

To model or measure: Estimating gas exchange to measure metabolism in shallow, low-gradient stream habitats

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Abstract: Stream metabolism is an important metric of ecosystem function. Accurate estimates of gross primary production (GPP) and respiration (ER) are based on metabolism models that require estimates of gas transfer rates at the surface–water interface. When the gas exchange rate K (d^{-1}) is measured directly from the environment, it can be used with dissolved O_2 data to estimate GPP and ER. However, inverse modeling methods can also be used to solve for GPP, ER, and K simultaneously. Estimates of K from inverse models have rarely been compared to direct estimates of K . Additionally, the effects of the method used to estimate K on estimates of ecosystem metabolism are unknown. We compared these methods in shallow, low-gradient, open-canopy experimental streams under a range of hydrologic conditions with (vegetated) and without (unvegetated) instream vegetation. The different methods gave similar results for K estimates in vegetated streams. In unvegetated streams, however, inverse modeling methods that simultaneously estimated K with GPP and ER gave higher K estimates than did our direct measurements. When K was modeled rather than measured, metabolism estimates were higher in unvegetated streams, and model fits struggled to replicate dissolved O_2 data. The different methods of estimating K resulted in similar metabolism estimates within vegetated streams. However, the linear relationships between ER and GPP were not significantly different among methods of estimating K for vegetated or unvegetated streams. This study demonstrates that in shallow, low-gradient, open-canopy streams, particularly those with high GPP and low K , practitioners can use inverse modeling approaches to estimate K . Estimates in unvegetated systems, which have lower GPP, may be hindered by uncertainty in measured K in low gas transfer environments or by process errors within existing models.

Key words: Bayesian, emergent vegetation, dissolved oxygen, gross primary production, respiration

Gross primary production (GPP) and respiration (ER) are fundamental processes that produce and consume oxygen (O_2) in aquatic environments, thereby enabling the presence and growth of aquatic organisms (Odum 1956, Connolly et al. 2004). GPP and ER are integral drivers of elemental cycling, including C, N, and P (Christensen et al. 1990, Cohen et al. 2013, Hensley and Cohen 2016). Vegetation in aquatic systems, especially vascular plants, can amplify the amount of dissolved O_2 within a given habitat and even increase gas flux (F) across the air–water interface (Caraco et al. 2006). Thus, quantifying patterns in variation of O_2 and other dissolved gases can allow ecologists to calculate flows of energy and elements within aquatic ecosystems.

The flux of gas across the surface water–air interface strongly influences estimates of GPP, ER, and the subse-

quent flow of elements in aquatic ecosystems. This flux is the product of the velocity (k , m/d) of gas transferred across the air–water interface and the relative saturation of the water. For example, $F = k(\alpha C_{\text{air}} - C_{\text{water}})$, where C_{air} and C_{water} are the concentrations of gas in the air and water, and α is the unitless Ostwald solubility coefficient. Gas exchange velocities (k , m/d) are commonly put into or estimated by metabolism models as a daily rate (K , d^{-1}) (Hall et al. 2016). Quantifying K is challenging, and a variety of measurement and modeling methods have been used to estimate K for metabolism models.

There are several common methods used to estimate K . The most common approach to estimate K is direct measurement with tracer gas additions (Wanninkhof et al. 1990, Hall and Madinger 2018). In this approach, tracer gases are

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bubbled into the stream at a known rate, either as a pulse or to a plateau, and then the decline from the peak tracer concentration is measured. This technique relies on scaling relationships based on Schmidt number (Sc) ratios between tracer gases and O_2 (Jahne et al. 1987). In addition to direct measurements, we can also estimate K from either published empirical equations that relate gas exchange rates to physical characteristics of streams (Raymond et al. 2012) or inverse modeling approaches that use diel O_2 curves to simultaneously solve for K and other metabolic parameters, including GPP and ER (Holtgrieve et al. 2010, Grace et al. 2015, Hall et al. 2016). These modeling approaches rely on Bayesian principles (Gelman et al. 2013) and can use prior information to inform estimates or search for solutions with minimally-informed priors.

Direct comparisons of measured and modeled gas exchange rates and their influence on metabolism estimates are lacking. Riley and Dodds (2013) compared measurements of K to predictive equations for gas transfer rates in several streams and demonstrated that the best method depended on site and temperature (but see Demars et al. 2015). However, measured and modeled K have only been compared in a single river (Dodds et al. 2008). Thus, despite decades of stream ecology research, systematic evaluation of how different approaches bias measurements of gas exchange rates and the resulting influence on metabolism estimates remains elusive, even as metabolic regimes continue to be an active theme of research (McDowell 2015, Bernhardt et al. 2018). Direct comparisons of measured and modeled K estimates could better inform researchers of the sensitivity of metabolism estimates to estimation approaches as well as provide the opportunity to assess hybrid approaches.

Headwater streams are biogeochemical hotspots that exert considerable control over C and N cycles in stream networks, and, thus, influence water quality and ecological integrity at landscape scales (Peterson et al. 2001, Freeman et al. 2007, Roberts et al. 2007). Headwater stream systems appear in agricultural landscapes as channelized headwater streams, agricultural ditches, and natural drainages. Measurements of diel dissolved O_2 and associated metabolism estimates in small, agricultural streams can address important questions related to nutrient and organic matter processing in modified landscapes. These measurements can also address methodological questions related to measuring gas exchange in shallow, low-gradient systems with vegetation. However, biologically-driven O_2 production from the presence of vegetation can dominate diel dynamics, making precise measurements of K even more challenging. Further, ecosystem metabolic processes are positively correlated with autotrophic biomass (Bernot et al. 2010), and metabolic rates are influenced by the availability of organic matter, which can be readily acted upon in productive streams with in situ vegetation (Minshall 1978, Kaplan and Bott 1989, Webster and Meyer 1997, Bernhardt et al. 2018). The com-

plex interaction of the biological influences of vegetation on gas transfer kinetics and ecosystem metabolism makes investigating the effects of vegetation on K in small, open canopy streams well suited to experimental testing.

Here, we compare 3 methods based on either direct measurements or inverse modeled estimates of K to estimate GPP and ER in a set of vegetated and unvegetated experimental stream mesocosms with varying hydraulic residence times (HRTs). More specifically, these methods used 3 different variations of a Bayesian inverse modeling procedure: a minimally informed prior on K , an informed prior on K , and a set K method. The set K method equates to having perfect prior knowledge of the parameter, is based on direct measurement of gas exchange in the stream mesocosms, and estimates only GPP and ER within the model. We used each of these models with daily diel dissolved O_2 data collected over time in the same experimental streams to assess the influence of these different modeling approaches on daily ecosystem metabolic rates. Specifically, we asked the following questions: 1) How does K vary with differences in hydrology or vegetation? 2) How similar is K between measured and modeled methods? and 3) How do differences among methods of calculating K influence estimates of daily GPP and ER rates across a range of hydrologic and vegetation conditions?

METHODS

Study site

We used 6 flow-through experimental stream mesocosms located at the University of Mississippi Biological Field Station in Lafayette County, Mississippi (Fig. 1A). Each stream had a 0.34- m^3 headpool followed by a sequence of run, pool, run, pool sections. Each of these sections had a pre-sediment-addition volume of 0.91 m^3 . Thus, the total volume of each stream mesocosm was 3.96 m^3 before we added sediment substrates. We filled streams with ~5 cm of a mixture of Dundee silty loam and Sharkey clay soil typical of the nearby Mississippi Alluvial Plain region. The streams had similar volumes after the sediment addition (1.54–1.74 m^3 ; Table 1). Inflow water entered each stream through a PVC pipe at the main headpool and then flowed through the run, pool, run, pool sequence. The inflow water came from a spring-fed pond located ~50 m from our experimental setup. This water had stable nutrient concentrations (0.091–0.224 NO_3^- -N mg/L, 0.004–0.012 PO_4^{3-} -P mg/L). All outflow water exited the stream from an outlet standpipe in the final pool and then flowed through a series of small wooded and vegetated wetlands before discharging into a local stream. We set the discharge manually with PVC spigot structures set inline within each stream to maintain desired flow rates for average HRTs of 2, 4, and 6 h.

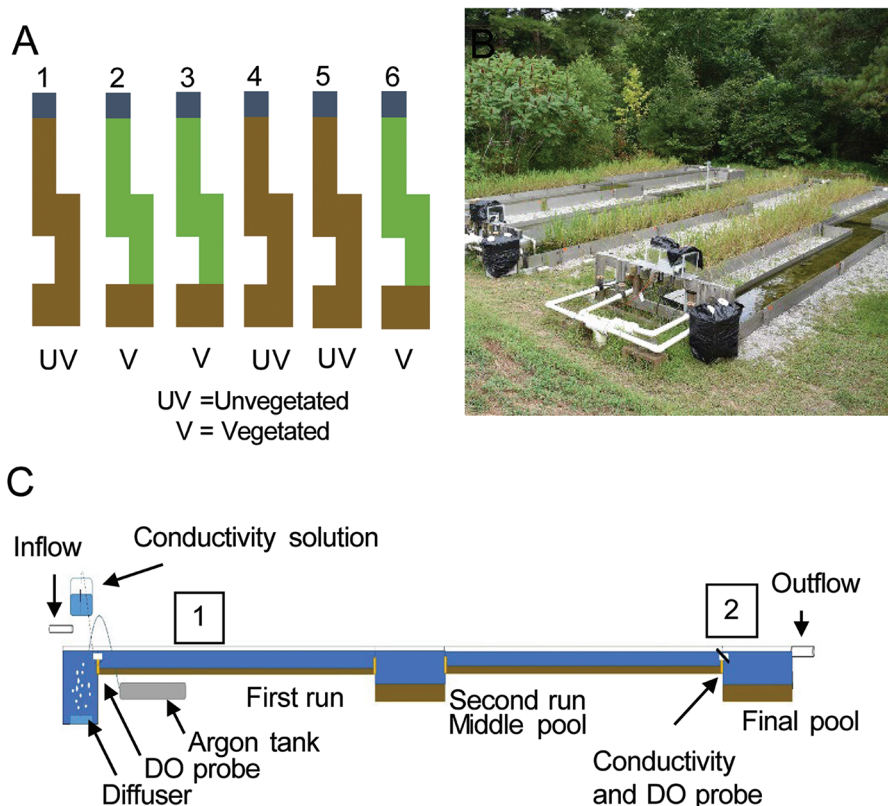


Figure 1. A.—Schematic diagram of the experimental streams setup with solid brown indicating unvegetated streams and patterned green indicating streams vegetated with *Leersia oryzoides* (rice cutgrass). B.—Picture of streams at University of Mississippi Field station. C.—Cross sectional view of unvegetated experimental stream (stream dimensions are 12.8-m long and 0.6-m wide, depths vary from 0.1-m in runs to 0.3-m in pools and 0.9-m in headpool). Sampling occurred at the upstream location (1) and the downstream location (2).

