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| 2 | Journal of Geophysical Research: Biogeosciences |
| 3 | Supporting Information for |
| 4 | Comprehensive multi-year carbon budget of a temperate headwater stream |
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Text S1. STUDY SITE

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We conducted this study in Watershed 1 (WS1), a 95.9-ha (~1 km²) catchment located in the H.J. Andrews Experimental Forest in the western Cascade Mountains of Oregon, USA (44° 10' N. 122° 15' W; Figure S1 and S2). The climate is characterized by wet, mild winters and dry, cool summers. Mean monthly air temperatures range from 1 °C in January to 18 °C in July. Precipitation is concentrated in autumn and winter and averages 2300 to 3550 mm per year depending on the elevation. Some precipitation occurs as snow; peak snow water equivalent is about 375 mm at highest elevation. Minimum stream flows occur at the end of the summer dry season, with discharge < 0.5 L s⁻¹. WS1 has maximum elevation of 1027 m and minimum elevation of 450 m, WNW aspect and an average slope of 29%. The watershed was logged and burned completely between 1962 and 1966, was aerially seeded in October 1967, and 10 ha of the watershed reseeded again, in October 1968 [Lutz and Halpern, 2006]. The establishment of new vegetation was poor so in April and May 1969, and April 1971, the watershed was replanted with 2-vr-old Douglas fir (Pseudotsuga menziesii [Mirbel] Franco; [Johnson and Jones, 2000]). Streamside vegetation is currently dominated by red alder (Alnus rubrus) at lower elevations [Lutz and Halpern, 2006], with some presence of vine maple (Acer circinatum), bigleaf maple (Acer macrophyllum) and black cottonwood (Populus trichocarpa, [Frady et al., 2007]), and by Douglas fir, in the rest of the catchment.

Text S2. STREAMFLOW AND WATER CHEMISTRY COLLECTION AND ANALYSIS

Stream gauging at WS1 started in October 1952. Since then, stage height has been measured continuously in a trapezoidal flume which is complemented with a v-notch weir mounted to the existing flumes to increase measurement sensitivity during low flows (i.e., from mid-July to late Sept). Collection of stream water for chemistry analysis started in October 2003. Stream chemistry samples are collected at the gauge, sampling frequency proportionally to flow (at least every 13.3 hours during low flows up to every 40 min at maximum flows) and composite over three-week periods (Figure S3). Water samples are stored in dark, cold conditions until filtered and processed the Cooperative Chemical Analytical Laboratory at Oregon State University (http://ccal.oregonstate.edu). One source of uncertainty in our results was the possible degradation of the samples while sitting unfiltered in the field. To test the extent of this degradation, the HJ Andrews Experimental Forest applied a QA/QC process which included the simultaneous collection of two samples, one filtered and processed within two days of collection and the other left unfiltered in the gauge house for 3-weeks. The samples were collected twice per year (summer and winter) in 9 gauges across the Andrews between 1989 and 2006 (18 years with a total of 36 samples, except for DOC which was collected between 2003 and 2006 with a total of 6 samples). The statistical analysis of these two types of samples using a paired t-test showed no significant differences in SSED or DOC (p>0.05) but a consistent decrease in alkalinity (mean \pm SE: -0.7 \pm 0.2%) when samples were left unfiltered in the field. Concentration of the sample filtered immediately was always able to predict the sample analyzed 3 weeks-later (Table S1).

Alkalinity and pH analysis are done using a ManTech PC-Titrate auto titrator system following a modification of the APHA 2320 method, using 0.02N Na₂CO₃ and 0.02N H₂SO₄, for alkalinity, and APHA 4500H method for pH [APHA, 2005]. Water temperature is measured every five minutes upstream of the gage using a Campbell Scientific model 107 temperature probe with a Fenwal Electronics UUT51J1 thermistor. Barometric pressure is measured at the Primary

Meteorological Station (PriMet), located at the Andrews headquarters (430 m asl) at 500 m linear distance from WS1. Barometric pressure from this station has been only available since Dec 2009 [Daly, 2015]. We established a relation between PriMet data and data from Redmond airport (80 km from WS1) and used the relationship to estimate barometric pressure for the days with no PriMet barometric data to estimate metabolism and CO₂ evasion rates to the atmosphere.

