Global Change Biology

Global Change Biology (2012), doi: 10.1111/gcb.12083

Evasion of CO_2 from streams – The dominant component of the carbon export through the aquatic conduit in a boreal landscape

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Abstract

Evasion of gaseous carbon (C) from streams is often poorly quantified in landscape C budgets. Even though the potential importance of the capillary network of streams as C conduits across the land–water–atmosphere interfaces is sometimes mentioned, low-order streams are often left out of budget estimates due to being poorly characterized in terms of gas exchange and even areal surface coverage. We show that evasion of C is greater than all the total dissolved C (both organic and inorganic) exported downstream in the waters of a boreal landscape. In this study evasion of carbon dioxide (CO_2) from running waters within a 67 km^2 boreal catchment was studied. During a 4 year period (2006–2009) 13 streams were sampled on 104 different occasions for dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). From a locally determined model of gas exchange properties, we estimated the daily CO_2 evasion with a high-resolution (5×5 m) grid-based stream evasion model comprising the entire ˜100 km stream network. Despite the low areal coverage of stream surface, the evasion of CO_2 from the stream network constituted 53% (5.0 (±1.8) g C m^{-2} yr^{-1}) of the entire stream C flux (9.6 (±2.4) g C m^{-2} yr^{-1}) (lateral as DIC, DOC, and vertical as CO_2). In addition, 72% of the total CO_2 loss took place already in the first- and second-order streams. This study demonstrates the importance of including CO_2 evasion from low-order boreal streams into landscape C budgets as it more than doubled the magnitude of the aquatic conduit for C from this landscape. Neglecting this term will consequently result in an overestimation of the terrestrial C sink strength in the boreal landscape.

Keywords: carbon budget, Greenhouse gases, headwaters, inland waters, water–atmosphere exchange

Received 5 June 2012 and accepted 1 November 2012

Introduction

Lateral export of carbon (C) from soils to running waters is a persistent output of C with terrestrial origin (Cole *et al*., 2007; Tranvik *et al*., 2009; Aufdenkampe *et al*., 2011). Even though the awareness of the fate of this C and its potential importance in regional and global C budgets is increasing, the scarcity of data from the stream section of the aquatic conduit is widely acknowledged (Cole *et al*., 2007; Battin *et al*., 2009; Buffam *et al*., 2011). Streams form the capillary network in the landscape that comprises most of the interface between terrestrial and aquatic ecosystems. A strong hydrochemical connectivity between the catchment soil and headwater streams has been shown in mid-to-high latitude regions for both organic carbon (as total organic carbon, TOC or dissolved organic carbon, DOC) (Creed *et al*., 2003; Billett *et al*., 2006; Köhler *et al*., 2009) and dissolved inorganic carbon/carbon dioxide (DIC/CO_2) (Jones & Mulholland, 1998; Hope *et al*., 2004; Öquist *et al*., 2009). Combining this knowledge with findings that the majority of the total stream length (80%–90%) is draining small catchments (typically <20 km^2) (Leopold *et al*., 1964; Bishop *et al*., 2008), makes low-order stream systems very important for the C budget of the northern hemisphere. But to include streams in landscape C budgets is challenging because 1) stream networks are heterogeneous and dynamic in their morphology and chemistry, 2) the C flux in and from streams is two dimensional with both a downstream (as dissolved or particulate phases) and a vertical dimension (evasion of gaseous phases), and 3) the length of, and area covered by, streams and rivers is not well documented, either at global or regional scales (Cole *et al*., 2007; Battin *et al*., 2008).

The loss of C by evasion from streams to the atmosphere has often been left out of landscape C budgets

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due to being poorly quantified. In the absence of reliable data, evasion from streams has also often been assumed to be of minor importance for the overall C budget. However, Butman & Raymond (2011) showed recently that streams and rivers in the United States are emitting a significant amount of CO_2 (corresponding to 10% of the net ecosystem exchange (NEE) in the United States). By scaling this to all temperate watercourses between 25°N and 50°N the release was estimated to be 0.5 Pg C yr^{-1}. Although the biogenic proportion of the CO_2 was not determined in this study, a similar large-scale study of the entire aquatic conduit of Sweden estimated that the majority of the aquatic CO_2 originated from organic terrestrial sources (Humborg *et al.*, 2010).

The aquatic loss of C from the terrestrial landscape might be especially important in boreal regions, where a significant part of the global C stock is stored in soil and vegetation (Gorham, 1991; Pregitzer & Euskirchen, 2004). However, few studies of boreal landscape C budgets consider fluvial export of both organic and inorganic C, and the few published investigations mainly focus on peatland systems (Nilsson *et al.*, 2008; Dinsmore *et al.*, 2010). However, Rantakari *et al.* (2010) estimated the combined downstream export of total organic carbon (TOC), total inorganic carbon (TIC), and the evasion of carbon dioxide (CO_2) from the stream surface for 11 small boreal catchments (<5 km^2) in eastern Finland. The study concluded that the downstream C export (TIC + TOC) ranged between 3.5 and 15.7 g C m^{-2} yr^{-1}, but it also indicated that the evasion of CO_2 from the surface area of the stream networks was a major component in the entire stream C flux despite a larger uncertainty in the evasion estimate compared with the downstream export. This is in agreement with similar findings of boreal streams as potentially significant sources for atmospheric CO_2 (Öquist *et al.*, 2009; Teodoru *et al.*, 2009; Koprivnjak *et al.*, 2010; Wallin *et al.*, 2010). But despite these studies, knowledge of how much of the entire aquatic C pool that is lost vertically along a stream network as CO_2 evasion is limited. Furthermore, existing estimates are often based on a number of assumptions concerning both CO_2 concentration and gas exchange ability. Consequently, there is a need to better understand the C exports in stream networks, in particular the diffuse vertical loss of CO_2.

Determining the evasion of CO_2 from the water surface is more challenging compared with estimating the downstream exports of DOC and DIC in a stream network as it is a diffuse and spatially very variable flux that takes place everywhere along the stream (Hope *et al.*, 2001). A key determinant when estimating the CO_2 evasion is the gas transfer coefficient (k_{CO_2}), which describes the exchange ability of CO_2 across the water–atmosphere interface. This exchange ability could also be described by the gas transfer velocity which is frequently used in the literature. Generalized or modeled estimates of k_{CO_2} or gas transfer velocities are, however, often used without field validation which renders large uncertainties in CO_2 evasion estimates (Wallin *et al.*, 2011). In this study, we used a stream slope-based model for determining spatial distribution of k_{CO_2} in the landscape (Wallin *et al.*, 2011). This model has the advantage of being based on detailed measurements of exchange ability determined in the same catchment as this work was conducted, but based on simple physical parameters, and hence applicable on any similar stream system. Similar slope-dependent equations can be found in the literature of reaeration of streams and rivers, and slope was also included in a recently suggested equation for scaling gas transfer velocities in streams and small rivers (Raymond *et al.*, 2012). Using the k_{CO_2} model and extensive data on stream CO_2 concentrations in combination with a high-resolution (5 × 5 m) digital elevation model (DEM) allowed us to determine the evasion of CO_2 from every grid cell of stream in the entire stream network.

