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# Dissolved Inorganic Carbon Export Across the Soil/Stream Interface and Its Fate in a Boreal Headwater Stream

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The aim of this investigation was to determine the lateral export of dissolved inorganic carbon (DIC) from soils of a Swedish boreal forest to a first order stream and to estimate the partitioning of this DIC into CO<sub>2</sub> evasion from the stream surface and the DIC pool exported down through the catchment by streamwater. The groundwater entering the stream was supersaturated with CO2 with values as high as 17 times equilibrium with the atmosphere. Up to 90% of the estimated daily soil DIC export to the stream was emitted to the atmosphere as CO<sub>2</sub> within 200 m of the water entering the stream. The annual DIC export from the soil to the stream was estimated to be 3.2 ( $\pm$ 0.1) g C m<sup>-2</sup> yr<sup>-1</sup> (normalized to catchment size). Ninety percent of the variation in soil DIC export could be explained by the variation in groundwater discharge and the DIC concentrations per se, were of minor importance. A significant correlation ( $R^2 = 0.74$ , P < 0.01) between soil DIC export and CO2 emission from the stream surface suggests that emission dynamics were primarily driven by the export of terrestrial DIC and that in-stream processes were less important. Our results reveal that current budget estimates of lateral DIC export from soils to aquatic conduits need to be revised because they do not account for conditions prevailing in headwater streams. Any quantification of lateral stream C export and CO<sub>2</sub> emissions from freshwater systems must include headwater streams as well as the lower parts of the aquatic conduit.

## Introduction

Boreal forests are important in global C cycling and the vertical exchange of  $CO_2$  between boreal forest soils and the atmosphere has been intensively studied. Less attention has

been directed toward surface waters in the boreal landscape and the role of these systems in the total C balance. Surface waters are conduits through which terrestrial C can be returned to the atmosphere by emission or exported to the ocean. The importance of inland waters for the terrestrial C cycle is becoming apparent and the most recent estimate of global C export from terrestrial systems via the "aquatic conduit" is 1.9 Pg C yr $^{-1}$ , including both dissolved organic carbon (DOC) and inorganic carbon (DIC) (1). UK studies, at various scales, of total C export via surface waters have produced estimates of 10.3 g C m $^2$  yr $^{-1}$  across England and Wales (2) and similar studies on major catchments in northern Sweden have estimated values of 3.1–8.6 g C m $^2$  yr $^{-1}$  (3, 4).

The terrestrial C cycle is dominated by photosynthesis and soil respiration; although the aquatic conduit is comparatively small, it accounts for a steady loss of C. For ecosystems close to equilibrium, including mature boreal forests (5) and boreal mires (6), the size of the aquatic conduit can be decisive in whether the long-term C balance is positive or negative. Indeed, several studies suggest that ignoring the C export through surface waters may significantly overestimate C accumulation within terrestrial ecosystems (2, 7-11).

One compartment in the aquatic conduit that has been neglected in both regional (e.g., 3, 4) and global (c.f. I) budget estimates is headwater streams. Studies attempting to quantify headwater C export have shown that streams draining terrestrial ecosystems may be important for the net C balance (6, 11-16). There are, however, few studies of the emission of DIC from headwaters. Those conducted on peatland catchments in Scotland and Canada show a vertical upward flux from headwater streams of  $3.1-14.1~{\rm g~C~m^2~yr^{-1}}$  (7, 14, 17).

One reason for the neglect of direct measurement in headwaters in the context of aquatic DIC export and CO2 emission to the atmosphere is the challenge of quantification, since downstream monitoring sites in rivers and lakes are more accessible. However, by only sampling the outlets of larger catchments, much of the variability in water chemistry is missed (18). This is especially important from a C-balance perspective because DIC export of carbon via surface waters is a two-dimensional flux, both lateral and vertical. CO2 emission from streams and rivers in northern Sweden is estimated to be 0.1–0.6 g C  $m^2$  yr $^{-1}$  (3) or 0.5–2.6 g C  $m^2$  yr $^{-1}$ (4). However, these studies have focused on the role of lakes and rivers in organic carbon cycling not on headwater CO2 emissions. Hence, the fractions of these estimates relating to headwater emissions are based on assumptions and literature values of concentrations and gas exchange rates of CO<sub>2</sub> that have not been tested against empirical measurements; this situation clearly needs to be rectified.

The aim of this investigation was to determine the lateral export of DIC from soils of a Swedish boreal coniferous forest to a first order stream and to estimate the partitioning of this DIC into CO<sub>2</sub> evasion from the stream surface and the DIC pool exported down through the catchment by streamwater. We hypothesized that soil DIC export can be estimated by direct measurements of groundwater DIC concentrations in combination with groundwater discharge modeling, and that the fraction of this DIC evading from the stream surface as CO<sub>2</sub> can be estimated by the difference between soil DIC and stream DIC export. Since vertical emission can be so rapid, this direct approach would be advantageous rather than have to reconstruct this from measurements of vertical emission and downstream export. We also hypothesized that the amount of DIC instantaneously lost from the small headwater stream as CO<sub>2</sub> emissions from the stream surface

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is large enough to significantly influence the C balance of the terrestrial system. Our hypotheses were tested by measuring the DIC concentrations in riparian soil profiles and the lateral flux of water from the soil to the adjacent stream. This soil-based estimate was compared to independent measurements of downstream transport and vertical emissions from the stream surface.

