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Factors Affecting Dissolved Oxygen Metabolism in Coastal Plain Streams of Virginia

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FACTORS AFFECTING DISSOLVED OXYGEN METABOLISM IN COASTAL

PLAIN STREAMS OF VIRGINIA

A thesis submitted in partial fulfillment of the requirements for the degree of Masters of
Science (Biology) at Virginia Commonwealth University.

by

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Abstract

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By Julie E. Frank, B.S.

A Thesis submitted in partial fulfillment of the requirements for the degree of Masters of Science (Biology) at Virginia Commonwealth University.

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I investigated seasonal and inter-site variation in factors influencing diel dissolved oxygen (DO) metabolism at four streams in the Virginia Coastal Plain. Data were collected monthly from January to August 2008 to characterize DO metabolism (diel DO amplitude, production, respiration), incident solar radiation (PAR), dissolved nutrients, fine benthic materials (mass, C:N, Chlα) and hydrology (discharge, water transit time, transient storage). Reach-scale metabolism estimates were determined using the one-station diurnal DO technique and transit time and transient storage were determined by conservative tracer additions. Incident solar radiation was the primary determinant of DO

metabolism as streams experiencing higher light levels (Herring and Powell Creeks) exhibited greater diel DO amplitudes, production and respiration. Streams with greater riparian shading (Courthouse and Crump Creeks) exhibited lower DO metabolism despite their higher nutrient concentrations. Higher incident solar radiation was associated with greater benthic algal biomass at some (Herring, Crump, and Courthouse Creeks) but not all (Powell Creek) sites. Diel DO amplitudes were significantly and positively correlated with benthic Chlα and incident solar radiation at less shaded sites. These factors were not significant predictors of DO amplitude, production or respiration at more shaded sites.

CHAPTER 1 Introduction

Ecosystem metabolism reflects the balance between autotrophic production and heterotrophic respiration. Metabolism is perhaps the most fundamental and unifying of ecosystem processes and is directly influenced by environmental factors (Izagirre et al., 2008; Williamson et al., 2008). In aquatic ecosystems, metabolism is monitored through changes in dissolved oxygen concentration which are subject to biological, physical and chemical processes (Wang et al., 2003). The three determinants of dissolved oxygen balance are: photosynthesis (P), respiration (R), and atmospheric exchange (K). Autotrophic production determines oxygen gain, heterotrophic respiration determines oxygen loss, and atmospheric exchange may be a gain or loss depending on whether the system is under- or over-saturated with oxygen. Daily variation in incident solar radiation drives characteristic diel patterns: daytime oxygen production is driven by photosynthesis whereas nighttime oxygen consumption is driven by respiration (Odum, 1956). Oxygen concentrations peak during the day and decline to a minimum at night; this 24-hour sinusoidal curve is referred to as a diel cycle. Diel patterns have been widely used to characterize variation in P and R among diverse aquatic ecosystems (e.g., lakes, estuaries, streams) and to evaluate factors controlling net ecosystem metabolism (NEM; the balance between P and R). Metabolic rates are determined in part by allochthonous inputs of nutrients and organic matter and by shade provided by riparian vegetation (Cummins,

1974; Lowe et al., 1986; Hill et al., 2001). In this way, stream metabolism is highly connected to adjacent terrestrial environments.

Prior studies have suggested that stream metabolism is strongly influenced by energy inputs via solar radiation. For example, Bott et al. (2006) showed that inter-stream variation in gross primary production (GPP) was highly correlated to variation in incident photosynthetically active radiation (PAR) among Catskill streams. Similarly, Hill et al. (2001) suggested that light is the principal driver of primary production in two headwater streams of eastern Tennessee. In this study, metabolism was measured on dates before and after leaf emergence to show that primary production was directly related to photon flux density. GPP decreased whereas nitrogen and phosphorus concentrations rose with decreasing light availability, indicating that shading surmounts the effects of nutrient availability. Mulholland et al. (2006) compared metabolic rates in the East and West Forks of Walker Branch (Tennessee) and showed that GPP followed PAR with higher rates observed on clear days than on overcast days. This study also reported that GPP influenced rates of nutrient retention as NO_3^- uptake rates were 50% greater on clear days than on overcast days. Thus, the more light a stream receives, the more autotrophic production and nitrate uptake will be observed. Hall and Tank (2003) showed similar results, as GPP explained more than 75% of the variability of NH_4^+ and NO_3^- uptake rates suggesting that autotrophic assimilation was the dominant mechanism for N removal. Overall, these studies suggest a strong correlation between light availability, primary production, and light-enhanced uptake of nutrients by algae.

The availability of nutrients can also play a significant role in the rates of metabolism in streams (Frost et at., 2002). Bott et al. (2006) found that light influences GPP but that streams receiving high nutrient inputs, such as wastewater effluents, had much higher rates of GPP. The effects of nutrient demands were also seen at Walker Branch (Tennessee) where production increased by 129% following the addition of nitrogen and phosphorous (Rosemond et al., 1993). In a study by Peterson et al. (1985), the addition of phosphorous to a tundra river resulted in a net increase in primary production. These studies suggest that when light is abundant for primary producers, inorganic nutrient availability can limit production due to assimilatory demands for nutrients.

Respiration represents the consumption of organic matter supplied by autochthonous and allochthonous sources. Respiration is one of the most commonly measured functional attributes of stream ecosystems and is a sensitive indicator of ecosystem stress (Hill et al., 2000). Respiration rates are influenced by temperature, the availability and quality of organic matter and the exchange of water between the stream and sub-surface storage zones (Grimm and Fisher, 1984; Bott et al., 1985; King and Cummins, 1989; Bonin et al., 2000; Fellows et al., 2001; Mulholland et al. 2001; Bonin et al. 2003). For instance, Sand-Jensen and Pedersen (2005) found that oxygen consumption and temperature were highly correlated in Denmark streams. Prior studies have also shown that temperature is an important determinant of respiration, accounting for 27% of the variation in respiration in a sub-tropical blackwater river (Edwards and Meyer, 1987)

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and 58% of the variation in temperate streams in four different biomes of the U.S. (Bott et al., 1985).

Temperature effects are directly related to microbial activity, however the quantity and quality of organic matter also plays an important role in determining respiration. For example, Izagirre et al. (2008) found that the effect of temperature on respiration was overridden by the inputs of organic sewage to Spanish streams. In this case, the availability of organic matter and its lability had a greater effect on respiration than temperature. Similarly, a study on urban and agricultural Japanese watersheds found that respiration in strongly heterotrophic streams was driven by organic matter loading from agriculture (Iwata et al., 2007). The presence of fine benthic organic matter (FBOM) in streams has been used as an indicator of substrate availability for microbial decomposition and has been shown to be highly correlated with respiration (Izagirre et al., 2008). Results from a study of FBOM in mountain streams (Bonin et al., 2000) suggest that low C:N ratios of FBOM (i.e., high N content) are associated with higher rates of respiration.

Lastly, the extent of the hyporheic zone and its rate of exchange with the stream has a strong effect on respiration by enhancing storage of organic matter and providing surface area for microbes to colonize (Grimm and Fisher, 1984; Fellows et al., 2001; Mulholland et al., 2001). Mulholland et al. (2001) reported that the size of the transient storage zone along with soluble reactive phosphorus (SRP) concentration together explained 73% of the variation in respiration in an inter-biome comparison of factors controlling metabolism. Overall, these studies suggest that temperature, organic matter, nutrients and transient storage are positively related to stream respiration.

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The extent to which P and R influence in-stream dissolved oxygen concentrations is determined in part by the exchange of oxygen between the stream and the atmosphere. Re-aeration rates are determined by oxygen concentrations and physical parameters such as depth and those influencing turbulent mixing (e.g., water velocity, channel morphology, discharge; Mulholland et al., 2001; Jha et al., 2004; Izagirre et al., 2007). The magnitude of these variables in addition to the amount of oxygen produced and consumed through photosynthesis and respiration determine the rate of re-aeration. In general, more turbulent streams will exchange oxygen more rapidly than will shallow streams and those exhibiting greater departures from atmospheric equilibrium (super- or under- saturated). Re-aeration is also influenced by seasonal variation in water temperature as warmer temperatures increase atmospheric exchange (Allan and Castillo, 2007).

Streams provide an important ecosystem service by mitigating downstream fluxes of nutrients which are determined in part by metabolism (Peterson et al., 2001; Alexander et al., 2007). For example, Chesapeake Bay, the largest estuary in North America, has exhibited symptoms of eutrophication (e.g., occurrence of algal blooms, hypoxia) which has led to wide-spread efforts to characterize sources and sinks of nutrients in the watershed (Wahl et al., 1997; Norton and Fisher, 2000; Royer et al., 2004; Stone et al., 2004; Robson et al., 2008). Coastal plain streams are potentially key sites for nutrient retention; however, little is known about metabolic rates in streams of this region. This study characterized inter-stream variation in dissolved oxygen metabolism in four coastal plain streams of Virginia. Factors affecting diel patterns in oxygen metabolism were investigated by characterizing seasonal and inter-stream differences in temperature,

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incident solar radiation, nutrient concentrations, transient storage and the quantity and

quality of fine benthic organic matter. The objectives of this research were to: (1)

characterize metabolic rates (P, R, NEM) in streams of the Virginia Coastal Plain, and (2)

identify environmental drivers of seasonal and spatial variation in metabolism.

CHAPTER 2 Methods

Environmental factors influencing dissolved oxygen metabolism were investigated at four sites: Herring Creek, Powell Creek, Courthouse Creek, and Crump Creek. These four sites exhibit a diversity of habitats (pools, riffles, debris dams) that are representative of Virginia coastal plain streams. Research was conducted from January through August 2008 to characterize seasonal variation in dependent (oxygen metabolism) and independent (hydrology, light, nutrients, and fine benthic matter) variables. Diel patterns in stream metabolism, incident light levels (Photosynthetically active radiation - PAR), the quality and quantity of fine benthic materials (FBM), water quality (temperature, pH, conductivity), nutrient chemistry (NO_3^-, NH_3, PO_4^{3-}), and hydrology (discharge, water transit time, transient storage) were measured monthly during this period (totaling eight sampling sets per site).

