Evasion of CO_2 from Streams

Quantifying a Carbon Component of the Aquatic Conduit in the Boreal Landscape

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Cover: Övre Krycklan (site 15), a “hot-spot” for CO_2 evasion.
(photo: Peder Blomkvist)

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Abstract

Lateral export of carbon (C) from soils to running waters is a persistent pathway for C with terrestrial origin. This "aquatic conduit" might be especially important in boreal regions where a significant part of the global C stock is stored in the soil. Even though the awareness of the fate of terrestrially derived C is increasing in regional and global C budgets, the scarcity of data on the contribution of streams is widely acknowledged. In particular, the evasion (degassing) of gaseous C (i.e. CO_2 and CH_4) from the water surface of streams requires better characterization. This thesis aims to quantify the evasion of CO_2 from boreal streams within the 67 km^2 Krycklan catchment, and explore the factors controlling this diffuse flux.

All streams in the Krycklan catchment were consistently supersaturated in CO_2 and were hence a source for atmospheric CO_2 all year around. The source for this supersaturation of CO_2 was to a great extent explained by the export of respired C from the catchment soils. This was shown by exploring the export of dissolved inorganic carbon (DIC) across the soil/stream/atmosphere interfaces in a headwater catchment. The study also found that CO_2 evasion from the stream surface is a rapid process, and that much of the DIC leaving the soils is returned to the atmosphere as CO_2 before leaving the headwaters. Evasion of CO_2 is dependent on the water-atmosphere concentration gradient, but also the gas exchange ability across the water-atmosphere interface (the gas transfer coefficient). The spatiotemporal variability of the gas transfer coefficient for carbon dioxide (K_{CO2}) was found to be large, but the slope of the stream can be used to predict the spatial component of this variability. The positive relationship between K_{CO2} and stream section steepness was used to determine the spatial distribution of gas exchange ability for the entire stream network of forested Sweden. By combining concentration measurements and field-determined relationships with a high resolution digital elevation model (DEM) we were able to model the CO_2 evasion for each grid-cell of stream in the Krycklan catchment. Evasion of CO_2 from the entire stream network constituted a major component (<69 %) of the entire aquatic C flux. This study highlights the importance of including CO_2 evasion from streams in estimates of the aquatic conduit for carbon in boreal regions.

Keywords: CO_2, DIC, Evasion, Carbon Export, Boreal streams, Krycklan

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Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I. **Wallin, M.**, Buffam. I., Öquist, M., Laudon, H., & Bishop, K. (2010). Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes. *Journal of Geophysical Research - Biogeosciences* 115: G02014, doi:10.1029/2009JG001100.

II. Öquist, M., **Wallin, M.**, Seibert, J., Bishop, K., & Laudon, H. (2009). Dissolved inorganic carbon export across the soil/stream interface and its fate in a boreal headwater stream. *Environmental Science & Technology* 43(19), 7364-7369. doi:10.1021/es900416h

III. **Wallin, M.**, Öquist, M., Buffam, I., Billett, M., Nisell, J., & Bishop, K. Spatiotemporal variability of the gas transfer coefficient (K_{CO2}) in boreal streams; implications for large scale estimates of CO_2 evasion (in review).

IV. **Wallin, M.**, Grabs, T., Buffam, I., Laudon, H., Ågren, A., Öquist, M., & Bishop, K. Evasion of CO_2 from streams – A major component of the carbon export through the aquatic conduit in a boreal catchment (manuscript).

The contribution of Marcus Wallin to the papers included in this thesis was as follows:

I. The respondent was involved in developing the method used for sampling. Data handling, writing and publishing was mainly done by the respondent.

II. The respondent was responsible for a portion of the data collection and handling. In addition, he was involved in the interpretation and writing of the paper.

III. The respondent was responsible for all data collection and analysis. In addition, data handling, interpretation and writing was mainly done by the respondent.

IV. The respondent was largely responsible for the data handling. In addition, he was responsible for the interpretation and writing of the paper.

Abbreviations

AHS	Acidified headspace method
CO_2	Carbon dioxide
DEM	Digital elevation model
DHS	Direct headspace method
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
GHG	Greenhouse gases
IPCC	Intergovernmental panel on climate change
K_{CO2}	Gas transfer coefficient of carbon dioxide
KCS	The Krycklan catchment study
MLR	Multiple linear regression
NEE	Net ecosystem exchange
NEP	Net ecosystem productivity
pCO_2	Partial pressure of carbon dioxide
POC	Particulate organic carbon
TOC	Total organic carbon

1. Introduction

1.1. The boreal landscape and its role in the global carbon cycle

From a distance, the boreal zone might seem rather simple and uniform, but from an ecosystem perspective the landscape is a complex mosaic of forest, peatlands and lakes. The landscape stores a significant part of the global carbon (C) stock in soils and vegetation (Pregitzer & Euskirchen, 2004; Gorham, 1991). Furthermore, boreal forests and peatlands are seen as important sinks for atmospheric carbon dioxide (CO_2) on a global scale (IPCC, 2007). The exchange of C between forest ecosystems and the atmosphere is however highly variable both on a spatial (Valentini *et al.*, 2000) and a temporal scale (Krishnan *et al.*, 2008; Zha *et al.*, 2004). A Swedish study emphasized that the inter-annual variability in Net Ecosystem Productivity (NEP) is large and that the same forest stand may act as a net sink during some years and a net source during other years (Lindroth *et al.*, 2008). This great variability in NEP in combination with the fact that mature forests in the boreal zone can be close to equilibrium with the atmosphere in terms of CO_2 exchange (Lagergren *et al.*, 2008; Lindroth *et al.*, 1998), means that the export of terrestrially derived C to aquatic ecosystems is a significant component in the sink/source relationship of the boreal landscape.

Similar findings of large spatial and temporal variability of the NEP in forested systems have been found for Net Ecosystem Exchange (NEE) in different unmanaged peatland systems. Despite a great variability in NEE, northern peatlands are concluded to generally be net sinks for atmospheric CO_2 (Lund *et al.*, 2010). However, the strength of this C sink component has been significantly altered (-30-(-)50%) when including fluvial export of C in the peatland C budget estimates (Dinsmore *et al.*, 2010; Nilsson *et al.*,

2008; Roulet *et al.*, 2007). Corresponding considerations of the potential importance of fluvial C export for C budgets of forested biomes are although rare in the literature.

1.2. The importance of aquatic systems in the global carbon budget

The importance of inland waters for the global terrestrial C cycle is becoming increasingly apparent and the most recent estimate of global C export from terrestrial systems via the "aquatic conduit" is 2.9 Gt C yr^{-1} (Tranvik *et al.*, 2009). Thus, the size of the aquatic C export is of the same magnitude as the global NEP, estimated as 2.0 Gt C yr^{-1} (Randerson *et al.*, 2002). About 50% of the C leaving terrestrial systems is concluded to be transferred back to the atmosphere (evasion) from the water surface of inland waters before reaching the sea. In addition, about 20% of the C is assumed to be buried in the sediments of lakes and impoundments resulting in only ~30% of the terrestrial C exported via the aquatic conduit actually reaching the sea (Tranvik *et al.*, 2009). However, estimates of the terrestrial C export via the aquatic conduit like this are to a large degree based on how much C reaches the sea and estimates of lake C processes (sedimentation and evasion). The importance of stream systems for C export is poorly characterized, especially at large scales, and estimates are associated with a large degree of uncertainty.

