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Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes

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[1] Carbon dioxide (CO_2) and dissolved inorganic carbon (DIC) concentrations and export were analyzed throughout a 67 km^2 boreal stream network in northern Sweden. 700 DIC and CO_2 samples from 14 subcatchments were collected in 2006 and 2007. All sites were consistently supersaturated in CO_2 with respect to the atmosphere. Temporal variability of DIC and CO_2 concentration was best correlated with discharge, with concentrations generally diluting at high discharge. However, the variability in CO_2 concentration was also dependent on the specific pH range of the stream, as variability was greatest in acidic headwater streams and lowest in larger circumneutral streams. In the larger ones the increase in the CO_2 proportion of DIC at increased discharge counteracts the dilution of CO_2. The shift toward proportionally more CO_2 of the DIC at higher discharge is caused by decline in pH. Spatial patterns showed that DIC and CO_2 concentrations were best correlated with peatland coverage of the subcatchment. The highest concentrations were found in headwater streams draining peatlands. The downstream export of DIC from the catchment outlet constitutes 19% of the total downstream export of carbon (DIC + DOC), or 0.7 (±0.09) g C m^{-2} yr^{-1}. This study demonstrates the importance of including fluvial fluxes of inorganic carbon in landscape carbon budgets via runoff, and also highlights the need to account for stream evasion of CO_2 to the atmosphere in such estimates since it can be larger than the downstream DIC export.

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1. Introduction

[2] Fluvial export of dissolved carbon from terrestrial systems has been identified as an important component of the terrestrial carbon cycle [*Kling et al.*, 1992; *Fiedler et al.*, 2006; *Hope et al.*, 1994; *Billett et al.*, 2004]. Even if this "aquatic conduit" of carbon is small in absolute numbers compared to the direct uptake and release of carbon from forested or peat dominated terrestrial systems, it is a persistent loss and an important component in the long-term carbon balance, especially for systems close to equilibrium with respect to atmospheric CO_2 [*Valentini et al.*, 2000; *Nilsson et al.*, 2008]. However, aquatic export of dissolved or gaseous carbon from lakes and streams is often neglected when discussing landscape carbon budgets. But studies have shown that estimating Net Ecosystem Exchange (NEE) in such systems without considering export of dissolved and gaseous carbon from surface waters might overestimate the accumulation significantly [*Hope et al.*, 2001; *Richey et al.*, 2002; *Nilsson et al.*, 2008]. *Cole et al.* [2007] reassessed the importance of inland waters in the terrestrial carbon budget. By considering sedimentation and evasion instead of looking on inland waters as passive pipes in the carbon transfer, they suggested an increase of the total export of terrestrial carbon via aquatic systems by a factor of two. The study concludes that 48% of the carbon leaving terrestrial systems enters the ocean, 12% is stored in sediments and the remaining 40% is lost via evasion to the atmosphere. They emphasized that the loss due to evasion is likely to be an underestimate since small headwater streams are excluded in the summary due to lack of global data of both evasion from headwaters and the unknown area represented by headwaters [*Cole et al.*, 2007]. The significance of headwaters for landscape-scale aquatic carbon assessments is further highlighted by the recent finding that 90% of the total stream length in Sweden has catchment areas under 15 km^2 [*Bishop et al.*, 2008]. This "aqua incognita" is especially interesting with respect to carbon balances due to the fact that the export of carbon in/from a stream is a two-dimensional flux, with both a vertical (evasion) as CO_2 and CH_4, and downstream transport of particulate and dissolved organic carbon (POC, DOC) as well as dissolved inorganic carbon (DIC). There is an obvious knowledge gap concerning the downstream export of carbon and gas exchange with the

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atmosphere from over a million kilometers of perennial headwater streams (catchment < 15 km^2) in Scandinavia alone, since only a limited amount of headwaters have been studied in the world. This lack of understanding has to be redressed in future landscape carbon budgets.

[3] Upland, riparian and groundwater processes are very important to the input of both solutes and gasses to aquatic habitats [*Jones and Mulholland*, 1998]. The riparian soil-stream linkage appears to be especially important for DIC in headwater streams. Studies from headwater streams draining a Scottish peatland, a Swedish forested catchment and a tropical Amazonian catchment all show in-stream DIC/CO$_2$ concentrations and dynamics that generally reflect DIC/CO$_2$ concentrations and dynamics in the riparian soil [*Hope et al.*, 2004; *Öquist et al.*, 2009; *Johnson et al.*, 2008]. *Johnson et al.* [2008] concluded that the CO$_2$ supersaturation in tropical headwater streams results primarily from groundwater discharge of terrestrially respired CO$_2$ dissolved within deep soils. In this respect, headwaters differ from larger rivers in tropical regions where in-stream processing of allochthonous organic carbon is the main driver of CO$_2$ supersaturation. *Öquist et al.* [2009] found a strong correlation (R^2 = 0.96) between concentrations of soil DIC in the riparian zone and stream DIC in the connecting headwater stream in the same catchment as this study was conducted.

[4] Most previous studies on the aquatic component of the carbon cycle at the small catchment scale have focused on dissolved organic carbon (DOC), while far less attention has been given to dissolved inorganic carbon (DIC) or gaseous forms (e.g., CO$_2$ and CH$_4$) [*Hope et al.*, 1994]. Higher concentrations and fluxes of DOC, and its manifold ecosystem functions is one explanation. Measuring concentrations of DIC in surface waters is also challenging because speciation between the different fractions (CO$_2$, HCO_3^-, CO_3^{2-}) in the bicarbonate buffer system is controlled by pH and the equilibrium is sensitive to degassing of CO$_2$ [*Stumm and Morgan*, 1996]. The effect of degassing between sampling and analysis can be substantial especially in headwater streams draining low-pH systems such as boreal forests or peatlands which are also often supersaturated with CO$_2$ [*Hope et al.*, 1994, 1995; *Laudon and Buffam*, 2008].

[5] Even if the literature is limited there are some studies on in-stream DIC and CO$_2$ variability at the landscape scale from temperate and boreal regions. These studies demonstrate that variability in hydrology and catchment characteristics control the DIC concentration to a great extent [*Finlay*, 2003; *Teodoru et al.*, 2009], but also that the ability of in-stream biota to consume CO$_2$ can be crucial for the seasonal variability of CO$_2$ [*Dawson et al.*, 2009]. There is a clear need for better understanding of headwater export of DIC, especially from boreal regions where a significant proportion of the terrestrial carbon stocks are located. An important need for determining the export is to define the temporal variation in DIC concentration and distribution among the fractions in the bicarbonate system. This information, together with defining the spatial patterns in stream concentrations of DIC and CO$_2$, is a step on the way to estimating fluxes of inorganic carbon downstream, as well as evasion from running waters on a landscape scale. The main aims of this study are therefore to (1) document spatial and temporal patterns of DIC and CO$_2$ concentrations in a boreal stream network, (2) identify likely causes of spatial and temporal variability by looking for relationships between DIC/CO$_2$ and physical parameters (discharge and temperature) as well as catchment characteristics, and (3) consider contribution of DIC to the total downstream carbon export.

2. Methods

2.1. Study Site

[6] 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 northwest of Umeå, northern Sweden (Figure 1). The area is well documented since it is a part of the Svartberget research park, established in 1923. 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 130–369 m asl. Snow covers the ground from the end of October to the beginning of May. The growing season starts at the end of May and ends in late September. Annual mean precipitation is 600 mm, approximately 35% of which falls as snow, and the annual daily mean temperature is 0°C [*Ottosson Löfvenius et al.*, 2003]. 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 [*Bishop et al.*, 1995]. 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. In the upper parts of the catchment there are a number of lakes and peatlands, which cover a large area in some subcatchments.

