PRIMARY RESEARCH PAPER

Water column oxygen demand and sediment oxygen flux: patterns of oxygen depletion in tidal creeks

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Abstract Low dissolved oxygen (DO) levels often occur during summer in tidal creeks along the southeastern coast of the USA. We analyzed rates of oxygen loss as water-column biochemical oxygen demand (BOD_5) and sediment oxygen flux (SOF) at selected tidal creek sites monthly over a 1-year period. Ancillary physical, chemical and biological data were collected to identify factors related to oxygen loss. BOD_5 rates ranged from 0.0 mg l^{-1} to 7.6 mg l^{-1} and were correlated positively with organic suspended solids, total suspended solids, chlorophyll a concentrations, temperature, and dissolved oxygen, and negatively with pH and nitrate + nitrite. SOF rates ranged from 0.0 to 9.3 g O_2 m^{-2} d^{-1}, and were positively correlated with temperature, chlorophyll a, and total suspended solids, but negatively with dissolved oxygen. Both forms of oxygen uptake were seasonally dependent, with BOD_5 elevated in spring and summer and SOF elevated in summer and fall. Average oxygen loss to sediments was greater and more variable than oxygen loss in the water column. Oxygen deficits at three of five locations were significantly related to BOD_5 and SOF, but not at two sites where ground water discharges were observed. Correlation and principal component analyses suggested that BOD_5 and SOF responded to somewhat different suites of environmental variables. BOD_5 was driven by a set of parameters linked to warm season storm water inputs that stimulated organic seston loads, especially chlorophyll a, while SOF behaved less strongly so. Runoff processes that increase loads of organic material and nutrients and ground water discharges low in dissolved oxygen contribute to occurrences of low dissolved oxygen in tidal creeks.

Keywords Dissolved oxygen · BOD · Sediments · Tidal creeks

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Introduction

Tidal creeks along the coast of the southeastern United States periodically experience low,

sub-saturating dissolved oxygen (DO) levels (Lerberg et al., 2000; Mallin et al., 2004), possibly related to anthropogenic inputs. Nutrient loading often drives an increased demand for oxygen (National Research Council, 2000, Mallin et al., 2006). Nutrient cycling and interactions among metals and sediments are heavily influenced by oxygen consumption or uptake (Medine et al., 1980). Toxic trace elements may also become a greater threat when DO levels are low. Some creeks also host periodic algal blooms (Mallin et al., 2004), which likely affect oxygen demand rates. Extreme oxygen consumption leading to hypoxia (<2 mg l^{-1} of oxygen) and anoxia can reduce available habitat for fish and other aquatic life and lead to mortality of sessile organisms. Dissolved oxygen concentrations integrate production and consumption processes, providing information about the balances of chemical, biochemical, and biological processes and, more generally, the ecological health of tidal creek ecosystems.

Processes that reduce oxygen concentrations in tidal creek ecosystems may be partitioned into those occurring in the water column and those associated with the substrata. Oxygen consumption in the water column is measured as Biochemical Oxygen Demand (BOD), a measure of the molecular oxygen (mg l^{-1}) utilized during a specific incubation period (5 or 20 days to give BOD_5 or BOD_{20}, for the biochemical degradation of organic material and the oxygen used to oxidize reduced forms of nitrogen, respectively) (Eaton et al., 1995). Oxygen consumption in the sediments is commonly measured as sediment oxygen demand (SOD). SOD is comprised of biological sediment oxygen demand (BSOD) and chemical sediment oxygen demand (CSOD). BSOD is dominated by aerobic heterotrophs that utilize organic material as an energy source, and tends to occur close to the sediment surface or proximal to macrofauna burrows owing to diffusivity constraints (Middelburg et al., 2005). CSOD occurs farther from the sediment–water interface in a hypoxic–anoxic region where anaerobic bacteria degrade organic matter releasing reduced compounds that react with molecular oxygen (Rounds & Doyle, 1997). SOD can be a significant percentage of the total oxygen uptake in aquatic systems (Caldwell & Doyle, 1995; Rounds & Doyle, 1997; Middelburg

et al., 2005). However, other processes complement diffusive oxygen fluxes. Respiration by macrobenthos can drive significant oxygen utilization by substrate communities (Hopkinson et al., 1991). Bioturbation and irrigation of the substrata can also drive significantly enhanced exchange rates of solutes, including oxygen and reduced compounds (Christenson et al., 1987). Water pumping by transient pressure gradients (Huettel & Gust, 1992) and discharges of groundwater can also contribute to oxygen fluxes across the sediment–water interface (Simmons, 1992). For these reasons sediment oxygen flux (SOF) is a more appropriate term for the effects of substrate processes on water column DO concentrations than sediment oxygen demand (SOD).

Water quality monitoring of tidal creeks in New Hanover County, North Carolina, USA, since 1993 (Mallin et al., 1998; 2000; 2004) has identified periodic low DO levels as a concern in these ecosystems, which support important biological and recreational functions, including as primary nursery areas for many species of fishes. DO levels in these creeks, particularly the upper reaches, were frequently below 5.0 mg l^{-1}, the North Carolina standard for these waters, and below saturating values for the observed temperatures and salinities. These observations indicated that primary production and aeration were insufficient to maintain oxygen concentrations at saturating levels throughout time and space in these creeks and that oxygen consuming processes were important. The objectives of this research were to determine the relative magnitudes of oxygen consumption by water column processes (measured as BOD_5) and substrate processes (measured as SOF), to compare the measured rates with other physical, chemical, and biological data collected concurrently by the University of North Carolina Wilmington/New Hanover County Tidal Creeks Program, and to identify factors controlling oxygen consumption in these ecosystems.

