QUANTIFYING THE EFFECTS OF LAND USE AND FLOW REGIME ON METABOLISM IN NEW ENGLAND STREAMS

Daniel R. Bolster
University of New Hampshire, Durham

Follow this and additional works at: https://scholars.unh.edu/thesis

Recommended Citation

This Thesis is brought to you for free and open access by the Student Scholarship at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in Master's Theses and Capstones by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact Scholarly.Communication@unh.edu.
QUANTIFYING THE EFFECTS OF LAND USE AND FLOW REGIME ON METABOLISM
IN NEW ENGLAND STREAMS

BY

Daniel Bolster
B.S., Le Moyne College, 2016

THESIS

Submitted to the University of New Hampshire
in partial fulfillment of
the requirements for the degree of
Master of Science

In

Natural Resources Soil and Water Resource Management

December, 2020
This thesis has been examined and approved in partial fulfillment of the requirements for the degree of Master of Science in Natural Resources Soil and Water Resource Management by:

Thesis Director, Wilfred M. Wollheim, Associate Professor of Natural Resources and the Environment

William H. McDowell, Professor of Natural Resources and the Environment

Gopal Mulukutla, Affiliate Research Scientist, Earth Systems Research Center, Institute for the Study of Earth, Oceans, and Space

On August 28, 2020

Approval signatures are on file with the University of New Hampshire Graduate School
DEDICATION

To complete anything in life takes endurance, courage, and a lot of support. I could not have made it to where I am today without my advisor, parents, family, friends, colleagues from UNH and Le Moyne, and my wife. Many hours of field and lab work have come to fruition with the help of late-night calls to my Dad (who helped foster my love of nature) from James Hall, time sensitive emails to Wil that he always finds a moment to answer, and some phone calls from the middle of the stream to my wife Rebecca. I am eternally grateful for everyone’s support and confidence in me. I truly know the meaning of dedication and hard work.
ACKNOWLEDGEMENTS

I am extremely grateful for the time, effort, challenging questions, guidance, help sampling, and support that my advisor Wil Wollheim has provided over my time at UNH. It started with a cup of coffee and a book on how to write scientifically and has blossomed into the ability to think like a scientist, ask better questions, and pass these skills on to my own students. It is not often you see an advisor spend so much time and effort on all students/staff in their lab, but Wil is one in a million. I would like to thank everyone in the Water Systems Analysis Group for their immense support. Special thanks to Chris Cook for teaching me how (and where) to sample, Chris Whitney for helping me code and make beautiful figures in R and answering all my questions in a prompt manner, Drew Robison for asking even harder questions and always helping me to step my ideas, sentences, and figures up a notch, Gopal Mulukutla for help with sensor deployments, data, and electronics, Mike Routhier for his support with my writing (and in the cafeteria), and Stanley Glidden for always finding the time to help with computer troubleshooting, model support, and car trouble. I’d also like to thank Wil, Chris, Drew, Gopal, Jake Gehrung, Brian Saccardi, and my wife for helping me sample and Jody Potter, the WQAL, Jake Gehrung, Drew, and Chris Whitney for help running samples. I am again extremely thankful for my wife Rebecca for truly teaching me what it means to support one another, in good times, and in bad. She is a continuous beacon of light, always guiding me in the right direction. Thanks also to my committee, the Water Quality Analysis Lab, all of my teachers, and for anyone’s time I may have used as a steppingstone to complete this thesis. This story would not be possible without the help of so many people, so thank you immensely. Funding for this research was provided by the University of New Hampshire Agricultural Experimental Station with a teaching assistantship in the Natural Resources Department.
TABLE OF CONTENTS

DEDICATION ........................................................................................................................ iii
ACKNOWLEDGEMENTS ..................................................................................................... iv
LIST OF TABLES .................................................................................................................. vi
LIST OF FIGURES ............................................................................................................... vii
ABSTRACT .......................................................................................................................... x
1. Introduction .................................................................................................................... 1
   1.1 Goal .......................................................................................................................... 5
2. Methods .......................................................................................................................... 6
   2.1 Overarching design ................................................................................................. 6
   2.2 Study Sites .............................................................................................................. 7
   2.3 High Frequency Sensor Measurements ............................................................... 8
   2.4 Discharge ................................................................................................................ 9
   2.5 Stream Reach Characterization ............................................................................ 9
   2.6 Stream Metabolism ............................................................................................... 10
   2.7 Grab Samples ......................................................................................................... 12
   2.8 Statistical Analysis ............................................................................................... 12
   2.9 Additional Measurements ...................................................................................... 13
3. Results ........................................................................................................................... 15
   3.1 Metabolism of Headwater Streams ...................................................................... 15
   3.2 Response to Storm Events ..................................................................................... 18
   3.3 Large River Response ............................................................................................ 19
4. Discussion ....................................................................................................................... 20
   4.1 Headwater GPP ....................................................................................................... 20
   4.2 Headwater ER ......................................................................................................... 23
   4.3 Response of GPP and ER to Storm Events in Headwaters ................................... 26
   4.4 Large River Metabolism and Storm Response ...................................................... 29
5. Conclusion ....................................................................................................................... 31
Literature Cited .................................................................................................................... 33
Appendix ............................................................................................................................. 52
LIST OF TABLES

Table 1: Land use statistics of watersheds draining to streams.................................45
Table 2: Physical and chemical properties of the Oyster River Watershed streams........46
Table 3: Average Daily Metabolism Estimates (g O$_2$ m$^{-2}$ day$^{-1}$)..........................47
Table 4: Average Change in Metabolism Post Storm (g O$_2$ m$^{-2}$ day$^{-1}$)..................48
Table 5: Average Change in Metabolism Post Storm (%)............................................49
Table 6: Absolute Change in GPP Post Storm (g O$_2$ m$^{-2}$ day$^{-1}$)............................50
Table 7: Absolute Change in ER Post Storm (g O$_2$ m$^{-2}$ day$^{-1}$).............................51
Table A1: SUNA Deployment dates and average nitrate during the deployment in headwater streams........................................................................................................53
Table A2: Diel Variability in NO$_3$ (mg N L$^{-1}$) in Oyster River Streams.......................54
Table A3: Diel Variability in DO (%) in Oyster River Streams......................................55
Table A4: Diel Variability in N$_2$:Ar ratios in Oyster River Streams...............................56
Table A5: Average Disequilibrium of N$_2$:Ar ratios in Oyster River Watershed Streams....57
Table A6: Average Daily and Nightly N$_2$:Ar disequilibrium ratios in Oyster River Watershed Streams for 1st Diel sampling round.........................................................58
Table A7: Average Daily and Nightly N$_2$:Ar disequilibrium ratios in Oyster River Watershed Streams for 2nd Diel sampling round.........................................................59
Table A8: Average Daily and Nightly N$_2$:Ar disequilibrium ratios in Oyster River Watershed Streams for 3rd Diel sampling round.........................................................60
LIST OF FIGURES

Figure 1: Map of Oyster River Watershed in Southeast NH, USA, showing the three headwater streams and the larger mainstem (MAIN). Land use statistics can be found in Table 1.................38

Figure 2: Timeseries of 15-minute DO concentration (A), Discharge (B), water temperature (C), and PAR (D) for URB to show streamMetabolizer model parameters.............................................39

Figure 3: Timeseries of daily GPP (A), ER(B), and K<sub>600</sub> (C) metabolism estimate model outputs from streamMetabolizer for the URB stream.................................................................40

Figure 4: Boxplots of mean GPP(A), ER(B), K<sub>600</sub>(C), and water temperature(D). Boxes show first and third quartiles, horizontal lines in the box are median values, while individual points are outliers. Letters above each boxplot show statistically significant groupings. .......................41

Figure 5: Linear regressions for GPP vs Q(A), PAR(B), and Temp (C). Only significant regressions, p values, and r<sup>2</sup> values are shown.................................................................42

Figure 6: Linear regressions for ER vs Q(A), PAR(B), and Temp (C). Only significant regressions, p values, and r<sup>2</sup> values are shown.................................................................43

Figure 7: Time series of high frequency Q data at the URB stream added to daily GPP (green) and ER (red) data from July 3rd, 2017 to August 28th, 2017. Note that days determined to be storm days were removed (hence gaps in the GPP and ER data). Pre and post GPP and ER were taken as the average values two modellable days before and after storms. Storms are highlighted as open circles. Not all storms are shown to more easily see the effect of Q on GPP and ER. .....44

Figure A1: Figure from Dave Cedarholms’ PowerPoint showing the location of the springs under the MIX stream (Chesley Brook). Being a spring fed system leads to more stable flows at the MIX stream.................................................................61

Figure A2: Power rating curve of Q vs stage height for the FOR stream. This equation was used to calculate instantaneous Q from logger stage heights throughout the entire study period..................62

Figure A3: Power rating curve of Q vs stage height for the MIX stream. This equation was used to calculate instantaneous Q from logger stage heights throughout the entire study period..................63

Figure A4: Power rating curve of Q vs stage height for the URB stream. This equation was used to calculate instantaneous Q from logger stage heights throughout the entire study period..................64

Figure A5: Timeseries of 15-minute DO concentration (A), Discharge (B), water temperature (C), and PAR (D) for MIX to show streamMetabolizer model parameters.............................................65

Figure A6: Timeseries of 15-minute DO concentration (A), Discharge (B), water temperature (C), and PAR (D) for FOR to show streamMetabolizer model parameters.............................................66
Figure A7: Timeseries of 15-minute DO concentration (A), Discharge (B), water temperature (C), and PAR (D) for MAIN to show streamMetabolizer model parameters. .................................67

Figure A8: Timeseries of daily GPP(A), ER(B), and $K_{600}$ (C) metabolism model estimate outputs from streamMetabolizer for the MIX stream. ........................................................................................................68

Figure A9: Timeseries of daily GPP(A), ER(B), and $K_{600}$ (C) metabolism model estimate outputs from streamMetabolizer for the FOR stream. ........................................................................................................69

Figure A10: Timeseries of daily GPP(A), ER(B), and $K_{600}$ (C) metabolism model estimate outputs from streamMetabolizer for the MAIN stream........................................................................................................70

Figure A11: Boxplots of mean PAR. Boxes show first and third quartiles, horizontal lines in the box are median values, while individual points are outliers. Letters above each boxplot show statistically significant groupings.................................................................71

Figure A12: Snapshot of Oyster River high frequency (15-minute) discharge data from June 29th, 2017 to July 17th, 2017 showing storms (black arrows) for each stream, especially the flashiness of urbanized storms, which can be seen at the URB stream without any response at the other streams (red arrows). ..............................................................................................72

Figure A13: Time series of daily P:R ratio for the MIX (orange), URB (red), FOR (green), and MAIN (purple) showing the two days (July 29th, 2017 and January 6th, 2018) where the P:R ratio at MAIN was >1 and net autotrophic........................................................................73

Figure A14: TSS for thesis streams 2016-2018........................................................................74

Figure A15: Correlations between K600 and ER for the URB (A), MIX(B), FOR(C), and MAIN(D). Low correlations suggest the K600 estimates are more accurate and not correlated to ER ........................................................................................................................................75

Figure A16: Correlations of storm size (maximum Q) vs change in GPP post storm for the URB (A), MIX(B), FOR(C), and MAIN(D). No significant relationships at any stream showing that higher Q’s statistically do not lead to higher changes in GPP..................................................................................76

Figure A17: TSS for all other streams collected 2016-2018. Days with multiple points during the summer of 2016 were storm samples .................................................................77

Figure A18: Oyster River monthly grab sample of Chloride (A), Fluoride (B), and Bromide (C). ........................................................................................................................................78

Figure A19: Oyster River monthly grab sample of Nitrate (A), Phosphate (B), and Sulfate (C). 79

