



Carbon dioxide evasion from a Boreal Catchment

Master thesis in Soil Science.

by

Marcus Wallin

Department of Environmental Assessment
Swedish University of Agricultural Sciences
Box 7050 SE 750 07 Uppsala

Supervisors: Prof. Kevin Bishop, Department of Environmental Assessment, SLU
Ishi Buffam, Department of Forest Ecology, SLU
Rasmus Sørensen, Department of Environmental Assessment, SLU

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Abstract

Boreal headwaters potentially represent important conduits for the exchange of gaseous carbon between the terrestrial ecosystem and the atmosphere. Even if the loss is small in absolute terms compared to the uptake and release directly from forested terrestrial systems, it is a persistent term that is important when discussing the landscape carbon budget. Earlier studies in Sweden by Algesten et al. (2004) estimate the flux of gaseous carbon between boreal streams and the atmosphere to $0.5 \text{ g C/m}^2\text{&year}$. Similar studies in Brocky Burn, Scotland by Hope et al. (2001) show a flux up to $14 \text{ g C/m}^2\text{&year}$.

The aim of this study is to determine the flux of carbon dioxide between streams in a typical Swedish boreal headwater catchment and the atmosphere. This was done by using the same method as in Brocky Burn. A comparison with other methods calculating the evasion was done in an attempt to get appropriate results. The study was performed within the headwater catchment of Krycklan in Västerbotten during 2003-2005. Totally around 570 water samples were taken during the period at different sites within the catchment and at different times of the year.

The results from this study show that the loss of carbon from a boreal headwater catchment is somewhere between 2 and $13 \text{ g C/m}^2\text{&year}$. The wide range depends on the annual variation and what measurements are used in the calculations. Earlier Swedish studies seem to have underestimated the evasion flux of carbon dioxide from headwater streams. The study also shows that the evasion is to a great extent regulated by the spring flood.

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Introduction

The debate about climate change and how human activities contribute to the global warming has increased in intensity over the last few decades. The Kyoto protocol of 1997 has given focus to the problem of increasing emissions of greenhouse gases (GHG). Although there still are opinions that the global warming is caused by natural climate fluctuations, the majority of scientists agree that the increase in global mean temperature the last 50-100 years mainly is caused by anthropogenic activities. The UN:s panel for climate issues, IPCC (Intergovernmental Panel on Climate Change) presented in 2001 the “Third Assessment Report” where it is written, “In the light of new evidence and taking into account the remaining uncertainties, most of the observed warming over the last 50 years is likely to have been due to the increase in greenhouse gas concentrations”. Different scenarios are described in the report where the mean global temperature, depending on scenario will rise up to 5.8°C during the period 1990-2100 (IPCC, 2001). The increased greenhouse effect is mainly caused by carbon dioxide (CO₂). CO₂ has, compared to other GHG:s like Methane and HFC etc, a low greenhouse effect on the molecular level, but the comparatively high concentrations in the atmosphere make it the greatest contributor to the global warming (Naturvårdsverket. 2005). This together with future plans for trading of emissions makes it necessary to get an improved understanding of the national/international carbon budget and especially CO₂ in our attempt to decrease the human influence on the global climate.

The aquatic component of the landscape carbon budget is small in absolute terms compared to the uptake and release from forested terrestrial systems (Valentini et al. 2002). However it is a persistent term that can not be neglected. Most studies done on the aquatic part of the carbon cycle within a catchment scale have focused on dissolved organic carbon (DOC) and less attention has been given to gaseous forms (e.g., carbon dioxide and methane) (Hope et al. 1994). But surface waters have been identified as an important conduit of carbon dioxide evasion from soils to the atmosphere and especially from headwaters (Hope et al. 2001). The chemical composition of stream water is a product of many factors and not only in-stream processes. Upland, riparian and groundwater processes are very important to the input of both solutes and gasses to aquatic habitats. Free CO₂ (pCO₂) and dissolved inorganic carbon (DIC) concentrations in stream result from the interplay between inorganic carbon fixation via aquatic primary production, organic matter decomposition, diffusion to the atmosphere (evasion) and groundwater inputs (Kling et al. 1992; Hope et al. 1994). Due to these factors streams are frequently supersaturated of DIC, especially in headwaters and evasion from surface waters may represent a significant pathway for carbon loss to the atmosphere for headwaters in boreal and temperate regions (Hope et al. 1994).

While considerable progress has been made on defining C fluxes from lakes (Algesten et al. 2005) much less attention has been paid to evasion from headwater streams. The estimated flux in Sweden are just estimates which are based on the assumption that CO₂ levels in streams are the same as in Swedish lakes and rivers, i.e. 3-5 times equilibrium with the atmosphere. Studies based on this assumption show an evasion from streams and rivers of up to 0.5 g C/m²&year (Algesten et al. 2004). This study will try to assess the spatial and seasonal variations in the CO₂ evasion flux within a 68 km² headwater catchment.