We randomly selected 3 of the stream mesocosms (2, 3, and 6) to be vegetated with *Leersia oryzoides* (commonly known as rice cutgrass). We transplanted *L. oryzoides* into the streams at an average density of 115 stems/m² (stream 2 density [$\mu \pm$ SE] = 152 \pm 26, stream 3 density = 108 \pm 14, stream 6 density = 132 \pm 27). These plants came from a nearby headwater stream-floodplain-wetland complex on the field station property. *Leersia oryzoides* is a native perennial grass species, widespread across the United States, that can tolerate seasonal to permanent flooding (NRCS 2008). Multiple studies have demonstrated that vegetation within agricultural ditch sediments, including *L. oryzoides*, influences biogeochemical processes including sediment O₂ demand and denitrification (Roley et al. 2012, Taylor et al. 2015, Speir et al. 2017). We left 3 streams (1, 4, and 5) unvegetated with bare sediments (Fig. 1B). We set up streams ~3 mo before the study began to allow vegetation and benthic assemblages to establish.

Flow and gas tracer amendments

Streams were randomly assigned to different HRTs on each day to create a dataset in which, over the course of 3 sam-

pling dates, 3 Ar tracer experiments were run in each stream for each different HRT (2, 4, and 6 h) for a total of 18 Ar tracer events. We used Ar gas to conduct a continuous tracer injection and model downstream gas exchange. Propane and sulfur hexafluoride have commonly been used as tracer gases, but neither gas is ideal as a tracer. Sulfur hexafluoride is a potent greenhouse gas, both potential tracers are flammable and expensive, and neither of them have the same physical characteristics as O₂. Recently, researchers have proposed that Ar is an ideal tracer gas for 3 reasons: 1) Ar and O₂ have similar Schmidt numbers and solubility; 2) Ar is non-toxic, inert, and not a greenhouse gas; and 3) Ar can be easily quantified with membrane inlet mass spectrometry (MIMS; Hall and Madinger 2018).

Prior to injection, we collected pre-plateau samples at sampling locations 1 and 2, located 2.36 m and 10.97 m, respectively, from the headpool in each stream (Fig. 1C). We collected triplicate dissolved gas samples with a dissolved gas sampler constructed from a PVC pipe (30-cm length with a 3.8-cm inner diameter). We inserted an outlet tube 4 cm above the bottom end of the sampler and sealed the insertion point with silicone (Reisinger et al. 2016, Hall and

Table 1. Physical stream characteristics including volume (m^3), average stream depth (z ; m), hydraulic residence time (min), median velocity (m/min), discharge (Q ; m^3/min), measured K gas exchange rates (K_m), K_{600Ar} , and temperature (T ; $^{\circ}C$) during tracer tests.

Stream	Volume (m^3)	z (m)	HRT Treatment (min)	Actual HRT (min)	Velocity (m/min)	Q (m^3/min)	K_m (d^{-1})	K_{600Ar} (d^{-1})	T ($^{\circ}C$)
Vegetated streams									
2	1.54	0.17	120	108.8	0.11	0.012	3.51	2.47	28.41
			240	184.2	0.07	0.006	7.42	5.14	28.90
			360	275.3	0.04	0.0006	10.32	7.41	27.82
3	1.73	0.19	120	172.1	0.07	0.017	1.92	1.29	29.65
			240	215.2	0.06	0.007	4.45	3.17	28.02
			360	366.8	0.03	0.006	–	–	28.05
6	1.57	0.18	120	145.4	0.08	0.011	3.01	2.19	27.45
			240	247.8	0.05	0.005	3.83	2.76	27.78
			360	246.8	0.05	0.001	6.50	4.56	28.47
Unvegetated streams									
1	1.54	0.17	120	134.6	0.09	0.011	5.91	4.23	27.92
			240	257.3	0.05	0.006	3.79	2.72	27.88
			360	381.1	0.03	0.002	4.12	3.49	22.95
4	1.74	0.19	120	130.8	0.09	0.013	3.85	2.78	27.61
			240	261.6	0.05	0.006	1.99	1.82	20.72
			360	259.7	0.05	0.001	6.54	4.54	28.81
5	1.62	0.18	120	119.1	0.10	0.019	1.69	1.13	29.87
			240	212.4	0.06	0.012	3.82	2.70	28.28
			360	308.4	0.04	0.002	4.42	3.13	28.18

Madlinger 2018). To take samples we first submerged the sampler below the water surface, held it parallel to the flow, and allowed water to flow through the pipe for 60 s before sealing the sampler with a rubber stopper while the sampler remained submerged. We then collected dissolved gas samples by lifting the sampler from the water, holding it upright to allow water to flow through the outlet tube, and allowing a 12-mL Exetainer[®] (Labco, Lampeter, Wales) to overflow 3× prior to being preserved with $ZnCl_2$ and capped.

Additionally, we measured specific conductivity, temperature, and barometric pressure at each sampling location with a handheld multiparameter conductivity sensor (YSI, Yellow Springs, Ohio) and Extech MODEL barometric pressure sensor (Nashua, New Hampshire).

After pre-injection sampling, we simultaneously added Ar and established a continuous NaCl solution drip entering the headpool of each stream. Industrial grade Ar was added by pumping it into the headpool at $\sim 0.14 m^3/h$ with a Point Four[™] (Cary, North Carolina) micro bubbler diffuser (30.5×6.03 cm) to allow for even bubbling and higher gas absorption. We concurrently dripped a solution of 14.9 g NaCl/L into each stream mesocosm at a constant rate with a peristaltic pump. Pumps were calibrated to deliver NaCl solution at 5 mL/min into the headpool, where

the solution could mix thoroughly with the Ar-rich water. We measured conductivity instead of Cl^- because conductivity was easier to monitor in the field to determine when a plateau had been reached. We used In-Situ[™] (Fort Collins, Colorado) water quality monitoring sondes to measure conductivity at 15-min intervals at sampling location 2 (Fig. 1B). Our goal was to increase conductivity by at least 10%. We installed sondes prior to tracer tests and allowed them to remain in the stream for up to 10 h to describe the conductivity plateau. We used these measurements to calculate HRTs within each stream. We also measured conductivity with a handheld water quality meter at all sampling locations every h during each experimental trial to determine when measurements were consistent across the stream and a plateau had been reached at the downstream location. When a plateau was reached, we sampled again for specific conductivity, stream temperature, and barometric pressure. We also collected triplicate dissolved gas samples following the pre-injection protocol.

MIMS analysis

We measured dissolved Ar concentrations in our dissolved gas samples with an MIMS (Bay Instruments, Easton, Maryland, USA) (Kana et al. 1994). The calibration standard

was purified water (18 M Ω resistance; Barnstead™ E-Pure™ Ultrapure Water Purifications Systems, Dubuque, Iowa) in a round-bottom flask maintained at field temperature with a circulating water bath (VWR International, Radnor, Pennsylvania). We kept this water equilibrated with the atmosphere by stirring continuously with an overhead stirring device (model # BDC250; Caframo Limited, Ontario, Canada) set at 300 rpm. We collected a set of 3 standard samples from the primary standard water bath every 5 to 10 samples. We recorded the current of mass 40, which represents Ar gas, for each unknown sample and standard sample set.

We experienced measurement error as we had high dissolved Ar enrichment in our streams even though we set the gas regulators to the lowest measurable discharge rate. Across our 2-, 4-, and 6-h HRT treatments the Ar concentration increased to 68, 82, and 91 \times the background concentration, respectively. We used absolute Ar concentrations because MIMS can measure absolute gas concentrations with high precision when concentrations are high. We observed an average % coefficient of variation of 0.03% for absolute Ar concentrations among standards within our sample runs, which are well within the range of previously-reported precision (0.05%) for ratio-based MIMS measurements (Kana et al. 1994). We converted mass to charge ratio of 40 currents to absolute Ar concentration ($\mu\text{mol/L}$) by calculating Ar concentrations in a primary standard set at the membrane temperature and assuming equilibrium with the atmosphere at a known temperature and barometric pressure. We estimated saturation concentrations in the flask based on Hamme and Emerson (2004) and corrected unknown Ar concentrations for instrument drift during each run based on changes in primary standard sets distributed throughout the run. Accuracy of MIMS measurements are related to factors controlling solubility (temperature, salinity, and barometric pressure), with nominal accuracy of \sim 0.3% for samples that measure close to the primary calibration point.

Analysis of HRT and Q

We determined HRT for each experimental stream mesocosm with the conductivity measurement time series (Table 1). We calculated the median reach residence time based on when the conductivity reached $\frac{1}{2}$ of the plateau peak value (Marzolf et al. 1994, Payn et al. 2008). We based the midpoint of the time series on the minimum conductivity value before the rising limb of the plateau and the maximum value in the plateau. We determined discharge, Q , by multiplying the rate of conductivity tracer injection by the ratio of the injected tracer conductivity to the increase in conductivity of the plateau. We calculated median velocity, v , as stream length divided by median reach residence time.

Gas exchange coefficient calculations

We calculated the measured gas exchange coefficient (K_m) with the following equation (Kilpatrick et al. 1989):

$$K_m = \ln\left(\frac{Ar_{\text{upstream}} \times Q_{\text{upstream}}}{Ar_{\text{downstream}} \times Q_{\text{downstream}}}\right) \times \left(\frac{1}{\text{HRT}}\right) \quad \text{Eq. 1}$$

where Ar_{upstream} and $Ar_{\text{downstream}}$ represent the measured concentrations of Ar at sampling locations 1 and 2, respectively. We assumed Q_{upstream} and $Q_{\text{downstream}}$ were equivalent within each stream because the inflow and outflow were constant and the mesocosms were not connected to groundwater sources. We converted HRT from min to d for this calculation. The 6-h HRT for stream 3 was excluded from subsequent analyses because of potential sampling errors.

K_m values were transformed to a K coefficient with a Schmidt number of 600 ($K_{600(\text{Ar})}$) values with the following equation from Raymond et al. 2012:

$$K_{600(\text{Ar})} = K_m \left(\frac{600}{(1799 - (\text{temp} \times 106.96) + (2.797 \times \text{temp}^2) - (0.0289 \times \text{temp}^3))} \right)^{-0.67} \quad \text{Eq. 2}$$

We used the exponent -0.67 instead of the common exponent -0.50 for streams because of the long HRTs and lack of turbulence in our streams (Wanninkhof 1992). We used $K_{600(\text{Ar})}$ values to predict K values (K_{pred}) for each stream based on relationships derived from mixed effects regressions based on hydraulic residence time and vegetation conditions (see Statistical analysis section, Fig. 2, Appendix 1).

