Estimating stream metabolism from oxygen concentrations: Effect of spatial heterogeneity

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[1]   Rivers are heterogeneous at various scales. River metabolism estimators based on oxygen time series provide average estimates of net oxygen production at the scale of a river reach. These estimators are derived for homogeneous river reaches. For this reason, they cannot be used to analyze how exactly they average over longitudinal variations in net production, reaeration, oxygen saturation concentration and flow velocity. We try to fill this gap by using a general analytical solution of the transport-reaction equation to (1) demonstrate how downstream oxygen concentration is affected by upstream concentration and (possible) longitudinally varying values of net production, reaeration, oxygen saturation concentration and flow velocity within a reach, and (2) derive how the net production estimate depends on varying upstream river parameters. In addition, we derive a new net production estimator that extends previously suggested estimators. The equations derived in this paper provide a general framework for understanding the assumptions underlying net production estimators. They are used to derive recommendations on the use of single station or two stations measurement layouts to get accurate river metabolism estimates. The estimator is implemented in the freely available statistics and graphics software package R (http://www.r-project.org). This makes it easily applicable to observed oxygen time series. Empirical evidence of the significance of heterogeneity in rivers is demonstrated by applying the estimator to four subsequent reaches of a river using oxygen measurements from the ends of all reaches.

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1.   Introduction

[2]   Primary production and respiration are key processes for turnover of organic matter, inorganic substances, and energy in a river. Primary production is usually the dominant process converting abiotic energy to chemical binding energy of organic matter and thus supporting growth and maintenance of ecosystems. Ecosystem respiration is the sum of the dissipation of this energy by all organisms of the ecosystem. The quantification of both processes, primary production and ecosystem respiration, is fundamental for understanding mass and energy balances of ecosystems.

[3]   Quantification of oxygen pools and transfer is an obvious way to gain information on primary production and ecosystem respiration rates. Oxygen production rates can directly be used to quantify primary production. In contrast to this, due to the possible presence of oxygen consumption by nitrification and the activity of anoxic and anaerobic mineralization processes, oxygen consumption rates are only an approximate quantification of ecosystem respiration. This approximation is reasonable if there are no important ammonia sources and no large anoxic sections of the water body.

[4]   The open-channel technique introduced by *Odum* [1956] provides a tool to estimate both processes in flowing water and has stimulated various studies on river metabolism [*Hoskin*, 1959; *Duffer and Dorris*, 1966; *Fisher*, 1976; *Meyer and Edwards*, 1990; *Uehlinger and Naegeli*, 1998; *Young and Huryn*, 1999; *Acuña et al.*, 2004] (and many more). The method is based on an analysis of the mass balance of dissolved oxygen or carbon dioxide in a stream reach and requires information on temporal changes of dissolved oxygen and on the air-water exchange of oxygen (typically called reaeration although oxygen will escape from the water during phases of supersaturation that may occur during the day). Modern equipment (oxygen probes and data loggers) [*Marzolf et al.*, 1994] enables rapid measurement of dissolved oxygen. Estimation of the reaeration coefficient is more difficult than measurement of dissolved oxygen but there exist a variety of methods to get this information [*Hornberger and Kelly*, 1975; *Thyssen et al.*, 1987; *Wanninkhof et al.*, 1990; *Chapra and Di Toro*, 1991; *Genereux and Hemond*, 1992]. The simplest form of the open-channel method requires that lateral inflow of dissolved oxygen by tributaries or groundwater seepage into the reach is small compared to in-stream processes such as photosynthesis and respiration. However, the method can easily be extended to the situation with tributaries, if the discharge and oxygen

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concentrations of the tributaries are known [*Hall and Tank*, 2005; *McCutchan and Lewis*, 2006].

[5] Primary production and respiration estimates cannot directly be obtained from dissolved oxygen time series. We will need a mathematical expression of how to get an estimate of net oxygen production in a reach based on measured downstream or upstream and downstream dissolved oxygen time series. Such an expression is called an estimator. During the night, the estimate can be interpreted as ecosystem respiration; primary production during the day can only be obtained with an assumption on respiration during the day. The simplest assumption would be having the same respiration as during the night. More sophisticated approaches assume a temperature dependence of respiration. Estimators of net oxygen production from dissolved oxygen time series are (usually) derived under the assumption of a homogeneous river reach upstream of the measurement site over a distance of at least $3v/K$ (v is flow velocity and K the reaeration coefficient, see equation (1)) or to the upstream measurement site [*Chapra and Di Toro*, 1991] (and extensive discussion below). Having in mind that flow velocities in rivers vary at least in a range between 0.1 and 1 m/s and reaeration coefficients in a range between 0.02 and 5 h^{-1} we get a reasonable range of values of $3v/K$ that extends at least from 100 m to 10 km (here, we already consider that large velocities will typically be associated with large reaeration coefficients and vice versa). Even larger values in the range of 20 to 26 km were reported [*Uehlinger*, 2006]. The assumption of homogeneity of river conditions over distances in this range may often not be realistic. Light controls primary production and influences biomass production and the spatial distribution of primary producers. Contrasting landscape elements (such as forest and grassland), gaps in the riparian tree vegetation or changing aspect in an incised river bed may result in heterogeneous light distribution and, as a consequence, in spatially heterogeneous primary production and (autotrophic) respiration. There is further evidence that the spatial distribution of respiration is not homogeneous, e.g., respiration rates in riffles and downwelling zones have been found to be much higher than in pools or upwelling zones [*Jones et al.*, 1995; *Pusch*, 1996]. In addition, upwelling zones can lead to the input of water with low oxygen concentration and could thus be interpreted as having high respiration activity. This can easily be considered if the inflow is known. We will therefore not address this issue in this paper. Changes in riverbed geometry (most importantly in slope) may cause heterogeneity in flow velocity and depth, which may also affect the spatial distribution of algae and reaeration. Heterogeneity in sediment grain size distribution (e.g., due to a change in river slope) may result in a heterogenous distribution of primary producers; substratum size has shown to be an important determinant of the biomass of epilithic algae and may not be uniformly distributed over the river bed [*McConnel and Sigler*, 1959; *Uehlinger*, 1991]. For all of these reasons, the assumptions underlying the derivation of the primary production and respiration estimators will usually not be fulfilled. As water parcels are flowing over areas with higher and lower production and respiration rates, the dissolved oxygen concentration reflects an average effect of these influence factors. For this reason, primary produc-

tion and respiration estimates derived from dissolved oxygen time series average to some degree over the heterogeneous conditions in the river. This implies that spatial heterogeneity in a river does not make such estimates useless, but there is a need of an analysis of how these estimators behave for heterogeneous rivers.

[6] Problems in estimating stream metabolism using the open-channel method have been addressed in several studies, which range from the setup of oxygen measurements [*Odum*, 1956; *Bott et al.*, 1978; *Marzolf et al.*, 1994; *Van de Bogert et al.*, 2007] to computation and error estimation [*Odum*, 1956; *Hornberger and Kelly*, 1972; *Schurr and Ruchti*, 1975; *Chapra and Di Toro*, 1991; *McCutchan et al.*, 1998]. However, to our knowledge, the effect of spatial heterogeneity on metabolism estimates has not been explicitly addressed so far. It is the goal of this paper to close this gap. In particular, we intend (1) to study the influence of spatial heterogeneity in the net oxygen production rate (= production − consumption), reaeration and flow velocity on oxygen concentration at the downstream station of a stream reach, (2) to derive new estimators of the net oxygen production rate in a homogeneous river reach, (3) to explore the effect of spatial heterogeneity on estimates of net oxygen production calculated from downstream oxygen time series under the assumption of a homogeneous river reach, and, finally (4) to derive recommendations on the use of single station versus two stations techniques for river metabolism estimation.

[7] The paper is structured as follows. We first derive the general solution of the transport-reaction equation for dissolved oxygen in a river reach, discuss its structure, and derive special solutions for a homogeneous river reach and for a heterogeneous reach consisting of two consecutive homogeneous reaches (section 2). On the basis of this solution we derive estimators of the net oxygen production rate for a homogeneous river reach, calculate the effect of spatial heterogeneities on estimates derived from these estimators, and give recommendations on the use of single station or two stations techniques (section 3). We then discuss some implementation features, in particular the use of a local quadratic regression procedure for smoothing and taking derivatives of measured dissolved oxygen time series (section 4). In the next section (section 5) we demonstrate the practical relevance of heterogeneity by analyzing data for five dissolved oxygen measurement sites along a river. Conclusions are drawn in the final section (section 6).

2. Analytical Solutions of the Transport-Reaction Equation

2.1. Assumptions

[8] Stream metabolism parameters can best be estimated from oxygen measurements of a river during sunny weather periods that lead to significant daily variations in dissolved oxygen concentrations under quasi steady state river hydraulics. Dominant processes affecting oxygen concentrations are advective transport and transformation processes. The effect of transformation processes is summarized by a net oxygen production term. As daily variations do not lead to sharp peaks, spreading by dispersion can usually be neglected. Furthermore, dry weather situations usually make

it possible to select a river reach for the investigation for which tributaries can be neglected or quantified with a reasonable degree of accuracy. This makes it meaningful to investigate oxygen dynamics in a river under the assumptions of (1) steady state river hydraulics, (2) no lateral inflows or tributaries, and (3) negligible effect of dispersion on oxygen concentrations.

[9] These assumptions make it possible to obtain analytical solutions to the transport-reaction equation for dissolved oxygen in the river without additional restrictive assumptions, such as a constant net oxygen production rate, a constant gas exchange coefficient, a constant saturation concentration, or a constant transport velocity.

2.2. Transport-Reaction Equation for Dissolved Oxygen

[10] Under the assumptions listed above, the transport-reaction equation for dissolved oxygen in the river is

$$\frac{\partial C}{\partial t} + v(x)\frac{\partial C}{\partial x} = NP(x,t) + K(x)(C_{sat}(x,t) - C), \quad (1)$$

where t is time (T), x is the location along the river (L), C is the concentration of dissolved oxygen in the river water (ML^{-3}), v is the cross-sectionally averaged flow velocity of the river (LT^{-1}), NP is net oxygen production per volume of the river water column by the difference of primary production and total ecosystem respiration (ML^{-3}T^{-1}), K is the reaeration coefficient (T^{-1}), and C_{sat} is the saturation concentration of dissolved oxygen under the given environmental conditions (ML^{-3}; water temperature is the most influential factor for a freshwater stream). Equation (1) describes the temporal change in dissolved oxygen concentration due to advection, production, respiration, and reaeration.

