Spatiotemporal variability of the gas transfer coefficient (K_{CO2}) in boreal streams: Implications for large scale estimates of CO_2 evasion

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[1] Boreal streams represent potentially important conduits for the exchange of carbon dioxide (CO_2) between terrestrial ecosystems and the atmosphere. The gas transfer coefficient of CO_2 (K_{CO2}) is a key variable in estimating this source strength, but the scarcity of measured values in lotic systems creates a risk of incorrect flux estimates even when stream gas concentrations are well known. This study used 114 independent measurements of K_{CO2} from 14 stream reaches in a boreal headwater system to determine and predict spatiotemporal variability in K_{CO2}. The K_{CO2} values ranged from 0.001 to 0.207 min^{-1} across the 14 sites. Median K_{CO2} for a specific site was positively correlated with the slope of the stream reach, with higher gas transfer coefficients occurring in steeper stream sections. Combining slope with a width/depth index of the stream reach explained 83% of the spatial variability in K_{CO2}. Temporal variability was more difficult to predict and was strongly site specific. Variation in K_{CO2}, rather than pCO_2, was the main determinant of stream CO_2 evasion. Applying published generalized gas transfer velocities produced an error of up to 100% in median instantaneous evasion rates compared to the use of actual measured K_{CO2} values from our field study. Using the significant relationship to local slope, the median K_{CO2} was predicted for 300,000 km of watercourses (ranging in stream order 1–4) in the forested landscape of boreal/nemoral Sweden. The range in modeled stream order specific median K_{CO2} was 0.017–0.028 min^{-1} and there was a clear gradient of increasing K_{CO2} with lower stream order. We conclude that accurate regional scale estimates of CO_2 evasion fluxes from running waters are possible, but require a good understanding of gas exchange at the water surface.

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1. Introduction

[2] The importance of aquatic export of terrestrially derived carbon (C) in the terrestrial C balance has been highlighted by several studies at different scales and in different environments during the last decade [*Richey et al.*, 2002; *Cole et al.*, 2007; *Battin et al.*, 2009; *Dinsmore et al.*, 2010]. Furthermore, the fate of the terrestrially derived C exported to aquatic systems is crucial to budget estimates, in particular whether it reaches a sink in oceanic or estuarine organic sediments or if it is lost to the atmosphere. The vertical export (often referred to as degassing or evasion) of carbon dioxide (CO_2) and other gases from surface waters is an aquatic flux term which has been intensively studied in lakes [e.g., *Jonsson et al.*, 2008], reservoirs [e.g., *Huttunen et al.*, 2002a], estuaries [e.g., *Frankignoulle et al.*, 1998] and oceans [e.g., *Wanninkhof*, 1992], but has received considerably less attention in headwaters and streams even though they make up a considerable part of the terrestrial aquatic environment [*Battin et al.*, 2008]. Stream networks draining peatlands and forests in boreal regions are often supersaturated in CO_2 mainly due to the close connectivity to organic-rich soils [*Hope et al.*, 2004; *Dinsmore and Billett*, 2008; *Wallin et al.*, 2010], thus the potential for significant evasion of CO_2 of terrestrial origin is high. Initial studies [*Kling et al.*, 1991; *Hope et al.*, 2001; *Öquist et al.*, 2009; *Dinsmore et al.*, 2010] suggest that evasion

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from streams is likely to be a significant term in C budgets of the arctic tundra, peatlands and boreal forest systems. Furthermore, *Öquist et al.* [2009] estimated the average "half life" of terrestrially derived dissolved inorganic carbon (DIC) entering a headwater stream to be 5.5 h, equal to the annual average time it took water to flow 400 m downstream. Even though this was estimated for a specific stream it indicates that the rapid evasion will cause that this part of the aquatic C pool will not likely reach rivers or lakes. In addition, small streams typically comprise the majority of stream length in a given area. For instance, headwater streams (catchment areas < 15 km^2) comprise 90% of the total stream length in Sweden [*Bishop et al.*, 2008]. Hence it is important that evasion rates from low-order stream systems are included in budget estimates and that the appropriate parameters needed are measured or modeled accurately.

[3] Collectively the partial pressure of an individual gas and its exchange ability at the water-atmosphere interface control its evasion rate to the atmosphere from surface waters [*Macintyre et al.*, 1995]. Several methods have been used to determine gas evasion rates from surface waters. Floating chambers and eddy covariance techniques directly measure gas exchange between water and the atmosphere. Floating chambers have been widely used on estuaries [*Borges et al.*, 2004], reservoirs/ponds [*Huttunen et al.*, 2002a, 2002b] and streams [*Billett et al.*, 2006; *Billett and Moore*, 2008], but have been criticized because they are likely to underestimate the evasion rate by removing the wind effect and also reducing water surface turbulence [*Raymond and Cole*, 2001]. The eddy covariance technique has successively been used on lakes [*Vesala et al.*, 2006; *Jonsson et al.*, 2008] but requires a large open water surface fetch-area around the point of measurement and is therefore not suitable for most streams.

[4] A third method that has been widely used to determine various evasion rates for all types of inland surface waters is the tracer gas method [*Wanninkhof et al.*, 1990; *Cole and Caraco*, 1998; *Hope et al.*, 2001; *Maprani et al.*, 2005]. The method involves an injection of an inert volatile gas tracer not naturally occurring in the water system (e.g., C_3H_8, SF_6, CH_3Cl) and aims to determine the gas exchange ability across the water-atmosphere interface. In lentic systems (lakes, reservoirs, estuaries and oceans) this ability is often described as the gas transfer velocity or piston velocity (here and throughout given as K_{TV}). Gas transfer velocity is defined as the height of water that equilibrates with the atmosphere per unit time (often expressed in cm h^{-1}) for a given gas at given temperature [*Cole and Caraco*, 1998; *Frankignoulle et al.*, 1998; *Raymond and Cole*, 2001]. In lotic systems (streams and rivers) where the channel depth often is hard to define, the gas transfer coefficient (here and throughout given as K_{TC}) is often used. K_{TC} is defined as the portion of the tracer gas that is lost over a specific reach per unit time. The relationship between K_{TV} and K_{TC} is defined as $K_{TC} = K_{TV}/z$, where z for lotic systems is the average channel depth [*Genereux and Hemond*, 1992; *Macintyre et al.*, 1995].

[5] The use of gas tracers in streams and rivers was first developed, and has been widely used, for determining reaeration of the water system where K_{TC} applies to the rate of oxygen uptake [*Bennett and Rathbun*, 1972; *Wanninkhof et al.*, 1990; *Marzolf et al.*, 1994]. Because morphological and hydrological conditions in most streams and rivers are dynamic, K_{TC} is an integrated measure of the gas exchange ability over a specific stream reach at a point in time (often expressed in min^{-1}). The measured K_{TV} or K_{TC} for the specific tracer gas used must be converted to the gas of interest (O_2, CO_2, CH_4 etc.), since the physical properties of the tracer and the gas of interest usually are different. The correction is made using the specific diffusion coefficients (d_x) for both the tracer and the studied gas [*Bennett and Rathbun*, 1972; *Jähne et al.*, 1987].

[6] Due to the difference between lentic and lotic systems it is difficult to apply methods developed for lakes or even worse, oceans, to sheltered first order forest streams. However, due to the lack of information on exchange rates of CO_2 in systems with running water, there are a number of examples where methods developed for lentic systems are used to estimate CO_2 exchange from streams to the atmosphere. There are only a few occasions where different approaches have been compared, but a wind speed based method to estimate K_{TV} developed for lentic systems [*Wanninkhof*, 1992] generally underestimated the CO_2 evasion (based on chamber measurements) from streams draining the Mer Bleue peatland (Ontario, Canada) [*Billett and Moore*, 2008]. The main driver for variability in gas exchange in open water systems besides the water-atmosphere concentration gradient is often concluded to be wind speed over the water surface [*Wanninkhof*, 1992; *Borges et al.*, 2004]. The corresponding main driver for streams is water turbulence created by variations in discharge and stream morphology [*Tsivoglou and Neal*, 1976; *Wanninkhof et al.*, 1990; *Hope et al.*, 2001]. Hence there is clearly a need to better understand and predict variability in gas exchange between low order stream networks and the atmosphere. This is also recognized in several studies carried out at the landscape scale, where this term is estimated or modeled from literature values without empirical field validation [*Jonsson et al.*, 2007; *Teodoru et al.*, 2009; *Humborg et al.*, 2010].

