Biochemical Oxygen Demand in the Savannah River Basin: Results from Six Years of Research

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Reference: McDowell RJ, CA Pruitt, RA Bahn (eds.), *Proceedings of the 2015 Georgia Water Resources Conference*, April 28-29, 2015, University of Georgia, Athens.

Abstract. Biochemical oxygen demand (BOD) is a regulatory parameter that is used to determine how much oxygen will be consumed by a particular natural or manmade discharge to a water body. Over the past six years, we have assessed oxygen demand dynamics within this river system by applying multiple methods, experiments, and analysis approaches. By using a Lagrangian sampling approach (sampling according to travel time) from 2006-2008, we found that the river acts as a conduit for dissolved organic material in the winter but undergoes moderate organic matter loss in the summer. Using the EPA approved Long Term Biochemical Oxygen Demand method, we found large seasonal intra-site variability (20% to 90% coefficient of variation) for all sampled sites but also found that the oxygen consumption rate used in the Total Maximum Daily Load calculations for the Savannah Basin underestimates the fast kinetic rate and overestimates the slow kinetic rate used in the current modeling effort. Using a real-time, in-situ Lagrangian sampling effort, we found that the conventional LTBOD test likely underestimates actual river respiration rates downstream of industrial and municipal discharges. Results from this research show that current sampling, analysis, and modeling of biochemical oxygen demand in river systems can be improved to better characterize actual river processes.

INTRODUCTION

Riverine food webs are fueled by organic material; that organic material is either transported to the river by surface water, groundwater, or point source discharges (allochthonous) or originates within the system as algal, bacterial, and aquatic vegetative biomass (autochthonous). Vegetation and land use in watersheds feeding most river systems are not homogenous or monoculture so the landscape can be thought of as a mosaic of individual patches. The Patch Dynamics Concept (Pringle et al., 1988; Townsend, 1989) of river systems provides a context for understanding river water quality as a function of the landscape that feeds it. Within this context, the concept also allows for understanding the presence, absence, and abundance of aquatic organisms at any given location in a river as a function of the drainage within each reach. The concept proposes that each patch has the ability to provide different organic and inorganic material to the river system at any given time. Since the biological assemblage at any given site is a function of the physical and chemical environment, then the assemblage itself will be a function of that material and will be patchy too. We used this concept as our foundational understanding of river systems and have developed sampling and analysis protocols through that conceptual lens.

Understanding the origination, quality, fate, and transport of organic material in rivers is the essence of understanding the overall water quality narrative, the capacity of the riverine food web to sustain a certain biomass of organisms, and to understand the overall metabolic processing potential of a river to sustain industries and municipalities above the natural background loads in order to meet water quality standards. Since organic material is the most significant bridge between ecosystem and economic sustainability, we have focused on it for the past 10 years in the Savannah River Basin. That research, its findings, and conclusions are summarized in this paper.

BACKGROUND

Over the past 10 years, we developed three distinct studies in order to understand how the river processes natural (tributaries and groundwater) and manmade (point sources) discharges. This section briefly defines the goals of each study.

2005-2008: Comprehensive Study. The goal of this study was to understand Savannah River water quality dynamics in terms of physical, chemical, and biological components from Thurmond Dam to near Clyo, GA with reference to physical, geological, and land use changes along that reach. We developed permanent monitoring stations at 10 mainstem and 3 tributary sites, all of which had continuous monitors for temperature, pH, specific conductance, and dissolved oxygen (DO). Each site was sampled monthly for over 90 dissolved and total chemical constituents. A subset of each monthly sampling event was collected according to travel time (Lagrangian sampling). During that time we collected aquatic insect samples from each site every other month, and collected a number of other physical parameters. The relevant data from that study for this paper was the mass transport of DOC.

