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Key Points:

- We propose a novel way to integrate biotic processes with concentration-discharge trends via process-discharge relationships
- Low and high flows induce distinct trends in gross primary production, ecosystem respiration, and net ecosystem production
- Interrelated physicochemical parameters and ecosystem processes, such as pH and net ecosystem production, follow mirrored trends

Supporting Information:

- Supporting Information S1
- Data Set S1
- Data Set S2
- Data Set S3
- Data Set S4

Correspondence to:

B. O'Donnell, brynnmodonnell@gmail.com

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Coupling Concentration- and Process-Discharge Relationships Integrates Water Chemistry and Metabolism in Streams

B. O'Donnell¹ D and E. R. Hotchkiss¹

¹Department of Biological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA

Abstract Stream ecosystem processes, such as metabolism, are dynamically impacted by flow intensity. Therefore, without integrating ecosystem processes with water quality, we miss opportunities to develop frameworks to understand metabolic responses to changing flow. Flow simultaneously affects the material transport and biological opportunities for material transformation. Combining the strengths of ecohydrology and stream ecology to understand how flow variation alters ecosystem processes, we analyzed more than 5 years of water quality and stream metabolism data. We created segmented process-discharge (P-Q) relationships to examine how metabolism rates vary across discharge and compared them to concentration-discharge (C-Q) relationships to explore the dynamic effects of discharge on processes and physicochemical parameters. Within the segmented P-Q relationships, we found the behavior of ecosystem respiration (ER), gross primary production (GPP), and net ecosystem production (NEP) to be different at high and low flows with varying degrees of statistical significance, demonstrating the potential for divergent metabolic responses across changing flows. GPP declined with increasing discharge. The rate of ER declined with discharge initially but then became unchanging at higher flows. NEP reflected the divergent trends between ER and GPP, as the relationship of NEP to Q was flat at lower discharge and declined at higher flows. Interrelated physicochemical parameters and ecosystem processes, such as pH and NEP, had mirrored responses to discharge. Coupling analyses of flow, water quality, and metabolism offers a more complete picture of interrelated ecosystem processes, allowing for a better understanding of ecosystem response to the physical and chemical changes that occur across flows.

Plain Language Summary Understanding how stream microorganisms respond to changes in water flow is needed to improve the health of aquatic ecosystems. While high discharge is frequent when nutrients and pollutants are swept downstream, we lack information about how biology and water quality change during high flow. To examine water quality across flows, concentration-discharge relationships are often quantified. However, by only looking at how water quality changes as a function of flow, we miss a key piece of information: Life within the stream. Life within a stream influences and is influenced by water quality and flow. Here, we used 5 years of chemistry and flow data to calculate stream metabolism: The processes of photosynthesis and respiration by the life within a stream. To assess how water quality changes across flow, we (1) identified how stream metabolism changes across flow via process-discharge analyses and (2) compared concentration-discharge and process-discharge trends to discover how they influenced one another. We found that stream metabolism exhibited different responses across flows. Moreover, multiple concentration-discharge relationships had mirrored responses to associated process-discharge relationships. This study ultimately reveals that both transport and biology respond to changes in flow, with the potential to regulate key ecosystem behaviors.

1. Introduction

Streams function along gradients of 'transformers' to 'transporters' of solutes (Cole et al., 2007). The degree to which a stream transports and transforms solutes can determine the extent to which a stream carries out the processes that make up many of the ecosystem services we value: Nitrogen is assimilated and reduced, and carbon is fixed and respired. However, different environmental factors can shift the dominant stream function between transformer or transporter, elongating or shortening biogeochemical processing length: Shifting stoichiometric limitations, hydrologic disturbance, or changing allochthonous inputs (Dodds et al., 2004; Fisher et al., 1998; Seybold & McGlynn, 2018). Arguably the most influential factor in shaping

©2019. American Geophysical Union. All Rights Reserved. whether a stream functions as a predominant transporter or transformer is flow (Poff et al., 1997). Flow has the ability to impact stream function by loading solutes from the surrounding catchment, changing concentrations of physicochemical constituents (e.g., turbidity and conductivity) within the stream, reducing water residence time, and inducing scour (Raymond et al., 2016; Wollheim et al., 2018). At low flows, a stream is more of an active transformer of nutrients and organic matter, as longer hydrologic residence times are conducive to biogeochemical transformations such as uptake, mineralization, and denitrification (Drummond et al., 2016; Hall et al., 2009). At high flows, upper stream reaches may be more of a "transporter" of materials, as higher flows can reduce biotic activity by scouring the benthos and decreasing transient storage (Fisher, 1982), ultimately shuttling more solutes to downstream ecosystems (Raymond et al., 2016; Zarnetske et al., 2018). The extent to which stream function is altered by the combination of flow-induced changes to physicochemical parameters has not yet been extensively quantified (Wollheim et al., 2018).