2.3. General Solution

[11] By applying a transformation into a coordinate system moving with river flow (this corresponds to using the method of characteristics for solving hyperbolic partial differential equations), equation (1) can be solved analytically. This leads to the general solution for the dissolved oxygen concentration as a function of location, $x > x_0$, and time, t:

$$
\begin{aligned}
C^{gen}(x,t) = &\int_{x_0}^{x} \frac{1}{v(x')}\left[K(x')C_{sat}\left(x', t - \int_{x'}^{x}\frac{dx''}{v(x'')}\right)\right.\\
&\left. + NP\left(x', t - \int_{x'}^{x}\frac{dx''}{v(x'')}\right)\right]\\
&\cdot \exp\left(-\int_{x'}^{x}\frac{K(x'')}{v(x'')}dx''\right)dx'\\
&+ C\left(x_0, t - \int_{x_0}^{x}\frac{dx'}{v(x')}\right)\\
&\cdot \exp\left(-\int_{x_0}^{x}\frac{K(x')}{v(x')}dx'\right) \qquad (x \geq x_0). \quad (2)
\end{aligned}
$$

This solution requires the (upstream) concentration at x_0 to be known as a function of time, $C(x_0, t)$. The first term on the right-hand side of equation (2) describes the effect of reaeration and net oxygen production within the river reach, the second term the influence of the upstream concentration at x_0 on the downstream concentration at x. In both terms, time shifts due to the transport time to the downstream location and concentration changes due to reaeration are considered.

[12] In order to facilitate the interpretation of the general solution, equation (2) can be rewritten in the alternative form

$$
C^{gen}(x,t) = (1 - \alpha) \cdot \overline{\left(C_{sat} + \frac{NP}{K}\right)}^{\beta} + \alpha \cdot C\left(x_0, t - \int_{x_0}^{x}\frac{dx'}{v(x')}\right)
$$
(3a)

with

$$
\begin{aligned}
\overline{\left(C_{sat} + \frac{NP}{K}\right)}^{\beta} = &\int_{x_0}^{x}\left\{C_{sat}\left(x', t - \int_{x'}^{x}\frac{dx''}{v(x'')}\right)\right.\\
&\left. + \frac{1}{K(x')}NP\left(x', t - \int_{x'}^{x}\frac{dx''}{v(x'')}\right)\right\}\beta(x',x)dx',
\end{aligned}
$$
(3b)

$$
\beta(x',x) = \frac{\frac{K(x')}{v(x')}\exp\left(-\int_{x'}^{x}\frac{K(x'')}{v(x'')}dx''\right)}{\int_{x_0}^{x}\frac{K(x'')}{v(x'')}\exp\left(-\int_{x''}^{x}\frac{K(x''')}{v(x''')}dx'''\right)dx''}\ (x_0 \leq x' \leq x) ,
$$
(3c)

and

$$
\alpha = \exp\left(-\int_{x_0}^{x}\frac{K(x')}{v(x')}dx'\right). \quad (3d)
$$

In the denominator of β we have used the identity

$$
\begin{aligned}
&\int_{x_0}^{x}\frac{K(x'')}{v(x'')}\exp\left(-\int_{x''}^{x}\frac{K(x''')}{v(x''')}dx'''\right)dx''\\
&= 1 - \exp\left(-\int_{x_0}^{x}\frac{K(x''')}{v(x''')}dx'''\right)
\end{aligned}
$$
(4)

to clarify normalization of the weighting factor β.

[13] The form (3) of the general solution facilitates its physical interpretation: Equation (3a) shows that $C(x, t)$ is the weighted average of the expression $\overline{\left(C_{sat} + \frac{NP}{K}\right)}^{\beta}$ and the time-shifted upstream concentration $C(x_0, t - \int_{x_0}^{x}\frac{dx'}{v(x')})$. As shown by equations (3b) and (3c), $\overline{\left(C_{sat} + \frac{NP}{K}\right)}^{\beta}$ is the

exponentially weighted average (by the weight β) of the equilibrium concentration resulting from C_{sat}, NP and K with adequate time shifts to account for transport time. Equation (3d) defines the weight between the two terms in equation (3a).

2.4. Solution for Spatially Homogeneous Conditions

[14] The most obvious task for estimating river metabolism is to estimate net oxygen production for a spatially homogeneous river reach. For this purpose, we need the analytical solution for the oxygen concentration under spatially homogeneous conditions. Usually there is a strong daily variation in net production and, due to temperature changes, also a significant daily variation in dissolved oxygen saturation. For this reason, the simplest case with spatially and temporally constant parameters of equation (1) is often not realistic. However, over relatively short periods in time (hours) centered at a given time, t_0, a local linear approximation to the daily variation seems to be reasonable. We therefore assume that both C_{sat} and NP vary linearly in time taking the same value over the whole reach at any point in time. This can be formalized by the following equations:

$$v(x) = v \qquad (5a)$$

$$K(x) = K \qquad (5b)$$

$$C_{sat}(x,t) = C_{sat}(t_0) \cdot (1 + \alpha_{sat}(t - t_0)) \qquad \text{for } x \geq x_0 \quad (5c)$$

$$NP(x,t) = NP(t_0) \cdot (1 + \alpha_{NP}(t - t_0)) \qquad \text{for } x \geq x_0. \quad (5d)$$

Substituting these expressions into the general solution given by equation (2) allows us to evaluate the integrals analytically. This leads to the following solution:

$$
\begin{aligned}
C^{\text{hom}}(x,t) = {} & \left(C_{sat}(t_0) + \frac{NP(t_0)}{K} \right) \left[1 - \exp\left(-K\frac{x - x_0}{v} \right) \right] \\
& + \left(\alpha_{sat} C_{sat}(t_0) + \alpha_{NP}\frac{NP(t_0)}{K} \right) \\
& \cdot \left\{ \left(t - t_0 - \frac{1}{K} \right) \left[1 - \exp\left(-K\frac{x - x_0}{v} \right) \right] \right. \\
& \left. + \frac{x - x_0}{v} \exp\left(-K\frac{x - x_0}{v} \right) \right\} \\
& + C\left(x_0, t - \frac{x - x_0}{v} \right) \exp\left(-K\frac{x - x_0}{v} \right).
\end{aligned} \qquad (6)
$$

The first term on the right-hand side of this equation represents the solution for a spatially homogeneous river in which the parameters are also constant in time. The second term corrects for linear time dependence of C_{sat} and NP according to equations (5a)–(5d). Finally, the third term represents the influence of the upstream boundary condition of the homogeneous reach. Obviously, the influence of this term decreases exponentially with increasing values of $K\frac{x - x_0}{v}$. The solution (6) is a generalization of a solution that was already presented in 1972 for determining primary production in a stream [*Hornberger and Kelly*, 1972].

[15] As the correction term for linear time dependence of C_{sat} and NP (second term on the right-hand side of equation (6)) is again linear in time, we can choose the time t_0 at which we evaluate C_{sat} and NP in such a way that this term becomes zero. According to equation (6) this is the case for t_0 equal to

$$
t_0^*(x,t) = t - \frac{1}{K} + \frac{x - x_0}{v} \frac{\exp\left(-K\frac{x - x_0}{v} \right)}{1 - \exp\left(-K\frac{x - x_0}{v} \right)}. \qquad (7)
$$

Making this choice of t_0 leads to the following simplification of equation (6):

$$
\begin{aligned}
C^{\text{hom}}(x,t) = {} & \left(C_{sat}\left(t_0^*(x,t) \right) + \frac{NP\left(t_0^*(x,t) \right)}{K} \right) \\
& \cdot \left[1 - \exp\left(-K\frac{x - x_0}{v} \right) \right] \\
& + C\left(x_0, t - \frac{x - x_0}{v} \right) \exp\left(-K\frac{x - x_0}{v} \right). \qquad (8)
\end{aligned}
$$

This equation relates the downstream concentration $C^{\text{hom}}(x, t)$ at time t to saturation, C_{sat}, and net oxygen production, NP, at time $t_0^*(x, t)$. It is remarkable that this relationship is independent of the gradients, α_{sat} and α_{NP}, of the linear trend in C_{sat} and NP. We will take advantage of this property for deriving an estimator in section 3.1.

[16] When equation (8) is written in the form

$$
\begin{aligned}
C^{\text{hom}}(x,t) = {} & (1 - \alpha) \cdot \left(C_{sat}\left(t_0^*(x,t) \right) + \frac{NP\left(t_0^*(x,t) \right)}{K} \right) \\
& + \alpha \cdot C\left(x_0, t - \frac{x - x_0}{v} \right) \qquad (9)
\end{aligned}
$$

with

$$\alpha = \exp\left(-K\frac{x - x_0}{v} \right) \qquad (10)$$

it becomes clear that under homogeneous conditions the downstream dissolved oxygen concentration is equal to the weighted mean of $C_{sat} + NP/K$ along the reach (and taken at the correct time, $t_0^*(x, t)$) and the upstream concentration taken one travel time earlier than the downstream concentration (compare to the general case given by equations (3a)–(3d)). If α is small, the effect of the upstream concentration can be neglected. This condition of $\alpha \ll 1$ is often quantified as $\alpha < 5\%$. Because $\exp(-3) \approx 5\%$, this implies that the downstream dissolved oxygen concentration is primarily determined by processes within a river reach of length [*Chapra and Di Toro*, 1991]

$$\Delta x = 3\frac{v}{K}. \qquad (11)$$

2.5. Solution for Spatially Heterogeneous Conditions

[17] To investigate the effect of spatial heterogeneity, we need an analytical solution for a typical type of heterogeneity. The most straightforward generalization of the solution derived in the preceding section is a solution for two homogeneous reaches in sequence. Such a solution is of high practical relevance as this type of heterogeneity occurs

frequently, e.g., in oxygen production due to changes in light intensity when a river leaves or enters a forest or in reaeration and transport velocity when the slope of a river changes.

