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Metabolism, gas exchange, and carbon spiraling in rivers

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Abstract

Ecosystem metabolism, i.e., gross primary productivity (GPP) and ecosystem respiration (ER), controls organic carbon (OC) cycling in stream and river networks and is expected to vary predictably with network position. However, estimates of metabolism in small streams outnumber those from rivers such that there are limited empirical data comparing metabolism across a range of stream and river sizes. We measured metabolism in 14 rivers (discharge range 14 to 84 m³ s⁻¹) in the Western and Midwestern United States (US). We estimated GPP, ER, and gas exchange rates using a Lagrangian, 2-station oxygen model solved in a Bayesian framework. GPP ranged from 0.6 to 22 g O₂ m⁻² d⁻¹ and ER tracked GPP, suggesting that autotrophic production supports much of riverine ER in summer. Net ecosystem production, the balance between GPP and ER was 0 or greater in 4 rivers showing autotrophy on that day. River velocity and slope predicted gas exchange estimates from these 14 rivers in agreement with empirical models. Carbon turnover lengths (i.e., the distance traveled before OC is mineralized to CO₂) ranged from 38-1190 km, with longest turnover lengths in high-sediment, arid-land rivers. We also compared estimated turnover lengths with the relative length of the river segment between major tributaries or lakes; the mean ratio of carbon turnover length to river length was 1.6, demonstrating that rivers can mineralize much of the OC load along their length at baseflow. Carbon mineralization velocities ranged from 0.05 to 0.81 m d⁻¹, and were not different than measurements from small streams. Given high GPP relative to ER, combined with generally short OC spiraling lengths, rivers can be highly reactive with regard to OC cycling.

Key words: rivers, gross primary production, ecosystem respiration, carbon spiraling, gas exchange, ecosystem metabolism

Introduction

There is a renewed interest in carbon cycling in freshwater ecosystems as ecologists link metabolic processes with regional carbon (C) budgets (Battin and others 2009; Tranvik and others 2009), but empirical measurements of metabolism in a wide variety of freshwater ecosystems are lacking, as is our understanding of processes that control variation within and across ecosystems. Ecosystem size and position in the landscape will control variation in rates of C supply and *in situ* metabolism; for example, lake size correlates with metabolism (Staeher and others 2012). In the case of streams and rivers, ecosystem processes such as C cycling will vary both as a function of size (as volumetric flow) and landscape position, given that the downstream movement of water connects headwaters with larger streams and rivers (Webster 2007). The effects of stream size and landscape position on C cycling were initially conceptualized as part of the River Continuum Concept (RCC) where headwater streams were predicted to have high rates of ecosystem respiration (ER) relative to gross primary production (GPP), whereas mid-order reaches were predicted to have higher GPP relative to ER because of increased light availability supporting autochthony combined with reduced allochthonous inputs of C (Vannote and others 1980). In contrast, large rivers with high sediment loads would revert to a pattern of higher ER relative to GPP, like headwater streams, because of decreased light penetration in the water column combined with the import of allochthonous particles from upstream. Data from selected river continua have supported the pattern of increasing

GPP/ER downstream from headwaters to non-wadeable rivers (Meyer and Edwards 1990; McTammany and others 2003).

Despite strong conceptual foundations and limited empirical data on how larger streams and rivers function, metabolism estimates in rivers are far fewer in number than those from small streams. Only 10% of reach-scale metabolism estimates (reviewed below) have been conducted in rivers with discharge $>10 \text{ m}^3 \text{ s}^{-1}$ ($\sim 20 \text{ m}$ width), while $> 50\%$ have been made in streams $< 0.1 \text{ m}^3 \text{ s}^{-1}$. Recent advances for estimating gas exchange from dissolved oxygen (O_2) data (Holtgrieve and others 2010; Dodds and others 2013) make estimating metabolism in rivers potentially as straightforward as in small streams. In addition, understanding variation and controls on metabolism in rivers will allow ecologists to answer a variety of unanswered questions in river networks. For example, river food webs are based to a large degree on *in situ* primary production (Thorp and Delong 2002; Cross and others 2013), but there are few data on the actual rates of primary production in rivers.

More broadly, ecosystem metabolism in rivers is of general interest because of the potential for rivers to store, mineralize, and transport terrestrial organic carbon (OC) before reaching the coastal zone (Battin and others 2008; Raymond and others 2013). It is well known that small streams can respire large quantities of terrestrial OC (Marcarelli and others 2011), yet the role of rivers is less understood, despite evidence showing that big rivers also transform terrestrial OC (Cole and Caraco 2001). Riverine metabolism estimates will also facilitate the calculation of OC spiraling lengths (Newbold and others 1982), allowing further comparison among small streams and larger rivers. The OC spiraling method examines downstream C flux relative to mineralization and is a direct

estimate of the degree to which rivers mineralize versus transport OC. Oddly, ecosystem ecologists rarely use this spiraling metric to describe the role of streams and rivers in C cycling despite strong theoretical (Webster 2007) and empirical (Thomas and others 2005; Taylor and others 2006; Griffiths and others 2012) examples.

Here, we measured metabolism of 14 rivers ranging in size from 14 to 84 m³ s⁻¹ to link metabolism metrics with OC cycling. We had 3 objectives: 1) develop a two-station model, solved via Bayesian inverse modeling of metabolism parameters, to measure metabolism in each of 14 rivers varying in physical attributes in Midwest and Western US; 2) combine riverine metabolism values with others from the literature to examine how the balance of GPP and ER varies across a large size range of streams and rivers; and 3) calculate instantaneous metrics of OC spiraling to estimate the degree to which river reaches can process OC.

Methods

Study sites

We chose 14 rivers in the Midwest and Western US that varied chemically, physically, and geomorphically (Table 1, Appendix 1). This study was part of a larger study investigating nutrient cycling in rivers, thus we chose sites to maximize variation in suspended sediment and nutrient concentrations. Sites in western Wyoming and eastern Idaho had low nutrient and low suspended sediment concentrations, central Wyoming and Utah rivers had low to medium nutrient concentrations and medium to high suspended sediments, and Midwestern rivers had generally higher nutrients and low to medium suspended sediments (Table 1). We chose the study reaches by taking in to

consideration the proximity of bridges for adding solutes, the presence of USGS gages for measurements of discharge, and the presence of boat ramps for reach-scale sampling logistics. Rivers varied in summer baseflow discharge from 14 to 84 m³ s⁻¹ with an average of 39 m³ s⁻¹.

