AGU PUBLICATIONS

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE

10.1002/2015JG003050

Key Points:

- Here we present a 10 year detailed C budget for a small headwater stream
- This headwater stream exported 159 kg C ha^{-1} y^{-1}, which is similar to global carbon river exports
- 27% of carbon exported from the stream occurred as evasion to atmosphere, and 73% was exported in streamflow

Supporting Information:

- Supporting Information S1

Correspondence to:
A. Argerich,
alba.argerich@oregonstate.edu

Citation:
Argerich, A., R. Haggerty, S. L. Johnson, S. M. Wondzell, N. Dosch, H. Corson-Rikert, L. R. Ashkenas, R. Pennington, and C. K. Thomas (2016), Comprehensive multiyear carbon budget of a temperate headwater stream, *J. Geophys. Res. Biogeosci.*, *121*, doi:10.1002/2015JG003050.

Received 6 MAY 2015
Accepted 26 APR 2016
Accepted article online 29 APR 2016

Comprehensive multiyear carbon budget of a temperate headwater stream

Alba Argerich[1], Roy Haggerty[2], Sherri L. Johnson[3], Steven M. Wondzell[3], Nicholas Dosch[2], Hayley Corson-Rikert[2], Linda R. Ashkenas[4], Robert Pennington[2], and Christoph K. Thomas[2,5]

[1]Department of Forest Engineering, Resources and Management, College of Forestry, Oregon State University, Corvallis, Oregon, USA, [2]College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA, [3]U.S. Forest Service Pacific Northwest Research Station, Corvallis, Oregon, USA, [4]Department of Fisheries and Wildlife, College of Agricultural Sciences, Oregon State University, Corvallis, Oregon, USA, [5]Micrometeorology Group, Now at University of Bayreuth, Bayreuth, Germany

Abstract Headwater streams comprise nearly 90% of the total length of perennial channels in global catchments. They mineralize organic carbon entering from terrestrial systems, evade terrestrial carbon dioxide (CO_2), and generate and remove carbon through in-stream primary production and respiration. Despite their importance, headwater streams are often neglected in global carbon budgets primarily because of a lack of available data. We measured these processes, in detail, over a 10 year period in a stream draining a 96 ha forested watershed in western Oregon, USA. This stream, which represents only 0.4% of the watershed area, exported 159 kg C ha^{-1} yr^{-1}, similar to the global exports for large rivers. Stream export was dominated by downstream transport of dissolved inorganic carbon (63 kg C ha^{-1} yr^{-1}) and by evasion of CO_2 to the atmosphere (42 kg C ha^{-1} yr^{-1}), leaving the remainder of 51 kg C ha^{-1} yr^{-1} for downstream transport of organic carbon (17 kg C ha^{-1} yr^{-1} and 34 kg C ha^{-1} yr^{-1} in dissolved and particulate form, respectively).

1. Introduction

The global increase in atmospheric CO_2 concentrations and the impacts of increased carbon (C) for climate change [*Intergovernmental Panel on Climate Change*, 2006] have stimulated interest in understanding carbon transport and transformation processes across and within ecosystems. Recent estimates suggest that streams and rivers collectively evade 121 ± 17 kg C ha^{-1} yr^{-1} (1.8 ± 0.25 Pg C yr^{-1}) to the atmosphere as CO_2 [*Raymond et al.*, 2013] and export 60 kg C ha^{-1} yr^{-1} (0.9 Pg C yr^{-1}) to the oceans as particulate organic carbon (POC), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) [*Battin et al.*, 2009; *Cole et al.*, 2007]. Together, the total amount of C exported from streams and rivers is around 181 kg C ha^{-1} yr^{-1}, similar to the terrestrial net ecosystem production (NEP, i.e., C fixed by terrestrial gross primary production minus total C released by respiration), which is about 143 kg C ha^{-1} yr^{-1} (2.1 Pg C yr^{-1}; [*Koffi et al.*, 2012]). Although the role of streams and rivers in transporting and processing C from the land to the oceans has been widely recognized [*Aufdenkampe et al.*, 2011; *Battin et al.*, 2009; *Richey et al.*, 2002], streams and rivers have largely been ignored in global C budgets [*Butman and Raymond*, 2011; *Cole et al.*, 2007].

Headwater streams comprise nearly 90% of the total length of perennial channels in global catchments [*Downing et al.*, 2012] and, because they are the primary linkage between terrestrial landscapes and oceans, are critical for global C estimates. Headwater streams are linked to adjacent terrestrial components of ecosystems through litter fall and by flows of soil, ground, and hyporheic water [*Öquist et al.*, 2014]. They mineralize organic C from riparian and hillslope soils and evade this and other terrestrially generated CO_2 to the atmosphere [*Butman and Raymond*, 2011; *Öquist et al.*, 2009]. Headwater streams also generate and remove considerable amounts of C through in-stream processes (i.e., primary production and respiration) occurring in the water column and in the benthic and hyporheic zones [*Battin et al.*, 2008]. Carbon from streams can be exported in two ways (Figure 1), (a) to the atmosphere as a gas (i.e., CO_2 or CH_4) or (b) downstream through transport in dissolved organic and inorganic forms, or in particulate forms. POC can be transported in suspended sediment (sPOC) or in bed load (bPOC).

The interest in characterizing C exports from headwater streams (first to third order) has increased in the last decade, as new technologies have developed. These new studies indicate that the role of headwater streams in the global C budget might be more important than initially thought [*Battin et al.*, 2009; *Cole et al.*, 2007].

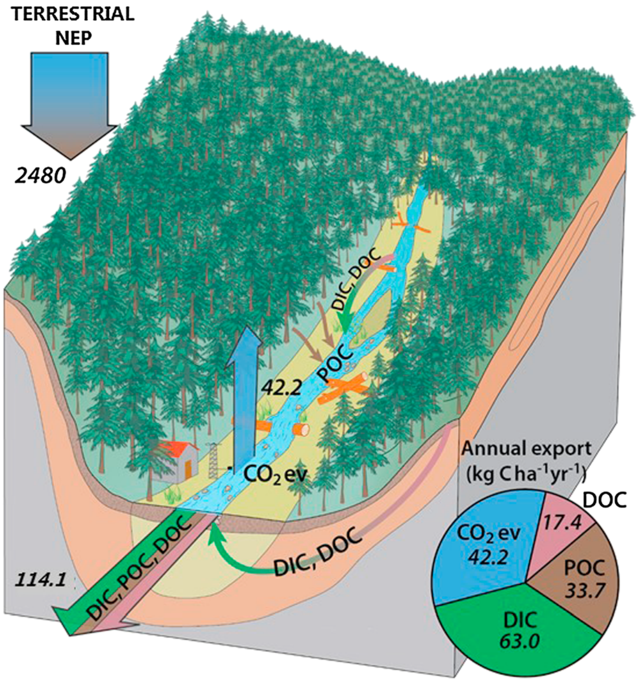

Figure 1. Annual carbon budget for Watershed 1, HJ Andrews Experimental Forest, western Oregon USA. Numbers are annual averages from 10 years of data collected continuously proportional to discharge during 3 week periods. Total export (158.7 kg ha^{-1} yr^{-1}) is not exactly equal to the sum of the components because each of the total and the components are the medians of their distributions. All values are in kg C ha^{-1} yr^{-1}, where the area basis (ha^{-1}) is the watershed area. NEP = net ecosystem production, CO_2ev = evasion of CO_2 from stream surface, DIC = dissolved inorganic carbon, POC = particulate organic carbon (both suspended and bed load), DOC = dissolved organic carbon.

Results from these studies also indicate that the role of forests as C sinks might be considerably overestimated if aquatic C exports are not taken into account [*Dillon and Molot*, 1997; *Hope et al.*, 2001; *Wallin et al.*, 2010].

Although there are numerous studies on aquatic C, few report particulate and dissolved exports downstream and evasion to the atmosphere simultaneously for extended periods of time [*Alvarez-Cobelas et al.*, 2012]. Here we constructed a detailed stream C budget considering DOC, POC, sPOC, bPOC, and evasion based on 10 years of measurements (2004–2013) from Watershed 1 (WS1) in the HJ Andrews Experimental Forest Long Term Ecological Research site. We also examine in-stream metabolic processes (i.e., respiration and primary production) with the objective to (a) characterize the contribution of each C species to the overall annual export and (b) to examine seasonal patterns in the contribution of each C species and possible factors driving these exports.

This second-order stream drains a small, steep silicate-bedrock watershed (95.9 ha) originally forested with large old-growth conifers. It was clear-cut harvested between 1962 and 1966, burned in 1966, and subsequently replanted with conifers that are now 49 years old. Water for the analysis of stream DOC, DIC, and sPOC was collected with a flow-proportional sampler since 2003. Additionally, bed load sediment has been measured annually, and discharge measured continuously. We supplemented these long-term measurements with an 11 month record of pCO_2 and DIC in surface water, with discrete measurements of gas evasion from the stream to the atmosphere, and with in-stream C processing by respiration and primary production. Confidence intervals for each component of the stream C budget were estimated using a Monte Carlo analysis. See supporting information and section 2 for more details.