[18] We therefore modify our assumptions made in equations (5a)–(5d) to distinguish a downstream subreach (dn) just upstream of the location x at which we calculate the solution and an upstream subreach (up) that extends from the beginning of the river reach at x_0 to a location x_1 at which the downstream reach starts. All parameters in equation (1) are assumed to be constant in space within both of these reaches. This leads to the following assumptions:

$$v(x) = \begin{cases} v^{dn} & \text{for } x_1 \leq x \\ v^{up} & \text{for } x_0 \leq x < x_1 \end{cases} \quad (12a)$$

$$K(x) = \begin{cases} K^{dn} & \text{for } x_1 \leq x \\ K^{up} & \text{for } x_0 \leq x < x_1 \end{cases} \quad (12b)$$

$$C_{sat}(x,t) = \begin{cases} C_{sat}^{dn}(t) = C_{sat}^{dn}(t_0^{dn}) \cdot \left(1 + \alpha_{sat}^{dn}(t - t_0^{dn})\right) & \text{for } x_1 \leq x \\ C_{sat}^{up}(t) = C_{sat}^{up}(t_0^{up}) \cdot \left(1 + \alpha_{sat}^{up}(t - t_0^{up})\right) & \text{for } x_0 \leq x < x_1 \end{cases} \quad (12c)$$

$$NP(x,t) = \begin{cases} NP^{dn}(t) = NP^{dn}(t_0^{dn}) \cdot \left(1 + \alpha_{NP}^{dn}(t - t_0^{dn})\right) & \text{for } x_1 \leq x \\ NP^{up}(t) = NP^{up}(t_0^{up}) \cdot \left(1 + \alpha_{NP}^{up}(t - t_0^{up})\right) & \text{for } x_0 \leq x < x_1 \end{cases} . \quad (12d)$$

Integrating the general solution (2) under these assumptions, or sequentially applying solution (6) to the two river reaches leads to the following solution for the sequence of two homogeneous river reaches:

$$C^{inh}(x,t) = \left(C_{sat}^{dn}(t_0^{dn}) + \frac{NP^{dn}(t_0^{dn})}{K^{dn}}\right)\left[1 - \exp\left(-K^{dn}\frac{x - x_1}{v^{dn}}\right)\right]$$
$$+ \left(\alpha_{sat}^{dn}C_{sat}^{dn}(t_0^{dn}) + \alpha_{NP}^{dn}\frac{NP^{dn}(t_0^{dn})}{K^{dn}}\right)$$
$$\cdot \left\{\left(t - t_0^{dn} - \frac{1}{K^{dn}}\right)\left[1 - \exp\left(-K^{dn}\frac{x - x_1}{v^{dn}}\right)\right]\right.$$
$$\left. + \frac{x - x_1}{v^{dn}}\exp\left(-K^{dn}\frac{x - x_1}{v^{dn}}\right)\right\}$$
$$+ \left\{\left(C_{sat}^{up}(t_0^{up}) + \frac{NP^{up}(t_0^{up})}{K^{up}}\right)\left[1 - \exp\left(-K^{up}\frac{x_1 - x_0}{v^{up}}\right)\right]\right.$$
$$+ \left(\alpha_{sat}^{up}C_{sat}^{up}(t_0^{up}) + \alpha_{NP}^{up}\frac{NP^{up}(t_0^{up})}{K^{up}}\right)$$
$$\cdot \left\{\left(t - \frac{x - x_1}{v^{dn}} - t_0^{up} - \frac{1}{K^{up}}\right)\left[1 - \exp\left(-K^{up}\frac{x_1 - x_0}{v^{up}}\right)\right]\right.$$
$$\left.\left. + \frac{x_1 - x_0}{v^{up}}\exp\left(-K^{up}\frac{x_1 - x_0}{v^{up}}\right)\right\}\right\}\exp\left(-K^{dn}\frac{x - x_1}{v^{dn}}\right)$$
$$+ C\left(x_0, t - \frac{x_1 - x_0}{v^{up}} - \frac{x - x_1}{v^{dn}}\right)$$
$$\cdot \exp\left(-K^{up}\frac{x_1 - x_0}{v^{up}} - K^{dn}\frac{x - x_1}{v^{dn}}\right). \quad (13)$$

The interpretation of this equation is analogous to that of equation (6) with the difference that the upstream boundary condition of the downstream reach is given as the downstream solution of the upstream reach.

[19] Similarly as we could simplify equations (6)–(8) by making an intelligent choice of the time t_0 in equation (7), we can make the following choices for t_0^{dn} and t_0^{up} to simplify the solution:

$$t_0^{dn*}(x,t) = t - \frac{1}{K^{dn}} + \frac{x - x_1}{v^{dn}}\frac{\exp\left(-K^{dn}\frac{x - x_1}{v^{dn}}\right)}{1 - \exp\left(-K^{dn}\frac{x - x_1}{v^{dn}}\right)}, \quad (14a)$$

$$t_0^{up*}(x,t) = t - \frac{x - x_1}{v^{dn}} - \frac{1}{K^{up}} + \frac{x_1 - x_0}{v^{up}}\frac{\exp\left(-K^{up}\frac{x_1 - x_0}{v^{up}}\right)}{1 - \exp\left(-K^{up}\frac{x_1 - x_0}{v^{up}}\right)}. \quad (14b)$$

This leads to the simplified solution:

$$C^{inh}(x,t) = \left(C_{sat}^{dn}\left(t_0^{dn*}(x,t)\right) + \frac{NP^{dn}\left(t_0^{dn*}(x,t)\right)}{K^{dn}}\right)$$
$$\cdot \left[1 - \exp\left(-K^{dn}\frac{x - x_1}{v^{dn}}\right)\right]$$
$$+ \left(C_{sat}^{up}\left(t_0^{up*}(x,t)\right) + \frac{NP^{up}\left(t_0^{up*}(x,t)\right)}{K^{up}}\right)$$
$$\cdot \left[1 - \exp\left(-K^{up}\frac{x_1 - x_0}{v^{up}}\right)\right] \cdot \exp\left(-K^{dn}\frac{x - x_1}{v^{dn}}\right)$$
$$+ C\left(x_0, t - \frac{x_1 - x_0}{v^{up}} - \frac{x - x_1}{v^{dn}}\right)$$
$$\cdot \exp\left(-K^{up}\frac{x_1 - x_0}{v^{up}} - K^{dn}\frac{x - x_1}{v^{dn}}\right). \quad (15)$$

This equation can again be written in a form that makes spatial averaging more explicit:

$$C^{inh}(x,t) = \left(1 - \alpha^{dn}\right) \cdot \left(C_{sat}^{dn}\left(t_0^{dn*}(x,t)\right) + \frac{NP^{dn}\left(t_0^{dn*}(x,t)\right)}{K^{dn}}\right)$$
$$+ \alpha^{dn}$$
$$\cdot \left\{\left(1 - \alpha^{up}\right) \cdot \left(C_{sat}^{up}\left(t_0^{up*}(x,t)\right) + \frac{NP^{up}\left(t_0^{up*}(x,t)\right)}{K^{up}}\right)\right.$$
$$\left. + \alpha^{up} \cdot C\left(x_0, t - \frac{x_1 - x_0}{v^{up}} - \frac{x - x_1}{v^{dn}}\right)\right\} \quad (16)$$

with

$$\alpha^{dn} = \exp\left(-K^{dn}\frac{x - x_1}{v^{dn}}\right) \quad , \quad \alpha^{up} = \exp\left(-K^{up}\frac{x_1 - x_0}{v^{up}}\right) \quad . \quad (17)$$

This solution demonstrates that the downstream dissolved oxygen concentration is equal to the weighted mean of

$C_{\text{sat}} + NP/K$ along the downstream subreach (and taken at the correct time, $t_0^{\text{dn}*}(x, t)$) and an upstream concentration of the downstream subreach that is again the weighted mean of $C_{\text{sat}} + NP/K$ along the upstream subreach (taken at the correct time, $t_0^{\text{up}*}(x,t)$) and the upstream concentration taken one complete travel time of both subreaches together earlier than the downstream concentration.

3. Estimating Net Oxygen Production

3.1. Estimators for Homogeneous Conditions

[20] After sunset, net oxygen production is negative and is dominated by respiration. Assuming respiration to be constant or to follow a given temperature dependence allows us in principle to estimate reaeration during this time of the day. However, in strongly reaerated rivers, the transition phase where oxygen concentration still deviates strongly enough from its dynamic equilibrium between respiration and gas exchange (due to production processes during the day) is too short to obtain a reliable estimate of the reaeration coefficient. This makes a reproduction of the measured oxygen time series with different combinations of values of the reaeration coefficient and net oxygen production possible. This is a well known identifiability problem [*Brun et al.*, 2001]. To avoid this problem, we limit our task to the estimation of the net primary production rate, NP, at a given time t_0, for given, but possibly uncertain, values of the reaeration coefficient, K, the river flow velocity, v, the dissolved oxygen saturation concentration, C_{sat}, at time t_0, and measured time series of dissolved oxygen concentration upstream and downstream of a homogeneous river reach.

[21] An estimator of the net primary production rate, $NP(t_0)$, for a homogeneous river reach can, in principle, be derived by solving the solution for the downstream concentration (6) for $NP(t_0)$. However, this involves a lot of unknowns, such as the gradients of the saturation concentration, α_{sat}, and of the net primary production rate, α_{NP}. For this reason, it is better to first replace these terms by an expression that can more easily be calculated from measured dissolved oxygen concentration time series. This is done by calculating the time derivative of the solution for the homogeneous river reach (6):

$$\frac{\partial C^{\text{hom}}}{\partial t}(x, t) = \left(\alpha_{\text{sat}} C_{\text{sat}}(t_0) + \alpha_{NP} \frac{NP(t_0)}{K}\right)\left[1 - \exp\left(-K\frac{x - x_0}{v}\right)\right]$$
$$+ \frac{\partial C}{\partial t}\left(x_0, t - \frac{x - x_0}{v}\right)\exp\left(-K\frac{x - x_0}{v}\right). \quad (18)$$

This equation can be solved for the term that contains the above mentioned variables:

$$\alpha_{\text{sat}} C_{\text{sat}}(t_0) + \alpha_{NP} \frac{NP(t_0)}{K}$$
$$= \frac{\frac{\partial C^{\text{hom}}}{\partial t}(x, t) - \frac{\partial C}{\partial t}\left(x_0, t - \frac{x - x_0}{v}\right)\exp\left(-K\frac{x - x_0}{v}\right)}{1 - \exp\left(-K\frac{x - x_0}{v}\right)}. \quad (19)$$

Substituting this expression into the solution (6) and solving for $NP(t_0)$ leads to:

$$NP(t_0)$$
$$= K\left(\frac{C^{\text{hom}}(x, t) - C\left(x_0, t - \frac{x - x_0}{v}\right)\exp\left(-K\frac{x - x_0}{v}\right)}{1 - \exp\left(-K\frac{x - x_0}{v}\right)} - C_{\text{sat}}(t_0)\right)$$
$$- \frac{\frac{\partial C^{\text{hom}}}{\partial t}(x, t) - \frac{\partial C}{\partial t}\left(x_0, t - \frac{x - x_0}{v}\right)\exp\left(-K\frac{x - x_0}{v}\right)}{\left[1 - \exp\left(-K\frac{x - x_0}{v}\right)\right]^2}$$
$$\cdot \left\{(K(t - t_0) - 1)\left[1 - \exp\left(-K\frac{x - x_0}{v}\right)\right]\right.$$
$$\left.+ K\frac{x - x_0}{v}\exp\left(-K\frac{x - x_0}{v}\right)\right\}. \quad (20)$$

