INSTREAM SWAMPS AND THEIR EFFECT ON DISSOLVED OXYGEN DYNAMICS WITHIN BLACKWATER STREAMS OF THE GEORGIA COASTAL PLAIN: ROLE OF HYDROLOGY AND SEDIMENT OXYGEN DEMAND

by

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(Under the Direction of George Vellidis and Catherine M. Pringle)

ABSTRACT

Blackwater streams on the Georgian Coastal Plain are distinguished by violation of the state's dissolved oxygen (DO) standard leading to TMDL development as required by the Clean Water Act. These streams are characterized by low slopes, high summertime temperatures, and extensive inundation of surrounding floodplains. Typically lasting from winter to early spring, the long inundation period creates a multitude of instream floodplain swamps that play a vital role in overall water quality. One of the hypothesized reasons for the relatively low DO levels in these systems is the slow movement or water and extended contact with underlying sediments. This dissertation investigated the role of these instream swamps on a watershed scale and focused specifically on the influences of sediment oxygen demand (SOD), the distribution of organic sediments and the role of hydrology on water column DO concentrations. Results support the idea of extended travel times through these instream swamps due to tortuous flow pathways and extensive transient storage. SOD values were measured well above previously published values and were correlated with increasing organic carbon content. Results show that organic sediments are widespread and become more prevalent in higher order streams. While DO dynamics are a complicated mix of natural and anthropogenic factors, instream swamps play a critical role in overall watershed oxygen dynamics and support the hypothesis that these systems are naturally low in DO. Further, these studies suggest that biota may be particularly vulnerable to any additional anthropogenically induced oxygen demand because of these already naturally lowered DO conditions.

INDEX WORDS: Dissolved oxygen, Blackwater streams, Hydrology, Sediment oxygen demand, Georgia coastal plain

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

INTRODUCTION

Dissolved oxygen (DO) levels within the four main blackwater river systems (Ochlocknee, Satilla, Suwannee, and St. Mary's) and their tributaries on the southern Georgia Coastal Plain regularly violate Georgia's Department of Natural Resources standard (Figure 1.1). These waterways, colored by the humic substances which leach into the water column, are distinguished by their low slopes, high summertime water temperatures, and extensive floodplain inundation. In addition, these stream systems are characterized by a series of instream

Figure 1.1. River systems of Georgia highlighting the four major blackwater river systems (Modified from Georgia Department of Natural Resources).

swamps and wetlands that dot the landscape during periods of high discharge. Heretofore, the effect of these swamps on dissolved oxygen is largely unexplored.

DO, a commonly measured water quality parameter, has been described as the "most important of all chemical methods available for the investigation of the aquatic environment" (Joyce et al. 1985). Upon violation of the state's standard, that waterway is required to be listed on the 303(d) list as mandated by the United States Clean Water Act (1972) (CWA). Upon listing, a total maximum daily load (TMDL), or the total amount of a pollutant that a given water body can sustain without compromising water quality standards, is developed. As part of that listing, an implementation plan is developed and enacted to bring the affected water body back into compliance. At the onset of this project, of the segments not supporting their designated uses with these basins, 90% of them were listed due to violation of the DO standard (GADNR 2000-2001). Normally, lowered DO in streams like those found in the Georgia Coastal plain are assumed to be a consequence of increased biological activity from nitrogen and phosphorus enrichment. Nutrient enrichment in these systems usually leads to increased algal biomass, dark respiration and biological oxygen demand (Mallin et al. 2001, Mallin et al. 2004).

However, recent research has shown lowered DO levels in many of these systems and not a sign of pollution or impairment (Joyce et al. 1985, Meyer 1992, Ice and Sugden 2003). Among the reasons hypothesized for these lowered DO levels are the high summertime water temperatures, slow movement of water, and extended contact with the underlying sediments. If streams are naturally deficient in DO and below the regulatory standard even in unimpacted reaches, development, implementation, and attainment of TMDLs stipulations as mandated under the CWA would prove difficult to achieve and may needlessly waste both manpower and economic resources.

In response to this growing body of evidence, the state has proposed delisting some listed segments under the premise of having “naturally low” DO concentrations. However, many of the blackwater streams in the Georgian Coastal Plain drain areas of intensive agriculture use that in recent years have supplemented the waterways with additional nutrients through the use of commercial fertilizers that could further exacerbate already low dissolved oxygen conditions (Carey 2005, Carey et al. 2007). Because of this mix of natural and anthropogenic factors, determining the actual natural DO level in blackwater streams is a time intensive and costly endeavor.

Objectives

This dissertation is part of an ongoing project and seeks to build on the growing body of information concerning lowered DO levels within the blackwater river systems of the Coastal Plain of Georgia (Cathey 2005, Carey et al. 2007, Utley et al. 2008). An under investigated feature of these systems is the influence and role of the numerous instream swamps. To that end the main objectives of this project are:

1) Characterize and document the magnitude and variability of sediment oxygen demand (SOD) in representative instream swamps found on the Georgia Coastal Plain and relate them to stream and floodplain sediment characteristics.
2) Investigate the movement and travel time of water moving through these instream swamp complexes.
3) Provide recommendations and guidance in advancing development of proper dissolved oxygen standards within the state of Georgia.

To that end, I have investigated SOD, sediment characteristics, and movement of water at two instream swamps of different size found within a representative blackwater system, the Little River Experimental Watershed.

LITERATURE REVIEW

Blackwater Streams

Blackwater streams and rivers are a common feature found throughout the Coastal Plain of the Southeastern United States. They offer a chance to investigate river processes in a stream system that is largely unimpacted by flow alteration or large impoundments and in many areas maintain their riparian buffer zones (Smock and Gilinsky 1992, Katz and Raabe 2005). They are characterized by low slopes, high summertime temperatures, and large inputs of dissolved organic material (Meyer 1990, Smock and Gilinsky 1992). The large inputs of dissolved organic materials stain the water their characteristic coffee or tea colored complexion. These large influxes of organic materials are attributed to the marked seasonal change in flow and extensive floodplain inundation (Mulholland and Kuenzler 1979, Benke and Meyer 1988). The marked seasonal change in discharge and areal extent is highly precipitation dependent with floodplain inundation typically lasting from winter to early spring, followed by extensive drying (sometimes completely) during the summertime months when evapotranspiration becomes dominant (Wharton 1978, Wharton et al. 1982). Many streams, up to at least 5^{th} order are intermittent.

Found throughout these blackwater systems are a series of instream swamps and floodplain wetlands that form a vital link between the terrestrial environment and the river channel as they alternate between landscapes and riverscapes. Owing to the low topography of the region, 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). The role of hydrology within this system is the principal force in the maintenance of floodplain environments through the movement and storage of sedimentary material as well a key player in biogeochemical processes (Mitsch and Gosselink 1986, Hupp 2000). Although blackwater basins are characterized by their low slopes, 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). This wide variety leads to difficulties in classification as these instream swamp areas are known by a variety of names such as southern deepwater swamps (Mitsch and Gosselink 1986, Conner and Buford 1998), blackwater river and swamp systems (Wharton 1978), southern floodplain forests (Sharitz and Mitsch 1993) and bottomland hardwood swamps (Wharton et al. 1982).

Water Quality

Maintenance of water quality in our nation's waterways is of growing concern, expense, and importance in the United States. In a recent water quality report, 45% of our nation's waterways were impaired for one or more reasons (USEPA 2007). Within the state of Georgia, 58% of its rivers and streams either partially support or do not support their designated uses (GADNR 2002-2003). As required by the U.S. Clean Water Act (1972) (CWA), states are required to set water quality standards for maintenance of waterbodies as either fishable, swimmable or drinkable and report results of those streams and river segments not meeting those standards under section 303(d). Those rivers and streams not meeting designated standards are required to develop a Total Maximum Daily Load (TMDL), or the total amount of a pollutant that a given water body can sustain without compromising water quality standards. The goal of the TMDL is to bring the affected water body back into compliance with water quality regulations. Upon approval and adoption of a TMDL, that water body is monitored until it is brought back into compliance. The development, implementation and monitoring of a given TMDL is a highly time intensive and costly endeavor.

DO is one of the many water quality parameters measured that is subject to regulation under the CWA. Measurement of dissolved oxygen is considered an excellent indicator of stream biological activity and the “most important of all chemical methods available for the investigation of the aquatic environment” (Joyce et al. 1985). With reduced levels of dissolved oxygen, biological activity and biotic integrity could suffer. Within the state of Georgia, they have listed the standard for dissolved oxygen as: “A daily average of 6.0 mg L^{-1} and no less than 5.0 mg L^{-1} at all times for waters designated as trout streams by the Wildlife Resources Division. A daily average of 5.0 mgL^{-1} and no less than 4.0 mgL^{-1} at all times for waters supporting warm water species of fish (GADNR 2005). However, the state recognizes that certain water quality parameters including DO oftentimes do not fall within water quality standards and should therefore be applied a standard of “Natural Water Quality.” Natural conditions are defined as:

> Those that would remain after removal of all point sources and water intakes, would remain after removal of man made or induced nonpoint sources of pollution, but may include irretrievable effects of man’s activities, unless otherwise stated. Natural conditions shall be developed by an examination of historic data, comparisons to reference watersheds, application of mathematical models, or any other procedure deemed appropriate by the Director (GADNR 2005).

Within the state of Georgia, stream and river segments often do not meet the set DO criterion. The major blackwater river basins within the southern Coastal Plain of Georgia are often referred to as the Lower Four River Basins for their similar water quality characteristics and are comprised of the Ochlocknee, Satilla, Suwannee, and St. Mary’s Rivers (Figure 1.1).

Upon initiation of this project, of the segments not supporting their designated uses within these basins, the majority (61 of 68 listed river segments or 90%) were listed due to violation of the state's minimum DO standards of 4.0 mg L^{-1} or 24-hour average of 5.0 mg L^{-1} (GADNR 2000-2001). In the 2004 303 (d) list for the four river basins, 98 out of 119 or 82% of listed river segments were listed for violation of the state's DO standard. In the following years, there has been a push towards delisting some of the listed water segments under the premise of "natural conditions." The conditions set for delisting for DO with one or multiple consecutive years of available data are:

1) New data with 10% or less exceedences of the water quality standards will be eligible for delisting. Recommended data set consisted of at least 12 samples.
2) For those segments where a DO TMDL has been approved and a natural DO was established, EPD will compare the DO data with the natural DO established in the TMDL. If no violations of the natural DO occurred, the segment would be eligible for delisting (GAEPD 2006)

Of the river segments listed in the 2004 303(d) in violation of the DO standard, the 2006 list delists or shortens designated lengths in 51% of those (50 of 98 listed river segments), oftentimes under the premise of naturally low conditions.

Low Dissolved Oxygen

Low DO levels in slow moving streams such as those found in the Georgia Coastal Plain are generally assumed to be a consequence of increased biological activity from nitrogen and phosphorus enrichment. Nutrient enrichment in these systems usually leads to increased algal biomass, dark respiration and biological oxygen demand (Mallin et al. 2001, Mallin et al. 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 in recent years have supplemented the waterways with additional nutrients through the use of commercial fertilizers that could further exacerbate already low dissolved oxygen conditions (Carey et al. 2007).

Low dissolved oxygen levels may indeed be a natural phenomenon of these systems and not a sign of pollution or impairment. Various studies have shown dissolved oxygen levels below the 5 mg L^{-1} 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 were below the 5 mg L^{-1} standard and close to 60% were below the proposed revised limit of 3 mg L^{-1}. 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.

Sediment Oxygen Demand

The reasons for low dissolved oxygen levels are unknown, but are likely due to a combination of the factors listed above. A further sink for dissolved oxygen in this system that has been poorly investigated is the effect of SOD, or benthic oxygen demand, and specifically within instream swamps and floodplain wetlands. Hatcher (1986a) defines SOD as "the rate that dissolved oxygen is removed from the water column …due to the decomposition of organic matter in the bottom sediments." The sources of these organic materials can come from either outside the system (allochthonous material) such as leaf litter and wastewater point sources 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 under-estimated, as it can be a critical sink of dissolved oxygen (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.

Measuring SOD

In order for a SOD method to be considered acceptable it must be consistent, reproducible, and efficient (Bowman and Delfino 1980). SOD is generally arrived at via three methods: estimation, laboratory measurement using sediment cores, and *in situ* measurements. Each method has its own benefits and disadvantages. Estimation of SOD, by comparing to known SOD values in the literature, is the easiest and most commonly done for routine uses (Bowie et al. 1985, Hatcher 1986b). While time efficient, these values can vary widely over space and time, having the potential to be inaccurate. For instance, a study done in the Willamette River, Oregon found SOD values nearly fourteen times lower than a previous study done during 1970 (Caldwell and Doyle 1995).

The two most common laboratory and *in situ* methods are either batch or continuous flow. Batch methods consist of chambers covering a known surface area of sediment with a known volume of water. Water within the chamber is usually circulated and the level of DO is monitored over time (Bowman and Delfino 1980). The continuous flow method measures the difference in DO concentration between the influent and effluent water. The *in situ* method is generally considered to be more accurate (Hatcher 1986b, Murphy and Hicks 1986). However, (Bowman and Delfino 1980) consider the laboratory method to better meet the acceptability criteria rather than *in situ* methodologies. Logistically, *in situ* methodologies need considerable lead time, special equipment, and training for field crews. Furthermore, there is more variation both spatially and temporally with many uncontrollable ambient variables. In comparison, the laboratory method allows control of conditions such as weather, current velocity, temperature, light, and turbulence (Bowman and Delfino 1980). *In situ* methods minimize manipulation of sediments and other ambient conditions giving a more "natural" representation, while allowing the investigator to evaluate the quality of data while on site (Murphy and Hicks 1986). Most researchers consider biological processes to be the major component of SOD, therefore changes to the microbial community and its metabolism due to compaction and handling of laboratory samples can lead to considerable changes in SOD (Murphy and Hicks 1986).

Factors Affecting SOD

Multiple factors have been studied to assess their affect on SOD. Among those factors investigated are oxygen concentration, thickness of the benthic sediment, organic matter content, sediment resuspension, photosynthetic activity, invertebrate activity, salinity, pH, chemical oxygen demand, oxygen concentration at the sediment interface and temperature (Bowman and Delfino 1980, Bowie et al. 1985). Despite these studies, many of them result in contradictory results. For instance, SOD is often assumed to increase with increasing organic matter. Thomann and Mueller (1987) stated that SOD values range from 0.2 g m^{-2} d^{-1} for sandy sediments to 10 g m^{-2} d^{-1} for very organic sediments. However, other studies have found no relation between organic matter content and the rate of SOD (Seiki et al. 1994, Caldwell and Doyle 1995). Further, it may be difficult to estimate SOD based on organic content because communities of similar content may support completely different benthic communities.

Two of most studied factors in terms of affecting SOD are temperature and water velocity. Numerous studies have shown that SOD increases with increasing temperature (Bowman and Delfino 1980, Seiki et al. 1994, Truax et al. 1995). The effect of velocity on SOD rates has also been widely studied. Whittemore (1986) found that a doubling of the overlying water velocity resulted in a near doubling of the SOD rate. A theory by Nakamura and Stefan (1994) postulated that SOD increases linearly with velocity at low velocities, but becomes independent of velocity at higher ones. At low velocities, SOD is determined wholly by the rate of oxygen transport across the sediment-water interface. At higher velocities, SOD is instead affected by biological and chemical consumption, DO concentration, and the apparent diffusion coefficient of oxygen within the sediment (Nakamura and Stefan 1994). While showing a wide degree in variation, subsequent studies confirmed this phenomenon (Bowman and Delfino 1980, Josiam and Stefan 1999). However, Ziadat and Berdanier (2004) found that velocity differences were not significant, while the depth of the water column was. If velocity of the overlying water column is high enough to cause resuspension of the sediment bed, SOD increases as well (Bowman and Delfino 1980). For these reasons, care must be taken when deploying *in situ* chambers to minimize resuspension of the sediment and maintain velocities within the chamber similar to those at the sediment-water interface (Doyle and Rounds 2003).

As shown above, temperature and chemical composition of the water affect measures of SOD, a variable which changes across time. Other variables that have been shown to affect SOD at times include velocity, depth and sediment characteristics. All of these are variable across a reach and cross section while being interdependent. Further, microbial and biological communities would be expected to change with time and across seasons possibly affecting SOD rates. For these reasons, SOD is an extremely variable process across space and time. In order to gain an accurate representation of SOD characteristics and realistic estimation of rates and variation, multiple measures are required (Bowie et al. 1985).

Travel Time

The primary factor in describing water quality in a river system is the movement of water principally in a downstream direction (Thomann and Mueller 1987) (Thomann and Mueller 1987). Any solute or pollutant mixing in a river system follows three main phases:

1) With depth through the water column
2) Laterally across the river channel
3) Longitudinally as it transported downstream (Figure 1.2).

Mixing with depth is usually the quickest process, followed by lateral mixing. As a solute or pollutant travels downstream, its concentration is dispersed until fully mixed throughout the water column. Another force involved in solute transport and retention is the process of transient storage. Transient storage is the process by which water is stored in dead zones within a stream channel (such as side eddies or pools) or exchanges through the hyporheic zone (Bencala and Walters 1983). These "dead" areas of the stream allow extended contact time with microbial communities and extend residence time through a reach. In a blackwater stream system these extended contact times with the bottom sediments could be a driving force in lowering dissolved oxygen levels. Despite this potentially strong influence on dissolved oxygen dynamics, the role of travel time in blackwater systems and specifically instream swamps has received minimal attention (but see Pernik and Roberts 1985).

Measuring travel time

The calculation of travel time is accomplished through the use of a conservative tracer. Ideally, a conservative tracer is one which behaves exactly how a water molecule traveling through the system would behave and not subject to decay, biological uptake, sorption to sediments or vegetation and loss. Finding a tracer that is truly conservative has been problematic as it is difficult to find one that is not affected by one of the processes listed above. Rhodamine WT is a common and recommended tracer because of its ease of use, economical price, and ease of detectability (Smart and Laidlaw 1977, Kilpatrick and Wilson 1989). However, rhodamine WT has shown to not be a truly conservative tracer due to mass loss via sorption to sediments (Smart and Laidlaw 1977, Bencala et al. 1983, Lin et al. 2003) and photochemical decay in experiments lasting longer than a week (Smart and Laidlaw 1977). Despite these limitations,

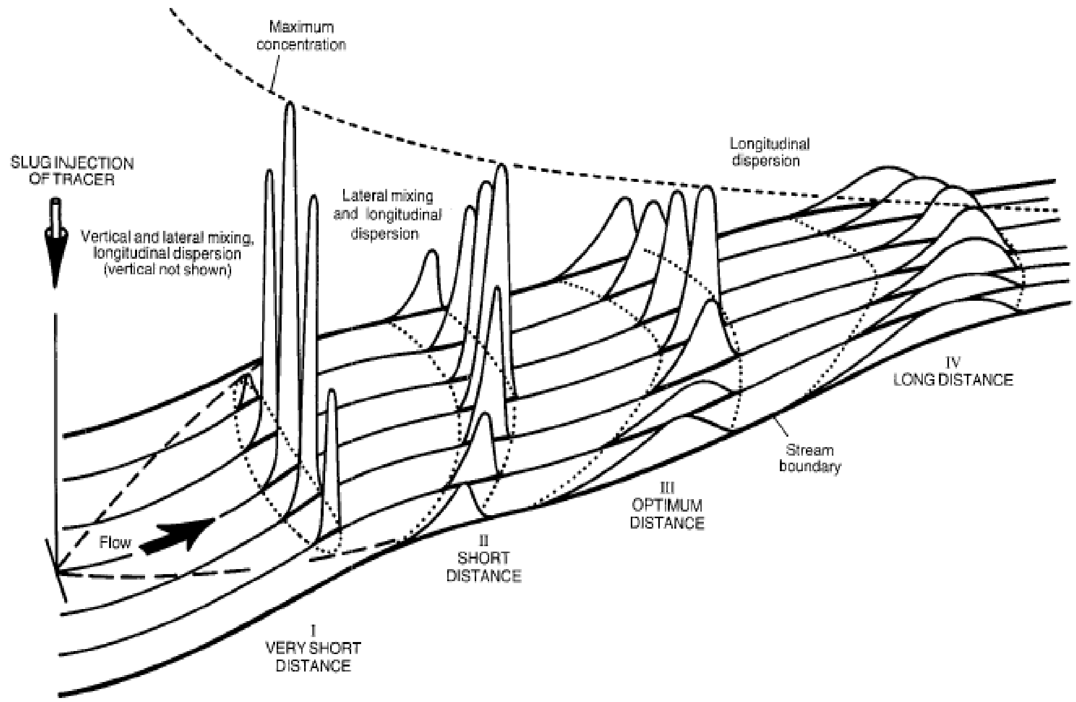

Figure 1.2. Lateral mixing and longitudinal dispersion patterns and changes in distribution of concentration downstream from a single, center slug injection of tracer (from Kilpatrick and Wilson 1989).

rhodamine WT is among the most common tracers used for analyzing travel time within a stream environment and is approved for use by the USGS.

Measurement of travel time is accomplished by adding the tracer to the stream water column and letting it diffuse and spread evenly across the river channel. Travel time is either measured via a continuous or slug injection. With a continuous injection, dye is added at a constant rate until reaching a plateau concentration at up and downstream measuring points. Time till reaching plateau between the stations is determined to be reach travel time. With a slug injection, a single pulse of known dye is injected usually into the center of flow and time between centers of concentration mass determined to be reach travel time. Dye concentrations are measured either via an *in situ* fluorometer or samples collected at known time intervals and brought back to the lab for analysis.

Stream Solute Transport Modeling

Modeling of stream transport has been aided in recent years by the development of OTIS, a quasi two-dimensional mathematical simulation model which is able to model the fate and transport of both conservative and nonconcervative solutes in rivers and streams (Runkel 1998). The model is based on the transient storage model first developed by Bencala and Walters (1983). The model is developed by creating mass balance equations for two conceptual areas: the main channel and the storage zone. The main channel is defined as the section of stream where advection and dispersion are the main transport properties while the storage zone is the area in which transient storage is the dominant process. The two areas are linked by an exchange term. The governing equations describing the spatial and temporal variation in solute concentrations are given by two coupled differential equations:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}(AD\frac{\partial C}{\partial x}) + \frac{q_{LIN}}{A}(C_L - C) + \alpha(C_s - C) \qquad [1]$$

$$\frac{dC_s}{dt} = \alpha\frac{A}{A_s}(C - C_s) \qquad [2]$$

Where A the main channel cross-sectional area (L^2); As the storage zone cross-sectional area (L^2); C is the main channel solute concentration (ML^{-3}); C_L is the lateral inflow solute concentration (ML^{-3}); C_s is the storage zone solute concentration (ML^{-3}); D is the dispersion coefficient (L^2T^{-1}); Q is the volumetric flow rate (L^3T^{-1}); q_{LIN} ($L^3T^{-1}L^{-1}$); t is time (T); x is distance along the main channel (L); and α, the storage zone exchange coefficient (T^{-1}). It is possible for all parameters to vary on a reach-by-reach basis as well as include terms for kinetic sorption and first-order decay in both the main channel and storage zones. For a complete write-up on the capabilities of the OTIS model see Runkel (1998).

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CHAPTER 2

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

[1] Todd, M.J., G. Vellidis, R.R. Lowrance and C.M. Pringle. To be submitted to the *Journal of the American Water Resources Association*.

Abstract. Blackwater streams are found throughout the Coastal Plain of the southeastern United States and are characterized by low gradients, high summertime temperatures, and extensive inundation of surrounding floodplains. Typically lasting from winter to early spring, the long inundation period creates a multitude of instream floodplain swamps that play a vital role in overall water quality. Over 90% of the blackwater streams listed as impaired on the Coastal Plain of Georgia are listed as being in violation of the state's dissolved oxygen (DO) standard. A key influence on the DO levels within these floodplain swamps is sediment oxygen demand (SOD), a critical and dominant sink for oxygen in many river systems that is often poorly investigated or roughly estimated in oxygen budgets. Results show SOD rates ranging from 0.491–14.189 g O_2 $m^{-2}d^{-1}$, 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 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 Words: sediment oxygen demand, dissolved oxygen, blackwater streams, organic carbon

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 (Meyer 1990, Smock and Gilinsky 1992). In large part, these rivers have been unimpacted by large impoundments and in many areas maintain an intact riparian buffer (Smock and Gilinsky 1992, Katz and Raabe 2005). The marked seasonal change in discharge and areal extent is largely precipitation-dependent with floodplain inundation lasting from winter to early spring, followed by extensive drying (sometimes completely) during the summertime months when evapotranspiration becomes dominant (Wharton 1978, Wharton et al. 1982). Many streams, up to at least 5th order, are intermittent during the summertime months.