2. Methods

Downstream fluxes of DOC, DIC, and sPOC were calculated between October 2003 and September 2013 by combining discharge data (measured continuously at the mouth of the watershed [*Johnson and Rothacher*, 2016]) with C concentrations measured in discharge-proportional water samples [*Johnson and Fredriksen*, 2015]. Water samples were collected every 13.3 h during low flows and up to every 40 min at maximum flows and composited over 3 week periods. DIC was estimated from total alkalinity, pH, water temperature, and barometric pressure using CO_2calc v 1.2.8 [*Robbins et al.*, 2010] and the CO_2 constants of *Millero* [1979]. In addition, stream DIC was measured from monthly water samples collected between August 2013 to July 2014 in a 60 mL luer-lock syringe that was sealed underwater to avoid outgassing, refrigerated, and analyzed within 48 h with a Shimadzu TOC-VCSH Combustion Analyzer [*Motter*, 2015; *Dosch*, 2014]. Carbon in sPOC was calculated from suspended sediment concentrations, corrected by the percentage of organic C content [*Smith*, 2013]. Annual bPOC flux was estimated from bed load sediment volume (measured yearly between 1997 and 2013 in a sediment collection basin, [*Johnson and Grant*, 2015]) corrected by the percentage of organic content (see supporting information for details on the study site and streamflow and water collection and analysis).

Gas transfer coefficients (k_{gas}; defined as the fraction of the tracer gas that is lost over a specific reach per unit of time) used for the calculations of evasion rates of CO_2 to the atmosphere and metabolism were calculated based on the decline in gas concentration during steady state co-injections of a gas and a conservative tracer [*Bott et al*., 2006; *Hall and Tank*, 2003] and by developing a relationship between k_{gas} and stream discharge (supporting information).

The instantaneous evasion rates of CO_2 to the atmosphere (ECO_2, 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 CO_2 evasion [*Hope et al*., 2001; *Wallin et al*., 2011, 2013]:

$$E_{CO_2} = (\Delta CO_2 \times k_{CO_2} \times \tau \times Q) \tag{1}$$

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

Concentrations of CO_2 in the stream were estimated using equation (2) from estimated DIC:

$$\mathrm{pCO_2} = \frac{[\mathrm{DIC}]10^{m[\mathrm{DIC}]-b}}{K_{CO_2}\left(K_1 + 10^{m[\mathrm{DIC}]-b}\right)} \tag{2}$$

where [ ] indicates molar concentration ($M = \mathrm{mol\ L^{-1}}$); K_{CO2} 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) $[CO_3{}^{2-}] \cong 0$, valid for the circumneutral pH of WS1, and (b) a strong linear relationship between [DIC] and pH. Based on stream samples from August 2013 through July 2014 where pCO_2 and DIC were measured simultaneously, we estimated $m = 0.111$ and $b = 8.50$ ($n = 7$, $r^2 = 0.990$). The pCO_2 in the stream was measured over 1 year using a Vaisala Carbocap GMM220, modified similar to *Johnson et al*. [2010], and attached to a Campbell Scientific data logger [*Haggerty and Dosch*, 2016]. *Dosch* [2014] used the above-mentioned pCO_2 and DIC data collected simultaneously and found that pCO_2 calculated using equation (2) was highly correlated to direct measurements ($r^2 = 0.94$). The pCO_2 calculated using DIC estimates obtained from alkalinity averaged 13% higher than directly measured pCO_2. Dosch' work suggests that in WS1, alkalinity is a reasonably accurate method for estimating pCO_2.

Concentrations of CO_2 in the atmosphere were measured between July 2012 and February 2014 at 15 min intervals from one inlet, attached to a float, and held 2.5 cm above the stream surface. The inlet was sampled continuously into a 1 L buffer volume at a flow rate of 0.6 L m^{-1}, 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 L min^{-1} for 85 s every 15 min.

The E_{CO2} was converted to a monthly or annual flux per unit area of stream (kg C m^{-2} yr^{-1}) by integrating the time series to the appropriate time step and dividing it by the stream surface area (m^2) estimated for this particular discharge (supporting information). So that fluxes could be compared at the landscape scale, E_{CO2} and all fluxes were reported in the figures as flux per hectare of watershed by normalizing to the watershed area (95.9 ha).

Stream metabolism (i.e., primary production and respiration) was calculated from field measurements during seven periods between July 2009 and June 2014 and include a total of 32 days (see Table S3 in the supporting information for exact dates) by measuring changes in dissolved oxygen (DO) between an upstream and downstream site following the open-channel method [*Marzolf et al*., 1994] and the following equation:

$$\Delta DO = GPP - ER \pm \mathrm{reaeration} \tag{3}$$

where ΔDO is the change in dissolved oxygen between upstream and downstream (mg O_2 m^{-2} d^{-1}), GPP- is the gross primary production (mg O_2 m^{-2} d^{-1}), ER is stream ecosystem respiration (mg O_2 L^{-1} m^{-2}), and reaeration refers to the flux of oxygen transferred to the atmosphere (mg O_2 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 oxygen transfer coefficient (k_{O2}), 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 photosynthetically active radiation 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 were transformed to C flux units by applying photosynthetic coefficients [*Bott*, 2006]. We applied linear interpolation between point measurements in time to calculate annual exports.

A Monte Carlo analysis was performed to estimate uncertainties for the total stream C budget and each of its components (i.e., DIC, DIC, sPOC, bPOC, and CO_2 evasion). We estimated uncertainties on all parameters upon which flux calculations directly or indirectly depended. Each parameter was assumed independent and normally distributed. We generated 10,000 sets of parameters in a MATLAB script and used these to calculate C flux. Because some of the same parameters appear in multiple equations, the confidence intervals of the fluxes are correlated. Consequently, we also calculated the total C flux within the same Monte Carlo script. We report median values with uncertainties bracketed by the 97.5 and 2.5 percentiles.

3. Results

3.1. Annual Carbon Exports

The WS1 stream exported $15,215\pm^{30,941}_{11,166}$ kg C yr^{-1} (where the upper and lower limits denote the 97.5th and 2.5th percentiles and bracket 95% of the Monte Carlo estimates), which is equivalent to $158.7\pm^{322.6}_{116.4}$ kg C per hectare of the watershed per year (kg C ha^{-1} yr^{-1}; Figure 1).

Annually, 73% of the stream-exported C from the watershed was transported downstream and 27% ($42.2\pm^{209.3}_{7.7}$ kg C ha^{-1} yr^{-1}) was evaded to the atmosphere. Downstream exports occurred mainly in the form of DIC (40% of the total exports, $63.0\pm^{63.9}_{62.0}$ kg C ha^{-1} yr^{-1}; Figure 1), followed by POC (22%, $33.7\pm^{63.1}_{19.3}$ kg C ha^{-1} yr^{-1}) and DOC (11%, $17.4\pm^{17.7}_{17.2}$ kg C ha^{-1} yr^{-1}). (Total export is not exactly equal to the sum of the components because the total and the components reported are the medians of each of their distributions).

3.2. Interannual Variability

Interannual variability was large over the 10 years of study. Exports of DOC ranged between 12.1 and 21.2 kg C ha^{-1} yr^{-1} (coefficient of variation (COV) of 16%), and exports of DIC ranged from 44.0 to 75.0 kg C ha^{-1} yr^{-1} (COV 15%). The C in bed load (bPOC) ranged from 5.4 to 47.7 kg C ha^{-1} yr^{-1} (COV 69%), which was slightly higher than the C in the suspended load (sPOC), which ranged from 1.1 to 39.0 kg C ha^{-1} yr^{-1} (COV 66%).

Highest DOC and DIC exports were observed in wet years (e.g., 2006, 2008, and 2011) and lowest during dry years (e.g., 2005 and 2010). The sPOC exports did not show the same pattern, however, being maximum in 2006, 2009, and 2011, and lowest in 2012 and 2013.

Stream ecosystem respiration generated 14.9 kg C ha^{-1} yr^{-1}, and aquatic primary production fixed 3.5 kg C ha^{-1} yr^{-1}, resulting in a negative balance for aquatic net primary production (i.e., a net loss of C from the stream in form of CO_2). Gross primary production (GPP) ranged from 0.02 to 0.37 g C m^{-2} d^{-1} per unit of stream area (or 0.08 and 1.19 g O_2 m^{-2} d^{-1}). Ecosystem respiration (ER) ranged from 0.30 to 2.32 g C m^{-2} d^{-1} per unit of stream area (or 0.41 and 5.25 g O_2 m^{-2} d^{-1}). Repeated measures during summers of 2010 to 2013 showed high interannual variability for both GPP and ER (COV 84% and 63%, respectively). Highest metabolic rates for ER and GPP were observed on July and August 2012 and lowest on July 2013 coinciding with lowest water temperatures and photosynthetic active radiation.

