

Measurement of gas-exchange rate in streams by the oxygen–carbon method

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Abstract: The gas-exchange rate between streams and the atmosphere is needed to measure in-stream ecological processes and C processing in rivers and streams. Current methods include empirical relationships to hydraulics, direct injection of a tracer gas, and modeling based on O₂ or C diel curves. All existing methods have strengths and drawbacks and most are limited to point measurements or are unable to measure diel variation in exchange rate. Researchers continue to search for better techniques, particularly for steep streams with high rates of gas exchange and low primary productivity. We present the O₂–C (OC) method for calculating gas-exchange rates via simultaneous measurement of O₂ and dissolved inorganic C (DIC). Gas-exchange rates are calculated by solving the combined stream transport equation for O₂ and DIC. The output is a time-series of aeration rates at the same sampling frequency as the input O₂ and C data. Field tests in a 4th-order montane stream in Oregon, USA, indicate that the method is suitable for stream reaches with high downstream gas-concentration gradients and saturation deficits. The mean modeled aeration rate adjusted to 17°C (3.25/h) agreed well with the value of 3.22/h from direct gas injection. Net ecosystem production calculated with the modeled aeration rate ($-1.69 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$) was consistent with the result obtained with direct gas injection ($-1.60 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$). An assumption of the model is a constant respiration quotient, but results indicated that the respiration quotient may be time variable. Sensitivity analysis indicated that application of the OC method is limited to reaches with a suitable change in combined O₂ and CO₂ concentration $\geq \sim 4 \mu\text{mol/L}$ and combined O₂ and CO₂ saturation deficits $\approx 4 \mu\text{mol/L}$, characteristic of smaller gaining streams. Preliminary application of the OC method indicates it could be useful to practitioners interested in continuous measurement of gas-exchange rates.

Key words: stream metabolism, aeration rate, gas transfer, efflux, evasion, stream carbon flux, community respiration, submersible CO₂ sensor

Measurement of rates of gas exchange between streams and the atmosphere is fundamental for quantifying stream ecosystem processes including primary productivity and respiration (Cole et al. 1991, Mulholland et al. 2001) and for calculating catchment to global-scale C budgets (Cole et al. 2007, Raymond et al. 2013). Gas exchange is a model parameter for ecosystem and water-quality models of rivers and lakes concerned with biological O₂ demand (Tsvoglou and Neal 1976). However, it is commonly a model parameter with great uncertainty (Aristegi et al. 2009, Demars et al. 2015), which results in poorly constrained estimates of stream metabolism and related rates of net ecosystem

production (*NEP*), gross primary production (*GPP*), and community respiration (*CR*) (McCutchan et al. 1998, Riley and Dodds 2013). When evasion of CO₂ from rivers to the atmosphere is poorly constrained, large errors in regional and global C budgets are expected (Raymond and Cole 2001).

Many methods are used to estimate gas-exchange rates including direct injection of a semi-inert gas (Rathbun et al. 1978, Kilpatrick et al. 1989, Wanninkhof et al. 1990) and empirical relationships based on hydraulic parameters (Palumbo and Brown 2013). Other methods estimate gas-exchange rates from attributes of a time-series of dissolved

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O₂ (DO). For example, the nighttime regression method (Hornberger and Kelly 1975) estimates the aeration coefficient of O₂ (K_{DO}) from the change in DO during nighttime in relation to the change in O₂ saturation deficit (DO_{def}) when the influence of GPP can be neglected. Others use the offset in time between the DO maximum and the solar maximum to estimate K_{DO} (the delta method; Chapra and Di Toro 1991). Multiparameter inverse models that optimize model parameters, including CR , GPP and K_{DO} , have been applied to fit observed DO time-series (Holtgrieve et al. 2010, Birkel et al. 2013, Riley and Dodds 2013).

Of the above methods, all but direct gas injection generally are considered inadequate for studies of stream metabolism in well-aerated streams. Even top-performing empirical relationships to hydraulic parameters applied over a wide range of stream velocities and depths have expected errors of 40 to 50% (Palumbo and Brown 2013). Gas-transfer rates from other indirect methods have similar errors with median discrepancies of 65% between measured and modeled values (Riley and Dodds 2013, Demars et al. 2015). Indirect techniques perform best in productive waters with relatively low aeration rates, and assume substantial lengths of homogenous stream conditions (Chapra and Di Toro 1991, Reichert et al. 2009). For less productive waters, streams with high rates of gas transfer, or heterogeneous reach conditions, indirect methods are generally considered inadequate, and the aeration rate typically is measured through direct gas injection (Bott 2006). However, direct gas injection generally results in a point measurement of the aeration rate representative of conditions at the time of the injection. For prolonged studies under varying hydrologic conditions, multiple gas injections must be made over the range in stream discharge (Roberts et al. 2007). This requirement is logistically challenging and time consuming, so an alternative but robust method to estimate gas-exchange rates is of continued interest.

We present a new approach to measure aeration and stream metabolic rates continuously through the simultaneous measurement of DO and CO₂ at an up- and downstream station. A few investigators have used inorganic C to estimate stream metabolism in rivers (Wright and Mills 1967, Kelly et al. 1974, 1983, Thyssen and Kelly 1985, Crawford et al. 2014), but DO data generally have been used for better accuracy and ease of continuous measurement. Relatively new technology that enables direct measurement of dissolved CO₂ at an affordable price has changed this paradigm and now continuous dissolved CO₂ can be measured at comparable cost and accuracy to DO (Johnson et al. 2010, Yoon et al. 2016). Simultaneous measurement of DO and CO₂ allows direct computation of continuous gas-transfer rates, and stream metabolism by independent data sets. We termed these methods the OC method, and it is applicable to streams where assumptions of the 2-station method are valid, and both:

- 1) measurable offset in combined dissolved gas concentration ($\Delta DO + \Delta CO_2$) is present and
- 2) measurable combined saturation deficit (CO₂ saturation deficit + DO saturation deficit) is present.

Theory

The DO concentration in a well-mixed river can be modeled with a 1-dimensional solute-transport equation adapted from Bencala and Walters (1983) to include 1st-order gas transfer with the atmosphere and stream metabolism source and sink terms. The equation accounts for fluxes in and out of an infinitesimally thin, yet entirely well-mixed, cross-section of water considering dispersion (longitudinal mixing), advection (stream flow), lateral inflow (groundwater), aeration, and stream metabolism:

$$\begin{aligned} \frac{\partial DO}{\partial t} = & \overset{\text{Dispersion}}{\frac{1}{A_x} \frac{\partial}{\partial x} \left(A_x D \frac{\partial DO}{\partial x} \right)} - \overset{\text{Advection}}{\frac{Q}{A_x} \frac{\partial (DO)}{\partial x}} + \overset{\text{Lateral Inflow}}{\frac{q_l}{A_x} (DO_l - DO)} \\ & + \overset{\text{Aeration}}{\frac{w K_v DO_{def}}{A_x}} + \overset{\text{Stream metabolism}}{\frac{(GPP + CR)p}{A_x}} \end{aligned} \quad (\text{Eq. 1})$$

where A_x is the stream channel cross-sectional area, D is dispersion, Q is discharge, q_l is lateral inflow of groundwater and hillslope water per unit stream length, w is stream width, K_v is gas transfer velocity, and p is wetted perimeter ($\approx w$ for shallow channels). See Table 1 for a complete list of variable definitions.

Equation 1 is simplified by assuming that the influence of dispersion is negligible, a nearly ubiquitous assumption in stream metabolism and aeration studies (Knapp et al. 2015). Hensley and Cohen (2016) questioned this assumption through the analysis of a low-gradient spring-fed river, but found that estimates of the influence of dispersion were orders of magnitude less than the influence of aeration or metabolic fluxes at a high-gradient study site. The wK_v/A_x term is substituted by K_{DO} , and p/A_x is approximated by the average depth (z).

$$\begin{aligned} \frac{\partial DO}{\partial t} = & -v \frac{\partial DO}{\partial x} + \frac{q_l}{A_x} (DO_l - DO) + K_{DO} DO_{def} \\ & + \frac{(GPP + CR)}{z} \end{aligned} \quad (\text{Eq. 2})$$

The above partial differential equation is transformed using the method of characteristics into an ordinary differential equation in Lagrangian coordinates (Eq. 3), whereby one can envision moving downstream with a volume or parcel of water (Fischer 1972). In the Lagrangian frame

Table 1. Variable definitions.