Metabolism

A multi-day deployment of the sensors was not feasible in each stream at each HRT, so we set 1 HRT for each stream

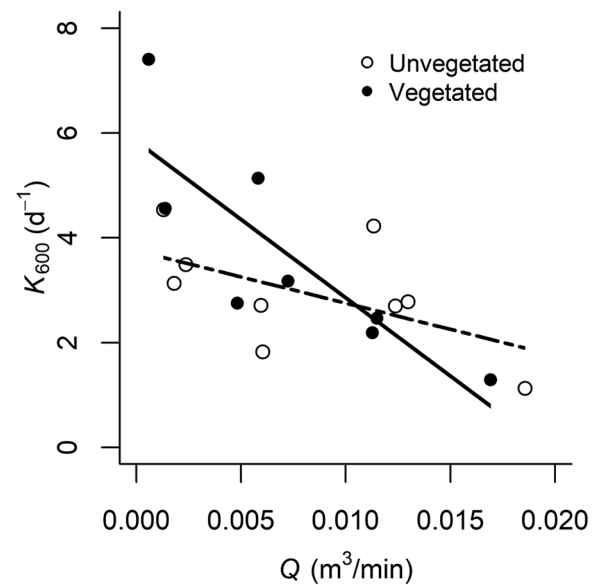


Figure 2. Measured gas exchange rate (K) declined with increasing discharge, Q , for vegetated streams (closed circles and solid line, slope $\mu \pm \text{SE}$, -299.72 ± 68.25 , $p < 0.001$) whereas there was no significant decline in unvegetated streams (open circles and dashed line, -92.16 ± 57.09 , $p = 0.07$).

and estimated metabolism rates based on changes in dissolved O_2 through time with the 2-station method (Marzolf et al. 1994, Young and Huryn 1998). We used 2 HOBO® (U26-001, Onset® Computer Corporation, Bourne, Maine) loggers placed in the middle of each stream channel to measure dissolved O_2 and temperature every 15 min at both sampling sites in each stream over a period of 9 d, which gave us 5 to 9 estimates of daily metabolism in each stream. The 2-station method was most appropriate due to the discrete nature of the experimental streams (Hall and Hotchkiss 2017). We used dissolved O_2 logger data to estimate GPP, ER, and K with the following equation in a Bayesian inverse modeling procedure following Hall et al. (2016):

$$O_{2\text{down}(t+\tau)} = \frac{O_{2\text{up}(t)} + \left(\frac{\text{GPP}}{z} \times \sum_t^{t+\tau} \frac{\text{PPFD}}{\text{PPFD}_{\text{total}}} \right) + \frac{\text{ER}}{z} \tau + K \tau \frac{(O_{2,\text{satup}(t)} - O_{2\text{up}(t)} + O_{2,\text{satdown}(t+\tau)})}{2}}{1 + \frac{K\tau}{2}} \quad \text{Eq. 3}$$

where $O_{2\text{up}(t)}$ is the upstream O_2 concentration ($\text{g } O_2/\text{m}^3$) and $O_{2\text{down}(t+\tau)}$ is the downstream O_2 concentration of that same parcel of water following travel time, τ . GPP and ER are expressed in $\text{g } O_2 \text{ m}^{-2} \text{ d}^{-1}$ and represent positive and negative rates of O_2 production and consumption, respectively. z is mean depth (m) calculated as stream volume (m^3) divided by surface area (m^2), $O_{2,\text{satup}}$ and $O_{2,\text{satdown}}$ are the saturation concentrations upstream and downstream ($\text{g } O_2/\text{m}^3$), K (d^{-1}) is the gas exchange rate, and PPFD is the sum of the photosynthetic photon flux density ($\mu\text{mol m}^{-2} \text{ s}^{-1}$) accumulated in the time interval from t to $(t + \tau)$ divided by the daily total of PPFD ($\text{PPFD}_{\text{total}}$) for any given parcel of water.

We fit each daytime period separately, with the d starting 1 full HRT before midnight and ending 1 full HRT after midnight the following d (2–6.5 h). We used the function `metrop` in the `mcmc` package (version 0.9–6; Geyer and Johnson 2019) in R to sample from the posterior probability distribution $P(\mu | D)$. Each chain was run for 20,000 iterations following a 1000 iteration burn-in. We did not thin chains, and we adjusted the proposal distribution to achieve an acceptance rate of ~20%. We used minimally-informative prior probability distributions for GPP and ER ($\text{GPP} \sim N[\mu = 5, \text{SD} = 10]$; $\text{ER} \sim N[\mu = -5, \text{SD} = 10]$).

We ran the model $3 \times$ for each d in each stream: once for a minimally-informed prior, once for informed prior probability distribution on K , and once where K was set (K_{pred}) and not part of the solution set. For the minimally-informed prior probability distributions, we used $K_{\text{uninformed}} \sim N(\mu = 5, \text{SD} = 5; \text{Hall et al. 2016})$. We based informed prior probability distributions on ANCOVA models that related K to vegetation and Q (see Statistical analysis). In vegetated streams we used $K_{\text{informed}} \sim N(\mu = K_{\text{pred}}, \text{SD} = \text{SD}[K_{\text{pred}}])$ where μ was the K_{pred} for that stream given its vegetation status and Q , $\text{SD}(K_{\text{pred}}) = ([\mu + 2\text{SE}] - [\mu - 2\text{SE}])$. For unvegetated streams, the slopes of the relationship between K and Q were not significantly different from 0. Thus, we used $K_{\text{informed}} \sim N$

($\mu = K_{\text{pred}}$, $\text{SD} = 2.865$), where SD was equal to the confidence interval for the intercept (Appendix 1). For informed priors, K_{O_2} was transformed from K_{pred} within the model with the daily average temperature for that stream with the following equation from Raymond et al. (2012):

$$K_{O_2} = K_{\text{pred}} \left/ \left(\frac{600}{(1568 - (\text{temp} \times 86.04) + (2.142 \times \text{temp}^2) - (0.0216 \times \text{temp}^3))} \right)^{-0.67} \right. \quad \text{Eq. 4}$$

The set K scenario used the same K_{O_2} as detailed above except the value of K_{O_2} was estimated outside the model, prior to model implementation, with results from Ar tracer tests. K_{O_2} was dependent on the stream temperature at each 15-min interval, resulting in small diel fluctuations in the value as the stream heated and cooled. For this scenario we modified the model to solve only for GPP and ER.

Statistical analysis of HRT and K

Our previously-described metabolism models used a Bayesian framework. In favor of pragmatism, however, we analyzed the field-collected data and patterns of GPP and ER outputs from Bayesian models with frequentist statistics to make our results accessible to a wider audience, although we recognize this may be controversial. All analyses were done in R version 3.5.0 (R Foundation for Statistical Computing, Vienna, Austria).

For our frequentist analysis of K based on the argon tracer test data, we employed a randomized block experimental design that involved repeated sampling of the set of 6 streams over 3 different d. As streams needed to acclimate to each HRT, it was not feasible to conduct more than 1 tracer test in 1 day. In this design, each d was a block that we used to examine relationships between measured K and Q associated with different HRTs within vegetation treatments. We used linear mixed effects (LME) models to account for the random effects of differences among individual streams (~1 | stream) when we compared how HRT changed with vegetation or depth. We also used the random effect of streams to account for multiple measurements from 1 stream when we analyzed the differences in K between treatments. We treated both vegetation and depth as factors when we tested for differences in HRT with vegetation or depth. When we tested for differences in K with HRT and vegetation, we converted HRT to Q and treated it as a continuous predictor whereas we treated presence or absence of vegetation as a categorical factor (LME ANCOVA). We used the restricted maximum likelihood criterion to fit all models. We assessed the assumptions of all models visually with normality plots (`qqnorm`) and standardized residual plots across treatments (Zuur et al. 2009). If error variances differed across levels of treatments, this heterogeneity was incorporated into our model by modeling variance separately among treatments with the `VarIdent` command (Zuur et al. 2009). The best

model was selected based on the Akaike Information Criterion adjusted for small sample sizes. We used Tukey's honestly significant difference multiple comparison of means to test for significant differences among levels of fixed factors and the *lstrends* function to estimate and compare slopes of K and discharge among vegetation treatments. We used the best fit model from this analysis (LME [$K \sim Q \times \text{vegetation}$, random = $\sim 1 | \text{stream}$]) to predict K (K_{pred}) and provide an informed prior for subsequent Bayesian metabolism models. The LME models were run in the *nlme* package version 3.1–140 (Pinheiro et al. 2019). Tukey honestly significant difference tests were run in the *multcomp* package version 1.4–10 (Hothorn et al. 2008), and differences in slope were tested with *lstrends* in the *lsmeans* package version 2.30–0 (Lenth 2016).

Bayesian metabolism models were run for each model version, stream, and d. We used the triplot function within the *learnBayes* package version 2.15.1 (Albert 2018) to extract posterior probability distributions to visualize differences between methods of estimating GPP, ER, and K (informed and minimally-informed prior only for K) for each stream based on multiple 24-h periods (range 5–9 d). We used daily estimates from metabolism model outputs based on medians of posterior probability distributions in LME models to assess how ER varied with GPP. Models included random effects to account for differences among d within individual streams ($\sim 1 | \text{stream/d}$). We ran models with GPP as a continuous predictor and the method for estimating K and presence or absence of vegetation were considered categorical factors that could potentially influence differences in slope among the 3 approaches (LME ANCOVA). Model fitting and assessment of assumptions followed methods presented earlier (Zuur et al. 2009).

RESULTS

Analysis of tracer test measurements

Measured K values were differentially influenced by HRT between unvegetated and vegetated streams. We found the interaction between stream discharge and vegetation influenced the measured $K_{600\text{Ar}}$ (LME ANCOVA, $F_{1,9} = 5.44$, $p = 0.04$) (Fig. 2). K values decreased as HRT values decreased (slope $\mu \pm \text{SE}$, -299.72 ± 68.25 , $p < 0.001$) in vegetated streams, but this effect was less clear in unvegetated streams (-92.16 ± 57.0 , 9; $p = 0.07$) (Table 1). HRT did not differ significantly between vegetation treatments (LME ANCOVA, $F_{1,4} = 0.7$, $p = 0.45$) or with stream depth ($F_{1,4} = 0.09$, $p = 0.78$). Average stream temperature did not significantly differ between vegetation treatments (LME ANCOVA, $F_{1,4} = 1.64$, $p = 0.26$).