Materials and methods

Site description

Five study sites were chosen in Futch Creek, Hewletts Creek and Pages Creek, located in New

Hanover County, North Carolina, USA (Fig. 1). Sites were chosen to reflect a range in the values of dissolved oxygen levels, chlorophyll *a* concentrations and nutrient (nitrogen and phosphorus) loading, based on data collected between 1993 and 2001 (Mallin et al., 1998; 2004). All sites experienced semi-diurnal tides with up to ~1.1 m amplitude.

Futch Creek has few algal blooms, low fecal coliform levels (Mallin et al., 2000) and numerous natural springs. Study site FC-17 (N 34.30378 W 77.76422), was in the upper southern branch, which has shallow surface feeder creeks (<30 cm deep at low tide) and a small upstream spring (Mallin et al., 1996). Its drainage was mostly rural, with a golf course nearby. The mouth of Futch Creek was dredged in 1995–1996 to promote flushing and improve microbiological water quality. Following the dredging lower portions of the creek were re-opened to shell fishing (Mallin et al., 2000).

Hewletts Creek drains a heavily developed watershed that receives high nutrient loading and experiences periodic algal blooms and has low dissolved oxygen levels in warmer months (Mallin et al., 2004). Portions of the creek run along roadways and receive run-off from golf courses and suburban areas. Study sites in this creek were HC-3 (N 34.19023 W 77.85083), adjacent to a private dock in the main channel of the creek, and HC-SBPGR (N 34.19025 W 77.86472), an anthropogenically impacted site on the creek's southern tributary.

Study sites in Pages Creek (generally not highly impacted by nutrient loading) were located in areas that experienced the highest levels of fecal coliforms, chlorophyll *a* and nutrients in that creek (Mallin et al., 1998). Both of the sites chosen

Fig. 1 Tidal creek study sites in coastal New Hanover County, North Carolina, USA
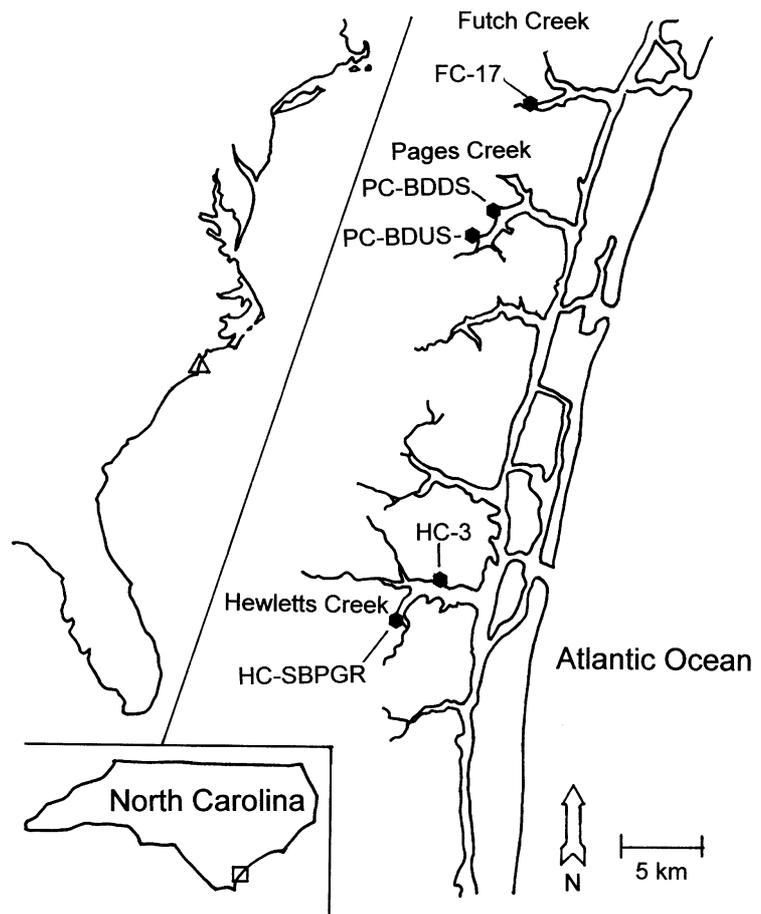
(PC-BDDS and PC-BDUS) have experienced periodic hypoxia in the summer months and rare algal blooms (Mallin et al., 1998). The downstream site, PC-BDDS (N 34.28143 W 77.79417), was adjacent to a private dock, and the upstream site PC-BDUS (N 34.27732 W 77.80153) was adjacent to a boat dock, near a natural spring, and along a tributary draining a residential neighborhood. The upper branches of Pages Creek have experienced high sedimentation due to runoff and development (Mallin et al., 2004).

Dissolved oxygen fluxes

Biochemical oxygen demand (BOD_5) was measured in duplicate water samples collected in one-liter Nalgene[TM] bottles between 6 and 9 AM (local) on the incoming tide at each site once each month between July, 2001 and August, 2002. Collection bottles were iced in darkened coolers and brought to the laboratory for analysis within six hours. Samples were processed using the 5-day BOD test described by Eaton et al. (1995), utilizing DO readings in 300 ml BOD bottles at the beginning and end of the incubation period. Dissolved oxygen levels were measured in mg l^{-1} with a YSI Model 57 dissolved oxygen meter (precision of ± 0.1 mg l^{-1}), with salinity corrections made as needed. BOD_5 was reported as mg oxygen consumed liter^{-1} d^{-1}, with a corresponding precision of ± 0.04 mg l^{-1} d^{-1} (Laws, 1993).