Measurements of carbon dioxide content in streams made it possible to estimate the evasion flux from stream to the atmosphere for a typical Swedish boreal catchment. Measurements from both monthly sampling at 15 sites, together with three synoptic surveys where around 90 sites were sampled were used. This made it possible to estimate both instantaneous and annual evasion rates at a certain point and also show the variations in evasion flux over the year.

Chemical theory

Background

Henry's law describes the solubility for an ideal gas in a liquid phase. The solubility of the gas in the liquid is proportional to the pressure of the gas over the solution.

$$c = K_H * p \quad (1)$$

Where c is concentration in liquid phase is in moles per liters (M). K_H is Henry's constant, an equilibrium constant which is different for different gasses and with the unit moles per atmosphere (M/atm). p is the pressure of the gas in the unit atmospheres (atm).

K_H is temperature dependent and has to be corrected according to:

$$K_H = H / (R * T) \quad (2)$$

where H is the dimensionless temperature independent equilibrium constant, R is the general gas constant, 0.082058 l*atm/K*mol) and T is the temperature in Kelvin (Stumm and Morgan 1996).

The general gas law describes the relationship between pressure, volume, and temperature for an ideal gas.

$$p * V = n * R * T \quad (3)$$

Where p is the pressure of the gas in atmospheres, V is the volume in litres, n is the quantity of the substance in moles, R is the general gas constant (0.0820578 l*atm/K*mol), and T is the temperature in Kelvin.

The apportionment of carbon dioxide between the gas and liquid phase is dependent on water pH, since carbon dioxide is buffered in water by the bicarbonate buffer system:



$H_2CO_3^*$ is including dissolved and hydrated CO_2 .

The partial pressure of CO₂ in natural waters is often higher than in the atmosphere. It can then be relevant to express the excess of pressure in number of times overpressure, where EpCO₂ is dimensionless.

$$EpCO_2 = \frac{\text{partial pressure of CO}_2 \text{ in natural water}}{\text{equilibrium partial pressure of CO}_2 (360 \mu atm)} \quad (7)$$

pH- and temperature dependency

The CO₂ concentration in water is buffered by the bicarbonate buffer system according to equations 3-5. The system is a chain of linked equilibrium reactions and sensitive to changes in temperature and pH. At pH-values more than 6, small changes in pH affects the distribution of carbon dioxide between different forms of C in the solution (figure 1). Henry’s constant, K_H is as seen in equation 7, temperature dependent and gives carbon dioxide different solubility at different temperatures (figure 2). Since this is the case in many natural waters, with variations in pH and temperature the DIC-concentration and the CO₂ solubility varies a lot over the year.

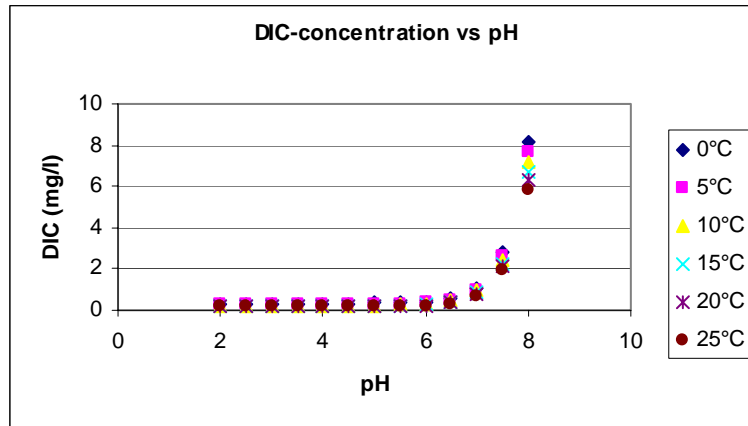


Figure 1. The potential DIC-concentration in water at different pH and at different temperatures

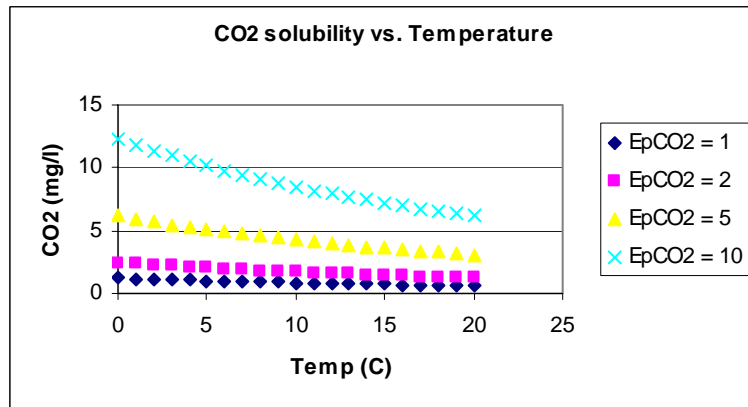


Figure 2. The solubility of carbon dioxide in water at different temperatures and at different levels of overpressure

Study areas

The study was conducted at two locations, Krycklan and Degerö-Stormyr in Västerbotten during 2003-2005.

