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# Estimating Components of Stream Metabolism Using the Free Water Dissolved Oxygen Method

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Estimating Components of Stream Metabolism Using the Free Water Dissolved Oxygen Method

Jay Raymond Zuidema Jr.

A Thesis Submitted to the Graduate Faculty of

# GRAND VALLEY STATE UNIVERSITY

In

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#### **Abstract**

Stream ecosystem metabolism is commonly measured in stream ecology studies in order to understand the functioning of the stream ecosystem and as an indicator of stream health. One common method for gathering the time series data required to estimate stream metabolism is the free water dissolved oxygen method, which involves measuring dissolved oxygen in freely moving water. This is accomplished by taking measurements at a single location (one-station monitoring method) or at two locations (two-station monitoring method). In conjunction with these data, a process-based model of dissolved oxygen dynamics is used to estimate gross primary production, respiration, and net production. There are two commonly used estimation methods: accounting and prediction. With the accounting method, estimates are derived directly from the time-series data. With the prediction method, estimates are derived statistically by fitting predicted dissolved oxygen concentrations to measured concentrations. In this study, we compared combinations of the one-station and two-station monitoring methods and the accounting and prediction estimation methods using data from Little Black Creek in Muskegon, MI gathered over two days each in July and December, 2017 using four monitoring stations within an 800 m reach. The time-series data permitted comparison of metabolism estimates for four individual stations (one-station monitoring) and six sub-reaches (two-station monitoring). We found differences in metabolic estimates between seasons, methods, and sub-reaches. One of the more significant results was the effect of spatial heterogeneity in physical and biological properties of the stream on metabolic estimates. We found a similar range in metabolic estimates for different stations and sub-reaches within the 800 m study reach as was found in published

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## **Key to Symbols and Abbreviations**

- A autotrophic respiration
- $a(t)$  rate of atmospheric exchange
- $C(t)$  modeled dissolved oxygen concentration at time t
- $c(t)$  measured dissolved oxygen concentration
- $c_e(t)$  air-water equilibrium concentration
- D-NAE daytime net atmospheric exchange
- DO dissolved oxygen
- DR daytime respiration
- $\varepsilon_{\pi}$ ,  $\varepsilon_{\rho}$ , and  $\varepsilon_{\alpha}$  temperature adjustment parameters
- $f(t)$  temperature adjust function
- *γ*20 gas exchange velocity
- GPP gross primary production
- *H* height of the water column
- Halloch heterotrophic respiration of allochthonously produced carbon
- Hautoch heterotrophic respiration of autochthonously produced carbon
- $I(t)$  measured irradiance at time t
- *K* flow-dependent constant
- *L* length between monitoring stations
- NAE 24 hr net atmospheric exchange
- N-NAE nighttime net atmospheric exchange
- NP net production
- NR nighttime respirations
- $\pi(t)$  gross primary productivity
- P/R ratio of gross primary production to respiration
- $R 24$  hr respiration
- $\rho(t)$  rate of respiration
- *s –* slope of the stream bed
- SRP-P soluble reactive phosphorus
- $\theta(t)$  measured water temperature at time t
- TP-P total phosphorus
- $\bar{u}$  average current velocity

# **Chapter 1: Introduction**

# **Introduction**

The metabolism of stream communities has historically been studied in the context of stream ecosystem ecology by looking at the balance between primary production and respiration to infer how these communities are functioning. More recently, stream metabolism estimates have also been used as a functional indicator of stream health that can be used to assess potential human impacts on streams at the reach and catchment scales.

Stream metabolism can be separated into three main components: gross primary production, respiration, and net production. Gross primary production (GPP) is the amount of biomass, expressed as carbon, produced by photoautotrophic organisms over a given period of time, mostly through oxygenic photosynthesis and subsequent biosynthesis, which involves the uptake of  $CO_2$  (as well as H<sub>2</sub>O, nitrogen, phosphorus, sulfur, etc.) and the release of  $O_2$ . Primary production can be represented via the following stoichiometric formula from Stumm & Morgan (1996):

$$
106 CO2 + 16 NO3- + HPO42- + 122 H2O + 18 H+ \rightleftarrows C106H263O110N16P + 138 O2
$$

with produced biomass being the first term on the right side of the formula. Conversely, community respiration (R) is the amount of biomass, expressed as carbon, broken down by aerobic organisms, involving the uptake of  $O_2$  and the release  $CO_{2}$  over the same period of time, and is often assumed to correspond to the left arrow in the above reaction formula, despite the fact that the community doing the respiring is composed of more than just primary producers and that different portions of biomass (carbohydrates, lipids, proteins) are metabolized at different rates. Net production (NP) is the net change in biomass over the same period of time and is calculated as the difference between GPP and R.

One method for quantifying GPP, R, and NP, first used by Sargent and Austin (1949, 1954) in a study on atoll productivity, then adapted and expanded by Odum (1956) in order to study productivity in streams, is termed the free water dissolved oxygen method, which involves obtaining time-series of dissolved oxygen (DO) concentrations in freely-moving water. There are two common methods of monitoring in the field: the one-station method and the two-station (or upstream-downstream) method. The one-station method involves monitoring DO at one point in the stream in order to determine how DO concentrations are changing at that point. Measured changes in DO concentrations are assumed to be the same throughout the vaguely defined upstream region being integrated by the single station. The two-station method involves monitoring DO at both an upstream and downstream location and calculating the change in concentration that occurs in water as it moves between the stations. This change is associated with the portion of the stream between the two stations.

Given that GPP, R, and NP are defined in terms of carbon, it might seem more natural to estimate these quantities by monitoring the concentration of dissolved  $CO_2$  instead of  $O_2$ . However, DO concentrations are preferred in studies of stream metabolism for multiple reasons: the free-water DO method was adapted from sanitary engineering studies specifically focused on DO dynamics, as discussed in Chapter 2; DO is easier and cheaper to measure using automatic recording sensors;  $CO<sub>2</sub>$  is involved in the bicarbonate buffering system, which complicates

interpretation of direct measurements; and the use of carbon fixation as a measure of gross primary production is complicated if photorespiration rates are high (Falkowski & Raven, 2007).

Stoichiometric ratios of  $O_2$  consumed and  $CO_2$  produced via respiration and  $CO_2$  consumed and  $O_2$  produced via photosynthesis can be used to convert  $O_2$  based metabolism estimates to  $CO<sub>2</sub>$  based estimates. These photosynthetic and respiratory quotients are based on assumptions made about, for example, different nitrogen sources in primary production and the form of organic carbon available for respiration (e.g., the above stoichiometric formula assumes nitrate is the nitrogen source, photoautotroph and heterotroph biomass has the same composition, and all biomass components are metabolized at the same rate). There are therefore different quotients that can be used. For example, Bott (2006) give a photosynthetic quotient of 1.2 and a respiratory quotient of 0.85, and Falkowski and Raven (2007) give an overall ratio of  $O_2$  released to  $CO_2$ assimilated of 1.05 based on a photosynthetic quotient of 1.0 and a respiratory quotient of 1.15. As a result of the different assumptions that can be made, there is uncertainty involved in this conversion.

To estimate GPP, R, and NP using DO concentration measurements, one must use a process-based model of DO dynamics (see Chapter 3). Along with primary production and respiration, this model must take into account DO exchange across the air-water interface at the stream surface. Most studies of stream metabolism have estimated GPP, R, and NP using a basic accounting procedure, formalized by Odum (1956), in which estimates are extracted directly from the measured time series data using a simple model of DO dynamics sans statistical methods. This procedure requires unnecessary and dubious assumptions regarding daytime

respiration and provides no way to assess the accuracy of the model of DO dynamics (McNair et al. 2013, 2015).

Another estimation approach has been developed for use in streams and lakes in a series of papers by Hornberger and Kelly (1975), Van de Bogert et al. (2007), Hanson et al. (2008), and McNair et al. (2013, 2015). It uses a model for which parametric forms of the production and respiration terms can be supplied, generating a predicted DO time series. The parameters can then be adjusted using appropriate statistical methods to match the predicted DO time series to the measured DO time series as accurately as possible. This comparison of observed and predicted DO time series allows assessment of the adequacy of the assumed model of DO dynamics, which the accounting approach does not permit. Also, unlike the accounting approach, this prediction-based approach allows separate estimation of daytime and nighttime respiration values, through the use of separate equations for each time period.

## **Objectives/Hypotheses**

Assessing the performance of methods for estimating metabolism components is complicated by the fact that in real streams, we do not know the true rates of metabolism. Our approach was therefore to implement several of the commonly used variants of the free water dissolved oxygen method at the same study site and compare the resulting estimates of 24 h GPP, R, and NP. More specifically, our objectives were to (1) assess the conceptual strengths and weaknesses of commonly used variants of the free water dissolved oxygen method, (2) implement versions of the accounting and prediction-based estimation approaches using both the one-station and two-station monitoring methods, (3) compare the resulting estimates of 24 h

GPP, R, and NP, (4) compare the results obtained in different sections of a spatially heterogeneous study site, (5) make these comparisons during the summer leaf-on period and the late fall leaf-off period, and (6) compare estimates obtained in the different stream reaches from this study with estimates published in the literature, most of which only include monitoring at a single station or one two-station reach within each stream studied.