Sediment oxygen flux measurements were made using opaque benthic chambers deployed sub-tidally on the rising tide at each study site each month between July, 2001 and August, 2002. This in situ approach was used in preference to core sampling and incubation techniques as it minimized disturbance artifacts and permitted operation of natural processes that might affect SOF, and followed techniques used to measure benthic primary production and respiration in other coastal habitats (Cahoon & Cooke, 1992; Cahoon et al., 1993). Chamber placements deliberately avoided visible macrofauna and groundwater discharges, but not less obvious infauna and slower seepages. Chambers were made of 16 cm diam PVC pipe sections 26 cm long with beveled bottom edges and a 2 cm diam opening on the side to permit chamber placement without compression-driven water discharges around the rim, as described by Cahoon (1996). The opening was stoppered after insertion into the sediment to a depth of 5 cm and withdrawal of initial samples. Whirling cup rotors used the natural flow of the creek to drive slow stirring (<15 rpm) in the chamber in proportion to external flows as slow as 0.02 m s^{-1} (Cahoon, 1988), allowing for continual mixing and thus uniform DO concentration within the chambers. Clear 0.3 cm diam PVC tubing inserted into the side of the chamber allowed for extraction of water samples. Initial and final samples were extracted from each chamber into glass 60 ml BOD bottles using large syringes. Final samples removed ~1.5% of chamber volume. A 2-h time span was allowed between extraction of initial and final samples (Rounds & Doyle, 1997). Collected samples were fixed in the field with Winkler reagents (Strickland & Parsons, 1972), kept on ice and brought back to the laboratory. Although efforts were made to avoid contamination of DO samples by air bubbles, limited visibility sometimes allowed sample withdrawal errors and air bubbles in the final samples. Data from these samples were not used in subsequent calculations or analyses. Laboratory analyses of triplicate water samples from SOF chambers were conducted within 48 h of collection using Winkler titrations (precision = ± 0.06 mg/l) and calculation procedures for non-standard volumes (Strickland & Parsons, 1972) in order to establish a rate of oxygen flux. Individual rates were calculated for each of the three chambers at each study site as g O_2 m^{-2} d^{-1}. Based on the precision of the Winkler titration technique and the dimensions of the sampling devices, precision of SOF measurements was approximately ± 0.14 g O_2 m^{-2} d^{-1}

Suspended sediments were analyzed in duplicate one-liter water samples collected at all study sites monthly. Total and organic suspended solids (TSS and OSS) were determined in duplicate by filtration and gravimetry following drying and combustion procedures, respectively. Sediment samples were collected in the creek beds after collecting water samples and deploying benthic chambers at each sampling time and site, taking care not to disturb the chambers. Sediment cores (10 cm and ''fluff layer'') were taken using 8 cm diam PVC pipe. For the purposes of this study

"fluff layer" was defined as the top few centimeters of substrate that, when cored, were different in color and texture than the remaining cored sediment and were more easily resuspended. Sediment core samples were frozen for later analysis. Sediment organic content and grain size were analyzed for samples taken in July and October (2001) and January and May (2002). Percent organic content of sediments in well-mixed sub-samples of thawed sediment was determined by gravimetry following drying and combustion procedures. Grain size analyses were also conducted using sediment cores that were thawed, well mixed, heated and treated with a 30% hydrogen peroxide solution to oxidize organic matter before analysis (Folk, 1980). Grain size distributions were then determined with an LS 230 Beckman Coulter Particle Sizer.

Water quality parameters

Nutrient and chlorophyll *a* data were obtained by the New Hanover County Tidal Creeks program (website: http://www.uncwil.edu/cmsr/aquatic-ecology/TidalCreeks/Index.htm) for all sites at high tide on the same day that oxygen demand sampling and measurements were conducted. Dissolved oxygen (mg l^{-1}), pH, temperature (°C), salinity and conductivity (mS/cm) were measured using a YSI Model 85 meter prior to placing benthic chambers in the water column. Flow velocity measurements were taken at each site using a Marsh-McBirney Flo-Mate Model 2000 flow meter with precision of ± 2% and a range of –0.15 to 6 m s^{-1}. Daily rainfall data (24 h total @ 0700 local) were obtained from the National Weather Service Eastern Regional Headquarters website for the Wilmington International Airport, ~10 km from the study area (NOAA).

Statistical analysis

Normality tests, using PROC UNIVARIATE or the Shapiro-Wilk test, were conducted for all variables using JMP and SAS statistical software (SAS Institute, 1998). Variables that were not normally distributed were log transformed using a function of $\log_{10}(X + 1)$; variables that could not

be transformed to normality were analyzed by non-parametric tests. ANOVA tests (SAS) were conducted using log-normalized BOD$_5$ and SOF data to identify differences among sites. Pair-wise correlations among parameters were identified using Spearman's rank correlation procedure as appropriate for non-normal data sets. Principal component analysis of all independent variables was conducted using SAS, and the response variables BOD$_5$ and SOF, transformed to normality as necessary, were regressed against individual principal components. Significance levels for these analyses were set at $p < 0.05$.

Results

Site characteristics

Site characteristics for physical parameters, chlorophyll *a*, nutrients and suspended solids varied seasonally and among sites (Table 1). Mean DO concentrations were highest at the HC-3 study site (5.4 mg l^{-1}) and the lowest at FC–17 (3.5 mg l^{-1}). Hypoxic dissolved oxygen levels (<2 mg l^{-1} of DO) occurred at the FC-17 study site in September 2001, March, July and August 2002 and at PC-BDUS in October 2001. DO concentrations were generally highest in the winter months (Fig. 2). Mean chlorophyll *a* was highest at the HC-SBPGR study site (12.3 μg l^{-1}) and lowest at the HC-3 study site (2.5 μg l^{-1}). Algal blooms (>25 μg l^{-1} of chlorophyll *a*) occurred at the HC-SBPGR site in June and July of 2002. Mean salinity levels were highest at PC-BDDS (32.1) and lowest at FC-17 (9.0). In general flow speeds during sampling periods were greatest at the HC-SBPGR study site and lowest at PC-BDDS, with means of 0.12 m s^{-1} and 0.01 m s^{-1}, respectively. Nitrate concentrations at the FC–17 study site were high compared to other sites (mean = 64.4 μg N l^{-1}) and lowest at HC-3 (mean = 4.1 μg N l^{-1}). Overall mean concentrations were 58.0 μg N l^{-1} for ammonium and 17.6 μg P l^{-1} for orthophosphate. Ammonium and orthophosphate concentrations were highest at the PC-BDUS site, the lowest concentrations of ammonium occurred at HC-SBPGR (22.5 μg N l^{-1}), and the lowest concentration of orthophosphate oc-

Table 1 Characteristics of tidal creek study sites, July 2001–August 2002, as mean (s.d.)