# **Experimental Section**

**Site Description.** The study site was Västrabäcken, a 13 ha subcatchment located in Vindeln's Experimental Forests, 60 km northwest of Umeå, Sweden. The altitude of the catchment ranges from 235 to 310 m.a.s.l.; it is forested with 90-year-old Norway spruce (*Picea abies*) in wetter areas and Scots pine (*Pinus sylvestris*) on drier soils. The annual mean temperature (1981–2000) was 1 °C, and mean annual precipitation is 646 mm with an average runoff of 323 mm (19, 20). The site is characterized by shallow groundwater which is typical for the boreal landscape (mainly within 1–2 m below ground surface). The open water surface of the Västrabäcken stream is 400 m long. The mean stream width and depth are 40 and 15 cm, respectively, based on measurements every 25 m along the stream. A more complete description of the site is presented in (21–24).

**Soil DIC and Export.** Samples for measuring CO<sub>2</sub> concentrations in the groundwater flowing into the stream were taken using soil gas probes (25, 23) weekly or biweekly from October 20, 2003 to September 19, 2004 (36 sampling occasions). CO<sub>2</sub> was analyzed by GC-FID (Varian 3400 equipped with a methanizer; detection limit 50  $\mu$ g C L<sup>-1</sup>) according to ref 25. Measurements were taken at three replicate sites from depths of 10, 25, 40, 60, and 80 cm. Soil temperatures and moisture (TDR) at the same depths were logged automatically every 4 h (Campbell CR10). The CO<sub>2</sub> concentrations in the probes were adjusted for solubility in the soil—water pool according to Henry's law (with modifications for nonideal gases according to 26 and to soil—water pH (cf 21, 27, 28.)).

The flow pathways along this transect have been studied previously, and it has been shown that by combining the principle of transmissivity feedback with Darcy's law, integrated lateral flow contributions from each 5 cm soil layer can be calculated for a given streamflow (29, 30).

**Stream DIC Export and Evasion.** Stream sampling of DIC was performed monthly from November 2003 to October 2004, and more intensively during the spring flood (a total of 28 occasions). The DIC was measured as  $\mathrm{CO}_2$  in the headspace of acidified samples collected in the field and analyzed by GC FID in the laboratory (see Supporting Information (SI) for details). Discharge was based on stage height measurements at a V-notch weir with a known rating curve. Stream water temperature was also recorded continuously at this location.

The emission of  $CO_2$  from stream to atmosphere was determined using a volatile gas tracer (propane,  $C_3H_8$ ) previously used in several similar studies (7, 14, 31–33). Emission measurements were made during 2006 and 2007 on eight occasions with different flow situations. The procedures for calculating  $K_{C_3H_8}$ ,  $K_{CO_2}$ , and concomitant  $CO_2$  emission are detailed in the Supporting Information.

**Flux Calculations.** Hereafter, C export across the soil/stream interface is referred to as *soil DIC export*, C exported from the catchment in streamwater at the outlet weir is referred to as *stream DIC export*. The "vertical" CO<sub>2</sub> emission from the stream surface is referred to as *CO*<sub>2</sub> *emission*.

Daily DIC concentrations in ground- and streamwater, as well as the excess pressure of  $CO_2$  used in  $CO_2$  emission calculations (see SI) were obtained by linear interpolation between sampling points. Interpolation was used because no relationship between measured variables and DIC con-

centrations facilitating empirical modeling could be observed. Vertical soil DIC concentration profiles were derived by linear interpolation between the data from different depths. Daily stream DIC export rates were derived by multiplying concentrations by mean daily discharge. For soil DIC export, the DIC concentration in each soil layer was multiplied by the lateral groundwater flow through each layer (see above). The volume-weighted groundwater DIC concentrations were obtained by adding the concentrations multiplied by the water flow for the soil layers with laterally flowing water. Water was assumed to flow laterally through saturated soil layers (i.e., below the groundwater table). Annual and seasonal lateral soil DIC export, stream DIC export, and CO<sub>2</sub> emission were obtained by summing the estimated daily exports. All DIC export rates were normalized to the catchment size (13 ha). The data were separated into four seasons, as well as growing season and nongrowing season based on the daily average temperature at standard 1.7 m above the ground. Threshold values for spring/fall were 0 °C, summer +10 °C, and growing season +5 °C (19).