The estimates presented in this study are oxygen-based, as opposed to carbon-based, with units of  $g O<sub>2</sub>/m<sup>2</sup>$ . This is for three reasons: the uncertainty in conversion between oxygen-based and carbon-based estimates mentioned above, which this study was not concerned with exploring; comparison of the methods, the main objective of this study, can be done equally well using oxygen or carbon-based estimates; and the estimates reported in the literature to which the estimates in this study will be compared are in oxygen-based units.

The two main comparisons that will be made, between the one- and two-station monitoring methods and between the accounting and prediction-based estimation approaches, lend themselves to a couple of qualitative hypotheses. The two-station method is likely to provide a better picture of metabolism than the one-station method in the stream reach, as it allows determination of DO changes within sections of water as they move from one station to the next and attributes those changes to the known region between the stations. The one-station method, on the other hand, determines changes in DO concentration at a single point between successive measurements and assumes those changes to be equal throughout a somewhat vaguely defined upstream region. The prediction-based estimation approach will likely provide better estimates because it doesn't require an assumed relationship between daytime and nighttime respiration as

required by the accounting approach. Also, as a result of the statistical methods used, model adequacy can be assessed by comparing predicted DO values to measured values. For these reasons, the two-station monitoring method combined with the prediction-based estimation approach will likely give the best estimates of metabolism components. As noted above, however, accuracy cannot be assessed, because the true values of GPP, R, and NP will not be known.

#### **Significance**

As mentioned above, and discussed in Chapter 2, stream metabolism estimates are used in various ways by stream ecologists to infer the function of stream ecosystems and assess potential impacts of human modifications of the catchment and riparian zone on this function. These are the main applications of stream metabolism estimates in the literature and the main basis for judging the significance of improved methods of estimation. Additionally, since the pioneering study by Cole et al. (2007) and the follow-up study by Tranvik et al. (2009) showed that inland waters, including streams and rivers, actively participate in the global cycling of carbon, there has been some interest in the role that stream ecosystems play in this cycle, mainly via the uptake and release of carbon dioxide due to metabolism (the editorial by Biddanda (2017) provides an overview of these ideas and additional references).

# **Chapter 2: Literature Review**

The free water dissolved oxygen method has been in use in streams and other aquatic systems since at least the mid-20<sup>th</sup> century. In early studies, Winkler titrations were used to obtain DO time series (Sargent & Austin, 1949, 1954; Odum, 1956). The use of in situ DO probes with automated data logging in streams began with Kelly et al. (1974). Aside from these free water methods, various closed system methods have also been used in stream metabolism studies, including light dark bottles and various chambers, which have had closed and open bottoms, have been closed and flow-through systems, and have been situated within the stream and on the stream bank (Bott et al., 1978; Naiman, 1983; Newbold et al., 1997; Uzarski et al., 2004). Additionally, there have been studies of stream metabolism in artificial channels in a laboratory setting (McIntire et al, 1964; McIntire & Phinney, 1965). Other methods used to generate the requisite gas concentration time series data include oxygen-18 isotope methods (Tobias et al., 2007; Hotchkiss & Hall, 2014), the use of pH and alkalinity measurements to estimate  $CO<sub>2</sub>$ concentrations (Beyers & Odum, 1959), and eddy covariance techniques (Koopmans & Berg, 2015).

The use of mathematical models representing the processes that control DO dynamics in conjunction with DO concentration measurements began in the field of sanitary engineering. Workers in this field were faced with the problem of highly polluted rivers, e.g. the Delaware River (Albert, 1998), which during the first half of the  $20<sup>th</sup>$  century had long reaches with extremely low DO concentrations (Fig 1), due mainly to untreated sewage and industrial effluent. As a result, the goal of these sanitary engineers was to understand DO dynamics in these systems

in order to determine safe effluent levels and the 'natural purification capacity' of the water bodies (Streeter & Phelps, 1925).

One of the first significant models of DO dynamics was developed by Streeter and Phelps in their 1925 publication detailing their studies on the Ohio River, which was also a highly polluted system. Streeter and Phelps noticed a pattern in DO concentrations downstream from effluent releases in which DO would decrease substantially immediately downstream and subsequently increase farther downstream. In an effort to model these dynamics, they considered the processes of respiration of the organic material within the effluent and reaeration, the movement of oxygen into the stream from the atmosphere – termed such specifically for these early engineering studies of highly polluted rivers because of the essentially one way movement of oxygen across the air-water interface, yet still commonly used today to refer to two-way exchange in unpolluted streams. Because of the focus of sanitary engineering studies on oxygen, there was use of the concept of biochemical oxygen demand, which is defined as the amount of oxygen that would be necessary to allow the oxidation of the amount of organic matter present. This is essentially a proxy measure of the amount of organic matter itself. The idea of the Streeter and Phelps model is that respiration is proportional to the organic matter concentration, and reaeration is proportional to the DO deficit, i.e. the difference between the theoretical oxygen concentration that would be in equilibrium with the atmosphere and the actual DO concentration in the water body. Downstream of an effluent discharge, organic matter is aerobically metabolized, thereby decreasing both the organic matter and DO concentrations as water moves downstream. Because of this decrease in DO concentration, reaeration increases, at some point

downstream overtaking respiration as the dominant process. The interplay of these two processes produces the pattern which Streeter and Phelps termed the oxygen sag curve.

These early engineering studies mostly ignored the photosynthetic oxygen production of organisms within these systems, because it was assumed that respiration of the high amount of organic matter within effluents and subsequent reaeration were the dominant processes. However, there were early studies which showed that photosynthetic oxygen production could be a significant factor (Schroepfer & Childs, 1931; Calvert, 1933; Purdy, 1935), so these engineers weren't ignorant of metabolic realities; they merely used the simplest models that could adequately describe the DO dynamics they were dealing with.

Along with the studies on polluted systems, the engineering literature later developed a focus on technical problems related to the use of DO concentration measurements. One significant topic addressed in many engineering studies was reaeration and various methods for estimating it. There were many attempts to derive equations that could be used to calculate reaeration based on easily measured physical properties of the system under study (e.g., Streeter & Phelps, 1925; O'Connor & Dobbins, 1956; Dobbins, 1964; Tsivoglou & Neal, 1976), some of which had coefficients with values estimated via regression analysis of measured reaeration rates (Churchill et al., 1962; Owens et al., 1964). There were also attempts to estimate reaeration via measurement of the exchange of various gases across the stream surface. One such method, the disturbed equilibrium-technique, involved measuring DO concentrations at two points in a stream before and after depressing the DO concentration with sodium sulfite and a cobalt catalyst and the subsequent use of an equation to estimate reaeration from these measurements (Gameson

& Truesdale, 1959). Another class of methods, called tracer methods, use measured exchange rates of various gases and relationships between the exchange rates of those gases and oxygen to estimate reaeration. These gases include krypton-85 (Tsivoglou, 1967), ethylene and propane (Rathbun et al., 1975), methyl chloride (Wilcock 1984), and sulfur hexafluoride (Wanninkhof et al. 1990). There are also methods to estimate reaeration from the measured DO concentration time series (Odum, 1956; Hornberger & Kelly, 1975; Kosinski, 1984). There have been several publications comparing different methods – usually formula-based with tracer methods – which have given mixed results as to the best methods to use (Dobbins, 1964; Wilson & Macleod, 1974; Grant & Skavroneck, 1980; Parker & Gay, 1987; Genereux & Hemond, 1992; Melching, 1998; Mulholland et al. 2001).

Subsequent to early engineering studies dealing with highly polluted systems, the ideas underlying the free water dissolved oxygen method were picked up for use in ecological studies of flowing water. This started with the atoll studies of Sargent and Austin (1949, 1954), and continued with the subsequent formalization of the method by Odum (1956) and Odum and Hoskin (1958). As the goal of Odum's study was investigating primary production, the model he proposed represented DO dynamics via respiration, primary production, and atmospheric exchange (reaeration). Subsequent ecological studies used models similar to that presented by Odum, and focused mainly on deriving estimates of ecosystem metabolism in an effort to understand ecosystem dynamics and to explore various practical applications these estimates could have.

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Many studies have used metabolism estimates in an effort to determine the relative autotrophy or heterotrophy of a given stream based on the relative amounts of GPP and R (Odum, 1956; Minshall, 1978; Dodds & Cole, 2007). This often includes discussion of the P/R ratio, i.e. the ratio of gross primary production to community respiration, and what it can reveal about the relative impacts in a given stream of carbon produced within the system (autochthonous) and carbon from without the system (allochthonous) (e.g., Wright & Mills, 1967; Bott et al., 1978; Young & Huryn, 1997; Bunn et al., 1999; Bott et al., 2006). However, there have been discussions about the problems with interpretation of the P/R ratio and what it can reveal about any transition points between majority autochthonous and allochthonous carbon use (Rosenfeld & Mackay, 1987; Meyer, 1989), problems arising because community respiration can be expressed as  $A + H_{\text{autoch}} + H_{\text{alloch}}$ , where A is aerobic respiration by photosynthetic autotrophs and  $H_{\text{autoch}}$  and  $H_{\text{alloch}}$  are aerobic respiration by heterotrophs metabolizing autochthonous and allocthonous organic carbon, respectively. Given only the P/R ratio, it is difficult to parse the relative contributions of allochthonous and autochthonous carbon to community respiration. In a related vein, there have also been studies which used metabolism estimates to investigate various ecological theories, notably the River Continuum Concept of Vannote et al. (1980) (Naiman, 1983; Wiley et al., 1990; McTammany et al., 2003), focusing on whether the metabolic pattern of longitudinally changing P/R ratio described in that theory (with maximal P/R at intermediate stream orders) holds in various systems.