Precipitation events activate different catchment sources and flow paths (McGlynn & McDonnell, 2003), with large influences on stream solute concentrations and physicochemical parameters (Boyer et al., 1997). The relationship between solute concentrations and discharge is often depicted using concentration-discharge (C-Q) curves (Williams, 1989). When specific flow paths become connected to running waters (e.g., deep groundwater, riparian zones, floodplains, and disconnected wetlands), solute concentrations change. Changes to concentrations with increasing flow induce either an enriching, positive C-Q relationship if the solute is transport-limited, or a diluted, negative relationship if the element is source-limited and not abundant within the catchment (Basu et al., 2011; Inamdar et al., 2004). If concentration does not have a significant relationship with discharge, and the slope of the C-Q relationship is zero, the C-Q is considered chemostatic. The relationships between discharge and solute concentrations often follow power law distributions; however, slope changes frequently occur at certain thresholds of discharge (Diamond & Cohen, 2018). The prevalence of these power-function slope changes in C-Q relationships has led to the use of segmented, piecewise regressions to better explain the consequences of changing discharge on concentrations (Meybeck & Moatar, 2012; Moatar et al., 2017). Physicochemical (e.g., turbidity, conductivity, and pH) relationships with discharge can be impacted by and segmented due to multiple factors, including availability within the catchment, source activation, or antecedent conditions (Diamond & Cohen, 2018; McMillan et al., 2018).

Flow intensity can also impact in-stream ecosystem processes, such as stream metabolism. Stream metabolism is a measure of the fixation of carbon by autotrophs as gross primary production (GPP) and the breakdown of organic carbon by both autotrophs and heterotrophs as ecosystem respiration (ER). The balance between GPP and ER is net ecosystem production (NEP). Increased flow at low amplitudes can have enriching effects on stream ecosystems, subsidizing biotic transformations of reactive solutes. For instance, low- to middle-intensity flows can load fresh supplies of organic carbon into streams (McLaughlin & Kaplan, 2013), which can stimulate ER (Demars, 2018). On the other hand, higher flows can stress and disturb the ecosystem, inducing drastic changes in temperature and prolonged increases in turbidity (Blaszczak et al., 2018; Roberts & Mulholland, 2007). Elevated flow also has the potential to impede biotic processing by reducing transient storage, diminishing light, and scouring benthos (Blaszczak et al., 2018; Uehlinger & Naegeli, 1998). As a result, the signal from in-stream biotic processes may diminish at higher discharges when either abiotic factors have more control or the footprint of the upstream area contributing to changes in dissolved oxygen crosses terrestrial-aquatic boundaries in ways we cannot account for in-stream metabolism modeling. Indeed, the divergent effects of different levels of flow influence stream processes along a "subsidy-stress gradient" (in the sense of Odum et al., 1979).

Because discharge affects stream processes along a subsidy-stress gradient, process-discharge (P-Q) relationships may exhibit contrasted, segmented trends. Although the adoption of piecewise regressions to quantify C-Q relationships has become more prevalent, most previous work has used linear or power law relationships to assess associations between metabolism and discharge (e.g., Demars, 2018; Lamberti & Steinman, 1997). At the scale of a single precipitation event, ER and GPP often exhibit hysteresis behavior with flow (Roberts & Mulholland, 2007). However, C-Q relationships are typically created for timescales longer than a single event, and we do not yet understand the relationship between discharge and metabolism that spans a range of flow magnitudes. To address this knowledge gap, we explored the dynamic and potentially segmented patterns of stream metabolism across discharges via a P-Q relationship. A segmented P-Q relationship between metabolism and discharge will yield a more comprehensive understanding of flow controls on ecosystem function and carbon transformations and transport.





Figure 1. One of many possible outcomes of coupled concentration- and process-discharge analyses (adapted from Moatar et al., 2017). The dashed vertical line represents a statistically derived breakpoint. Below the breakpoint, in this example, the stream acts as a predominant "transformer" of solutes as flow has not yet created conditions that drastically inhibit biology. Above the breakpoint, in this example, flow creates conditions unfavorable to biological processes and elevates transport-limited solutes, making the stream a dominant "transporter."

