HOW MUCH DOES STREAM-GROUNDWATER EXCHANGE INFLUENCE
WHOLE-STREAM METABOLISM IN A SMALL MOUNTAIN STREAM?

by

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find that both the content and the form meet acceptable presentation standards
of scholarly work in the above mentioned discipline.

ABSTRACT

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How much does stream-groundwater exchange influence whole-stream metabolism in a small mountain stream?

Thesis directed by Associate Professor Michael N. Gooseff

To estimate whole-stream metabolism, the open-channel oxygen method has traditionally provided underlying assumptions for modeled estimates of gross primary productivity (GPP) and ecosystem respiration (ER). The open-channel oxygen method employs the diel stream dissolved oxygen (DO) curve, which attributes stream metabolism to four processes: photosynthesis by primary producers, oxidative respiration, reaeration, and, in the model used here, groundwater flux. Of these processes, groundwater flux is often assumed to be negligible when modeling whole-stream metabolism, which may introduce bias in estimates of GPP and ER. For example, if net groundwater flux is into the main channel, we may expect an overestimation of modeled ER due to dissolved oxygen dilution effects from influent groundwater. Although this error is recognized, there is a lack of continuous and spatial data that quantify the extent of bias that is introduced by not including groundwater flux in model parameters. To investigate this bias, whole-stream metabolism and groundwater flux were measured in Como Creek, a headwater catchment 26 km west of Boulder, CO. DO sensors were deployed in the stream and groundwater wells in June 2018 at 3 sites along 300 m of the reach. BASE (Bayesian Single-station Estimation), a package available through R, was used for modeling whole-stream metabolism between peak streamflow and baseflow. BASE also optimizes the reaeration coefficient, K , which was estimated both including and neglecting groundwater discharge and

DO concentration. Results indicate that Como Creek experiences a groundwater flux both into and out of the stream, with significant model bias observed during periods of anoxic groundwater input. Modeled rates of ER are lower with the groundwater-corrected model, while GPP and K remain relatively constant. These data suggest that the underlying assumption that groundwater flux is negligible in the open-channel oxygen method is inadequate for modeling whole-stream metabolism in highly-aerated alpine streams. However, results are highly susceptible to the treatment of reaeration and primary productivity priors, as well as the methodology for computing net gains or losses from water budget analyses.

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CHAPTER 1

HOW MUCH DOES STREAM-GROUNDWATER EXCHANGE INFLUENCE WHOLE-STREAM METABOLISM IN A SMALL MOUNTAIN STREAM?

1.1 Introduction

Whole-stream metabolism is useful in understanding nutrient cycling, carbon sources or sinks, as well as the trophic status of an ecosystem (Hall & Tank, 2003; Jones & Mulholland, 1998; Riley & Dodds, 2013). As photoautotrophic production and heterotrophic respiration occur, the metabolic activity of an ecosystem is regulated, dictating the chemistry and nutrient surplus or deficit vital for organism habitat. This regulation occurs through the production and consumption of oxygen and carbon dioxide from gross primary productivity (GPP) and ecosystem respiration (ER). Whole-stream metabolism is defined as the net difference between GPP and ER, and can be estimated via numerous methods (Grace & Imberger, 2006; Hanson et al., 2003; Wright & Mills, 1967). These include the use of benthic chambers, measuring carbon dioxide fluxes, and monitoring diel changes in dissolved oxygen (DO) concentrations. The open-channel oxygen method, however, is perhaps the most widely used due to the ease and low cost of in-situ DO sensor deployment. This method utilizes a mass balance approach on a parcel of water to attribute a change in DO concentration to four processes indicative of metabolic ecosystem activity (Odum 1956). These processes include reaeration, GPP, ER, and groundwater flux. Reaeration will either increase or decrease concentrations as a function of the level of saturation surplus or deficit at the air-water interface, while GPP and ER will increase and decrease DO levels, respectively. Reaeration will either be into or out of the stream depending on the relative degree of saturation in the reach. This is calculated as the net difference between the DO concentration required for saturation and the current concentration measured in the water

column. Since higher water temperatures cannot dissolve as much oxygen, the DO concentration required for saturation decreases with temperature, which typically corresponds to a negative reaeration flux observed during the midday as temperatures rise and the stream becomes supersaturated at the air-water interface. Groundwater flux is expected to decrease DO concentrations in a stream by having a “dilution effect”, where low DO, or even anoxic, groundwater enters the reach through hyporheic exchange.

Several assumptions are made in practice for computing whole-stream metabolism from the open diel oxygen method. These include neglecting GPP at night since photoautotrophic production requires sunlight, as well as assuming ER is constant throughout the day. This assumption is made because up until recently, we have not been able to separate photosynthesis and respiration rates during the day (Demars et al., 2015). Another assumption that is commonly made in practice is that groundwater flux, or “dilution”, is negligible. Therefore, influent or effluent groundwater is assumed to be small relative to the other terms in the mass balance equation. However, as the interest in surface and subsurface interactions increases, the validity of this assumption is questioned (Hall & Tank, 2005; McCutchan et al., 2002). Although it is known that groundwater will contribute to the diel oxygen concentration in a stream, there does not currently exist a framework for identifying when this assumption is justified.

Previous studies indicate that neglecting groundwater flux in the open-channel oxygen method results in model bias. Models that do not include groundwater in the DO mass balance have been found to overestimate ER and underestimate GPP (Hall & Tank, 2005). The bias in ER and GPP are both a function of the groundwater flux, but the bias in GPP is also related to the difference between day and night oxygen concentrations. Bias increases with the

groundwater discharge and the difference between groundwater and surface water DO, but this relationship has not yet been developed for larger time and spatial scales.

The purpose of this study is to quantify model bias resulting from the assumption that groundwater flux is negligible in the diel oxygen mass balance equation. This bias will be calculated continuously from peak streamflow to baseflow to assess the validity of this assumption seasonally. Previous studies have computed groundwater flux on shorter reaches in a variety of hydroclimates (Fellows et al., 2001; Marzolf et al., 1994; Mulholland et al., 1997; Ortiz-Zayas, 1998), so this work will focus on a longer reach in the alpine to subalpine zone. The model that does not include groundwater flux in its mass balance equation will be referred to in this paper as the baseline or uncorrected model, whereas the model that includes groundwater flux will be identified as the corrected model. Field work and continuous in-situ experimentation will allow whole-stream metabolism to be modeled over the 2018 summer season, which can help establish new methodologies for quantifying groundwater flux and computing model bias in ER and GPP. Parameters of interest for groundwater identification include dissolved oxygen, temperature, and electrical conductivity (EC). This work seeks to contribute to the available literature on surface and subsurface interactions by further investigating the bias in metabolism estimates and suggesting a framework for field and monitoring efforts.

1.2 Objectives, Hypotheses, and Predictions

This study aims to utilize the open-channel oxygen method and Bayesian linear regression to quantify bias and compare parameter optimizations between corrected and uncorrected model simulations. Specifically, this study will: 1) estimate rates of ER, GPP, and the reaeration coefficient, K , and 2) define the relationship between model bias, groundwater flux, and the difference between groundwater and surface water DO in Como Creek, a steep

Colorado mountain stream near the Niwot Ridge Long-Term Ecological Research (LTER) project field site. This work also seeks to develop a framework for continuous measurements of groundwater flux and whole-stream metabolism, with data collected along the falling limb of the summer hydrograph, post-snowmelt. Uncertainties and challenges in sampling and modeling practices will also be discussed, with emphasis on the calculation of groundwater discharge in a headwater stream and the reaeration coefficient.

Surface-subsurface flow regimes are strongly influenced by topography, aquifer geometry, hydraulic properties, and depression-based recharge (Harvey & Bencala, 1993). In this study, we focus on groundwater recharge in a steep catchment, where fluxes may be as large as 40% of the total discharge. We hypothesize that the magnitude of groundwater influx will be dominant from mid-June to early July, based on previous work conducted along Niwot Ridge in the Green Lakes Valley and Martinelli catchments (Liu et al., 2004). We therefore expect the pattern of the water table to transition from a greater hydraulic head following snowmelt, to lower water table elevations later in the summer. As a greater proportion of total streamflow is sourced as groundwater, unsaturated water with respect to DO is expected to enter the main channel, inducing a potential for bias in modeled metabolism. We predict that ER and GPP will be over- and underestimated, respectively, in the baseline model at this time, and bias will be greatest at the time of peak groundwater discharge. Therefore, we predict that bias will increase proportionally with groundwater influx.