Preliminary data collected during fall 2007 revealed that the four sites differed with respect to nutrient and light availability. Incident solar radiation was generally higher at Herring and Powell Creeks relative to Crump and Courthouse Creeks. In contrast, dissolved inorganic nitrogen (DIN) concentrations were higher at Crump and Courthouse Creeks (0.63 and 0.54 mg/L, respectively) as compared to Herring and Powell Creeks (0.07 and 0.06 mg/L, respectively). PO_4^{3-} was low at all sites (< 0.02 mg/L) but inter-site

differences followed trends in DIN. These preliminary results led to the formulation of two hypotheses:

H1: If light availability is the primary determinant of metabolism in Coastal Plain streams, then streams experiencing higher light levels (Herring Creek and Powell Creek) should exhibit greater metabolism.

H2: If nutrient availability is the primary determinant of metabolism in Coastal Plain streams, then streams experiencing higher nutrient levels (Crump Creek and Courthouse Creek) should exhibit greater metabolism.

<u>Study Sites</u>

The four study sites are 2nd and 3rd order streams located within the James River and York River Basins (Table 1). The composition of land use in the James River watershed is approximately 71% forest, 7% water/wetland, 6% urban, and 16% agriculture. The York River watershed is composed of approximately 64% forest, 11% water/wetlands, <4% Urban, and 22% agriculture (Va. Dept. of Forestry, 2008). The four sites are similar in watershed area, stream order, width, depth, and substrate composition (Table 1). The study sites differed in the ways by which they were impacted by local land use activities. Courthouse Creek received approximately 18,927 L of effluent each day released from an on-site wastewater treatment plant ('package plant' for the Charles City County Elementary and Middle Schools). Crump Creek is adjacent to Georgetown Road and downstream of an agricultural area. Herring Creek is downstream of Harrison Lake and adjacent to the fish ponds of the Harrison Lake National Fish Hatchery. Effluent from the

hatchery ponds is released into this creek. Powell Creek is downstream of a large wetland complex.

<u>Field and Laboratory Techniques</u>

At each site, a reach of approximately 200 m in length was established and marked at 20 m intervals. At each of the 20-m sampling locations, incident solar radiation and channel width/depth were measured and samples of fine benthic material were obtained. Discharge was measured at the top of the study reach; transit time, transient storage and diel oxygen concentrations were measured at the bottom of the study reach. Nutrient samples were collected at both the top and bottom of the reach. Each sampling event was conducted over three days; (1) day one entailed conservative tracer injections to determine discharge, transit time, and transient storage and the deployment of Hydrolab minisondes for diel measurements, (2) day two was a continuation of diel measurements, and (3) day three entailed measurements of stream morphology (widths and depths), incident solar radiation, and fine benthic materials.

Stream Water chemistry. Samples for Nitrate (NO_3^-), Ammonia (NH_3), Phosphate (PO_4^{3-}) and dissolved organic carbon (DOC) analyses were filtered in the field using a syringe and filter apparatus (pre-combusted GF-A glass fiber). DOC samples were refrigerated and analyzed on a Shimadzo TOC Analyzer. Nutrient concentrations were determined by a Skalar auto-analyzer using methods of analysis established by the Environmental Protection Agency (EPA; EPA 1997). Alkalinity was determined during three seasons (winter, spring, and summer) by titrating with a standard sulfuric acid solution and a pH meter (Lind, 1985).

Stream Morphometry and Photosynthetically Active Radiation (PAR). Incident

solar radiation was measured four times between 10:00 am and 2:00 pm at 20-m intervals

along the study reach. Light measurements were taken using a Li-Cor data logger 1400.

Widths and depths were measured at the same locations and used in conjunction with the

diel O_2 data to estimate reaeration. Surveys to determine stream slope, stream orientation,

and dominant substrate types were conducted on a one-time basis to characterize inter-site

differences.

Hydrology. Discharge (Q) was estimated prior to and at the end of each diel

sampling period using a flow meter and the measured cross-channel area. Discharge was

also derived by conservative tracer (NaCl) injection using the Cl^- concentration of the

injection solution, the rate of injection and the observed in-stream increase in Cl^- (Stream

Solute Workshop, 1990; Bukaveckas, 2007). Transient storage (TS) and Transit time (TT)

were also determined from the conservative tracer injection based on the shape of the

tracer curve and time required for the tracer to travel through the reach. Dal values were

used to determine if the reach length was appropriate for calculating TS. Dal values of 0.5-

5.0 are considered acceptable (Hall et al., 2002) and therefore 4 experiments were excluded

due to exceedingly high Dal values. Remaining Dal values ranged from 0.4 to 10.9 with a

mean value of 8.1.

Benthic sampling. Fine benthic materials (FBM) were sampled at 20-m intervals

along the study reach. The method for sample collection was similar to that used by

Mulholland et al. (2001). A bottomless bucket was pressed into the stream channel to

isolate a known area of the stream bottom. Sediments were re-suspended (mixing by hand)

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into the volume contained inside the bucket. The volume within the bucket was measured and a sub-sample collected. The sub-sample was passed through a 1 mm sieve to remove coarse particulate matter and filtered upon return to the laboratory through a pre-weighed and combusted filter (GF-A glass). The samples were dried at 60° C and re–weighed to determine the dry mass of fine sediments. A sub-sample of the filter was run on a Perkin-Elmer CHN Analyzer to determine the content of carbon (C) and nitrogen (N). The C and N content of FBM was used as an indicator of organic matter content and sediment quality. Duplicates of a subset of samples were acidified to determine whether inorganic carbon was present. Acidified samples had approximately 5% less carbon than non-acidified samples suggesting that organic carbon was slightly over-estimated by this method. Benthic chlorophyll (Chlα) was measured as part of a related study (M. Brandt, thesis project).

Dissolved oxygen (DO) metabolism. Diurnal dissolved oxygen measurements were used to estimate production, respiration and air-water gas exchange using the single station open-water method. Dissolved oxygen measurements were obtained using Hydrolab minisondes which also recorded temperature (C°), pH, and specific conductance (μS/cm). The key challenge to estimating P and R from diel DO measurements is the uncertainty associated with the estimation of re-aeration (K). The estimation of K is critical to calculating metabolism in open-channels (Iwata et al., 2007; Izagirre et al, 2008) as re-aeration rates vary depending on turbulence, slope, depth, oxygen concentrations, and velocity (Young and Huryn, 1999; Izagirre et al., 2007 & 2008, Roberts et al., 2007). A direct method of measuring re-aeration using tracer gas injection (e.g., propane) can be

problematic due to difficulties in achieving complete mixing of the tracer during injections (Mulholland et al., 2001). This method also requires advanced instrumentation for measuring propane in water. There are a number of empirical methods used to derive re-aeration based on slope, depth, and velocity (Jha et al., 2004). Following the recommendations of Moog and Jirka (1998) who emphasized the importance of stream slope in determining K, two equations were tested: Cadwallader and McDonnell (1969) and Krenkel and Orlob (1962). The two equations yielded values that were not significantly different when comparing all sites daily values (one-way ANOVA: $p = 0.1$, df = 1,210) and hereafter we use re-aeration estimates derived from the equation of Krenkel and Orlob (1962) where H specifies mean depth in meters, S refers to slope in meters, and V represents velocity in meters per second:

$$K_2 = 173(SV)^{0.404}H^{-0.66}$$

We used the average (reach-scale) velocity (determined by tracer injection) and depth to derive re-aeration rates for each 3-day sonde deployment.

Production (P) and respiration (R) estimates were derived using two methods of calculation: the extreme value method (EVM; Wang et al., 2003) and the approximate delta method (ADM; McBride and Chapra, 2005). Estimates of P and R derived by EVM were not significantly different than those derived by ADM (one-way ANOVA for P: $p = 0.09$, R: $p = 0.23$, df = 1,210). EVM results were used in subsequent analyses for consistency with a related study (Dougherty, 2008). In addition to deriving P and R, we used the maximum and minimum deficits of dissolved oxygen to calculate the daily amplitude of oxygen change (Mulholland et al., 2005).   Both EVM results and daily DO

amplitudes were used as dependent variables in correlation analyses with environmental

parameters (temperature, light, nutrients, and fine benthic materials). The times of the

minimum and maximum DO deficit were also compared to determine if there were

consistent differences among the four streams.

Statistical analysis. Data were analyzed using ANOVAs and multiple regressions

(SAS 9.1). Two-way ANOVAs were used to identify seasonal and inter-stream

differences. Eight months were aggregated into three seasons: winter (January –

February), spring (March – May) and summer (June – August). Regression analysis was

used to identify relationships between environmental factors and metrics of metabolism (P,

R, diel DO amplitudes). To assess inter-site differences in the timing of diel DO patterns,

time of day was transformed into elapsed time and tested as a predictor for the minimum

and maximum DO deficit.

CHAPTER 3 Results

Stream Hydrology. Average discharge varied five-fold among the four study sites with Courthouse Creek exhibiting the lowest mean value (44 L/s) and Powell and Herring the highest (ca. 210 L/s; Table 2). Inter-site differences in average discharge followed differences in watershed area (Court < Crump < Herring = Powell) and were also related to differences in water velocity. The site with the lowest discharge exhibited the lowest average water velocity (0.06 m/s). Water velocities at the higher discharge sites were 2-3 fold greater (0.15-0.21 m/s). Discharge was also a good predictor of velocity across sampling dates at each of the four sites (Figure 1). Highest correlations were observed among the three sites exhibiting the widest range of discharge ($R^2 = 0.62$-0.77), whereas a weaker correlation was observed at the low discharge site (Courthouse; $R^2 = 0.30$). Transient storage also varied by 3-fold, inter-stream differences were related to discharge ($p = 0.01$) but were unrelated to water velocity. Highest transient storage was observed in Powell Creek (0.65) where discharge and velocity were high. Lowest transient storage was in Crump Creek (0.18) which exhibited high velocity and intermediate discharge. Neither site nor season was a significant predictor of variation in transient storage; site was a significant predictor of variation in discharge, whereas both were significant predictors of water velocity. Thus, statistical analyses suggest that seasonal and inter-site differences in water velocity were more consistent than those for discharge or transient storage.