[7] A number of studies have used injections of gas tracers to measure K_{TC} for CH_4 and CO_2 in small streams [*Wanninkhof et al.*, 1990; *Jones and Mulholland*, 1998; *Hope et al.*, 2001; *Öquist et al.*, 2009]. Although the majority of those studies focused on just one stream the results have sometimes been used as the basis for regional (upscaled) estimates. Here we present the first in-depth study of measured (n = 114) K_{CO2} values from 14 different streams in a boreal stream network, and then use these results to model the K_{CO2} of the entire length of perennial streams (stream order 1–4) in boreal/nemoral forested Sweden. This provides a basis for producing realistic, upscaled estimates of evasion fluxes from large landscape units. This study specifically aimed to;

[8] 1) quantify spatial and temporal variability in the gas transfer coefficient of CO_2 (K_{CO2}) within a boreal stream network,

[9] 2) explore relationships of K_{CO2} to physical parameters that might be used to make continuous spatial and temporal estimates of K_{CO2},

[10] 3) define the relative importance of variability in K_{CO2} and pCO_2 for estimating CO_2 evasion from boreal streams, and

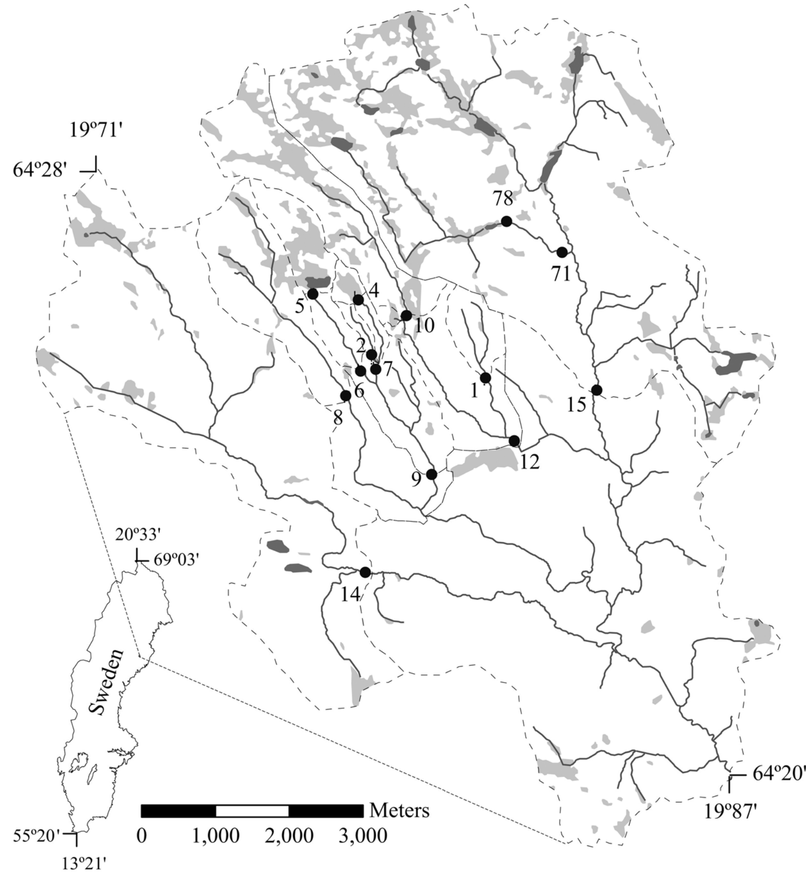

Figure 1. The Krycklan catchment with the stream network and location of the sampled stream reaches (black dots). Lakes are in dark grey and peatlands in light grey.

[11] 4) upscale the results and predict the K_{CO2} for all 300,000 km of perennial running waters (stream order 1–4) in the boreal/nemoral forested area of Sweden

2. Site Description

[12] The field study was conducted within the upper 67 km^2 of the Krycklan catchment, which is situated ca. 60 km northwest of Umeå, in northern Sweden (Figure 1). The area is well documented since it is a part of the Vindeln Experimental Forests, established in 1923 (http://vfp.esf.slu.se), and stream water chemistry has been monitored regularly from one subcatchment for more than 25 years [*Bishop et al.*, 1990; *Köhler et al.*, 2008]. The catchment stream network is typical of forested catchments in Scandinavia. The average length of the growing season is 152 days (1997–2007) and snow covers the ground from the end of October to the end of April. Annual mean precipitation is 600 mm (about 35% falls as snow) and ~50% of this is lost as runoff; annual daily mean temperature is 1.3°C [*Ottosson Löfvenius et al.*, 2003]. Elevation range in the catchment is 126 to 369 m a.s.l. The catchment is mainly forested with Norway spruce (*Picea abies, L*) and Scots pine (*Pinus sylvestris, L*), with deciduous trees commonly found in the riparian zone of 3rd and 4th order 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 (1st and 2nd order streams). 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 [*Ågren et al.*, 2007].

[13] Data from 14 stream sites ranging in subcatchment area from 0.03 to 19.7 km^2 are presented in this study (Figure 1). The main land cover elements in the subcatchments are forest and peatland (Table 1). Stream order ranges from 1st to 4th order with a typical annual pH range of 3.7–6.3 in headwaters and 5.7–7.4 in 4th order streams. Typical 1st order stream carbon concentrations are; dissolved organic carbon (DOC); 5.0–40.0 mg L^{-1} and dissolved inorganic carbon (DIC); 0.5–25.0 mg L^{-1} with the majority of the DIC (>90%) in the form of CO_2. Corresponding concentration ranges in 4th order streams are DOC; 5.0–15.0 mg L^{-1} and DIC; 1.0–5.0 mg L^{-1} with ~50% of the DIC in the form of CO_2. Furthermore, lowest pH and highest DOC and DIC concentrations are seen in streams characterized by a high proportion of peatland (30–75%) in the catchment [*Buffam et al.*, 2007; *Wallin et al.*, 2010]. More detailed descriptions of the sites and stream chemistry dynamics can be found in the work of *Buffam* [2007], *Wallin et al.* [2010] and *Björkvald et al.* [2008].

3. Methods

3.1. Field Procedures

[14] The gas transfer coefficient (K_{CO2}) was determined using a volatile gas tracer, propane (C_3H_8) previously used

Table 1. Characteristics of the Subcatchments and Stream Reaches for the 14 Sampling Sites[a]

	Catchment Characteristics							Stream Reach Characteristics			
Site	Catchment Area (km^2)	Stream Density (km/km^2)	Total Upstream Stream Length Above Sampling Location (km)	Forest (%)	Peatland (%)	Lake (%)	Arable (%)	Stream Order	Reach Length (m)	Stream Slope (%)	Altitude[b] (m a.s.l.)
1	0.7	2.9	2.0	98.7	1.3	0	0	1	30	6.8	227
2	0.1	8.0[c]	0.8[c]	100.0	0	0	0	1	21	3.8	247
4	0.2	0.2	0.03	59.6	40.4	0	0	1	22	2.1	282
5	0.8	0.03	0.02	59.0	36.3	4.7	0	1	35	3.7	286
6	1.3	1.1	1.4	72.8	24.1	3.1	0	1	27	0.2	236
7	0.5	3.8	1.9	85.1	14.9	0	0	2	22	4.4	245
8	2.5	1.9	4.8	87.8	12.2	0	0	2	18	1.8	234
9	3.1	2.4	7.5	84.9	13.8	1.3	0	3	21	1.2	184
10	2.9	0.9	3.0	74.2	25.8	0	0	3	22	3.3	256
12	5.4	1.5	8.7	84.1	15.5	0	0.3	3	19	0.4	184
14	13.6	1.2	14.5	90.4	5.1	0.6	3.9	3	21	1.5	172
15	19.7	1.4	27.4	83.2	14.0	1.7	1.0	4	25	5.8	181
71	3.8	1.7	6.3	79.0	14.8	1.4	0	2	16	2.5	225
78	3.3	1.5	5.2	79.7	15.9	1.5	0	2	16	0.5	245

[a]Proportion of land cover elements are given as % of the subcatchment area.
[b]Determined at the lower end of the stream reach.
[c]Manually determined since the stream is not on maps.

in several similar studies [*Genereux and Hemond*, 1992; *Hope et al.*, 2001; *Maprani et al.*, 2005; *Öquist et al.*, 2009]. A total of 114 propane injections were made during 2006 and 2007 at 14 different stream reaches (16–35 m long) spread over the catchment and under different discharge conditions. The stream reaches were typical of the sites and included a range of pools and sections with high turbulence to make sure the geomorphological heterogeneity of the stream network was captured. This was supported by more than 50 chamber measurements to show the wide range of small scale spatial variability in CO_2 evasion that occurred within the stream reaches [*Ingvarsson*, 2008]. The number of injections at each site varied between 3 and 20, with the majority of the injections carried out in 2nd order streams. This was due to practical difficulties of using the tracer method in smaller 1st order streams during low summer discharge (slow mixing) and in 3rd or 4th order streams during high discharge events (incomplete mixing). Despite the practical difficulties in performing tracer injections at discharge extremes, we covered a wide hydrological range valid for more than 90% of the range in daily discharge in 1st to 3rd order streams and 70% of the time in the 4th order stream. This analysis was based on frequency analysis of almost 30 years of daily specific discharge at one of the sites in this study (site 7) (unpublished data, 2010).