Processes captured in P-Q analyses have the potential to influence and be influenced by C-Q trends. Although hydrology and catchment connectivity are critical to understanding solute-discharge relationships, they only capture part of the picture; the feedbacks between in-stream biotic processes and C-Q relationships are missing. C-Q trends often seek to quantify biogeochemical processes via relationships between solute and flow (Godsey et al., 2009; Thomas et al., 2016; Wagner et al., 2019); however, they do not include direct measurements of process and may not take into consideration the potential impact of ecosystem processes on solute dynamics. In-stream biotic processes can alter solute concentrations and physicochemical parameters (Mulholland, 1992; Mulholland & Hill, 1997; Roberts & Mulholland, 2007). Thus, quantifying the impact stream biology has on C-Q dynamics is essential to furthering our understanding of solute transformation and export. For instance, stream metabolism includes the net production or consumption of dissolved organic carbon (Hall & Hotchkiss, 2017). ER also alters stream chemistry by lowering dissolved oxygen (DO) concentrations and elevating CO2 (Hall & Hotchkiss,

2017), with associated pH changes (Maberly, 1996). Similarly, physicochemical parameters affect stream metabolism. Both temperature and DO can affect respiration (Sinsabaugh et al., 1997), and turbidity can decrease GPP by inhibiting access to light (Hall et al., 2015; Young & Huryn, 1996). The interactions among solutes, biota, and flow may be represented by coupling analyses of segmented C-Q and P-Q relationships (Figure 1, Moatar et al., 2017).

To quantify P-Q relationships and examine the interconnection of C-Q and P-Q behavior, we analyzed over 5 years of stream water quality and metabolism data in a mixed urban and agricultural catchment in southwest Virginia. Our objectives were to (1) assess P-Q dynamics to improve our understanding of stream metabolism and function at different flows and (2) compare C-Q and P-Q results across discharges to examine the relationship between biogeochemical processes and physicochemical parameters as they are both acted upon by changes in flow. We predicted that physicochemical parameters will have opposite, mirrored trends compared to the processes they are affected by (e.g., pH and ER) or affect (e.g., turbidity and GPP).

2. Materials and Methods

2.1. Study Site

Stroubles Creek (37°12′36″N, 80°26′42″W) is a 15-km, third-order stream draining a 15-km² subwatershed of the New River in Montgomery County of southwest Virginia (Figure 2). Land use in the contributing catchment is approximately 87% developed, 10.9% agriculture, and 2.9% forest (Homer et al., 2015; Figure 2a), resulting in excess sediment and pathogen loads. Our study site is within the Stream Research, Education, and Management Lab (StREAM Lab, https://vtstreamlab.weebly.com/) that has been monitored by the Virginia Tech Biological Systems Engineering (BSE) Department since 2008 (Thompson et al., 2012). In 2010, BSE completed a restoration project that involved removing cattle and sloping back and stabilizing vertical banks in efforts to remove Stroubles Creek from the Environmental Protection Agency 303(d) impaired list for benthic impairment caused by excessive sediment (Wynn et al., 2010). During summer 2018, NO₃ ranged from 0.97 to 1.7 mg/L, Dissolved organic carbon (DOC) from 3.0 to 5.6 mg/L, phosphate was consistently below 0.02 mg/L, and ammonium ranged from 0.01 to 0.03 mg/L. Our study reach along the stream was selected for its data availability, accessibility, and land use type.

2.2. Data Collection

High temporal resolution measurements of physicochemical parameters were collected from 10 December 2012 to 1 May 2018. An in situ YSI 6920V2 sonde measured conductivity, pH, dissolved oxygen, turbidity, and temperature at 15-min intervals. We also recorded dissolved oxygen data with a PME MiniDOT at 15-min intervals from 31 August 2017 to 1 May 2018, and these were used for metabolism measurements from 1 September 2017 to 14 April 2018 after a freeze event impaired dissolved oxygen measurements from the YSI (Figure S1 in the supporting information). Sensors were calibrated every 2–4 weeks, and all data were quality checked to exclude outliers due to sensor error (Text S1 and Figures S2–S4). A Campbell Scientific



Figure 2. (a) Map of Stroubles Creek watershed and land use. Black line encompasses the drainage area for our study site. (b) Photos immediately downstream of our study reach at low (left) and high (right) flows.

CS451 pressure transducer recorded stage at 10-min intervals. A stage-discharge relationship developed in 2013 and confirmed using salt dilution gaging in 2018 was used to calculate discharge. Velocity and width measurements were taken across multiple years to create relationships with stage. We obtained light measurements from a local weather station that uses a Campbell Scientific CS300. We applied the *interp* function in R to merge discharge, light, and water quality data sets at matching 30-min intervals using linear interpolation (R Core Team, 2017).

Because daily aggregated medians of physicochemical parameters were needed for the C-Q analysis, we calculated the daily median of each parameter for days in which sensors collected measurements for at least 80% of the complete 24-hr period, a percentage we confirmed had minimal impacts on estimating central tendencies. Daily medians were then natural log-transformed. pH was not logged because it is log-transformed [H⁺]. We binned seasons as following June–August as summer (n = 205 total days of data), September–November as fall (n = 180), December–February as winter (n = 237), and March–May as spring (n = 311).