We hypothesized that CO_2 evasion from the stream surface was a major component in the entire flux of C exported by boreal streams due to the high concentrations of CO_2 and the range in k_{CO_2} that have been previously observed (Wallin *et al.*, 2010, 2011). To test this, we investigated the two-dimensional flux of organic and inorganic carbon within a boreal stream network over a 4 year period (2006–2009). The overall purpose of this work was to give more complete representation of boreal streams as conduits for C export. The specific aims of the study were as follows:

- Estimate the evasion of CO_2 from streams in a boreal catchment and relate this to the downstream export of DOC and DIC,
- Determine the spatial variability in relative contribution of the different C species to the entire C export and
- Identify hot spots in the stream network, where high rates of vertical CO_2 evasion occur

Site description

The study was conducted in the upper 67 km^2 of the Krycklan catchment, which drains into the Vindeln River and is situated ca 60 km north west of Umeå, northern Sweden (Fig. 1). The area is well documented as it is a part of the Svartberget LTER site, established in 1923, and where observations of catchment hydrology and biogeochemistry have been ongoing since 1980 (Laudon *et al.*, 2011). The catchment is typical for

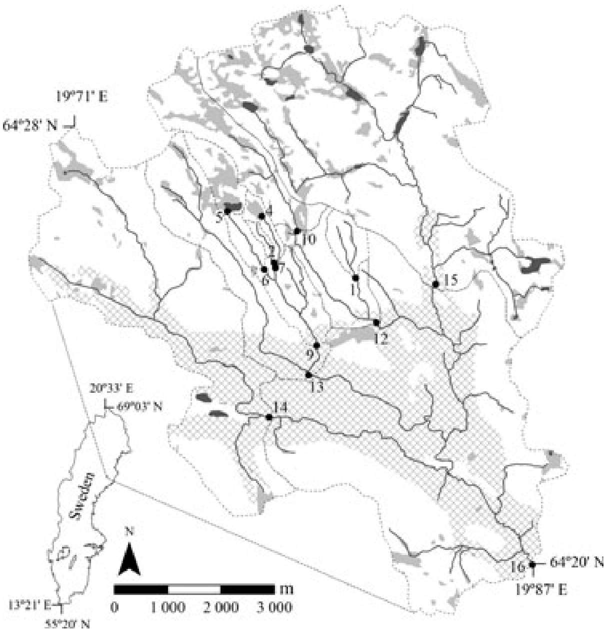

Fig. 1 The Krycklan catchment with the stream network and location of the sampled subcatchment outlets (black dots) which are referred to in the text as C-plus subcatchment number (ex. C7). Lakes are in dark gray, peatlands in light gray, and silty sediments are crosshatched.

forested catchments in Scandinavia, characterized by a climate with short summers and long winters. Elevation range in the catchment is 130 to 369 m.a.s.l. The growing season typically starts at the end of May and ends in late September, with snow cover persisting from the end of October to the beginning of May. Annual mean precipitation is 612 mm, approximately 35% of which falls as snow, and the annual daily mean temperature is 1.7 °C (Haei *et al.*, 2010). The catchment is mainly forested with Norway spruce (*Picea abies*) and Scots pine (*Pinus Sylvestris*), but deciduous trees are commonly found in the riparian zone of larger streams. The forest soils are mainly well-developed iron podzols with organic-rich soils commonly found in the near stream zone in the upper parts of the catchment. At lower elevation below the highest postglacial coastline, glaciofluvial sediments are more commonly found with a large proportion of silt deposits formed by a postglacial river delta. A number of lakes and peatlands are found in the upper parts of the catchment (Ågren *et al.*, 2007; Buffam *et al.*, 2007).

Data from 13 stream sites ranging in catchment area from 0.03 to 67 km^2 and stream orders (SOs) first to four are presented in this study (Fig. 1, Table 1). The lowest pH and highest DOC, DIC, and CO_2–C concentrations are found in streams with catchments characterized by high proportion of peatland (30–75%) (Buffam *et al.*, 2007; Wallin *et al.*, 2010). The median width and depth of the stream channels are generally <1 m; ~10 cm in the headwaters and ~7 m; ~50 cm at the outlet of the catchment (Fig. 1 and Table 1) (Nathanson *et al.*, 2012). As in the majority of the Scandinavian boreal region many of the low-order streams in the catchment network are characterized by man-made deepening conducted 75

Table 1 Subcatchment characteristics of the 13 sampling sites within the Krycklan catchment

Site	Stream order*	Catchment area (km^2)	Stream surface area (ha)	Total stream† length (km^2)	% stream surface of catchment	Stream density ($km\ km^{-2}$)	Altitude‡ (masl)	Stream slope‡ (%)	Stream flow§ ($L\ s^{-1}$)
C1	2	0.46	0.2	2.0	0.33	4.3	258	6.7	3.4
C2	1	0.13	0.04	0.6	0.34	4.9	251	5.5	0.7
C4	1	0.17	0.01	0.05	0.08	0.3	280	1.9	1.0
C5	1	0.65	0.002	0.03	0.004	0.1	283	0.4	4.9
C6	1	1.1	0.1	1.5	0.09	1.4	258	4.0	7.3
C7	2	0.46	0.1	1.9	0.28	4.1	257	4.5	2.6
C9	3	2.9	0.8	7.8	0.27	2.7	232	4.0	16.3
C10	2	3.3	0.3	2.9	0.09	0.9	271	1.4	15.2
C12	3	5.4	1.0	9.2	0.19	1.7	240	3.6	28.0
C13	3	7.0	1.9	17.1	0.27	2.5	238	3.4	37.4
C14	2	13.8	1.4	15.1	0.10	1.1	200	2.0	70.5
C15	4	18.8	3.6	31.4	0.19	1.7	255	3.0	103
C16	4	66.9	15.5	106.7	0.23	1.6	214	3.1	347

*Determined at sampling site.
†Total stream length upstream of sampling site
‡Average altitude and slope of the stream channels.
§Estimated median stream flow (2006–2009) using specific discharge measured at C7
Note: C3, C8, and C11 does not exist in this study.

–200 years ago to improve the forest productivity by drainage. More detailed descriptions of the sites and stream chemistry dynamics can be found in Cory *et al.* (2006), Buffam (2007) and Björkvald *et al.* (2008).