Dissolved organic carbon (DOC) was defined as the carbon contained in particles smaller than 0.7 μ m. Particulate organic carbon in suspended sediments (sPOC) was defined as the carbon contained within particulate organic matter between 0.7 and 1.2 μ m, and was estimated from suspended sediments. Suspended sediments were obtained by filtering an aliquot of the three-week composited stream water sample using Whatman GF/F and GF/C glass microfiber pre-weighted filters. Filters were then dried at 80 °C for five days and reweighed to measure the amount of suspended solid per unit of filtered volume [*Motter and Jones*, 2013]. A selection of 29 filters from composite samples collected between 2004 and 2006 which were processed to remove carbonates, powdered, and combusted with oxygen using a Costech flash Elemental Analyser [*Smith*, 2013] to estimate the carbon content in suspended sediments. Average sPOC was 2.75 \pm 2.1% of suspended sediments.

Dissolved inorganic carbon (DIC is the sum of inorganic carbon species in solution: carbon dioxide (CO₂), carbonic acid (H₂CO₃), bicarbonate anion (HCO₃⁻) and carbonate (CO₃²-). DIC was estimated for the 2004-2013 water years from total alkalinity, pH, water temperature, and barometric pressure using CO₂calc v 1.2.8 [*Robbins et al.*, 2010] and the CO₂ constants of *Millero* [1979]. In addition, DIC was measured monthly in stream water simultaneously to pCO₂ measurements between August 2013 and July 2014 and from a set of 6 samples (3 replicates each) collected at the end of the 40-m reach on 4 different days during August 2012 (but also see section S2.4). Stream water samples were collected in a 60 ml luer-lock syringe that was sealed underwater to avoid outgassing, refrigerated, and analyzed in the lab with a Shimadzu TOC-VCSH Combustion Analyzer [*Motter*, 2015].

Downstream fluxes for DOC, sPOC, and DIC were calculated using three-weekly composite stream chemistry samples and streamflow measurements recorded at the mouth of the watershed following:

$$F = a \sum_{j=1}^{j=dy} f_j = a \sum_{j=1}^{j=dy} c_j Q_j$$
 (1)

99 where:

a is a unit conversion factor

F is the estimated solute flux (in kg C mo⁻¹ or yr⁻¹) for a time period (i.e., month or year)

j is the day since the start of the time period

dy is the total number of days in the time period

 f_i is the solute flux on day j (in g C d⁻¹)

 C_j is the solute concentration on the composite sample collected on day j (in mg C L⁻¹)

 Q_j is the accumulated streamflow between day j and the day when the last chemistry sample was collected (in Ls⁻¹)

The annual bedload particulate organic carbon (bPOC) was calculated from the bedload sediment flux in WS1 based on data from 1997 - 2013. This period is 31 - 47 years after the watershed was burned and follows the year with the flood of record, 1996, which had a sediment export nearly four times the post-fire average. While 1996 would be valuable to include in the overall carbon budget, we did not have concomitant records of water chemistry, and so elected to start the bPOC budget in 1997. Bedload sediment is accumulated in a sediment collection basin at the bottom of WS1 and its volume is measured yearly. In July, 2014, we collected approximately 200 g (dry weight) of sediment from random locations and depths (n = 6) in the basin after one year of sediment accumulation. Organic matter was largely wood chips, leaves, and biofilms on sand and gravel by visual inspection. Organic matter fraction was measured by loss on ignition. The proportion of carbon in the organic matter (i.e., bPOC) was calculated by multiplying the organic matter fraction by 0.58, the Van Bemmelen factor, which is the typical average of organic carbon in organic matter [Nelson et al., 1996]. Average bPOC was $2.85 \pm 0.81\%$ of bedload sediment.