The uncertainty estimates for the flux compartments were 27%, 12%, and 24% (SD) for daily soil DIC export, stream DIC export, and  $CO_2$  emission, respectively. These uncertainties were based on the estimated accuracy of measuring DIC/ $CO_2$  concentrations and discharge and the uncertainties introduced by the various calculations. In addition, our export estimates were also affected by interpolating measured DIC concentrations to obtain daily export rates. To evaluate the resilience of our estimates we also present the annual and seasonal export rates assuming that the daily DIC concentrations are represented by the 25% and 75% quartiles of the measured DIC concentrations. See SI for further details.

#### **Results**

Stream discharge, streamwater temperatures, and groundwater temperatures were recorded from March 2003 to November 2004. The mean discharge rate at the outlet was  $1.2~L~s^{-1}$ , ranging from a trickle at low flow to  $\sim 10~L~s^{-1}$  at spring flood and in association with heavy precipitation. The annual discharge over the period investigated was 293 mm. For details on streamwater and groundwater temperatures see SI.

The average DIC concentrations in the soil—water ranged from ca. 9 to 13 mg C L $^{-1}$  (Figure 1). The highest concentrations were found at 40 and 60 cm, where they were significantly (P < 0.05) higher than at the other depths. The groundwater table varied from 15 to 100 cm below the surface. The groundwater movement through the soil resulted in the majority of lateral water flow traversing the riparian soil at a depth of 20–60 cm (Figure 1).

DIC concentrations were consistently higher in the groundwater (7–23 mg L $^{-1}$ ; volume-weighted concentrations) than in the adjacent stream (2–6 mg C L $^{-1}$ ; Figure 2). The excess pressure of  $CO_2$  in the stream was 5–17 times the equilibrium with the atmosphere; the average during the sampling period was 8.3  $\pm$  0.5 ( $\pm$ SE; Figure 2).

Soil DIC export ranged from zero during midwinter (when no water flow occurred), up to ca. 0.1 g m<sup>-2</sup> day<sup>-1</sup> during high flow events (Figure 4). The variation in soil DIC export was proportional to the stream DIC export, although export rates for the latter ranged from 0 to ca. 0.02 g DIC m<sup>-2</sup> day<sup>-1</sup> (Figure 3). The volume-weighted DIC concentrations in the groundwater flowing into the stream (Figure 3) were not correlated with the soil DIC export rates ( $R^2 = 0.003$ ; P = 0.33). There were 12 occasions when soil DIC and stream DIC measurements were taken simultaneously, and these displayed a strong positive correlation ( $R^2 = 0.96$ ; P < 0.01).

The estimated daily  $K_{\rm CO_2}$  values ranged from 0 to 0.0482 min<sup>-1</sup> (average 0.0255  $\pm$  0.0121(SD); Figure 3, insert). The

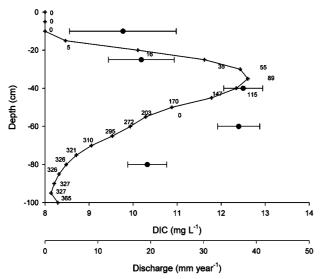


FIGURE 1. Average DIC concentrations in the soil—water at different depths below the soil surface (n=3, error bars are SE) and the annual lateral flow through each soil horizon (values next to the curve indicate the number of days on which water flowed through each horizon during the study period). Note that the DIC concentrations reflect the annual average concentration in the soil—water regardless of whether lateral flow is occurring through the specific horizon. The total discharge over the year is 293 mm.

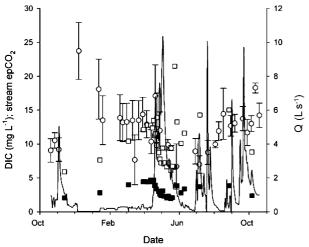


FIGURE 2. DIC concentrations in the soil groundwater ( $\bigcirc$ ; volume weighted), in the stream ( $\blacksquare$ ), and the excess pressure of  $\mathrm{CO}_2$  in the stream ( $\square$ ; relative atmosphere;  $\mathrm{epCO}_2$ ) for the different sampling occasions. The line represents stream discharge ( $\mathcal{Q}$ ). Error bars for soil groundwater DIC concentrations are SE from the replicate riparian soil profiles of  $\mathrm{CO}_2$  (n=3).

highest  $K_{\rm CO_2}$  values occurred at flows of 3–4 L s<sup>-1</sup>;  $K_{\rm CO_2}$  decreased during higher flows (see SI). The estimated rates of CO<sub>2</sub> emission from the stream surface ranged from 0 to 0.03 g DIC m<sup>-2</sup> day<sup>-1</sup>. The temporal dynamics of CO<sub>2</sub> emission correlated significantly with both stream DIC export ( $R^2 = 0.50$ ; P = 0.007; n = 28) and soil DIC export ( $R^2 = 0.74$ ; P = 0.004; n = 12). The average "half-life" of DIC entering the stream was estimated to be 5.5 h (average  $K_{\rm CO_2} = 0.0255$  min<sup>-1</sup> and the volume-weighted average DIC concentration in laterally flowing groundwater was 12 mg L<sup>-1</sup>).