Table 1 Terms Used in Equation (1)						
Parameter symbol	Parameter description (units)					
mO Δt GPP ER z K _o O _{sat} PAR	Modeled O_2 (g O_2 m ⁻³) Measurement interval (d) Gross primary production (g O_2 m ⁻² d ⁻¹) Ecosystem respiration (g O_2 m ⁻² d ⁻¹) Depth (m) Air-water gas exchange of O_2 (d ⁻¹) Oxygen at saturation (g O_2 m ⁻³) Photosynthetically active radiation (umol m ⁻² s ⁻¹)					

2.3. Metabolism Estimates

We used Bayesian inverse modeling to estimate daily GPP and ER using the *streamMetabolizer* R package (Appling et al., 2018). This modeling approach iteratively seeks to find the combination of GPP, ER, and airwater gas exchange of oxygen (K_O) that gives the best match between modeled (mO) and measured (O) dissolved oxygen (Hall & Hotchkiss, 2017; Equation (1)). All parameters are defined, with units, in Table 1.

$${}_{m}O_{i} = {}_{m}O_{i-t} + \frac{\text{GPP*PAR}_{t}}{z^{*}\Sigma\text{PAR}} + \frac{\text{ER}}{z}t + K_{O}(O_{\text{sat}(i-t)} - {}_{m}O_{i-t})t$$
(1)

Average stream channel depth (z) was calculated as $\frac{Q}{v^*w}$, where we divided discharge (Q) by velocity (v) and wetted width (w), to create a stage-depth rating curve. Oxygen at saturation was calculated using sonde water temperature and barometric pressure (Garcia & Gordon, 1992).

To decrease the likelihood of equifinality of parameter estimates by simultaneously solving for GPP, ER, and K (Appling et al., 2018), we took the difference between maximum and minimum discharge and divided Q into six bins per year. The hierarchal modeling framework used by *streamMetabolizer* then established K~Q relationships by using the bins to constrain air-water gas exchange of oxygen (K_0 ; d⁻¹) as a function of discharge (Appling, Hall, Arroita, & Yackulic, 2018). We confirmed modeled K using nighttime linear regression of dissolved oxygen (Hall & Hotchkiss, 2017, supporting information Figures S5 and S6). We found that the relationship between K-ER is lowest and potential for equifinality reduced when constraining K according to a K~Q relationship, compared to using air-water gas exchange scaled to a temperature of 20 °C, as in Rovelli et al. (2018); supporting information Figures S7 and S8). Additionally, we removed 30 days with K values below the 1% (<3.38 d⁻¹) and above the 99% (>27.21 d⁻¹) quantiles to further decrease the chances of using biased metabolism estimates in our P-Q analyses (Figure S6).

Within *streamMetabolizer*, we configured specifications for our metabolism estimates (supporting information Code S1). We specified a Bayesian model with observation error and process error. We visualized model convergence of four chains via a *traceplot* in the *rstan* package (Stan Development Team, 2018). Based off this traceplot, we used a conservative number of burn-in steps: 500. Saved steps were set to 2,000, and the Markov chain Monte Carlo (mcmc) model objects were kept on model run to inspect the traceplot. Default package specifications were otherwise used.

Metabolism estimates passed our model output quality checks for 87% of days with complete 24-hr data sets (1,405/1,621 days). Two hundred sixteen days had complete data sets but were removed from analysis either due to biologically impossible values (negative GPP or positive ER), poor model convergence, or poor fit of the modeled O₂ data to observed O₂. We used diagnostics from *fit()* in *rstan* to quantify model fit, including *Rhat* and *N_eff* (Stan Development Team, 2018). Convergence of mcmc occurs when *Rhat* is equal to 1, so we removed days with *Rhat* exceeding 1.1 (Gelman & Rubin, 1992). *N_eff* is the number of effective samples and should be less than the product of the number of mcmc chains run (4) and the number of saved steps (2,000; Howell, 2017). Therefore, if the *N_eff* value ended on or exceeded 8,000, we assumed no convergence and we removed those days. We removed an additional 472 days due to unreasonable K values or missing physicochemical data. Only days that had solute, discharge, and metabolism estimates were included in our assessment of site-specific C-Q and P-Q relationships, totaling 933 dates from 2013 to 2018.

2.4. C-Q and P-Q Analysis

Varying methods exist to characterize segmented C-Q relationships beyond single-power functions, such as segmenting regressions around statistically derived breakpoints in the discharge data (Diamond & Cohen, 2018) or median discharge (Meybeck & Moatar, 2012; Moatar et al., 2017). We used the Davies test from the *segmented* package in R to iteratively search across 10 quantiles for a significant change of slope in the model of the ln[C]- and ln[P]-ln[Q] relationships and subsequently identified breakpoints (Muggeo, 2008). The *segmented* package tests for the point of segmentation on the explanatory variable (Muggeo, 2008) and requires the user to input a starting value to estimate the breakpoint. We did not find any influence of choosing different starting values (Table S1). We compared using the Davies test to inform segmentation with





Figure 3. Estimates of Stroubles Creek daily discharge, gross primary production (GPP), and ecosystem respiration (ER) from 2013 to 2018.

segmenting at median daily Q (as in Meybeck & Moatar, 2012, Moatar et al., 2017; see supporting information Figures S9 and S10 and Table S2); the trends below and above median Q breakpoints did not differ from the Davies segmentation, so we chose to focus on parameter-specific, statistically derived C-Q and P-Q breakpoints for our study.