Text S3. ESTIMATION OF GAS TRANSFER COEFFICIENTS

In order to calculate primary production, respiration, and CO_2 evasion to the atmosphere, we estimated oxygen and CO_2 gas transfer coefficients (k_{gas} ; defined as the portion of the tracer gas that is lost over a specific reach per unit of time). Estimations were based on the decline in gas concentration during steady-state injections of a gas tracer (propane – C_3H_8 or sulfur hexafluoride – SF_6) and a conservative tracer, sodium chloride [Bott et al., 2006; Hall and Tank, 2003]. Gas samples were analyzed in an Agilent 7890A gas chromatograph system and the measured values were corrected for dilution using electrical conductivity (EC) readings as a surrogate of conservative tracer concentration at the two stations following:

$$K_{gas} = \frac{1}{\tau} \ln \left(\frac{G_{upst} E C_{downst}}{G_{downst} E C_{upst}} \right)$$
 (2)

where K_{gas} is reaeration rate (min⁻¹), L is length of the stream reach (m), τ (min) is the nominal travel time measured as the time since the start of the tracer injection needed for the downstream site to reach half of the maximum EC, G is gas concentration, EC is electrical conductivity, and upst and downst refer to upstream and downstream locations, respectively.

Propane or SF₆ gas transfer coefficients were then converted to the target gas transfer coefficient (i.e., K_{02} or K_{C02}) according to *Mulholland et al.* [2004]:

$$K_{O2 \ or \ CO2} = K_{gas} \left(\frac{d_{O2 \ or \ CO2}}{d_{gas}} \right)^n$$
 (3)

where *n* is a coefficient describing the characteristics of the water surface in relation to the process dominating diffusion [Jähne et al., 1987; Ledwell, 1984; MacIntyre et al., 1995], in this case set to 0.5, and *d* are the gas diffusion coefficients calculated from temperature dependent equations. Because at a given temperature, the kinematic viscosity of water is the same in the numerator and denominator of equation 3, we can substitute the diffusion coefficients for the Schmidt numbers

 $(Sc = A - BT + CT^2 - DT^3)$, where T is temperature in degrees Celsius and coefficients are described in Table S2), which results in the following conversion factors:

$$K_{O2} = 1.345 K_{SF6} \tag{4}$$

$$K_{O2} = 1.396 K_{C3H8}$$
 (5)

$$K_{CO2} = 1.267 K_{SF6} \tag{6}$$

$$K_{CO2} = 1.282 K_{C3H8}$$
 (7)

A total of 9 injections of a gas and a conservative tracer were performed in the same reach between 2009 and 2013. We used these results to estimate metabolism and to develop a relationship between k and stream discharge.

Text S4. STREAM METABOLISM

Stream metabolism was calculated from field measurements during 7 periods between July 2009 and June 2014, and include a total of 32 days (see Table S3 for exact dates) using the open-channel, two-station approach [Marzolf et al., 1994] and the following equation:

$$\Delta DO = GPP - ER \pm reaeration \tag{8}$$

where ΔDO is the change in dissolved oxygen between upstream and downstream (mg O₂ m⁻² d⁻¹), GPP is the gross primary production (mg O₂ m⁻² d⁻¹), ER is stream ecosystem respiration (mg O₂ L⁻¹ m⁻²) and reaeration refers to the flux of oxygen transferred to the atmosphere (mg O₂ m⁻² d⁻¹). Dissolved oxygen (DO) concentration and temperature were automatically recorded at 5-min intervals using two YSI 6600 V2 sondes, which were located at the upstream and downstream ends of the study reach. Recording periods lasted a minimum of 48 h. The DO exchange with the atmosphere (i.e., reaeration flux) was calculated based on the average DO saturation deficit in the reach, the reaeration rate (k_{O_2}), the travel time between the two stations, and stream discharge [*Young and Huryn*, 1998]. Percent DO saturation was determined using DO concentration and temperature data [*Bales and Nardi*, 2008] together with a standard altitude-air pressure algorithm to correct for site altitude. During stream metabolic measurement campaigns, we measured photosyntetically active radiation (PAR) data every 10 min using a LiCor 190SA sensor (LiCor Biosciences, Lincoln, NE, USA) connected to a Campbell Scientific logger. Respiration, primary production and net metabolism expressed in oxygen-flux units (Figure S4) were transformed to carbon flux units by applying photosynthetic coefficients [*Bott*, 2006].

