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MODELING BIOCHEMICAL OXYGEN DEMAND THROUGH THE MIDDLE AND LOWER SAVANNAH RIVER[1]

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ABSTRACT: In order to improve modeling accuracy and general understanding of lotic biochemical oxygen demand (BOD), this study characterized river metabolism with the current Georgia Environmental Protection Division method for the middle and lower Savannah River basin (MLSRB) and several alternative methods developed with 120-day, long-term biochemical oxygen demand (LTBOD) data from the MLSRB. The data were a subset of a larger two-year LTBOD study to characterize and understand BOD in the MLSRB, located approximately between Augusta, Georgia, and Savannah, Georgia, along the border of Georgia and South Carolina. The LTBOD data included total oxygen loss and nitrogen speciation for separately quantifying nitrification. Results support the following insights and opportunities for modeling methods: (1) it is important to modeling accuracy that residuals be checked for even dispersion to avoid areas of over- and underprediction; (2) modeling with bounded, yet unfixed, rates is a sufficiently simple alternative to fixed-rate modeling that can eliminate the need for manual adjustments and provide additional system understanding to inform regulation; (3) if fixed rates modeling is desired, model quality for this system might be improved through revising the current low rate (along with the associated *f*-ratio updates) from 0.02/day rate to 0.006/day and potentially adding a new rate at 1.0/day in some cases; and (4) the current 57/43 ratio of slow/fast BOD is reasonable based on the 52/45/3 slow/fast/faster BOD proportions of this study.

(KEY TERMS: environmental impacts; environmental regulations; microbiological processes; rivers/streams; simulation; total maximum daily load; transport and fate.)

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INTRODUCTION

Based on the requirements of the Clean Water Act, a total maximum daily load (TMDL) has been developed for the middle and lower Savannah River basin (MLSRB). Part of this TMDL development was the establishment of regulatory limits for oxygen demanding substances from dischargers in the MLSRB. These limits ensure that sufficient dissolved oxygen concentrations exist in Savannah Harbor to meet numeric targets that are intended to safeguard various ecological services (USEPA, 2006). These regulatory limits, which limit municipal and industrial

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discharges to the river, are highly dependent upon river models to ensure that discharges are appropriately limited without causing either undue hardship or license. Modeling has proven to be a useful tool in characterizing and understanding natural processes. An accurate model allows practitioners to efficiently project trajectories for natural resources and respond to changes in environmental stresses. However, model accuracy is of utmost importance to this utility and the desire for answers to complex questions can sometimes lead to predictive weakness prior to sufficient model refinement. This predictive weakness can sometimes lead to conclusions and regulations that cause more harm than good. Therefore, in order to both ensure the protection of ecological services and avoid unnecessary restriction on economic development, it is imperative that these models are continuously reviewed and improved based on as much data as possible to represent the best possible understanding of river processes.

The current regulatory modeling effort for the MLSRB is comprised of the Savannah Harbor Model (a WASP derivative) (Di Toro *et al.*, 1983; Connolly and Winfield, 1984; Ambrose *et al.*, 1988) and the Savannah River Model (a CE-QUAL-RIV1) (USEPA, 2012), which interface near Clyo, Georgia, 98 km (61 miles) from the mouth of the river. This study was an assessment of the mathematical modeling methods for analyzing the biochemical oxygen demand (BOD) data that provides input to these larger-scale water-quality models. These water-quality models were used to develop waste load allocations, which are used for compliance testing by the point-source dischargers with a combination of five-day BOD tests and previously developed correlations or "*f*-ratios" that estimate a long-term biochemical oxygen demand (LTBOD) value from the five-day BOD test result.

The BOD component of the Savannah River Model was developed with a combination of long-term 120-day BOD (LTBOD) and five-day BOD data. For reference, the residence time of the river distance associated with the Savannah River Model at a 4,000 cfs discharge is about 4.5 days. This estimate is based on prior work by the authors including peak-matching of chemograph data and mean velocities from acoustic Doppler profiling conducted over 68 miles of the river. The residence time of the Savannah Harbor Model portion is 10-30 days based on a tracer study of a 1991 accidental tritium release from the Department of Energy Savannah River Site (Blanton *et al.*, 2009). A multicomponent, fixed-rate, first-order exponential equation was applied to LTBOD data in order to model the BOD transport and degradation rates from various sources to the interface at RM61 (GAEPD, 2010). The development of these fixed rates, and the associated mathematical equation they parameterize were determined through a curve fitting procedure described in the Savannah River Long-Term BOD Study by EPA Region 4 (USEPA, 2007). The basic procedure starts with either a best fit, sometimes lagged, first-order exponential model or a logistic model to nitrogenous BOD (NBOD) data estimated from nitrogen analysis. This NBOD curve is then subtracted from total BOD (TBOD) data from dissolved oxygen measurements and followed by a best fit of a dual first-order exponential model to the resulting residual in order to characterize two-component carbonaceous BOD (CBOD). The sole purpose of the NBOD analysis in the curve-fitting procedure is to determine the CBOD parameters (ultimates and *k*-rates) for the CE-QUAL-RIV1 water-quality model. The rate of the NBOD equation is allowed to be flexible during the curve fitting in the method described by USEPA (2007).

The rates of the two CBOD curves were set based on previous research and modeling considerations to 0.15/day and 0.02/day (USEPA, 2007; GAEPD, 2010). The selection of the best-fit curve was based on "judicious use of the 'eyeball' fit … and attempting to minimize the value of RMS (USEPA, 2007)." According to USEPA (2007), the use of this method produced "reasonable representation" for almost all of the data, with the exception of one river location. River model calibration was accomplished with five-day BOD data that was apportioned into slow-degrading and fast-degrading components by a fixed 20/80 ratio, respectively, and extrapolated with *f*-ratios of 1.9 for slow and 10.5 for fast to estimate the ultimate oxygen demand along the river (GAEPD, 2010). The resulting proportion for a 120-day BOD exertion (BOD_{120}) from these values would be 57/43 for slow/fast.

The modeling efforts for USEPA, Georgia Environmental Protection Division (GAEPD), and this study were based on the use of the short-term, five-day BOD and GAEPD, amplified, long-term, 120-day BOD bottle tests (GAEPD, 1989; NCDENR, 1995; APHA *et al.*, 2005). These bottle tests are meant to represent or predict metabolism of oxygen demanding substances in the river. However, closed system conditions of the bottle test differ in several ways from the open system conditions in the river including temperature fluctuations, continued carbon inputs, elimination or dilution of limiting metabolic products, additional pH buffering or pH fluctuations/alterations, turbulence, replenished nutrient sources, and changing biological assemblages (i.e., patch dynamics) (Pringle *et al.*, 1988).

The common assumption of a first-order exponential model (Volkmar and Dahlgren, 2006; Sullivan *et al.*, 2010) is likely an imperfect estimate of the theoretical substrate decomposition dynamic, which is generally accepted to be Monod kinetics for microbial growth and maintenance metabolisms (Gates *et al.*, 1969). However, Monod models, especially those that include growth, are typically based on an intact substrate and low minimal microbial population at time zero. A more realistic representation of the river is probably a truncation of Monod as sampling at any point in the river is not a time-zero condition relative to substrate or microbes. Even in the case of industrial discharges or wastewater discharges, initial treatment usually occurs in ponds or other processes that prime the kinetics before the substrate reaches the river and enters the modeling effort. To further the complexity, these initial treatment systems are subject to seasonal bacterial dynamics as they are open to the atmosphere. Based on these factors, some form of exponential may be a valid alternative to the much more complex Monod model for modeling in-river BOD processing. This validity is supported by the exponential and stationary phases following a lag phase as described by Madigan and Martinko (2006). However, in the experience of the authors, a standard first-order exponential often proves inadequate to describe experimental BOD data from river samples adequately. One possible alternative to the standard first-order exponential is to remove the first- or zero-order limitation of the exponential model and instead allow for a mixed-order model as proposed by Borsuk and Stow (2000). One of the procedures tested in this study is based on that approach. Another alternative, used by Sullivan *et al.* (2010) involves the use of both a first-order exponential and a zero-order decay rate; however, over a 120-day period, this type of model is almost indistinguishable mathematically from a dual first-order exponential with one very low *k*-rate (<0.005/day). In another study, Cao and Alaerts (1996) favored the first-order model for moderately polluted systems whereas the zero-order was more applicable for sewers and drains.