1.3. Why study stream systems?

The areal coverage of lakes, ponds and impoundments has been estimated to cover 4.6 million km^2 or about 3% of the earth´s "land" surface (Downing *et al.*, 2006). This number was almost twice as high as previous estimates and has contributed to the increased awareness the role inland waters play in the global C cycle (Tranvik *et al.*, 2009; Cole *et al.*, 2007). Comparable knowledge concerning the global area covered by running waters is however very limited and often highlighted as a potential source of error in global C budget estimates (Battin *et al.*, 2008; Cole *et al.*, 2007). Furthermore, much of the scientific work on aquatic systems and their role in the global C cycle has been focused on lakes, while much less attention has been given to running waters. One exception is a study by Battin *et al.* (2008) that highlighted the importance of fluvial networks and their role in the global C cycle. Their study emphasized that metabolism of carbon with

terrestrial origin in fluvial networks (streams and rivers) was responsible for a large amount of the CO_2 being outgassed to the atmosphere. They estimated the vertical C flux from fluvial networks to 0.95 and 0.50 Gt C yr^{-1} for global respiration and global net heterotrophy respectively. However, their estimate only considered in-stream processed organic carbon. Soil and groundwater inputs of DIC therefore have to be added to this estimate in order to give an accurate estimate of all CO_2 emissions from fluvial networks. Humborg *et al.* (2010) estimated the CO_2 efflux from the entire Swedish aquatic conduit (including streams, rivers and lakes) to be 2.58 Tg C yr^{-1}. Their estimate was based solely on modelling of both the degree of supersaturation and gas transfer velocities. They concluded that streams, despite their low area coverage, were responsible for a large part of the C exchange (27%; stream order 1-4) between inland waters and the atmosphere. Furthermore, they estimated that terrestrial respiration was responsible for 50% of the vertical CO_2 flux for the entire aquatic conduit.

Small streams often comprise the majority of the length of a fluvial network in a given area. For instance, small streams (catchment areas < $15km^2$) comprise 90% of the total stream and river length in Sweden (Bishop *et al.*, 2008). These low order streams form the capillary network in the landscape and provide the first possibility for direct gas exchange between water leaving the soil and the atmosphere. In addition, such low order streams in forested and peatland systems in the boreal region are often highly supersaturated in CO_2 with respect to the atmosphere (Koprivnjak *et al.*, 2010; Rantakari *et al.*, 2010; Nilsson *et al.*, 2008). This supersaturation has been concluded for peatland systems to be a result of the close hydrochemical connectivity between the soil and the adjacent stream (Dinsmore & Billett, 2008; Hope *et al.*, 2004). Furthermore, the evasion of CO_2 from low order stream systems has been found to be a rapid process (a matter of hours) and the supersaturation of CO_2 typically decreases downstream along the stream network (Temnerud, 2005; Dawson *et al.*, 2004; 1995). These stream features make them potentially important in the calculation of landscape C budgets. Although the awareness of stream systems and their role in biome specific C balances is increasing, the knowledge gap at regional and global scales is still large.

1.4. Sources of DIC in streams

Dissolved inorganic carbon (DIC) (including HCO_3^-, CO_3^{2-} and CO_2) in streams can be derived from both biogenic, geogenic and atmospheric sources (Figure 1). The biogenic contributions are groundwater inputs of CO_2 derived from respiration processes in the soil, in-stream degradation of C through microbial processes and photo-oxidation. The geogenic sources are dissolution of carbonate and weathering of silicate minerals in soils and underlying bedrock. In addition, there is a potential atmospheric source (atmospheric draw-down or invasion) in streams under-saturated in CO_2 (Palmer *et al.*, 2001; Atekwana & Krishnamurthy, 1998). The stream DIC concentration has been found to be strongly influenced by the degree of hydrochemical connectivity between the riparian soil and the adjacent stream in peatland systems (Dawson *et al.*, 2004; Hope *et al.*, 2004), a pattern also seen in boreal forested systems (Paper II). The contribution of in-stream processes to the DIC concentration is highly dependent upon catchment-specific characteristics but is generally suggested to increase downstream along the stream network. In-stream processing of C is considered to be of minor influence for DIC in boreal low-order streams (Paper II). Controlling factors such as water residence time, stream gradient, water temperature, light conditions and nutrient availability support this statement. However, in-stream metabolism for example is known to be an important component in the global C cycle (Battin *et al.*, 2008) and will thus significantly affect the DIC/CO_2 concentration in larger streams and rivers of various biomes (Dawson *et al.*, 2009; McTammany *et al.*, 2003).

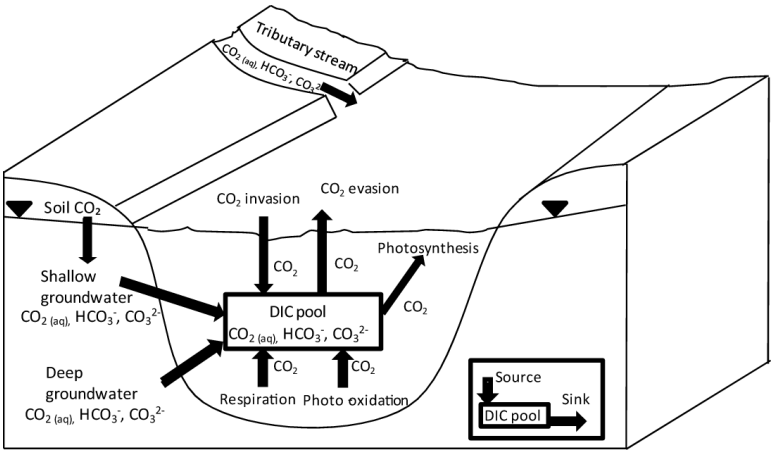

Figure 1. Processes controlling stream DIC concentrations. Triangles indicate groundwater level. Revised version of an original figure by Atekwana and Krishnamurthy (1998).

1.5. Factors controlling CO_2 evasion

Evasion of a given gas across the water-atmosphere interface requires a concentration difference. A higher concentration of the gas in the water compared to the air result in a concentration gradient driving diffusion across the interface. The rate of diffusion is controlled by the partial pressure of the individual gas and its exchange ability at the water-atmosphere interface (*K)* (Macintyre *et al.*, 1995). The main driver for variability in gas exchange in open water systems (oceans, estuaries and lakes) besides the water-atmosphere gas concentration gradient is often concluded to be wind speed over the water surface (Borges *et al.*, 2004; Wanninkhof, 1992). The corresponding main driver for streams is instead suggested to be water turbulence created by variations in discharge and stream morphology (Hope *et al.*, 2001; Wanninkhof *et al.*, 1990; Tsivoglou & Neal, 1976). In the absence of a turbulent water surface, streams can show moderate evasion rates although being highly CO_2 supersaturated. Such findings have been made for streams and ponds draining the Mer Bleu peatland in Canada (Billett & Moore, 2008). Furthermore, turbulence conditions are often very variable along a stream, thus the evasion can vary greatly at a small scale with local hot-spots occurring along the stream network. Hence, it is important to have a good understanding of the small scale variability in CO_2 exchange at the water surface before making accurate regional estimates of CO_2 evasion fluxes from running waters.

2. Objectives

The overall aim of this thesis is to improve the understanding of the concentration dynamics and fluxes of dissolved inorganic carbon (DIC) in boreal streams, especially the evasion of CO_2 from the stream surface. The thesis also investigates the potential importance of the two-dimensional flux of inorganic carbon (both laterally as DIC and vertically as CO_2) for the aquatic conduit in the landscape C budget. The paper specific objectives were:

I. Document spatial and temporal patterns of DIC and CO_2 concentrations in a boreal stream network and indentify likely causes for those patterns

II. Determine the lateral export of DIC from soils of a boreal coniferous forest to a first order stream and estimate the partitioning of the DIC into CO_2 evasion from the stream surface and the DIC exported downstream

III. Quantify spatial and temporal variability in the gas transfer coefficient of CO_2 (K_{CO2}) within a boreal stream network and explore relationships of K_{CO2} to physical parameters

IV. Estimate the evasion of CO_2 from streams within a boreal catchment and relate it to the downstream export of DOC and DIC

3. Study site

All studies included in this thesis (except the synoptic samplings described in 4.4 and 5.6) were conducted in the upper part of the Krycklan catchment, (64° 14´N, 19° 46´E) situated ca 60 km north-west of Umeå, northern Sweden (Figure 2). The area is well documented since it is a part of the Svartberget, Long Term Ecological Research (LTER), originally established in 1923 (http://vfp.esf.slu.se). Hydrological and biogeochemical research has been performed in one of the subcatchments, the 0.5 km^2 Nyänget catchment, for more than 30 years (Köhler *et al.*, 2008; Bishop *et al.*, 1990). Starting in 2002, research in the area expanded to cover the upper 67 km^2 catchment of the river Krycklan and the Krycklan Catchment Study (KCS) was born (Buffam, 2007). A great number of scientific papers, reports, doctoral and master thesis have been published since then and they all contribute to the Krycklan catchment being the most investigated watershed in Sweden today regards to hydrological, biogeochemical and stream ecological research. The stream network is typical in many regards for 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 until the end of April. Annual mean precipitation is 600 mm (about 35% falls as snow) and ~50% of this is lost as runoff. The 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).

