JOURNAL OF THE AMERICAN WATER RESOURCES ASSOCIATION
Vol. 45, No. 6 AMERICAN WATER RESOURCES ASSOCIATION December 2009

HIGH SEDIMENT OXYGEN DEMAND WITHIN AN INSTREAM SWAMP IN SOUTHERN GEORGIA: IMPLICATIONS FOR LOW DISSOLVED OXYGEN LEVELS IN COASTAL BLACKWATER STREAMS[1]

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ABSTRACT: Sediment oxygen demand (SOD) is considered a critical and dominant sink for dissolved oxygen (DO) in many river systems including blackwater streams and is often poorly investigated or roughly estimated in oxygen budgets. The purposes of this study are to (1) characterize and document the magnitude and variability of SOD in representative instream swamps found on the Georgia Coastal Plain; (2) predict SOD from more readily measured parameters such as soil, sediment, and litter organic carbon; and (3) obtain an accurate representation of SOD values within this understudied habitat to help improve water quality models and the continued development of DO as an appropriate water quality standard. Results show SOD rates ranging from 0.491 to 14.189 g O_2/m^2/day, up to 18 times higher than values reported for southeastern sandy-bottomed streams and suggest that instream swamps are repositories of large amounts of organic matter and are thus areas of intense oxygen demand and a major factor in determining the oxygen balance of the watershed as a whole. These areas of intense oxygen demand in relatively unimpacted areas indicate that low DO concentrations may be a natural phenomenon. SOD rates were significantly correlated (alpha = 0.05) with a number of sediment parameters, with organic carbon and total organic carbon being the best predictors of SOD rate. When developing water quality models, managers should pay closer attention to the influence of SOD as it plays a critical role in determining DO levels within instream swamps and the river system.

(KEY TERMS: sediment oxygen demand; dissolved oxygen; blackwater streams; organic carbon; total maximum daily load.)

Todd, M. Jason, George Vellidis, R. Richard Lowrance, and Catherine M. Pringle, 2009. High Sediment Oxygen Demand Within an Instream Swamp in Southern Georgia: Implications for Low Dissolved Oxygen Levels in Coastal Blackwater Streams. *Journal of the American Water Resources Association* (JAWRA) 45(6):1493-1507. DOI: 10.1111/j.1752-1688.2009.00380.x

INTRODUCTION

Blackwater streams are a common and dominant hydrological feature of the Southeastern Coastal Plain. Within Georgia, the four main blackwater river systems are the Ochlocknee, Satilla, St. Mary's, and Suwannee Rivers. These rivers are characterized by having low slopes, high summertime temperatures, and large inputs of dissolved organic materials

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[1] Paper No. JAWRA-09-0047-P of the *Journal of the American Water Resources Association* (JAWRA). Received March 2, 2009; accepted September 22, 2009. © 2009 American Water Resources Association. **Discussions are open until six months from print publication**.

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(Meyer, 1990; Smock and Gilinsky, 1992). These large allochthonous inputs of organic matter drive high respiration rates and lead to blackwater systems being very heterotrophic (Edwards and Meyer, 1987; Meyer and Edwards, 1990). In large part, they have been unaffected by large impoundments and in many areas maintain an intact riparian buffer (Smock and Gilinsky, 1992; Katz and Raabe, 2005). Blackwater rivers are characterized by a marked seasonal change in discharge and areal extent that is largely precipitation-dependent, with floodplain inundation lasting from winter to early spring (December to May), followed by extensive drying (sometimes completely) during the summer and autumn months (June to November) when evapotranspiration becomes dominant (Wharton, 1978; Wharton *et al.*, 1982). Many streams, up to at least fifth order, are intermittent during summer and autumn months.

A critical and frequently encountered feature of blackwater systems are large instream swamps which form a vital link between the terrestrial and aquatic landscape. Due to the lack of topographical relief, during periods of high discharge, floodplains can become inundated for hundreds of meters in width and lead to "orders of magnitude difference in wetted perimeter, width/depth, suspended sediment load and hydraulic roughness" (Hupp, 2000). Although blackwater floodplains are characterized by low gradients, the slight changes in elevation that are present lead to an assortment of hydrologic, soil, and vegetational patterns (Conner and Buford, 1998; Burke *et al.*, 2003).

Blackwater stream systems are also characterized by extremely low dissolved oxygen (DO) levels, one of the many water quality parameters subject to regulation under the United States Clean Water Act (CWA). DO levels are considered to be an excellent indicator of stream biological activity and health and the "most important of all chemical methods available for the investigation of the aquatic environment" (Joyce *et al.*, 1985; Wetzel and Likens, 2000) as biological activity and biotic integrity can suffer at reduced levels. Within the state of Georgia, the standard for DO is defined as: "A daily average of 5.0 mg/l and no less than 4.0 mg/l at all times for waters supporting warm water species of fish" (GADNR, 2005). Any water body not meeting this standard is listed as impaired on the state's 303(d) list as required by the CWA (GADNR, 2009). Following listing, the state is required to develop and implement a total maximum daily load (TMDL) to bring that water body back into compliance. A TMDL is the total amount of a pollutant that a given water body can sustain without compromising water quality standards. Upon approval and adoption of a TMDL, the affected water body is monitored until it is brought back into compliance (GADNR, 2002). The development, implementation, and monitoring of a given TMDL is a highly time intensive and economically costly endeavor.

The four main blackwater river systems within the state of Georgia often do not meet the set DO criteria. Of the river segments listed as impaired within these four river basins in 2000-2001, 90% failed to meet the DO standard (GADNR, 2000-2001). In the 2004 303(d) list, the number of segments still listed as impaired for the DO standard made up 82% of all listed segments. Stream segments suffering from lowered DO levels, such as those found in the Georgia Coastal Plain, are generally assumed to be a consequence of increased biological activity resulting from nitrogen and phosphorous enrichment. Nutrient enrichment in these systems usually leads to increased algal biomass, dark respiration, and biochemical oxygen demand (Mallin *et al.*, 2001, 2004). This phenomenon generally is absent from streams with shading by overhead canopy or when the bottom substrate is loose such as sand, both common conditions in the "listed" blackwater rivers and streams in the Southeastern Coastal Plain (Carey *et al.*, 2007). However, many of the blackwater streams in the Georgia Coastal Plain drain areas of intensive agriculture use that may provide additional nutrients to streamflow due to the use of fertilizers (Carey, 2005; Carey *et al.*, 2007).

Low DO levels may indeed be a natural phenomenon of these systems and not a sign of pollution or impairment. Various studies have shown that DO levels below the 5 mg/l limit are common during the summer months even in areas with extensive riparian forests or in forested watersheds (Joyce *et al.*, 1985; Meyer, 1992; Ice and Sugden, 2003). Working in the Louisiana South Central Plains, Ice and Sugden (2003) found over 80% of their summertime observations (August) were below the 5 mg/l standard and close to 60% were below the proposed revised limit of 3 mg/l. Multiple reasons have been hypothesized for this phenomenon including: high summertime air and water temperatures (Joyce *et al.*, 1985), slow movement of water (Ice and Sugden, 2003), and high inputs of dissolved organic carbon (DOC) (Meyer, 1992).