Metabolism estimates have been employed as functional indicators of stream health (Young et al., 2008) that complement the more commonly used structural indicators based on patterns of relative abundance and pollution tolerance or sensitivity within the algae, benthic macroinvertebrate, and fish assemblages. Specifically, estimates of metabolism have been used to assess the impacts of disturbance (Uehlinger & Naegeli, 1998; Uehlinger, 2000; Mulholland et al., 2005; Snyder & Minshall, 2005) and the effects of remediation efforts in streams (Bott et al., 2012; Roley et al., 2014). Parkhill and Gulliver (2002) used ecosystem metabolism estimates to investigate the impacts of inorganic sediment introduction via erosion on stream ecosystem function. The impacts of land use on streams have also been assessed (Young & Huryn, 1999; Bott et al., 2006; Bernot et al., 2010; Clapcott et al., 2016). There have been studies related to nutrients: the relationship between metabolism and nitrogen uptake (Hall & Tank, 2003; Webster et al., 2003) and phosphorus uptake (Stutter et al., 2010), and the use of productivity estimates in assessing eutrophication potential (Hornberger et al., 1977). The effects of differing light levels on primary production in streams has also been studied (Hill et al., 1995; Hill et al, 2001). This often involves the production of photosynthesis-irradiance curves, which relate organic carbon production via photosynthesis to light levels (Gulliver & Stefan, 1984; Boston & Hill, 1991; Parkhill & Gulliver, 1998).

There has been discussion within the ecological literature as to the impact of metabolism within the hyporheic zone on whole-system metabolism, with several studies showing that there is significant exchange between the hyporheic zone and the water column. This has included studies which compared whole-stream and chamber derived metabolic estimates in order to determine the relative impact of the hyporheic zone (Grimm & Fisher, 1984; Naegeli &

Uehlinger, 1997; Fellows et al., 2001). Uzarski et al. (2004) compared metabolism estimates using chambers with both closed and open bottoms.

Metabolism estimates are also used to compare different systems, often in an effort to determine differing factors which affect metabolism (Lamberti & Steinman, 1997). Bott et al. (2006) compared 10 different streams in New York State. Inter-biome comparisons have also been made (Minshall et al., 1983; Mulholland et al., 2001). Hall et al. (2016) measured metabolism in several larger rivers in the US, as opposed to the small streams usually studied.

There are several issues related to the free water dissolved oxygen method as it is commonly used. One such problem is that measurements are usually made only over a short period of time (typically one 24-h period), often only in one season. An early counterexample is the work of Kelly et al. (1974) and Hornberger & Kelly (1975), who used automated continuous monitoring of a reach of the Mechums River, Virginia, for a period of nearly two years. More recently, several studies have used continuous monitoring techniques, from 15 months up to 5 years (Roberts et al., 2007; Izagirre et al., 2008; Birkel et al., 2013; Roley et al., 2014). Another problem is that many natural stream reaches are spatially heterogeneous, which defies the assumption of homogeneity in the models used. There have been efforts recently to deal with the uncertainties brought about by spatial heterogeneity (Reichert et al., 2009; Demars et al., 2011; Hondzo et al., 2013). The inflow of groundwater into the reach under study is also a problem, as the DO concentration of any groundwater is likely not known. McCutchan et al. (2002) present a method to correct for groundwater inflow if it is significant in the reach (this method was

criticized by Hall  $&$  Tank (2005), but the arguments presented are incorrect; see McCutchan  $&$ Lewis (2006)).

The basic modeling approach, i.e. the accounting approach, formalized by Odum has been used in most studies of stream metabolism in the ecological literature. More recently, there have been ecological studies which have used prediction-based modeling approaches (Grace & Imberger, 2006; Holtgrieve et al., 2010; Hotchkiss & Hall, 2014; Roley et al., 2014). However, this approach was started in the engineering literature by Hornberger and Kelly (1975), who presented both one and two-station prediction-based models.

As a result of the widespread use of the free water dissolved oxygen method in streams, there have been several reviews of the ecological literature and the methods involved. Bott (2006), Grace and Imberger (2006), and Hall and Hotchkiss (2017) give reviews of methods for both acquiring and analyzing data, though Hall and Hotchkiss (2017) restrict attention to onestation monitoring. Tank et al. (2010) and Demars et al. (2015) present reviews of the ecological literature on stream metabolism, but neither of these reviews adequately cover the seminal contributions of the engineering literature.



Figure 1. Longitudinal patterns of dissolved oxygen concentration (mg/L) in the Delaware River near Philadelphia in 1946, 1958, and 1986. River mile is distance upstream from the mouth of the river. Source: Albert (1998).

# **Chapter 3: Methods**

### **Study Site**

This study was conducted on a portion of Little Black Creek (USGS GNIS ID 630565, latitude 43.1258333, longitude −86.2527778) in Muskegon County, MI. (Note: The provincial name of this stream, stated in the Michigan Geographic Framework, is Little Black Lake Drain. The official name in the national Geographic Names Information System, which is assigned by the U.S. Board of Geographic Names and is used in the National Hydrography Dataset and all other national spatial data, is Little Black Creek.) This stream flows from Little Black Lake to Lake Michigan, flowing through Oak Ridge Golf Course and Hoffmaster State Park en route (Figure 2).

The portion of the stream used was an 800 m reach within Oak Ridge Golf Club, which has alternating areas of open and closed canopy along its length. The land cover types of the area surrounding the study site are mostly developed land and forest (Figure 3). The soil of the surrounding area is made up mostly of various types of sand, with the stream channel within the study area being composed of Roscommon and Au Gres sands (Figure 4). For more detailed information regarding Little Black Lake see the publication by Steinman et al. (2011).

Separate instrument deployments were made in July and December 2017. In July, the closed canopy portions of the stream were shaded due to the presence of leaves, while the open canopy portions received abundant light (specific light levels discussed below). Consequently, the open canopy sections of the stream had abundant submersed macrophyte growth, and the closed canopy sections had none. The dominant macrophyte species was sago pondweed

(*Stuckenia pectinata*; synonym: *Potamogeton pectinatus*), which formed dense submersed beds in open reaches of the stream. Other abundant submersed macrophytes included curly-leaf pondweed (*Potamogeton crispus*) and Richardson's pondweed (*Potamogeton richardsonii*). In December, the trees were completely bare of leaves, and the macrophytes had senesced.

## **Time Series**

Time series measurements of DO concentration, temperature, and light intensity were taken at four stations within the stream reach for two consecutive 24 hr periods during both July 28-31 and December 1-4. The four stations will be referred to as stations 1, 2, 3, and 4. Station 1 was located approximately 60 m downstream from the outfall from Little Black Lake. Station 2 was 200 m downstream from station 1, station 3 was 300 m downstream from station 2, and station 4 was 300 m downstream from station 3 (Figure 5). Originally in July, 5 sondes were put into the stream, with sonde 5 being 300 m downstream of station 4, but the data were unusable, as the sonde malfunctioned. As a result, only the first four stations were analyzed in July, and in December sondes were placed only at the first four stations.

At each station, DO and temperature time series were recorded every 2 min in July and every 5 min in December using YSI 6600 recording sondes placed within the thalweg. The sondes were calibrated before deployment and were run side-by-side before and after deployment to check for any sensor drift. Light intensity was recorded using HOBO data logging pendants every 2 min in both July and December. The sondes were fixed to the stream bed via metal fence posts, and the HOBO pendants were attached to the top of these posts (Figure 6). Time series data were smoothed using the R function smooth.spline() with a smoothing

parameter of 0.50 for analyses in order to reduce random data scatter. Different degrees of smoothing were experimented with until this value was arrived at.

### **Stream Physical Properties**

The average width of the stream and height of the water column were measured across transects perpendicular to the direction of flow. On July 31, 2017, three transects were measured: one approximately 10 m upstream of station 1, another approximately 10 upstream of station 4, and the final approximately 100 upstream of station 4. On December 1, 2017, one transect was measured within 10 m of each station. Width was measured across the transect from the edge of the water on the left bank (facing downstream) to the edge on the right. The depth of the water column was measured every 0.5 m across the transect. The area of the transect was estimated by multiplying each depth measurement by 0.5 m (the distance between successive depth measurements) and summing the results.

Average current velocity, stream flow, and time of travel were estimated using two methods. The first method was based on current velocity measurements taken using a Marsh-McBirney Flo-Mate 2000 along the same transects mentioned in the previous paragraph. In July, current velocity measurements were made every 0.5 m along the transect. In December, the wetted width was greater, and measurements were made every 1 m along the transect, and half meter estimates were obtained by averaging the two surrounding measurements. Average current velocity and flow were estimated using the current velocity measurements taken along the transect and the calculated rectangular area via a method detailed by Gordon et al. (2004). Travel time for any given distance could then be estimated by dividing the distance by the average current velocity.