About 90% of the variation in soil DIC export and stream DIC export rates could be explained by variations in discharge (Q; Figure 4). During high flows (>4 L s<sup>-1</sup>) the variation in soil DIC export among the three replicate sites

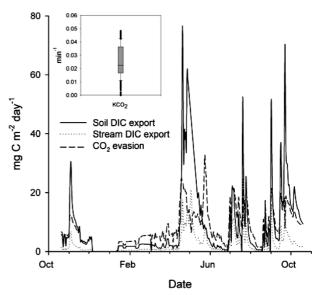


FIGURE 3. Estimated daily rates of soil DIC export, stream DIC export, and  $CO_2$  emission from the stream surface. The distribution of the  $K_{CO_2}$ -values used for calculating emission estimates (inserted).

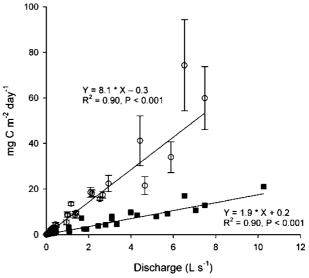


FIGURE 4. Soil DIC export (○) and stream DIC export (■) expressed as functions of stream discharge.

was large compared to that during low flows. Restricting the regression expressing soil DIC export at flow rates <4 L s $^{-1}$  improved the fit ( $R^2=0.95$ ) but the parameter estimates were not substantially affected (7.3 and -0.4 for the slope and intercept, respectively; Figure 4). The  $\rm CO_2$  emission from stream pCO $_2$  was not significantly correlated with discharge.

On an annual basis, the total DIC export from the soil to the stream was estimated to be 3.2  $(\pm 0.1)$  g C m $^{-2}$  year $^{-2}$ . An estimated 0.9  $(\pm 0.01)$  g m $^{-2}$  year $^{-1}$  was exported from the catchment as DIC in streamwater. The total estimated vertical CO $_2$  emission from the stream was 2.9 g  $(\pm 0.10)$  C m $^{-2}$  year $^{-1}$ . Almost twice as much DIC was exported from the soil to the stream during the growing season than outside this season (2.1  $(\pm 0.07)$  and 1.1  $(\pm 0.02)$  g C m $^{-2}$ , respectively); the same pattern was observed for stream DIC export (Table 1). Spring was the main season for soil DIC export; the other seasons contributed about equally to the annual export. Similar patterns were observed for stream DIC export, but the total amounts were smaller (Table 1).

TABLE 1. Estimated Annual and Seasonal DIC Export ( $\pm$  SD) from Soil Groundwater to the Stream and Its Partitioning into DIC Stream Export and CO<sub>2</sub> Emission (Values in Parentheses Represent Export Assuming Daily DIC Concentrations Represented by the 25% and 75% Quartiles, Respectively)

time period	days (no.)	soil DIC export (g C m <sup>-2</sup> )	stream DIC export (g C m <sup>-2</sup> )	$K_{\mathrm{CO_2}}$ emission (g C m $^{-2}$ )
annual	365	$3.2\pm0.1~(2.9/4.1)$	$0.9 \pm 0.01  (0.7/1.2)$	$2.9 \pm 0.1$ (2.0/3.7)
winter	168	$0.5\pm0.02~(0.4/0.6)$	$0.1 \pm 0.002  (0.1/0.2)$	$0.7 \pm 0.01  (0.6/1.1)$
spring	56	$1.3 \pm 0.07  (1.2/1.6)$	$0.3 \pm 0.01  (0.3/0.5)$	$0.8 \pm 0.08  (0.6/1.1)$
summer	99	$0.7 \pm 0.04  (0.7/1.0)$	$0.3 \pm 0.01 \; (0.2/0.3)$	$0.9 \pm 0.05  (0.4/0.8)$
fall	42	$0.8 \pm 0.04  (0.6/0.8)$	$0.2 \pm 0.004  (0.1/0.2)$	$0.5 \pm 0.04  (0.4/0.7)$
growing season	160	$2.1 \pm 0.07$ (2.0/2.8)	$0.6 \pm 0.01~(0.5/0.8)$	$1.8 \pm 0.1  (1.1/2.0)$
nongrowing season	205	1.1 $\pm$ 0.02 (0.8/1.2)	$0.3 \pm 0.004  (0.3/0.9)$	$1.1 \pm 0.03  (0.9/1.7)$

#### **Discussion**

There have been a number of previous attempts to estimate the lateral C export from terrestrial to aquatic ecosystems on a range of different spatial and temporal scales. In this discussion we confine our comparison with existing studies to those that (i) explicitly contain information on headwater streams, or (ii) are relevant for budget estimates in the investigated region. The temporal variations in discharge and temperature were typical for the site (23, 24, 34). The spring flood constitutes the main hydrological event when ca.40% of the annual discharge occurs over just 56 days. The total annual discharge (293 mm) was ca.10% lower than the 30-year average of 323 mm.