The definitive reasons for lowered DO levels in these systems are ultimately unknown, but likely are a combination of the factors listed above. Another critical sink for DO in this system (and especially in instream swamps and floodplain wetlands) is sediment oxygen demand (SOD). Hatcher (1986a) defines SOD as "the rate that DO is removed from the water column …due to the decomposition of organic matter in the bottom sediments." These organic materials can come from either outside the system (allochthonous material) such as leaf litter and settling of organic particles from wastewater point discharges or from within the system (autochthonous material) such as decomposing plant materials. Once organic matter reaches the sediment matrix, SOD is influenced by two different phenomena: (1) the rate at which oxygen diffuses into the sediments and is then consumed and (2) the rate at which reduced organic substances are conveyed into the water column and then oxidized (Bowie *et al.*, 1985). The literature is consistent in describing SOD as the combination of two processes: (1) biological respiration of benthic organisms residing in the sediment and (2) chemical oxidation of reduced substances found within the sediment matrix (Bowman and Delfino, 1980; Hatcher, 1986a; Chau, 2002). The effect of SOD on the oxygen budget of an entire river system should not to be underestimated, as it can be a critical sink of DO (Wu, 1990). Indeed, in some rivers SOD can account for over half of the total oxygen demand and can play a primary role in the water quality of a stream system (Rutherford *et al.*, 1991; Matlock *et al.*, 2003). While being a potentially major influence on the total oxygen demand within a system, this parameter is often assumed (or estimated) in water quality models (Hatcher, 1986a; Matlock *et al.*, 2003). Errors in this measurement could lead to inaccurate models for the stream environment, at great biological and financial cost.

The purposes of this study are to: (1) characterize and document the magnitude and variability of SOD in representative instream swamps found on the Georgia Coastal Plain; (2) predict SOD from more readily measured parameters such as soil, sediment, and litter organic carbon (LOC); and (3) obtain an accurate representation of SOD values within this understudied habitat to help improve water quality models and the continued development of DO as an appropriate water quality standard.

METHODS

Study Site

Research was conducted in part of the Little River Experimental Watershed (LREW), a 334 km^2 research watershed of the Southeast Watershed Research Laboratory of the USDA Agricultural Research Service (Sheridan and Ferreira, 1992). Instrumented for the measurement of rainfall and streamflow beginning in 1967, the LREW has been designated as representative of the soils, topography, geography, and land use within the Southern Coastal Plain. Land usage across the watershed is 50% forested, 31% agricultural, 10% pasture, 7% urban, and 2% open water (Bosch *et al.*, 2006). Of the 50% of the landscape that is forested, 28% is considered riparian forest and vegetated buffers remains largely intact along portions of the river, with swamp hardwood communities consisting of a closed canopy and thick undergrowth. The instream swamp selected for the majority of this experiment is a 1,550 m long stretch of river located in the lower part of the LREW above the gauging site designated Station B (Figure 1) (Sheridan and Ferreira, 1992). The stream at this point is a fifth-order stream and can be as wide as 350 m during periods of complete inundation. Inundation of the floodplain usually begins in December with complete inundation until April or May. During summertime months (June to August), flow may stop along with complete drying of the river channel (Figure 2). Additional measurements were made in a small headwater watershed (third order) located above gauging site Station J, with a main channel 5-10 m in width and subject to overbank flooding during high flow events and cessation of flow during summertime months (Figure 1). Both of the

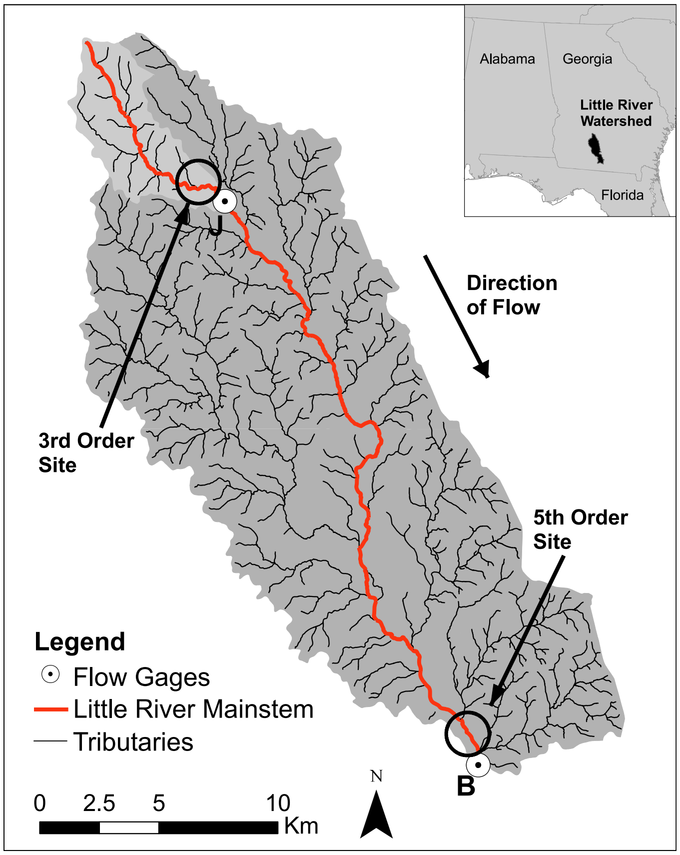

FIGURE 1. Map of Little River Experimental Watershed With Selected Sampling Locations.

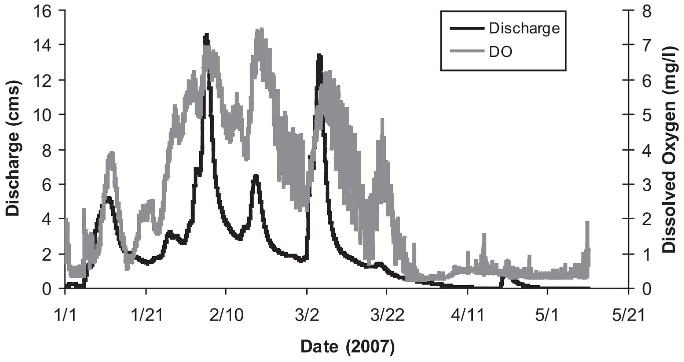

FIGURE 2. Measure of Discharge and Dissolved Oxygen for 2007 Experimental Season at Downstream End of Fifth-Order Site. Zero flow first occurred May 8, 2007 and did not resume for the remainder of the calendar year.

sites used in this study have intact riparian buffers.

Sediment Oxygen Demand

SOD was measured using chambers originally designed by Murphy and Hicks (1986) and modified by Utley *et al.* (2008). Each chamber has a volume of 65.15 l and covers a surface area of 0.27 m^2 on the stream bottom (Figure 3a). The cutting flange sinks the chamber 5.08 cm into the stream sediment. Water circulates throughout the chamber via a 12 V DC submersible pump, powered by a 14 V submersible, gel-cell, lead acid battery. The pump continuously withdraws water from one diffuser and injects it back into the chamber via the second diffuser. The diffusers force the water within the chamber to circulate around the chamber annulus, promoting continuous mixing and a similar velocity among all chambers. The control chamber differs from the experimental chamber by having a sealed bottom which is used to measure water column respiration. Oxygen concentration was measured within the chamber using an oxygen optode (Aanderaa Instruments Oxygen Optode 3975, Bergen, Norway) logging to a handheld computer (Dell Axim X50, Round Rock, Texas) (Figure 3b). For each sampling event, SOD chambers were pushed into the sediment to create a solid seal and then oxygen and temperature levels logged within chambers every 2 min for 2-3 h. The circulating pumps and recording computers for each chamber were not started until all chambers had been sealed and filled. The total time between seal of the first chamber and the final chamber was between 45 and 90 min.

SOD is calculated as the decline in oxygen concentration over the elapsed time. SOD was calculated using:

$$\mathrm{SOD} = 1.44\frac{V}{A}(b_1 - b_2), \tag{1}$$

where SOD is the sediment oxygen demand (g O_2/m^2/day), b_1 is the slope from the oxygen depletion curve (mg/l/min), b_2 is the slope from the oxygen depletion curve of the control chamber (mg/l/min), V is the volume of the chamber (l), A is the area of bottom sediment covered by the chamber (m^2), and 1.44 refers to a unit conversion constant (converting mg/min to g/day).