2009-2011: Long-Term Biochemical Oxygen Demand study. The goal of this study was to determine sources, transport, and respiration rates of biochemical oxygen demanding substances, with an emphasis on the carbonaceous biochemical oxygen demand (CBOD), within the Savannah River. The study reach stretched from RM 215 to the Savannah Harbor (RM 11) and focused on land use changes and seasonality effects on oxygen demanding substances by applying a Lagrangian sampling scheme.

2012: Lagrangian cruise study. The goal of this study was to develop a truly Lagrangian perspective of the river and its biogeochemical processes by traveling with, and continuously collecting data from, the same packet of water as it flowed from RM 190 (approximately 2 miles above NSBL&D) to RM 45 (near Ebenezer Creek). Our intention was to focus on the carbon dioxide and dissolved oxygen dynamics to develop an understanding of the rate and amount of organic material that was processed by the entire river community along the study reach.

Figure 1 shows sampling locations and the extent of the Lagrangian cruise (RM 190 to RM 45).

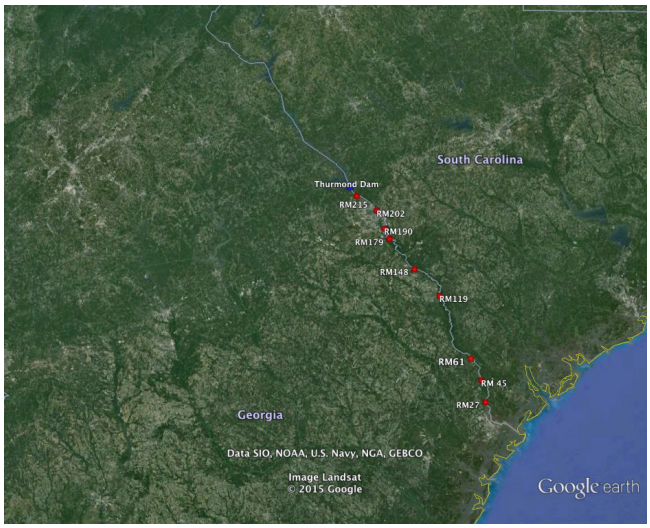

Figure 1: Map of study area showing sampling locations and extent of Lagrangian cruise.

METHODS

2005-2008: Comprehensive Study. When possible, all water samples were collected using a US-D96-A1 collapsible bag sampler, developed by the Federal Interagency Sedimentation Project (FISP). This device allowed for the collection of flow-weighted, depth-integrated samples. Based on depth and water velocity, the device was lowered and raised at a constant rate to collect approximately three liters of water. A total of 20 L of water was collected at each sampling location, with approximately one-third of the total volume collected at the right, center, and left thirds of the transect. The sampler could not collect water at velocities below 1.5 – 2.0 ft/sec. At sites where water velocities were below this threshold, depth-integrated samples were collected with an electric pump. Each 20-L carboy containing samples was placed on ice for transport to the lab. For each sampling event, a duplicate and field blank were included for QA/QC purposes. Water samples were homogenized in the lab using a 37-L polyethylene churn splitter. Water samples were then either poured directly into sample containers or filtered through a 0.45-m cellulose acetate filter using a peristaltic pump for total and dissolved constituent analysis, respectively. Shealy Environmental Services (Cayce, SC) conducted all analyses according to EPAs Contract Laboratory Program (CLP) specifications except for fecal coliform concentrations, they were determined by MicroBac (New Ellington, SC).