[7] Data from 14 stream sites ranging in subcatchment area from 0.03 to 67 km^2 are presented in this paper (note that sites 8 and 11 do not exist in this study). The main land cover elements in the subcatchments are forest and peatland (Table 1). Stream order ranges from first to fourth order with a typical pH range between peak and base flow of 5.9–3.9 in headwaters and 6.5–6.0 in fourth-order streams. The DOC concentration range between peak and base flow is 7–41 mg L^{-1} in headwaters and 4–14 mg L^{-1} in fourth-order streams. The lowest pH and highest DOC concentrations are seen in streams characterized by a high proportion of peatland in the catchment (>35%) [*Buffam et al.*, 2007]. Further site descriptions are given by *Buffam* [2007] and *Ågren et al.* [2007].

2.2. Sampling and Analysis

[8] Stream DIC was sampled at the 14 sites in conjunction with other chemical and physical stream parameters including DOC, metals, major cations and anions, pH, and stream temperature. Sampling was performed monthly, and during spring flood and summer more intensively during 2006 and 2007 for a total of 49 occasions. Samples for pH analysis were collected without headspace in high-density polyethylene bottles, and kept cold and dark during transport to the laboratory. The pH was always measured within 24 h 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 equil-

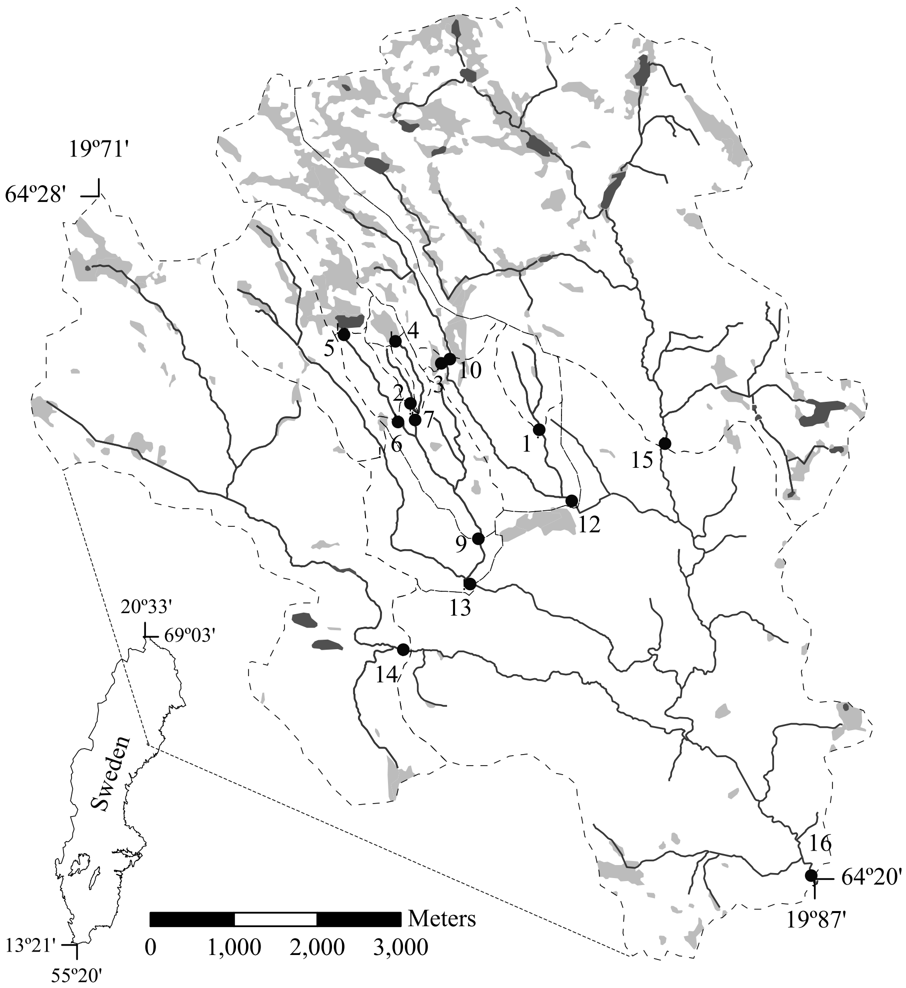

Figure 1. The Krycklan catchment with the stream network, the 14 subcatchments (dotted), and the sampled sites (solid circles). Lakes are in dark gray, and peatlands are in light gray.

Table 1. Subcatchment Characteristics of the 14 Sampling Sites[a]

Site	Catchment Area (km^2)	Stream Order[b]	Total Upstream Stream Length Above Sampling Location (km)	Altitude[b] (m asl)	Forest	Peatland	Lake	Arable	Silt	Till	Alluvial	Thin Soils	Rock
1	0.7	2	2.0	227	98.7	1.3	0	0	0	94.3	0	7.2	0
2	0.1	1	0.8	247	100.0	0	0	0	0	90.6	0	9.4	0
3	0.03	1	0.05	256	24.0	76.0	0	0	0	24.0	0	0.1	0
4	0.2	1	0.03	282	59.6	40.4	0	0	0	17.1	0	27.5	0
5	0.8	1	0.02	286	59.0	36.3	4.7	0	0	49.5	0	4.7	0
6	1.3	1	1.4	236	72.8	24.1	3.1	0	0	58.4	0	9.3	2.0
7	0.5	2	1.9	245	85.1	14.9	0	0	0	68.0	0	14.2	0
9	3.1	3	7.5	184	84.9	13.8	1.3	0	5.9	68.9	0	6.1	1.6
10	3.2	2	3.0	256	74.2	25.8	0	0	0	58.7	0	10.7	0
12	5.7	3	8.7	184	84.1	15.5	0	0.3	3.4	63.4	0	8.4	0
13	7.3	3	15.2	177	89.1	9.9	0.6	0.4	15.7	60.7	0	8.9	1.2
14	12.6	2	14.5	172	90.4	5.1	0.6	3.9	30.8	50.2	1.8	8.1	1.8
15	19.7	4	27.4	181	83.2	14.0	1.7	1.0	2.3	65.7	7.9	7.6	0.8
16	66.8	4	96.5	130	88.0	8.3	0.7	3.0	25.7	51.9	3.0	7.5	1.3

[a] Proportion of land cover elements and quaternary deposits are given in percent of the subcatchments. Note that sites 8 and 11 do not exist in this study.
[b] Determined at sampling site.

ibrated 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 (site 7) 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; *Björkvald et al.*, 2008; *Laudon et al.*, 2007]. The median annual runoff during 1981–2000 was 323 mm [*Ottosson Löfvenius et al.*, 2003].

[9] For DIC and CO_2 determination, a headspace method was used where a sample of bubble-free water (2 ml in 2006 and 5 ml in 2007 to increase the detection of CH_4, which was measured from the same samples but not presented in this study) was injected in a 22.5 ml glass vial sealed with a bromobutyl rubber septa. The injection was made by using a sterile syringe which was flushed with stream water before sampling. The vial was prefilled with 0.5 ml of 0.6% HCl and nitrogen at atmospheric pressure. Samples were stored in the dark at 8°C for on average 3 days until analysis. A storage study of samples showed an increase in headspace CO_2 concentration by ~5% during storage for one month before analysis (M. Wallin, unpublished data, 2009). Any effect of respiration in the bottles during storage was thus assumed to be insignificant for the actual storage times in this study. Headspace CO_2 concentrations were analyzed by GC-FID (Perkin Elmer Autosystem Gas chromatograph) equipped with a methanizer operating at 375°C and connected to an auto sampler. Separation was carried out on a Haysep N column using N_2 (40 ml min^{-1}) as carrier gas.