In addition to the type of equation used for the model, the strict division of CBOD at all river locations into exactly two components, especially with set rates, is quite restrictive to data fitting, and can potentially propagate incorrect assumptions through data while masking longitudinal or temporal variations. It is also contrary to the patch dynamics paradigm where new substrates or environmental conditions may give rise to completely new rates. In some cases, new substrates may be readily degradable or catalytic to existing substrates (Hee *et al.*, 2001) and river temperature fluctuations are possible, especially downstream of reservoirs, as is the case for the Savannah River. Although averaging rates or rate groups may be necessary at some point to enter assumptions into large-scale models, it may be better to apply this averaging postfit rather than prefit. This opportunity for improvement in modeling was exemplified by the large variation in first-order model coefficients and incomplete modeling of several portions of the curve even for the same wastewater source (Mason *et al.*, 2006). Mason *et al.* (2006) also found that a dual, first-order exponential model had a fit to the data that was superior to a mixed-order model, but was still not completely capable of accurately representing the complex kinetics involved.

Therefore, it was desirable to investigate improved modeling methodologies to enhance the accuracy of mathematical descriptions for BOD processing. A purely theoretical approach based upon fingerprinting the kinetics of individual substrates followed by summation of these components was initially compelling. However, the potentially enormous number of unique substrates (Wei and Kuo, 1969), dynamic nature of these substrates and their various metabolites (Madigan and Martinko, 2006), and complex interactions when they are metabolized concurrently (Hee *et al.*, 2001) made this type of analysis prohibitively complicated. In contrast, a single BOD curve fit with a single averaged rate may have been an oversimplification that limits the ability of regulatory efforts to capture the complexities of the system. A typical compromise between these methods is the substrate-lumping approach (Wei and Kuo, 1969; Li *et al.*, 1996). The current USEPA method for the MLSRB is arguably a form of substrate lumping; however, the restrictions on rate and use of manual adjustments could impose external assumptions of substrate lumping on the data that may not have statistical significance for that particular dataset. An alternative approach was based loosely on the study by Mason *et al.* (2006) but goes further. This approach used a statistical selection process to characterize a particular dataset with an undetermined number of lumps and no set rates. Each additional lump had to be statistically justified based on (1) the statistical difference in the rates from the rates of other lumps and (2) the absolute significance of the ultimate BOD of that lump above the analytical limit of the instrument. One potential advantage to characterizing CBOD in this manner was that particular samples could be compared against one another in order to characterize longitudinal changes in BOD processing. This dynamic processing of BOD is more consistent with the patch dynamics framework (Pringle *et al.*, 1988).

Aside from CBOD modeling, NBOD in the current BOD curve-fitting process is estimated based on a single-stage assumption that attributes 4.57 mg-O/mg-N for incremental increases in nitrate-N. Depending on river conditions, this assumption may unnecessarily oversimplify the much more nuanced two-stage nitrification process, which includes a 3.43-mg-O/mg-N nitritation stage followed by a 1.14-mg-O/mg-N nitritation stage (Chapra, 1997; Fang *et al.*, 2009). Nitrite data are often available to improve the NBOD estimate, and because the NBOD is the initial subtraction from the model, it could also improve the CBOD curve fit as any shortcomings in the NBOD estimation may create artifacts in the CBOD characterization. However, as most laboratory bottle tests are conducted at 20°C where the nitrification process is limited by ammonium-oxidizing bacteria and large nitrite accumulations are not predicted, this factor may be limited in LTBOD data (Hellinga *et al.*, 1998).

Detailed laboratory studies of the nitrification process revealed insights into whether a first-order exponential model accurately depicted this process. Studies by Moussa *et al.* (2005) and Fang *et al.* (2009) both produced oxygen-use rate curves that resembled the first derivative of the first-order exponential curve more accurately at lower initial concentrations (Figure 1A) than at higher initial concentrations (Figure 1C). Higher initial concentrations displayed a sustained initial rate followed by a rapid rate decrease. The period of sustained rate was consistent with the zero-order NBOD kinetics reported by Wong-Chong and Loehr (1975). Approximate integration of the oxygen-use rate curves of Fang *et al.* (2009) (Figures 1B and 1D) produced NBOD data where the first-order exponential model overestimated or underestimated in certain regions. With even higher concentrations than those shown in Figure 1, the estimated NBOD curve began to resemble a logistic function more closely. This tendency may become important for modeling BOD in industrial discharge samples with higher initial ammonium concentrations.

However, it was important to recognize two factors separating the batch experiment studies of Moussa *et al.* (2005) and Fang *et al.* (2009) from river samples. First, the lowest initial ammonium concentrations in Fang *et al.* (2009) (Figure 1) were still quite high compared with typical river concentrations (18-150 *vs.* <1.0 mg-N/l), and the plotted rate and integral for the lowest ammonium concentration (Figures 1A and 1B) indicated that, at lower concentrations of ammonium, NBOD approached the first-order model. Secondly, in these studies, there was plenty of inorganic ammonium-N available initially, so the NBOD kinetics could only be limited by ammonium or nitrite oxidation. By contrast, river samples often

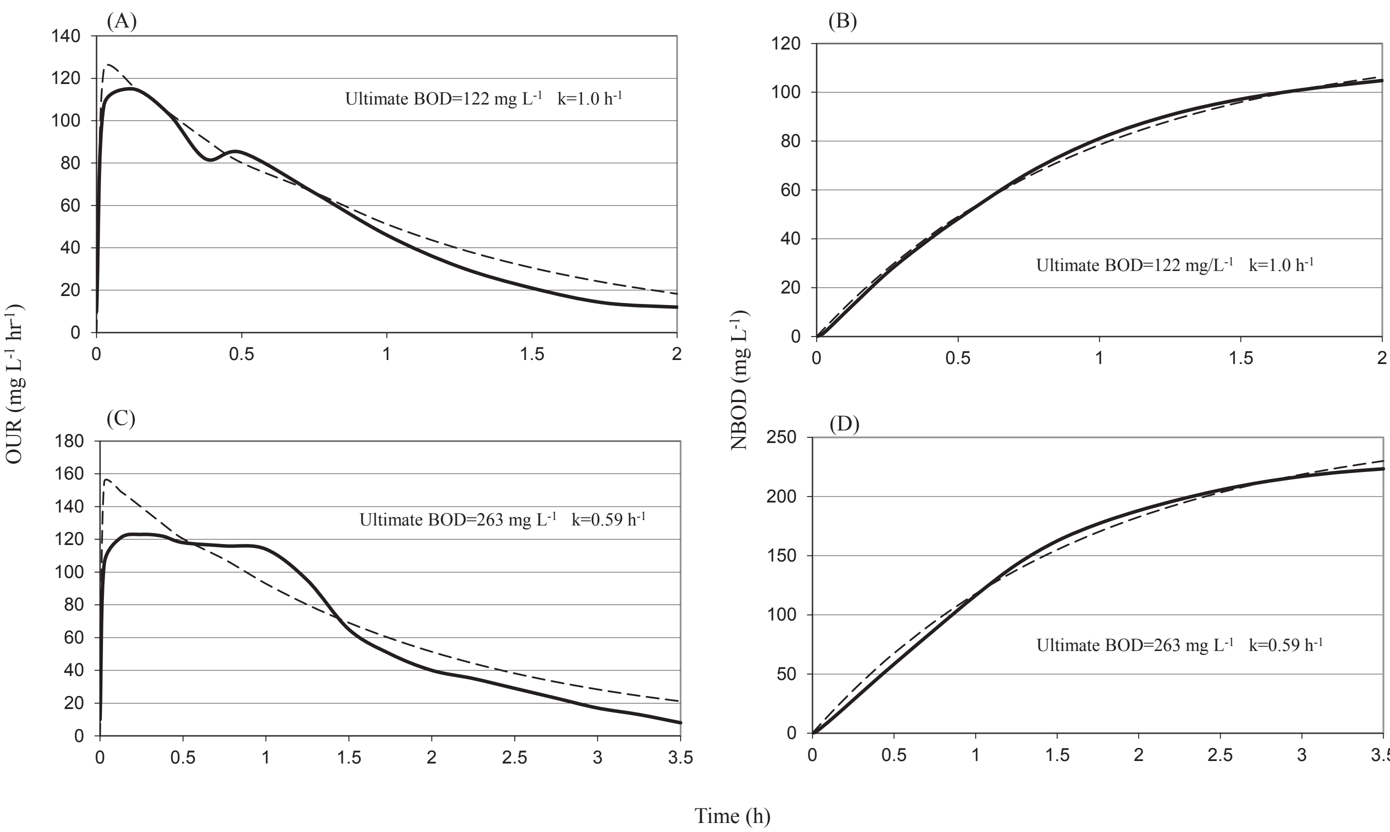

FIGURE 1. Oxygen Utilization Rates (OUR) (solid lines) Shown with the First Derivative of the First-Order Exponential (dashed line) for (A) 18.8 mg-N/l Initial Ammonium and (C) 44.5 mg-N/l Initial Ammonium. NBOD estimates are based on integration of the OUR data and are shown with first-order exponential curves for (B) 18.8 mg-N/l initial ammonium and (D) 44.5 mg-N/l initial ammonium (Adapted from Fang *et al.*, 2009).