Text S5. STREAM-ATMOSPHERE FLUXES OF CO2

The instantaneous evasion rates of CO₂ to the atmosphere (E_{CO2} , mg C s⁻¹) for the 2003-2010 water year period were calculated following the equation described in *Young and Huryn* [1998] for oxygen evasion and posteriorly applied to calculate CO₂ evasion [*Hope et al.*, 2001; *Wallin et al.*, 2011; 2013]:

$$E_{CO2} = \left[\Delta CO_2 \times k_{CO_2} \times \tau \times Q \right] \tag{9}$$

where ΔCO_2 (mg C L⁻¹) is the difference between CO₂ concentration in the stream and CO₂ concentration in the atmosphere, k_{CO_2} (min⁻¹) is the gas specific transfer coefficient, τ (min) is the nominal travel time, and Q (L s⁻¹) is streamflow.

Concentrations of CO₂ in the stream were estimated using equation 10 from DIC which, in turn, was estimated from water temperature, barometric pressure, and total alkalinity and pH (from the 3-weekly composite samples), using CO₂calc v 1.2.9 [*Robbins et al.*, 2010] and the CO₂ constants recommended for freshwaters [*Millero*, 1979].

$$pCO_2 = \frac{[DIC] \ 10^{m[DIC]-b}}{K_{CO_2}(K_1 + 10^{m[DIC]-b})}$$
(10)

where [] indicates molar concentration (M = mol L⁻¹), K_{CO_2} is the equilibrium constant between dissociated carbonic acid, $H_2CO_3^0$, and pCO_2 ($10^{-1.47}$ M bar⁻¹), K_1 is the equilibrium constant between H⁺, HCO_3^- , and $H_2CO_3^0$ ($10^{-6.35}$ M), and m and b are empirical coefficients for $pH = -\log[H^+] = -m$ [DIC] + b. This model is geochemically self-consistent, assuming (a) [CO_3^{2-}] $\sim = 0$, valid for the circumneutral pH of WS1; and (b) a strong linear relationship between [DIC] and pH. Based on stream samples from Aug 2013 through Jul 2014 where pCO₂ and DIC were measured simultaneously, we estimated m = 0.111 and b = 8.50 (n = 7, $r^2 = 0.990$). pCO₂ in the stream was measured over one year using a Vaisala Carbocap GMM220, modified similar to *Johnson et al.* [2010], and attached to a Campbell Scientific datalogger.

Concentrations of CO₂ in the atmosphere were measured at 15 min intervals from one inlet located at 2.5 cm above the stream surface on a float. The inlet was sampled continuously into a 1 liter buffer volume at a flow rate of 0.6 liters per minute, from which subsamples were drawn by a cavity-ringdown spectrometer (Model CFFDS with 16-port multiplexer; Picarro instruments, Santa Clara, CA, USA) at a flow rate of 0.3 liters per minute for 85 s seconds every 15 minutes.

A time series of instantaneous evasion flux (E_{CO2}) was then created by multiplying ΔCO_2 by k_{CO_2} and τ estimated from the relationship that we developed between these variables and streamflow. E_{CO2} was converted to a monthly or annual flux per unit of area of stream (kg C m⁻² y⁻¹) by integrating the time series to the appropriate time step and dividing it by the total stream surface area (m²). E_{CO2} was also reported as monthly and annual flux per hectare of watershed by dividing the flux per unit of stream area by the watershed area (95.9 ha).