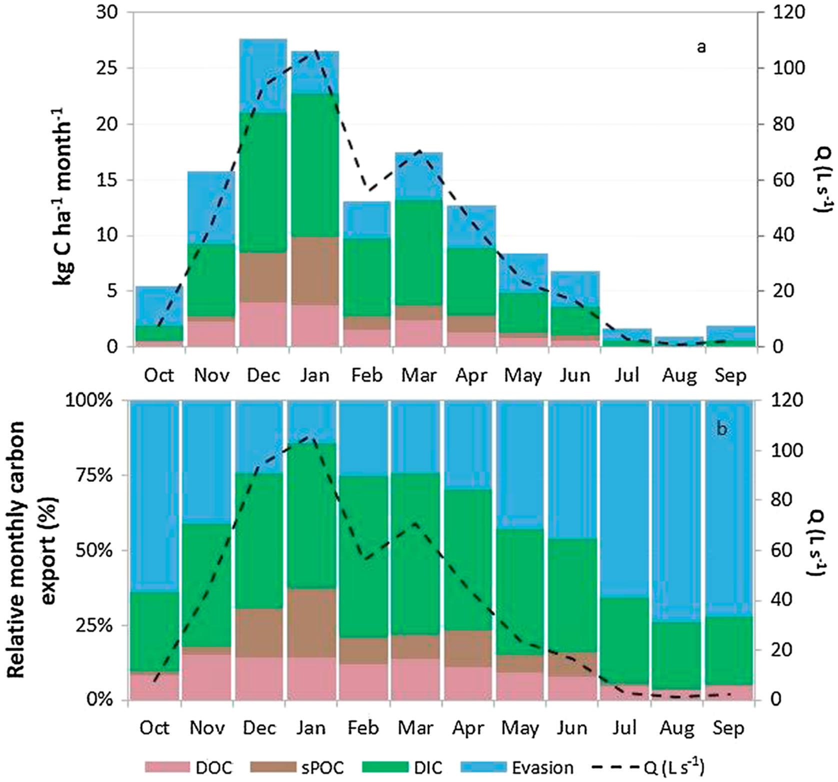

Figure 2. (a) Total and (b) relative monthly contribution of different carbon compartments to the stream carbon export and mean monthly discharge (*Q*). Values are calculated from 3-weekly composite samples collected during the 2004–2013 water year period.

3.3. Seasonal Variability

The stream exported C throughout the year, both downstream and to the atmosphere. The bulk of C export (i.e., 90% of annual C export) happened in 6 months, from November to April, coinciding with high flows (Figure 2a), and only 3% of the annual C flux occurred in summer (July to September).

DOC and DIC exports showed a bimodal distribution, peaking on December, before the maximum discharge, decreasing in February, and peaking again in March, with the increase in discharge. Transport of POC in suspended sediment remained moderately low throughout the year except in December and January. Despite most C exports increasing with discharge (Figure 2), C concentrations did not respond uniformly to changes in flow. DOC concentrations started rising in October with the first precipitation events after the dry summer season and peaked during November and December, while maximum discharge was observed during December and January (Figure 2). Conversely, DIC concentrations were inversely proportional to discharge, ranging between 4.0 and 10.3 mg C L^{-1}, with maxima in summer, during base flow conditions, and minima in winter.

Evasion to the atmosphere peaked in November coinciding with the rise in discharge after the onset of the seasonal rains, decreased in January when maximum discharge was observed, and remained moderately constant until June (Figure 2a). Evasion decreased in July and remained low for the rest of the summer. Although the amount of C exported through evasion was low during summer months, evasion was the dominant export process between May and October, peaking in August, when it represented 74% of the monthly C exports (Figure 2b).

The stream was always supersaturated, with CO_2 ranging from 472 to 3353 μatm (Figure 3). The pCO_2 was lowest between February and April and highest during August and September (Figure 3). Evasion was strongly controlled by individual storm events, peaking during the highest recorded discharge. If that rate was maintained throughout the year, it would have resulted in an annual export of 218 kg C ha^{-1} yr^{-1}.

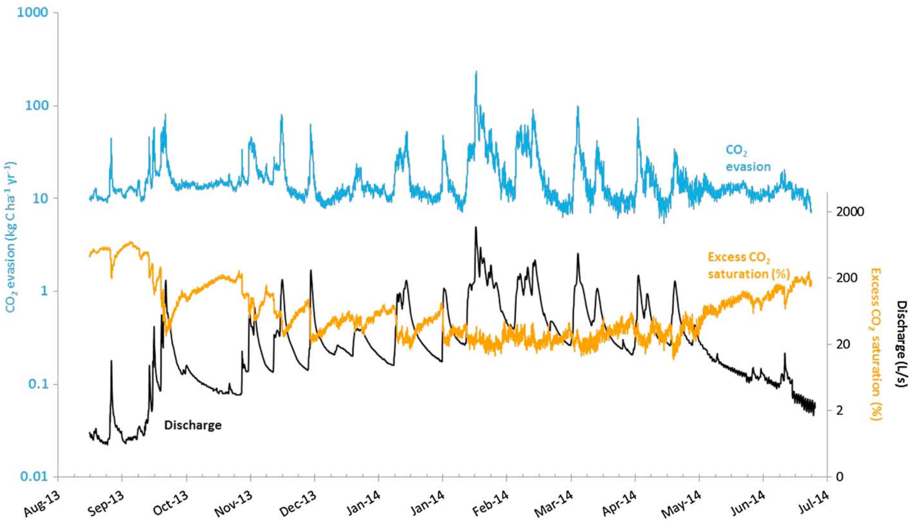

Figure 3. Modeled daily CO_2 evasion and excess CO_2 saturation in the stream, calculated by direct pCO_2 measurement from August 2013 to July 2014 [*Haggerty and Dosch*, 2016], and measured daily discharge.

Stream ecosystem respiration showed maxima during summer (1.30 ± 0.37 g C m^{-2} stream surface per day) and minima in winter (0.30 g C m^{-2} stream surface per day; supporting information). Aquatic primary production was low throughout the year with values below 0.18 g C m^{-2} stream surfaceper day during spring and summer, and with a peak of 0.37 g C m^{-2} stream surface per day in late winter.

3.4. Natural Variability and Uncertainty

There are multiple potential sources of uncertainty in calculating monthly and annual export. A Monte Carlo analysis was performed to estimate uncertainties for the total stream C budget and each of its components (i.e., DOC, DIC, sPOC, bPOC, and CO_2 evasion). Fluxes are reported in section 3.1. The stream exports $158.7\pm^{322.6}_{116.4}$ kg C ha^{-1} yr^{-1}. The largest sources of uncertainty are in the CO_2 evasion, $42.2\pm^{209.3}_{7.7}$ kg C ha^{-1} yr^{-1}, and POC export $33.7\pm^{63.1}_{19.3}$ kg C ha^{-1} yr^{-1}.

Another possible uncertainty was potential for degradation of the stream water samples after collection while unfiltered in the field. We tested for degradation by comparing aliquots of grab samples analyzed immediately versus those left to sit in the field, unfiltered, for 3 weeks. There were no significant differences in sPOC or DOC ($p > 0.05$), but there was a consistent decrease in alkalinity (mean ± SE: −0.7 ± 0.2%; supporting information).

4. Discussion

4.1. Annual Carbon Exports

The C exported by the stream draining WS1 during a year ($158.7\pm^{322.6}_{116.4}$ kg C ha^{-1} of the watershed) was comparable to the global average of stream and river export (181 kg C ha^{-1} yr^{-1}) [*Battin et al.*, 2009; *Cole et al.*, 2007; *Raymond et al.*, 2013].

Evasion to the atmosphere was 42.2 kg C ha^{-1} yr^{-1} or 27% of the total carbon export, in agreement with values reported for low-order streams in temperate and boreal regions [*Dawson and Smith*, 2007] but in the lower range of estimated by *Butman and Raymond* [2011] for the West region of the United States (i.e., 70 ± 26 kg C ha^{-1} yr^{-1}). Downstream exports were mostly in the form of DIC (40.4% of the total export), followed by POC (22%) and DOC (11.2%). The dominance of inorganic forms in total C export has also been reported in boreal streams [*Dillon and Molot*, 1997], in contrast to what has been reported in temperate peat-dominated watersheds where DOC is the most prominent from of dissolved export [*Dawson and Smith*, 2007]. However, DIC and POC exports were higher than observed in nearby watersheds [*Johnson and Fredriksen*, 2015]. Increased export of particulate C potentially could be attributed to legacy effects of the clear-cutting and burning in WS1 during the 1960s. Sediment transport in WS1 increased dramatically after clear-cutting and burning [*Grant and Wolff*, 1991]; these increases have diminished with time but are still substantially higher than pretreatment fluxes more than 50 years later [*Johnson and Grant*, 2015]. Sources of high DIC have not been identified.