Physical-chemical. During the period of study, stream temperature ranged from 5° to 30 °C and season was found to be a significant predicator of variation in temperature (Table 2). Inter-site differences in temperature were small by comparison (range of means = 15.4° to 17.3°) and were not significantly different (Figure 2a). Variation in incident solar radiation followed expected trends based on preliminary data collected in fall 2007. Incident PAR differed by 3-fold among sites with Courthouse exhibiting the lowest average value (135 $\mu E\ m^{-2}\ s^{-1}$) and Herring the highest (395 $\mu E\ m^{-2}\ s^{-1}$; Figure 2b). Site was a highly significant predictor of variation in PAR ($p = 0.005$) whereas season was only marginally significant ($p = 0.06$). Seasonal variation in PAR was most apparent at the heavily shaded site (Courthouse) where highest values occurred in April (ca. 350 $\mu E\ m^{-2}\ s^{-1}$) and declined to less than 100 $\mu E\ m^{-2}\ s^{-1}$ by May. Two other sites exhibited clear maxima prior to leaf-out (Herring – March; Powell – April) whereas Crump did not exhibit any clear seasonal trend.

Crump and Courthouse Creeks had the highest average values of SRP and were 2-fold greater than Powell and Herring Creeks. However, inter-site differences were not statistically significant (Table 2). Season was a significant predictor for site with highest concentrations at all sites occurring in summer months (Figure 2c). On the other hand, both site and season were significant predictors of variation in DIN (Table 2). DIN concentrations were greatest at Crump Creek (0.477 mg/L) and Courthouse Creek (0.467 mg/L) and were lowest at Herring Creek (0.083 mg/L) and Powell Creek (0.124 mg/L). At the high DIN sites (Crump and Courthouse Creeks) peak concentrations occurred during the winter and dropped 3-4-fold in summer (Figure 2d). The low DIN sites did not exhibit

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consistent seasonal patterns and thus there was a significant interaction effect between site and season. At the high DIN sites, nitrate was the dominant N fraction with ammonia contributing less than 20%. Thus seasonal and inter-site differences for NO_3^- followed patterns described for DIN. At the low DIN sites, ammonia contributed a greater proportion of DIN (ca. 30-50%; Table 2).

Benthic Materials. Neither site nor season was a significant predictor of fine benthic detrital matter (FBDM) as well as for mass of carbon (FBCM) and nitrogen (FBNM; Table 2). Mass of FBDM was greatest at Powell and Courthouse Creeks (300-500 g/m^2) and was lowest at Crump and Herring Creeks (200-300 g/m^2). FBDM was variable throughout the study with a small spring peak for Crump and Powell Creeks and a 2-fold increase during the summer at Powell Creek (Figure 3a). Inter-site differences in the mass of C and N in benthic materials generally followed trends in FBDM with the exception of Herring Creek. Sediments at this site were particularly rich in C relative to other sites (mean = 6.2 % vs. 3.0-3.5%, respectively) as well as N (0.58% vs. 0.22-0.28%, respectively). Thus site was a highly significant predictor of variation in C% and N% (p < 0.0001 for both). Due to its higher C and N content, the mass of C and N in benthic sediments was higher relative to Courthouse and Crump Creeks despite lower FBDM. Although the C and N content of benthic materials was constant across sites and was strongly related among all sites (R^2 = 0.95; Figure 3b) the N content of Herring Creek sediments was disproportionately high relative to C. Thus, the molar relationship between carbon and nitrogen differed among sites (p < 0.0001) with lowest values at Herring Creek

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(mean C:N = 9.3) and higher values at the other three sites (range of means = 10.8 to 12.1; Table 2).

Metabolism -

Diel Dissolved Oxygen. Significant inter-site differences in diel dissolved oxygen amplitudes were found among the four streams. Average DO amplitudes were greatest at Herring Creek (1.56 mg/L) and Powell Creek (1.76 mg/L) and lowest at Courthouse Creek (0.99 mg/L) and Crump Creek (1.04 mg/L). Site was a significant predictor of DO amplitude (p = 0.048) as was season (p = 0.0007; Table 2). DO amplitudes peaked during the spring when incident light was greatest prior to leaf emergence (Figure 4a). After leaf emergence, DO amplitude concentrations steadily declined. At Herring Creek a second peak was observed in the summer months (June-August).

Production and Respiration. Despite no inter-site differences in P, site predicted variation in R (p = 0.03). Subsequently, season was a significant predictor of P (p = 0.02) but was not a significant predictor for variation in R (Table 2). P was greatest at Powell Creek (4.12 g O_2 m^{-2} d^{-1}) and Herring Creek (3.07 g O_2 m^{-2} d^{-1}) and was lowest at Crump Creek (1.16 g O_2 m^{-2} d^{-1}) and Courthouse Creek (0.87 g O_2 m^{-2} d^{-1}; Figure 4b). Herring Creek (16.95 g O_2 m^{-2} d^{-1}) and Powell Creek (14.8 g O_2 m^{-2} d^{-1}) had the greatest R and Courthouse Creek (13.17 g O_2 m^{-2} d^{-1}) and Crump Creek (7.82 g O_2 m^{-2} d^{-1}) had the lowest R (Figure 4c). P and R were lowest during the winter and summer at all sites except for Herring Creek. Variation in P and R for Herring Creek had the same pattern as DO amplitude; during the summer these rates returned to rates seen before leaf emergence.

Estimated re-aeration rates were greatest at Crump Creek, the shallowest study site, and there was no inter-site variation or seasonal variation for re-aeration (Table 2). Gross primary production (GPP; the sum of P and R), however, showed significant inter-site variation ($p = 0.007$) and variation in GPP was not predicted by season ($p = 0.09$; Table 2). Of the four sites, Crump Creek ($8.98 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$) had the lowest GPP and Powell Creek had the greatest ($18.94 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$). In a comparison of the ratio between P and R (P:R), all sites were heterotrophic, with Courthouse Creek being the most heterotrophic (0.04) and the Powell Creek value being closest to 1 (Table 2). There were no significant differences in site P:R ratios, but season was a significant predictor of variation in P:R ($p = 0.05$; Table 2).

In supplementary examinations of DO amplitude and the occurrence of DO maximums and minimums, significant differences occurred in the timing of DO maximum (minimum DO deficit) at Powell and Crump Creeks ($p = 0.005$). The DO minimum (maximum DO deficit) timing was not found to be different between any sites (Figure 5). When DO amplitude was compared to independent variables, Chlα ($R^2 = 0.72$, $p = 0.008$) and DIN ($R^2 = 0.57$, $p = 0.03$) were significant predictors of variation in DO amplitude at Herring Creek but were not drivers at other sites (Figure 6a and c). Light, however, was a significant driver at Powell Creek ($R^2 = 0.86$, $p = 0.001$; Figure 6b).

P was greatest at Herring and Powell Creeks where significant relationships were observed between DO amplitude and parameters. However, when P was compared to independent variables, no relationships were found between expected parameters (DIN and PAR; Figure 7a and b). A relationship was found between P and DO amplitude and the

two were significantly correlated ($R^2 = 0.56$, $p < 0.0001$; Figure 7c), as well as for R and DO amplitude and GPP and DO amplitude, when data were pooled for all sites (R: $R^2 = 0.24$, $p = 0.004$; GPP: $R^2 = 0.41$, $p < 0.0001$). When R was compared to independent variables, no significant correlations were found between R and temperature, FBDM, or transient storage (Figure 8).

In a comparison of mean values for P, R, DO amplitude, PAR, and transient storage, Herring and Powell Creeks had the greatest values when compared to Courthouse and Crump Creeks (Figure 9). DIN mean values were greatest for Courthouse and Crump Creeks as expected and lowest for Herring and Powell Creeks. FBDM showed no differences between sites and contrasting paired sites comparisons where Courthouse Creek and Powell Creek had the greatest means and Crump and Herring Creek had the lowest means. Velocity also had contrasting pairs where mean values were comparable at Herring, Powell, and Crump Creeks and was lowest at Courthouse Creek (Figure 9).

CHAPTER 4 Discussion

My results suggest that the amount of light reaching coastal plain streams is more important at influencing stream metabolism than the effect of nutrient availability, thus supporting my first hypothesis. I presume that similarities between P and R of sites were a result of analogous biological demands for light and nutrients by stream autotrophs. Other similarities in hydrology and organic matter between sites are due to the same geographical region. I predicted that light levels would influence stream metabolism rates according to season and in streams with relatively low DIN levels because of the greater energy demands by autotrophic biosynthesis in relation to the demand of nutrients.