Data from 17 stream sites ranging in subcatchment area from 0.03-67 km^2 are presented in this thesis (Figure 2 and Table 1). The main land cover elements in the subcatchments are forest and peatland. 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}, dissolved inorganic carbon (DIC), 0.5-25.0 mg L^{-1}, and carbon dioxide carbon (CO_2-C), 0.5-17.0 mg L^{-1}. Respective concentration ranges in 4th order streams are 5.0-15.0 mg L^{-1}, 1.0-5.0 mg L^{-1} and 0.5-2.0 mg L^{-1}. Furthermore, lowest pH and highest DOC, DIC and CO_2-C concentrations are seen in streams characterized by a high proportion of peatland (30-75%) in the catchment (Wallin *et al.*, 2010; Buffam *et al.*, 2007). More detailed descriptions of the sites and stream chemistry dynamics can be found in Buffam (2007) and Ågren *et al.* (2007).

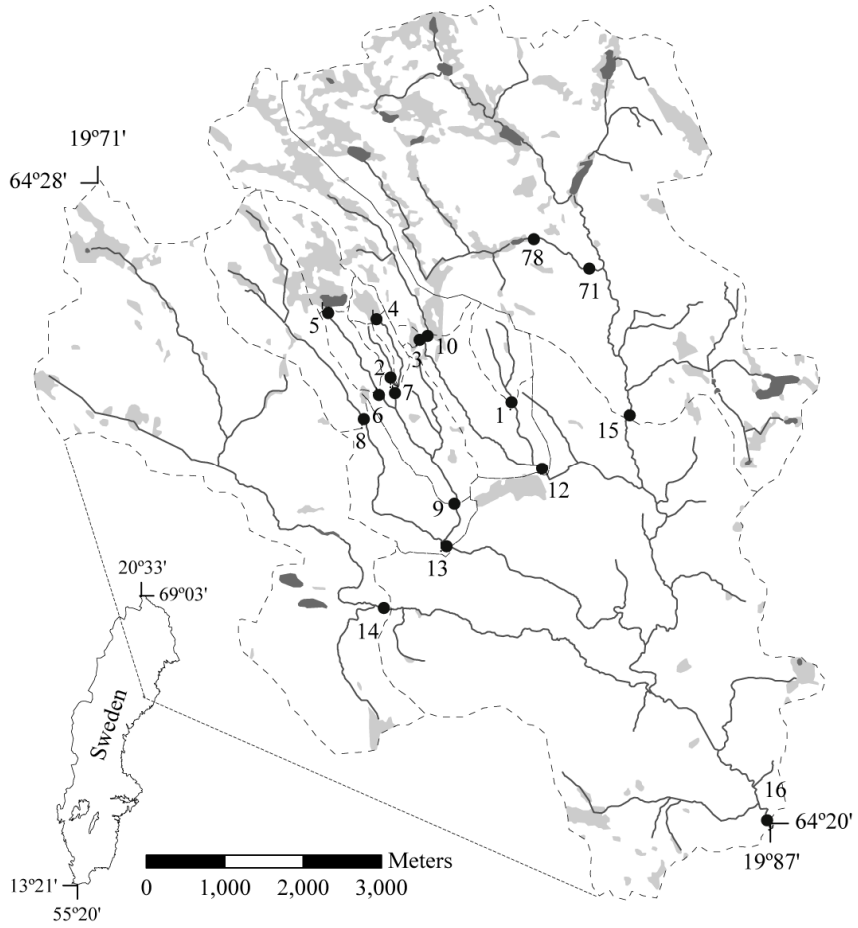

Figure 2. The Krycklan catchment with the stream network and location of the 17 stream sites presented in this thesis (black dots). Lakes are in dark grey and peatlands in light grey.

Table 1. Subcatchment characteristics of the 17 stream sites and their appearance in the different papers.

Site	Name	Catchment area (km^2)	Stream order[a]	Tot. upstr. stream length	Altitude[a] (masl)	Paper
1	Risbäcken	0.5	2	2.0	227	I,III,IV
2	Västra bäcken	0.1	1	0.6	247	I-IV
3	Lillmyrbäcken	0.03	1	0.05	256	I
4	Kallkällsmyren	0.2	1	0.03	282	I,III,IV
5	Stortjärnen outlet	0.8	1	0.03	286	I,III,IV
6	Stortjärnsbäcken	1.1	1	1.4	236	I,III,IV
7	Kallkällsbäcken	0.5	2	1.9	245	I,III,IV
8	Fulbäcken	2.5	2	4.8	234	III
9	Nyängesbäcken	2.9	3	7.8	184	I,III,IV
10	Stormyrbäcken	3.3	2	2.9	256	I,III,IV
12	Nymyrbäcken	5.4	3	9.2	184	I,III,IV
13	Långbäcken	7.0	3	17.1	177	I,IV
14	Åhedbäcken	13.8	2	15.1	172	I,III,IV
15	Övre Krycklan	18.8	4	31.4	181	I,III,IV
16	Krycklan	66.9	4	106.7	130	I,IV
71	Renbergstjärnsbäcken	3.8	2	6.3	225	III
78	Renbergstjärnen outlet	3.3	2	5.2	245	III

[a]determined at sampling site

4. Methods

4.1. Field sampling

Papers I and IV are based on the regular stream sampling of 14 or 13 stream sites respectively, streams which are all included in the KCS program (Buffam *et al.*, 2007; Ågren *et al.*, 2007). The streams were sampled biweekly to monthly and more intensively during the spring floods from 2006 to 2009 for a total of 104 occasions. Paper II is based on measurements of DIC export from the riparian zone into an adjacent headwater stream, combined with estimates of the downstream and vertical fluxes of DIC and CO_2. Soil and stream DIC concentrations were measured during one year 2003/2004. Measurements of gas exchange ability of the headwater stream using tracer gas injections (supporting information paper II) were carried out during 2006-2007. Paper III is based on tracer gas injections conducted in 14 stream reaches of various stream orders and during different seasons in 2006-2007. In addition to papers I-IV, δ^{13}C-DIC data of the Krycklan streams and synoptic samplings of DIC and pCO_2 across Sweden are presented in this thesis (described in 4.3. and 4.4).

4.2. Method used for determining DIC and pCO_2

An acidified headspace method (AHS) has been used in all papers to measure DIC in the stream water. DIC, CO_2-C concentrations 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. The methodology and required calculations are described in detail in paper I. The method is further evaluated in terms of accuracy

and sample storage effects by Wallin *et al.* (Manuscript)(Figure 3A and B). A well -direct headspace method (DHS) (Jonsson *et al.*, 2003; Kelly *et al.*, 2001; Cole *et al.*, 1994; Hesslein *et al.*, 1991) was used as a reference. Both the field and lab study showed good agreement between the AHS and DHS methods in terms of pCO_2 (Figure 3A). The sample storage test showed that despite lowering the pH to ~2 and keeping the samples dark and cold (5°C) prior to analysis, microbial processes affect the concentration of inorganic carbon in the sample bottle (Figure 3B). The mean increase in DIC concentration (%) due to storage was well approximated with a logarithmic function indicating a substrate limitation. The results also showed that GC-analysis should be done within a few days after sampling.