2.3. Calculations

[10] Since the samples were acidified (pH ~ 2) essentially all DIC was in the form of CO_2, partitioned between $H_2CO_3{}^*$ in the dissolved phase, and CO_2 in the headspace. The amount of CO_2 in headspace was determined by using the general gas law

$$CO_{2HS} = \frac{pCO_{2HS} V_{HS}}{RT} \tag{1}$$

where CO_{2HS} is the amount of carbon dioxide in headspace in moles, pCO_{2HS} is the partial pressure of CO_2 in headspace in atmospheres, V_{HS} is the volume of headspace in liters, R is the general gas constant (0.0820578) and T is the temperature (K) which is set to 293.15 for equations (1)–(9) since the analysis is done under laboratory conditions.

[11] The concentration of the dissolved inorganic carbon (DIC) was calculated as a sum of the three fractions ($H_2CO_3{}^*$, HCO_3^- and CO_3^{2-}).

$$[DIC]_{Water} = [H_2CO_3^*]_{Water} + [HCO_3^-]_{Water} + [CO_3^{2-}]_{Water} \tag{2}$$

The concentration of each fraction was calculated according to equations (3), (5), and (6) [*Stumm and Morgan*, 1996], where equation (3) is Henry's law and $H_2CO_3{}^*$ includes hydrated and dissolved CO_2.

$$[H_2CO_3^*] = \frac{pCO_{2HS}}{K_H} \tag{3}$$

$$\ln K_H = A_1 + A_2 \frac{100}{T} + A_3 \ln \frac{T}{100} \tag{4}$$

K_H is Henry's constant according to equation (4). A_1, A_2 and A_3 represent the constants −58.0931, 90.5069 and 22.2940, respectively [*Weiss*, 1974].

$$[HCO_3^-] = \frac{[H_2CO_3^*]K_1}{[H^+]} \tag{5}$$

$$[CO_3^{2-}] = \frac{[HCO_3^-]K_2}{[H^+]} \tag{6}$$

$[H^+]$ is the proton concentration at pH set to 2, K_1 and K_2 are the equilibrium constants in equations (7) and (8) according to *Gelbrecht et al.* [1998] adjusted for laboratory temperature.

$$\log K_1 = \left(\frac{-3404.71}{T}\right) + 14.844 - 0.033T \tag{7}$$

$$\log K_2 = \left(\frac{-2902.39}{T}\right) + 6.498 - 0.0238T \tag{8}$$

The total concentration of DIC in the sample was a simple sum of the headspace and the dissolved fraction.

$$[DIC]_{Tot} = \frac{CO_{2HS}}{V_{Water}} + [DIC]_{Water} \tag{9}$$

V_{Water} is the volume of the sampled water. To determine the CO_2 concentration in the stream during natural conditions we used equation (10) [*Stumm and Morgan*, 1996] together with in-stream pH and equilibrium constants (equations (7) and (8)) adjusted for in-stream temperature. $H_2CO_3{}^*$ is set equal to $CO_{2Stream}$ and reported as CO_2.

$$[CO_{2Stream}] = \frac{[DIC]_{Tot}}{1 + \left(\frac{K_1}{[H^+]}\right) + \left(K_1 \frac{K_2}{[H^+]^2}\right)} \tag{10}$$

Concentrations are reported in units of mg of C per liter, and all fluxes reported as g C m^{-2} yr^{-1} based on catchment area.

2.4. Data Treatment and Statistical Analysis

[12] Since the sampling occasions were unevenly distributed over the period, daily time series of DIC concentration, CO_2 concentration and pH were created by linear interpolation between sampling days. Linear interpolation was chosen to be consistent since significant regression models between DIC/CO_2 concentrations and physical parameters were not found at all sites. Median values of DIC, CO_2, pH and coefficients of variation were based on interpolated data instead of just sampled data to get representative annual values. Average flow-weighted concentrations of DIC and CO_2-C were obtained by normalizing to annual runoff. Annual downstream export of DIC was estimated as the sum of daily DIC export (daily concentrations times mean daily discharge), which was then divided by the area of each subcatchment to obtain areal specific export. If one subcatchment was embedded in a larger catchment that was also

Table 2. Median Concentration of DIC and CO_2-C, CV, the Median Proportion CO_2-C of DIC, Median pH, Flow-Weighted DIC Concentration, Flow-Weighted CO_2-C Concentration, and Areal Specific Downstream Export of DIC From 14 Sites Within the Krycklan Catchment[a]

Site	DIC ($mg\ L^{-1}$)	CV (%)	CO_2-C ($mg\ L^{-1}$)	CV (%)	Proportion CO_2-C (%)	pH	Flow-Weighted DIC ($mg\ L^{-1}$)	Flow-Weighted CO_2–C ($mg\ L^{-1}$)	Areal Specific DIC Export (±SD) ($g\ C\ m^{-2}\ yr^{-1}$)
1	1.1 (0.6–2.4)	39	1.0 (0.6–2.1)	35	93 (68–99)	5.5 (6.3–4.8)	1.0	0.9	0.3 ± 0.04
2	2.8 (1.4–18.5)	65	2.7 (1.3–17.1)	63	98 (84–99)	4.9 (5.9–4.5)	2.3	2.2	0.7 ± 0.09
3	6.1 (2.9–14.4)	41	6.1 (2.9–12.4)	37	100 (86–100)	4.0 (5.9–3.7)	4.9	4.9	1.5 ± 0.20
4	5.9 (1.9–15.4)	46	5.8 (1.9–14.0)	39	99 (64–100)	4.3 (6.3–3.9)	4.6	4.5	1.4 ± 0.18
5	2.6 (1.0–23.0)	84	2.5 (0.8–14.8)	70	98 (77–100)	4.8 (6.0–4.2)	2.7	2.6	0.8 ± 0.11
6	1.7 (0.9–6.2)	53	1.5 (0.8–3.5)	37	87 (39–100)	5.7 (6.7–4.5)	1.5	1.4	−0.3 ± 0.04
7	1.4 (0.9–3.6)	40	1.3 (0.8–3.5)	39	97 (57–100)	4.9 (6.5–4.2)	1.5	1.5	−0.7 ± 0.09
9	1.9 (1.0–5.1)	45	1.4 (0.8–3.1)	33	78 (48–99)	6.0 (6.7–4.8)	1.6	1.2	0.5 ± 0.07
10	1.8 (1.1–4.5)	43	1.5 (1.1–3.4)	29	93 (44–99)	5.3 (6.6–4.4)	1.6	1.5	0.5 ± 0.06
12	1.2 (0.7–3.8)	52	1.0 (0.7–2.7)	27	85 (36–99)	5.7 (6.8–4.6)	1.1	1.0	0.1 ± 0.01
13	2.9 (1.0–12.0)	67	2.4 (1.0–9.9)	63	86 (64–99)	5.7 (6.3–4.9)	2.4	2.1	0.9 ± 0.12
14	2.6 (1.5–5.4)	30	1.5 (1.0–2.5)	18	56 (31–88)	6.5 (6.9–5.8)	2.2	1.5	0.7 ± 0.09
15	1.9 (0.8–3.5)	34	0.9 (0.5–2.0)	32	52 (20–90)	6.5 (7.1–5.7)	1.5	0.9	0.5 ± 0.06
16	3.2 (1.1–6.1)	39	1.2 (0.7–2.2)	29	43 (13–86)	6.7 (7.4–5.9)	2.3	1.2	1.0 ± 0.13

[a] Data presented are based on 2 years, 2006–2007. Note that sites 8 and 11 do not exist in this study. Ranges are given in parentheses. CV, coefficients of variation.

sampled, export from the upstream subcatchment was subtracted from the downstream export using the method proposed by *Ågren et al.* [2007]. If the export from the entire catchment is lower then export obtained in the upstream subcatchment, i.e., the evasion rate for the stream reach between the measured sites is higher then the input of DIC to the stream, then the downstream subcatchment will show a negative areal specific downstream DIC export. Uncertainty estimates for downstream export of DIC are given according to similar studies using Monte Carlo simulations for error propagation [*Nilsson et al.*, 2008].