Parameter	FC-17	HC-3	HC-SBPGR	PC-BDDS	PC-BDUS
Temp.	19.5 (4.1)	21.5 (6.5)	21.0 (6.9)	21.2 (6.8)	21.0 (5.5)
DO, mg l^{-1}	3.5 (1.7)	5.4 (2.1)	5.3 (2.3)	4.8 (1.9)	4.2 (1.9)
Salinity	9.0 (7.1)	25.5 (6.4)	15.5 (6.2)	32.1 (2.4)	20.9 (9.4)
pH	7.1 (0.4)	7.3 (0.4)	6.9 (0.3)	7.5 (0.5)	7.1 (0.4)
Flow, m s^{-1}	0.07 (0.05)	0.06 (0.03)	0.13 (0.06)	0.01 (0.01)	0.02 (0.02)
Chl a, mg l^{-1}	5.9 (5.0)	2.5 (1.9)	12.3 (24.8)	5.2 (4.2)	8.0 (6.0)
Nitrate, mg l^{-1}	64.4 (58.8)	4.1 (1.9)	10.4 (10.2)	11.9 (12.9)	10.0 (8.5)
Ammonium, mg l^{-1}	50.7 (78.2)	N/A	22.5 (10.5)	25.9 (11.1)	58.0 (48.3)
Ortho-PO$_4$, mg l^{-1}	14.7 (7.0)	6.9 (2.2)	10.6 (5.2)	11.3 (5.4)	17.6 (5.9)
TSS, mg l^{-1}	21.7 (17.3)	15.6 (9.0)	16.7 (13.2)	21.8 (10.2)	30.5 (21.0)
OSS, μg l^{-1}	2.7 (1.5)	2.0 (0.6)	2.4 (1.0)	2.2 (0.52)	3.4 (2.4)
Sed. % organic	4.4 (1.3)	3.7 (0.6)	18.3 (1.6)	13.8 (1.9)	2.8 (0.2)
Modal grain size, μm	144.7 (8.0)	164.0 (9.9)	10.0 (2.2)	10.6 (0.6)	175.5 (61.7)

DO = dissolved oxygen; Chl a = chlorophyll a; TSS = total suspended solids; OSS = organic suspended solids

Fig. 2 Dissolved oxygen concentrations for each study site, July 2001–August 2002
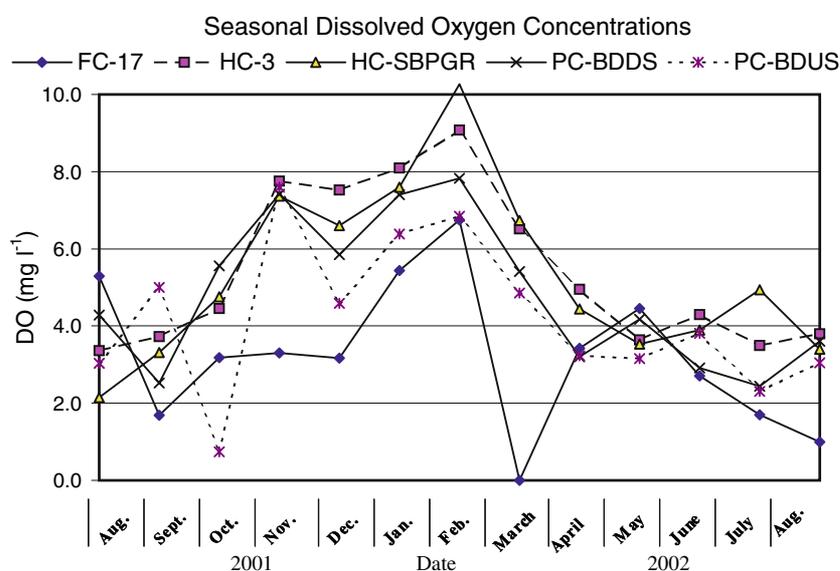
curred at HC-3 (6.9 μg P l^{-1}). The Tidal Creeks Monitoring Program did not analyze ammonium at the HC-3 study site, so these data were not available. Average DIN:DIP (dissolved inorganic N:ortho-P) ratios were highest at FC-17 (17.3) and lowest at PC-BDDS (7.2). TSS and OSS changed seasonally, with the highest levels occurring in the summer and spring months. Organic suspended solids comprised 15% of the total suspended solids measured in these tidal creek sites on average. TSS and OSS concentrations were highest at PC-BDUS, where mean TSS and OSS were 30.5 mg l^{-1} and 3.4 mg l^{-1}, respectively

(Table 1). Suspended solids were the lowest at HC-3, with means of 15.6 mg l^{-1} for TSS and 2.0 mg l^{-1} for OSS.

Sediment characteristics also differed among sites (Table 1). Modal grain size of bottom sediments changed very little over the sampling period. Modal sediment grain sizes at the FC-17, HC-3 and PC-BDUS study sites were coarser than modal grain sizes at other sites. The coarsest material, 175 μm fine sand, occurred at PC-BDUS. The finest modal grain size, 10.0 μm silty mud, occurred at HC-SBPGR. Organic percentages varied little over the sampling period.

Mean organic content of bottom sediments was highest at HC-SBPGR (18.3%) and lowest at PC-BDUS (2.8%).