The slope for both control and experimental chambers was taken as the linear best fit for the oxygen depletion curve (Figure 4a). For most cases, the entire dataset was used. In some instances, the initial oxygen concentration was low and the oxygen depletion curve deviated from linear, due to lack of oxygen within the chamber (Figure 4b). In these instances only the linear portion of the line was used to calculate SOD. At other times, initial DO concentrations

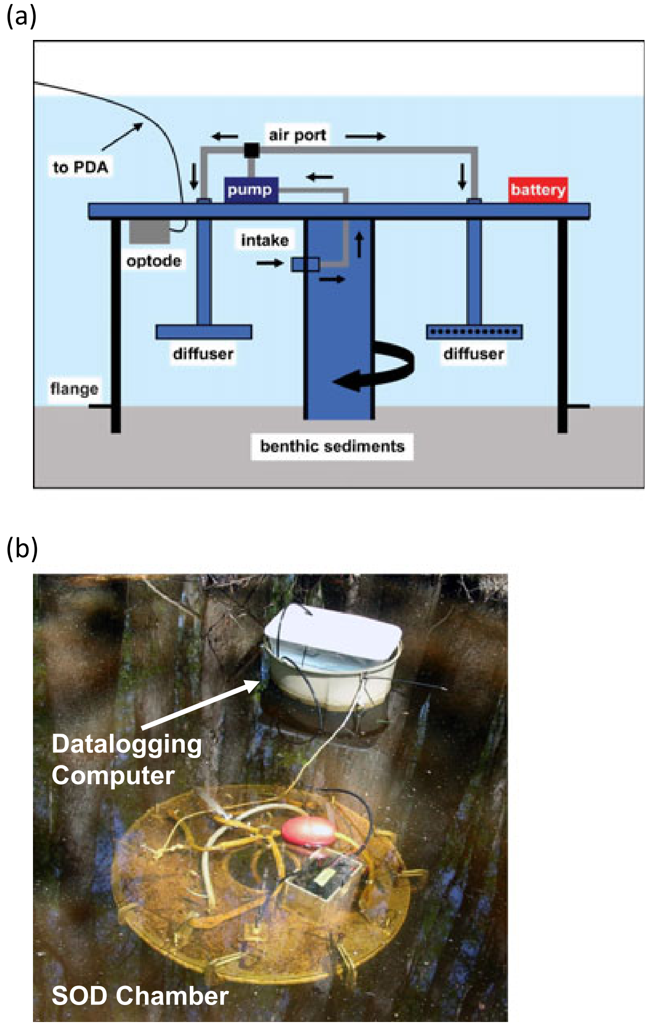

FIGURE 3. (a) Schematic of Sediment Oxygen Demand Chamber and (b) Typical Deployment of Sediment Oxygen Demand Chamber and Associated Data Logger in the Field.

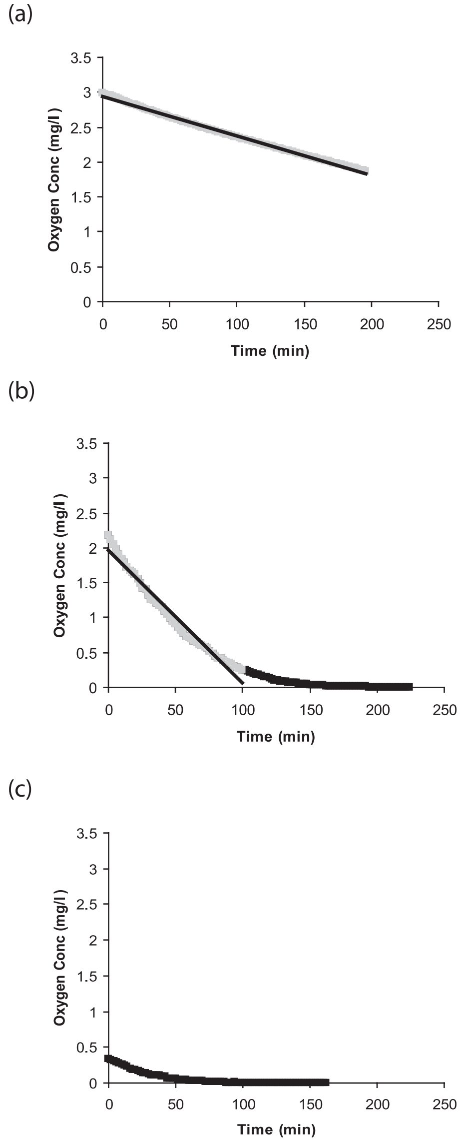

FIGURE 4. Oxygen Decline Curves During Sediment Oxygen Demand (SOD) Runs Showing (a) Typical Decline Curve Exhibiting a Linear Loss of Oxygen Concentration With Time. Data represent Chamber 3 from March 15, 2006; (b) example of nonlinear loss of oxygen concentration with time. Slope for calculation of SOD was taken from initial linear portion. Data represent Chamber 3 from April 13, 2006; (c) example of low initial dissolved oxygen concentration with time. Calculation of SOD was not possible due to zero oxygen remaining in chamber during run. Data represent Chamber 1 from April 13, 2006.

were below 1 mg/l (Figure 4c) (see Results, first paragraph). SOD rates were then corrected to 20°C using the modified van't Hoff form of the Arrhenius equation (Hatcher, 1986b; Truax *et al.*, 1995):

$$\mathrm{SOD}_T = \mathrm{SOD}_{20}\theta^{(T-20)}, \tag{2}$$

where SOD_T is the SOD rate at temperature T, SOD_{20} is the SOD rate at 20°C, and θ is a temperature correction coefficient chosen from literature.

Values for θ, based on the type of DO model, are given by Bowie *et al.* (1985). Because this project was designed to generate SOD data for use in Georgia, a θ of 1.047 was used. The temperature (T) was calculated as the average temperature within the chamber over the SOD run.

SOD values were measured at both the third-order and fifth-order location throughout the period of flowing water and adequate DO (generally DO > 1 mg/l; see Results section below) where it was possible to achieve a reliable measure of SOD. Measurement of SOD is limited by depth within the stream channel as water must be ~36 cm to fully submerge the chamber and depths of over ~90 cm would require the use of artificial breathing equipment, thereby restricting sampling to time periods when hydrologic conditions permitted (generally January to May). Nevertheless, the sampling regime encompassed the time period critical for lowered DO in the LREW as lowered DO levels begin in late winter and early spring (February to March) followed oftentimes by complete drying of stream channels during the summer and fall months (June to November) (Figure 2). Effort was taken to get a variety of sampling sites within each location to give a representative range of sediment and hydrologic conditions. SOD was sampled a total of 33 times over 11 dates, with two dates (3/6/07 Chamber 1 and 3/20/07 Chamber 2) (Table 1), omitted because of chamber leakage. In total, five usable measures of SOD were gathered at the third-order location and 19 measures from the fifth-order location (see Results).

Sediment and Water Sample Preparation

Sediment samples were taken immediately following an SOD run with one sample taken from each quadrant under a chamber. Sediment samples were taken to a depth of 15 cm with each set of four 5.7 cm diameter cores separated into 0-5 cm and 5-15 cm depth classes. All four cores from each depth class were composited into a single Ziploc bag and were stored in a refrigerator until analysis. Samples were dried in an oven at 35°C, rolled with a rolling pin to crush soil, and then sieved with a #10 sieve (<2 mm). Material that passed the sieve was considered soil matter with that remaining above as litter/residue. Care was taken to avoid crushing organic pieces larger than 2 mm by removing them prior to rolling and prevent biasing the sample.