Materials and methods

Sampling and analysis

Stream DOC and DIC were sampled at the 13 sites in conjunction with other chemical and physical stream parameters including metals, major cations and anions, pH, and stream temperature. Sampling was performed monthly during winter, every second week during summer and fall, and more intensively during spring flood. Here, data are used for the period between 2006 and 2009 with a total of 104 sampling occasions in each of the 13 streams. Samples for DOC and pH analysis were collected without headspace in 250 mL high-density polyethylene bottles, and kept cold and dark during transport to the laboratory. DOC samples were frozen until analyzed. Prior to analysis samples were acidified and sparged to remove inorganic carbon. Then DOC was analyzed using a Shimadzu TOC-C_{PCH} analyzer (Ågren *et al.*, 2007; Buffam *et al.*, 2007). The particulate fraction of TOC in these Krycklan streams and in similar types of streams in boreal Scandinavia is generally insignificant with TOC being equivalent to DOC. The particulate fraction of TOC is less than 0.6% for the Krycklan catchment (Laudon *et al.*, 2011). For DIC, a separate stream sample of 5 ml of bubble-free water was taken and injected into a 22.5 ml glass vial (containing N_2 at atmospheric pressure) sealed with a rubber septa using a syringe. The vial was prefilled with 0.5 ml of 0.6% HCl to shift the carbonate equilibrium toward CO_2. Headspace CO_2 concentration was analyzed during 2006–2008 by GC-FID (Perkin Elmer Autosystem Gas chromatograph) equipped with a methanizer operating at 375 °C and connected to an autosampler (HS40) (Wallin *et al.*, 2010). During 2009 the samples were analyzed by GC-FID (Perkin-Elmer Clarus 500) equipped with a methanizer operating at 250 °C and connected to an autosampler (Turbo Matrix 110). DIC concentrations were then determined from headspace CO_2, and field $p\mathrm{CO_2}$ was calculated from the DIC using temperature-dependent equations for the carbonate equilibrium (Gelbrecht *et al.*, 1998) and Henry's Law (Weiss, 1974), together with measured stream water pH and temperature. Further description of the DIC/$p\mathrm{CO_2}$ method can be found in Wallin *et al.* (2010). The pH was always measured within 24 hours using an Orion 9272 pH meter equipped with a Ross 8102 low-conductivity combination electrode with gentle stirring at ambient temperature (20 °C) on the nonair equilibrated sample. Stream temperature was measured in the field. Discharge measurements were made using a V-notch weir in a heated dam house at the Svartberget/Nyänget catchment (C7), where stage height and water temperature were recorded continuously. This 0.5 km^2 subcatchment has been used as a representative site for specific discharge for the Krycklan catchment in several studies (Ågren *et al.*, 2007; Laudon *et al.*, 2007; Björkvald *et al.*, 2008; Wallin *et al.*, 2010). The average annual run-off during 1981–2008 was 323 mm (Haei *et al.*, 2010). The stream network was the focus of this study; internal processes of the lakes within the catchment (covering 0.7% of the catchment area) were not included in this study, but their potential role is addressed in the discussion section.

CO_2 evasion calculations and uncertainty estimation

The CO_2 evasion was calculated using the flux equation first proposed for reaeration of streams by Young & Huryn (1998) and used for determining stream CO_2 evasion (Hope *et al.*, 2001; Billett *et al.*, 2004; Öquist *et al.*, 2009; Dinsmore *et al.*, 2010; Wallin *et al.*, 2011).

$$E_{\mathrm{CO_2}} = \Delta\mathrm{co_2} \times k\mathrm{co_2} \times \tau \times Q \qquad (1)$$

where $E_{\mathrm{CO_2}}$ is the evasion of CO_2 over a specific reach of stream (mg s^{-1}); $\Delta\mathrm{co_2}$ is the difference between the in-stream CO_2 concentration and the concentration that would exist if the stream was in equilibrium with the atmosphere (mg C L^{-1}); $k_{\mathrm{CO_2}}$ is the gas-specific transfer coefficient (min^{-1}); τ is the reach travel time (min); and Q is the mean daily stream discharge (L s^{-1}). Median annual values of $k_{\mathrm{CO_2}}$ and specific daily τ for each grid cell (see section 3.4 for information of the GIS work) of stream were modeled using equations 2 and 3, respectively, both derived from the findings in Wallin *et al.* (2011).

$$k_{\mathrm{CO_2}} = \frac{a_k \times \tan\beta \times 100 + b_k}{1.01^{(20-T)}} \qquad (2)$$

$$\tau_{norm} = \exp(a_\tau \cdot \ln(\mathrm{Q}) + b_\tau) \qquad (3)$$

where a_k and b_k are regression parameters; tan β is the slope of the stream segment (m m^{-1}); T the mean daily stream temperature (°C); τ_{norm} the reach travel time normalized for stream distance (min m^{-1}); a_τ and b_τ are regression parameters; and Q the mean daily stream discharge (L s^{-1}).

Daily time series of $\Delta\mathrm{co_2}$ concentrations (assuming an atmospheric $p\mathrm{CO_2}$ of 380 μatm) and $p\mathrm{CO_2}$ were created by linear interpolation between sampling days (Fig. 2). The spatiotemporal variability in atmospheric CO_2 just above a stream surface in forested regions is, however, hard to estimate. But for example assuming 450 μatm would imply a reduction in evasion by <3% based on the average $p\mathrm{CO_2}$ observed in the Krycklan streams. Linear interpolation was chosen as general regression models between $p\mathrm{CO_2}/\Delta\mathrm{co_2}$ and physical parameters were not found at all sites (Wallin *et al.*, 2010). Daily evasion of CO_2 from the stream surface of each grid cell was determined using equation 1 and assuming a daily median SO-specific $\Delta\mathrm{co_2}$ concentration. Daily $k_{\mathrm{CO_2}}$ was given according to equation 2 with the stream slope for each grid cell and with daily median SO-specific temperature. Daily discharge for each grid cell was obtained using specific discharge adjusted for catchment area, i.e., assuming a constant stream flow generation. The CO_2 evasion was calculated separately for each grid cell of stream and expressed per stream surface area or per catchment area.

Mean evasion rates with associated standard deviations were determined using a Monte Carlo experiment. A total 50,000 random parameter sets (13 parameters per set) were drawn from a multivariate normal distribution to compute stochastic CO_2 evasion for each of the 13 subcatchments as well as per SO. For more detailed description of the modeling and uncertainty estimation for CO_2 evasion see the Supporting Information.

Downstream export of DOC and DIC

For consistency, daily time series of DIC and DOC were created in the same manner to that for $p\mathrm{CO_2}$ by linear interpolation between sampling days (Fig. 2). The discrepancy in downstream DOC export between linearly interpolated daily data and daily data based on discharge-dependent regression models has been shown to be low (<10%), given the sampling frequency in this study (Laudon *et al.*, 2004). Flow-weighted values of DOC and DIC were based on interpolated data to get representative annual values. Annual flow-weighted concentrations of DOC and DIC were obtained by normalizing to annual discharge. Annual downstream export of DOC and DIC was estimated as the sum of daily export (daily concentrations times mean daily discharge), which was then divided by the area of each subcatchment to obtain area-specific export. Uncertainty estimates for lateral export of DOC and DIC (13% and 12% (SD of mean), respectively, including uncertainties associated with sampling, analysis, and discharge determination) are given according to similar studies in Krycklan or in the nearby region using Monte Carlo simulations for error propagation (Ågren *et al.*, 2007; Nilsson *et al.*, 2008). Uncertainties are given as standard deviation for all export and evasion rates.

