

RESEARCH ARTICLE

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Key Points:

- Here we present a 10 year detailed C budget for a small headwater stream
- This headwater stream exported $159 \text{ kg C ha}^{-1} \text{ yr}^{-1}$, 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

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Comprehensive multiyear carbon budget of a temperate headwater stream

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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 (CO₂), 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 $159 \text{ kg C ha}^{-1} \text{ yr}^{-1}$, similar to the global exports for large rivers. Stream export was dominated by downstream transport of dissolved inorganic carbon ($63 \text{ kg C ha}^{-1} \text{ yr}^{-1}$) and by evasion of CO₂ to the atmosphere ($42 \text{ kg C ha}^{-1} \text{ yr}^{-1}$), leaving the remainder of $51 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ for downstream transport of organic carbon ($17 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ and $34 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ in dissolved and particulate form, respectively).

1. Introduction

The global increase in atmospheric CO₂ 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 $121 \pm 17 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ ($1.8 \pm 0.25 \text{ Pg C yr}^{-1}$) to the atmosphere as CO₂ [Raymond *et al.*, 2013] and export $60 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ (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 $181 \text{ kg C ha}^{-1} \text{ yr}^{-1}$, 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 $143 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ (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 CO₂ 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., CO₂ or CH₄) 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].

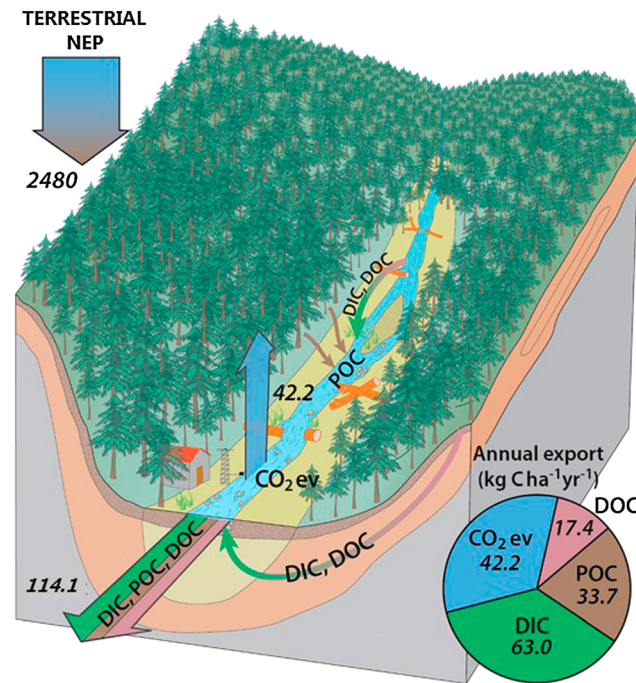


Figure 1. Annual carbon budget for Watershed 1, HJ Andrews Experimental Forest, western Oregon USA. Numbers are annual averages from 10 years of data collected continuously proportional to discharge during 3 week periods. Total export ($158.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$) is not exactly equal to the sum of the components because each of the total and the components are the medians of their distributions. All values are in $\text{kg C ha}^{-1} \text{ yr}^{-1}$, 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 $\text{CO}_2\text{calc v 1.2.8}$ [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 (E_{CO_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]:

$$E_{\text{CO}_2} = (\Delta\text{CO}_2 \times k_{\text{CO}_2} \times \tau \times Q) \quad (1)$$

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_{CO_2} (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:

$$\text{pCO}_2 = \frac{[\text{DIC}] 10^{m[\text{DIC}] - b}}{K_{\text{CO}_2} (K_1 + 10^{m[\text{DIC}] - b})} \quad (2)$$

where [] indicates molar concentration ($\text{M} = \text{mol L}^{-1}$); K_{CO_2} is the equilibrium constant between dissociated carbonic acid, H_2CO_3^0 , and pCO_2 ($10^{-1.47} \text{ M bar}^{-1}$); K_1 is the equilibrium constant between H^+ , HCO_3^- , and H_2CO_3^0 ($10^{-6.35} \text{ M}$); and m and b are empirical coefficients for $\text{pH} = -\log[\text{H}^+] = -m[\text{DIC}] + b$. This model is geochemically self-consistent, assuming (a) $[\text{CO}_3^{2-}] \cong 0$, 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 min^{-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_{CO_2} was converted to a monthly or annual flux per unit area of stream ($\text{kg C m}^{-2} \text{ yr}^{-1}$) 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_{CO_2} 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:

$$\Delta\text{DO} = \text{GPP} - \text{ER} \pm \text{reaeration} \quad (3)$$

where ΔDO is the change in dissolved oxygen between upstream and downstream ($\text{mg O}_2 \text{ m}^{-2} \text{ d}^{-1}$), GPP is the gross primary production ($\text{mg O}_2 \text{ m}^{-2} \text{ d}^{-1}$), ER is stream ecosystem respiration ($\text{mg O}_2 \text{ L}^{-1} \text{ m}^{-2}$), and reaeration refers to the flux of oxygen transferred to the atmosphere ($\text{mg O}_2 \text{ m}^{-2} \text{ d}^{-1}$). 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_{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 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 $15,215 \pm \begin{smallmatrix} 30,941 \\ 11,166 \end{smallmatrix}$ 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 $158.7 \pm \begin{smallmatrix} 322.6 \\ 116.4 \end{smallmatrix}$ 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% ($42.2 \pm \begin{smallmatrix} 209.3 \\ 7.7 \end{smallmatrix}$ 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, $63.0 \pm \begin{smallmatrix} 63.9 \\ 62.0 \end{smallmatrix}$ kg C ha⁻¹ yr⁻¹; Figure 1), followed by POC (22%, $33.7 \pm \begin{smallmatrix} 63.1 \\ 19.3 \end{smallmatrix}$ kg C ha⁻¹ yr⁻¹) and DOC (11%, $17.4 \pm \begin{smallmatrix} 17.7 \\ 17.2 \end{smallmatrix}$ 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 $14.9 \text{ kg C ha}^{-1} \text{ yr}^{-1}$, and aquatic primary production fixed $3.5 \text{ kg C ha}^{-1} \text{ yr}^{-1}$, 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 $0.37 \text{ g C m}^{-2} \text{ d}^{-1}$ per unit of stream area (or 0.08 and $1.19 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$). Ecosystem respiration (ER) ranged from 0.30 to $2.32 \text{ g C m}^{-2} \text{ d}^{-1}$ per unit of stream area (or 0.41 and $5.25 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$). 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.

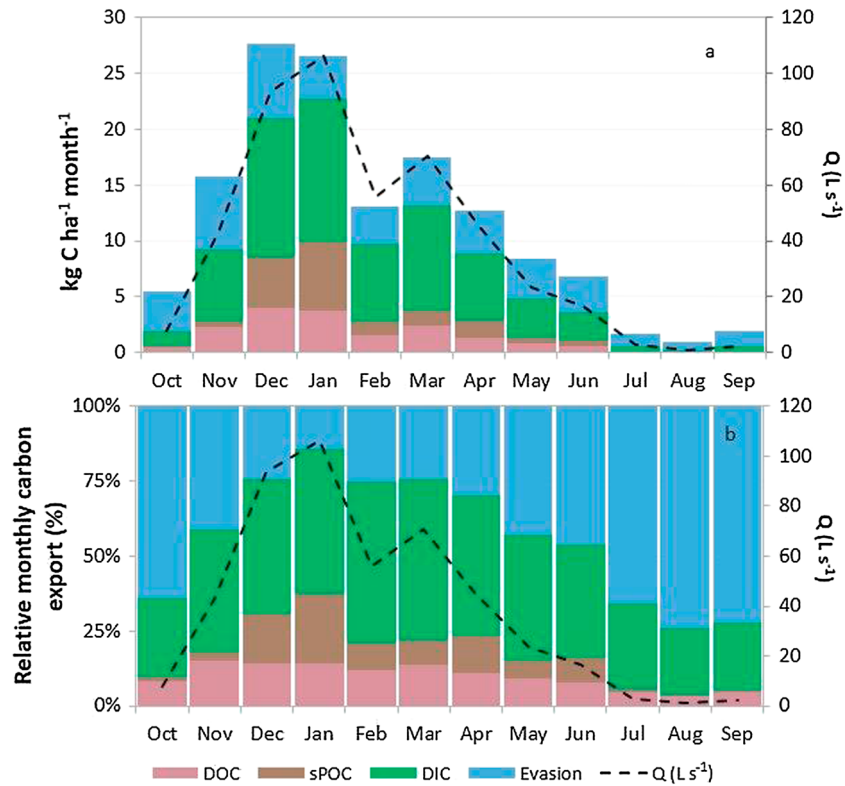


Figure 2. (a) Total and (b) relative monthly contribution of different carbon compartments to the stream carbon export and mean monthly discharge (Q). Values are calculated from 3-weekly composite samples collected during the 2004–2013 water year period.