Comparison of model estimates to measured values of dissolved O_2

Model estimates of dissolved O_2 in the unvegetated stream performed worse when compared to observed dissolved O_2

values than model fits in the vegetated stream (Fig. 3A, B). All methods under predicted dissolved O_2 saturation recovery during the morning and failed to capture the magnitude of the overnight saturation deficit in this unvegetated stream. The largest difference between methods was between the minimally-informed and informed methods with the set K method in the unvegetated stream (Fig. 3A). In contrast, all methods predicted similar patterns in modeled dissolved O_2 in vegetated stream and better replicated the observed downstream values, even for the early morning sag in dissolved O_2 (Fig. 3B).

Comparison of methods to calculate gas exchange rate coefficients

When estimating K , the minimally-informed and informed prior methods had a greater degree of overlap in posterior probability densities (PPD) in vegetated streams (Fig. 4A, C, E) than in unvegetated streams (Fig. 4B, D, F). In unvegetated streams, posterior means of K overlapped less at shorter HRTs. Mean $\pm 95\%$ credible intervals ($\mu \pm 95\% \text{ CI}$) were: minimally informed = 7.85 ± 0.62 and informed = 7.02 ± 0.54 for stream 1, and minimally informed = 4.86 ± 0.77 and informed = 3.37 ± 0.62 for stream 4 (Fig. 4B, D, respectively). For stream 5, which had a longer HRT of 6.4 h, the different modeling methods had similar posterior probability distributions (Fig. 4F).

Moreover, differences in K estimates were observable between vegetated and unvegetated streams. Based on the set K method, vegetated streams had higher values of K than unvegetated streams for both 4 and 6 h HRTs (Table 2). This result may be driven by the increased turbulence caused by stream vegetation but may not be commonly observed in experiments because of the decreasing velocity associated with in-stream vegetation growth. However, K values from the 2-h HRT treatments (Fig. 4A, B; Table 2) did not follow this pattern. The lower K estimate for the vegetated stream could be because of the significantly-longer measured HRT (~ 53 min longer), which had more pronounced decreases in K with increasing discharge that were similar to patterns of K changes in streams with shorter HRTs (Fig. 2). Furthermore, stream 1 and stream 5 (Fig. 4B, F) had exceptionally high posterior means relative to their vegetated stream counterparts (Fig. 4A, E) based on both the informed and minimally-informed methods. The set K method in these streams also resulted in much lower K values than the informed and minimally-informed methods (Table 2). Across all streams, the set K method resulted in higher posterior means with increasing HRT, which was similar to measured trends (Table 2).

Effects on metabolism

We present our estimates of GPP as PPD, which provide some evidence that the method used to measure or estimate K influences measures of ecosystem function in both

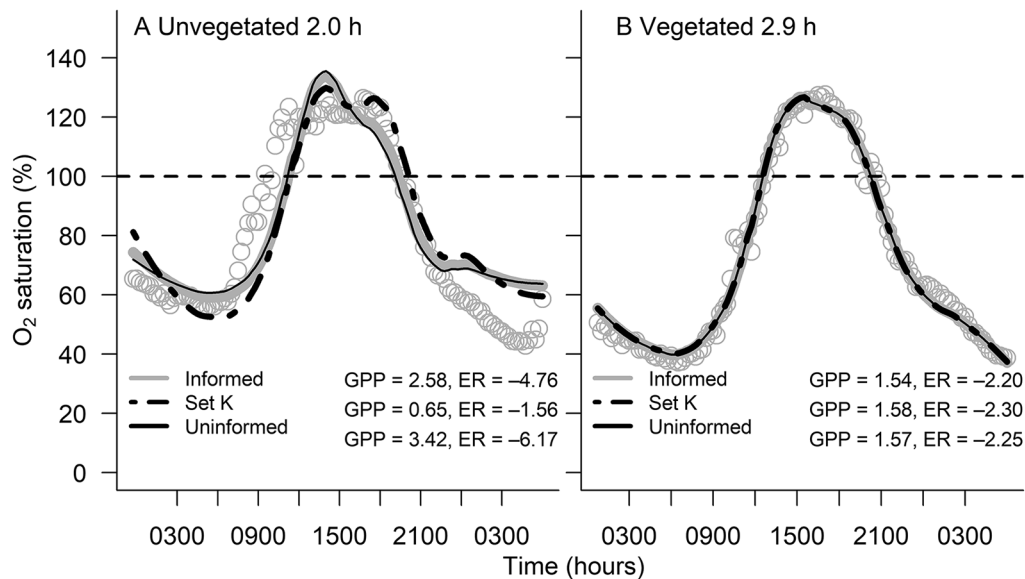


Figure 3. Modeled and observed downstream dissolved O₂ concentrations shown as % O₂ saturation for unvegetated stream 5 (A) and vegetated stream 3 (B). Open gray circles represent observed downstream dissolved O₂ values whereas solid gray lines, dashed black lines, and solid black lines represent informed, set *K*, and minimally-informed model output, respectively. GPP and ER estimates for the unvegetated stream differ among methods, while all methods result in consistent GPP and ER estimates in the vegetated stream.

vegetated and unvegetated streams (Fig. 5A–L). GPP estimates among methods were similar in vegetated streams because there was a high degree of overlap in PPD (Fig. 5A, E, I). In vegetated streams, GPP estimates increased with increasing HRT. GPP estimates were less consistent among methods, and there was no clear relationship with HRT in unvegetated streams (Fig. 5B, F, J). Informed and minimally-informed models resulted in high estimates of GPP that did not overlap significantly with GPP estimates based on set *K* in streams 1 and 5 (Fig. 5B, J). However, the results all 3 methods overlapped for stream 4 (Fig. 5F).

Across the different streams and HRT treatments, the ER estimates, also presented as PPD, from the 3 different methods were less consistent than the GPP estimates. ER estimates generally increased with increasing HRT in vegetated streams, but this trend was not observed in unvegetated streams (Table 2). The most overlap among PPD occurred in streams 2 (vegetated; Fig. 5C) and 4 (unvegetated; Fig. 5H). The biggest observed differences between the informed and minimally-informed models and the set *K* estimates occurred in stream 5 (unvegetated; Fig. 5D). Further, estimates of ER in stream 1 between models based on minimally-informed and set *K* did not overlap substantially (unvegetated; Fig. 5L). ER estimates overlapped moderately among methods of estimating *K* in the 2 other vegetated streams (Fig. 5G, K). Overall, the lowest ER estimates in unvegetated streams came from metabolism models that used the set *K* method.

Scatterplots contrasting results from the 3 different methods provide further evidence that vegetation influenced how similar the estimates of GPP and ER from metab-

olism models were based on the methods used to estimate *K* (Fig. 6A–I). In vegetated streams, GPP and ER estimates from minimally-informed (Fig. 6A, B) or informed (Fig. 6D, E) priors increased as estimates from set *K* models increased. However, model estimates based on minimally-informed or informed priors in vegetated streams tended to have larger error bars than set *K* estimates at high GPP and ER rates. In contrast, set *K* models in unvegetated streams produced estimates for both GPP and ER that did not vary consistently with output from either the minimally-informed or informed models (Fig. 6A, B, D, E). GPP estimates based on a set *K* were higher than estimates from minimally-informed or informed models at the low range of estimates but were lower at the high range of estimates. Additionally, in several instances the estimates based on informed and minimally-informed priors were greater and contained more error than estimates based on set *K*. Informed priors and minimally-informed priors gave similar estimates of GPP and ER in vegetated streams (Fig. 6G, H). These models also gave similar results in unvegetated streams, although there were 2 instances where minimally-informed estimates were higher than informed estimates (Fig. 6G, H).

Comparisons of set *K* to *K* modeled with minimally-informed or uninformed priors show that minimally-informed priors (Fig. 6C) lead to greater uncertainty than do informed priors (Fig. 6F). The error in *K* values consistently overlapped with the 1:1 line for the contrast between the informed and uninformed models but increased at higher *K* values (Fig. 6I).

Choice of method to determine *K* did not influence broad patterns in ER and GPP. Positive slopes >1 between

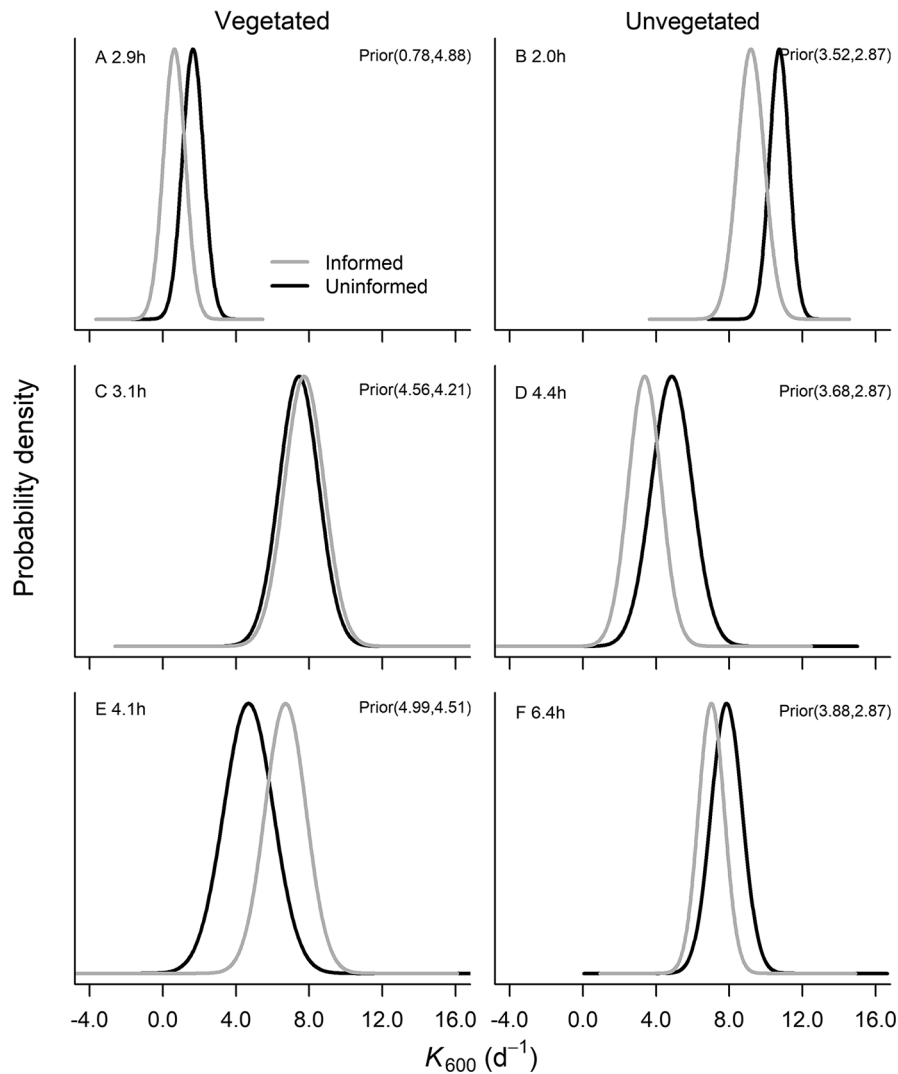


Figure 4. Bayesian posterior probability density plots of the gas exchange rate (K) summarizing data estimates from different prior probabilities. Informed priors are represented by the solid gray line, and minimally-informed priors are represented by the black line. Panels A, C, and E represent streams 3, 2, and 6, respectively, which are vegetated. Panels B, D, and F represent streams 5, 4, and 1, respectively, which are unvegetated. Informed priors are provided in the top right corner of each panel. The average value for set K is in Table 2.