After segmenting the hydrograph according to where the *segmented* package found a breakpoint, we retrieved the slopes (β) of the ln-ln relationship between each concentration or metabolism parameter and discharge above and below the breakpoint (supporting information Code S2). The slopes can be used to characterize the trends of physicochemical parameters (e.g., Godsey et al., 2009; Moatar et al., 2017) and metabolism. To test for chemostasis (when $\beta = 0$), we used an analysis of variance test of independence (Ott & Longnecker, 2015). We calculated significant slope differences using a two-tailed *z* test (Paternoster et al., 1998). All analyses were conducted in R (R Core Team, 2017).

3. Results

3.1. Hydrology and Chemistry

The Stroubles Creek hydrograph was characterized by frequent flow increase events (Figure 3). Median daily discharge ranged from 0.03 to 0.47 m³ s⁻¹, with an average of 0.11 m³ s⁻¹. Spring flow typically exceeded annual medians, with an average median spring discharge of 0.14 m³ s⁻¹. Ranges in median discharge were similar across 2013, 2014, and 2015 (0.05–0.41, 0.06–0.0.39, and 0.04–0.47 m³ s⁻¹ respectively); however, there was a notable decline in flow in 2016 and 2017, lessening to a maximum of 0.31 and 0.26 m³ s⁻¹ respectively. Time series of physicochemical parameters can be found in Figures S2–S4.

3.2. Ecosystem Metabolism

ER mirrored GPP seasonally, but rates of ER exceeded GPP in all seasons except for occasionally in the spring (Figures 3 and 4). GPP ranged from 0 to 17.3 g O_2 m⁻² d⁻¹, with an average of 4.23 and a median of 3.69 g O_2 m $^{-2}$ d⁻¹ (Figures 3 and 4). High GPP in Stroubles Creek exceeded GPP in other studies that have examined the influence of flow on metabolism in urban streams (Reisinger et al., 2017; Smith & Kaushal, 2015) but was within the range of metabolism found in other agriculturally impacted streams (Griffiths et al., 2013; Roley



Figure 4. Relationship between GPP and ER. Different symbols reflect different seasons of metabolism estimates. Points above the dashed 1:1 line depict when the stream was autotrophic (GPP > ER and net ecosystem production > 0); Stroubles Creek was almost always heterotrophic (ER > GPP and net ecosystem production < 0).

et al., 2014). ER, reported as a negative flux of O₂ consumption, ranged from -2.19 to -20.46 g O₂ m⁻² d⁻¹, with an average of -9.60 and a median of -9.56 g O₂ m⁻² d⁻¹. NEP ranged from -15.36 to 4.86 g O₂ m⁻² d⁻¹. There were 29 measured days (3% total) when GPP was greater than ER (positive NEP), all of which occurred in the spring (Figure 4). K estimates ranged from 3.9 to 27.1 d⁻¹, with an average of 18.0 d⁻¹. Our K-ER correlation was negative and weak ($R^2 = 0.19$; supporting information Figure S9), suggesting low equifinality issues related to simultaneously estimating GPP, ER, and K with *streamMetabolizer*.

3.3. C-Q

Discharge had a significant effect on all parameters above and below their breakpoint, most of which were close to median discharge (Table 2). However, dissolved oxygen and conductivity were both chemostatic above their breakpoints but increased below ($\beta = 0.16$, and 0.80 respectively; Figure 5 and Table S3). Turbidity was chemostatic below the breakpoint but followed common upward trends above the breakpoint ($\beta = 1.15$; Moatar et al., 2017; Figure 5 and Table S3). pH increased below but declined above the breakpoint ($\beta = 0.17$, -0.23; Figure 5 ad Table S3).

DO and temperature varied seasonally, where DO decreased at lower flows below the breakpoint in summer but increased during fall and

Table 2	
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Statistical Results for Slope Segmentation of Concentration-Discharge and Process-Discharge Relationships