A critical and frequently encountered feature of these 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).

These 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^{-1} and no less than 4.0 mg L^{-1} at all times for waters supporting warm water species of fish” (GADNR 2005). Any waterbody not meeting this standard is listed as impaired on the state’s 303(d) list as required by the CWA. Following listing, the state is required to develop and implement a Total Maximum Daily Load (TMDL) to bring that waterbody 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. 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 biological oxygen demand (Mallin et al. 2001, Mallin et al. 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 DO levels below the 5 mg L^{-1} 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 percent of their summertime observations were below the 5 mg L^{-1} standard and close to 60 percent were below the proposed revised limit of 3 mg L^{-1}. 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 (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 dissolved oxygen 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 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 under-estimated, as it can be a critical sink of dissolved oxygen (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 purpose of this study is to: (1) characterize and document the magnitude and variability of SOD in representative instream swamps found on the Georgia Coastal Plain; (2) describe the relationship between SOD, soil and water column properties; (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. Although land use is primarily agricultural, riparian vegetation 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 1550 m long stretch of river located in the lower part of the LREW above the gauging site designated Station B (Sheridan and Ferreira 1992) (Figure 2.1). The stream at this point is a 5th 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, flow may stop along with complete drying of the river channel (Figure 2.2). Additional measurements were made in a small headwater watershed (3rd order), with a main channel 5-10 meters in width and subject to overbank flooding during high flow events and cessation of flow during summertime months (Figure 2.1).

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 liters and covers a surface area of 0.27 m^2 on the stream bottom (Figure 2.3a). The cutting flange sinks the chamber 5.08 cm into the stream sediment. Water circulates throughout the chamber via a 12 volt DC submersible pump, powered by a 14 volt 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 amongst 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) logging to a handheld computer (Dell Axim X50) (Figure 2.3b). For each sampling event, SOD chambers were pushed into the sediment until sealed and then oxygen and temperature levels logged within chambers every two minutes for 2-3 hours. 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 45-90 minutes.

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

$$SOD = 1.44\frac{V}{A}(b_1 - b_2) \qquad [1]$$

Where:

SOD = the sediment oxygen demand (g O_2 m^{-2} day^{-1})

b_1 = the slope from the oxygen depletion curve (mg L^{-1} $minute^{-1}$)

b_2 = the slope from the oxygen depletion curve of the control chamber (mg L^{-1} $minute^{-1}$)

V = the volume of the chamber (L),

A = the area of bottom sediment covered by the chamber (m^2)

1.44 = a units conversion constant (Caldwell and Doyle 1995)

The slope for both control and experimental chambers was taken as the linear best fit for the oxygen depletion curve (Figure 2.4a). For most cases, the entire data set 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 2.4b). In these instances only the linear portion of the line was used to calculate SOD. SOD rates were then corrected to 20˚C using a modified van't Hoff form of the Arrhenius equation (Hatcher 1986b, Truax et al. 1995):

$$SOD_T = SOD_{20}\theta^{(T-20)} \qquad [2]$$

Where:

SOD_T = SOD rate at temperature T

SOD_{20} = SOD rate at 20˚C

θ = temperature correction coefficient chosen from literature

Values for θ, based on the type 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 3rd order and 5th order location throughout the period of flowing water and adequate DO to achieve a reliable measure of SOD. Measurement of SOD is limited by depth within the stream channel as water must be approximately 36 cm to fully submerge the chamber and depths of over approximately 90 cm would require the use of artificial breathing equipment, thereby restricting sampling to time periods when hydrologic conditions permitted (generally winter to spring). Nevertheless, the sampling regime encompassed the time period critical for lowered DO in the LREW as stream channels are oftentimes completely dry during the summer and fall months (Figure 2.2). 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; 3/20/07-Chamber 2; Table 2.1), omitted because of chamber leakage. In total, five usable measure of SOD were gathered at the 3rd order location and 19 measures from the 5th 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, approximately 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 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) 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 (<2mm, 2-5mm, and >5mm diameter). Litter <2mm diameter was separated from inorganic material by placing material in a beaker and then adding deionized 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 was removed by extracting with room temperature deionized (DI) water. The second step involved extracting labile components of soil carbon using a water bath at 80ºC for 16 hours. The two steps are hereafter referred to as water soluble carbon and total nitrogen (WSC and WSTN respectively) and hot water extractable carbon and total nitrogen (HWC and HWTN respectively).

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 one hour on a Fisher Scientific Hematology Mixer, centrifuged for 30 minutes at 2500 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 seconds to ensure complete resuspension. The tubes were then placed in a hot water bath for 16 hours at 80ºC. 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 total nitrogen using a Shimadzu TOC-V Combustion Analyzer.

Water Sample Preparation

Before and after each deployment, temperature, pH, conductivity, ambient DO level and percent saturation were measured using a YSI 6920 sonde. 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^+), total nitrogen (TN), total phosphorus (TP), and dissolved organic carbon (DOC) concentrations. NO_3-N, OP, NH_4-N, and Cl were measured on a Technicon Instruments TrAAcs 800 Autoanalyzer. TN and TP were measured on an Bran+Luebbe AA3 Autoanalyzer. TOC and was analyzed using a Shimadzu TOC-5050a Total Organic Carbon Analyzer with a Shimadzu ASI-5000A Auto Sampler. K^+ was analyzed using a Perkin-Elmer AAnalyst 100 Atomic Absorption Spectrometer.

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 amongst 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^{-1} like those displayed in Figure 2.4c despite the lack of stratification through the water column.]

Since 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; 4/19/06 Chamber 1-3; Table 2.1). 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 – 14.19 g O_2 $m^{-2}d^{-1}$ with an average SOD rate of 5.37 g O_2 $m^{-2}d^{-1}$ (Table 2.1). For the points measured at the instream swamp in the 5th order stream, the SOD rate was shown to significantly correlate with the initial DO concentration measured at the beginning of a run (Figure 2.5; $r^2 = 0.527$, p=<0.0001). None of the measured ambient water quality parameters were significantly correlated with the measurements of SOD (Table 2.2).

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^{-1}) at all size classes (<2 mm, 2-5 mm, and >5 mm) as well as total concentration were significantly correlated with SOD (Table 2.3). The measures of extractable carbon (WSC, HWC, TWC) and extractable total nitrogen (WSTN, HWTN, 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 ($r^2 = 0.2318$, p = 0.0200) the best predictors in their respective pools (Table 2.3). 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}^{-1}) or TOC (mg g_{total}^{-1}) alone was the single best predictor of SOD rate (Table 2.3, Figure 2.6a 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 cm and 5-15 cm depth fractions is found within the SOC pool (Figure 2.7a). SOC represents significantly more of the carbon pool at both depth fractions with around 80% of total carbon (0-5 cm: $F = 436.50$, $p = <0.0001$; 5-15 cm: $F = 295.80$, $p = <0.0001$). Additionally, the average SOC concentration is significantly higher in the 0-5 cm depth fraction as compared to the 5-15 cm depth fraction (Figure 2.7b; $F = 37.59$, $p = <0.0001$). 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 2.8a; $F=24.19$, $p=<0.0001$). However, in the 5-15 cm depth class, significantly more of the litter is found in the largest >5mm size class as compared to the other two classes (Figure 2.8b; $F=9.59$, $p=0.0001$).

DISCUSSION

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 – 0.77 g O_2 $m^{-2}d^{-1}$. All but one (23 of 24 measures) of the SOD measurements in this study are higher and, in some cases, much higher (up to 18 times) than this range. The average SOD rate across all samples is 5.37 g O_2 $m^{-2}d^{-1}$, 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 – 1.4 g O_2 $m^{-2}d^{-1}$ in the agricultural catchment and 0.9 – 2.5 g O_2 $m^{-2}d^{-1}$ in the forested catchment (Crompton 2005, Utley et al. 2008). The previous studies failed to look at rates within instream swamps and focused sampling at more easily accessible road crossing. These locations had the potential to be impacted anthropogenically and may not represent actual conditions across the watershed. 75% of the measurements made in the instream swamp during this study are above the highest value recorded during the previous study (Table 2.1). These results indicate that SOD plays an even greater role than previously believed in the LREW. This is the first time SOD has been measured in instream swamps and our results suggest that instream swamps are areas of intense oxygen demand and are a major factor in the oxygen balance of the watershed as a whole.

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 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^{-1} there is a total of 3050 mg of O_2. Assuming no reaeration, photosynthesis or movement of water, available DO within the water column would be consumed in just over a half a day using the average SOD rate of 5.37 g O_2 $m^{-2}d^{-1}$ measured in this study. Using the maximum rate of SOD measured in this study (14.19 g O_2 $m^{-2}d^{-1}$), 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 2.4). Comparison among these different measures is hampered by the differing water temperatures across season and location. Since all SOD rates in this study have been corrected to 20˚C, to aid in comparison between CR and SOD, we corrected community respiration rates to 20˚C using a modified form of Equation 2:

$$CR_T = CR_{20}\theta^{(T-20)} \qquad [3]$$

Where:

CR_T = CR rate at temperature T

CR_{20} = 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 $m^{-2}d^{-1}$ in the 4th order Black Creek to 7.18 g O_2 $m^{-2}d^{-1}$ in the 6th order Ogeechee River (Table 2.4). 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 $m^{-2}d^{-1}$) indicates that SOD makes up a large portion of total CR within blackwater systems as it is higher than the total of the 4th order site and 75% of the total respiration measured in the 6th 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 – 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 discussed above (Sinsabaugh 1997). Although the streams in that comparison measured CR, the average measure of SOD alone in this study would place it with the 5th 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 $m^{-2}d^{-1}$ 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 $m^{-2}d^{-1}$ 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 this study however 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 measure *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.

SOC or TOC in the 0-5 cm depth fraction were the best predictors of SOD rate within the instream swamp system, both explaining 35 percent of the variation. The reason for their similar relationship is likely due to the majority of the TOC being made up of SOC (Figure 2.7a). In both depth classes ~80 percent of the TOC is compromised 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 percent of TOC in both depth classes (Figure 2.7a) with no significant differences between average concentrations (Figure 2.7b), 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 2.8). 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 towards smaller size fractions.

HWC 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 2.2). 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 sediment DO concentrations 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 $m^{-2}d^{-1}$ for sandy sediments to 10 g O_2 $m^{-2}d^{-1}$ 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 85-87% 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. In the case of instream swamps such as this one with highly organic sediments, SOD may at some point become carbon saturated, which may have contributed to some of the variation.

SOD increased linearly with increasing initial concentration of DO (Figure 2.5). 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 using the mass transfer coefficients of oxygen to the sediments as a more relevant measure for water quality modeling. Additionally, as mentioned in the methodology, the chambers were not started for data collection till all chambers had been sealed. This led to a lag in time of 45-90 minutes 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 2.5 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 DO in the water column may be one of the leading limiting factors of SOD in these systems.

Conclusion

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 literature values for similar stream environments. This study showed that SOD can be widely variable and considerably different from literature values. Additionally, SOD rates were higher than previously measured rates even 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 times 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 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 of having naturally low DO conditions thereby bypassing 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, this study measured low nutrient levels (Table 2.2) in line with natural blackwater stream systems (Meyer 1992, Smock and Gilinsky 1992). Therefore, any TMDL designed around limiting nutrients into the system may show little actual improvement to instream DO levels. Furthermore, the already lowered DO concentrations suggest that stream biota would be particularly vulnerable to any added anthropogenically induced increases in oxygen demand.

This study shows that low DO concentrations might be 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 2.5), SOD could increase and actually increase demand. Matlock et al. (2003) showed that SOD rates are often oxygen limited below 2 mg L^{-1} 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 must be diagnosed.

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 (Chapter 4) as well as the distribution of these sediment properties on a reach scale (Chapter 3). Additional work looking at instream swamps of different sizes and in other watersheds would be beneficial. Finally, further investigation of the role initial DO concentration may have on oxygen demand within this system would be beneficial in determining whether proposed oxygen increases through TMDL implementation would be sustained.

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Table 2.1 Individual chamber measurements of SOD_{20}, dissolved oxygen and temperature

Date	Site Location	Chamb.	SOD_{20} ($g\ O_2\ m^{-2} day^{-1}$) Ind	Avg	Chamb. DO ($mg\ L^{-1}$)	DO Change ($mg\ L^{-1}$)	Chamb. Temp (°C)
3/15/06	5th 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	5th 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	5th 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	5th Order	1	Low DO	4.95	0.34 – 0.00	0.34	-----
		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	5th 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	3rd 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	3rd 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	5th 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	5th 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	5th 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	5th 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

Table 2.2. Ambient water quality parameters for each sediment oxygen demand sampling date including temperature, pH, total P, dissolved organic carbon (DOC), nitrate (NO_3-N), ammonium (NH_4-N), orthophosphate (OP), chloride (Cl^-) and potassium (K^+)

Date	Site Location	Amb. Temp (°C)	Avg. pH	Total N (mg L^{-1})	Total P[a] (mg L^{-1})	DOC (mg L^{-1})	NO_3-N (mg L^{-1})	NH_4-N (mg L^{-1})	OP (mg L^{-1})	Cl^- (mg L^{-1})	K^+ (mg L^{-1})
3/15/06	5th 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	5th 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	5th 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	5th Order	17.04 – 18.96	5.78	0.6637	<0.2	14.55	0.042	0.052	0.018	12.602	3.2
4/19/06	5th 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	3rd 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	3rd Order	12.37 –	5.73	0.317	0.006	8.01	0.087	0.015	0.008	9.817	1.2
3/6/07	5th 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	5th 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	5th 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	5th Order	14.13 – 15.95	6.30	0.660	0.007	22.42	0.003	0.021	0.028	11.798	3.6

[a]Difference in precision between 2006 and 2007 due to change in laboratory analysis methodology

Table 2.3. Results of regression analysis (alpha = 0.05) relating SOD rate (g O_2 $m^{-2}d^{-1}$) to carious individual soil property measurements

OC Pool	Class	R^2	P<
Extractable C (mg kg^{-1})	WSC	0.3107	0.0057
	HWC	0.2629	0.0124
	TWC	0.2830	0.0090
Extractable TN (mg kg^{-1})	WSTN	0.2318	0.0200
	HWTN	0.1922	0.0364
	TWTN	0.2064	0.0294
LOC (mg g^{-1})	<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}^{-1})		0.3523	0.0022
TOC (mg g_{total}^{-1})		0.3579	0.0020

Table 2.4. Measures of community respiration (CR) and adjusted community respiration (CR_{20}) in other blackwater river systems

River	Stream Order	Sampling Period	Mean CR[a] ($g\ O_2\ m^{-2}\ d^{-1}$)	Temp (˚C)	Adjusted CR_{20}[b] ($g\ O_2\ m^{-2}\ d^{-1}$)	Reference
Ogeechee River, GA	6th	Annual	6.7 (3.70 – 11.75)	18.5	7.18	Edwards and Meyer (1987)
		Spring	6.93			Meyer et al. (1997)
		Summer	8.3			
		Autumn	5.82			
		Winter	5.48			
Black Creek, GA	4th	Annual	4.1 (2.3 – 9.6)	18.5[c]	4.39	Meyer and Edwards (1990)
Buzzards Branch, VA	1st	Annual	3.01	15	3.79	Fuss and Smock (1996)
						Smock (1997)
Kissimmee River, FL	4th-5th	Annual	9.44	25.0	7.50	Colangelo (2007)
		Wet (June-Nov)	13.91	27.8	9.72	
		Dry (Dec-May)	4.97	22.2	4.49	

[a]Data in parentheses represents the range of measurements during the annual period
[b]CR was adjusted to 20˚C using Equation 3
[c]Black Creek is a subwatershed of the larger Ogeechee River watershed. Temperature data was not reported for Black Creek so mean temperature was assume to be same as reported for the larger Ogeechee River watershed reported in Meyer et al. (1997)

Figure Captions

Figure 2.1. Map of Little River Ecological Watershed with Selected Sampling Locations.

Figure 2.2. Measure of discharge and dissolved oxygen for 2007 experimental season. Zero flow first occurred on Julian Day = 128 (7/8/2007) and did not resume for the remainder of the calendar year.

Figure 2.3a. Schematic of sediment oxygen demand chamber.

Figure 2.3b. Typical deployment of sediment oxygen demand chamber and associated data logger in the field.

Figure 2.4a. Typical oxygen decline curve during a sediment oxygen demand run showing a linear loss of oxygen concentration with time.

Figure 2.4b. Example of nonlinear loss of oxygen concentration with time during a sediment oxygen demand run. Slope for calculation sediment oxygen demand taken from initial linear portion.

Figure 2.4c. Example of low initial dissolved oxygen concentration with time during a sediment oxygen demand run. Calculation of sediment oxygen demand not possible due to zero oxygen remaining in chamber during run.

Figure 2.5. Relationship between initial dissolved oxygen (DO) concentration and sediment oxygen demand (SOD) rate within the 5th order instream swamp location.

Figure 2.6a. Relationship between soil organic carbon (SOC) and sediment oxygen demand rate (SOD).

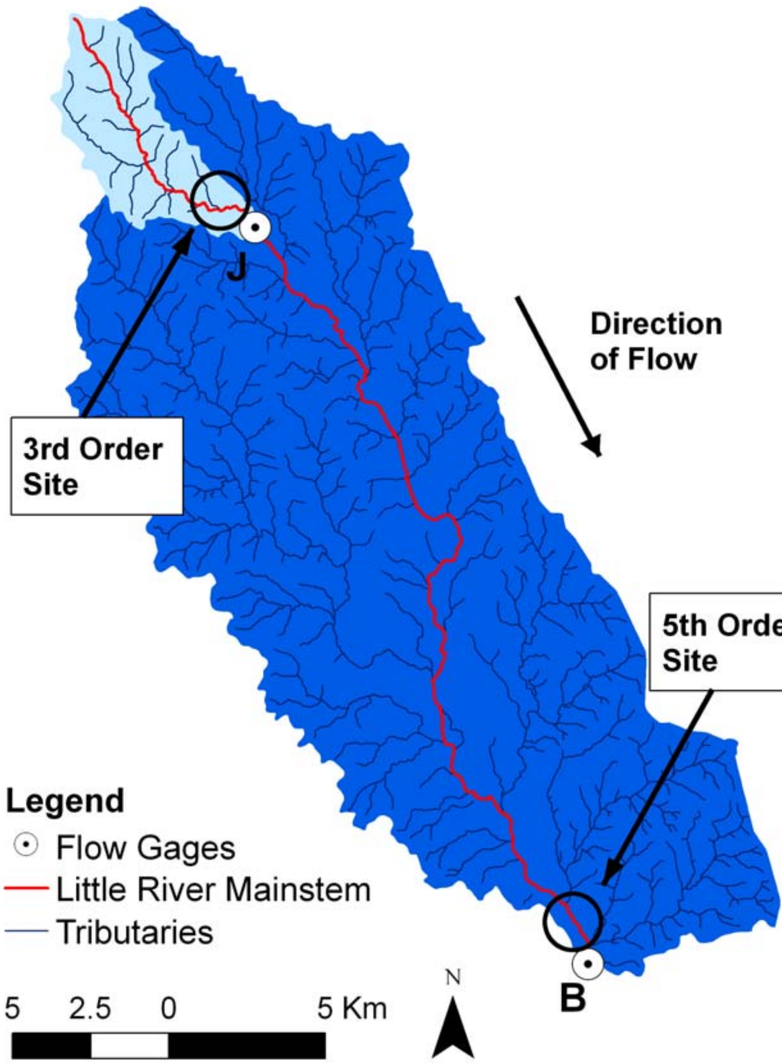
Figure 2.6b. Relationship between total organic carbon (TOC) and sediment oxygen demand (SOD).

Figure 2.7a. Percentage of soil organic carbon (SOC) and litter organic carbon (LOC) within each depth class. Different letters denote significant differences between bars. Error bars = ±1 standard error.

Figure 2.7b. Average concentration of soil organic carbon (SOC) and litter organic carbon (LOC) with depth. Different letters denote significant differences between bars. Error bars = ±1 standard error.

Figure 2.8. Percentage of litter organic carbon at different size classes with depth. Different letters denote significant differences between bars. Error bars = ±1 standard error.

Figure 2.1



J
Direction
of Flow
3rd Order
Site
5th Order
Site
Legend
Flow Gages
Little River Mainstem
Tributaries
5 2.5 0 5 Km
N
B

Figure 2.2

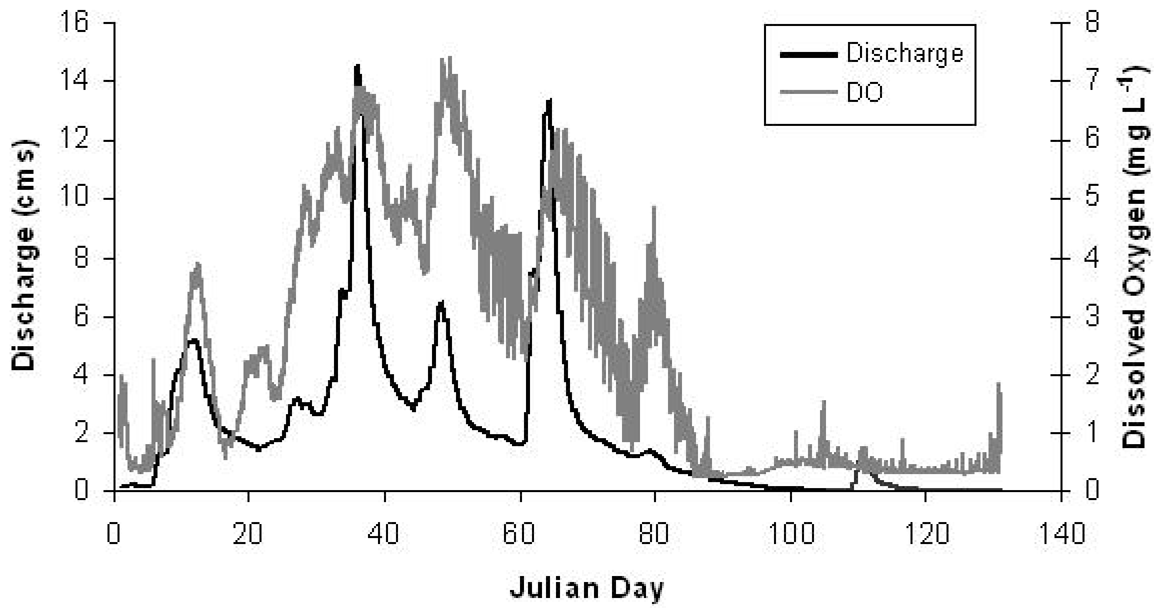
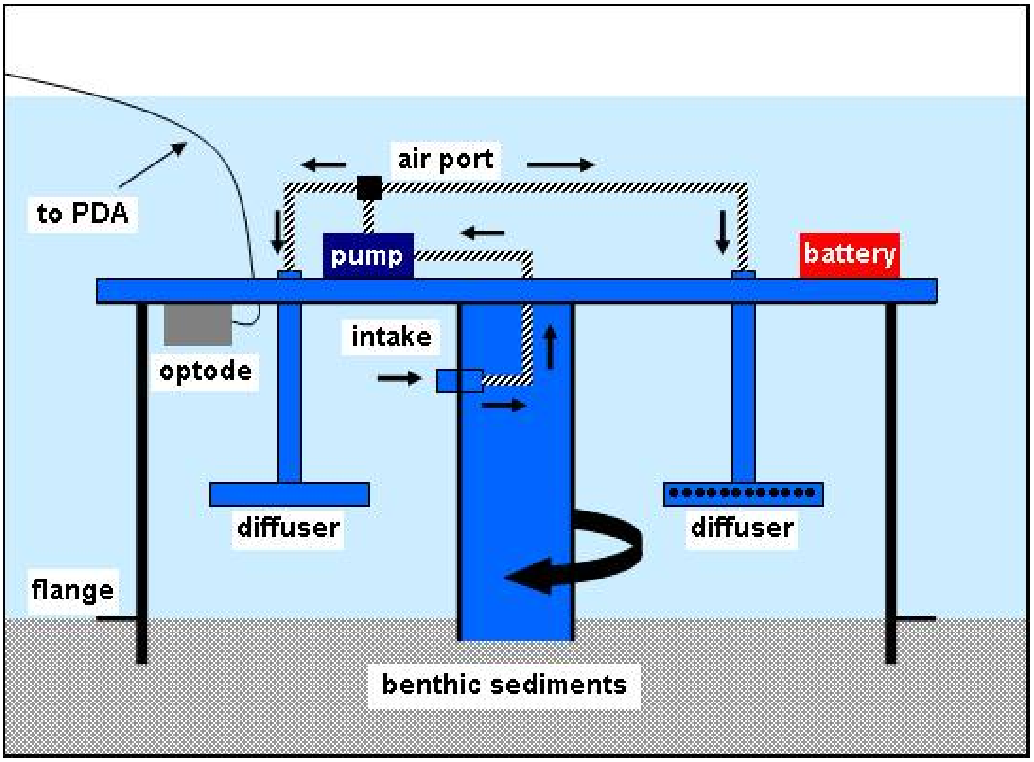