As with all transect studies, we assumed that the soil atmosphere sampled at the riparian sites is representative of all zones draining to the stream. The catchment area in this study is small (13 ha), and the vegetation and soil morphology of the transect were similar to those of other sites within the catchment. Previously, a stable isotope investigation of water sources and flow pathways (36) and a study of the major constituents of stream chemistry (30) found that this assumption is justified.

The soil groundwater and headwater stream concentrations of DIC were similar to those recorded in other studies from the boreal region (6, 7, 16, 36, 37). The relatively large difference in DIC concentrations of the soil groundwater and the streamwater implies the rapid disappearance of DIC from water after it enters the stream. Because the entire DIC pool, including different fractions of the bicarbonate system, was accounted for in both the soil groundwater and the streamwater, this decrease must be attributed to either rapid degassing of CO2 as the groundwater flows into the stream or in-stream processes involving CO<sub>2</sub> consumption (38). The "package" of laterally flowing groundwater entering the stream is supersaturated with CO<sub>2</sub> with values as high as 17 times equilibrium with the atmosphere. This excess pressure should be released quickly from the surface waters. This is strongly supported by our results: the loss in DIC can be primarily attributed to degassing of CO<sub>2</sub> from the stream surface. Furthermore, the significant correlation between CO<sub>2</sub> emission and soil DIC export suggests that emission dynamics are primarily driven by the export of terrestrial DIC and that in-stream processes are much less important. This conclusion is also supported by the large DIC loss along the stream, in conjunction with relatively low rates of primary productivity therein (24). Our results also show that this CO<sub>2</sub> degassing is very fast and, on average, ca. 65% of the DIC in the groundwater is lost within 200 m of the water entering the stream. The average water transit time in the 200 m between the riparian soil measurements and the subcatchment's outlet is ca. 4.5 h, a value similar to the estimated 5.5 h "half-life" of DIC entering the stream. Although there is some discrepancy between these figures they do suggest that CO<sub>2</sub> degassing occurs very rapidly.

The findings that both soil DIC and stream DIC export rates are mainly determined by discharge and that the variations in DIC concentrations are relatively small compared to the flow variation agree with other work, e.g., 15. During the study period the discharge varied by up to 10-fold; the corresponding variations in DIC concentrations in the groundwater and the streamwater were 2-3 times. Since export is the product of these variables, the influence of discharge will, consequently, be much larger. However, the soil DIC concentration becomes increasingly important for soil DIC export rates with increasing discharge, as indicated by the substantial increase in variation among replicates under high flow conditions. During high flow events the groundwater level rises quickly, hydrologically "connecting" higher soil layers to the stream via lateral groundwater flow. These higher layers contain greater concentrations of DIC than the deeper layers. During the spring flood, high concentrations are linked to the winter soil frost regime: in spring there is a strong correlation between the maximum soil frost depth and soil DIC concentrations (23). Thus, activation of previously frozen layers during spring flood may cause increased variation in groundwater DIC concentrations among replicates, caused by different soil frost regimes.

There are few investigations of lateral soil DIC export rates across the soil/stream interfaces of boreal headwaters. The annual export of DIC that we observed (3.2  $\pm$  0.1 g C m $^{-2}$  yr $^{-1}$ ) is in the same range as estimates made for a mire-dominated catchment in the area (3–6 g C m $^{-2}$  yr $^{-1}$  (6)) and a catchment in Scotland (2.1 g C m $^{-2}$  year $^{-1}$  (14)). It is, however, lower than values reported from temperate forest systems in Germany (ca.10 g C m $^{-2}$  yr $^{-1}$  (15)). Nonetheless, this study shows that annual soil DIC export is of the same magnitude as estimates of dissolved organic carbon (DOC) reported from the same headwater catchment (4.2 g C m $^{-2}$  yr $^{-1}$  (34)).

The  $K_{CO_2}$  range recorded (0-0.0482) corresponds to that reported from a similar sized headwater stream in Scotland (7). Our estimated CO<sub>2</sub> emission rates (2.9 ( $\pm 0.10$ ) g C m<sup>-2</sup> yr<sup>-1</sup>) are slightly lower than previous measurements of peatland-dominated catchments (4.6 g C m<sup>-2</sup> yr<sup>-1</sup> (14) and ca. 3.1-3.9 g C m<sup>-2</sup> yr<sup>-1</sup> (17). The excess pressure of CO<sub>2</sub> in the streamwater (5-17 times atmosphere) was in the same range as literature values used by 4 in their estimate of CO<sub>2</sub> emissions from streams in a catchment in northern Sweden. In addition, the estimated annual CO<sub>2</sub> emissions based on these excess pressures (4) are similar to our investigation, albeit slightly lower  $(0.5-2.6 \text{ g C m}^{-2} \text{ yr}^{-1})$ and 2.9 g ( $\pm 0.10$ ) C m<sup>-2</sup> yr<sup>-1</sup> (herein)). The value of pCO<sub>2</sub> in the water is important for estimating emissions because the efflux is mainly driven by the concentration gradient between the water surface and the atmosphere. For example 3 assumed that the excess pressure in headwater streams and rivers was similar to that typically observed in lakes (3-5 times atmosphere). Consequently, the

estimated C loss through emissions from streams in that study (<0.6 g C  $m^{-2}\ yr^{-1})$  was low in comparison to those in this investigation. Thus, it is critical that any assumptions about  $pCO_2$  are thoroughly validated against actual conditions.