ER and GPP indicated that streams became increasingly net heterotrophic at higher GPP rates for both vegetated and unvegetated streams (Fig. 7A–C). Overall, ER increased more quickly in response to increasing GPP in vegetated streams ($\mu \pm \text{SE}$, 1.93 ± 0.08) than in unvegetated streams (1.47 ± 0.06) (LME ANCOVA; $F_{1,76} = 45.45$, $p < 0.0001$). Slope did not vary with the approach used to estimate K ($F_{2,76} = 0.61$, $p = 0.55$), though there was evidence that differences in slope among approaches for estimating K were associated with vegetation status of a stream ($F_{2,76} = 3.39$, $p = 0.04$). Slopes derived from the set K method were not different between vegetated and unvegetated streams. However, this potential pattern could have been driven by the

much smaller range of ER and GPP estimates for unvegetated streams based on the set K method (Fig. 7C).

DISCUSSION

The gas exchange rate is a key variable that influences the accurate estimation of dissolved gas fluxes and associated ecosystem process including GPP, ER, and denitrification in streams (Pribyl et al. 2005, Tobias et al. 2009, Holtgrieve et al. 2010). We experimentally manipulated the presence of vegetation and HRT to better understand how hydrology and vegetation influence gas exchange in low gradient headwater streams, how K varies among different estimation

Table 2. Gross primary production (GPP), ecosystem respiration (ER), and gas exchange values (K) for concurrent deployment by vegetation and hydraulic residence time (HRT) treatment. Values include informed priors used to model results as well as the mean values of the 50th percentile model output, representing several daily estimates ($n = 5-9$ d) and the associated 95% confidence intervals (CI) for each method.

Stream	Vegetation HRT treatment (Actual HRT)	Informed prior on K ($\mu \pm$ SD)	Average (informed prior method) ($\mu \pm$ 95% CI)	Average (minimally-informed prior method) ($\mu \pm$ 95% CI)	Average (set K method) ($\mu \pm$ 95% CI)
3	Vegetated 2 h (172.1 min)	K (0.78, 4.88)	GPP (1.75 ± 0.36)	GPP (1.75 ± 0.40)	GPP (1.82 ± 0.35)
			ER (-3.27 ± 0.81)	ER (-3.24 ± 0.80)	ER (-3.28 ± 0.61)
			K (0.90 ± 1.22)	K (0.87 ± 1.17)	K (1.14 ± 0.03)
2	Vegetated 4 h (184.2 min)	K (4.56, 4.21)	GPP (2.47 ± 0.38)	GPP (2.46 ± 0.40)	GPP (2.04 ± 0.44)
			ER (-4.05 ± 1.00)	ER (-4.03 ± 1.03)	ER (-3.05 ± 0.64)
			K (8.16 ± 2.49)	K (8.12 ± 2.61)	K (6.71 ± 0.13)
6	Vegetated 6 h (246.8 min)	K (4.99, 4.51)	GPP (3.35 ± 0.49)	GPP (3.40 ± 0.54)	GPP (3.27 ± 0.37)
			ER (-5.94 ± 1.62)	ER (-6.28 ± 2.25)	ER (-5.95 ± 0.57)
			K (5.57 ± 2.60)	K (6.00 ± 3.34)	K (7.32 ± 0.11)
5	Unvegetated 2 h (119.1 min)	K (3.52, 2.87)	GPP (3.29 ± 0.90)	GPP (3.77 ± 1.02)	GPP (1.19 ± 0.59)
			ER (-6.03 ± 1.01)	ER (-6.83 ± 1.15)	ER (-2.64 ± 0.73)
			K (9.10 ± 1.60)	K (10.56 ± 1.54)	K (2.68 ± 0.05)
4	Unvegetated 4 h (261.6 min)	K (3.68, 2.87)	GPP (1.71 ± 0.48)	GPP (1.83 ± 0.56)	GPP (1.63 ± 0.24)
			ER (-2.74 ± 0.81)	ER (-2.97 ± 0.97)	ER (-2.58 ± 0.53)
			K (3.54 ± 2.07)	K (4.16 ± 2.50)	K (4.62 ± 0.07)
1	Unvegetated 6 h (381.1 min)	K (3.88, 2.87)	GPP (2.27 ± 0.62)	GPP (2.39 ± 0.73)	GPP (1.48 ± 0.22)
			ER (-2.71 ± 0.76)	ER (-2.87 ± 0.73)	ER (-1.61 ± 0.22)
			K (7.92 ± 1.52)	K (8.35 ± 1.81)	K (5.34 ± 0.09)

methods, and how these differences impact estimates of GPP and ER.

Effects of hydrology and vegetation on K

In the shallow, low-gradient stream mesocosms we used, measured K was attenuated by vegetation as discharge increased, whereas measured K in unvegetated streams was less predictable. These patterns suggest that interactions between vegetation and stream flow are important in low gradient headwater streams (Thyssen et al. 1987, Wilcock et al. 1999, Kaenel et al. 2001; Fig. 2). Vegetated streams had more consistent K and metabolism estimates among the 3 methods than did unvegetated streams, as well as better model fits. We did not observe clear patterns in metabolism estimates between modeled and measured K approaches for unvegetated streams across a range of HRTs. These results suggest considerable error in either modeled, measured, or both estimates of K in unvegetated streams. Informed priors did not appear to improve metabolism model output over minimally-informed priors in either in vegetated or unvegetated streams. This result is probably because our data exhibited strong diel patterns in gas concentrations, which may outweigh prior information in our metabolism models. Scaling relationships between GPP and ER indicated

that net heterotrophy increased with increasing GPP in all streams, regardless of which approach was used to estimate K .

The parameter K is a metric of how fast a change in gas concentration in stream water occurs given gas equilibration with the atmosphere. K can be affected by physical parameters such as slope, turbulence, and stream velocity particularly in small, steep mountainous streams (Hall et al. 2012, Hall and Madinger 2018). In shallow, low-gradient streams, stream depth and volume can be important influences, although our experimental streams had similar volumes and channel configurations. However, the factors affecting K may be especially influenced by vegetation in shallow, low-gradient systems. The greater negative slope of K with increasing Q in vegetated streams than in unvegetated streams could have occurred because vegetation influences hydraulic roughness, disrupts laminar flow, and increases small-scale turbulence (Bansal 1973, Watson 1987, Wilcock et al. 1999). Several studies have measured higher K after the removal of vegetation and attributed this difference to the modification of physical controls on current velocity, which is a major influence on K (Wilcock et al. 1999, Kaenel et al. 2001, Arroita et al. 2019). However, Soana et al. (2018) found higher K in densely-vegetated (1200–1900 plants/m²) mesocosms experiments with velocities ranging from 0 to 6 cm/s relative

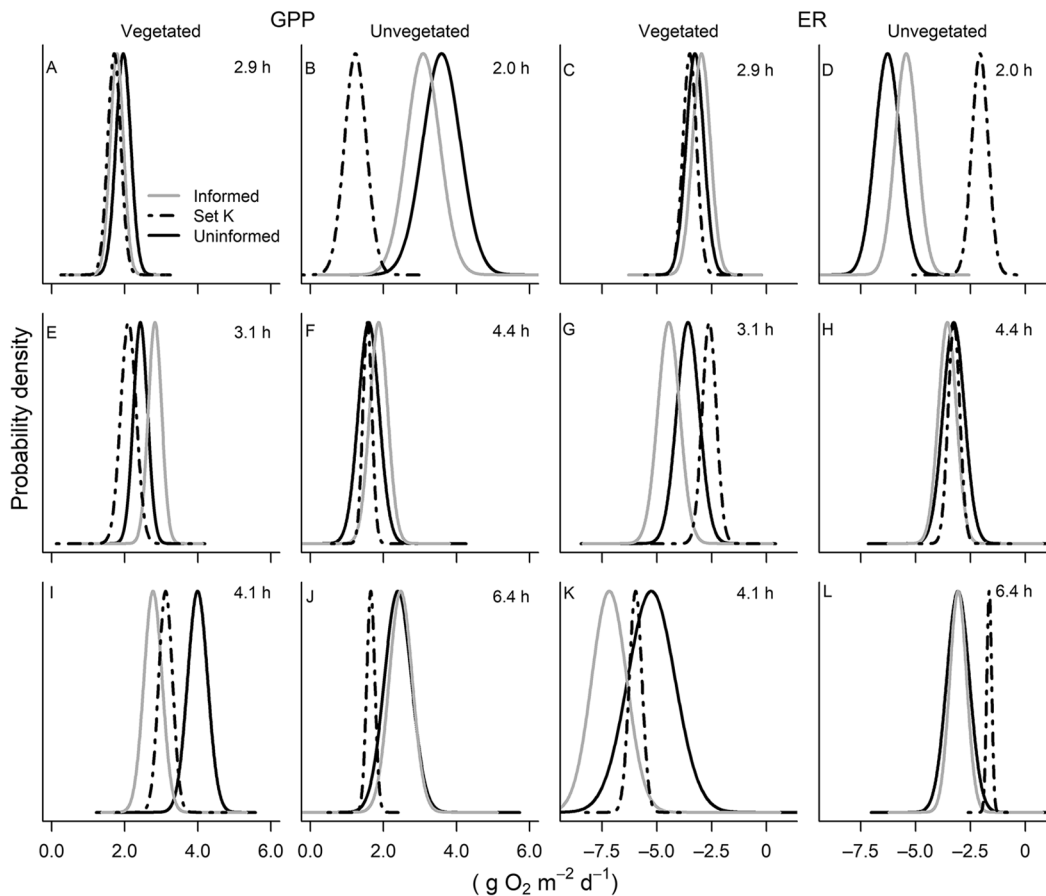


Figure 5. Bayesian posterior probability density plots of gross primary production (GPP) and ecosystem respiration (ER) summarizing data estimates from different prior probabilities on K including informed priors represented by the solid gray line, minimally-informed priors represented by the black gray line, and set the gas exchange rate (K) represented by the dashed black line. Panels A, E, and I represent GPP estimates for vegetated streams 3, 2, and 6 respectively. Panels B, F, and J represent GPP estimates for unvegetated streams 5, 4, and 1, respectively. ER estimates for vegetated streams 3, 2, and 6 are in panels C, G, and K, respectively. Panels D, H, and L represent ER estimates for streams 5, 4, and 1, respectively.

to unvegetated mesocosms. Together, these results suggest a nonlinear response in K as velocities in vegetated streams increase from 0. Additionally, observational studies in low-slope streams suggest factors other than physical turbulence, including turbidity and total organic C content through indirect effects on stream temperature, may drive gas exchange in these systems particularly at low flows (Parker and DeSimone 1988, Demars and Manson 2013). Lastly, the range of measured K was greatest in vegetated streams (Fig. 2). This suggests that the presence of vegetation could generate more dynamic rates across a given range of HRTs because of nonlinear relationships between the behavior of plant material in response to increasing flows (Watson 1987, Sand-Jensen et al. 1989, Wilcock et al. 1999).