Field and laboratory methods

At most sites we performed two-station metabolism estimates based on sampling dissolved O₂ through time. To measure dissolved O₂ we anchored 2-4 multi-parameter Hydrolab Minisondes equipped with optical O₂ sensors in areas of moderate downstream flow, at stations 2.5-10.7 km apart (mean 6.1 km) along each river, with mean distance between sondes corresponding to an average of 2.7 h of travel time. We calibrated the sondes river-side in a 100-L pot of air-saturated water that we vigorously bubbled using an aquaculture air pump and air stone. This method of bubbling oversaturates O₂ by 2%. Bubbling this pot in the laboratory and measuring Ar (which has similar diffusivity as O₂) on a membrane-inlet mass spectrometer, we found that Ar was 2% (±0.15%) oversaturated. This phenomenon is likely due to oversaturation due to bubble-mediated gas exchange (e.g., Hall et al. 2012). We corrected our oxygen data downwards by 2% to counter this over calibration. Following initial calibration, we recorded O₂ readings in this air saturated water to check calibration and that all sondes remained within 2% of saturation; O₂ readings from sondes drifted little during the deployments and thus did not need drift correction. We recorded O₂, temperature, and turbidity using these sondes at 5-min intervals during 3-d deployments during summer baseflow conditions (i.e., July or August).

We also collected physical and chemical data at each site; discharge (Q , $\text{m}^3 \text{s}^{-1}$) came from nearby USGS gaging stations or gages associated with upstream dams. We measured wetted channel width (w , m) of the reach at ~ 70 locations throughout the study reach using a laser rangefinder operated from a boat. We also conducted solute tracer additions as part of nutrient uptake experiments, adding Rhodamine WT (RWT) and NaBr in separate pulse additions with target downstream concentrations of $10 \mu\text{g RWT L}^{-1}$ or $50 \mu\text{g Br}^{-1} \text{L}^{-1}$. We monitored RWT at 4 stations downstream of the release point using 4 Hydrolab Minisondes equipped with fluorometric sensors programmed to record RWT concentration every 10 seconds while Br^{-} samples were manually collected from the river thalweg at timed intervals and analyzed using ion chromatography (Dionex models ICS-5000) using US-EPA standard method 300.0. These tracer releases were used to calculate nominal travel time (i.e., the time for 50% of the solute to pass the downstream station), and mean velocity (V , m min^{-1}) was then calculated as reach length/nominal travel time, while mean depth (z , m) was estimated based on continuity, $z = Q/(wV)$. We also measured background water column nutrients at each site as part of the nutrient uptake experiments and reach-scale estimates were based on the average of 3 to 5 samples collected at 4 sites. We analyzed $\text{NH}_4^{+}\text{-N}$ using the phenol-hypochlorite method (Solorzano 1969), $\text{NO}_3^{-}\text{-N}$ using the cadmium reduction method (APHA 1995) and SRP using the ascorbic acid method (Murphy and Riley 1962) on a Lachat Flow Injection Autoanalyzer (Lachat Instruments, Loveland, CO, USA).

To estimate C spiraling, we sampled particulate OC (POC) and dissolved OC (DOC). We collected POC from 3 grab samples taken in the thalweg at 4 locations from each river. Rivers averaged 0.6 to 1.3 m deep and were turbulent; hence, we did not take

depth-integrated samples. For POC, we immediately filtered a known volume of water in the field onto pre-ashed and weighed glass fiber filters (Whatman GF/F), air dried the filters and stored them for transport to the lab where we dried them at 60°C, weighed them, and combusted at 500°C. We reweighed the filters to obtain an ash-free dry mass (AFDM) and converted to mg AFDM/L given the volume of sample filtered; we assumed that 50% of AFDM was C. Samples for DOC came from triplicate samples at one location. These were filtered with pre-ashed glass fiber filters (Whatman GF/F), acidified with HCl to a pH of 2, and then stored in acid washed and ashed borosilicate amber vials (I-Chem, 40mL). We transported samples on ice to the laboratory, and refrigerated them until analysis on a Shimadzu Total Organic Carbon Analyzer (TOC-5000A; measurement precision of $\pm 0.05 \text{ mg C L}^{-1}$).

Metabolism estimation

We estimated metabolism and gas exchange by fitting a two-station Lagrangian model to the dissolved O₂ data, except for the Muskegon, North Platte, and Bear rivers where we used a one-station method due to instrument failures or burial of the upstream sondes. A two-station procedure measures metabolism in a defined reach of river between the upstream and downstream O₂ sensors, which allows estimation of reach-scale metabolism, even below river discontinuities, such as dams, which may be included in the upstream footprint of one-station O₂ measurements. A general model for two-station metabolism is:

$$O_{down(t+\tau)} = O_{up(t)} + GPP + ER + \text{gas exchange}$$

(1)

207 where $O_{up(t)}$ is the upstream O_2 concentration ($g\ O_2\ m^{-3}$) and $O_{down(t+\tau)}$ is downstream
 208 O_2 concentration of that same parcel of water following travel time, τ . GPP and ER are
 209 both expressed in $g\ O_2\ m^{-2}\ d^{-1}$, and represented as positive and negative rates of O_2
 210 production and consumption, respectively.