Figure A20: Oyster River monthly grab sample of Ammonium (A), Non-purgeable organic carbon (B), Total dissolved nitrogen (C), and dissolved organic nitrogen (D) .....................80
Figure A21: Timeseries of nitrate at the MIX(A), FOR(B), and MAIN(C) streams from September 2017 to December 2017. .................................................................81

Figure A22: N$_2$:Ar disequilibrium values for Diel 1. Samples were collected every two hours for 24 hours straight between June 26th and June 27th, 2017. .................................................................82

Figure A23: N$_2$:Ar disequilibrium values for Diel 2. Samples were collected every two hours for 24 hours straight between August 2nd and August 3rd, 2017. .................................................................83

Figure A24: N$_2$:Ar disequilibrium values for Diel 3. Samples were collected every two hours for 24 hours straight between August 10th and August 11th, 2017. .................................................................84

Figure A25: DO(%) handheld measurements for Diel 1. Samples were collected every two hours for 24 hours straight between June 26th and June 27th, 2017. .................................................................85

Figure A26: DO(%) handheld measurements for Diel 2. Samples were collected every two hours for 24 hours straight between August 2nd and August 3rd, 2017. .................................................................86

Figure A27: DO(%) handheld measurements for diel 3. Samples were collected every two hours for 24 hours straight between August 10th and August 11th, 2017. .................................................................87

Figure A28: Nitrate (mg N L$^{-1}$) grab sample measurements for Diel 1. Samples were collected every two hours for 24 hours straight between June 26th and June 27th, 2017. .........................88

Figure A29: Nitrate (mg N L$^{-1}$) grab sample measurements for Diel 2. Samples were collected every two hours for 24 hours straight between August 2nd and August 3rd, 2017. .........................89

Figure A30: Nitrate (mg N L$^{-1}$) grab sample measurements for Diel 3. Samples were collected every two hours for 24 hours straight between August 10th and August 11th, 2017. .........................90

Figure A31: Timeseries of 15-minute DO% for the URB (A), MIX (B), FOR (C), and MAIN (D). .........................................................................................................................91

Figure A32: Timeseries of 15-minute Specific Conductivity (uS cm$^{-1}$) for the URB (red), MIX (orange), FOR (green), and MAIN (purple). .........................................................................................................................92
ABSTRACT

QUANTIFYING THE EFFECTS OF LAND USE AND FLOW REGIME ON METABOLISM IN NEW ENGLAND STREAMS

By

Daniel Bolster

University of New Hampshire

Metabolism in aquatic ecosystems influences food webs and water quality but is potentially altered by changes in land use and flow regime. The interacting effects of storms and land use on stream metabolism are largely understudied. The goal of this study was to understand how flow variability and land use interact to affect biogeochemical cycling in headwater streams. 

In situ measurements of stage, water temperature, and dissolved oxygen (DO) were made in three headwater streams draining different land uses (urban, forest, and mixed) and one larger river site from July 2017 to January 2018. All streams were located in the Oyster River Watershed in coastal New Hampshire, USA. Metabolism was quantified using the single station dissolved oxygen method and the streamMetabolizer package in the R statistical program. StreamMetabolizer is a state space inverse Bayesian model with partial pooling to constrain process error. It was hypothesized that Gross Primary Productivity (GPP) and ecosystem respiration (ER) in the urbanized stream (URB) would be higher than the mixed (MIX) and forested (FOR) streams because of more open canopy cover and higher nutrients, but that GPP and ER would decline more following storm events because of the flashier (larger and quicker flows) hydrology. It was also hypothesized that GPP and ER in the larger mainstem (MAIN) would remain constant following storms due to more attenuated storm peaks. All streams were net heterotrophic with GPP estimates from 0.0 to 0.96 g O₂ m⁻² day⁻¹ and ER from 0.0 to 14.2 g
O₂ m⁻² day⁻¹. GPP was higher at the urban stream (0.32 g O₂ m⁻² day⁻¹) than at all other streams. Pre and post storm disturbance metabolism estimates were compared across all streams for 11 to 28 storms. In general, GPP declined more due to storms than ER at the urbanized and forested streams respectively. Mainstem GPP and ER were most affected by storms; however; GPP and ER were very low. The urbanized stream demonstrated that, despite being subject to constant flashy flow events and being in a constant state of recovery, urbanized streams could rebound quickly and still exhibit high GPP and ER. Future changes in global climate and land use could lead to more frequent and more harmful episodic disturbances in headwater streams.
1. Introduction

Anthropogenic effects on aquatic ecosystems such as pollution, increased nutrients due to runoff, destruction of riparian vegetation, and changes in physical and hydrological properties of these ecosystems are coming to the forefront of environmental awareness. Streams are increasingly affected by land use and climate change (Malmqvist and Rundle, 2002; Meyer et al., 2007; Swain and Hayhoe, 2015). This effect can be seen through the lens of ecosystem services (food web support, water supply, water filtration, flood mitigation, and aesthetic beauty), which are at risk of declining as a result of land use changes such as urbanization, agriculture and the imminent threat of climate change (Hanratty et al., 1996). The construction of impervious surfaces (or those which prevent precipitation from absorbing into the ground) such as driveways, roads, and parking lots along with increased nutrient concentrations and runoff from lawns, farms, and human waste are a few of the major modifications made by humans. Increased impervious surface cover leads to more water being diverted directly into the streams through storm drains (Walsh et al., 2005).

Flashy hydrological regimes can have large effects on gross primary productivity (GPP) and ecosystem respiration (ER) which are the estimates of total autotrophic production and total autotrophic and heterotrophic respiration of the system. Flashier (larger and quicker) flows can lead to a scouring of primary producers and attenuation of light, thus lowering GPP in the system (Qasem et al., 2019). Conversely, increased organic matter (OM) transported during high flows could bring organic matter from upstream and make it available for heterotrophs, increasing ER. Increased OM can also lead to the depletion of oxygen as it is used by heterotrophs, causing hypoxic conditions (Williamson et al., 2008), until higher flows replenish O₂ or increase gas exchange (Blaszczak et al., 2019), or primary producers reestablish and produce O₂ through
photosynthesis. Additionally, warmer water temperatures and flashier flows alter the function of streams (Malmqvist and Rundle, 2002). Warmer water temperatures can stimulate photosynthetic autotrophs and also heterotrophs, thus increasing both GPP and ER, but also leads to a decreased solubility of O$_2$ in the water (Williamson et al., 2008). Climate change is projected to lead to moderate increases in total precipitation, however it is also projected to increase the frequency of extreme precipitation events (Wake et al., 2014; Kirshen et al., 2014), meaning less steady precipitation throughout the year but more precipitation during these extreme events. This leads to responses in streams such as longer periods of low flow during droughts associated with less frequent precipitation events but also flow events at larger magnitudes during the larger storms. Despite these changes in distal (such as regional climate and land use) and proximal (such as light and nutrients) factors, the effects of storm events in general and in different land uses are poorly understood in headwater streams.

Stream metabolism, or the combination of gross primary productivity (GPP) and ecosystem respiration (ER), is a fundamental metric of stream health (Bernot et al., 2010; Hall et al., 2016). Changes in the production of Oxygen gas (O$_2$) are produced during photosynthesis and consumed during respiration. Measurements of dissolved oxygen (DO) are key in determining the importance of metabolism to healthy streams. Metabolism is the biological processing of energy and materials (Brown et al., 2004). Energy is the basic unit of function in a biological system, and a streams metabolism can be very informative about that systems total biotic activity (Dodds, 2007). Additionally, metabolism can be used as an indicator of stream structure and function (Izagirre et al., 2008), one that is sensitive to many important stressors such as changes in temperature, riparian cover, salinization, nutrient status, organic matter content, and discharge regime (Young et al., 2004). These stressors are caused by humans,
accelerated by humans, or both, and thus are pivotal to our understanding of managing stream health. Additionally, as the sum of all biotic activity, metabolism is useful in comparing different stream ecosystems and their responses to environmental changes (Hoellein et al., 2013). The amount of DO in a stream is also connected to water quality. High amounts of instream DO is a product of GPP. This DO is used through ER to produce energy. Less DO leads to lower species richness as hypoxic conditions can be stressful on aquatic macro-organisms (Blaszczak et al., 2019). Another source of DO is the atmosphere. Reaeration, the gas exchange between the surface of the water and the atmosphere, is usually estimated as a daily rate (d⁻¹) but can be converted into a gas exchange velocity \(K_{600}, \text{m day}^{-1}\) by multiplying it by depth (m). \(K_{600}\) strongly influences GPP and ER rates estimated from DO measurements in aquatic ecosystems (Nifong et al., 2020; Hall et al., 2018). Much effort has been put into understanding these gas exchange velocities, especially in regard to reducing equifinality, i.e. where multiple estimates of GPP and ER can be fit to the data (Appling et al., 2018).

Metabolism often varies in streams draining different land use types due to distal factors such as regional vegetation, climate, soil, and land use. Interactions of proximal and distal factors together are largely undescribed within scientific literature (Bernot et al., 2010). Small shaded headwater streams often show negligible rates of GPP (Hall et al., 2016) and large values of ER (Hollein et al., 2013). However, some studies show similar metabolism rates despite broader ranges of land use categories and different regions (Bernot et al., 2010). So why does metabolism change (or not) with different controlling factors in different land uses? While the primary factors influencing GPP are light availability, nutrient availability, and the presence of algal biomass in the streams and those influencing ER are OM and nutrients in the ecosystem, these controlling factors vary over different land use types and flow regimes. Light, as the primary
driver of photosynthesis, is essential for GPP. Streams differ in how much light they get due to land use. For example, a forested stream typically has low light (and thus low GPP) due to high riparian vegetation cover, while an urbanized stream, one that has lost riparian zone vegetation, has a larger amount of light reaching the surface of the water leading to higher GPP (Walsh et al., 2005; Young et al., 2008). Changes in light can also lead to changes in temperature, where more light hitting the stream means higher water temperatures throughout the year. This is important because temperature has been known to increase both autotrophic and heterotrophic activity (Williamson et al., 2008).

Nutrient availability drastically changes between land uses as well. Forested streams usually contain lower concentrations of nutrients, as they are absorbed and stored in the riparian vegetation and thus are less likely to enter the stream (Golay et al., 2013). Urbanized and agricultural streams tend to have elevated nutrient levels due to runoff over impervious surface cover and from excess fertilizer usage. This leads to increased GPP and ER as there is no nutrient limitation in the system (Qasem et al., 2019). Izagirre et al. (2008) found that GPP increases with more nutrient loading and ER increases with increased availability of labile organic matter. However, high GPP could ultimately lead to low values of DO in the water overall due to the presence of more algal biomass, using the increased nutrients. This could cause hypoxic conditions as ER and decomposition uses up available DO. Riparian and whole watershed land cover can also be correlated with nutrient concentrations (Dodds and Oakes 2008).

Reisinger et al. (2017) focused on urbanized stream metabolism and how it changed during storms, including superstorm Sandy. Overall, their study showed that GPP decreased by 84% and 92% in suburban and urban streams (respectively) and ER decreased by 72% and 86% in suburban and urban streams (respectively) after storm events. A larger reduction in GPP than
ER was also observed by Qasem et al. (2019), where they concluded that, while GPP and ER are affected by storms (with larger storms depressing GPP more than smaller storms), the recoveries of GPP and ER were different and varied by location, and thus hard to predict due to the many factors that control metabolism. Such factors that have an effect on the recovery of GPP include the turbidity that ensues after storm events as organic materials and sediments are washed downstream (decreasing GPP) and the fact that GPP recovers according to rates of regrowth of the primary producers that were scoured away due to the higher flows. ER was predicted to recover faster because, as opposed to the autotrophs, heterotrophs are not scoured from surfaces in the same manner but transported downstream along with organic material to use as food for ER (Qasem et al., 2019). Blaszczak et al. (2019) also stated that light extinction could persist long after storms ended, decreasing productivity in urbanized watersheds. They also concluded that the predicting power of incoming light at the stream surface as a driver of GPP decreased as hydrological flashiness increased. While it is not a new idea that high flow events are controlling factors for stream ecosystems (Poff et al., 1997) more studies are needed to investigate the effects of hydrologic disturbances on stream metabolism, especially across an urbanization gradient (Qasem et al., 2019). As greater variability of precipitation is predicted throughout the world due to climate change (Milly et al., 2005; Swain et al., 2018) the effects of land use and hydrology on stream metabolism are of utmost importance as we seek to understand what the future may hold for headwater streams.