2009-2011: Long-Term Biochemical Oxygen Demand study. River samples were collected bimonthly from several of the mainstem sampling sites; most of those samples were collected according to a Lagrangian sampling scheme. Due to the complexity of regulated flows and tidal influences, samples were collected while water was discharging from the dam (RM 215) and from the mainstem river prior to the tidally influenced reach. Samples were collected in triple rinsed 20-L carboys, stored on ice until arrival at the lab, and refrigerated until processing. We followed an EPA amended (John Marlar-EPA, personal communication, 2009) methodology developed by GAEPD (1989) for determination of ultimate BOD (uBOD). In short, all samples were divided into a ground glass stoppered,

2-L BOD bottle and a 1-L reservoir bottle after being homogenized with a churn splitter. All samples and reservoir bottles were incubated at 20 C for 120 days. DO was checked daily for the first week, once every other day during weeks 2 and 3, every third day during weeks 4- 6, and weekly for the remaining time period. If needed, samples were reaerated before the DO reached 4 mg/L by vigorously shaking the entire 3-L sample for 30 seconds between two BOD bottles. In order to determine DO loss due to nitrification, ~4 mL of sample was removed from each bottle on each day the DO concentrations were assessed. Nitrate, nitrite, and ammonia concentrations were determined using an AQ2 discrete autoanalyzer (SEAL Analytical, Mequon, WI) while TKN was assessed on day 1 and day 120 by permanganate digestion and subsequent ammonium analysis on the AQ2. All data were entered and analyzed within GAEPDs (2008) LtBod software program (version 3.0.). Dissolved oxygen consumption was modeled according to GAEPDs Amplified BOD protocol (GAEPD, 1989). The modeling philosophy included accounting for oxygen loss due to nitrogen species oxidation (NBOD), a labile or fast-reacting carbonaceous component (CBOD k1), and a recalcitrant or slow-reacting carbonaceous component (CBOD k2). This modeling philosophy was also consistent with EPA and GAEPDs model efforts for the Savannah Harbor DO TMDL. Ultimate oxygen consumption (uBOD) was calculated as a summation of a lagged first order equation for NBOD and first order equations for both CBOD1 and CBOD2.

2012: Lagrangian cruise study. Lagrangian data was collected from a 30-ft research vessel equipped with a data sonde (temperature, DO, pH, and conductivity), GPS, an instrument capable of measuring the partial pressure of CO_2 in air and water (Apollo SciTech Inc. model AS-P2), and drifter floats. Water for the CO_2 analyzer, BOD samples, and water bath was continuously pumped from a depth of 0.5m below the water surface from a pipe that extended 1m off the front of the vessel; the sonde was deployed off the side of the boat at a similar depth.

The cruise was initiated on June 26, 2012 from RM 190 (~2 miles above New Savannah Bluff Lock & Dam (NSBL&D)) and ended on July 1, 2012 at RM 45 (near Ebeneezer Creek). We intended the cruise to be conducted continuously but our actual travel time (0.52m/s) was consistently faster than our pre-calculated and measured (drifters) travel time (0.46m/s). As a result, we anchored the boat and switched to an Eulerian scheme for up to four hours each day while the theoretical centroid of the packet of water caught up to our position. This methodology would have been most important early on in the cruise and less important later in the cruise because dispersion of the tracked water packet would have exceeded the small deviation in travel time relative to our starting point at RM 190. Conversely, our stoppages may have slightly altered the Lagrangian perspective for discharges to the river that were well downstream of our starting point at RM 190.

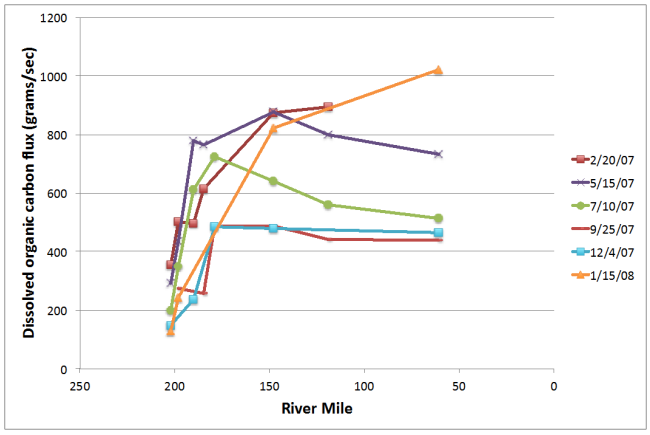

Figure 2: Dissolved organic carbon flux for 2007 and 2008 Lagrangian sampling events.