4.2. Interannual Variability

Annual flow was a good predictor of DIC and DOC exports, with higher exports occurring during wet years and lower exports during dry years, and is consistent with results reported by other authors [*Striegl et al.*, 2007]. Interannual variability of POC was substantial and did not vary in synchrony with annual flow. POC interannual variability was probably related to the frequency and magnitude of high discharge events as well as to the legacy effects of clear-cutting and burning. In a long-term study in the HJ Andrews, the sequence of storm events of different magnitudes explained interannual variability of sediment transport [*Grant and Wolff*, 1991]. In-stream carbon transformation processes, estimated by summer metabolism calculations, also varied year-to-year, in relation to changes in water temperature and photosynthetic active radiation, coinciding with results reported by *Mulholland et al*. [2001] and *Bernot et al*. [2010].

4.3. Seasonality

Carbon fluxes showed strong seasonality. During periods of low flow (July–October), fluxes were small and evasion to the atmosphere was the dominant export process. At high flows evasion to the atmosphere declined to 10–30% of the total flux.

The DOC concentrations increased markedly with the first rainstorms after the dry summer, peaked in early in the rainy season and then declined, a pattern consistent with the flushing hypothesis, where C accumulates in the riparian zone and near-stream hillslopes during summer and is subsequently flushed by storms and as the water table raises [*Hornberger et al*., 1994; *Mei et al*., 2014]. In contrast, DIC concentrations were inversely proportional to discharge with maxima in summer, during base flow conditions, and minima in winter. This pattern suggests that DIC sources (e.g., hyporheic and benthic respiration and DIC input from groundwater) may be diluted by short-residence-time, low-DIC water during the wet season.

The pCO_2 also showed an inverse relationship with discharge, consistent with the findings of *Peter et al*. [2014], where strong seasonal variability in stream and hyporheic pCO_2 were observed, and with those of *Dinsmore et al*. [2013], where seasonal variations were observed in an intermittent headwater stream in the Fraser Lowland of British Columbia, Canada. The stream was always supersaturated with CO_2, and values were within the range reported by similar studies [*Cole and Caraco*, 2001; *Raymond et al*., 2013].

Monthly patterns in evasion and pCO_2 suggest that during some periods of the year, evasion is source-limited by the amount of CO_2 in the stream. At other times, it appears to be transport-limited by the capacity to evade CO_2 to the atmosphere (i.e., by the gas exchange coefficient, which is driven by the turbulence generated by stream discharge). *Dosch* [2014] estimated that hyporheic DIC constituted a major source of C to the stream (37.5 $\mathrm{kg\,C\,ha^{-1}\,yr^{-1}}$), which represents 35% of the inorganic carbon evaded as CO_2 or exported downstream as DIC in WS01. Comparison of evasion and stream DIC export rates with hyporheic DIC from *Dosch* [2014] reveals a strongly coupled relationship that appears to drive stream pCO_2. In periods of low flow, turbulence limits evasion to the atmosphere, and hyporheic exchange is large relative to discharge [*Wondzell*, 2011], so stream pCO_2 tends to increase. At high discharge, evasion rates surpass input rates and stream pCO_2 decreases.

Highest pCO_2 values coincided with highest stream respiration rates and lowest discharge, further supporting the hypothesis that evasion during summer is transport-limited by the capacity to evade CO_2 to the atmosphere and that sources become more important in regulating pCO_2. This was further supported by the fact that although general patterns of evasion could be associated with changes in flow, evasion did not correlate with discharge, suggesting that other controls, in addition to hydrology, may play a significant role in determining the balance between pCO_2 and evasion during low flows.

Stream ecosystem respiration, which is mostly respiration from heterotrophic bacteria located on substrates and in the hyporheic zone [*Battin et al*., 2003; *Fellows et al*., 2001], was influenced by stream temperature as well as availability of high-quality detrital material. Warm summer stream temperatures, which coincide with summertime leaf senescence and small amounts of litter input, result in high respiration compared to other seasons. In fall, litter inputs from deciduous trees in the downstream portion of the riparian zone are much greater than other seasons, but because they occur at the same time as cooler temperatures and higher streamflows, it is not a period of high stream respiration in Oregon. In other forested systems, respiration showed lowest rates during summer low flows and high rates of respiration following storms [*Roberts et al.*, 2007].

Carbon originating from stream ecosystem respiration has the potential to be fixed by in-stream primary production. Aquatic primary production in WS1 was low, typical of shaded headwater streams of the Pacific Northwestern USA [*Naiman and Sedell*, 1980; *Sobota et al.*, 2012]. Low primary productivity results in a net loss of C from the stream in form of CO_2. This net difference between CO_2 generated by respiration and C fixed by primary production represents 7% of DIC and evasion exports between February and May but more than 85% between June and August. This highlights the major role of in-stream biological activity as a source of C exports during low flows, in concordance with studies by *Battin et al.* [2008] and *Dawson et al.* [2001].

4.4. Uncertainty

The uncertainty in calculating C exports by the stream was large (see Table S4). Each component has a seasonal cycle and measurement error. The largest uncertainties were in the CO_2 evasion and POC export, the latter because of the variability in the C fraction in the bed load sediment. In addition to the natural variability of the stream C components, the number of samples available for each measurement was a source of both variability and uncertainty in our estimates. Components with the fewest measurements, such as bPOC or metabolism, or the ones that extrapolated reach-scale measurements to the whole wetted stream surface, like evasion, showed the largest uncertainties.

Both DIC and DOC fluxes were estimated with small uncertainty because both the concentrations and the stream discharge were well constrained by sampling type and frequency. In small streams the bulk of solute export happens during storms, coinciding with rapid changes in solute concentrations. Composite flow-proportional sampling increases the sampling frequency at high flows, and therefore, the method gives very accurate estimates of annual solute fluxes, better than sampling at fixed time intervals regardless of flow conditions [*Schleppi et al.*, 2006; *Rabiet et al.*, 2010]. However, the composited samples are not useful for interpretations at time scales finer than the three week composite. The storage of composited samples has the potential to introduce errors (see supporting information), which were not included in the Monte Carlo analysis. These errors would likely be greater for samples collected during summer low flows when temperatures were higher. However, the summer periods contribute very little to calculations of annual budget of fluxes.

There is large uncertainty in the CO_2 evasion that results from uncertainty in the reaeration coefficient. The reaeration coefficient is poorly constrained due to spatial variation along the stream network and temporal variation with changes in discharge. Reaeration varies with turbulence and surface area, both of which vary in time and space. Calculations of uncertainty for evasion involved alkalinity, pH, and DIC measurements as well of direct pCO_2 measurements, for which we only had 1 year of data. Reducing the uncertainty in reaeration is a significant challenge. This uncertainty is not easily reduced with current methods, which depend on making measurements with injections of a conservative tracer (typically propane or SF_6) and are constrained temporally and spatially. Reducing the uncertainty in other measurements, such as C content of bed load POC, could also improve our C flux budget. However, most studies do not include any bed load measurements, due to challenges of sampling during storms.

4.5. WS1 in Relation to Global C Budgets

Carbon export from WS1 was comparable to the global estimates for rivers and streams, even though this headwater stream is much smaller than many of those evaluated in the literature [*Battin et al.*, 2009; *Cole et al.*, 2007; *Raymond et al.*, 2013]. Small streams might be expected to have more terrestrialy originated C than large streams, due to their higher proportion of stream water volume in direct contact with adjacent soils. Alternatively, larger streams might have more autochthonous carbon, as a function of in-stream C production [*Dawson and Smith*, 2007; *Vannote et al.*, 1980].

Global C export from streams and rivers is around 181 kg C ha^{-1} yr^{-1}, similar to the terrestrial net ecosystem production (NEP, i.e., C fixed by terrestrial gross primary production minus total C released by respiration), which is about 143 kg C ha^{-1} yr^{-1} (2.1 Pg C yr^{-1} [*Koffi et al.*, 2012]). WS1 is exporting an amount similar to the average from large rivers; however, this is only a small proportion of terrestrial NEP of this watershed (6% of 2480 kg C ha^{-1} yr^{-1}, NEP modeled by Dr. Turner for WS1 using the model described at *Turner et al.* [2011]). This percentage (6%) is much smaller than the global average, but few studies have site-specific comparisons of stream and terrestrial carbon fluxes. Also, note the differences in NEP in the Pacific Northwestern wet coniferous forests and the global average for terrestrial ecosystems; these coniferous forests accumulate and store large amounts of carbon in multiple forms for decades to centuries [*Harmon et al.*, 2007; *Harmon et al.*, 1986].

5. Conclusions

We have shown that this small headwater stream is a significant exporter of C to the atmosphere and river network to which it is connected. Despite representing a small percentage of the total area of the watershed (0.4%), this headwater stream processes and transports 159 kg C ha^{-1} yr^{-1}, similar to the global stream and river exports. Most of the C was exported in streamflow as DIC. Evasion of CO_2 to the atmosphere was the second largest export. Discharge is the main driver for dissolved and particulate exports; however, in-stream and hyporheic biological activity plays a major role during summer low-flow periods, but total stream exports were small at this time of year. Because headwater streams are approximately 90% of the total global river length [*Downing et al.*, 2012], small streams collectively might substantially contribute to the transformation and export of carbon with repercussions for the global carbon cycle.