Krycklan

The headwater catchment of Krycklan is a sub catchment to the catchment of Vindelälven and situated near Vindeln ca 60 km north-west of Umeå. The area is well documented since it is a part of the Svartberget research park. It has an area of 68 km² and is a typical Swedish boreal catchment characterized by climate conditions with short summers and long winters. Snow is covering the ground from the end of October to the beginning of May. The growing season starts at the end of May and ends in late September. Annual mean precipitation is 600 mm, where about 35% falls as snow and the annual day mean temperature is 0°C (Vindelns Science Parks. 2005) The catchment is mainly forested with Norway spruce (*Picea abies*) and Scots pine (*Pinus Sylvestris*). But in the downstream areas deciduous trees are more commonly found near the streams. The soils are mainly well-developed iron podzols. In the upper parts of the catchment there are a few lakes and mires, which in some sub catchments cover a large area.

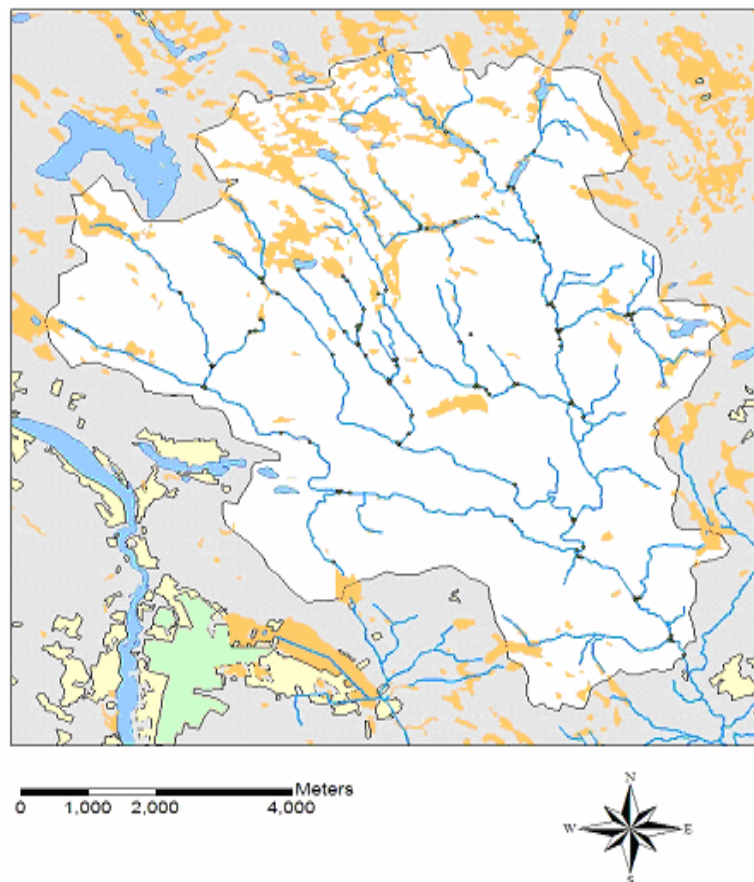


Figure 3. The headwater catchment of Krycklan

Degerö -Stormyr

Degerö-Stormyr is a mixed acid mire system with an area of 6.5 km² in the research park Kulbäcksliden situated 9 km south-west of Vindeln. The mire is on a highland between two major rivers, the Umeälven and the Vindelälven. It consists of a rather complex system of interconnected smaller mires divided by islets and ridges of glacial till. The total catchment area including Degerö Stormyr is ca 10 km² (Malmström 1923). The depth of the peat is mostly between 3 and 4 m, but with 7.8 meters as maximum. The climate is more or less the same as in Krycklan since the distance between the areas only is ca 10 km. Records from the closest national reference climate station, Kulbäcksliden had the following long-term (1961–1990) average values: mean annual total precipitation, 523 mm; mean annual temperature +1.2°C (Alexandersson et al. 1991).

Methods

Field procedures

Degerö-Stormyr

During one day in February 2005 the evasion of carbon dioxide from the stream surface was measured at 4 study reaches along the stream draining the Degerö mire (figure 4). This was done by measuring the carbon dioxide concentration in stream from the upwelling on the edge of the mire and downstream to 250 meters from the source. Temperature, width, and depth of the stream were measured at the upwelling and at the reach at 250 meters downstream (SR4). It was assumed that groundwater flowing into the reach had a negligible effect on the stream CO₂, so that all changes in CO₂ concentration were related to evasion from the stream surface.