Alternatively, we hypothesize that if groundwater flux is out of the stream, the main channel DO concentration will not change. As a result, we predict that the baseline and corrected model simulations will produce similar results if Como Creek is losing surface water. This will pertain to a low level of bias in the baseline model. We expect that the groundwater discharge

will be out of the reach following snowmelt, or just after peak discharge because the lateral head gradient will force flow toward lower water table elevations.

Finally, we hypothesize that the groundwater will be unsaturated with respect to DO, and at times of groundwater influx, we predict that there will be a relationship between model bias and the difference between subsurface and surface DO concentrations. As the DO deficit in the groundwater relative to the main channel increases, we expect that the error in the baseline model will increase, overestimating ER.

1.3 Background on Model Selection and Dissolved Oxygen Mass Balance

We will use and modify the BASE (BAYesian Single-station Estimation) model developed by Grace et al. (2015) to process multiple diel oxygen curves with and without groundwater flux. BASE utilizes the single-station approach (as opposed to the two-station method) to simulate the diel oxygen curve, which is then processed with a Bayesian estimation framework. The difference between single-station and two-station methods for calculating a change in DO concentration relate to the selected control volume. For the two-station method, a Lagrangian framework monitors changes in DO between upstream and downstream transects, adjusting for travel time. The two-station method, therefore, requires at least two transects equipped with instrumentation. One problem associated with the two-station method pertains to assuming spatial homogeneity of reach properties such as travel time, lateral inflows, depth, reaeration, and the saturation deficit. If reach characteristics change due to fine scale spatial heterogeneity between two sensors, the distance upstream contributing to the observed signal can either shrink or expand. Length thresholds have been established depending on the stream velocity and reaeration that capture the appropriate upstream influence. Reichert et al. (2009) identified the limits of the distance between two loggers as $0.4U/K < L < 3U/K$. Below $0.4U/K$,

the downstream station is predominantly affected by the upstream station as opposed to within reach processes. Conversely, above $3U/K$, the two stations are essentially independent. It is optimal when the downstream station is approximately $\frac{1}{3}$ to $\frac{2}{3}$ affected by the upstream transect, but this can be difficult to determine in turbulent streams. The single-station method, however, only utilizes one downstream transect, of which DO concentrations above this site are assumed to be equal (Lieth & Whittaker, 1975). This assumption is valid in well-mixed scenarios, but a comparison of the two techniques proves that outputs are similar, even though there is much disagreement on which model should be used in practice (Genereux & Hemond, 1992; Parkhurst & Pomeroy, 1972).

Bayesian linear regression is a statistical analysis in which the mean and standard deviation of the errors have an assumed probability density function (McCarthy, 2007). As opposed to fitting the parameter coefficients to a single value that best fits, or explains, the data, Bayesian linear regression aims to determine the posterior distribution of the model parameters. This distribution is assumed to be Gaussian, or normally distributed. BASE computes whole-stream metabolism by optimizing instantaneous rates of K , respiration, and the primary production per quantum of light, A :

$$\Delta C_i / \Delta t = AI_i^p - ER_i(\theta^{(T_i - T)}) + K(1.0241^{(T_i - T)})(S_i - C_i) \quad \text{Equation 1}$$

where i is the timestep of interest, ΔC is the change in DO concentration between timesteps, Δt , I is the incident light intensity at the water surface, and p represents the ability for primary producers to use incident light. GPP by default is assumed to be proportional to photosynthetically active radiation (PAR) (Bott, 2006; Grace et al., 2015; Kilpatrick et al., 1989; Wilcock et al., 1998), which is expressed by the AI_i^p term in Equation 1. Instantaneous rates of both reaeration, K , and respiration, ER , are temperature dependent, corrected by applying a

power law with the difference between the instantaneous, T_i , and average, T , daily temperatures. Reaeration is also a function of the saturation deficit, $S_i - C_i$, or the difference between the DO concentration at saturation and that which was observed in the stream. The model is then examined and passed for convergence through the posterior predictive fit (PPP) within and between multiple Markov Chain Monte Carlo (MCMC) samples.

BASE uses both R (R Development Core Team) and JAGS (Plummer 2003) software to estimate model parameters. Groundwater is incorporated to the model by adjusting the DO mass balance equation in the JAGS interface. The mass balance of DO from the Eulerian framework is best conceptualized in Figure 1. Here, a change in DO within the control volume is the result of reaeration, metabolism, downstream transport, and lateral exchange.

Figure 1. Conceptual model of the single-station oxygen method. A change in DO concentration in the Eulerian control volume is attributed to reaeration, metabolism, advection, and groundwater flux.

1.4 Considerations for the Reaeration Coefficient

One complication in the open-channel oxygen method is the reaeration coefficient because it can be difficult and costly to directly measure, and empirical approaches are highly

subjective (Riley & Dodds, 2013). BASE provides the option to estimate reaeration through Bayesian modeling, but the reaeration coefficient will be dependent on concurrent optimizations of respiration and A . Therefore, it is important to have realistic limits or priors set for K that are representative of the physical system. Empirical methods are based on the characteristics of a given stream such as stream velocity, slope, and mean depth (Parker and Gay, 1987), and studies have been conducted to determine the best model for a variety of applications (Benson et al., 2014; Cox, 2003; Raymond et al., 2012). However, there is not one relationship that accommodates every channel, and these equations can disagree even within the same reach. As a result, direct measurements or estimations of the reaeration coefficient are preferred. By using an inert gas tracer such as sulfur hexafluoride (SF_6) and a conservative solute to estimate travel time, the reaeration rate can be approximated without the use of empirical relationships or model optimization.

For the purposes of this study, a prior will be set for the reaeration coefficient that is dependent on data measured upstream of the study reach, limiting the maximum K value in the model. Field measurements were completed by the National Ecological Observatory Network (NEON), where the loss of injected SF_6 between two sampling locations serves as a proxy for gas exchange. NEON uses sodium chloride (NaCl) or sodium bromide (NaBr) as the conservative solute to calculate travel time and, subsequently, stream velocity (Cawley, 2018). Reaeration rates expressed in this thesis are normalized to a Schmidt number of 600, pertaining to oxygen at 17.5 °C in freshwater, as is the typical convention.

1.5 Background on Salt Dilution Gauging Methodology

Salt dilution gauging is one technique used to calculate channel discharge and net hydrologic gains or losses resulting from bidirectional exchange. This study will employ

methods outlined in Payn et al. (2008), where we will represent groundwater exchange as a net gain or loss from water balance calculations. The upstream-downstream water balance approach has been critiqued as neglecting gross fluxes, which may underestimate tracer dilution from gross gains and neglect tracer mass lost (Payn et al., 2009). In relation to the objectives of this study, the potential of gross gains or losses that are not accounted for in the net flux calculation may introduce small scale dilution effects that are not captured in model adaptation. Although the drawbacks of this approach are recognized, we have chosen to utilize this method so that analyses are conducted on a continuous time scale from the development of a stage-discharge rating curve.

The relationship between river stage and discharge is assumed to be log-linear, and if preliminary data are collected to identify the site-specific relationship between these parameters, stream discharge may be computed without further manual field measurements (World Meteorological Organization, 1994). Discharge is computed by applying the function, or rating curve, to the water depth at the time of interest. Errors associated with manual flow and depth measurements as well as imperfect estimations by the rating curve introduce compounded uncertainties in the groundwater flux calculation described above (Baldassarre & Montanari, 2009). These uncertainties inherent in the methods portion of this analysis are recognized and limitations are discussed later in this thesis.

CHAPTER 2

METHODS

We identified the groundwater signature and flux along Como Creek during summer 2018 through continuous in-situ measurements and multiple tracer studies. Following field experimentation, the BASE model was adjusted to include groundwater exchange. Differences between the baseline and corrected model simulations were used to quantify bias in *ER*, *GPP*, and *K*. Data was collected along the falling limb of the hydrograph, between peak streamflow and baseflow. Deployment spanned from 6/25/18 to 9/4/18, and gas tracer experiments were conducted by NEON on 6/19/18 and 8/06/18. At this time, measurements of stage, DO, EC, PAR, barometric pressure, and temperature were recorded and later implemented to BASE. These data were collected at multiple transects and wells along 300 m of the reach. The heterogeneity of subsurface biogeochemical properties was accounted for by measuring DO and conductivity in several groundwater wells approximately 1 meter in depth. The magnitude and direction of groundwater discharge were calculated from flow and EC mass balances. Separate rating curves for each transect were developed by manual field measurements and applied for continuous approximations. However, only one day for each week of deployment was selected at equal intervals to model in BASE because the reaeration prior changed with time, as indicated by the data. In total, 11 days were simulated and assessed for model bias.