The second method used was a slug injection method, similar to that from Kilpatrick & Cobb (1985). Two YSI 6600 recording sondes were placed in the stream 50 m apart, and 5 kg of NaCl mixed with stream water was injected as a line source 25 m upstream of the upstream sonde. Time series salinity values were recorded at each sonde (the sonde has a conductivity probe and calculates salinity). Salinity increase due to the injected salt solution was estimated by subtracting background salinity from the recorded values. Time series of cumulative salinity were constructed, and stream flow  $(m^3 s^{-1})$  was estimated as the total mass of salt injected (5 kg) divided by the product of the asymptote of cumulative salinity (kg m<sup>-3</sup>) and the sampling interval (s). The time of travel from the injection location to each sonde was estimated by determining the 50th percentile on the curve of cumulative salt mass versus time, which represents the median travel time for water. Current velocity was estimated by dividing the distance from the release point to the station by the travel time to that station. Two slug injections were done on July 21, 2017, one near station 1 and the other near station 4. One slug injection was done on December 1, 2017 near station 1.

The average depth and width of the stream at the measured transects in July was 0.26 m and 3.5 m respectively (Table 1). The average flow was  $0.042 \text{ m}^3/\text{s}$ , and the average current velocity estimated with the current meter was 0.05 m/s while that estimated using the flow and rectangular area was 0.055 m/s. The averages at the December transects were 0.3 m depth, 4.7 m width,  $0.26$  m<sup>3</sup>/s flow,  $0.2$  m/s current meter velocity, and  $0.21$  m/s calculated velocity. The

average 75 m travel time in July was 22.9 min and in December was 5.9 min. The July estimates derived using the salt release data were  $0.029 \text{ m}^3/\text{s}$  average flow,  $0.085 \text{ m/s}$  median velocity, and 14.9 min 75 m travel time (Table 2). The December estimates were  $0.24 \text{ m}^3/\text{s}$  flow,  $0.20 \text{ m/s}$ median velocity, and 6.21min 75 m travel time.

Sediment samples were collected from the four monitoring stations on 18 July 2018. At each station, five 11-cm cores were taken and composited, using a clear plastic cylinder with an inside diameter of 5 cm. Samples were transported to the Annis Water Resources Institute, Muskegon, Michigan, where they were dried and analyzed for ash free dry mass. Percent organic matter was 0.65, 0.66, 0.27, and 0.53 at stations 1, 2, 3, and 4, respectively.

To characterize longitudinal variation in light availability, light levels (as PAR) were measured at 18 locations along the stream on 18 July 2018. The first location was 50 m upstream from Station 1; the remaining locations were at 50-m intervals downstream, ending at Station 4. PAR at each location was measured as a 15-s average using a LI-COR LI-250 light meter with an upward-pointing LI-COR LI-190SA quantum sensor attached to a tripod. Areas with macrophytes were also mapped at this time by recording the position downstream in m at which the macrophyte beds started and ended (Figure 7).

## **Nutrients**

In July, triplicate water samples were taken at one location in Little Black Lake just before the outfall into Little Black Creek, and at four more locations along the study reach in Little Black Creek. These samples were kept on ice until they were returned to the lab. Samples were

analyzed for  $SO_4$ ,  $NO_3$ ,  $NH_3$ ,  $SRP-P$  (soluble reactive phosphorus), and  $TP-P$  (total phosphorus) by the Environmental Chemistry laboratories at Annis Water Resources Institute.

Nutrient data from July are presented in Table 3. The mean  $\pm$  SE of the SO<sub>4</sub> concentrations were  $11 \pm 0$  mg/L in the lake and  $11.42 \pm 0.15$  mg/L in the stream. NO<sub>3</sub> concentrations were 0.08  $\pm$  0.01 mg/L in the lake and 0.09  $\pm$  0 mg/L in the stream. NH<sub>3</sub> concentrations were 0.03  $\pm$  0 mg/ L in the lake and  $0.15 \pm 0.1$  mg/L in the stream. SRP concentrations at all sampling locations were below the detection limit of 0.005 mg/L. TP concentrations were  $0.1 \pm 0$  mg/L in the lake and stream. These nutrient concentrations are comparable to those measured at the outfall of Little Black Lake in July 2007 reported in Steinman et al. (2011).

#### **Metabolism Estimates**

Estimating metabolism components requires a model of DO dynamics to use in conjunction with the time-series data. Which model is used depends on whether the one-station or two-station method is being used. The four stations in this study were analyzed separately using the one-station method and in all six possible upstream-downstream pairwise combinations using the two-station method. The equation that is the basis for the one-station method has the form

$$
\frac{dC}{dt} = \pi(t) - \rho(t) + \alpha(t),
$$
\n(1)

where *C*(*t*) is the concentration of DO at time *t* [mass per volume], *dC*/*dt* is the instantaneous rate of change in dissolved oxygen concentration,  $\pi(t)$  is gross primary productivity,  $\rho(t)$  is the rate of community respiration, and  $\alpha(t)$  is the rate of atmospheric exchange of oxygen across the water

surface (also known as the reaeration rate). The dimensions of  $\pi(t)$ ,  $\rho(t)$ , and  $\alpha(t)$  are mass per volume per time. The atmospheric exchange rate  $\alpha(t)$  has the form

$$
\alpha(t) = \gamma_{20} f(t) [c_e(t) - c(t)] / H \tag{2}
$$

where  $\gamma_{20}$  is the gas-transfer velocity for O<sub>2</sub> at 20<sup>o</sup>C,  $f(t)$  is a known function that adjusts  $\gamma_{20}$  to the measured water temperature at time *t*, *H* is the average height of the water column,  $c_e(t)$  is the air-water equilibrium ("saturation") concentration of DO at time *t*, and *c*(*t*) is the measured DO concentration at time *t*. For purposes of estimating parameter values, measured DO concentration  $c(t)$  was used instead of model-predicted concentration  $C(t)$  in Eq. (2), because the measured concentration yields a more accurate estimate of the atmospheric exchange rate  $\alpha(t)$  at each measurement time.

Integrating Eq. (1) between any two times *ta* and *tb* yields the equation,

$$
C(t_b) = C(t_a) + \int_{t_a}^{t_b} \pi(t) dt - \int_{t_a}^{t_b} \rho(t) dt + \int_{t_a}^{t_b} \alpha(t) dt,
$$
 (3)

The first integral on the right represents gross primary production of  $O_2$  between times  $t_a$  and  $t_b$ . The second represents total respiration of  $O_2$  between times  $t_a$  and  $t_b$ , and the third represents total atmospheric exchange of  $O<sub>2</sub>$ .

The equation that is the basis of the traditional two-station method has the form

$$
\frac{\partial C}{\partial t} + \bar{u} \frac{\partial C}{\partial x} = \pi(t, x) - \rho(t, x) + \alpha(t, x), \tag{4}
$$

where *t* is time, *x* is downstream distance in the stream,  $\bar{u}$  is mean current velocity, and the other quantities are defined as above except that they depend on both *t* and *x*. This plug-flow model assumes that the water column of a stream behaves like a loaf of sliced bread on a conveyor belt.

The slices remain intact, and there is no longitudinal exchange (hence, no longitudinal dispersion) between neighboring slices. Thus, if a slice passes the upstream station at time *t* , the model implies that the intact slice will pass the downstream station at time  $t + L/\bar{u}$ , where *L* is the distance between stations and  $L/\bar{u}$  is the travel time between stations. Changes in DO concentration are due entirely to processes occurring within each moving slice and on its interfaces with the atmosphere and stream bed; no exchange across its interfaces with neighboring slices occurs. Though ignoring longitudinal dispersion is clearly unrealistic, the plug-flow transport model greatly simplifies the estimation of metabolism components and for that reason has been the model of choice since the 1950s. A summary of the one-station and twostation equations and the assumptions leading to each is presented in Figure 8.

By using monitoring data to estimate the terms in these equations, we can estimate 24 hr GPP, R, and NP. Three methods were compared for estimating the terms in Eq. (3). These methods are briefly outlined here; for additional details, see the papers by McNair et al. (2013, 2015).

The first method is the accounting method used by Odum (1956). This method treats *γ*20 in Eq. (2) as a known parameter and therefore requires a method for calculating its value; we used two well-known formula-based methods called the surface renewal method and the energy dissipation method (Bott 2006). The formula for the surface renewal method has the form

$$
\gamma_{20} = (6.17 \times 10^{-5}) \bar{u}^{0.67} H^{-0.85}
$$
 (5)

where  $\gamma_{20}$  is gas transfer velocity in m⋅s<sup>-1</sup>,  $\bar{u}$  is mean current velocity in m⋅s<sup>-1</sup>, and *H* is mean height of the water column in m. The formula for the energy dissipation method has the form
$$
\gamma_{20} = K s \bar{u} H \tag{6}
$$

where  $\gamma_{20}$  is gas transfer velocity in m⋅s<sup>-1</sup>, *s* is the slope of the stream bed (m⋅m<sup>-1</sup>), *u* is mean current velocity in m⋅s<sup>-1</sup>, *H* is height of the water column in m, and *K* is a flow-dependent constant, the value of which is 0.328, 0.247, or 0.177  $m^{-1}$  depending on which of the following ranges estimated stream flow falls in:  $Q \le 0.28$ ,  $0.28 < Q \le 0.56$ , or  $Q > 0.56$  m<sup>3</sup>·s<sup>-1</sup>, respectively. The accounting-formula method, as detailed by Bott (2006), also requires the assumption that the instantaneous daytime respiration rate is constant and equal to the time average of the nighttime respiration rate (see McNair et al. (2013, 2015)). No other assumptions are required. This method does not generate predicted DO concentrations and therefore cannot be assessed by comparing observed and predicted time series.