[15] Prior to propane injection a pulse injection of NaCl was made to measure stream reach discharge (Q), travel time (τ) and potential groundwater inputs along the reach. Electrical conductivity (EC) was measured at each end of the reach using a system of duplicate CS547A probes connected to a CR10X data logger (both EC probes and logger, Campbell Scientific Inc). Water travel time within the reach was taken as the difference in time between maximum EC at the upper and lower reach end. The net effect of groundwater inputs between the stream and the riparian zone was determined by comparing the integral of the EC curves over time (equal to the difference in stream discharge) between the upper and lower reach ends. The mean difference in stream discharge between the upper and lower reach end was 0.5% (90th percentile; 4%). Since the precision of the pulse injection method is concluded to be 5% [*Day*, 1976], it was not sufficient to measure differences in discharge along the study reaches. An area specific discharge increase was used instead and added to equation (1) to compensate for any dilution by groundwater inputs. The mean difference in discharge between the upper and lower reach end using area specific discharge increase was 0.8% (90th percentile; 2%). Propane (Airliquid, Malmö, Sweden) from 6 or 10 kg cylinders was injected 10–20 m upstream from start of the stream reach through an air curtain (a 60 cm long perforated plastic tube creating fine bubbles; Karlie, Haaren, Germany) with a constant rate at a fixed pressure set to 0.8–1.4 bar (injection rates were linked to stream discharge). Propane was injected for 10–25 min (depending on reach travel time) prior to sampling to achieve steady state within the reach. Stream samples were taken at each end of the stream reach. The difference in sampling time between each pair of upstream and downstream samples was set equal to the reach travel time in order to sample the same water mass. The procedure was repeated two or three times at each sampling occasion. To measure in-stream concentrations of propane and DIC (and pCO_2) simultaneously, a stream water sample of 5 ml of bubble-free water was collected and immediately injected using a syringe into a 22.5 ml glass vial (containing N_2 at atmospheric pressure) sealed with a bromobutyl rubber septa. The vial was pre-filled with 0.5 ml of 0.6% HCl in order to shift the carbonate equilibrium toward CO_2. Further descriptions of the headspace method are described by *Wallin et al.* [2010] and *Wallin* [2011].

[16] Measurements of depth and width of the stream reach were made manually at the time of each tracer injection. Stream depth and width were measured at meter intervals along the stream reach; stream depth was calculated from 3 to 5 measurements evenly distributed across the stream profile. Median values of stream depth and width for the whole stream reach were calculated for each tracer injection. The slope (%) of the stream was calculated as the elevation

difference over the length of the stream reach. The elevation difference at each stream reach was determined using a rotary laser (DeWalt, DW074K) with a precision of 1–2 cm. Figures of catchment characteristics and percent of various land cover types (Table 1) were used from, or determined according to, *Buffam et al.* [2007] and *Ågren et al.* [2007].

3.2. Laboratory Procedures

[17] Headspace propane and 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 autosampler (HS40). Separation was carried out on a Heysep Q column using N_2 (40 ml min^{-1}) as carrier gas [*Öquist et al.*, 2009; *Wallin et al.*, 2010]. The precision of propane and CO_2 sampling and analysis were estimated to average 10% (SD), based on replicate sampling [*Nilsson et al.*, 2008; *Öquist et al.*, 2009]. The pH was always measured within 24 h of sampling 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 non-air equilibrated sample. The precision of the pH determination was within 0.1 pH units of closed cell pH [*Buffam et al.*, 2007].

3.3. Calculations

[18] The gas transfer coefficient for propane (K_{C3H8}) was calculated according to [*Genereux and Hemond*, 1990], with the modification that differences in streamflow instead of electrical conductivity between upper and lower ends of the stream reach were used to compensate for any tracer gas dilution by inflowing groundwater.

$$K_{C_3H_8} = \frac{1}{\tau} \times \ln\left(\frac{[C_3H_8]_U \times Q_U}{[C_3H_8]_L \times Q_L}\right) \tag{1}$$

where τ is the reach travel time (min), $[C_3H_8]_U$ and $[C_3H_8]_L$ are the relative concentrations of propane at the upper and lower sampling reach end, respectively and Q_U and Q_L are the discharge (L s^{-1}) at the upper and lower end of the sampling reach. We used the average discharge over the entire reach with the dilution effect corresponding to the increase in catchment area between the upper and lower reach end (ranging from 0.1 to 2% among the 14 sites according to catchment areas determined with a LIDAR-based digital elevation model [*Grabs*, 2010]).

[19] The K_{C3H8} value is then converted to K_{CO2} according to *Jones and Mulholland* [1998].

$$K_{CO_2} = K_{C_3H_8}\left(\frac{d_{CO_2}}{d_{C_3H_8}}\right)^n \tag{2}$$

where the coefficient *n* describes the characteristics of the water surface [*Macintyre et al.*, 1995]; here the value was set to 0.5. There is substantial variability among the possible range in *n* given in the literature. *Genereux and Hemond* [1992] give a range of $0.5 \leq n \leq 1$, whereas *Hope et al.* [2001] state that the range in *n* can vary from −0.66 to unity. Our use of a fixed value of *n* (0.5) is probably conservative since the turbulence conditions are variable among the investigated stream reaches. The sensitivity in the calculated K_{CO2} is ±~1.5% per 0.1 change in *n*. d_{CO2} and d_{C3H8} are the respective gas diffusion coefficients calculated from temperature dependent equations based on data by *Jähne et al.* [1987] (equation (3)) and *Wise and Houghton* [1966] (equation (4)), where T is stream temperature (°C).

$$d_{CO_2} = 0.9477\exp^{(0.0274T)} \tag{3}$$

$$d_{C_3H_8} = 1.092\exp^{(0.0235T)} \tag{4}$$

Since gas transfer coefficients are influenced by temperature, K_{CO2} values were normalized for temperature effects when determining spatial and temporal variability. The K_{CO2} values were corrected to 20°C (equation (5)).

$$K_{CO2}(20^\circ) = K_{CO2}(T)\theta^{(20-T)} \tag{5}$$

where T is the water temperature of the stream reach of interest. The value of θ was set to 1.01 based on literature values of reaeration [*Metzger and Dobbins*, 1967]. Normalized K_{CO2} values are used henceforth in all text, figures and tables except for Table 1.

[20] Stream water DIC concentration and pCO_2 were calculated from GC-determined headspace pCO_2 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 method can be found in the work of *Wallin et al.* [2010].

[21] The evasion rate in μmol s^{-1} was calculated by using the flux equation first proposed for reaeration by *Young and Huryn* [1998] and used for determining stream CO_2 evasion [*Hope et al.*, 2001; *Billett et al.*, 2004; *Öquist et al.*, 2009].

$$CO_{2_{ev}} = CO_{2_{str-atm}} \times K_{CO_2} \times \tau \times Q \tag{6}$$

$CO_{2_{str-atm}}$ is the difference between stream CO_2 concentration and the concentration that would exist if the stream were in equilibrium with the atmosphere (μmol L^{-1}), K_{CO2} is the gas specific transfer coefficient (min^{-1}), τ is the reach travel time (min), and Q is the stream discharge (L s^{-1}). Area specific CO_2 evasion was calculated by dividing the evasion rate with the stream reach surface area (m^2).