2.1 Site Description

Como Creek is a subalpine headwater stream approximately 26 km west of Boulder, CO. It is one of the multiple field sites monitored by the Boulder Creek Critical Zone Observatory (CZO), and the watershed resides within the Niwot Ridge Biosphere Reservation (Boulder Creek

CZO, Niwot Ridge LTER). The catchment area is 6.64 km², and the site spans an elevation of 2900 and 3560 meters. The watershed is shown in Figure 2, and the 300 m subreach studied resides between the C-1 Niwot LTER Meteorological Station and the CU Mountain Research station. This portion of the reach is fairly steep, with a high elevation gradient and slope.

Figure 2. Contour map of Como Creek basin. *Source:* Boulder Creek CZO

The soil of this region is moderately well-drained with minimal clay content and is classified as loamy sand to gravel. Approximately 80% of the watershed is below treeline, including the study site. Engelmann spruce, subalpine fir, limber pine, lodgepole pine, and aspen are all tree species that may be found within the predominantly coniferous forest (Boulder Creek CZO).

There is a weir at Como Creek near the CU Mountain Research Station that has hourly stage data dating from 2004 to present (through main flow season only, not maintained during the winter). The weir is approximately 150 m downstream from the last transect of the studied

subreach. The average discharge at the weir is 82 L/s, with peak flow rates ranging from 230 L/s (June 19, 2004) to 1200 L/s (June 13, 2015). Snowmelt typically occurs early to late May, with peak streamflows observed mid June. Como Creek usually reaches baseflow during the month of August, where discharge can be as low as less than 1 L/s. The 3-year hydrograph for the years 2014 - 2017 is plotted in Figure 3 to provide context for the discharge measurements from the rating curve analysis along the 300 m subreach.

Figure 3. 3-year hydrograph for Como Creek at the weir near the CU Mountain Research Station. *Data Source:* Ryan Webb

Qualitative observations indicate that periphyton production increases during the month of July, following peak discharge. Phylum appear to be dominated by green algae, although periphyton and chlorophyll samples were not taken. Algal biomass visibly decreases approaching

fall, as stream temperatures decline. These physical observations are important in relation to the hypotheses, as they directly contribute to *GPP* and *ER* (but are not directly tested as potential controls here). Figure 4 provides a comparison of in-reach periphyton abundance during the months of June and July.

Figure 4. Visible observations of periphyton biomass on June 28, 2018 (left) and July 17th, 2018 (right). *Source:* Ricardo Gonzalez-Pinzon

2.2 Field Experiments and Sensor Deployment

Three sampling/monitoring transects were established along the 300 m subreach of Como Creek, equipped with HOBO data loggers (Onset). The furthest upstream site will be referred to as Transect 1, or T1, while the remaining transects from upstream to downstream will be identified as T2 and T3. The distance between T1 and T2 is approximately 200 m, while the distance between T2 and T3 is 100 m (Figure 5). Although each transect is equipped with full instrumentation, DO, temperature, and conductivity data from T3 is directly inputted to BASE, while data from the other transects are used for flux calculations and to account for heterogeneity

in PAR and groundwater DO concentrations. We installed three groundwater wells at each transect on north-facing and south-facing slopes. The orientation of well installment relative to river-right or river-left was dependent on the slope, soil, and depth-to-water table at each transect. The well installed at T2 became dry early in deployment after evaluation of EC and temperature data, so we installed an additional well 50 m downstream to collect groundwater DO data. Each transect was equipped with a HOBO U26 dissolved oxygen data logger (dissolved oxygen accuracy: ± 0.2 mg/L up to 8 mg/L, temperature accuracy: 0.2°C), HOBO U24 fresh water conductivity data logger (conductivity accuracy: $\pm 0.3\%$), a HOBO U20 water level logger (pressure accuracy: $\pm 0.3\%$), and a 64K HOBO Pendant®.

Figure 5. Transect and well deployment along the 300 m subreach of Como Creek.

We installed these instruments at each transect in a similar fashion depicted in Figures 6 and 7. PVC and fishing line were used to secure sensors to the streambed, and we downloaded and monitored sensors on a weekly basis. Grace et al. (2015), suggest the stable threshold for data entered into BASE be 15 minutes, so to optimize storage space availability while maintaining an appropriate time interval, sensors were initiated to record data every 10 minutes.

Figure 6. In-situ instrumentation for monitoring surface water stage, DO, EC, and temperature.

Figure 7. HOBO EC and water level logger deployed in groundwater well.

We conducted multiple tracer studies at each transect to generate three stage-discharge rating curves. These studies were completed throughout the deployment period to capture a full range of flow rates, and repetitions were performed 7-10 times at each transect. The purpose of developing multiple rating curves was to generate continuous discharge measurements at upstream and downstream sites. These streamflows were then incorporated into the water balance to compute net groundwater gains or losses.

We manually computed discharge through salt-dilution gauging. During each tracer study, we measured stage at each transect with a ruler relative to an established datum. The HOBO pressure transducer reading at the time of manual depth measurements was calibrated to the same reference datum employed by the rating curve. We used NaCl as our conservative solute and released the injectate instantaneously approximately 15 m upstream of each transect. HOBO EC sensors at each downstream location were adjusted to a timestep of 1 second to capture the entire

breakthrough curve. The injected mass ranged from 600 to 200 grams for higher and lower discharge, respectively. We established this threshold through trial and error by analyzing the breakthrough curves from different injectate masses at variable flow rates, and followed the procedures outlined in Wood & Dykes (2002). Discharge via dilution gauging was derived from the downstream conductivity data by dividing the known mass of injected NaCl by the area under the breakthrough curve (Equation 2):

$$Q = \frac{M}{\int_0^t C(t)} \quad \text{Equation 2}$$

where Q is the discharge in units of $[\frac{L^3}{T}]$, M is the mass of injectate in grams [M], C is the concentration of the conservative tracer $[\frac{M}{L^3}]$, and t is time [T]. The rating curves for each transect are included for reference in Appendix A.

We computed groundwater discharge by conducting a flow and mass balance on EC, with EC data from upstream and downstream sites and wells:

$$Q_D = (Q_U C_U + Q_G C_G) / C_D \quad \text{Equation 3}$$

where subscripts u, g, and d correspond to upstream, groundwater, and downstream parameters. The variables indicated by Q represent discharge $[\frac{L^3}{T}]$ and C represents the measured concentration of electrical conductivity $[\frac{\mu S}{cm}]$, adjusted for travel times between the upstream and downstream transects. We were able to use EC data in sourcing groundwater because groundwater conductivity is higher in the subsurface due to greater residence times and solute dissolution.

Finally, we used field measurements of (wetted) stream width and depth along the 300 m subreach to calculate cross-sectional areas to be implemented to the DO mass balance equation.

We measured these parameters every 15 m to develop an average cross-sectional area at each transect along the reach.

2.3 NEON Reaeration Coefficient

Although we did not conduct inert gas tracer studies to measure reaeration, NEON performed multiple continuous SF₆ injections upstream of the sampling site, which we will use as a prior in BASE for modeled K . Although NEON measures reaeration each month along Como Creek, only data for June (6/19/18) and August (8/6/18) were complete and available for analysis. Since SF₆ was continuously injected into the stream via a drip station, the plot of the log of SF₆ concentration versus downstream distance yields a slope of $-K/U$. Four downstream stations monitored approximately 18, 38, 68, and 93 meters from the injection site monitored electrical conductivity, temperature, and specific conductance for the computation of stream travel time and velocity. The travel time was assumed to be the time difference between the upstream and downstream peak of the slug (Cowley, 2018), which was close to 10 minutes in June and 40 minutes in August for a distance of 74 and 83 meters, respectively. Grab samples were collected throughout the rising limb, plateau, and falling limb of the breakthrough curve, and samples were analyzed at the Loecke Lab at the University of Kansas (SF₆ detection limit: 0.000041 ppm). After the slope of the semi-log linear relationship between downstream distance and SF₆ concentration was determined, the reaeration rate of SF₆ is given by:

$$K_{SF_6} = LR_{SF_6} \times U \quad \text{Equation 4}$$

where LR_{SF_6} is the slope of the regression and U is the stream velocity. From Wanninkhof (1992), the gas transfer velocity of SF₆ is converted to K_{O_2} by multiplying K_{SF_6} by 1.34. This rate is represented with a Schmidt number of 600 by accounting for oxygen in fresh water at 17.5°C (Jahne et al., 1987).

$$K_{600} = \left(\frac{600}{S_{CO_2}} \right)^{-0.5} \times K_{O_2} \quad \text{Equation 5}$$

$$S_{CO_2} = 1800.6 - 120.10 \times T + 3.7818 \times T^2 - 0.047608 \times T^3 \quad \text{Equation 6}$$

where T is the mean temperature in degrees Celsius during the tracer study.