211 An expansion of this model is:

$$O_{down(t+\tau)} = O_{up(t)} + \left(\frac{GPP}{z} \times \frac{\sum_t^{t+\tau} PPFD}{PPFD_{total}} \right) + \frac{ER}{z} \tau$$

$$+ K\tau \left(\frac{O_{satup(t)} + O_{satdown(t+\tau)}}{2} - \frac{O_{up(t)} + O_{down(t+\tau)}}{2} \right)$$

212 (2)

213 where z is mean depth (m), O_{satup} and $O_{satdown}$ are O_2 saturation concentrations
 214 upstream and downstream ($g\ O_2\ m^{-3}$). Gas exchange flux was the gas exchange rate, K
 215 (d^{-1}) multiplied by the dissolved O_2 saturation deficit, which we averaged for the
 216 upstream and downstream stations. We use light to drive GPP in this model (Van de
 217 Bogert and others 2007). For any parcel of water, the fraction of light it accumulates is
 218 the sum of the photosynthetic photon flux density (PPFD, $\mu mol\ m^{-2}\ s^{-1}$) accumulated in
 219 the time interval from t to $(t + \tau)$ divided by the daily total of PPFD ($PPFD_{total}$). Equation
 220 2 has O_{down} on both sides; we need O_{down} on the left side of the equation because we
 221 are comparing modeled O_{down} with the data. Following some algebra we get:

222

$$O_{down(t+\tau)}$$

$$= \frac{O_{up(t)} + \left(\frac{GPP}{z} \times \frac{\sum_t^{t+\tau} PPFD}{PPFD_{total}} \right) + \frac{ER}{z} \tau + K\tau \left(\frac{O_{satup(t)} - O_{up(t)} + O_{satdown(t+\tau)}}{2} \right)}{1 + \frac{K\tau}{2}}$$

223 (3)

Assumptions of this model are that GPP is a linear function of light intensity, ER is constant throughout the day, and that the average of up and down station O₂ saturation deficit is representative for the entire reach. We tested the assumption of linear light relationships by using 1-station models (equation 4 below) for 1 day on each river with a Jassby-Platt light saturation function exactly following Holtgrieve and others (2010). Eight of 14 rivers had linear light response curves. Six showed slightly curvilinear relationships, with increase in GPP 3-10%, with a concomitant two-fold increase in the credible intervals. In a two-station model with 3-h travel times, it would be necessary to divide these travel times into 5-min intervals to calculate and sum GPP for each. We felt that a potential increase in accuracy of 10% for 6 of the rivers did not warrant this increased model complexity. We did not include a diel temperature response for ER because the relationship of ER to temperature is highly variable (Huryn and others 2014, Jankowski and others 2014), and thus we would have needed to estimate this parameter in addition to GPP, ER, and *K*, possibly producing an overfitted model. Gas exchange is estimated as *K*₆₀₀ (d⁻¹) and is corrected for temperature at each time step based on Schmidt number scaling (Jähne and Haußecker 1998). We convert this per time rate to a gas exchange velocity (*k*₆₀₀, m/d) by multiplying by mean depth, *z*, to facilitate comparisons with published gas exchange velocities. We used modeled solar insolation data for Eq 3 based on geographic location and time of day and year.

For the 3 rivers using a one station method (North Platte, Bear, and Muskegon), we used the following model (Van de Bogert and others 2007):

$$O_t = O_{t-\Delta t} + \frac{GPP}{z} \times \frac{PPFD_t}{PPFD_{total}} + \frac{ER}{z} \Delta t + K \Delta t (O_{sat_{t-\Delta t}} - O_{t-\Delta t}) \quad (4)$$

where t is time of day and Δt is the time between O_2 measurements. This model measures O_2 change in one place rather than tracking it downstream and in a longitudinally homogenous river, one-station analyses will give the similar results to a two-station model (Reichert and others 2009). Of the 3 rivers, only the Muskegon had a dam located 47 km upstream, but we suggest that its influence was negligible because the dam was located twice the distance ($1.6V/K$) for 80% of O_2 turnover (Chapra and Di Toro 1991) .

Based on the above models, we used a Bayesian inverse modeling procedure to estimate metabolism (GPP and ER) and gas exchange rate (K_{600}) roughly following Holtgrieve and others (2010). Bayesian analysis treats parameters as random variables with a corresponding probability distribution and allows estimating uncertainty for the modeled parameters. Because we solved for gas exchange as well as GPP and ER, there is the risk of overfitting the model, and posterior probability distributions solved via a Bayesian approach allowed us to examine this assumption closely. At all but one sites we had two full days of data, and we fit each daytime period separately starting at 22:00 the night before to 06:00 the day after for a total of 32 h.

Following Bayes rule, we calculated the posterior probability distribution of the parameters as:

$$P(\theta|D) \propto P(D|\theta) \times P(\theta) \quad (5)$$

where θ is a vector of parameters, GPP, ER and K , and D is the O_2 data for the downstream or single station. The likelihood of the data given θ assumes normally distributed error and is calculated as:

$$\mathcal{L}(D|\theta) = \prod_{i=1}^n N(D_i|\mu_i, \sigma_i^2) \quad (6)$$

where the likelihood of D given θ is the product of likelihoods of the data relative to modeled downstream O_2 concentrations (μ_i) and variance (σ_i^2). We simulated the posterior distribution $P(\theta | D)$ using a Metropolis algorithm and Markov-chain Monte Carlo (MCMC) using function *metrop* in the *mcmc* package for R (Geyer 2010, R Development Core Team 2011). We ran each chain for 20,000 iterations following burn in and we started all MCMC chains with different parameter values to ensure a global solution. We did not thin chains and we adjusted the proposal distribution of the Metropolis algorithm to achieve an acceptance rate near 20%. For metabolism parameters, we used minimally informative prior probability distributions ($GPP \sim N(\mu=5, sd=10)$, $ER \sim N(\mu=-5, sd=10)$). For gas exchange, we used the nighttime regression method (Hornberger and Kelly 1975) or empirical equation 7 from Raymond and others (2012) to assign a normal prior probability distribution, where the mean and standard deviation of the prior probability distribution were the mean and standard deviation respectively of the 4 slopes from nighttime regression measured by the two O_2 sondes over two nights or the error in the predictive equation. Code for one- and two-station models is in Appendix 5.