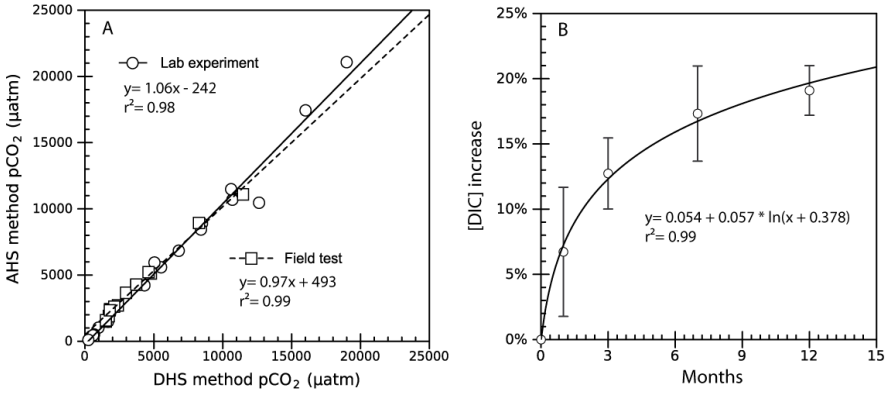

Figure 3. A) Comparing results of pCO_2 determination between the direct headspace method (DHS) (x-axis) and the acidified headspace method (AHS) (y-axis). B) Percent increase in DIC concentration as a function of storage time (months) of the acidified headspace method (AHS). Average value of three different stream sites is presented, with error bars showing SD.

4.3. Sampling and analysis of δ^{13}C-DIC

In order to investigate the sources of DIC within the Krycklan catchment, determination of the stable isotopic composition, δ^{13}C-DIC, was made. The stable isotopic composition of C is defined as the ratio between ^{13}C and ^{12}C related to an international carbonate standard (in this study the Pee Dee Belemite), and given as the per mil (‰) deviation from the standard (Equation 1).

$$\delta^{13}C = \left(\frac{R_{sample}}{R_{std}} - 1 \right) \times 1000 \qquad (1)$$

Different DIC sources have specific isotopic signatures making analysis of isotopic composition a useful tool for tracing the C origin. Distinct DIC sources are (with typical $\delta^{13}C$ values in parenthesis): atmospheric C (-8 ‰), carbonate bedrock C (0 ‰) and respired DOC-C (-28 ‰) (Parker *et al.*, 2010; Billett *et al.*, 2007; Finlay, 2003). Stream water samples for analysis of $\delta^{13}C$-DIC were collected from 15 stream sites at two or three occasions during 2006 (in June after spring flood, in August at an extreme low flow situation and in November at a moderate flow situation). Six stream sites were not sampled during the August occasion due to dry stream beds. All samples were collected in 12 ml gas tight exetainer tubes, which were evacuated and pre-filled with nitrogen at atmospheric pressure before sampling. The water samples were acidified prior to analysis and analyzed using IRMS technique (Europa Scientific Ltd, ANCA TG system) at the soil chemistry laboratory SLU, Umeå, Sweden.

4.4. CO_2 supersaturation of streams across Sweden

In order to evaluate how representative the studies conducted in the Krycklan catchment (papers I-IV) are in relation to the entire forested landscape of Sweden, we sampled low order streams in three different forested regions (n=~100 per region) along a latitude gradient across Sweden. A variety of chemical variables were assessed, including DIC, TOC and pH. Synoptic sampling was performed:

1) during one day within the Krycklan catchment in July 2007, where every stream junction was sampled for a total of 103 stream sites ranging from stream order 1-4.
2) 108 selected first order stream sites were sampled in the catchment of Dalälven during two weeks in late September 2009 at a stable discharge condition.
3) 94 selected first order stream sites were sampled along the west-coast of Sweden (Västkusten) in the Viskan, Ätran, Nissan and Lagan catchments during one week in early June 2010 at a stable discharge condition.

The stream sites for sampling surveys 2 and 3 were statistically representative sites and were randomly selected. The conditions for the site selection were that the upstream stream length of the sampling site was <2500 m and that the catchment did not include urban areas or more than 5% agricultural land.

5. Results and Discussion

5.1. DIC dynamics in a boreal stream network (paper I)

This study showed that all stream sites within the 4th order catchment of Krycklan were consistently supersaturated in CO_2 with respect to the atmosphere (Figure 4). Thus they are a constant source of atmospheric CO_2 due to vertical evasion. The ranges in DIC and pCO_2 are similar to findings made for boreal systems in eastern Finland (Rantakari *et al.*, 2010) and in Ontario, Canada (Koprivnjak *et al.*, 2010). The temporal variability in DIC concentration was to a great extent controlled by variability in discharge. However, the variability in CO_2 was also dependent on the pH range of the streams. The clear gradient in pH along the stream network and the hydrological control of acidity in the Krycklan catchment influenced 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 counteracted the dilution of CO_2. The low temporal CO_2 variability in the larger streams was controlled more by temperature. This emphasizes that headwaters are more likely to be variable than larger streams in their role as source for atmospheric CO_2.

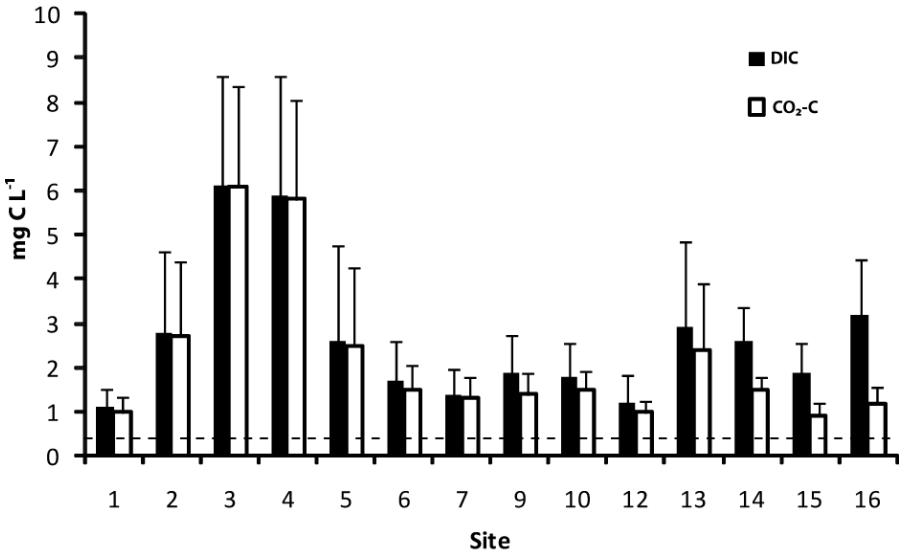

Figure 4. Median annual DIC concentration (black bar) and part as CO_2-C (white bar) for 14 stream sites within the Krycklan catchment. Error bars show coefficient of variation (CV). The hatched line indicates atmospheric equilibrium at a water temperature of 5°C and assuming an atmospheric concentration of 380 μatm.

Peatland coverage was the most important factor for controlling the spatial variability in the landscape stream concentrations of DIC and CO_2, as well as when estimating area-specific flux of DIC. The sites with a large proportion of peatland in their catchment by far exceeded the other sites in terms of annual median DIC and CO_2 concentration. Nearness to an extended peatland may also be an important contributing factor to spatial variability since the elevated signal of CO_2 in the stream disappeared a short distance downstream due to rapid evasion of CO_2.

5.2. Connecting soil with stream and the fate of DIC entering a headwater stream (paper II)

The aim of this investigation was to determine the annual lateral export of DIC from soils in a Swedish boreal coniferous forest to a first order stream and to partition this into CO_2 evasion from the stream surface and downstream export of DIC. The annual DIC export from the soil to the stream was estimated to be 3.2 g C m^{-2} yr^{-1} (Table 2). Up to 90% of this DIC was found to be evaded as CO_2 from the stream surface within a few hundred meters downstream. Furthermore, there was a strong positive correlation between the DIC concentration found in the riparian soil and DIC found in the adjacent stream (R^2 = 0.96), suggesting a strong hydrochemical connectivity. Similar findings of strong soil-stream linkages for CO_2 have been made for peatland systems (Dinsmore *et al.*, 2009; Hope *et al.*, 2004).