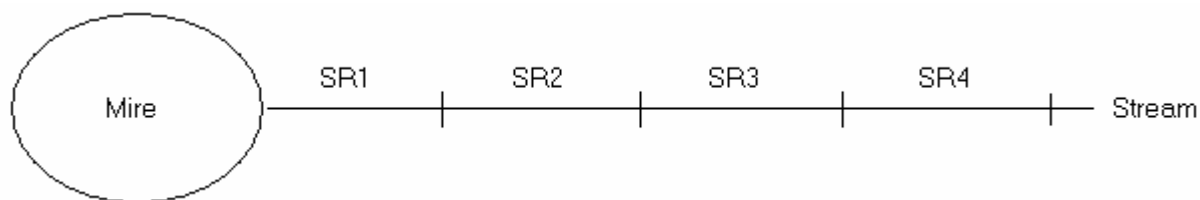


Figure 4. Schematically picture of mire and study reaches at Degerö-Stormyr

	Study reaches			
	1	2	3	4
Length of study reach (m)	50	60	80	60
Mean width (m)	0.5	0.5	0.5	0.5
Stream surface area per study reach (m ²)	25	30	40	30
Mean flow (l/s)*	0.5	0.5	0.5	0.5
Mean wind speed (m/s)**	1.0	1.0	1.0	1.0

Table 1. Physical characteristics for the stream draining Degerö-Stormyr

* Personal comment, Ishi Buffam ** Estimated value

Krycklan

During the period of study (January 2003-March 2005) the carbon dioxide concentration in stream water within the headwater catchment of Krycklan was measured in two types of samplings to determine CO₂ evasion flux. 1) Synoptic surveys, to cover the CO₂ evasion for the entire catchment based on measurements at one occasion. 2) Time series, to determine the variations in CO₂ evasion over the year for a number of sub catchments with streams ranging from stream order 1-4.

Surveys

Once a year between 2003 and 2005 around 90 sites within the catchment were sampled from the headwaters down to the outlet covering stream orders from one to four. The sampling dates were:

2003-05-02 just after the spring flood

2004-04-22 in the middle of spring flood

2005-02-17 - 2005-02-25 at low flow

Samples were taken at every stream junction within the catchment and each confluence was sampled according to figure 5. This was done in order to compare streams and see how each stem affect the main stem. Other sites sampled were for example at entrances and outlets to/from lakes and mires.

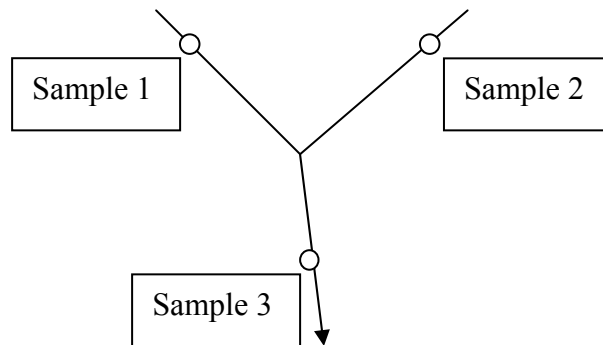


Figure 5. Each stem at the junctions were sampled

	May 2003	April 2004	February 2005
Number of sample sites	97	85	87
Discharge at sampling day (mm/day)	1.004	2.673	0.207
Annual discharge (mm/yr)	210	300	300*
Mean stream width (m)**	1.3	1.5	1.0
Mean stream depth (m)**	0.22	0.3	0.17
Mean stream surface area per study reach (m ²)**	1292	1701	1108

*Table 2. Physical characteristics of the surveys of Krycklan, *Estimated value based on twenty years of sampling. ** Values based on simplified measurements when sampling*

Time series

Sampling was performed monthly, and during spring flood more intensively at 15 sites within the catchment representing stream order 1-4 in 2003 and 2004. Totally ca 30 samples per site and year. To get time series with values for every day I assumed that the change in pCO₂ between the sampling days was linear.

Study reach	Stream order	Catchment area (km ²)	% Mire within catchment	Area rep. study reach (km ²)*	Study reach length (m)	Annual mean flow (l/s) 2003/2004
1	1	0.66	1.3	0.66	2022	3.8/5.9
2	1	0.13	0	0.13	811	0.9/1.4
3	1	0.03	36.5	0.03	109	0.4/0.7
4	1	0.2	40.4	0.2	49	0.9/1.4
5	1	1.0	36.0	1.0	67	5.6/8.6
6	1	1.4	24.1	0.43	1325	8.3/12.8
7	2	0.5	14.9	0.20	1320	3.0/4.7
8	2	2.5	11.3	0.66	1358	15.4/23.8
9	2	3.1	13.8	0.42	660	19.8/30.6
10	2	2.9	25.8	2.9	2961	18.4/28.4
12	3	5.4	15.5	0.07	113	32.4/50.2
13	3	7.2	9.9	1.52	2543	45.5/70.3
14	3	13.6	5.1	0.07	152	73.4/113.5
15	4	19.9	14.0	0.11	128	114.9/177.8
16	4	67.8	8.3	0.02	71	398.7/616.7

*Table 3. Physical characteristics of the time series study reaches of Krycklan. * Area which represents each specific reach, upstream area excluded.*

Sampling

At every study reach/site a water sample of approximately 15 ml of bubble-free water was injected in a 60 ml glass vial sealed with a bromobutyl rubber septa. The injection was made by using a sterile syringe which was flushed with stream water from every site before sampling. The bottle was filled with nitrogen at atmospheric pressure. Additional samples were taken at every site/reach in 100 ml acid washed plastic bottles for pH measurements and other chemical parameters.