Calculation of C spiraling

We calculated turnover length of OC for each river following (Newbold and others 1982) where spiraling length (S_{OC} , m) is the ratio of downstream transport relative to mineralization and is calculated as:

$$S_{OC} = \frac{Q \times [OC]}{-HR \times w} \quad (7)$$

Discharge (Q) and stream width (w) were estimated as described above, and the sum of POC and DOC gives the organic C concentration [OC]. However, to calculate S_{OC} requires an estimate of heterotrophic respiration (HR, which is a negative flux) that equals $ER - AR$, where AR is the respiration by algae and macrophytes themselves. Typically researchers assume that AR is some fraction of GPP (e.g., 0.2 to 0.5) but a recent analysis suggests that the daily fraction of GPP (AR_f) consumed by respiration by algae is about 44% (Hall and Beaulieu 2013). Assuming this fraction, we estimated HR as:

$$HR = ER - AR_f \times GPP \quad (8)$$

Turnover length of OC will depend strongly of the size of the river. To compare mineralization relative to [OC] (i.e., [DOC] + [POC]) we calculated a “mineralization velocity” (v_{f-OC} , $m\ d^{-1}$) of OC as:

$$v_{f-OC} = \frac{-HR}{[OC]} \quad (9)$$

analogous to uptake velocity measured in nutrient uptake studies (Hall and others 2013). We converted HR in O_2 units to $g\ C\ m^{-2}\ d^{-1}$ by assuming a 1:1 molar relationship between C and O in respiration and we then compared v_{f-OC} to those measured in other rivers and streams where OC spiraling length was reported. Error in not perfectly knowing AR_f may introduce error into estimates of v_{f-OC} . Therefore we calculated v_{f-OC} 1000 times with each replicate using a randomly selected estimate of AR_f from Hall and Beaulieu (2013) and 3 subsequent studies (Roley and others 2014, Genzoli and Hall in revision, R. O. Hall et al, unpublished data). Finally, we compared S_{OC} to the estimate of river length estimated from GIS; we defined the segment distance for each river as the length of river downstream of a major reservoir or confluence of large tributary and upstream of a lake,

reservoir, or much larger river. This designation of river length was not meant as a definition, but rather to provide some context for considering OC turnover length, *Soc*.

Statistical inference

We used Pearson correlations to relate rates of metabolism to predictor variables, and rates of C spiraling to river size. Inference on this correlation coefficient (r) was based on calculating default Bayes factors for correlation (Wetzels and Wagenmakers 2012), which can be interpreted as the relative probability that a linear relation exists between 2 variables. Bayes factors >6 constitute strong evidence in support of the alternative hypothesis (linear relation) versus a null. We estimated error on metabolism estimates, GPP, ER and K_{600} , not as the parameter error from the MCMC solutions, but rather on the bootstrap 95% confidence intervals from the 2-8 metabolism estimates (i.e., the median value of the posterior probability distributions) at each site. This approach assumes no within-estimate error, which follows the fact that the among-estimate error exceeded the parameter error from any one MCMC solution. We performed all statistics using R (R Development Core Team 2011).

We compared rates of metabolism in this study to those from many other streams and rivers, collating estimates of reach-scale, open channel metabolism from Marcarelli and others (2011). We also added newer studies to this data set, of which several are from similar sized rivers as the ones studied here (Appendix 4). We used locally weighted regression (Trexler and Travis 1993) with a smoothing parameter of 0.75 to visualize trends in metabolism as a function of river discharge.

Results

Models fit the data closely and had low error in estimates of the parameters, GPP, ER, and K (Fig 1). The 95% credible interval on metabolism parameters for any model fit averaged $< 10\%$ of the value of the parameter itself (Table 1). Variation in parameter estimates between the two measurement days or among sondes was higher than credible intervals within any one day (Table 1, Appendix 2).

GPP and ER varied strongly among the 14 rivers (Table 1, Fig 3); variation in GPP ranged from 0.6 to 22 $\text{g O}_2 \text{ m}^{-2} \text{ d}^{-1}$, and encompassed much of the range of GPP measured previously in small streams. However, for these rivers, unlike many smaller streams, GPP and ER fell closer to the 1:1 line (Fig 3) suggesting that these 14 rivers had low rates of HR relative to GPP. Neither turbidity nor nutrient concentrations correlated with GPP or ER in any of the rivers (Appendix 3). Nearly all Pearson correlation coefficients were $< |-0.48|$, with corresponding Bayes factor of < 0.9 , which provided no support for a linear relationship between the metabolism parameters and potential covariates (Appendix 3). Two exceptions were benthic chlorophyll and total chlorophyll which positively correlated with ER ($r=0.76$ and 0.78 respectively with Bayes factor > 27 indicating strong evidence). Log transformed GPP and $|ER|$ were strongly positively correlated with each other (Fig 3, $r=0.74$, Bayes factor = 18.6).

River size affected variation in metabolic rates and $GPP/|ER|$. GPP and ER were highly variable, but peaked in mid-sized rivers (Fig 4). Estimates of heterotrophic respiration in our 14 rivers spanned a broad range, but were not as high as some streams with $< 10 \text{ m}^3 \text{ s}^{-1}$ discharge. The ratio $GPP/|ER|$ increased with increasing river size, and large streams and rivers did not have low values of $GPP/|ER|$. For example, 50% of

361 rivers with $Q < 10 \text{ m}^3 \text{ s}^{-1}$ had $\text{GPP}/|\text{ER}| < 0.3$. On the other hand, in rivers with $Q > 10$
362 $\text{m}^3 \text{ s}^{-1}$, only 14% had $\text{GPP}/|\text{ER}| < 0.3$.

363 Gas exchange (K_{600}) varied among the rivers (Table 1), with a mean of 5.7 d^{-1} and
364 a range of 0.5 to 16 d^{-1} ; gas exchange rates corresponded to a mean gas exchange velocity
365 (k_{600}) of 20.8 cm h^{-1} with a range of 2 to 71 cm h^{-1} . Gas exchange rate was uncorrelated
366 with river depth, but river depth only varied two-fold among the 14 rivers. River slope
367 strongly predicted gas exchange velocity (Fig 2), and k_{600} fell closely to the prediction
368 estimate based on empirical equations used for many studies (Raymond and others 2012)
369 (Fig 2). The 1:1 prediction line explained 84% of the variation in these 14 rivers relative
370 to the 76% R^2 in Raymond and others (2012).