The second method is the prediction method, first used (in a somewhat different form) by Hornberger & Kelly (1975). Here, it is assumed that  $\pi(t)$ ,  $\rho(t)$ , and  $\alpha(t)$  have the forms

$$
\pi(t) = \psi_{20}(1+\varepsilon_{\pi})^{\theta(t)-20} I(t)
$$
\n
$$
\rho(t) = \begin{cases}\n\rho_{20}^{(N)}(1+\varepsilon_{\rho})^{\theta(t)-20} & (\text{nighttime}) \\
\rho_{20}^{(D)}(1+\varepsilon_{\rho})^{\theta(t)-20} & (\text{daytime})\n\end{cases}
$$
\n
$$
\alpha(t) = \gamma_{20}(1+\varepsilon_{\alpha})^{\theta(t)-20} [c_{e}(t)-c(t)]/H,
$$
\n(7)

where  $I(t)$  is measured solar radiation,  $\theta(t)$  is measured water temperature in <sup>o</sup>C,  $c_e(t)$  is the airwater equilibrium DO concentration, *c*(*t*) is the measured DO concentration in the stream, *H* is the measured average height of the water column, and  $\varepsilon_{\pi}$ ,  $\varepsilon_{\rho}$ , and  $\varepsilon_{\alpha}$  are temperature adjustment parameters that were treated as known, with values  $\varepsilon_{\alpha} = \varepsilon_{\rho} = 0.072$  and  $\varepsilon_{\alpha} = 0.024$ (Grace & Imberger 2006). The remaining quantities ( $\psi_{20}$ ,  $\rho_{20}^{(N)}$ ,  $\rho_{20}^{(D)}$ ,  $\gamma_{20}$ ) are parameters to be estimated, using the statistical method detailed by McNair et al. (2013, 2015). Note that the

respiration rate is allowed to differ between nighttime (dark) and daytime (light), which is desirable based on the physiology of photoautrophic respiration (Raven & Beardall 2005; Falkowski & Raven 2007). The prediction method allows two separate ways in which daytime and nighttime  $y_{20}$  can be estimated. Either the statistically predicted nighttime value can be used for the daytime period as well, or the daytime and nighttime values can be separately predicted. We employed both methods for comparison.

The third method, called the accounting-statistical method, is the same as the first, except that the statistically estimated daytime and nighttime *γ*20 values from the prediction method are used instead of formula based estimates. Thus, the atmospheric exchange rate in this method is exactly the same as in the prediction method. A summary of the three methods is presented in Table 4.

All three methods provide estimates of gross primary production, total respiration, and atmospheric exchange as mass of  $O_2$  per unit volume of water over a 24-h period of time. These metabolism estimates are being reported in terms of oxygen instead of carbon for the reasons listed in Chapter 1. GPP and *R* are the integrals of *π*(*t*) and *ρ*(*t*) over a 24-h period, and NP is the integral of  $\pi(t) - \rho(t)$  over the same period (also, NP = GPP – R). GPP, R, and NP have dimensions of mass  $O_2$  per volume but can be converted to dimensions of mass  $O_2$  per (horizontal) area by multiplying by *H*.

Table 1. Stream physical properties estimated at transects measured in the stream. Measurements were taken at three transects on July 31, 2017 and at four transects on December 1, 2017. The transects are numbered in the downstream direction in the first column, with an average for each monitoring date.

<b>Transect</b>		Average		<b>Average Velocity (m/s)</b>	75 m Travel	
	Width (m)	Depth (m)	Flow $(m^3/s)$	<b>Meter</b>	<b>Calculated</b>	Time (min)
July 1	4.5	0.16	0.043	0.065	0.067	18.7
July 2	3.3	0.35	0.050	0.045	0.048	26.2
July 3	2.7	0.27	0.034	0.040	0.049	25.3
July average	3.5	0.26	0.042	0.050	0.055	22.9
December 1	5.5	0.28	0.23	0.16	0.16	7.6
December 2	4.2	0.28	0.36	0.29	0.31	4.0
December 3	5.0	0.22	0.21	0.21	0.21	5.9
December 4	4.0	0.43	0.25	0.15	0.16	7.7
December average	4.7	0.30	0.26	0.20	0.21	5.9

Table 2. Stream physical properties estimated using the salt tracer method. Two salt releases were done on July 31, 2017 (one upstream and one downstream), and one salt release was done on December 1, 2017.



Table 3. Triplicate nutrient concentration data from July 31, 2017. The L samples are from Little Black Lake just before the outfall into Little Black Creek. The S samples are from the creek. The numbers 1-4 represent the longitudinal position along the creek at which the samples were taken with 1 being upstream and 4 being downstream. A, B, and C represent the triplicate samples at each location.

<b>Station</b>		$SO_4$ (mg/L) $NO_3-N$ (mg/L)	$NH3-N (mg/L)$	$SRP-P(mg/L)$	$TP-P(mg/L)$
LA	12	0.0969	0.0368	< 0.005	0.0094
LB	12	0.0764	0.0293	< 0.005	0.0119
LC	12	0.0765	0.0262	< 0.005	0.0121
S <sub>1</sub> A	12	0.0785	0.0174	< 0.005	0.0090
S <sub>1</sub> B	12	0.0685	< 0.01	< 0.005	0.0104
S1C	11	0.0735	0.0239	< 0.005	0.0107
S <sub>2</sub> A	12	0.0923	0.0406	< 0.005	0.0114
S <sub>2</sub> B	12	0.0879	0.0375	< 0.005	0.0103
S <sub>2</sub> C	12	0.0791	0.0323	< 0.005	0.0104
S <sub>3</sub> A	11	0.0876	0.0543	< 0.005	0.0102
S3B	11	0.0948	1.2693	< 0.005	0.0091
S <sub>3</sub> C	11	0.0851	0.0498	< 0.005	0.0096
S <sub>4</sub> A	11	0.1150	0.0897	< 0.005	0.0104
S <sub>4</sub> B	11	0.1073	0.1013	< 0.005	0.0106
S <sub>4</sub> C	11	0.1178	0.0715	< 0.005	0.0103

Table 4. Summary of the attributes of the three methods used to estimate metabolism components. Each of the three methods can be used with either the one-station or two-station equations and will therefore carry the assumptions of whichever equation used, as outlined in Figure 8.





Figure 2. Map showing Little Black Creek relative to the larger Muskegon, MI area.



Figure 3. NOAA 2016 CCAP (Coastal Change Analysis Program) landcover map for the area surrounding Little Black Creek and Little Black Lake.



Figure 4. NRCS (Natural Resource Conservation Service) soil type map for the area surrounding Little Black Creek.



Figure 5. Map showing the study site and sonde deployment locations. Station 5 was used only in July, and the data were unusable due to sonde malfunction. Source: 2014 National Agricultural Imagery Program (NAIP) and National Hydrography Dataset (NHD).



Figure 6. Photograph of the sonde deployment set-up.



Figure 7. Plot showing longitudinal light patterns (blue line and open circles) and locations of macrophyte beds (green rectangles) in m downstream from station 1. The locations of each of the four stations is marked along the top of the plot. PAR is the downward vertical flux of photosynthetically active radiation, with units of  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>.



Figure 8. Flow chart starting with a general advection-diffusion model of DO transport and dynamics (top row). Alternative specializing assumptions lead to the standard models for onestation and two-station monitoring (middle row). Further alternative specializing assumptions then lead to the accounting and prediction-based estimation approaches (bottom row). Symbols are defined in the text.

# **Chapter 4: Results/Discussion**

### **Time series/physical properties**

As expected, there were marked differences in the time series data between July and December (Figures 9–11). In July, maximum light intensities were about 175 – 200 klx at stations 1, 2, and 4, which were located in areas with little or no canopy cover. These light intensity values were much higher than those measured in December after the trees had lost their leaves, where maximum light intensity values were about 40 klx at Station 1, 70 klx at station 2, 30 klx at station 3, and 25 klx at station 4. Interestingly, the lowest maximum light intensity in July, about 18 klx measured at station 3 within an area fully covered with trees, was lower than all the maximum December measurements. Despite the much higher light intensities in July, the canopy cover at station 3 blocked the vast majority of light from reaching the stream. Because all the leaves were off the trees in December, station 3 got more light than it did in July.

As a result of the higher light intensities (the main determinant of stream water temperature: Sinokrot & Stefan 1993) and air temperatures in July, water temperatures were also much higher (Figures 9–16). DO concentrations were lower in July than in December despite the fact that July production rates were much higher (Tables 5–12), mainly due to lower air-water equilibrium DO concentrations (roughly 8.0 versus 12.5 mg/L, on average: Figures 9–16). On the other hand, the diel range in DO concentration was much larger in July (roughly 3 mg/L) than in December (roughly 0.3 mg/L), as there were dense submersed macrophyte beds in the open portions of the stream where high light intensities provided ample energy for photosynthesis. The metabolic activities of these macrophytes, as well as microorganisms,

resulted in the large range in DO values over the diel cycle. In December, light intensities and water temperatures were much lower, and the submersed macrophytes had senesced. Only the metabolism of microorganisms, lowered as a result of lower light intensities and water temperatures, contributed to the DO dynamics of the stream, resulting in the very small diel DO ranges in December.