3.4. Statistical Analysis

[22] Correlation matrices were constructed with catchment characteristics, stream reach characteristics and physical/chemical variables (Tables 1 and 2). A number of physical measures of the stream channels were also incorporated in the analysis (water volume, water surface area etc.). The significance of each correlation was tested using the non-parametric Spearman's rank correlation test; correlations were considered significant if $p < 0.05$. Least square linear regression analysis was used to explore and model simple temporal and spatial relationships. Coefficient of variation (CV) was used to describe both temporal and spatial variability in K_{CO2}. Uncertainty in the CV determination related to the use of a fixed value for the coefficient *n* in equation (2) was estimated to be <5%. Stepwise multiple linear regressions (MLR) was used to model spatial variability in median

Table 2. Stream Channel Geometry, Physical Stream Parameters, and Evasion Rates at the 14 Stream Reaches[a]

		Stream Channel Geometry			Physical Stream Parameters						CO_2 Supersaturation and Evasion Rates		
Site	n	Reach Width (cm)	Reach Depth (cm)	Width/Depth Index	Temperature (°C)	Reach Travel Time (min)	Discharge (L s^{-1})	Specific Discharge (mm day^{-1})	Velocity (m min^{-1})	K_{CO2} (min^{-1})	pCO_2 (µatm)	CO_2 Evasion (µmol L^{-1})	CO_2 Evasion[b] (µg C m^{-2} s^{-1})
1	8	66	9	7.8	5.3 (1.3–7.5)	2.44–6.28	5.9 (2.4–9.4)	0.7 (0.3–1.2)	7.4 (4.6–11.0)	0.104 (0.090–0.123)	713–894	8.3–15.1	21.2–54.5
2	8	39	12	3.2	1.1 (0.1–6.1)	1.36–19.24	3.0 (0.4–11.0)	2.0 (0.3–7.3)	3.9 (1.1–13.1)	0.034 (0.023–0.067)	1364–3713	7.4–118.7	55.6–116.9
4	6	50	10	4.8	2.7 (0.1–6.7)	2.00–11.04	2.7 (1.4–15.1)	1.2 (0.7–6.9)	3.5 (2.0–11.0)	0.030 (0.017–0.071)	3504–6141	25.1–95.2	71.0–529.8
5	3	49	18	2.7	4.8 (4.8–5.6)	3.08–5.44	14.4 (8.7–19.0)	1.5 (0.9–1.9)	9.0 (6.1–11.2)	0.055 (0.045–0.068)	1985–5019	25.6–63.7	152.2–810.5
6	11	72	23	3.1	3.4 (1.1–8.3)	1.28–3.32	33.9 (12.2–83.3)	2.3 (0.8–5.5)	14.4 (7.6–18.4)	0.009 (0.001–0.025)	1043–1314	0.2–2.9	1.9–66.9
7	11	54	9	6.0	5.7 (0.4–10.2)	0.52–15.00	7.0 (1.6–41.4)	1.2 (0.1–7.2)	6.0 (0.7–25.3)	0.059 (0.006–0.201)	1116–1891	1.0–28.9	9.5–578.4
8	20	63	16	4.2	8.0 (0.4–11.0)	0.48–8.32	12.1 (0.9–97.8)	0.4 (0.1–3.4)	8.0 (2.1–22.5)	0.016 (0.001–0.044)	1082–3383	0.1–29.8	3.3–100.9
9	11	82	17	4.8	5.8 (1.3–8.1)	1.24–5.24	45.0 (5.0–134.5)	1.3 (0.1–3.8)	4.9 (3.9–15.0)	0.040 (0.018–0.207)	1033–2262	1.6–16.8	26.5–1625.8
10	13	78	23	3.4	7.6 (−0.1–10.9)	1.00–8.00	24.3 (2.5–104.5)	0.7 (0.1–3.1)	8.7 (2.8–22.0)	0.027 (0.009–0.048)	1234–3725	1.9–25.4	31.4–419.8
12	5	122	25	4.9	5.5 (3.2–13.4)	1.24–7.24	35.0 (2.3–90.9)	0.6 (0.1–1.5)	8.6 (2.6–13.6)	0.011 (0.004–0.038)	756–2035	0.6–2.5	3.2–96.6
14	3	127	60	2.1	5.3 (4.1–12.5)	2.12–3.08	71.8 (7.8–114.0)	0.5 (0.1–0.7)	7.3 (6.7–9.5)	0.033 (0.009–0.042)	1106–2232	0.9–11.9	48.9–75.5
15	5	162	22	8.1	10.5 (3.0–11.9)	1.08–4.32	38.6 (22.6–154.1)	0.2 (0.1–0.7)	8.4 (5.7–21.2)	0.085 (0.047–0.180)	910–1667	7.4–16.8	100.1–228.7
71	5	90	10	9.0	11.9 (10.5–12.5)	2.52–6.08	5.3 (4.1–7.8)	0.1 (0.1–0.2)	3.7 (2.3–5.6)	0.031 (0.010–0.060)	1700–2112	3.9–14.5	17.1–78.1
78	5	135	8	16.9	15.2 (14.9–18.6)	2.24–5.24	4.1 (1.9–5.8)	0.1 (0.1–0.2)	4.1 (3.0–6.7)	0.040 (0.010–0.073)	4860–6253	7.6–48.8	22.7–122.7

[a]Median values are given for parameters with range in parenthesis.
[b]CO_2 evasion rates expressed per unit water surface area.

K_{CO2} based on variables of interest derived from the correlation matrices. All variables used in the MLR-analysis were normally distributed according to the Shapiro Wilks W test. A "leave one out" cross-validation approach was used to evaluate the performance of the MLR-model [*Hope et al.*, 1997]. In this procedure one stream reach at a time was excluded in the regression analysis and refitted models were made to predict median K_{CO2} of the missing stream reach. The average sum of squares for the difference between predicted and measured values was given as the degree of prediction of the model. JMP 8.0.1 (SAS Institute Inc., Cary, NC, USA) was used for all statistical calculations.

3.5. Slope Determination of Running Waters Across Sweden

[23] The official digital hydrography for Sweden (1:250.000 scale) covers only about half of the perennial stream length [*Bishop et al.*, 2008]. To define the entire network of running waters, a virtual stream network, VIVAN [*Nisell et al.*, 2007], was derived from the national digital elevation model (50 × 50 m), with hydrography from the Swedish road map (1:100.000 scale) and subcatchment boundaries according to the Swedish Metrological and Hydrological Institute (SMHI). This was done to extend the digital stream network to include the full length of perennial running waters on the assumption that stream initiation occurred at a threshold value of accumulated catchment area (see *Nisell et al.* [2007] for more details). Stream length, catchment area, Strahler stream order and slope were derived from VIVAN for each segment of running waters. The median segment length was ~650 m and slope was defined as the elevation difference (m) between the highest and the lowest point of each stream segment divided by the stream length (m) and expressed in %. Land use for each stream segment was defined as the major land use class within a 50 m buffer zone around the segment. The slopes were then used to predict median K_{CO2} for each stream segment in streams (stream order 1–4) (i.e., for segments with land use forest or peatland) according to the equation in the caption of Figure 2b. Stream segments with other land use types (area above tree line and agricultural dominated areas) were not included in the analysis because the conditions in these areas could be different from those where K_{CO2} were determined in field.

4. Results

4.1. Discharge, Stream Channel Geometry, and Reach Travel Time

[24] Discharge ranged from 0.4 to 154.1 L s^{-1} across all tracer injections, which corresponded to a specific discharge range of 0.1 to 7.2 mm day^{-1} when considering the site specific catchment area (Table 2). Median specific discharge for the measurements at the 14 sites ranged from 0.1 to 2.5 mm day^{-1}.