371 Organic C spiraling lengths (S_{OC}) averaged 319 km and ranged from 38 to 1193
372 km, and S_{OC} lengths were generally similar to their respective river segment lengths;
373 median ratio of S_{OC} to segment length was 1.6 with a range of 0.2 to 4.7 (Table 2). Arid-
374 land rivers with high suspended organic sediment loads and low HR (e.g., Green River at
375 two Utah sites, Colorado River, and Bear River, UT) had much longer S_{OC} than other
376 rivers (Table 2). Mineralization velocities (v_{fOC}) for the 14 rivers averaged 0.37 m d^{-1} and
377 ranged from 0.05 to 0.81 m d^{-1} and when combined with previous studies, v_{fOC} correlated
378 positively with discharge ($r = 0.50$, Bayes factor = 127, strong evidence) (Fig 5).

380 Discussion

381 Gross primary production and ER varied strongly in our 14 rivers; this variation
382 corresponded to that of other previous measurements in similar-sized rivers. One river,
383 the Henry's Fork, ID had among the highest GPP ever measured for a stream or river.

Others, like the Bear River, UT had low rates of metabolism. The 4 rivers in the Midwestern US had moderate rates of metabolism with low variation among them. Despite evidence showing that GPP can increase as a function of stream or river size (Fig 4) (Finlay 2011), variation in metabolism among rivers was large enough that rivers have no characteristic rate of metabolism.

Because we measured metabolism on only 2 days, during summer baseflow conditions, we did not have a large within-river dataset to examine uncertainty on our estimates. As such, we used a Bayesian method that allowed us to examine parameter error within any one day (Holtgrieve and others 2010). This approach becomes necessary when solving for gas exchange as well as metabolic parameters to avoid equifinality among parameter estimates. In fact, we found low rates of parameter error. Variation among sondes, or between the two measurement days, were higher than error estimated via computational Bayesian approach on any one day, suggesting that these within-day error estimates may not represent day-to-day error well.

GPP and ER

GPP ranged widely in our 14 rivers from among the highest rate ever measured (e.g., Henry's Fork) to low rates that were similar to those measured in small, forested streams. Despite this high variability, we were unable to statistically assess controls on variation of GPP among our 14 rivers. Time series of metabolism clearly show that turbidity can control rates of GPP in a river (Hall et al. 2015). We certainly expected that variation in turbidity would control GPP among rivers, but we found only weak

correlation between GPP and turbidity (Appendix 3), even though variation in turbidity was high, suggesting that some other processes were controlling variation.

We acknowledge that we only measured metabolism for two days; it is very likely that antecedent conditions (e.g., time since last flood) may have controlled the rates of GPP that we measured. Variation in the metabolism of one river can be as large as variation among rivers, and a strong role for antecedent conditions has been noted (Uehlinger 2006; Roberts and others 2007; Beaulieu and others 2013). One river, the Muskegon, had an unexpected dam release, tripling discharge the day before our metabolism estimates. This spate may have affected metabolism.

Despite these limitations, we can observe some anecdotal evidence for controls on GPP; for example, the rivers with the two highest rates of GPP (Green River, WY and Henry's Fork, ID) were located below water storage impoundments. Rivers below dams typically have stable flow and low turbidity and can have high benthic algal biomass with correspondingly high rates of GPP (Davis and others 2012). Henry's Fork also has substantial inputs of groundwater-fed springs; high metabolism has been measured previously in other spring streams (Odum 1957; Hall and others 2003; Heffernan and Cohen 2010). In contrast, Buffalo Fork, WY drains mountain wilderness and is oligotrophic, and had correspondingly low rates of metabolism. However, we emphasize that we did not design the overall study to statistically tease out controls on river metabolism, but rather to assess rates and variation of riverine nutrient uptake (J. L. Tank and others, unpublished data). Statistically examining controls on metabolism would have required many more rivers (Bernot and others 2010), or we would have selected all

428 rivers along a gradient of a predicted controlling variable, such as nutrient concentrations,
429 in one region of the country.

430 GPP and ER were highly coupled in these 14 rivers (Fig 3), and unlike in some
431 streams, we did not find high riverine ER associated with low rates of GPP. This finding
432 suggests that despite an overall pattern of $GPP/|ER| < 1$, rivers may not have extremely
433 high rates of HR, at least during baseflow when they are not transporting large amounts
434 of terrestrial C and GPP is high. The relationship between $GPP/|ER|$ as a function of river
435 discharge across the 14 rivers, combined with the full meta-analysis data set, supports
436 this conclusion with small streams having the potential for both low and high ratios of
437 $GPP/|ER|$, whereas rivers $> 10 \text{ m}^3 \text{ s}^{-1}$ had $GPP/|ER| > 0.3$ in 85% of the observations.
438 Higher rates of GPP in rivers have been previously noted in other meta-analyses of
439 stream metabolism, with the interesting twist that human perturbation has a stronger
440 effect on metabolism in small streams relative to rivers (Finlay 2011). Studies that
441 measure metabolism within a river network have found a similar pattern of increasing
442 $GPP/|ER|$ with downstream position in the network (Meyer and Edwards 1990;
443 McTammany and others 2003); increasing $GPP/|ER|$ with river size could be due to
444 increasing GPP, decreasing HR, or both.

445 Theory predicts that lower rates of HR should occur in downstream reaches
446 because most terrestrial (i.e., allochthonous) OC inputs are mineralized in the headwaters
447 (Webster 2007), yet HR peaks in middle river discharge (Fig. 4). Rather, rivers tended to
448 have high rates of ER, but do not have the negligible rates of GPP found frequently in
449 small, often shaded, headwater streams (Fig. 4). Alternatively, the pattern of somewhat
450 lower HR in larger rivers may be an artifact of the rivers and time chosen for metabolism

estimates. Rivers occupying a floodplain may have large spikes in HR during flooding periods (Colangelo 2007; Dodds and others 2013), which are notably not included in the 14 estimates of river metabolism that we present here. In addition, as shown by Meyer and Edwards (1990), rivers with large quantities of terrestrially-derived DOC may have high rates of ER relative to GPP, though we note that they too found a pattern of increasing $GPP/|ER|$ with increasing stream order.