Organic Carbon Determination. From separated sample, ~20 g of soil was pulverized with a rolling table until the sample attained a powder-like consistency. Three 3 g subsamples were taken from

TABLE 1. Individual Chamber Measurements of SOD$_{20}$, DO, and Temperature.

Date	Site Location	Chamber	SOD$_{20}$ (g O$_2$/m^2/day)		Chamber DO (mg/l)	DO Change (mg/l)	Chamber Temperature (°C)
			Individual	Average			
3/15/06	Fifth order	1	2.61	2.34	3.10-1.81	1.29	15.04-17.57
		2	2.11		3.10-2.13	0.97	15.12-17.72
		3	2.30		2.99-1.87	1.12	15.11-17.53
4/5/06	Fifth order	1	Low DO	—	0.32-0.05	0.27	16.44-17.75
		2	Low DO		0.23-0.00	0.23	16.31-17.80
		3	Low DO		0.60-0.01	0.59	16.31-17.91
4/11/06	Fifth order	1	13.37	12.45	4.81-1.07	3.74	15.48-17.28
		2	14.19		9.35-1.13	8.22	15.30-16.79
		3	9.79		7.84-0.47	7.37	15.37-17.18
4/13/06	Fifth order	1	Low DO	4.95	0.34-0.00	0.34	17.21-18.30
		2	2.74		1.43-0.47	0.96	17.16-18.43
		3	7.17		2.18-0.24	1.94	17.02-18.48
4/19/06	Fifth order	1	Low DO	—	0.57-0.00	0.57	20.13-20.33
		2	Low DO		0.53-0.00	0.53	20.30-20.85
		3	Low DO		0.95-0.06	0.89	20.15-20.47
2/19/07	Third order	1	0.49	2.36	9.19-9.35	−0.16	6.33-8.56
		2	4.62		9.43-8.32	1.11	6.25-8.53
		3	1.96		9.43-9.11	0.32	6.42-8.53
2/21/07	Third order	1	4.18	2.36	9.46-7.36	2.10	11.87-13.34
		2	1.60		7.81-7.30	0.51	12.01-13.37
		3	1.31		7.34-6.94	0.40	11.91-13.36
3/6/07	Fifth order	1	Leak	7.16	Leak	Leak	Leak
		2	5.15		6.60-4.15	2.45	11.50-12.92
		3	9.16		9.92-5.79	4.13	11.40-13.05
3/7/07	Fifth order	1	3.23	6.41	4.66-3.47	1.19	12.05-14.02
		2	7.84		5.11-3.69	1.42	12.14-13.96
		3	4.26		5.02-4.82	0.20	12.13-12.45
3/19/07	Fifth order	1	4.57	8.03	3.38-1.66	1.72	12.56-13.80
		2	7.69		3.33-0.53	2.80	12.65-13.80
		3	11.83		9.24-5.64	3.60	12.50-13.77
3/20/07	Fifth order	1	3.20	3.35	3.65-1.74	1.91	13.97-15.48
		2	Leak		Leak	Leak	Leak
		3	3.50		3.87-1.63	2.24	14.02-15.53

Notes: DO, dissolved oxygen; SOD, sediment oxygen demand.
Dates are mm/dd/yy notation.
Site locations and orders represented identified in Figure 1.

pulverized sample, with organic matter determined by loss on ignition (LOI) (Nelson and Sommers, 1996). After measuring of soil organic matter via LOI, organic matter content of each sample was converted to soil organic carbon (SOC) by assuming a 0.5 proportion of C by weight (Nelson and Sommers, 1996). The litter/residue sample was separated into size classes of organic material (<2, 2-5, and >5 mm diameter). Litter <2 mm diameter was separated from inorganic material by placing material in a beaker and then adding deionized (DI) water. Organic material that floated on top was decanted off, dried at 60°C, and weighed. After separation, forceps were used to separate any additional organic matter that might have been missed. Carbon content in litter residues (LOC) was assumed to be 0.4 by weight (Schlesinger, 1997). SOC and LOC were added together to form total organic carbon (TOC).

Water Extractable Carbon and Nitrogen. Water extractable carbon and nitrogen were determined following a modified methodology of Ghani *et al.* (2003). In the first step, readily soluble carbon and total nitrogen (TN) was removed by extracting with room temperature DI water. During the second step, labile components of soil carbon were extracted using a water bath at 80°C for 16 h. The two steps are hereafter referred to as water soluble carbon and TN (WSC and WSTN, respectively) and hot water extractable carbon and TN (HWC and HWTN, respectively). WSC and HWC were summed to calculate total water extractable carbon (TWC), while WSTN and HWTN were summed to calculate total water extractable total nitrogen (TWTN).

For the WSC procedure, 3 g of dried soil was placed in a 40 ml glass tube. These samples were extracted by adding 30 ml of DI water and shaken for 1 h on a

Fisher Scientific Hematology Mixer (Pittsburgh, Pennsylvania), centrifuged for 30 min at 2,500 rpm, and the supernatant then decanted and filtered through 0.7 μm Whatman GF/F filters into separate vials. Following extraction, these tubes were reweighed to calculate the entrained water volume. The HWC procedure was performed by adding an additional 30 ml of DI water to the tubes and shaken on a vortex shaker for 10 s to ensure complete resuspension. The tubes were then placed in a hot water bath for 16 h at 80°C. Following the hot water bath, the tubes were again shaken on a vortex sampler to ensure full resuspension of the HWC and followed the centrifuge and filtering procedure as before. Both WSC and HWC samples were analyzed for organic carbon and TN using a Shimadzu TOC-V Combustion Analyzer (Columbia, Maryland).

Water Sample Preparation. Before and after each deployment, temperature, pH, conductivity, ambient DO level, and percent saturation were measured using a YSI 6920 sonde (Yellow Springs, Ohio). A water quality sample was collected in a 1-liter glass bottle for the measurement of nitrate (NO_3-N), orthophosphate (OP), ammonium (NH_4-N), chloride (Cl), potassium (K^+), TN, total phosphorus (TP), and DOC concentrations. NO_3-N, OP, NH_4-N, and Cl were measured on a Technicon Instruments TrAAcs 800 Autoanalyzer (Tarrytown, New York). TN and TP were measured on a Bran + Luebbe AA3 Autoanalyzer (Delavan, Wisconsin) and DOC was analyzed using a Shimadzu TOC-5050a Total Organic Carbon Analyzer with a Shimadzu ASI-5000a Auto Sampler (Columbia, Maryland). K^+ was analyzed using a Perkin-Elmer Analyst 100 Atomic Absorption Spectrometer (Waltham, Massachusetts).

Statistical Analyses

The relationship between SOD and various water quality and soil physical properties were initially determined using regression analysis at an alpha = 0.05. Further, various models using soil physical properties were created using multiple linear regression and forward and backward stepwise linear regression to attempt to better explain the variability in SOD measurements. For comparisons among the soil properties, a mixed model analysis of variance was used (alpha = 0.05).

RESULTS

After data collection, it was observed that seven SOD runs started with DO levels of less than 1 mg/l like those displayed in Figure 4c despite the lack of stratification through the water column. As little oxygen is available to be consumed during these runs, the calculated SOD rates were not considered representative of their underlying sediment characteristics and were omitted from the analyses relating SOD to sediment characteristics (4/5/06 Chamber 1-3, 4/13/06 Chamber 1, and 4/19/06 Chamber 1-3 – Table 1). However, these locations were included in the analyses looking at the sediment characteristics as a whole as the sediment properties found at these locations were considered representative of the instream swamp system. For the remaining 24 measures, rates of SOD ranged from 0.49 to 14.19 g O_2/m^2/days with an average SOD rate of 5.37 g O_2/m^2/day (Table 1). For the points measured at the instream swamp in the fifth-order stream, the SOD rate was shown to significantly correlate with the initial DO concentration measured at the beginning of a run (Figure 5 – $r^2 = 0.527$, $p \leq 0.0001$). None of the measured ambient water quality parameters were significantly correlated with the measurements of SOD (Table 2).