Modeling gas exchange

PPD of gas exchange from the minimally-informed and informed models were consistent with the set K method in veg-

etated streams (Fig. 4A, C, E; Table 2). In contrast, model estimates differed more in unvegetated streams (Fig. 4B, D, F; Table 2). Generally, vegetated streams are more likely to have high GPP values, which may have contributed to consistent estimates of K between models (Holtgrieve et al. 2010). In contrast, unvegetated streams may lack turbulence, especially over the short channel length of the stream mesocosm, and therefore be incompletely mixed. Incomplete mixing could contribute to heterogeneity in gas exchange rates along unvegetated channels. Additionally, the error structure of the current model addresses parameter error within a single day well but lacks the ability to represent errors across days adequately (Hall et al. 2016). This error structure could thereby contribute to observed differences among methods, particularly in unvegetated systems. Finally, inverse modeling approaches can suffer from equifinality, which occurs when model estimates that predict the observed data can be reached by several potential combinations of parameter estimates (Appling et al. 2018). Inconsistency in parameter

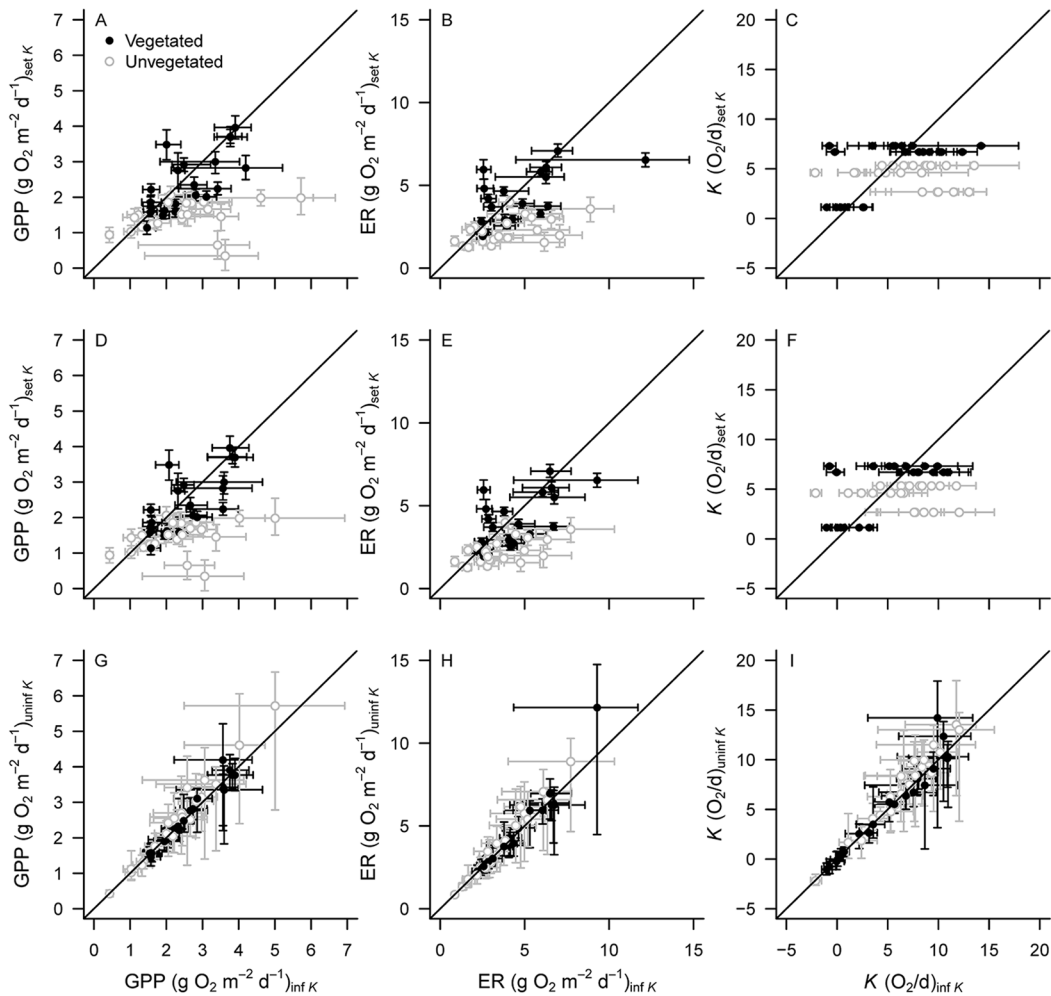


Figure 6. Biplots of Bayesian median and 95% credible intervals that show the degree of overlap in gross primary production (GPP), ecosystem respiration (ER), and the gas exchange rate (K) among contrasting methods. Model output is based on set K vs minimally-informed (uninf K) prior to model K for (A) GPP, (B) ER, and (C) K . Model output is based on set K vs informed prior to model K for (D) GPP, (E) ER, and (F) K . Model output is based on minimally-informed (uninf K) vs informed (inf K) prior to model K for (G) GPP, (H) ER, and (I) K . Gray points represent unvegetated streams and black points represent vegetated streams. The black line in each panel is the 1:1 line.

estimates among methods within unvegetated streams suggests potential equifinality. However, poor model agreement with observed diel curves in unvegetated streams suggests a greater issue within the model to replicate observed diel patterns in O_2 . In vegetated streams, more consistent conclusions among models and associated parameter estimates suggest that equifinality was not an issue, possibly because of strong linkages between GPP, autotrophically-fueled ER, and resulting gas transfer estimates (Bernot et al. 2010, Hall and Beaulieu 2013, Solomon et al. 2013).

Effects of method choice on metabolism estimates

The effect of different methods on estimates of K transferred to metabolism results. Overall, there was a greater

degree of agreement among methods for estimates of GPP and ER in vegetated streams. In contrast, in the unvegetated streams both informed and minimally-informed models yielded higher, sometimes more than $3\times$ higher, GPP estimates with more error than the set K method. Previous investigations suggest temperature and light may be more significant drivers of GPP and associated variability in unvegetated streams than in vegetated streams (Mulholland et al. 2001, Valett et al. 2008, Bernot et al. 2010, Beaulieu et al. 2013). Average temperatures were similar among our study streams, but differences between upstream and downstream sondes in unvegetated streams were slightly greater than vegetated streams (unvegetated: $1.06^\circ\text{C} \pm 3\%$ [$\mu \pm$ coefficient of variation], vegetated: $0.59 \pm 2\%$). This difference may have contributed to a wider range of metabolism parameter

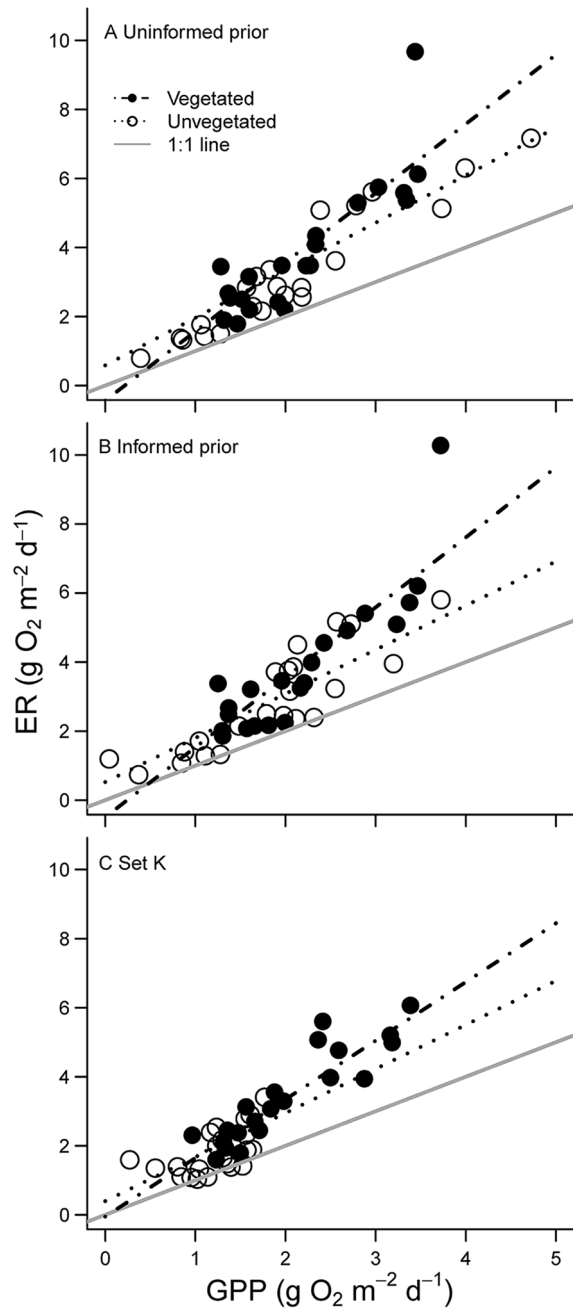


Figure 7. Gross primary production (GPP) vs ecosystem respiration (ER) from metabolism models based on minimally-informed prior probability distributions on the gas exchange rate (K) solved in a Bayesian framework (A), informed prior probability distributions on K solved in a Bayesian framework (B), and a set K (C). The gray line in each panel is the 1:1 line. Circle size indicates K , such that larger circles indicate higher K .

estimates in unvegetated vs vegetated streams as the model sought to accurately estimate downstream dissolved O₂ curves, but this possibility is unlikely. ER rates were also higher based on both informed and minimally-informed models in unvegetated streams (Fig. 6B, E), which indicates the

possibility of smaller C fluxes than predicted by modeling efforts. An alternative explanation may be that lower activation energy requirements for respiration than for photosynthesis yield even greater divergence among methods for posterior means of ER (Enquist et al. 2003, Acuña et al. 2008). To support this, Demars et al. (2011) found the relationship of ER with temperature is stronger than the relationship of GPP with temperature in groundwater-fed Icelandic streams.