Applying this equation to a river reach from x^{up} to x^{dn} and introducing the variables

$$x^{\text{up}} = x_0 \,, \; x^{\text{dn}} = x \,, \; \tau = \frac{x^{\text{dn}} - x^{\text{up}}}{v} \,,$$
$$C^{\text{up}}(t) = C(x_0, t) \,, \; C^{\text{dn}}(t) = C(x, t) \quad (21)$$

leads to an equation that underlies our estimators. x^{up} and x^{dn} are the locations of the upstream and downstream ends of the river reach, $C^{\text{up}}(t)$ and $C^{\text{dn}}(t)$ are the dissolved oxygen concentrations at these locations, and τ is the travel time from x^{up} to x^{dn}. For a given time t_0 at which the estimate of the net oxygen production rate is to be calculated, we can still choose the time, t, at which the downstream concentration is to be used (according to equation (20), the upstream concentration will have to be used at time $t - \tau$). The linear trend in time of oxygen saturation and net oxygen production (5) underlying the analytical solution (6) on which our estimator is based is only a good approximation over short periods of time (hours). To not challenge this approximation too much, t_0 should not deviate too much from t. The straightforward choice

$$t = t_0 \quad (22)$$

leads, after substituting t for t_0, to the estimator

$$\widehat{NP}^{(1)}(t) = K\left(\frac{C^{\text{dn}}(t) - C^{\text{up}}(t - \tau)\exp(-K\tau)}{1 - \exp(-K\tau)} - C_{\text{sat}}(t)\right)$$
$$+ \frac{\frac{dC^{\text{dn}}(t)}{dt} - \frac{dC^{\text{up}}(t - \tau)}{dt}\exp(-K\tau)}{[1 - \exp(-K\tau)]^2}$$
$$\cdot [1 + (K\tau - 1)\exp(-K\tau)] \quad . \quad (23)$$

This equation allows us to estimate the net primary production rate from concentration time series of dissolved oxygen. However, we will have to interpolate these time series and calculate derivatives to apply this estimator. As discussed in section 4, this can best be done by a smoothing procedure that provides joint smoothed results and derivatives.

[22] Note that if the homogeneous reach is long ($K\tau \gg 1$; typically quantified as $K\tau > 3$ which implies that $\exp(-K\tau) < 5\%$) we get the simplified estimator:

$$K\tau \gg 1 : \quad \widehat{NP}^{(1)}(t) \approx K\left(C^{\mathrm{dn}}(t) - C_{\mathrm{sat}}(t)\right) + \frac{dC^{\mathrm{dn}}(t)}{dt}. \quad (24)$$

This simplified estimator requires data only from the downstream station.

[23] As, due to travel time, the downstream solution is influenced by production rates within the river reach at earlier points in time, the choice (22) may not be optimal. As the term with the slopes α_{sat} and α_{NP} corrects for saturation and production not equal to their values at time t_0 (see discussion following equation (6)), it seems a reasonable alternative to choose the value of t such that this correction term becomes zero. This is the case for

$$t = t_0 + \frac{1}{K} - \tau \frac{\exp(-K\tau)}{1 - \exp(-K\tau)}. \quad (25)$$

Again after changing our notation from t_0 to t, we then get the alternative estimator

$$\widehat{NP}^{(2)}(t) = K$$
$$\cdot \left(\frac{\left(C^{\mathrm{dn}}\left(t + \frac{1}{K} - \tau\frac{\exp(-K\tau)}{1-\exp(-K\tau)}\right) - C^{\mathrm{up}}\left(t + \frac{1}{K} - \tau\frac{\exp(-K\tau)}{1-\exp(-K\tau)} - \tau\right)\exp(-K\tau)\right)}{1 - \exp(-K\tau)} - C_{\mathrm{sat}}(t) \right) \quad (26)$$

This estimator frees us from the need of calculating derivatives of the measured oxygen time series by an adequate choice of the point in time at which the oxygen time series are evaluated (by interpolation or smoothing). This is a significant advantage if poor methods are applied to take derivatives.

[24] Again, if the homogeneous reach is long ($K\tau \gg 1$) we get a simplified estimator that only needs data from the downstream station:

$$K\tau \gg 1 : \quad \widehat{NP}^{(2)}(t) \approx K\left(C^{\mathrm{dn}}\left(t + \frac{1}{K}\right) - C_{\mathrm{sat}}(t)\right). \quad (27)$$

[25] Note that our first estimator (23) is a generalization of an estimator based on finite difference approximations to the derivatives, as presented by *Hornberger and Kelly* [1972]. In contrast, to our knowledge, our second estimator (26) has not been published before.

3.2. Effect of Using the Homogeneous Estimator Under Heterogeneous Conditions

[26] By substituting the analytical solution for a given type of heterogeneity as the downstream dissolved oxygen time series in the estimator derived under the assumption of homogeneous conditions, we can calculate how exactly the estimator averages over the heterogeneity. On the basis of the equations derived in the preceding section this can be done for a large class of heterogeneities.

[27] In this paper we focus on the most important case. In section 2.5 we derived the downstream dissolved oxygen concentration for a simple heterogeneous condition that consists of two homogeneous reaches in sequence. Inserting

this solution (15) into the estimator (26) leads to the relatively complicated result:

$$\widehat{NP}^{(2)}(t) \approx \frac{K}{1 - \exp(-K\tau)}$$

$$\cdot \left(\left\{ C_{\mathrm{sat}}^{\mathrm{dn}}\left(t_0^{\mathrm{dn}*}\left(x^{\mathrm{dn}}, t + \frac{1}{K} - \tau\frac{\exp(-K\tau)}{1-\exp(-K\tau)}\right)\right) \right. \right.$$

$$\left. + \frac{NP^{\mathrm{dn}}\left(t_0^{\mathrm{dn}*}\left(x^{\mathrm{dn}}, t + \frac{1}{K} - \tau\frac{\exp(-K\tau)}{1-\exp(-K\tau)}\right)\right)}{K^{\mathrm{dn}}} \right\}$$

$$\cdot \left[1 - \exp\left(-K^{\mathrm{dn}}\frac{x^{\mathrm{dn}} - x_1}{v^{\mathrm{dn}}}\right) \right]$$

$$+ \left\{ C_{\mathrm{sat}}^{\mathrm{up}}\left(t_0^{\mathrm{up}*}\left(x^{\mathrm{dn}}, t + \frac{1}{K} - \tau\frac{\exp(-K\tau)}{1-\exp(-K\tau)}\right)\right) \right.$$

$$\left. + \frac{NP^{\mathrm{up}}\left(t_0^{\mathrm{up}*}\left(x^{\mathrm{dn}}, t + \frac{1}{K} - \tau\frac{\exp(-K\tau)}{1-\exp(-K\tau)}\right)\right)}{K^{\mathrm{up}}} \right\}$$

$$\cdot \exp\left(-K^{\mathrm{dn}}\frac{x^{\mathrm{dn}} - x_1}{v^{\mathrm{dn}}}\right) \cdot \left[1 - \exp\left(-K^{\mathrm{up}}\frac{x_1 - x^{\mathrm{up}}}{v^{\mathrm{up}}}\right)\right]$$

$$+ C^{\mathrm{up}}\left(t + \frac{1}{K} - \tau\frac{\exp(-K\tau)}{1-\exp(-K\tau)} - \frac{x^{\mathrm{dn}} - x_1}{v^{\mathrm{dn}}} - \frac{x_1 - x^{\mathrm{up}}}{v^{\mathrm{up}}}\right)$$

$$\cdot \exp\left(-K^{\mathrm{dn}}\frac{x^{\mathrm{dn}} - x_1}{v^{\mathrm{dn}}} - K^{\mathrm{up}}\frac{x_1 - x^{\mathrm{up}}}{v^{\mathrm{up}}}\right)$$

$$- C^{\mathrm{up}}\left(t + \frac{1}{K} - \tau\frac{\exp(-K\tau)}{1-\exp(-K\tau)} - \tau\right)\exp(-K\tau) \right)$$

$$- K C_{\mathrm{sat}}(t) \quad (28)$$

This expression quantifies how the estimate of net production at time t depends on the input to the estimator and on the true values of influencing factors in the river. Input to the estimator (derived for a homogeneous reach) consists of the downstream and upstream positions of the reach, x^{dn} and x^{up}, the retention time in the reach, $\tau = (x^{\mathrm{dn}} - x^{\mathrm{up}})/v$, the reaeration coefficient, K, the dissolved oxygen concentration at saturation in the reach, $C_{\mathrm{sat}}(t)$, and the measured dissolved oxygen concentrations at the downstream and upstream ends of the reach, C^{dn} and C^{up}. The true conditions (for the assumed class of heterogeneities) are characterized by the location in the river reach, at which the properties change from "upstream" to "downstream" values, x_1, the cross-sectionally averaged flow velocity in the upstream and downstream subreaches, v^{up} and v^{dn}, the reaeration coefficient in the upstream and downstream subreaches, K^{up} and K^{dn}, the dissolved oxygen saturation concentration in the upstream and downstream subreaches, $C_{\mathrm{sat}}^{\mathrm{up}}$ and $C_{\mathrm{sat}}^{\mathrm{dn}}$ as a linear function of time (see equation (12)), and the net oxygen production rate in the upstream and downstream subreaches, NP^{up} and NP^{dn} as a linear function of time (see equation (12)). Finally, $t_0^{\mathrm{dn}*}$ and $t_0^{\mathrm{up}*}$ are defined by equations (14a) and (14b).

[28] Equation (28) looks very complicated and it is not possible to simplify it considerably at this level of generality.

However, the equation simplifies considerably when making more specific assumptions. If the reaeration coefficient does not change considerably between the two subreaches and is well estimated ($K^{up} \approx K^{dn} \approx K$) and the total retention time is also well estimated ($(x_1 - x^{up})/v^{up} + (x^{dn} - x_1)/v^{dn} = \tau^{up} + \tau^{dn} \approx \tau$) then the terms with the upstream concentration, C^{up} cancel out. If in addition, the saturation concentration does not considerably change between the subsections and over time, the terms with C_{sat} cancel out also. In this simplified situation, we end with

$$\widehat{NP}^{(2)}(t) \approx \frac{\begin{aligned}&NP^{dn}\left(t_0^{dn*}\left(x^{dn}, t + \frac{1}{K} - \tau \frac{\exp(-K\tau)}{1 - \exp(-K\tau)}\right)\right) \cdot [1 - \exp(-K\tau^{dn})]\\ &+ NP^{up}\left(t_0^{up*}\left(x^{dn}, t + \frac{1}{K} - \tau \frac{\exp(-K\tau)}{1 - \exp(-K\tau)}\right)\right) \cdot \exp(-K\tau^{dn})\\ &\qquad\qquad\qquad \cdot [1 - \exp(-K\tau^{up})]\end{aligned}}{1 - \exp(-K\tau)}$$

(29)

which simplifies even further if the upstream reach is long ($K\tau^{up} \gg 1$):

$$\widehat{NP}^{(2)}(t) \approx NP^{dn}\left(t_0^{dn*}\left(x^{dn}, t + 1/K\right)\right) \cdot \left[1 - \exp\left(-K\tau^{dn}\right)\right] \\ + NP^{up}\left(t_0^{up*}\left(x^{dn}, t + 1/K\right)\right) \cdot \exp\left(-K\tau^{dn}\right). \quad (30)$$

This demonstrates that, for this simplified situation, the estimator provides a weighted mean between the net oxygen production rates within the two subreaches. This clearly demonstrates that the two situations shown in Figure 1 with the same mean net production over a reach of length $3v/K$ lead to different net oxygen production estimates. The estimate for situation A will be significantly smaller than that of situation B as net production closer to the downstream measurement site gets more weight.