Oxygen flux

Rates of five-day biochemical oxygen demand (BOD$_5$) for all sites over the entire sampling period varied from 0.0 mg l^{-1} to 7.6 mg l^{-1} (Fig. 3). Station mean rates ranged from 2.0 mg l^{-1} to 3.0 mg l^{-1} (Table 1). Overall mean BOD$_5$ rates did not differ significantly among study sites (1-way ANOVA, $F = 1.60$, df = 1,65, $p = 0.184$). The maximum rate of 7.6 mg l^{-1} occurred at the south branch study site in Hewletts Creek (HC-SBPGR) in June 2002 and the minimum rate of 0.0 mg l^{-1} was found at the mid-creek station (HC-3) in the lower part of Hewletts Creek in October 2001.

Rates of SOF for all study sites varied from 0.0 to 9.3 g O$_2$ m^{-2} d^{-1} (Fig. 4). Mean rates were highest at PC-BDDS (2.15 g O$_2$ m^{-2} d^{-1}) and lowest at FC-17 (1.16 g O$_2$ m^{-2} d^{-1}), but no site means were significantly different (1-way ANOVA on transformed SOF data, $F = 0.89$, df = 4,59, $p = 0.47$). The maximum rate of 9.3 g O$_2$ m^{-2} d^{-1} occurred in Futch Creek (FC-17) in July 2001 and the minimum rate of 0.0 g O$_2$ m^{-2} d^{-1} occurred a total of five times, at least once at each site except PC-BDUS, between November 2001 and April 2002.

Mean SOF rates were significantly greater than mean BOD$_5$ rates at all study sites when con-
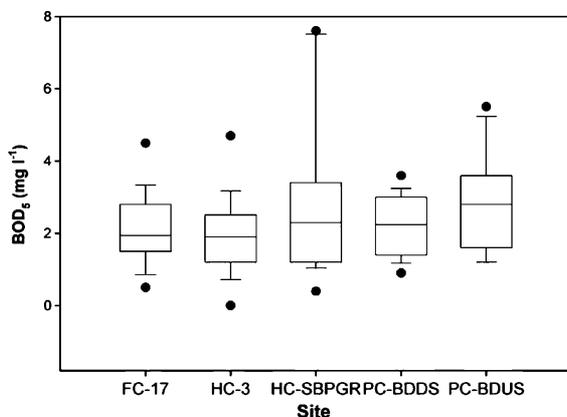
Fig. 3 Box plots of median, confidence intervals, and outliers for BOD$_5$ data for each site, July 2001–August 2002
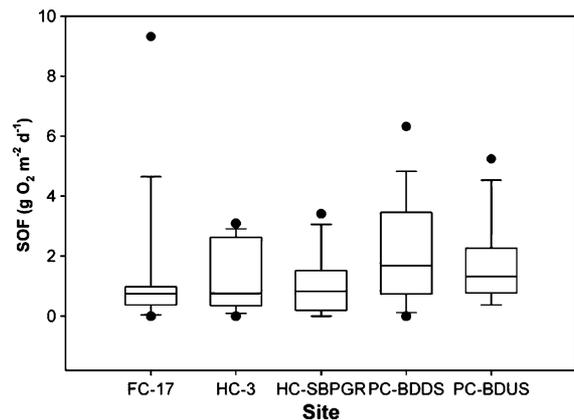

Fig. 4 Box plots of median, confidence intervals, and outliers for SOF data for each site, July 2001–August 2002

verted to common units (g O$_2$ m^{-2} d^{-1}) (Table 2). Coefficients of variation for BOD$_5$ and SOF rates were 0.61 and 0.92, respectively. SOF, therefore, was a larger but more variable sink for oxygen than BOD$_5$ (Fig. 5). Concurrent measures of BOD$_5$ and SOF were not significantly correlated ($r^2 = 0.005$, $F = 0.31$, df = 1,67, $p = 0.59$), suggesting that different factors controlled these oxygen sinks. BOD$_5$ rates were highest in spring and summer, and were positively correlated with temperature, chlorophyll a, total suspended solids, organic suspended solids and negatively with dissolved oxygen (Table 3a). In contrast SOF rates were higher in the summer and fall months (Fig. 5), and were positively correlated with temperature, chlorophyll a, and TSS, but negatively correlated with dissolved oxygen (Table 3a).

The effects of BOD$_5$ and SOF (g O$_2$ m^{-2} d^{-1}), on dissolved oxygen deficits (mg l^{-1}), defined as the difference between the 100% DO saturation level for the corresponding temperature and salinity (Strickland & Parsons, 1972) and measured DO concentrations at the tidal creek sites, were examined by plotting resulting values for each site and time (Fig. 6 a, b). Subsequent regression analyses showed that there were significant effects of BOD$_5$ ($F = 6.26$, df = 1,34, $p = 0.017$) and SOF ($F = 10.21$, df = 1,33, $p = 0.003$) on dissolved oxygen deficits at the HC-3, HC-SBPGR, and PC-BDDS sites combined, although there were no significant regressions for all five sites together. Multiple regression of dissolved oxygen deficits against

Table 2 Comparisons of mean BOD_5 and SOF rates (g O_2 m^{-2} d^{-1}) over the sampling period July 2001–August 2002; data are means ± standard deviation and results of 1-way ANOVA on log-transformed data

Study site	BOD_5	SOD	ANOVA
FC-17	0.14 ± 0.10	1.43 ± 2.65	$F = 42.2$, df = 1,23, $P < 0.0001$
HC-3	0.15 ± 0.07	1.31 ± 1.16	$F = 43.3$, df = 1,25, $P < 0.0001$
HC-SBPGR	0.26 ± 0.23	1.16 ± 1.16	$F = 56.8$, df = 1,26, $P < 0.0001$
PC-BDDS	0.19 ± 0.06	2.15 ± 1.93	$F = 28.1$, df = 1,26, $P < 0.0001$
PC-BDUS	0.27 ± 0.15	1.80 ± 1.54	$F = 61.5$, df = 1,24, $P < 0.0001$
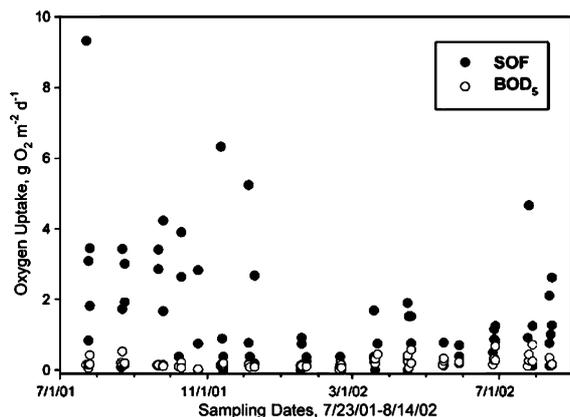
Fig. 5 Oxygen demand rates (BOD_5 and SOF) in common units for all sites, July 2001–August 2002