have low or negligible initial ammonium concentrations compared with organic-N and NBOD could be limited by ammonium availability. Although uninhibited nitrogen processing should be limited by nitritation before ammonification (Wong-Chong and Loehr, 1975; Kadlec and Wallace, 2009), it is possible with sufficiently high C:N ratios that ammonium availability for nitrification can be limited due to competitive uptake by heterotrophic microbes (Strauss and Lamberti, 2000). This competition for ammonium by CBOD processes could be responsible for slowing NBOD expression in the river and could potentially create extreme complexity in NBOD kinetics as the growth of heterotrophic microbes, the C:N ratio, and the labile-to-refractory carbon ratio vary interactively. A limitation in ammonium availability for nitrification was also consistent with the initial lag-phase seen in many NBOD-modeling examples (Chapra, 1997) where CBOD processing of the most labile organic carbon may take place prior to sufficient availability of ammonium for nitrification. However, this lag had several other possible explanations including analytical and sampling effects. In this study, the above factors (nitrite buildup, ammonium availability, and model fit) were evaluated in the context of the overall modeling process.

This study evaluated the current standard method for amplified LTBOD used by USEPA Region 4 and GAEPD to characterized BOD for TMDL modeling against several alternative methods. The goal was to seek to improve upon the ability to model the transport and degradation of oxygen-consuming substances. Study objectives were: (1) to determine whether, given the conditions observed in the MLSRB, a first-order NBOD and dual first-order CBOD model with fixed rates is the best available set of model components; (2) to determine from four possible modeling alternatives whether there is a sufficiently simple alternative method that can more accurately partition and characterize oxygen demand in river samples; (3) to determine whether the single-stage NBOD assumption is valid compared with a more thorough two-stage estimate; and (4) to investigate whether the multiple first-order model can characterize patch dynamics in the river by describing longitudinal rate changes in river metabolism.

MATERIALS AND METHODS

Study Site

The data used in this study to evaluate the various modeling methodologies came from a larger LTBOD analysis project conducted by Southeastern Natural Sciences Academy, Augusta, Georgia, during 2009-2010. The overall LTBOD data collected included nine mainstem river stations and two tributaries (Figure 2), industrial effluents, and municipal wastewater effluents. This study utilized data from four of the mainstem river stations (Table 1) including a cold weather (March 2010) and a warm weather (August 2009) sample for each mainstem river station. The March 2010 sample followed an approximately three-month-long period of unusually high flow that was sufficient to inundate the flood plain. The August 2009 sample was taken in the middle of an approximately three-month-long, low-flow period. This study also utilized two contributing tributary samples from the overall dataset, which were taken in March 2009 (Butler Creek) and June 2009 (Brier Creek).

Sample Collection and Analysis Procedures

All samples were collected in 20-l bottles submerged mid-stream in the top meter of the water column. Samples were either processed immediately or preserved below 4°C until processing. Entire samples were homogenized in a 25-l churn splitter and split into a 2-l BOD bottle and a 1-l reservoir for each sample. Both bottle and reservoir were then incubated at 20°C in the dark for 120 days, based on the accepted regulatory protocol. Samples were reaerated every time the dissolved oxygen concentration fell below 4 mg/l by splitting the sample (BOD bottle and reservoir) into two BOD bottles, shaking each bottle approximately 50 times, and returning the sample to the original bottle and reservoir. LTBOD analysis was conducted in accordance with the specific requirements of the 120-day, Amplified Long-Term BOD Test (GAEPD, 1989). This test involved the collection of two distinct datasets including changes in dissolved oxygen used for TBOD, and changes in oxidized nitrogen species (NO_x) used to estimate NBOD. The test required a specific schedule for both dissolved oxygen measurements (YSI 5010 BOD Probe; Yellow Springs, Ohio) and subsampling for nitrogen species analysis (SEAL AQ2 + Discrete Analyzer; Mequon, Wisconsin). Ammonium (EPA-103-A Rev. 5), nitrite (EPA-115-A Rev. 3), and nitrate/nitrite (EPA-114-A Rev. 6) were independently measured throughout the analysis for each subsample and total Kjeldahl nitrogen (TKN) (EPA-110-A Rev. 4) was analyzed at the beginning (Day 0) and end (Day 120) of each sample's analysis period with a separate subsample. Ammonium, nitrite, and nitrate/nitrite analysis of subsamples occurred either immediately or within two days of storage below 4°C in capped, glass vials. TKN analysis occurred within two months of

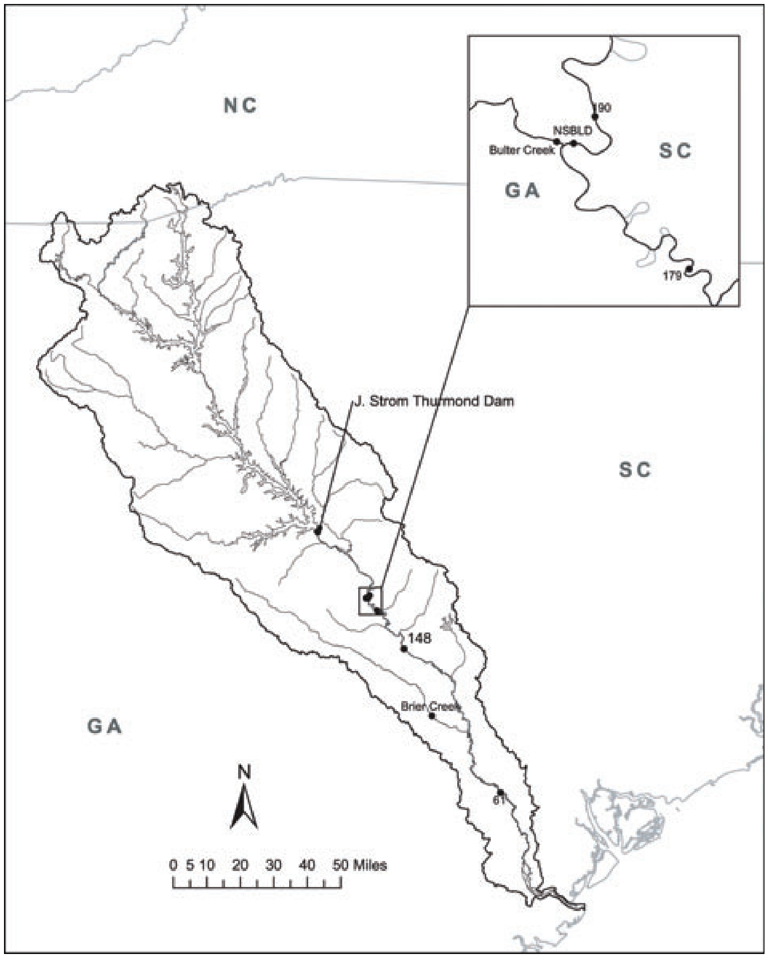

FIGURE 2. Map of All Sampling Sites in SNSA LTBOD Study (2009-2010) Identified by River Miles from the Mouth of the River (e.g., RM190).

TABLE 1. The 120-Day BOD Analysis Samples Were Used for Model Development in This Study.