Parameter (units)	<i>p</i> value from Davies ^a	Estimated breakpoint $(m^3 s^{-1})$	Estimated breakpoint standard error	β below breakpoint	β below breakpoint standard error	β above breakpoint	β above breakpoint standard error	p valueZ test ^b			
Temp (°C)	0.001*	0.11	0.12	-0.32	0.08	0.18	0.09	< 0.001*			
pН	< 0.001*	0.10	0.06	0.17	0.03	-0.23	0.03	< 0.001*			
$DO (mg L^{-1})$	0.001*	0.10	0.12	0.16	0.03	-0.006	0.03	< 0.001*			
Conductivity (ms cm ^{-1})	< 0.001*	0.08	0.04	0.80	0.06	-0.03	0.03	< 0.001*			
Turbidity (NTU)	< 0.001*	0.07	0.09	0.01	0.23	1.15	0.08	< 0.001*			
ER (g $O_2 m^{-2}$)	0.03*	0.07	0.14	-0.29	0.11	0.03	0.03	0.005*			
$GPP(gO_2 m^{-2})$	0.14	0.23	0.16	-0.51	0.05	-1.48	0.53	0.07			
NEP ($g O_2 m^{-2}$)	0.07	0.08	0.16	-0.03	0.07	-0.26	0.04	0.004*			

^asegmented output for the Davies p value. ^bDifference in slopes according to two-sided Z test. *Significant p values (p < 0.05).

winter (Figure 5 and Table S4). Above breakpoints at higher flows, DO declined in fall and winter but increased in summer. Changes to DO slopes at low and high flows during spring were not significant. At lower discharges below season-specific breakpoints, temperature declined in the fall and increased in the winter (Figure 5 and Table S4). Above the breakpoint at higher flows, temperature declined in the winter and increased in fall. Spring and summer temperatures did not have significant slope breaks above and below breakpoints.

3.4. P-Q

ER and NEP had significantly different slopes below and above their P-Q breakpoints. ER declined below the breakpoint and was chemostatic above, whereas NEP was chemostatic below the breakpoint and declined above (Figure 6 and Table S3). GPP had the highest breakpoint across all parameters (Q = 0.23 m³ s⁻¹), but with an insignificant slope change (p = 0.07, α = 0.05). GPP's rate of change across Q did steepen from



Figure 5. Concentration-discharge (C-Q) graphs of segmented physicochemical parameters (turbidity, temperature, dissolved oxygen, pH, and conductivity) in Stroubles Creek. Graphs are natural log-scaled, but numbers on axes are not log-transformed for more intuitive interpretation of values. The dashed vertical line represents the statistically derived breakpoint; the solid regression lines below and above the breakpoint were all significantly different (Table 2).

 $\beta = -0.51$ below the breakpoint to $\beta = -1.48$ above (Table 2 and Figure 6). Moreover, seasonality may significantly influence segmented P-Q patterns. Although we did not have enough data to detect significant differences for most P-Q relationships when data were subset by season or year, several different analyses of GPP across discharge supported the findings of the pooled GPP relationship with discharge that, while not significantly different below and above the breakpoint, did show that GPP consistently declined above the breakpoint (Figures 6 and S11). The lack of a significant breakpoint for GPP across discharge does not suggest that there is no relationship with flow; rather, the lack of a significant change in slope may indicate that there are no fundamental changes to the underlying factors that shape the relationship between GPP and discharge.

We observed coupled responses between pH and NEP and GPP and turbidity (Figure 6). pH and NEP had breakpoints at approximately the same discharge. As NEP declined, so did pH (Table 2). GPP and turbidity followed predicted, mirrored trends; as turbidity β increased (from chemostasis to $\beta = 1.15$), the β for GPP-Q became more negative above the breakpoint (Figure 6 and Table 2). GPP's breakpoint occurred at a much higher discharge than turbidity (0.23 versus 0.07 m³ s⁻¹). ER had the same breakpoint as turbidity; however, it did not appear to follow coupled trends with any of the physicochemical parameters.

4. Discussion

Increasing flow does more than just scour the bed or introduce solutes; it influences metabolism by changing the physicochemical conditions that underlie microbial carbon fixation and respiration. In addition to finding statistical support for using segmented regressions to quantify distinct changes in ER and NEP with varying discharge above and below breakpoints, we found that C-Q and P-Q relationships of parameters predicted to directly affect one another, such as turbidity and GPP or pH and NEP, followed coupled breakpoint behaviors, with varying degrees of statistical significance. These couplings illustrate the potential utility for using P-Q and C-Q relationships together to explain both functional responses and biogeochemical consequences of flow changes.

4.1. P-Q

Precipitation events generate multiple abiotic changes that can influence stream ecosystem processes: Flow increases, physicochemical parameters are altered, and cloud cover reduces photosynthetically active radiation. Yet, we do not account for likely thresholds or breakpoints in processes the same way we do for C-Q relationships. Ultimately, statistically derived segmented P-Q relationships allow us to quantify when a stream becomes a predominant "transporter" from "transformer" by determining if and when a significant threshold of process resistance to discharge exists.