Delineation of the stream network and catchment characteristics

Characteristics of the stream network of Krycklan are presented for the 13 subcatchments and per SO in Tables 1 and 2. Stream network characteristics were calculated from a high-resolution (5 × 5 m) DEM derived from LIDAR data. The stream network was obtained using the "Channel Network" module in the open source software SAGA GIS (SAGA User Group Association, Göttingen, Germany) (Conrad, 2007; Böhner *et al.*, 2008), with an initiation threshold area of 5 ha calculated using a multiple-flow-direction algorithm (Seibert & Mcglynn, 2007). The derived stream network was further compared with the stream network presented on a digital land-cover map (1:100000) (Lantmäteriet, Gävle, Sweden). To ensure that the originally derived network only contained perennial streams, all stream segments that were not shown on the land-cover map were removed. Local slope values for each grid cell of stream were determined using the down-slope index by Hjerdt *et al.* (2004). In this approach, local slope (tan β) is calculated by dividing a fixed elevation difference (d) by the length of a flow path (L_d), i.e., $\tan \beta = d/L_d$. The value of L_d corresponds to the downstream distance over which the change in elevation equals d. The value of d was optimized to 40 cm as it showed the strongest correlation ($r = 0.64$, $n = 14$) between values of the down-slope index and stream slopes measured in the field (Wallin *et al.*, 2011). Further descriptions of the LIDAR-based GIS work in the Krycklan catchment can be found in Grabs (2010) and Laudon *et al.* (2011).

The stream surface area of the network was assumed to be constant over the year and estimated from the length and width of all streams. Stream length was computed from the DEM-based stream network, and as previously mentioned, only representing perennial streams. Stream width and depth were estimated as mean width and depth per SO based on field measurements ($n = 136$) of the channel network at low to moderate flow conditions (Jaremalm and Nolin, unpublished) (Table 2). The width estimates for Krycklan are 25%–40% lower than estimates made for the River Öre catchment (Jonsson *et al.*, 2007) or for Sweden as a whole (Humborg *et al.*, 2010). To summarize, our estimate of the stream surface area should be seen as a moderately conservative estimate as it is based on perennial stream length.

Results

Run-off

The mean annual discharge was 306 mm (2006, 331 mm; 2007, 291 mm; 2008, 295 mm; 2009, 306 mm) with a specific discharge ranging from 0.01 to 11.1 mm day^{-1} (median: 0.5 mm day^{-1}) during the 4 year period (Fig. 2). According to frequency analysis, 80% of the days had a specific discharge <1 mm day^{-1}. Despite the few days with discharge >5 mm day^{-1} (<5% of the entire period), those days accounted for 25% of the accumulated discharge. The majority (>80%) of these high discharge days occurred during the snow melt, April–May.

Stream water $p\mathrm{CO_2}$, DIC, and DOC

The mean annual flow-weighted concentration of DIC ranged from 1.0 to 4.7 mg L^{-1} across the 13 sites, the site-specific median annual $p\mathrm{CO_2}$ ranged from 1251 to 7852 μatm (equal to 3.3–20.7 times equilibrium with the atmosphere) (Table 3). The highest DIC concentration and highest $p\mathrm{CO_2}$ were found in the peatland dominated C4 (4.7 mg L^{-1}: 7852 μatm). The remaining sites had a mean flow-weighted DIC concentration ranging from 1.0 to 2.8 mg L^{-1}. Although the highest DIC concentrations were found in headwater streams, there was no pattern of decreasing DIC with increased SO. As the speciation of the different DIC constituents is highly pH dependent, sites with relatively high DIC and low pH had high $p\mathrm{CO_2}$ (C2, C5, and C13), whereas sites with similar DIC concentration but with higher pH showed significantly lower supersaturation of CO_2 (C14 and C16). However, SO-specific median $p\mathrm{CO_2}$ tended to decrease with increasing SO, but with a clear step shift between SO 1 and SO 2 where SO 1 was more than twice as CO_2 supersaturated as SO 2. Stream

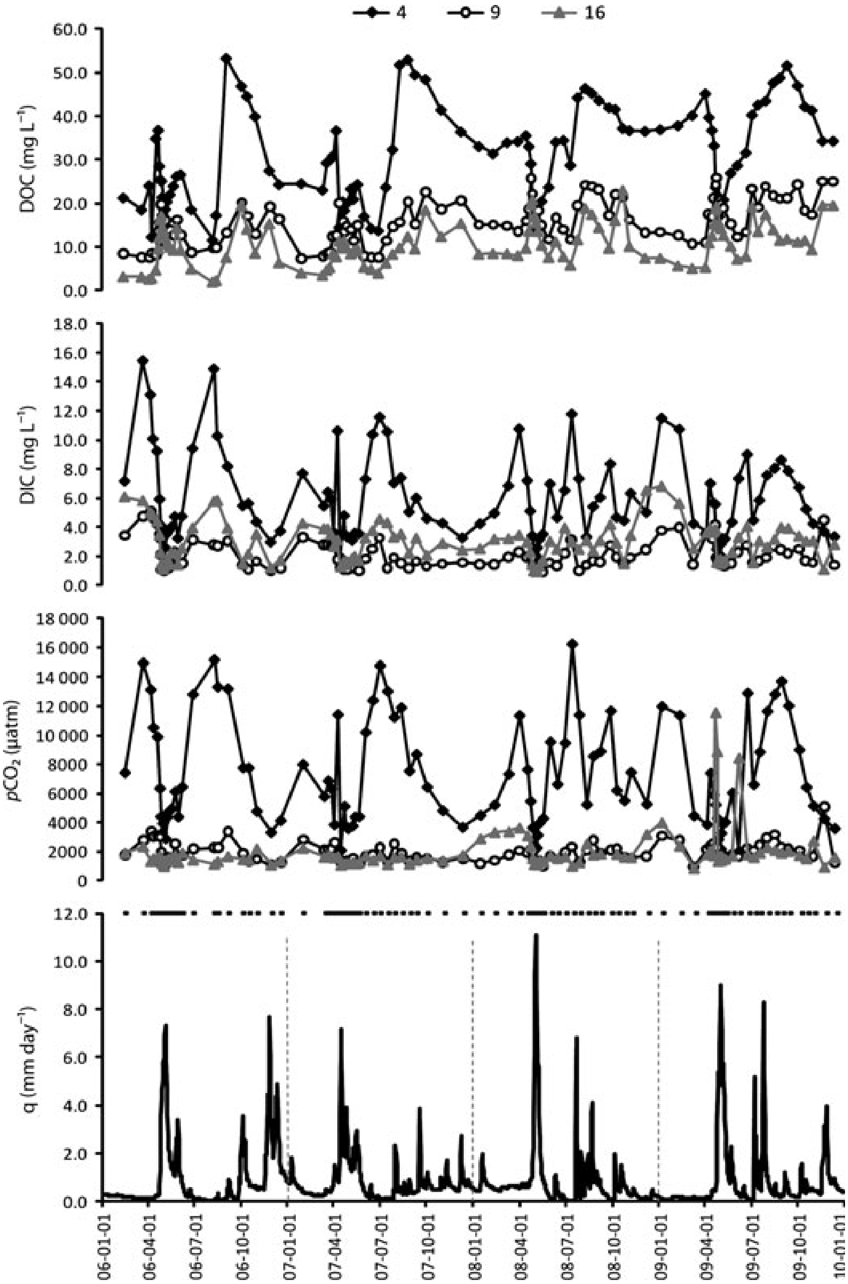

Fig. 2 Temporal changes in DOC, DIC, and pCO$_2$ during 2006–2009 at three representative sites within the Krycklan catchment. C4; peatland outlet (filled circles), C9; intermediate-sized stream (open circles), and C16; outlet of Krycklan (gray triangles). Specific discharge (q) (black line) from a representative site (C7) and the collection times of water samples for analysis of carbon content (black dots at the top of the graph).