Acknowledgments
Access to all data sets used for this study are available through the HJ. Andrews Experimental Forest data repository (http://andrewsforest.oregonstate.edu/lter/data.cfm?frameURL=8). Funding for A.A., long-term data, and facilities were provided by the HJ Andrews Experimental Forest research program, funded by the National Science Foundation's Long-Term Ecological Research Program (DEB 08-23380), U.S. Forest Service Pacific Northwest Research Station, and Oregon State University. Parts of this study were funded by NSF grants EAR 14–17603 and AGS0955444, the OSU Hollis Dole Fund for Environmental Geology, and the U.S. Forest Service Pacific Northwest Research Station (Joint Venture Agreement 10-JV-11261991-055).

References

Alvarez-Cobelas, M., D. G. Angeler, S. Sánchez-Carrillo, and G. Almendros (2012), A worldwide view of organic carbon export from catchments, *Biogeochemistry*, *107*(1-3), 275–293.

Aufdenkampe, A. K., E. Mayorga, P. A. Raymond, J. M. Melack, S. C. Doney, S. R. Alin, R. E. Aalto, and K. Yoo (2011), Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, *Front. Ecol. Environ.*, *9*(1), 53–60.

Bales, J. D., and M. R. Nardi (2008), Automated routines for calculating whole-stream metabolism: Theoretical background and user's guide rep., U.S. Geol. Surv. Tech. and Methods 4–C2, 1-33 pp. [Available at http://pubs.water.usgs.gov/tm4c2/.]

Battin, T. J., L. A. Kaplan, J. D. Newbold, and S. P. Hendricks (2003), A mixing model analysis of stream solute dynamics and the contribution of a hyporheic zone to ecosystem function, *Freshwater Biol.*, *48*(6), 995–1014, doi:10.1046/j.1365-2427.2003.01062.x.

Battin, T. J., L. A. Kaplan, S. Findlay, C. S. Hopkinson, E. Martí, A. I. Packman, J. D. Newbold, and F. Sabater (2008), Biophysical controls on organic carbon fluxes in fluvial networks, *Nat. Geosci.*, *1*(2), 95–100, doi:10.1038/ngeo101.

Battin, T. J., S. Luyssaert, L. A. Kaplan, A. K. Aufdenkampe, A. Richter, and L. J. Tranvik (2009), The boundless carbon cycle, *Nat. Geosci.*, *2*(9), 598–600, doi:10.1038/ngeo618.

Bernot, M. J., et al. (2010), Inter-regional comparison of land-use effects on stream metabolism, *Freshwater Biol.*, *55*(9), 1874–1890.

Bott, T. L. (2006), Primary productivity and community respiration, in *Methods in Stream Ecology*, edited by F. R. Hauer and G. A. Lamberti, pp. 663–690, Academic Press, Paris.

Bott, T. L., J. D. Newbold, and D. B. Arscott (2006), Ecosystem metabolism in Piedmont streams: Reach geomorphology modulates the influence of riparian vegetation, *Ecosystems*, *9*(3), 398–421, doi:10.1007/s10021-005-0086-6.

Butman, D., and P. A. Raymond (2011), Significant efflux of carbon dioxide from streams and rivers in the United States, *Nat. Geosci.*, *4*(12), 839–842, doi:10.1038/ngeo1294.

Cole, J. J., and N. F. Caraco (2001), Carbon in catchments: Connecting terrestrial carbon losses with aquatic metabolism, *Mar. Freshwater Res.*, *52*(1), 101–110, doi:10.1071/MF00084.

Cole, J. J., Y. T. Prairie, N. F. Caraco, W. H. McDowell, L. J. Tranvik, R. G. Striegl, C. M. Duarte, P. Kortelainen, J. A. Downing, and J. J. Middelburg (2007), Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, *Ecosystems*, *10*(1), 172–185, doi:10.1007/s10021-006-9013-8.

Dawson, J. J. C., and P. Smith (2007), Carbon losses from soil and its consequences for land-use management, *Sci. Total Environ.*, *382*(2–3), 165–190.

Dawson, J. J. C., C. Bakewell, and M. F. Billett (2001), Is in-stream processing an important control on spatial changes in carbon fluxes in headwater catchments? *Sci. Total Environ.*, *265*(1–3), 153–167.

Dillon, P., and L. Molot (1997), Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments, *Water Resour. Res.*, *33*(11), 2591–2600, doi:10.1029/97WR01921.

Dinsmore, K. J., M. B. Wallin, M. S. Johnson, M. F. Billett, K. Bishop, J. Pumpanen, and A. Ojala (2013), Contrasting CO_2 concentration discharge dynamics in headwater streams: A multi-catchment comparison, *J. Geophys. Res. Biogeosci.*, *118*, 445–461.

Dosch, N. T. (2014), Spatiotemporal dynamics and drivers of stream pCO2 in a headwater catchment in the Western Cascade Mountains, Oregon, MS thesis, College of Earth, Ocean & Atmospheric Sciences, Oregon State Univ., Corvallis, Oregon. [Available at http://andrewsforest.oregonstate.edu/pubs/pdf/pub4861.pdf (15 October 2015).]

Downing, J. A., J. J. Cole, C. A. Duarte, J. J. Middelburg, J. M. Melack, Y. T. Prairie, P. Kortelainen, R. G. Striegl, W. H. McDowell, and L. J. Tranvik (2012), Global abundance and size distribution of streams and rivers, *Inland Waters*, *2*(4), 229–236, doi:10.5268/IW-2.4.502.

Fellows, C. S., H. M. Valett, and C. Dahm (2001), Whole-stream metabolism in two montane streams: Contribution of the hyporheic zone, *Limnol. Oceanogr.*, *46*(3), 523–531, doi:10.4319/lo.2001.46.3.0523.

Grant, G., and A. Wolff (1991), Long-term patterns of sediment transport after timber harvest, western Cascade Mountains, Oregon, USA, in *Sediment and Stream Water Quality in a Changing Environment: Proceedings of the Vienna IAHS Symposium. International Association of Hydrological Sciences Publ. No. 203*, edited by D. E. Walling and N. Peters, pp. 31–40, IAHS, Oxfordshire, U. K.

Haggerty, R., and N. Dosch (2016), Stream and hyporheic carbon dioxide (CO_2) measurements in a headwater catchment, Watershed 1, and throughout Lookout Creek watershed at the HJ Andrews Experimental Forest, July 2013 to July 2014, Long-Term Ecological Research, Forest Science Data Bank, Corvallis, Oreg. [Available at http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=CF010.]

Hall, R. O., and J. L. Tank (2003), Ecosystem metabolism controls nitrogen uptake in streams in Grand Teton National Park, Wyoming, *Limnol. Oceanogr.*, *48*(3), 1120–1128, doi:10.4319/lo.2003.48.3.1120.

Harmon, M. E., J. F. Franklin, F. J. Swanson, P. Sollins, S. V. Gregory, J. D. Lattin, N. H. Anderson, S. P. Cline, N. G. Aumen, and J. R. Sedell (1986), Ecology of coarse woody debris in temperate ecosystems, *Adv. Ecol. Res.*, *15*(133), 302.

Harmon, M. E., D. L. Phillips, J. J. Battles, A. Rassweiler, R. O. Hall Jr., and W. K. Lauenroth (2007), Quantifying uncertainty in net primary production measurements, in *Principles and Standards for Measuring Primary Production*, edited by T. J. Fahey and A. K. Knapp, pp. 238–260, Oxford Univ. Press, Cary, N. C.

Hope, D., S. M. Palmer, M. F. Billett, and J. J. C. Dawson (2001), Carbon dioxide and methane evasion from a temperate peatland stream, *Limnol. Oceanogr.*, *46*(4), 847–857, doi:10.4319/lo.2001.46.4.0847.

Hornberger, G. M., K. E. Bencala, and D. M. McKnight (1994), Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado, *Biogeochemistry*, *25*(3), 147–165.

Intergovernmental Panel on Climate Change (2006), Climate change 2001: Impacts, adaptation, and vulnerability, in *Contribution of Working Group II to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. J. McCarthy et al., pp. 879–906, Cambridge Univ. Press, Cambridge.

Johnson, M. S., M. F. Billett, K. J. Dinsmore, M. Wallin, K. E. Dyson, and R. S. Jassal (2010), Direct and continuous measurement of dissolved carbon dioxide in freshwater aquatic systems: Method and applications, *Ecohydrology*, *3*(1), 68–78, doi:10.1002/eco.95.

Johnson, S., and G. Grant (2015), Bedload data from sediment basin surveys in small gauged watersheds in the Andrews Experimental Forest, 1957 to present, Long-Term Ecological Research, Forest Science Data Bank, Corvallis, Oreg. [Available at http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=HS004 (15 October 2015).]