Reaeration was computed as 201 d⁻¹ on 6/19/18 and 52 d⁻¹ on 8/6/18. We then applied a power function to the measured K with time to estimate the required prior on a weekly interval throughout deployment because the reaeration rate measured in August is likely close to the minimum, as discharge returned to baseflow between August and September. We selected the same day for each week to model based on days where minimal precipitation was expected. A hyetograph for the 2018 summer season is provided in Figure 8 from the meteorological station at the C1 site along Como Creek, approximately 430 meters upstream of T1 with an elevation of 3018 meters (Niwot Ridge LTER). Cumulative daily precipitation is plotted versus time, which was used to determine the day of the week during deployment with the least amount of precipitation to be modeled. The selected day of the week was Tuesday, and dates corresponding to those implemented to BASE are also shown in Figure 8, totalling 22 simulations of cumulative baseline and corrected scenarios.

Figure 8. The Como Creek hyetograph from the 2018 summer season at the C1 site was used to determine the day of the week throughout deployment with the lowest average precipitation. The selected dates for analysis are therefore at weekly intervals on Tuesday, which was the day of the week with the lowest observed precipitation. Selected dates implemented to BASE and analyzed in this study are depicted by the black marker in the figure.

2.4 BASE Relevant Equations and Adaptation

We altered the governing equation in the BASE model (Equation 1) to include groundwater in order to compare outputs of ER , GPP , and K from the baseline and corrected simulations. The DO mass balance that BASE, and many other models that function on the open-channel oxygen method, utilizes does not include groundwater exchange (Equation 7). The

relevant parameters and units in the original and adapted mass balance equation implemented to BASE are summarized in Table 1.

Table 1. Relevant parameters with provided units and descriptions used in baseline and corrected DO mass balances.

Variable	Description	Units
C_t	Stream DO concentration at a given time, t	$\frac{mg}{L}$
C_0	Initial stream DO concentration	$\frac{mg}{L}$
C_g	Groundwater DO concentration	$\frac{mg}{L}$
M	Net rate of whole-stream metabolism	$\frac{mg}{m^2d}$
z	Water depth	m
A_s	Surface area of reach	m^2
K	Oxygen reaeration coefficient	d^{-1}
S	Saturated concentration of DO	$\frac{mg}{L}$
Δt	Difference between two timesteps	d
Q_g	Groundwater discharge into or out of the reach	$\frac{L}{d}$

Before and after correcting for groundwater flux, the DO mass balance is:

$$C = C_0 + [\frac{M}{z \times 1000} + K(S - C)]\Delta t \quad \text{Equation 7}$$

$$C = C_0 + [\frac{C_g Q_g}{A_s z \times 1000} - \frac{Q_g C}{A_s z \times 1000} + \frac{M}{z \times 1000} + K(S - C)]\Delta t \quad \text{Equation 8}$$

In Equation 8, $(\frac{C_g Q_g}{A_s z \times 1000} - \frac{Q_g C}{A_s z \times 1000})$ is the groundwater flux, which can be positive or negative as a function of net groundwater gains or losses. The factor of 1000 is simply a unit

conversion for consistent dimensional analysis. BASE accounts for the temperature dependence of respiration and reaeration, as well as the saturation concentration of DO being a function of salinity, barometric pressure, and temperature. BASE also employs the daytime regression model (Kosinski, 1984) to calculate *GPP* and *ER*, where *ER* is assumed to be constant throughout its diel cycle and *GPP* is set to zero during the night, when there is not sufficient solar radiation to conduct photoautotrophic production. As a result, *ER* is computed as an average of instantaneous rates optimized at each timestep during a 24-hour period, while *GPP* is the sum of only daily increases in DO above saturation.

By default, the posterior distribution of the errors of the estimated parameters for the respiration rate, *K*, and *A* are assumed to be Gaussian with a mean of 0 and precision of 0.25. We additionally constrained the parameters *A* and *K* so that the groundwater-corrected model output was physically realistic of the Como Creek system. This was necessary in model development because unbounded values of these parameters resulted in an increase of modeled *GPP* that was several orders of magnitude greater than the baseline output and a lack of convergence in model performance between timesteps that was due to the reaeration term in the mass balance equation. If *K* was not constrained, modeled DO concentrations would increase and subsequently decrease between each timestep, centered around an average concentration. This behavior is attributed to the model overcorrecting low and high DO values by altering reaeration at each timestep as modeled values increased and decreased above and below the average concentration. Parameters *A* and *K* were constrained either through direct measurements of reaeration or by limiting the maximum value of *A* in the groundwater corrected model by setting the mean of the distribution of *A* to the output from the baseline model. We ran 20,000 iterations with 10,000 burn-in for each

day simulated to generate multiple MCMC samples. These defaults allow for model convergence and fit is assessed through PPP criteria.

Comparisons between the baseline and corrected models will be normalized to a bias index, as detailed in Hall and Tank (2005). The bias index is the ratio of the uncorrected to corrected model rates of *ER*, *GPP*, and *K*. A sensitivity analysis for the addition of saturated, semi-saturated, and anoxic groundwater will be conducted to determine the model's response to varying degrees of groundwater saturation and flow rates. The results will be discussed relative to this analysis in order to provide context of output variables.

CHAPTER 3

RESULTS

3.1 Groundwater Flux and Dissolved Oxygen Deficit

Groundwater flux was quantified between T1 and T3 from late June to early September (Figure 10). Groundwater gains or losses were estimated from the water balance between two transects, and discharge generally decreased downstream, indicating a net flux out of the main channel. The maximum and minimum flow rates at T1 were approximately 5 and 70 L/s, respectively. Peak rates occurred in late June following snowmelt, and baseflow was as low as 1 L/s at T2 (Figure 9). Streamflow at T2 ranged between 1 and 50 L/s, and the discharge at T3 was between 2 and 20 L/s (Table 2).

Table 2. Transect hydrologic and geomorphic properties.

Transect	Minimum Discharge (L/s)	Maximum Discharge (L/s)	Average Discharge (L/s)	Standard Deviation (L/s)	Average Width (m)	Average Stage (cm)
1	4.9	61	15	12	2.2	0.98
2	1.2	40	11	8.4	2.3	1.8
3	2.3	22	9.2	6.3	2.7	1.5

These statistics agree with the historical hydrograph from the weir, but indicate that we captured only the falling limb of the hydroperiod as opposed to additionally sampling throughout snowmelt and peak flows. The average daily discharge at each transect and computed groundwater flux between T1 and T3 for each of the selected modeled days are included in Appendix B.

Figure 9. Stream discharge computed from rating curves at each transect indicate that we expect to observe a groundwater loss by performing a flow balance between T1 and T3. Days implemented into the BASE model are depicted by open circles.

Groundwater enters the reach periodically throughout the month of July, with groundwater gains calculated between 7/6/18 - 7/22/18 and 7/27/18 - 8/3/18 (Figure 10). We therefore expect to see a difference in modeled rates of *GPP*, *ER*, and *K* between the baseline and corrected simulations during this time. We implemented a daily moving average of hyporheic flow into the BASE model, which had a maximum loss of 8.3 L/s, as depicted in Figure 10.

Figure 10. Groundwater flux along the 300 m subreach of Como Creek was generally represented as a net loss to the water table except for groundwater gains between 7/6/18 - 7/22/19 and 7/27/18 - 8/3/18.

We hypothesized that the groundwater would be undersaturated with respect to DO and lower in concentration than the surface water. We averaged the heterogeneous well concentrations to establish an average groundwater DO concentration that we included in the corrected BASE model. The groundwater became anoxic in early August, with prior concentrations having a maximum value of 2.7 mg/L. Relative to the main channel, there was an observed DO deficit in the groundwater, with the surface water being 89 to 102% saturated while the wells were only 0 to 34% saturated (Figure 11). We see a decreasing temporal trend in both surface and groundwater percent saturation, with greater diel variability during July. DO concentrations decrease and increase at night and during the day, respectively, due to primary productivity resulting from sunlight. The greater observed difference between nighttime and

daily degrees of saturation during the month of July may be due to the qualitative observation of increased periphyton communities in the reach and/or the groundwater influx during this time.

Figure 11. DO concentrations at T3 (top) and averaged between groundwater wells (bottom) along 300 m of Como Creek. Wells became anoxic in August, and concentrations follow a diel day-night cycle.