order-specific median pCO$_2$ values were as follows: SO 1, 4075 μatm; SO 2, 1843 μatm; SO 3, 1941 μatm; SO 4, 1480 μatm.

The mean annual flow-weighted concentration of DOC ranged from 12.7 to 30.3 mg L^{-1} across the 13 sites (Table 3). The sites can be grouped according to their DOC concentration. The highest concentration 30.3 mg L^{-1} was found in the headwater stream (C4) with the highest proportion of peatland in the catchment. This was the same site that had the highest DIC concentrations and pCO$_2$. The headwater sites dominated by forest in the catchment (C1 and C2) and the intermediate-sized mixed peatland/forest sites (C6, C7, C9, C10, C12, and C13) had DOC concentrations ranging from 15 to 25 mg L^{-1}. The lowest DOC concentrations (<15 mg L^{-1}) were found in the largest

Table 2 Stream order characteristics of the Krycklan stream network

Stream order	Stream width* (m)	Stream depth* (m)	Total catchment area (km^2)	Stream surface area (ha)	Total stream length (km)	% of total stream length	% stream surface of catchment	Stream density ($km\ km^{-2}$)	Altitude† (masl)	Stream slope† (%)
1	0.6/0.6 (0.3–0.9)	0.16/0.14 (0.05–0.34)	31.7	3.6	51.6	48	0.11	1.6	238	4.3
2	1.3/1.1 (0.7–2.0)	0.38/0.31 (0.11–0.70)	22.5	4.7	34.3	32	0.21	1.5	207	2.3
3	2.8/2.5 (1.0–5.4)	0.31/0.30 (0.10–0.60)	6.9	2.8	12.2	11	0.40	1.8	184	2.0
4	5.1/5.0 (3.7–6.6)	0.32/ 0.32 (0.15–0.56)	6.3	4.5	8.9	9	0.72	1.4	143	0.9

*Stream width and depth are given as mean/median (10th–90th percentiles).
†Average altitude and slope of the stream channels.

third- and fourth- order streams (C14, C15, and C16). The flow-weighted concentration of DOC expressed as a SO-specific median decreased with increasing SO: SO 1, 20.9 mg L^{-1}; SO 2, 20.2 mg L^{-1}; SO 3, 18.5 mg L^{-1}; SO 4, 13.0 mg L^{-1}.

CO_2 evasion

The CO_2 evasion from the water surface ranged between 1455 (±525) and 6411 (±3012) g C m^{-2} yr^{-1} based on stream surface area for the 13 catchments (Fig. 3). The highest mean annual CO_2 evasion rates were found for C6 and C14 which vertically exported 6411 (±3012) and 4224 (±1415) g C m^{-2} yr^{-1}, respectively. The lowest rates, 1455 (±525) and 1839 (±239) g C m^{-2} yr^{-1} were found in the first-order C4 and C5. The remaining catchments had evasion rates between 2060 (±891) and 2875 (±878) g C m^{-2} yr^{-1}. The CO_2 evasion rates per stream surface area decreased with increasing SO: SO 1, 4192 (±1852) g C m^{-2} yr^{-1}; SO 2, 1995 (±636) g C m^{-2} yr^{-1}; SO 3, 1555 (±654) g C m^{-2} yr^{-1}; SO 4, 1166 (±227) g C m^{-2} yr^{-1}. Median k_{CO_2} by SO was as follows: SO 1, 0.070 min^{-1}; SO 2, 0.042 min^{-1}; SO 3, 0.038 min^{-1}; SO 4, 0.023 min^{-1}.

Contribution of CO_2 evasion to the catchment C flux

In addition to the stream surface area-based flux, the evasion of CO_2 was expressed per catchment area for comparison with downstream export of DIC and DOC. The catchment area-based evasion of CO_2 ranged from 0.07 (±0.01) to 9.2 (±4.9) g C m^{-2} yr^{-1} (Fig. 4). The highest catchment area-based evasion rate was obtained for C1 (9.2 (±4.9) g C m^{-2} yr^{-1}). Lowest rates were found in the two first-order catchments, C4 and C5 (C4, 1.1 (±0.4) g C m^{-2} yr^{-1} and C5, 0.07 (±0.01) g C m^{-2} yr^{-1}). The remaining sites ranged between 2.5 (±0.8) and 7.8 (±4.0) g C m^{-2} yr^{-1} in catchment area-based evasion. The CO_2 evasion should be compared with the downstream export of DIC and DOC that ranged from 0.3 (±0.04) to 1.4 (±0.2) g C m^{-2} yr^{-1} for DIC and from 3.9 (±0.5) to 9.3 (±1.2) g C m^{-2} yr^{-1} for DOC

Table 3 Annual flow-weighted concentration of DOC (mg L^{-1}) and DIC (mg L^{-1}), annual median pCO_2 (μatm), and 4 year mean of DOC, DIC, and pCO_2 of the 13 sites within the Krycklan catchment 2006–2009.

	2006			2007			2008			2009			Mean 2006–2009		
Site	DOC	DIC	pCO_2	DOC	DIC	pCO_2	DOC	DIC	pCO_2	DOC	DIC	pCO_2	DOC	DIC	pCO_2
C1	17.7	1.0	1364	16.3	1.0	1301	22.6	0.9	1124	23.5	1.2	1698	20.0	1.0	1372
C2	17.5	2.1	3778	16.1	2.7	5131	19.7	2.4	3652	23.2	2.6	5176	19.1	2.5	4434
C4	28.0	4.4	8890	30.4	4.8	7319	30.5	4.8	7536	32.3	4.6	7663	30.3	4.7	7852
C5	19.3	2.4	3776	21.2	2.9	4361	24.1	2.6	2958	25.2	3.2	3770	22.5	2.8	3716
C6	17.1	1.4	2249	17.2	1.6	2067	20.3	1.4	1841	22.4	1.6	2210	19.3	1.5	2092
C7	21.9	1.4	1681	21.4	1.6	1895	25.2	1.3	1453	27.3	1.6	1848	24.0	1.5	1719
C9	15.7	1.5	2024	15.5	1.6	1765	18.7	1.6	1759	21.0	2.1	2214	17.7	1.7	1941
C10	18.3	1.6	2305	18.5	1.6	1948	21.4	1.5	1776	23.4	1.8	2156	20.4	1.6	2046
C12	16.9	1.2	1484	16.9	1.1	1221	20.4	1.1	1256	22.4	1.2	1464	19.2	1.2	1356
C13	18.4	2.3	5277	18.0	2.6	3357	21.4	2.9	3747	23.6	2.6	4002	20.4	2.6	4096
C14	12.4	2.1	2101	11.5	2.3	1870	14.0	2.2	1773	16.0	2.4	2121	13.5	2.3	1966
C15	12.6	1.3	1167	11.3	1.6	1235	14.2	1.4	1110	14.9	1.6	1520	13.3	1.5	1258
C16	11.8	2.1	1574	10.1	2.5	1556	14.0	2.3	1903	14.9	2.4	1769	12.7	2.3	1701

Note: C3, C8 and C11 do not exist in this study.