In order to incorporate the CO_2 data into the conventional LTBOD methodology, we transformed the CO_2 into DO data by assuming that 1 mole of CO_2 evolved through respiration would have consumed 1 mole of O2. We then used the converted data to construct an oxygen loss curve over time in order to determine the rates of oxygen demand and associated BOD.

RESULTS

2005-2008: Comprehensive Study. The overall upstream to downstream trend (Lagrangian sampling) of DOC flux from January 2007 through January 2008 indicated a seasonal trend where the cooler months exported significantly more carbon than the warmer months (>1.0 kg DOC/s versus >0.8 kg DOC/s). During the cooler months, presumably due to decreased respiration rates, carbon flux increased steadily with decreasing river mile, even through the floodplain section of the study reach. However in the warmer months, DOC flux often decreased through the reach from RM 179 to RM 61 (Fig. 2).

2009-2011: Long-Term Biochemical Oxygen Demand study. The average measured bottle rate for the CBOD k1 (fast rate) was 0.225/d and the average measured bottle rate for CBOD k2 (slow rate) was 0.009/d for all river sites from RM 215 to RM 61 (n=60) (Table 1). Of all sites, RM 148 had the lowest average CBOD k1 and CBOD k2 rates of all river samples while

Table 1: Results from Savannah River long-term biochemical oxygen demand (LTBOD) samples.

Site (river mi.)	BOD_{120} (mg L^{-1})	CBOD k1 (day^{-1})	CBOD k2 (day^{-1})	NBODu (mg L^{-1})	NBOD k (day^{-1})	NBOD lag (days)	BODu (mg L^{-1})	Total N (mg L^{-1})	Mean RMSE	n
215	3.20 (0.562)	0.334 (0.2063)	0.009 (0.0026)	0.66 (0.168)	0.075 (0.0270)	10.5 (6.44)	4.22 (0.900)	0.84 (0.246)	0.06	7
190	4.26 (2.509)	0.220 (0.1890)	0.008 (0.0036)	0.81 (0.319)	0.066 (0.0592)	7.0 (4.23)	5.84 (2.988)	0.93 (0.177)	0.06	11
185	4.43 (3.194)	0.291 (0.2539)	0.011 (0.0066)	0.80 (0.320)	0.061 (0.0413)	6.3 (2.78)	5.71 (3.719)	1.23 (0.451)	0.06	7
179	6.39 (1.432)	0.214 (0.0969)	0.012 (0.0072)	0.95 (0.132)	0.067 (0.0345)	6.5 (1.83)	7.68 (0.775)	0.85 (0.063)	0.07	6
148	5.35 (1.294)	0.139 (0.0471)	0.007 (0.0023)	1.02 (0.187)	0.053 (0.0213)	4.0 (2.62)	7.47 (1.231)	0.75 (0.085)	0.07	6
119	4.23 (0.200)	0.183 (0.0931)	0.007 (0.0028)	0.71 (0.391)	0.070 (0.0389)	6.8 (3.10)	6.05 (0.877)	0.80 (0.121)	0.06	6
61	4.98 (1.221)	0.215 (0.0971)	0.008 (0.0031)	0.82 (0.333)	0.063 (0.0373)	6.6 (3.02)	6.75 (1.606)	0.87 (0.136)	0.07	11
27	5.56 (1.460)	0.180 (0.0448)	0.009 (0.0019)	0.72 (0.388)	0.085 (0.0512)	9.6 (4.28)	7.37 (2.206)	0.98 (0.167)	0.06	6

BOD120 = biochemical oxygen demand at 120 days, CBOD k1 = carbonaceous biochemical oxygen demand fast rate, CBOD k2 = carbonaceous biochemical oxygen demand slow rate, NBODu = ultimate nitrogenous biochemical oxygen demand, NBOD k, nitrogenous biochemical oxygen demand rate, NBOD lag = nitrogenous biochemical oxygen demand lag time, BODu = ultimate biochemical oxygen demand, Total N = total nitrogen in sample, Mean RMSE = mean Root Mean Square Error for all samples, and n = number of samples at particular river mile.