3.2 BASE Sensitivity Analysis

We conducted a sensitivity analysis of groundwater discharge and concentration on modeled rates of *GPP*, *ER*, and *K* in order to understand how the BASE model responds to adaptation and provide context for physical results. We selected a single day, 7/10/18, for input manipulation that was representative of gaining conditions along the reach. We did not consider groundwater losses, as we found that there was not a significant difference, other than stochastic model variations inherent in the applied methods, in the two models after the incorporation of flux out of the system. Groundwater gains of anoxic, saturated, and semi-saturated water were compared to both the measured data and baseline simulation. We adjusted the magnitude of groundwater discharge from 5 to 100% of the absolute value of the maximum observed stream flow rate. This value was calculated as 8.3 L/s during the entire deployment period. Therefore, cases identified as 5, 15, 30, and 50% in Figure 12 pertain to their respective portions of the total, or maximum, 8.3 L/s. It should be noted here that this is an extreme case for the observed groundwater gain during deployment, as the maximum flux into the stream was only 3.6 L/s (43.3% of 8.3 L/s).

The model proves to be sensitive to changes in groundwater magnitude and its DO concentration, which influences parameterization of *ER* more than that of *GPP* and *K*. The baseline simulation overestimates *ER* and *GPP* relative to the semi-saturated and anoxic cases. *ER* is computed as 3.6 mg O₂/L/d in the baseline model and ranges between 0.2 and 4.4 mg O₂/L/d for undersaturated simulations. For saturated groundwater entering the reach through lateral exchange, *ER* is greater than the baseline model and increases slightly with increasing groundwater discharge. The model appears to be more sensitive to changes in the magnitude of groundwater flux, with rates of *ER* increasing with hyporheic exchange. This may be due to the

nature of the Bayesian framework being dependent on posterior distributions or the tradeoff of model fit as a result of decreasing the computed DO concentration in the mass balance equation. *GPP* is smaller relative to the baseline for all corrected model simulations, which may also be due to the iterative processing of model parameters to achieve convergence. Finally, *K* does not vary significantly between simulations, as we set a prior of 111 d^{-1} for reaeration from interpolation of physical measurements conducted by NEON. However, we do see that *K* decreases in the DO saturated-groundwater scenario and increases to the predefined limit in DO unsaturated model runs. Since Como Creek is typically undersaturated with respect to DO at the water-atmosphere interface, this may result in the conclusion that the addition of higher DO groundwater results in a smaller DO deficit in the stream, and therefore, a smaller reaeration estimate. Conversely, lower DO groundwater might increase the reaeration coefficient to offset dilution effects.

Figure 12. Sensitivity of the BASE model to groundwater flux. Sensitivities in *ER*, *GPP*, and *K* parameter estimation were analyzed as a function of groundwater magnitude and DO concentration. The selected day for analysis was July 10, 2018, and semi-saturated conditions were modeled as 4 mg/L. Anoxic concentrations were implemented as 1E-13 mg/L. Saturated concentrations were computed from temperature, pressure, and salinity at each timestep.

We also analyzed the diel model fit for 7/10/18 under the 100% groundwater gain scenario to assess how the tradeoff of model fit was made in BASE after the inclusion of undersaturated groundwater (Figure 13). It should be noted here first that the diel variability of DO within Como Creek is not consistent with theoretical expectations of maximum concentrations occurring during the mid-to-late afternoon (Odum, 1956). This expectation is due to the fact that reaeration may only increase DO concentrations up to 100% saturation, since oversaturated conditions would result in gas exchange out of the water column and into the atmosphere. Therefore, primary producers are responsible for increasing DO concentrations

above 100% saturation, which would typically be observed after a temporal lag when the maximum solar radiation is available (around noon). We see in our results, however, that peak concentrations are early in the morning, which may be attributed to the presence of a wetland upstream of the 300 m subreach.

The model's response to anoxic gains is the most dramatic, and saturated conditions do not significantly alter the output parameters from the baseline. As the groundwater becomes more anoxic, the observed DO cannot be fit as well, increasing the difference between measured and modeled concentrations. While the baseline model has an R^2 value of 0.98, the semi-saturated and anoxic simulations yield R^2 values of 0.64 and 0.24, respectively. This could be due to the daytime regression model employed by BASE. At night, *GPP* is assumed to be equal to zero, but since the influent groundwater decreases calculated oxygen concentrations, the reaeration term alone is not sufficient for increasing modeled concentrations to those observed. Therefore, the modeled DO concentration under the anoxic simulation only reaches a maximum value of 4.8 mg/L, while measured concentrations were 8.37 mg/L. We also see that for saturated groundwater concentrations, the model fit does not change significantly from the baseline, even though we observed a response in *GPP*, *ER*, and *K*.

Figure 13. Sensitivity of model fit to groundwater concentration for the 100% gaining scenario. Data is from July 10, 2018, and we see that although the shape of the diel curve is consistent throughout simulations, undersaturated groundwater results in a negative transformation where maximum modeled concentrations are lower than observed. This relationship is dependent on the groundwater DO deficit and is more extreme for increasingly anoxic conditions.

The results of this sensitivity analysis are used to better understand the model results for baseline and corrected simulations for the 2018 summer season. Later we will discuss the BASE model and constraints for groundwater adaptation as it relates to this analysis and the physical data.

3.3 Weekly Baseline and Corrected Simulations

BASE optimized *ER*, *GPP*, and *K* as instantaneous rates over 10-minute intervals for each of the selected model days and simulation types. We selected 11 days, each a week apart, during the deployment period to model baseline and corrected scenarios, totaling 22 simulations and parameter estimations. We used this approach due to temporal variability in the reaeration coefficient and to maximize data storage while minimizing computation time. These instantaneous rates were aggregated to daily fluxes for model comparison. We used a bias index similar to that which is presented in Hall and Tank (2005) to compare uncorrected and corrected model outputs between variables of different magnitudes. The bias index was represented as the uncorrected model output divided by the corrected model output for parameters *ER*, *GPP*, and *K*. Values greater than 1 indicate that the uncorrected model overestimated the parameter of interest. Conversely, values less than 1 indicate that baseline outputs are smaller than the parameter estimation from the corrected model. Table 3 summarizes these results for the days when groundwater entered the system and presents the bias index for each parameter.

Table 3. Comparison of the daily rates of *GPP*, *ER*, and *K* for both model simulations and bias indices for days with groundwater influx.

Date	Baseline Output			Corrected Output			Bias Index		
	GPP (mg O ₂ /L/d)	ER (mg O ₂ /L/d)	K (d ⁻¹)	GPP (mg O ₂ /L/d)	ER (mg O ₂ /L/d)	K (d ⁻¹)	GPP	ER	K
7/10/18	0.0971	3.65	108	0.0501	0.475	111	1.94	7.67	0.972
7/17/18	0.0900	0.113	88.4	0.0464	0.947	91.1	1.94	0.119	0.970
7/31/18	0.0278	1.25	61.1	0.0140	0.105	61.6	1.98	11.9	0.990

Appendix C includes also includes a summary table of these rates for each of the modeled days, including both groundwater gains and losses. Figures 14 and 15 graphically

represent the baseline and corrected outputs for *GPP* and *ER*, and *K*, respectively. Dates with groundwater gains are represented through plot background shading and are important for assessing bias, since the sensitivity analysis proved that groundwater losses do not significantly influence model response. We see that the temporal trend of *ER* and *GPP* increases and decreases, respectively, into August, and baseline and corrected outputs for *ER* are the same late in deployment. For days with groundwater flux into the system, 7/10/18, 7/17/18, and 7/31/18, we see that uncorrected rates of *ER* are greater for $\frac{2}{3}$ of the modeled days. On 7/17/18, the corrected modeled output for *ER* is greater than the baseline, even though *GPP* follows the same trend of baseline outputs being greater than the corrected model. We do see, however, that at this time, uncorrected *K* is less than that of the corrected model, which may explain the reason that *ER* is smaller for this day.

Reaeration follows a decreasing trend due to the priors initiated for each model simulation. The power law governing the temporal trend was assumed in the selection of the prior, so should not be considered in bias analyses, rather, the difference between the uncorrected and corrected outputs. Differences between the two simulations are observed on 6/26/18, 7/10/18, 7/17/18, 7/24/18, and 7/31/18. All of the days where grounder influx was calculated produced different outputs of *K*, but only 2 of the days where a loss was observed yielded variations in uncorrected and corrected model output. These 2 days, 6/26/18 and 7/24/18, both have agreeable rates of *GPP* and *ER* relative to the baseline and corrected simulations, which may explain the difference in estimated *K*. These days, however, differ from the groundwater gain scenarios, as *K* is greater in uncorrected model runs. This may be due to the model fit being more sensitive to changes in *ER* as opposed to *GPP*, since corrected rates of *ER* were smaller, so BASE compensated for observed DO concentrations by also reducing *K*.