Table 2. Estimated annual and seasonal DIC export (± SD) from soil ground water to the stream and its partitioning into DIC stream export and CO_2 evasion (values in parenthesis represents export assuming daily DIC concentrations represented by the 25% and 75% quartiles, respectively).

Time period	Days #	Soil DIC Export (g C m^{-2})	Stream DIC Export (g C m^{-2})	Stream CO_2 evasion (g C m^{-2})
Annual	365	3.2 ±0.1 (2.9/4.1)	0.9 ±0.01 (0.7/1.2)	2.9 ±0.1 (2.0/3.7)
Winter	168	0.5 ±0.02 (0.4/0.6)	0.1 ±0.002 (0.1/0.2)	0.7 ±0.01 (0.6/1.1)
Spring	56	1.3 ±0.07 (1.2/1.6)	0.3 ±0.01 (0.3/0.5)	0.8 ±0.08 (0.6/1.1)
Summer	99	0.7 ±0.04 (0.7/1.0)	0.3 ±0.01 (0.2/0.3)	0.9 ±0.05 (0.4/0.8)
Fall	42	0.8 ±0.04 (0.6/0.8)	0.2 ±0.004 (0.1/0.2)	0.5 ±0.04 (0.4/0.7)
Growing season	160	2.1 ±0.07 (2.0/2.8)	0.6 ±0.01 (0.5/0.8)	1.8 ±0.1 (1.1/2.0)
Non-growing season	205	1.1 ±0.02 (0.8/1.2)	0.3 ±0.004 (0.3/0.9)	1.1 ±0.03 (0.9/1.7)

In addition, temporal dynamics of the CO_2 evasion from the stream correlated positively with the soil DIC export ($R^2 = 0.74$). This suggested that the CO_2 evasion was primarily driven by soil DIC export, with in-stream processes playing a minor role. Based on our results, we concluded that current budget estimates of lateral DIC export from soils to aquatic conduits need to be revised because they do not account for prevailing conditions in headwater steams. Data from headwater systems is rare, so any quantification of lateral stream C export and CO_2 emissions from freshwater systems must include headwater streams as well the lower parts of the aquatic conduit.

5.3. Variability in the water-atmosphere exchange ability of CO_2 across a boreal stream network (paper III)

We concluded in this study that the spatiotemporal variability of the gas transfer coefficient for carbon dioxide (K_{CO2}) is large in boreal streams, but that the slope and the morphology of the stream can be used to predict the spatial component of this variability (Figure 5). This finding is supported by studies that have shown that topographic slope is one of the primary hydraulic properties that influence reaeration in streams (Gualtieri *et al.*, 2002; Tsivoglou & Neal, 1976; Bennett & Rathbun, 1972). Although the influence of stream slope on reaeration is well described in the literature it is poorly described in studies of K_{CO2} and CO_2 exchange. Furthermore, for specific stream sections, the slope of the stream was also correlated to the size of the temporal variability in K_{CO2}, with steeper stream sections showing larger variability. Large-scale response functions for K_{CO2} based solely on discharge are inappropriate since the patterns between these variables appear to be highly site specific. Furthermore, we found that variability in K_{CO2} is the main determinant of between site variations in CO_2 evasion from boreal streams.

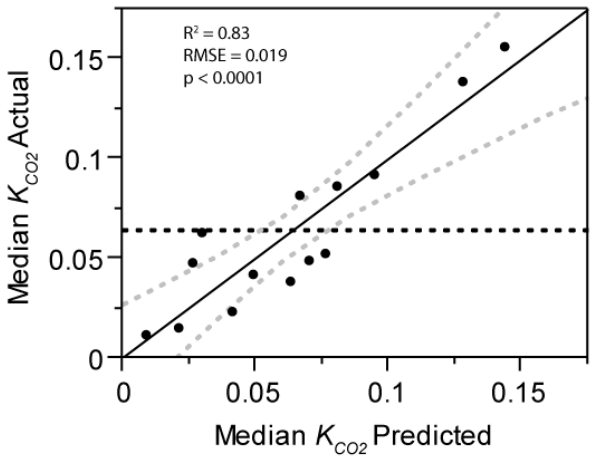

Figure 5. Measured versus MLR-modelled values of median gas transfer coefficient of CO_2 (K_{CO2}) normalized to 20 °C from the 14 studied stream reaches. Predictive variables were slope of the stream reach (%) and the ratio, median stream width over median stream depth (-). Confidence interval is given by grey hatched lines and mean value of the medians is given in black hatched line.

Even though we did not find an influence of stream order on 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} in higher stream orders. This finding is in agreement with a study of the entire stream network of Sweden (Humborg *et al.*, 2010). However, the trend of decreasing K_{CO2} at higher stream orders was due to the prevalence of low order streams with a higher slope, rather than an issue related to the size of the stream *per se*. Furthermore, this study showed 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 be associated with a very high degree of uncertainty.

5.4. Evasion of CO_2 from boreal streams – a major carbon component of the aquatic conduit (paper IV)

By combining concentration measurements and field determined relationships (paper I & III) with a high resolution digital elevation model (DEM) (Grabs, 2010), we were able to calculate the CO_2 evasion from the entire stream network of the Krycklan catchment in detail. Evasion of CO_2 from the stream surface was hypothesized as a major carbon component of the aquatic conduit due to the degree of CO_2 supersaturation observed in paper I. The annual evasion of CO_2 from the Krycklan catchment was 10.4 g C m^{-2} yr^{-1},which corresponded to 69 % of the entire aquatic C flux (lateral as DIC, DOC and vertical as CO_2) (Figure 6). The 1st and 2nd order streams contributed to 50 % of the entire CO_2 evasion from the stream network. Although the CO_2 evasion flux was associated with a relatively higher uncertainty compared to the lateral DOC and DIC flux (mainly derived from uncertainty of the length and area of the stream network), it was clear that it constituted a major component of the entire aquatic C flux. This was in agreement with findings of streams draining 1st order boreal catchments in Eastern Finland (Rantakari *et al.*, 2010) and streams draining peatland systems in Scotland (Dinsmore *et al.*, 2010; Hope *et al.*, 2001). This study highlighted the importance of including evasion of CO_2 from boreal streams in landscape C budgets at various scales. It also indicated that previous estimates of C export from soils to surface waters might have been significantly underestimated, since a major C component is lost to the atmosphere shortly after crossing the soil-stream interface.

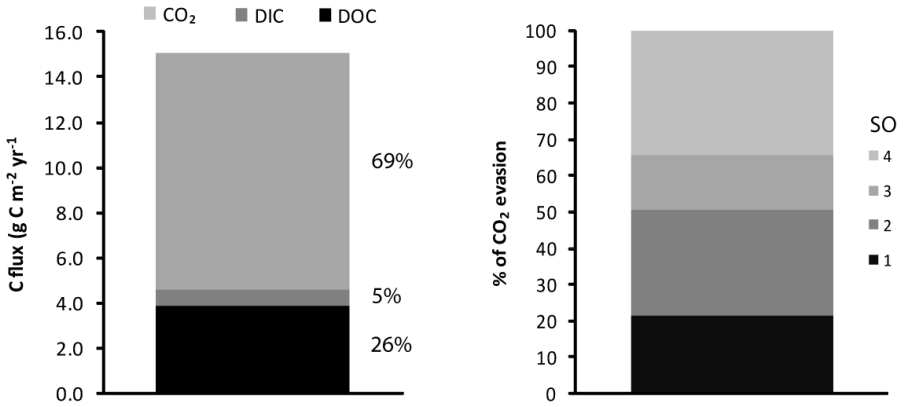

Figure 6. Contribution of the various C species to the entire aquatic C flux from the Krycklan catchment, including lateral flux of DOC, DIC and vertical flux of CO_2 (left graph). Contribution of the different stream orders to the CO_2 evasion (right graph).