RM 215 had the highest average CBOD k1 rate and RM 179 had the highest average CBOD k2 rate. Since the total CBOD is partitioned between a fast (CBOD1) and slow (CBOD2) component, changes in rates will result in changes in how much CBOD, in terms of CBOD concentration (mg/L), will be apportioned between the fast and slow CBOD components. When compared to the fixed rate results (0.15/d and 0.02/d), the partition of the total CBOD between fast and slow components changed as a result of changes in CBOD k1 and CBOD k2. We found that changes resulting from the fixed to unconstrained rate analysis methodology that we applied resulted in an average increase of CBOD1 for half of the samples. The data also showed a regular periodicity to the partitioning where CBOD1 partitioning was highest around August and March and lowest around December and May of each year.

2012: Lagrangian cruise study. Using a two CBOD rate characterization, a fixed CBOD k2 (slow rate) of 0.02/d, and an ultimate biochemical oxygen demand (uBOD) of 7.0 mg/L, we found that the LTBOD bottle test data (from a 2011 sampling event) were best fit with a CBOD k1 (fast rate) of 0.3/d and that the in-situ Lagrangian CO_2 data were best fit with a CBOD k1 (fast rate) of 0.9/d.

CONCLUSIONS

2005-2008: Comprehensive Study. The trend in DOC flux most likely indicated that significant respiration was ongoing, especially in July 2007 when a loss of $\sim$ 0.2 kg DOC/s was observed from RM 179 to RM 61. This loss, which was equivalent to nearly 30% of the total load below all CSRA dischargers, decreased carbon flux to levels observed within the CSRA pool (above the dischargers with the largest biochemical oxygen demanding loads) for that time period and may indicate that a significant amount of CSRA effluent material was respired within river, prior to the harbor.

2009-2011: Long-Term Biochemical Oxygen Demand study. The current rates used in the Savannah River TMDL modeling effort are 0.15/d for CBOD k1 and 0.02/d for CBOD k2. This study showed that the average measured bottle rate for CBOD k1 was 0.225/d and the average measured bottle rate for CBOD k2 was 0.009/d for all river sites from RM 215 to RM 61 (n=60).

2012: Lagrangian cruise study. When comparing the results to the fixed CBOD rates of 0.02/d and 0.15/d that are currently being used in the TMDL model for the Savannah River, our results translate to 2.3% less Total BOD transported to RM 61 using the LTBOD bottle test result and 12% less Total BOD transported to RM 61 when using the Lagrangian CO_2 data result for only the 12 hour period below the Augusta dischargers (RM 179). In pounds of BOD/d, this result indicates that an additional 25,000-30,000 lbs/d of BOD was being respired in this portion of the river over what was currently being modeled (Fig. 3).

Each method we used to understand the fate of oxygen demanding substances in the Savannah River below Thurmond Dam showed that patches of high respiration exist in certain reaches of the river below Augusta, GA. When directly compared to respiration rates, the patches were shown to have rates that were higher than rates used in the TMDL modeling effort for the Savannah River below Augusta. Data from these studies shows that model parameters could be updated to reflect the new data and analysis and to better reflect the actual ecosystem services that bacteria provide in this river system.