3.3. Uncertainty of Net Production Estimates

[29] Dissolved oxygen and temperature measurements required for the calculation of dissolved oxygen saturation concentration are quite accurate. On the other hand, measurements of mean river depth, d (needed to calculate the per area net production from the per volume values provided by our estimates $\widehat{NP}$), stream velocity and thus transport time, τ, and, in particular, the reaeration coefficient, K, are quite uncertain. For this reason, we can assume that the uncertainty of the estimate of net oxygen production is dominated by the uncertainty of the parameters d, τ and K.

[30] As a first step, we therefore need the joint probability distribution of K, d and τ. We can get estimates of the standard deviation of these quantities either by multiple measurements or by quantifying the error of the measurement process. It seems then to be reasonable to assume the joint probability distribution of these three influence factors to be the product of independent marginals of the individual factors. To consider only the positive values of these parameters and to avoid unrealistic tails of the distribution, we used lognormal distributions, truncated at the 1 and 99% quantiles, to describe the marginal distributions of the three parameters.

[31] In a second step, we can derive the probability distribution of net oxygen production estimates by propagating this probability distribution of K, d and τ through the estimator (equations (23), (24), (26), or (27)). The resulting probability distribution of the estimates can be visualized by bands of values that cover a prescribed probability value (e.g., 90%).

[32] To get an assessment of the relative contributions of the different parameters to total uncertainty, we can calculate the first-order sensitivity coefficients

$$S_{1,i} = \frac{\text{Var}_{\Theta_i}\left[E_{\Theta \backslash \Theta_i}[NP(\Theta)|\Theta_i]\right]}{\text{Var}_{\Theta}[NP(\Theta)]} \quad (31)$$

where $\Theta = (K, d, \tau)$ [*Cukier et al.*, 1978; *Saltelli et al.*, 1999, 2004]. As we assume independence between the influencing parameters, the sum of the three sensitivity coefficients will be smaller or equal to unity, the difference being responsible for interactions of the parameters to the result (for an additive model and independent parameters, the coefficients would sum to unity) [*Saltelli et al.*, 2004].

3.4. Recommendations Regarding the Use of Measurement Stations

[33] Our analytical solutions (2), (3), (6), (8), (9), (13), (15), and (16) clarify how the downstream dissolved oxygen concentration in a river reach depends on the upstream concentration and the processes within the river reach. For the homogeneous case (6), (8), and (9) the essential conclusion is that the influence of the upstream concentration can be estimated as $\exp(-K\Delta x/v)$, that of the processes within the reach as $(1 - \exp(-K\Delta x/v))$. For the heterogeneous case (2), (3), (13), (15), and (16) the influence of upstream subreaches decays exponentially with distance from the downstream measurement station in a similar way as it is the case for the upstream concentration.

[34] This has the following consequences for our estimators (23), (24), (26), and (27):

[35] 1. If a reach is homogeneous over distances for which the influence of the upstream reach, $\exp(-K\Delta x/v)$, becomes small, the use of a single (downstream) measurement station using one of the estimators (24) or (27) is sufficient. If we choose the critical length by requiring $\exp(-K\Delta x/v) \approx 5\%$, we get a required length of the homogeneous reach of $\Delta x \geq 3v/K$ or a required retention time fulfilling $K\tau \geq 3$. A second station can still be used to check the homogeneity of the reach. If the reach is heterogeneous over shorter distances and still the single station technique is applied, we have to accept that the resulting estimate is a relatively complicated weighted average of the true net production rate with more weight on subreaches close to the measurement station (see equations (28)–(30) for details). Such heterogeneities can considerably influence the estimate.

[36] 2. If a reach is not homogeneous over a reach longer than about $3v/K$, a two station technique using one of the estimators (23) or (26) should be applied. However, if the reach is very short, the downstream concentrations are dominated by the upstream concentrations rather than the processes within the reach. If we require the influence of the within reach processes to be at least 1/3, this requires the length of the homogeneous reach to fulfill $\Delta x \geq 0.4v/K$ or $K\tau \geq 0.4$. If the reach is shorter, the extraction of the within reach process rates becomes more and more difficult and requires very precise measurements.
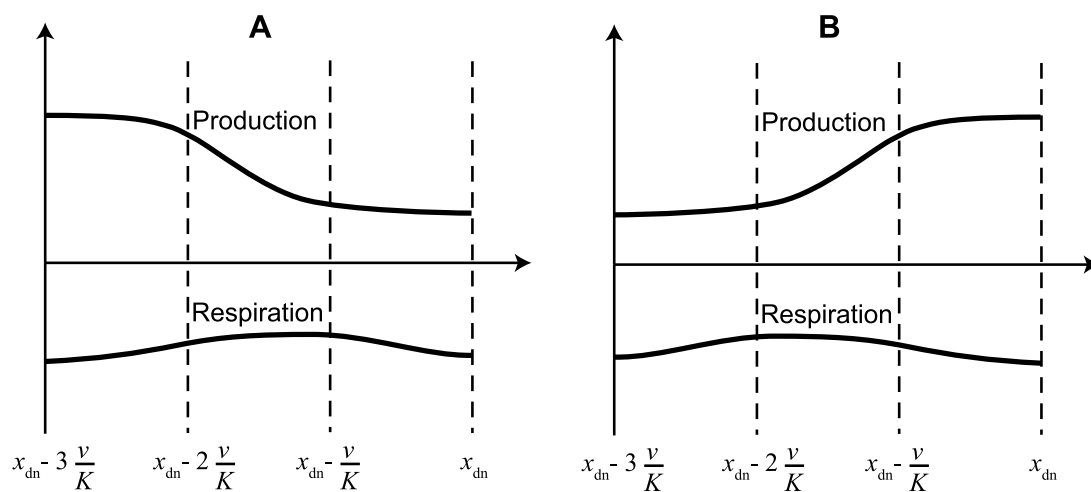
Figure 1. Two situations with the same mean net oxygen production over a river reach of length $3v/K$. The downstream station is assumed to be on the right-hand end of the reach. (left) Situation A. (right) Situation B.

[37] To conclude, for homogeneous stream reaches with $\Delta x \leq 0.4v/K$ or $K\tau \leq 0.4$ it will be difficult to extract metabolism rates with sufficient accuracy, for homogeneous reaches with $0.4v/K < \Delta x \leq 3v/K$ or $0.4 < K\tau \leq 3$, use of two stations using one of the estimators (23) or (26) is required, and for homogeneous reaches with $\Delta x > 3v/K$ or $K\tau > 3$ a single station using one of the estimators (24) or (27) is sufficient (but the two station technique is still good, too).

[38] A consequence of these considerations is that the ideal placement of measurement stations is at the interfaces between homogeneous stream subreaches, with a practical lower limit of the reaches in the order of $\Delta x = 0.4v/K$ or $K\tau = 0.4$. Somewhat shorter reaches may still be possible if high-quality data is available, for much shorter reaches it will be impossible to extract within reach process rates from very small upstream and downstream concentration differences.

[39] Whether to use our first, derivative-based estimators (23) and (24) or the time-correction based estimators (26) and (27) should not affect the result considerably if a good smoothing technique is used to estimate the derivatives required for the former approach. If such an algorithm is not available, the latter approach using time corrections instead of derivatives is recommended as interpolation is less susceptible to numerical errors than taking derivatives.

[40] To conclude, we would recommend researchers to apply the following guideline for placement of measurement stations: (1) Determine v and K in the stream segment of interest. (2) Estimate the critical lengths $0.4v/K$ and $3v/K$. (3) Analyze the river segment for heterogeneities such as varying exposition to light, river bed shape and river slope as well as to tributaries or groundwater input. (4) Try to identify homogeneous river reaches without significant tributaries of length $>0.4v/K$ and plan to place a measurement station at the downstream end of the reach. (5) For homogeneous reaches that are shorter than $3v/K$, plan to place another station at the upstream end of the reach.

[41] Please note that although tributaries could be considered in the estimator, it is usually a better strategy to search for river reaches without tributaries. This is because discharge and dissolved oxygen concentration in the tributaries are additional sources of uncertainty to the estimation procedure. This is particularly difficult for ground water input.

4. Numerical Implementation

[42] The crucial issue in using any of the four estimators given by the equations (23), (24), (26), and (27) is the use of adequate procedures for smoothing and taking derivatives from noisy data. We describe our concept of doing this in section 4.1 and its implementation in the statistics and graphics package R (http://www.r-project.org) in section 4.3.

4.1. Smoothing and Taking Derivatives

[43] To calculate from a data time series a smoothed value and its derivative at an arbitrary point in time, we use local quadratic regression. We fit a parabola to the data applying weights proportional to the density of a normal distribution of a given width centered at the point in time at which the value and derivative are to be calculated. The width of the standard deviation controls the degree of smoothing. This procedure produces highly consistent results for value and derivative at any point in time. This procedure is applied for all suggested estimators given by the equations (23), (24), (26), and (27).