[13] Linear regressions were used to describe the relationship of log discharge and temperature against DIC, CO_2 and pH. Regressions were considered significant if $p < 0.05$. In order to explore the spatial variability in DIC and CO_2 concentrations between the subcatchments, we used Partial Least Squares Regression (PLS) since it is suitable for covarying descriptor variables [*Sobek et al.*, 2003; *Eriksson et al.*, 1995]. Catchment characteristics (Table 1) and concentration data (Table 2) were used as variables. The data were logarithmically transformed to achieve normally distributed data when needed. JMP 7.0.1 (SAS Institute Inc., Cary, NC, USA) was used for all statistical calculations except for the PLS where SIMCA-P 11.5.0.0 (Umetrics, Umeå, Sweden) was used.

3. Results

[14] Stream discharge and stream water temperature were recorded for the 2 year study period from January 2006 to December 2007 (Figure 2d). The mean specific discharge rate over the study period at the representative site (site 7) described above, was 0.9 mm d^{-1}, ranging from 0.005 mm d^{-1} at low flow to 7.7 mm d^{-1} at spring flood and in association with intense precipitation events. The annual runoff over the investigated years was 331 mm for 2006 and 291 mm for 2007.

3.1. Spatial Variability

[15] Flow-weighted DIC concentration based on 2 years of data ranged from 1.0 to 4.9 mg L^{-1} for the 14 sites (Table 2). The highest DIC concentrations (4.9 and 4.6 mg L^{-1}) were found in the two headwater streams that had high peatland proportions in their catchments (sites 3 and 4, respectively). The flow-weighted DIC concentration of the remaining 12 sites was lower, ranging from 1.0 to 2.7 mg L^{-1}, while the higher concentrations (2.2 to 2.7 mg L^{-1}) were found in either headwater streams (sites 2 and 5) or in the largest third- or fourth-order streams (sites 13, 14 and 16). The lower numbers (1.0 to 1.6 mg L^{-1}) were found in the intermediate sized second- and third-order streams.

[16] Flow-weighted CO_2-C concentration based on 2 years of data ranged from 0.9 to 4.9 mg L^{-1} for the 14 sites (Table 2), and all sites were consistently supersaturated in CO_2 with respect to the atmosphere (>~0.3 mg C L^{-1}). The highest CO_2-C concentrations were found in the same two headwater streams with the highest DIC (sites 3 and 4). Sites 2, 5 and 13 had concentrations ranging from 2.1 to 2.6 mg $L^{-1}$and the remaining 9 sites from headwaters to fourth-order streams had flow-weighted CO_2-C concentrations ranging from 0.9 to 1.5 mg L^{-1}.

[17] There was large spatial variability in pH among the 14 sites with a clear gradient from acidic peatland-connected headwater sites to more circumneutral fourth-order streams. Median pH among the sites spanned a range of almost three pH units (6.7–4.0) (Table 2). The strong pH gradient in the catchment controls the distribution of the different fractions in the bicarbonate system of the streams. The dominant DIC fraction in most of the streams was CO_2 based on median concentration (Table 2). The median proportion of CO_2 in the total DIC over the period was almost 100% in the headwater sites with low pH. There were however a few exceptions at low-discharge conditions in some headwaters during summer when a higher stream pH shifts the bicarbonate equilibrium toward a higher proportion of HCO_3^-. The variability was higher in the intermediate sized streams where the median proportion of CO_2 ranged

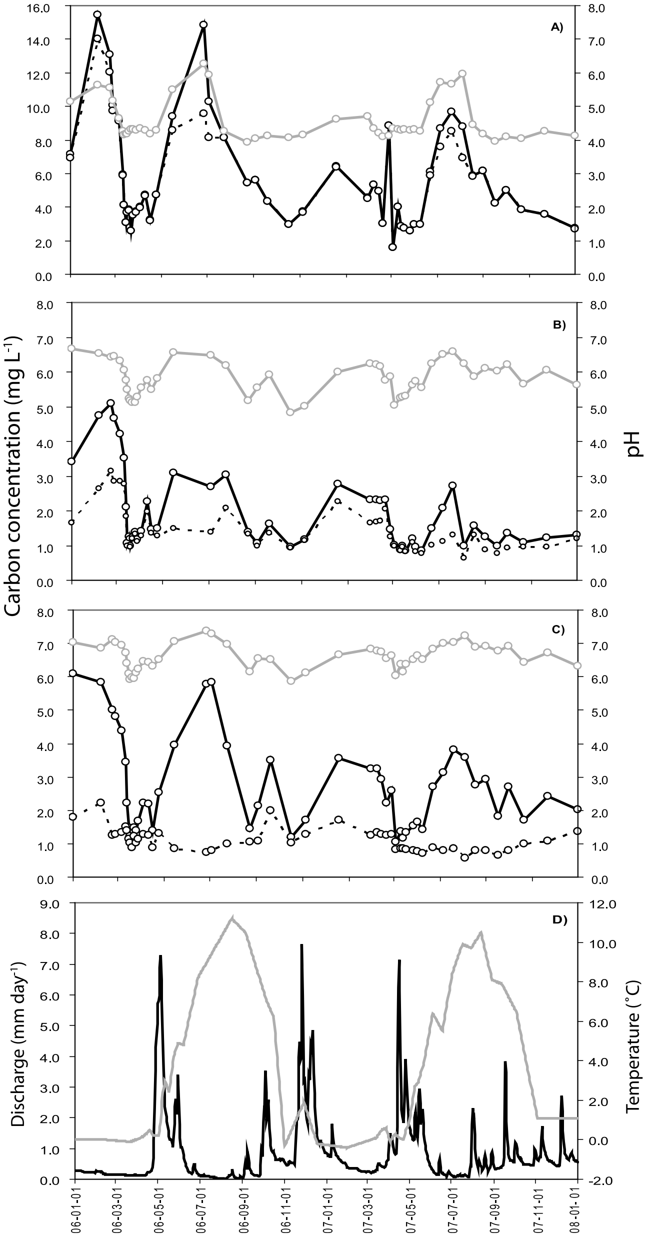

Figure 2. Time courses from (a) site 4, first-order stream, (b) site 9, third-order stream, and (c) site 16, fourth-order stream, outlet of entire catchment. Graphs show DIC concentration (black line), CO_2-C concentration (dotted line), and pH (gray line). (d) Specific discharge (black line) and stream temperature (gray line) from a representative site (site 7). Note that the *y* axis scale for DIC/CO_2-C goes twice as high on the first-order stream (Figure 2a) as that for the third- and fourth-order streams in Figures 2b and 2c.

from 78 to 97% among the sites. The variability at specific sites ranged from 31 to 100%. The median proportion of CO_2 in the fourth-order streams (sites 15 and 16) was 52 and 43%, respectively, while the annual range at these two sites was 13–90% (Table 2).