Johnson, S., and J. Rothacher (2016), Stream discharge in gaged watersheds at the Andrews Experimental Forest, 1949 to present. Long-Term Ecological Research, Forest Science Data Bank, Corvallis, Oreg. [Available at: http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=HF004 (15 October 2015).]

Johnson, S., and R. Fredriksen (2015), Stream chemistry concentrations and fluxes using proportional sampling in the Andrews Experimental Forest, 1968 to present, Long-Term Ecological Research, Forest Science Data Bank, Corvallis, Oreg. [Available at: http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=CF002 (15 October 2015).]

Koffi, E., P. Rayner, M. Scholze, and C. Beer (2012), Atmospheric constraints on gross primary productivity and net ecosystem productivity: Results from a carbon-cycle data assimilation system, *Global Biogeochem. Cycles*, *26*, GB1024, doi:10.1029/2010GB003900.

Marzolf, E. R., P. J. Mulholland, and A. D. Steinman (1994), Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams, *Can. J. Fish. Aquat. Sci.*, *51*(7), 1591–1599, doi:10.1139/f94-158.

Mei, Y., G. M. Hornberger, L. A. Kaplan, J. D. Newbold, and A. K. Aufdenkampe (2014), The delivery of dissolved organic carbon from a forested hillslope to a headwater stream in southeastern Pennsylvania, USA, *Water Resour. Res.*, *50*(7), 5774–5796, doi:10.1002/2014WR015635.

Millero, F. J. (1979), The thermodynamics of the carbonate system in seawater, *Geochim. Cosmochim. Acta*, *43*(10), 1651–1661, doi:10.1016/0016-7037(79)90184-4.

Motter, K. (2015), Standard operating procedure for the analysis of dissolved inorganic carbon report, Cooperative Chemical Analytical Laboratory, College of Forestry, Oregon State Univ., Corvallis, Oreg.[Available at http://ccal.oregonstate.edu/sites/ccal/files/sop/CCAL%20DIC%20SOP%202015.pdf (15 October 2015).]

Mulholland, P. J., et al. (2001), Inter-biome comparison of factors controlling stream metabolism, *Freshwater Biol.*, *46*, 1503–1517.

Naiman, R. J., and J. R. Sedell (1980), Relationships between metabolic parameters and stream order in Oregon, *Can. J. Fish. Aquat. Sci.*, *37*(5), 834–847, doi:10.1139/f80-112.

Öquist, M. G., M. Wallin, J. Seibert, K. Bishop, and H. Laudon (2009), Dissolved inorganic carbon export across the soil/stream interface and its fate in a boreal headwater stream, *Environ. Sci. Technol.*, *43*(19), 7364–7369, doi:10.1021/es900416h.

Öquist, M., et al. (2014), The full annual carbon balance of boreal forests is highly sensitive to precipitation, *Environ. Sci. Technol. Lett.*, *1*(7), 315–319.

Peter, H., G. A. Singer, C. Preiler, P. Chifflard, G. Steniczka, and T. J. Battin (2014), Scales and drivers of temporal pCO2 dynamics in an Alpine stream, *J. Geophys. Res. Biogeosci.*, *119*, 1078–1091, doi:10.1002/2013JG002552.

Rabiet, M., C. Margoum, V. Gouy, N. Carluer, and M. Coquery (2010), Assessing pesticide concentrations and fluxes in the stream of a small vineyard catchment – Effect of sampling frequency, *Environ. Pollut.*, *158*(3), 737–748, doi:10.1016/j.envpol.2009.10.014.

Raymond, P. A., J. Hartmann, R. Lauerwald, S. Sobek, C. McDonald, M. Hoover, D. Butman, R. Striegl, E. Mayorga, and C. Humborg (2013), Global carbon dioxide emissions from inland waters, *Nature*, *503*(7476), 355–359, doi:10.1038/nature12760.

Richey, J. E., J. M. Melack, A. K. Aufdenkampe, V. M. Ballester, and L. L. Hess (2002), Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2, *Nature*, *416*, 617–620, doi:10.1038/416617a.

Robbins, L. L., M. E. Hansen, J. A. Kleypas, and S. C. Meylan (2010), CO_2calc: A user-friendly carbon calculator for windows, Mac OS X, and iOS (iPhone) *U.S. Geol. Surv. Open File Rep.*, 1280, 42.

Roberts, B. J., P. J. Mulholland, and W. R. Hill (2007), Multiple scales of temporal variability in ecosystem metabolism rates: Results from 2 years of continuous monitoring in a forested headwater stream, *Ecosystems*, *10*(4), 588–606, doi:10.1007/s10021-007-9059-2.

Schleppi, P., P. A. Waldner, and M. Stähli (2006), Errors of flux integration methods for solutes in grab samples of runoff water, as compared to flow-proportional sampling, *J. Hydrol.*, *319*(1), 266–281.

Smith, J. C. (2013), Particulate organic carbon mobilisation and export from temperate forested uplands PhD dissertation thesis, Univ. of Cambridge, U. K.

Sobota, D. J., S. L. Johnson, S. V. Gregory, and L. R. Ashkenas (2012), A stable isotope tracer study of the influences of adjacent land use and riparian condition on fates of nitrate in streams, *Ecosystems*, *15*(1), 1–17, doi:10.1007/s10021-011-9489-8.

Striegl, R. G., M. M. Dornblaser, G. R. Aiken, K. P. Wickland, and P. A. Raymond (2007), Carbon export and cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001–2005, *Water Resour. Res.*, *43*, W02411, doi:10.1029/2006WR005201.

Turner, D. P., W. D. Ritts, Z. Yang, R. E. Kennedy, W. B. Cohen, M. V. Duane, P. E. Thornton, and B. E. Law (2011), Decadal trends in net ecosystem production and net ecosystem carbon balance for a regional socioecological system, *For. Ecol. Manage.*, *262*(7), 1318–1325, doi:10.1016/j.foreco.2011.06.034.

Vannote, R. L., G. W. Minshall, K. W. Cummins, J. R. Sedell, and C. E. Cushing (1980), The river continuum concept, *Can. J. Fish. Aquat. Sci.*, *37*(1), 130–137.

Wallin, M., I. Buffam, M. Öquist, H. Laudon, and K. Bishop (2010), Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes, *J. Geophys. Res.*, *115*, G02014, doi:10.1029/2009JG001100.

Wallin, M. B., M. G. Öquist, I. Buffam, M. F. Billett, J. Nisell, and K. H. Bishop (2011), Spatiotemporal variability of the gas transfer coefficient (KCO_2) in boreal streams: Implications for large scale estimates of CO_2 evasion, *Global Biogeochem. Cycles*, *25*, GB3025, doi:10.1029/2010GB003975.

Wallin, M. B., T. Grabs, I. Buffam, H. Laudon, A. Ägren, M. G. Öquist, and K. Bishop (2013), Evasion of CO_2 from streams: The dominant component of the carbon export through the aquatic conduit in a boreal landscape, *Global Change Biol.*, *19*(3), 785–797, doi:10.1111/gcb.12083.

Wondzell, S. M. (2011), The role of the hyporheic zone across stream networks, *Hydrol. Processess*, *25*(22), 3525–3532, doi:10.1002/hyp.8119.

Young, R. G., and A. D. Huryn (1998), Comment: Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams, *Can. J. Fish. Aquat. Sci.*, *55*(7), 1784–1785, doi:10.1139/f98-052.

Journal of Geophysical Research: Biogeosciences

Supporting Information for

Comprehensive multi-year carbon budget of a temperate headwater stream

A. Argerich[1], R. Haggerty[2] , S. L. Johnson[3], S. M. Wondzell[3], N. Dosch[2], H. Corson-Rikert[2], L. R. Ashkenas[4], R. Pennington[2], and C. K. Thomas[2,5]

[1]Department of Forest Engineering, Resources and Management, College of Forestry, Oregon State University, Corvallis, Oregon, USA, [2]College of Earth, Ocean & Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA, [3]US Forest Service Pacific Northwest Research Station, Corvallis, Oregon, USA, [4]Department of Fisheries and Wildlife, College of Agricultural Sciences, Oregon State University, Corvallis, Oregon, USA, [5]now at: University of Bayreuth, Micrometeorology Group, Bayreuth, Germany.

Contents of this file

Text S1 to S8
Figures S1 to S4
Tables S1 to S4

Additional Supporting Information (Files uploaded separately)

None

Introduction

This file contains expanded information on the study site and the methods used.

Text S1. STUDY SITE

We conducted this study in Watershed 1 (WS1), a 95.9-ha (~1 km^2) catchment located in the H.J. Andrews Experimental Forest in the western Cascade Mountains of Oregon, USA (44º 10’ N, 122º 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 ºC in January to 18 ºC 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-yr-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 at 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 ± SE: -0.7 ± 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 Na_2CO_3 and 0.02N H_2SO_4, 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 CO_2 evasion rates to the atmosphere.