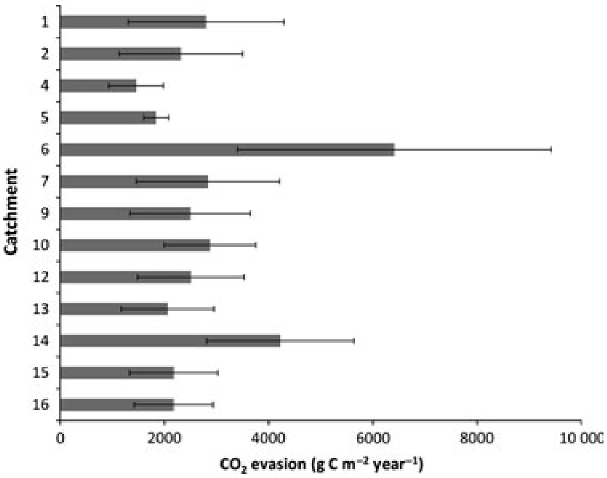

Fig. 3 Mean annual CO_2 evasion expressed per stream surface area from the 13 subcatchments of Krycklan. The fluxes are presented as mean evasion rates based on 4 years, 2006–2009, and with error bars showing SD.

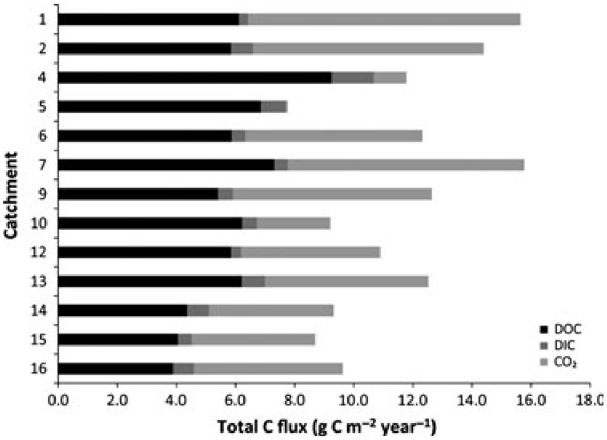

Fig. 4 Mean annual downstream export of DOC and DIC as well as CO_2 evasion from the 13 subcatchments of Krycklan. The fluxes are mean numbers based on 4 years, 2006–2009, and expressed per catchment area.

across the 13 catchments. Furthermore, the contribution of CO_2 evasion to the entire stream C flux varied significantly across the 13 catchments from <10% in two of the headwater catchments (C4 and C5) to >50% in two of the other headwater catchments (C1 and C2). The CO_2 evasion from the streams of the Krycklan catchment represented 53% (5.0 (±1.8) g C m^{-2} yr^{-1}) of the entire catchment's stream C flux (9.6 (±2.4) g C m^{-2} yr^{-1}) (Fig. 5).

To determine where the CO_2 evasion takes place in the Krycklan catchment, the entire evasion flux was separated into the different SOs (1–4) (Fig. 5). The first- and second-order streams which comprised 80% of the total stream length and 53% of the total stream surface area (Table 2) were responsible for 72% of the entire vertical flux of CO_2 from the stream network. Hence, the remaining 28% of CO_2 was evaded from the third- and fourth-order streams which comprised 47% of the entire stream surface area and 20% of the total stream length, respectively.

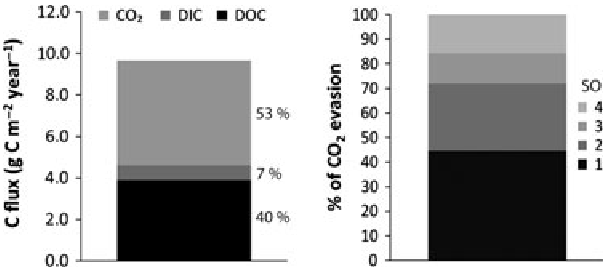

Fig. 5 Total aquatic C flux (including CO_2 evasion and lateral exports of DOC and DIC) from the Krycklan catchment and contribution of the various C species (left graph). Contribution of the different SOs to the entire CO_2 evasion from the stream network of Krycklan (right graph).

Discussion

Combining field measurements and relationships with a five meter DEM provided a novel way to quantify the CO_2 evasion from the stream network in a boreal landscape. The study showed that CO_2 evasion from the stream surface was the dominant component of the entire C flux via the aquatic conduit for these boreal streams. Neglecting this underestimates the strength of the aquatic pathway for the terrestrial net ecosystem carbon balance (NECB) (Chapin *et al.*, 2006) and consequently results in an overestimation of the terrestrial uptake of atmospheric C. The CO_2 evasion rates (both per stream surface and catchment area) for the Krycklan catchment were within the range (upper half) found in similar studies of supersaturated streams in boreal and temperate regions (Table 4). In addition, the degree of CO_2 supersaturation (722–24167 μatm) covers almost the full range observed in the literature illustrating the large spatiotemporal variability and hence the complexity of estimating evasion rates from streams on a landscape level. There was a large spatial variability in CO_2 evasion, with stream surface-based CO_2 evasion rates generally decreasing with increased SO. To our knowledge, no such detailed quantification of CO_2 evasion from a landscape drainage system (SOs 1–4) has been previously published, although significant evasion rates have been concluded to occur in highly CO_2 supersaturated streams/river systems in boreal (Rantakari *et al.*, 2010), peatland (Hope *et al.*, 2001; Dins-

Table 4 A summary of CO_2 evasion data from published studies of streams/rivers in temperate and boreal regions