4.2. Uncertainty Analysis

[44] As described in section 3.3, we can approximate the probability distribution of the net oxygen production rate by propagating the joint probability distribution of the parameters K, d and τ through the estimator (equations (23), (24), (26), or (27)). Numerically, this is implemented by Monte Carlo simulation and subsequent construction of the probability band based on quantiles of the empirical distribution function of the sample of net production estimates. The first-order sensitivity coefficients, S_1, were calculated by applying the Extended Fourier Analysis Sensitivity Test [*Cukier et al.*, 1978; *Saltelli et al.*, 1999, 2004] as imple-
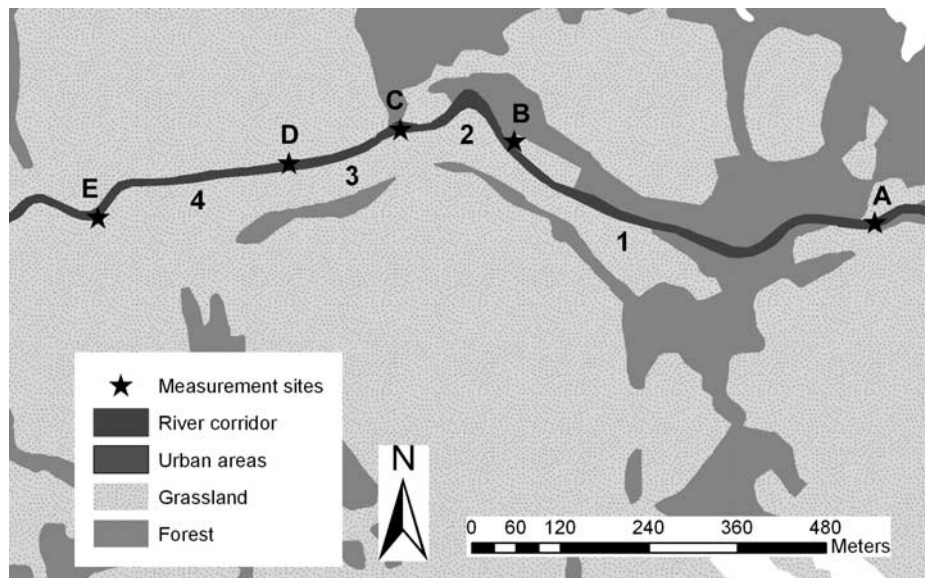
Figure 2. Overview of the investigated river segment with the measurement stations bounding four reaches of the river.

mented in the package "sensitivity" of the statistics and graphics package R (http://www.r-project.org).

4.3. Implementation of Estimators in R

[45] We implemented a function "smooth" that performs local quadratic regression of an arbitrary (time) series and returns smoothed values and derivatives. This function is not specific to our estimators. In addition we implemented a function to calculate estimates based on the equations (23), (24), (26), and (27). When using our procedure of smoothing and calculating derivatives, the two alternative estimators (23) and (26) produced nearly indistinguishable results as did the two alternatives (24) and (27). Monte Carlo simulation was also implemented in R. All scripts and data sets required to reproduce our results or to be adapted for the evaluation of other data sets can be downloaded from http://www.eawag.ch/~reichert.

5. Practical Relevance

[46] To demonstrate the practical relevance of spatial heterogeneity in rivers we took oxygen measurements in June 2008 at five sites along the small river Luteren near Rietbad (47°14′46.00″ N, 9°14′59.87″ E, 940 m a.s.l.) at the northeastern front range of the Swiss Alps. We then compared the evaluation of our estimators on subreaches between different stations.

5.1. Study Site

[47] Figure 2 gives an overview of the five measurement stations along the river. The five stations divide the investigated river segment into four reaches of approximately homogeneous conditions. Mean stream discharge was about 220 l/s, mean river width about 5 m. The most upstream reach 1 is completely shaded by a forest and riparian vegetation, reach 2 is partially shaded and reaches 3 and 4 are not shaded (see Figure 3). For this reason, we can expect considerable differences in the net oxygen production rate along the river. Table 1 summarizes the characteristics of all

four river reaches bounded by these measurement sites. The values in the last column of Table 1 demonstrate that the reaches are not long enough ($K\tau < 3$) to make the downstream dissolved oxygen concentration approximately independent of the upstream concentration. Three of the four reaches are even close to the limit of $K\tau = 0.4$ below which we expect considerable uncertainty in river metabolism estimates. The discharge did only slightly increase along the river segment and the dissolved oxygen concentrations in the (small) tributaries were similar to those in the main stream. This indicated that there was not a significant influence of possibly hypoxic groundwater entering the river.

5.2. Measurement Techniques

[48] At all five measurement stations dissolved oxygen, temperature and conductivity were recorded in 5-min intervals with optical dissolved oxygen probes YSI 6150
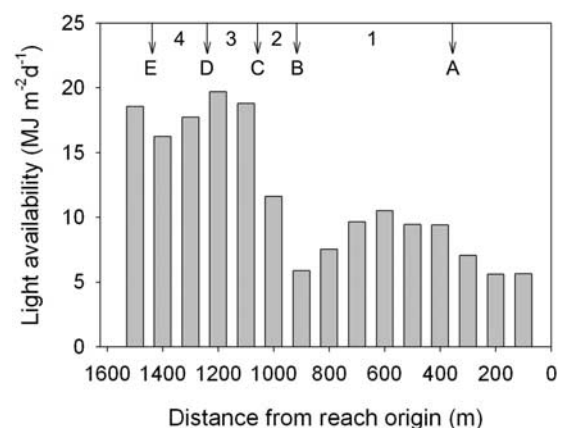
Figure 3. Light availability along the study stream segment of the river Luteren on 25 June 2008. The positions of the measurement stations and the reaches are indicated at the top.

Table 1. Characteristics of the Four Subsequent River Reaches and Their Estimated Standard Deviations[a]

Reach	Mean Depth d (m)	Reaeration Coefficient K (1/min)	Travel Time τ (min)	$K\tau$
1	0.111 ± 0.018	0.046 ± 0.014	28 ± 2.9	1.28 ± 0.41
2	0.180 ± 0.045	0.031 ± 0.015	14 ± 1.4	0.44 ± 0.22
3	0.191 ± 0.029	0.056 ± 0.020	8 ± 0.8	0.45 ± 0.17
4	0.178 ± 0.007	0.038 ± 0.026	12 ± 1.2	0.46 ± 0.31

[a]The last column is derived from the second and third columns.

connected to YSI 600 OMS V2 multiparameter sonde (YSI Inc., Yellow Springs, Ohio, USA). The probes were deployed in the thalweg of the stream, about 5 cm below the water surface, from 24 to 27 June 2008. On 26 June, dissolved oxygen was measured in all visible inflows within the study reach using a handheld HQ 40d oxygen meter (HACH Company, Loveland, Colorado, USA). Before deployment, the dissolved oxygen sensors were calibrated according the manufacturer's manual. After the field measurements, sonde-to-sonde variability was determined by simultaneously immersing the 5 probes in a thermo-regulated and aerated water bath (±0.1 °C). The temperature of the water bath was successively adjusted to 20, 18, 16, 14, 12, 10, 8, and 6°C and dissolved oxygen recorded every 30 s. Saturation concentration of dissolved oxygen was calculated using recorded temperatures and barometric pressure from a nearby meteorological station in Kloten (Federal Office of Meteorology and Climatology, MeteoSwiss) according to *Bührer* [1975]. Deviations from the calculated saturation concentrations were determined and used to correct the field dissolved oxygen records.

[49] Above-canopy global radiation data was obtained from the meteorological station at the top of the mountain Säntis (Federal Office of Meteorology and Climatology, MeteoSwiss). Hemispherical photographs of the canopy were taken with a high-resolution digital camera (Nikon D-70s, NIKON Corporation, Tokyo, Japan) fitted with a 180° fisheye lens every 100 m along the entire study reach. To calculate the direct global radiation reaching the stream bed, above canopy global radiation data was filtered with the computer program Hemiview (Dynamax Inc., Houston, USA) using the obtained canopy images.

[50] Discharge at each location and travel time between locations was measured twice during the study period. Fifty L NaCl solution (10 kg NaCL) were released (slug injection) 200 m upstream of the first location, and electrical conductivity was recorded in 1-min intervals at each of the five stations. Discharge was calculated according to *Gordon et al.* [2004]. Travel time of water was calculated based on the time when the conductivity peak passed a station. Stream widths (width of the wetted channel) measured every 100 m were used to calculate average stream width between the stations. Mean depth (d) was calculated as $d = Q/(vw)$, where Q is the discharge, v is the average flow velocity, and w is the average stream width.

[51] Estimates of reaeration coefficients were based on measurements for the gas exchange of sulfur hexa-fluoride (SF_6) [*Wanninkhof et al.*, 1990; *Genereux and Hemond*, 1992]. Gas injections of SF_6 were done twice during the deployment simultaneously to the slug additions of NaCl. Samples for volatile tracer concentrations were collected in

all locations 60 min after the conductivity pulse passed the downstream end of the study reach. A more detailed description of the sampling procedure and the subsequent analysis is given by *Cirpka et al.* [1993]. The gas exchange coefficient for dissolved oxygen, K, was calculated by multiplying the obtained gas exchange coefficient for SF_6 by 1.4 [*O'Connor and Dobbins*, 1958; *Haydik and Laudie*, 1974].

5.3. Results and Discussion

[52] Figure 4 (left) shows the saturation concentration in all four river reaches and the measured dissolved oxygen concentrations at both ends of the four river reaches. At all measurement sites, the river is undersaturated during the courses of all days. This is probably due to a significant contribution of mineralization rates of allochthonous organic material from the forest in addition to mineralization of autochthonous organic material. As mentioned above, we assumed the input of anoxic groundwater to be insignificant. Owing to primary production, the undersaturation is significantly smaller in the early afternoon than during the night.

[53] Figure 4 (middle) shows the net oxygen production rate estimates and their 90% probability intervals for all reaches based on the two stations technique. We present estimates for per area net production, $d \cdot \widehat{NP}$, rather than for the per volume net production, $\widehat{NP}$ given by our estimators (d is mean river depth). The results are based on the estimators (23) and (26) using the smoothing procedure described in section 4.1 with a standard deviation of 0.5 h for the weighting Gaussian distribution. The results for applying the two different estimators were nearly the same (not shown). The 90% uncertainty bands indicate a significant uncertainty of the estimates. This is in particular true for the reaches 2 and 4 in which the uncertainty of the reaeration coefficient is particularly large.