Methodology. The open-system one-station method has been used for many studies to estimate metabolism using diel changes in dissolved oxygen (Odum, 1956; Marzolf et al., 1994; Young and Huryn, 1996 and 1999; Mulholland et al., 2001 and 2005). This method had not been used in the coastal plain of Virginia and provided comparable values for these experiments conducted on shaded and unshaded streams of this study. Diel DO profiles were also useful indicators for comparisons of metabolism across sites. Re-aeration measurements were determined using an empirical equation incorporating slope, depth, and velocity that provided comparable values for K as suggested by Moog and Jirka (1998), in spite of the potential for under- or over-estimation of metabolism rates as proposed by Genereux and Hemond (1992) and Mulholland et al. (2001). Despite the

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inability to directly measure re-aeration rates through volatile gas tracer injections that are costly and time consuming, the re-aeration rates determined were < 100 day^{-1} at all sites and are in the ranges observed by other studies, for example Young and Huryn (1996; 1-255 K_a 1/d) and Wilcock et al. (1998; 0.5 - 40 K_a 1/d). The P rates ranged from $<1 - 10.1$ g O_2 m^{-2} d^{-1}and were similar to those found by Marzolf et al. (1994; 0.1 -1.7 g O_2 m^{-2} d^{-1} and Young and Huryn (1996; 0.5-3.6 g O_2 m^{-2} d^{-1}). In addition, R estimates ranged from $4.5 - 20.9$ g O_2 m^{-2} d^{-1} and fell amongst typical stream values such as those from Wilcock et al. (1998; $3.5 - 55$ g O_2 m^{-2} d^{-1}), Wiley et al. (1990; $6.2 - 42$ g O_2 m^{-2} d^{-1}) and Mulholland et al. (2001; > 2 - >10 g O_2 m^{-2} d^{-1}). These estimates suggest that the extreme value method established by Wang et al. (2003) is a suitable method and shows consistent and comparable results to other research.

Metabolism. My results indicate that light is the primary driver of metabolism in coastal plain streams. Streams that received more light had higher rates of P, R, and DO amplitude than more shaded streams. In addition, P, R, and DO amplitude peaked during the spring and decreased after leaf emergence, similar to observations by Hill et al. (2001). These rates did however, increase at the end of summer in Herring Creek but not at the other sites. P rates potentially could have been influenced by benthic substrates that varied by site, similar to a study that examined how velocity and sediment disturbance had an effect on P (Tett et al., 1978; Biggs et at. 1999). Biggs et al. (1999) found that production and chlorophyll biomass were greater in streams with more stable substrate, particularly during the summer, than in streams with unstable substrate and frequent high velocities. Herring Creek had the most stable substrate and the greatest chlorophyll biomass of all

sites, which likely caused the higher P rates and diel DO amplitudes. However, the substrate at Powell Creek was sand and despite this unstable substrate had the highest P rates and the second greatest chlorophyll biomass of all sites. According to Biggs et al. (1999) streams with infrequent high velocities and unstable substrate had the highest P rates during the summer, consistent with results from Powell Creek.

In other studies, high algal productivity in streams is related to light intensity; however, when light is limited, algal growth is positively correlated with nutrient concentrations (McTammany et al., 2007). McTammany found that agricultural streams with higher light and nutrient levels had greater chlorophyll content in comparison to recovery watersheds that had reduced primary production due to reforestation. Light appeared to be the main driver of GPP in both the agricultural and recovered streams studied and DIN was only weakly correlated to GPP (McTammany et al., 2007). There was no statistically significant correlation between P and DIN at all sites; however, diel DO at Herring Creek was positively correlated with DIN and Chlα and at Powell Creek diel DO was positively correlated with light. These results suggest a strong relationship between the production of oxygen and light as well as nutrients for some of but not all of my sites. Turbidity and shading explained 77% of the variation in P during the summer growing season in a study of agricultural prairie streams by Wiley et al. (1990). Wiley et al. (1990) also found that when neither N nor SRP could be associated with P, nutrient constraint was inconsequential, suggesting that the supply of nutrients to those streams was insignificant if no relationship existed between nutrients and P. My results similarly

suggest that light had a greater effect on production rates than nutrients. Solar irradiance appeared to be the most significant factor in metabolic rates of coastal plain streams.

Unlike many other studies, temperature, quality of benthic materials, and hydraulics were not drivers of stream respiration for the streams we examined. My results do not suggest that these drivers significantly impact R rates despite the well known effect that nutrients and temperature have on microbial processes (Elwood et al., 1981; Bott et al., 1985; Edwards and Meyer, 1987; Izagirre et al. 2008). Previously cited studies did however collect measurements during all seasons, unlike the study I conducted, in which I sampled during only three seasons; nonetheless a wide range of temperature conditions was captured. Similarly, a lack of evidence to support the impact of temperature on R was also found in a study by Mulholland et al. (2001), suggesting that the effects of temperature on R may have been influenced by organic matter supply and nutrient concentration. In a study by Young and Huryn (1999), on streams of varying land use types, organic matter supply and retention contributed to R rates that were magnitudes greater than seen at my study sites. However, the quality (C:N ratio) of the organic matter supply is more important than quantity as seen by Bonin et al. (2000) and Fellows et al. (2006). Herring Creek R rates were the greatest of all sites and that rate could be attributed to its having the lowest C:N ratios of the sites. Benthic materials might have had little influence on R rates due to shifting substrates and burying of materials as a result of disturbance in some of the streams, similar to what was seen by Houser et al. (2005) at Fort Benning Military Reservation (Georgia). R rates were greatest in the winter and spring in my study except at Herring Creek where R increased during the summer. Houser et al.

(2005) also observed greater R in winter and spring that they attributed to increased lability of organic matter. Besides benthic materials, hyporheic and transient storage zones also have an effect on R and in a study by Mulholland et al. (2001), the size of the transient storage zone predicted 17% of the variation in R. My results however do not suggest a correlation between R and transient storage or between temperature and benthic materials. Bott et al. (2006) also did not find a significant relationship between transient storage and respiration, concluding that hyporheic respiration did not make significant contributions to total respiration.

The P: R ratios observed in my study suggest the importance of allochthonous sources of carbon in coastal plain streams of Virginia (Vannote et al., 1980; McTammany et al., 2003; Fellows et al., 2006). Respiration was greater than production in all our streams and all ratios were very low (< 0.31). The river continuum concept (RCC) suggests that a shift in ecosystem metabolism from heterotrophic to autotrophic is characteristically dependent upon the amount of shading or light a stream receives (Vannote et al., 1980). In addition to a shift in light regimes, there is a shift from dependence on allochthonous to autochthonous materials, suggesting that in small streams organic matter fuels the food web and in larger rivers, primary production supplies energy (Vannote et al., 1980; McTammany et al., 2003). In regions that are forested, many studies have demonstrated support for the RCC (Bott et al., 1985; Mulholland et al., 2001; Iwata et al., 2007); streams in the Virginia coastal plain are also heterotrophic as expected. Despite higher levels of light at several of the sites that were significant to autotrophy, the streams' small size and close connection with the riparian zone maintained heterotrophy.

My results suggest that light is the most prominent driver of ecosystem metabolism in coastal plain streams and that nutrients are most likely the secondary determinant. Variation in ecosystem metabolism found among coastal plain streams is most likely due to the response of P and R to variation in environmental parameters (i.e. hydrology, physical parameters, chemistry, and benthic materials); nonetheless, estimated values are comparable to other studies. My study of metabolism researched a region that had not yet been examined, providing an opportunity to explore the function of coastal plain streams in Virginia and their role in ecosystem processes for the Chesapeake Bay.

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Tables

Table 1. Geographic location, stream order, river drainage, stream chemistry, and watershed area for four streams located in the Virginia coastal plain. Channel widths and depths and chemistry are average values from monthly surveys.

	Stream Site			
	Courthouse	Crump	Herring	Powell
Geographic Setting				
Lat./Long.	37.335, -77.06139	37.703, -77.36419	37.311, -77.13583	37.244, -77.15442
River Drainage	James	York	James	James
Watershed				
Stream Order	2nd	2nd	3rd	3rd
Watershed Area (Sq. km)	23	33	48	51
Slope	0.667%	0.265%	0.283%	0.208%
Canopy	Closed	Semi-closed	Semi-closed	Semi-closed
Stream Characteristics				
Substrate	Cobble/sand	Sand	Cobble	Sand
Width (m)	3.59	4.44	5.34	4.95
Depth (cm)	21	15	27	25
Stream Chemistry				
pH	6.79	6.35	6.11	7.24
Specific Conductance (μS/cm)	85.98	57.76	84.13	182.18
DOC (mg/L)	4.2	4.3	9.2	3.8
Alkalinity (mg $CaCO_3$/L)	27.3	9.1	30.9	69.5

Table 2. Means and ranges for hydrological, physical, chemical and metabolic parameters of four streams located in the Virginia Coastal Plain. Statistical results are from a 2-way ANOVA using stream, season, and the interaction of stream and season as model components.