For most of the year the temporal dynamics of soil and stream DIC export show reasonable agreement with respect to CO2 emissions. However, during winter and early summer our results suggest that more CO2 is being emitted from the stream surface than can be attributed to soil DIC export. During winter this discrepancy may result from ice formation on the stream surface, which may trap dissolved CO<sub>2</sub>. This would increase the pCO<sub>2</sub> of the streamwater but would also decrease the rate of gas exchange. However, we do not have adequate data on stream ice conditions to correct the calculations. It is unlikely that this  $CO_2$  originates from microbial activity in the stream sediments since it compares to emission rates of ca. 1.5 g CO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup> during winter and 4.5 g m<sup>-2</sup> day<sup>-1</sup> during summer (assuming a stream area of 140 m<sup>2</sup>) and it is unlikely that the sediments can sustain such high production rates even at summer temperatures (e.g., 39). Based on previous investigations of in-stream CO<sub>2</sub> production (40) we can also conclude that such contribution is negligible in comparison to our CO<sub>2</sub> emission rates. In theory, the amount of DIC available for emission is the difference between the soil export pool and the stream export pool. Annually, this amounts to 2.1 g C m<sup>-2</sup> yr<sup>-1</sup>; for comparison, our CO<sub>2</sub> emission estimate is 2.9 ( $\pm 0.10$ ) g C  $m^{-2}$  yr<sup>-1</sup>. Although there is some discrepancy between these estimates, they are similar. Further research is needed to determine the cause of these discrepancies, but we can conclude that the two independent methods used for estimating lateral and vertical flux dynamics agree well with the annual loss of C from the stream surface, as well as losses occurring during spring and fall.

The key part of the year in terms of soil DIC export to the stream is spring, accounting for ca. 40% of the total annual export over 56 days. This result is expected, since discharge was found to greatly affect export rates; in addition, the spring flood is the main hydrological event during the year. It is also evident that most of the soil DIC export to the headwaters, as well as CO2 emissions from the stream surface, occurs during the growing season. This is consistent with the discharge characteristics at the site, with very little groundwater movement and discharge during the winter. Nevertheless, 35% of the soil DIC export occurred outside the growing season: stream DIC export and CO<sub>2</sub> emissions accounting for 33% and ca. 40%, respectively, of the annual total. This implies that the cold season can not be ignored in budget estimates although discharge rates are low. Export outside the growing season also occurs when the terrestrial system is inactive in terms of CO<sub>2</sub> uptake through photosynthesis, implying that soil DIC export greatly affects winter C balances in boreal

The results of this investigation are in agreement with our underlying hypotheses and we judge that the difference between groundwater DIC and stream DIC adequately represents the fraction of DIC evading from the stream surface as  $CO_2$ , although some discrepancies remain to be resolved. Both the stream DIC export and the stream  $CO_2$  emissions in this headwater system are driven by the soil DIC export. Other sources, such as in-stream production of  $CO_2$  thorough the activity of heterotrophic microorganisms is negligible. Our results also reveal that current estimates of lateral DIC export from boreal forest soils to aquatic conduits need to be revised because they often do not account for conditions in headwater steams.

# Acknowledgments

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## **Supporting Information Available**

Experimental details of DIC concentrations analysis,  $CO_2$  emission rates from the stream surface, and procedures used to estimate uncertainty. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **Literature Cited**