[18] The PLS showed that the seven most important catchment characteristics and DOC concentration together explained 85% of the variability in DIC and CO_2 concentration (Figure 3). High DIC and CO_2 concentrations were closely associated with small peatland streams, rich in DOC and located high up in the stream network. Peatland, forest and till coverage were the catchment character variables that explained most of the spatial variability in median concentrations of DIC and CO_2 (data not shown). Forest and till coverage were negatively correlated with DIC and CO_2 concentrations and closely correlated with the peatland cover. The peatland coverage was positively correlated with DIC and CO_2 concentrations and was the catchment character variable that best explained spatial variability in DIC and CO_2. The relationship was significant for both DIC and CO_2, but was slightly stronger for CO_2 (DIC, $R^2 = 0.50$; CO_2, $R^2 = 0.62$). This can be explained by the pH gradient in the catchment, but also indicates potential for other sources of DIC in the lower areas of the catchment. The correlation of CO_2 versus percentage of peatland in the catchment is seen in Figure 4.

3.2. Temporal Variability

[19] There was a negative correlation between DIC and discharge at 12 of 14 sites (Table 3). Sites 5 and 7 were the exceptions without a significant correlation to discharge ($p = 0.05$). The slope of the regressions ranged from −0.17 to −0.43, with the steepest slopes at sites with high variability in DIC concentration (Table 2). The highest R^2 for regression models were seen at two headwaters sites, sites 3 and 4 ($R^2 = 0.71$ and 0.81, respectively) and at the two fourth-order sites, sites 15 and 16 ($R^2 = 0.71$ and 0.90, respectively).

[20] Nine sites showed a significantly negative correlation between CO_2 and discharge. However, the correlations were weak ($R^2 < 0.20$) at four of the sites, which means that even if the relationship was significant, discharge explained only a small proportion of the variability in CO_2. At four sites (sites 2, 3, 4 and 13), the correlations were stronger ($R^2 > 0.62$). The stronger correlations between discharge and CO_2/DIC were associated spatially with till soils in the upper portion of the catchment (Figure 3).

[21] At all sites except site 3 (one of the peatland streams that was consistently acid), there were significant correlations between pH and discharge. Discharge explained much of the variability in pH ($R^2 = 0.58–0.88$) except at site 5.

[22] The strong negative correlations between discharge and DIC were not seen between discharge and CO_2 in the larger streams. Even if DIC was diluted by increasing discharge, CO_2 remained relatively stable due to decreases in pH which shifted the bicarbonate equilibrium toward a higher proportion of CO_2 (Figure 2 and Table 3). This was particularly evident when DIC sampling was performed at base discharge 2–4 weeks before the event and during the peak. The periods were April/May 2006 (spring flood), September/October 2006 (rain event) and March/April 2007 (spring flood). All three events showed a decrease in DIC concentration between base and peak discharge for all sites, independent of stream size or catchment character (Figure 5). The balance between CO_2 and HCO_3^- changed especially in the intermediate and large sized streams where the decline in pH during peak discharge increased the proportion of CO_2, keeping it at a relatively stable concentration.

[23] Weak but significant positive correlations ($R^2 > 0.35$) were found between DIC concentration and temperature at

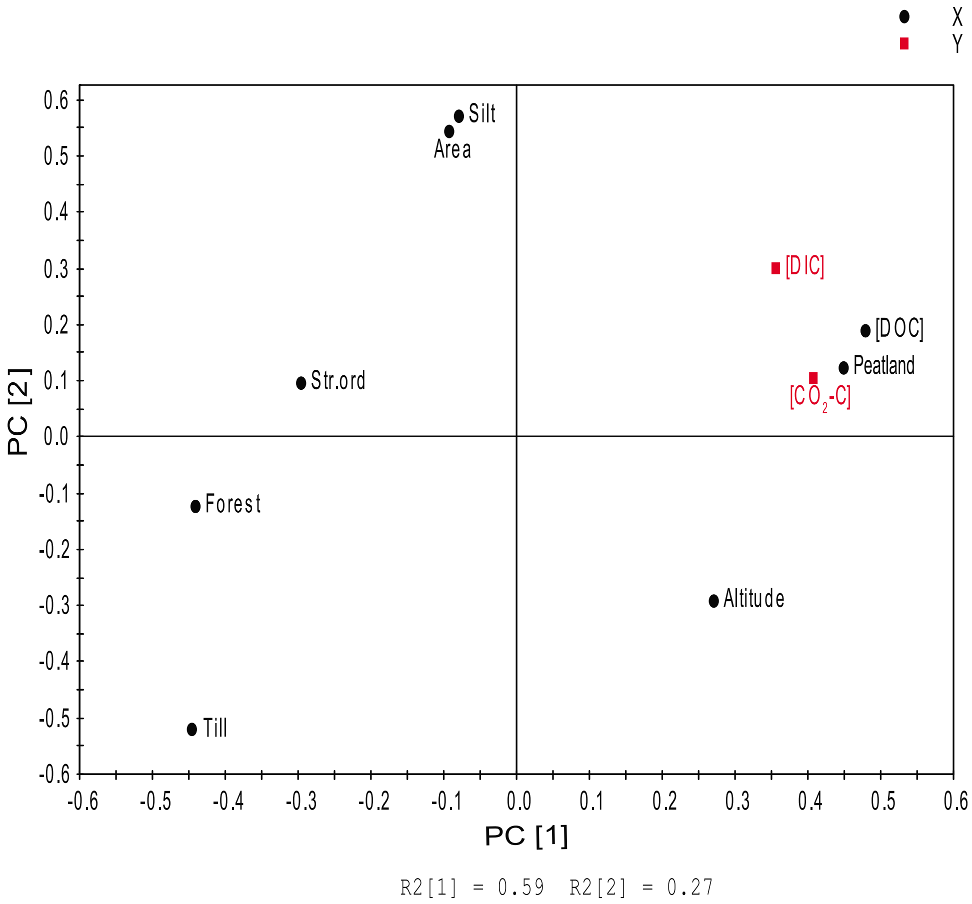

Figure 3. PLS score plot on principle components describing variability with median DIC and CO_2-C concentrations (Table 2) as response variables and catchment characteristics (Table 1) and median DOC concentration as predicting variables for the 14 sampled sites. R^2 and Q^2 are 0.85 and 0.60, respectively.

three of the headwater sites (sites 2, 3 and 4), while sites 5 and 7 had weak but significant negative correlations ($R^2 > 0.30$) (Table 3). Since these sites are all characterized by low pH, almost all DIC was in the form of CO_2. Thus the correlations between CO_2 and temperature were almost the same as those for DIC. No significant temperature relationships with DIC were found at the rest of the sites. Eleven of the sites had a significant correlation between CO_2 and temperature. As described above, correlations were positive at 3 of the headwater sites, but all other relationships were negative. The strongest correlations were found in the two large, fourth-order streams (R^2 = 0.47 and 0.46 for sites 15 and 16, respectively).

3.3. Fluxes

[24] A total of 47 tons (0.7 (±0.09) g C m^{-2} yr^{-1}) were fluvially exported as DIC per year from the entire 67 km^2 catchment. Annual areal specific export of DIC from the 14 subcatchments ranged from −0.7 to 1.5 g C m^{-2} yr^{-1} (Table 2), where negative numbers indicate that DIC has been lost between upstream and downstream measured sites. The highest areal specific DIC exports (1.5 (±0.20) and 1.4 (±0.18) g C m^{-2} yr^{-1}) were found in the two headwater streams draining two major peatlands (sites 3 and 4, respectively). *Ågren et al.* [2007] reported DOC export from those sites to be 9.9 and 8.8 g C m^{-2} yr^{-1}, respectively.