| | Stream Site | | | | Statistics: p, df =3,28 | | |
Means ± SE or (range)	Courthouse	Crump	Herring	Powell	Stream	Season	Stream*Season
Hydrology							
Discharge (L/s)	44.1 ± 10.5	100.9 ± 23.4	216.1 ± 52.1	211.3 ± 50.6	0.01	0.08	0.9
Velocity (m/s)	0.058 ± 0.009	0.212 ± 0.014	0.149 ± 0.031	0.215 ± 0.028	0.0002	0.03	0.3
Transient Storage (K1/K2)	0.328 ± 0.062	0.183 ± 0.054	0.369 ± 0.056	0.648 ± 0.318	0.8	0.4	0.5
Physical Parameters							
Light/Irradiance (μE m^{-2}s^{-1})	134.6 ± 14.1	287.0 ± 30.1	394.8 ± 44.1	299.3 ± 46.5	0.005	0.06	0.4
Temperature (C°)	16.37 (5.6-26.1)	15.42 (8.6-23.9)	17.3 (4.0-30.5)	17.26 (8.6-26.2)	0.7	< 0.0001	0.4
Chemistry							
NO_3 (mg/L)	0.437 ± 0.054	0.390 ± 0.025	0.032 ± 0.008	0.097 ± 0.009	< 0.0001	0.04	0.1
NH_4 (mg/L)	0.041 ± 0.006	0.064 ± 0.005	0.037 ± 0.006	0.013 ± 0.004	0.0003	1.0	0.4
DIN (mg/L)	0.467 ± 0.089	0.477 ± 0.052	0.083 ± 0.014	0.124 ± 0.021	< 0.0001	0.008	0.004
P-SRP (mg/L)	0.058 ± 0.006	0.046 ± 0.003	0.023 ± 0.003	0.027 ± 0.008	0.9	0.04	1.0
Benthic Materials							
FBDM (g/m^2)	314.96 ± 50	266.26 ± 45	203.92 ± 54	497.40 ± 156	0.08	0.1	0.5
FBCM (gC/m^2)	11.10 ± 1.94	7.22 ± 1.42	12.47 ± 2.29	16.58 ± 6.44	0.4	0.1	0.7
FBNM (gN/m^2)	0.85 ± 0.14	0.49 ± 0.16	1.17 ± 0.20	1.21 ± 0.40	0.3	0.1	0.5
FBDM C%	3.54% ± 0.22%	3.03% ± 0.22%	6.21% ± 0.47%	2.96% ± 0.27%	<0.0001	0.02	0.5
FBDM N%	0.28% ± 0.02%	0.22% ± 0.02%	0.58% ± 0.05%	0.24% ± 0.02%	<0.0001	0.03	0.08
C:N Molar	10.94 ± 0.31	12.06 ± 0.32	9.31 ± 0.28	10.85 ± 0.53	<0.0001	0.08	0.08
Metabolism							
P (g O_2 m^{-2} d^{-1})	0.87 ± 0.93	1.16 ± 0.16	3.07 ± 0.38	4.12 ± 0.56	0.1	0.02	0.3
R (g O_2 m^{-2} d^{-1})	13.17 ± 6.55	7.82 ± 6.18	16.95 ± 14.36	14.8 ± 0.56	0.004	0.4	0.7
K_2 (1/d)	30.24 ± 2.93	45.96 ± 2.56	31.38 ± 4.19	31.40 ± 3.18	0.4	0.8	0.05
GPP (g O_2 m^{-2} d^{-1})	14.04 ± 1.51	8.98 ± 0.56	20.02 ±0.91	18.94 ± 0.9	0.007	0.09	0.5
P:R	0.04 ± 0.08	0.14 ± 0.12	0.18 ± 0.03	0.27 ± 0.04	0.3	0.05	0.4
0_2 amplitude (mg/L)	0.99 ± 0.28	1.04 ± 0.27	1.56 ± 0.23	1.76 ± 0.32	0.048	0.0007	0.04
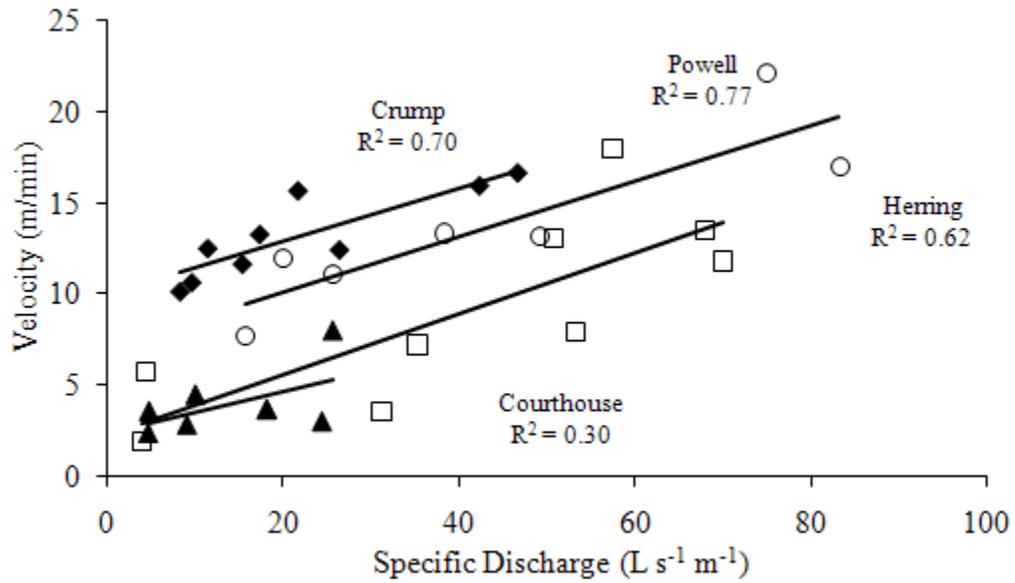
Figure 1. Relationships between stream water velocity and specific discharge determined from monthly injection experiments for four Virginia coastal plain streams.
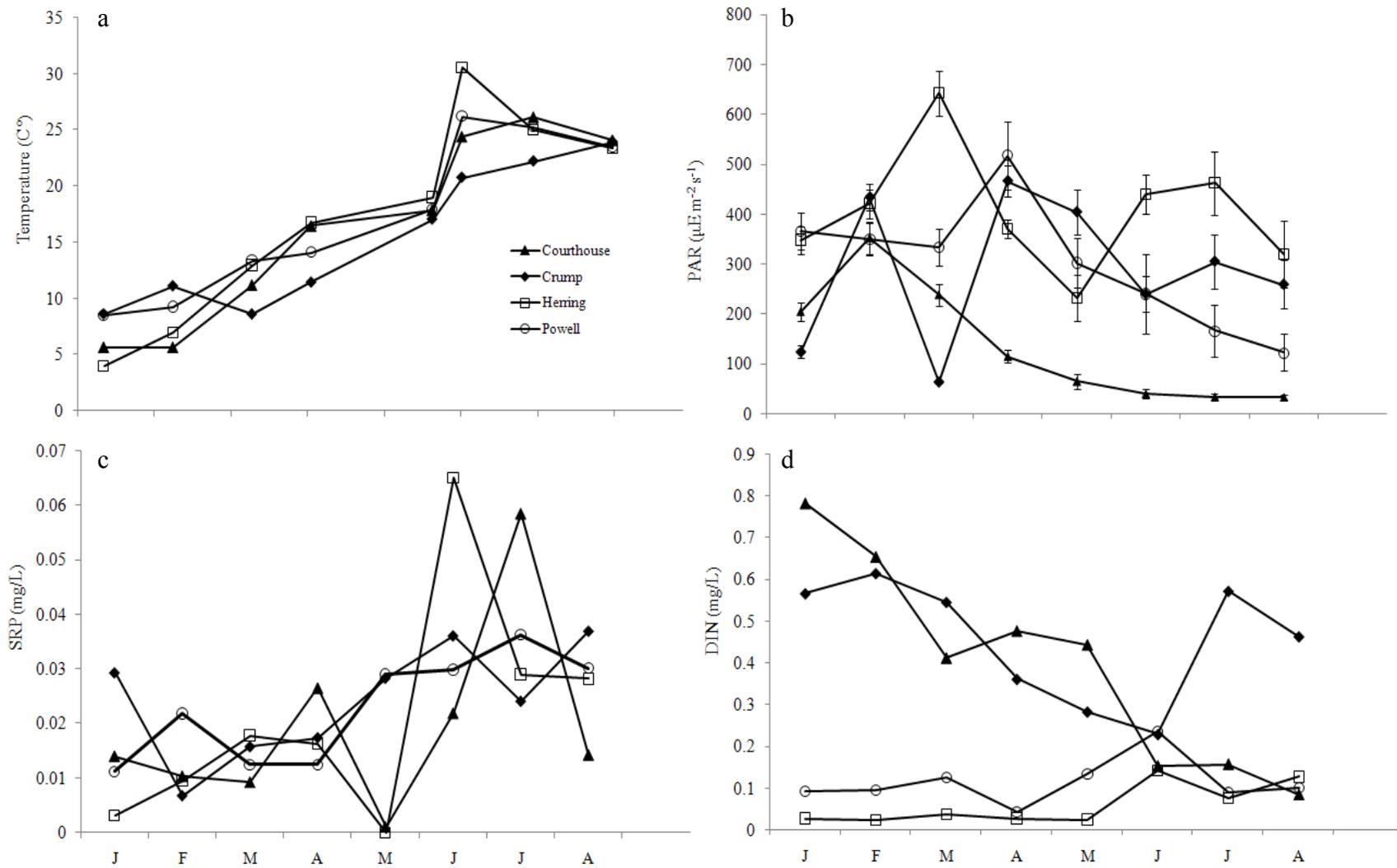
Figure 2. Seasonal variation in temperature (a), incident solar radiation (PAR) (b), SRP (c), and DIN (d) for four Virginia coastal plain streams during January to August 2008. .
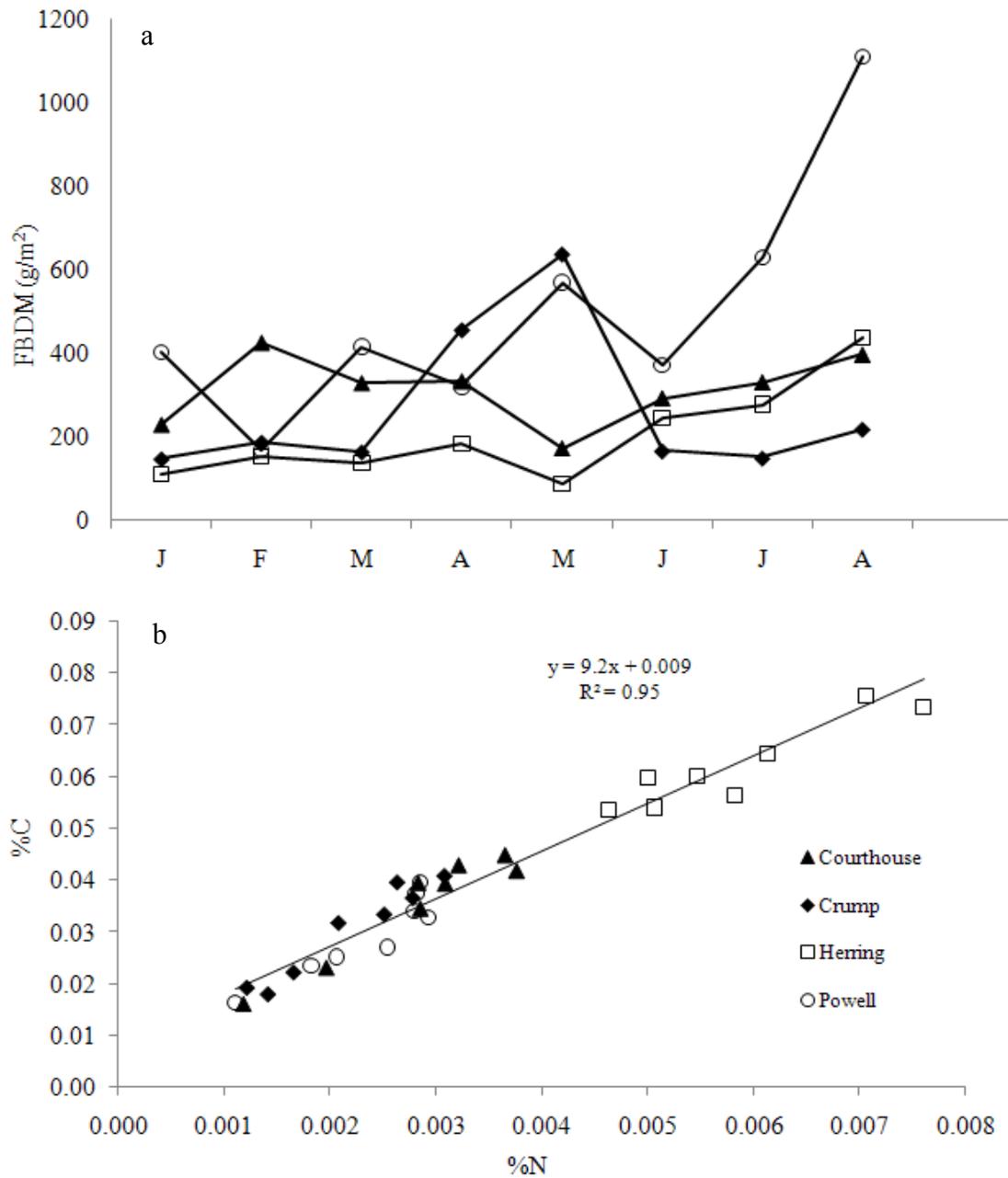
41