There is an interesting phenomenon revealed in Figures 17 and 18 in which DO concentrations at all four stations are plotted together in July and December, respectively. Station 1 has a visibly different DO pattern than the rest of the stations in both seasons. It can also be seen, especially in the December plot, that station 2, while being much closer to stations 3 and 4 in pattern, still has traces of the station 1 pattern. Little Black Creek flows out from Little Black Lake, and station 1 was located  $\sim 60$  m downstream from this outfall. It seems that station 1 is representative of a transition zone between the dynamics of the lake and the stream. If this is the case, it is a significant aspect of heterogeneity in this system and is a phenomenon to be aware of when planning studies. It would be helpful and interesting to have time series data within the lake near the outfall in order to more fully explore this transition zone.

There were also significant differences in physical properties in the streams between the two seasons (Tables 1 and 2). Flow and velocity were lower in July than in December, and consequently the travel time was longer. It is also interesting to note that the estimates derived from the salt tracer experiments were closer to those from the transects in December than July. The transect estimates are dependent upon the channel morphology of where the transects are measured, and can easily lead to averages that are not representative of the reach, especially in small streams (Grace & Imberger, 2006). The tracer estimates, on the other hand, are likely to be more representative of an average, because they are not dependent on the geometry of specific sections of the stream.

### **Metabolism estimates**

Metabolism estimates also showed large seasonal variation, regardless of which methods were used to obtain them. Comparing Tables 5–8 from July and 9–12 from December, it is clear that there is much less metabolic activity in December than July. This is to be expected given the lower light intensities, lower water temperature, absence of submersed aquatic macrophytes, and much smaller diel DO range in December. Not only are the estimates of components of metabolism higher in July, the P/R ratios are also higher (Table 13), indicating a greater proportion of GPP in July along with the greater overall metabolic activity. All P/R ratios were well below 1, indicating that respiration is the dominant metabolic process in this system, especially in December. There was not much variation in metabolic estimates over the two days that were measured in each season. This indicates that there were likely not large changes is metabolic processes on this short time scale. Previous studies (Roberts et al., 2007; Izagirre et al., 2008; Birkel et al., 2013; Roley et al., 2014) using continuous monitoring over longer time periods have shown metabolic variation over time scales intermediate between the two day and seasonal time periods in this study. This indicates that more frequent monitoring than is typically used in stream metabolism studies is preferable in order to assess temporal variation in metabolic processes.

Along with seasonal variation, there was variation between the different methods used. Within the accounting-formula method, there were differences in metabolism estimates depending on which formula was used for estimating gas transfer velocity  $\gamma_{20}$ . The surface renewal method produced higher gas exchange and metabolism estimates than the energy dissipation method in both July and December. This is one hint as to how important the gas transfer velocity estimate is when using the accounting method. The two formulas used produce different estimates of gas exchange, and subsequently different metabolism estimates. In both seasons, the prediction method produced lower metabolism estimates than the accountingformula method in conjunction with the surface renewal formula. Metabolism estimates derived using the accounting-formula method with the energy dissipation formula were closer to the results from the prediction method, and in most cases were lower.

The use of the prediction method allows visual assessment of model adequacy by comparing observed and predicted DO curves (Figures 19–22, 23a–28a). These figures show a range in goodness of fit between the predicted and measured DO time-series, indicating that the model was able to fairly accurately predict the DO time-series in some cases, and not in others. This suggests that there are processes at work in some cases that the model is not able to fully account for.

The use of the accounting-statistical method reveals some interesting things. When the daytime and nighttime estimates of  $\gamma_{20}$  are taken from the prediction program and used as the estimates in the accounting program, the estimates of NAE, NP, and NR are brought in line with those from the prediction program. This once again points out the importance of  $\gamma_{20}$  estimates in

the accounting program. The way in which one estimates this parameter can have major impacts on the metabolism estimates produced, because NAE is a major component of the total DO budget of the stream, comparable in magnitude to GPP and R (Tables 5–12). Where the accounting-statistical and prediction methods differ is in their estimates of DR (and therefore R) and GPP, and this points out the other major problem with the accounting method. The prediction method uses separate equations for the daytime and nighttime periods and is therefore able to statistically estimate DR and NR separately. On the other hand, in the accounting method, DR is estimated directly from NR by assuming that the daytime rate is equal to the average nighttime rate. This assumption produces DR, R, and subsequently GPP estimates that are mainly quite different than those from the prediction program.

Another result which further shows the importance of the method for estimating  $\gamma_{20}$  is the comparison between the prediction method wherein  $\gamma_{20}$  is estimated separately for the daytime and nighttime periods and the prediction method wherein the nighttime estimate of  $\gamma_{20}$  is used for the daytime as well (Table 14). The latter method was proposed by Hornberger & Kelly (1975) and is discussed by Grace & Imberger (2006). Looking at Figures 23b–28b from the prediction program with nighttime  $γ_{20}$  used for daytime and comparing them to Figures 23a–28a where  $γ_{20}$ is estimated separately, it is clear that there is no advantage in estimating  $\gamma_{20}$  only from the nighttime data and that estimating it separately for nighttime and daytime often produces significantly better fits. This also points back to the way in which  $\gamma_{20}$  is often estimated when using the accounting approach, i.e. only one estimate is used for both the daytime and nighttime periods, whether this is calculated using a formula or estimated using a gas evasion method. It is

clear from the comparison of the different ways that  $\gamma_{20}$  can be estimated within the prediction method that separate daytime and nighttime estimates are preferable.

In this study, we were unable to estimate  $\gamma_{20}$  via a gas-evasion method to compare the resulting estimate with the formula-based estimates. However, it has been shown elsewhere that estimates of the gas-transfer velocity derived using gas-evasion methods and the formula-based methods employed here may be similar or that the formula-based methods may underestimate relative to gas-evasion methods (Grant & Skavroneck, 1980; Young & Huryn, 1999; Mulholland et al., 2001; Bott et al. 2006). There are also conceptual reasons to believe that gas evasion methods, especially as typically applied, do not produce reliable estimates of  $\gamma_{20}$ . These methods are usually only done a single time in a stream (on one day, during daytime), so there is no way to adequately account for temporal differences between days or between daytime and nighttime, nor is there any way to estimate measurement error (because the true value of  $\gamma_{20}$  is never known), which is likely to be substantial due to the complexity of the field procedures employed and the fact that estimates are based on fitting a simple spatially-homogeneous plug-flow model to field estimates of residual gas concentrations, thus ignoring spatial heterogeneity and longitudinal dispersion.

One of the most significant aspects of this study is spatial heterogeneity. There are differences in metabolism estimates between the four single stations and between the various two-station combinations. In July, when using the accounting-formula and prediction methods, station 2 always had the highest estimates of GPP among the single-station results, and the reach between stations 1 and 2 had the highest estimates of both GPP and R among the two-station

results. These correspond to roughly the same reach, which was the reach with the greatest area of stream without tree cover, hence the reach with the greatest area containing submersed macrophytes. Comparing the reach between stations 1 and 2 with the reaches between stations 2 and 3 and between 3 and 4 in July, it is clear that there is significant spatial heterogeneity in estimates of metabolism in the study reach. This is interesting to note as the total length of the study reach was 800 m. Many studies use a single two-station reach comparable in length to those we used, or even a single station, to estimate metabolism and compare different streams (Mulholland et al., 2001; Hall & Tank, 2003; Bott et al., 2006). Even some studies which directly address longitudinal patterns or spatial heterogeneity either space their observation stations much farther apart than our study reach or only use a single two-station reach (McTammany et al., 2003; Demars et al., 2011; but see Siders et al. 2017).

The importance of spatial heterogeneity is further highlighted when looking at plots comparing the results derived in this study using the prediction and accounting-statistical methods with published results (Figure 29). The literature results are from several studies on both temperate and tropical streams (Fellows et al., 2001; Mulholland et al., 2001; Hall & Tank, 2003; Ortiz-Zayas et al., 2005; Bott et al., 2006; Bott & Newbold, 2013; Riley & Dodds, 2013; Silva-Junior et al., 2014; Masese et al., 2017; Saltarelli et al., 2018). With few exceptions, these studies were conducted using either a single station or one two-station reach within each stream. The comparison plots show that the range in GPP, R, and P/R ratio estimates in the results from the single 800 m reach in the present study is similar to the range of estimates from the combined results of many different streams of different types reported in the literature. This finding draws

into question the validity of comparing or assessing different streams based on metabolism estimates made at a single station or in a single reach.

Another interesting aspect of heterogeneity in this study involves the reach between stations 1 and 2 in December. The estimates of R in this case are negative, which is biologically impossible. Looking at Figure 18, in which DO concentrations at all four stations are plotted together, it can be seen when looking at stations 1 and 2 that this is the only case in which DO concentrations at the downstream station are higher than those at the upstream station over the entire 24 h period. During the nighttime period, the only way for the model to legitimately increase DO downstream is through atmospheric exchange. The formulas used in the accounting method produce only a single estimate based on physical parameters estimated as averages over the entire reach, so they wouldn't be able to account for conditions local to a specific reach or time period. Theoretically the prediction program should be able to produce atmospheric exchange velocities high enough to account for the increase, but it seems not to be able to, instead using negative respiration values. This is a situation similar to that pointed out by Demars et al. (2011). Their solution was to average the two stations together and analyze the average as a single station, but this doesn't seem like a legitimate solution to the underlying problem of spatial heterogeneity, and Demars et al. provide no derivation or other justification for their approach. It seems the model of DO dynamics is not able to account for this phenomenon, and that is where the problem should be addressed. The problem may be related to the proximity of the first station to the lake outfall, in which case a monitoring station within the lake could perhaps provide necessary information to address the situation.