Dissolved organic carbon (DOC) was defined as the carbon contained in particles smaller than 0.7 µm. Particulate organic carbon in suspended sediments (sPOC) was defined as the carbon contained within particulate organic matter between 0.7 and 1.2 µm, 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 ºC 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 ± 2.1% of suspended sediments.

Dissolved inorganic carbon (DIC is the sum of inorganic carbon species in solution: carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate anion (HCO_3^-) and carbonate (CO_3^{2-}). DIC was estimated for the 2004-2013 water years from total alkalinity, pH, water temperature, and barometric pressure using CO_2calc v 1.2.8 [*Robbins et al.*, 2010] and the CO_2 constants of *Millero* [1979]. In addition, DIC was measured monthly in stream water simultaneously to pCO_2 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:

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

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_j	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 ± 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:

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

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 SF_6 gas transfer coefficients were then converted to the target gas transfer coefficient (i.e., K_{O2} or K_{CO2}) according to *Mulholland et al.* [2004]:

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

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 :

$$K_{O2} = 1.345\ K_{SF6} \qquad (4)$$

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

$$K_{CO2} = 1.267\ K_{SF6} \qquad (6)$$

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

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:

$$\Delta DO = GPP - ER\ \pm reaeration \qquad (8)$$

where ΔDO is the change in dissolved oxygen between upstream and downstream (mg O_2 m^{-2} d^{-1}), GPP is the gross primary production (mg O_2 m^{-2} d^{-1}), ER is stream ecosystem respiration (mg O_2 L^{-1} m^{-2}) and reaeration refers to the flux of oxygen transferred to the atmosphere (mg O_2 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 CO_2

The instantaneous evasion rates of CO_2 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 CO_2 evasion [*Hope et al.*, 2001; *Wallin et al.*, 2011; 2013]:

$$E_{CO2} = \left[\,\Delta\, CO_2 \times k_{CO_2} \times \tau \times Q\right] \qquad (9)$$

where $\Delta\, CO_2$(mg C L^{-1}) is the difference between CO_2 concentration in the stream and CO_2 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 CO_2 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 CO_2calc v 1.2.9 [*Robbins et al.*, 2010] and the CO_2 constants recommended for freshwaters [*Millero*, 1979].

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

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-}] ~ = 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 pCO_2 and DIC were measured simultaneously, we estimated m = 0.111 and b = 8.50 (n =7, r^2 = 0.990). pCO_2 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 CO_2 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 (m^2). 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.

Text S6. ESTIMATION OF TERRESTRIAL NEP

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 CO_2 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:

DOC (kg C ha^{-1} yr^{-1}) = Q (L s^{-1}) x DOC (mg C L^{-1}) x β/ ws area (ha)

DIC (kg C ha^{-1} yr^{-1}) = Q (L s^{-1}) x DIC (mg C L^{-1}) x β / ws area (ha)

sPOC (kg C ha^{-1} yr^{-1}) = Q (L s^{-1}) x SSED (mg C L^{-1}) x f_{SSED} x β / ws area (ha)

bPOC (kg C ha^{-1} yr^{-1}) = Bedload (m^{3} ha^{-1} yr^{-1}) x Bulk density (kg m^{-3}) x f_{BED} (-)

β = 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} = fraction of carbon in suspended sediments = 0.0275 ± 2.1%

Bulk density (kg m^{-3}) = mineral density (kg m^{-3}) x (1 - porosity (-))

Mineral density = 2650 ± 100 kg m^{-3}

Porosity = 0.35 ± 0.1

f_{BED} = fraction of carbon in bedload = f_{om} (-) x f_{C} (-)

f_{OM} = fraction of organic matter in bedload = 0.0492 ± 0.0139

f_{C} = fraction of carbon in organic matter in bedload = 0.58 ± 0.1

Evasion (kg C ha^{-1} yr^{-1}) = E_{CO2} (µg CO_2 s^{-1}) x 3.1558e^{-2}/ws area (ha)

$$E_{CO2}\ (\mu g\ CO_2\ s^{-1}) = \left[\Delta CO_2 \times K_{CO_2} \times \tau \times Q\right]$$

$$\Delta CO_2\ (\mu g\ CO_2\ L^{-1}) = (CO_2\text{-stream - } CO_2\text{-atm})$$

$$CO_2\text{-stream}\ (\mu g\ CO_2\ L^{-1}) = CO_2\text{stream-v}\ \frac{M}{R\ (273.15+T_{water})} \times 0.9877^{\frac{alt}{100}}$$

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

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

b = empirical coefficient = 8.5036 ± 0.1314

m = empirical coefficient = 0.11143 ± 0.1725

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

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

K_1 = equilibrium constant between H^+, HCO_3^-, and $H_2CO_3^0 = 10^{-6.35}$ M)

$$CO_2\text{-atm}\ (\mu g\ CO_2\ L^{-1}) = CO_2\text{atm-v}\ \frac{M}{R\ (273.15+T_{water})} \times 0.9877^{\frac{alt}{100}}$$

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

$$E_{CO2} = \gamma\, \Delta CO_2$$

Text S8. DATA AVAILABILITY

Long term data are publically available on the Andrews website: http://andrewsforest.oregonstate.edu/lter/data.cfm?frameURL=8. Specifically we relied on data sets:

CF002 -stream chemistry and suspended sediment [*Johnson and Fredriksen*, 2015]

CF010 -stream carbon dioxide [*Haggerty and Dosch*, 2016]

GI010 -bare earth LiDAR [*Spies*, 2013]

HF004 -stream discharge [*Johnson and Rothacher*, 2016]

HS004 -bedload measurements [*Johnson and Grant*, 2011]

MS001 -climate measurements [*Daly and McKee*, 2015]

REFERENCES

APHA (2005), Standard methods for the examination of water and wastewater, American Public Health Association (APHA): Washington, DC, USA.

Bales, J. D., and M. R. Nardi (2008), Automated routines for calculating whole-stream metabolism: theoretical background and user's guide Rep., 1-33 pp.

Bott, T. L. (2006), Primary productivity and community respiration, in *Methods in Stream Ecology*, edited by F. R. Hauer and G. A. Lamberti, pp. 663-690, Academic Press, Paris.

Bott, T. L., J. D. Newbold, and D. B. Arscott (2006), Ecosystem metabolism in Piedmont streams: reach geomorphology modulates the influence of riparian vegetation, *Ecosystems*, 9(3), 398-421, doi: 10.1007/s10021-005-0086-6.

Daly, C. and W. McKee (2015), Meteorological data from benchmark stations at the Andrews Experimental Forest, 1957 to present. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR. [Database]. Available at: http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=MS001 (15 October 2015).

Frady, C., S. Johnson, and J. Li (2007), Stream macroinvertebrate community responses as legacies of forest harvest at the HJ Andrews Experimental Forest, Oregon, *Forest Sci.*, 53(2), 281-293.

Haggerty, R. and N. Dosch (2016), Stream and hyporheic carbon dioxide (CO2) measurements in a headwater catchment, Watershed 1, and throughout Lookout Creek watershed at the HJ Andrews Experimental Forest, July 2013 to July 2014. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR. [Database]. Available upon publication of this manuscript at: http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=CF010.

Hall, R. O., and J. L. Tank (2003), Ecosystem metabolism controls nitrogen uptake in streams in Grand Teton National Park, Wyoming, *Limnol. Oceanogr.*, 48 (3), 1120-1128, doi: 10.4319/lo.2003.48.3.1120.

Hope, D., S. M. Palmer, M. F. Billett, and J. J. C. Dawson (2001), Carbon dioxide and methane evasion from a temperate peatland stream, *Limnol. Oceanogr.*, 46(4), 847-857, doi: 10.4319/lo.2001.46.4.0847.

Jähne, B., K. O. Münnich, R. Bösinger, A. Dutzi, W. Huber, and P. Libner (1987), On the parameters influencing air-water gas exchange, *J. Geophys. Res.*, 92, 1937-1949, doi: 10.1029/JC092iC02p01937.

Johnson, M. S., M. F. Billett, K. J. Dinsmore, M. Wallin, K. E. Dyson, and R. S. Jassal (2010), Direct and continuous measurement of dissolved carbon dioxide in freshwater aquatic systems: method and applications, *Ecohydrology*, 3(1), 68-78, doi: 10.1002/eco.95.

Johnson, S. L., and J. A. Jones (2000), Stream temperature responses to forest harvest and debris flows in western Cascades, Oregon, *Can. J. Fish. Aquat. Sci.*, 57(S2), 30-39, doi: 10.1139/cjfas-57-S2-30.

Johnson, S. and R. Fredriksen (2015), Stream chemistry concentrations and fluxes using proportional sampling in the Andrews Experimental Forest, 1968 to present. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR. [Database]. Available at: http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=CF002 (15 October 2015).