Laboratory procedures

The samples for 2004 and 2005 were acidified to pH 2-3 with 1 drop of 30% ultrapure HCl (0.5% v/v). Samples for 2003 were adjusted for changes in pH according to Laudon et al. (2000). All samples were then stored at 8°C. The CO₂ concentration was measured by headspace analysis. Prior to analysis, samples were warmed to 20 °C and shaken for 1 hour to achieve equilibrium.

Headspace CO₂ concentrations were analyzed by GC-FID (Perkin Elmer Autosystem Gas chromatograph) equipped with a methanizer operating at 375 °C. Separation was carried out on a Haysep N column using He (70ml min⁻¹) as carrier gas. Duplicate injections of 0.5 ml were performed for all samples, with additional injections as necessary to attain a coefficient of variation of less than 5%. pH was measured on an Orion 9272 in lab.

Measurements of discharge

At Krycklan all discharge values are based on the measurements from site 7 (damhuset). The flow is measured every hour by loggers (figure 6). Mean daily values are then used in the calculations. By knowing the area, a specific discharge was determined. At all other sites the flows were estimated by using the specific discharge from site 7 and extrapolated with respect to the area that every site represents. The flow at Degerö on the sampling day in February 2005 was estimated to 0.5 liters per second by comparing with the conditions at Krycklan (personal comment, Buffam).

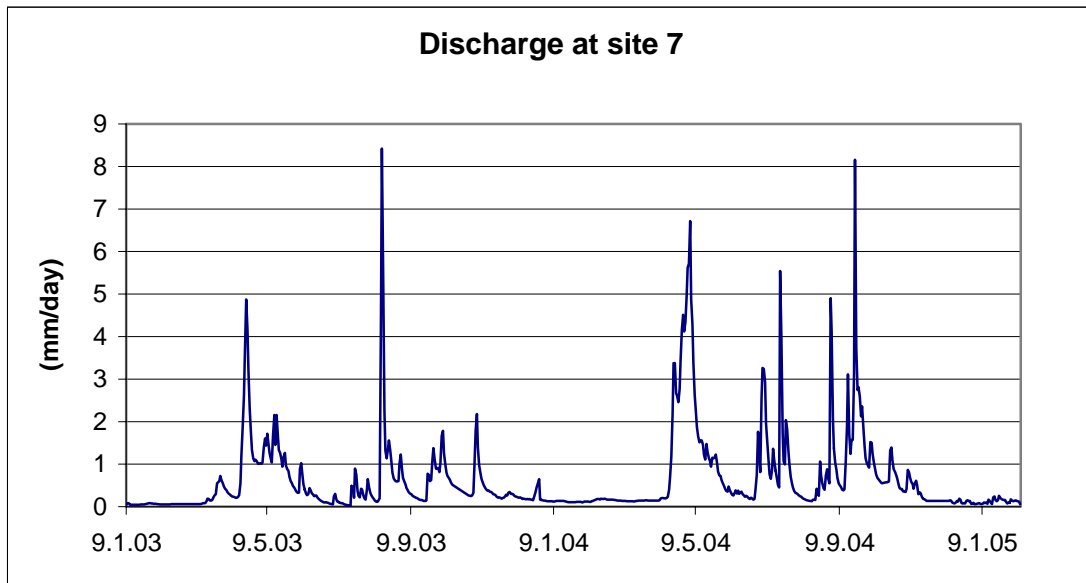


Figure 6. Water discharge at site 7, Kallkällbäcken in the Krycklan catchment from 2003 to the beginning of 2005

Calculations

DIC calculations

With the pCO₂ values that the GC-analysis resulted in, the CO₂ concentration in the water was determined by using equation 1. But CO₂ is not an ideal gas and Henry's constant, K_H was corrected by Weiss, 1974 for the non-ideality according to:

$$\ln K_H = A_1 + A_2(100/T) + A_3 \ln(T/100) \quad (8)$$

where A_1 , A_2 and A_3 represents the constants -58.0931, 90.5069 and 22.2940 respectively, and T is the temperature in Kelvin, laboratory conditions were used with $T=293.15$ K.