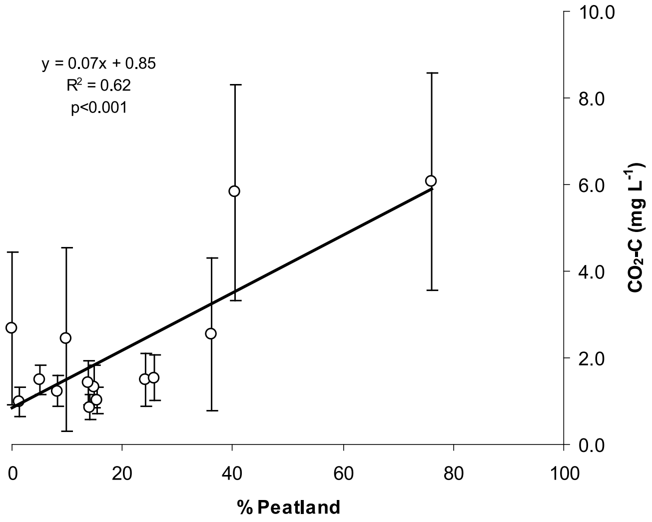

Figure 4. Median concentrations of CO_2-C (mg L^{-1}) as a function of percentage peatland (including lakes) of the catchment area for the 14 stream sites. Concentrations are based on daily values interpolated between sampling occasions. Error bars show standard deviation.

Table 3. R^2 and K From Least Squares Linear Regressions Between DIC, CO_2-C, as Well as pH and Log Discharge or Temperature[a]

	DIC[b] ($mg\ L^{-1}$)		CO_2-C[b] ($mg\ L^{-1}$)		pH	
Site	R^2	K	R^2	K	R^2	K
			Discharge ($L\ s^{-1}$)			
1	0.31	−0.17	0.16	−0.11	0.83	−0.31
2	0.66	−0.36	0.62	−0.33	0.65	−0.23
3	0.71	−0.29	0.71	−0.28	n.s.	n.s.
4	0.81	−0.35	0.76	−0.31	0.58	−0.36
5	n.s.	n.s.	n.s.	n.s.	0.29	−0.12
6	0.51	−0.29	0.32	−0.17	0.82	−0.41
7	n.s.	n.s.	n.s.	n.s.	0.63	−0.41
9	0.52	−0.28	0.20	−0.13	0.84	−0.37
10	0.47	−0.22	0.13	−0.08	0.86	−0.51
12	0.47	−0.27	0.10	−0.08	0.82	−0.47
13	0.69	−0.43	0.62	−0.36	0.64	−0.21
14	0.70	−0.21	n.s.	n.s.	0.86	−0.22
15	0.71	−0.27	n.s.	n.s.	0.72	−0.21
16	0.90	−0.36	n.s.	n.s.	0.88	−0.28
			Temperature (°C)			
1	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
2	0.16	0.06	0.17	0.06	n.s.	n.s.
3	0.34	0.06	0.37	0.06	n.s.	n.s.
4	0.12	0.04	0.09	0.03	0.09	0.04
5	0.13	−0.03	0.15	−0.03	0.19	0.02
6	n.s.	n.s.	0.09	−0.02	n.s.	n.s.
7	0.30	−0.06	0.32	−0.06	n.s.	n.s.
9	n.s.	n.s.	0.12	−0.03	n.s.	n.s.
10	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
12	n.s.	n.s.	0.10	−0.02	n.s.	n.s.
13	n.s.	n.s.	n.s.	n.s.	0.08	0.02
14	n.s.	n.s.	0.11	−0.01	0.10	0.02
15	n.s.	n.s.	0.47	−0.04	0.23	0.03
16	n.s.	n.s.	0.46	−0.04	0.23	0.04

[a] Not significant correlations are marked with n.s. (significance level $p = 0.05$).

[b] Logarithmical transformed.

Negative areal export of DIC was found at sites 6 and 7 (−0.3 (±0.04) and −0.7 (±0.09) $g\ C\ m^{-2}\ yr^{-1}$, respectively). These two sites are situated up to 1.5 km downstream from two headwater sites (sites 5 and 4). As described above site 4 is a stream draining a peatland, and site 5 is the outlet of a lake. Both these upstream sites are characterized by high in-stream DIC concentration and low pH. The negative areal export of DIC from sites 6 and 7 downstream from these headwaters indicates a rapid vertical evasion from the stream taking place in the first several hundred meters of the stream.

4. Discussion

[25] In order to quantify downstream export of DIC and CO_2 evasion from a stream network, it is fundamentally important to understand what controls DIC and CO_2 concentrations in space and time. It would also be advantageous to find relationships between DIC/CO_2 concentrations and more readily available parameters in order to help determine downstream export as well as vertical evasion fluxes of inorganic carbon from stream networks in the landscape.

[26] The flow-weighted in-stream concentrations of DIC (1.0 to 4.9 $mg\ L^{-1}$) and CO_2-C (0.9 to 4.9 $mg\ L^{-1}$) among the 14 sites in the catchment are of the same order of magnitude as found in studies of similar systems. The CO_2-C concentrations were in the same range as in streams draining peatland systems in Scotland [*Hope et al.*, 2001; *Billett et al.*, 2004; *Dinsmore and Billett*, 2008] where the range was from 0.3 to 5.1 $mg\ L^{-1}$, but lower than the CO_2-C concentrations (2.7–47.9 $mg\ L^{-1}$) found in a headwater spring draining a Norway spruce forest in southwestern Germany [*Fiedler et al.*, 2006]. The DIC concentrations from this study were in the same range as observed in a similar system in Canada (1.15–3.21 $mg\ L^{-1}$) [*Teodoru et al.*, 2009], but lower than figures found in a stream draining an oligotrophic minerogenic mire (6.0 to 13.2 $mg\ L^{-1}$ with 70% peatland in the catchment) 10 km from the Krycklan catchment [*Nilsson et al.*, 2008].

4.1. Spatial Variability

[27] Northern peatlands (including the peatlands in this study) and their role in the global carbon cycle have been intensively studied for decades. They contain about one third of the global carbon soil pool and can potentially act as a major carbon source with a changing climate [*Gorham*, 1991]. The importance of peatlands for fluvial DOC export has been emphasized by several studies from this [*Ågren et al.*, 2007; *Laudon et al.*, 2004], and at other temperate/boreal catchments [*Dawson et al.*, 2002; *Mattsson et al.*, 2005; *Hinton et al.*, 1997]. Furthermore a strong connection between DOC and partial pressure of CO_2 (pCO_2) has been found in boreal lakes along a latitudinal gradient in Sweden [*Sobek et al.*, 2003]. This is confirmed by the PLS loading plot (Figure 3), which shows strong connections between median DIC, CO_2-C, DOC and peatland coverage. DOC and peatland coverage actually had the highest influence in the PLS model and correlate closely to DIC and CO_2-C also when considered as single independent variables in linear regression analysis (peatland coverage, Figure 4; DOC, data not shown). The sites with the highest DIC and CO_2-C concentrations (sites 3 and 4) are located in headwater streams, which are rich in DOC and drain peatlands. It may be, however, that the distance from the peatlands is also important. The samples at sites 3 and 4 are taken within 50 m from the peatland outlets (see stream length, Table 1) which results in a short residence time of the water in the stream before sampling. The short residence time is important, especially in streams with low pH (4.0 and 4.3 for sites 3 and 4, respectively), since almost all DIC is in form of CO_2 that can start to evade immediately to the atmosphere when the water reaches the stream. The rapid CO_2 evasion is supported by several studies [*Palmer et al.*, 2001; *Fiedler et al.*, 2006]. *Öquist et al.* [2009] estimated the annual average "half life" of DIC to be 5.5 h once it entered a headwater stream (site 2 in this catchment with annual median pH of 4.9).