Variable	Description	Units
DO	Dissolved O ₂ in stream	mol/L ³
DO _l	Dissolved O ₂ of lateral inflow (groundwater)	mol/L ³
DIC	Total dissolved inorganic C	mol/L ³
DIC _l	Total dissolved inorganic C of lateral inflow	mol/L ³
CO ₂	Dissolved CO ₂ in stream	mol/L ³
DO _{def}	Dissolved O ₂ deficit	mol/L ³
CO _{2def}	Dissolved CO ₂ deficit	mol/L ³
EC	Electrical conductivity	μS/cm
<i>t</i>	Time	T
τ	Mean travel time through reach	T
<i>L</i>	Reach length	L
<i>z</i>	Mean water depth	L
<i>w</i>	Mean width	L
<i>p</i>	Wetted perimeter	L
<i>A</i>	Streambed area	L ²
<i>A_x</i>	Cross-sectional area	L ²
<i>v</i>	Stream velocity	L/T
<i>Q</i>	Stream discharge	L ³ /T
<i>Q_l</i>	Lateral inflow	L ³ /T
<i>D</i>	Longitudinal dispersion	L ² /T
<i>q_l</i>	Lateral inflow per unit stream length	L ² /T
<i>SF</i>	Spatial factor for computation of optimal reach length	–
<i>E</i>	Measurement error	mol/L ³
<i>K_c</i>	Coefficient of gas transfer for gas <i>c</i> . Subscript may be DO, CO ₂ , propane, or left as <i>c</i> if unspecified.	1/T
<i>K₆₀₀</i>	Coefficient of gas transfer for O ₂ at 17°C	1/T
<i>K_v</i>	Gas-transfer velocity	L/T
<i>n</i>	Exponent for calculation of β from <i>Sc</i>	–
<i>Sc</i>	Schmidt number, relation of viscosity to molecular diffusion	–
β	Ratio of <i>K_{CO2}</i> to <i>K_{DO}</i>	–
<i>IAP</i>	Ion activity product	–
<i>SI</i>	Saturation index	–
<i>K_{sp}</i>	Solubility constant	–
<i>NEP</i>	Net ecosystem production measured as amount of O ₂ produced	M L ⁻² T ⁻¹
<i>CR</i>	Community respiration measured as amount of O ₂ produced	M L ⁻² T ⁻¹
<i>G</i>	Gross primary productivity measured as amount of O ₂ produced	M L ⁻² T ⁻¹
<i>RQ</i>	Respiratory quotient measured as amount of CO ₂ released to O ₂ absorbed	–
<i>PQ</i>	Photosynthetic quotient measured as amount of O ₂ released to CO ₂ absorbed	–

of reference, all aspects of a volume of water, including chemistry, are a function of time, not space.

$$\frac{\Delta DO}{\tau} = \frac{Q_l}{zA} (DO_l - DO) + K_{DO} DO_{def} + \frac{(GPP + CR)}{z} \quad (\text{Eq. 3})$$

An Euler approximation also is made by substituting ∂t with τ , the mean travel time through the reach. ΔDO represents the change in DO from the up- to downstream ends of a study reach. q_l/A_x when scaled up from a thin cross-channel section to an entire reach is equivalent to Q_l/zA where Q_l is total lateral inflow into the reach and A is total streambed area. Equation 3 is consistent with

equations for stream metabolism with groundwater inflow by Hall and Tank (2005).

We developed a transport model of dissolved inorganic C (DIC) similar to the DO model in Eq. 3 and consistent with that formulated by Kelly et al. (1974):

$$\frac{\Delta DIC}{\tau} = \frac{Q_l}{zA} (DIC_l - DIC) + K_{CO_2} CO_{2def} - \frac{(GPP/PQ + RQ CR)}{z} \quad (\text{Eq. 4})$$

In this equation, the aeration flux is driven by the CO₂ saturation deficit (CO_{2def}), but concentration is DIC. DIC includes dissolved CO₂ gas, H₂CO₃, HCO₃⁻, and CO₃²⁻. We collectively refer to dissolved CO₂ gas and H₂CO₃ as CO₂. The respiratory quotient (RQ) is the molar ratio of CO₂ released to O₂ used in respiration. The photosynthetic quotient (PQ) is the molar ratio of O₂ released to CO₂ used in photosynthesis. In the production or metabolism of simple carbohydrates PQ and RQ are both 1. For other organic molecules, RQ and PQ are generally assumed to range from 0.8 to 1.2 (del Giorgio and Williams 2005), and Bott (2006) recommended a value of 0.85 for RQ and 1.2 for PQ. The reciprocal of 0.85 is 1.18, a value quite close to 1.2. Therefore, we assume ¹/PQ = RQ.

$$\frac{1}{RQ} \frac{\Delta DIC}{\tau} = \frac{1}{RQ} \frac{Q_l}{zA} (DIC_l - DIC) + \frac{1}{RQ} K_{CO_2} CO_{2def} - \frac{(GPP + CR)}{z} \quad (\text{Eq. 5})$$

In pursuit of the aeration rate, and after rearranging to solve for the stream metabolism term $\frac{(GPP+CR)}{z}$, Eq. 5 for DIC transport is combined with the transport equation for DO (Eq. 3), and the stream metabolism terms cancel out:

$$\frac{\frac{\Delta DIC}{RQ} + \Delta DO}{\tau} = \frac{Q_l}{zA} \left(\frac{(DIC_l - DIC)}{RQ} + DO_l - DO \right) + K_{DO} \left(\frac{\beta}{RQ} CO_{2def} + DO_{def} \right) \quad (\text{Eq. 6})$$

The coefficient β relates K_{DO} to K_{CO₂}. The gas-transfer velocity of 2 gases is commonly related by a friction-velocity model (Bennett 1972, Jähne et al. 1987).

$$\beta = \frac{K_{CO_2}}{K_{DO}} = \left(\frac{Sc_{CO_2}}{Sc_{DO}} \right)^{-n} \quad (\text{Eq. 7})$$

Temperature-dependent Schmidt numbers (Sc) can be calculated from regression coefficients provided by Raymond et al. (2012).

Equation 6 is rearranged to solve for K_{DO}. The resulting equation (Eq. 8) is the generalized form of the OC method

and includes a change term, a lateral inputs term, and deficit term.

$$K_{DO} = \left(\frac{\frac{\Delta DIC}{RQ} + \Delta DO}{\tau} - \frac{Q_l}{zA} \left(\frac{(DIC_l - DIC)}{RQ} + DO_l - DO \right) \right) \left/ \left(\frac{\beta}{RQ} CO_{2def} + DO_{def} \right) \right. \quad (\text{Eq. 8})$$

The temporal resolution of the input variables will define the temporal resolution of the output. A continuous estimate of K_{DO} is made with time-series of DO, DIC, and CO₂ and estimates of hydraulic and geometric terms (that may generally be related to stream discharge). However, Eq. 8 also could be used with point measurements of DO, DIC, and CO₂ in time, in which case the output would consist of discrete point estimates of K_{DO}.

The ratio of the lateral inputs term to the longitudinal change in concentrations term of Eq. 8 can be used to assess the relative importance of groundwater/hillslope water to estimates of K_{DO} from OC. If this ratio is <~10%, Eq. 8 may be simplified by assuming that lateral inflows and outflows are negligible:

$$K_{DO} = \left(\frac{\frac{\Delta DIC}{RQ} + \Delta DO}{\tau} \right) \left/ \left(\frac{\beta}{RQ} CO_{2def} + DO_{def} \right) \right. \quad (\text{Eq. 9})$$

However, the value of the lateral inputs term may be difficult to define because both the inflow rate and chemistry of groundwater are often poorly constrained.

In low-alkalinity waters (alkalinity < 500 μeq/L), common in geologic settings without limestone and other carbonate type rocks, ΔDIC can be substituted by ΔCO₂. This substitution is possible because the relation of CO₂ to DIC is nearly 1 : 1 over a large range of CO₂ concentrations (Appendix S1, Figs S1, S2). $\frac{\Delta DIC}{\Delta CO_2}$ is ~1 for low-alkalinity water, particularly at higher CO₂ concentrations. However, for waters with alkalinity >500 μmol/L, we do not recommend substituting ΔCO₂ for ΔDIC. Under these circumstances DIC should be measured or calculated from 2 of the following concentrations: pH, CO₂, alkalinity, HCO₃⁻, and CO₂³⁻ (Stumm and Morgan 1996). However, practical challenges exist to collection of accurate carbonate chemistry data.