[25] Median stream reach width (w) and depth (z) ranged from 40 to 180 cm and from 5 to 55 cm respectively, with stream width generally increasing with stream order (Table 2). Median stream depth was spatially more unpredictable and showed no correlation with stream order or width. On a temporal scale discharge correlated positively with both

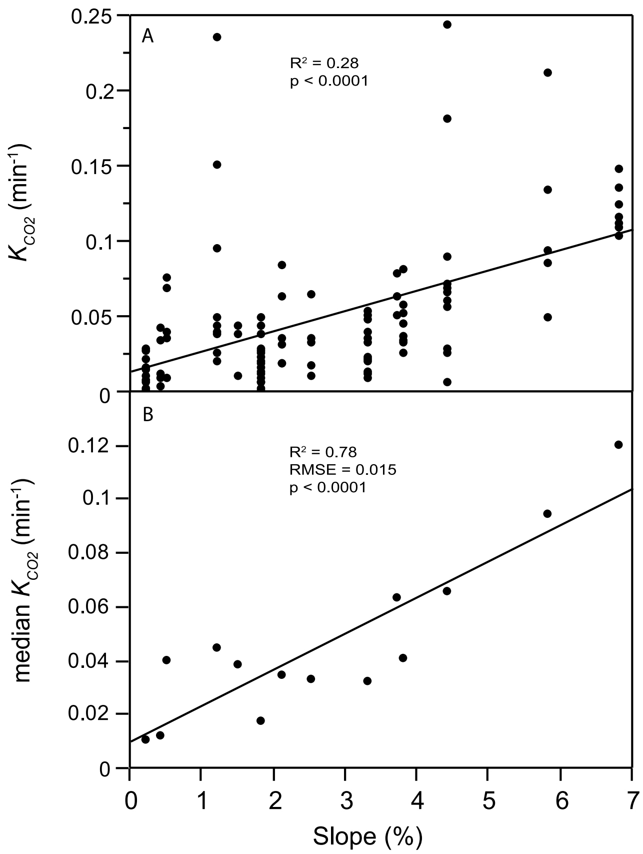

Figure 2. (a) Measured values (n=114) of the gas transfer coefficient of CO_2 (K_{CO2}) (min^{-1}) as a function of slope (%) of the stream reach (K_{CO2} = 0.014 × Slope + 0.022), (b) Median gas transfer coefficient of CO_2 (K_{CO2}) (min^{-1}) as a function of slope (%) of the stream reach (K_{CO2} = 0.017 × Slope + 0.018). Numbers of measurements for each median value of K_{CO2} are shown in Table 2. All K_{CO2} values are normalized to 20 °C.

median stream depth (R = 0.94) and width (R = 0.95; given as an average R for all 14 sites). The median stream reach depth at site 14 was much deeper (55 cm) compared to the rest of the stream reaches, which had median depths ranging from 5 to 25 cm. Median w/z ratio was used as an index of stream channel geometry and ranged from 2.7 to 16.6 across the 14 sites. The w/z index was strongly correlated with specific discharge (R > 0.90) at 10 of the 14 sites (Table 3). Stream channel geometry expressed as a w/z index was also significantly correlated to discharge when all the individual tracer injections were combined, with a decrease in index with increased discharge (Figure 3).

[26] Reach travel times for the different stream reaches ranged from 0.52 to 19.24 min depending on hydrological conditions, with most between 1.54 and 5.20 min (25th and 75th percentile; Table 2). The reach travel time was negatively correlated with specific discharge at 12 of the 14 sites (R > 0.90). The reach travel times normalized for stream reach length ranged from 0.04 to 0.92 min m^{-1} among all sites. Normalized reach travel time also had a significant negative relationship to specific discharge when combining all individual tracer injections (Figure 3).

4.2. pCO_2

[27] All stream reaches were consistently supersaturated in CO_2 with pCO_2 values ranging from 713 to 6253 μatm (Table 2), equal to a supersaturation of 1.9–16.5 times with respect to atmospheric equilibrium (assuming an atmospheric concentration of 380 μatm). The highest values were found in the headwater streams closely connected to peatlands and lakes (sites 4, 5 and 78). Median pCO_2 decreased with increasing stream order (SO); SO 1, 1961 μatm → SO 2, 1718 μatm → SO 3, 1553 μatm → SO 4, 1308 μatm).

4.3. K_{CO2}

[28] The values of K_{CO2} from all individual measurements ranged from 0.001 to 0.207 min^{-1} among the 14 sites (Table 2 and Figure 2a). The highest median K_{CO2} values were observed in sites 1 and 15 (0.104 and 0.085 min^{-1} respectively), whereas the lowest were found in sites 6 and 12 (0.009 and 0.011 min^{-1} respectively).

4.4. Spatial variability of K_{CO2}

[29] The spatial variability of K_{CO2} (normalized to 20°C) expressed as the coefficient of variation of site median K_{CO2} values was 66%. According to the correlation matrices stream reach slope was the only variable that significantly correlated with median K_{CO2} (R = 0.75), with higher gas exchange potential associated with steeper stream sections. Slope explained 78% of the between site variability in median K_{CO2} according to least square linear regression analysis (Figure 2b). In addition to slope, the ratios width/depth (w/z) and 1/depth (1/z) (equal to water surface area/water volume) were related to median K_{CO2} even though they were not statistically significant (R = 0.48, p = 0.11 and R = 0.53, p = 0.09 respectively). Since w/z and 1/z are not independent variables they were combined separately with slope in MLR analysis, with resulting models that explained 83% and 78% of the variability in median K_{CO2} for w/z and 1/z, respectively. Slope together with w/z were used in the final model (equation (7) and Figure 4) due to the higher degree of explanation combined with a lower root mean square error (RMSE) (0.014, slope + w/z; 0.015, slope + 1/z).

$$\text{median}\, K_{CO2} = 0.013 \times \text{Slope} + 0.002 \times \text{w/z} - 0.000003 \quad (7)$$

where K_{CO2} is the gas transfer coefficient normalized for 20°C (min^{-1}), slope is the gradient (%) of the stream reach, and w/z is the ratio of mean width over mean depth for each stream reach. The "leave one out" cross-validation of the model produced an average sum of squares of 0.0007 and with refitted models ranging in R^2 from 0.74 to 0.88. The improvement of the model by including w/z index compared to using slope as a single explanatory variable was mainly an effect of site 78, that showed a high median K_{CO2} despite a relatively flat stream reach (slope = 0.5%) (Figure 2b). The median w/z index for site 78 was 16.9 and far exceeded the rest of the stream reaches studied (Table 2). By excluding site 78 in the least square linear regression analysis with slope as the only explanatory variable, the model explained 83% of the variability in between site median K_{CO2}. The performance of this model was similar to the MLR model (Figure 4), but using just slope as an explanatory variable excludes an important stream morphology type (wide and

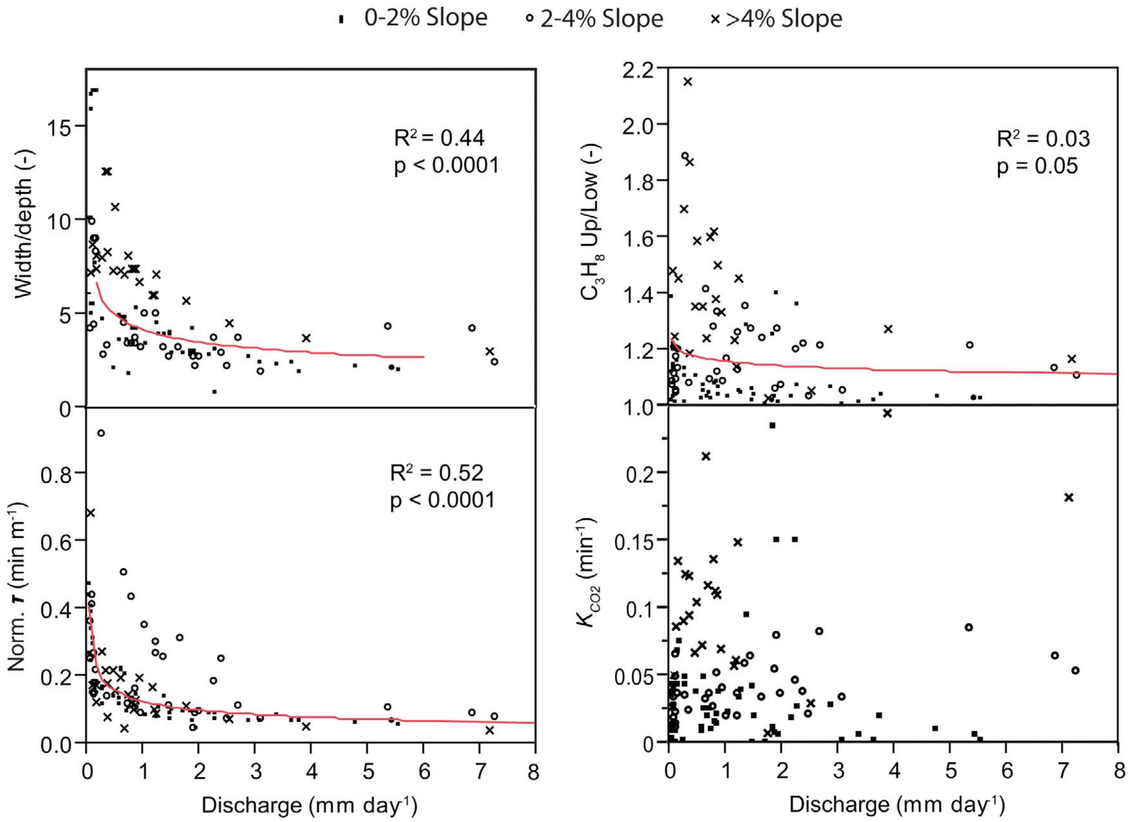

Figure 3. Stream width/depth index, normalized reach travel time, ratio in relative C_3H_8 concentration between the upstream and the downstream stream reach ends and K_{CO2} as a function of specific discharge. Regressions are given for the entire data set but individual data points are given according to three different slope classes, filled circles; 0–2 % slope (n = 55), open circles; 2–4 % slope (n = 35), and crosses; > 4 % slope (n = 24). The significant correlations shown are based on ln-transformed x and y (p < 0.05).