BOD_5 and SOF for the three sites, HC-3, HC-SBPGR, and PC-BDDS, yielded the following equation:

$$DO\,Deficit = 0.93 + 2.30(BOD_5) + 0.34(SOF) \quad (1)$$

The intercept and coefficients were all significant at $p < 0.001$, indicating that both BOD_5 and SOF were important in creating dissolved oxygen deficits at those sites. In contrast, there was no significant effect of BOD_5 or SOF on oxygen deficits at the other two sites, FC-17 and PC-BDUS. Significant groundwater discharges from springs in the vicinity of these two sites likely had a greater effect than BOD_5 or SOF on water column DO concentrations and deficits, as evidenced by occurrence of all the dissolved oxygen deficit values >4 mg l^{-1} at these two sites (Fig. 6a, b) and hypoxic oxygen concentrations in groundwater discharges from nearby springs (Douglas Parsons, UNC Wilmington Center for Marine Science, Wilmington, NC 28409, unpublished data).

Correlation analysis for all sites combined

Pair-wise correlation analysis revealed many significant associations among the independent and response variables in the data set pooled for all sites and the entire 14-month sampling period (Table 3a). BOD_5 was positively correlated with temperature, chlorophyll a, TSS, OSS, and dissolved oxygen. Chlorophyll a in turn was positively correlated with TSS, OSS, water temperature, dissolved oxygen, and cumulative rainfall over 24 h, 48 h and 72 h prior to sampling, and negatively correlated with pH. There was a significant positive relationship between SOF rates and temperature, chlorophyll a, and TSS, but a significant negative relationship between SOF and dissolved oxygen. Dissolved oxygen was positively correlated with chlorophyll a, pH, and BOD_5, but negatively correlated with temperature, OSS, TSS, and SOF.

The correlation matrix demonstrated that many variables co-varied in this data set, so it was inappropriate to try to identify cause-and-effect relationships from simple pair-wise analyses of the independent variables and BOD_5 and SOF. Principal Components Analysis (PCA) of the 16 independent environmental variables analyzed was conducted using SAS statistical software. Only the first four principal components were significant ($P < 0.05$), and they collectively explained 74% of the variability in the data set. Eigenvalues and percent variance for principal components 1 to 4 were 4.77 and 30%, 2.90 and 18%, 2.11 and 13%, and 2.05 and 13%, respectively. Principal component 1 was most strongly driven by the variables temperature, chlorophyll a, total suspended solids and rainfall (Table 3b). Principal component 2 was most strongly associated with nutrients and (negative) salinity.

Table 3 (a) Spearman's rho correlation matrix for all study sites using un-transformed data, (b) Weightings of independent variables in principal components axes 1–4

	SOF	BOD$_5$	Chl a	NH$_4$	NIT	PO$_4$	TSS	OSS	pH	Sal	OrgC	Temp.
(a)												
BOD$_5$	–0.08	1.00										
Chl a	0.35*	0.50*	1.00									
NH$_4$	0.12	–0.08	–0.09	1.00								
NIT	0.21	–0.25*	0.09	0.27	1.00							
PO$_4$	0.10	0.06	0.07	0.58*	0.48*	1.00						
TSS	0.26*	0.61*	0.56*	0.19	–0.08	0.20	1.00					
OSS	0.20	0.73*	0.66*	–0.04	–0.04	0.21	0.77	1.00				
pH	–0.09	–0.30*	–0.40*	0.06	–0.06	–0.02	–0.21	–0.41*	1.00			
Sal	0.11	–0.05	–0.15	0.12	–0.36*	–0.27*	0.19	–0.15	0.40*	1.00		
OrgC	0.12	0.04	0.30	–0.59*	–0.26	–0.35	–0.11	–0.06	0.18	0.09	1.00	
Rain$_{24}$	0.18	0.14	0.30*	–0.03	0.20	0.03	0.11	0.09	–0.23	–0.07	0.14	0.31*
Rain$_{48}$	0.18	0.06	0.34*	–0.12	0.38*	0.01	0.06	0.04	–0.23	–0.22	0.18	0.34*
Rain$_{72}$	0.14	0.21	0.36*	–0.10	0.29*	0.06	0.25*	0.17	–0.21	–0.18	0.00	0.51*
Temp	0.44*	0.33*	0.69*	–0.09	0.01	–0.07	0.59*	0.57*	–0.36*	0.10	0.02	1.00
DO	–0.34*	–0.28*	0.60*	0.12	–0.15	–0.08	–0.37*	–0.44*	0.33*	0.16	0.21	–0.68*

Parameter	PC1	PC2	PC3	PC4
(b)				
Depth	0.218	0.146	0.296	0.154
Temp	0.404	0.033	–0.197	0.067
(L)DO	–0.253	–0.107	0.219	0.034
pH	–0.187	–0.147	0.259	–0.049
Sal	0.109	–0.389	0.390	0.252
Cond	0.206	–0.364	0.318	0.226
(L)Chl a	0.342	–0.016	–0.310	0.067
(L)NH$_4$	0.069	0.320	0.221	0.419
(L)Nit	–0.005	0.482	0.187	0.040
(L)Phos	–0.063	0.360	0.068	0.324
(L)N:P	0.066	0.395	0.278	0.149
(L)TSS	0.310	–0.069	–0.129	0.343
(L)OSS	0.217	0.008	–0.336	0.302
(L)Rain24	0.351	0.071	0.204	–0.334
(L)Rain48	0.340	0.105	0.215	–0.360
(L)Rain72	0.352	0.140	0.158	–0.308