Figure 3. Seasonal variation in fine benthic materials (a) and the lability of the benthic materials

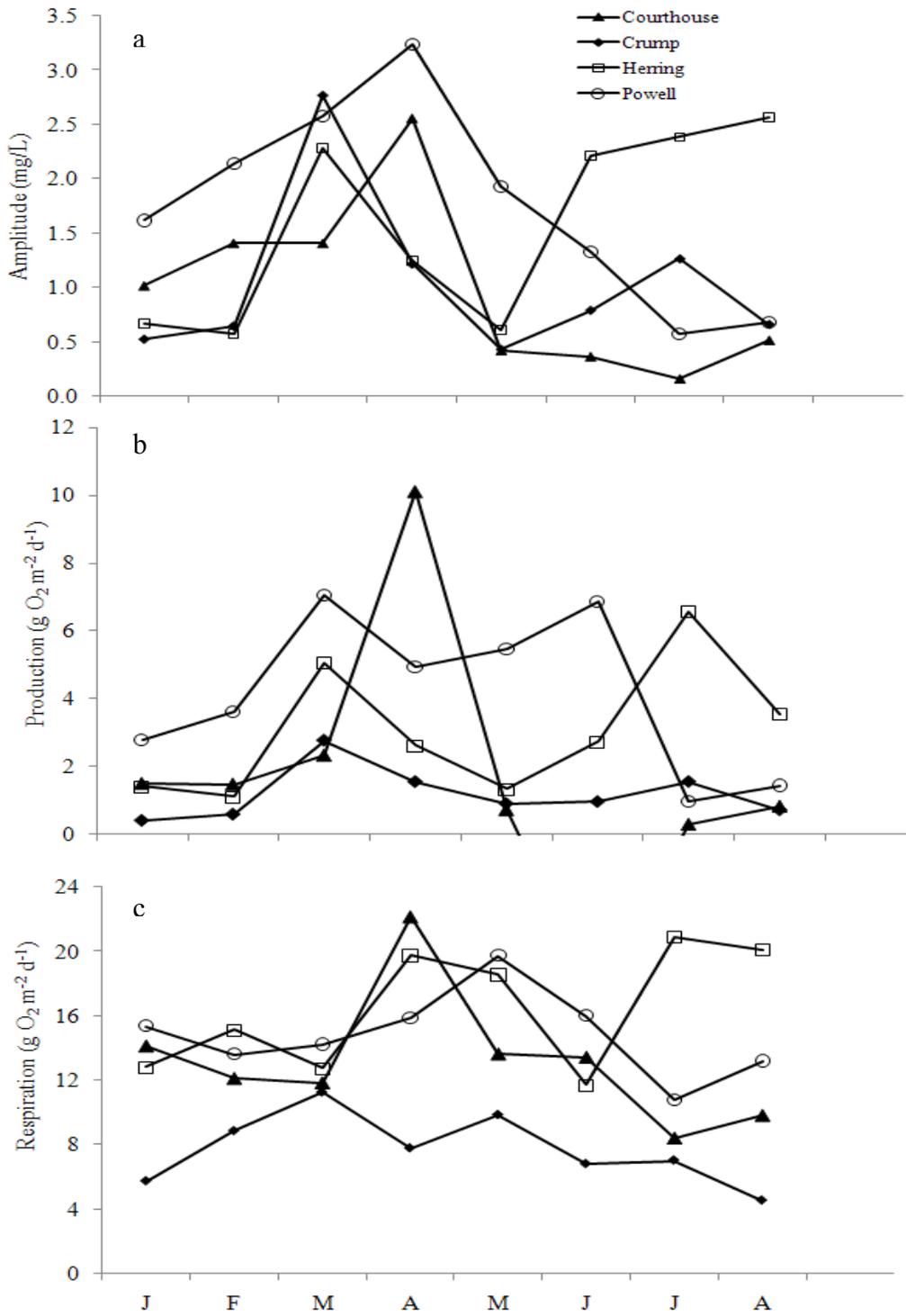(b) based on monthly measurements from January to August 2008.

Figure 4. Seasonal variation in DO amplitudes (a), production (b) and respiration (c) for four

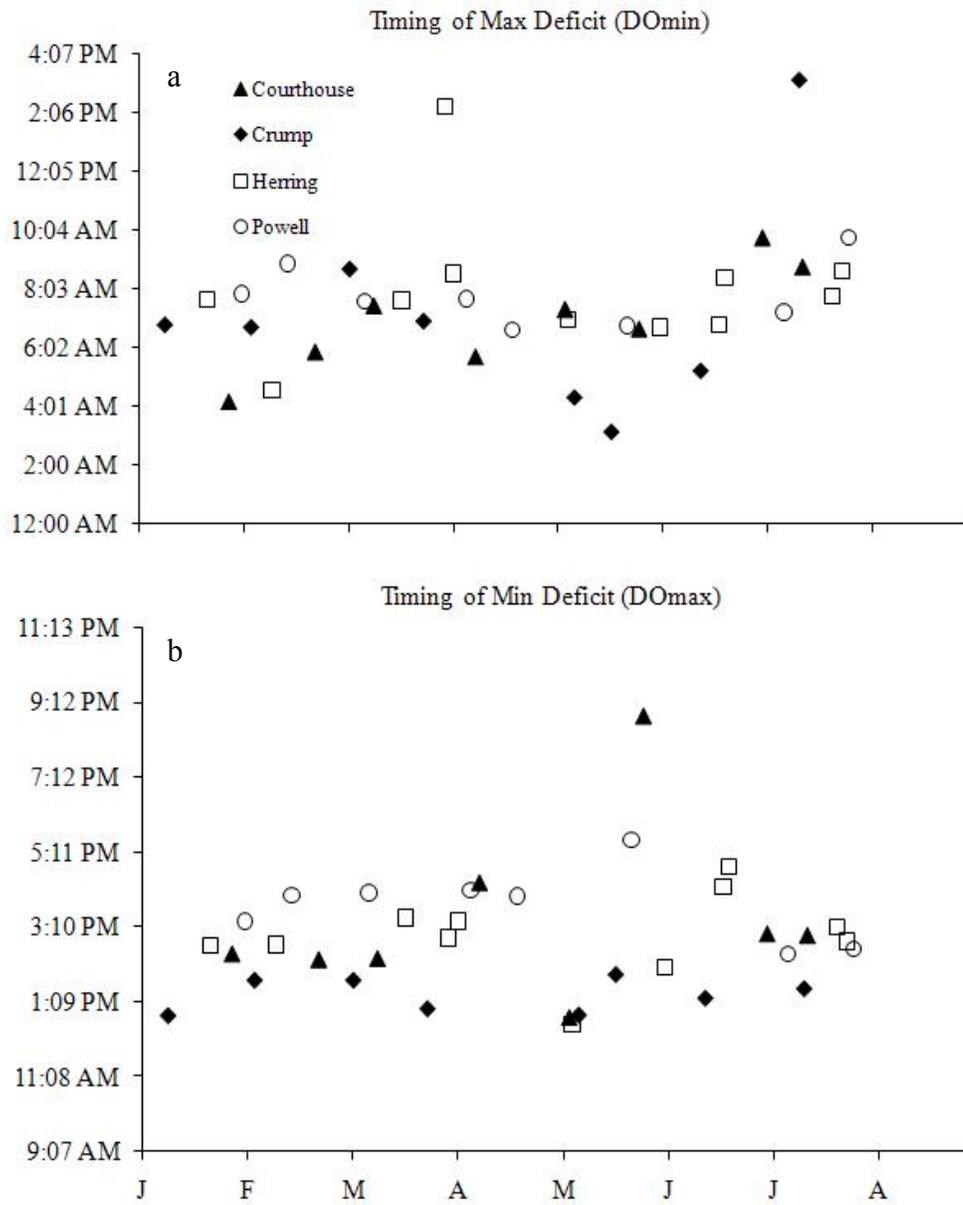VA Coastal Plain Streams during January to August 2008.