Many small streams had $|ER| \gg GPP$; but we suggest that it is not possible to have $GPP \gg |ER|$ because of a necessary upper limit to $GPP/|ER|$. For example, high rates of GPP will result in higher ER because of the combination of associated respiration of the autotrophs along with heterotrophic organisms contained in stream biofilms. The fraction of GPP that is autotrophic respiration (AR) will determine this upper limit; given a mean fraction of GPP respired each day (AR_f) of 0.44 (Hall and Beaulieu 2013), we calculate that $GPP/|ER| = GPP/(GPP \times 0.44) = 2.2$. Thus we predict that the upper limit of $GPP/|ER|$ is 2.2 because, on average, 44% of GPP constitutes daily autotrophic respiration. Indeed only 1.1 % of $GPP/|ER|$ values exceeded 2.2, suggesting that this value may represent an upper bound for autotrophy in rivers.

Gas exchange

The 14 rivers had variable gas exchange and river slope was the primary predictor of gas exchange velocity (k_{600} , Fig. 2); gas exchange was lowest in Bear River, UT which had gas exchange similar to a low-wind lake (Cole and Caraco 1998). Gas exchange was highest in the Henry's Fork, which at 71 cm h^{-1} approached that of the steep, whitewater section of the Colorado through Grand Canyon (Hall and others 2012). The slope of the

regression line between river slope and k_{600} was lower for these 14 rivers than for multiple measurements in the Colorado River in Grand Canyon (Hall et al. 2012), likely due to the broad range of reaches through the Grand Canyon, ranging from nearly still to extremely turbulent rapids. Our 14 rivers here did not display this within-river variation in river morphology, even for the pool-drop section of the Green River in Gray Canyon. Nevertheless, gas exchange predicted using empirical equations matched closely with our data, even more closely than the original data used to derive these equations (Raymond and others 2012).

There is much interest in understanding gas exchange in rivers to estimate global gas fluxes (Raymond and others 2013). With this study, we show that across a few medium-sized continental rivers, gas exchange can vary widely. For the purposes of an accurate metabolism estimate, it is necessary to estimate gas exchange for each river because the log-log relationship in Fig. 2 has 2-fold prediction error. Optimistically, with high GPP and low rates of O₂ turnover (K_{600}), it is possible to model gas exchange using solely O₂ data, with no need to perform an experimental gas tracer addition (e.g., SF₆) in these rivers. For the purposes of scaling gas exchange, where it is impractical to empirically measure gas exchange for an entire river network, the method employed by Raymond et al. (2012) is likely the best available for these medium-sized rivers in the sense that it is unbiased (though with large prediction error) and captures much of the variability in k_{600} .

C spiraling

Spiraling lengths for OC were generally long, but variable, in these 14 rivers. In 7 cases S_{OC} was shorter than the length of the river segment that we measured, suggesting that there can be complete turnover of the OC pool along the length of some rivers. Functionally, rivers with an S_{OC} roughly equal to segment length have turned over > 50% of the OC pool in that length, although a caveat to this conclusion is that we evaluated these rivers at baseflow discharge. High flows associated with storms or snowmelt would assuredly result in much longer OC spiraling lengths because the OC flux would increase more than any increase in organic matter processing (i.e., HR) during high flow periods. Notably, the singular aspect of C cycling that most C spiraling studies (ours and others) generally overlook is that most OC transport will occur during periods of high flow, resulting in substantial intra-annual variation in S_{OC} (Meyer and Edwards 1990). However, our analysis shows that, at least at baseflow, heterotrophic activity can drive substantial mineralization of OC along a river's length. Given scaling relationships between element spiraling length and river length, a constant v_{f-OC} means that spiraling length increases less than proportionally with downstream distance from headwaters (Hall and others 2013). We suggest that OC mineralization and subsequent turnover of OC pools occurs to the same degree in larger streams and rivers as in the more well-studied small streams.

It is important to note that although $GPP/|ER|$ is higher in rivers than headwaters, it is clear that there is substantial processing of allochthonous C in rivers supported by the high rates of HR across a range of stream and river sizes (Fig. 4). This point has also been noted previously by Cole and Caraco (2001) for large rivers; these findings suggest that rivers are important sites for the mineralization for OC. Alternatively this

“allochthonous” C fueling excess ER downstream could be C produced via autochthonous production that is subsequently transported, and then mineralized, in downstream river segments (Genzoli and Hall in revision).

From the perspective of C cycling, data from these 14 rivers combined with that from the literature support that rivers are reactive ecosystems. With the current interest in examining how freshwater ecosystems contribute to regional and global C budgets (Battin and others 2008; 2009; Raymond and others 2013), we suggest that rivers may strongly influence mineralization and fixation of new C in addition to their more obvious role in the longitudinal transport of C. In fact at baseflow, mineralization and transport are balanced such that OC can turn over completely in some river reaches. In rivers without substantial groundwater inputs containing terrestrial sources of dissolved CO₂, we may expect that net ecosystem production (NEP) for rivers will roughly equal CO₂ emissions, as has been found for the Hudson River (Cole and Caraco 2001). Metabolism and C spiraling data from this study represent an approach to examine the biogeochemical mechanisms controlling riverine C cycling, but only represent a snapshot in time. In the future, we expect that time series of metabolism data will provide estimates across a range of seasonal and hydrologic conditions, supporting a more thorough understanding of the role of rivers in C cycling.

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Table 1. Physical and chemical properties and metabolism of the 14 rivers in this study. Values in parentheses represent 95% bootstrap confidence intervals for metabolism based on 2 to 8 metabolism estimates at each site.