Discharge
DO
Discharge (cms)
Dissolved Oxygen (mg L-1)
Julian Day
0
2
4
6
8
10
12
14
16
0
1
2
3
4
5
6
7
8
0
20
40
60
80
100
120
140

Figure 2.3a and 2.3b



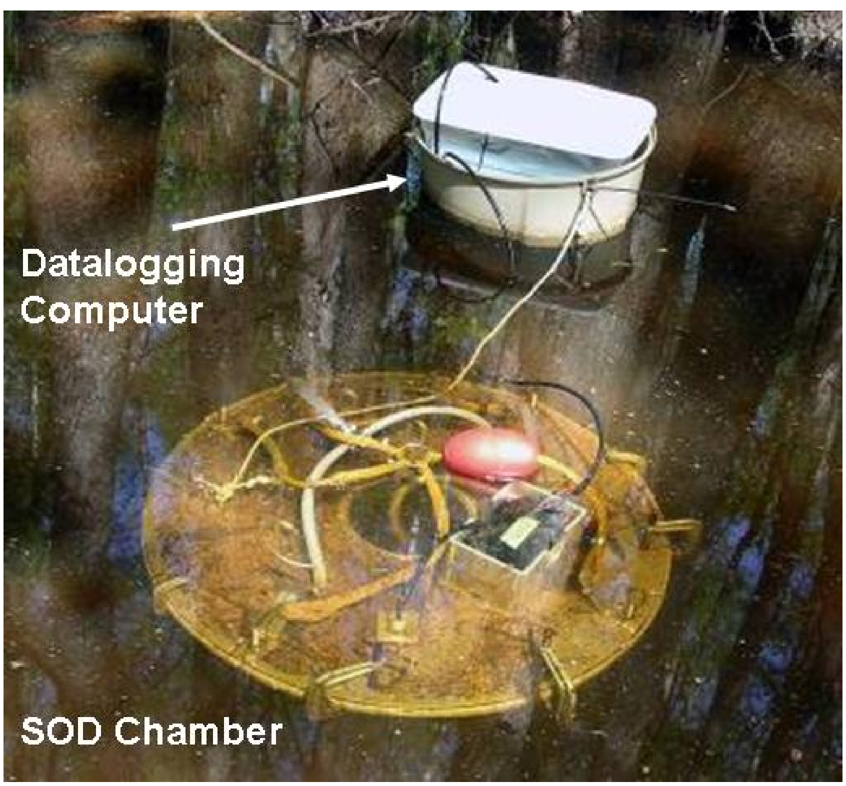


Figure 2.4a, 2.4b and 2.4c

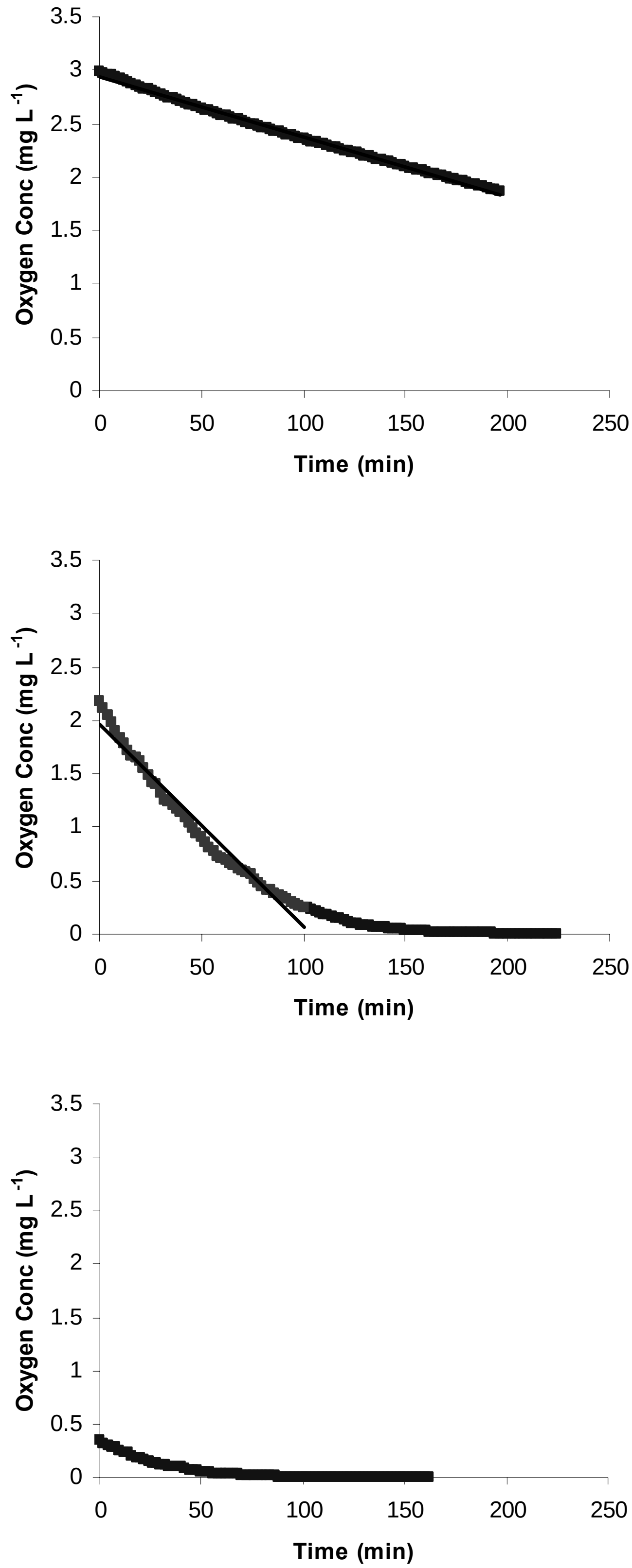
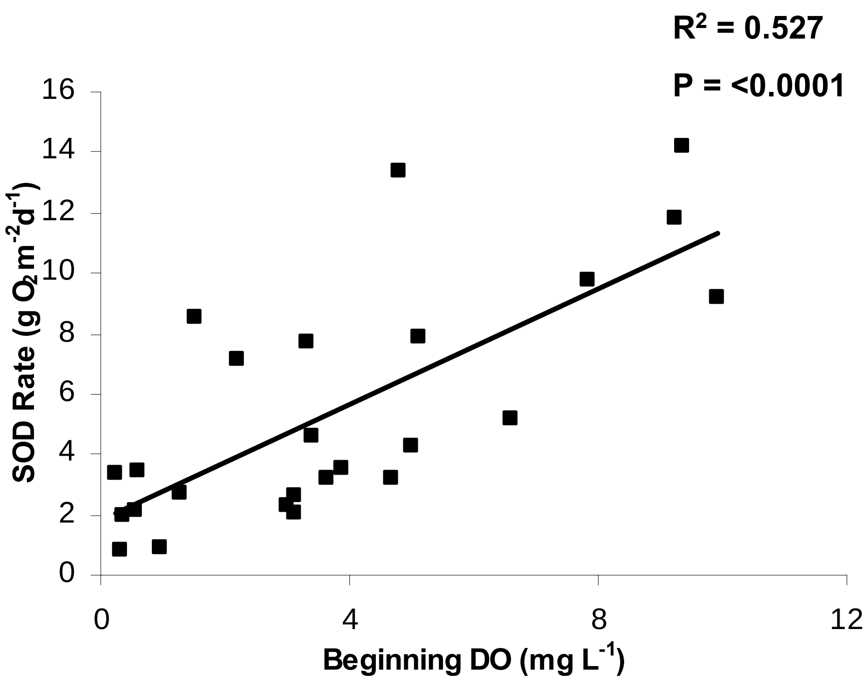
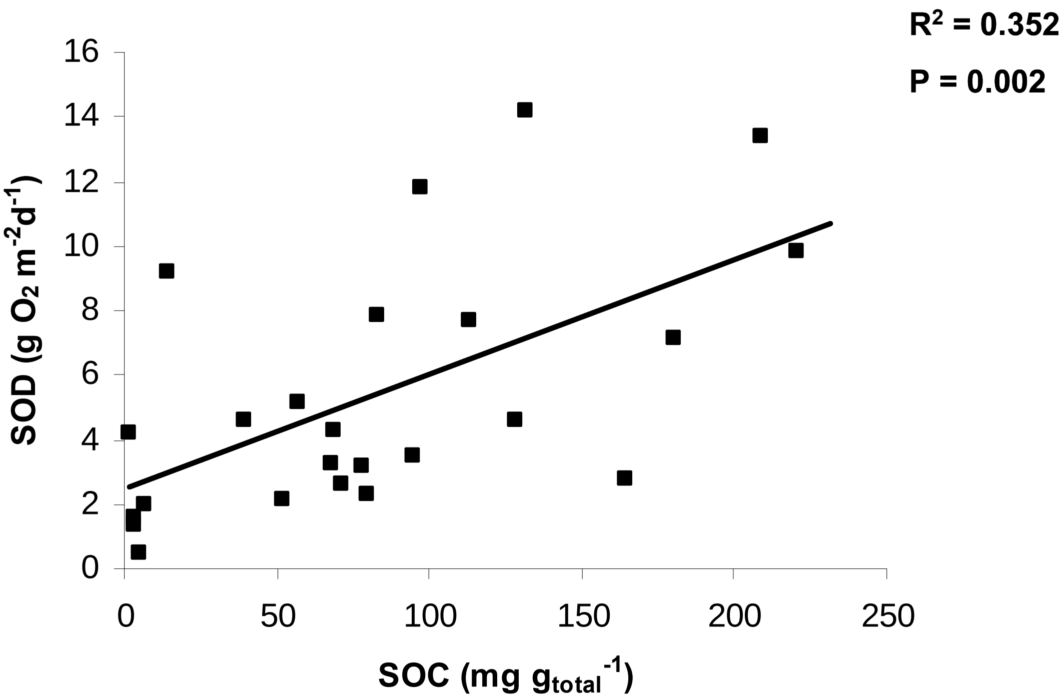


Figure 2.5



R2 = 0.527
P = <0.0001
16
14
12
10
8
6
4
2
0
SOD Rate (g O2 m-2d-1)
0
4
8
12
Beginning DO (mg L-1)

Figure 2.6a and 2.6b



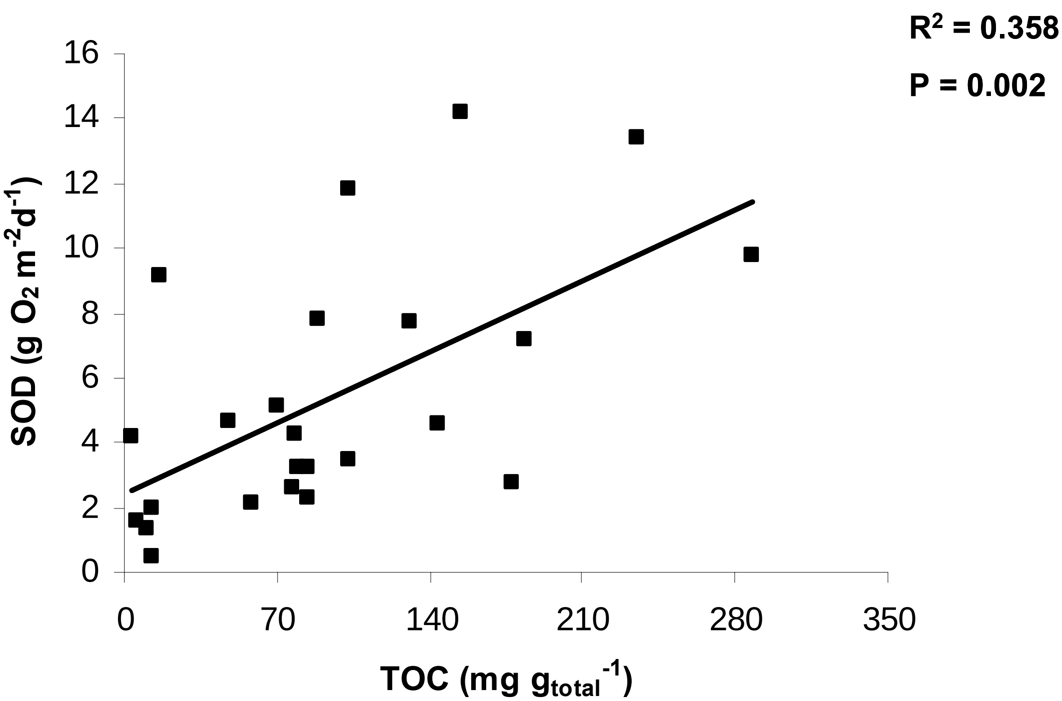
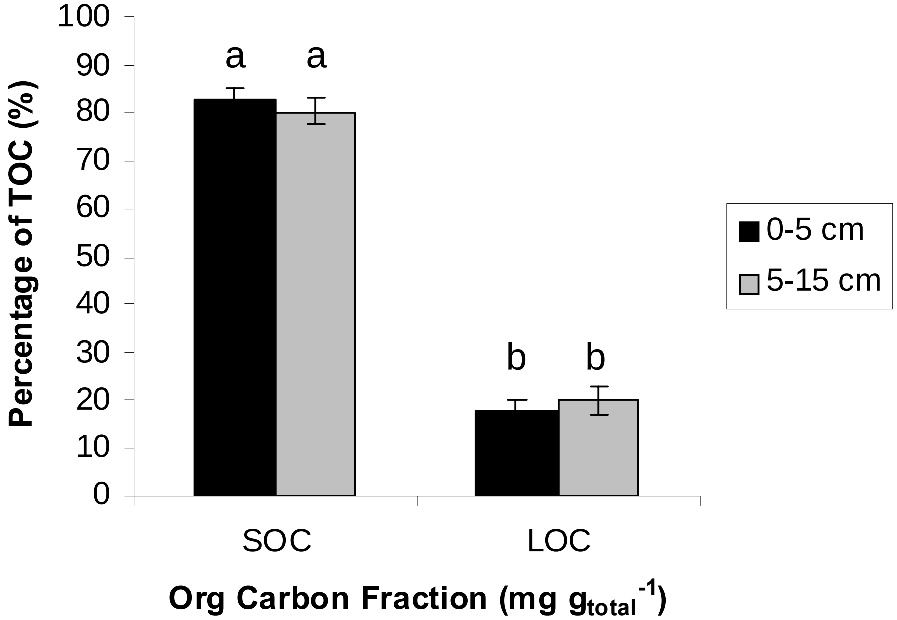


Figure 2.7a and 2.7b



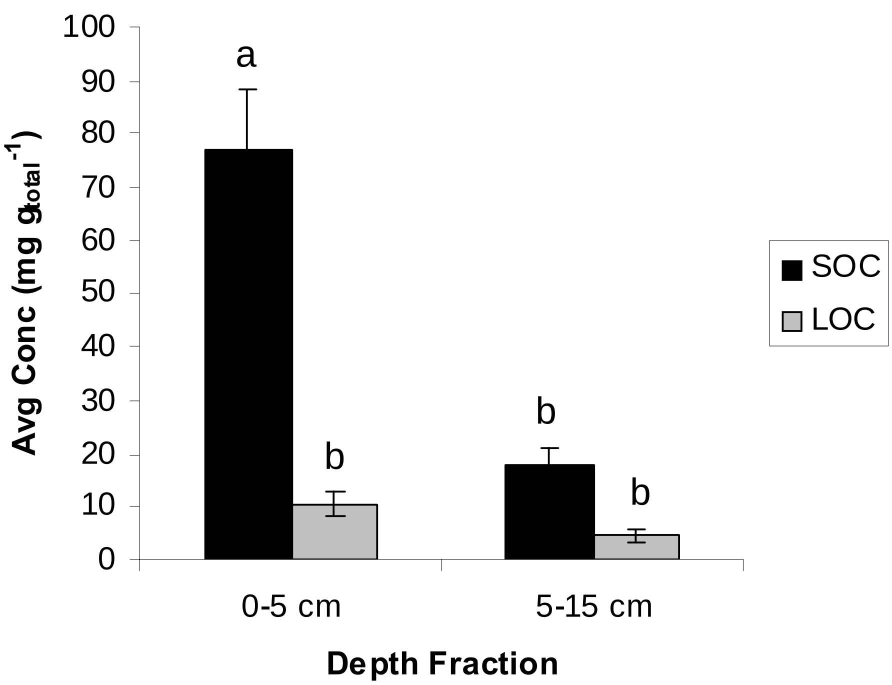
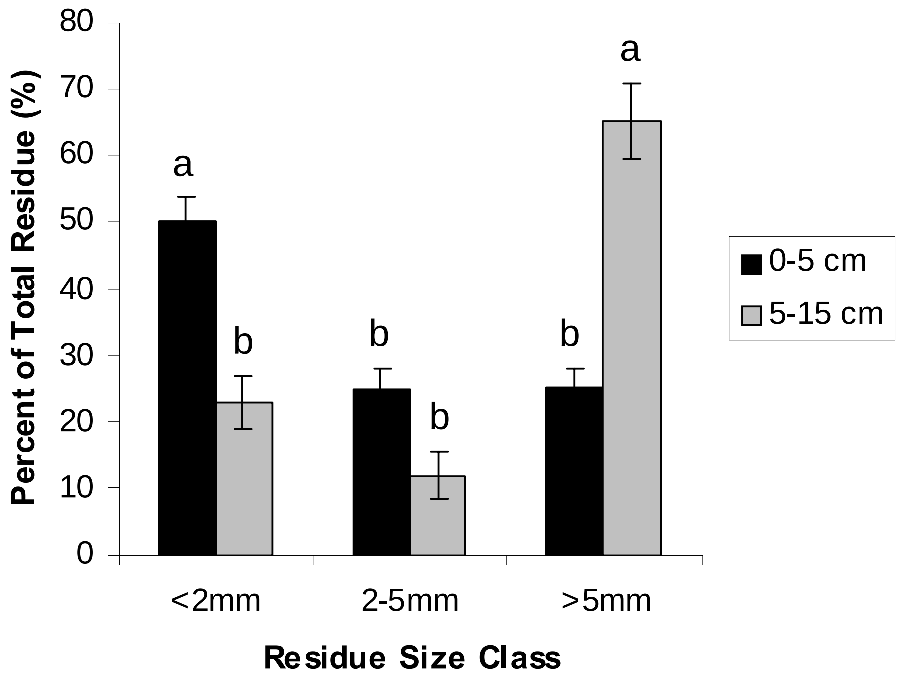


Figure 2.8



80
70
60
50
40
30
20
10
0
Percent of Total Residue (%)
a
b
b
b
b
a
0-5 cm
5-15 cm
<2mm
2-5mm
>5mm
Residue Size Class

CHAPTER 3

GEOSTATISTICAL MODELING OF THE SPATIAL DISTRIBUTION OF SEDIMENT OXYGEN DEMAND WITHIN A COASTAL PLAIN BLACKWATER WATERSHED: EVIDENCE FOR THE IMPORTANCE OF INSTREAM SWAMPS IN CONTRIBUTING TO LOW INSTREAM OXYGEN LEVELS

Abstract. Blackwater streams are found throughout the Coastal Plain of the southeastern United States and are characterized by a series of instream floodplain swamps that play a critical role in determining the water quality of these systems. Within the state of Georgia, many of these streams are listed in violation of state's dissolved oxygen (DO) standard and previous work has shown that sediment oxygen demand (SOD) to be elevated in instream floodplain swamps and positively correlated with the concentration of total organic carbon. This study builds on previous work by using geostatistics and Sequential Gaussian Simulation to investigate the patchiness and distribution of sediment properties at the reach scale. Additionally, this study identifies areas within the stream system prone to high SOD at representative 3rd and 5th order locations. Results show that SOD at both locations was spatially correlated with the differences in distribution of sediment properties likely a result of the differing hydrologic regime and watershed position. Mapping of floodplain soils at the landscape scale shows that areas of organic sediment are widespread and become more prevalent in higher order streams. DO dynamics within blackwater systems are a complicated mix of natural and anthropogenic influences, but this paper illustrates the importance of instream swamps in enhacing SOD at the watershed scale. Moreover, our study illustrates the influence of instream swamps on oxygen demand while providing support that many of these systems are naturally low in DO.

Keywords: Sediment oxygen demand, Geostatistics, Sequential Gaussian Simulation, Blackwater streams, Dissolved oxygen

INTRODUCTION

The study of riverine ecosystems has been furthered by extending a principle of landscape ecology to aquatic ecosystems—namely that streams should be viewed as a diverse assemblage of multiple habitat patches that act as a mosaic across the landscape (Pringle et al. 1988). The River Continuum Concept was one of the first attempts to differentiate waterways into more discrete patches and compare different lotic environments based on location within a longitudinal gradient and across stream order (Vannote et al. 1980). Aquatic ecologists have further subdivided these reaches into relatively homogenous units such as riffles, pools, and runs for ease of study and comparison (Pringle et al. 1988). These designations have proved useful in characterizing different aspects of stream function and processes that occur within them. The ability to quantify and map these patches or the features within them on a reach scale could be of particular benefit.

The changing viewpoint of a stream as an integral, variable force operating as a connected entity to the surrounding catchment has modified the ways streams are studied and perceived (Bencala 1993). Today, a stream is less often viewed primarily as a pipe transporting water, solutes and materials downstream, but rather as a dynamic system, involving bidirectional connections between the stream and landscape as a whole (Bencala 1993). One such system where this mosaic of patches and dynamic bidirectional connections are readily evident is within blackwater river watersheds of the southern Atlantic Coastal Plain. Within Georgia, blackwater rivers have not been impacted by large impoundments and in many areas maintain intact riparian buffers over the majority of their length (Smock and Gilinsky 1992, Katz and Raabe 2005). These streams are characterized by a marked seasonal change in discharge and areal extent that are driven largely by precipitation events which cause extensive floodplain inundation lasting from winter to early spring, followed by drying (sometimes completely) when evapotranspiration becomes dominant (Wharton 1978, Wharton et al. 1982). Streams up to at least 5th order flow intermittently.

Because of this pronounced change in discharge and areal extent, a critical and abundant feature of blackwater streams are large instream swamps which form a vital link between the aquatic and terrestrial environment. Because of a lack of topographical relief, floodplains can become inundated for hundreds of meters in width during periods of high discharge. This marked change in inundation between periods of high and low discharge can lead to drastic differences in wetted perimeter, width/depth ratio and hydraulic roughness (Hupp 2000). Blackwater watersheds are characterized by low gradients, but the slight changes in elevation that are present cause a variety of hydrologic, soil and vegetational patterns (Conner and Buford 1998, Burke et al. 2003).

Many blackwater streams are also characterized by having extremely low dissolved oxygen (DO) levels, one of the many measures of water quality subject to regulation under the Clean Water Act (CWA). Considered to be an excellent indicator of stream biological activity and health and among the most important methods when investigating instream habitats (Wetzel and Likens 2000), many of the streams draining the Georgia Coastal Plain are listed in violation of the state's DO criteria. Within the state of Georgia, the standard for DO is defined as: "A daily average of 5 mg L^{-1} and no less than 4 mg L^{-1} at all times for waters supporting warm water species of fish" (GADNR 2005). Of the river segments listed as impaired within the four main blackwater river basins in 2000-2001, 90% of the listings were a result of failure 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.

Despite the high prevalence of impaired streams due to low DO, evidence suggests that low DO may be a natural phenomenon in these systems and not a sign of pollution or impairment. Levels of DO below the 5 mg L^{-1} limit have been shown in several studies, even those in largely forested watersheds or where there is extensive riparian vegetation (Joyce et al. 1985, Benke and Meyer 1988, Ice and Sugden 2003). One of the hypothesized reasons for relatively low DO is the extended contact time with organic sediments.