1.1 Goal

This study used continuous, high frequency DO measurements to quantify how land use affects metabolism in headwater streams. The study had two objectives: 1) Quantify GPP and ER in three headwater streams draining different land use types as well as in a larger mainstem river;
and 2) Quantify how GPP and ER respond to storm events in each stream reach. These goals enable us to infer responses of GPP and ER at ecosystem scales if the climate changes and how these responses will differ with land use type and changing hydrologic regimes. It was hypothesized that 1) the urbanized (URB) stream would have higher GPP and ER than the forested (FOR) and mixed (MIX) streams because of increased light (increasing GPP), increased organic matter in the catchment (increasing ER), and higher nutrients due to anthropogenic inputs (increasing GPP and ER). 2) The URB stream, because of its flashier hydrology which scours primary producers and reduces light in the water column, would show a greater change in GPP and ER following storms than in the FOR and MIX headwater streams which have more stable flows. It was also hypothesized that 3) The larger river (MAIN) would maintain stable GPP and ER following storms because of more attenuated hydrographs, decreasing potentially flashy flows that could lower GPP and ER.

2. Methods

2.1 Overarching design

Combining reliable DO probes that have little to no sensor drift with new mathematical models of stream metabolism makes it feasible to study longer periods of stream GPP and ER through observing and calculating changes in diel DO curves (Odum, 1956). As sensor technology increases and new model iterations are developed, we can now observe and measure these characteristics to a greater degree than ever.

*In situ* sensor suites were installed at three headwater streams and one river mainstem in the Oyster River watershed in order to quantify the effects of land use and flow on stream metabolism, which is comprised of both GPP and ER. These sensor suites measured water temperature, water depth, DO, photosynthetically active radiation (PAR), conductivity and
(occasionally) nitrate. Continuous discharge data was obtained via power rating curve equations created by measuring flow using the area-velocity method. Storm events were identified and responses of GPP and ER to storm flows quantified in each stream. We also collected monthly handheld meter readings, and physical grab samples to characterize each stream’s chemistry through time. We also characterized diel variability in each stream using three diel, or 24 hour, sampling events to identify variation in nitrate, N₂:Ar, and DO during the course of a day. Diel samples were collected every two hours for 24 hours at all four sample locations on the same days.

2.2 Study Sites

The Oyster River watershed in southeastern New Hampshire is a coastal watershed that drains an area of approximately 50.6 km² (Figure 1). This watershed is characterized by multiple land use types and is predominantly forest (59.1%), followed by developed (17.3%), wetland (11.6%) and agricultural (11.1%) land cover (Wollheim et al., 2017). Four intensive stream sampling sites, each with their own unique land covers surrounding them (Table 1) and chemical and physical properties (Table 2), were identified to look at the effects of storm flow impacts on metabolism. These consist of Dube Brook, a forested stream, College Brook, an urbanized stream, and Chesley Brook, a mix between College Brook and Dube Brook land use types. Samples were also collected at a channelized mainstem of the Oyster River at Oyster River Road. Dube Brook, Chesley Brook, College Brook and the Mainstem at Oyster River Road will be referred to as FOR, MIX, URB, and MAIN respectively. The FOR stream (watershed area = 3.3 km²) consists of 59.4% forest, 17.3% wetlands, 15.4% agricultural, and 7.9% developed. The URB stream (watershed area = 2.3 km²) consists of 68.7% developed, 20.8% forest, 9.8% agricultural, and 0.7% wetland. The MIX stream (watershed area = 4.0 km²) consists of 48.9%
forest, 24.5% agriculture, 13.8% wetland, and 12.9% developed. The MIX stream, which includes the Spruce Hole bog in its watershed, has been permitted for water withdraw in the past (NHDES, 2014). This stream seems to behave like a spring fed system due to this bog, leading to more stable flows (Cedarholm, 2012, Figure A1). The MAIN (watershed area = 45km²) is 63% forest, 13% wetland, and 12% developed, and 11% agricultural. Impervious service cover (ISC) is part of the “developed” category but is important when thinking in terms of runoff from anthropogenic structures such as roads and parking lots. ISC for each stream site was 28.4% (URB), 6.2% (MIX), 4.8% (FOR), and 2.2% (MAIN, Table 1).

2.3 High Frequency Sensor Measurements

High frequency sensors were deployed at the four Oyster River Watershed streams for a 7-month period that spanned approximately from solstice to solstice (June 23rd, 2017 to January 10th, 2018). Each of the three headwater streams had water temperature, water level, conductivity, and DO loggers (Onset Inc.) and PAR loggers (Odyssey). Water temperature, stage water level, and DO loggers were deployed in stilling wells near the thalweg. The stilling well is comprised of a PVC tube which was attached to rebar driven into the stream bed. The PVC tube had holes drilled in it to allow adequate water circulation. PAR loggers were deployed on rebar 25 meters upstream of the DO loggers (in the streams for FOR, MIX, and URB, and on the bank for MAIN) in order to characterize light hitting upstream and accounting for the production in the reach. A barometric pressure logger, which is needed to convert logger DO to percent saturation, and logger stage to depth, was located at nearby Wednesday Hill Brook, with data maintained by Lisle Snyder of the UNH Water Quality Analysis Lab (WQAL). The MAIN was equipped with only water temperature, DO, and PAR loggers while stage data was transformed from the upstream USGS gaging station #01073000 (drainage area = 31 km²) near Durham, NH.
Data was transformed by lining up concurrent stage data at the MAIN with the gaging station data. Then a nonlinear second order polynomial was fit to binned means and applied to the gage data starting in 2016 to create a dataset of MAIN stage spanning July 2016 to December 2018. This was used under the assumption that the fit was valid going forward and backwards in time. All sensor measurements were taken at 15-minute intervals and sensors were maintained, downloaded, and cleaned at weekly to monthly intervals, or when thought necessary (such as after large storms). DO and PAR loggers were calibrated before deployment.

**2.4 Discharge**

Stream discharge (Q) was calculated using continuous measurements from stage depth pressure loggers and site-specific power rating curves of discharge (m³ sec⁻¹) to stage height (m). Rating curves were created for the FOR, URB, and MIX streams by measuring flow via the area-velocity method with a Marsh-McBirney Flo-Mate (Hach Company) several times (at least 10 measurements at each stream) between the summer of 2016 and the spring of 2018 (Figures A2, A3, and A4). Flows were measured across a range of stage heights, with the highest being 0.45m, 0.4m, and 0.65m for the FOR, URB, and MIX streams respectively.

**2.5 Stream Reach Characterization**

Each stream was characterized with a series of measurements of average width, depth, and canopy cover. Measurements were taken over five transects throughout the stream reach. Depth was measured in feet with a weighted rod and converted to meters. Width was measured with transect tape in meters. Canopy cover was measured at each transect by using a spherical densiometer and standing in the stream, holding it far enough away so your head is just out of view, and counting the number of dots (out of 17) that touch any canopy overhead. This was done four times, once upstream, rotate 90° from upstream, rotate again to get the downstream
value, and lastly rotate 90° from that. Average canopy cover (%) is the total number of dots shaded divided by 17*4 (68) dots multiplied by 100. Since the stage loggers are not representative of the mean reach depth, they needed to be corrected to turn logger stage depth into a mean reach scale depth (MRSD). MRSD was calculated by subtracting an average offset at each stream found by comparing the logger depths at the time of sampling from the average depths calculated in the stream characterizations above. This gives you a correction to use (FOR=0.204m, MIX=0.027m, URB = 0.069m, MAIN=0.318m) for estimating MRSD in each stream.

2.6 Stream Metabolism

Stream metabolism was calculated via the one station diel DO curve method using a hierarchical state-space, inverse Bayesian model run through the streamMetabolizer package (Appling et al., 2018) in the R statistical program version 3.4.4. Inputs to this model include 15-minute DO concentration (mg L⁻¹), DO at saturation (mg L⁻¹), water depth (m), water temperature (°C), Q (m³ sec⁻¹), and light (µmol photons m² sec⁻¹, Figures 2, A5, A6, and A7), while the outputs the model solves for are GPP (g O₂ m⁻² day⁻¹), ER (g O₂ m⁻² day⁻¹), and K₆₀₀ (day⁻¹, Figures 3, A8, A9, and A10). K₆₀₀, also called the reaeration rate, is the gas exchange velocity between the surface of the water and the atmosphere. Often normalized to a Schmidt number of 600, K₆₀₀ is essential in answering questions about aquatic ecosystems because it defines the flow of gasses between the water and the atmosphere (Hall et al., 2018). Six argon tracer gas additions were performed throughout the study period, two at each stream. Pre-addition nutrient samples, N₂:Ar samples, and handheld meter measurements were collected. Argon gas was bubbled into the stream at the same time as a NaCl solution. These acted as conservative and non-conservative tracers to evaluate when a plateau in conductivity occurred.
and post samples (of nutrients, N₂:Ar, and handhelds) were to be collected. Obtaining gas exchange coefficients, especially for the air/water interface, is challenging because the exchange velocity is highly variable and correlated to stream slope and water velocity (Hall et al., 2018). That being said, the tracer additions performed did not compare to the modeled K₆₀₀ estimates, most likely due to short reach lengths and that well mixed parts of the stream were hard to find during low flow conditions. Gas tracer additions, when done correctly, are a good option for calculating this exchange of gasses because they represent direct exchange measured at spatial scales. Scaling of these measurements however from typical addition gasses (SF₆, Propane, ³He) to the ecological gasses of interest (CO₂, O₂, CH₄) is often not as straightforward, but is improved for O₂ with the use of Argon gas (Hall et al., 2018).

Because the model simultaneously solves for all three variables (GPP, ER, and K₆₀₀), partial pooling of the K₆₀₀ data was allowed under the assumption that similar Q’s have similar K₆₀₀’s. Partial pooling relates the Q data to the K₆₀₀ values from the entire time series to better predict K₆₀₀ on individual days (Appling et al., 2018). This reduces uncertainty and equifinality in the model, resulting in more robust GPP and ER estimates. Due to the hierarchical nature of the streamMetabolizer model, days with weak diel variation or trending DO tend to increase equifinality. In order to combat this, assigned storm days themselves (those with highly variable flows) were removed from the model to improve accuracy of the given time series metabolism estimates. Since storm days were removed, this study compares GPP and ER two days before the storm to GPP and ER two days after the storm once the DO signal returns. The Bayesian model was run for 1000 warmup steps to determine the number of model iterations for the burn-in process and 500 saved steps on 4 cores, just as Appling et al. (2018) used in their model. Error
bars for GPP, ER, and $K_{600}$ are represented as confidence intervals of the variance of the daily modeled estimate.

### 2.7 Grab Samples

Monthly grab samples were collected from each stream to characterize their biogeochemistry in order to understand patterns of GPP and ER and to validate sensor measurements. For example, the SUNA data can be compared to a nitrate grab sample and the DO loggers can be compared to the handheld values as a benchmark to evaluating the accuracy of the sensor data. Nutrient samples were filtered through GF/F (0.7 μm) filters in the field, stored on ice, and then frozen in the lab until analysis by the WQAL at the University of New Hampshire (UNH). Grab samples were analyzed for chloride (Cl$^-$), nitrate-N(NO$_3^-$-N), ammonium-N(NH$_4^+$-N), phosphate (PO$_4^{3-}$), and total dissolved N (TDN: DON = TDN - NO$_3^-$-N - NH$_4^+$-N). NO$_3^-$ and Cl$^-$ were measured via ion chromatography (Dionex ICS 1000), while PO$_4^{3-}$ and NH$_4^+$ were analyzed using a SmartChem 200 discrete automated colorimetric analyzer using the alkaline phenate standard method (MDL: 5 lg N/L). DOC (as NPOC) and TDN were measured via high temperature catalytic oxidation (Merriam et al., 1996) on a Shimadzu TOC-V.