The CO_2 concentration in the headspace was determined by using equation 3
By using the CO_2 concentration in the water it was possible to determine the total concentration of inorganic carbon (DIC) in the liquid. This was done according to Stumm and Morgan (1996).

$$DIC = \left([H_2CO_3^*] * (1 + (K_1 / [H^+]) + (K_1 * K_2 / [H^+]^2)) \right) \quad (9)$$

where the concentrations are in molar and K_1 and K_2 are the equilibrium constants adjusted for temperature according to Gelbrecht (1998).

$$\log K_1 = (-3404.71/T) + 14.844 - 0.033 * T \quad (10)$$

$$\log K_2 = (-2902.39/T) + 6.498 - 0.0238 * T \quad (11)$$

By knowing the concentrations of DIC in water and the CO_2 concentration in the headspace a total DIC concentration for both the water and the headspace was calculated

$$DIC_{Total} = DIC_{Water} + CO_{2Air} \quad (12)$$

The analyses were made under laboratory conditions with a temperature at 20°C, samples for 2004 and 2005 were acidified to drive the CO_2 to the headspace according to figure 1. To determine the partial pressure of CO_2 in water during natural conditions, it was necessary to use equation 10 and use pH in stream and the equilibrium constants K_1 and K_2 adjusted for the actual temperature in stream at sampling. By knowing the concentration of DIC, it was possible to determine the in stream concentration of CO_2 according to Gelbrecht (1998)

$$[H_2CO_3^*]_{calc} = \left(DIC / (1 + (K_1 / [H^+]) + (K_1 * K_2 / [H^+]^2)) \right) \quad (13)$$

Evasion calculations

Degerö-Stormyr

By knowing the partial pressure of CO_2 in the stream was it possible to determine the gas evasion flux from stream surface at a study reach. This was done in four ways in order to compare the methods. Only the instantaneous evasion per stream surface area was calculated since it is hard to know how much of the catchment area each reach represents.

A. By using the reaeration flux equation by Young and Huryn (1998)

$$\begin{aligned} & CO_{2\ evasion} \ (\mu mol / s) \\ & = CO_{2\ streamwater-air} * K_{CO_2} * \tau * Q \end{aligned} \quad (14)$$

$CO_{2,streamwater-atm}$ is the difference between the reach stream water CO_2 concentration and the atmospheric equilibrium CO_2 concentration ($\mu\text{mol/L}$) and Q is the stream flow (L/s) from the study reach. τ is the reach travel time (min), and K_{CO_2} is the gas specific transfer coefficient (/min) calculated from $K_{propane}$ by Jones and Mulholland (1998) according to:

$$K_{propane} = \frac{155.3 * Q}{2.41 + Q} \quad (15)$$

$$K_{CO_2} = K_{propane} * 1.3 \quad (16)$$

where $K_{propane}$ and K_{CO_2} is in (/day), Q is in (L/s). K_{CO_2} was then transformed to (/min) by dividing with 1440 when using in equation 15.

B. By using the wind dependent evasion flux equation from water surfaces by Wanninkhof (1992).

$$F = K_0 * 0.31u^2 (Sc / 660)^{-1/2} * \Delta pCO_2 \quad (17)$$

where K_0 is the solubility of CO_2 , u is wind speed at 10 m, Sc is the Schmidt number, and ΔpCO_2 is the difference in CO_2 partial pressure between surface waters and atmosphere.

The equation is constructed to describe the effect of wind speed on CO_2 evasion flux between air and sea, and is not adjusted for conditions in forest. A rough estimation of the wind speed was used, 1.0 meters per second, but as seen in figure 7 small variations in wind speed gives large differences in evasion since the flux increases exponentially with wind speed.

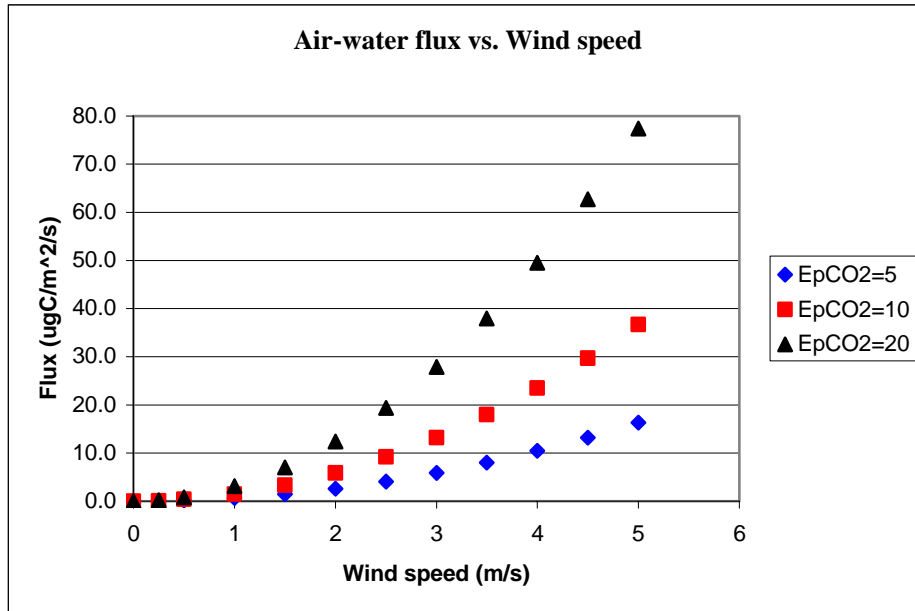


Figure 7. The equation by Wanninkhof showing the flux of carbon dioxide between air and water at different wind speed and at different levels of overpressure