Further caution is recommended for streams draining watersheds with abundant carbonate type rocks, or clastic rocks with carbonate cement that may result in waters being at or near saturation with respect calcite, aragonite, dolomite, and other carbonates. At such sites, changes in dissolved CO₂ and DIC through the reach may occur not only from repartitioning of inorganic carbonate species, stream

metabolism, and aeration, but also from precipitation and dissolution (Barnes 1965, Spiro and Pentecost 1991). Tobias and Böhlke (2011) found that 40% of US Geological Survey stream-monitoring stations in the contiguous USA were at or above the equilibrium saturation state for calcite. The OC method, as formulated in our study, should not be applied for water at or above solid-phase saturation. Under continuously or intermittently saturated conditions with respect to solid-phase carbonates, additional kinetic terms for precipitation and dissolution are necessary (Lorah and Herman 1988, de Montety et al. 2011, Tobias and Böhlke 2011, Khadka et al. 2014).

METHODS

Study site

The study was conducted at a 60-m-long study reach on McRae Creek in the H. J. Andrews Experimental Forest and Long-Term Ecological Research (LTER) site, Oregon, USA (HJA) during baseflow conditions. The reach had a slope of 3%, boulder and cobble substrate, contributing drainage area of 15.3 km², and site elevation of 560 m asl. The study reach was selected with the expectation that complicating factors including lateral inflow were small. No distinct cascades or riffles were present, and the stream could be classified as plane-bed (Montgomery and Buffington 1997). Abundant riparian forest of alder and mixed conifer provided roughly 30% shade to the channel at midday. Water was of low alkalinity and low ionic strength with a background electrical conductivity (EC) of ~30 μS/cm. The bedrock of the catchment is entirely volcanic in origin with no mapped carbonate rock units (Swanson and James 1975).

Measurements

We conducted stream metabolism measurements 11–14 August 2015 by monitoring DO and CO₂ concentrations up- and downstream following the 2-station open-channel method (Marzolf et al. 1994, 1998, Young and Huryn 1998). We conducted a constant-rate coinjection of NaCl tracer and propane gas on 11 August 2015. We calculated discharge, mean travel time, and mean velocity from the conservative-tracer breakthrough curves (Kilpatrick and Cobb 1985) with EC as a surrogate for concentration (Appendix S1). We measured wetted channel width at 10 locations evenly spaced through the reach, and averaged measurements to give mean channel width. On day 1 of the study, we collected 2 replicate 250-mL water samples at the top and bottom of the reach for alkalinity analysis (Appendix S1).

We measured and logged EC, CO₂ concentration, DO, and temperature, at the up- and downstream ends of the reach with WTW (Weilheim, Germany) Cond 3310 meters (EC), modified Vaisala (Vantaa, Finland) CARBOCAP GMM220 CO₂ sensors (Johnson et al. 2010) wired to Campbell Scientific (Logan, Utah) data loggers (CO₂)

and YSI 600 OMS-V2 sondes (model 6150 ROX DO; Yellow Springs Instruments, Yellow Springs, Ohio; DO and temperature). We attached sensors to the bottom of floats to maintain a consistent water depth. We calibrated sensors in the laboratory before and after deployment to check for drift and cross-calibrated them in the field to check for differences between sensors (Appendix S1). No sensor drift was observed through the measurement period.

We calculated O₂ saturation for each time-step according to equations detailed by Weiss (1970) and used barometric pressure recorded at the HJA PRIMET station (4.9 km down-valley at 430 m asl) and transformed to the elevation of the study reach (560 m asl) (USGS 1981). CO₂ data were post-processed and converted to partial pressure CO₂ (*p*CO₂) according to barometric pressure, water temperature, and water depth per Johnson et al. (2010).

We calculated DIC and CO₂ from the continuous record of *p*CO₂ and mean alkalinity of point samples with CO2SYS (version 1.1; coded in Matlab; Lewis and Wallace 1998) and temperature-dependent equilibrium constants published by Millero (1979). To estimate dissolved CO₂ at saturation, necessary to compute *CO*_{2def} we assumed a constant value of 400 μatm for atmospheric CO₂ concentration, equal to the global annual mean CO₂ concentration for 2015 (NOAA 2016).

Assumptions and model validation

We calculated *K*_{DO} by the OC method with Eq. 9, which assumes negligible lateral inputs of groundwater. We explored potential bias related to this assumption. *K*_{DO} was often converted to *K*₆₀₀, the aeration coefficient of O₂ at 17°C when water has an *Sc* value of 600, by Eq. 7 and temperature-dependent *Sc* from regression coefficients provided by Raymond et al. (2012).

We estimated the gas-transfer coefficient independently of the OC method by co-injecting propane gas into the stream with an air-stone and a salt tracer to correct for dilution. We collected 6 gas samples at each of 3 stations along the reach during steady-state and analyzed them within 24 h on an Agilent (Santa Clara, California) 7890A gas chromatograph system. We calculated the value of the gas-transfer coefficient for propane (*K*_{propane}) from the decline in dilution-adjusted propane concentration following Tsivoglou and Neal (1976) and Kilpatrick et al. (1989):

$$K_{propane} = \frac{1}{\tau} \ln \left[\frac{Propane_{upstream} EC_{downstream}}{Propane_{downstream} EC_{upstream}} \right]. \quad (\text{Eq. 10})$$

We used Eq. 7 and the *Sc* calculated from regression coefficients provided by Raymond et al. (2012) to convert *K*_{propane} to *K*_{DO}.

To ensure that stream water was undersaturated with respect to carbonate minerals, we calculated calcite

(CaCO₃) and dolomite (CaMg(CO₃)₂) saturation indices using solubility constants (*K_{sp}*) published by Plummer and Busenberg (1982) and Sherman and Barak (2000), respectively. The saturation index (SI) of a given mineral is equal to the logarithm of the ratio of the ion activity product (IAP) to the mineral's *K_{sp}*. A positive SI indicates the mineral is oversaturated and precipitation is thermodynamically favored, whereas a negative SI indicates that the mineral is undersaturated and the dissolution of the mineral is thermodynamically favored. IAP at low concentrations is approximated by the product of concentrations (e.g., for calcite, IAP = [Ca²⁺][CO₃²⁻]). We obtained [Ca²⁺] and [Mg²⁺] during August 2015 from the HJA long-term chemistry data set at Lookout Creek (Johnson and Fredriksen 2016).

To check whether our assumption of a constant RQ = 0.85 was reasonable, we rearranged Eq. 9 to solve for RQ and used *K_{DO}* obtained from direct gas injection:

$$RQ = (\tau\beta K_{DO}CO_{2def} - \Delta DIC) / (\Delta DO - \tau K_{DO}DO_{def}) \quad (\text{Eq. 11})$$

To check whether our assumption of constant 400 μL/L atmospheric CO₂ was reasonable, we rearranged Eq. 9 to solve for CO_{2def}, then converted CO_{2def} to partial pressure atmospheric CO₂.

Error analysis

We used a Monte-Carlo approach to estimate the confidence intervals of modeled *K_{DO}* based on the OC method. For each input parameter and constant of the Monte-Carlo model, we estimated a 95% confidence interval (CI). DO and CO₂, temperature, and travel time were all given an error of 1%. Atmospheric CO₂, alkalinity, and β values were given an error of 5%, and RQ was given an error of 10%. We assumed variables were normally distributed and independent. We assumed errors were systematic, rather than random. For time-series with thousands of data points, random errors (noise) tend to be insignificant to summary results. In contrast, systematic errors can alter summary results substantially (Révész 1967, Kadmon et al. 2003). A systematic error of +1% for temperature means that all values of temperature in the time-series are 1% higher than the measured value for that model run. We coded model equations in Matlab and evaluated 10,000 model runs. The model calculated and saved *K_{DO}* for each time-step of each 1 run. After all model runs were complete, 2.5, 50, and 97.5 percentiles from the results were computed for each time-step to estimate the *K_{DO}* 95% CI.