Total suspended sediment (TSS) samples were collected by filtering a 1L stream water sample and measuring the difference between a pre-weighed filter and filter plus sample (Figure A14 and 17). Handheld measurements of DO, water temperature, and specific conductance were collected at every site during monthly sampling regiments with a YSI ProDO and YSI Pro30 water quality meters.

### 2.8 Statistical Analysis

The statistical aspects of this study consisted of spatial comparisons of whether streams differed, temporal regressions of what controls caused changes in GPP and ER over time at each
stream, and the storm analysis. All data (except for temperature) was log transformed to meet assumptions of normality. On top of this, simple linear regression analysis was used to look at relationships over time between GPP and ER and potential controls such as temperature, Q, and PAR. ANOVA tests were used in conjunction with Tukey HSD tests to see which means were significantly different from each other in the different streams. Storm flows and base flows were calculated using the “BaseflowSeperation” function in the “EcoHydRology” package in R. This function was run with a recursive filter (Fuka et al., 2014), 3 passes, and a filter parameter of 0.9 (Blaszczak et al., 2019). The maximum Q’s were then separated from the storm flow data and storms were determined by visual analysis of a typical flood peak on the hydrograph and a response in discharge value of 0.05 m³ sec⁻¹ or higher at FOR and URB, and 0.04 m³ sec⁻¹ or higher at MIX. A lower threshold was used at the MIX because it had more stable flows. To look at the effect of storm events on GPP and ER, indices of response and storm disturbance were developed to look at changes in Q with what was called a storm index ratio (SIR) of maximum Q during the storm event divided by Q before the storm. This is similar to the rate that Reisinger et al. (2017) used in their response ratio for GPP and ER post floods. Indices comparing pre and post storm disturbance such as absolute changes in Q, PAR, and temperature were also used. It was also a point of interest to see how the nitrogen cycle compares in the different streams at different flows. Diel variability in NO₃⁻ allows you to visualize nitrate assimilation while looking at N₂:Ar disequilibrium (N₂:Ar observed in the streams minus N₂:Ar at equilibrium) allows you to get at nitrogen fixation or denitrification (Reisinger et al., 2016). For this study the diel variability in nitrate and DO was simply summarized, as were the disequilibrium values of N₂:Ar during the day and at night.

**2.9 Additional Measurements**
Additional measurements that were taken but not interpreted ranged from diel sampling, SUNA deployments, monthly grab samples and TSS samples. On three separate occasions (June 26th-27th, August 2nd-3rd, and August 10th-11th 2017) 24-hour diel sampling rounds took place at all four streams. Diel samples included grab samples of NO₃ (Table A2), handheld meter measurements of DO (Figure A3), and N₂:Ar samples (Table A4) which were taken every two hours for a total of 24 hours. Diel variability (max – min) of NO₃ in the FOR ranged from 0.07, 0.06, and 0.05 mg N L⁻¹ on diel sampling days 1, 2, and 3 respectively. The change in NO₃ at the MIX stream was 0.09, 0.09, and 0.07 mg N L⁻¹ for each diel respectively. URB saw the largest difference (during Diel 1) in maximum and minimum NO₃ with variability from 0.16, 0.04, and 0.02 mg N L⁻¹ over the three diel days. The MAIN differences were small at 0.04, 0.03, and 0.01 mg N L⁻¹ for diel 1, 2, and 3 respectively (Table A2, Figures A28, A29, and A30). Diel variability in DO was largest at the FOR stream and ranged from 19.7, 20.6, and 22.2% over the three diel sampling days. MIX saw changes of 10.3, 6.4, and 6.7%. The URB saw small changes of 8.6, 6.3, and 7.0% DO over the three diels, and the MAIN varied by 5.7, 6.9, and 8.4% over diel 1, 2, and 3 respectively (Table A3, Figures A25, A26, and A27). Diel variability in N₂:Ar ratios for the FOR ranged from 0.05, 0.57, and 0.21 over the three diels respectively. The MIX changed by 0.07, 0.47, and 0.26 respectively. The URB changed by 0.03, 0.34, and 0.56 over the three rounds respectively and the MAIN changed by 0.26, 1.6, and 1.3 during diel 1, 2, and 3 respectively (Table A4). One TSS sample was also taken at each site in the middle of the day and added to the database of monthly TSS samples (Figure A14). All constituents above were analyzed for each DIEL sampling round. Grab samples are run through traditional methods by the WQAL while N₂:Ar samples were kept in the cooler until analyzed in the lab by drawing water through a semipermeable microbore silicone tubing inside of the inlet vacuum line of a
membrane inlet mass spectrometer (MIMS) for dissolved gas ratios of N₂, O₂, and Ar in the water (Kana et al., 1994).

A Submersible Ultraviolet Nitrate Analyzer (SUNA, Satlantic, LLC) was deployed periodically to measure nitrate levels in certain streams (Table A1, Figure A21). The SUNA was equipped with only a copper antifouling guard (i.e. no automatic wiper), so it was cleaned weekly to prevent biofouling. The SUNA was calibrated periodically throughout the year. The SUNA was deployed at FOR twice (September 11th to September 12th, 2017 and October 10th to November 16th, 2017), at the MIX from November 16th to December 19th, 2017, and at the MAIN from September 29th to October 17th, 2017 (Table A1). These nitrate data were used to look at the diel cycling of nitrate in headwater streams and to get an idea of ambient nitrate in each stream for that particular time of the year. This data could also be compared to the nutrient grab samples to check the accuracy of the sensors.

N₂:Ar disequilibrium values, or the difference between the ratio that is measured in the stream minus what would be present at saturation, differed amongst all streams. In diel 1, 2, and 3 the average disequilibrium values were -0.2, -0.14, and 0.12 respectively for the FOR. They were 0.006, 0.2, and 0.12 for the MIX, -0.16, 0.30, and 0.12 for the URB, and -0.34, -0.04, and -0.02 for the MAIN (Table A5, Figures A22, A23, and A24). Average daytime, nighttime, and changes between day and night were also calculated (Tables A6, A7, and A8).

3. Results

3.1 Metabolism of Headwater Streams

All headwater streams were net heterotrophic (P:R ratio <1) with average ER greater than GPP for the entire study period. Daily GPP ranged from 0.0 to 0.96 g O₂ m⁻² day⁻¹, ER from 0.12 to 14.2 g O₂ m⁻² day⁻¹, and modeled K₆₀₀ from 0.02 to 5.5 m day⁻¹ (Figures 3, A8, A9, and A10).
Mean GPP over the entire study period ranged from 0.04 g O₂ m⁻² day⁻¹ at the MIX stream to 0.32 g O₂ m⁻² day⁻¹ at the URB stream and 0.08 g O₂ m⁻² day⁻¹ for the FOR stream (Table 3). Mean ER ranged from 2.1 g O₂ m⁻² day⁻¹ at the FOR stream to 7.6 g O₂ m⁻² day⁻¹ at the URB stream with MIX ER at 2.3 g O₂ m⁻² day⁻¹ (Table 3). GPP and ER at the URB stream were both significantly higher than the other two headwater streams (p = <0.001: Figure 4A and 4B). GPP in URB was 75% higher than the FOR stream, while ER was on average 72% higher. Daily K₆₀₀ in the headwaters ranged from 0.02 to 5.5 m day⁻¹ with averages (excluding storm events themselves) of 1.6, 1.04, and 2.9 m day⁻¹ in FOR, MIX, and URB streams respectively (Figure 4C). Modeled K₆₀₀ vs ER can be found in figure A15.

Potential environmental controls of GPP and ER differed among the streams. Daily Q ranged from 0.19 m³ sec⁻¹ to 0.81 m³ sec⁻¹ in the headwater streams. Average Q, not including storms themselves, ranged from 0.024 m³ sec⁻¹ at the URB stream to 0.039 m³ sec⁻¹ for both the MIX and FOR streams (Table 2). PAR values ranged from 0 to 2214.3 μmol photons m⁻² sec⁻¹ across all streams and seasons, with average PAR values highest (74.0 μmol photons m⁻² sec⁻¹) at the FOR stream, intermediate at the mixed stream (45.0 μmol photons m⁻² sec⁻¹) and lowest (23.6 μmol photons m⁻² sec⁻¹) at the URB stream. The URB streams average PAR was approximately 68% lower than that of the FOR stream. This is atypical as forested streams are usually shaded and urbanized streams are usually open due to riparian zone loss. Furthermore, average PAR values at all three headwater streams were significantly different from each other (p <0.01, Figure A11). Water temperature did not vary significantly between streams with average temperatures ranging 10.5-12.5°C (p>0.06, Table 2, Figure 4D). The MIX stream did have temperatures that were much less variable through time compared to the other streams (Figure 4). Mean nitrate-N from the grab samples ranged from 0.22 mg N L⁻¹ at the FOR, 0.85 mg N L⁻¹
at the URB and 1.08 mg N L\(^{-1}\) at the MIX. Mean chloride ranged from 36.3 mg Cl\(^{-}\) L\(^{-1}\) at the MIX, to 64.5 mg Cl\(^{-}\) L\(^{-1}\) at FOR, and 333.1 mg Cl\(^{-}\) L\(^{-1}\) at URB. DON ranged from 0.28 mg N L\(^{-1}\) at the MIX, 0.29 mg N L\(^{-1}\) at the FOR, to 0.7 mg N L\(^{-1}\) at the URB. Mean phosphate ranged from 8.1 \(\mu g\) P L\(^{-1}\) at the MIX, 16.5 \(\mu g\) P L\(^{-1}\) at the FOR, and 26.3 \(\mu g\) P L\(^{-1}\) at the URB. Mean canopy cover at the FOR, URB, and MIX were 50%, 88%, and 93% respectively (Table 2, Figures A18, A19, and A20).

GPP decreased from summer into fall at all headwater sites (Figure 3, A8, A9) but showed a secondary increase in the fall at URB (Figure 3). PAR, temperature, and Q were explored as potential seasonal controls. GPP declined seasonally as baseflow increased at the FOR and MIX streams (FOR: \(p<0.01, r^2=0.09\); MIX \(p<0.01, r^2=0.22\)), but no significant relationship with baseflow occurred at URB (\(p=0.09\)). PAR decreased as the year progressed in FOR and MIX (figure A6D), though MIX had a brief increase when canopy cover dropped (Figure A5D). URB PAR is quite variable throughout the year but shows increases after leaf drop in the fall (Figure 2D). GPP declined as PAR increased at the MIX stream (\(p<0.01, r^2=0.08\)) and increased with PAR at the FOR stream (\(p<0.016, r^2=0.04\), Figure 5). Despite these being significant relationships, PAR only explained 4% and 8% of the variability in GPP at the FOR and MIX sites respectively. Increased water temperature (Figures 2C, A5C, A6C, and A7C) was associated with increased GPP at the FOR and MIX streams (FOR: \(p<0.016, r^2=0.04\); MIX \(p<0.01, r^2=0.19\)) and decreased GPP at URB (\(p<0.01, r^2=0.09\), Figure 5C).