C. By comparing the concentration at the reach with upstream reach was it possible to calculate the evasion and a K_{CO_2} value for every study reach. Lateral groundwater inputs assumed to be negligible so the difference in pCO_2 above atmospheric pressure between the reaches assumed to have degassed.

D. By using the reaeration flux equation by Young and Huryn as in A and K_{CO_2} values calculated from measurements in C, using equation 14.

Krycklan

Surveys

Equations 14-16 were used to determine the evasion for the surveys of Krycklan. To cover the entire catchment I assumed that every sample point corresponds to an equally large reach length. This reach length was calculated by dividing the total stream length of the catchment, 96,308 meters with the number of sampling points. Up scaling from evasion per stream area to evasion per catchment area was done by dividing the sum of the evasion from all reaches with the total catchment area. Up scaling to annual values was done in two ways, by multiplying the total daily evasion with annual discharge for the specific year, or by multiplying the total daily evasion with 365.

Time series

Equations 14-16 were used to determine the evasion for the time series of Krycklan. Every study reach is representing a site specific area and stream length. The evasion is calculated both as annual evasion per catchment area and instantaneous evasion per stream surface area.

Stream morphology

Since the evasion is dependent of the reach travel time, τ , which are dependent of the volume of the study reach, the measurements are used in the calculations of the time series. The data are mean values for each stream order based on simplified measurements at sampling (table 4).

	Stream order			
	1	2	3	4
Mean width (m)	0.8	1.4	1.6	2.5
Mean depth (m)	0.15	0.19	0.23	0.27

Table 4. Mean measurements of width and depth used in the calculations of the time series

Results

Degerö-Stormyr

The sampling shows a high super saturation of CO₂ in the water with EpCO₂ ranging from 28.4 at upwelling to 15.0 250 meters downstream, and with decreasing EpCO₂ with distance from the upwelling (Figure 8). The decrease was almost 10 times overpressure between SR 1 and SR 4, a distance of 200 meters. By comparing each reach with next upstream reach the difference was assumed to be the evasion. By knowing the evasion, a K_{CO2}-value for each reach was calculated according to equation 14. This ranged from 0.0029 to 0.0058. K_{CO2} was also calculated according to the flow dependent equation by Jones and Mulholland (equation 15-16). Since I assumed that the flow was same for all reaches, 0.5 liters per second, K_{CO2} was also the same, 0.0241 (table 5). The ratio between the K_{CO2}-value by Jones and Mulholland and mean measured K_{CO2}-value (0.0042) was calculated as 5.74.

The instantaneous evasion per square meter stream surface area ranged from 340 to 567 µg C/m²&s using the equation by Young and Huryn. Using the equation by Wanninkhof, the instantaneous evasion per square meter stream surface area were ranging from 2.3 to 3.8 µg C/m²&s. The instantaneous evasion per square meter stream surface area ranged from 53 to 85 µg C/m²&s using equation 14 with K_{CO2} from measurements

	Study reaches			
	1	2	3	4
EpCO ₂	24.4	19.4	16.1	15.0
K _{CO2} by Jones & Mulholland	0.0241	0.0241	0.0241	0.0241
K _{CO2} measured	0.0029	0.0046	0.0035	0.0058
A. Instantaneous evasion rate by Young & Huryn with K _{CO2} by Jones & Mulholland	567	444	367	340
B. Instantaneous evasion rate by Wanninkhof	3.8	3.0	2.5	2.3
C. Instantaneous evasion rate from measurements	13.6	14.2	6.8	13.7
D. Instantaneous evasion rate by Young & Huryn with K _{CO2} measured	68	85	53	82

Table 5. EpCO₂, K-values, and evasion rates per square meter stream surface area (µg C/m²&s) for the four reaches at Degerö-Stormyr