River	Discharge m ³ s ⁻¹	Width m	Velocity m min ⁻¹	Mean		NH ₄ ⁺ μg N L ⁻¹	NO ₃ ⁻ μg N L ⁻¹	SRP μg P L ⁻¹	Turbidity fmu	GPP g O ₂ m ⁻² d ⁻¹	ER g O ₂ m ⁻² d ⁻¹	K ₆₀₀ d ⁻¹
				depth m	depth m							
Buffalo Fork Green River, WY	19.1 25.5	35.2 62.5	55.8 32.4	0.58 0.76	5 5	3 5	3 15	44 21	3 3	0.8 (0.7, 0.8) 19.9 (18.3, 21.5)	-3.4 (-3.5, -3.3) -17.5 (-20.0, - 15.0)	8.7 (8.5, 8.9) 8.3 (6.5, 10.0)
Henry's Fork	69.6	62.0	61.7	1.09	3	6	16	16	1	22.1 (20.6, 23.6)	-18.1 (-20.2, - 15.9)	15.6 (13.9, 17.3)
Snake River	71.7	65.3	63.4	1.04	5	bd	7	7	0	3.0 (2.9, 3.1)	--5.1 (-5.6, - 4.7)	7.0 (7.0, 7.0) 15.2 (14.2, 16.4)
Salmon River Tippecanoe River	25.9 19.0	50.5 50.6	59.2 37.9	0.52 0.59	5 15	2 1850	4 67	4 67	2 17	4.0 (3.9, 4.2) 2.6 (2.5, 2.7)	-5.1, (-5.8, -4.7) -5.3 (-5.4, -5.2)	2.1 (2.0, 2.3)
East Fork, White River	14.0	47.9	21.4	0.82	1	1650	60	60	43	4.7 (4.4, 5.0)	-5.6 (-5.6, -5.5)	1.7 (1.6, 1.8)
Muskegon River	33.0	67.0	28.3	1.05	14	330	9	9	23	3.0 (3.0, 3.0)	-4.8 (-4.8, -4.7)	3.0 (3.0, 3.1)
Manistee River North Platte River	36.5 83.9	52.5 81.3	33.4 58.9	1.25 1.05	30 5	120 20	10 20	10 20	3 19	3.9 (3.5, 4.2) 4.0 (3.7, 4.5)	-4.4 (-4.6, -4.2) -6.8 (-7.6, -6.1)	2.0 (1.9, 2.1) 4.4 (4.0, 4.9)
Bear River Green River at Ouray	16.0 37.9	37.3 111.8	26.6 31.6	0.97 0.64	12 2	49 7	18 3	18 3	53 16	1.1 (1.0, 1.3) 1.1 (1.1, 1.2)	-1.1, (-1.6, -0.7) -1.2, (-1.5, -1.0)	0.5 (-0.5, 1.6) 2.1 (1.7, 2.6)
Green River at Gray Canyon	41.0	79.1	23.2	1.34	14	19	22	22	607	0.3 (0.2, 0.5)	-3.0 (-3.1, -2.9)	2.1 (2.0, 2.2)
Colorado River	63.4	83.1	34.3	1.33	1	697	12	12	116	4.5 (4.3, 4.8)	-2.7 (-3.3, -2.2)	6.3 (6.2, 6.5)

Table 2. Parameters for estimating C spiraling length: dissolved organic C concentration (DOC), particulate OC concentration (POC), and heterotrophic respiration (HR). S_{OC} is OC spiraling length, values in parentheses represent 5% to 95% quantiles of a bootstrap distribution from varying HR. Segment length is length of river between major upstream tributaries and larger downstream rivers or lakes. v_{fOC} is the OC mineralization velocity.

River	DOC g m ⁻³	POC g m ⁻³	HR g C m ⁻² d ⁻¹	S_{OC} (km)	Segment length (km)	v_{fOC} m d ⁻¹
Buffalo Fork	2.87	0.43	1.2	134 (123, 143)	44	0.351
Green River, WY	3.64	0.39	3.3	43 (25, 112)	103	0.812
Henry's Fork	2.91	1.06	3.1	123 (66, 433)	120	0.787
Snake River	2.53	0.46	1.4	200 (159, 254)	136	0.473
Salmon River	3.03	0.41	1.2	123 (88, 183)	184	0.360
Tippecanoe River	4.32	0.69	1.6	104 (87, 125)	173	0.310
East Fork, White River	1.53	0.43	1.3	38 (27, 59)	246	0.672
Muskegon River	4.9	0.07	1.3	164 (127, 215)	235	0.259
Manistee River	1.74	0.10	1.0	108 (74, 177)	169	0.553
North Platte River	5.27	0.08	1.9	251 (199, 321)	217	0.354
Bear River	4.08	1.08	0.2	814 (508, 1605)	323	0.045
Green River at Ouray	3.09	0.98	0.3	422 (283, 709)	542	0.069
Green River at Gray Canyon	3.48	14.52	1.1	748 (719, 773)	542	0.060
Colorado River	2.98	2.17	0.3	1194 (403, inf)	264	0.055

Figure legends

Figure 1. Data (thick gray lines) and model fit (thin black line) for 1 representative example of the 2 to 8 metabolism model fits for each of the 14 rivers. Each model fitting procedure was based on one day's worth of oxygen data. Y axis units are % O₂ saturation to facilitate comparison among rivers.

Figure 2. Panel A. Gas exchange velocity from O₂ metabolism model (k_{600} , cm h⁻¹) increased as a function of river slope (%). Line is linear regression, $\log_{10}(k_{600}) = 2.07 + 0.79 \times \log_{10}(\text{slope})$, $r^2 = 0.89$. Panel B. Modeled gas exchange velocity lies to close to that predicted by model # 7 in (Raymond and others 2012). Line is 1:1.

Figure 3. Gross primary production (GPP) versus ecosystem respiration (ER) for our 14 rivers (black points) and other data (gray circles) show high variation among studies. Line is GPP = ER. Axes are log scaled.

Figure 4. Gross primary production (GPP, Panel A), Ecosystem respiration (|ER|, Panel B), and GPP / |ER| (Panel C) as a function of river discharge. Black points are the 14 rivers from this study, gray are other data. Axes are log scaled. Lines are locally weighted regression with smoothing factor = 0.75, The point far to the right is from the Mississippi river and represents the largest possible size for a North American river (Dodds and others 2013). Because of the zero density in points between the Mississippi River and the second largest river in the data set, we did not fit the regression line to the Mississippi River.