ER significantly increased with baseflow Q at the FOR and MIX streams (FOR: \(p<0.01, r^2=0.5\), MIX: \(p<0.01, r^2=0.61\)) and decreased with Q at URB (\(p<0.01, r^2=0.3\), Figure 6A). These strong relationships of ER to Q differ from those of GPP and Q. Also in contrast with GPP vs. Q, a lot of the variation in ER is explained by Q variability (based on \(r^2\) values). 50% and 61% of
the variation in the increase of ER as Q increases is explained in the FOR and MIX streams respectively, while 30% is explained at the URB stream. As PAR increased, ER decreased significantly at MIX (p<0.01, r²=0.06) and FOR (p<0.01, r²=0.09) streams, although r² values were low, with no significant relationship (p=0.06, Figure 6B) at the URB stream (like GPP vs PAR). Increasing temperature was associated with a decrease in ER in the FOR and MIX streams (FOR: p<0.01, r²=0.04, MIX: p<0.01, r²=0.05) and an increase in ER at URB (p<0.01, r²=0.3, Figure 6C), although again, little of the variability was explained by water temperature.

3.2 Response to Storm Events

Responses to individual storms in each headwater stream were quantified by comparing the average GPP and ER for the two days before the storm at baseflow conditions with the average of the next two modellable days (when diel variability returns) after the storm. Anywhere from 11 (MIX) to 28 (URB) storms of varying sizes were isolated throughout the study period (Figure 7). More storms occurred in the URB where flashy discharges cause storm responses that might not be picked up at any of the other streams (Figure A12). Both GPP and ER decreased after storms at the URB stream with GPP decreasing on average 0.11 g O₂ m⁻² day⁻¹ and ER decreasing 1.6 g O₂ m⁻² day⁻¹ (Table 4). These equate to a 34% decrease in average daily GPP and 21% decrease of average daily ER values. Larger storms did not always lead to larger changes in GPP as there was no significant relationship between storm size (maximum Q) and absolute change in GPP (Figure A16). The URB stream was the only location where decreases in both GPP and ER were observed. The FOR stream saw a decrease in GPP (0.03 g O₂ m⁻² day⁻¹, or 38%) and an increase in ER (0.31 g O₂ m⁻² day⁻¹, or 15% increase). The MIX stream showed essentially no change after storms with GPP decreasing by 0.003 g O₂ m⁻² day⁻¹ (7.5% decrease) and ER increasing by 0.046 g O₂ m⁻² day⁻¹ (2% of average ER, Table 4). In
general, there was a greater change in GPP (38%, 7.5%, and 34%) due to storms than in ER (15%, 2%, and 21%) at FOR, MIX, and URB, respectively (Table 5).

3.3 Large River Response

The mainstem Oyster (MAIN) was net heterotrophic like the three headwater streams where ER was almost exclusively higher than GPP except for two days, one on July 29th, 2017 and the other January 6th, 2018 (Figure A13). Daily GPP in MAIN ranged from 0.0 to 0.40 g O₂ m⁻² day⁻¹ with an average daily GPP of 0.06 g O₂ m⁻² day⁻¹ (Table 3). ER ranged from 0.003 g O₂ m⁻² day⁻¹ to 4.5 g O₂ m⁻² day⁻¹ with an average of 0.71 g O₂ m⁻² day⁻¹ (Table 3). K₆₀₀ ranged from 0.02 to 4.8 m day⁻¹ with an average of 0.87 m day⁻¹. MAIN GPP was lower than URB (p<0.01), but not different from the MIX and FOR streams (p=0.31; p = 0.69, Figure 4A). In contrast, ER in MAIN was lower than all the headwater streams (P=<0.01, Figure 4B). Modeled daily K₆₀₀ was on average lower than all headwater streams, but the difference with MIX was not statistically significant (Figure 4C). Average discharge in the MAIN was 0.34 m³ sec⁻¹. PAR values ranged from 0 to 715.8 μmol photons m⁻² sec⁻¹ with an average daily PAR of 17.7 μmol photons m⁻² sec⁻¹. MAIN PAR was similar to that of the URB stream (p=0.44) and lower than the MIX and FOR streams (p<0.01). Average water temperature was 12.1°C, similar to the headwater streams (p >0.16). In general, the MAIN showed an increase in GPP with increasing temperatures (p<0.01, r²= 0.35, Figure 5C). Increased Q (p<0.01, r²=0.09), PAR (p=0.023, r²=0.03), and water temperature (p<0.01, r²=0.12) all led to an increase in ER (Figure 6A, 6B, 6C). Mean nitrate-N was 0.25 mg N L⁻¹, mean chloride was 55.1 mg Cl⁻ L⁻¹, mean DON was 0.31 mg N L⁻¹, mean phosphate was 11.5 μg P L⁻¹, and average canopy cover was 96% (Table 2). MAIN saw increases in both GPP and ER after storms with GPP increasing by an average of 0.10 g O₂ m⁻² day⁻¹ and ER increasing by 1.1 g O₂ m⁻² day⁻¹ (67% and 55% of average GPP and
ER, respectively, Table 5). It was the only stream to see increases in both GPP and ER after storms, as opposed to a decrease in GPP and an increase in ER (MIX and FOR) or decreases in both (URB). Looking at MAIN GPP and ER in an absolute basis, GPP increases after storms from as little as 0.002 g O$_2$ m$^{-2}$ day$^{-1}$ to as much as 0.31 g O$_2$ m$^{-2}$ day$^{-1}$ while ER minimum and maximum absolute changes are 0.13 g O$_2$ m$^{-2}$ day$^{-1}$ to 3.01 g O$_2$ m$^{-2}$ day$^{-1}$ respectively (Table 6, Table 7).

4. Discussion

4.1 Headwater GPP

Streams are increasingly affected by land use and climate change (Malmqvist and Rundle, 2002; Meyer et al., 2007; Swain and Hayhoe, 2015) while the urban stream syndrome continues to alter stream structure and function (Walsh et al. 2005). Therefore, using GPP and ER as indices of ecosystem change can allow us to evaluate the health and function of headwater streams (Izagirre et al., 2008). GPP rates from this study (0.0 to 0.96 g O$_2$ m$^{-2}$ day$^{-1}$) were lower than but within the range of other metabolism studies (Reisinger et al., 2017; Hoellein et al., 2013; Qasem et al., 2019; Bernot et al., 2010; Blaszczak et al., 2018) especially when it came to urban, suburban, and agricultural streams. Qasem et al. (2019) saw GPP estimates up to 6.61 g O$_2$ m$^{-2}$ day$^{-1}$ in urban and suburban streams, Blaszczak et al. (2018) saw GPP up to 9.1 g O$_2$ m$^{-2}$ day$^{-1}$ in urbanized streams, while Bernot et al. (2010) saw estimates up to 16.2 g O$_2$ m$^{-2}$ day$^{-1}$ in their agricultural streams with lower maximum GPP’s for the forested (3.9 g O$_2$ m$^{-2}$ day$^{-1}$) and urban (11.9 g O$_2$ m$^{-2}$ day$^{-1}$) streams. Higher GPP was observed in these studies than in my study because these studies focused on more productive months (Blaszczak et al., 2018), or because the urban and agricultural streams did not have any canopy cover (Bernot et al., 2010). Unlike Bernot et al., (2010) who were surprised to see similar ranges of metabolism over a diverse
selection of land uses, my study saw different GPP and ER among the headwaters of differing land use (Figure 4), although all were relatively low. Since light and nutrients are key drivers of GPP, differences in GPP between the URB and FOR streams could be associated with the fact that the higher shaded URB still had adequate light for GPP, along with enough nutrients and a conducive substrate. The FOR had more light, but potential limits on nutrients and unstable substrates. Bernot et al. (2010) also found a correlation between increased nutrients and higher metabolism estimates.

The higher GPP at URB came despite the higher canopy cover (Table 2) and associated lower light levels (Figure A11) compared to FOR and MIX streams. Light, which was measured by a PAR logger placed halfway up the reach in a spot representative of the average canopy cover, is the primary driver of GPP, yet the URB stream showed higher GPP and ER than the FOR or MIX headwater streams, as hypothesized. Normally, increased light due to the loss of riparian vegetation is characteristic of urban streams (Walsh et al., 2005), however, the riparian zone of the URB stream, which flows east/west, has been maintained, especially on the south side, with a lot of low shrubby vegetation overhanging the bank. This vegetation, even if just shrubs, present on the south side is more likely to block more of the sun in an east/west flowing stream such as this one. Unlike typical forested streams with higher canopy covers, the FOR stream in this study had a mostly open canopy (Table 2), likely because it flows through a beaver meadow recovering from being a beaver pond.

Because of the relatively closed canopy in URB, seasonal PAR variation was less than at the other streams and its range of light conditions was not enough to identify a relationship between GPP and PAR (Figure 5B). Bernot et al. (2010) also saw no correlation between GPP and light within land uses, however, in open streams, light was correlated to increased GPP.
URB showed an increase in GPP in the fall when the canopy cover opened up following leaf drop. Letting more light into the catchment and adding a supply of course particulate organic matter (CPOM) through leaf litter. This was not seen in the other streams, suggesting something other than light is limiting GPP. This effect of opening canopy cover at the URB is consistent with the close coupling of GPP to PAR reported in multiple studies of metabolism and throughout different land use types.

The FOR stream had the highest average daily PAR values of the three headwater streams (Figure A11). In contrast to URB, there was a significant positive relationship between PAR and GPP at the FOR stream, perhaps because of the greater range in light conditions due to the more open canopy (Figure 5B). Although light was relatively high in FOR, this stream had lower concentrations of NH$_4^+$, NO$_3^-$, and PO$_4^{3-}$ (Table 2) as is typical of forested watersheds.

On top of light, nutrients can also be a driver of GPP. The higher nutrient concentrations in URB could have contributed to higher GPP and ER. Other studies have shown relationships between nutrients and GPP in a wide range of stream types (Izagirre et al., 2008). Elevated nutrients at URB result from fertilizer applied to UNH lawns and athletic fields, as well as from manure applications to one of the UNH dairy fields located where the stream begins (Wollheim et al., 2017). Neither Bernot et al. (2010), Blaszczak et al. (2018) or Reisinger et al. (2017) listed specific nutrient data but Blaszczak et al. (2010) brings up a good point that it is difficult to predict the cumulative effects of both higher amounts of limiting nutrients and flashier flows in urbanized streams, since they are opposing drivers of GPP and ER.

URB GPP was higher than FOR and MIX GPP despite having a much flashier hydrograph. Higher Q’s can cause a decrease in GPP for many reasons, including the scouring of primary producers and increasing turbidity in the water column by mobilizing bed sediments
Qasem et al., 2019; Reisinger et al., 2017). While studies have shown that urbanization can lead to a decrease in ecosystem functions like GPP and ER, sometimes the opposite is seen where urbanized streams could also exhibit rates equal to or higher than other streams, suggesting that processes like GPP and ER could be more resistant to urbanization than the biodiversity in the stream communities (Reisinger et al., 2017). Stimulation of GPP was reported by Qasem at al. (2019) but not by Reisinger et al. (2017). However, after the initial decreases, GPP and ER in Reisinger’s streams tended to increase higher than pre-storm levels. Interestingly, there was not a significant relationship between GPP and baseflow Q in the URB over the whole time period, although storm response indicates a small decline (Table 4). Qasem et al. (2019) did not see a relationship between GPP and ER with Q either. GPP also declined following storm Q in the FOR and MIX sites, which was expected due to scouring of primary producers and increased turbidity (thus decreased light to the stream surface). This could be supported by more resilient species of primary producers present in the URB stream, which despite many physiochemical disturbances, remain more tolerant to the altered hydrology of the stream.

MIX GPP was lower than the FOR and URB. This difference in GPP could be explained by the mean canopy cover, which was high at the MIX stream, and water temperatures, which were cooler and very stable throughout the study period compared to the other streams.