Sediment oxygen demand is defined as the rate which DO is consumed from the water column due to the decomposition of organic matter in bottom sediments (Hatcher 1986). Organic materials can come from either outside the system (allochthonous material such as leaf litter and 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 1986, Chau 2002). SOD has been shown to play a major role on instream water quality as it can be a critical sink of DO on the oxygen budget of a river system (Wu 1990), and in some rivers has been shown to be over half of the total oxygen demand (Rutherford et al. 1991, Matlock et al. 2003). Despite this major influence on the total oxygen demand within a system, SOD is often assumed (or estimated) in modeling exercises (Hatcher 1986, Matlock et al. 2003) possibly leading to inaccurate water quality models. These errors have the potential to cause great biological and financial cost.

Previous work has showed that organic sediments with high SOD are a critical sink for oxygen in blackwater streams (Utley et al. 2008). These studies showed that SOD is often higher than estimated values for southeastern sandy bottomed rivers and streams, especially within instream swamps, and is a major factor in the oxygen budget of a stream as a whole. Despite SOD's importance, measurements in the field can prove difficult, as many areas are difficult to access and the measurement procedure requires specialized equipment and training. Chapter 2 correlated SOD measurements with easier to measure sediment properties and found that SOD was most significantly correlated with total organic carbon (TOC) in the top 5 cm of the sediments (Figure 3.1). Despite this significant relationship, it can be difficult to gauge the total impact of SOD on a stream system since measurements of SOD are localized in nature with sediment properties potentially changing markedly across a stream bottom. The purpose of this study is to: 1) Investigate the patchiness and distribution of sediment properties across a stream bottom at two different sites subject to different flooding regimes; 2) Using the relationship of TOC within the top 5 cm and SOD rate, predict the distribution of SOD values across a reach scale to identify possible areas of intense oxygen demand; and 3) Utilize these finding to address the importance of instream swamps in contributing to high DO demand.

METHODS

Study Site

Research was conducted in part of the Little River Experimental Watershed (LREW), a 334 km^2 research watershed located in the western headwaters of the Suwannee River Basin (Figure 3.2) (Sheridan and Ferreira 1992). The LREW was instrumented by the Southeast Watershed Research Laboratory of the USDA Agricultural Research Service for the measurement of rainfall and streamflow beginning in 1967 and has been designated as representative of the soils, topography, geography and land use within the southern Coastal Plain. While land use is primarily agriculture and forestry, riparian vegetation remains largely intact along portions of the river, with swamp hardwood communities consisting of a closed canopy and thick undergrowth. The areas selected for measurement are in two locations. The first is a 270 m long stretch of stream located in the headwaters of the LREW above the gauging site designated as Station J (Figure 3.2, Figure 3.3a) (Sheridan and Ferreira 1992). The stream at this point is 3rd order, with a bankful main channel 5-15 m in width and subject to overbank flooding during high flow events where floodplain width can extends for over 100 m. The second location is a 1600 m long stretch of river located in the lower part of the LREW above the gauging site designated Station B (Figure 3.2, Figure 3.3b). The stream at this point is 5th order and can be as wide as 350 m during periods of complete inundation. At this site, inundation of the floodplain usually begins in December with complete inundation until April or May. During the summer months, flow may stop along with complete drying of the river channel at both locations

Soil Collection and Preparation

Soil samples were taken at the 5th order site in summer 2006 and the 3rd order site in fall 2006 when the channel was completely dry. Samples at the 5th order site were taken every 25 m along five transects spaced roughly 150 m apart (Figure 3.3b). The 3rd order site had a total of 9 transects spaced roughly 35 m apart (Figure 3.3a). Due to the narrower area of inundation at this location and to capture areas that were flooded most often, a sample was taken at the center of the channel, 5 meters on either side of center and then 10 meters apart thereafter. One soil core

(5.7 cm diam.) was taken from each quadrant surrounding a sampling point. Soil samples were taken to a depth of 15 cm with each set of four cores separated into two depth classes (0-5 cm and 5-15 cm) in the field. All four cores from each depth class were composited into a single Ziploc bag.

Upon return to the lab, soil samples were stored in a refrigerator until analyzed. They were dried in an oven at 35°C and were then crushed and sieved with a #10 sieve (<2 mm). Material that passed the sieve was considered soil matter with that remaining above as litter/residue. Samples were collected at a total of 80 points for the 5th order site (49 soil cores + 31 sediment cores collected from the stream bed covered by SOD chambers (Chapter 2)) and 68 points were collected for the 3rd order site (all being soil cores).

Organic Carbon Determination

From seived samples, approximately 20 g of soil was pulverized using a rolling table until the sample was of a powder like consistency. Three 3 g subsamples were taken from the pulverized sample and organic matter was determined by loss on ignition (LOI) (Nelson and Sommers 1996). After soil organic matter determination by LOI the 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). Carbon content in litter residues (LOC) was assumed to be 0.4 by weight (Schlesinger 1997). The litter and soil organic carbon pools were added together to estimate total organic carbon (TOC).

Geostatistical Analysis

Geostatistics is a set of statistical tools that incorporate the spatial coordinates of observations into the description and modeling of spatial patterns, predictions at unknown locations, and assessment of the uncertainty associated with those predictions. This section highlights the methods used for the present analysis including a procedure known as Sequential Gaussian Simulation (SGS), but a more complete discussion of this and other geostatistical methodologies is given by Goovaerts (1997, 2001). SGS was used to generate realizations of the spatial distribution of TOC at both experimental sites. Each realization exactly matches the sampled data (conditional simulation) while reproducing their spatial pattern as modeled from the semivariogram ($\gamma(\mathbf{h})$) that measures the average dissimilarity between data separated by a vector **h**:

$$\gamma(\mathbf{h}) = \frac{1}{2N(\mathbf{h})}\sum_{\alpha=1}^{N(\mathbf{h})}[z(\mathbf{u}_\alpha) - z(\mathbf{u}_\alpha + \mathbf{h})]^2 \qquad [1]$$

where $[z(\mathbf{u}_\alpha) - z(\mathbf{u}_\alpha + \mathbf{h})]$ is an **h**-increment of attribute *z*. In theory, as the distance between observations increases, the semivariogram increases until it levels out when the semivariance becomes independent of the distance separating two points.

To apply SGS, the data must follow a standard normal (Gaussian) distribution. In this study, TOC data at 0-5 cm depth were normal score transformed to give a normal distribution with zero mean and unit variance. The steps for simulation were as follows: 1) a random path is established to visit all *N* grid nodes (excluding the conditioning data) only once; 2) the value of TOC and its associated variance are estimated at the visited location using simple kriging and the variogram model of the normal transformed data; 4) a value is randomly drawn from the local Gaussian probability distribution characterized by the kriging estimate and variance; 5) the simulated value is added to the data set and the process repeated for each node until all locations have been simulated (Goovaerts 2001, Vann et al. 2002). Finally, the simulated normal score values are back transformed to give a grid of simulated TOC at 0-5 cm depth values. In total, 10 realizations of TOC were generated at both sites, using a spacing of 2 m at the 5th order site and 1 m at the 3rd order site.

Let $y(\mathbf{u})$ and $z(\mathbf{u})$ be the SOD and TOC values at a given location $\mathbf{u}$, respectively. Using the significant linear relationship (Figure 3.1, p=0.0027) developed between these two attributes in Chapter 2, the expected SOD value at any unsampled location $\mathbf{u}_i$ can be predicted as:

$$y(\mathbf{u}_i) = f(z(\mathbf{u}_i)) = a + bz(\mathbf{u}_i) \qquad [2]$$

The uncertainty about the predicted y-value arises from the uncertainty attached to: 1) the z-value (i.e. TOC), and 2) the regression coefficients a and b. The uncertainty associated with the TOC value was modeled through the generation of L'=10 simulated TOC maps, $\{z^{(l)}(\mathbf{u}_i), i = 1,...,N; l = 1,...,L'\}$, using the SGS procedure described above. The parameter uncertainty can be modeled by building the probability distributions of each parameter a and b as well as their joint distribution. For linear regression, these distributions are Gaussian and fully characterized by the parameter estimates and standard errors, as well as the covariance between parameters. Both sources of uncertainty can then be incorporated numerically by sampling randomly the two parameter distributions and combining the simulated coefficient values

$\{(a^{(l)}, b^{(l)}), l-1,...,L\}$ with the simulated TOC values in the regression equation to retrieve the corresponding simulated SOD value:

$$y^{(l)}(\mathbf{u}_i) = f(z^{(l)}(\mathbf{u}_i)) = a^{(l)} + b^{(l)} z^{(l)}(\mathbf{u}_i) \qquad [3]$$

The main technical difficulty is caused by the strong negative correlation between the intercept and the slope of the regression equation (r = -0.7899), which means that their probability distributions cannot be sampled independently. The propagation of uncertainty was achieved using a modified version of the method described by Rossel et al (2001):

1. Sample the standard normal probability distribution (zero mean and unit variance) using Latin Hypercube sampling (M = 40 classes). Repeat the procedure as many times as there are parameters. For this study, the procedure is repeated twice, producing two sets of 40 random numbers that can be combined into 1600 pairs, $[v^{(l)}, w^{(l)}], l = 1,...,1600$.
2. Decompose the variance-covariance matrix of parameters, C, into the product of a lower and an upper triangular matrix: C=LU (lower-upper decomposition).
3. Premultiply each vector of two random numbers $[v^{(l)}, w^{(l)}]$ by the lower triangular matrix L, and add the vector of means of the two parameters $[m_a, m_b]$:

$$\begin{bmatrix} a^{(l)} \\ b^{(l)} \end{bmatrix} = \begin{bmatrix} L_{11} & 0 \\ L_{12} & L_{22} \end{bmatrix} * \begin{bmatrix} v^{(l)} \\ w^{(l)} \end{bmatrix} + \begin{bmatrix} m_a \\ m_b \end{bmatrix}$$

In summary, a total of 10 simulated TOC maps were generated at each site and then multiplied by the 1600 pairs of regression coefficients, yielding 16,000 possible realizations of SOD. For each realization, the area-wide average was calculated as:

$$y_A^{(l)} = \frac{1}{N}\sum_{i=1}^{N} y^{(l)}(\mathbf{u}_i) \qquad l=1\ldots,L \qquad [4]$$

The distribution of 16,000 area-wide averages provides a numerical model of the uncertainty attached to the mean SOD value over the site *A*. Extreme scenarios, such as the map of simulated SOD values out of the 16,000 possible realizations that yields the minimum or the maximum area-wide average $y_A^{(l)}$ can be identified easily.

All geostatistical analyses were conducted using Stanford Geostatistical Modeling Software (SGeMS) (Remy 2004) and the variograms modeled using TerraSeer Space-time Information System (STIS). All statistical computations were performed using SAS for Windows (Version 9.1, SAS Institute Inc., Cary, North Carolina, 2002-2003)

Floodplain Soils Calculation

Floodplain soils are a common feature of the LREW and the experimental locations described above are only an example of the extent of instream swamps within the greater LREW. An estimate of areas subject to elevated SOD was calculated using existing geographical data layers. The extent of the basin was delineated as described by Sheridan and Ferreira (1992). The soils data for the watershed were retrieved from the USDA-NRCS Soil Survey Geographic (SSURGO) database with all datasets at the 1:24,000 scale, but publication dates range from 1999-2004 for individual counties (USDA-NRCS 2008). After combination of datasets, hydric soils meeting either of two criteria were extracted: 1) Those soils having a landform designation of "Floodplains" and/or 2) Those soils having a hydric criterion of 3 or 4. A designation of 3 is defined as "soils that are frequently ponded for long or very long duration during the growing season" and a designation of 4 is defined as "soils that are frequently flooded for long or very long duration during the growing season" (USDA-NRCS 2008). A hydrological layer with all streams within the LREW from the USGS National Hydrography Dataset (NHD) at the 1:24,000 scale was used and individual stream segments delineated by the Strahler stream order classification method. Each stream segment was buffered to encompass all extracted hydric soil along that segment and area of floodplain soil along each segment calculated and summed by stream order. Additionally, the gradient was computed in each watershed by downloading digital elevation models at the 1:24,000 scale from the USGS National Elevation Dataset (NED).

All geographical analysis was completed using ESRI ArcMap (Version 9.2, ESRI Inc., Redlands, California, 1999-2006) and ArcView (Version 3.3, ESRI Inc., Redlands, California, 1991-2000).

RESULTS

Geostatistical Analysis

Each site showed a distinct spatial correlation as illustrated by differences between the TOC variograms (Figure 3.4a and 3.4b). At the 3rd order stream site, the experimental variogram, created using 10 lags of 14 m, was fitted by an exponential model with a nugget of 0.41, a range of 27.3 meters, and a total sill of 1.02 (Figure 3.4a). The nugget effect is much smaller for the variogram computed at the 5th order stream site ($9.92*10^{-8}$) which was created using a series of 20 lags of 20 m (Figure 3.4b). The model is also exponential with a sill of 1.03 and a range of 64.46 m.

The average TOC value of all ten realizations at the 3rd order stream site was 73.47 mg g_{total}^{-1} and ranged between 22.68 and 225.91 mg g_{total}^{-1} at individual nodes (Table 3.1). In contrast, the concentration of TOC at the 5th order stream site was on average nearly double that of the 3rd order stream site averaging 145.61 mg g_{total}^{-1} and ranging between 15.11 and 275.28 mg g_{total}^{-1}. The average SOD rate for the mean of all realizations at the 3rd order stream site was 4.90 g O_2 $m^{-2}d^{-1}$ (Table 3.1; Figure 3.5a). The area-wide minimum and maximum realizations had average SOD rates of 2.32 g O_2 $m^{-2}d^{-1}$ and 7.49 g O_2 $m^{-2}d^{-1}$ respectively (Table 3.1; Figure 3.5b and 3.5c). The average SOD rate for the mean of all realizations at the 5th order site was higher than the 3rd order site with a rate of 7.13 g O_2 $m^{-2}d^{-1}$ (Table 3.1; Figure 3.6a). The area-wide minimum and maximum averages of SOD were also higher than their 3rd order counterparts showing rates of 4.37 g O_2 $m^{-2}d^{-1}$ and 11.13 g O_2 $m^{-2}d^{-1}$ respectively (Table 3.1; Figure 3.6b and 3.6c). The realizations also show a difference in distribution patterns and patchiness between the two locations. The higher rates of SOD tend to occur away from the center of flow (dashed line) in the 3rd order site while at the 5th order site the higher rates are generally found in areas following the center of flow (Figure 3.4a and 3.5a).

Floodplain Soils Extent

The LREW is characterized by an extensive floodplain network along all stream orders (Figure 3.7). The three soil types meeting the hydric soil criteria defined above were Grady sandy loam (Gr), Kinston and Osier soils (KO), and Olustee sand (Os) with the majority being KO soils. There are a total of 553.46 km of streams within the LREW with 89% of that length classified as headwater streams (1st through 3rd order streams). Within the entire watershed, nearly 2,700 ha are identified as floodplain soils with increasing area of floodplain per stream km with increasing stream order (Table 3.2).

DISCUSSION

Streams have often been stratified into patches of differing hydrological and physical properties such as riffles, pools, and runs for ease of comparison across locations. With the increased study of the hyporheic zone, additional differentiation of the streambed into areas such as the identification of upwelling and downwelling zones of groundwater and solute movement have occurred. This study has extended the principle of patchiness and zonation of the streambed to sediment properties found therein with a specific emphasis on the distribution of organic carbon and its relationship to SOD.

Previous work has shown a significant positive linear relationship between TOC concentration at 0-5 cm depth and SOD rates in blackwater streams (Chapter 2), but measuring SOD *in situ* can prove difficult and time consuming. Furthermore, measurement of SOD rates at specific locations give point measurements that are difficult to extrapolate across a reach or landscape due to SOD's expected variation in spatial distribution as a result of sediment physical and chemical properties along with differing rates of deposition (Bowie et al. 1985). Nevertheless, accurately predicting SOD across a landscape is of vital importance as previous work in the LREW has shown that SOD is the most important variable to accurately predict DO levels at the watershed scale (Cathey et al. 2005). The ability to use TOC, a less time intensive and more easily measured variable, in conjunction with geostatistical analysis allows for not only the accurate mapping of SOD across a landscape but also the ability to quantify the importance of instream swamps.

The mapping of TOC (and by relation SOD rates) at our two sites shows distinct differences. While concentrations of TOC are high at both sites, the 5th order site has a TOC concentration that is nearly double that of the headwater, 3rd order site (Table 3.1). Highly organic soils are not an uncommon feature of many blackwater coastal plain environments. For example, *Burke et al.* (2003) reported floodplain organic matter levels on a South Carolina blackwater river ranging from 1.1 to 8.1% depending on the flooding and vegetation regime. Higher levels of organic content are possible given that organic matter levels as high as 35% are reported in backswamps characterized by water tupelo stands (Wharton et al. 1982, Sharitz and Mitsch 1993). In our study, percentages of organic matter content in some sediment samples were greater than 50% at both sites, indicating levels of organic carbon higher than previously reported for blackwater systems.

The use of geostatistical analyses allows for not only the accurate mapping of sediment properties on a reach scale, but also the identification of distributional patterns and patchiness (Figures 3.5 and 3.6). In the headwater, 3rd order site, lowest SOD values (dark green colors) are found in conjunction with the stream center line, while highest SOD values are in floodplain areas (Figure 3.5a). This is especially evident in the area-wide maximum realization (Figure 3.5c) that shows high SOD rates on the eastern floodplain (brown colors). In contrast, the distributional pattern of SOD rates in the larger, 5th order site is reversed (Figure 3.6). At this location, highest SOD rates (orange to red colors) are primarily found in the middle of the stream in line with the delineated stream center (Figure 3.6a), while the lowest SOD rates (blue to dark green colors) are located on the margins of the stream. Again this phenomenon is shown in the most extreme using the area-wide maximum realization (Figure 3.6c) since the center of the stream is dominated by high SOD (red to brown colors) with lower SOD (blue to green colors) on the periphery. Additionally, along the flow line at the 5th order location there are alternating patches of high and low values while the values along the flow line at the 3rd order site are consistently low. The alternating high and low patches of SOD in the 5th order site are likely a result of localized depressions found within the stream channel that promotes the deposition of organic matter.

Observed patchy distributional patterns of SOD rates are likely to be driven by the hydrology. Both sites have intact riparian buffers and are completely covered by overhead canopy, but with different hydrological patterns as a result of their watershed position and gradient. The entire LREW has a low watershed gradient of 0.15%, typical of many coastal plain systems, but the majority of that elevation change occurs in the headwaters area. The gradient for the 3rd order watershed (from the topographic divide to Station J) is 0.39% and the gradient from Station J to Station B (outlet of 5th order watershed) is 5.3 times less with a gradient of 0.07%. Over 63% of the total elevation change in the entire LREW is located within this third order watershed. The difference in watershed gradients between these two sites likely plays a key role in the hydrology and transport of organic carbon within this system. The 3rd order site receives overbank flooding during high flow events which causes water to spread over the floodplain and cover much of the sampled area. However, such events are typically short in duration and typically do not persist for more than a few days. Normally, the stream is within a more confined channel roughly the extent of the 10 m width designated in Figure 3.3a leaving much of the mapped area dry and not an active part of instream oxygen demand. In contrast, the 5th order site is completely inundated across its entire width for a period of months at a time with high discharge events leading to increased connection of the side channels (Figure 3.3b). However, even during baseflow these areas remain inundated.

Differences in flow permanence and transport of organic materials likely determine observed spatial differences in SOD rate. Prior to data collection, we hypothesized that areas of higher organic carbon (and hence SOD) would be located on the periphery at both locations since there tends to be a marked reduction in flow velocity in coastal plain streams as water exits the main channel and travels onto the more hydraulically dynamic floodplain (Hupp 2000). This phenomenon is supported at the 3rd order site since the floodplain is intermittently flooded, allowing organic material to fall out of suspension. In contrast, during high discharge events the channel is subject to higher velocities allowing the flushing of organic material out of the deeper, more defined channel. Meanwhile, the 5th order site is flooded for extended periods of time, has a less defined channel and is characterized by extensive vegetative interference as a result of debris dams and multiple overstory trees growing in the flooded area (Figure 3.8). Regardless of flow intensity, the heavy vegetative interference and lower watershed gradient likely prevents large increases in velocity even during storm events and retards the movement of materials out of the flooded area including the stream channel. This allows for the observed material accumulation and development of highly organic sediments. The combination of low gradient and heavy vegetative interference has been seen in other blackwater ecosystems containing swamp-stream complexes. Mulholland (1981) states, "Organic carbon loading potential in Creeping Swamp is very large, primarily because of its great width and complete canopy; however its low gradient and dense vegetation enhance organic carbon retention especially of CPOC by maintaining low water velocities with little erosive force, tortuous flow pathways and debris dams."

Chapter 2 highlighted the importance that SOD could have in determining water column DO concentrations, especially within instream swamps. This paper extends the principle of point measurements of SOD to a reach scale. When looking at the area-wide mean realization, the 5th order site had an average SOD rate of 7.13 g O_2 $m^{-2}d^{-1}$ over the entire mapped area and oxygen demand of 1.56 kg O_2 $d^{-1}m^{-1}$ length of stream (Table 3.1; Figure 3.6a). In contrast, the 3rd order site has a smaller area of inundated sediment available for oxygen demand. If one considers the entire flooded area, the area-wide mean realization has an average SOD rate of 4.90 g O_2 $m^{-2}d^{-1}$ and oxygen demand of 0.34 kg O_2 $d^{-1}m^{-1}$ of stream (Table 3.1; Figure 3.5a). If only the area that is most often flooded (10 m wide strip identified in Figure 3.2a) is considered, the average SOD rate in the area-wide mean realization drops slightly to 4.54 g O_2 $m^{-2}d^{-1}$, but total area decreases by 86% decreasing oxygen demand by nearly 96% to 0.015 kg O_2 $d^{-1}m^{-1}$ of stream. While the average rates of oxygen demand are high regardless of stream order, the rates per meter of stream are over two orders of magnitude higher in the 5th order stream than in the 3rd order stream due to its greater area of constant inundation (1.56 kg O_2 $d^{-1}m^{-1}$ vs. 0.015 kg O_2 $d^{-1}m^{-1}$ of stream length). Even if one allows for complete inundation at the 3rd order site (a rare hydrologic occurrence), the 5th order site has a rate of oxygen demand per meter of stream over four times that of the 3rd order site.

Although these two experimental locations only give examples of the effects of SOD on the watershed scale, the mapping of floodplain soils (and by relation highly organic areas most prone to high SOD) across the entire LREW shows that these locations are very common (Figure 3.7). In fact, their prevalence and scale becomes more pronounced as the stream system gets larger, a situation most closely resembling the 5th order location. For instance, 89% of all stream length within the watershed is found in the smaller headwater streams (1st-3rd order).

Meanwhile, the total area of floodplain soil is split approximately evenly between the headwater streams (48%) and the larger 4th-5th order stream segments (52%). However, with only 11% of the total stream length in the watershed located in 4th-5th order segments, the floodplains are disproportionately more abundant on these larger order stream segments having 7.4 times more area per stream km (21.15 ha km^{-1} to 2.87 ha km^{-1}). When combined with the higher rates of oxygen demand (per unit length of stream) and longer and more sustained periods of inundation, locations such as the 5th order site appear to be common and a major driver of oxygen dynamics on the watershed scale.

Conclusions

Blackwater streams of the Georgia Coastal Plain are often listed as impaired due to chronically low DO levels. Previous research has shown that high SOD values, a hypothesized cause of lowered DO within these waters, are significantly positively correlated with TOC within the stream sediments (Chapter 2). SOD measurements in the previous study were point measurements, making it difficult to characterize SOD values at the reach and watershed scale. However, the use of geostatistics and SGS allowed for the mapping of SOD across a reach in two study locations through its relationship with TOC. The results showed TOC to be spatially correlated at both experimental locations. However, the corresponding distribution and patchiness of SOD differed between the sites as a result of different hydrological regimes. The 5th order site, with a larger, more persistent area of inundation had higher average rates of oxygen demand and as a function of stream length when compared to the 3rd order site.

While only measured at two experimental locations, the mapping of floodplain soils on the watershed scale showed that areas subject to inundation are common in this watershed and that these areas are more expansive per unit stream length in larger order streams. The greater area per unit stream length in the larger order streams demonstrates the importance of areas such as the 5^{th} order experimental area. This study highlights the importance of instream swamp areas in coastal blackwater streams and further illustrates their importance to oxygen dynamics on a watershed scale. Additionally, this research provides support for the hypothesis that many blackwater streams draining Georgia's coastal plain are naturally low in DO as a result of elevated SOD.

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Table 3.1. Mean and range of total organic carbon (TOC) and sediment oxygen demand (SOD) rate for the mean and area-wide minimum and maximum realizations.