Mainstem Sampling Sites	**Description**
River Mile 190 (306 km)	Contributions from reservoir, urban streams, industry, small WWTPs (<100 l/s)
River Mile 179 (288 km)	Additional contributions from urban streams (Butler), industry, large WWTP (1,100 l/s)
River Mile 148 (238 km)	Additional contributions from blackwater creeks, groundwater
River Mile 61 (98 km)	Additional contributions from blackwater creeks (Brier), groundwater, industry
Contributing influents	
Butler Creek	Urban watershed and large WWTP (1,100 l/s)
Brier Creek	Rural/agricultural/wetland watershed and small WWTPs

Notes: WWTP, wastewater treatment plant. Descriptions provide a general idea of the potential land use factors influencing each additional reach. River miles are measured from the mouth of the Savannah River at Savannah, Georgia.

storage below 4°C, acidified with 4N sulfuric acid, and in capped, plastic containers.

Evaluation of nitrogen data also included: (1) nitrite occurrence across all samples regarding potential for two-stage estimation, (2) ammonium:TKN ratio, and (3) goodness of fit for a first-order exponential model (Table 2). An example case (Figure 3) revealed an initial spike in nitrite and lag in the production of nitrate, indicating that lumping nitrification into one 4.57 mg-O/mg-N phase may result in slight overestimation of NBOD during the first 10 days and slight underestimation of NBOD during the second 10 days. Although application of a best-fit curve should dampen most of this estimation error, there could be some tendency with a first-order exponential to model an inaccurate k-rate with the single-stage estimation. An NBOD

TABLE 2. A Summary Is Given of Nitrogen Speciation During the LTBOD Analysis.

	% of Nitrite Samples						
River Sampling Sites	**0.00-0.02**	**0.02-0.04**	**0.04-0.06**	**0.06-0.10**	**Initial NO_3**	**Final NO_3**	**Initial NH_4:TKN**
River Mile 190 Summer	16	0	0	3	0.29	0.45	0.10
River Mile 179 Summer	6	3	6	0	0.30	0.49	0.10
River Mile 148 Summer	16	0	0	0	0.28	0.52	0.00
River Mile 61 Summer	6	6	0	0	0.31	0.48	0.09
River Mile 190 Winter	21	11	4	4	0.27	0.57	0.22
River Mile 179 Winter	33	4	7	0	0.34	0.59	0.23
River Mile 148 Winter	26	4	4	4	0.31	0.61	1.00
River Mile 61 Winter	16	8	0	4	0.26	0.64	0.00

Notes: Columns 2-5 provide the percentage of samples during the run that fell in the given range, indicating a potential buildup of nitrite. Subtraction of Columns 7 and 8 provides an assessment of total nitrification during the 120-day test.

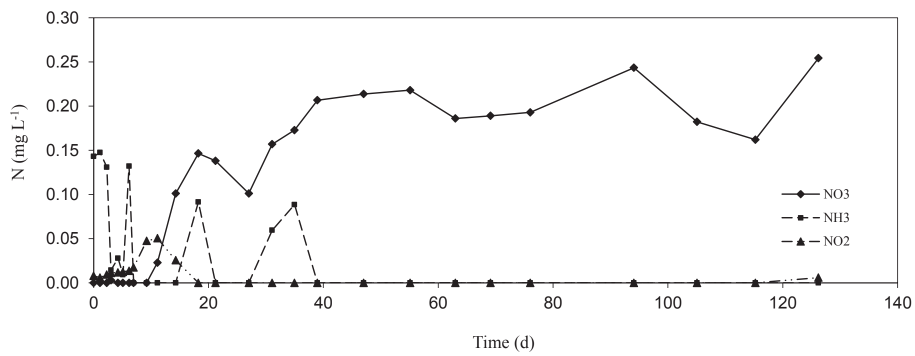

FIGURE 3. Nitrogen Data for River Mile 179 During Winter, Which Represented a "Worst Case" for Nitrite Accumulation Among All the Included Sites (NO_3 data shown is $NO_3[t]$-$NO_3[0]$).

fingerprinting test within this study involved spiking two river samples that had already completed a 120-day LTBOD incubation period with ammonium in order to isolate the NBOD curve resulting from the introduction of ammonium specifically. This was performed in order to compare this fingerprinted NBOD curve with the NBOD curves produced for river samples.

Curve-Fit Methods

The measures described above were used to compare the following alternative curve-fit methods (Table 3) for TBOD in river samples: (1) current method as described by GAEPD (2010) and USEPA (2007), (2) current method with two-stage NBOD estimation procedure, (3) single mixed-order curve-fit for BOD, (4) two-stage NBOD estimation together with multiple first-order curve-fit for CBOD by forward selection based on the statistical significance of model parameters, and (5) two-stage NBOD estimation together with rate-bracketed first-order curve-fit for CBOD by backward selection based on statistical significance.

Methods 1 and 2 followed the exact procedure described above as the USEPA (2007) process with two exceptions. First, for both methods, the least-squares solution was used with no manual corrections. Second, for Method 1, NBOD was estimated based on a single-stage NBOD equation (Equation 5) *vs.* the two-stage process of Method 2 (Equations 1-4). In both cases, NBOD parameters were estimated first and then included as fixed parameters in the TBOD model that was used to determine CBOD parameters.

$$NO_{2,\text{oxidized}} = \Delta NO_3 \quad (1)$$

$$NH_{4,\text{oxidized}} - NO_{2,\text{oxidized}} = \Delta NO_2 \quad (2)$$

$$NH_{4,\text{oxidized}} = \Delta NO_2 + \Delta NO_3 = \Delta NO_x \quad (3)$$

$$NBOD_{\text{two-stage}} = 3.43 \times \Delta NO_x + 1.14 \times \Delta NO_3 \quad (4)$$

$$NBOD_{\text{single-stage}} = 4.57 \times \Delta NO_x \quad (5)$$

For Method 3, TBOD was modeled based on the mixed-order model (Equation 6) developed by Borsuk and Stow (2000)

TABLE 3. A Summary Is Given of the Alternative Curve-Fit Methods Evaluated in This Study Including the NBOD Approach, CBOD Approach, and Appropriate References for Each Method.

Method	NBOD	CBOD	Reference
1	One-stage, lagged, first-order exponential	Dual, nonlagged, first-order exponential, fixed rates	USEPA (2007)
2	Two-stage, lagged, first-order exponential	Dual, nonlagged, first-order exponential, fixed rates	USEPA (2007); Fang *et al.* (2009)
3	TBOD estimated from single, mixed-order curve		Borsuk and Stow (2000)
4	Two-stage, lagged, first-order exponential	Statistically determined number of rate groups, nonlagged, unfixed rates	Mason *et al.* (2006)
5	Two-stage, lagged, first-order exponential	Statistically determined number of rate groups (max 3), nonlagged, binned, and unfixed rates	Mason *et al.* (2006)

$$\mathrm{BOD} = \mathrm{BOD_{ult}} - \left\{\mathrm{BOD_{ult}^{1-n}} - k_m \times t \times (1-n)\right\}^{\frac{1}{1-n}}, \tag{6}$$

where n is the "pseudo-order" parameter and k_n is a rate constant with units of $(\mathrm{mg/l})^{(1-n)}/\mathrm{day}$. In this analysis, n was set at 2 (Method 3a) and then 6 (the highest order that would converge for any sample, Method 3b). All samples converged for an n value of 2, but 2 of the 10 samples did not converge (DNC) for an n value of 6.

Method 4 modeled BOD with an initially undetermined number of lagged or unlagged first-order curves (Equation 7) developed based on forward selection and retained as long as each successive curve displayed the following: (1) convergence of the nonlinear least-squares curve-fit algorithm, (2) dissimilar rate coefficients based on a 70% confidence interval for each rate parameter, and (3) $\mathrm{BOD}_{\mathrm{ult},n}$ values >0.2 mg/l (based on limitation of the analytical instrument) at a 70% confidence interval. This method was performed both with and without including NBOD based on a lagged or unlagged, first-order exponential curve based on the two-stage estimate (Equation 5).

$$\mathrm{BOD} = \mathrm{BOD_{ult,n}} \times \left(1 - \mathrm{e}^{-k_n t - T}\right) + \mathrm{BOD_{ult,n+1}} \times \left(1 - \mathrm{e}^{-k_{n+1} t - T}\right) + \ldots \tag{7}$$

Method 5 modeled BOD as in Method 4 (Equation 7) after the two-stage NBOD curve was initially subtracted. However, in divergence with Method 4, there was a maximum of three first-order curves and the three initial rates were bracketed in adjoining bins (0.005-0.05/day, 0.05-0.5/day, 0.5-1.0/day). Each of the resulting three curves were retained as long as the entire model displayed the following: (1) convergence of the nonlinear least-squares curve-fit algorithm, (2) dissimilar rate coefficients based on a 70% confidence interval for each rate parameter, and (3) $\mathrm{BOD}_{\mathrm{ult},n}$ values >0.2 mg/l at a 70% confidence interval. If the initial three-component CBOD model did not meet these criteria, the component with the worst fit was removed and the process was repeated. The reasoning for the lower bound of 0.005/day was that, with increasingly lower rates, the relative portion of the curve's predicted BOD exertion that was within the 120-day test was increasingly smaller. The 0.005/day value was chosen because it represented just >50% of the predicted BOD being expressed within the 120-day data window (Figure 4). The reasoning for the upper bound of 1.0/day was the converse. With an increasing rate, the majority of the BOD exertion occurred over such a short time period that only a few data points were available to model it. The 1.0/day value was chosen so that a minimum of three data points were relevant for model development with daily measurements.