Stream area was estimated based on the relationship between streamflow and stream area at a 40-m reach obtained from measurements in different times of the year. Stream area was estimated for every 10-m segment of the stream network based on that relationship and the estimated values of streamflow at the end of this 10-m segments. For every streamflow recorded at the gage, we Streamflow at the end of the 10-m segments was estimated using the streamflow at the gage and the contributing area of the segment to the total streamflow.

Terrestrial NEP of watershed 1 was modelled by Dr. Turner for WS1 using the model described at Turner et al. [2011] using 1-km grid GIS data for the watershed [Spies, 2013]. It was estimated to be 2,480 kg C ha⁻¹ yr⁻¹.

Text S7. MONTE CARLO ANALYSIS

Uncertainties in many of our estimates may be large, so we performed a Monte Carlo analysis on each estimate and the total stream carbon budget. For each component of the stream carbon budget – DIC, DIC, sPOC, bPOC, and CO₂ evasion, we placed all equations into a numerical computing software (Matlab, The Mathworks Inc.). For every variable in every equation we estimated a 95% confidence interval (CI). All variables were assumed to be independent and normally distributed. Error was sometimes assumed to be random (changes for each 3 week interval), and sometimes assumed to be systematic (changes each iteration). Some variables appear in more than one equation (e.g., stream discharge), causing CIs for each component to be correlated with other CIs. For this reason, we also calculated the overall CI for the total stream carbon budget. Using equation 10 as an example, the parameters m and b had significant uncertainty because of a small data set. Using a regression analysis, we estimated the uncertainty on the parameters as $m = 0.111 \pm 0.173$, and $b = 8.50 \pm 0.13$.

The final equations used in the Monte Carlo analysis were:

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DOC (kg C ha<sup>-1</sup> yr<sup>-1</sup>) = Q (L s<sup>-1</sup>) x DOC (mg C L<sup>-1</sup>) x \beta/ ws area (ha)
DIC (kg C ha<sup>-1</sup> yr<sup>-1</sup>) = Q (L s<sup>-1</sup>) x DIC (mg C L<sup>-1</sup>) x \beta/ ws area (ha)
sPOC (kg C ha<sup>-1</sup> yr<sup>-1</sup>) = Q (L s<sup>-1</sup>) x SSED (mg C L<sup>-1</sup>) x f_{SSED} x \beta/ ws area (ha)
bPOC (kg C ha<sup>-1</sup> yr<sup>-1</sup>) = Bedload (m³ ha<sup>-1</sup> yr<sup>-1</sup>) x Bulk density (kg m<sup>-3</sup>) x f<sub>BED</sub> (-)
\beta = 10e^{-6} (kg mg^{-1}) x 86400 (sec d^{-1}) x 365.25 (d yr^{-1})
ws area = watershed area = 96 ha
SSED = suspended sediments
f_{SSED} = \text{fraction of carbon in suspended sediments} = 0.0275 \pm 2.1\%
Bulk density (kg m<sup>-3</sup>) = mineral density (kg m<sup>-3</sup>) x (1 - porosity (-))
Mineral \ density = 2650 \pm 100 \ kg \ m^{-3}
Porosity = 0.35 \pm 0.1
f_{BED} = \text{fraction of carbon in bedload} = f_{om} (-) x f_{C} (-)
f_{OM} = \text{fraction of carbon in organic matter in bedload} = 0.0492 \pm 0.0139
f_{C} = \text{fraction of carbon in organic matter in bedload} = 0.58 \pm 0.1
Evasion (kg C ha<sup>-1</sup> yr<sup>-1</sup>) = E_{CO2} (µg CO<sub>2</sub> s<sup>-1</sup>) x 3.1558e<sup>-2</sup>/ws area (ha)
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$$E_{CO2}$$
 (µg CO₂ s⁻¹) = [$\Delta CO_2 \times K_{CO_2} \times \tau \times Q$]
 ΔCO_2 (µg CO₂ L⁻¹) = (CO₂-stream - CO₂-atm)
CO₂-stream (µg CO₂ L⁻¹) = CO₂stream-v $\frac{M}{R (273.15+T_{water})} \times 0.9877^{\frac{alt}{100}}$