shallow streams). Hence equation (7) was chosen as being more representative for stream systems with these characteristics.

4.5. Temporal Variability of K_{CO2} and Tracer Loss

[30] Temporal variability of K_{CO2} (normalized to 20°C) expressed as a coefficient of variation (CV) ranged from

Table 3. Spearman's Rank Correlation Coefficients Between a Number of Variables and ln-Transformed Specific Discharge (mm day^{-1})[a]

Site	Width/Depth (-)	τ (min)	C_3H_8 Loss (-)	K_{CO2}[b] (min^{-1})
1	−0.97*	−0.93*	−0.83*	0.10
2	−0.01	−0.95*	−0.90*	0.60
4	−0.58	−0.94*	−0.37	0.71
5[c]	−1.0*	−1.0*	−0.50	1.0*
6	−0.90*	−0.95*	−0.55	−0.36
7	−0.94*	−0.99*	−0.81*	0.21
8	−0.99*	−0.96*	−0.73*	−0.43
9	−0.92*	0.05	0.26	0.30
10	−0.89*	−0.94*	0.42	0.46
12	−0.97*	−0.90*	0.90*	0.90*
14[c]	−1.0*	−1.0*	−1.0*	−1.0*
15	−0.70	−0.97*	−0.50	0.90*
71	−0.95*	−0.80	−0.20	0.50
78	0.78	−0.90*	−0.20	0.70

[a]Significant correlations (p < 0.05) are marked with *.
[b]Values are normalized to 20°C.
[c]Correlations based on three values.

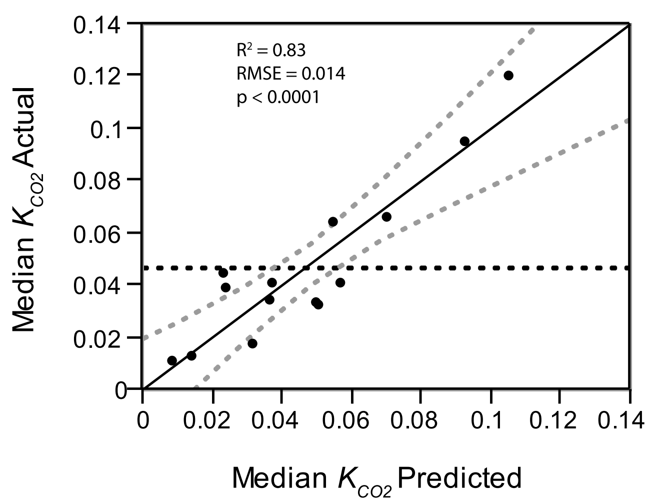

Figure 4. Measured versus MLR-modeled values of median gas transfer coefficient for CO_2 (K_{CO2}) normalized to 20 °C from the for the 14 stream reaches. Predicting variables were slope of the stream reach (%) and the ratio median stream width over median stream depth (-). Confidence interval is given by grey hatched lines and mean value of the medians is given in black hatched line.

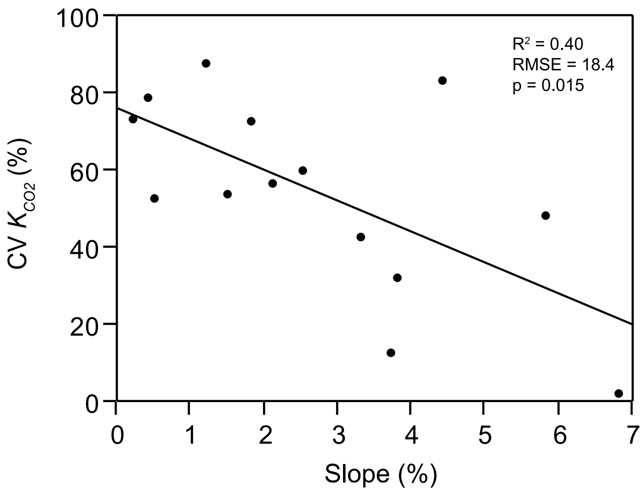

Figure 5. Coefficient of variation, CV (%), for normalized K_{CO2} values to 20°C as a function of slope of the stream reach (%). Least square linear regression: CV K_{CO2} = - 8.4 × Slope + 80.0.

12% to 89% across the 14 stream reaches with a median CV of 60%. Temporal variability was negatively correlated with stream reach slope with a least square linear regression model that explained 40% of the variation in CV between the sites (Figure 5). At four sites the specific discharge significantly explained some of the variability in K_{CO2}, but correlations were both positive and negative (site 5, R = 1.0; site 12, R = 0.90; site 14, R = −1.0 and site 15, R = 0.90; Table 3).

[31] In order to explore temporal variability further we used the loss of tracer gas (C_3H_8) over the stream reach (ratio of relative C_3H_8 concentration between the upper and lower ends of the stream reach) which is related to K_{CO2} [*Öquist et al.*, 2009]. The downstream loss of C_3H_8 showed significant correlations to specific discharge for six of the 14 sites; these six sites were located in 1st, 2nd as well as in 3rd order streams (Table 3). It was noticeable that both positive (site 5, 12 and 15) and negative (sites 1, 2, 7, 8 and 14) discharge dependent correlations were found for C_3H_8 loss or K_{CO2}. Discharge dependent correlation for both C_3H_8 loss and K_{CO2} were only found at sites 12 and 14.

4.6. Importance of K_{CO2} for CO_2 Evasion

[32] Instantaneous CO_2 evasion rates ranged from 1.9 to 1625.8 μg C m^{-2} s^{-1} across all sites (Table 2). The variability in K_{CO2} generally explained >80% of the variability in evasion rate with a smaller component of the variability related to pCO$_2$ (Table 4). There were however two exceptions found at headwater sites 1 and 2, where CO_2 evasion rates were more closely linked to variability in pCO$_2$ (R = 0.86 and R = 0.69 respectively). The variability (CV) across the 14 sites was similar for K_{CO2} and instantaneous CO_2 evasion rate, but less for pCO$_2$ (data not shown).

4.7. Upscaling of K_{CO2}

[33] We used the model of median K_{CO2} (equation in Figure 2b) to upscale the results from the Krycklan catchment to the whole of the forested area of boreal/nemoral Sweden. This was based on modeling a median K_{CO2} for each unique stream segment (Table 5). In the absence of width and depth data for the whole Swedish stream network, slope was used as the single predicting variable. Median K_{CO2} was highest in the 1st order streams which comprise the majority of the length in the network of running waters. There was a clear gradient in decreasing K_{CO2} with higher stream orders. The spatial variability (CV) in median K_{CO2} was almost 40% higher in the 1st order compared to the 4th order streams (82 and 59% respectively).