- (1) Cole, J. J.; Prairie, Y. T.; Caraco, N. F.; McDowell, W. H.; Tranvik, L. J.; Striegl, R. G.C.; Duarte, M.; Kortelainen, P. J.; Downing, A.; Middelburg, J. J.; Melack, J. Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. *Ecosystems* 2007, 10, 171–184.
- (2) Worrall, F.; Guilbert, T.; Besien, T. The flux of carbon from rivers: the case for flux from England and Wales. *Biogeochemistry* 2007, 86, 63–75
- (3) Algesten, G.; Sobek, S.; Bergstrom, A. K.; Agren, A.; Tranvik, L. J.; Jansson, M. Role of lakes for organic carbon cycling in the boreal zone. Global Change Biol. 2004, 10, 141–147.
- (4) Jonsson, A.; Algesten, G.; Bergström, A.-K.; Bishop, K.; Sobek, S.; Tranvik, L.; Jansson, M. Integrating aquatic carbon fluxes in a boreal catchment carbon budget. *J. Hydrol.* 2007, 334, 141–150.
- (5) Valentini, R.; Matteucci, G.; Dolman, A. J.; Schulze, E. D.; Rebmann, C.; Moors, E. J.; Granier, A.; Gross, P.; Jensen, N. O.; Pilegaard, K.; Lindroth, A.; Grelle, A.; Bernhofer, C.; Grunwald, T.; Aubinet, M.; Ceulemans, R.; Kowalski, A. S.; Vesala, T.; Rannik, U.; Berbigier, P.; Loustau, D.; Guomundsson, J.; Thorgeirsson, H.; Ibrom, A.; Morgenstern, K.; Clement, R.; Moncrieff, J.; Montagnani, L.; Minerbi, S.; Jarvis, P. G. Respiration as the main determinant of carbon balance in European forests. Nature 2000, 404, 861–865.
- (6) Nilsson, M.; Sagerfors, J.; Buffam, I.; Laudon, H.; Eriksson, T.; Grelle, A.; Klemedtsson, L.; Weslien, P.; Lindroth, A. Contemporary carbon accumulation in a boreal oligotrophic minerogenic mire - a significant sink after accounting for all C-fluxes. Global Change Biol. 2008, 14, 2317–2332.
- (7) Hope, D.; et al. Carbon dioxide and methane evasion from a temperate peatland stream. *Limnol. Oceanogr.* 2001, 46, 847– 957
- (8) Richey, J. E.; Melack, J. M.; Aufdenkampe, A. K.; Ballester, V. M.; Hess, L. L. Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO<sub>2</sub>. *Nature* **2002**, *416*, 416–420.
- (9) Grace, J.; Malhi, Y. Global change carbon dioxide goes with the flow. *Nature* **2002**, *416*, 594–595.
- (10) Jones, J. B.; Mulholland, P. J. Carbon dioxide variation in a hardwood forest stream: an integrative measure of whole catchment soil respiration. *Ecosystems* 1998, 1, 183–196.
- (11) Worrall, F.; Burt, T.; Adamson, J. Fluxes of dissolved carbon dioxide and inorganic carbon from an upland peat catchment: implications for soil respiration. *Biogeochemistry* 2005, 73, 515– 530
- (12) Pacala, S. W.; Hurtt, G. C.; Baker, D.; Peylin, P.; Houghton, R. A.; Birdsey, R. A.; Heath, L.; Sundquist, E. T.; Stallard, R. F.; Ciais, P.; Moorcroft, P.; Caspersen, J. P.; Shevliakova, E.; Moore, B.; Kohlmaier, G.; Holland, E.; Gloor, M.; Harmon, M. E.; Fan, S. M.; Sarmiento, J. L.; Goodale, C. L.; Schimel, D.; Field, C. B. Consistent land- and atmosphere-based US carbon sink estimates. Science 2001, 292, 2316–2320.
- (13) Cole, J. J.; Carpenter, S. R.; Kitchell, J. F.; Pace, M. L. Pathways of organic carbon utilization in small lakes: Results from a wholelake C-13 addition and coupled model. *Limnol. Oceanogr.* 2003, 47, 1664–1675.
- (14) Billett, M. F.; Palmer, S. M.; Hope, D.; Deacon, C.; Storeton-West, R.; Hargraves, K. J.; Flechard, C.; Fowler, D. Linking land-atmosphere-stream carbon fluxes in a lowland peatland system. Global Biogeochem. Cycles 2004, 18, doi: 10.1029/2003GB002058.
- (15) Fiedler, S.; Höll, B. S.; Jungkunst, H. F. Discovering the importance of lateral CO<sub>2</sub> transport from a temperate spruce forest. Sci. Total Environ. 2006, 368, 909–915.
- (16) Teodor, C. R.; Giorgio, P. A.; Prairie, Y. T.; Camire, M. Patterns in  $pCO_2$  in boreal streams and rivers of northern Quebec, Canada. *Global Biogeochem. Cycles* **2009**, *23*, doi: 10.1029/2008GB003404.
- (17) Billet, M. F.; Moore, T. R. Supersaturation and evasion of  $CO_2$  and  $CH_4$  in surface waters at Mer Bleu peatland, Canada. *Hydrol. Process.* **2007**; doi: 10.1002/hyp.