	3rd Order Location		**5th Order Location**	
	Mean	Range	Mean	Range
TOC ($mg\ g_{total}^{-1}$)				
Area-wide minimum	68.91	7.76 – 317.72	132.52	14.46 – 288.00
Mean of all realizations	73.47	22.68 – 225.91	145.61	15.11 – 275.28
Area-wide maximum	76.05	7.76 – 317.72	162.85	14.46 – 288.00
SOD Rate ($g\ O_2\ m^{-2} d^{-1}$)**				
Area-wide minimum	2.32	0.25 – 10.72	4.37	1.26 – 8.45
Mean of all realizations	4.90	3.33 – 9.61	7.13	3.10 – 10.62
Area-wide maximum	7.49	5.10 – 15.94	11.13	3.21 – 16.87

**Also see Figures 3.5 (3rd order) and 3.6 (5th order) for visual representation of rates

Table 3.2. Stream length, floodplain area, and floodplain area per length of stream by stream order in the Little River Experimental Watershed

Stream Order	Stream Length (km)	Area of Floodplain (ha)	(ha km^{-1})
1^{st}	289.68	275.72	0.95
2^{nd}	138.65	616.79	4.45
3^{rd}	64.45	522.52	8.11
4^{th}	46.11	785.86	17.04
5^{th}	14.58	497.50	34.13
Total	553.46	2,698.53	4.88

Figure Captions

Figure 3.1. Relationship between total organic carbon (TOC) and sediment oxygen demand (SOD). From Chapter 2.

Figure 3.2. Map of Little River Ecological Watershed with selected sampling sites.

Figure 3.3. Map of 3rd order sampling site (a) and 5th order sampling site (b).

Figure 3.4. Experimental variograms used for Sequential Gaussian Simulation for analysis of 3rd order site (a) and 5th order site (b)

Figure 3.5. Mean (a), area-wide minimum (b), and area-wide maximum (c) realizations of SOD (g O_2 $m^{-2}d^{-1}$) at 3rd order site. SOD classes constitute equally populated intervals of total data set at 3rd order location.

Figure 3.6. Mean (a), area-wide minimum (b), and area-wide maximum (c) realizations of SOD (g O_2 $m^{-2}d^{-1}$) at 5th order site. SOD classes constitute equally populated intervals of total data set at 5th order location.

Figure 3.7. Map of floodplain soils within the Little River Ecological Watershed

Figure 3.8. Picture of 5th order location showing tortuous flowpaths and heavy vegetative interference.

Figure 3.1

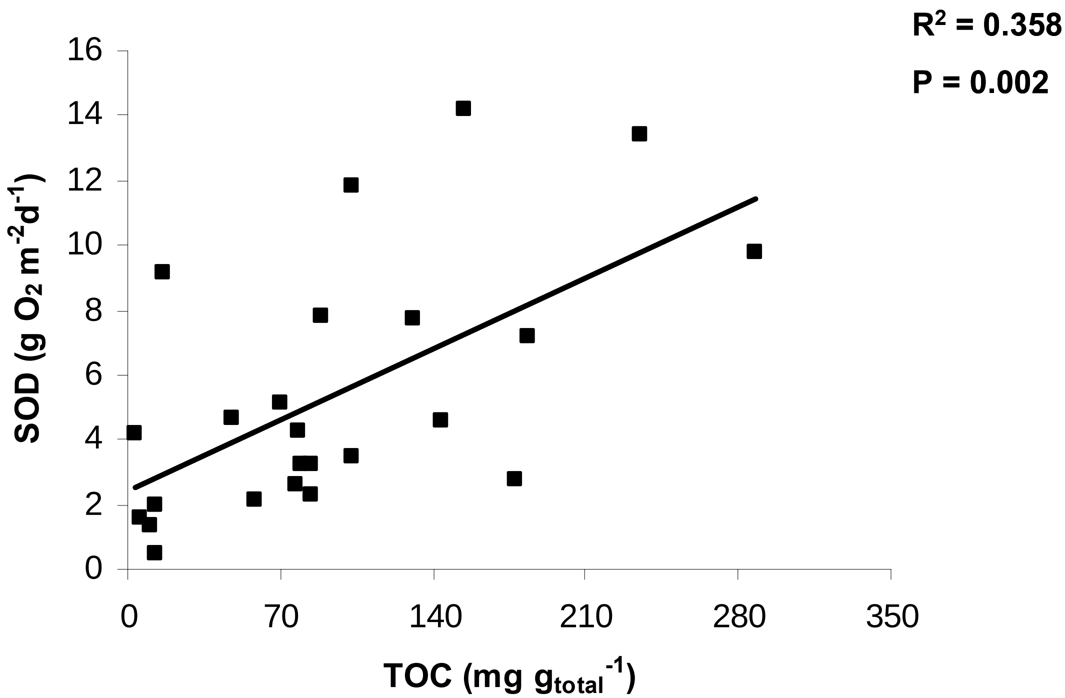

R2 = 0.358
P = 0.002
16
14
12
10
8
6
4
2
0
0
70
140
210
280
350
SOD (g O2 m-2d-1)
TOC (mg gtotal-1)

Figure 3.2

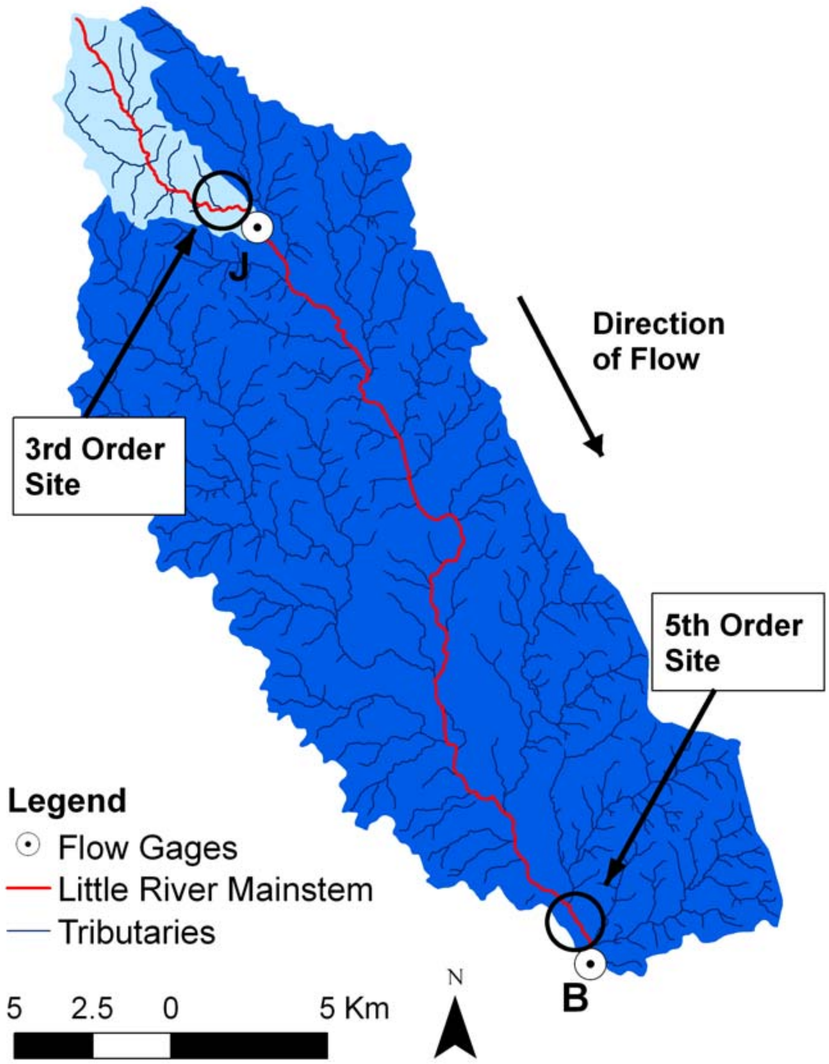

J
Direction
of Flow
3rd Order
Site
5th Order
Site
Legend
Flow Gages
Little River Mainstem
Tributaries
5 2.5 0 5 Km
N
B

Figure 3.3

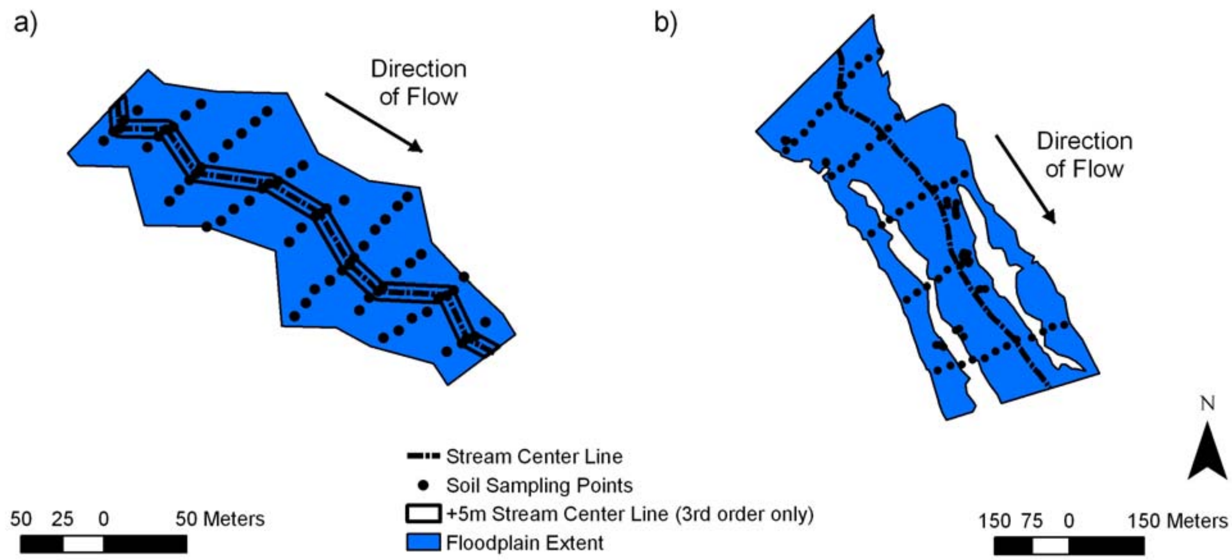
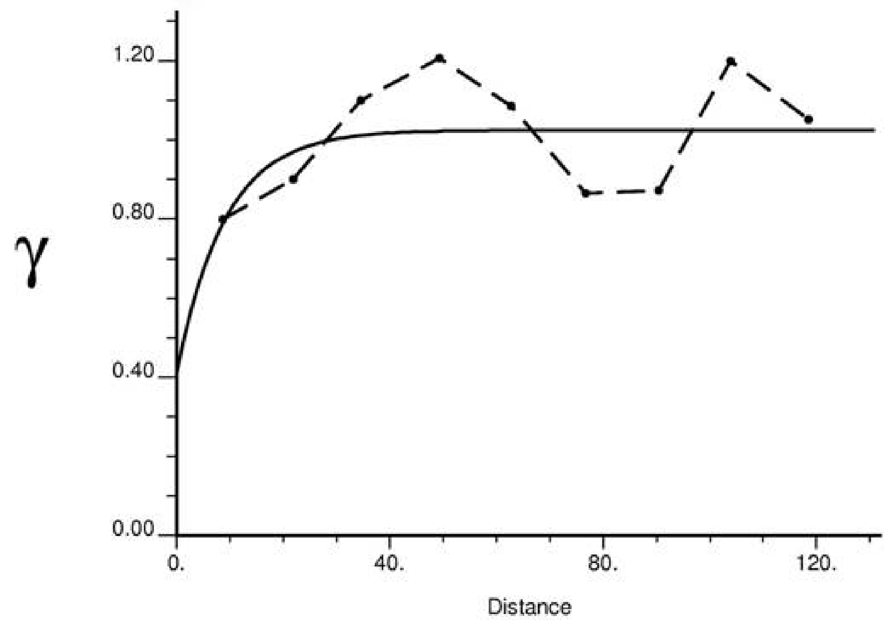

a)
Direction of Flow
b)
Direction of Flow
N
Stream Center Line
Soil Sampling Points
+5m Stream Center Line (3rd order only)
Floodplain Extent
50 25 0 50 Meters
150 75 0 150 Meters

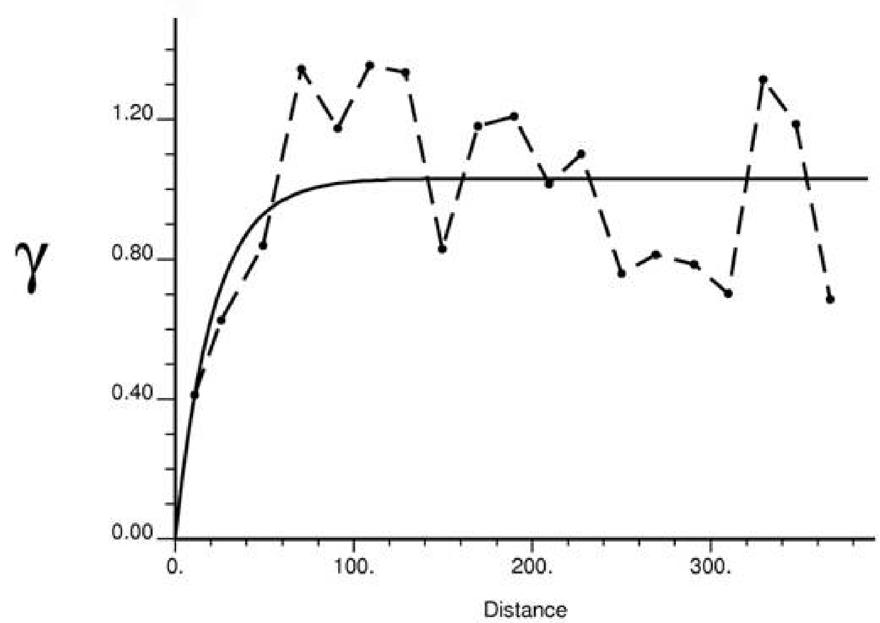
Figure 3.4

a)



1.20
0.80
0.40
0.00
γ
0.
40.
80.
120.
Distance

b)



1.20
0.80
0.40
0.00
γ
0.
100.
200.
300.
Distance

Figure 3.5

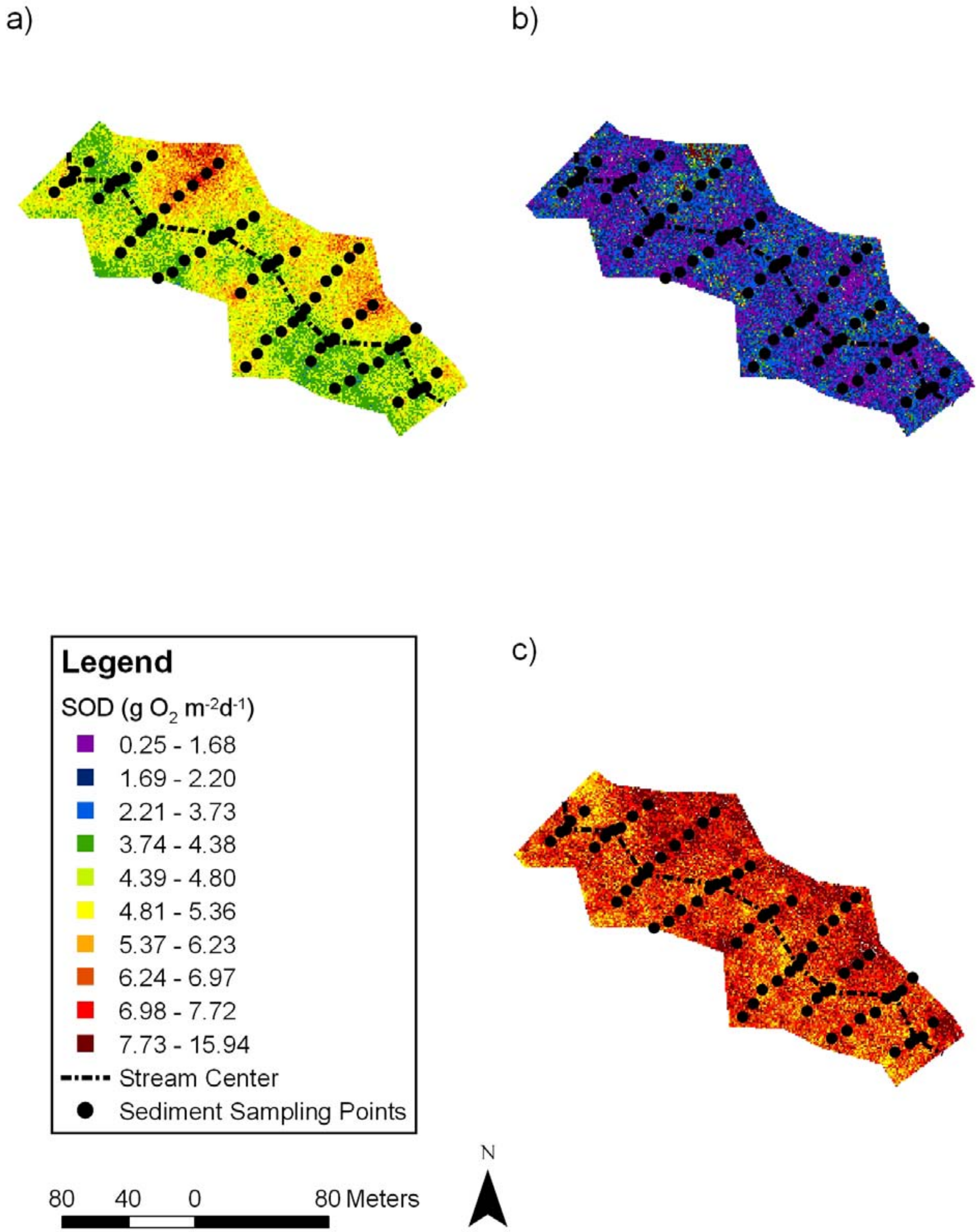

a)
b)
c)
Legend
SOD (g O2 m-2d-1)
0.25 - 1.68
1.69 - 2.20
2.21 - 3.73
3.74 - 4.38
4.39 - 4.80
4.81 - 5.36
5.37 - 6.23
6.24 - 6.97
6.98 - 7.72
7.73 - 15.94
Stream Center
Sediment Sampling Points
80 40 0 80 Meters
N

Figure 3.6

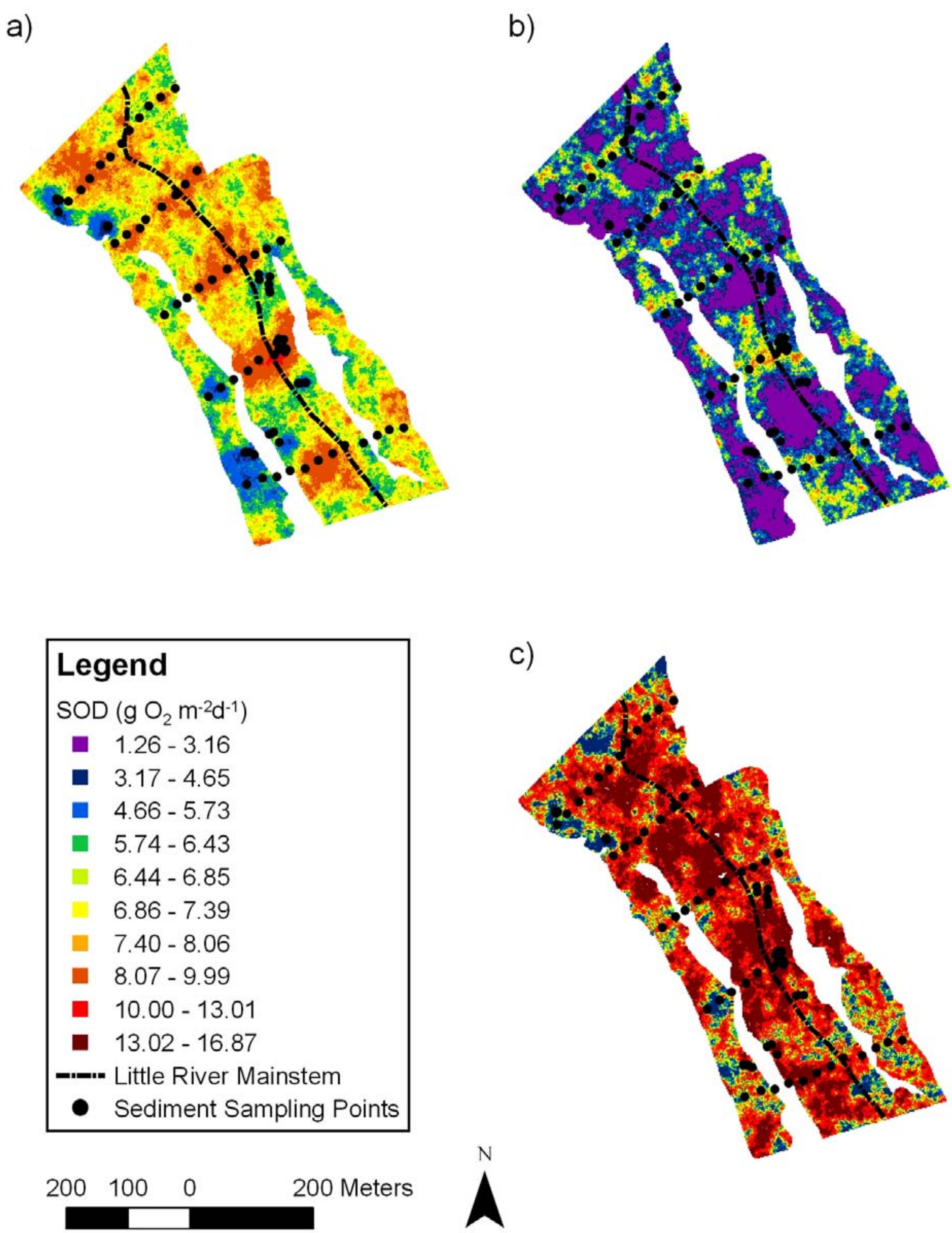

a)
b)
c)
Legend
SOD (g O_2 $m^{-2}d^{-1}$)
1.26 - 3.16
3.17 - 4.65
4.66 - 5.73
5.74 - 6.43
6.44 - 6.85
6.86 - 7.39
7.40 - 8.06
8.07 - 9.99
10.00 - 13.01
13.02 - 16.87
Little River Mainstem
Sediment Sampling Points
200 100 0 200 Meters
N

Figure 3.7

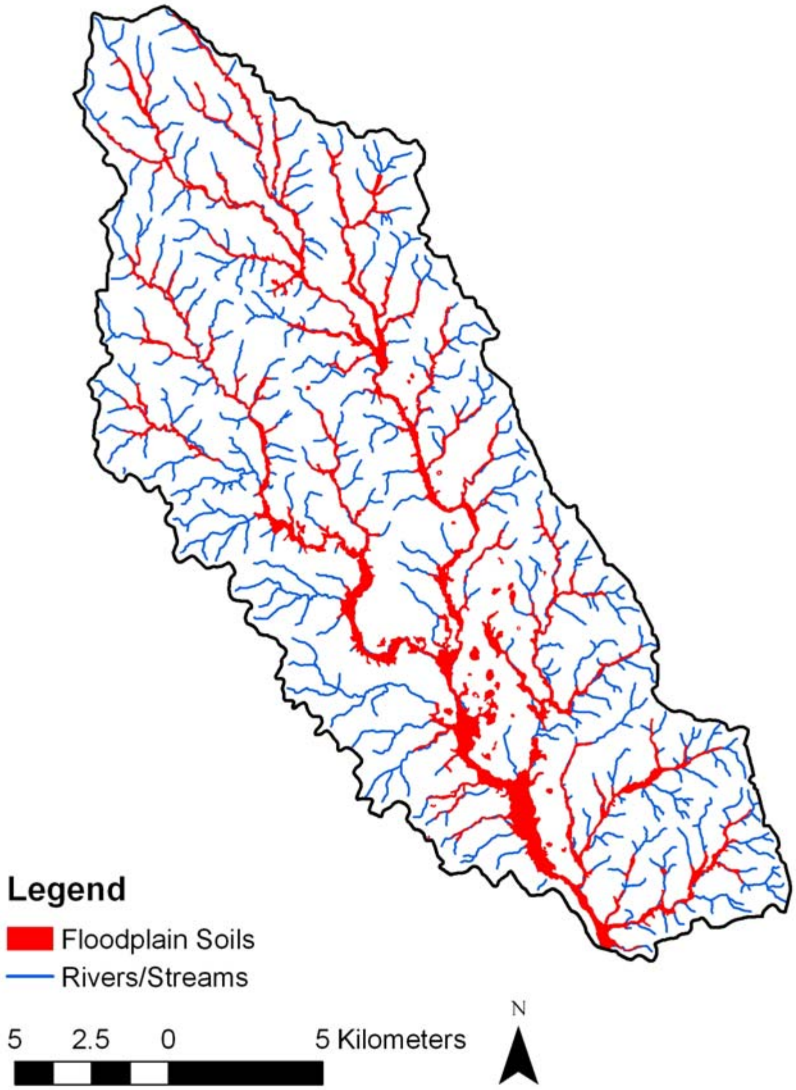

Legend
Floodplain Soils
Rivers/Streams
5
2.5
0
5 Kilometers
N

Figure 3.8

CHAPTER 4

SLOW TRAVEL TIME AND TRANSIENT STORAGE WITHIN INSTREAM SWAMPS ON THE GEORGIA COASTAL PLAIN: IMPLICATIONS FOR LOW RIVER DISSOLVED OXYGEN LEVELS[2]

[2] Todd, M.J., G. Vellidis, D.D. Bosch, R.R. Lowrance, and C.M. Pringle. To be submitted to *Water Resources Research*

Abstract. Blackwater streams on the southeastern Coastal Plain are distinguished by violation of the state's dissolved oxygen (DO) standard leading to the requirement of TMDL development. These streams are characterized by low slopes, high summertime temperatures, and extensive inundation of surrounding floodplains. Typically lasting from winter to early spring, the long inundation period creates a multitude of instream floodplain swamps that play a vital role in overall water quality. One of the hypothesized reasons for the lowered DO levels in this system is the slow movement or water and extended contact with the underlying sediments. Instream swamps are locations of particular interest as they are widespread in blackwater river systems and characterized by having highly organic sediments and hypothesized tortuous flowpaths. This study investigated the movement of water through two representative instream swamps using rhodamine dye as a hydrologic tracer and modeling of water transport parameters through a one-dimensional solute transport model with components for inflow and storage (OTIS). Results showed extended travel times and low velocities even during periods of high flow. Modeling using OTIS illustrated the prominent influence of transient storage on travel times. When coupled with intense oxygen demand in the underlying sediments, these instream swamps play a critical role in overall watershed oxygen dynamics and lend support to these systems being naturally low in DO.