Modeling was performed with methods from the R-Project (R Development Core Team, 2005), specifically the nonlinear least-squares regression analysis along with the accompanying confidence interval method.

Temperature Correction

One of the known limitations of the bottle test in predicting *in situ* BOD dynamics was the fixed incubation temperature of 20°C. Although this approach has benefits for standardization and comparison, it may not completely represent the dynamic of a much colder or much warmer river. In this study, a modified Arrhenius Equation (8) was used as postprocessing on Method 5 results to explore possible variations in BOD rates and totals:

$$k_{\mathrm{adjusted}} = k_{\mathrm{unadjusted}} \times 1.407^{(T-20)}, \tag{8}$$

where T is given in units of °C. The T value used for each mainstem river sample was based on a weighted average of typical temperatures seen along the river

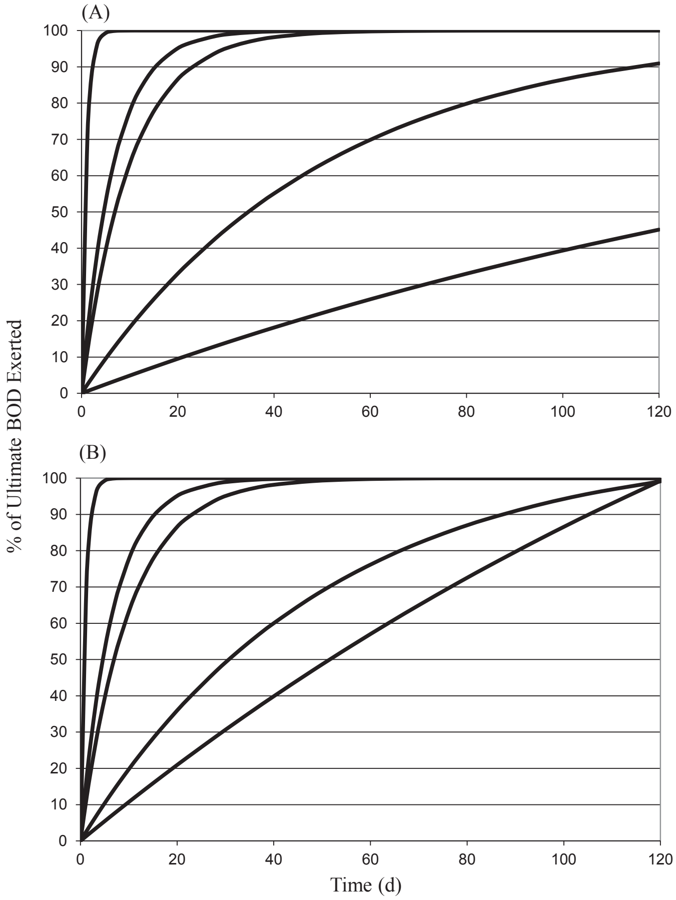

FIGURE 4. Example Rates from Bottom to Top (0.005/day, 0.02/day, 0.10/day, 0.15/day, 1.0/day, and 2.0/day) Showing (A) Percent of a Common BOD_{ult} Exerted Over Time and (B) Percent of a Common BOD_{120} Exerted Over Time.

starting at each sampling site in the month when the sample was taken. For instance, T for the RM190S sample was a weighted average of typical temperatures observed from RM190 to the mouth of the river for the days the sample was collected. Weighting factors were based on the distances between river locations with temperature data available. Summer T values used for RM190, RM179, RM148, and RM61 were 26.8, 27.0, 27.2, and 28.1°C, respectively. Winter T values used for RM190, RM179, RM148, and RM61 were 14.2, 14.2, 14.3, and 14.6°C, respectively. T values used for tributary samples were the T values of the appropriate season for the river mile they were closest to when reaching the river.

Measures of Modeling Quality

Two measures of modeling quality were used to evaluate all methods in this study: (1) the root mean square (RMS) error and (2) dispersion of model residuals. The RMS is minimized during a statistical best-fit procedure and RMS was used in this study as a measure of the overall ability of the model to represent the data. The RMS error value represents a "typical" error between the actual measured value and the model predicted value. As RMS values are not normalized, they must be referenced to the magnitude of data values for a particular sample in order to compare between samples. However, values should be compared directly between different modeling efforts for the same sample. The second measure of modeling quality was a graphical analysis of the model residuals (observed values minus model-predicted values), where an ideal model fit has residuals that are evenly dispersed around the horizontal line $y = 0$ (BOD) and dispersed equidistantly from that line at all points along the x-axis (time).

Residual distributions with varying dispersion distance at various points along the x-axis (Figure 5A) revealed an unequal variance in the data throughout the 120-day incubation for that sample. This condition may be partially attributed to the sampling protocol, which includes more frequent sampling toward the beginning of the 120-day test, thereby increasing the potential for a larger spread in that portion of the data. In situations where this condition is pervasive, it may be desirable to use a weighted least-squares approach with lower variability portions of the curve weighted more heavily. Residuals that also displayed uneven dispersion around $y = 0$ (Figure 5B) indicated the existence of remaining trends in the data that were not captured by the model (underparameterized model). In the example case given, residual dispersion indicated a tendency to overpredict BOD between Day 20 and Day 80 whereas underpredicting BOD prior to Day 20 and after Day 80 (Figure 5D).

RESULTS AND DISCUSSION

Measures of Modeling Quality

Average RMS error decreased from Method 1 to Method 5 with Method 1 displaying the highest RMS error values (Table 4). However, a typical residual of 0.1-0.4 mg/l must be kept in perspective with BOD_{120} values of 3.0-10.0 mg/l and with an instrument error of 0.1 mg/l. Residual analysis showed a similar trend with increasing numbers of samples displaying ideal residuals from Method 1 to Method 5 and the increase was more pronounced. In Method 1, only one of the samples exhibited ideal residuals whereas seven of the samples displayed ideal residuals with

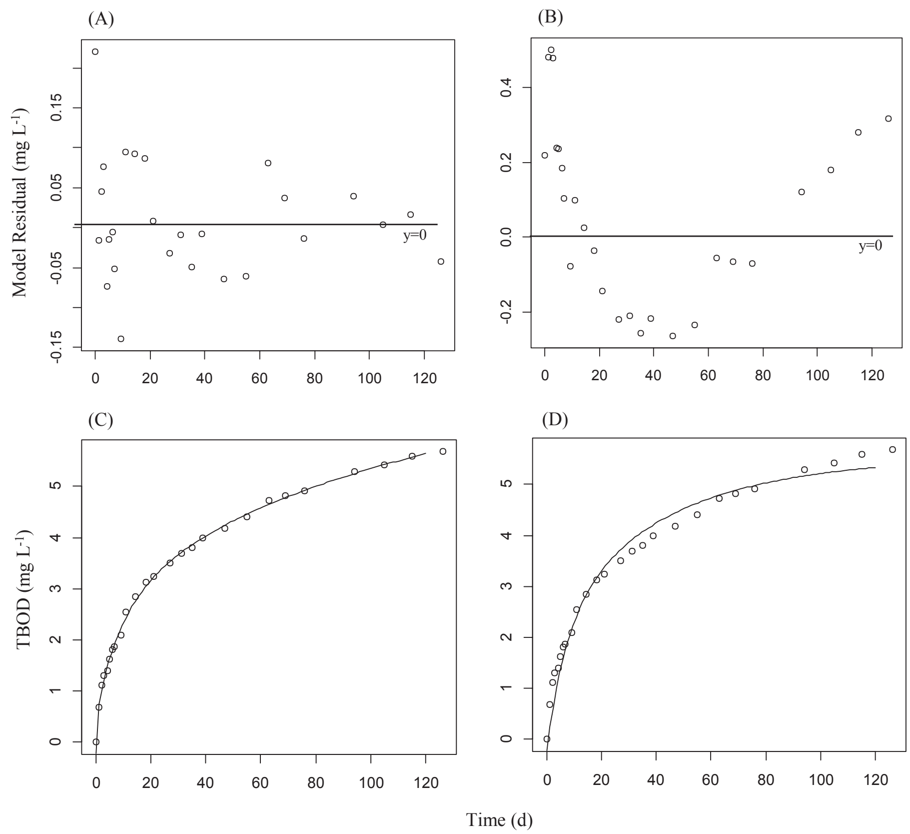

FIGURE 5. Two-Model Residual Plot Examples Including One with Ideal Residual Except for Unequal Variance (A) and One That Clearly Indicates a Remaining Trend Not Captured in the Model (B) Along with the Fit of a First-Order Exponential Model to the Example with Unequal Variances (C) and with Remaining Trend (D).