Analysis of sensitivity to site conditions

To create a rough guideline for application of the OC method, we performed a sensitivity analysis of the OC method

to the longitudinal change in the combined DO and DIC concentrations through the study reach and to the reach-averaged combined DO and CO₂ deficits. We used simple rules of error propagation for addition and division on Eq. 9 and assumed error was primarily attributed to measurement errors of DO and CO₂. For a more complete error analysis, we advise using a Monte-Carlo method based on site-specific data and error distributions of all input parameters (discussed above). We assumed that CIs were ~±0.1 μatm for DO and ±20 μatm CO₂. When converted into consistent molar units, error (*E*) for both the combined longitudinal change in concentrations (ΔDIC + ΔDO) and combined deficit (CO_{2def} + DO_{def}) terms were ~4 μmol/L. We approximated the % error of *K_{DO}* by the OC method as:

% error *K_{DO}* by OC

$$\approx 100 \left(\frac{E}{\Delta DIC + \Delta DO} \pm \frac{E}{CO_{2def} + DO_{def}} \right) \quad (\text{Eq. 12})$$

For the purpose of considering where best to apply the OC method, we calculated % error by Eq. 12 over a range of possible reach conditions.

Stream metabolism

We calculated *NEP* with the 2-station open-channel method, accounting for the influence of lateral inflow (Odum 1956, Marzolf et al. 1994, 1998, McCutchan et al. 2002, Hall and Tank 2005), assuming that *CR_{nighttime}* = *NEP_{nighttime}* and that *CR_{nighttime}* = *CR_{daytime}*. We applied various combinations of aeration-rate and stream-chemistry data, including *K_{DO}* from propane injection with either DO or carbonate data sets or *K_{DO}* from OC with either DO or carbonate data sets:

$$NEP_{from\ DO} = z \left(\frac{\Delta DO}{\tau} - K_{DO}DO_{def} \right) - \frac{Q_l}{A} (DO_l - DO) \quad (\text{Eq. 13})$$

or

$$NEP_{from\ C} = \frac{[-z(\frac{\Delta DIC}{\tau} - K_{CO2}CO_{2def}) + \frac{Q_l}{A}(DIC_l - DIC)]}{RQ} \quad (\text{Eq. 14})$$

NEP from DO or C are both in units of DO produced per unit area per unit time. We calculated instantaneous *NEP* for each 5-min time-step. For summary results, we averaged instantaneous *NEP*, *CR*, and *GPP* for each day, then over the 4-d period.

We generally assumed that lateral inflows were 0, but we used the ratio of the lateral inputs term to aeration/advection to *NEP* estimates.

RESULTS

Hydraulic conditions

Our study was conducted during steady summer base-flow conditions over a 72-h period (11–14 August 2015). Dilution gauging on August 11 measured Q as 17.0 L/s at the downstream end of the 60-m-long reach and 17.7 L/s at a point 140 m farther downstream. Day (1976) found that median errors for dilution gauging ranged from 4.7 to 7.3%. Thus, measured increase in streamflow of 4% over the 140-m distance was within the error of Q measurements. Median travel time between the up- and downstream DO and CO₂ sensors was 13.7 min, median channel width was 4.5 m, and mean depth was 5.2 cm. No precipitation events occurred over the study period, nor had any rain fallen for weeks prior to the experiment, resulting in steady flow conditions through the study period. US Geological Survey gauging station 14161500, 5 km downstream of the study site on Lookout Creek, recorded no change in streamflow through the study period. Thus, hydraulic conditions for 11–14 August were well-represented by the 11 August propane/solute injection.

We calculated a dimensionless spatial factor ($SF = LK_{DO}/v$), where L was reach length, to assess the potential influence of L and spatial heterogeneity on our results (Reichert et al. 2009). Optimum reach lengths have SF values between 0.4 and 1. Applying the aeration rate from direct gas injection (2.88 L/h; see below) we estimated $SF = 0.66$, indicating effective station spacing.

Time-series data

Time-series data for temperature, solar radiation, DO, CO₂, and DIC showed expected diel fluctuations (Fig. 1A–C), but % saturation of CO₂ was high compared to DO (Fig. 1B). DO curves roughly resembled incoming solar radiation with a defined peak near solar noon close to 100% saturation and a broad, flat trough through the night at ~95% saturation (Fig. 1A, B). CO₂ and DIC concentration curves followed an inverse DO pattern and, unlike DO, concentrations were far from saturation with the atmosphere (Fig. 1C). CO₂ concentrations ranged between 250 and 450% saturation, and at midday, when DO was near equilibrium with the atmo-

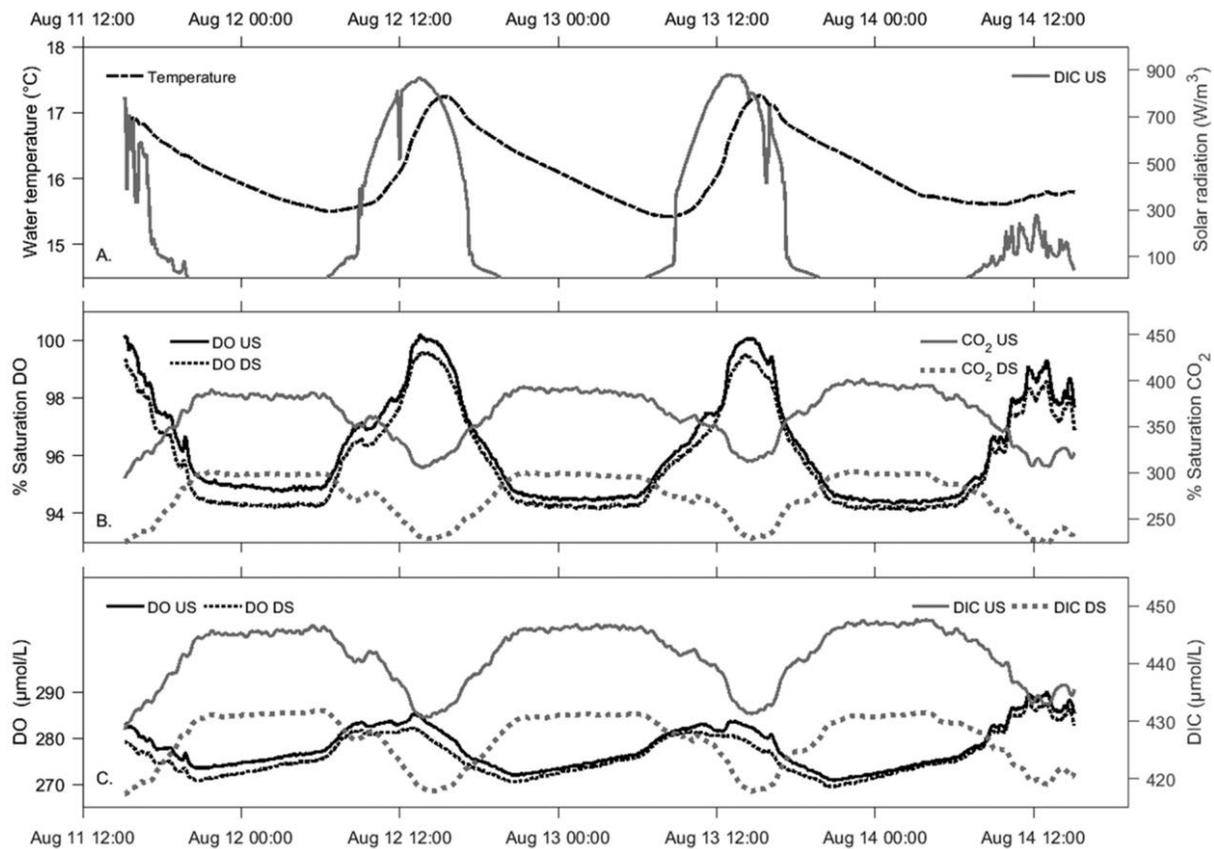


Figure 1. Upstream (US) and downstream (DS) changes in water temperature, solar radiation, and streamflow (A); dissolved O₂ (DO) and CO₂ saturation (B); and DO and dissolved inorganic C (DIC) concentration (C) during the study period. Water temperature record shows a diel fluctuation that lags behind incoming solar radiation. CO₂, DO, and DIC curves follow expected diel patterns attributable to photosynthesis and respiration. Note the large change in DIC from up- to downstream compared with change in DO. This difference in behavior is necessary to constrain errors of the O₂-C (OC) method. US = upstream, DS = downstream.

sphere, CO_2 was at a minimum but still well above saturation.