[28] The peatland coverage turned out to be the best predictor of stream DIC and CO_2 concentrations in the landscape. However, riparian peat is not available in the map information used in this study, but in terms of fluvial DOC export, riparian peat deposits are a major source of DOC in forested catchments [*Bishop et al.*, 1993; *Creed et al.*, 2003]. Furthermore, the DIC export from the riparian peat to the stream at site 2 in this catchment has been estimated to be 3.2 $g\ C\ m^{-2}\ yr^{-1}$, and with typical soil CO_2-C concentrations that ranged from 3.4 to 8.1 $mg\ L^{-1}$ [*Öquist and Laudon*, 2008; *Öquist et al.*, 2009] (even though the map information does not show any peatland cover in the specific catchment). The impact of extended peatlands fur-

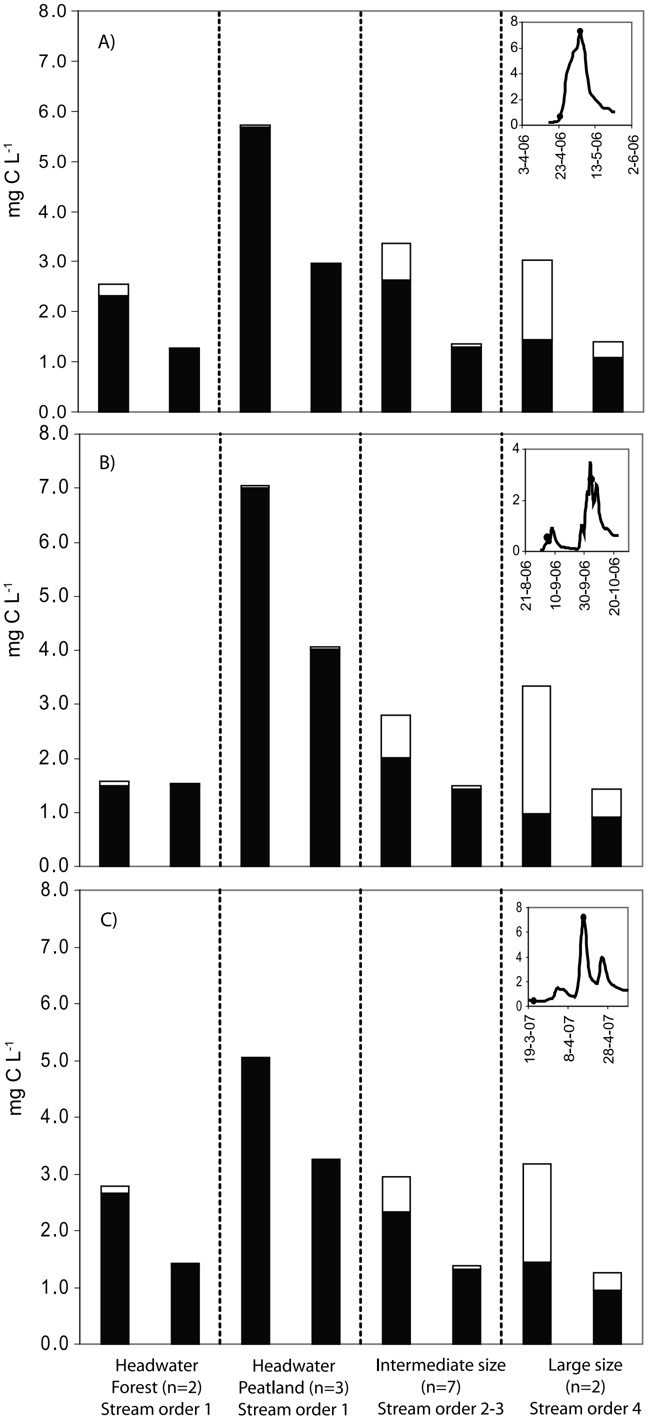

Figure 5. DIC concentration and partitioning between CO_2-C (black) and HCO_3^--C (white) at base flow (left bar) and high flow (right bar) conditions grouped by stream type during three discharge events. (a) Spring flood, 2006, (b) rain storm, fall 2006, and (c) spring flood, 2007. Specific discharge from representative site is shown on *y* axis and given in mm d^{-1}.

ther downstream in the catchment on in-stream concentration of DIC and CO_2 is best illustrated at site 13, where the key may not be that there is a large peatland percentage, but that the sampling site lies close to the peatland. Site 13 is 30 m downstream from a major peatland outlet, but the total peatland coverage of the subcatchment is only ca 10% (Table 1 and Figure 4). This third-order stream has a different chemical composition than the other larger sites, identified with relatively high DIC and CO_2-C concentration (2.4 and 2.1 mg L^{-1}) and low median pH (5.7). The peatland may act as a source for DIC to the passing stream. A similar pattern has also been seen in a Scottish headwater catchment where areas rich in peat are located downstream from the headwaters, and DIC/CO_2 concentrations in the stream increased when it passes through these areas [*Dawson et al.*, 2002]. It is likely that the elevated CO_2 signal disappears within a short distance downstream due to evasion and/or dilution.

[29] Other catchment characteristics besides peatland coverage that were highly influential in the PLS model were stream order, till coverage and forest coverage (Figure 3). All were negatively correlated and the latter two are highly autocorrelated with peatland coverage. They were therefore considered to be of minor interest although they are influential in the model. The negative correlation to stream order is also seen as an influence of peatland coverage since the subcatchments covered by a high proportion of peatland are generally drained by small headwater (low order) streams. Catchment area did not turn out to be a good predictor for in-stream DIC or CO_2-C according to the PLS model. Correlations between catchment size and CO_2 have been found in studies of boreal streams and rivers in Canada [*Teodoru et al.*, 2009] and in upland streams and rivers in Scotland [*Dawson et al.*, 2009]. However, those two studies covered a much wider range in catchment size that included larger rivers in which in situ primary production has a strong influence on the CO_2 supersaturation [*Dawson et al.*, 2009] and which might explain why we did not find such correlations.

4.2. Temporal Variability

[30] Stream discharge was negatively correlated with DIC concentration at 12 of the 14 sites. One site (site 5) that lacked a significant correlation between DIC and discharge was the outlet of a humic headwater lake. The hydrological and chemical conditions of the stream at site 5 are likely more connected to the hydrology and internal processes of the lake.

[31] CO_2 was not as strongly correlated with discharge as DIC. Changes in CO_2 over time are a function of both DIC and pH dynamics. But even though both pH and DIC decrease with increased discharge, the pattern for CO_2 might be different, since partitioning between the DIC fractions is not a linear relationship [*Stumm and Morgan*, 1996]. This is emphasized by the strong correlations between discharge and CO_2 found in the most acidic streams and in the streams with the highest CO_2 concentrations (sites 2, 3, 4 and 13). There the effect of changing pH with changing discharge was minor compared to the dilution effect on CO_2. This is supported by a study from a small stream draining a peatland in Scotland which showed a strong negative relationship between discharge and CO_2 ($R^2 = 0.81$) [*Dinsmore and Billett*, 2008]. However, correlations between discharge and CO_2 concentration were weak or nonexistent in the larger streams. This was because their discharge-related pH

changes compensate for the dilution in DIC by shifting the bicarbonate system toward more CO_2 (Figure 5).

