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

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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...
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 CO₂ (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 CO₂ 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 CO₂ 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; Fregitzer & 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 (CO₂) from the stream surface for 11 small boreal catchments (<5 km²) 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 CO₂ 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 CO₂ (Oquist 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 CO₂ evasion is limited. Furthermore, existing estimates are often based on a number of assumptions concerning both CO₂ 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 CO₂.

Determining the evasion of CO₂ 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 CO₂ evasion is the gas transfer coefficient (k_{CO₂}), which describes the exchange ability of CO₂ 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_{CO₂} or gas transfer velocities are, however, often used without field validation which renders large uncertainties in CO₂ evasion estimates (Wallin et al., 2011). In this study, we used a stream slope-based model for determining spatial distribution of k_{CO₂} 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_{CO₂} model and extensive data on stream CO₂ concentrations in combination with a high-resolution (5 × 5 m) digital elevation model (DEM) allowed us to determine the evasion of CO₂ from every grid cell of stream in the entire stream network.

We hypothesized that CO₂ 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 CO₂ and the range in k_{CO₂} 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 CO₂ 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 CO₂ evasion occur

Site description

The study was conducted in the upper 67 km² 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 Svarretberget 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...
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 (Hæi 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 km² and stream orders (SOs) first to four are presented in this study (Fig. 1, Table 1). The lowest pH and highest DOC, DIC, and CO₂–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 years ago.

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

<table>
<thead>
<tr>
<th>Site</th>
<th>Stream order*</th>
<th>Catchment area (km²)</th>
<th>Stream surface area (ha)</th>
<th>Total stream length (km²)</th>
<th>% stream surface of catchment</th>
<th>Stream density (km km⁻²)</th>
<th>Altitude ‡ (masl)</th>
<th>Stream slope ‡ (%)</th>
<th>Stream flow § (L s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>2</td>
<td>0.46</td>
<td>0.2</td>
<td>2.0</td>
<td>0.33</td>
<td>4.3</td>
<td>258</td>
<td>6.7</td>
<td>3.4</td>
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<tr>
<td>C2</td>
<td>1</td>
<td>0.13</td>
<td>0.04</td>
<td>0.6</td>
<td>0.34</td>
<td>4.9</td>
<td>251</td>
<td>5.5</td>
<td>0.7</td>
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<tr>
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<td>0.17</td>
<td>0.01</td>
<td>0.05</td>
<td>0.08</td>
<td>0.3</td>
<td>280</td>
<td>1.9</td>
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<tr>
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<td>0.002</td>
<td>0.03</td>
<td>0.004</td>
<td>0.1</td>
<td>283</td>
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<tr>
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<td>1</td>
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<td>0.1</td>
<td>1.5</td>
<td>0.09</td>
<td>1.4</td>
<td>258</td>
<td>4.0</td>
<td>7.3</td>
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<td>0.1</td>
<td>1.9</td>
<td>0.28</td>
<td>4.1</td>
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<td>3</td>
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<td>0.8</td>
<td>7.8</td>
<td>0.27</td>
<td>2.7</td>
<td>232</td>
<td>4.0</td>
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<td>0.3</td>
<td>2.9</td>
<td>0.09</td>
<td>0.9</td>
<td>271</td>
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<td>0.19</td>
<td>1.7</td>
<td>240</td>
<td>3.6</td>
<td>28.0</td>
</tr>
<tr>
<td>C13</td>
<td>3</td>
<td>7.0</td>
<td>1.9</td>
<td>17.1</td>
<td>0.27</td>
<td>2.5</td>
<td>238</td>
<td>3.4</td>
<td>37.4</td>
</tr>
<tr>
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<td>13.8</td>
<td>1.4</td>
<td>15.1</td>
<td>0.10</td>
<td>1.1</td>
<td>200</td>
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<td>15.5</td>
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<td>1.6</td>
<td>214</td>
<td>3.1</td>
<td>347</td>
</tr>
</tbody>
</table>

* Determined at sampling site.
† Total stream length upstream of sampling site.
‡ Average altitude and slope of the stream channels.

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-CR1 analyzer (Agren 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 N2 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 carbon 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 (HS400) (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 pCO$_2$ 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/pCO$_2$ 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 Svarterberget/Nyånger 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 (Agren 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; Oquist et al., 2009; Dinsmore et al., 2010; Wallin et al., 2011).

\[
E_{CO_2} = \Delta CO_2 \times k_{CO_2} \times \tau \times Q
\]  

where $E_{CO_2}$ is the evasion of CO$_2$ over a specific reach of stream (mg s$^{-1}$); $\Delta CO_2$ 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$^{-1}$); $k_{CO_2}$ is the gas-specific transfer coefficient (min$^{-1}$); $\tau$ is the reach travel time (min); and $Q$ is the mean daily stream discharge (L s$^{-1}$). Median annual values of $k_{CO_2}$ and specific daily $\tau$ 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).

\[
k_{CO_2} = \frac{a_k \times \tan \beta \times 100 + b_k}{1.01^{(20-T)}}
\]  

\[
\tau_{norm} = \exp(a_s \cdot \ln(Q) + b_s)
\]  