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 CO₂ ranging from 472 to 3353 μatm (Figure 3). The pCO₂ 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.

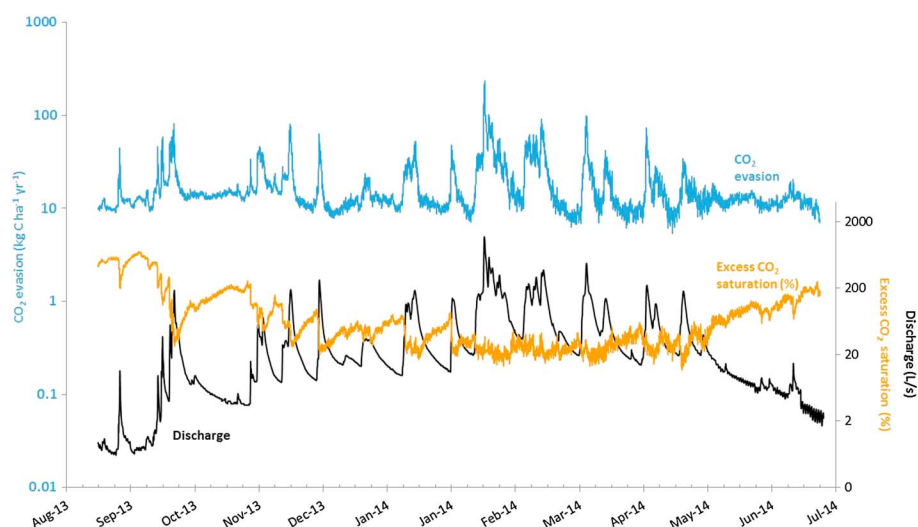


Figure 3. Modeled daily CO₂ evasion and excess CO₂ saturation in the stream, calculated by direct pCO₂ measurement from August 2013 to July 2014 [Haggerty and Dosch, 2016], and measured daily discharge.

Stream ecosystem respiration showed maxima during summer ($1.30 \pm 0.37 \text{ g C m}^{-2}$ 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 surface per 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 CO₂ evasion). Fluxes are reported in section 3.1. The stream exports $158.7 \pm_{116.4}^{322.6} \text{ kg C ha}^{-1} \text{ yr}^{-1}$. The largest sources of uncertainty are in the CO₂ evasion, $42.2 \pm_{7.7}^{209.3} \text{ kg C ha}^{-1} \text{ yr}^{-1}$, and POC export $33.7 \pm_{19.3}^{63.1} \text{ kg C ha}^{-1} \text{ yr}^{-1}$.

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 \pm SE: $-0.7 \pm 0.2\%$; supporting information).

4. Discussion

4.1. Annual Carbon Exports

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

Evasion to the atmosphere was $42.2 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ 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., $70 \pm 26 \text{ kg C ha}^{-1} \text{ yr}^{-1}$). 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 form 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 $p\text{CO}_2$ also showed an inverse relationship with discharge, consistent with the findings of Peter *et al.* [2014], where strong seasonal variability in stream and hyporheic $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 ($37.5 \text{ kg C ha}^{-1} \text{ yr}^{-1}$), 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 $p\text{CO}_2$. In periods of low flow, turbulence limits evasion to the atmosphere, and hyporheic exchange is large relative to discharge [Wondzell, 2011], so stream $p\text{CO}_2$ tends to increase. At high discharge, evasion rates surpass input rates and stream $p\text{CO}_2$ decreases.

Highest $p\text{CO}_2$ 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 $p\text{CO}_2$. 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 $p\text{CO}_2$ 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 CO₂. This net difference between CO₂ 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 CO₂ 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 CO₂ 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 pCO₂ 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 SF₆) 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 terrestrially 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 $159 \text{ kg C ha}^{-1} \text{ yr}^{-1}$, 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.

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