DO concentration was consistently higher up- than downstream with mean offset of $1.7 \mu\text{mol O}_2/\text{L}$ ($0.05 \text{ mg O}_2/\text{L}$), but this apparent offset was within sensor error. CO_2 and DIC concentrations were consistently higher up- than downstream with a mean offsets of $14.4 \mu\text{mol C/L}$ (0.17 mg C/L) and $14.6 \mu\text{mol C/L}$ (0.17 mg C/L), respectively, which were an order of magnitude larger than the observed change in DO. Changes in CO_2 and DIC were nearly identical, an expected result given the low alkalinity and relatively high CO_2 concentration of the stream (Figs S1, S2).

Aeration rates and model validation

Based on our estimates of uncertainty, we found no meaningful differences between aeration estimates from the OC method and direct tracer-addition studies (Fig. 2). K_{600} from propane injection was $3.2/h \pm 1.2\%$, whereas mean estimated K_{600} from OC was $3.3/h \pm 0.7\%$ (Fig. 3A). The mean estimates were nearly identical and well within

confidence bounds. Instantaneous estimates of K_{600} by OC showed a clear diel fluctuation of $\sim 30\%$ ($0.7/h$). The values had a repeating diel structure with a steady value through the night, a minimum near solar noon, and a maximum in late afternoon.

Alkalinities measured from samples collected 11 August at the up- and downstream ends of the study reach were equal ($382 \mu\text{eq/L}$). EC was relatively steady through the study period ($\pm 2 \mu\text{S/cm}$), and we assume that alkalinity was constant through the study period because of the strong correlation between alkalinity and EC for streams at the HJA ($R^2 = 0.95$ for Lookout Creek; Johnson and Fredriksen 2016). Nevertheless, we built a 5% error for alkalinity into the error analysis.

Calcite and dolomite concentrations were well below equilibrium saturation state ($\text{SI} = -1.57$ and -2.6 , respectively). The bedrock of the HJA is entirely volcanic, with low rates of chemical weathering relative to water-residence time (Fredriksen et al. 1982). The apparent result that solute concentrations are below equilibrium saturation states supports the assumption that precipitation and dissolution fluxes are negligible in regard to reach-scale processes.

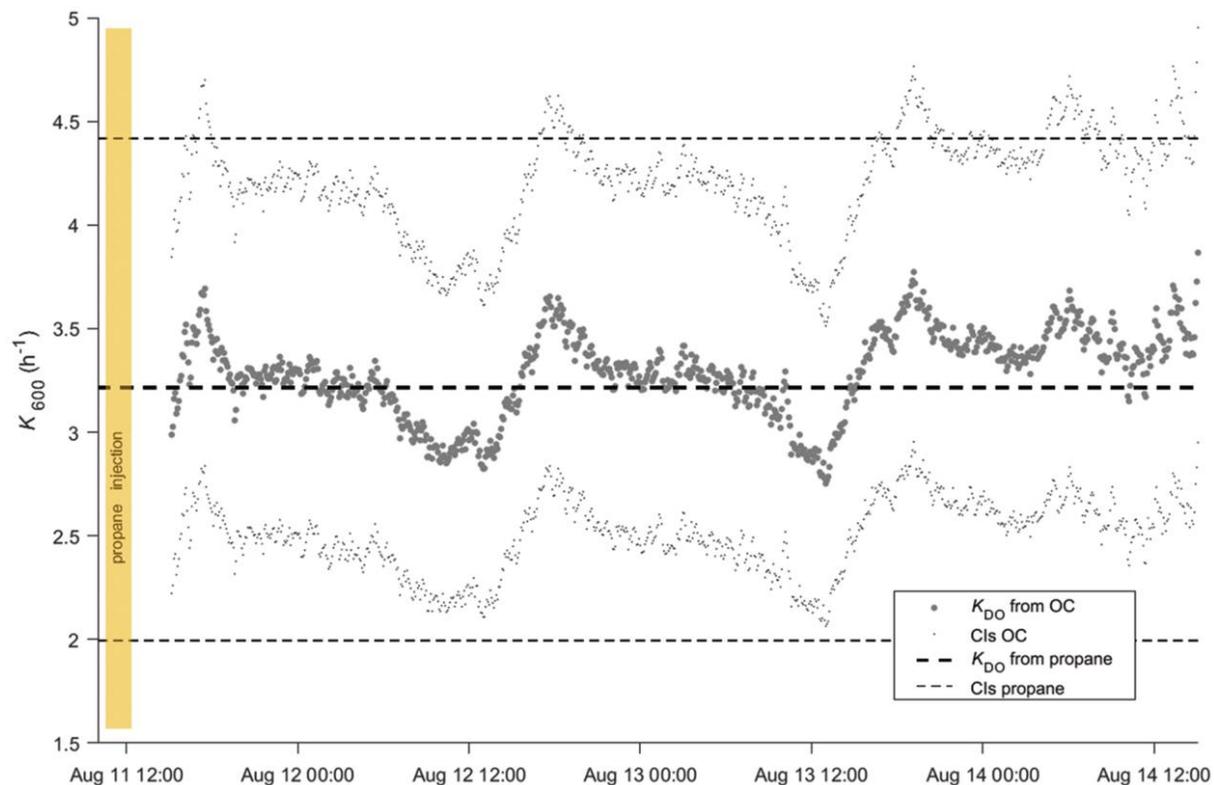


Figure 2. Mean (95% CI) K_{600} (aeration coefficient of O_2 [K_{DO}]) corrected to 17°C from the O_2 -C (OC) method and from propane injection. K_{600} from propane is extrapolated from a 1.5-h steady-state gas injection that was performed prior to the beginning of the time-series conducted on 11 August. Estimates of K_{600} by the 2 methods are in general agreement. However, the diel structure of the OC method indicates that transient factors, such as wind, are important to the diel signal or assumed constants (respiratory quotient, photosynthesis quotient, and atmospheric CO_2) change through the day and affect modeled aeration rates.