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

Daily time series of $\Delta CO_2$ concentrations (assuming an atmospheric pCO$_2$ of 380 µatm) and pCO$_2$ 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 pCO$_2$ observed in the Krycklan streams. Linear interpolation was chosen as general regression models between pCO$_2$/$\Delta CO_2$ 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 $\Delta CO_2$ concentration. Daily $k_{CO_2}$ 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 CO₂ evasion for each of the 13 subcatchments as well as per SO. For more detailed description of the modeling and uncertainty estimation for CO₂ 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 pCO₂ 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 (Agren 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 x 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 downslope 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 β = 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 pCO₂, 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 pCO₂ 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 pCO₂ 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 pCO₂ (C2, C5, and C13), whereas sites with similar DIC concentration but with higher pH showed significantly lower supersaturation of CO₂ (C14 and C16). However, SO-specific median pCO₂ 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 CO₂ supersaturated as SO 2.
order-specific median $p$CO$_2$ 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 $p$CO$_2$. 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

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.

**CO₂ evasion**

The CO₂ 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 CO₂ 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 CO₂ 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 kCO₂ 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 CO₂ evasion to the catchment C flux**

In addition to the stream surface area-based flux, the evasion of CO₂ was expressed per catchment area for comparison with downstream export of DIC and DOC. The catchment area-based evasion of CO₂ 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 CO₂ 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 2** Stream order characteristics of the Krycklan stream network

<table>
<thead>
<tr>
<th>Stream order</th>
<th>Stream width* (m)</th>
<th>Stream depth* (m)</th>
<th>Total catchment area (km²)</th>
<th>Stream surface area (ha)</th>
<th>Total stream length (km)</th>
<th>% of total stream length</th>
<th>% stream surface of catchment</th>
<th>Stream density (km km⁻²)</th>
<th>Altitude† (masl)</th>
<th>Stream slope‡ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6/0.9 (0.3–0.9)</td>
<td>0.16/0.14 (0.05–0.34)</td>
<td>31.7</td>
<td>3.6</td>
<td>51.6</td>
<td>48</td>
<td>0.11</td>
<td>1.6</td>
<td>238</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>1.3/1.1 (0.7–2.0)</td>
<td>0.38/0.31 (0.11–0.70)</td>
<td>22.5</td>
<td>4.7</td>
<td>34.3</td>
<td>32</td>
<td>0.21</td>
<td>1.5</td>
<td>207</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>2.8/2.5 (1.0–5.4)</td>
<td>0.31/0.30 (0.10–0.60)</td>
<td>6.9</td>
<td>2.8</td>
<td>12.2</td>
<td>11</td>
<td>0.40</td>
<td>1.8</td>
<td>184</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>5.1/5.0 (3.7–6.6)</td>
<td>0.32/0.32 (0.15–0.56)</td>
<td>6.3</td>
<td>4.5</td>
<td>8.9</td>
<td>9</td>
<td>0.72</td>
<td>1.4</td>
<td>143</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*Stream width and depth are given as mean/median (10th–90th percentiles).
†Average altitude and slope of the stream channels.
‡Annual flow-weighted concentration of DOC (mg L⁻¹) and DIC (mg L⁻¹), annual median pCO₂ (μatm), and 4 year mean of DOC, DIC, and pCO₂ of the 13 sites within the Krycklan catchment 2006–2009.

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

across the 13 catchments. Furthermore, the contribution of CO2 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 CO2 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 CO2 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 CO2 from the stream network. Hence, the remaining 28% of CO2 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.

Discussion
Combining field measurements and relationships with a five meter DEM provided a novel way to quantify the CO2 evasion from the stream network in a boreal landscape. The study showed that CO2 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 CO2 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 CO2 supersaturation (722–2416 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 CO2 evasion, with stream surface-based CO2 evasion rates generally decreasing with increased SO. To our knowledge, no such detailed quantification of CO2 evasion from a landscape drainage system (SOs 1–4) has been previously published, although significant evasion rates have been concluded to occur in highly CO2 supersaturated streams/river systems in boreal (Rantakari et al., 2010), peatland (Hope et al., 2001; Dins-
Table 4  A summary of CO₂ evasion data from published studies of streams/rivers in temperate and boreal regions