Multiple soil properties were significantly correlated with SOD rate with all significant relationships occurring in the 0-5 cm depth fraction. The concentration of LOC in the soil (mg/g) at all size classes (<2, 2-5, and >5 mm) as well as total concentration were significantly correlated with SOD (Table 3). The measures of extractable carbon (WSC, HWC, and TWC) and extractable TN (WSTN, HWTN, and TWTN) at the 0-5 cm depth class all were significantly correlated with SOD rate with WSC ($r^2 = 0.3107$, $p = 0.0057$) and WSTN ($r^2 = 0.2318$,

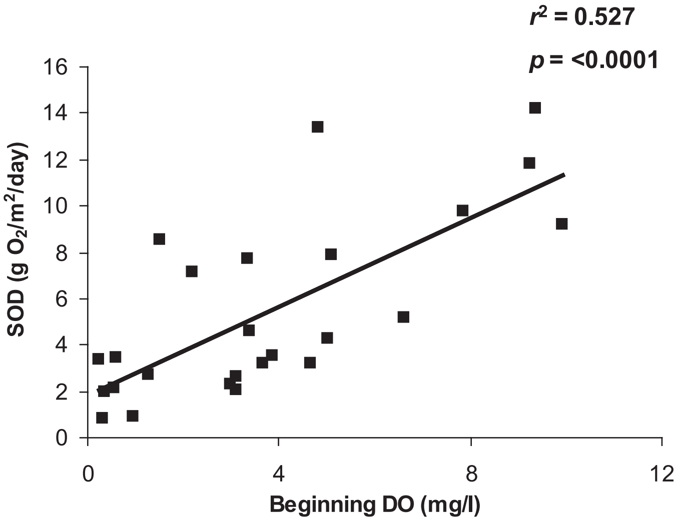

FIGURE 5. Relationship Between Initial Dissolved Oxygen (DO) Concentration and Sediment Oxygen Demand (SOD) Rate Within the Fifth-Order Instream Swamp Location.

TABLE 2. Ambient Water Quality Parameters for Each Sediment Oxygen Demand Sampling Date Including Temperature, pH, Total P, DOC, NO_3-N, NH_4-N, OP, Cl$^-$, and K$^+$.

Date	Site Location	Ambient Temp (°C)	Average pH	Total N (mg/l)	Total P[1] (mg/l)	DOC (mg/l)	NO_3-N (mg/l)	NH_4-N (mg/l)	OP (mg/l)	Cl$^-$ (mg/l)	K$^+$ (mg/l)
3/15/06	Fifth order	15.90-18.09	5.78	0.607	<0.2	13.09	0.033	0.030	0.035	11.298	3.2
4/5/06	Fifth order	16.75-18.73	5.27	0.696	<0.2	13.93	0.036	0.095	0.013	11.235	3.1
4/11/06	Fifth order	15.98-18.13	5.85	0.652	<0.2	14.56	0.035	0.065	0.028	11.355	3.3
4/13/06	Fifth order	17.04-18.96	5.78	0.664	<0.2	14.55	0.042	0.052	0.018	12.602	3.2
4/19/06	Fifth order	19.97-20.84	5.99	0.816	<0.2	16.36	0.012	0.117	0.049	13.098	3.1
2/19/07	Third order	6.92-8.77	5.83	0.367	0.041	7.56	0.122	0.019	0.026	9.693	1.2
2/21/07	Third order	12.37-	5.73	0.317	0.006	8.01	0.087	0.015	0.008	9.817	1.2
3/6/07	Fifth order	11.82-13.15	6.34	0.594	0.022	18.24	0.013	0.004	0.006	10.273	3.2
3/7/07	Fifth order	12.47-14.40	6.26	0.539	0.017	17.53	0.006	0.000	0.001	10.306	3.2
3/19/07	Fifth order	13.13-14.76	6.22	0.661	0.018	22.20	0.003	0.018	0.003	11.818	3.6
3/20/07	Fifth order	14.13-15.95	6.30	0.660	0.007	22.42	0.003	0.021	0.028	11.798	3.6

Notes: Cl$^-$, chloride; DOC, dissolved organic carbon; K$^+$, potassium; NH_4-N, ammonium; NO_3-N, nitrate; OP, orthophosphate.
Dates are mm/dd/yy notation.
Site locations and orders represented identified in Figure 1.
[1] Difference in precision between 2006 and 2007 due to change in laboratory analysis methodology.

TABLE 3. Results of Regression Analysis (alpha = 0.05) Relating SOD Rate (g O_2/m^2/day) to Various Individual Soil Property Measurements.

OC Pool	Class	r^2	$p<$
Extractable C (mg/kg)	WSC	0.3107	0.0057
	HWC	0.2629	0.0124
	TWC	0.2830	0.0090
Extractable TN (mg/kg)	WSTN	0.2318	0.0200
	HWTN	0.1922	0.0364
	TWTN	0.2064	0.0294
LOC (mg/g)	<2 mm	0.1905	0.0330
	2-5 mm	0.2022	0.0275
	>5 mm	0.1592	0.0535
	Total	0.2041	0.0267
SOC (mg/g_{total})		0.3523	0.0022
TOC (mg/g_{total})		0.3579	0.0020

Notes: HWC, hot water extractable carbon; HWTN, hot water total nitrogen; LOC, litter organic carbon; SOC, soil organic carbon; SOD, sediment oxygen demand; TN, total nitrogen; TOC, total organic carbon; TWC, total water extractable carbon; TWTN, total water extractable total nitrogen; WSC, water soluble carbon; WSTN, water soluble total nitrogen.

$p = 0.0200$) the best predictors in their respective pools (Table 3). Use of both a forward and backward stepwise linear regression model involving multiple soil property factors was employed, but use of multiple factors did not significantly better explain the relationship with SOD. Instead, measurement of SOC (mg/g_{total}) or TOC (mg/g_{total}) alone was the single best predictor of SOD rate (Table 3, Figures 6a and 6b; SOC, $r^2 = 0.3523$, $p = 0.0022$; TOC, $r^2 = 0.3579$, $p = 0.0020$).

When looking at the soil carbon pools as a whole across all sampling dates, the majority of the organic carbon in both the 0-5 and 5-15 cm depth fractions is found within the SOC pool (Figure 7a). SOC represents significantly more of the carbon pool at both depth fractions with around 80% of total carbon (0-5 cm: $F = 436.50$, $p \leq 0.0001$; 5-15 cm: $F = 295.80$, $p \leq 0.0001$). Additionally, the average SOC concentration is significantly higher in the 0-5 cm depth fraction when compared with the 5-15 cm depth fraction (Figure 7b; $F = 37.59$, $p \leq 0.0001$). Within the LOC pool, there are significant differences both within a depth class and between size classes. Within the 0-5 cm depth, significantly more of the LOC is in the <2 mm size class as compared to the other two size classes (Figure 8; $F = 24.19$, $p \leq 0.0001$). However, in the 5-15 cm depth class, significantly more of the litter is found in the largest >5 mm size class when compared with the other two classes (Figure 8; $F = 9.59$, $p = 0.0001$).