Groundwater Influx Results in Overestimation of ER

Figure 14. Weekly BASE model parameter estimations of *ER* and *GPP* for the 2018 summer season. Shading represents days where hyporheic exchange was into the main channel, 7/10/18, 7/17/18, and 7/31/18. *ER* was overestimated in uncorrected simulations for a majority of these days, while *GPP* was always smaller in corrected simulations relative to the baseline model. The temporal relationship between *ER* and *GPP* in Como Creek shows that *ER* increases seasonally while *GPP* decreases. Note the logarithmic y-axis.

BASE Model Output With and Without Groundwater

Figure 15. Weekly BASE model parameter estimation of K for the 2018 summer season. Shading represents days where hyporheic exchange was into the main channel, 7/10/18, 7/17/18, and 7/31/18. The temporal power relationship was developed from the treatment of the K prior interpolated from direct in-reach measurements conducted by NEON. Reaeration decreased during deployment, and K is higher for corrected simulations when a groundwater gain was observed. Two days where a groundwater loss was computed produced outliers, where corrected simulations produced lower estimations of K than the baseline model, 6/26/18 and 7/24/18.

We also analyzed the model fit for the same data utilized in the sensitivity analysis, July 10, 2018, to compare extreme scenarios with the physical results (Figure 16). For this day, the groundwater discharge was 0.9 L/s into the reach. Consistent with the sensitivity analysis, we see that the shape of the diel oxygen curve agrees with the observed concentrations and baseline model, but the maximum and minimum DO concentrations are lower. While the uncorrected model overestimates the DO concentration in the trough between 9:00 and 18:00, the corrected model underestimates DO at all times. The greatest variability between the corrected model and observed data occurs between 0:00 and 7:00, which may be explained by the daytime regression assumption, or that *GPP* at night is set as negligible so dilution effects cannot be offset to yield model convergence. As mentioned in the context of the sensitivity analysis, we may see peak DO concentrations around 6:00 in Como Creek due to processes within an upstream wetland, which may introduce downstream loading of high conductivity water throughout the day.

Oxygen Concentrations for 7/10/18 (Anoxic Gain)

Figure 16. Diel oxygen curve produced from measured and modeled data. The baseline model neglects groundwater flux entering the system, while the corrected model simulates a groundwater gain computed from the water balance. Data is from T3 on July 10, 2018, and groundwater concentrations into the system at this time were anoxic, or less than 1 mg/L.

3.4 Bias Indices

We plotted bias in ER , GPP , and K as a function of groundwater DO deficit relative to in-reach concentrations and the proportion of influx contributing to total streamflow. We studied these relationships because we hypothesized that bias would increase with influent hyporheic exchange and the difference between stream and groundwater DO. The results show that there is not a statistically significant relationship between bias and the groundwater DO deficit for any of the optimized parameters (Figure 17). However, there is a negative linear relationship between bias in ER and the total proportion of groundwater flux as total streamflow (Figure 18). This relationship was unexpected, but may be due to smaller scale gains having a more profound

influence on observed concentrations prior to baseflow. We also plotted the bias index from the results of the sensitivity analysis discussed previously as a function of groundwater discharge and the DO deficit (Figure 19). The range of bias in ER , GPP , and K are consistent between the theoretical results from the sensitivity analysis and the physical output from Como Creek, with a maximum bias index of ER between 14 and 16. As the proportion of total streamflow from groundwater influx increases, the bias of ER decreases nonlinearly for undersaturated scenarios. This indicates that ER becomes underestimated in the baseline model when there is a large influx of groundwater. Conversely, the results show that saturated groundwater entering the main channel results in an underestimation of ER in the baseline model. These results are consistent with those depicted in Figure 18, however, the regression of ER is an exponential decay. The findings of the sensitivity analysis are also validated in that BASE is more sensitive to variations in groundwater flux as opposed to the concentration in undersaturated scenarios.

Figure 17. Model bias versus groundwater DO deficit, represented as the difference between main channel and groundwater DO concentrations. Results indicate that, while *ER* is typically overestimated in the uncorrected model, there is not a statistically significant relationship between bias and groundwater concentration.

Model Bias Versus Proportional Groundwater Influx

Figure 18. Model bias versus groundwater flux, as percent of total observed streamflow from influent groundwater. There is a negative linear relationship between bias in *ER* proportion of streamflow as groundwater. The baseline model overestimates *ER* except with larger groundwater contributions, when rates are smaller than produced by the corrected model.

Figure 19. Model bias versus groundwater flux from results of sensitivity analysis. Flux is represented as the percent of total observed streamflow from influent groundwater. Data from 7/10/18 was used to manipulate input data and compare to baseline rates of *ER*, *GPP*, and *K*. Bias in *ER* decreases exponentially for undersaturated conditions, where *ER* becomes underestimated as more groundwater contributes to the total streamflow. When the DO concentration of groundwater is assumed to be saturated, *ER* is slightly underestimated in the baseline model.

CHAPTER 4

DISCUSSION

The results of this study indicate that the inclusion of groundwater flux into the BASE metabolism model do effect estimates of ER , GPP , and K . We see that bias is introduced to the uncorrected model when groundwater is accounted for, and error associated with a groundwater loss is due to uncertainty in stochastic modeling. ER is overestimated in the baseline model when groundwater enters the system. However, the importance of accurate measurements of reaeration is emphasized through the treatment of a K prior distribution because the model will respond to low DO inputs by dramatically increasing K and GPP . Therefore, GPP must also be restricted to realistically represent the physical constraints of the system. When K and GPP were constrained in the groundwater corrected model, we saw that K was underestimated in the baseline model, while GPP was overestimated. This is because reaeration must be higher in the adapted model to offset low DO loading from influent groundwater, and GPP decreases since the primary productivity per quantum of light, A , is limited throughout the day. Limiting A decreases total GPP since there is less primary productivity for the same amount of solar radiation, and GPP is expressed as the sum of each of the instantaneous rates throughout the day. The sensitivity analysis reveals the model's behavior to dilution effects, and proves that reaeration will approach its predefined limit, while GPP and reaeration alone are unable to compensate for lower inputs by employing the daytime regression model. Reaeration and primary production may be quantified by the use of other modeling strategies such as the Lagrangian, or 2-station approach, or the use of benthic chambers. The groundwater magnitude and flux varies seasonally in the reach, with gains observed during the month of July. However, there is uncertainty associated

with the quantification of net groundwater inputs by the rating curve and water balance methods, so observed gains or losses could be attributed to other processes. The physical observation of periphyton biomass revealed that green algae was present in July, and may have contributed to the greater diel variability in DO concentrations. The percent bias was found to decrease with baseflow, proving that the assumption of negligible groundwater contribution to metabolism measurements may be influenced seasonally. In other words, gross gains are increasingly important during periods where a greater difference in surface and subsurface concentrations are observed.

4.1 Flux Calculation and Water Budget Uncertainty

Although our hypothesis was supported by the data showing that low DO groundwater influx did influence metabolism results, it was not supported in the timing that net groundwater gains or losses were observed. While we hypothesized that gains would be prevalent between peak streamflow and the falling limb of the hydrograph, groundwater entered the main channel only periodically throughout the month of July. The observed temporal lag in maximum influx may be attributed to variability in channel morphology or errors in the computation of flux by the rating curve and water balance methodologies.

We hypothesized that the magnitude of groundwater influx would be greatest during June and July from a previous study by Liu et al. (2004). However, we know that a 1000 year flooding event affected the Boulder Creek Watershed during September 2013 (Dailey et al., 2015), which likely increased sediment loading and changed the reach-scale channel morphology in Como Creek. Variables controlling groundwater exchange that were potentially disrupted include step-pool, pool-riffle, and braided sequences as well as pressure divergence and the spatial variation of hydraulic conductivity (Buffington & Tonina, 2009). As a result, observed

differences in the timing of groundwater gains may be due to the time distribution between this study and prior work.

Additionally, we computed discharge and groundwater flux from the rating curve method and an upstream-downstream water budget. Appendix A shows the rating curves developed for each transect, and it is apparent in these curves that the uncertainty associated with each discharge computation is compounded by both positive and negative residuals of the linear regression. We also offset each downstream discharge calculation by an average weekly travel time to incorporate into the water balance. Travel times ranged between approximately 15 minutes to 1 hour, but are also susceptible to uncertainty in flood-pulse responses. The error associated with the water balance method for computing net groundwater gains or losses has been found to underestimate gross groundwater gains in net losing conditions (Payn et al., 2009), and simultaneous gains and losses are ignored in this approach. However, studies have found that bidirectional hyporheic exchange at the same time-step can be significant (Covino & McGlynn, 2007; Ruehl et al., 2006). Therefore, the hyporheic flow paths of modeled days represented by gaining or losing conditions may be more complex than that which was simplified for model adaptation. This influences model response by days represented as a net loss actually having small-scale dilution effects that are ignored in the DO mass balance equation. Likewise, gross losses are neglected for days identified by a net groundwater gain, where dilution is buffered by time-steps where DO concentration does not change.