5. Discussion

[34] Understanding what controls the spatial and temporal variability of gas transfer coefficients (K_{CO2}) is a key step in quantifying the importance of CO_2 evasion from streams in terms of the landscape C budget. Even though tracer data from reaeration studies can be used for estimating K_{CO2}, the number of K_{CO2} values reported in the literature is very limited and even fewer publications address the issue of K_{CO2} variability in time and space and link these to measured pCO$_2$ values. In addition, few gas tracer studies have been conducted in boreal forest and peatland dominated stream systems. Here we have presented data from 114 independent measurements of K_{CO2} from 14 sites, more than double the amount of K_{CO2} values found reported in the literature to date. K_{CO2} values, which ranged from 0.001 to 0.207 min^{-1} across the 14 stream reaches (Table 2), were similar to the range described in the literature, with the exception of several high values from a study of UK peatlands (Billett and Harvey, unpublished data, 2010), related to high discharge rates (Table 6). Our study showed that the variability in K_{CO2} is large both on a spatial and a temporal scale, with coefficients of variation of 66% and 60% for spatial and temporal variability respectively. By comparing K_{CO2} values in space and time, this study allow us to define relationships, or lack thereof, to readily measured physical variables, most notably slope of the stream reach and discharge.

5.1. Spatial Patterns

[35] Slope of the stream reach explained much of the between site variability in median K_{CO2}. This finding is supported by studies which have shown that topographic slope is one of the primary hydraulic properties that influence

Table 4. Spearman's Rank Correlation Coefficients Between a Number of Variables and CO_2 Evasion (μg C m^{-2} s^{-1})[a]

Site	pCO$_2$ (μatm)	K_{CO2}[b] (min^{-1})	τ (min)	Q (L s^{-1})
1	0.86*	0.62	−0.76*	0.74*
2	0.69*	0.17	−0.14	0.17
4	−0.20	0.86*	−0.54	0.60
5[c]	1.0*	1.0*	−1.0*	1.0*
6	−0.08	0.83*	−0.01	0.09
7	0.42	0.63*	−0.65*	0.62*
8	−0.11	0.88*	0.12	−0.07
9	−0.06	0.70*	0.12	0.81*
10	−0.03	0.84*	−0.53	0.47
12	−0.50	0.90*	−0.90*	1.0*
14[c]	0.50	−0.50	−0.50	0.50
15	−0.70	1.0*	−0.87	0.90*
71	−0.30	0.90*	−0.50	0.10
78	−0.10	0.90*	−0.70	0.60

[a]Significant correlations ($p < 0.05$) are marked with *.
[b]Values are normalized to 20°C.
[c]Correlations based on three values.

Table 5. Total Stream Length, Proportion of Total Stream Length in Boreal Sweden, Median Catchment Size, Median Slope, Modeled Median K_{CO2} and Variability in K_{CO2} Expressed as Coefficient of Variation for Streams in Forested Sweden Grouped by Strahler Stream Order 1–4

Stream Order	Stream Length (km)	Proportion of Total Stream Length (%)	Catchment Size (km^2)[a]	Slope (%)[a]	K_{CO2} (min^{-1})[a, b]	CV K_{CO2} (%)[b]
1	172867	56	0.7 (0.3–1.9)	1.3 (0.2–4.9)	0.028 (0.013–0.076)	82
2	74271	24	3 (1–8)	0.9 (0.1–3.5)	0.022 (0.012–0.057)	78
3	33810	11	12 (4–38)	0.7 (0.1–2.4)	0.020 (0.012–0.042)	70
4	16273	5	55 (17–177)	0.5 (0.1–1.8)	0.017 (0.011–0.034)	59

[a]10th and 90th percentiles are given in parenthesis.
[b]At a stream temperature of 20°C.

reaeration in streams [*Bennett and Rathbun*, 1972; *Tsivoglou and Neal*, 1976; *Gualtieri et al.*, 2002]. Despite that the influence of stream slope on reaeration is well described in the literature it is poorly described in studies of K_{CO2}. Moreover, the sites with highest median K_{CO2} (sites 1 and 15) had the lowest observed pCO_2 values among the 14 sites (Table 2); this suggests that high K_{CO2} is a feature of steeper stream sections leading to increased vertical CO_2 loss to the atmosphere. In fact, slope has actually been found to be closely connected to the supersaturation of CO_2 in small streams located in temperate forested watersheds in California, USA [*Finlay*, 2003]. This study found a strong negative relationship between stream gradient and CO_2 concentration in small streams draining watersheds ranging in size from 1.7 to 8 km^2. In our study including the width/depth (w/z) index of the stream channel in a MLR-analysis improved the predictability of median K_{CO2} in the landscape, although median w/z was not correlated to median K_{CO2} as a single explanatory variable. The geometry of the stream channel is known to be significantly correlated with the reaeration rate of small streams [*Wanninkhof et al.*, 1990; *Genereux and Hemond*, 1992]. Wide and shallow stream sections generate a larger water surface area compared to narrow and deep sections assuming the same flowing water mass. In addition, a shallow stream section creates more surface turbulence affecting the aquatic boundary layer, which enhances gas exchange at the water-air interface [*Macintyre et al.*, 1995].

[36] There was a gradient in decreasing median pCO_2 with increased stream order, suggesting that there is a higher degree of CO_2 supersaturation in headwaters than downstream. Similar patterns have been found with decreasing pCO_2 as a function of distance from the source of the stream in Scottish upland stream systems [*Dawson et al.*, 1995, 2004], and in a boreal Swedish catchment geographically close to the Krycklan catchment where DIC concentrations decreased with increasing catchment area [*Temnerud*, 2005]. However, the lowest site specific median pCO_2 value (769 μatm) was found in a headwater stream (site 1), reflecting the high degree of spatial variability in the Krycklan catchment.

5.2. Temporal Patterns

[37] Temporal patterns in K_{CO2} were more unpredictable than spatial patterns and showed most site specific variability. Discharge is generally thought to control much of the temporal variability in reaeration of streams [*Tsivoglou and Neal*, 1976; *Roberts et al.*, 2007] and variability in K_{CO2} [*Hope et al.*, 2001]. We found however that specific discharge and K_{CO2} were only significantly correlated at four sites out of a total of 14, with one site negatively and three positively correlated. Part of the reason for the lack of a consistent relationship between K_{CO2} and discharge is that decreasing reach travel time tends to counteract the effect of increased turbulence. By relating C_3H_8 loss over the stream reach to specific discharge we were able to indirectly model temporal variability in K_{CO2} for four more sites. We believe that differences in how turbulence is related to changes in discharge in stream reaches with different morphological characteristics are the main reason why discharge is not a better predictor of temporal variability in K_{CO2} at all sites. Our study therefore emphasizes that discharge as control on the temporal variability in K_{CO2} is highly site specific and

Table 6. K_{CO2} Values Based on Similar Tracer Injection Studies Using Propane as Tracer Gas and Conducted in Low Order Stream Systems

K_{CO2} Range[a] (min^{-1})	Measurements	Discharge Range (L s^{-1})	Region	Reference
0.025–0.076	26	3.0–33	Tennessee, USA	*Genereux and Hemond* [1992]
0.04–0.07[b]	31	5–57	Tennessee, USA	*Roberts et al.* [2007]
0–0.10[b]	11	10–770	Alaska, USA	*Morse et al.* [2007]
0.0004–0.003	3	154–244	Wisconsin, USA	*House and Skavroneck* [1981]
0.023–0.061	7	12.9	Maine, USA	*Maprani et al.* [2005]
0.005–0.151	3	36–137	Scotland, UK	*Billett et al.* [2004]
0.015–0.344	8	4.3–22.4	Scotland, UK	*Hope et al.* [2001]
0–1.41	17	1.9–188.4	N. England, UK	Billett and Harvey (unpublished data, 2010)
0–0.048[c]	8	0–10	Northern Sweden	*Öquist et al.* [2009]
0.001–0.207	114	0.4–154.1	Northern Sweden	This study

[a]Values are transformed to K_{CO2} and to the unit min^{-1} where needed.
[b]Based on approximate figure data and with temperature set to 10°C.
[c]Modeled daily values from a first order stream (site 2 in this study) based on eight tracer injections. The eight injections are included in the data set of this study.