5.5. Isotopic composition of DIC within the Krycklan stream network

The streams within the Krycklan catchment showed a spatial variability in the isotopic composition of DIC (δ^{13}C-DIC) ranging from -10.8 to -24.9 ‰ and with site-specific median range from -13.5 to -24.4 ‰. The majority of the streams had a median δ^{13}C-DIC between -18 and -22 ‰, suggesting that most of the DIC is derived from respired organic matter in the soil or from in-stream processing of DOC. Both catchment area (Figure 7A) and peatland coverage in the catchment (Figure 7B) came out as important explanatory variables for the δ^{13}C-DIC, although exclusion of the high peatland site (site 3, 76 % peatland) in the regression (Figure 7B) made the relationship statistically insignificant. A heavier δ^{13}C-DIC with increased distance downstream is in agreement with findings made in river systems in Michigan, USA (Atekwana & Krishnamurthy, 1998), in small streams in California, USA (Finlay, 2003) and in a small peatland stream in North East Scotland (Palmer *et al.*, 2001). The enrichment in δ^{13}C-DIC with increased stream size can be explained by a number of potential causes. The influence of CO_2 being lost to the atmosphere by evasion along the stream network would explain the pattern with enrichment in δ^{13}C-DIC since ^{12}C is evaded faster than ^{13}C (Parker *et al.*, 2010; Finlay, 2003).

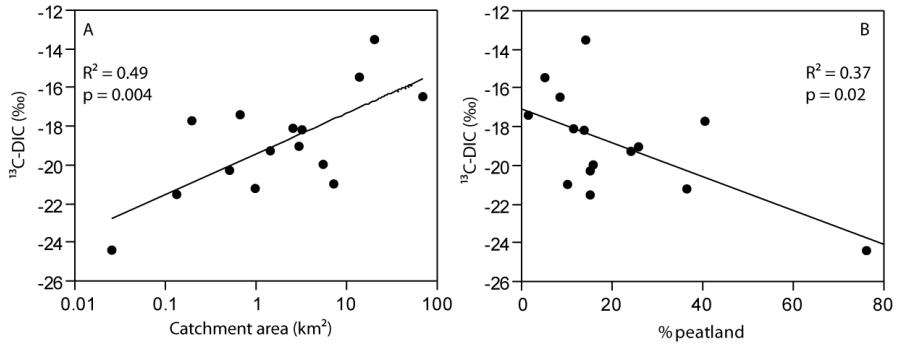

Figure 7. Mean $\delta^{13}C_{DIC}$ as a function of catchment area (A) and percentage peatland in the catchment (B) of 15 streams within the Krycklan catchment. Data are based on two or three sampling occasions (June, August and November).

As discussed in Buffam *et al.* (2008), in the lower parts of the Krycklan catchment a greater contribution of deep groundwater, rich in base cations, is affecting the chemistry of the stream water. This could suggest a larger influence of DIC with a geogenic source, although the weathering rates of carbonate containing bedrock in the catchment are concluded to be low (Klaminder *et al.*, in press). The strong pH gradient in the catchment from acidic headwaters (pH ~4) to more circumneutral 4th order streams (pH ~6.5) could also explain the enrichment in δ^{13}C-DIC, since a much higher proportion of the DIC pool will be in the form of HCO_3^- in the larger streams. Such shift in the distribution of the DIC species can cause a large enrichment in δ^{13}C-DIC (<10 ‰) (Waldron *et al.*, 2007; Finlay, 2003). A draw-down or mixing of atmospheric CO_2 with a typical isotopic composition of -7-(-)8 ‰ could also potentially cause the pattern, but since the entire stream network is constantly supersaturated in CO_2 (paper I), this is unlikely to have an significant influence

5.6. DIC and pCO_2 in streams along a latitude gradient across Sweden

This study showed that all sampled streams (n = 305) across Sweden were supersaturated in CO_2 and hence a source for atmospheric CO_2 (Table 3). The full range in pCO_2 (744-36229 µatm) was found in the Krycklan catchment. The regions were sampled during different parts of the growing-season, thus observed geographical patterns and trends should be interpreted with caution. However, the data indicates that the supersaturation of the streams was much higher in the Västkusten region (median pCO_2 = 4821 µatm). Determining whether this pattern has a biogeochemical explanation or is just an artefact resulting from the seasonal difference in time of sampling, requires further research. Since pH is controlling the chemical equilibrium and speciation of the DIC components (Stumm & Morgan, 1996), the lower pH in the streams of the Västkusten region also leads to a higher proportion of the DIC being in the form of CO_2. Furthermore, a higher pH in Krycklan compared to the Dalälven streams explained why the supersaturation was lower despite having a higher DIC concentration. The pH decrease along the north-south latitude gradient observed in this study reflects the historical influence of acid deposition, and the same pH-gradient has been documented for forest soils in Sweden (Karltun, 1994).

Table 3. Stream water chemistry data from three sampling surveys of low order streams along a latitude gradient across Sweden

	Krycklan[a]	Krycklan[b]	Dalälven[c]	Västkusten[c]
Latitude	64°N	64°N	60-62°N	56-57°N
Sampling time	July 2007	July 2007	September 2009	June 2010
(n)	103	64	108	94
DIC ($mg\ L^{-1}$)	2.7 (1.4-6.6)	2.9 (1.0-7.4)	1.9 (1.1-4.7)	4.0 (1.8-9.4)
pCO_2 (µatm)	1862 (1072-8718)	2564 (1248-10168)	2632 (1488-6341)	4821 (2412-9835)
TOC ($mg\ L^{-1}$)	10.0 (4.6-16.3)	11.9 (6.6-18.4)	22.5 (9.9-37.9)	26.2 (13.8-38.3)
pH	6.55 (5.63-6.61)	6.26 (5.42-6.80)	5.82 (4.64-6.69)	5.44 (4.75-6.73)

Data are presented as median values with 10^{th} and 90^{th} percentiles in parenthesis
[a] Sampling of each junction in the stream network, 1^{st} to 4^{th} order streams
[b] Just 1^{st} and 2^{nd} order streams from a.
[c] Statistically randomly selected stream sites independent of each other

6. Conclusions and future perspectives

This thesis concludes that:

- All streams within the Krycklan catchment are constantly supersaturated in CO_2 and hence a source for atmospheric CO_2.
- The amount of peatland in the catchment area controls the degree of supersaturation to a great extent. The most CO_2 supersaturated streams were found in close connection to peatland outlets.
- The soil export of DIC is the main source of the observed stream supersaturation of CO_2.
- The evasion of CO_2 from the stream surface is a rapid process and much of the DIC crossing the soil/stream interface is transferred back to the atmosphere within hours and before leaving the headwater stream systems.
- The gas exchange ability of CO_2 across the water-atmosphere interface (K_{CO2}) in stream systems is very variable but to a large degree controlled by the slope of the stream.
- Evasion of CO_2 is a major component (~70%) of the C export via the aquatic conduit in the Krycklan catchment.
- Accurate landscape scale estimates of the evasion 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 be associated with a very high degree of uncertainty.

However, it also raises a number of questions requiring further research:

- The hydrochemical connectivity between the catchment soils (especially the riparian zone) and low-order streams, in order to improve the understanding of boreal stream networks and their role in the terrestrial/aquatic C cycle.
- This thesis briefly explores the degree of CO_2 supersaturation in streams across the forested Sweden. However, further large scale investigations are needed to be able to explain geographical patterns of CO_2 in streams across larger scales.
- Determining the source of DIC in the observed streams is essential for carbon balance estimates. Investigation of the stable isotopic composition (δ^{13}C-DIC) is a useful tool in this work.
- To be able to incorporate evasion of CO_2 from streams in national and global C budgets requires a better knowledge of the physical occurrence of stream networks and also their temporal behaviour. We need to know how many streams there are and what area they cover!

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References

Ågren, A., Buffam, I., Jansson, M. & Laudon, H. (2007). Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. *Journal of Geophysical Research-Biogeosciences,* 112, doi:10.1029/2006jg000381

Atekwana, E.A. & Krishnamurthy, R.V. (1998). Seasonal variations of dissolved inorganic carbon and delta C-13 of surface waters: application of a modified gas evolution technique. *Journal of Hydrology,* 205(3-4), 265-278.