TABLE 4. RMS Values and Evaluation of Residual Distributions Are Provided for Each Method Evaluated Including Some That Did Not Converge (DNC).

Sampling Sites	Method 1 Overall	Methods 1/2 NBOD	Method 3a Overall	Method 3b Overall	Method 4a Overall	Method 4b Overall	Method 5 Overall
River Mile 190 Summer RMS	0.09	0.11/0.12	0.08	0.08	0.09	0.09	0.08
River Mile 179 Summer RMS	0.09	0.12/0.11	0.11	0.08	0.07	0.08	0.07
River Mile 148 Summer RMS	0.07	0.12/0.12	0.06	0.06	0.10	0.05	0.05
River Mile 61 Summer RMS	0.09	0.12/0.12	0.09	0.06	0.05	0.07	0.05
River Mile 190 Winter RMS	0.12	0.15/0.15	0.14	0.09	0.06	0.05	0.06
River Mile 179 Winter RMS	0.25	0.12/0.12	0.22	0.12	0.06	0.05	0.05
River Mile 148 Winter RMS	0.18	0.12/0.12	0.13	0.08	0.07	0.06	0.07
River Mile 61 Winter RMS	0.31	0.16/0.12	0.26	0.17	0.05	0.16	0.06
Butler Creek RMS	0.15	0.92/0.92	0.07	DNC	0.06	0.06	0.06
Brier Creek RMS	0.39	0.12/0.12	0.16	DNC	0.05	0.05	0.05
Average RMS	0.17	0.21/0.21	0.13	0.09	0.07	0.07	0.06
Displayed ideal residuals	1	7/7	1	5	5	6	7
Ideal residuals except unequal variance	1	10/10	1	5	8	8	10

Note: Instrument error for the dissolved oxygen probe used in the test was 0.1 mg/l.

Method 5. Furthermore, the only unevenness in residual dispersion observed for Method 5 was unequal variance.

Overall, Method 5 had the highest measures of modeling quality for RMS error and residual dispersion, performed adequately in terms of convergence with available numerical methods, and enabled partitioning of BOD between different rates in order to characterize patch dynamics (compared with Method 3). The Method 5 limitation of three rate groups was consistent with Method 4 results, which provided no more than three statistically justified rate groups for any sample. Therefore, the best performing method in measures of modeling quality (Method 5) also captures as much or more rate information as any other method. Therefore, the results for Method 5 are presented below in contrast to Method 1 results (current regulatory methodology for the MLSRB) to compare BOD rates and proportions.

Nitrogenous Biochemical Oxygen Demand Estimation

Results from Methods 1 and 2 suggested that there were no significant differences in model parameters between the single-stage and the two-stage NBOD estimates of these two methods. Both in the case of *k*-rates (Figure 6; Table 5) and estimated lag times, the 70% confidence range of model parameters far overshadowed any difference in the estimates between methods. This wide confidence range also reveals the potential for artifacts in CBOD parameters caused by uncertainty in the NBOD curve fit. NBOD rate results generally fell somewhere between Method 1

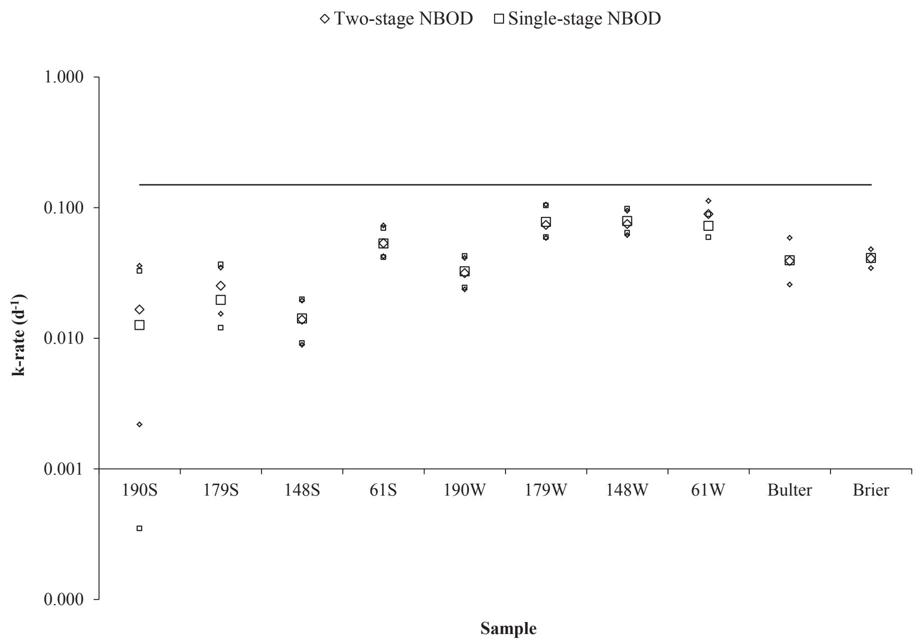

FIGURE 6. NBOD Estimates from Methods 1 and 2, 70% Confidence Intervals for Those Rates (smaller icons of the same type). The ammonium-NBOD rate from the fingerprinting test (0.31/day) is shown with a solid line.

TABLE 5. *k*-Rate Values for Each Method Evaluated.

Sampling Sites	Methods 1/2 NBOD	Method 3a BOD	Method 3b BOD	Method 4b CBOD1	Method 4b CBOD2	Method 4b CBOD3	Method 5 CBOD1	Method 5 CBOD2	Method 5 CBOD3
River Mile 190 Summer	0.013/0.017	3.8E-3	7.6E-8	0.021	-	-	0.005	0.06	-
River Mile 179 Summer	0.020/0.025	6.6E-3	9.8E-8	0.007	0.085	-	0.005	0.10	-
River Mile 148 Summer	0.014/0.014	6.3E-3	1.4E-7	0.003	0.059	-	0.005	0.07	-
River Mile 61 Summer	0.053/0.053	8.8E-3	2.6E-7	0.010	0.095	-	0.006	0.14	-
River Mile 190 Winter	0.033/0.032	9.7E-3	6.5E-7	0.007	0.125	-	0.005	0.16	-
River Mile 179 Winter	0.078/0.074	9.9E-3	2.3E-7	0.011	0.113	1.62	0.008	0.20	1.00
River Mile 148 Winter	0.079/0.075	5.8E-3	6.1E-8	0.010	0.109	-	0.006	0.19	-
River Mile 61 Winter	0.073/0.089	7.4E-3	5.5E-8	0.029	-	0.68	0.005	0.14	1.00
Butler Creek	0.040/0.039	1.4E-3	DNC	0.019	0.153	-	0.014	0.26	-
Brier Creek	0.041/0.041	6.7E-4	DNC	0.006	0.086	-	0.005	0.10	-

Note: Method 1 is omitted here as the rates are set at 0.15/day and 0.02/day, and Method 4 with separate NBOD is omitted due to its close similarity to Method 5.