Asterisks denote correlations significant at $p < 0.05$

SOF = sediment oxygen flux, BOD$_5$ = 5-day biochemical oxygen demand, Chl a = chlorophyll a, NH$_4$ = ammonium, NIT = nitrate + nitrite, PO$_4$ = orthophosphate, TSS = total suspended solids, OSS = organic suspended solids, Sal = salinity, OrgC = organic carbon, Rain$_{24}$, Rain$_{48}$, and Rain$_{72}$ = cumulative rainfall in 24, 48 and 72 hours prior to sampling, respectively

Temp = temperature, DO = dissolved oxygen, Cond = conductivity, and N:P = dissolved inorganic nitrogen:orthophosphate

Principal component 3 was most strongly driven by salinity, (negative) chlorophyll a and (negative) organic suspended solids. Principal component 4 was most strongly driven by ammonium, phosphorus, suspended solids and (negative) cumulative rainfall totals. Measured values of BOD$_5$ and SOF were regressed against values of each principal component to determine which sets of independent variables controlled the two oxygen consumption variables, which were not correlated with each other. Regression analyses revealed significant relationships between BOD$_5$ and principal components 1 ($P < 0.0001$) and 3 ($P < 0.0001$): BOD$_5$ = 2.57 + 0.31 PC1 – 0.56 PC3. Values of BOD$_5$ increased with positive values of principal component 1, with a strong seasonal increase from winter to summer. Values of BOD$_5$ decreased with increasing values of

Fig. 6 (**a**) Dissolved oxygen deficits for each study site versus BOD_5. (**b**) Dissolved oxygen deficits for each study site versus SOF

chemical oxygen demand in the water column (BOD_5), oxygen uptake across the sediment–water interface (SOF), replacement of oxygenated surface waters by oxygen-depleted groundwater, and other factors not addressed in this study, such as respiration by nekton, e.g., deaths of large schools of menhaden in adjacent ICW waters during December, 2005, have been attributed to localized oxygen depletion (Richard Carpenter, N.C. Division of Marine Fisheries, pers. comm.) and macrobenthos, and advection of oxygen-depleted water from outside the tidal creeks. SOF frequently exceeded BOD_5 as a sink for dissolved oxygen, but not at all sampling times and locations. Average SOF for all locations and times was approximately 8 times higher than BOD_5 (1.58 vs. 0.21 g O_2 m^{-2} d^{-1}, respectively), but variability in SOF was substantially higher as well, creating some situations in which BOD_5 was the dominant oxygen sink. Thus, prediction and management of oxygen depletion must consider sediment oxygen consumption as well as other factors in these very shallow and well-flushed estuarine ecosystems.

Principal components analysis indicated that BOD_5 and SOF were controlled by different suites of environmental factors in these tidal creek ecosystems. BOD_5 responded positively to a combination of temperature, chlorophyll a, TSS, and OSS that may be viewed collectively as warm season characteristics that support higher organic seston loads. Tidal creeks in this area typically exhibited higher densities of organic suspended matter during the warm season, partly as a result of rainfall-driven runoff and partly as a result of increased phytoplankton production (Mallin et al., 2004; Johnson, 2005), so increases in water column oxygen demand are to be expected. Chlorophyll a biomass makes strong contributions to the BOD of a variety of fresh and brackish water bodies (Mallin et al., 2006). Measured values of SOF increased with higher values of principal component 1, which implied a temperature effect similar to that driving BOD_5, but SOF was also positively correlated with some of the seston indicators that were important in PC 1. These patterns suggested that BOD_5 rose immediately following runoff events and that SOF subsequently rose when plankton blooms depleted nutrient levels and their organic seston loads

principal component 3, and were lower in winter when chlorophyll a levels and organic suspended solid concentrations were lower. Regression analysis for SOF revealed a significant relationship with principal component 1 only ($P = 0.038$): SOF (inverse log-transformed to normality) = 0.57 – 0.01 PC1, representing a positive relationship between untransformed values of SOF and values of principal component 1. SOF increased with higher temperatures and was related to warm weather algal bloom formation and their expression as chlorophyll a (Table 3a), but in a different manner than BOD_5.

Discussion

Oxygen depletion in tidal creeks ecosystems can be attributed to a variable combination of bio-

settled to the bottom to become an organic source for SOF. Nutrient addition experiments have demonstrated that phytoplankton biomass responds rapidly (one day) to nutrient inputs in these tidal creeks, creating substantial chlorophyll *a* concentrations, particularly during late spring and summer (Mallin et al., 2004). Thus temperature, a variable frequently identified as a major determinant of respiration rates and, presumably, oxygen demand in tidal creek ecosystems, did drive water column and sediment oxygen fluxes in this study, but with different combined effects when other variables are considered. Chlorophyll *a* biomass and phytoplankton production are both positively correlated with water temperature in these creeks (Mallin et al., 2004; Johnson, 2005), providing a source of labile organic material (i.e., organic suspended solids) to stimulate water column BOD. Models of oxygen demand in these shallow ecosystems must therefore take into account a complex set of driving parameters and temporal variability in attempting to predict oxygen deficits.