While DO was lower and even anoxic in the groundwater wells during deployment, we observed a greater variability of in-reach DO saturation when periphyton was present in the channel. Periphyton increases stream DO concentrations through photoautotrophic production, which directly increases the rate of *GPP*. The model output of *GPP* in mid-July indicates that

productivity was relatively high compared to modeled rates in August. The rate of *GPP* was approximately 0.09 mg O₂/L/day during this time, compared to 0.01 mg O₂/L/day in August. The physical observation of periphyton in the reach on July 17th therefore validates the BASE model. Furthermore, modeled rates agree with those from Grace et al. (2015) for multiple sites within the United States, Australia, and New Zealand. Grace et al. used the BASE model with fixed p and θ parameters, and output rates of *GPP* ranged from 0.1 to 10 mg O₂/L/day while *ER* was between 1 and 20 mg O₂/L/day. Reaeration, however, was smaller in magnitude for these reaches, with K between 0.1 and 50 d⁻¹ (Grace et al., 2015). This indicates that Como Creek is relatively unproductive, heterotrophic, and highly-aerated, since the maximum rate of *GPP* pertains to the lower threshold of values from other studies, while *ER* reached maximum values of approximately 5 mg O₂/L/day. We also see that groundwater flux was into the reach prior to this qualitative analysis of algal biomass. This introduces the idea of periphyton habitat in Como Creek and can help better understand the groundwater flow regime. We know that periphyton production is typically light-limited, but studies have also found that growth can be nutrient (nitrogen and phosphorus) or carbon limited (Carey et al., 2007). Deep groundwater is generally low in organic matter, nutrients, and DO (Schmidt & Hahn, 2012). Therefore, if the periphyton production in Como Creek was secondary-limited by nutrient availability, we might expect recharge from shallow groundwater inputs, as opposed to deeper, more anoxic, DO. This influences the model, as we assumed that the groundwater influx had low DO concentrations, as observed in the wells. However, it is possible that the subsurface flow regime had a short residence time and concentrations into the reach were not as low as observed in the wells. It would therefore be beneficial to concurrently monitor deep and shallow groundwater DO and nutrient concentrations. Additionally, we see that on July 17th, the day when periphyton was

observed in the channel, the corrected modeled optimization of ER was greater than the baseline simulation. This was the outlier for the modeled groundwater gaining days, and higher ER may be due to the increased algal biomass, fostering higher populations of benthic invertebrates at this time.

4.2 BASE Model Strengths and Limitations

The results alone provide justification for questioning the validity of the assumption that groundwater is negligible not only in BASE, but also for other models that calculate whole-stream metabolism from the open-channel oxygen method. We see that ER is overestimated under groundwater gaining conditions from the baseline simulation. However, in order to compensate for large inputs of low DO groundwater, the model sacrifices fit between the observed and modeled data to maintain the treatment of priors under the daytime regression model.

The daytime regression model (Kosinski, 1984) assumes that the relationship between photosynthesis and light is governed by a power law that corrects for the ability of primary producers to use incident PAR. At night, PAR is equal to zero, so a change in oxygen within the reach is attributed only to respiration. We assume that the nighttime and daytime respiration rates are equal, and can subsequently compute GPP by subtracting the daytime respiration from the measurement of net ecosystem metabolism. BASE utilizes this assumption in parameter optimization, and by default the variable describing the ability of primary producers to use incident PAR is set to 1. This treats GPP as a linear function of PAR, scaled by A , or the primary productivity per quantum of light. However, studies have found that the assumption that daytime and nighttime respiration are equal produces different results relative to separately computing nighttime and daytime respiration (Karakaya, 2011). Variability in simulated rates of GPP and

ER between the two assumptions is seasonal, with *GPP* and *ER* being higher and lower under the daytime regression model during early to late fall and late summer months, respectively. This assumption is crucial when modeling whole-stream metabolism, as there are not currently any empirically based methods for estimating *GPP* at the whole reach scale (Gilmanov et al., 2003). Due to the limitations of the daytime regression model, at night, modeled DO concentrations do not fit those observed after the inclusion of groundwater. This is because daytime and nighttime respiration rates are assumed to be equal, so at night when *GPP* is negligible, the only processes that can compensate for the decrease of oxygen in the mass balance (resulting from influent groundwater) are *ER* and reaeration. *ER* and *K* may decrease and increase, respectively, in an attempt for model convergence, but since *K* is limited by a prior condition realistic of the system, *ER* can only decline. We see in the sensitivity analysis that with a greater influx of anoxic groundwater, both *K* and *ER* increase. This is due to the model iteratively approaching a solution, where *ER* will drastically decrease, but then increase as the model attempts to fit the observed data. Reaeration also follows this pattern, but drastically increases as *ER* decreases. The reason *ER* increases with DO deficit and the magnitude of influx is because BASE computes *ER* as an average of instantaneous rates.

Therefore, we see that the physical constraints of the system are important to provide justification and context for the BASE model output. We initiate the prior information, or maximum values, of *GPP* and *K* because the model responds to dilution effects by significantly increasing these parameters, and in scenarios where inputs are high, the JAGS estimation may be unrealistic. For example, when *GPP* was not restricted to reasonable limits output from the baseline simulation, the corrected model attempted to converge by increasing *A* several orders of magnitude. This resulted in a diel oxygen curve with a shape that followed PAR and not the

observed data. We therefore suggest that these parameters be constrained in corrected models either based on the output from the baseline simulation or physical measurements. This requires analyzing the parameter output of the model and comparing rates of *GPP*, *ER*, and *K*, to relevant literature focusing on similar study reaches. Therefore, even though BASE identifies model convergence through PPP criteria between the measured and modeled DO concentrations, the model may not be adequate if assessed through alternative performance criteria such as the root mean square error.

We also saw an inconsistency between the theoretical timing of maximum DO concentrations and those which were observed in Como Creek. Rather than observing a maximum concentration around mid-afternoon, or approximately 14:00, we see that DO concentrations peak earlier in the day, around 6:00. This may be due to increases in stream electrical conductivity throughout the night, resulting in decreased solubility of DO. Therefore, our system can become oversaturated even without gross primary productivity increasing DO concentrations. The source of this high electrical conductivity water may be from an upstream wetland that was approximately 100 m upstream of the 300 m subreach. Although we did not record electrical conductivity in this wetland, we did observe the stage throughout the deployment period. We saw that the wetland stage decreased throughout the day, which may be due to evapotranspiration. As a result, the downstream contribution of high electrical conductivity water is smaller throughout the daytime, and our stream becomes less saturated. Conversely, throughout the night, evapotranspiration is expected to be small or negligible, so a greater proportion of high electrical conductivity water is released and advected downstream, potentially susceptible to a temporal lag.

We described several methods including empirical approaches and gas tracer injections for estimating reaeration in a reach. If groundwater flux into the main channel is observed, it is vital to couple measurements of metabolism with reaeration. Since tracer experiments can be expensive and time consuming, we consider other modeling and field approaches to generate these data. One method that is typically used is an assaying technique for measurements of metabolism are benthic chambers. Benthic chamber techniques are different than open channel techniques for measuring the diel variation in DO because they isolate a small area of benthos and overlying water to represent metabolism for a particular environment (Grace & Imberger, 2006). This approach reduces uncertainties associated with the reaeration term, which has been found to increase errors in measurements of *GPP* and *ER* in highly aerated streams. The reach needs to be extremely productive if *K* is high in order to accurately quantify rates of *GPP* and *ER*. Benthic chambers exclude reaeration since the air-water interface is not within the control volume of the apparatus. It has been suggested that chambers be used if groundwater flux exceeds 5% of the total streamflow (Grace & Imberger, 2006), which was observed in Como Creek, with a maximum influx of approximately 14%. Chambers may be open or closed based, and various substrate such as cobbles or woody material may be added. However, there are limitations with this approach including the requirement of a tight seal which may not be achieved in cobble reaches or channels that have significant hyporheic flow paths which creates a Venturi effect that leaks solutes and gases. They are also unrealistic in shallow streams because there must be ample water above the chamber for installment, but can provide more accurate estimates in ‘flashier’ watersheds with a high runoff ratio. Others have also found that chambers become anaerobic when water is not circulated through the control volume, so careful design considerations or maintenance are required (Hall et al., 1979).