Johnson, S. and G. Grant (2011), Bedload data from sediment basin surveys in small gauged watersheds in the Andrews Experimental Forest, 1957 to present. Long-Term Ecological

Research. Forest Science Data Bank, Corvallis, OR. [Database]. Available at: http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=HS004 (15 October 2015).

Johnson, S. and J. Rothacher (2016), Stream discharge in gaged watersheds at the Andrews Experimental Forest, 1949 to present. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR. [Database]. Available at: http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=HF004 (15 October 2015).

Ledwell JJ (1984) The variation of the gas transfer coefficient with molecular diffusity, in *Gas transfer at water surfaces*, edited by W. Brusaert and G. H. Jirka, pp. 293–302, Springer, New York.

Lutz, J. A., and C. B. Halpern (2006), Tree mortality during early forest development: a long-term study of rates, causes, and consequences, *Ecol. Monogr.*, 76(2), 257-275, doi: 10.1890/0012-9615(2006)076[0257%3ATMDEFD]2.0.CO%3B2.

MacIntyre, S., R. Wanninkhof, and J. Chanton (1995), Trace gas exchange across the air-water interface in freshwater and coastal marine environments, in *Biogenic trace gases: Measuring emissions from soil and water*, edited by P.A. Matson and C. Hariss. Wiley–Blackwell. pp. 52–97.

Marzolf, E. R., P. J. Mulholland, and A. D. Steinman (1994), Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams, *Can. J. Fish. Aquat. Sci.*, 51(7), 1591-1599, doi: 10.1139/f94-158.

Millero, F. J. (1979), The thermodynamics of the carbonate system in seawater, *Geochim. Cosmochim.*, 43(10), 1651-1661, doi:10.1016/0016-7037(79)90184-4.

Motter, K. (2015), Standard operating procedure for the analysis of dissolved inorganic carbonRep., Cooperative Chemical Analytical Laboratory, College of Forestry, Oregon State University, Corvallis, Oregon, USA. Available at: http://ccal.oregonstate.edu/sites/ccal/files/sop/CCAL%20DIC%20SOP%202015.pdf (15 October 2015).

Motter, K. and C. Jones (2013), Standard operating procedure for the determination of suspended sediments, Cooperative Chemical Analytical Laboratory, College of Forestry, Oregon State University, Corvallis, Oregon, USA. Available at : http://ccal.oregonstate.edu/sites/ccal/files/sop/CCAL%20SSED%20SOP%202015.pdf (15 October 2015).

Mulholland, P. J., H. M. Valett, J. R. Webster, S. A. Thomas, L. W. Cooper, S. K. Hamilton, and B. J. Peterson (2004), Stream denitrification and total nitrate uptake rates measured using a field ^{15}N tracer addition approach, *Limnol. Oceanogr.*, 809-820, doi: 10.4319/lo.2004.49.3.0809.

Nelson, D., L. Sommers, D. Sparks, A. Page, P. Helmke, R. Loeppert, P. Soltanpour, M. Tabatabai, C. Johnston, and M. Sumner (1996), Total carbon, organic carbon, and organic matter, in *Methods of soil analysis. Part 3-chemical methods*, SSSA Book Series No. 5. D. L. Sparks et al., eds. Madison, WI: Soil Science Society of America, Inc. pp. 961-1010.

Robbins, L. L., M. E. Hansen, J. A. Kleypas, and S. C. Meylan (2010), CO2calc: a user-friendly carbon calculator for windows, Mac OS X, and iOS (iPhone): US geological survey open file report, 1280, 42.

Smith, J. C. (2013), Particulate organic carbon mobilisation and export from temperate forested uplands, PhD dissertation thesis, University of Cambridge, UK.

Spies, T. (2013), LiDAR data for the Andrews Experimental Forest and Willamette National Forest study areas, August 2008. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR. [Database]. Available at: http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=GI010 (15 October 2015).

Wallin, M. B., M. G. Öquist, I. Buffam, M. F. Billett, J. Nisell, and K. H. Bishop (2011), Spatiotemporal variability of the gas transfer coefficient (KCO_2) in boreal streams: Implications for large scale estimates of CO_2 evasion, *Global Biogeochem. Cy.*, 25(3), doi: 10.1029/2010GB003975.

Wallin, M. B., T. Grabs, I. Buffam, H. Laudon, A. Ägren, M. G. Öquist, and K. Bishop (2013), Evasion of CO_2 from streams: The dominant component of the carbon export through the aquatic conduit in a boreal landscape, *Glob. Change Biol.*, 19(3), 785-797, doi: 10.1111/gcb.12083.

Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97, 7373-7382, doi: 10.1029/92JC00188.

Witherspoon, P. A., and D. N. Saraf (1965), Diffusion of methane, ethane, propane, and n-butane in water from 25 to 43°, *J. Phys. Chem.*, 69(11), 3752-3755, doi: 10.1021/j100895a017.

Young, R. G., and A. D. Huryn (1998), Comment: Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams, *Can. J. Fish. Aquat. Sci.*, 55(7), 1784-1785, doi: 10.1139/f98-052.

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

Figure S2. Image of the stream draining WS1

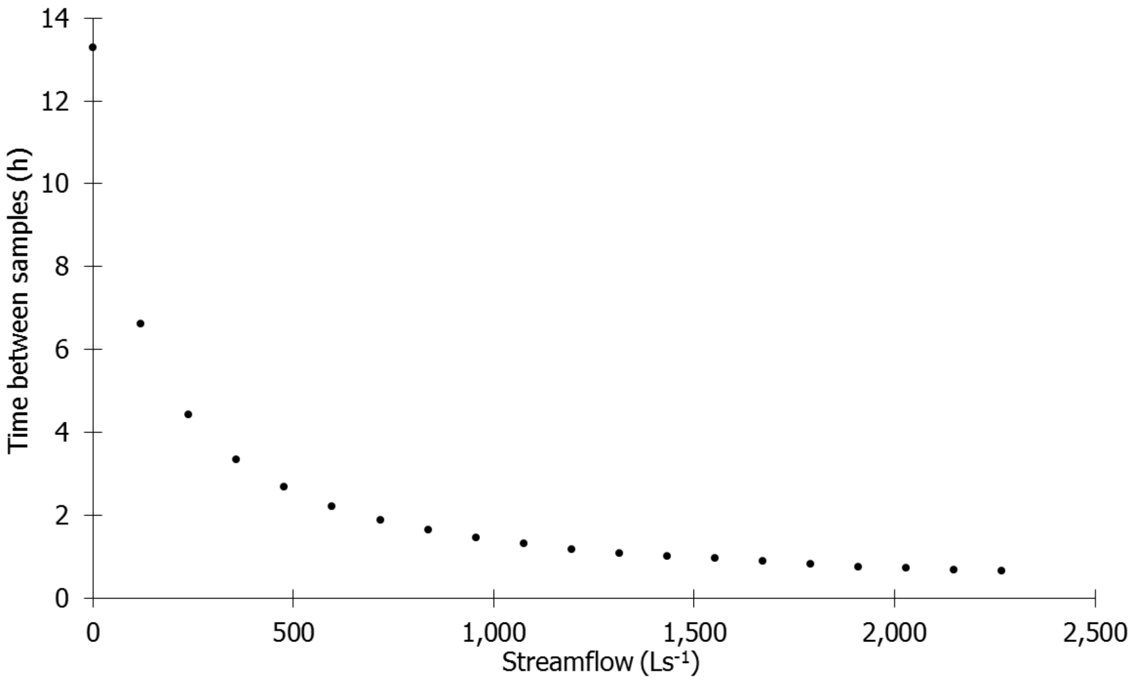

Figure S3. Water sampling scheme for the WS1 stream. Samples were collected every 13.3 h at low flows and up to every 40 minutes at high flows and composite over 3-week periods.

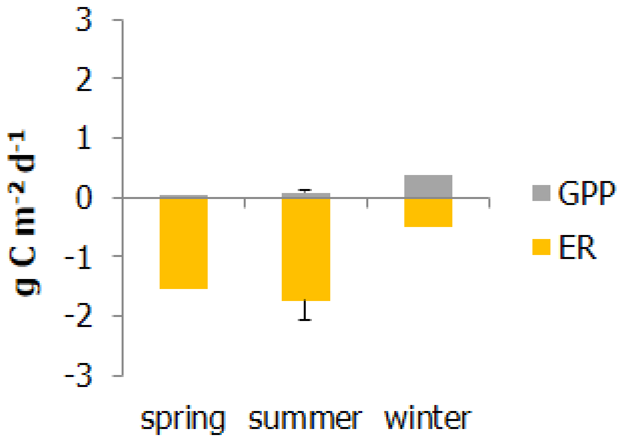

Figure S4. Fluxes in ecosystem respiration and gross primary production measured in WS1. Error bars are SEM, number of measurements were 1, 2, 29 for winter, spring and summer, respectively.

Analyte	Slope	Intercept	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
pH	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	B	C	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.

	Annual concentrations (mg C L^{-1})			Annual fluxes (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

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}.