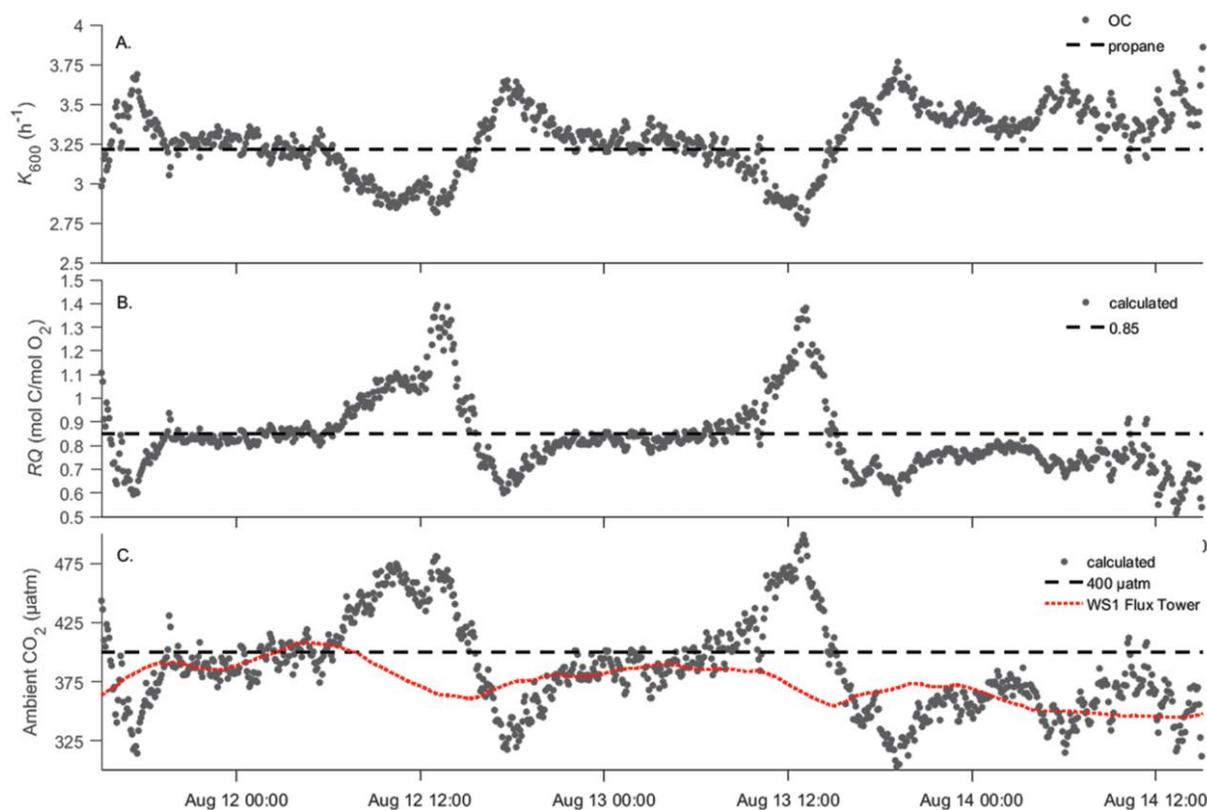


Figure 3. A.— K_{600} (aeration coefficient of O_2 [K_{DO}] corrected to $17^\circ C$) from the O_2 -C (OC) method, calculated assuming a respiratory quotient (RQ) = 0.85 and atmospheric CO_2 = 400 $\mu L/L$, demonstrating diel structure with minimum near midday and maximum in later afternoon. B.— RQ calculated assuming constant K_{DO} from propane injection and atmospheric CO_2 = 400 μatm . Calculated RQ had a diel structure with large maximum through the day and minimum in late afternoon. Given that hydraulic conditions were steady and calculated CO_2 was inconsistent with measured values, we suspect diel structure of K_{600} was related to variation in metabolic rates and parameters, including RQ . C.—Atmospheric CO_2 calculated assuming a constant K_{DO} from propane injection and RQ = 0.85 and atmospheric CO_2 concentration measured at the flux tower at Watershed 1, H. J. Andrews Experimental Forest (HJA). The calculated and measured values were in general agreement at night, but deviated substantially during the day.

We calculated RQ for every time-step based on K_{DO} from the propane injection and ambient CO_2 (400 μatm ; Fig. 3B). The mean calculated RQ was 0.83 and the median was 0.81, suggesting that the assumed value of 0.85 was generally appropriate. However, calculated RQ presented diel fluctuations. RQ was ~ 0.85 through the night, rose rapidly to a maximum of 1.5 near midday, when K_{600} based on the OC method was at a minimum, and dropped to a minimum of ~ 0.6 around 1800 h, when K_{600} by the OC method was at a maximum.

Calculated atmospheric CO_2 followed a similar pattern (Fig. 3C). The calculated CO_2 remained close to 385 μatm through the first 2 nights, with peaks of up to 500 μatm near midday, when K_{600} by the OC method was at a minimum. After the midday peak, calculated ambient CO_2 dropped to a minimum of ~ 325 μatm at ~ 1800 h. The mean calculated ambient CO_2 was 386 μatm and median was 382 μatm , suggesting the assumed value of 400 μatm was ~ 15 μatm too high. Measured CO_2 concentrations at

Watershed 1, HJA, a tributary stream 5 km downstream, showed similar concentrations.

OC method sensitivity to site conditions

We tested model sensitivity to longitudinal change in combined CO_2 and DO, and combined CO_2 and DO saturation deficits to help define suitable conditions for application of the OC method (see Eq.12). When either the combined change or the combined deficit was ≤ 4 $\mu mol/L$, the 95% CI in modeled K_{DO} increased rapidly to values $>100\%$ (Fig. 4). The study reach selected for this proof-of-concept study had a large longitudinal change in DIC (mean = 14.6 $\mu mol C/L$ or 350 μatm) compared with change in DO (mean = 1.7 $\mu mol O_2/L$). The mean combined change in DO + DIC was 16.0 $\mu mol/L$. The mean combined deficit was 25 $\mu mol/L$. Thus, the study reach was well suited for the OC method with a 95% CI = $\sim 41\%$ according to Eq. 12. This value was higher than estimated through our Monte-Carlo analysis (22%).

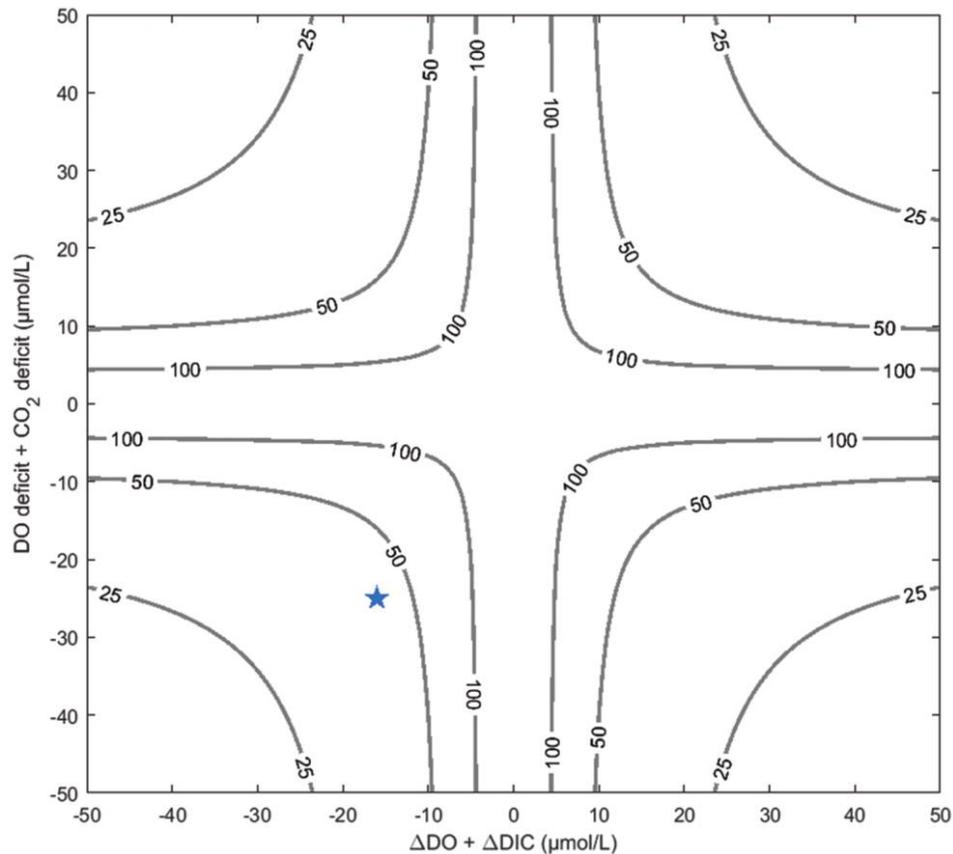


Figure 4. Approximate % error for K_{DO} (aeration coefficient of O_2) by the O_2 -C (OC) method contoured over a range of possible combined gas gradients (x -axis) and combined gas deficits (y -axis). Errors are $>100\%$ if either the combined change or the combined deficit term is $<4 \mu\text{mol/L}$. The star indicates average conditions for our study.

Stream metabolism

Stream metabolic metrics estimated for various combinations of aeration rates with DO and CO_2 data sets were relatively consistent (Table 2). All estimates of NEP were negative, indicating the reach was net heterotrophic. Ranges were -1.56 to $-1.69 \text{ g } O_2 \text{ m}^{-2} \text{ d}^{-1}$ for NEP , -2.00 to $-2.15 \text{ g } O_2 \text{ m}^{-2} \text{ d}^{-1}$ for CR , and 0.44 to $0.46 \text{ g } O_2 \text{ m}^{-2} \text{ d}^{-1}$ for GPP . Note that stream metabolic rates based on K_{DO} from the OC method gave identical results regardless of whether DO or CO_2 data sets were used. This result is inherent to the OC method, which solves for aeration rate by canceling out the stream metabolism terms.