Linear relationships between GPP and ER always indicated increased heterotrophy in response to increasing GPP, regardless of which approach was used to estimate K (Fig. 7A–C). Slopes describing this response were always higher in vegetated vs unvegetated streams, consistent with previous findings that slopes describing GPP–ER relationships increased in macrophyte dominated habitats relative to unvegetated streams (Alnoee et al. 2016). Additionally, overall patterns of increasing heterotrophy with increasing photosynthetic capacity in these shallow, low-gradient, open-canopy streams were similar among all approaches to estimating K . Patterns within our streams suggest that as GPP increased, ER rates exceeded photosynthetic capacity, which is similar to results from highly-productive, open-canopy streams (Rosenfeld and Mackay 1987, Frankforter et al. 2010, Marcarelli et al. 2011, Roley et al. 2014).

Implications for conducting studies in low-gradient streams

Methods for measuring gas exchange and stream metabolism continue to evolve because of improvements in knowledge and technology (Bernhardt et al. 2018, Hall and Madinger 2018). Our results contribute to understanding how gas exchange and associated metabolism estimates are influenced by the practitioner's choice of method in shallow, low-gradient, open-canopy streams. Our findings show that 1) K decreases as discharge, Q , increases; 2) different methods produce wide variation in K estimates; and 3) this variation in K estimates affects metabolism estimates, particularly for unvegetated streams. High rates of gas exchange in small, steep-sloped streams necessitate empirical measurements for accurate estimates of K (Hall and Madinger 2018). In contrast the ability to infer gas exchange from diel variation in O₂ data shows promise in larger rivers with low gas exchange and high GPP (Hall et al. 2016). This study demonstrates that given high GPP and low gas transfer in shallow, low-gradient, open-canopy streams, practitioners can consider the use of minimally-informed or informed models to estimate gas exchange rates within these habitats. This is especially apparent in vegetated streams, where minimally-informed or informed models and models based on empirical measurements of K (set K) predicted similar measured trends in dissolved O₂ and estimated metabolism parameters. However, model fits struggled to replicate dissolved O₂ data in unvegetated streams, possibly because of process

errors (sensu Appling et al. 2018) within the model and uncertainty in measured K in environments with low gas transfer contribute to inconsistencies between modeled and observed diel patterns.

ACKNOWLEDGEMENTS

Author contributions: Rachel Nifong organized and led data collection, data analysis, and manuscript preparation. Jason Taylor and Lindsey Yasarer facilitated research and experimental design; aided with data collection, laboratory processing, statistical analyses; and helped prepare and edit the final manuscript for submission.

We would like to thank the University of Mississippi Biological Field Station, particularly Scott Knight, for providing space, maintenance, and logistical support for the mesocosm facility. We thank Mark Griffith, Tate Hillhouse, and James Gledhill for assisting in data collection and sample processing. Terry Welch, Sam Testa, Tim Sullivan, and Matt Moore put forth a significant effort to establish Lower Mississippi River Basin ditch sediments and vegetation in stream mesocosms. Robert Payn, Bob Hall, Justin Murdock, Daniel Wren, and 1 anonymous reviewer provided greatly appreciated comments that improved an earlier draft of this manuscript. Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture. The US Department of Agriculture is an equal opportunity employer and provider.

LITERATURE CITED

- Acuña, V., A. Wolf, U. Uehlinger, and K. Tockner. 2008. Temperature dependence of stream benthic respiration in an Alpine river network under global warming. *Freshwater Biology* 53:2076–2088.
- Albert, J. 2018. Functions for learning Bayesian inference. (Available from: <https://cran.r-project.org/web/packages/LearnBayes/LearnBayes.pdf>)
- Alnoe, A. B., T. Riis, and A. Baatrup-Pedersen. 2016. Comparison of metabolic rates among macrophyte and nonmacrophyte habitats in streams. *Freshwater Science* 35:834–844.
- Appling, A. P., R. O. Hall Jr, C. B. Yackulic, and M. Arroita. 2018. Overcoming equifinality: Leveraging long time series for stream metabolism estimation. *Journal of Geophysical Research: Biogeosciences* 123:624–645.
- Arroita, M., A. Elozegi, and R. O. Hall Jr. 2019. Twenty years of daily metabolism show riverine recovery following sewage abatement. *Limnology and Oceanography* 64:S77–S92.
- Bansal, M. K. 1973. Atmospheric reaeration in natural streams. *Water Research* 7:769–782.
- Beaulieu, J. J., C. P. Arango, D. A. Balz, and W. D. Shuster. 2013. Continuous monitoring reveals multiple controls on ecosystem metabolism in a suburban stream. *Freshwater Biology* 58:918–937.
- Bernhardt, E. S., J. B. Heffernan, N. B. Grimm, E. H. Stanley, J. W. Harvey, M. Arroita, A. P. Appling, M. J. Cohen, W. H. McDowell, R. O. Hall Jr, J. S. Read, B. J. Roberts, E. G. Stets, and C. B. Yackulic. 2018. The metabolic regimes of flowing waters. *Limnology and Oceanography* 63:S99–S118.
- Bernot, M. J., D. J. Sobota, R. O. Hall Jr., P. J. Mulholland, W. K. Dodds, J. R. Webster, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, S. V. Gregory, N. B. Grimm, S. K. Hamilton, S. L. Johnson, W. H. McDowell, J. L. Meyer, B. Peterson, G. C. Poole, H. M. Valett, C. Arango, J. J. Beaulieu, A. J. Burgin, C. Crenshaw, A. M. Helton, L. Johnson, J. Merriam, B. R. Neiderlehner, J. M. O'Brien, J. D. Potter, R. W. Sheibley, S. M. Thomas, and K. Wilson. 2010. Inter-regional comparison of land-use effects on stream metabolism. *Freshwater Biology* 55:1874–1890.
- Caraco, N., J. Cole, S. Findlay, and C. Wigand. 2006. Vascular plants as engineers of oxygen in aquatic systems. *Bioscience* 56:219–225.
- Christensen, P. B., L. P. Nielsen, J. Sorensen, and N. P. Revsbech. 1990. Denitrification in nitrate-rich streams: Diurnal and seasonal variation related to benthic oxygen metabolism. *Limnology and Oceanography* 35:640–651.
- Cohen, M. J., M. J. Kurz, J. B. Heffernan, J. B. Martin, R. L. Douglass, C. R. Foster, and R. G. Thomas. 2013. Diel phosphorus variation and the stoichiometry of ecosystem metabolism in a large spring-fed river. *Ecological Monographs* 83:155–176.
- Connolly, N. M., M. R. Crossland, and R. G. Pearson. 2004. Effect of low oxygen on survival, emergence, and drift of tropical stream macroinvertebrates. *Journal of North American Benthological Society* 23:251–270.
- Demars, B. O. L., and J. R. Manson. 2013. Temperature dependence of stream aeration coefficients and the effect of water turbulence: A critical review. *Water Research* 47:1–15.
- Demars, B. O. L., J. R. Manson, J. S. Olafsson, G. M. Gislason, R. Gudmundsdottir, G. Woodward, J. Reiss, D. E. Pichler, J. J. Rasmussen, and N. Friberg. 2011. Temperature and the metabolic balance of streams. *Freshwater Biology* 56:1106–1121.
- Demars, B. O. L., J. Thompson, and J. R. Manson. 2015. Stream metabolism and the open diel oxygen method: Principles, practice, and perspectives. *Limnology and Oceanography: Methods* 13:356–374.
- Dodds, W. K., J. J. Beaulieu, J. J. Eichmiller, J. R. Fischer, N. R. Franssen, D. A. Gudder, A. S. Makinster, M. J. McCarthy, J. N. Murdock, J. M. O'Brien, J. L. Tank, and R. W. Sheibley. 2008. Nitrogen cycling and metabolism in the thalweg of a prairie river. *Journal of Geophysical Research Biogeosciences* 113:G04029.
- Enquist, B. J., E. P. Economo, T. E. Huxman, A. P. Allen, D. D. Ignace, and J. F. Gillooly. 2003. Scaling metabolism from organisms to ecosystems. *Nature* 423:639–642.
- Frankforter, J. D., H. S. Weyers, J. D. Bales, P. W. Moran, and D. L. Calhoun. 2010. The relative influence of nutrients and habitat on stream metabolism in agricultural streams. *Environmental Monitoring and Assessment* 168:461–479.
- Freeman, M. C., C. M. Pringle, and C. R. Jackson. 2007. Hydrologic connectivity and the contribution of stream headwaters to ecological integrity at regional scales. *Journal of American Water Resources Association* 43:5–14.
- Gelman, A., J. B. Carlin, H. S. Stern, D. B. Dunson, A. Vehtari, and D. B. Rubin. 2013. Bayesian data analysis. CRC Press, Boca Raton, Florida.
- Geyer, C. J., and L. T. Johnson. 2019. Mcmc: Markov chain monte carlo. (Available from: <https://cran.r-project.org/web/packages/mcmc/mcmc.pdf><http://CRAN.R-project.org/packages=mcmc>)