DISCUSSION

Our results suggest that instream swamps of the LREW are areas of intense oxygen demand and a major factor in the oxygen balance of the watershed as a whole. Further, this is the first study to measure SOD within instream swamps of blackwater rivers. Previous research in the LREW has shown that SOD is the most important variable to accurately predict DO levels (Cathey *et al.*, 2005). Despite the importance of accurate measures of SOD, it is oftentimes estimated from literature values because of the difficulty in obtaining SOD measurements. Truax *et al.* (1995) stated that SOD rates for Southeastern United States rivers range between 0.33 and 0.77 g O_2/m^2/day. All but one (23 of 24 measures) of the SOD measurements in our study are higher and, in some cases, much higher (up to 18 times) than this

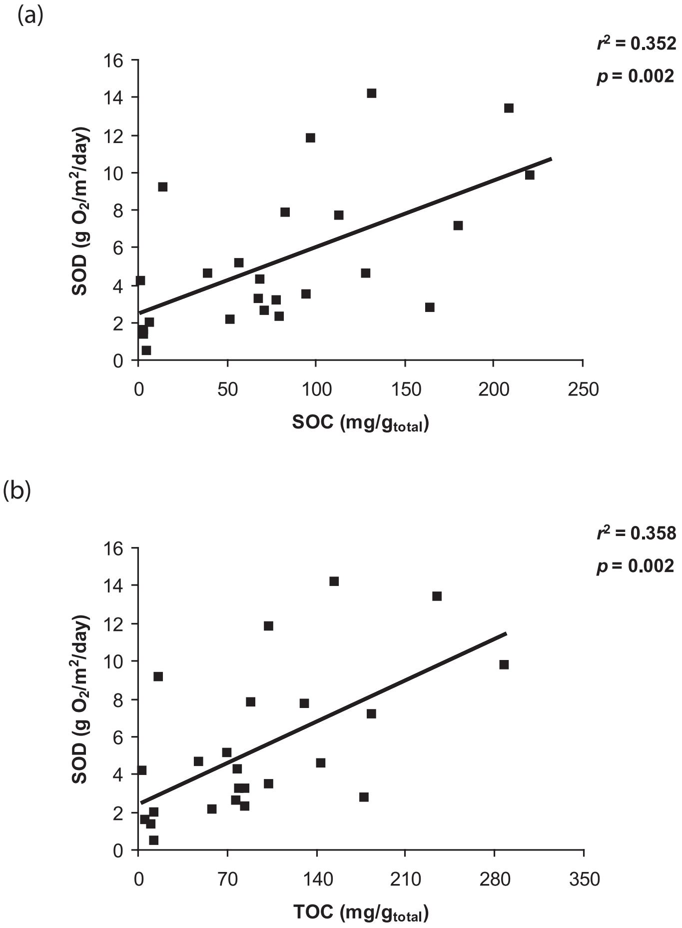

FIGURE 6. Relationship Between (a) Soil Organic Carbon (SOC) and Sediment Oxygen Demand (SOD), and (b) Total Organic Carbon (TOC) and Sediment Oxygen Demand (SOD).

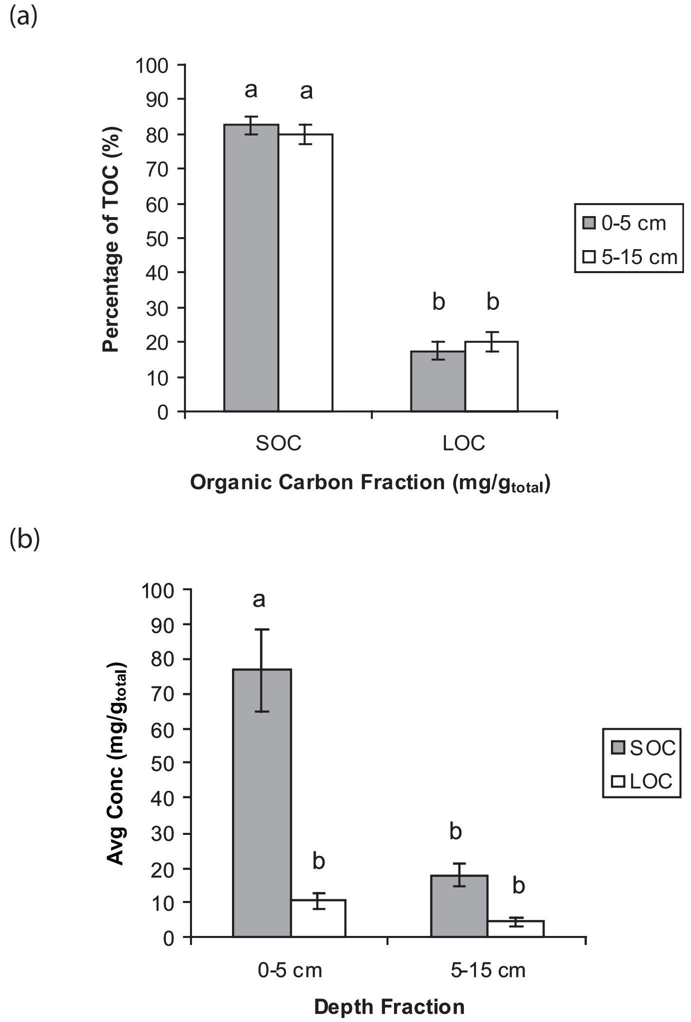

FIGURE 7. Characterization of Organic Carbon Pools Showing (a) Percentage of Soil Organic Carbon (SOC) and Litter Organic Carbon (LOC) Within Each Depth Class and (b) Average Concentration of Soil Organic Carbon (SOC) and Litter Organic Carbon (LOC) with Depth. Within a graph, different letters above bars denote significant differences between bars. Error bars, ±1 SE.

range. The average SOD rate across all samples is 5.37 g O_2/m^2/day, a rate seven times higher than the upper limit of this range. Further, a previous study measuring SOD within forested and agricultural catchments of the LREW found SOD rates between 0.6 and 1.4 g O_2/m^2/day in an agricultural catchment and 0.9-2.5 g O_2/m^2/day in a forested catchment (Crompton, 2005; Utley *et al.*, 2008). The previous study failed to look at rates within instream swamps and focused sampling at more easily accessible road crossings. These locations had the potential to be impacted anthropogenically and may not represent actual conditions across the watershed. Seventy-five percent of the measurements made in the instream swamp during our study are above the highest value recorded during the previous study (Table 1). The majority of measures of SOD during this study took place at the fifth-order location as measures at the third-order location were limited by adequate depth for complete chamber submersion except during periods of high flow. Due to the lack of measures at this location, it makes robust comparisons among sites difficult, but results indicate that SOD rates are similar to those at the more heavily sampled fifth-order location and higher than previously published results for southeastern streams. In total, our results indicate that SOD plays an even greater role than previously believed in the LREW.

When looking at the potential effect of these rates on water column DO concentrations, their influence is prominent. As previously mentioned, blackwater streams are characterized by slow-moving water that limits reaeration and have decreased photosynthesis due to darkly colored water and overhead shading. If one envisions a square meter of sediment overlain by water 0.61 m deep with an initial DO concentration of 5 mg/l there is a total of 3,050 mg of O_2. Assuming no reaeration, photosynthesis, or movement of water, available DO within the water column would be

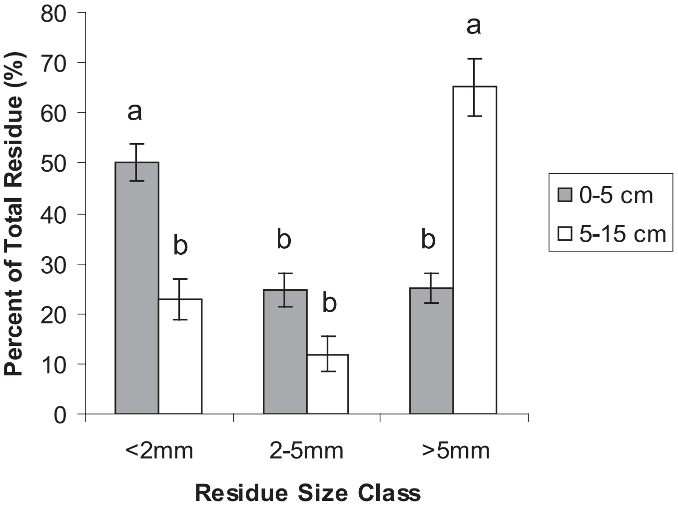

FIGURE 8. Percentage of Litter Organic Carbon at Different Size Classes With Depth. Different letters denote significant differences between bars. Error bars, ±1 SE.

consumed in just over half a day using the average SOD rate of 5.37 g O_2/m^2/day measured in this study. Using the maximum rate of SOD measured in this study (14.19 g O_2/m^2/day), DO would be depleted from the hypothetical water column in 0.2 days. While water movement, reaeration, and photosynthesis are rarely zero, this hypothetical example shows that SOD is a major sink of DO in blackwater river systems and instream swamps in particular.