M = carbon molecular weight =12.01078 g mol⁻¹

R = Universal Gas Law Constant = 0.08205734 L atm K⁻¹ mol⁻¹

 T_{water} = Water temperature in °C

Alt = altitude = 450 m

CO₂stream-v (ppmv) = 2449x
$$\frac{[DIC] \ 10^{m[DIC]-b}}{K_{CO_2}(MK_1 + 10^{m[DIC]-b})}$$

b = empirical coefficient = 8.5036 ± 0.1314

 $m = \text{empirical coefficient} = 0.11143 \pm 0.1725$

[DIC] = DIC concentration in mols L^{-1}

 K_{CO_2} = equilibrium constant between dissociated carbonic acid, $H_2CO_3^0$, and $pCO_2 = 10^{-1.47} \,\text{M bar}^{-1}$

 K_1 = equilibrium constant between H⁺, HCO₃⁻, and H₂CO₃⁰ = $10^{-6.35}$ M)

CO₂-atm (µg CO₂ L⁻¹) = CO₂atm-v
$$\frac{M}{R (273.15 + T_{water})} \times 0.9877^{\frac{alt}{100}}$$

$$Y = K_{CO_2} \times \tau \times Q$$

$$E_{CO2} = \Upsilon \Delta CO_2$$

221 Text S8. DATA AVAILABILITY

- 222 Long term data are publically available on the Andrews website:
- 223 <u>http://andrewsforest.oregonstate.edu/lter/data.cfm?frameURL=8</u>. Specifically we relied on data
- 224 sets:

- 225 CF002 -stream chemistry and suspended sediment [Johnson and Fredriksen, 2015]
- 226 CF010 -stream carbon dioxide [*Haggerty and Dosch*, 2016]
- GI010 -bare earth LiDAR [Spies, 2013]
- 228 HF004 -stream discharge [Johnson and Rothacher, 2016]
- 229 HS004 -bedload measurements [Johnson and Grant, 2011]
- 230 MS001 -climate measurements [Daly and McKee, 2015]

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Figure S1. Study site location (Lat 44.21, Long -122.26)

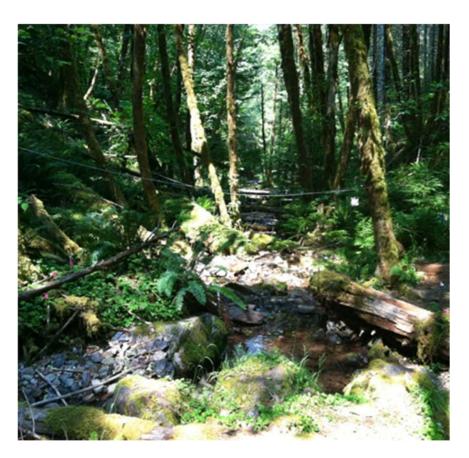


Figure S2. Image of the stream draining WS1

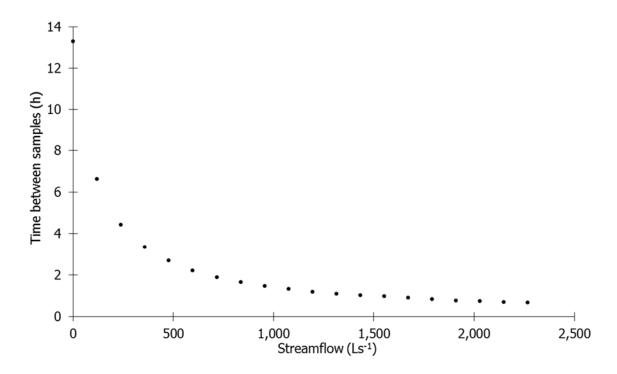


Figure S3. Water sampling scheme for the WS1 stream. Samples were collected every 13.3 h at low flows and up to every 40 minutes at high flows and composite over 3-week periods.