Figure 5. Patterns of DO amplitude minimums (a) and maximums (b) for four VA Coastal Plain
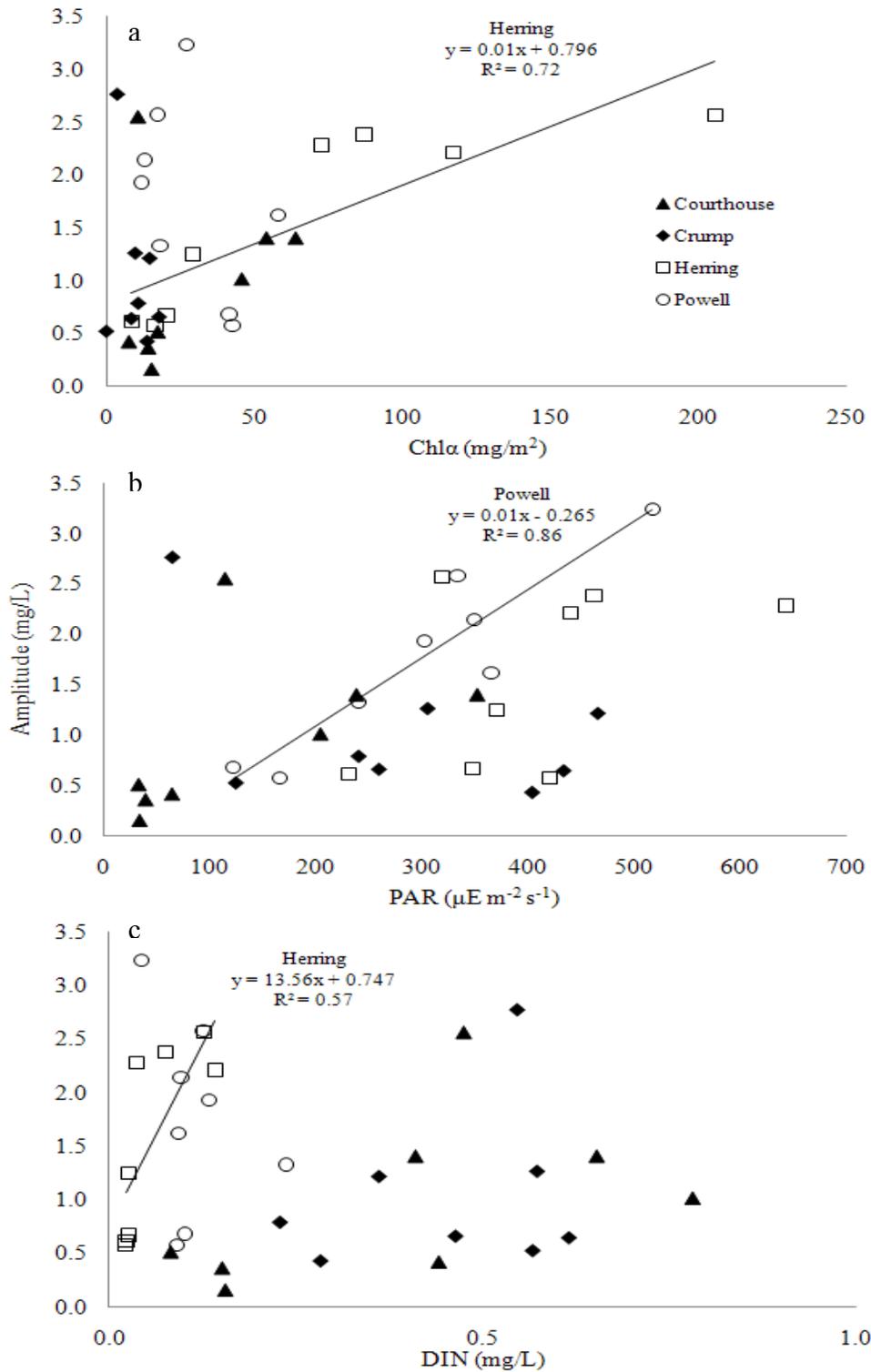Streams during January to August 2008.

Figure 6. Relationships between DO amplitudes and (a) benthic chla, (b) incident solar radation (PAR), and (c) dissolved inorganic nitrogen (DIN) for four Virginia Coastal streams. Regression lines shown where significant relationships were observed. Chlα data from M. Brandt thesis.
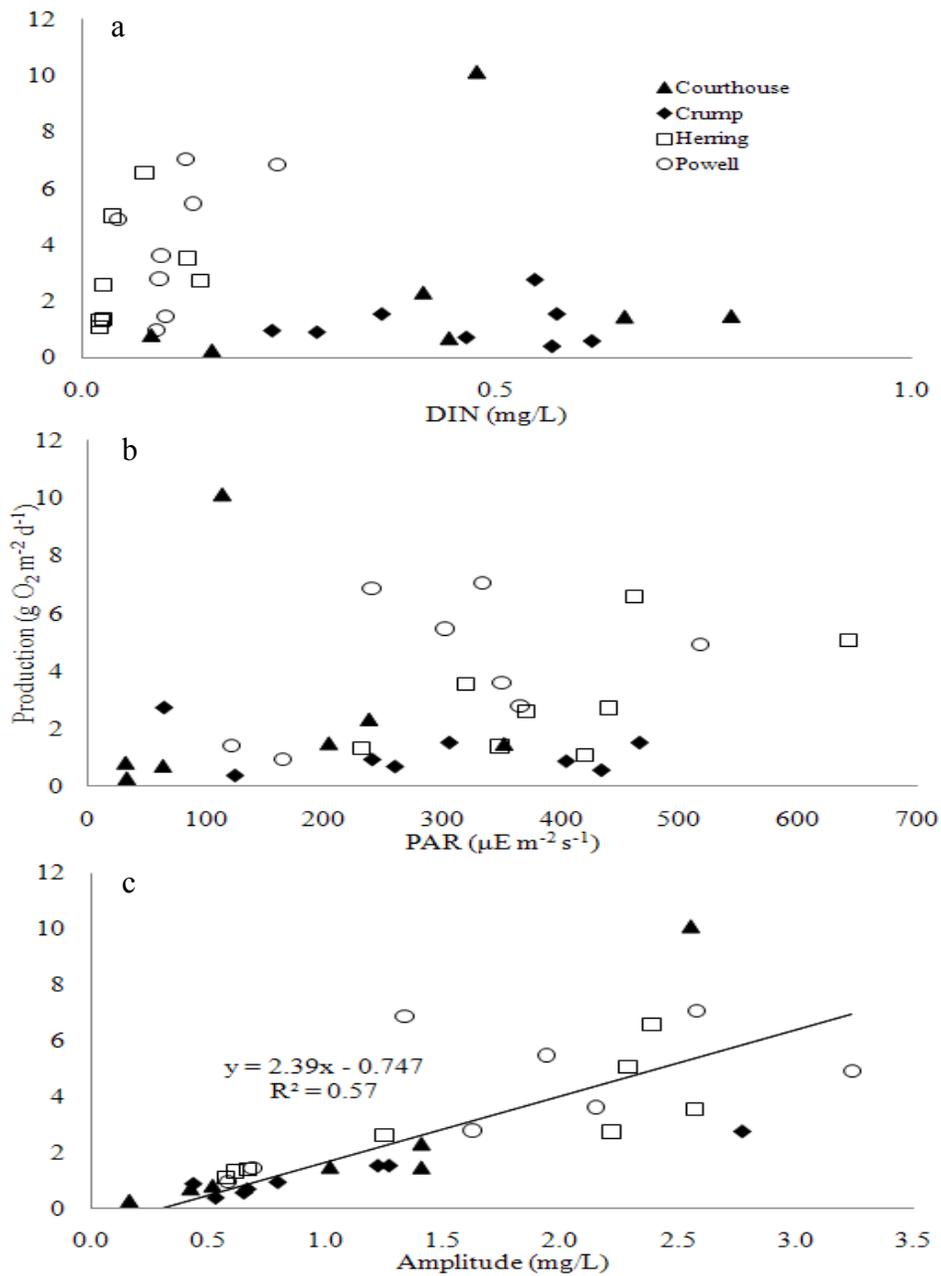
Figure 7. Relationships between production and (a) dissolved inorganic nitrogen (DIN), (b) inciden solar radation (PAR), and (c) diel DO amplitude in four Virginia Coastal streams. Regression line shows that a statistically significant relationship was observed for all sites.
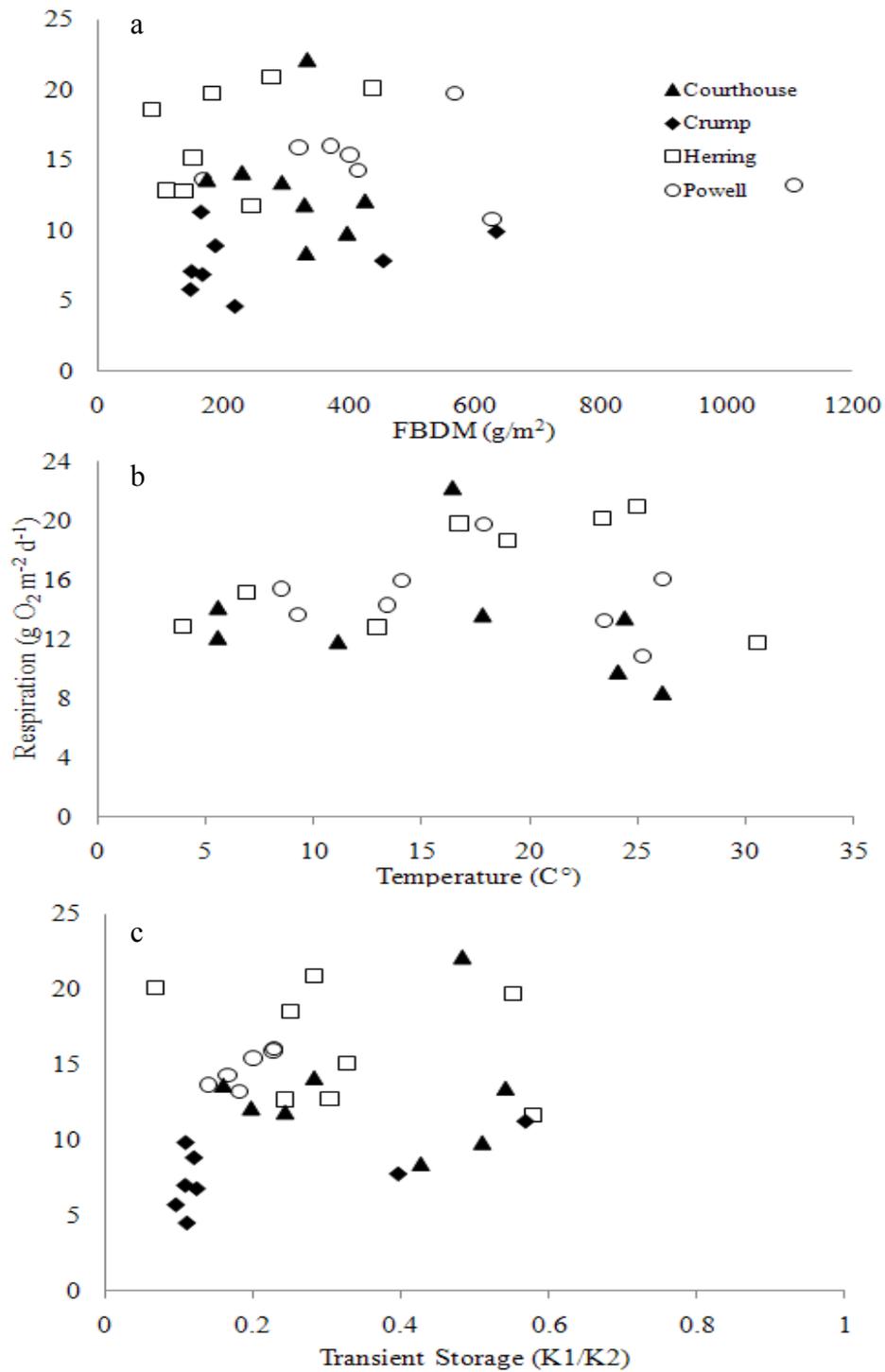
Figure 8. Relationships between respiration and (a) fine benthic detrital matter (FBDM),