At a precipitation event scale, GPP declines as flow increases (Fisher, 1982; Reisinger et al., 2017). GPP also declined with increasing flow at our study site. We did not detect a significantly greater GPP reduction (i.e., a significantly steeper negative slope of GPP-Q) at higher flows as a result of the compounding influence of elevated turbidity, reduced light, or intensified scour (Table 2). While our data suggest a breakpoint at higher discharge $(0.23 \text{ m}^3 \text{ s}^{-1})$ for GPP relative to any other metabolism or C-Q relationships (Figure 6), we ultimately did not have enough estimates of GPP from high-flow events to find a statistically significant change in slope (Table 2).

ER is also affected by flow-induced changes: Reductions in residence time, scour that may remove respiring microbes, and influxes of terrestrial organic matter. Storms frequently increase ER (Roley et al., 2014), potentially as a result of the increased concentrations of stimulating organic matter (Demars, 2018). We found no evidence for flow-induced stimulation of ER in Stroubles Creek, perhaps due to reductions in residence time and mild scouring concomitant with loading of bioreactive organic matter subsidies. The prebreakpoint ER reduction may have been a result of disproportionate autotrophic scouring relative to heterotrophic, as GPP declined at a much faster rate than ER below the breakpoint (Table 2). Heterotrophs tucked away in the hyporheic zone may be more resistant to scour than autotrophs exposed on the stream bed (Uehlinger, 2000; Uehlinger & Naegeli, 1998). However, ER was chemostatic above the breakpoint (Figure 6 and Table S3). As catchment connectivity increases, organic matter may be flushed into the stream (Buffam et al., 2001). Consequently, this shift to chemostasis above the breakpoint could be due to balanced stimulation from fresh organic matter when Stroubles Creeks spills overbank and disturbance caused by scour. Additionally, statistically significant breakpoint analyses by season or year (Figure S11) suggest



Figure 6. Process-discharge graphs for GPP, ER, and net ecosystem production (NEP). Insets are C-Q plots that correlate with metabolism. Graphs are natural log-scaled, but numbers on axes are not log-transformed for more intuitive interpretation of values. The vertical dashed line is the statistically derived breakpoint; regression lines below and above the breakpoint illustrate changing metabolism trends across discharge. ER and NEP had a significant slope break, and the slopes were significantly different. GPP did not have a significant slope break and the slopes above and below the statistically derived breakpoint were not significantly different.

inconsistent slope trends for ER above and below the breakpoint according to year or season of data collection. Ultimately, lower or higher flows can induce contrasting effects on ER.

NEP remained relatively constant below the NEP-Q breakpoint (Table S3), likely because there was not a great enough change in either GPP or ER to drive a shift in NEP. Chemostasis below this point signifies that the balance between GPP and ER was not significantly impacted by discharge, suggesting that other factors at lower flows may control NEP. Above the breakpoint, the significant decline of NEP was a result of increased ER relative to GPP. The resistance of hyporheic heterotrophs to scour relative to the vulnerability of surface autotrophs can lead to a greater reduction in GPP than ER (Uehlinger, 2000; Uehlinger & Naegeli, 1998), a trend observed in other storm and metabolism studies (Reisinger et al., 2017; Roley et al., 2014). Further work is needed to understand how other drivers of metabolism change across flows to truly discern what dictates segmented P-Q relationships and metabolic balance in different ecosystems.

In ecosystems with lower GPP or less flashy hydrology, NEP may reflect different responses from GPP and ER. High GPP in our study reach gave us a unique opportunity to view potentially contrasting responses of ER or GPP at low and high flows (Walsh et al., 2005). Because the range of GPP is generally narrower in less impacted streams, distinguishing significant statistical changes as a result of precipitation events is much more difficult. Across other human-modified sites with high GPP, however, the opportunity exists to select streams or stream reaches across a gradient of transient storage to evaluate the influence of surface-subsurface connectivity and highly variable flows (e.g., "flashiness" in many urban streams) on NEP. The segmented response of NEP to discharge can potentially yield insights into how different channel morphology and water flowpaths can alter ecosystem resistance.

4.2. C-Q

Precipitation events are influential moments of solute export, shuttling disproportionately large fluxes of solutes downstream (Raymond et al., 2016). Transport or source limitations are frequently used to explain C-Q enrichment or dilution trends at higher flows, respectively (Basu et al., 2011; Moatar et al., 2017). In Stroubles Creek, C-Q trends were similar to findings of other segmented C-Q studies. Although conductivity often exhibits source-limited dilution across discharge (Diamond & Cohen, 2018), the initial increase observed below the breakpoint in our study reach may be a result of the dominantly developed catchment that drains into our study site, as urban streams are inundated with ions that elevate conductivity (Kaushal et al., 2018; Paul & Meyer, 2001). However, higher flows may reverse this trend after depleting the sources of ions and diluting the concentrations that remain. The enrichment of

turbidity at higher flows at our study site aligned with common dynamics of total suspended solids across discharge, due to erosion and transport limitation (Moatar et al., 2017). At higher flows, Stroubles pH exhibited the decline seen in other C-Q studies, potentially as a result of accessing CO₂-rich groundwater or soils (Diamond & Cohen, 2018; Jenkins, 1989). Overall, the similarity of Stroubles Creek physicochemical trends to those seen in other streams suggests that our findings of coupled C-Q and P-Q relationships may apply to other systems. However, classifying C-Q dynamics by transport or source limitations alone may not capture physicochemical behavior across discharge.