### **Sensitivity analysis**

There are two hydraulic parameters, estimated directly from field measurements rather than by fitting the model of DO dynamics to the time series data, whose values appear to be particularly uncertain and for which different choices are likely to produce differing results. The uncertainty in these parameters and its effects on estimates of GPP, R, NP, and NAE arise mainly because the standard model of stream flow and DO dynamics employed in studies of stream metabolism treats the stream channel as uniform in width and depth and assumes plug flow with spatially and temporally constant velocity and no longitudinal dispersion. In fact, channel morphology is spatially heterogeneous, the stream does not exhibit plug flow, and current velocity is spatially and temporally variable along the stream.

One such parameter is current velocity (and the associated estimate of reach travel time), which we measured in two different ways. All results presented previously were derived using the current velocity measurement from the tracer studies. Table 15 shows results from July 28– 29, 2017 in which the estimate of current velocity obtained using the transect current meter readings was used; the corresponding results based on the tracer studies are shown in Tables 5 and 6. (Analogous results from December are not presented, because the current velocity estimate obtained using the current meter was the same as that from the tracer release.) Estimates from the accounting-formula method are smaller by roughly 51 % when using the lower current velocity estimate from the transect data, as can be seen by comparing the results in Table 15 for this method with those in Table 5. Only the estimates derived using the surface renewal formula for the gas transfer velocity are presented in Table 15, as the estimates derived using the energy

dissipation formula were similarly smaller when using the current velocity measurement from the current meter. Comparison of the results in Table 15 with those in Table 6 reveals that the estimates derived using the prediction method were more variable in their response to the lower current velocity estimate, with the absolute value of differences being roughly 23 %. Only twostation results using the prediction and accounting-statistical methods are presented in Table 15, as the one-station version of this method does not take current velocity into account in calculating the estimates, and the one-station results are therefore the same as those in Table 6.

Another parameter for which different values could be chosen is the average depth. Previously presented results were derived using the overall average depth for all transects measured in a season. To check the sensitivity of the results to the chosen depth, the lowest (0.16 m) and highest (0.35 m) average depth at an individual transect was used for the July 28-29, 2017 data (Tables 16 and 17). The use of the higher and lower depth measurements produced a fairly large range in metabolism estimates, the range being a rough average of 63 % of the original estimates in Table 5 when using the accounting-formula method with the surface renewal formula and a rough average of 73 % of the original estimates in Table 6 when using the prediction method. This shows that the estimate of depth used is important. Different depth measurements similarly produced a range of metabolism estimates in December, although the range was smaller because of the overall smaller metabolism estimates.

## **Conclusions**

Based on the results presented herein, and on an assessment of the conceptual underpinnings of the various methods addressed in this study, we believe the two-station prediction method in which daytime and nighttime  $\gamma_{20}$  are separately estimated is the soundest method for estimating components of stream metabolism. The two-station method is sounder conceptually than the one-station method as DO is measured in two places, and the change is ascribed to a specific area of stream, while with the one-station method, DO changes are measured over time at a single location, and those changes are ascribed to a vague upstream area. The prediction method is sounder than the accounting-formula method as model adequacy can be assessed by comparing observed and predicted DO concentrations (one station) or observed and predicted changes in DO concentration between stations during transit (two stations). This allows one to see that in some cases there are likely processes that the model cannot fully account for, which the accounting approach does not show. Also, the prediction method allows separate estimation of daytime and nighttime atmospheric exchange velocities and doesn't require the assumption that the daytime respiration rate is constant and equal to the time-averaged nighttime respiration rate. These two assumptions have been shown to be dubious by the results presented herein.

A significant aspect of stream metabolism which needs more study is spatial heterogeneity. Using four stations in an 800 m reach, results of this study show that there is the possibility of substantial differences in metabolism estimates within short distances when there are differing physical factors within the area under study (e.g., dense versus little or no canopy cover). The comparison between the results from this study and results from many different streams in the literature shows that the spatial differences within a stream segment roughly 1 km in length can produce a range of reach-scale metabolism estimates comparable to the range across individual

reaches in different streams that would be missed when using a single station or two-station reach. In order to more adequately explore this aspect of stream metabolism, studies should be undertaken using the greatest number of recording stations possible, and variation in metabolism between reaches within streams should be quantified.

Table 5. Metabolism estimates from July 28-29, 2017 derived using the accounting-formula method with both the surface renewal (top) and energy dissipation (bottom) formula methods for estimating the gas exchange velocity. The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of g  $O_2/$  $m<sup>2</sup>$ .



**Accounting-formula – Surface Renewal**

#### **Accounting-formula – Energy Dissipation**



Table 6. Metabolism estimates from July 28-29, 2017 derived using the prediction (with separate daytime and nighttime estimates of the gas transfer velocity) and accounting-statistical methods. The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of  $g O_2/m^2$ .





Table 7. Metabolism estimates from July 29-30, 2017 derived using the accounting-formula method with both the surface renewal (top) and energy dissipation (bottom) formula methods for estimating the gas exchange velocity. The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of g  $O_2/$  $m<sup>2</sup>$ .



**Accounting-formula – Surface Renewal**

#### **Accounting-formula – Energy Dissipation**



Table 8. Metabolism estimates from July 29-30, 2017 derived using the prediction (with separate daytime and nighttime estimates of the gas transfer velocity) and accounting-statistical methods. The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of  $g O_2/m^2$ .





Table 9. Metabolism estimates from December 1-2, 2017 derived using the accounting-formula method with both the surface renewal (top) and energy dissipation (bottom) formula methods for estimating the gas exchange velocity. The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of g  $O_2/$  $m<sup>2</sup>$ .



**Accounting-formula – Surface Renewal**

### **Accounting-formula – Energy Dissipation**



Table 10. Metabolism estimates from December 1-2, 2017 derived using the prediction (with separate daytime and nighttime estimates of the gas transfer velocity) and accounting-statistical methods. The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of  $g O_2/m^2$ .

<b>Prediction</b>									
	<b>GPP</b>	<b>NR</b>	DR	R	NP	N-NAE	D-NAE	<b>NAE</b>	Total DO Change
Station 1	0.05	0.12	0.11	0.23	$-0.18$	0.03	0.07	0.10	$\overline{\phantom{0}}$
Station 2	0.04	0.06	0.14	0.20	$-0.17$	$-0.01$	0.10	0.10	$\overline{ }$
Station 3	0.04	$-0.09$	0.26	0.17	$-0.13$	$-0.12$	0.21	0.09	$\overline{\phantom{0}}$
Station 4	0.07	$-0.30$	0.50	0.19	$-0.12$	$-0.32$	0.42	0.09	$\overline{\phantom{0}}$
1,2	0.32	$-2.11$	$-1.24$	$-3.34$	3.66	0.95	0.73	1.69	5.35
1,3	0.20	1.58	0.78	2.36	$-2.16$	1.00	0.40	1.40	$-0.76$
1,4	0.15	2.68	1.49	4.17	$-4.02$	0.95	0.30	1.25	$-2.77$
2,3	0.08	3.75	1.94	5.69	$-5.61$	0.73	0.04	0.77	$-4.84$
2,4	0.05	3.97	2.16	6.13	$-6.08$	0.63	$-0.04$	0.59	$-5.49$
3,4	0.03	3.90	2.32	6.22	$-6.19$	0.21	$-0.17$	0.04	$-6.14$



Table 11. Metabolism estimates from December 2-3, 2017 derived using the accounting-formula method with both the surface renewal (top) and energy dissipation (bottom) formula methods for estimating the gas exchange velocity. The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of g  $O_2/$  $m<sup>2</sup>$ .



**Accounting-formula – Surface Renewal**

### **Accounting-formula – Energy Dissipation**



Table 12. Metabolism estimates from December 2-3, 2017 derived using the prediction (with separate daytime and nighttime estimates of the gas transfer velocity) and accounting-statistical methods. The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of  $g O_2/m^2$ .