[54] As expected from the oxygen concentrations shown in Figure 4 (left), net oxygen production is always negative. However, Figure 4 (middle) clearly demonstrates that there are large differences in the net oxygen production rates within the four different river reaches. From the net oxygen production rates we can estimate respiration rates during the night when there is no light available for primary production. Primary production can then be estimated from the difference between net production rates during the night and day. Analyzing the amplitudes, we conclude that primary production is smallest in the reaches 1 and 2. This is exactly what we can expect due to the presence of riparian forest. Primary production is somewhat larger in reach 4 and much larger in reach 3. The large differences in respiration are more difficult to explain. While reaches 1 and 3 do not differ very strongly, respiration is significantly smaller in
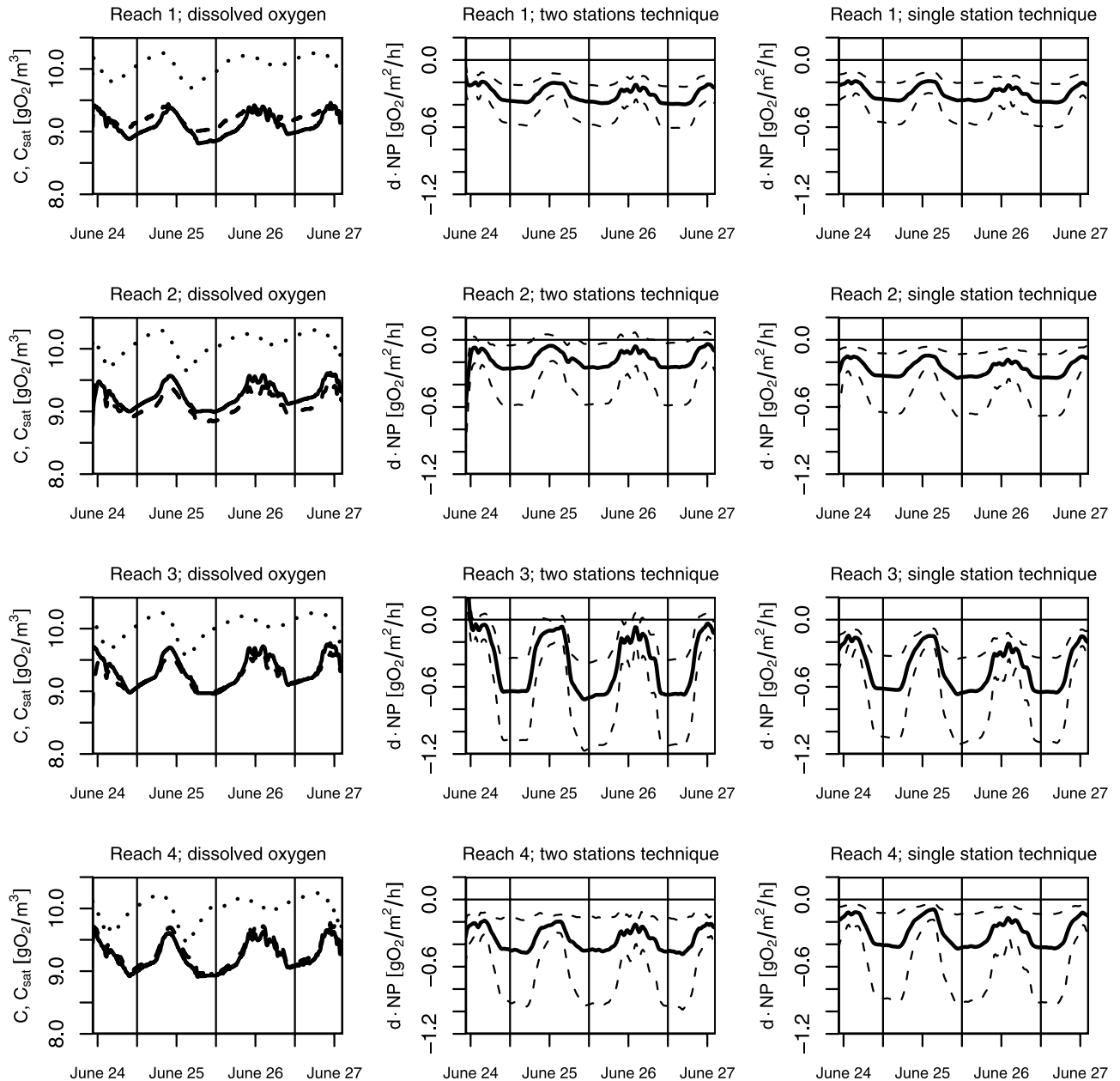
Figure 4. (left) Downstream (solid) and upstream (dashed) dissolved oxygen concentrations and oxygen saturation concentration (dotted) in all four river reaches. (middle) Best estimate (solid) and 90% predictive uncertainty interval (dashed) of net production in the four river reaches based on the two station technique (equations (23) or (26)). (right) Best estimate (solid) and 90% predictive uncertainty interval (dashed) of net production in the four river reaches based on the single station technique (equations (24) or (27)). See text for more details.

reach 2 and much larger in reach 4. The cause for theses differences could be different potential for retention of particulate organic matter transported in the river.

[55] To demonstrate the error of assuming the continuation of homogeneous conditions upstream of the river reaches under consideration, we applied the single station technique to all reaches also. Figure 4 (right) shows the results of the application of the single station estimator given by the equations (24) and (27). Again, the results of these two estimators were nearly identical (not shown). As shown in section 3.2, instead of getting an estimate just of

the upstream reach, we get a weighted average between this reach and further upstream reaches. For this reason, the differences between net production rate estimates of the different reaches are less pronounced for these estimators than those shown in Figure 4 (middle). The difference in amplitude between these estimates is particularly large for reach 3, as the single station estimate is influenced by reach 2 which is more strongly shaded than reach 3.

[56] Figure 4 (middle and right) demonstrates the high uncertainty of the estimates particularly during the night. The uncertainty is dominated by multiplicative effects of K
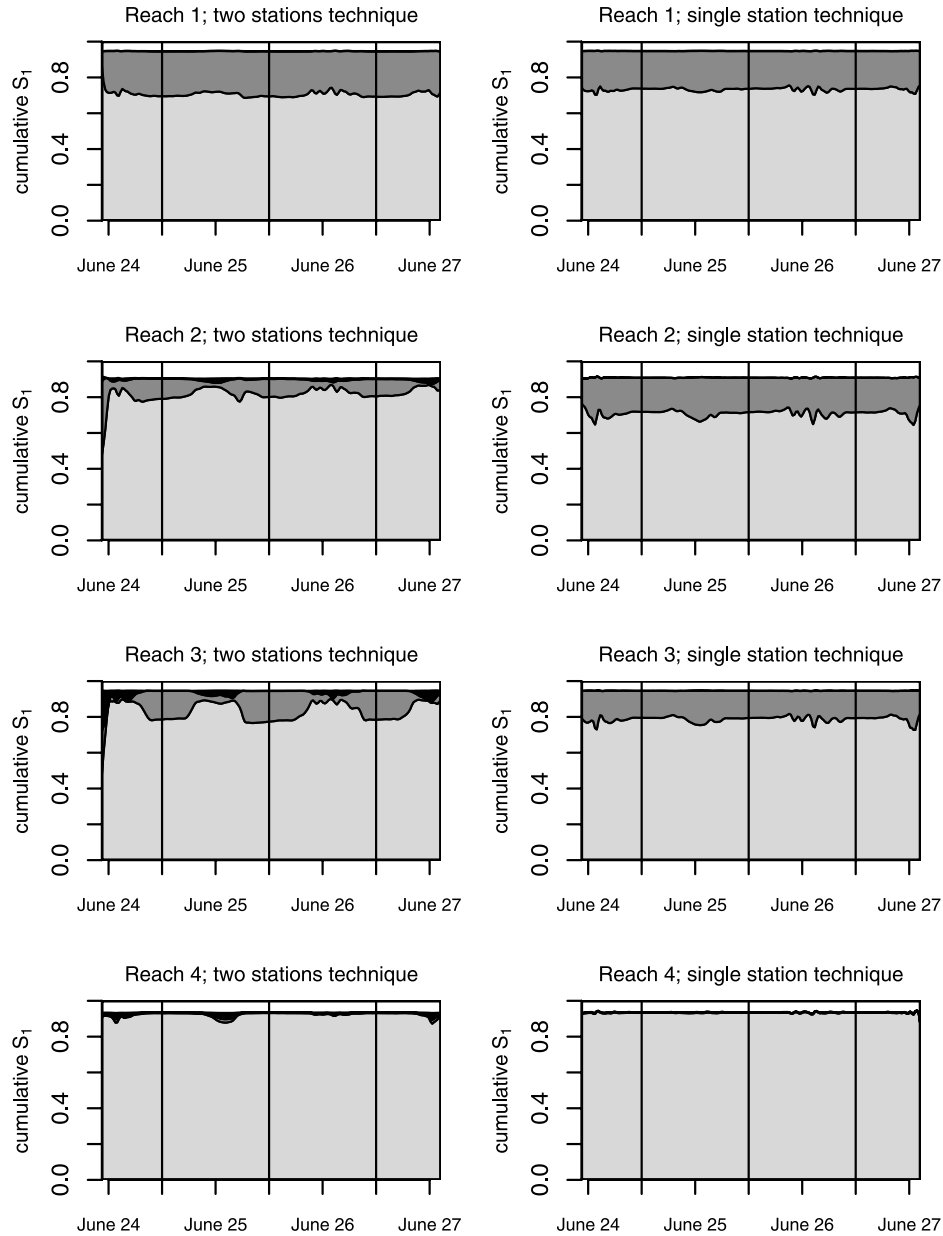
Figure 5. Cumulative plots of first-order sensitivity coefficients for all eight estimations shown in Figure 4. The areas indicate the first-order contributions to relative variance by the parameters K (light grey), d (dark grey), and τ (black).

and d; this is the reason why it increases with increasing absolute value of net oxygen production. To get an assessment of the relative contributions of the three parameters K, d and τ to the overall uncertainty, we calculated the first-order variance-based sensitivity coefficients S_1 according to equation (31) [*Saltelli et al.*, 1999, 2004]. The results for all four reaches and both, the two station and single station techniques, are shown in Figure 5. These results clearly demonstrate the dominant contribution of the reaeration coefficient, K, to estimation uncertainty (note that the results for the single station technique presented in Figure 5 (right) do not depend on τ). Our results very clearly indicate that careful measurement of the reaeration coefficient is crucial for getting good net oxygen production estimates in our case study. As it is much more difficult to accurately

measure K compared to d and τ, this result will apply for most other cases also.

[57] To visualize the weighted averaging process of the estimator, Figure 6 compares the best estimates for all four subreaches (Figure 6, left) with the best estimates of composite reaches of increasing length (Figure 6, right). The results demonstrate that the estimate is dominated by the most downstream reach, but, due to the short nondimensional length of this subreach ($K\tau \approx 0.46$), the upstream reaches still affect the estimate.