4.3. C-Q and P-Q Coupling

The true promise of P-Q relationships lies in coupling them with C-Q dynamics to explore the influence that flow-induced changes of C-Q and P-Q can have on one other. Flow-induced changes to physicochemical parameters have the potential to either stimulate or suppress metabolism. For instance, turbidity hinders the permeability of light throughout the stream. As light is a key driver of GPP (Blaszczak et al., 2018; Larsen & Harvey, 2017; Mulholland et al., 2001), increasing turbidity induces a decline of GPP (Hall et al., 2015). Therefore, we predicted that increasing turbidity above the breakpoint would decrease GPP. As the upward slope of turbidity's changes with Q intensified above its breakpoint, so did GPP's rate of decline with Q, although the change in the rate of GPP was not significant (Figure 6). If directly influenced by the enrichment of turbidity, GPP had a lagged effect, with a breakpoint much later than turbidity (Table 2). Most breakpoints were close to median flow (Table 2), lending support to fixing the breakpoints at median discharge (e.g., Moatar et al., 2017). However, by standardizing the point of inflection for breakpoints to the median discharge, we may miss processes or fluxes that have delayed reactions to changes in physicochemical parameters or flow. Ultimately, changes to physicochemical parameter trends across flows can stimulate or constrain stream metabolism.

The relationship between physicochemical parameters and ecosystem processes is not unidirectional; processes can also influence physicochemical parameters and potentially reduce solute export. Respired or fixed CO_2 reduces or increases pH (Maberly, 1996). Here, we observed coupled responses of pH and NEP (Figure 6), exhibiting slope changes at approximately the same discharge breakpoint (Table 2). Above the breakpoint, the decline of pH and NEP at similar rates could be a result of more CO_2 production due to increased rates of ER relative to GPP. Ultimately, biotic processes do not happen in isolation; they have the potential to influence the physicochemical parameters in their surrounding environment, and we expect there may be many more instances of common breakpoints and linked trends in water chemistry and ecosystem processes.

Although comparing physicochemical parameters with processes is informative, a missing piece within this long-term sensor data set is the ability to directly compare P-Q relationships with carbon and nutrients, such as DOC and NO₃, that are frequently the limiting elements of stream metabolism. When we quantify export regimes of solutes such as DOC and NO₃ based on transport or source limitation, we exclude the biological processes that produce or transform these solutes. For instance, the ratio of DOC:NO₃ declined or remained about the same in most of the catchments studied by Moatar et al. (2017). Depending on the most limited element in a stream, a changing ratio of DOC:NO₃ could stimulate or repress biological processes by enriching the limiting solute or further diluting it. DOC predominantly enriches at higher flows (Moatar et al., 2017; Musolff et al., 2017). Would systems with greater DOC limitation and higher respiration potential be more capable of reducing the higher DOC loads at high flows?

Expanding the coupling of C-Q and P-Q relationships to include solutes such as NO_3 and DOC is an exciting next step to further understand how P-Q patterns can both directly influence, and be acted upon by, reactive solute dynamics. As logging sensor deployments become more prevalent, our capacity to create coupled C-Q and P-Q analyses will drastically expand. The data will likely soon be available to simultaneously assess DOC-Q and metabolism-Q relationships across variable systems and conditions. For example, through using high-frequency United States Geological Survey sensor data, it is possible to analyze sites across the U.S. that have metabolism and discharge estimates (Appling et al., 2018) and physicochemical data. By combining our existing knowledge of export regimes with a quantitative understanding of how flow can change biological processes, we can better understand the mechanisms behind ecosystemlevel responses to changing flow and export of solutes downstream.

5. Conclusion

Stream flow changes have hydrologic and biogeochemical consequences. Hydrologically, higher flows are regarded as agents of catchment connectivity, simultaneously unleashing or diluting solutes into freshwater ecosystems. Biogeochemically, physical disturbances caused by higher flows disrupt ecosystem processes by moving the stream bed or reducing transient storage. However, insight into the mechanisms behind C-Q and P-Q dynamics across flow is stunted when we view one without the other; physicochemical parameters



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influence, and are influenced by, in-stream biology. To truly comprehend ecosystem responses at different flows, we must integrate the interactions between flow, ecosystem process, and C-Q dynamics into our analyses of stream function. By coupling C-Q and P-Q relationships, we can better understand how ecosystems respond to, influence, and recover from the many physical and chemical changes that occur with altered flow.

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