"fast" and "slow" rates and indicated that NBOD rates may experience large variation. These rates were significantly lower than for the ammonium NBOD fingerprinting test (average of 0.31/day). Compared with values given in GAEPD (2010), the NBOD fingerprinting test result was close to the 0.30/day nitrification rate whereas the sample NBOD rates were closer to the 0.05/day ammonification rate. Lag times for river samples fell between 0 and 19 days with an average value of 6.0 days and a typical 70% confidence interval of ±2.0 days. The average lag for NBOD in the ammonium spike bottles was 5.4 days. Even though there was more theoretical basis for an exponential equation on river samples, a logistic NBOD equation was applied to a few samples. This equation produced RMS values and BOD parameters that were similar to those produced with the first-order exponential equation. Observation of lower rates in river samples than in the ammonia fingerprinting test supports the hypothesis that NBOD in the river may be rate limited, potentially by the availability of ammonium to nitrifiers. This limited availability would likely be caused, at least in part, by competition from heterotrophic microbes for available ammonium in areas of high C:N ratio (Strauss and Lamberti, 2000), an example of a patch dynamic.

A reasonable possibility exists that the lag was an artifact of either the LTBOD bottle test procedure not accurately representing the river or a difficulty in measuring small changes in concentration early in the test with colorimetric nitrogen analysis. However, observed lags on undiluted industrial samples, with initial ammonium concentrations higher than river samples (results not shown), weighs against a nitrogen analysis explanation of the lag as these higher concentrations can be measured with more reliability. Given the tendency of nitrifying bacteria to associate most successfully with sediments or other structure (Diab and Shilo, 1988; Pauer and Aeur, 2000; Fisher and Pusch, 2001), it is also possible that the lag was an artifact of sampling. After samples were extracted from the water column, the amount of accessible surface area already colonized with nitrifiers may have been significantly decreased relative to such surface area in the river downstream of the sample location. Time required for colonization of the available surfaces (Hochheimer and Wheaton, 1998) in the bottle may have contributed to the observed lag phase. In this explanation, the lag seen may not be descriptive of actual conditions in the river; however, the previously described ammonium competition explanation is another valid possibility and if verified would indicate that the modeled lag probably is descriptive of actual conditions in the river. In any case, this is an important area for further research.

Biochemical Oxygen Demand Rates

Method 5 results indicated that the rates of Method 1 might not have fully characterized the BOD dynamics (Figure 7; Table 5). Although both methods supported the existence of a rate in the

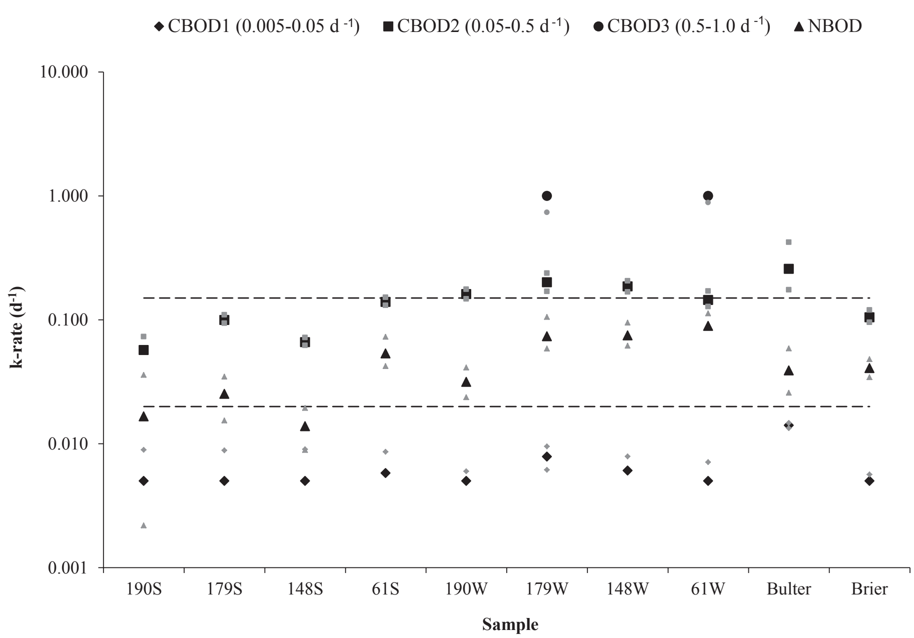

FIGURE 7. Method 5 Estimates Shown on Log Scale for Rates (large icons) Along with Upper and Lower Bounds of the 70% Confidence Interval for Those Rates (smaller icons of the same type). The fixed rates of Method 1 (0.15/day and 0.02/day) are shown with dashed lines.

range of 0.10-0.15/day (average Method 5 CBOD2 rate was 0.14/day), some samples deviated from 0.15/day significantly. Furthermore, the fixed rate of 0.02/day was most likely higher than the "slow" rate found in these samples by almost a factor of 10 (average Method 5 CBOD1 rate was 0.006/day). There was also a possible "faster" rate found that was approximately a factor of 10 higher than the Method 1 "fast" rate of 0.15/day (average Method 5 CBOD3 rate was 1.0/day). The multiple rates found in this study bracketed the single rates found by Volkmar and Dahlgren (2006) on the lower San Joaquin River and were slightly lower than those rates found by Sullivan *et al.* (2010) on the upper Klamath River. The San Joaquin River study also found that the decay of instream algae contributed 28-39% of the

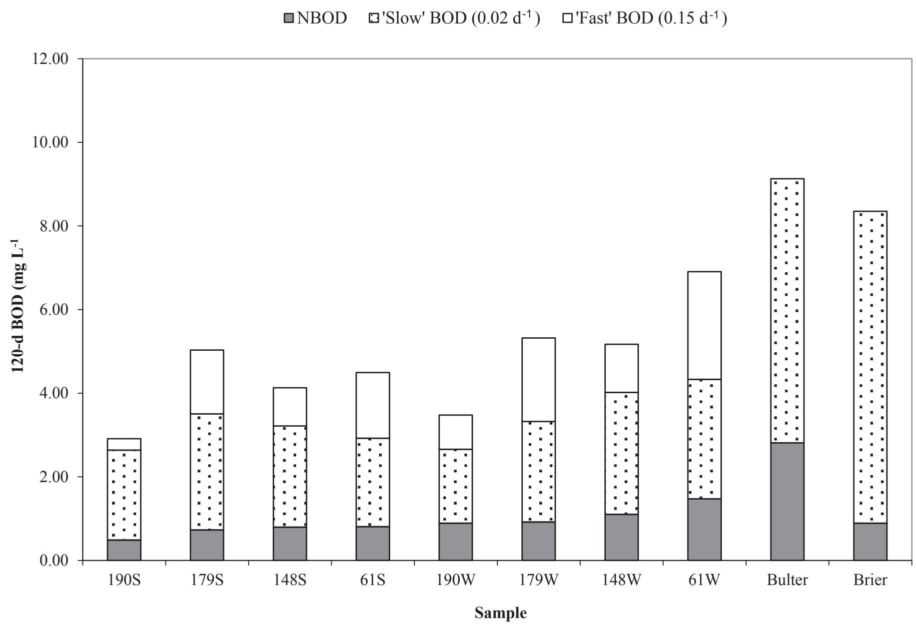

FIGURE 8. Method 1 Estimates for BOD_{120} Apportioned into Respective Rate Groups.

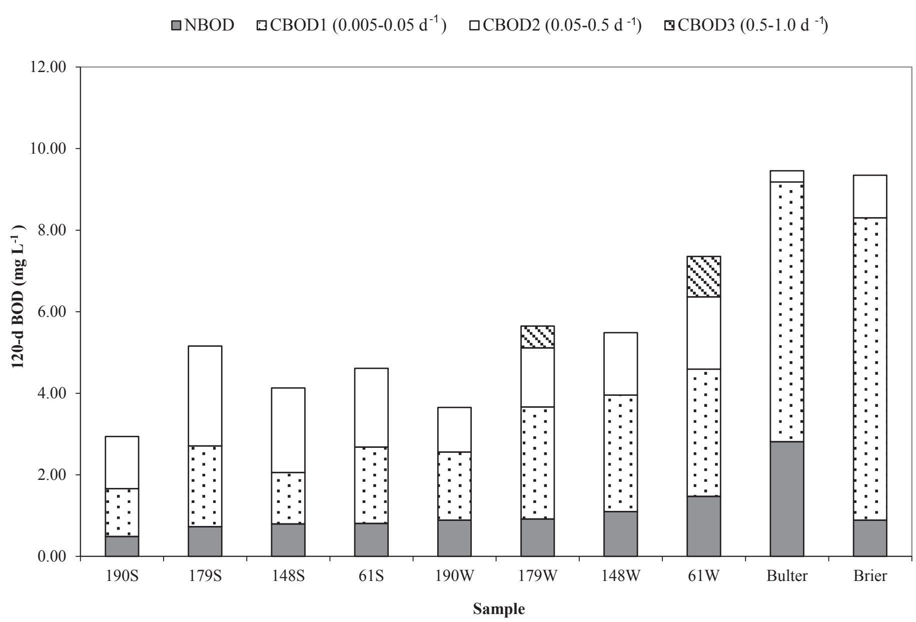

FIGURE 9. Method 5 Estimates for BOD_{120} Apportioned into Respective Rate Groups.