6. Summary and Conclusions

[58] This paper presents the following results:

[59] 1. A general solution of the transport-reaction equation for dissolved oxygen in a river reach demonstrates how

Net Production by Individual Reach   **Net Production by Extended Reach**
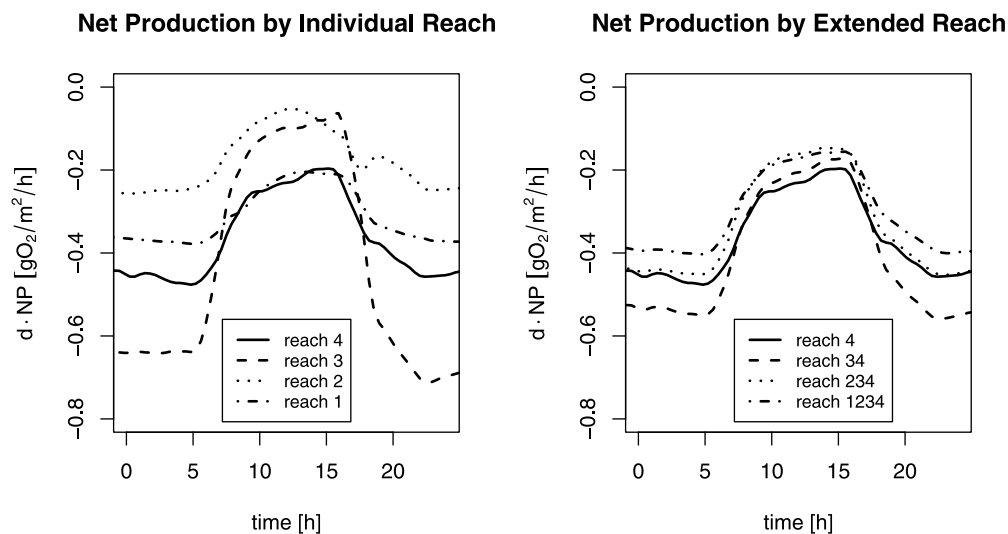
Figure 6. Comparison of best estimates of (left) the individual stream reaches with (right) those of a reach of increasing length starting with the most downstream reach. The horizontal axis represents hours of 25 June 2008.

downstream oxygen concentration depends on the flow velocity, the reaeration coefficient, dissolved oxygen saturation concentration and the net oxygen production rate along the river reach and on upstream dissolved oxygen concentration (equations (2) and (3)).

[60] 2. A special case of this solution for spatially homogeneous conditions links this general solution to earlier work on river metabolism (equations (6), (8), and (9)).

[61] 3. Another special case for two homogeneous river reaches in sequence explicitly demonstrates that the downstream dissolved oxygen concentration is a weighted sum of concentrations that would result for the two homogeneous subreaches (equations (13), (15), and (16)).

[62] 4. The equation for the homogeneous reach is then used to derive two estimators of the net oxygen production rate from transport time, the reaeration coefficient, oxygen saturation coefficient, and upstream and downstream dissolved oxygen time series (equations (23) and (26). These estimators generalize previously published estimators and the second one even eliminates the need of taking derivatives of measured time series.

[63] 5. For long river reaches (length larger than 3 times the reaeration coefficient times the transport time in the reach) these estimators become nearly independent of the upstream dissolved oxygen concentration and therefore simplify considerably (equations (24) and (27)).

[64] 6. We then clarify how the estimates calculated by applying these equations depend on river characteristics of a river consisting of two homogeneous reaches in sequence (equation (28)). In the simplest case, the estimate will be the weighted mean of net oxygen production of the two subreaches (equations (29) and (30)).

[65] 7. The analysis of the paper is used to derive practical recommendations of how to place measurement stations for estimating river metabolism rates (section 3.4).

[66] 8. The methodological part is concluded by presenting a smoothing procedure that allows its users to derive stable estimates of concentration and time derivatives from dissolved oxygen time series as they are required for the estimators described above (section 4.1).

[67] 9. The estimators described in this paper were implemented in the publicly available software package for graphics and statistics R (http://www.r-project.org) and can be downloaded from http://www.eawag.ch/~reichert.

[68] 10. The practical relevance of heterogeneity in river reaches and of the applicability of our estimators is demonstrated by a case study (section 5). Besides the demonstration of the usefulness of our estimators and their implementation, this case study demonstrates the dominance of the uncertainty of the reaeration coefficient on net production estimation uncertainty. This may be typical for other cases also.

[69] With the presentation of our study we intend to contribute to raising the awareness of the effect of heterogeneity in river reaches on river metabolism estimates. Our equations provide a general framework unifying past methods of river metabolism estimation and clarifying the way these estimators integrate over varying conditions in an investigated river reach.

References

Acuña, V., A. Giorgi, I. Muñoz, U. Uehlinger, and S. Sabater (2004), Flow extremes and benthic organic matter shape the metabolism of headwater Mediterranean stream, *Freshwater Biol.*, *49*, 960–971.

Bott, T. L., J. T. Brock, C. E. Gregory, D. King, and R. C. Peterson (1978), A comparison of methods for measuring primary productivity and community respiration in streams, *Hydrobiologia*, *60*, 3–12.

Brun, R., P. Reichert, and H.-R. Künsch (2001), Practical identifiability analysis of large environmental simulation models, *Water Resour. Res.*, *37*(4), 1015–1030.

Bührer, H. (1975), Computerprogramm zur Bekanntgabe aktueller Seedaten, *Schweiz Z. Hydrol.*, *37*, 332–346.

Chapra, S. C., and D. M. Di Toro (1991), Delta method for estimating primary production, respiration, and reaeration in streams, *J. Environ. Eng.*, *117*(5), 640–655.

Cirpka, O., P. Reichert, O. Wanner, S. R. Müller, and R. P. Schwarzenbach (1993), Gas exchange at river cascades: Field experiments and model calculations, *Environ. Sci. Technol.*, 27, 2086–2097.

Cukier, R. I., H. B. Levine, and K. E. Schuler (1978), Nonlinear sensitivity analysis of multiparameter model systems, *J. Comput. Phys.*, 26, 1–42.

Duffer, W. R., and T. C. Dorris (1966), Primary productivity in a southern great plain stream, *Limnol. Oceanogr.*, 11, 143–151.

Fisher, S. G. (1976), Organic matter processing by a stream-segment ecosystem: Fort River, Massachusettes, USA, *Int. Rev. Hydrobiol.*, 62, 701–727.

Genereux, D. P., and H. H. Hemond (1992), Determination of gas exchange rate constants for a small stream on Walker Branch watershed, Tennessee, *Water Resour. Res.*, 28, 2365–2374.

Gordon, N. D., T. A. McMahon, B. L. Finlayson, C. J. Gippel, and R. J. Nathan (2004), *Stream Hydrology—An Introduction for Ecologiests*, 2nd ed., John Wiley, New York.

Hall, R. O., and J. L. Tank (2005), Correcting whole-stream estimates of metabolism for groundwater input, *Limnol. Oceanogr. Methods*, 3, 222–229.

Haydik, W., and H. Laudie (1974), Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions, *Am. Inst. Chem. Eng. J.*, 20, 611–615.

Hornberger, G. M., and M. G. Kelly (1972), The determination of primary production in a stream using an exact solution to the oxygen balance equation, *Water Res. Bull.*, 8(4), 795–801.

Hornberger, G. M., and M. G. Kelly (1975), Atmospheric reaeration in a river using productivity analysis, *J. Environ. Eng. Div. Am. Soc. Civ. Eng.*, 101, 729–739.

Hoskin, C. M. (1959), Studies of oxygen metabolism of streams of North Carolina, *Publ. Inst. Mar. Sci. Univ. Tex.*, 6, 186–192.

Jones, J. B., S. G. Fisher, and N. B. Grimm (1995), Vertical hydrological exchange and ecosystem metabolism in a Sonoran Desert stream, *Ecology*, 76, 942–952.

Marzolf, E. R., P. J. Mulholland, and A. D. Steinmann (1994), Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole stream metabolism in streams, *Can. J. Fish. Aquat. Sci.*, 51, 1591–1599.

McConnel, W. J., and W. F. Sigler (1959), Chlorophyll productivity in a mountain river, *Limnol. Oceanogr.*, 4, 335–351.

McCutchan, J. H., and W. M. Lewis (2006), Groundwater flux and open-channel estimation of stream metabolism: Response to Hall and Tank, *Limnol. Oceanogr. Methods*, 4, 213–215.

McCutchan, J. H., W. M. Lewis, and J. F. Saunders (1998), Uncertainty in the estimation of stream metabolism from open-channel oxygen concentrations, *J. N. Am. Benthol. Soc.*, 17, 155–164.

Meyer, J. L., and R. T. Edwards (1990), Ecosystem metabolism and turnover of organic carbon along a blackwater river continuum, *Ecology*, 71, 668–677.

O'Connor, D. J., and W. E. Dobbins (1958), Mechanism of reaeration in natural streams, *Trans. Am. Soc. Chem. Eng.*, 123, 631–684.

Odum, H. T. (1956), Primary productivity in flowing waters, *Limnol. Oceanogr.*, 1, 102–117.

Pusch, M. (1996), The metabolism of organic matter in the hyporheic zone of a mountain stream, and its spatial distribution, *Hydrobiologia*, 323, 107–118.

Saltelli, A., S. Tarantola, and K. P.-S. Chan (1999), A quantitative model-independent method for global sensitivity analysis of model output, *Technometrics*, 41(1), 39–56.

Saltelli, A., S. Tarantola, F. Campolongo, and M. Ratto (Eds.) (2004), *Sensitivity Analysis in Practice—A Guide to Assessing Scientific Models*, John Wiley, Chichester, U. K.

Schurr, J. M., and J. Ruchti (1975), Kinetics of oxygen exchange, photosynthesis, and respiration in rivers determined from time-delayed correlations between sunlight and dissolved oxygen, *Hydrologie*, 37(1), 144–174.

Thyssen, N., M. Erlandsen, E. Jeppesen, and C. Ursin (1987), Reaeration of oxygen in shallow, macrophyte rich streams: I - Determination of the reaeration coefficient, *Int. Rev. Hydrobiol.*, 72, 405–429.

Uehlinger, U. (1991), Spatial and temporal variability of periphyton biomass in a prealpine river (Necker, Switzerland), *Arch. Hydrobiol.*, 123, 219–237.

Uehlinger, U. (2006), Annual cycle and inter-annual variability of gross primary production and ecosystem respiration in a floodprone river during a 15-year period, *Freshwater Biol.*, 51, 938–950.

Uehlinger, U., and W. M. Naegeli (1998), Ecosystem metabolism, disturbance, and stability in a prealpine gravel bed river, *J. N. Am. Benthol. Soc.*, 17, 165–178.

Van de Bogert, M. C., S. R. Carpenter, J. J. Cole, and M. L. Pace (2007), Assessing pelagic and benthic metabolism using free water measurements, *Limnol. Oceanogr. Methods*, 5, 145–155.

Wanninkhof, R., P. J. Mulholland, and J. W. Elwood (1990), Gas exchange rates for a first-order stream determined with deliberate and natural tracers, *Water Resour. Res.*, 26, 1621–1630.

Young, R. G., and A. D. Huryn (1999), Effects of land use on stream metabolism and organic matter turnover, *Ecol. Appl.*, 9(4), 1359–1376.

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