The low dissolved oxygen content of groundwater discharged from natural springs in the vicinity of two of the study sites noted above suggested that groundwater inputs may have also reduced dissolved oxygen concentrations in tidal creek water, particularly at those two sites. The failure of a multiple regression model to predict dissolved oxygen deficits based on a combination of BOD_5 and SOF values at sites FC-17 and PC-BDUS suggested that inputs of oxygen-depleted groundwater by springs observed in those locations obscured the effects of these two oxygen sinks and yielded generally lower dissolved oxygen values at these sites. Submarine groundwater discharges are widespread in nearshore zones in aquatic ecosystems generally (Simmons, 1992; Roberts, 2002) so efforts to predict oxygen deficits when groundwater discharges are significant will have to consider this physical, site-specific factor in addition to BOD_5 and SOF. Groundwater discharges are likely driven by longer-term rainfall patterns, and thus may lag surface runoff events, so effects of rainfall may vary considerably among basins.

Comparisons of the results of this study with those of studies in other estuarine and shallow coastal habitats highlight several additional points (Table 4). The ranges and means of values we report here for relatively small, shallow tidal creeks of southeastern North Carolina, USA, are similar to those reported from most other estuarine systems, which are in turn generally somewhat higher than values from coastal ecosystems, where sediment organic loads are likely to be lower than in estuarine habitats, e.g., Hopkinson (1985), Cahoon & Cooke (1992). Concurrent measures of SOF and water column oxygen consumption in other ecosystems frequently show

Table 4 Values of sediment oxygen demand (SED) and water column oxygen consumption (WC; g O_2 m^{-2} d^{-1}; values originally reported in carbon units converted using respiratory quotient of 1.0) reported from estuarine and coastal marine habitats as overall mean values or ranges; "E"—estuary, "C"—coastal

Location/Country/Habitat	SED	WC	Reference
La Jolla, CA/USA/C	0.1–0.84	–	Hartwig (1978)
Ems-Dollard/Netherlands/E	0.1–4.7	–	van Es (1982)
Netarts Bay, OR/USA/E	0.17–0.51	–	Davis & McIntire (1983)
Bay of Fundy/Canada/E	0.70–1.85	–	Hargrave et al. (1983)
Chesapeake Bay/USA/E	1.5–3.1	3.2–19.1	Boynton & Kemp (1985)
Georgia Bight/USA/C	1.0–3.4	0.5–2.2	Hopkinson (1985)
Gulf of Trieste/Yugoslavia/C	1.02	3.36	Herndl et al. (1989)
Southwest lagoon/New Caledonia/C	0.93–1.92	–	Boucher & Clavier (1990)
Roskjilde Fjord/Denmark/E	2.5	3.8	Sand-Jensen et al. (1990)
Tomales Bay, CA/USA/E	0.06–0.15	–	Dollar et al. (1991)
Oosterschelde/Netherlands/E	1.57	–	Hofman et al. (1991)
Onslow Bay, NC/USA/C	0.07–1.01	–	Cahoon & Cooke (1992)
Chesapeake Bay/USA/E	0–1.64	–	Kemp et al. (1992)
Albufera, Majorca/Spain/E	0.52–1.55	–	López et al. (1995)
Chesapeake Bay/USA/E	0.33–0.85	–	Reay et al. (1995)
Gulf of Fos/France/C	0.08–1.4	–	Barranguet et al. (1996)
Gulf of Trieste/Italy/C	0.16–0.64	–	Bertuzzi et al. (1997)
Tidal creeks, NC/USA/E	0–9.3	0–0.68	This study
Tidal creeks, NC/USA/E	1.58	0.21	This study

relatively higher areal oxygen consumption in deeper water columns, e.g., Boynton & Kemp (1985), Herndl et al. (1989), Sand-Jensen et al. (1990), however, highlighting the role of shallow depth in the relative importance of SOF in this study. Many studies demonstrated the importance of temperature as a controlling factor for sediment and water column oxygen consumption. Analysis of our data showed that temperature, a strongly seasonal variable, covaries with other factors whose effects are more difficult to identify than temperature alone in larger, more complex, and less responsive ecosystems, such as large estuaries or coastal ocean waters, than in small and highly responsive tidal creek ecosystems.

Results from this study suggest that models for predicting BOD_5 and SOF must incorporate suites of environmental variables, particularly in small tidal creek ecosystems that are tightly coupled to both terrestrial and marine influences. It is especially difficult to create simple models to predict SOF rates because numerous variables need to be taken into account, there is high variability for all water quality parameters measured in dynamic tidal creek systems, and time lags between runoff events and SOF responses may obscure causal relationships.

Patterns of oxygen availability in tidal creek ecosystems also reflect oxygen inputs as well as the consumption processes discussed above. Aeration, inflows of oxygen-saturated rain water, and oxygenation by planktonic and benthic primary producers all contribute to oxygen content, and, as with consumption processes, are driven by event- and seasonal-scale variability. The magnitudes of these competing processes determine the extent in space and time of hypoxic events in tidal creek ecosystems. The relatively frequent occurrence of hypoxia in warmer seasons and after major rain events observed in these tidal creek ecosystems (Mallin et al., 1998, 2000, 2004), and, as noted by Mallin and Corbett (2006) in the Cape Fear River Estuary following flooding by Hurricanes Fran, Bonnie, and Floyd, which struck the southeastern U.S. in 1996, 1998, and 1999, respectively, highlights the importance of biologically driven respiration as a major control of water column oxygen levels. This study shows how important sediment oxygen fluxes, which

respond significantly to temperature and the consequences of rain events, can be in total ecosystem respiration.

Conclusions

Simultaneous measurements of Biochemical Oxygen Demand (BOD) and Sediment Oxygen Flux (SOF) in small tidal estuaries demonstrated strong variability in response to complex interaction of parameters. Oxygen depletion in these important ecosystems is driven by both sources, usually more so by SOF than by BOD, but not always. Factors driving these oxygen sinks include seasonal variation in primary production (mostly phytoplankton), which contributes to organic suspended solids, and are highly related to temperature and run-off driven responses in the water column and benthos. Groundwater inputs can alter or obscure the SOF signal in these land–water interface habitats. SOF is thus particularly hard to predict using single effects models.

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