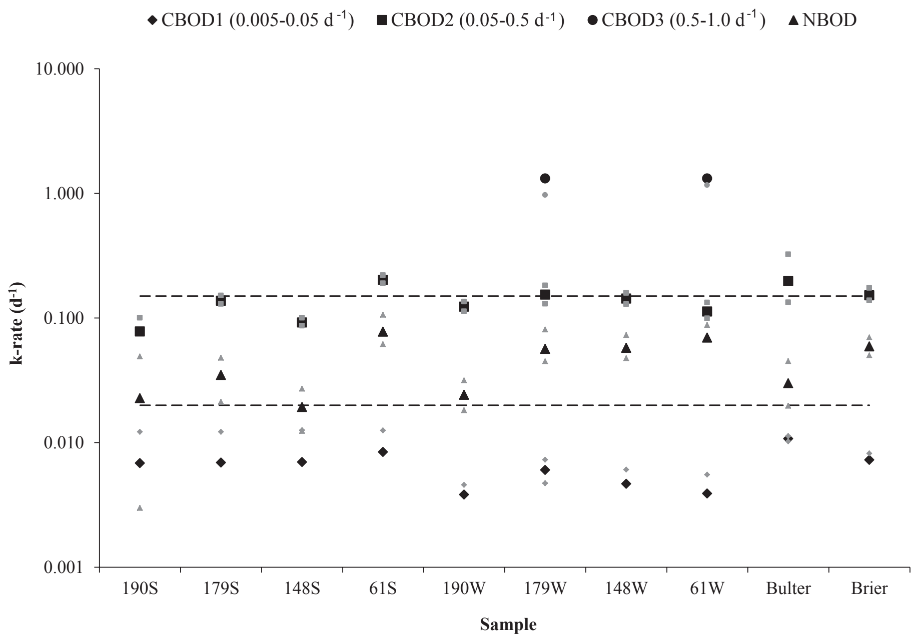

FIGURE 10. Method 5 Rate Estimates Shown on Log Scale for Rates with Temperature Correction (large icons) Along with Upper and Lower Bounds of the 70% Confidence Interval for Those Rates (smaller icons of the same type; compare with Figure 7). The fixed rates of Method 1 (0.15/day and 0.02/day) are shown with dashed lines.

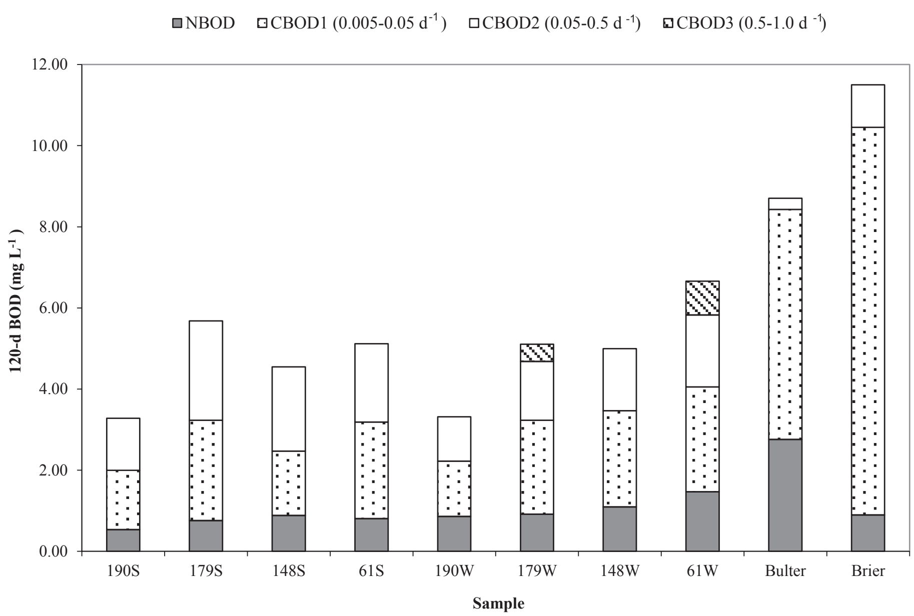

FIGURE 11. Method 5 Estimates for BOD_{120} Apportioned into Respective Rate Groups with Temperature Correction (compare with Figure 9).

BOD at one of the downstream sampling stations again supporting importance of capturing patch dynamics within modeling efforts.

The "faster" rate observed in some river samples might largely be explained by initial sample temperatures moving to the incubation temperature of 20°C; however, the "faster" rate was also seen with more confidence in full-strength effluent samples analyzed along with river samples (results not shown). Examination of the theoretical oxygen loss associated with the temperature changes in the cases where the faster rate was found revealed that this mechanism was probably sufficient to account for the oxygen loss observed; however, other samples in the study had similar initial temperature changes but did not exhibit this "faster" rate in analysis.

120-Day Biochemical Oxygen Demand Proportions

Another implication of the differences in rate characterization was seen in how BOD partitions between rates for Method 1 (Figure 8) and Method 5 (Figure 9). It is necessary to point out that although the proportions for Method 1 were based on a particular rate, the proportions for Method 5 were based on the rate brackets described for that method. As the Method 5 rates were well grouped (Figure 7), it was still reasonable to compare them in this way. Compared with the 57/43 ratio for slow/fast BOD, Method 1 proportions for the river in this study averaged 66/34. However, the average proportions for Method 5 were approximately 52/45/3 for slow/fast/faster BOD, which was quite close to the current ratio. Of note, a previous BOD study of the Savannah River by the authors found somewhat higher ratios for slow/fast BOD. The differences are likely explained by the following factors, with the first factor being the most dominant: (1) the previous study reported BOD_{ult} ratios whereas this study reports BOD_{120} ratios, an important distinction as the ratio changes with time and BOD_{120} and BOD_{ult} values diverge when the "slow" rate is modeled below 0.02/day; (2) the sample set in the previous paper only included warm weather samples, which tend to have higher slow/fast BOD ratios; and (3) one of the sample sites included in the previous study was below a large reservoir and is known to have a substantially different ratio.

It is generally understood that BOD addition to a river can occur in patches, such as urban corridors, industrial areas, riparian zones, or bottomland hardwood swamp. However, what may be less obvious, but indicated by this study and highlighted through Method 5, is that river processing of BOD probably also exhibits patch dynamics. In several cases, Method 5 apportioned the sample into different and possibly more rate groups in some cases than did Method 1. These areas of more or different rates are likely evidence of patch dynamics and demonstrate the ability of Method 5 to capture such information. The changes in occurrence and proportions of various rate groups may provide a more nuanced assessment of longitudinal changes in oxygen utilization. These patches may also support the possibility of a reset in river processes based on the serial discontinuity concept described by Ward and Stanford (1983). They theorized that an impoundment with a hypolimnetic release (such as J. Strom Thurmond Lake) could cause a large drop in nutrients at the outlet, significantly altering the continuum of nutrient transport downstream. This relatively low-nutrient water could potentially have effects on CBOD processing or create lag in NBOD as the river slowly begins to acquire and process organic and inorganic forms of nitrogen. A slight longitudinal increase in NBOD was observed, particularly in winter samples (Figures 8 and 9). Whether caused entirely by the nature of the substrate additions in a given patch or simultaneously affected by the physical, biological, and chemical environment of that patch, the variations in the rates of oxygen use and proportions of rates indicated patch dynamics in the Savannah related to BOD.

Temperature Adjustments

Adjustments for temperature tended to consolidate rates for NBOD, fast CBOD, and faster CBOD, while slightly differentiating the slow CBOD rates (Figures 10 and 11). Temperature correction affected BOD_{120} totals in general by decreasing the difference between summer and winter totals for the river. Temperature had a more notable affect on tributary samples than on river samples, probably because of their higher percentage of slow-degrading BOD_{120}, which would be more sensitive to rate adjustment as a lower percentage of that portion has been degraded over 120 days.

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