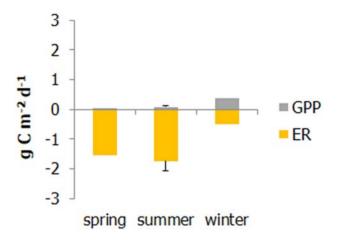


Figure S4. Fluxes in ecosystem respiration and gross primary production measured in WS1. Error bars are SEM, number of measurements were 1, 2, 29 for winter, spring and summer, respectively.

| Analyte | Slope | Intercept | \mathbb{R}^2 | N | p |
|------------|-------|-----------|----------------|----|--------|
| Alkalinity | 1.017 | ns | 0.998 | 36 | <0.001 |
| sPOC | 0.539 | ns | 0.567 | 36 | <0.001 |
| DOC | 0.733 | ns | 0.966 | 6 | <0.001 |
| рН | 0.828 | ns | 0.973 | 36 | <0.001 |

Table S1. Regression coefficients between samples collected simultaneously during different times of the year, one filtered and analyzed within two days of collection, the other filtered and analyzed 3 weeks after collection. "ns"= not significant. For sPOC, the relationship considering only samples collected in winter, i.e., when the majority of the sPOC export happens, is slope= 0.676, R^2 =0.795, N=18, p<0.001.

| gas | A | В | С | D | reference | |
|----------|--------|--------|--------|----------|-------------------------------|--|
| O_2 | 1800.6 | 120.1 | 3.7818 | 0.047608 | [Wanninkhof, 1992] | |
| CO_2 | 1911.1 | 118.11 | 3.4527 | 0.04132 | [Wanninkhof, 1992] | |
| C_3H_8 | 3343 | 259.43 | 9.601 | 0.1336 | [Witherspoon and Saraf, 1965] | |
| SF_6 | 3255.3 | 217.13 | 6.837 | 0.08607 | [Wanninkhof, 1992] | |

Table S2. Coefficients for the calculation of Schmidt numbers for gases relevant to our study.

| Spring | Summer | Winter | | |
|-----------------|-------------------|------------------|--|--|
| 5/4 to 5/5/2010 | 7/27 to 8/2/2009 | 2/8 to 2/10/2010 | | |
| | 8/2 to 8/5/2010 | | | |
| | 7/31 to 8/4/2012 | | | |
| | 8/21 to 8/23/2012 | | | |
| | 7/24 to 8/1/2013 | | | |

Table S3. Dates of metabolism measurements.

| | Annua | l concent | rations | Annual fluxes | | |
|---------|--------|----------------------|---------|---|-------|-------|
| | (| mg C L ⁻¹ |) | (kg C ha ⁻¹ yr ⁻¹) | | |
| | Median | 2.5% | 97.5% | Median | 2.5% | 97.5% |
| DOC | 1.16 | 0.88 | 2.25 | 17.4 | 17.2 | 17.7 |
| DIC | 5.46 | 4.33 | 7.73 | 63.0 | 62.0 | 63.9 |
| CO_2 | 0.47 | 0.27 | 1.09 | 42.2 | 7.7 | 209.3 |
| sPOC | 0.14 | 0.02 | 5.90 | 16.5 | 15.9 | 17.1 |
| bPOC | na | na | na | 17.2 | 3.4 | 46.0 |
| Total C | 7.2 | 5.5 | 17.0 | 158.7 | 116.4 | 322.6 |
| bPOC | na | na | na | 17.2 | 3.4 | 46.0 |

Table S4. Annual carbon concentrations and fluxes. Fluxes were estimated using concentration and streamflow. Na = not available. Mean annual streamflow for the study period was 38.96 L s^{-1} .