- Grace, M. R., D. P. Giling, S. Hladyz, V. Caron, R. M. Thompson, and R. Mac Nally. 2015. Fast processing of diel oxygen curves: Estimating stream metabolism with BASE (BAYesian Single-station Estimation). *Limnology and Oceanography: Methods* 13:103–114.
- Hall, R. O. Jr, and J. J. Beaulieu. 2013. Estimating autotrophic respiration in streams using daily metabolism data. *Freshwater Science* 32:507–516.
- Hall, R. O. Jr, and E. R. Hotchkiss. 2017. Stream metabolism. Pages 219–233 in G. A. Lamberti and F. R. Hauer (editors). *Methods in stream ecology*. 3rd edition. Academic Press, San Diego, California.
- Hall, R. O. Jr, T. A. Kennedy, and E. J. Rosi-Marshall. 2012. Air-water oxygen exchange in a large whitewater river. *Limnology and Oceanography: Fluids and Environments* 2:1–11.
- Hall, R. O. Jr, and H. L. Madinger. 2018. Use of argon to measure gas exchange in turbulent mountain streams. *Biogeosciences* 15:3085–3092.
- Hall, R. O. Jr, J. L. Tank, M. A. Baker, E. J. Rosi-Marshall, and E. R. Hotchkiss. 2016. Metabolism, gas exchange, and carbon spiraling in rivers. *Ecosystems* 19:73–86.
- Hamme, R., and S. Emerson. 2004. The solubility of neon, nitrogen and argon in distilled water and seawater. *Deep Sea Research Part I: Oceanographic Research Papers* 51:1517–1528.
- Hensley, R. T., and M. J. Cohen. 2016. On the emergence of diel solute signals in flowing waters. *Water Resources Research* 52:759–772.
- Holtgrieve, G. W., D. E. Schindler, T. A. Branch, and Z. T. A'Mar. 2010. Simultaneous quantification of aquatic ecosystem metabolism and reaeration using a Bayesian statistical model of oxygen dynamics. *Limnology and Oceanography* 55:1047–1063.
- Hothorn, T., F. Bretz, and P. Westfall. 2008. Simultaneous inference in general parametric models. *Biometrical Journal* 50:346–363.
- Jahne, B., G. Heinz, and W. Dietrich. 1987. Measurement of the diffusion coefficients of sparingly soluble gases in water. *Journal of Geophysical Research* 92:10767–10776.
- Kaenel, B. R., H. Buehrer, and U. Uehlinger. 2001. Effects of aquatic plant management on stream metabolism and oxygen balance in streams. *Freshwater Biology* 45:85–95.
- Kana, T. M., C. Darkangelo, M. D. Hunt, J. B. Oldham, G. E. Bennett, and J. C. Cornwell. 1994. Membrane inlet mass spectrometer for rapid high-precision determination of N₂, O₂, and Ar in environmental water samples. *Analytical Chemistry* 66:4166–4170.
- Kaplan, L. A., and T. L. Bott. 1989. Diel fluctuations in bacterial activity on streambed substrata during vernal algal blooms: Effects of temperature, water chemistry, and habitat. *Limnology and Oceanography* 34:718–733.
- Kilpatrick, F. A., R. E. Rathburn, N. Yotsukura, G. W. Parker, and L. L. DeLong. 1989. Techniques of water-resources investigations of the United States Geological Survey: Determination of stream reaeration coefficients by use of tracers. United States Geological Survey, Denver, Colorado.
- Lenth, R. V. 2016. Least-squares means: The R package lsmeans. *Journal of Statistical Software* 69:1–33. (Available from: <https://www.jstatsoft.org/article/view/v069i01>)
- Marcarelli, A. M., C. V. Baxter, M. M. Mineau, and R. O. Hall Jr. 2011. Quantity and quality: Unifying food web and ecosystem perspectives on the role of resource subsidies in freshwaters. *Ecology: Ecological Society of America* 92:1215–1225.
- Marzolf, E. R., P. J. Mulholland, and A. D. Steinman. 1994. Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences* 51:1591–1599.
- McDowell, W. H. 2015. NEON and STREON: Opportunities and challenges for the aquatic sciences. *Freshwater Science* 34:386–391.
- Minshall, G. W. 1978. Autotrophy in stream ecosystems. *Bioscience* 28:767–771.
- Mulholland, P. J., C. S. Fellows, J. L. Tank, N. B. Grimm, J. R. Webster, S. K. Hamilton, E. Martí, L. Ashkenas, W. B. Bowden, W. K. Dodds, W. H. McDowell, M. J. Paul, and B. J. Peterson. 2001. Inter-biome comparison of factors controlling stream metabolism. *Freshwater Biology* 46:1503–1517.
- NRCS (Natural Resources Conservation Service). 2008. Plant fact sheet: Rice cutgrass. US Department of Agriculture, Natural Resources Conservation Service, Plant Materials Center, Corvallis, Oregon.
- Odum, H. T. 1956. Primary production in flowing waters. *Limnology and Oceanography* 1:102–117.
- Parker, G. W., and L. A. DeSimone. 1988. Estimating reaeration coefficients for low-slope streams in Massachusetts and New York, 1985–88. Report 91–4188. United States Geological Survey, Water-Resources Investigations, Denver, Colorado. (Available from: <https://pubs.usgs.gov/wri/1991/4188/report.pdf>)
- Payn, R. A., M. N. Gooseff, D. A. Benson, O. A. Cirpka, J. P. Zarnetske, W. B. Bowden, J. P. McNamara, and J. H. Bradford. 2008. Comparison of instantaneous and constant-rate stream tracer experiments through non-parametric analysis of residence time distributions. *Water Resources Research* 44. (Available from: <https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2007WR006274>)
- Peterson, B. J., W. M. Wollheim, P. J. Mulholland, J. R. Webster, J. L. Meyer, J. L. Tank, E. Martí, W. B. Bowden, H. M. Valett, A. E. Hershey, W. H. McDowell, W. K. Dodds, S. K. Hamilton, S. Gregory, and D. D. Morrall. 2001. Control of nitrogen export from watersheds by headwater streams. *Science* 292:86–90.
- Pinheiro, J. C., D. M. Bates, S. Debroy, D. Sarkar, and R Core Team. 2019. nlme: Linear and nonlinear mixed effects models. R package version 3.1–142 (Available from: <https://CRAN.R-project.org/package=nlme>)
- Pribyl, A. L., J. H. McCutchan Jr, W. M. Lewis Jr, and J. F. Saunders III. 2005. Whole-system estimation of denitrification in a plains river: A comparison of two methods. *Biogeochemistry* 73:439–455.
- Raymond, P. A., C. J. Zappa, D. Butman, T. L. Bott, J. Potter, P. Mulholland, A. E. Laursen, W. H. McDowell, and D. Newbold. 2012. Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. *Limnology and Oceanography: Fluids and Environments* 2:41–53.
- Reisinger, A. J., J. L. Tank, T. J. Hoellein, and R. O. Hall Jr. 2016. Sediment, water column, and open-channel denitrification in rivers measured using membrane-inlet mass spectrometry. *Journal of Geophysical Research: Biogeosciences* 121:1258–1274.

- Riley, A. J., and W. K. Dodds. 2013. Whole-stream metabolism: Strategies for measuring and modeling diel trends of dissolved oxygen. *Freshwater Science* 32:56–69.
- Roberts, B., P. Mulholland, and W. Hill. 2007. Multiple scales of temporal variability in ecosystem metabolism rates: Results from 2 years of continuous monitoring in a forested headwater stream. *Ecosystems* 10:588–606.
- Roley, S. S., J. L. Tank, N. A. Griffiths, R. O. Hall Jr, and R. T. Davis. 2014. The influence of floodplain restoration on whole-stream metabolism in an agricultural stream: Insights from a 5-year continuous data set. *Freshwater Science* 33:1043–1059.
- Roley, S. S., J. L. Tank, M. L. Stephen, L. T. Johnson, J. J. Beaulieu, and J. D. Witter. 2012. Floodplain restoration enhances denitrification and reach-scale nitrogen removal in an agricultural stream. *Ecological Applications* 22:281–297.
- Rosenfeld, J. S., and R. J. Mackay. 1987. Assessing the food base of stream ecosystems—Alternatives to the P/R ratio. *Oikos* 50:141–147.
- Sand-Jensen, K., E. Jeppesen, K. Nielsen, L. Van der Bijl, L. Hjermand, L. W. Nielsen, and T. M. Iversen. 1989. Growth of macrophytes and ecosystem consequences in a lowland Danish stream. *Freshwater Biology* 22:15–32.
- Soana, E., E. A. Fano, and G. Castadelli. 2018. Estimate of gas transfer velocity in the presence of emergent vegetation using argon as a tracer: Implications for whole-system denitrification measurements. *Chemosphere* 213:526–532.
- Solomon, C. T., D. A. Bruesewitz, D. C. Richardson, K. C. Rose, M. C. Van de Bogert, P. C. Hanson, T. K. Kratz, B. Larget, R. Adrian, B. Leroux Babin, C. Chiu, D. P. Hamilton, E. E. Gaiser, S. Hendricks, V. Istvánovics, A. Laas, D. M. O'Donnell, M. L. Pace, E. Ryder, P. A. Staehr, T. Torgerson, M. J. Vanni, K. C. Weathers, and G. Zhu. 2013. Ecosystem respiration: Drivers of daily variability and background respiration in lakes around the globe. *Limnology and Oceanography* 58:849–866.
- Speir, S. L., J. M. Taylor, and J. T. Scott. 2017. Seasonal differences in relationships between nitrate concentration and denitrification rates in ditch sediments vegetated with rice cutgrass. *Journal of Environmental Quality* 46:1500–1509.
- Taylor, J. M., M. T. Moore, and J. T. Scott. 2015. Contrasting nutrient mitigation and denitrification potential of agricultural drainage environments with different emergent aquatic macrophytes. *Journal of Environmental Quality* 44:1304–1314.
- Thyssen, N., M. Erlandsen, E. Jeppesen, and C. Ursin. 1987. Reaeration of oxygen in shallow, macrophyte rich streams: I - Determination of the reaeration rate coefficient. *Internationale Revue der gesamten Hydrobiologie und Hydrographie* 72:405–429.
- Tobias, C. R., J. K. Bohlke, and E. Busenberg. 2009. A simple technique for continuous measurement of time-variable gas transfer in surface waters. *Limnology and Oceanography: Methods* 7:185–195.
- Valett, H. M., S. A. Thomas, P. J. Mulholland, J. R. Webster, C. N. Dahm, C. S. Fellows, C. L. Crenshaw, and C. G. Peterson. 2008. Endogenous and exogenous control of ecosystem function: N cycling in headwater streams. *Ecology* 89:3515–3527.
- Wanninkhof, R. 1992. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research* 97:7373–7382.
- Wanninkhof, R., P. J. Mulholland, and J. W. Elwood. 1990. Gas exchange rates for a first-order stream determined with deliberate and natural tracers. *Water Resources Research* 26:1621–1630.
- Watson, D. 1987. Hydraulic effects of aquatic weeds in U.K. rivers. *Regulated Rivers: Research and Management* 1:211–287.
- Webster, J. R., and J. L. Meyer. 1997. Organic matter budgets for streams: A synthesis. *Journal of North American Benthological Society* 16:141–161.
- Wilcock, R. J., P. D. Champion, J. W. Nagels, and G. F. Croker. 1999. The influence of aquatic macrophytes on the hydraulic and physico-chemical properties of a New Zealand lowland stream. *Hydrobiologia* 416:203–214.
- Young, R. G., and A. D. Huryn. 1998. Comment: Improvements to the diurnal upstream- downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences* 55:1784–1785.
- Zuur, A. F., E. N. Ieno, N. J. Walker, A. A. Saveliev, and G. M. Smitt. 2009. *Mixed effects models and extensions in ecology with R*. Springer, New York, New York.