Region	Stream order*	pCO_2 (μatm)	Stream flux[†] (g C m^{-2} yr^{-1})	Catchment flux[‡] (g C m^{-2} yr^{-1})	Method[§]	Reference
Ontario, Canada	1–2	570–23500	641–2440	–	L.D.	(Koprivnjak *et al.*, 2010)
Ontario, Canada	1	3200–9320	311–4347	3.1–3.9	F.C.	(Billett & Moore, 2008)
Quebec, Canada	1–5	481–5410	1138	1.6	L.D.	(Teodoru *et al.*, 2009)
Tennessee, USA	1	360–6228	688–1634	3.2	E.D.	(Jones & Mulholland, 1998)
Entire USA	1–10	1588–4326[¶]	882–4008	4.5–22.9[¶]	E.D.	(Butman & Raymond, 2011)
Scotland, UK	1	420–4500	95–16745	14.1	E.D.	(Hope *et al.*, 2001)
Scotland, UK	1	1300–6000**	1390–9450	4.6	E.D.	(Billett *et al.*, 2004)
Scotland, UK	1	906–8112	25418	11.5–13.9	E.D.	(Dinsmore *et al.*, 2010)
Eastern Finland	1	890–8320	–	3.5–48	M.D.	(Rantakari *et al.*, 2010)
Entire Sweden	1–6	794–1950	473–3032	–	M.D.	(Humborg *et al.*, 2010)
Northern Sweden	1–5	3400[††]	471	0.5–2.6	L.D	(Jonsson *et al.*, 2007)
Northern Sweden	1	2015–7838	2356	2.9	E.D.	(Öquist *et al.*, 2009)
Northern Sweden	1–4	722–24167	1455–6411	5.0	E.D.	This study

*Estimated where not given

[†] CO_2 evasion expressed per stream surface area

[‡] CO_2 evasion expressed per catchment area

[§] Method used to determine CO_2 evasion:

E.D.: Experimentally determined data of *k* (the gas transfer coefficient/velocity)

F.C.: Direct method of determining CO_2 evasion by floating chamber

L.D.: Literature-based data of *k*

M.D.: Modelled-based data of *k*

[¶] Regional average values

**Estimated from data expressed as CO_2–C in mg L^{-1}

[††] Literature value used for pCO_2

more *et al.*, 2010), temperate (Butman & Raymond, 2011) and tropical biomes (Richey *et al.*, 2002).

Downstream DOC and DIC exports at the Krycklan outlet (C16) were estimated to represent 40% (3.9 (±0.5) g C m^{-2} yr^{-1}) and 7% (0.7 (±0.1) g C m^{-2} yr^{-1}), respectively, of the entire stream C flux of Krycklan. The range in downstream DOC export across the 13 stream sites in this study (3.9 –9.3 g C m^{-2} yr^{-1}) was on the same order as TOC export rates found for small boreal streams in eastern Finland (2.3–14.8 g C m^{-2} yr^{-1}) (Rantakari *et al.*, 2010), but lower than TOC and DOC exports reported for small streams draining peatland systems in Sweden (TOC; 11.9–14.0 g C m^{-2} yr^{-1}) (Nilsson *et al.*, 2008), Canada (DOC; 13.2–21.0 g C m^{-2} yr^{-1}) (Roulet *et al.*, 2007), and in Scotland (DOC; 18.6–32.2 g C m^{-2} yr^{-1}) (Dinsmore *et al.*, 2010). This is expected as peatland coverage was only 9% of the Krycklan basin. The downstream DIC export found in this study (0.3–1.4 g C m^{-2} yr^{-1}) was similar to the range found in the Finnish study (0.4 –1.4 g C m^{-2} yr^{-1}) (Rantakari *et al.*, 2010) and the range found for the River Öre catchment, northern Sweden (0.8–1.1 g C m^{-2} yr^{-1}) (Jonsson *et al.*, 2007).

The DIC in the Krycklan streams is mainly a product of mineralization of organic C and root respiration as the occurrence of carbonate-containing bedrock is low in the area. Input of HCO_3^- derived from weathering of silicate minerals is suggested to be of importance only for the chemistry of the larger (SOs 3–4), lower elevation streams in Krycklan (Klaminder *et al.*, 2011). The DIC source is supported by the typical stream water range in the stable isotopic composition of DIC ($\delta^{13}C$-DIC) ranging between −24 ‰ and −12 ‰ across the stream network (Wallin, 2011). The range in isotopic composition was similar to those in the nearby River Öre catchment, where similar conclusions about the DIC source were made (Jonsson *et al.*, 2007). In addition, the trend in changing stable isotopic composition ($\delta^{13}C$-DIC) toward enrichment in ^{13}C with increasing catchment area also supports the finding of significant evasion rates (Venkiteswaran *et al.*, in review). A loss of the lighter ^{12}C (diffusional fractionation) along the streams would cause the observed pattern in isotopic composition of DIC (Parker *et al.*, 2010). The lowest CO_2 evasion rates per catchment area were found in the headwater catchments (C4 and C5) although they were the sites that had the highest pCO_2. Those catchments are outlets of a peatland (C4) and an isolated headwater lake (C5) that are sampled <50 m downstream from the outlets. A short stream length in relation to the catchment area (low stream density) (Table 1) results in a low catchment area-based CO_2 evasion.

The CO_2 evasion from the streams in this study is assumed to take place all year around. If the evasion of CO_2 was considered to be zero during the ice-covered season (Dec–April), the annual evasion fluxes should be reduced by an average of 27%. Ice cover is often described to prevent gas exchange across the water–atmosphere interface in lakes (Striegl *et al.*, 2001; Sobek *et al.*, 2006) and streams (Jonsson *et al.*, 2007; Teodoru *et al.*, 2009; Rantakari *et al.*, 2010). But compared with lakes, low-order streams in boreal regions are much more heterogeneous in their water surface and fine-scale morphology, so the ice and snow cover at winter time is highly variable across the stream network. As the stream water is moving, CO_2 can be rapidly lost from the stream to the atmosphere along the parts of the stream network with open water or fragile ice cover. CO_2 flux through the snow pack has been concluded to be a significant component in the annual CO_2 emissions from soils in seasonally snow-covered regions (Sommerfeld *et al.*, 1993; Hubbard *et al.*, 2005).

An essential factor when determining CO_2 evasion from streams is the estimated surface area of the stream network. A recent study suggests that the stream surface area has globally been significantly underestimated, and as a consequence, resulting in large-scale estimates of greenhouse gas evasion from fluvial systems being too low (Benstead & Leigh, 2012). In addition, streams in boreal regions can be very dynamic in their occurrence over the year due to the variable hydrological conditions. According to the five meter DEM used in this study, the stream network could potentially double its length from ~100 km (used in this study) to ~200 km when going from base flow to high flow (spring flood, rain storms). Hence, the estimates of CO_2 evasion (both based on stream surface area and catchment area) are associated with an additional uncertainty coupled to both the length and width (i.e., surface area) of the stream network. The stream surface area presented in this study, 0.004%–0.37% of the catchment area among the 13 catchments (Table 1), represents low-to-moderate flow conditions. Those numbers could be compared with the range 0.23%–0.84% representing stream and river surface areas (SOs 1–10) across the entire United States (Butman & Raymond, 2011). The dynamics of the stream network occurrence, especially during high flows, and its influence on the estimates of CO_2 evasion require further investigation.