Battin, T.J., Kaplan, L.A., Findlay, S., Hopkinson, C.S., Marti, E., Packman, A.I., Newbold, J.D. & Sabater, F. (2008). Biophysical controls on organic carbon fluxes in fluvial networks. *Nature Geoscience,* 1(2), doi:10.1038/ngeo101

Bennett, J.P. & Rathbun, R.E. (1972). Reaeration in open channel flow. *U.S. Geological survey professional paper,* 737.

Billett, M.F., Garnett, M.H. & Harvey, F. (2007). UK peatland streams release old carbon dioxide to the atmosphere and young dissolved organic carbon to rivers. *Geophysical Research Letters,* 34(23), doi:10.1029/2007gl031797

Billett, M.F. & Moore, T.R. (2008). Supersaturation and evasion of CO2 and CH4 in surface waters at Mer Bleue peatland, Canada. *Hydrological Processes,* 22(12), doi:10.1002/hyp.6805

Bishop, K., Buffam, I., Erlandsson, M., Fölster, J., Laudon, H., Seibert, J. & Temnerud, J. (2008). Aqua Incognita: the unknown headwaters. *Hydrological Processes,* 22(8), doi:10.1002/hyp.7049

Bishop, K.H., Grip, H. & Oneill, A. (1990). The origin of acid runoff in a hillslope during storm events. *Journal of Hydrology,* 116(1-4), 35-61.

Borges, A.V., Vanderborght, J.P., Schiettecatte, L.S., Gazeau, F., Ferron-Smith, S., Delille, B. & Frankignoulle, M. (2004). Variability of the gas transfer velocity of CO2 in a macrotidal estuary (the Scheldt). *Estuaries,* 27(4), 593-603.

Buffam, I. (2007). *Linking landscape characteristics, streamwater acidity and Brown trout (Salmo trutta) distributions in a boreal stream network.* Doctoral thesis, Umeå:Swedish University of Agricultural Sciences. 37pp.

Buffam, I., Laudon, H., Seibert, J., Mörth, C.M. & Bishop, K. (2008). Spatial heterogeneity of the spring flood acid pulse in a boreal stream network. *Science of the Total Environment,* 407, doi:10.1016/j.scitotenv.2008.10.006

Buffam, I., Laudon, H., Temnerud, J., Mörth, C.M. & Bishop, K. (2007). Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network. *Journal of*

Geophysical Research-Biogeosciences, 112, doi:10.1029/2006jg000218
Cole, J.J., Caraco, N.F., Kling, G.W. & Kratz, T.K. (1994). Carbon-dioxide supersaturation in the surface waters of lakes. *Science,* 265(5178), 1568-1570.
Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J. & Melack, J. (2007). Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems,* 10(1), doi:10.1007/s10021-006-9013-8
Dawson, J.J.C., Billett, M.F., Hope, D., Palmer, S.M. & Deacon, C.M. (2004). Sources and sinks of aquatic carbon in a peatland stream continuum. *Biogeochemistry,* 70(1), 71-92.
Dawson, J.J.C., Hope, D., Cresser, M.S. & Billett, M.F. (1995). Downstream changes in free carbon-dioxide in an upland catchment from Northeastern Scotland. *Journal of Environmental Quality,* 24(4), 699-706.
Dawson, J.J.C., Soulsby, C., Hrachowitz, M., Speed, M. & Tetzlaff, D. (2009). Seasonality of epCO2 at different scales along an integrated river continuum within the Dee Basin, NE Scotland. *Hydrological Processes,* 23(20), doi:10.1002/hyp.7402
Dinsmore, K.J. & Billett, M.F. (2008). Continuous measurement and modeling of CO2 losses from a peatland stream during stormflow events. *Water Resources Research,* 44(12), doi:10.1029/2008wr007284
Dinsmore, K.J., Billett, M.F. & Moore, T.R. (2009). Transfer of carbon dioxide and methane through the soil-water-atmosphere system at Mer Bleue peatland, Canada. *Hydrological Processes,* 23(2), doi:10.1002/hyp.7158
Dinsmore, K.J., Billett, M.F., Skiba, U.M., Rees, R.M., Drewer, J. & Helfter, C. (2010). Role of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland catchment. *Global Change Biology*, doi:10.1111/j.1365-2486.2009.02119.x
Downing, J.A., Prairie, Y.T., Cole, J.J., Duarte, C.M., Tranvik, L.J., Striegl, R.G., McDowell, W.H., Kortelainen, P., Caraco, N.F., Melack, J.M. & Middelburg, J.J. (2006). The global abundance and size distribution of lakes, ponds, and impoundments. *Limnology and Oceanography,* 51(5), 2388-2397.
Finlay, J.C. (2003). Controls of streamwater dissolved inorganic carbon dynamics in a forested watershed. *Biogeochemistry,* 62(3), 231-252.
Gelbrecht, J., Fait, M., Dittrich, M. & Steinberg, C. (1998). Use of GC and equilibrium calculations of CO2 saturation index to indicate whether freshwater bodies in north-eastern Germany are net

sources or sinks for atmospheric CO2. *Fresenius Journal of Analytical Chemistry,* 361(1), 47-53.
Gorham, E. (1991). Northern peatlands - role in the carbon-cycle and probable responses to climatic warming. *Ecological Applications,* 1(2), 182-195.
Grabs, T. (2010). *Water quality modeling based on landscape analysis: Importance of riparian hydrology.* Doctoral thesis, Stockholm:Stockholm university. 39pp.
Gualtieri, C., Gualtieri, P. & Doria, G.P. (2002). Dimensional analysis of reaeration rate in streams. *Journal of Environmental Engineering-Asce,* 128(1), 12-18.
Hesslein, R.H., Rudd, J.W.M., Kelly, C., Ramlal, P. & Hallard, K.A. (1991). *Carbon-dioxide pressure in surface waters of Canadian lakes*. New York: Amer Soc Civil Engineers. (Air-Water Mass Transfer - Selected Papers from the Second International Symposium on Gas Transfer at Water Surfaces. ISBN 0-87262-846-9.
Hope, D., Palmer, S.M., Billett, M.F. & Dawson, J.J.C. (2001). Carbon dioxide and methane evasion from a temperate peatland stream. *Limnology and Oceanography,* 46(4), 847-857.
Hope, D., Palmer, S.M., Billett, M.F. & Dawson, J.J.C. (2004). Variations in dissolved CO2 and CH4 in a first-order stream and catchment: an investigation of soil-stream linkages. *Hydrological Processes,* 18(17), doi:10.1002/hyp.5657
Humborg, C., Mörth, C.-M., Sundbom, M., Borg, H., Blenckner, T., Giesler, R. & Ittekot, V. (2010). CO2 supersaturation along the aquatic conduit in swedish watersheds as constrained by terrestrial respiration, aquatic respiration and weathering. *Global Change Biology*, doi:10.1111/j.1365-2486.2009.02092.x
IPCC (2007). *Climate Change 2007: Synthesis Report*: Intergovernmental Panel on Climate Change.
Jonsson, A., Karlsson, J. & Jansson, M. (2003). Sources of carbon dioxide supersaturation in clearwater and humic lakes in northern Sweden. *Ecosystems,* 6(3), 224-235.
Karltun, E. (1994). Principal geographic-variation in the acidification of Swedish forest soils. *Water Air and Soil Pollution,* 76(3-4), 353-362.
Kelly, C.A., Fee, E., Ramlal, P.S., Rudd, J.W.M., Hesslein, R.H., Anema, C. & Schindler, E.U. (2001). Natural variability of carbon dioxide and net epilimnetic production in the surface waters of boreal lakes of different sizes. *Limnology and Oceanography,* 46(5), 1054-1064.
Klaminder, J., Grip, H., Mörth, C.M. & Laudon, H. (in press). Carbon mineralization and pyrite oxidation in groundwater: Importance for