Keywords: Blackwater streams, Dissolved Oxygen, OTIS, Rhodamine, Transient storage, Travel Time

INTRODUCTION

Southeastern Coastal Plain blackwater streams are characterized by their low slopes and extensive seasonal floodplain inundation (Meyer 1990, Smock and Gilinsky 1992). In addition, many of these rivers are unimpacted by large impoundments and maintain riparian buffers with overhead canopies. Due to the lack of topographical relief, hydrology plays a principal role in these environments leading to orders of magnitude difference in wetted perimeter, areal extent and hydraulic roughness (Mitsch and Gosselink 1986, Hupp 2000). These large changes in discharge and areal extent are principally precipitation driven, with floodplain inundation up to hundreds of meters in width lasting from winter to early spring, and drying (with streams up to 5^{th} order being intermittent) occurring in the summer when evapotranspiration becomes dominant (Wharton 1978, Wharton et al. 1982). An important, but understudied hydrologic feature within these systems is the presence of instream swamps and floodplain wetlands, highly dynamic, changeable features that highlight the importance of lateral linkages in a riverine system (Meyer 1990). While understudied, these instream swamps play a vital role in the water quality of blackwater streams throughout the southeastern Coastal Plain.

These blackwater systems are also characterized by having extremely low dissolved oxygen levels (DO), one of the many parameters subject to regulation under the United States Clean Water Act (CWA). Within the state of Georgia, 57% of its rivers and streams either partially support or do not support their designated uses (GADNR 2000-2001). For those streams not supporting their designated uses in the southern Coastal Plain of Georgia in 2000-2001, 90 percent were listed due to violation of the state's minimum DO standards of 4.0 mg L^{-1} or 24-hour average of 5.0 mg L^{-1} (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.

Measurement of DO is considered an excellent indicator of stream biological activity and the "most important of all chemical methods available for the investigation of the aquatic environment" (Joyce et al. 1985, Mitsch and Gosselink 1986). With reduced levels of DO, biological activity and biotic integrity can suffer. As required by the CWA, any stream segment not meeting this standard is listed as impaired and subject to TMDL development requiring a considerable investment of labor and financial resources.

Generally, lowered DO levels in slow moving streams is assumed to be a consequence of increased biological activity from nitrogen and phosphorus enrichment. Nutrient enrichment in these systems usually leads to increased algal biomass, dark respiration and biological oxygen demand (Mallin et al. 2001, Mallin et al. 2004). This phenomenon generally is absent from shaded streams having an overhead canopy or a bottom substrate of loose sand, conditions common in many "listed" streams in the southeastern Coastal Plain. However, many of the blackwater streams in the Georgian Coastal Plain drain areas of intensive agriculture use that in recent years have supplemented the waterways with additional nutrients through the use of commercial fertilizers that could further exacerbate already low DO conditions (Carey 2005, Carey et al. 2005).

Recent evidence shows that low DO levels may be a natural occurrence in many of these systems and not a sign of pollution or impairment. Various studies have shown DO levels below the 5 mg L^{-1} 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). For instance, Ice and Sugden (2003) found over 80 percent of their summertime observations were below the 5 mg L^{-1} standard and close to 60 percent were below the proposed revised limit of 3 mg L^{-1} working in forested watersheds in the Louisiana South Central Plains. 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 (Meyer 1992).

Hydrological properties are paramount in a river system as the primary factor in describing water quality in a river system is the movement of water principally in a downstream direction (Thomann and Mueller 1987). Previous work on this project investigated the prevalence and role of sediment oxygen demand (SOD) and highly organic sediments within instream swamps on DO levels. These studies found *in situ* SOD rates ranging from 0.49–14.19 g O_2 $m^{-2}d^{-1}$, values much higher than those previously reported in the literature (Chapter 2). Further, Chapter 3 showed that areas subject to elevated SOD are widespread at the watershed scale. To fully quantify the effects of high SOD on DO, it is necessary to understand the effects of hydrology and travel time within these instream swamp systems. The purposes of this study were to: 1) investigate travel times through two representative instream swamps within a characteristic blackwater stream system; 2) use established solute transport models and investigate transport properties including the influence of transient storage under different flow regimes; 3) characterize the impact of these transport properties on DO dynamics.

METHODS

Study Site

Research was conducted within the Little River Experimental Watershed (LREW), a 334 km^2 research watershed located in the western headwaters of the Suwannee River Basin (Figure 4.1) (Sheridan and Ferreira 1992). The LREW was instrumented by the Southeast Watershed Research Laboratory of the USDA Agricultural Research Service for the measurement of rainfall and streamflow beginning in 1967 and has been designated as representative of the soils, topography, geography and land use within the southern Coastal Plain. While land use is primarily agriculture and forestry, riparian vegetation remains largely intact along portions of the river, with swamp hardwood communities consisting of a closed canopy and thick undergrowth. Two locations were selected for measurement. The first is a 270 m long stretch of stream determined by measurement in a geographic information system (GIS) as the distance between upstream and downstream measuring station along the stream center line. This location is located in the headwaters of the LREW above the gauging site designated as Station J (Figure 4.1, Figure 4.2a) (Sheridan and Ferreira 1992). The stream at this point is 3rd order, with a bankful main channel 5-15 m in width for most flow intensities (designated by outline in Figure 4.2a) and subject to overbank flooding during high flow events where floodplain width can extend for over 100 m. The second location is a 1601 m long stretch of river measured as the difference between sampling locations along the stream centerline. It is located in the southern end of the LREW above the gauging site designated Station B (Figure 4.1, Figure 4.2b). The stream at this point is 5th order and can be as wide as 350 m during periods of complete inundation. At this site, complete inundation of the floodplain usually begins in December and lasts until April or May. During the summer months, flow usually stops and during most years, the river channel dries completely at both locations.

Rhodamine Dye Trace

One way to calculate travel time and conservative water transport parameters is through the use of a conservative tracer. Ideally, a conservative tracer is one which behaves as a water molecule traveling through the system would and not be subject to decay, biological uptake, sorption to sediments or vegetation and loss. Finding a tracer that is truly conservative has been problematic as it is difficult to find one that is not affected by one of these processes. Rhodamine WT is a common and recommended tracer because of its ease of use, economical price, and ease of detectability (Smart and Laidlaw 1977, Kilpatrick and Wilson 1989). However, rhodamine WT has been shown to not be a truly conservative tracer due to mass loss via sorption to sediments (Smart and Laidlaw 1977, Bencala et al. 1983, Lin et al. 2003, Keefe et al. 2004) and photochemical decay in experiments lasting longer than a week (Smart and Laidlaw 1977). Despite these limitations, rhodamine WT is among the most common tracers used for analyzing travel time within a stream environment and is approved for use by the United States Geological Survey.

Measurement of travel time through the experimental locations was achieved through the release of rhodamine WT dye (Fluorescent Red, Norlab Inc., Amherst, OH) and the deployment of automated discrete water samplers (Teledyne Isco 3700, Teledyne Isco Corp., Lincoln, NE). The 3rd order location was a 270 m reach consisting of upstream and downstream samplers (Figure 4.2a). The 5th order location was a 1601 m reach consisting of three samplers in the center of the stream channel (Samplers A, D, and B) and two additional samplers (Samplers C and E) placed in a latitudinal transect parallel to Sampler D for dye concentration measurement (Figure 4.2b). At both locations, a broad-crested V-notch weir was used to measure flow continuously at the downstream end of the sampling runs during the experiment. To obtain measurement of rhodamine transport during different hydrologic conditions, there were a total of four releases at the 3rd order location and three at the 5th order location. As stated previously, streams throughout the watershed are intermittent, so releases occurred during the winter and early spring and dye releases conducted under both high and low flow conditions. The time period of dye releases for this study coincides with the period of the year subject to lowered DO levels within this watershed. Effort was taken to minimize flow variation by planning releases during periods when precipitation was not forecast for multiple days.

For each sampling run, rhodamine WT dye was released as a single slug far enough upstream to ensure adequate mixing of the dye prior to reaching the first sampler. At the 3rd order location, this distance was approximately 100 meters, but lack of access points to the river at the 5th order location required the dye to be released approximately 6500 m upstream of the first sampler. Following sampling, mass balances were calculated to assess conservation of mass. The automated samplers were programmed to take water samples at time intervals that allowed adequate capture of the dye concentration curve at each location. At the 3rd order location these time intervals were most often 10-15 minutes between sampling bottles, whereas the samples at the 5th order location were most often hourly samples. Multiple samples were composited into a single bottle giving an average over the programmed time interval. For instance, at the 5th order location, an hourly sample consisted of four 70 mL subsamples taken every 15 minutes and composited into a single bottle to give the hourly average. Upon return to the lab the concentration of rhodamine dye in each sample was measured on a fluorometer (TD-700 Laboratory Fluorometer, Turner Designs, Sunnyvale, CA). Prior to measurement, standard solutions were prepared from stream water taken prior to dye release.

Modeling using OTIS

Modeling of stream transport has been aided in recent years by the development of OTIS (One-dimensional Transport with Inflow and Storage), a quasi two-dimensional mathematical simulation model which is able to model the fate and transport of both conservative and nonconcervative solutes in rivers and streams (http://co.water.usgs.gov/otis) (Runkel 1998). The model is based on the transient storage model first developed by Bencala and Walters (1983). The model is developed by creating mass balance equations for two conceptual areas: the main channel and the storage zone (Figure 4.3). The main channel is defined as the section of stream where advection and dispersion are the main transport properties while the storage zone is the area in which transient storage is the dominant process. Transient storage is the process by which water is stored in dead zones within a stream channel (such as side eddies or pools) or exchanges through the hyporheic zone (Bencala and Walters 1983). These "dead" areas of the stream allow extended contact time with microbial communities and extend residence time through a reach. The two areas are linked by an exchange term. The governing equations describing the spatial and temporal variation in solute concentrations are given by two coupled differential equations:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}(AD\frac{\partial C}{\partial x}) + \frac{q_{LIN}}{A}(C_L - C) + \alpha(C_s - C) \qquad [1]$$

$$\frac{dC_s}{dt} = \alpha\frac{A}{A_s}(C - C_s) \qquad [2]$$

Where:

A main channel cross-sectional area (m^2);

A_s storage zone cross-sectional area (m^2);

C main channel solute concentration ($\mu g\ L^{-1}$);

C_L lateral inflow solute concentration ($\mu g\ L^{-1}$);

C_s storage zone solute concentration ($\mu g\ L^{-1}$);

D dispersion coefficient (m^2 s^{-1});

Q volumetric flow rate (m^3 s^{-1});

q_{LIN} lateral inflow rate (m^3 s^{-1} m^{-1});

t time (s);

x distance along the main channel (m);

α storage zone exchange coefficient (s^{-1}).

OTIS can be utilized with the non-linear regression package STARPAC (Donaldson and Tryon 1990) which estimates parameter values by minimizing the sum-of-squared errors between measured and predicted values to determine optimal sets of parameter values. Convergence is achieved by a trial-and-error approach involving the running of multiple model iterations by substituting modeled parameter values from one iteration into the following iteration until stable. Convergence is measured by the relative change of sum-of-squared errors or relative change of the parameter estimates (Martinez and Wise 2003).

The 3rd order location was modeled as a single 270 m reach (Figure 4.2a). The 5th order location was modeled as two individual reaches with the first reach being 632 m (distance from Sampler A to D) and the second being 969 m (distance from Sampler D to B). Both locations were modeled with steady state flow and average flow computed for the time period of dye tracing using measurements taken at the weir. Flow was adjusted for the upstream sampling locations based on calculations of contributing watershed area. For the 3rd order location, watershed area was shown to not have a significant change on flow between the upstream and downstream sampling locations, so the average flow measured at the downstream weir was used for flow across the whole reach. At the 5th order location, the timing and magnitude of flow was considered. The magnitude of flow was adjusted at the upstream samplers (Stations A and D) according to the percentage difference in contributing watershed area when compared to the downstream weir (Sampler B). Flow adjustments due to timing differences in flow between the upstream stations and the downstream weir was accomplished using established time to peak relationships developed for the watershed (Sheridan 1994).

As stated above, rhodamine has been shown to be affected by sorption to sediments (Smart and Laidlaw 1977, Bencala et al. 1983, Lin et al. 2003, Keefe et al. 2004). To account for loss of rhodamine in the OTIS model structure, photodegredation was assumed to be minimal and sorption was modeled using the first-order decay option (R. Runkel pers. comm.). Sorption was only considered in the transient storage areas as it was assumed to occur primarily in the areas where flow is slowest and most likely to interact with organic materials on the streambed and in the hyporheic zone. The equation governing the decay of rhodamine in the transient storage zone is given by:

$$\frac{dC_s}{dt} = S(C_s) - \lambda_s C_s \qquad [3]$$

Where:

$S(C_s)$ = physical processes in the storage zone (the right hand side of equation 2)

λ_s = storage zone first-order decay coefficient (s^{-1}).

Modeling of advection, dispersion and transient storage proceeds with concentrations measured downstream adjusted to represent values as if rhodamine was conservative (e.g. if mass balance was 90%, measured concentration values are divided by 0.90 to give "conservative" values). Initial values of the conservative transport parameters (A, A_s, D, and α)

were estimated and OTIS was executed in conjunction with the non linear regression package STARPAC as described above. Trial runs were repeated until the change in parameter estimates or the residual sum of squares between model runs was minimal. Following convergence of the conservative transport parameters, the original data (non conservative values) was substituted back into the model structure and first-order decay modeled to reach final estimates of all five parameters. Following modeling runs, modeled solute concentration curves were used for calculation of travel time as center of mass. For those curves not modeled with OTIS, measured solute concentration data was used for calculation of center of mass. Center of mass was calculated by integrating the area under the modeled or measured solute concentration curves and then determining the time when 50 percent of the rhodamine dye had passed.

RESULTS

Hydraulic Conditions

The LREW has a long history of measuring discharge and rainfall at various points in the watershed since the late 1960s. As mentioned previously, both are these sites are subject to drying during the summer time months. The 3rd order site over a period of 40 years (1968-2007) has averaged 231.5 flowing days year^{-1} and is dry for much of the summer and fall months (Figure 4.4a). Flows peak in February with a long term median daily average flow of 0.39 m^3 s^{-1} (Figure 4.4a). Traces 1 and 2 occurred during February and both had flows higher than the long term median daily average flow (0.506 and 0.714 m^3 s^{-1} respectively) along with overbank flooding and floodplain inundation (Table 4.1). Traces 3 and 4 took play in late April with flows of 0.035 and 0.017 m^3 s^{-1} (Table 4.1). Both of these traces were under low flow conditions and

Trace 4 was particularly representative of this time period as the median daily average flow for the month of April is 0.15 $m^3 s^{-1}$ (Figure 4.4b).

The 5th order site over a period of 36 years (1971-2007) has averaged 281.8 flowing days $year^{-1}$. Flows peak in February at 5.39 $m^3 s^{-1}$ and generally reach a minimum by May (Figure 4.4b). Trace 1 occurred in late January and was representative of the long term condition for this month as the measured flow of 3.83 $m^3 s^{-1}$ was near the long term median average daily discharge of 3.58 $m^3 s^{-1}$ (Table 4.1, Figure 4.4b). Traces 2 and 3 were conducted during the 2007 calendar year, a period of extreme drought in the study area. Consequently, the measured flow rates were well below the long term median daily average flow as Trace 2 (Q = 0.75 $m^3 s^{-1}$) was lower than the long term median daily average of between 2.05 – 4.75 $m^3 s^{-1}$ for March and April and Trace 3 (Q = 1.72 $m^3 s^{-1}$) was similarly less than the long term median daily average flow of between 4.75 – 5.39 $m^3 s^{-1}$ (Table 4.1, Figure 4.4b). Mass balances across both sites yielded low recovery rates as less than 30% of dye was recovered across all traces (Table 4.1).

OTIS Parameter Modeling

OTIS was able to model three of the four releases at the 3rd order location and one of the releases at the 5th order location (Table 4.2). In those instances where OTIS parameter results are not reported (Trace 1, 3rd order location; Trace 1 and 3, 5th order location), the STARPAC regression package either did not reach convergence after multiple iterations or the estimated parameters after multiple iterations had such high standard deviations so as to make those results functionally unreliable. Figures 4.5 and 4.6 illustrate field observations with modeled simulation results for both the 3rd and 5th order locations. Figure 4.5 shows that OTIS was able to closely model the rhodamine concentration curves at the 3rd order location for a variety of flow conditions. Under lower flow conditions (Figure 4.5b and 4.5c) rhodamine dye concentration curves had a longer time of travel along with a more elongated tail and return to background concentrations illustrating the slow movement of water through the system when compared to a high flow condition (Figure 4.5a). Figure 4.6 shows that OTIS overestimated the tail of the curve at both downstream sampling locations.

For the 3rd order location, parameter estimates for dispersion (D) ranged from 0.034 to 0.587 across all rhodamine dye traces, while for the one modeled run at the 5th order location, values for each Reach 1 and 2 were 0.016 and 0.012 respectively (Table 4.2). At the 3rd order site, dispersion (D) decreased with decreasing discharge (Q), while the relationship between the storage zone cross-sectional area (A_s) and main channel cross-sectional area (A) varied. F_{mean} ($A_s/A+A_s$) is a measure of the fraction of the total reach volume occupied by the storage zone or the fraction of the mean travel time due to transient storage. Results for the 3rd order watershed showed that during instances of overbank flooding (Trace 2) or when flow was very low (Trace 4) that transient storage was a large fraction of the mean travel time at 50% and 35% respectively. F_{med} was proposed by Runkel (2002) as a measure of the median travel time due to transient storage. It is given by the equation:

$$F_{med} \cong (1 - e^{-L(\alpha/u)}) \frac{A}{A + A_s} \qquad [4]$$

Where:

L = Length of the reach (m)

u = Advective velocity (Q/A) (m s^{-1})

Under this metric, reaches where downstream transport of solute mass is substantially affected by transient storage will have high values while those reaches where storage has lesser effect on downstream transport will have lower values. Under the differing flow scenarios, F_{med} had values between 9% and 29% with the highest values at the highest and lowest flows. Further parameters of interest are u and u', measures of velocity through the study reach with u representing advective velocity through the main channel (Q/A) and u' representing depth-averaged velocity of tracer ($u \cdot A/(A+A_s)$) which is a function of flow through the main channel as well as the transient storage component (Harvey et al. 2005). Velocities were slow for all three runs with a maximum velocity of 10.5 cm s^{-1} during the high discharge run. However, due to the large transient storage area during that run, the depth-averaged velocity was half of the advective velocity. As indicated by the relationship between u and u' for each trace, the transient storage had the greatest impact on the tracer transport during the tracer test with the highest streamflow (Table 4.2).

Although OTIS was only able to be calibrated for one of the dye tracer runs at the 5th order location, the trace that was calibrated showed that parameters for the two reaches are similar (Table 4.2, Figure 4.6). Although D was the most uncertain parameter term during calibration, both reaches had similarly low values. Additionally, values for velocity were low with both reaches having velocities of less than 2 cm s^{-1} and F_{med} values of 12% for both reaches.

Travel Time Calculations

Median travel time (T_{med}) was calculated as the difference in time between solute center of mass reaching the upstream and downstream sampling locations for all dye traces. At both locations, as Q increased travel time decreased (Table 4.1). Velocities were calculated as reach length divided by reach travel time. Velocities at the 3rd order location ranged from 0.80 cm s^{-1} to 9.34 cm s^{-1}. The highest velocities were recorded during Trace 1 and 2 when there was substantial overbank flooding and floodplain inundation. The velocities for all dye tracing runs calculated through center of solute mass (Table 4.1) were slightly less, but comparable to those calculations of velocity through OTIS parameter estimation (Table 4.2).

Due to difficulty in OTIS parameter estimation for the 5th order site, comparison between modeling and center of mass calculation was only possible for Trace 2. Nevertheless, velocities calculated through the two methods were in agreement as velocities for both methods were between 1-2 cm s^{-1}.

The additional sampling locations in the side channels (Samplers C and E) offer alternative methods of comparison amongst rhodamine dye tracing runs at the 5th order location. Trace 1 (1/24/06-1/30/06) had a total reach time of travel of 12.67 hours and an average downstream discharge of 3.83 m^3 s^{-1} (Table 4.1). Observation of the rhodamine concentration curves showed they reach a characteristic peak and then quickly returned to background concentrations (Figure 4.7). Additionally, the two side channel samplers showed dye concentrations well above background and reached a peak a few hours following Sampler D located in the center of the channel.

Trace 2 (3/29/06-4/7/06) had a total reach travel time of 30.93 hours due to its lower average discharge of 0.75 m^3 s^{-1} (Table 4.1). In contrast to Trace 1, Trace 2 showed characteristic differences in its dye response curves (Figure 4.8). Curves for Samplers A, D, and B, all located in the center of the channel, showed characteristic response curves but with concentrations of rhodamine above background at the downstream outlet more than seven days following maximum concentrations at the upstream sampling location. Additionally, despite the continuous presence of water in these side channel locations, the movement of rhodamine dye through these locations was less pronounced (Figure 4.8).

Measurement of rhodamine dye tracer travel through these natural systems made having consistent flow throughout a tracer run difficult. Hydrology is affected by natural daily variation and weather phenomena. Care was taken to limit flow changes by choosing dates when precipitation was not forecast for multiple days. Time of travel was calculated for Trace 3 for the initial 80 hours (2/26/07-3/1/07). During this time, average flow at the downstream terminus was 1.72 $m^3 s^{-1}$ with a time of travel for the entire reach of 18.93 hours. During this time period, the center channel samplers (A, D, and B) again showed a characteristic response curve with an elongated tail back to background (Figure 4.9). During Trace 2 the side channels appeared to not transmit flow as no dye signal was recorded at Samplers C and E during that run. In contrast, average flow was 2.3 times higher in Trace 3 and dye again was transmitted through the side channel locations (Sampler C), albeit many hours after the center sampler channel parallel to it (Sampler D). Following this initial measure of rhodamine dye a precipitation event caused an increase in discharge (Figure 4.9). This event led to an additional unexpected pulse of rhodamine dye through the study reach before returning to background concentrations approximately 190 hours following the initiation of the run.