<b>Prediction</b>									
	<b>GPP</b>	<b>NR</b>	DR	R	NP	N-NAE	D-NAE	<b>NAE</b>	Total DO Change
Station 1	$-0.01$	0.33	$-0.09$	0.24	$-0.25$	0.33	$-0.05$	0.28	$\overline{\phantom{a}}$
Station 2	$-0.02$	0.24	$-0.01$	0.23	$-0.25$	0.26	0.03	0.29	$\overline{\phantom{a}}$
Station 3	$-0.05$	0.45	0.06	0.51	$-0.55$	0.47	0.12	0.59	$\overline{\phantom{a}}$
Station 4	$-0.02$	0.58	0.16	0.74	$-0.76$	0.60	0.19	0.79	$\overline{\phantom{a}}$
1,2	0.24	$-0.82$	$-1.42$	$-2.24$	2.49	2.17	0.83	3.00	5.49
1,3	0.24	1.55	0.84	2.39	$-2.15$	1.08	0.54	1.62	$-0.52$
1,4	0.18	2.31	1.52	3.83	$-3.66$	0.71	0.40	1.11	$-2.55$
2,3	0.19	2.81	2.09	4.90	$-4.71$	0.02	0.16	0.18	$-4.53$
2,4	0.12	3.00	2.24	5.24	$-5.11$	$-0.14$	0.03	$-0.11$	$-5.22$
3,4	0.06	3.24	2.26	5.50	$-5.44$	$-0.26$	$-0.22$	$-0.48$	$-5.92$



Table 13. P/R ratios calculated from the GPP and R estimates in Tables 5 – 12. P/R ratios are omitted in the table if either or both the GPP and R values used to calculate them were negative, which is physically impossible. SR and ED refer to the surface renewal and energy dissipation formula methods for estimating the gas exchange velocity using the accounting-formula method. The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used.

		$P/R$ Ratio July 28 – 29		$P/R$ Ratio December $1-2$				
				Accounting Accounting Prediction Accounting	Accounting	Accounting		Prediction Accounting
	<b>SR</b>	ED		Statistical	<b>SR</b>	ED		Statistical
Station 1	0.44	0.62	0.81		0.06	0.10	0.22	0.06
Station 2	0.49	0.57	0.75	0.37	0.09	0.11	0.20	
Station 3	0.35	0.42	0.47	0.18	0.08	0.08	0.24	
Station 4	0.34	0.40	0.34	0.46	0.05	0.04	0.37	
1,2	0.53	0.58	0.49	0.62				
1,3	0.34	0.33	0.30	0.29	0.12	0.16	0.08	0.19
1,4	0.35	0.34	0.36	0.38	0.06	0.06	0.04	0.11
2,3	0.23		0.20	0.11	0.06	0.06	0.01	0.12
2,4	0.33	0.03	0.31	0.30	0.04	0.04	0.01	0.10
3,4	0.39	0.64	0.44	0.65	0.03	0.02	0.00	0.06



Table 14. Select metabolism estimates from July and December derived using the prediction method with the nighttime predicted atmospheric exchange velocity being used for the daytime as well, as opposed to estimating them separately. The one-station estimates are labeled with their respective station number, and the two-station estimates are labeled with the combination of the two stations used. The label columns that include '[2]' are from the second 24 hr monitoring period of the month; all others are from the first 24 hr monitoring period. ST is Station, GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of  $g O_2/m^2$ .



3,4 [2] 0.08 3.24 2.34 5.58 -5.50 -0.26 -0.15 -0.41 -5.92

**Prediction – nighttime atmospheric exchange rate**

Table 15. Metabolism estimates from July 28-29, 2017 derived using current velocity estimated via the transect method in conjunction with the accounting-formula method with the surface renewal formula for estimating the gas exchange velocity (top), the prediction method (middle), and the accounting-statistical method (bottom). The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of g  $O_2/m^2$ .







Table 16. Metabolism estimates from July 28-29, 2017 derived using the lowest average depth measurement from the transect data (0.16 m) in conjunction with the accounting-formula method with the surface renewal formula for estimating the gas exchange velocity (top) and the prediction method (bottom). The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of  $g O_2/m^2$ .




Table 17. Metabolism estimates from July 28-29. 2017 derived using the highest average depth measurement from the transect data (0.35 m) in conjunction with the accounting-formula method with the surface renewal formula for estimating the gas exchange velocity (top) and the prediction method (bottom). The one station estimates are labeled with their respective station number, and the two station estimates are labeled with the combination of the two stations used. GPP is gross primary production, R is total respiration, NR and DR are the separated nighttime and daytime estimates of respiration, NP is net production, NAE is net atmospheric exchange, N-NAE and D-NAE are the separated nighttime and daytime estimates of net atmospheric exchange, and total DO change is the net change in DO between the two stations analyzed. These estimates all have units of  $g O_2/m^2$ .









Figure 9. Time series data for station 1 in July, 2017. (Top) DO concentration and theoretical DO saturation concentration in mg/L. (Middle) Water temperature in degrees C. (Bottom) Light intensity in klx. The grey dotted lines represent the first sunset, sunrise, and second sunset, denoting one full 24 hr period.



Figure 10. Time series data for station 2 in July, 2017. (Top) DO concentration and theoretical DO saturation concentration in mg/L. (Middle) Water temperature in degrees C. (Bottom) Light intensity in klx. The grey dotted lines represent the first sunset, sunrise, and second sunset, denoting one full 24 hr period.



Figure 11. Time series data for station 3 in July, 2017. (Top) DO concentration and theoretical DO saturation concentration in mg/L. (Middle) Water temperature in degrees C. (Bottom) Light intensity in klx. The grey dotted lines represent the first sunset, sunrise, and second sunset, denoting one full 24 hr period.



Figure 12. Time series data for station 4 in July, 2017. (Top) DO concentration and theoretical DO saturation concentration in mg/L. (Middle) Water temperature in degrees C. (Bottom) Light intensity in klx. The grey dotted lines represent the first sunset, sunrise, and second sunset, denoting one full 24 hr period.



Figure 13. Time series data for station 1 in December, 2017. (Top) DO concentration and theoretical DO saturation concentration in mg/L. (Middle) Water temperature in degrees C. (Bottom) Light intensity in klx. The grey dotted lines represent the first sunset, sunrise, and second sunset, denoting one full 24 hr period.



Figure 14. Time series data for station 2 in December, 2017. (Top) DO concentration and theoretical DO saturation concentration in mg/L. (Middle) Water temperature in degrees C. (Bottom) Light intensity in klx. The grey dotted lines represent the first sunset, sunrise, and second sunset, denoting one full 24 hr period.



Figure 15. Time series data for station 3 in December, 2017. (Top) DO concentration and theoretical DO saturation concentration in mg/L. (Middle) Water temperature in degrees C. (Bottom) Light intensity in klx. The grey dotted lines represent the first sunset, sunrise, and second sunset, denoting one full 24 hr period.



Figure 16. Time series data for station 4 in December, 2017. (Top) DO concentration and theoretical DO saturation concentration in mg/L. (Middle) Water temperature in degrees C. (Bottom) Light intensity in klx. The grey dotted lines represent the first sunset, sunrise, and second sunset, denoting one full 24 hr period.



Figure 17. Time series DO concentrations for all four stations in July, 2017.



Figure 18. Time series DO concentrations for all four stations in December, 2017.



Figure 19. Observed (blue line) and predicted (red line) DO concentrations at station 3 on July 28-29, 2017. This plot was generated using the one-station prediction method.



Figure 20. Observed (blue line) and predicted (red line) DO change during transit between stations 1 and 3 on July 28-29, 2017. This plot was generated using the two-station prediction method.



Figure 21. Observed (blue line) and predicted (red line) DO concentrations at station 2 on December 2-3, 2017. This plot was generated using the one-station prediction method.



Figure 22. Observed (blue line) and predicted (red line) DO change during transit between stations 1 and 4 on December 1-2, 2017. This plot was generated using the two-station prediction method.



Figure 23. a) Observed (blue line) vs predicted (red line) DO concentrations at station 1 on July 28-29, 2017. b) Observed (blue line) and predicted (red line) DO concentrations at station 1 on July 28-29, 2017 using the predicted nighttime atmospheric exchange velocity during the daytime period. These plots were generated using the one-station prediction method.



Figure 24. a) Observed (blue line) and predicted (red line) DO change during transit between stations 2 and 3 on July 29-30, 2017. b) Observed (blue line) and predicted (red line) DO change during transit between stations 2 and 3 on July 29-30, 2017 using the predicted nighttime atmospheric exchange velocity during the daytime period. These plots were generated using the two-station prediction method.



Figure 25. a) Observed (blue line) and predicted (red line) DO change during transit between stations 3 and 4 on July 28-29, 2017. b) Observed (blue line) and predicted (red line) DO change during transit between stations 3 and 4 on July 28-29, 2017 using the predicted nighttime atmospheric exchange velocity during the daytime period. These plots were generated using the two-station prediction method.



Figure 26. a) Observed (blue line) and predicted (red line) DO concentrations at station 3 on December 1-2, 2017. b) Observed (blue line) and predicted (red line) DO concentrations at station 3 on December 1-2, 2017 using the predicted nighttime atmospheric exchange velocity during the daytime period. These plots were generated using the one-station prediction method.



Figure 27. a) Observed (blue line) and predicted (red line) DO change during transit between stations 2 and 4 on December 1-2, 2017. b) Observed (blue line) and predicted (red line) DO change during transit between stations 2 and 4 on December 1-2, 2017 using the predicted nighttime atmospheric exchange velocity during the daytime period. These plots were generated using the two-station prediction method.



Figure 28. a) Observed (blue line) and predicted (red line) DO change during transit between stations 3 and 4 on December 2-3, 2017. b) Observed (blue line) and predicted (red line) DO change during transit between stations 3 and 4 on December 2-3, 2017 using the predicted nighttime atmospheric exchange velocity during the daytime period. These plots were generated using the two-station prediction method.



Figure 29. Comparison between estimates of GPP, R, and P/R ratio derived in this study via the prediction and accounting-statistical methods in both July and December, 2017 and estimates from several papers in the literature.

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