silicate weathering in boreal forest soils and stream base-flow chemistry. *Applied Geochemistry*.
Köhler, S.J., Buffam, I., Laudon, H. & Bishop, K.H. (2008). Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements. *Journal of Geophysical Research-Biogeosciences,* 113(G3), doi:10.1029/2007jg000629
Koprivnjak, J.F., Dillon, P.J. & Molot, L.A. (2010). Importance of CO2 evasion from small boreal streams. *Global Biogeochemical Cycles,* 24(Gb4003), doi:10.1029/2009gb003723
Krishnan, P., Black, T.A., Barr, A.G., Grant, N.J., Gaumont-Guay, D. & Nesic, Z. (2008). Factors controlling the interannual variability in the carbon balance of a southern boreal black spruce forest. *Journal of Geophysical Research-Atmospheres,* 113(D9), doi:10.1029/2007jd008965
Lagergren, F., Lindroth, A., Dellwik, E., Ibrom, A., Lankreijer, H., Launiainen, S., Molder, M., Kolari, P., Pilegaard, K. & Vesala, T. (2008). Biophysical controls on CO2 fluxes of three Northern forests based on long-term eddy covariance data. *Tellus Series B-Chemical and Physical Meteorology,* 60(2), 143-152.
Lindroth, A., Grelle, A. & Moren, A.S. (1998). Long-term measurements of boreal forest carbon balance reveal large temperature sensitivity. *Global Change Biology,* 4(4), 443-450.
Lindroth, A., Klemedtsson, L., Grelle, A., Weslien, P. & Langvall, O. (2008). Measurement of net ecosystem exchange, productivity and respiration in three spruce forests in Sweden shows unexpectedly large soil carbon losses. *Biogeochemistry,* 89(1), doi:10.1007/s10533-007-9137-8
Lund, M., Lafleur, P.M., Roulet, N.T., Lindroth, A., Christensen, T.R., Aurela, M., Chojnicki, B.H., Flanagan, L.B., Humphreys, E.R., Laurila, T., Oechel, W.C., Olejnik, J., Rinne, J., Schubert, P. & Nilsson, M.B. (2010). Variability in exchange of CO2 across 12 northern peatland and tundra sites. *Global Change Biology,* 16(9), 2436-2448.
Macintyre, S.R., Wanninkhof, R. & Chanton, J.P. (1995). Trace gas exchange across the air-water interface in freshwater and coastal marine environments. In: Matson, P.A*., et al.* (Eds.) *Biogenic trace gases: Measuring emissions for soil and water*. pp. 52-97. Oxford: Blackwell Science.
McTammany, M.E., Webster, J.R., Benfield, E.F. & Neatrour, M.A. (2003). Longitudinal patterns of metabolism in a southern Appalachian river. *Journal of the North American Benthological Society,* 22(3), 359-370.
Nilsson, M., Sagerfors, J., Buffam, I., Laudon, H., Eriksson, T., Grelle, A., Klemedtsson, L., Weslien, P. & Lindroth, A. (2008). Contemporary

carbon accumulation in a boreal oligotrophic minerogenic mire - a significant sink after accounting for all C-fluxes. *Global Change Biology,* 14(10), doi:10.1111/j.1365-2486.2008.01654.x

Ottosson Löfvenius, M., Kluge, M. & Lundmark, T. (2003). Snow and soil frost depth in two types of shelterwood and a clear-cut area. *Scandinavian Journal of Forest Research,* 18(1), 54-63.

Palmer, S.M., Hope, D., Billett, M.F., Dawson, J.J.C. & Bryant, C.L. (2001). Sources of organic and inorganic carbon in a headwater stream: Evidence from carbon isotope studies. *Biogeochemistry,* 52(3), 321-338.

Parker, S.R., Poulson, S.R., Smith, M.G., Weyer, C.L. & Bates, K.M. (2010). Temporal variability in the concentration and stable carbon isotope composition of dissolved inorganic and organic carbon in two Montana, USA rivers. *Aquatic Geochemistry,* 16(1), 61-84.

Pregitzer, K.S. & Euskirchen, E.S. (2004). Carbon cycling and storage in world forests: biome patterns related to forest age. *Global Change Biology,* 10(12), 2052-2077.

Randerson, J.T., Chapin, F.S., Harden, J.W., Neff, J.C. & Harmon, M.E. (2002). Net ecosystem production: A comprehensive measure of net carbon accumulation by ecosystems. *Ecological Applications,* 12(4), 937-947.

Rantakari, M., Mattsson, T., Kortelainen, P., Piirainen, S., Finer, L. & Ahtiainen, M. (2010). Organic and inorganic carbon concentrations and fluxes from managed and unmanaged boreal first-order catchments. *Science of the Total Environment,* 408(7), 1649-1658.

Roulet, N.T., Lafleur, P.M., Richard, P.J.H., Moore, T.R., Humphreys, E.R. & Bubier, J. (2007). Contemporary carbon balance and late Holocene carbon accumulation in a northern peatland. *Global Change Biology,* 13(2), doi:10.1111/j.1365-2486.2006.01292.x

Stumm, W. & Morgan, J.J. (Eds.) (1996). *Aquatic Chemistry*. New York: John Wiley & Sons, Inc.

Temnerud, J. (2005). *Spatial variation of dissolved organic carbon along streams in Swedish boreal catchments.* Doctoral thesis, Örebro:Örebro University. 43pp.

Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dillon, P., Finlay, K., Fortino, K., Knoll, L.B., Kortelainen, P.L., Kutser, T., Larsen, S., Laurion, I., Leech, D.M., McCallister, S.L., McKnight, D.M., Melack, J.M., Overholt, E., Porter, J.A., Prairie, Y., Renwick, W.H., Roland, F., Sherman, B.S., Schindler, D.W., Sobek, S., Tremblay, A., Vanni, M.J., Verschoor, A.M., von Wachenfeldt, E. & Weyhenmeyer, G.A. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography,* 54(6), 2298-2314.

Tsivoglou, E.C. & Neal, L.A. (1976). Tracer measurement of reaeration: III. Predicting the reaeration capacity of inland streams. *Journal Water Pollution Control Federation,* 48(12), 2669-2689.

Valentini, R., Matteucci, G., Dolman, A.J., Schulze, E.D., Rebmann, C., Moors, E.J., Granier, A., Gross, P., Jensen, N.O., Pilegaard, K., Lindroth, A., Grelle, A., Bernhofer, C., Grunwald, T., Aubinet, M., Ceulemans, R., Kowalski, A.S., Vesala, T., Rannik, U., Berbigier, P., Loustau, D., Guomundsson, J., Thorgeirsson, H., Ibrom, A., Morgenstern, K., Clement, R., Moncrieff, J., Montagnani, L., Minerbi, S. & Jarvis, P.G. (2000). Respiration as the main determinant of carbon balance in European forests. *Nature,* 404(6780), 861-865.

Waldron, S., Scott, E.M. & Soulsby, C. (2007). Stable isotope analysis reveals lower-order river dissolved inorganic carbon pools are highly dynamic. *Environmental Science & Technology,* 41(17), doi:10.1021/es0706089

Wallin, M., Buffam, I., Öquist, M., Laudon, H. & Bishop, K. (2010). Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes. *Journal of Geophysical Research-Biogeosciences,* 115, doi:10.1029/2009jg001100

Wallin, M.B., Åberg, J. & Bishop, K. (Manuscript). Evaluating a headspace method for measuring DIC and pCO2 in surface waters – laboratory and field determination.

Wanninkhof, R. (1992). Relationship between wind-speed and gas-exchange over the ocean. *Journal of Geophysical Research-Oceans,* 97(C5), 7373-7382.

Wanninkhof, R., Mulholland, P.J. & Elwood, J.W. (1990). Gas-exchange rates for a 1st-order stream determined with deliberate and natural tracers. *Water Resources Research,* 26(7), 1621-1630.

Weiss, R.F. (1974). Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chemistry,* 2, 203-215.

Zha, T., Kellomaki, S., Wang, K.Y. & Rouvinen, I. (2004). Carbon sequestration and ecosystem respiration for 4 years in a Scots pine forest. *Global Change Biology,* 10(9), 1492-1503.