Another approach that should be compared to the methods described in this study is the 2-station, or Lagrangian, method for computing the diel change in DO within a parcel of water. We inherently assumed that the conditions above the downstream transect, T3, were well mixed in this analysis. This may introduce error resulting from longitudinal and water-column stratification of DO concentrations. The 2-station method constrains metabolism measurements to a defined area of the reach, and has been found to perform well in steep, rough, and low productivity streams (Young & Huryn, 1999).

Finally, other metabolism models such as BaMM (Holtgrieve et al., 2010) and ModelMaker (Atkinson et al., 2008) should be investigated for bias in a similar manner as shown in this study. Both BaMM and ModelMaker use the open-channel oxygen method to calculate net ecosystem metabolism, but also may include other features such as $\delta^{18}\text{O}$ isotopic ratio (Grace et al., 2015). These should be tested for groundwater bias in different hydroclimates in order to find the best model for a variety of site descriptions.

4.3 Implications of Transient Storage

We hypothesized that the bias index would increase with a greater proportion of total streamflow sourced as groundwater. We expected deep groundwater recharge during low flow periods when baseflow recession occurred on the hydrograph. This was predicted to introduce low DO groundwater into the main channel and therefore bias uncorrected modeled rates of *ER*. However, the results do not show this relationship, rather, there is a negative linear relationship between bias and the percent of streamflow corresponding to hyporheic exchange. The potential reason for this observed relationship may be due to the assumption that influent subsurface water has the same DO concentration as measured in the wells.

Although groundwater may be low in nutrients, carbon, and oxygen, subsurface flow regimes are complex and not accounted for in our approach. In addition to groundwater discharge, a net gain or loss in a channel may be attributed to releases from transient storage. Transient storage varies along a reach depending on hydraulic conditions and morphological gradients (Briggs et al., 2010). It is defined more clearly as the temporary delay of downstream solute transport resulting from small eddies, stagnant pockets of water that are moving slowly relative to the mean channel velocity (channel dead zones), and the movement through porous media, which increases residence time (Bencala & Walters, 1983; Kelleher et al., 2013; Runkel, 1998). Therefore, a net gain or loss calculated by the water budget method may be attributed to transient releases or storage, respectively, and not simply the recharge of old groundwater. As a result, the chemistry of the water entering the system may be different than what was assumed by measurements obtained in the groundwater wells. The influent groundwater may have actually had higher observed concentrations of DO than what was modeled because a net gain may be from the release of a slow-moving pool or shallow subsurface flow paths. The issue regarding net versus gross gains is reiterated here, and it is important to track the water signature of the influx since results and bias are highly dependent on this variable. Various pathways of transient storage are depicted in Figure 20, adapted from Runkel and Bencala (1995).

Figure 20. Transient storage introduces alternative pathways to deep groundwater recharge for computed groundwater gains. These include a) releases from dead zones or slower moving water such as pools and b) shallow subsurface flow through porous media.

This consideration in the context of the results indicates that the linear relationship between bias and the proportion of streamflow sourced as groundwater may be influenced by transient storage. The relationship shows that for high proportions of streamflow assumed to be from deep groundwater, bias is small and the magnitude of *ER* for corrected and baseline simulations agree. However, this may not be due to the percent of groundwater flux, rather, the fact that for the plotted data point the gain was actually associated with the release from shallow subsurface or small eddy transient storage. It would be therefore be beneficial to longitudinally measure water quality parameters such as DO, EC, temperature, nitrate, and carbon to find hotspots of deep groundwater influx so that gross gains or losses may be quantified, sourced, and implemented to the model.

Finally, we propose that this study is extended to other headwater and higher order reaches to validate our findings and understand the potential bias spatially. It would also be useful to look at hyporheic zone metabolism and focus monitoring efforts during cooler months

when K and GPP are small relative to ER due to lower incident light and temperatures. We see that the difference between baseline and corrected outputs of ER decreases as Como Creek reaches baseflow, which may be due to estimations of ER having a greater certainty when the other parameters are not as important. Despite the uncertainty in the findings of this study, we do see that this reach experiences a dynamic groundwater flux that influences model outputs. This provides justification for further investigation of this bias, and we recommend that groundwater is not assumed to be negligible when modeling whole-stream metabolism.

CHAPTER 5

CONCLUSION

We modified the BASE (BAYesian Single-station Estimation) metabolism model to include groundwater flux within the diel oxygen mass balance equation. Groundwater flux was quantified during the summer 2018 season in Como Creek, CO, capturing the falling limb of the hydrograph. We utilized manual stage and discharge readings to develop a rating curve so that flux could be computed continuously throughout the deployment period. Net gains or losses were analyzed through a flow and EC mass balance, where the difference between downstream and upstream discharge represented groundwater exchange. We also monitored groundwater DO and EC to both source and implement groundwater flow into the BASE metabolism model. We compared outputs of corrected and baseline simulations to represent a bias index for GPP , ER , and K . We found that after the BASE model was adapted to include groundwater flux, response was sensitive to the estimation of K , and outputs were dependent more on the magnitude of groundwater influx than DO concentration. Bias was introduced to the uncorrected model when the stream was gaining anoxic groundwater, and ER was typically overestimated by assuming negligible groundwater contributions. The tradeoff of including dilution effects within the BASE model was poorer model fit due to the daytime regression assumption that GPP is equal to zero at night, and daily and nighttime respiration rates are the same. Reaeration alone cannot offset the high loading of low DO from groundwater, which emphasizes the importance of proper physical measurements of K when modeling metabolism. We failed to accept our hypothesis that the relationship between the percent of total streamflow and model bias would be proportional since bias was inversely related to the proportion of streamflow sourced as groundwater. This

result, however, may be due to variable conditions within Como Creek, such as transient storage releases that are not considered in the net water budget approach. A net gain may subsequently be accompanied by gross losses, or vice versa, which influences the source water chemistry and flux parameter included in BASE. Therefore, future work should focus on quantifying gross gains or losses and the seasonal and spatial patterns of bias. It would be beneficial to analyze other models and assaying techniques for validation of these findings. Nonetheless, we suggest that groundwater be included, or at least quantified, prior to initiating metabolism models since we see that even small inputs of lower DO groundwater may drastically bias results.

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APPENDIX A

RATING CURVES FROM MANUAL DISCHARGE MEASUREMENTS

APPENDIX A (CONTINUED)

APPENDIX B

AVERAGE DAILY DISCHARGE AND GROUNDWATER FLUX FOR SELECTED MODEL DAYS

Date	Q_{T1} (L/s)	Q_{T2} (L/s)	Q_{T3} (L/s)	Q_g (L/s)
6/26/18	50.7	26.9	22.0	-6.81
7/3/18	28.5	20.1	14.9	-2.80
7/10/18	16.1	16.2	15.1	0.894
7/17/18	14.7	15.5	14.3	1.96
7/24/18	24.0	23.3	17.7	-1.78
7/31/18	6.80	6.77	5.86	0.142
8/7/18	7.85	5.83	4.85	-0.537
8/14/18	7.48	3.82	4.00	-1.15
8/21/18	7.29	4.22	4.51	-0.471
8/28/18	6.68	1.43	2.77	-1.59
9/4/18	5.94	1.23	2.26	-1.75

APPENDIX C

COMPARISON OF BASE OUTPUTS AND BIAS INDICES FOR GPP, ER, AND K

	Baseline Output			Corrected Output			Bias Index		
Date	GPP (mg O ₂ /L/d)	ER (mg O ₂ /L/d)	K (d ⁻¹)	GPP (mg O ₂ /L/d)	ER (mg O ₂ /L/d)	K (d ⁻¹)	GPP	ER	K
6/26/18	2.37	0.116	149	1.86	0.108	144	1.28	1.07	1.03
7/3/18	0.107	0.305	131	0.0438	0.294	131	2.45	1.04	0.998
7/10/18	0.0971	3.65	108	0.0501	0.475	111	1.94	7.67	0.972
7/17/18	0.0900	0.113	88.4	0.0464	0.947	91.1	1.94	0.119	0.970
7/24/18	1.16	0.0551	69.8	0.907	0.0517	68.1	1.27	1.07	1.03
7/31/18	0.0278	1.25	61.1	0.0140	0.105	61.6	1.98	11.9	0.990
8/7/18	0.0289	2.96	50.2	0.0121	2.94	50.2	2.39	1.00	1.00
8/14/18	0.0180	6.12	41.3	0.00769	6.11	41.3	2.34	1.00	1.00
8/21/18	0.0455	2.82	33.6	0.0220	2.79	33.5	2.07	1.01	1.00
8/28/18	0.0254	3.66	28.0	0.0107	3.66	28.0	2.36	1.00	1.00
9/4/18	0.0338	5.14	22.9	0.0144	5.11	22.9	2.35	1.01	1.00