The residence time of the stream water from crossing the soil–stream interface to leaving the catchment at downstream sites is among the key factors in determining eventual effects of in-stream processing of DOC within the catchment boundaries. Studies in the Krycklan catchment of in-stream bacterial respiration (Berggren *et al.*, 2007, 2009) and photochemical oxidation (Köhler *et al.*, 2002) of DOC have quantified the magnitude of these processes. Average bacterial respiration rate was estimated to be <0.2 mg C L^{-1} day^{-1}, whereas photochemical oxidation rates were higher with an average rate for stream water of 1.1 mg C L^{-1} day^{-1}. Assuming a combined constant degradation rate (1.3 mg C L^{-1} day^{-1}) throughout the entire year, the contribution of in-stream processes to the DIC stream flux was on the order of ~0.3 g C m^{-2} yr^{-1} at the catchment outlet (C16). Both the bacterial respiration and the photochemical oxidation rates were, however, determined at room temperature (15 °C–20 °C) and with optimized light conditions (equivalent to full sunlight) in the latter study. Consequently, the estimated maximum in-stream mineralization flux rate (~0.3 g C m^{-2} yr^{-1}) is likely an overestimation compared with mineralization occurring during *in-situ* conditions. Furthermore, it has been previously reported that given the short water residence times in most parts of the catchment in combination with shaded streams and low water temperatures, in-stream processing of DOC to CO_2 was believed to not significantly affect the stream concentration of DIC within the catchment (Wallin *et al.*, 2010). Our study further supports these findings as the Krycklan catchment's stream water residence time at an annual median discharge situation (0.5 mm day^{-1}) is 1–2 days from the furthest headwater to the outlet if not passing a lake. Whether the DOC will be processed further downstream (outside the catchment boundaries) and evaded to the atmosphere, or be buried in lake or ocean sediments, is, however, crucial for estimates of the C budget at larger scales.

Measurements in the nearby (20 km) Flakaliden research forest show a NEE of 96 (±14) g C m^{-2} yr^{-1} (for 2001–2002) for a forest stand representative in age for this study (Lindroth *et al.*, 2008). Assuming a similar productivity for the forest in our study area implies that export and evasion of C by fluvial systems in the Krycklan catchment accounts for 10% (8%–17% among the subcatchments) of NEE. Of this aquatic component, just over half is due to evasion of CO_2 from streams. In addition, for streams in this study draining subcatchments with a high proportion of peatland, the export and evasion of C could potentially account for more than the upper range of 17% given above. NEE for the nearby (10 km) Degerö mire was concluded to be 52 g C m^{-2} yr^{-1} (for 2004–2005) with fluvial C loss accounting for 34% of the terrestrial C uptake (Nilsson *et al.*, 2008).

Our results highlight the importance of CO_2 evasion from headwater streams relative to other carbon fluxes in freshwater ecosystems. Freshwater ecosystems in turn have been found in recent studies to substantially impact the overall net carbon balance at the watershed, regional and global scale. In regional studies, freshwater export + evasion + sedimentation have been measured ranging 6–19 g C m^{-2} yr^{-1}, equaling 6% to 40% of terrestrial NEE (Christensen *et al.*, 2007; Jonsson *et al.*, 2007; Buffam *et al.*, 2011). Globally the processing of carbon in freshwaters is estimated to average 18 g C m^{-2} of terrestrial area yr^{-1}, equal to 60% of the total terrestrial NEE (Battin *et al.*, 2009). But in many of these studies, the evasion of CO_2 from headwaters is a much smaller proportion than found in our study. It will be important to see whether this is a correct reflection of the evasion from headwaters, or an underestimate resulting from the headwater evasion of biogenic C entering streams as CO_2 having been overlooked.

The lakes within the Krycklan catchment (covering 0.7% of the area) are not included in the study, and the above paragraphs are not considering internal C processes or the much longer water residence times, months to years, typically observed for these kinds of boreal lakes. In-lake C processes such as mineralization, photosynthesis, sedimentation, and evasion are important contributors to the C balance of lakes and hence the landscape (Christensen *et al.*, 2007; Tranvik *et al.*, 2009; Buffam *et al.*, 2011). Published CO_2 evasion rates from small boreal lakes (<0.1 km^2) (Kortelainen *et al.*, 2006; Vesala *et al.*, 2006; Huotari *et al.*, 2011) suggest an ice-free season catchment area-based flux from the Krycklan lakes ranging between 0.3 and 0.8 g C m^{-2} yr^{-1}. This flux should be compared with the 5.0 ($\pm$1.8) g C m^{-2} yr^{-1} lost to the atmosphere from the streams. In addition to emitting CO_2, lakes also affect the downstream fluvial concentrations of all C species. However, the concentration effect for CO_2 caused by a lake in Krycklan has been found to rapidly disappear downstream due to evasion and/or by contribution of incoming groundwater (Ingvarsson, 2008).

Much of the existing literature on the aquatic conduit for C, and in particular the evasion of C from inland waters, has focused on organic C being mineralized in rivers and lakes. The mineralization of DOC with allochthonous origin within the water body is often considered as the main source for the CO_2 supersaturation in boreal lakes (Sobek *et al.*, 2003) and hence the water–atmosphere exchange. But taking the 67 km^2 Krycklan catchment as a case study, the evasion of biogenic CO_2 from relatively small streams is the dominant C component of the aquatic conduit for this landscape, even if all DOC is ultimately mineralized in lakes or rivers before reaching the sea. This implies the need for a paradigm shift in our conceptualization of the aquatic conduit for C in boreal landscapes. We suggest the need to consider evasion from all types of surface waters and all C with organic origin, whether it is exported from soils as CO_2 to a stream and lost to the atmosphere within hours, or exported as DOC which can be mineralized/degassed further downstream in rivers and lakes.

This study demonstrates the importance of including CO_2 evasion from the stream surface when estimating C loss in low-order boreal stream networks. Evasion of CO_2 from the streams comprises the dominant component, 53%, (5.0 g C m^{-2} yr^{-1}) of the entire stream C flux in the Krycklan landscape. Neglecting this significantly underestimates the strength of the aquatic pathway for C leaving terrestrial systems. Although the spatial variability in CO_2 evasion is large, the stream surface area-based flux decreases with increasing SO, and first- and second-order streams were responsible for 72% of the total CO_2 evasion from the stream network. Considering the vertical loss of C from low-order stream systems gives a more complete representation of the aquatic conduit for C and increases the significance of aquatic C loss in landscape C budgets.

Acknowledgements

The financial support for this work was provided by The Swedish Research Council with a grant to K. B. (2005-4157) and by the Department of Aquatic Sciences and Assessment at the Swedish University for Agricultural Sciences. The study is a part of the Krycklan Catchment Study which is funded by The Swedish Research Council, Formas (ForWater), Future Forests, SKB, Kempe foundation, and involves many skilled, helpful scientists and students. Particular thanks go to Peder Blomkvist and the Krycklan crew for excellent field and lab support. Thanks also to Anders Jonsson for GC analysis during 2009.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Data S1. Evasion modeling and uncertainty estimation