings provide a description of biogeochemical responses at the km scale, with a sampling of sediment and water column variables at a spatial intensity greater than many studies of these processes. Because eliminating hypoxia that is produced as a result of eutrophication is a goal of most nutrient management efforts, our study informs our understanding of

estuarine ecosystem oligotrophication. We identify the most critical findings of our experiment as the large spatial extent to which the aerators affect bottom water oxygen concentrations. Clearly, the engineered re-aeration of Rock Creek was effectively designed to ameliorate low oxygen conditions, as is indicated by the changed relationship between dissolved oxygen concentration and distance from the aerator zone. However, our study adds to this general finding by exposing the accompanying change in sediment and water column chemistry that occurs when shifting from anoxic/hypoxic conditions to oxic bottom water conditions.

Our results suggest the potential for a regime shift scenario in estuarine systems where hypoxic conditions prevail. In this case, sediments are subject to oxygen-limitation, reducing the probability of coupled nitrification–denitrification and dampening the capacity of the ecosystem to remove incoming nitrogen inputs. Whether the existence of this feedback will lead to behavior consistent with hysteresis when the system is subjected to reduced nutrient inputs, as has been suggested by others, remains a key question in our field (e.g., Scheffer, 1998; Scheffer et al., 2001; Mayer and Rietkerk, 2004; Kemp et al., 2009; Wang et al., 2012). That the metabolic processes in the sediments suspected of controlling this behavior responded quickly to re-oxygenation in our experiment provides an intriguing, small window into these dynamics. Conley et al. (2009a) review this concept of thresholds for estuarine hypoxia and emphasize the positive feedbacks that can retain biogeochemical conditions favoring eutrophication.

Our study is far from the comprehensive experimental framework we would idealize to answer these questions. Key rate processes were not measured (e.g., primary production, denitrification, nitrification), we have no documentation of the functional diversity of the bacterial community, and we were unable to ask questions related to time lags, seasonal variability, or the effect of climate effects such as precipitation or wind. Because the observations described here leveraged a monitoring effort with alternative goals, future efforts would benefit from improved experimental design and replication with an emphasis on the oxic–anoxic transition. More frequent sampling of the system during baseline (aeration) conditions may be warranted to document diurnal fluctuations. We also did not capture the transitions through alternate terminal electron acceptors (Froelich et al., 1979; Zopfi et al., 2001) that would have occurred in the water-column during the onset of anoxia during the experiment. However, we did document that shallow estuarine sediments are remarkably plastic in their response to environmental conditions, changing the magnitude and direction of rate processes rapidly. We also identified that destratification of the water column at one localized area can impact dissolved oxygen concentrations across a large spatial scale. In addition to future efforts that might attempt a more exhaustive experimental study, we are encouraged that coupling these findings to a modeling framework would enable us to explore the various ways that these metabolic reactions are connected. In this way, we might learn from the optimization efforts of our wastewater engineer colleagues, configuring our numerical models and experiments for multiple optimization objectives. As we have explored through our preliminary experimental and modeling results here, optimizing denitrification may involve more than the re-introduction of bottom water DO to impacted estuaries via reductions in nutrient loads. In these “aerated” conditions, should bottom water nitrate or organic matter also be reduced, there is the potential that denitrification could again be limited (Cornwell et al., 1999).

The early mesocosm experiments of Nixon et al. (1986), Twilley et al. (1985), and Petersen et al. (1997) focused attention on the role of increasing nutrients on subtidal and lagoon ecosystems. What is called for now are more experiments in line with the one



described here, experimentally manipulating nutrients, oxygen, light, or sediment nutrient concentrations and improving measurement replication to enable us to ask questions that will inform our understanding of how coastal waters will respond to management efforts to promote oligotrophication.

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