- (18) Bishop, K.; Buffam, I.; Erlandsson, M.; Folster, J.; Laudon, H.; Seibert, J.; Temnerud, J. Aqua Incognita: the unknown headwaters. *Hydrol. Process.* 2008, 22, 1239–1242.
- (19) Ottosson-Lofvenius, M. Referensmätninga av klimat vid skogligal försöksparkerna, Årsrapport 2003; Swedish University of Agricultural Sciences, 2004; 36 pp.
- (20) Ottosson-Lofvenius, M. *Referensmätninga av klimat vid skogligal försöksparkerna*, Årsrapport 2004; Swedish University of Agricultural Sciences, 2005; 36 pp.
- (21) Nyberg, L.; Stahli, M.; Mellander, P. E.; Bishop, K. H. Soil frost effects on soil water and runoff dynamics along a boreal forest transect: 1. Field investigations. *Hydrol. Process.* 2001, 15, 909– 926.
- (22) Seibert, J.; Bishop, K.; Rodhe, A.; McDonnell, J. J. Groundwater dynamics along a hillslope: A test of the steady state hypothesis. *Water Resour. Res.* 2003; ARTN 1014.
- (23) Oquist, M. G.; Laudon, H. Winter soil frost conditions in boreal forests control growing season soil CO<sub>2</sub> concentrations and its atmospheric exchange. *Global Change Biol.* 2008, 14, doi: 10.111/ j.1365-2486.2008.01669.x.
- (24) Kohler, S. J.; Buffam, I.; Laudon, H.; Bishop, K. H. Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements. J. Geophys. Res. 2008, 113, doi:10.1029/ 2007IG000629.
- (25) Klemedtsson, L.; Kasimir-Klemedtsson, Å.; Moldan, F.; Weslien, P. Nitrous oxide emission in Swedish forest soils in relation to liming and simulated increased N-deposition. *Biol. Fert. Soil* 1997, 25, 290–295.
- (26) Weiss, R. F. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar. Chem. 1974, 2, 203–215.
- (27) Stumm W.; Morgan, J. M. Aquatic Chemistry, 3rd ed.; John Wiley & Sons: New York, 1996.
- (28) Gelbrecht, J.; Fait, M.; Dittrich, M.; Steinberg, C. Use of GC and equilibrium calculations of CO<sub>2</sub> saturation index to indicate whether freshwater bodies in north-eastern Germany are net sources or sinks for atmospheric CO<sub>2</sub>. Fresenius J. Anal. Chem. 1998, 361, 47–53.
- (29) Stahli, M.; Nyberg, L.; Mellander, P. E.; Jansson, P. E.; Bishop, K. H. Soil frost effects on soil water and runoff dynamics along a boreal transect: 2. Simulations. *Hydrol. Process.* 2001, 15, 927– 941

- (30) Bishop, K.; Seibert, J.; Köhler, S.; Laudon, H. Resolving the Double Paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. *Hydrol. Process.* 2004, 18, 185– 189
- (31) Genereux, D. P.; Hemond, H. F. Naturally-Occurring Rn-222 as a Tracer for Streamflow Generation - Steady-State Methodology and Field Example. Water Resour. Res. 1990, 26, 3065–3075.
- (32) Genereux, D. P.; Hemond, H. F. Determination of Gas-Exchange Rate Constants for a Small Stream on Walker Branch Watershed, Tennessee. Water Resour. Res. 1992, 28, 2365–2374.
- (33) Maprani, A. C.; Al, T. A.; MacQuarrie, K. T.; Dalziel, J. A.; Shaw, S. A.; Yeats, P. A. Determination of mercury evasion in a contaminated headwater stream. *Environ. Sci. Technol.* 2005, 39, 1679–1687.
- (34) Agren, A.; Buffam, I.; Jansson, M.; Laudon, H. Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. *J. Geophys. Res.* 2007, 112, G03003,; doi: 10.1029/2006JG000381.
- (35) Laudon, H.; Seibert, J.; Kohler, S.; Bishop, K. Hydrological flow paths during snowmelt: Congruence between hydrometric measurements and oxygen 18 in melt water, soil water, and runoff. Water Resour. Res. 2004, 40, W03102, doi:10.1029/ 2003WR002455.
- (36) Temnerud, J. Spatial variation of dissolved organic carbon along streams in Swedish boreal catchments; Örebro Studies in Environmental Science 6; Örebro University, 2005; 43 pp; ISSN: 1650-6278, ISBN: 91-7668-437-7.
- (37) Magnusson, T. Carbon-dioxide and methane formation in forest mineral and peat soils during aerobic and anaerobic incubations. Soil Biol. Biochem. 1993, 25, 877–883.
- (38) Dawson, J. J. C.; Bakewell, C.; Billett, M. F. Is in-stream processing an important control on spatial changes in carbon fluxes in headwater catchments? Sci. Total Environ. 2001, 265, 153–167.
- (39) Likanen, A.; Huttunen, J. T.; Murtoniemi, T.; Tanskanen, H.; Vaisanen, T.; Silvola, J.; Alm, J.; Matikainen, P. J. Spatial and seasonal variation in greenhouse gas and nutrient dynamics and their interactions in the sediments of a boreal eutrophic lake. *Biogeochemistry* 2003, 65, 83–103.
- (40) Berggren, M.; Laudon, H.; Jansson, M. Landscape regulation of bacterial growth efficiency in boreal freshwaters. *Global Bio-geochem. Cycles* 2007, 21, Art no. GB4002.

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