Influence of lateral inflow

Lateral inflow of hillslope/groundwater to the study reach was estimated to be $<2\%$ of stream flow. Q measured at the downstream end of the study reach and a point 140 m farther downstream indicated a lateral inflow rate of $0.005 \text{ L s}^{-1} \text{ m}^{-1}$, a 4% increase in stream flow over this distance. The increase in stream flow was within the error of gauging measurements, but for consideration of the influence of lateral inflow, we assumed it was real. Over the

60-m study reach, lateral inflow was estimated to be 0.3 L/s (1.8% of stream flow). If stream flow was proportional to contributing area, it would have increased by 0.09 L/s (0.5%).

Based on expected lateral inflow rates and chemistry, potential bias to stream metabolic rates attributed to lateral inflows was moderate when based on DO data and large when based on C data. In contrast, lateral inflows had little influence on K_{DO} estimated by the OC method. DO and CO_2 concentrations of groundwater/hillslope waters were not measured at the study site. However, $DO < 5 \text{ mg/L}$ has rarely been observed in hillslope/groundwater-dominated piezometers at nearby Watershed 1, and observed DO is usually closer to saturation (S. Serchan, Oregon State, unpublished data). We applied values of 5 mg DO/L and 0.3 L/s lateral inflow and found a mean NEP correction factor of -28% , a value we consider moderate. Maximum values of DIC observed in the same piezometers were $\sim 9.4 \text{ mg C/L}$, equivalent to equilibrium with $10,000 \mu\text{atm } CO_2$ at 16°C and alkalinity of $382 \mu\text{eq/L}$ (Corson-Rikert et al. 2016). Applying a value of 9.4 mg DIC/L and 0.3 L/s lateral inflow, we found a mean NEP correction factor of -99% , a value we consider large. A

Table 2. Mean stream metabolism estimates for the period 11–14 August 2015 obtained by 4 different combinations of data. Positive values indicate production of O_2 , and consumption of C . K_{DO} from the propane injection and instantaneous values calculated from the OC method were applied independently to DO and CO_2 time-series. Estimates from CO_2 time-series assume $RQ = 1/PQ = 0.85$. Stream metabolism rates NEP , CR , and GPP are in general agreement by all pairs of data and applied gas exchange rate. See Table 1 for abbreviations.

Aeration rate origin	Time-series used as input	NEP (g O_2 m ⁻² d ⁻¹)	CR (g O_2 m ⁻² d ⁻¹)	GPP (g O_2 m ⁻² d ⁻¹)
OC method	DO ^a	-1.69	-2.15	0.46
OC method	CO_2 ^a	-1.69	-2.15	0.46
Propane injection	DO	-1.64	-2.09	0.45
Propane injection	CO_2	-1.56	-2.00	0.44
Mean		-1.63	-2.08	0.45

^a Stream metabolism rates obtained using K_{DO} from OC were identical whether DO or CO_2 data sets were used. This result is inherent to the OC method, which solves for aeration rate by canceling out the stream metabolism terms.

similar check can be made for K_{DO} by the OC method from the ratio of the lateral-inflow term to the longitudinal change in concentrations term in Eq. 8. After applying expected groundwater chemistries, we found a correction of only +1%. Thus, for our study site, the potential influence of lateral inflows to estimated rates of stream metabolism were moderate to large, but potential influence on the estimated aeration rate was small. However, correction factors may be sizeable at sites with relatively little lateral groundwater input, depending on water chemistry, and should be checked based on site-specific conditions.

DISCUSSION

We estimated the gas-transfer velocity and stream metabolic metrics of a 4th-order montane stream by applying the 2-station open-channel method for estimating stream metabolism combined with measurement of both DO and CO_2 . Estimated values of K_{DO} based on the OC method were consistent with and had similar CI to values obtained through the standard technique of direct gas injection.

An advantage provided by the OC method is the ability to monitor rates of gas transfer continuously over days to weeks to months in small streams without the need for multiple gas-tracer injections spread over the range in discharge. The nighttime regression method, the delta method, and multiparameter inverse-modeling methods also provide continuous estimates of gas-exchange rates, but work best in productive water bodies that have relatively low gas-transfer rates (Chapra and Di Toro 1991, Holtgrieve et al. 2010, 2016, Demars et al. 2015). Holtgrieve et al. (2016) clarified that inverse modeling is not limited to productive/low gas-transfer-rate waterbodies because the method relies on a dynamic DO signal, which may be driven by temperature fluctuation in place of photosynthesis, but sites with little fluctuation in the DO signal are difficult to model with confidence. Another important characteristic is that these methods provide a temporally averaged estimate of gas-transfer rate, commonly at a daily interval. The OC method differs

from methods that use attributes or inverse modeling of a DO time-series because it is best suited to low-order streams and provides instantaneous estimates of gas transfer rather than daily means. The OC method has no inherent limitation related to productivity or aeration rate. Thus, if site conditions permit, the OC method is suitable for extended monitoring at high temporal resolution, which enables observation of the influence of transient factors on stream metabolism including discharge, wind, and rain, among others.

Method application and limitations

The greatest limiting factor of the OC method is the need for a large longitudinal change in combined gas concentrations and combined gas deficits through the study reach. Combined concentration changes and combined deficits (defined in relation to Eq. 12) should both be $> \sim 4 \mu\text{mol/L}$ or CIs become large (Fig. 4). How frequently suitable longitudinal changes in concentration and deficit conditions occur and whether they persist throughout the year are not clear, but we expect them to be common to the Oregon Cascades and to gaining headwater streams and spring-fed systems in general. Stream CO_2 concentrations recorded in a 2nd-order stream 5.0 km downstream (Watershed 1, HJA) exhibited large longitudinal gas concentration gradients with differences in pCO_2 as high as 1000 μatm over tens of meters (Dosch 2014) and DO concentrations near saturation with little longitudinal change. Crawford et al. (2013) observed differences in pCO_2 up to 1000 μatm ($\sim 40 \mu\text{mol/L}$ or 0.5 mg C/L) over reach lengths of hundreds of meters throughout the year in an investigation of a boreal stream. We suspect that the elevated CO_2 concentrations that we observed in our study reach were caused by high-DIC lateral inflows *above* the upstream end of the study reach. Lateral inflows of hillslope/groundwater emerging at the transition from hillslope to riparian zone have been observed at the HJA. These inflows were supersaturated in CO_2 (with values 10–25 \times that of satu-

rated conditions (400 μatm) and had DO concentrations near saturation (Corson-Rikert et al. 2016). These seemingly contradictory concentrations are thought to be a result of soil and vadose-zone processes, where soil water equilibrates with the high- CO_2 and high- O_2 soil atmosphere typical of well-drained upland soils (Oh and Richter 2004, Zhou and Yiqi 2010). Thus, lateral inflow of hill-slope/groundwater provides a potential mechanism to create large combined gas concentration changes and deficits appropriate for the OC method.

The requisite combined gas-concentration change (ΔDIC and ΔDO) may preclude the application of the OC method based on the 1-station open-channel method. In our experience, concentration changes between time-steps (e.g., 10 min) at a single sensor location are typically small ($<1 \mu\text{mol/L}$). Thus, accurate estimates of aeration rates (given current sensor technology) with the OC method based on a single station would be unlikely. We did not test application of the single-station method, and the additional requirement for a suitably large combined gas-deficit term also may be limiting. In locations with suitably large and well-defined lateral inputs of groundwater, solving the equations in the OC method based on the single-station method might be possible. In this circumstance, the numerator and denominator terms of Eq. 8 may both be suitably large enough to constrain errors. However, a site-specific error analysis would be necessary to define uncertainty.