DISCUSSION

OTIS Parameter Modeling

OTIS has been used extensively to model the transient storage of solutes in stream environments. Many of these studies have been conducted in small, high gradient stream systems (for a complete reference list see Transient Storage Reader 1 and 2 at http://smig.usgs.gov/smig/reading_refs.html). Recently the use of OTIS has been extended to wetland systems with good results (Martinez and Wise 2003, Keefe et al. 2004, Harvey et al. 2005). In the latter two instances, OTIS was used to model a constructed wetland system with the former using natural flow through constructed channels in the Everglades. This paper is one of the first examples using OTIS in an instream wetland complex. OTIS was able to model a total of 4 out of the 7 total runs with the majority occurring at the 3rd order location, a stream more similar to those by which the model was developed. The lack of convergence for the first trace at the 3rd order location was likely not a result of the OTIS model structure, but rather because of poor measurement of the dye concentration curve due to excessive time gaps between sample capture.

Unlike the 3rd order location that tended to calibrate well, OTIS had a difficult time modeling the 5th order location, a stream that was nearly seven times the cross sectional area of the 3rd order location even during a period of relatively low flow. OTIS had difficulty modeling the 5th order location at higher flow levels. One of the major assumptions of one-dimensional models like OTIS model is that flow path is in a straight line distance from inlet to outlet (Martinez and Wise 2003), but the 5th order location more closely resembles a flooded forest floor with heavy vegetative interference and minimal evidence of a defined channel (Figure 4.10). Increasing flow levels would only increase that interference, possibly creating multiple, tortuous solute flow paths. Additionally the model assumes one general transient storage zone area with a single exchange rate between it and the main channel. In reality, under higher flows there are likely multiple different transient storage zone areas each with different exchange rates that would make accurate calibration difficult. Finally, we used an average steady-state flow at both locations due to the inability to accurately model the change in cross-sectional area with flow. It is apparent that due to the length in time associated with a dye tracing run at the 5th order location that flow and cross-sectional area change. The changing flow and cross-sectional area during higher discharge runs may have compromised the ability to effectively calibrate the model.

Despite these difficulties, the attained solute parameter estimates were considered well estimated under the criteria set forth by Wagner and Harvey (1997). The experimental Damköhler number (*DaI*) is a measure of parameter uncertainty and an indicator of the reliability of stream storage parameters (A_s and α) and was adapted from subsurface transport research conducted by Bahr and Rubin (1987) defined as:

$$DaI = \frac{\alpha(1+\frac{A}{A_s})L}{u} \qquad [5]$$

Under this parameter, values are "well-estimated" between values of 0.1-10.0. *DaI* values much less than 1 (due to high velocity, long exchange timescale, and/or short reach length) have high parameter uncertainty due to very little tracer interacting with the storage zone within the reach. When *DaI* is very high, solute exchange rates are high in comparison to the stream reach water velocity. As shown in Table 4.2, all values of *DaI* are within the "well-estimated" range.

With multiple traces done at the 3rd order site, comparisons amongst the parameter estimates for the different runs are possible. At this site, dispersion (*D*) and exchange between the main channel and transient storage zones (α) increased with increasing flow and water velocity. Hart et al. (1999) found similar trends for a small mountain stream in North Carolina, but found that dispersion leveled off at higher discharges. The relationship between the effect of transient storage area on median travel time (F_{med}) and reach volume (F_{mean}) is less clear as F_{med} and F_{mean} have their highest values at the highest and lowest levels of discharge. The increase at the lowest flow (Trace 4) is due to the bigger transient storage area when compared to Trace 3. Regardless of flow level, reach travel time is significantly affected by transient storage. Trace 1 shows that at times of high flow when water is flooded onto the floodplains and transient storage areas are high (F_{mean} = 50%), F_{med} is nearly 29% of reach travel time. At times of extremely low flow (Trace 4), transient storage plays a similarly large role as F_{med} = 24%. Keefe et al. (2004) working in a constructed wetland found similarly high levels of F_{med} due to the lateral spreading of the flowpath due to islands. The heavy vegetative interference due to canopy trees growing in the stream channel at this location may serve to make solute transport more two-dimensional in nature.

One of the limitations of the OTIS modeling structure is its inability to reliably extrapolate measured parameter values to different flow and seasonal conditions (Hart et al. 1999, Martinez and Wise 2003). The results reported in this study are a first approximation of water solute transport parameters within a dynamic instream swamp environment under differing flow conditions. To reliably assess how these transport parameters change at both locations under different seasonal and hydrologic conditions additional dye traces are needed.

Time of Travel Calculations

Calculation of median travel times (T_{med}) through center of mass calculations and observation of rhodamine dye response curves allows for the comparison of water transport dynamics between differing hydrologic conditions. At the 3rd order location, time of travel increased with decreasing flow and decreasing velocities through the reach. Even during periods when high stream flows occurred and water spread onto the floodplain (Traces 1 and 2), relatively slow velocities were encountered as all traces had velocities of less than 10 cm s^{-1}. When comparing the velocities calculated via the center of mass calculations versus the OTIS parameter calculations, they are in similar ranges indicating general agreement between the two methods (Table 4.1 and 4.2).

The 5th order location showed dramatic differences in the response of the rhodamine tracer curves depending on flow magnitude. Trace 1 had the highest velocities (3.51 cm s^{-1}) and consequently the lowest travel time through the reach of 12.67 hours (Table 4.1; Figure 4.7). Dye response curves reached a maximum and then returned to background concentrations at the downstream end of the reach by 75 hours following maximum rhodamine concentrations at the upstream sampler. The occurrence of dye within the side channel samplers during this run highlights the movement of water through this region (Figure 4.7). Further, the delayed response to peak at these locations (Sampler C and E) in comparison to the center channel sampler (Sampler D) indicated that water may be moving more slowly through these locations.

In contrast, the second trace was conducted at the lowest average flow and had the longest travel time of nearly 31 hours and lowest average velocity of 1.44 cm s^{-1} (Table 4.1; Figure 4.8). Upon inspection of the rhodamine concentration curves for the multiple samplers, it appears the majority of the water during this trace is conveyed through the main channel as responses are seen primarily in Samplers A, D, and B. The side channel samplers during this run do not show the distinctive response curves displayed during the first trace indicating less movement of water through these locations. Martinez and Wise (2003) investigated flow through different cells of a constructed wetland and found that in addition to modeling a main channel storage area and a transient storage area, the dye response curves were best modeled by adding a third storage area, one of purely "dead" water. The lack of dye moving through these side channel locations, even though they remained fully inundated, indicated that at lower flows parts of instream swamp complexes contain these same areas of virtually no movement or hydrologic exchange. Additionally, when compared to the first tracing run when dye concentrations returned to background concentrations relatively quickly, rhodamine dye above background is measured at the downstream sampler at least 170 hours following maximum concentration measurements at the upstream sampler (Figure 4.8). The long tails on these curves indicates the presence of long, tortuous pathways for water movement as dye labeled water slowly traveled downstream. The velocities calculated through the two methodologies are in general agreement and highlight this slow movement of water as both are between 1-2 cm s^{-1} (Table 4.1 and 4.2).

Finally, the third dye trace at the 5th order location offered the opportunity to see the effect of changes in watershed hydrology on water transport through this location. As mentioned in the results, rhodamine tracing runs were planned to minimize changes in flow intensity. However, with rhodamine tracing runs taking multiple days it was difficult to fully avoid precipitation events as the third trace exemplifies. Travel time was calculated during this run for the initial 80 hours of data when flow was relatively constant. This trace occurred at an intermediate flow to Traces 1 and 2 with a travel time of nearly 19 hours and a velocity of 2.35 cm s^{-1} (Table 4.1; Figure 4.9). During this initial 80 hours, characteristic rhodamine dye response curves are seen with flow moving through all sampling locations (Sampler E malfunctioned during this run and returned no data). Concentration curves reach a peak and return close to background levels at all samplers by the 80 hour mark. As seen in the flow measured at the downstream sampler (Sampler B), a precipitation event (2.8 – 4.3 cm across the watershed) led to over an eight fold increase in flow. Surprisingly, this led to measurement of another pulse of dye through all samplers within the reach. Since access points are limited on the river system dye had to be injected well upstream of Sampler A and this additional pulse of flow through the system highlights that the trapping of water in transient storage zones is a pervasive feature of the system. Only during periods of high flow do these pockets of slowly moving water get flushed through the system.

Conclusion

One of the hypothesized reasons for low DO levels in blackwater streams on the southeastern Coastal Plain has been tortuous low velocity pathways in conjunction with areas of elevated SOD (Ice and Sugden 2003). Previous work has shown that SOD rates within instream swamps are elevated above previously published values for southeastern streams and that areas subject to elevated SOD are widespread (Chapter 2 and 3). These two factors in combination have the ability to decrease DO levels on a watershed scale.

Work in this study compared travel times through two representative locations in this watershed and found generally low velocities as even during periods of high flow at the 3rd order reach velocities were less than 10 cm s^{-1}. However, the lowered velocities have more impact on oxygen demand at the 5th order location as previous work at these same study locations showed that average SOD rates on a reach scale were higher in the 5th order location when compared to the 3rd order location (Chapter 3). This difference is highlighted when compared on a per meter length of stream due to the larger floodplain width and more constant period of inundation at larger order sites. For example, the two traces exhibiting the most similar velocities are Trace 3 at the 3rd order location and Trace 3 at the 5th order location where velocity was just over 2 cm s^{-1}. At this flow level, the stream at the 3rd order location would be within its banks and have an oxygen demand of 0.015 kg O_2 $d^{-1}m^{-1}$ length of stream (Chapter 3). In contrast, the 5th order location with its more constant area of inundation has an oxygen demand of 1.56 O_2 $d^{-1}m^{-1}$ length of stream. Therefore, even if stream velocities between the two locations are the same, the total oxygen demand would be greater at the 5th order location highlighting their heightened importance in DO dynamics.

DO dynamics within a stream are a complex mosaic of natural and anthropogenic factors, but this research shows that flow pathways in these streams are low velocity with extended reach travel times. The long travel times ensure extended contact with the underlying organic sediments providing an environment for intense oxygen demand and lowered DO levels. These areas of intense oxygen demand offer support that many of these streams exhibiting lowered DO may in fact be naturally low and not a sign of impairment.

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Table 4.1. Calculation of median travel time (T_{med}), velocity (u), and rhodamine dye mass balance at 3rd and 5th order locations across different flow regimes

	Date	Length (m)	Q^a ($m^3\ s^{-1}$)	T_{med} (hours)	u ($cm\ s^{-1}$)	Mass Bal. (%)
3rd Order Location						
Trace 1	2/06/07	270	0.506	0.88	8.53	6.93
Trace 2	2/14/07	270	0.714	0.82	9.11	3.76
Trace 3	4/24/07	270	0.035	3.39	2.22	12.06
Trace 4	4/25/07	270	0.017	9.34	0.80	29.22
5th Order Location						
Trace 1	1/24/06 – 1/30/06					
Reach 1		632	3.57 (2.52 – 3.86)	6.30	2.79	
Reach 2		969	3.83 (2.70 – 4.13)	6.37	4.23	
Total		1601		12.67	3.51	7.87
Trace 2	3/29/06 – 4/7/06					
Reach 1		632	0.68 (0.296 – 0.941)	12.37	1.42	
Reach 2		969	0.75 (0.318 – 1.009)	18.56	1.45	
Total		1601		30.93	1.44	2.63
Trace 3	2/26/07 – 3/9/07					
Reach 1		632	1.60 (1.53 – 1.76)[b]	6.02	2.92	
Reach 2		969	1.72 (1.64 – 1.89)	12.91	2.08	
Total		1601		18.93	2.35	12.42

[a]Discharge measurements for 5th order location represent the average value across the entire study run at the downstream end of the study reach with average daily flow in parentheses

[b]While dye was measured through 3/9/07, flow measurements and calculation of T_{med} are from first 80 hrs (2/26/07 – 3/1/07) (See Figure 4.9)

Table 4.2. OTIS model parameters[a] estimation for 3rd and 5th order locations (±1 SD) including calculation of velocity (u), depth-averaged velocity (u'), F_{med}, F_{mean}, and DaI

	3rd Order Location			5th Order Location	
	Trace 2	Trace 3	Trace 4	Reach 1	Reach 2
Date	2/14/07	4/24/07	4/25/07	3/29/06 – 4/7/06	3/29/06 – 4/7/06
Q ($m^3 s^{-1}$)	0.714	0.035	0.017	0.675	0.752
D ($m^2 s^{-1}$)	0.587 (±0.027)	0.062 (± 0.005)	0.034 (±0.004)	0.016 (±0.026)	0.012 (±0.036)
A (m^2)	6.773 (±0.043)	1.385 (±0.014)	1.505 (±0.024)	40.398 (±0.658)	54.396 (±1.999)
A_s (m^2)	6.906 (±.316)	0.2566 (±0.012)	0.819 (±0.044)	19.783 (±1.385)	13.650 (±1.621)
α (s^{-1})	$3.32 \cdot 10^{-4}$ ($\pm 3.16 \cdot 10^{-1}$)	$8.06 \cdot 10^{-5}$ ($\pm 1.02 \cdot 10^{-5}$)	$4.83 \cdot 10^{-5}$ ($\pm 5.13 \cdot 10^{-6}$)	$1.21 \cdot 10^{-5}$ ($\pm 1.36 \cdot 10^{-6}$)	$1.30 \cdot 10^{-5}$ ($\pm 4.38 \cdot 10^{-6}$)
λ_s (s^{-1})	$1.52 \cdot 10^{-4}$ ($\pm 1.28 \cdot 10^{-5}$)	$1.17 \cdot 10^{-5}$ ($\pm 4.27 \cdot 10^{-6}$)	$1.27 \cdot 10^{-5}$ ($\pm 2.47 \cdot 10^{-6}$)	$3.86 \cdot 10^{-6}$ ($\pm 6.14 \cdot 10^{-7}$)	$2.17 \cdot 10^{-6}$ ($\pm 6.98 \cdot 10^{-7}$)
u (cm s^{-1})	10.5	2.55	1.14	1.67	1.38
u' (cm s^{-1})	5.22	2.15	0.74	1.12	1.11
F_{med} (%)	28.89	8.97	24.02	12.07	11.97
F_{mean} (%)	50.49	15.63	35.25	32.87	20.06
DaI	1.68	5.46	3.25	1.39	4.53

[a]OTIS Model Parameters are discharge (Q), main channel cross-sectional area (A), storage zone cross-sectional area (A_s), storage zone exchange coefficient (α), storage zone first-order decay coefficient (λ_s)

Figure Captions

Figure 4.1. Map of Little River Ecological Watershed with selected sampling sites.

Figure 4.2. Map of 3rd order sampling site (a) and 5th order sampling site (b). Stream width is most often found within the dotted line displayed in Figure 4.2a, but subject to cover the entire shaded area during high flow events.

Figure 4.3. Conceptual model of OTIS transient storage model (Runkel 1998).

Figure 4.4. Median daily average flows by month at the (a) 3rd order location and (b) 5th order location .

Figure 4.5. Rhodamine tracer test field data along with OTIS simulation curves (a) Trace 2 (2/06/07); (b) Trace 3 (4/24/07); (c) Trace 4 (4/25/07) at the 3rd order location. Note differing scale for Figure 4.4c.

Figure 4.6. Rhodamine tracer test field data along with OTIS simulation curve for 5th order location Trace 2 (3/29/06 – 4/7/06)

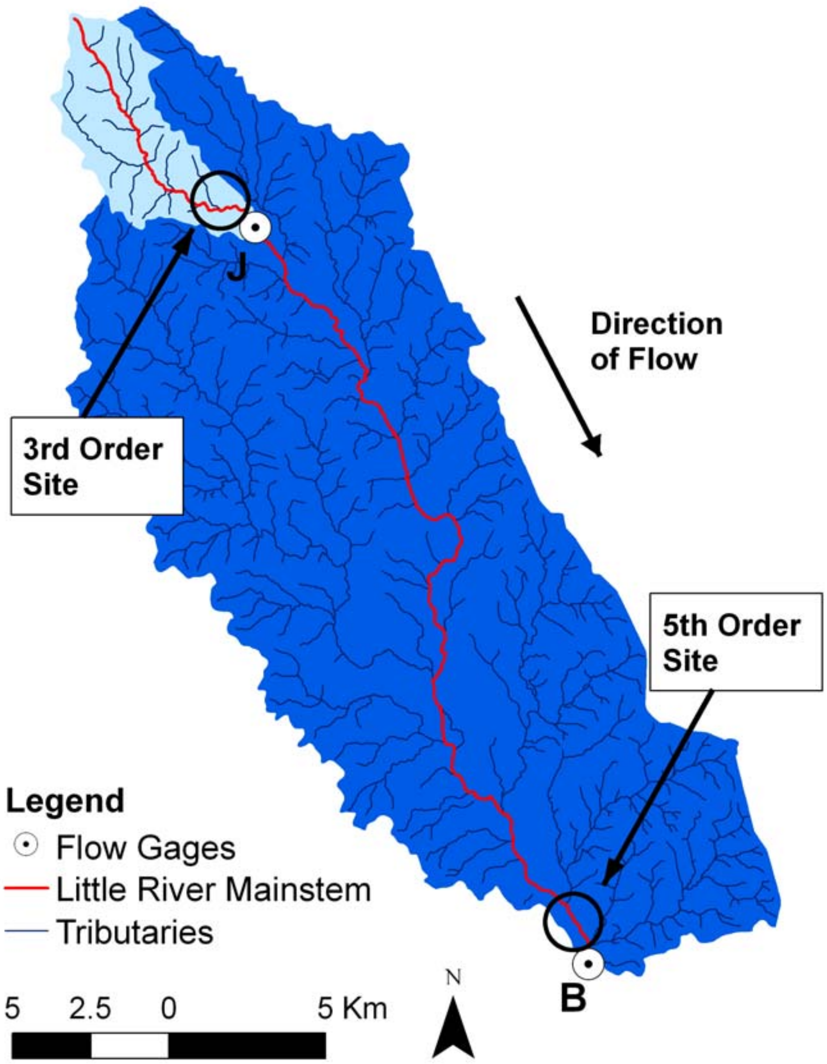
Figure 4.7. First rhodamine tracer test (1/24/06 – 1/30/06) at 5th order location showing tracer response curves for representative samplers and measured flow. Gap in data for Sampler E due to equipment malfunction during tracer run.

Figure 4.8. Second rhodamine tracer test (3/29/06 – 4/7/06) at 5th order location showing tracer response curves for representative samplers and measured flow.

Figure 4.9. Third rhodamine tracer test (2/26/07 – 3/9/07) at 5th order location showing tracer response curves for representative samplers and measured flow. Equipment malfunction for Sampler E led to no data during this tracing run.

Figure 4.10. Picture of 5th order location showing tortuous flowpaths and heavy vegetative interference

Figure 4.1



J
Direction
of Flow
3rd Order
Site
5th Order
Site
Legend
Flow Gages
Little River Mainstem
Tributaries
5 2.5 0 5 Km
N
B

Figure 4.2

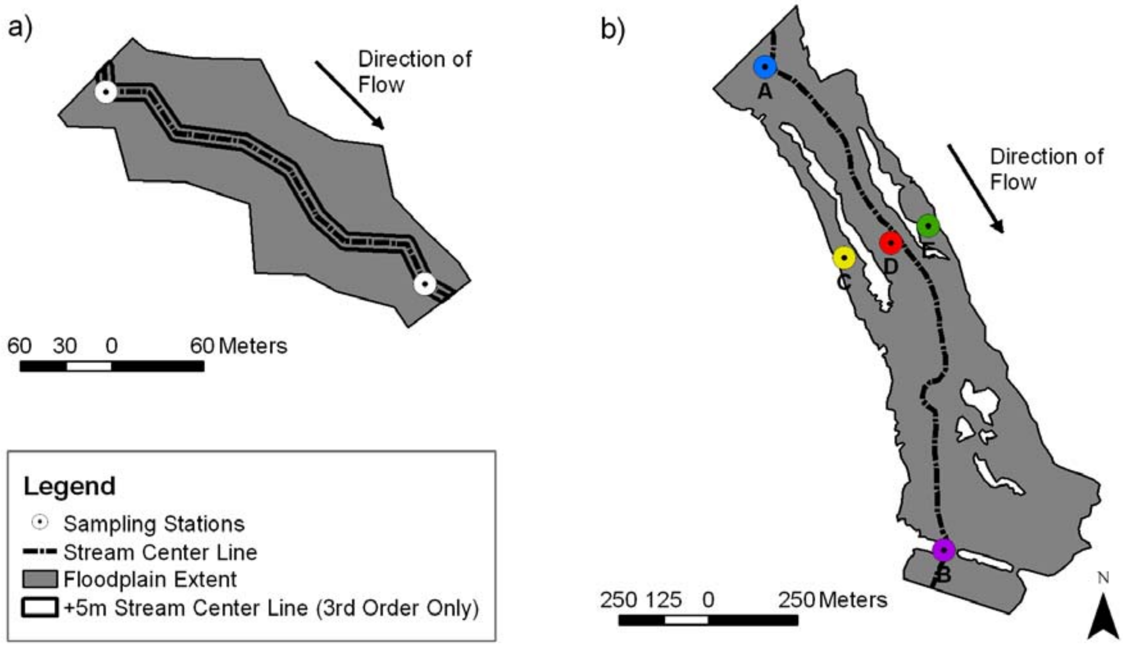

a)
Direction of
Flow
60 30 0 60 Meters
Legend
Sampling Stations
Stream Center Line
Floodplain Extent
+5m Stream Center Line (3rd Order Only)
b)
A
Direction of
Flow
E
D
C
B
250 125 0 250 Meters
N

Figure 4.3

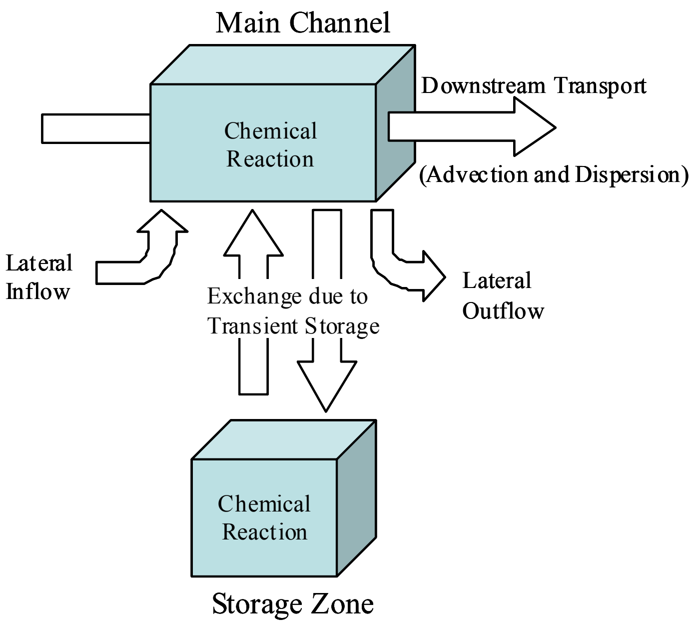
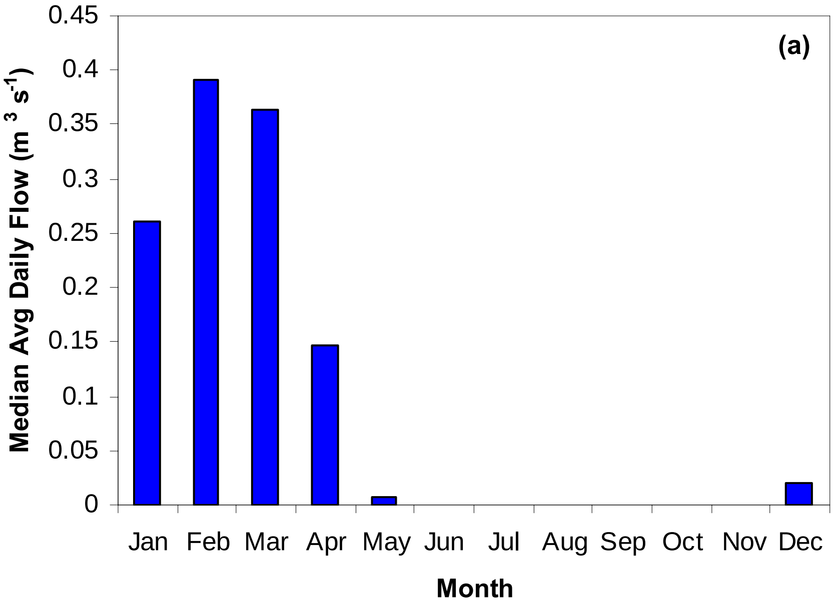
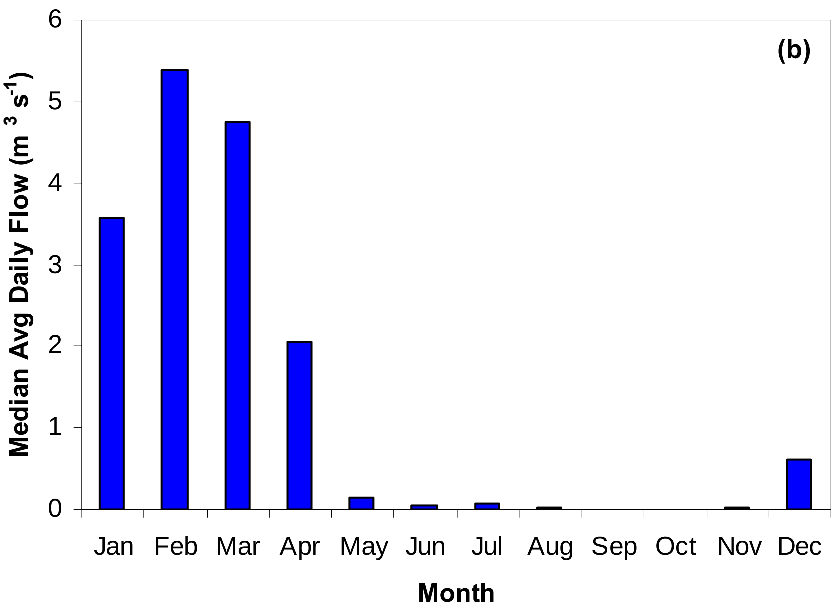