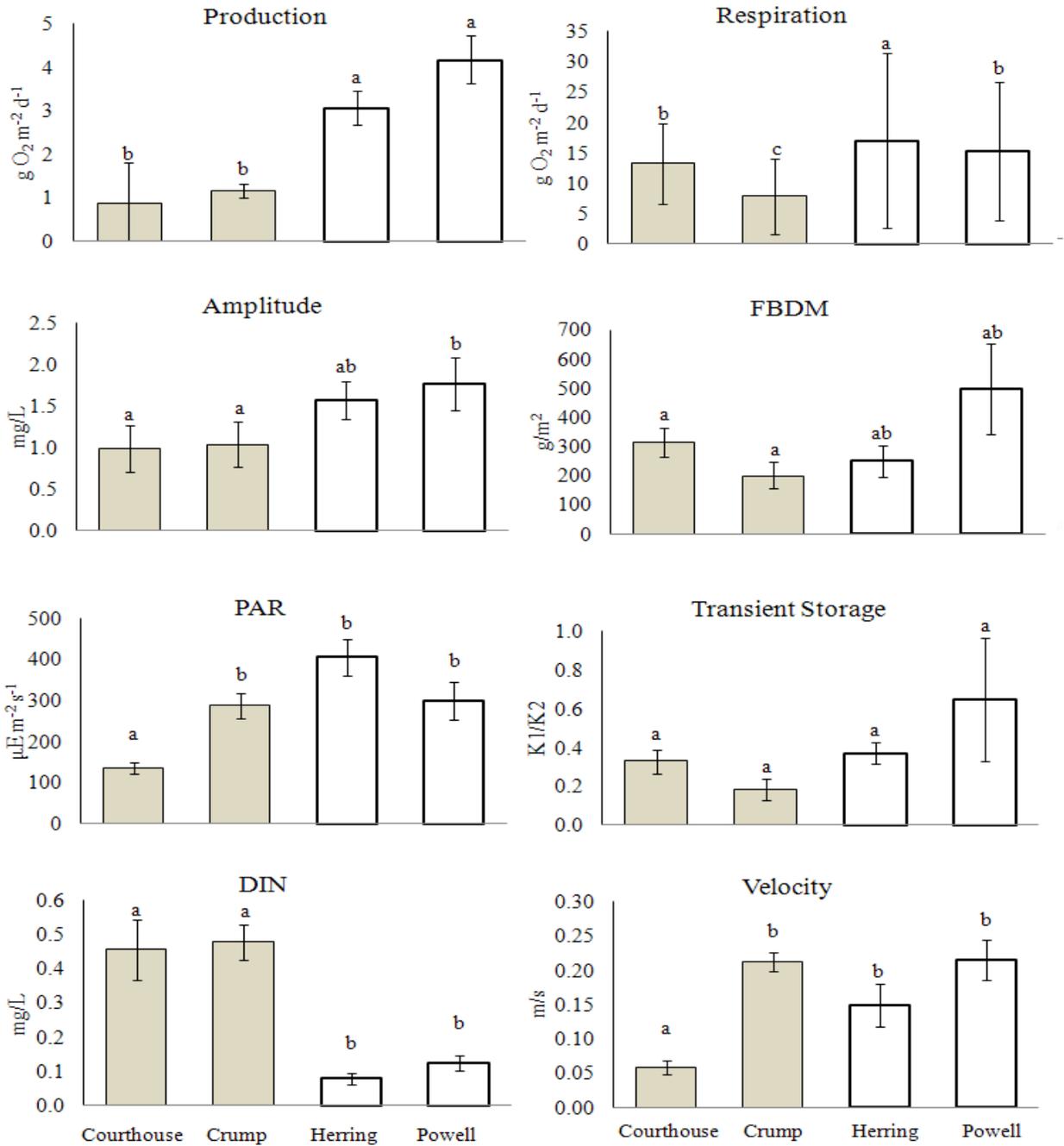(b) temperature, and (c) transient storage in four Virginia Coastal streams.

Figure 9. Mean values of production, respiration, diel O_2 amplitude, FBDM, light, transient storage, DIN and among four Virginia Coastal Plain Streams. Means are based on monthly measurements from January to August 2008.

Site	FBDM (g/m^2)		FBCM (g C/m^2)		FBNM (g N/m^2)		FBDM C%		FBDM N%		C:N Molar		Chlα (mg/m^2)	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Upstream Herring Creek	245	87	14.7	4.66	1.62	0.48	0.073	0.013	0.008	0.001	7.55	0.21	112.58	31.14
Fish Hatchery Ponds	993	202	92.7	24.59	7.68	1.76	0.099	0.020	0.009	0.002	10.30	1.69	254.86	50.06

Table 1. Fine benthic materials were collected in June 2008 at an upstream location on Herring Creek as well as several ponds adjacent to the study research at U.S. Fish and Wildlife Service, Harrison Lake National Fish Hatchery. Five ponds were sampled closest to the study reach and six samples were collected upstream of the study reach below the Harrison Lake dam; samples were collected to compare and possibly determine the source of the quality and quantity of benthic materials of the study reach. The mass of fine benthic materials upstream were similar to those of the study reach, however, a small increase in carbon and nitrogen content resulted in a lower C:N ratio upstream. Benthic materials (mass and nutrient content) were magnitudes greater in the fish hatchery ponds yet the quality of the matter was poor (4% increase in C content), resulting in a higher C:N ratio. The C:N ratio of the study reach was 9.31, just slightly above the average of the ponds and upstream location. Chlα at the upstream location was less than 2-fold greater than the study reach whereas the ponds were more than 3-fold greater in algal biomass. The availability of nutrients and unlimited supply of light most likely drives algal biomass levels in the ponds and the quality of benthic materials at the upstream site is most likely driving algal biomass. These data do not suggest a primary source of nutrients to the study reach, however, the benthic nutrient content and mass most likely have an effect on the quality and quantity of fine benthic materials at the study site on Herring Creek.

VITA

Julie E. Frank was born in Fairfax, Virginia on July 7, 1982. She graduated from Ad Fontes Academy in 2001 and attended Virginia Polytechnic Institute and State University. During her time at Virginia Tech, she conducted an undergraduate research project on the importance of hemlock wood input into stream ecosystems, under guidance by Dr. Jack R. Webster. She was also a laboratory assistant for the Virginia Tech Stream Team and gained further experience assisting the team with many research projects at and near Coweeta Hydrological Laboratory, LTER (NC). In 2006, she graduated with two Bachelors of Science in Biology and Psychology. After which, she perused a graduate career at Virginia Commonwealth University, in the River and Ecosystem Ecology Laboratory, under direction of Dr. Paul A. Bukaveckas. Julie was funded by grants and graduate teaching and research assistanceships and was a teaching assistant for Stream Ecology and taught biology laboratories. She also was involved with several environmental outreach programs for local schools. Her teaching experiences continued at Piedmont Virginia Community College (PVCC) where she taught biology laboratory and worked with special needs students. In the summer of 2009, will be working at Stroud Water Research Center in the Ecosystems Laboratory for Dr. J. Denis Newbold. She also plans to work on a manuscript for publication and in the fall she will continue teaching at PVCC. She hopes to continue to develop her academic and teaching career in ecological sciences.