Figure 5. Mineralization velocity of organic carbon (v_{f-OC}) was positively correlated with discharge. Gray points are data from other studies, black points are 13 rivers in this study. Error bars are the 5% to 95% quantiles of v_{f-OC} calculated from a

bootstrap of heterotrophic respiration (HR) from Hall and Beaulieu (2013). This error represents uncertainty in HR estimates. Pearson correlation ($r=0.5$) and Bayes factor (127) support strong evidence for a positive relationship.

Fig. 1

Fig 2

Fig 3

Fig 4

Fig. 5

Appendix 1. River physical data.

River	latitude	longitude	Reach length km	Discharge $\text{m}^3 \text{ s}^{-1}$	Width m	Velocity m min^{-1}	Mean depth m	slope m/m	temp $^{\circ}\text{C}$	k_{600} cm h^{-1}
Buffalo Fork	43° 50' 57.775" N	110° 19' 39.240" W	10.74	19.1	35.2	55.8	0.58	0.0016	12.0	21.2
Green River, WY	41° 57' 58.508" N	109° 58' 24.282" W	4.34	25.5	62.5	32.4	0.76	0.0011	18.7	26.1
Henry's Fork	44° 6' 14.008" N	111° 20' 55.190" W	8.86	69.6	62.0	61.7	1.09	0.0033	18.6	71.0
Snake River	43° 49' 40.163" N	110° 131' 49.238" W	7.96	71.7	65.3	63.4	1.04	0.0013	16.3	30.3
Salmon River	44° 16' 58.211" N	11° 19' 36.731" W	9.72	25.9	50.5	59.2	0.52	0.0034	16.1	32.9
Tippecanoe River	41° 1' 25.971" N	86° 35' 5.982" W	4.86	19.0	50.6	37.9	0.59	0.0002	26.2	5.2
East Fork, White River	39° 10' 0.043" N	85° 54' 40.264" W	7.41	14.0	47.9	21.4	0.82	0.0003	28.2	5.8
Muskegon River	43° 20' 48.584" N	85° 56' 25.359" W	5.01	33.0	67.0	28.3	1.05	0.0004	24.9	13.1
Manistee River	44° 16' 3.389" N	86° 0' 57.689" W	5.07	36.5	52.5	33.4	1.25	0.0003	22.6	10.4
North Platte River	42° 45' 46.750" N	105° 23' 41.987" W	8.15	83.9	81.3	58.9	1.05	0.0012	23.1	19.3
Bear River	41° 58' 30.905" N	111° 56' 13.003" W	2.50	16.0	37.3	26.6	0.97	0.0001	23.6	2.0
Green River at Ouray	40° 10' 56.773" N	109° 35' 44.690" W	3.97	37.9	111.8	31.6	0.64	0.0003	23.6	5.6
Green River at Gray Canyon	39° 11' 47.847" N	110° 4' 38.751" W	5.25	41.0	79.1	23.2	1.34	0.0011	25.1	11.7
Colorado River	38° 48' 45.218" N	109° 18' 29.116" W	5.15	63.4	83.1	34.3	1.33	0.0016	25.1	35.0

Appendix 2. Error estimates for metabolism parameters

Appendix 2, Figure 1. GPP for 2 to 8 estimates in each of the rivers. Points are median estimate of the posterior probability distribution of the GPP parameter. Line symbols are the 2.5% and 97.5% quantiles of the posterior probability distribution.

Appendix 2, Figure 2. Ecosystem respiration (ER) for 2 to 8 estimates in each of the rivers. Points are median estimate of the posterior probability distribution of the ER parameter. Line symbols are the 2.5% and 97.5% quantiles of the posterior probability distribution.

Appendix 2, Figure 3. Gas exchange (K_{600} , d^{-1}) for 2 to 8 estimates in each of the rivers. Points are median estimate of the posterior probability distribution of the K_{600} parameter. Line symbols are the 2.5% and 97.5% quantiles of the posterior probability distribution.

Appendix 3. Pearson correlation coefficients (r) between nutrient concentrations, turbidity and metabolism (gpp= gross primary production, er = |ecosystem respiration|). All data except temperature were ln transformed. Bold indicate correlations with strong evidence for a linear relationship ($r > 0.72$ corresponding to Bayes Factor > 10 with $n=14$) GPP and |ER| were positively correlated with Bayes factor = 18.6, showing strong evidence for a linear relationship. The only other variable to correlate with metabolism was benthic and total chlorophyll standing stocks.

	er	no3	nh4	srp	turbidity	DOC	pelagic chla	benthic chla	total chla	temp	width
gpp	0.79	0.07	-0.28	-0.02	-0.50	-0.12	-0.02	0.48	0.53	-0.10	-0.07
er		-0.08	-0.05	0.25	-0.48	-0.03	-0.17	0.76	0.74	-0.26	-0.17
no3			-0.01	0.50	0.56	-0.05	0.83	0.24	0.32	0.81	-0.11
nh4				0.04	-0.04	0.30	-0.11	0.21	0.21	-0.02	-0.32
srp					0.27	-0.02	0.44	0.36	0.27	0.21	-0.52
turbidity						0.24	0.71	-0.15	-0.10	0.75	0.28
DOC							-0.05	0.05	0.15	0.05	0.21
pelagic chla								0.00	0.08	0.89	0.08
benthic chla									0.95	-0.09	-0.38
total chla										0.02	-0.29
temp											0.30

Units for this table:

gpp and er ($\text{g O}_2 \text{ m}^{-2} \text{ d}^{-1}$), no3 and nh4 ($\mu\text{g N L}^{-1}$), srp ($\mu\text{g P L}^{-1}$), turbidity (FNU), DOC (mg C L^{-1}), chla ($\text{mg chlorophyll } a \text{ m}^{-2}$), temp ($^{\circ}\text{C}$)

Appendix 4. Metabolism data used in meta-analysis. Units are $\text{g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ for GPP and ER. Q is discharge in L s^{-1} . Table is .csv file.

Appendix 5. R code used to estimate 2 station metabolism via a Bayesian framework.