Accurate in situ measurements of DO and CO_2 are important to the OC method. Recent technological advancements allow maintenance-free deployment of sensors for weeks or even longer periods. Optical DO sensors have become increasingly robust, and minimal drift has been observed over periods of 2 to 3 wk (Johnston and Williams 2006). In-stream CO_2 sensors are a relatively young technology and less proven, but none of the multiple investigators who deployed submersible infrared gas analyzer (IRGA) CO_2 sensors in headwater streams for extended periods documented significant sensor drift (Johnson et al. 2010, Crawford et al. 2013, Leith et al. 2015). In more productive waters, biofouling may be problematic and frequent maintenance may be required. Yoon et al. (2016) recommended service every 3 to 5 d for sensors deployed in an urbanized river system in South Korea. When protected by Cu mesh the IRGA-type sensor-maintenance interval was extended to 1 to 2 wk. Thus, even in productive waters continuous monitoring of DO and CO_2 is possible. One additional limitation to CO_2 measurement for long-term deployment is that current technology needed for CO_2 measurement is energy intensive relative to for DO sensors. We found that a 35 amp-h deep-cycle battery allowed ~ 2 wk of data collection at a 5-min sampling interval when using a Vaisala CARBOCAP GMM220 CO_2 sensor wired to a Campbell Scientific CR200 data logger. By comparison, the relatively lightweight YSI 600 OMS-V2 sonde powered by AA alkaline batteries allowed 1 mo of sampling at 5-min

intervals. For remote sites and extended monitoring, transporting and maintaining charged batteries for CO_2 data collection may be a challenge.

Field recommendations

The OC method is viable for reaches with a relatively large combined gas concentration change and combined gas deficit when fluxes related to dissolution or precipitation of carbonates can be quantified or disregarded. Watershed geology may be helpful in considering potential for dissolution and precipitation fluxes. Characterization of SIs for calcite, dolomite, and other possible carbonate minerals is recommended. To this end, measurement of carbonate chemistry and knowledge of the expected range of $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, and other relevant solutes is necessary (Stumm and Morgan 1996). If near or above saturation with respect to a given carbonate mineral, then reformulation of the OC method derived in our paper to include precipitation or dilution fluxes would be necessary (de Montety et al. 2011). To verify that suitably large combined gas-concentration changes and combined gas deficits exist, we recommend a reconnaissance longitudinal survey of DO and CO_2 through the study reach before deciding to apply the OC method. Ideally, the longitudinal survey should be conducted in a Lagrangian frame by moving with the stream at the average water velocity, following and sampling a parcel of water. In practice, this type of survey may be difficult, so care should be taken to consider whether observed changes in combined concentration are representative of a discrete parcel of water (as they should be for application of the OC method). Submersible CO_2 sensors require ~ 10 min (dependent on water flow) to achieve 100% equilibration (Yoon et al. 2016).

Once a reach with a suitable longitudinal change in gas concentrations and deficits is found and selected, standard methods to measure reach hydraulics, including wetted width, travel time, stream gauging, and groundwater inflow, are necessary (Bott 2006). In our study, inclusion of relatively small lateral inflows of high-DIC groundwater, on the order of 1.7% of stream flow with 10,000 μatm CO_2 and 5 mg DO/L increased estimated aeration rates by only 1%. However, if lateral inputs had been 5% of stream flow, with a DO concentration at saturation with the atmosphere and 10,000 μatm CO_2 , the estimated aeration rate would have been 79% higher. Thus, accurate estimates of groundwater inflow and chemistry are important. Demars et al. (2011) noted that groundwater commonly does not enter a stream evenly distributed in space, but travels along preferential flow paths and enters the stream in spatially concentrated seeps. Spatial anomalies in EC during a plateau solute injection could indicate areas of lateral inflow. Longitudinal surveys of DO and CO_2 also may also be useful for detecting inflows of groundwater, but we know of no investigators who have

used this technique to evaluate lateral inflows. Conceptually, an abrupt increase in CO_2 could indicate high- CO_2 groundwater inflow.

DO and CO_2 sensors should be placed at the up- and downstream ends of the study reach. Ideally, a 3rd CO_2 sensor should be deployed in the air above the stream to measure atmospheric CO_2 concentrations. In our experience, well-calibrated and cross-checked sensors are very important. Calibration procedures for Vaisala-type CO_2 sensors were detailed by Johnson et al. (2010). We advise further cross-checks in the field before and after sampling. All CO_2 sensors should be hung together above the stream in the shade for 2 h, then placed together in the stream at the station with highest CO_2 concentration for another 2 h. These readings can be used to cross-check sensors across the range of CO_2 values. This process should be reversed at the end of the study, or intermittently, for long-term deployment.

In general, DIC also must be measured or calculated at the up- and downstream ends of the study reach. We made point measurements of alkalinity and assumed it was constant over the 4-d study period. For low-alkalinity waters $< \sim 500 \mu\text{eq/L}$, particularly if CO_2 concentrations are $\geq \sim 800 \mu\text{atm}$, $\Delta\text{DIC} \approx \Delta\text{CO}_2$ and calculation or measurement of DIC is unnecessary (Appendix S1). However, if this substitution is unwarranted, DIC can be calculated from CO_2 and pH, CO_2 and alkalinity, or another combination of 2 carbonate-related variables (Stumm and Morgan 1996).

Reach-scale metabolic quotients

The OC method has a number of assumptions related to environmental and biological processes that influence ratios of C to O_2 consumption and production. We assumed metabolic quotients $RQ = 1/PQ = 0.85$. This value was prescribed by Bott (2006) and supported by RQ values referenced by del Giorgio and Williams (2005) and PQ values referenced by Ryther (1956). RQ ranges from 0.5 for methane to 1.33 for glycolic acid for aerobic respiration, whereas simple sugars and carbohydrates have RQ values of 1.0. Values of RQ associated with anaerobic respiration including denitrification or fermentation are much higher, so reaches with substantial anaerobic respiration may have a larger RQ . To our knowledge, no values of metabolic quotients at the reach scale have been published, and recent studies pairing DO and CO_2 data have been based on assumed metabolic quotients of 1.0 (Roberts et al. 2007, Crawford et al. 2014, Hotchkiss et al. 2015). We found consistent rates of NEP , CR , and GPP from independent DO and data sets that support the applied RQ value of 0.85. Estimates of NEP based on C were 3.7% less than those based on DO. If $RQ = 1.0$ were applied, the discrepancy would increase to 18.5%.

We assumed constant RQ with respect to time. However, evidence suggests that RQ might change during the day. Modeled K_{600} had an unexpected diel signal given that stream flow was recorded as stable and the reach was sheltered from the wind. Assuming K_{600} was truly constant, the apparent signal could be attributed to time-variable RQ or atmospheric CO_2 . Calculated atmospheric CO_2 concentrations (assuming the aeration rate and other parameters were constant) were inconsistent with diel patterns observed at nearby Watershed 1 (Fig. 3C). Thus, we suspect that RQ is time variable. Calculated RQ (assuming the aeration rate and other parameters are constant) had a repeating diel structure with peak at midday and minimum in late afternoon (Fig. 3B). A number of recent investigators using $\delta^{18}\text{O}_2$ found large increases in respiration rates during the day (Tobias et al. 2007, Hotchkiss and Hall 2014). Increases in respiration are hypothesized to result from a combination of multiple processes including: 1) increased respiration of bioavailable C produced and released in association with photosynthesis (Kaplan and Bott 1982, del Giorgio and Williams 2005), 2) photorespiration (Raven and Beardall 2005), 3) photoreactions of organic C and respiration of newly produced of bioavailable by-products (Moran and Zepp 1997), and 4) increased respiration with temperature (Perkins et al. 2012). The variety of respiration pathways, photoreactions, and the potentially changing character of bioavailable C suggest that RQ would change through the day. Similar changes in respiration pathways and C character probably also occur seasonally. A lack of studies pertaining to RQ in riverine environments makes formation of a hypothesis regarding temporal dynamics of RQ difficult. Further study is certainly needed to better define metabolic quotients in stream systems at the reach scale.

Conclusion

Predicted gas-exchange rates by the OC method over a 3-d period during steady baseflow conditions were consistent with the measured aeration rate found through direct gas injection. The method is based on the dual measurement of DO and CO_2 according to general procedures of the commonly applied 2-station open-channel method for measurement of stream metabolism. Submersible CO_2 sensors are now common and inexpensive, making automated and continuous collection of DO and carbonate chemistry data easily attainable. Thus, the OC method can be easily applied to measure gas-exchange rates continuously in real time over extended periods if suitable reach conditions are present. The method hinges on the existence of a suitable downstream change in combined DO and CO_2 , a common condition in low-order streams of the Oregon Cascades. Our study provides added impetus for dual measurement of DO and CO_2 of streams for esti-

mation of gas exchange and characterization of C sources, processing, and transport. Our study is based on a single short-duration study of a single reach. We hope the greater community will implement and verify whether the OC method is broadly applicable, accurate, and convenient.

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