[32] The temporal variability of CO_2 in this stream network is large in headwaters but lower in larger streams. But this pattern would likely be different if the median pH was higher in the headwaters or lower in the larger streams. There are however not many larger streams in temperate/boreal Sweden (catchments > 15 km^2) with pH values low enough to keep all the DIC as CO_2 [*Bishop et al.*, 2008].

[33] Since the solubility of CO_2 in water decreases with increased temperature [*Stumm and Morgan*, 1996] it is not surprising that temperature was negatively correlated with CO_2 at eight of the sites. However, the correlation between CO_2 and temperature in the three headwaters (sites 2, 3 and 4) was positive (Table 3). This can be explained by higher soil respiration rates with increased temperature, and hence higher soil water CO_2 concentrations being exported to the stream, which would be congruent with strong hydrochemical connectivity between soils and headwaters. The negative correlations were strongest in the two largest streams (sites 15 and 16) but otherwise the temperature correlations were generally weak. Since the larger streams have generally stable CO_2 concentrations that are not strongly affected by changes in discharge, temperature appears to be the main driver for CO_2 dynamics in larger streams, likely explained by temperature influence on solubility.

[34] Most of the spatial and temporal variability in DIC and CO_2 concentrations in the stream network are related to physical catchment characteristics such as peatland distribution and variability in hydrology. Two factors that might also influence the temporal and spatial variability in stream water DIC and CO_2 are in-stream bacterial respiration and photochemical degradation of DOC. Biological degradation of DOC has been found to strongly influence DIC and CO_2 concentrations in lakes with long residence times [*Sobek et al.*, 2003]. Except in lakes and at base flow conditions, the residence time of surface water in Krycklan is likely too short for any considerable in-stream production of CO_2 to occur. Stream water residence time at average discharge in most places of the stream network is on the order of hours (M. Wallin, unpublished data, 2009) and temperature is well below those of room temperature, it is not likely that the flux of DIC and CO_2 is significantly affected by biological degradation of DOC. This was confirmed in studies by *Berggren et al.* [2007, 2009] on the same stream network, where the maximum bacterial respiration was less than 0.1 mg L^{-1} of CO_2-C per day in room temperatures. The rates of in-stream photooxidation of DOC to CO_2 can be somewhat higher [*Köhler et al.*, 2002], but are also unlikely to contribute substantially to spatial variation in stream DIC concentrations in the face of short stream water residence times within the catchment, and by shading of the forest.

4.3. Fluxes

[35] The fluvial downstream export of DIC from the outlet (site 16) constitutes 0.7 (±0.09) g C m^{-2} yr^{-1}, or 19% of the entire carbon export (DIC + DOC) (DOC export figures are from *Ågren et al.* [2007]). POC is neglected in this study since total organic carbon (TOC) often is concluded to be equivalent to DOC for these types of streams in the boreal zone [*Buffam et al.*, 2008]. Furthermore, *Laudon et al.* [2004] did not find a statistical significant difference in organic carbon concentration between a set of filtered and unfiltered samples taken both at base flow and peak flow. The DIC export figures are similar to the estimates of carbon export for the 3025 km^2 Öreälven catchment (0.9 g C m^{-2} yr^{-1}, or 20% of the entire carbon export (DIC + DOC)) [*Jonsson et al.*, 2007]. The higher DIC concentrations found in the more peatland dominated headwater catchments (sites 3 and 4) also reflect the higher fluxes (1.5 (±0.20) and 1.4 (±0.18) g C m^{-2} yr^{-1}, respectively). The contribution of DIC with respect to total carbon export was, however, less at sites 3 and 4 (13 and 14%, respectively) compared to the export from the entire Krycklan catchment (site 16). The negative export numbers of DIC at sites 6 and 7 (−0.3 (±0.04) and −0.7 (±0.09) g C m^{-2} yr^{-1}, respectively) highlight the occurrence of evasion rates exceeding the input rate of "new" DIC to the stream. The stream passing site 6 originates in a lake where highly elevated DIC and CO_2 concentrations are observed at the lake outlet (site 5) 1.5 km upstream from site 6. The second-order stream passing site 7 originates from two tributaries that both have highly elevated DIC and CO_2-C concentrations (sites 2 and 4). We believe that the elevated DIC and CO_2 concentrations in the upstream sites are lost from the stream as evasion along the stream reaches (up to 1.5 km) between the upstream and downstream sites, and that this evasion rate exceeds the input rate of DIC with diffuse groundwater inputs along the stream. Applying the discharge-driven regression models for the DIC concentration changed the annual export figures slightly (±5%) compared to using the daily linearly interpolated data.

[36] The fluvial DIC export should not be neglected in estimates of the landscape carbon balance. However, the fluvial downstream export of DIC is not a complete representation of the landscape export of DIC since it only measures one dimension of a two-dimensional flux. The DIC also has a vertical flux in the form of CO_2 evasion. This must be accounted for to estimate the total contribution of aquatic inorganic carbon fluxes to the catchment carbon export on a landscape scale. The importance of CO_2 evasion is particularly evident in the sites which showed negative downstream DIC export numbers (Table 2). But evasion of CO_2 is a diffuse flux that is occurring everywhere along the stream network where there is a supersaturation of CO_2. The amount of CO_2 lost by evasion from headwater streams is poorly characterized, but *Öquist et al.* [2009] has shown in a recent small-scale study from a headwater stream in this stream network (site 2) that carbon export from the stream surface to the atmosphere (evasion) was 2.9 (±0.1) g C m^{-2} yr^{-1} based on catchment area. This represented 30% of the total export of terrestrial carbon (DIC + DOC) via surface water. Similar figures (13–34%) for the evasion contribution have been found in Scotland for small streams draining peatlands [*Billett et al.*, 2004; *Hope et al.*, 2001]. It indicates that the evasion component of the aquatic export of terrestrial derived carbon can be significant in headwater stream systems.

5. Conclusions

[37] This study shows that all stream sites within the fourth-order catchment are consistently supersaturated in CO_2 with respect to the atmosphere. Thus they are a con-

stant source of atmospheric CO_2 due to vertical evasion. The temporal variability in DIC concentration is controlled by variability in discharge to a great extent. However, the variability in CO_2 is also dependent on the specific pH range of the stream. The clear gradient in pH along the stream network and the hydrological control of acidity in the Krycklan catchment is reflected in the variability in CO_2. The greatest dilution of CO_2 with increased stream discharge was seen in the low-pH headwater sites. The variability was less in the larger streams where the increase in the CO_2 proportion of DIC at increased discharge caused by a lowering of the pH counteracts the dilution of CO_2. The low temporal CO_2 variability in the larger streams is controlled more by temperature. This emphasizes that headwaters are more likely to be variable than larger streams in their role as a source of CO_2 evasion from the water surface to the atmosphere.

[38] Peatlands were the most important factor for spatial variability in the landscape stream concentrations of DIC and CO_2, as well as when estimating areal specific flux of DIC. The sites with a large proportion of peatland in their catchment by far exceed the other sites in terms of annual median DIC and CO_2 concentration. Nearness to an extended peatland may also be an important factor for the spatial variability since the elevated signal of CO_2 in the stream disappears a short distance downstream due to the rapid evasion process.

[39] It is evident from this study that fluvial export of inorganic carbon from boreal catchments like this one needs to be incorporated in landscape carbon budgets. The study also highlights the importance of including the vertical evasion term in those estimates. Knowledge from this study concerning temporal and spatial variability of DIC and CO_2 concentrations in a stream network will be a useful basis for future work in estimating vertical fluxes of CO_2 from surface waters in the landscape.

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