Whole stream community respiration rates (CR) have also been measured for a variety of blackwater stream systems (Table 4). Comparison among these different measures is hampered by the differing water temperatures across season and location. As all SOD rates in this study have been corrected to 20°C, to aid in comparison between CR and SOD, we corrected CR rates to 20°C using a modified form of Equation (2):

$$\mathrm{CR}_T = \mathrm{CR}_{20}\theta^{(T-20)}, \qquad (3)$$

where CR_T is CR rate at temperature T and CR_{20} is CR rate at 20°C. For the purposes of this comparison, θ was assumed to be the same value of 1.047.

One of the most intensively studied blackwater systems is the Ogeechee River in Georgia, a neighboring blackwater system to the LREW (Edwards and Meyer, 1987; Edwards *et al.*, 1990; Meyer *et al.*, 1997). Corrected annual rates of community respiration (CR_{20}) ranged from 4.39 g O_2/m^2/day in the fourth-order Black Creek to 7.18 g O_2/m^2/day in the sixth-order Ogeechee River (Table 4). Studies in other blackwater river systems show similarly high rates of CR in locations as varied geographically as Virginia and Florida (Fuss and Smock, 1996; Smock, 1997; Colangelo, 2007). While whole system CR was not measured in this study, SOD is a portion of CR. Assuming similar rates of respiration in the LREW, the average rate of SOD in this study (5.37 g O_2/m^2/day) indicates that SOD makes up a large portion of total CR within blackwater systems as it is higher than the total of the fourth-order site and 75% of the total respiration measured in the sixth-order Ogeechee River. Fuss and Smock (1996) also showed that 70% of the total respiration at Buzzards Branch, Virginia came from the hyporheic sediments (depth 2-20 cm) while between 8 and 13% was from the surface sediment, leaf litter, or woody debris. This large percentage of total respiration coming from the sediments further supports the dominant influence of SOD on oxygen dynamics within blackwater streams and instream swamps in particular. Finally, a large scale comparison of benthic respiration in 22 streams nationwide found the highest rates of respiration at the Ogeechee River and Buzzards Branch locations discussed above (Sinsabaugh, 1997). Although the streams in that comparison measured CR, the average measure of SOD alone in our study would place it with the fifth highest respiration rate among all streams studied, highlighting the role of elevated levels of SOD within blackwater systems.

DO was previously modeled in the LREW using the Georgia DOSag model – a steady-state, one-dimensional, advection dispersion, mass transport, deterministic model – used by the Georgia Environmental Protection Division for TMDL development (Cathey, 2005; Cathey *et al.*, 2005). In this previous study, most model input parameters were determined from data collected within the watershed over 20 years, but data for reaeration and SOD were unavailable. Reaeration was estimated using the O'Conner and Dobbins equation. SOD was used as the equilibrating factor during calibration of the model. For proper calibration, an SOD value of 6.0 g O_2/m^2/day was necessary. Additionally, during the sensitivity analysis, SOD was found to be the most sensitive parameter within the model. The average rate of 5.37 g O_2/m^2/day found in this study is slightly less than the calibrated value in the model, but much closer than those values reported by Utley *et al.* (2008). Cathey *et al.* (2005) questioned whether the calibrated value for SOD would correspond to actual values within the real system due to its deviation from previously published values and method of calculation. The similarity of the modeled value and the values in our study confirm that the modeled parameter is compatible with real system values and that SOD does indeed play an important if not dominant role in whole system DO dynamics.

Measurement of SOD is a labor and time intensive process that requires specialized equipment to mea-

TABLE 4. Measures of CR and CR_{20} in Other Blackwater River Systems.

River	Stream Order	Sampling Period	Mean CR[1] (g $O_2/m^2/day$)	Temp (°C)	Adjusted CR_{20}[2] (g $O_2/m^2/day$)	Reference
Ogeechee River, Georgia	Sixth	Annual	6.7 (3.70-11.75)	18.5	7.18	Edwards and Meyer (1987)
		Spring	6.93	20	6.93	Meyer *et al.* (1997)
		Summer	8.3	27.84	5.79	Edwards (1985)
		Autumn	5.82	20.87	5.59	
		Winter	5.48	10.03	8.66	
Black Creek, Georgia	Fourth	Annual	4.1 (2.3-9.6)	18.5[3]	4.39	Meyer and Edwards (1990)
Buzzards Branch, Virginia	First	Annual	3.01	15	3.79	Fuss and Smock (1996) Smock (1997)
Kissimmee River, Florida	Fourth to fifth	Annual	9.44	25.0	7.50	Colangelo (2007)
		Wet (June to November)	13.91	27.8	9.72	
		Dry (December to May)	4.97	22.2	4.49	

Notes: CR, community respiration; CR_{20}, adjusted community respiration.

[1] Data in parentheses represents the range of measurements during the annual period.

[2] CR was adjusted to 20°C using Equation (3).

[3] Black Creek is a subwatershed of the larger Ogeechee River watershed. Temperature data were not reported for Black Creek so mean temperature was assumed to be the same as reported for the larger Ogeechee River watershed reported in Meyer *et al.* (1997).

sure *in situ*. In addition, *in situ* measurements require access to areas that may be difficult to enter. An easier to measure property that correlates with SOD and may predict areas of intense SOD would be beneficial. We observed that multiple sediment properties were significantly related to SOD rate. Despite the presence of multiple factors, using a model involving multiple factors did little to significantly explain more variation than a single factor alone.

Soil organic carbon or TOC in the 0-5 cm depth fraction were the best predictors of SOD rate within the instream swamp system, both explaining 35% of the variation (Figures 6a and 6b). The reason for their similar relationship is likely due to the majority of the TOC being made up of SOC (Figure 7a). In both depth classes ~80% of the TOC is comprised of SOC. Additionally, while SOC makes up a similar percentage of TOC in both depth classes, the average concentration within the 0-5 cm depth class is over four times higher as compared to 5-15 cm depth fraction. This is not surprising as the freshest organic material is deposited on the surface sediments and is decomposed as it works into the soil column.

Although LOC is around 20% of TOC in both depth classes (Figure 7a) with no significant differences between average concentrations (Figure 7b), there are significant differences between the size classes that are most prevalent in the different depth classes. Although the 0-5 cm depth fraction is comprised mostly of the smallest size class (<2 mm), that situation is reversed in the 5-15 cm depth fraction with most of the litter being the largest size class (>5 mm) (Figure 8). The difference between size classes within the 5-15 cm fraction might be even more pronounced as the largest size class could be under represented. During sampling the coring device was unable to push through especially large pieces of wood and the sample was biased toward smaller size fractions.

Hot water extractable carbon is a measure of the labile portion of organic C within the soil and has been shown to be positively correlated with microbial biomass in terrestrial soils (Sparling *et al.*, 1998; Ghani *et al.*, 2003). Many aspects of SOD are microbially driven and we hypothesized this source of readily utilizable C would be positively correlated with SOD. While all measures of both extractable C and extractable TN at the 0-5 cm depth class were significantly positively related to SOD, it was not the strongest predictor of SOD rate among measured soil properties (Table 3). In fact measuring WSC alone was a better predictor of SOD than HWC or TWC.