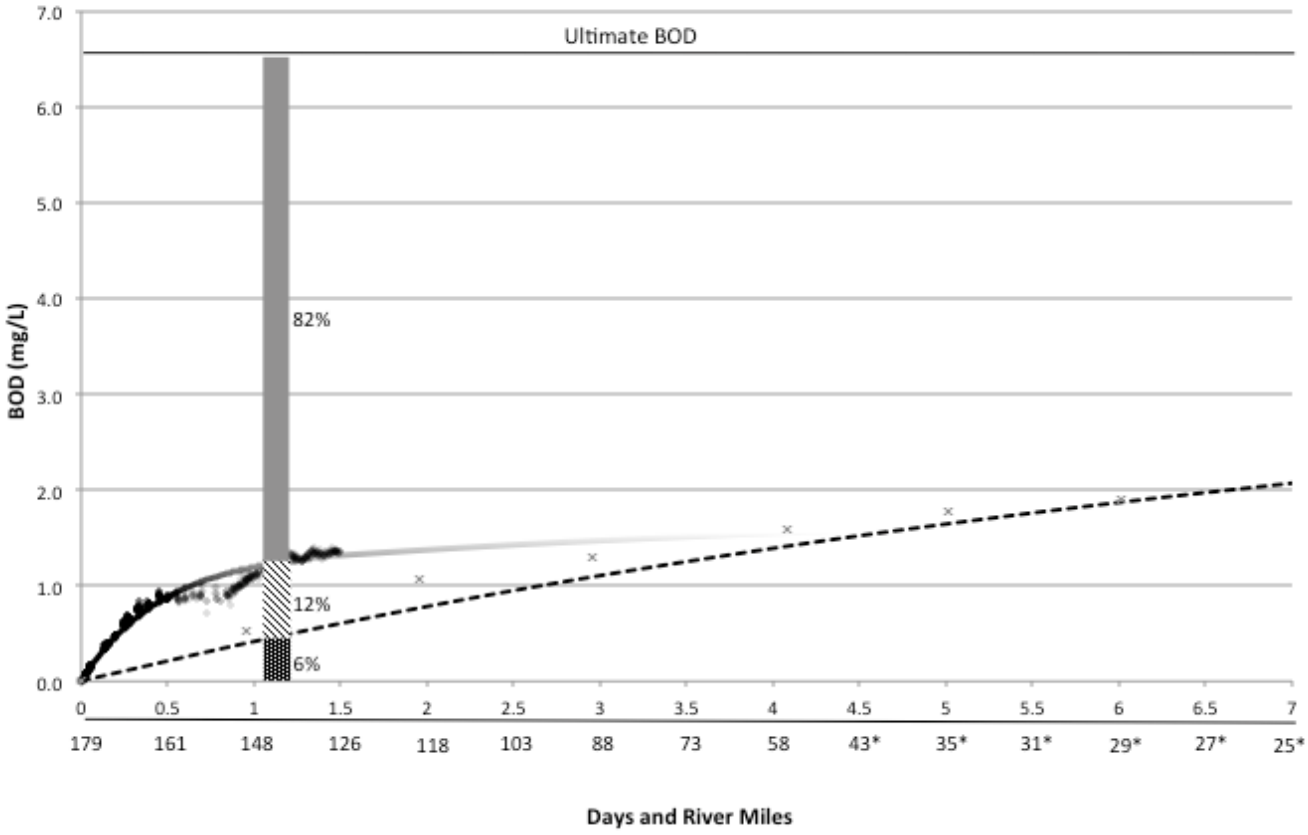

Figure 3: Oxygen demand results from the 2012 Lagrangian river cruise showing an ultimate biochemical oxygen demand of 6.6 mg BOD/L of which a total of 6% is consumed after day 1.1 using the long-term biochemical oxygen demand test results (dashed line) and 18% is consumed for the same time period using the converted CO_2 data (solid line through the data points (dots)).

Acknowledgements. The Savannah River data were collected as part of Phinizy Centers Savannah River Monitoring Program, which is funded by municipalities (Richmond and Columbia County, GA; City of North Augusta), industries (PCS Nitrogen, International Paper, DSM Chemical, and Kimberly Clark- Beech Island), Georgia Environmental Protection Division, and from individuals that support our organization through philanthropy and memberships.

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