4.2 Headwater ER

ER in this study (0.0 to 14.2 g O$_2$ m$^{-2}$ day$^{-1}$) fell within the range of other studies (Reisinger et al., 2017; Hoellein et al., 2013; Qasem et al., 2019; Bernot et al., 2010; Blaszczak et al., 2018) but again at the low end as some ER estimates reach 25.3 g O$_2$ m$^{-2}$ day$^{-1}$ (Blaszczak et al., 2018). Higher ER than in my study was observed in other studies due to warmer water temperatures stimulating respiration (Blaszczak et al., 2018) and higher availability of OM
(Bernot et al., 2010). The URB streams higher ER could be a result of its higher canopy cover compared to the other headwater streams, whereas the FOR only has small shrubs on its banks. While the high canopy of the MIX is similar to URB, suggesting a similar input of OM, its DOC is lower, which could be associated to lower ER overall (Schindler et al., 2017). DOC, or OM dissolved in the water column, has been linked to increasing ER in other studies (Schindler et al., 2017). DOC is also the lowest in the FOR stream, but so is the supply of OM from low canopy cover and larger beaver cuts present which release OM more slowly over time as compared to leaves and smaller woody debris. While PAR only has an indirect relationship to ER, it does lead to increased water temperatures over time, which can stimulate ER in streams (Williamson et al., 2008). The significant relationships with ER and water temperature at all three of the headwater streams, and the similarities of the average temperature, shows the importance of other proximal factors such as OM, nutrient concentrations, and Q in explaining the variation in GPP and ER. Proximal factors affecting ER, such as organic matter and nutrient concentrations, can be controlled by land use (Bernot et al., 2010). Organic matter, in the form of particulate organic matter (POM) and other allochthonous inputs can play a large part in ER by adding organic carbon for respiring organisms. The largest source of this allochthonous POM is from leaf litter (Hoellein et al., 2007).

Higher ER in the URB stream, as hypothesized, could also come from high organic matter loading. Organic matter dynamics can be affected by land use and land use change (Tank et al., 2010). Sources of OM input vary across the headwater streams from a very closed canopy at URB and MIX to low canopy cover at FOR. Since all streams are net heterotrophic, most OM is likely coming in from the catchment. Lower ER in the FOR could simply be a result of less OM as an effect of altered litter composition, which can have cascading effects on aquatic food,
webs (Tank et al., 2010). Additionally, ER in the FOR could be lower than the MIX as a result of a higher probability of scouring of what OM exists if a storm is to come through the system. The URB stream, with the highest probability of scouring from potentially higher flows, also has the largest source of OM in its thicker riparian vegetation, which could more easily replace OM after disturbances and relate to the higher ER at that stream.

On top of OM, nutrients can be a proximal factor influencing GPP and ER (Bernot et al., 2010). Nutrient enrichment (from increased amounts of ammonium and phosphate) can lead to increased presence of algae and other producers (Frankforter et al., 2010). Higher nutrients, specifically nitrate, have been detected in streams with agricultural inputs (Frankforter et al., 2010). This could support why the URB stream has higher averages of ammonium, DON, and phosphate than the MIX stream, but not higher nitrate (Table 2) as the MIX stream is not fully within an agricultural land use but does have agricultural inputs. MIX ER was not significantly different from the FOR stream, while it was lower than the URB, but higher nitrate has been connected to higher ER (Duncan et al., 2017; Marcarelli et al., 2011).

ER showed more significant relationships with potential seasonal controls (Q, PAR, and water temperature) than GPP (Figure 6A, 6B, 6C). A negative relationship of ER to Q (Figure 6A) at the URB was expected with flashy flows but higher mean ER did persist. This could suggest that although greater scouring of OM and/or heterotrophs occurs, and ER following storms declines, the response is short lived. The FOR and MIX streams, with positive relationships between ER and Q show that higher flows increase ER as opposed to decreasing it like in the URB. This suggests that the MIX and FOR streams could be limited by the amount of organic matter present, which is often replenished after higher flows carry new POM
downstream (Qasem et al., 2019). This stimulation of ER after storms is seen in studies like Qasem et al. (2019) but not by Reisinger et al. (2017).

According to the river continuum concept (RCC, Vannote et al., 1980) downstream communities are adapted to capitalize on the inefficiencies of upstream communities when it comes to the utilization of OM, and more labile terrestrially derived DOM is mobilized and pushed downstream during storm events (Raymond et al., 2016). With this being said, the FOR stream has the lowest amount of riparian vegetation, larger beaver cuts which could be utilized slowly, and less flashy storms compared to the URB stream. Higher flows at the URB could also transport larger forms of POM (such as woody debris) downstream, however these are very slowly utilized by producers and consumers.

4.3 Response of GPP and ER to Storm Events in Headwaters

Storm events had varying effects on streams of different land use types. Hypothesis 2 was supported as the URB stream did show a larger decrease in GPP and ER than the FOR and MIX streams (Table 4). Both the FOR and MIX streams have low ISC and low flashiness, making them less likely to be disturbed during storm events. On top of this the location of primary producers and heterotrophs is of key importance. Primary producers are located in exposed areas on the streambed due to their need for light. While heterotrophic biofilms are usually more protected by substrates in the streambed, sediments, and hyporheic zone (O’Donnell and Hotchkiss, in review). A major characteristic of the urban stream syndrome is a flashier hydrograph, leading to an increased frequency and magnitude of erosive flows during storms of all sizes (Blaszczak et al., 2019). This can have significant positive impacts on ER by bringing in more sediments and POM (Poff et al., 1997) from upstream or from terrestrial sources (Roberts et al., 2007) or negative effects on GPP such as scouring primary producers and increasing
turbidity in the water column (Blaszczak et al., 2019). In this study, the responses of flow following storm events across all three headwater streams were mixed, with most storms showing decreases in GPP and ER. However, unlike Reisinger et al. (2017), the FOR and MIX headwater streams corresponded with an increase in ER in the 1-2 days following storms, perhaps due to storm delivery of OM. A similar effect can be seen in Qasem et al. (2019) where more than 80% of flood events increased ER.

Decreasing GPP in all the headwater streams and decreases in ER in the URB but not the MIX and the FOR shows that storm flows affect these sites differently. Reduced GPP, on average, after storms at all the headwater streams is an expected reaction due to increased flows which scour primary producers, block light, and increase turbidity. The higher reduction in the URB could be caused by higher flows scouring more organisms. However, the percent reduction of GPP at the FOR stream was not significantly different from zero.

Although ER increased at the MIX and FOR streams following storms, the change was not significantly different from zero. An increase in ER at these two streams could be explained by mobilization of OM and the transportation of heterotrophs with their organic substrates downstream (Qasem et al., 2019) along with increased inputs of organic carbon from terrestrial sources that stimulate respiration (Roberts et al., 2017; Demars et al., 2019). A decrease in ER at URB could have resulted from high enough storm flows and water velocities to scour heterotrophs just as much as autotrophs, resulting in a reduction of benthic storage of OM and more OM being washed downstream (Qasem et al., 2019; Meyer et al., 2005; Larsen and Harvey 2017).

Despite the relatively large declines in GPP and ER (Table 5) after storms and the greater frequency of storms events (Figure A12) in the URB stream, GPP and ER during baseflows
remained higher in URB than the other streams. This suggests that urban streams have considerable resiliency and ability to recover more quickly from storms. Reisinger et al. (2017) suggested that urban stream metabolism may be in a frequent if not constant state of recovery due to the flashy hydrology and effects of the urban stream syndrome. This is reinforced with the conclusion from Qasem et al. (2019) where even minor flood events have been found to scour primary producers. Similarly, Qasem et al. (2019) also concluded that more than 80% of floods increased ER levels, while less than 40% of floods increased GPP, which is consistent with what was found in the MIX and FOR streams in the Oyster River Watershed as storms affected ER more than GPP. Interestingly, Reisinger did not report any increases in GPP or ER like Qasam et al. (2019) or like this study. This could be related to the fact that their measurements were taken after superstorm Sandy, where peak Q hit ~500 m³ sec⁻¹, which exceeds the high flow values of both this study and Qasem’s. The degree of reduction in GPP and ER in Reisinger’s study were also greater than other studies (Uehlinger, 2000; Uehlinger et al., 2003; and Roberts et al., 2007). O’Donnell and Hotchkiss (in review) reported stimulation and repression of both GPP and ER, suggesting that there is a resistance threshold of processes to flow disturbances (O’Donnell and Hotchkiss, 2019). Despite varying states of stimulation and repression, and similar to other studies (Reisinger et al., 2017; Qasem et al., 2019), GPP was less resistant to changes in storm flow, despite the magnitude of the storm flow, than ER was, which tended to decrease more as flows increased (O’Donnell and Hotchkiss, in review). All these studies build upon the idea that, despite declines in GPP and ER and more frequent storm events, that baseflow GPP and ER has been known to be as high, if not higher, than other agricultural and forested streams (Reisinger et al., 2017; Mulholland et al., 2008; Bernot et al., 2010). This could result from elevated nutrients transported in city runoff or farm fertilizers or from generally open canopies (although this is not
the case at URB). Reisinger et al. (2017) reports that despite constant press disturbances, processes like GPP and ER may actually be more resistant to the effects of urbanization than the biota in the stream.

4.4 Large River Metabolism and Storm Response

GPP at the mainstem (MAIN) was similar to that of the MIX and FOR headwater streams (Figure 4, Table 3) while ER was lower than all headwater streams. Contrary to what was hypothesized, the MAIN showed the largest percent changes in GPP (67% increase) and ER (55% increase) after storms (Table 5), with absolute changes similar to URB and higher than in FOR and MIX. Other studies showed that nutrients can be flushed downstream during storm events (Blaszcak et al., 2019). This increase of nutrients could be fueling the rise in GPP after storms events. ER increased for all 14 storms in the MAIN, increasing on average 1.1 g O2 m⁻² day⁻¹. Surprisingly, with an average ER around 0.71 g O2 m⁻² day⁻¹, this average increase in ER after storms is large (55%) compared to the headwater streams (Table 5). Out of the 14 storms, 10 of them showed an increase in ER. This increase is possibly the result of increased organic inputs from upstream that are mobilized during storm events and settling into the reach, which are then respired, with higher flows leading to OM being washed downstream (Blaszczak et al., 2019). However, this could also partially be explained by the low baseflow GPP and ER averages, leading to any change being large relative to the average daily values.

Since GPP and ER were so low at the MAIN, absolute changes in GPP and ER were compared to the other streams as well. Absolute maximum change in GPP was higher at the MAIN than the headwaters, while absolute minimum change in GPP was low, similar to the headwaters (Table 6). This shows a larger increase in GPP at the MAIN than the headwaters, perhaps due to rewetting of benthic algae that comes out of the water until higher flows come
through, rewetting the substrate, which is generally cobbles and boulders. Nutrients such as nitrate, phosphate, and DON were all lower in the MAIN than in the URB. Absolute maximum change in ER at the MAIN is in-between the headwaters while the absolute minimum change in ER is higher. This suggests that the maximum change is similar to the headwaters, but the minimum change is usually higher (Table 7). The MAIN did have higher DOC than the URB, which could be a source of the larger increase in ER post storm. The following results do not suggest any nutrient limitations for GPP or OM limitations for ER as the absolute changes of both are similar to that of the URB, which is much flashier than the MAIN.

When compared to the headwater streams, the MAIN was the only one to exhibit an increase of both GPP and ER in the 1-2 days after storm events. Many storms showed no change in GPP due to low rates of primary productivity in general due to the fact that baselevel GPP is often undetectable despite a similar average. With a small (0.10 g O$_2$ m$^{-2}$ day$^{-1}$) increase in GPP and most (9/14) of the isolated storms showing GPP at 0.0 g O$_2$ m$^{-2}$ day$^{-1}$ before the storm event, it is difficult to make any specific conclusions, but it can be deducted that storms either had no effect on MAIN GPP or a small positive effect, which is still an interesting find considering GPP decreased on average at the URB, MIX, and FOR streams.