Main Channel
Chemical Reaction
Downstream Transport
(Advection and Dispersion)
Lateral Inflow
Exchange due to Transient Storage
Lateral Outflow
Chemical Reaction
Storage Zone

Figure 4.4

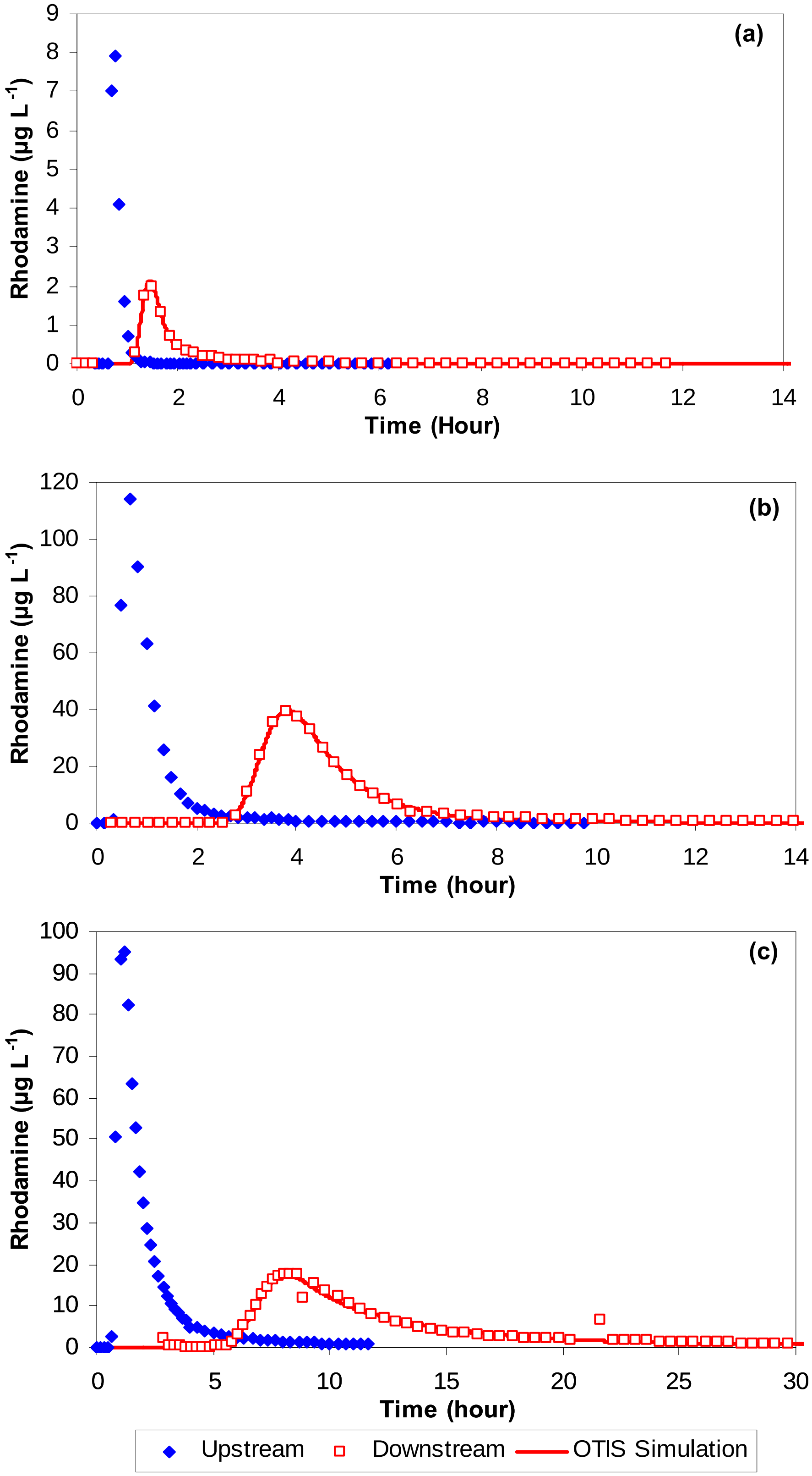


0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
(a)
Median Avg Daily Flow (m 3 s-1)
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
Month



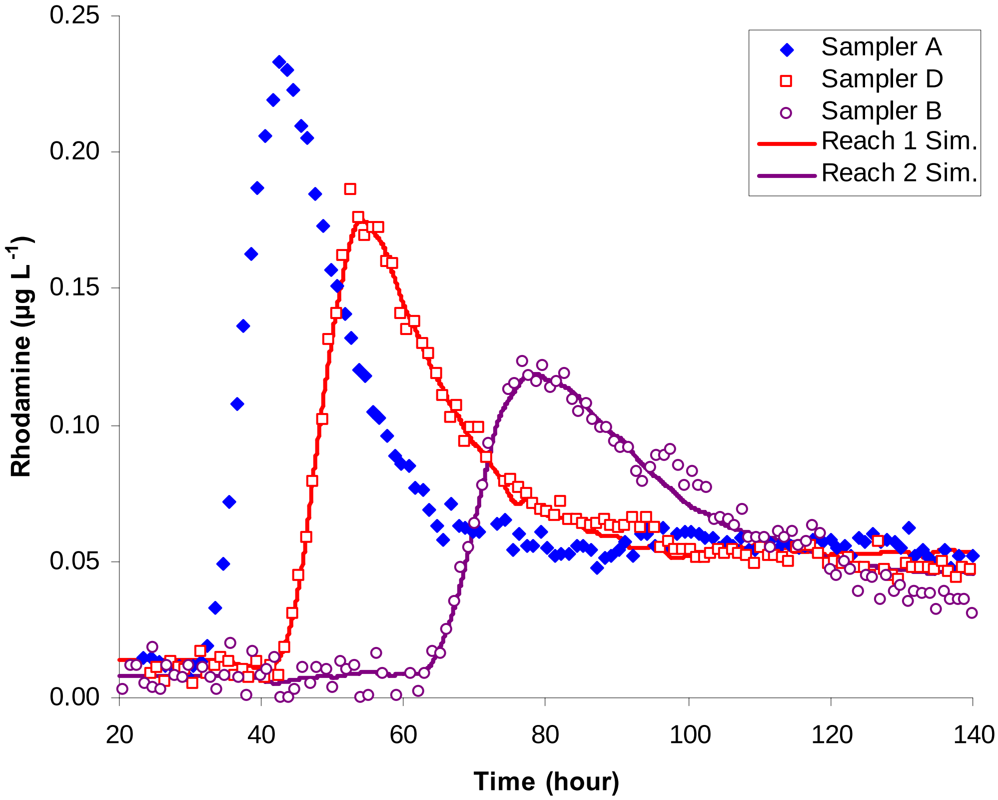
6
5
4
3
2
1
0
(b)
Median Avg Daily Flow (m 3 s-1)
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
Month

Figure 4.5



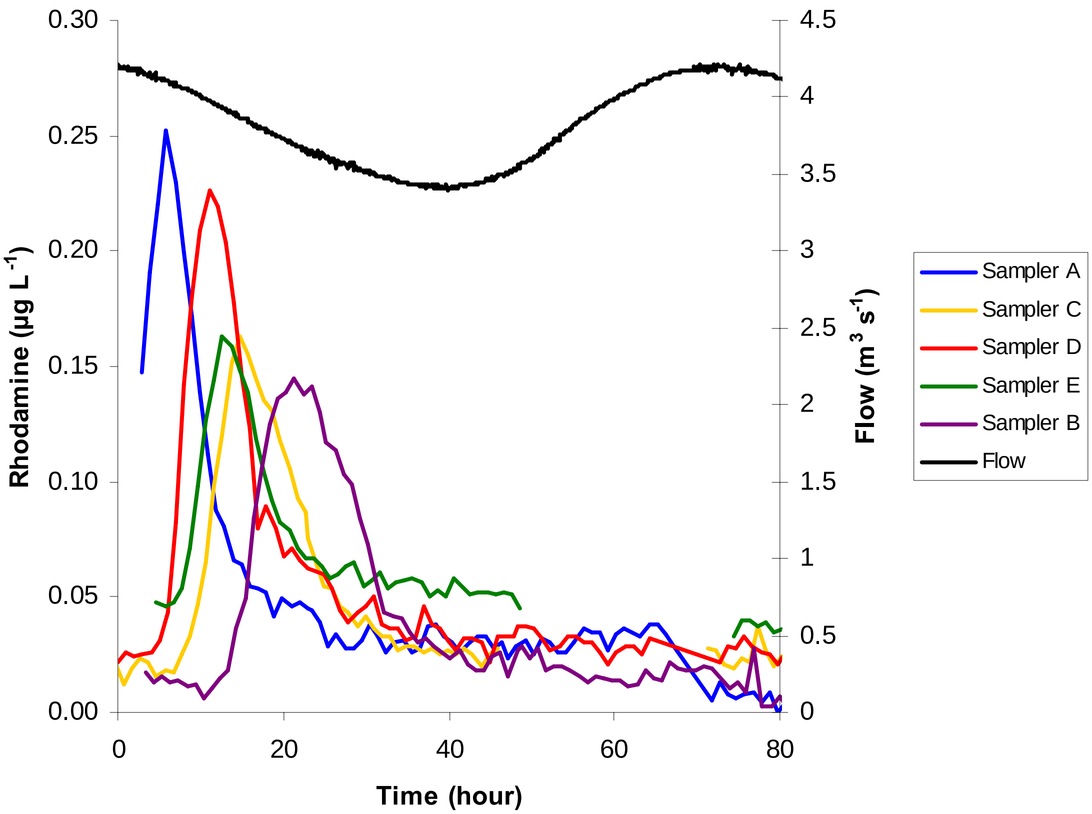
(a)
Rhodamine (µg L -1)
0
1
2
3
4
5
6
7
8
9
0
2
4
6
8
10
12
14
Time (Hour)
(b)
Rhodamine (µg L -1)
0
20
40
60
80
100
120
0
2
4
6
8
10
12
14
Time (hour)
(c)
Rhodamine (µg L -1)
0
10
20
30
40
50
60
70
80
90
100
0
5
10
15
20
25
30
Time (hour)
Upstream
Downstream
OTIS Simulation

Figure 4.6



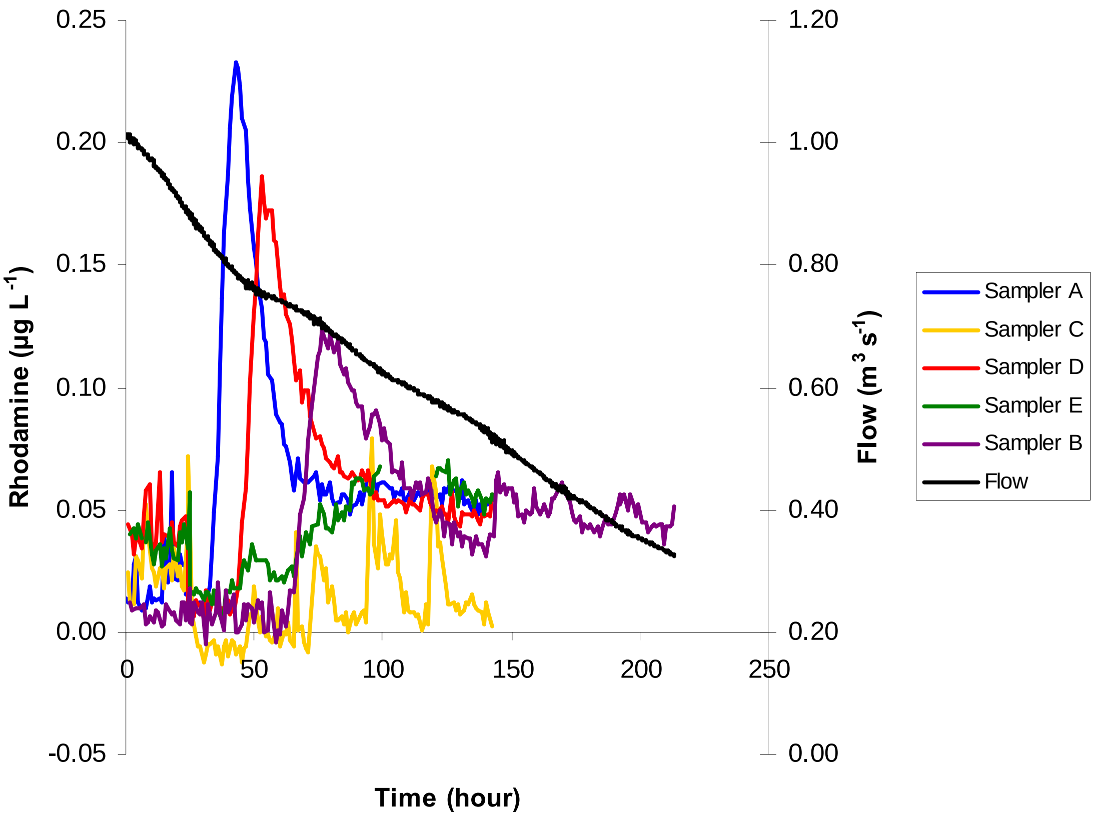
0.25
0.20
0.15
0.10
0.05
0.00
Rhodamine (μg L^{-1})
20
40
60
80
100
120
140
Time (hour)
Sampler A
Sampler D
Sampler B
Reach 1 Sim.
Reach 2 Sim.

Figure 4.7



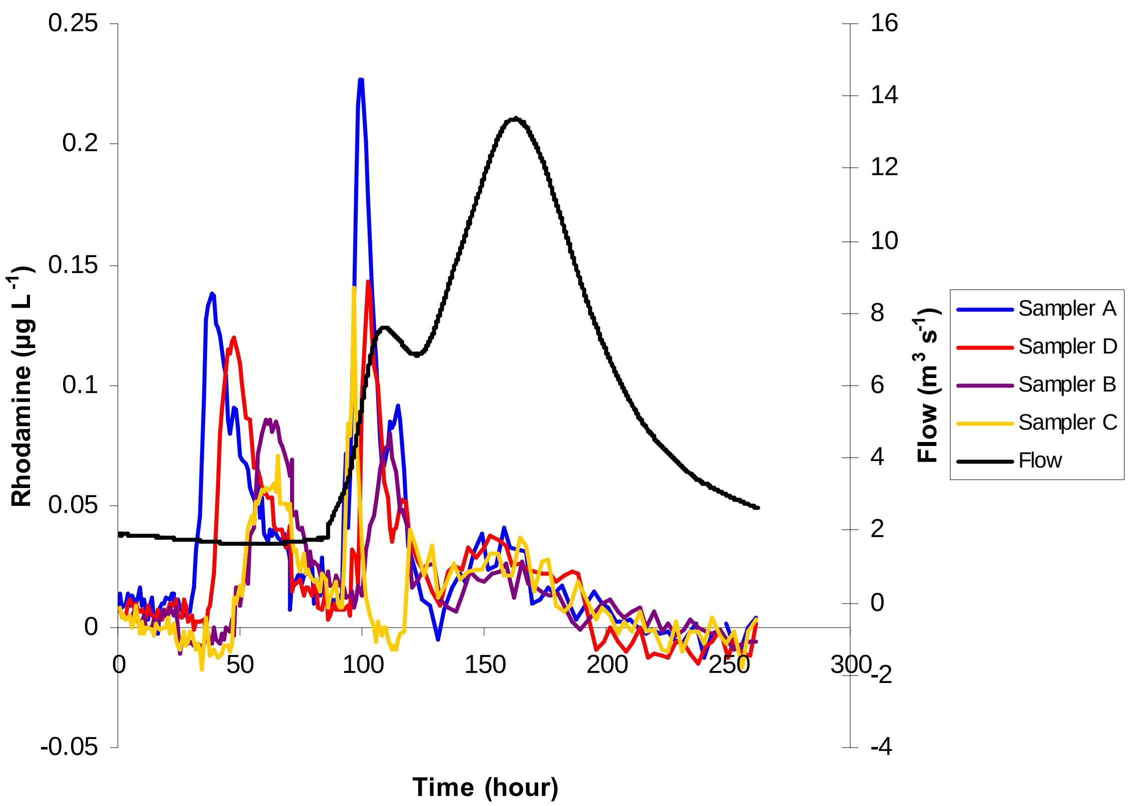
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Rhodamine (µg L -1)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Flow (m3 s-1)
0
20
40
60
80
Time (hour)
Sampler A
Sampler C
Sampler D
Sampler E
Sampler B
Flow

Figure 4.8



0.25
0.20
0.15
0.10
0.05
0.00
-0.05
Rhodamine (µg L-1)
0
50
100
150
200
250
Time (hour)
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Flow (m3 s-1)
Sampler A
Sampler C
Sampler D
Sampler E
Sampler B
Flow

Figure 4.9



0.25
0.2
0.15
0.1
0.05
0
-0.05
Rhodamine (µg L^{-1})
0
50
100
150
200
250
300
Time (hour)
16
14
12
10
8
6
4
2
0
-2
-4
Flow (m^{3} s^{-1})
Sampler A
Sampler D
Sampler B
Sampler C
Flow

Figure 4.10

CHAPTER 5

SUMMARY

DO is considered an excellent indicator of stream biological activity and the "most important of all chemical methods available for the investigation of the aquatic environment" (Joyce et al. 1985, Mitsch and Gosselink 1986). Blackwater streams of the Georgia Coastal Plain are characterized by chronic deficiencies in dissolved oxygen (DO) that frequently fall below the minimum standard of 4.0 mg L^{-1} or 24-hour average of 5.0 mg L^{-1} a condition assumed to be a consequence of increased biological activity due to nitrogen and phosphorus enrichment. As required by the Clean Water Act (CWA), those streams violating the standard are required to be brought into compliance through TMDL development, a process that usually begins with limiting nutrient addition to affected waterways. At the start of this study, 90 percent of the streams not meeting their designated uses within this region were listed due to violation of the DO standard. On the 2004 303(d), list the number of segments still listed as impaired due to violation of the DO standard made up 82 percent of all listed segments. The state has since proposed delisting segments under the premise of having "naturally low" conditions. If streams are naturally deficient in DO and below the regulatory standard even in unimpacted reaches, development, implementation, and attainment of TMDL stipulations as mandated under the CWA, would prove difficult to achieve and may needlessly waste economic resources.

The overarching goal of this dissertation was to characterize instream swamps and their effect on DO levels. To that end, the hydrology, travel time and sediment characteristics of these areas were investigated at a watershed level with the ultimate goal of furthering the understanding of DO dynamics within these areasand helping determine whether the 4 mg L^{-1} standard is appropriate and achievable. Two study areas were selected within the Little River Experimental Watershed, a watershed instrumented by the Agricultural Research Service of the United States Department of Agriculture and considered representative of the soils, topography, geography and land use within the southern Coastal Plain. These two study areas were located on a 3rd and 5th order stream to better characterize conditions on a watershed scale.

Investigation of sediment characteristics found that SOD was most strongly related with organic carbon content in the upper 5 cm and that those rates up to 18 times higher than previously published values for the southeastern Coastal Plaind and that the average rate of SOD was 7 times higher (Chapter 2). TMDL development usually uses estimated literature values for SOD. This research indicates that SOD values are many times higher and, if values had been estimated from literature values, accurate modeling of the watershed would have been difficult. Additionally, SOD was positively correlated with the initial DO concentration in the water column. These two factors suggest that instream swamps are a major sink of DO within this watershed and that even if a TMDL succeeded in elevating DO concentrations, SOD would increase as well counterbalancing those gains. In total, actual benefits by TMDL development would be minimal.

The previous study recorded point measurements of stream sediment conditions and their relationship with SOD. Chapter 3 takes the relationships established in Chapter 2 and extrapolates them to the reach and watershed scale. Through the use of geostatistics, measured soil organic carbon contents were related to SOD measurements to create reach scale measures of SOD through Simple Gaussian Simulation. Results showed that SOD at both locations was spatially correlated with the differences in the distribution of TOC likely a result of the differing hydrologic regime and watershed position. Further, results at the watershed scale showed that areas similar to those investigated are common and prevalent, with increasing magnitude in the higher order streams. These findings further support the idea that TMDL development for lowered DO levels would likely result in minimal overall water quality improvement as areas of sediment withhigh oxygen demand are widespread.

With the establishment of highly organic sediments, leading to high oxygen demand in instream swamps, the effect of hydrology was assessed through the use of hydrologic tracers (Chapter 4). Additionally, modeling was conducted through established solute transport models to estimate transport properties and specifically the magnitude of transient storage. One of the hypothesized reasons for lowered DO in these systems was the tortuous, low velocity flow pathways allowing extended contact time with highly organic sediments. Results show that flow pathways are indeed tortuous with low velocities leading to long travel times. Transient storage was shown to be a critical factor in water transport regardless of flow intensity. While velocities were low at both study locations, the larger areas of inundation and established higher SOD rates at the 5th order location would cause the lowered velocities to play a larger role on watershed DO dynamics.

The ultimate question that this dissertation attempted to address is whether the established DO standard is appropriate and achievable for blackwater streams on the southeastern Coastal Plain. DO dynamics within blackwater systems are a complicated mix of natural and anthropogenic influences, with the principle cause of lowered levels difficult to pinpoint. Nevertheless, this research shows instream swamps play a major if not dominant role on watershed DO dynamics through the presence of extensive areas of elevated SOD and long, tortuous flow pathways. Even in a watershed showing little anthropogenic impairment, DO levels were often well below the established criteria for "clean" water. All evidence in this dissertation supports the idea that these streams are naturally low in DO and that TMDLs designed to raise instream DO levels would likely see little actual improvement. Additionally, this research suggests that stream biota would be particularly vulnerable to any added anthropogenically induced increases in oxygen demand. Nevertheless, measurements such as these should be conducted in additional similar watersheds to assess the extent of these conditions and add to the body of evidence concerning DO dynamics on the southeastern Coastal Plain.

Despite the evidence of lowered DO levels, care must be taken in labeling all blackwater streams "naturally low". Within Georgia, proposals for delisting streams based on natural conditions have considered streams "naturally low" when stream DO conditions are 90% of ambient conditions. DO varies on a diel and seasonal time frame and determination of what is an "ambient" condition can be difficult to assess. Anthropogenic impairment is a very real cause of lowered DO in some stream systems and prior to delisting, extensive measurement of streams to accurately determine ambient conditions is suggested.

Additionally, incorporation of metrics of biotic integrity, tied to DO levels, could further differentiate streams naturally low in DO from impaired ones. The DO standard was established primarily as an indicator of biological health and if streams are indeed naturally low in DO, certain forms of biotic life have adapted to fit these conditions. Developing metrics that assess the presence or absence of critical biotic indicator species would add a further complement to simply listing of a stream for violation due to lowered DO.

Finally, Georgia is a large state with multiple climatic and geographic regions resulting in high variation of hydrologic conditions. Ecologically and functionally we would not expect a stream draining a mountainous watershed in the north to mimic, or have the same features, as a Coastal Plain stream in the south. Why then, are most streams expected, regardless of region, to meet the same water quality standards? While having one set of consistent standards is functionally easier to implement, not building in flexibility with regards to ecological realities makes enforcement more difficult and may require the expenditure of unnecessary funds.

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