<table>
<thead>
<tr>
<th>Region</th>
<th>Stream order*</th>
<th>pCO₂ (μatm)</th>
<th>Stream flux¹ (g C m⁻² yr⁻¹)</th>
<th>Catchment flux² (g C m⁻² yr⁻¹)</th>
<th>Method§</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ontario, Canada</td>
<td>1–2</td>
<td>570–23500</td>
<td>641–2440</td>
<td>–</td>
<td>L.D.</td>
<td>(Koprivnjak et al., 2010)</td>
</tr>
<tr>
<td>Tennessee, USA</td>
<td>1</td>
<td>3200–9320</td>
<td>311–4347</td>
<td>3.1–3.9</td>
<td>F.C.</td>
<td>(Billett &amp; Moore, 2008)</td>
</tr>
<tr>
<td>Quebec, Canada</td>
<td>1–5</td>
<td>481–5410</td>
<td>1138</td>
<td>1.6</td>
<td>L.D.</td>
<td>(Teodoru et al., 2009)</td>
</tr>
<tr>
<td>Tennessee, USA</td>
<td>1</td>
<td>360–6228</td>
<td>688–1634</td>
<td>3.2</td>
<td>E.D.</td>
<td>(Jones &amp; Mulholland, 1998)</td>
</tr>
<tr>
<td>Entire USA</td>
<td>1–10</td>
<td>1588–4326²</td>
<td>882–4008</td>
<td>4.5–22.9³</td>
<td>E.D.</td>
<td>(Butman &amp; Raymond, 2011)</td>
</tr>
<tr>
<td>Scotland, UK</td>
<td>1</td>
<td>420–4500</td>
<td>95–16745</td>
<td>14.1</td>
<td>E.D.</td>
<td>(Hope et al., 2001)</td>
</tr>
<tr>
<td>Scotland, UK</td>
<td>1</td>
<td>1300–6000**</td>
<td>1390–9450</td>
<td>4.6</td>
<td>E.D.</td>
<td>(Billett et al., 2004)</td>
</tr>
<tr>
<td>Eastern Finland</td>
<td>1</td>
<td>906–8112</td>
<td>25418</td>
<td>11.5–13.9</td>
<td>E.D.</td>
<td>(Dinsmore et al., 2010)</td>
</tr>
<tr>
<td>Western Finland</td>
<td>1–6</td>
<td>890–8320</td>
<td>–</td>
<td>3.5–48</td>
<td>M.D.</td>
<td>(Rantzakari et al., 2010)</td>
</tr>
<tr>
<td>Entire Sweden</td>
<td>1–6</td>
<td>794–1950</td>
<td>473–3032</td>
<td>–</td>
<td>M.D.</td>
<td>(Humborg et al., 2010)</td>
</tr>
<tr>
<td>Northern Sweden</td>
<td>1–5</td>
<td>3400††</td>
<td>471</td>
<td>0.5–2.6</td>
<td>L.D.</td>
<td>(Jonsson et al., 2007)</td>
</tr>
<tr>
<td>Northern Sweden</td>
<td>1</td>
<td>2015–7838</td>
<td>2356</td>
<td>2.9</td>
<td>E.D.</td>
<td>(Öquist et al., 2009)</td>
</tr>
<tr>
<td>Northern Sweden</td>
<td>1–4</td>
<td>722–24167</td>
<td>1455–6411</td>
<td>5.0</td>
<td>E.D.</td>
<td>This study</td>
</tr>
</tbody>
</table>

*Estimated where not given  
†CO₂ evasion expressed per stream surface area  
‡CO₂ evasion expressed per catchment area  
§Method used to determine CO₂ evasion:  
E.D.: Experimentally determined data of k (the gas transfer coefficient/velocity)  
F.C.: Direct method of determining CO₂ 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 CO₂ in mg L⁻¹  
††Literature value used for pCO₂  

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 HCO₃⁻ 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 in the stable isotopic composition of DIC (δ¹³C-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 (δ¹³C-DIC) toward enrichment in ¹³C with increasing catchment area also supports the finding of significant evasion rates (Venkiteswaran et al., in review). A loss of the lighter ¹²C (diffusional fractionation) along the streams would cause the observed pattern in isotopic composition of DIC (Parker et al., 2010). The lowest CO₂ evasion rates per catchment area were found in the headwater catchments (C4 and C5) although they were the sites that had the highest pCO₂. Those catchments are outlets of a peatland (C4) and an isolated headwater lake (C5) that are sampled <50 m downstream from the outlet. A short stream length in relation to the catch-
ment area (low stream density) (Table 1) results in a low catchment area-based CO₂ evasion.

The CO₂ evasion from the streams in this study is assumed to take place all year around. If the evasion of CO₂ 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 finescale morphology, so the ice and snow cover at winter time is highly variable across the stream network. As the stream water is moving, CO₂ can be rapidly lost from the stream to the atmosphere along the parts of the stream network with open water or fragile ice cover. CO₂ flux through the snow pack has been concluded to be a significant component in the annual CO₂ emissions from soils in seasonally snow-covered regions (Sommerfeld et al., 1993; Hubbard et al., 2005).

An essential factor when determining CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ evasion rates from small boreal lakes (<0.1 km²) (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 (±1.8) g C m⁻² yr⁻¹ lost to the atmosphere from the streams. In addition to emitting CO₂, lakes also affect the downstream fluvial concentrations of all C species. However, the concentration effect for CO₂ 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 CO₂ supersaturation in boreal lakes (Sobek et al., 2003) and hence the water–atmosphere exchange. But taking the 67 km² Krycklan catchment as a case study, the evasion of biogenic CO₂ 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 CO₂ 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 CO₂ evasion from the stream surface when estimating C loss in low-order boreal stream networks. Evasion of CO₂ 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 CO₂ 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 CO₂ 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.

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