Increasing watershed area can lead to changes in GPP and ER. In the river continuum concept (RCC, Vannote et al. 1980), as watershed size of a stream increases there is reduced importance of terrestrial organic inputs and an increased importance of autochthonous primary production and organic transport from upstream. Both GPP and ER in MAIN remain low compared to the headwater streams, while ER is greater than GPP in the MAIN, suggesting that the MAIN is still too small for the canopy to open and light to enter that would increase GPP. The low ER is consistent with lower terrestrial OM inputs, consistent with the RCC. The
increase in ER following storms may reflect the increasing importance of upstream organic matter inputs (Del Giorgio and Pace, 2008). These could include elevated DOC which is increasingly shunted downstream during storms (Raymond et al. 2016) or downstream transport and settling of particulate organic matter.

5. Conclusion

This study contributes to improved understanding of stream metabolism and how it reacts to the projected increase in frequency of extreme precipitation events. This study also shows the extent to which urban streams can recover following storm events, despite their flashy hydrograph and other symptoms of the urban stream syndrome. Although we studied only one urban stream, this and other studies (Qasem et al., 2019; Blaszczak et al., 2019) suggest it could be possible for other urbanized streams to exhibit higher GPP and ER despite being battered almost constantly by high flow events. This implies that increased urbanization may not reduce function. Despite being less resistant to storm events than the forested or mixed site, URB GPP and ER were able to quickly recover and thereby maintain the highest overall metabolism of all four streams. Future research should explore a greater diversity of headwater streams, especially urban streams with their potentially greater range of characteristics, to see the responses and recoveries of GPP and ER at more than one stream of each land use type and over a greater range of storm events. It would also be beneficial to better understand how the URB stream rebounds so rapidly despite being in a constant state of recovery and the implications of GPP and ER responding to land use changes in a changing climate. The results of this study show how important it is to understand the changing metabolic regime of GPP and ER in headwater streams and how key ecosystem services such as food web support, water supply, water filtration, flood
mitigation, and aesthetic beauty stand up to urbanization, especially with the expansion of urbanization world-wide and the projected changes in climate of our common home.
Literature Cited


Figure 1: Map of Oyster River Watershed in Southeast NH, USA, showing the three headwater streams and the larger mainstem (MAIN). Land use statistics can be found in Table 1.
Figure 2: Timeseries of 15-minute DO concentration (A), Discharge (B), water temperature (C), and PAR (D) for URB to show streamMetabolizer model parameters.
Figure 3: Timeseries of daily GPP (A), ER(B), and $K_{600}$ (C) metabolism estimate model outputs from streamMetabolizer for the URB stream.
Figure 4: Boxplots of mean GPP(A), ER(B), $K_{600}$ (C), and water temperature(D). Boxes show first and third quartiles, horizontal lines in the box are median values, while individual points are outliers. Letters above each boxplot show statistically significant groupings.
Figure 5: Linear regressions for GPP vs Q(A), PAR(B), and Temp (C). Only significant regressions, p values, and $r^2$ values are shown.
Figure 6: Linear regressions for ER vs Q(A), PAR(B), and Temp (C). Only significant regressions, p values, and $r^2$ values are shown.
Figure 7: Time series of high frequency Q data at the URB stream added to daily GPP (green) and ER (red) data from July 3rd, 2017 to August 28th, 2017. Note that days determined to be storm days were removed (hence gaps in the GPP and ER data). Pre and post GPP and ER were taken as the average values two modellable days before and after storms. Storms are highlighted as open circles. Not all storms are shown to more easily see the effect of Q on GPP and ER.
Table 1: Land use statistics of watersheds draining to streams.

<table>
<thead>
<tr>
<th>Stream Name</th>
<th>Reference Name</th>
<th>Watershed Area (km²)</th>
<th>ISC area* (%)</th>
<th>Developed (%)</th>
<th>Agriculture (%)</th>
<th>Forest (%)</th>
<th>Wetlands (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dube Brook</td>
<td>FOR</td>
<td>3.3</td>
<td>4.8</td>
<td>7.9</td>
<td>15.4</td>
<td>59.4</td>
<td>17.3</td>
</tr>
<tr>
<td>Chesley Brook</td>
<td>MIX</td>
<td>4.0</td>
<td>6.2</td>
<td>12.9</td>
<td>24.5</td>
<td>48.9</td>
<td>13.8</td>
</tr>
<tr>
<td>College Brook</td>
<td>URB</td>
<td>2.3</td>
<td>28.4</td>
<td>68.7</td>
<td>9.8</td>
<td>20.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Oyster River Road</td>
<td>MAIN</td>
<td>45.0</td>
<td>2.2</td>
<td>12</td>
<td>11</td>
<td>63</td>
<td>13</td>
</tr>
</tbody>
</table>

*Impervious surface cover (ISC) are surfaces that prevent water infiltration into the ground and promote runoff into the streams. ISC is part of the “developed” land use category.
Table 2: Physical and chemical properties of the Oyster River Watershed streams.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Mean Discharge (m^3 sec^{-1})</th>
<th>Mean Width (m)</th>
<th>Mean Depth (m)</th>
<th>Mean Water Temp (°C)</th>
<th>Mean NH₄⁺ (µg N L⁻¹)</th>
<th>Mean NO₃⁻ (mg N L⁻¹)</th>
<th>Mean Cl⁻ (mg Cl L⁻¹)</th>
<th>Mean DON (mg N L⁻¹)</th>
<th>Mean PO₄³⁻ (µg P L⁻¹)</th>
<th>Mean NPOC (mg C L⁻¹)</th>
<th>Mean Canopy Cover (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>0.039</td>
<td>1.7</td>
<td>0.14</td>
<td>10.9</td>
<td>21.1</td>
<td>0.22</td>
<td>64.5</td>
<td>0.29</td>
<td>16.5</td>
<td>6.2</td>
<td>50</td>
</tr>
<tr>
<td>MIX</td>
<td>0.039</td>
<td>2.5</td>
<td>0.25</td>
<td>10.5</td>
<td>11.7</td>
<td>1.08</td>
<td>36.3</td>
<td>0.28</td>
<td>8.1</td>
<td>2.8</td>
<td>93</td>
</tr>
<tr>
<td>URB</td>
<td>0.024</td>
<td>2.0</td>
<td>0.21</td>
<td>12.5</td>
<td>38.1</td>
<td>0.85</td>
<td>333.1</td>
<td>0.7</td>
<td>26.3</td>
<td>4.2</td>
<td>88</td>
</tr>
<tr>
<td>MAIN</td>
<td>0.342</td>
<td>8.8</td>
<td>0.21</td>
<td>12.1</td>
<td>20.6</td>
<td>0.25</td>
<td>55.1</td>
<td>0.31</td>
<td>11.5</td>
<td>5.7</td>
<td>96</td>
</tr>
</tbody>
</table>

Measurements are from June 2017 to January 2018. Mean discharge, width, depth, and canopy cover were calculated during multiple stream characterization events while nutrient data was collected for monthly and diel sampling regimes.
Table 3: Average Daily Metabolism Estimates (g O₂ m⁻² day⁻¹)

<table>
<thead>
<tr>
<th>Stream</th>
<th>GPP</th>
<th>ER</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>0.08 (0.006)</td>
<td>2.1 (0.01)</td>
</tr>
<tr>
<td>MIX</td>
<td>0.04 (0.005)</td>
<td>2.3 (0.07)</td>
</tr>
<tr>
<td>URB</td>
<td>0.32 (0.02)</td>
<td>7.6 (0.20)</td>
</tr>
<tr>
<td>MAIN</td>
<td>0.06 (0.007)</td>
<td>0.71 (0.06)</td>
</tr>
</tbody>
</table>

Measurements are from June 2017 to January 2018. Standard error (the standard deviation divided by the square root of the sample size) is given in parenthesis.
Table 4: Average Change in Metabolism Post Storm (g O₂ m⁻² day⁻¹)

<table>
<thead>
<tr>
<th>Stream</th>
<th>GPP</th>
<th>ER</th>
<th># Storms</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>-0.03 (0.02)</td>
<td>0.31 (0.17)</td>
<td>14</td>
</tr>
<tr>
<td>MIX</td>
<td>-0.003 (0.008)</td>
<td>0.046 (0.17)</td>
<td>11</td>
</tr>
<tr>
<td>URB</td>
<td>-0.11 (0.04)</td>
<td>-1.6 (0.41)</td>
<td>28</td>
</tr>
<tr>
<td>MAIN</td>
<td>0.10 (0.03)</td>
<td>1.1 (0.31)</td>
<td>12</td>
</tr>
</tbody>
</table>

Measurements are from June 2017 to January 2018. Standard error (the standard deviation divided by the square root of the sample size) is given in parenthesis.
Table 5: Average Change in Metabolism Post Storm (%)

<table>
<thead>
<tr>
<th>Stream</th>
<th>GPP</th>
<th>ER</th>
<th># Storms</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>-38%</td>
<td>15%</td>
<td>14</td>
</tr>
<tr>
<td>MIX</td>
<td>-7.5%</td>
<td>2%</td>
<td>11</td>
</tr>
<tr>
<td>URB</td>
<td>-34%</td>
<td>-21%</td>
<td>28</td>
</tr>
<tr>
<td>MAIN</td>
<td>67%</td>
<td>55%</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 6: Absolute Change in GPP Post Storm (g O$_2$ m$^{-2}$ day$^{-1}$)

<table>
<thead>
<tr>
<th>Stream</th>
<th>MAX</th>
<th>MIN</th>
<th># Storms</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>0.15 (0.02)</td>
<td>0.004 (0.02)</td>
<td>14</td>
</tr>
<tr>
<td>MIX</td>
<td>0.05 (0.008)</td>
<td>0.01 (0.008)</td>
<td>11</td>
</tr>
<tr>
<td>URB</td>
<td>0.17 (0.04)</td>
<td>0.05 (0.04)</td>
<td>28</td>
</tr>
<tr>
<td>MAIN</td>
<td>0.31 (0.03)</td>
<td>0.002 (0.03)</td>
<td>12</td>
</tr>
</tbody>
</table>

Measurements are from June 2017 to January 2018. Standard error (the standard deviation divided by the square root of the sample size) is given in parenthesis. GPP for the FOR, MIX, and URB decreased overall, while GPP for the MAIN increased.
Table 7: Absolute Change in ER Post Storm (g O₂ m⁻² day⁻¹)

<table>
<thead>
<tr>
<th>Stream</th>
<th>MAX</th>
<th>MIN</th>
<th># Storms</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>2.38 (0.17)</td>
<td>0.01 (0.17)</td>
<td>14</td>
</tr>
<tr>
<td>MIX</td>
<td>0.84 (0.17)</td>
<td>0.04 (0.17)</td>
<td>11</td>
</tr>
<tr>
<td>URB</td>
<td>5.93 (0.41)</td>
<td>0.04 (0.41)</td>
<td>28</td>
</tr>
<tr>
<td>MAIN</td>
<td>3.01 (0.31)</td>
<td>0.13 (0.31)</td>
<td>12</td>
</tr>
</tbody>
</table>

Measurements are from June 2017 to January 2018. Standard error (the standard deviation divided by the square root of the sample size) is given in parenthesis. ER for the FOR, MIX, and MAIN increased overall, while ER for the URB decreased.
Appendix
Table A1: SUNA Deployment dates and average nitrate during the deployment in headwater streams.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Dates Deployed</th>
<th>Duration (days)</th>
<th>Average Nitrate (mg N L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>2017-09-11 to 2017-09-12</td>
<td>1</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>and 2017-10-17 to 2017-11-16</td>
<td>31</td>
<td>0.28</td>
</tr>
<tr>
<td>MIX</td>
<td>2017-11-16 to 2017-12-19</td>
<td>34</td>
<td>0.96</td>
</tr>
<tr>
<td>MAIN</td>
<td>2017-09-29 to 2017-10-17</td>
<td>19</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Table A2: Diel Variability in NO\textsubscript{3} (mg N L\textsuperscript{-1}) in Oyster River Streams

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>0.07</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>MIX</td>
<td>0.09</td>
<td>0.09</td>
<td>0.07</td>
</tr>
<tr>
<td>URB</td>
<td>0.16</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>MAIN</td>
<td>0.04</td>
<td>0.03</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Diel Variability is calculated as maximum minus minimum concentration of NO\textsubscript{3} (mg N L\textsuperscript{-1}) analyzed in each grab sample.
Table A3: Diel Variability in DO (%) in Oyster River Streams.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>19.7</td>
<td>20.6</td>
<td>22.2</td>
</tr>
<tr>
<td>MIX</td>
<td>10.3</td>
<td>6.4</td>
<td>6.7</td>
</tr>
<tr>
<td>URB</td>
<td>8.6</td>
<td>6.3</td>
<td>7.0</td>
</tr>
<tr>
<td>MAIN</td>
<td>5.7</td>
<td>6.9</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Diel Variability is calculated as maximum minus minimum concentration of DO (%) recorded with a YSI ProDO handheld water quality meter in each grab sample.
Table A4: Diel Variability in N₂:Ar ratios in Oyster River Streams.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>0.05</td>
<td>0.57</td>
<td>0.21</td>
</tr>
<tr>
<td>MIX</td>
<td>0.07</td>
<td>0.47</td>
<td>0.26</td>
</tr>
<tr>
<td>URB</td>
<td>0.03</td>
<td>0.34</td>
<td>0.56</td>
</tr>
<tr>
<td>MAIN</td>
<td>0.26</td>
<td>1.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Diel Variability is calculated as maximum minus minimum N₂:Ar ratio as analyzed on a MIMS.
Table A5: Average Disequilibrium of N$_2$:Ar ratios in Oyster River Watershed Streams.