All the properties that were significant predictors of SOD were found within the 0-5 cm depth class indicating this topmost later is most important in driving the water column DO dynamics. It appears the most labile and biologically available components of the sediment matrix were the driving influences on SOD. The measures best correlated with SOD were SOC, the smallest size fractions within LOC, WSC, and WSTN. In contrast, the carbon buried deeper in the sediments was not significantly correlated with SOD as it was lower in average concentration and comprised of larger particles, corresponding with harder to decompose, more recalcitrant fractions. While DO concentrations within the sediment were not measured in this study, oxygen demand is by nature an aerobic process and the lack of a significant relationship between SOD and any soil properties measured within the 5-15 cm depth fraction lends support that oxygenation within the already depleted water column may not extend past that upper sediment layer. However, a study in a perennial blackwater stream in Virginia found that despite water column DO concentrations always near saturation, anaerobic conditions in the sediments were found 5 cm below the surface in the summer and early autumn and 10 cm below the surface during the rest of the year (Strommer and Smock, 1989).

Previous studies have had mixed results when correlating SOD to the organic matter content of soils. Thomann and Mueller (1987) stated that SOD values range from 0.2 g O_2/m^2/day for sandy sediments to 10 g O_2/m^2/day for very organic sediments. Fuss and Smock (1996) working in a Virginia blackwater stream found that respiration rates were positively related to particulate organic matter content in the sediments and explained between 85 and 87% of the variation in sediment respiration. However, other studies have found no relation between organic matter content and the rate of SOD (Seiki *et al.*, 1994; Caldwell and Doyle, 1995). Bowie *et al.* (1985) stated that the varied spatial distribution in sediment physical and chemical characteristics along with differing rates of deposition would likely lead to considerable variation in measurements of SOD. Further, it may be difficult to estimate SOD based on organic content because communities of similar content may support completely different benthic communities. Although there was considerable variation in the results, this study supports the idea that the organic carbon content of the underlying sediments can be a useful predictor of SOD particularly at lower levels of organic carbon. At higher levels of organic carbon there was considerably more variation and in the case of instream swamps such as this one with highly organic sediments, SOD may at some point become carbon saturated possibly contributing to some of the variation.

SOD increased linearly with increasing initial concentration of DO (Figure 5). A possible reason for this relationship is that as DO increases (gets closer to saturation), a greater variety and multitude of heterotrophic communities become active. At low concentrations of DO, respiration may be limited to those communities best adapted to lowered conditions. Chiaro and Burke (1980) also showed this same relationship when investigating SOD in the Saginaw River system in Michigan. These authors suggested that the mass transfer coefficients of oxygen to the sediments was a more relevant measure for water quality modeling. Additionally, as mentioned in the methodology, the chambers were not started for data collection until all chambers had been sealed. This led to a lag in time of 45-90 min between seal of the first and final chambers. During this time, DO would be consumed in the first sealed chamber without data being recorded. As Figure 5 shows, the amount of initial DO within the chamber was positively related to SOD and could lead to a low bias and conservative estimate of average SOD rates within this system. Nevertheless, this work highlights that the beginning concentration of DO in the water column may be one of the leading limiting factors of SOD in these systems.

Policy and TMDL Implications

Low DO concentrations are a chronic and widespread feature of the Georgia Coastal Plain, with the majority of impaired water segments listed for failing to meet the listed DO criteria. In developing water quality models for TMDL compliance, SOD is often estimated from published literature values for similar stream environments. However, our study showed that SOD can be widely variable and considerably different from literature values. Additionally, SOD rates measured in this study were higher than previously measured rates within the same watershed. Instream swamps are a common feature on the Georgia Coastal Plain and appear to play a dramatic role in oxygen dynamics locally and possibly across a watershed scale. The combined influences of extended residence time and elevated oxygen demand highlight the importance of instream swamps across the landscape and should not be ignored when developing water quality models. This paper also supports the hypothesis that areas of high organic carbon are significant predictors of SOD and may be a good initial step in determining areas of high SOD. However, there is no substitute for actually measuring SOD *in situ* whenever possible.

In the most recent state water quality report, the Georgia Environmental Protection Division proposes delisting some impaired segments under the premise that low DO conditions occur naturally and should not be subject to TMDL development (GAEPD, 2006). TMDL development for streams not meeting DO standards generally assumes perturbation due to anthropogenic nitrogen and phosphorus enrichment. Plans often propose removal of point sources or limiting nonpoint source additions of these nutrients. However, our study measured low nutrient levels (Table 2) in line with natural blackwater stream systems (Meyer, 1992; Smock and Gilinsky, 1992). Therefore, any TMDL design based on limiting nutrients may result in little actual improvement to instream DO levels. Furthermore, the already lowered DO concentrations suggest that stream biota would be particularly vulnerable to any additional anthropogenically induced increases in oxygen demand.

Our study strongly suggests that low DO concentrations are a natural phenomenon due to areas of intense oxygen demand such as instream swamps. Further, this work shows that even if DO concentrations in the water column were higher (Figure 5), SOD could actually increase. Matlock *et al.* (2003) showed that SOD rates are often oxygen limited below 2 mg/l due to diffusion limitations across the water-sediment boundary. Potential SOD rates were considerably higher under higher ambient DO conditions and resuspension events. Therefore, any TMDL that was designed to raise instream DO levels may see little actual improvement due to increased SOD. Nevertheless, prior to delisting stream segments, the anthropogenic influence on the stream system should be evaluated.

Future work looking at the role of instream swamps is paramount to understanding DO dynamics within blackwater streams of the Georgia Coastal Plain. Ongoing work is investigating the role of movement and residence time of water as it moves through these instream swamp complexes, as well as the distribution of these sediment properties on a reach scale. Additional work examining instream swamps of different sizes and in other watersheds would be beneficial. Finally, further investigation of the role that initial DO concentration may have on oxygen demand would be of help in determining whether proposed oxygen increases through TMDL implementation would be sustained.

CONCLUSIONS

1. SOD rates for instream swamps averaged 5.37 g O_2/m^2/day and ranged from 0.491 to 14.189 g O_2/m^2/day, up to 18 times higher than values reported for southeastern sandy-bottomed streams.
2. SOD rates were significantly correlated with a number of sediment parameters, with SOC and TOC in the 0-5 cm depth fraction the best predictors of SOD rate within the instream swamp system, both explaining 35% of the variation.
3. Instream swamps in blackwater streams play a principal role in determining the oxygen balance of the watershed as a whole due to areas of intense oxygen demand.
4. Low DO concentrations may be a natural phenomenon in many southeastern blackwater streams and TMDLs based on limiting nutrients may result in little actual improvements to instream DO levels.
5. When developing water quality models, managers should pay closer attention to the influence of SOD as it plays a critical role in determining DO levels within instream swamps and the river system.

ACKNOWLEDGMENTS

This work has been supported by a grant from the USDA-CSREES Integrated Research, Education, and Extension Competitive Grants Program – National Integrated Water Quality Program (Award No. 2004-5113002224), Hatch and State funds allocated to the Georgia Agricultural Experiment Stations, and USDA-ARS CRIS project funds. We would like to thank Wynn Bloodworth, Chris Clegg, Debbie Coker, Jerry Davis, Herman Henry, Paige Gay, Mike Gibbs, Rodney Hill, Lorine Lewis, and Andrew Mehring for field, laboratory, and technical assistance. We would also like to thank James Walker and Pat Bailey for generously allowing access onto their land.

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