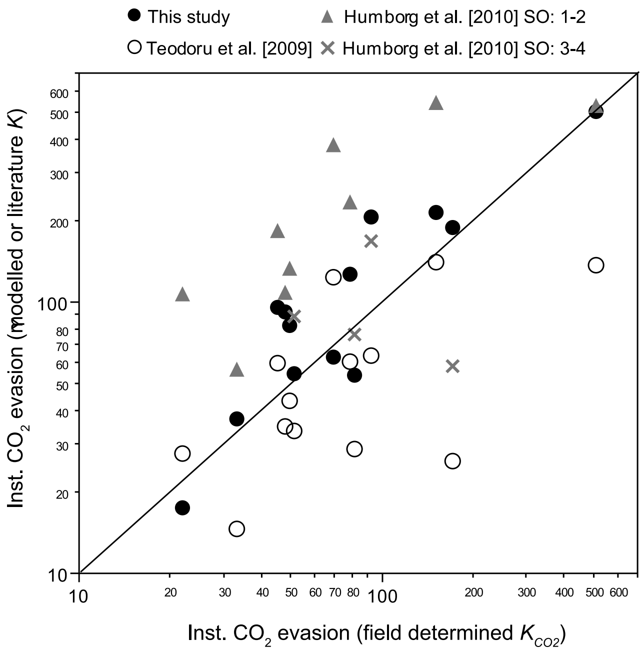

Figure 6. Measured instantaneous CO_2 evasion rates compared to evasion rates based on measured pCO_2 combined with estimated gas transfer coefficient (K_{CO2}) or gas transfer velocity (K_{TV}). The filled circles used K_{CO2} modeled by this study (as determined by cross-validation for each site). The open circles used literature values of gas transfer velocity (K_{TV}) according to *Teodoru et al.* [2009], the triangles and crosses according to *Humborg et al.* [2010], with triangles for stream order 1–2, and crosses for stream order 3–4. Data are presented as site specific median evasion rates and are expressed in μg C m^{-2} s^{-1}.

generalizations cannot be made at the regional scale. Generalized temporal models for larger landscape units are therefore likely to require more site specific input variables encompassing e.g., the fine-scale morphological differences of the stream channels. In the absence of that information, temporal variability is best treated as a random variable at a landscape scale, with slope defining the variability of K_{CO2} in space.

[38] To understand the contribution of groundwater inputs and/or hyporheic exchange is important when working on studies of metabolism and gas exchange within a stream reach. This was shown for estimates of whole-stream metabolism in a 180 m long study reach in Wyoming, USA [*Hall and Tank*, 2005]. The study concluded that by considering diffuse groundwater inputs significantly lowered the estimates of both community respiration and gross primary production. The effect of groundwater inputs or loss of tracer into the hyporheic zone on our measured K_{CO2} values was however insignificant because the difference according to the low difference in tracer mass (measured as integrated EC) between the upper and lower ends of the reach was only 0.5% (mean value for all tracer injections). The relatively short length of our stream reaches (16–35 m) compared to many other reaeration studies minimizes the influence of gaining or losing reaches. Furthermore, detailed measurements of groundwater levels and hydraulic gradients have been conducted in one subcatchment of the Krycklan catchment [*Bishop*, 1991]. In addition, during the last years a dozen hydrometrically instrumented riparian zones at different sites within Krycklan have been studied, measuring spatial variability in riparian groundwater levels and hydraulic gradients [*Grabs*, 2010]. None of these studies conducted in the near stream zone have discovered hydraulic gradients that indicate losing stream reaches. There might be many explanations for this, but one of the most obvious is that most streams in the area (and in most of Scandinavia) were deepened to improve drainage during the last century, increasing the hydraulic gradient from the riparian zone to the stream.

5.3. The Importance of K_{CO2} for CO_2 Evasion Estimates and Regional Upscaling

[39] Variability in the exchange of CO_2 between the stream surface and the atmosphere was largely controlled by K_{CO2} (Table 4). This result is very important in the context of integrating streams into estimates of landscape C budgets. It also indicates that previously published landscape estimates of CO_2 evasion from streams might need to be revised, since the exchange ability is often estimated from a generalized gas transfer velocity independent of spatial or temporal variability [*Jonsson et al.*, 2007; *Teodoru et al.*, 2009]. An attempt to give a more accurate representation of streams and rivers in evasion estimates were recently presented by *Humborg et al.* [2010], where they estimated the evasion component for the entire surface water area in Sweden to be 2.58 Tg C yr^{-1}. For lotic systems they applied different gas transfer velocities according to their Strahler stream order (stream order 1–6), with decreasing gas transfer velocities with increased stream order. Here we conclude, however, that stream slope rather than stream size or stream order is the key spatial determinant of K_{CO2}. In fact, the highest K_{CO2} values obtained in our study were found in both a 1st and a 4th order stream (sites 1 and 15). Thus, steeper stream sections create turbulence to a higher degree which generates a greater gas exchange potential, and this feature cannot be unconditionally coupled to stream order.

[40] We found that the relationship between the absolute numbers of K_{TV} from *Humborg et al.* [2010] and our modeled median K_{CO2} numbers for 1st order streams corresponds well to similar relationships found for streams in Wisconsin, USA [*Grant and Skavroneck*, 1980] and compiled by *Wanninkhof et al.* [1990]. We then compared our measured median instantaneous evasion rates with estimated rates computed from the gas transfer velocities used in other studies [*Teodoru et al.*, 2009; *Humborg et al.*, 2010] and measured pCO_2 from this study (Figure 6), in order to highlight the importance of adequately derived gas transfer velocities on C budget estimates. The average site specific median instantaneous evasion rate from our study (100 μg C m^{-2} s^{-1}) was almost twice as high as the corresponding rate (59 μg C m^{-2} s^{-1}) using a fixed gas transfer velocity (16.7 cm h^{-1}) reported for streams in northern Quebec by *Teodoru et al.* [2009]. Using the method proposed by *Humborg et al.* [2010] with gas transfer velocities based on stream order (64.5–37.4 cm h^{-1} for stream orders 1–4), the median instantaneous evasion rate were overestimated by almost 100% (197 μg C m^{-2} s^{-1}). However, if we considered stream orders 1–2 and 3–4 separately, the median evasion rates were 255% higher (stream

orders 1–2) and 8% lower (stream orders 3–4). Similar difficulties when applying general predictive models for estimating reaeration on streams were also found for rivers of various sizes in New York State, USA [*Stedfast and Draper*, 1986]. By using modeled K_{CO2} (determined by the cross-validation procedure) in the evasion calculations we were able to compare our modeled evasion rates with field measures and also with evasion rates calculated from literature values of K_{TV} (Figure 6). Using modeled K_{CO2} overestimated the median instantaneous evasion rate by an average of 13% independent of stream order. Even though the error can be larger at individual sites, the improved prediction of evasion rates in terms of average error show that the K_{CO2} model based on stream slope and stream channel geometry (equation (7)) gives a better spatial representation of CO_2 evasion from running waters at a landscape scale compared to using pre-existing literature values of K_{TV}.

[41] Since stream slope was the most important predictor of spatial variability in K_{CO2}, we used the distribution of slope for the stream network (stream order 1–4) of forested boreal/nemoral Sweden to model the landscape distribution in K_{CO2}. Since there is a lack of reliable estimates of geomorphological conditions (i.e., measures of width and depth) in the Swedish stream network, we choose to use slope as the single predicting variable. We grouped the results by stream order to facilitate comparison with the study by *Humborg et al.* [2010]. While our field study did not find any difference in K_{CO2} based on stream size among the 14 stream reaches, upscaling the model showed however that 1st order streams (median catchment size 0.7 km^2), which represent the majority of all stream length of the forested Swedish landscape, had a K_{CO2} almost 40% higher than the 4th order streams due to steeper slopes in the headwaters (Table 5). We believe that this represents a better and more accurate approach to upscaling evasion rates from the small catchment to the regional scale.

6. Conclusions

[42] We conclude that the spatiotemporal variability of the gas transfer coefficient for carbon dioxide (K_{CO2}) is large in boreal streams, but that the slope of the stream can be used to predict the spatial component of this variability. For specific stream sections the slope of the stream is also correlated to the size of the temporal variability in K_{CO2} where steeper stream sections show larger variability. Large scale response functions for K_{CO2} based on discharge are inappropriate since the relationship between these variables appears to be highly site specific. Furthermore, we found that variability in K_{CO2} is the main determinant of CO_2 evasion from boreal streams. Even though we did not find a relationship between stream order and K_{C02} in our field study, the pattern for the majority (>95%) of the Swedish forested boreal/nemoral stream network (stream order 1–4) was different with a clear trend in lower median K_{CO2} at higher stream order. This was due to the prevalence of low order streams with higher slope, rather than being related to the size of the stream per se. This study shows that accurate landscape scale estimates of the evasion fluxes of CO_2 require a good understanding of the controls on gas exchange at the water surface. Without this information estimates of landscape scale evasion loss from lotic systems will always be associated with a very high degree of uncertainty.

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