<table>
<thead>
<tr>
<th>Stream</th>
<th>DIEL 1</th>
<th>DIEL 2</th>
<th>DIEL 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>-0.2</td>
<td>-0.14</td>
<td>0.12</td>
</tr>
<tr>
<td>MIX</td>
<td>0.006</td>
<td>0.2</td>
<td>0.12</td>
</tr>
<tr>
<td>URB</td>
<td>-0.16</td>
<td>0.30</td>
<td>0.12</td>
</tr>
<tr>
<td>MAIN</td>
<td>-0.34</td>
<td>-0.04</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

Average daily disequilibrium of N$_2$:Ar ratios in the FOR, MIX, URB, and MAIN over the three separate diel sampling days.
Table A6: Average Daily and Nightly N$_2$:Ar disequilibrium ratios in Oyster River Watershed Streams for 1st Diel sampling round.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Max Day</th>
<th>Min Day</th>
<th>Max Night</th>
<th>Min Night</th>
<th>Change Day</th>
<th>Change Night</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>-0.06</td>
<td>-0.35</td>
<td>-0.1</td>
<td>-0.21</td>
<td>0.29</td>
<td>0.11</td>
</tr>
<tr>
<td>MIX</td>
<td>0.08</td>
<td>-0.11</td>
<td>0.06</td>
<td>-0.007</td>
<td>0.19</td>
<td>0.007</td>
</tr>
<tr>
<td>URB</td>
<td>-0.09</td>
<td>-0.2</td>
<td>-0.1</td>
<td>-0.2</td>
<td>0.11</td>
<td>0.1</td>
</tr>
<tr>
<td>MAIN</td>
<td>-0.27</td>
<td>-0.51</td>
<td>-0.33</td>
<td>-0.35</td>
<td>0.24</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Diel Variability is calculated as maximum minus minimum N$_2$:Ar ratio as analyzed on a MIMS. Samples were collected during the first Diel sampling round between 6/26/2017 and 6/27/2017. Max day is the average maximum disequilibrium value from all N$_2$:Ar samples for that stream during that particular diel sampling day. It was then compared to minimum for the day, and a maximum and minimum for the night to look at all the total change in N$_2$:Ar day vs night.
Table A7: Average Daily and Nightly N₂:Ar disequilibrium ratios in Oyster River Watershed Streams for 2nd Diel sampling round.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Max Day</th>
<th>Min Day</th>
<th>Max Night</th>
<th>Min Night</th>
<th>Change Day</th>
<th>Change Night</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>0.27</td>
<td>-0.45</td>
<td>0.05</td>
<td>-0.25</td>
<td>0.72</td>
<td>0.3</td>
</tr>
<tr>
<td>MIX</td>
<td>0.41</td>
<td>0.15</td>
<td>0.57</td>
<td>0.17</td>
<td>0.26</td>
<td>0.4</td>
</tr>
<tr>
<td>URB</td>
<td>0.55</td>
<td>0.07</td>
<td>0.38</td>
<td>0.27</td>
<td>0.43</td>
<td>0.11</td>
</tr>
<tr>
<td>MAIN</td>
<td>0.1</td>
<td>-1.4</td>
<td>0.21</td>
<td>0.0003</td>
<td>1.5</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Diel Variability is calculated as maximum minus minimum N₂:Ar ratio as analyzed on a MIMS. Samples were collected during the first Diel sampling round between 8/2/2017 and 8/3/2017. Max day is the average maximum disequilibrium value from all N₂:Ar samples for that stream during that particular diel sampling day. It was then compared to minimum for the day, and a maximum and minimum for the night to look at all the total change in N₂:Ar day vs night.
### Table A8: Average Daily and Nightly N₂:Ar disequilibrium ratios in Oyster River Watershed Streams for 3rd Diel sampling round.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Max Day</th>
<th>Min Day</th>
<th>Max Night</th>
<th>Min Night</th>
<th>Change Day</th>
<th>Change Night</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR</td>
<td>0.26</td>
<td>-0.1</td>
<td>0.3</td>
<td>0.02</td>
<td>0.36</td>
<td>0.28</td>
</tr>
<tr>
<td>MIX</td>
<td>0.26</td>
<td>-0.02</td>
<td>0.33</td>
<td>0.25</td>
<td>0.28</td>
<td>0.08</td>
</tr>
<tr>
<td>URB</td>
<td>0.19</td>
<td>-0.03</td>
<td>0.48</td>
<td>0.13</td>
<td>0.22</td>
<td>0.35</td>
</tr>
<tr>
<td>MAIN</td>
<td>1.2</td>
<td>0.1</td>
<td>-0.02</td>
<td>-0.1</td>
<td>1.1</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Diel Variability is calculated as maximum minus minimum N₂:Ar ratio as analyzed on a MIMS. Samples were collected during the first Diel sampling round between 8/10/2017 and 8/11/2017. Max day is the average maximum disequilibrium value from all N₂:Ar samples for that stream during that particular diel sampling day. It was then compared to minimum for the day, and a maximum and minimum for the night to look at all the total change in N₂:Ar day vs night.
Figure A1: Figure from Dave Cedarholms’ PowerPoint showing the location of the springs under the MIX stream (Chesley Brook). Being a spring fed system leads to more stable flows at the MIX stream.
Figure A2: Power rating curve of Q vs stage height for the FOR stream. This equation was used to calculate instantaneous Q from logger stage heights throughout the entire study period.

\[ y = 12.621x^{0.0743} \]

\[ R^2 = 0.9747 \]
Figure A3: Power rating curve of Q vs stage height for the MIX stream. This equation was used to calculate instantaneous Q from logger stage heights throughout the entire study period.

\[ y = 6.6801x^{3.7344} \]

\[ R^2 = 0.9886 \]
Figure A4: Power rating curve of Q vs stage height for the URB stream. This equation was used to calculate instantaneous Q from logger stage heights throughout the entire study period.

\[ y = 3.1126x^{3.9419} \]

\[ R^2 = 0.9889 \]
Figure A5: Timeseries of 15-minute DO concentration (A), Discharge (B), water temperature (C), and PAR (D) for MIX to show streamMetabolizer model parameters.
Figure A6: Timeseries of 15-minute DO concentration (A), Discharge (B), water temperature (C), and PAR (D) for FOR to show streamMetabolizer model parameters.
Figure A7: Timeseries of 15-minute DO concentration (A), Discharge (B), water temperature (C), and PAR (D) for MAIN to show streamMetabolizer model parameters.
Figure A8: Timeseries of daily GPP(A), ER(B), and K_{600}(C) metabolism model estimate outputs from streamMetabolizer for the MIX stream.
Figure A9: Timeseries of daily GPP(A), ER(B), and $K_{600}(C)$ metabolism model estimate outputs from streamMetabolizer for the FOR stream.
Figure A10: Timeseries of daily GPP(A), ER(B), and K_{600}(C) metabolism model estimate outputs from streamMetabolizer for the MAIN stream.
Figure A11: Boxplots of mean PAR. Boxes show first and third quartiles, horizontal lines in the box are median values, while individual points are outliers. Letters above each boxplot show statistically significant groupings.
Figure A12: Snapshot of Oyster River high frequency (15-minute) discharge data from June 29th, 2017 to July 17th, 2017 showing storms (black arrows) for each stream, especially the flashiness of urbanized storms, which can be seen at the URB stream without any response at the other streams (red arrows).
Figure A13: Time series of daily P:R ratio for the MIX (orange), URB (red), FOR (green), and MAIN (purple) showing the two days (July 29th, 2017 and January 6th, 2018) where the P:R ratio at MAIN was >1 and net autotrophic.
Figure A14: TSS for thesis streams 2016-2018.
Figure A15: Correlations between K600 and ER for the URB (A), MIX(B), FOR(C), and MAIN(D). Low correlations suggest the K600 estimates are more accurate and not correlated to ER.
Figure A16: Correlations of storm size (maximum Q) vs change in GPP post storm for the URB (A), MIX(B), FOR(C), and MAIN(D). No significant relationships at any stream showing that higher Q’s statistically do not lead to higher changes in GPP.
Figure A17: TSS for all other streams collected 2016-2018. Days with multiple points during the summer of 2016 were storm samples.
Figure A18: Oyster River monthly grab sample of Chloride (A), Fluoride (B), and Bromide (C).
Figure A19: Oyster River monthly grab sample of Nitrate (A), Phosphate (B), and Sulfate (C).
Figure A20: Oyster River monthly grab sample of Ammonium (A), Non-purgeable organic carbon (B), Total dissolved nitrogen (C), and dissolved organic nitrogen (D).
Figure A21: Timeseries of nitrate at the MIX(A), FOR(B), and MAIN(C) streams from September 2017 to December 2017.
Figure A22: $\text{N}_2: \text{Ar}$ disequilibrium values for Diel 1. Samples were collected every two hours for 24 hours straight between June 26th and June 27th, 2017.
Figure A23: N₂:Ar disequilibrium values for Diel 2. Samples were collected every two hours for 24 hours straight between August 2nd and August 3rd, 2017.
Figure A24: N$_2$:Ar disequilibrium values for Diel 3. Samples were collected every two hours for 24 hours straight between August 10th and August 11th, 2017.
Figure A25: DO(%) handheld measurements for Diel 1. Samples were collected every two hours for 24 hours straight between June 26th and June 27th, 2017.
Figure A26: DO(%) handheld measurements for Diel 2. Samples were collected every two hours for 24 hours straight between August 2nd and August 3rd, 2017.
Figure A27: DO(%) handheld measurements for diel 3. Samples were collected every two hours for 24 hours straight between August 10th and August 11th, 2017.
Figure A28: Nitrate (mg N L$^{-1}$) grab sample measurements for Diel 1. Samples were collected every two hours for 24 hours straight between June 26th and June 27th, 2017.
Figure A29: Nitrate (mg N L\(^{-1}\)) grab sample measurements for Diel 2. Samples were collected every two hours for 24 hours straight between August 2nd and August 3rd, 2017.
Figure A30: Nitrate (mg N L\(^{-1}\)) grab sample measurements for Diel 3. Samples were collected every two hours for 24 hours straight between August 10th and August 11th, 2017.
Figure A31: Timeseries of 15-minute DO% for the URB (A), MIX (B), FOR (C), and MAIN (D).
Figure A32: Timeseries of 15-minute Specific Conductivity (μS cm⁻¹) for the URB (red), MIX (orange), FOR (green), and MAIN (purple).