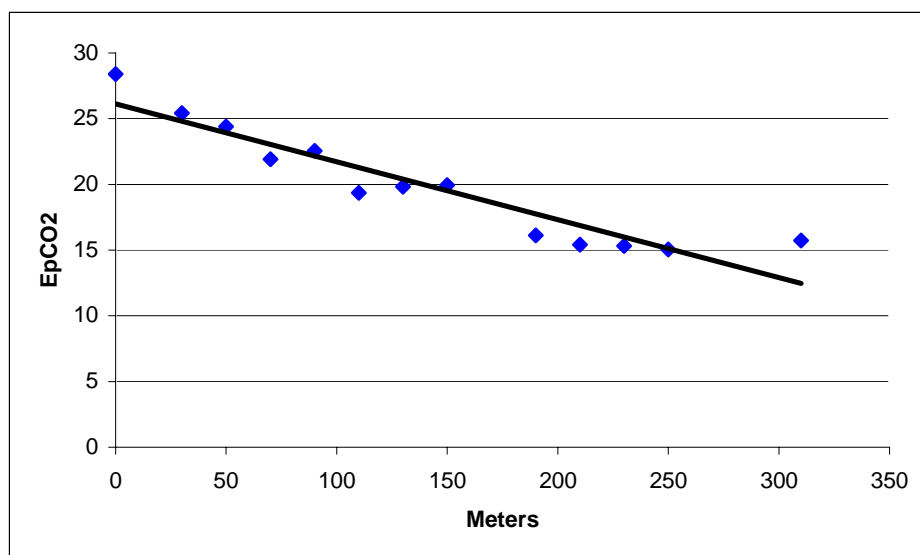


Figure 8. The change in $EpCO_2$ with distance from upwelling at Degerö

Krycklan

Extrapolated results by measured K_{CO_2} from Degerö-Stormyr

The results from the surveys and time series of Krycklan are calculated with the flow dependent equation for the gas specific transfer coefficient, K_{CO_2} by Jones and Mulholland (equation 15-16). However, measurements from Degerö-Stormyr show that using these equations can be an overestimation of the K_{CO_2} -value. By using the ratio of 5.74 between the K_{CO_2} values of Jones and Mulholland and the mean value from the measurements of Degerö, the evasion was extrapolated for the surveys and the time series according to that.

Surveys

The results from the three surveys are found in table 6. $EpCO_2$, DIC-concentration, pH, and instantaneous evasion from stream surface are presented with a range for the around 90 sample sites and a median instead of a mean value to minimize the effect of outliers due to the wide range.

There were large differences among the three surveys with respect to $EpCO_2$ and DIC-concentration. This together with differences in pH and discharge caused the wide range of evasion between the years. But depending on how the evasion was up scaled to the entire catchment different years have the highest evasion values (table 6). Since the comparatively low instantaneous evasion for 2005, median $153 \mu g C/m^2$ was measured at a day with low flow, this resulted in lower evasion than 2003 and 2004 when multiplying by 365. When normalizing the evasion with annual discharge when up scaling resulted in that the evasion of 2005 was the highest when comparing the years, $42.0 g C/m^2$ and 11.6 and $29.9 g C/m^2$ for 2003 and 2004 respectively. The median instantaneous evasion was over four times higher at sampling date in 2004 than in 2003 and over nine times higher than in 2005 (table 6).

Extrapolated results by using measured K_{CO_2} were estimated for the synoptic surveys to **2.0**, **5.2**, and **7.3** g C/m²&year for 2003, 2004, and 2005 respectively, by normalizing with annual discharge.

By dividing the streams into different stream orders, it seems like $EpCO_2$ is lower at sites further down in the catchment. But the trend is not so clear for all three years and the variation is great between sites with same stream order and size. The decrease in $EpCO_2$ from stream order 1 to stream order 4 is 2.5, 1.2 and 4.1 times with equilibrium to the atmosphere for 2003, 2004 and 2005 respectively (figure 9-10).

	May 2003	April 2004	February 2005
$EpCO_2$ range (median)	2.0-11.7 (4.0)	5.4-17.2 (9.9)	1.4-25.7 (3.1)
DIC-concentration (mg/l) range (median)	1.0-3.9 (1.7)	2.1-6.3 (3.6)	0.8-14.2 (2.1)
pH range (median)	4.0-6.8 (6.0)	4.1-6.3 (5.6)	4.6-6.9 (6.5)
Instantaneous evasion rate from stream surface area ($\mu\text{g C/m}^2\&\text{s}$) range (median)	98-1267 (333)	702-2821 (1411)	15-1521 (153)
Daily evasion for entire catchment ($\text{mg C/m}^2\&\text{day}$)	56.7	273.0	28.4
Annual evasion for entire catchment based on sampling day *365 ($\text{g C/m}^2\&\text{yr}$)	20.7	99.5	10.4
Annual evasion for entire catchment normalized by discharge ($\text{g C/m}^2\&\text{yr}$)	11.6	29.9	42.0
Extrapolated by measured K_{CO_2} , annual evasion for entire catchment normalized by discharge ($\text{g C/m}^2\&\text{yr}$)	2.0	5.2	7.3

Table 6. $EpCO_2$, pH, evasion rate, daily and annual evasion for the Krycklan catchment.

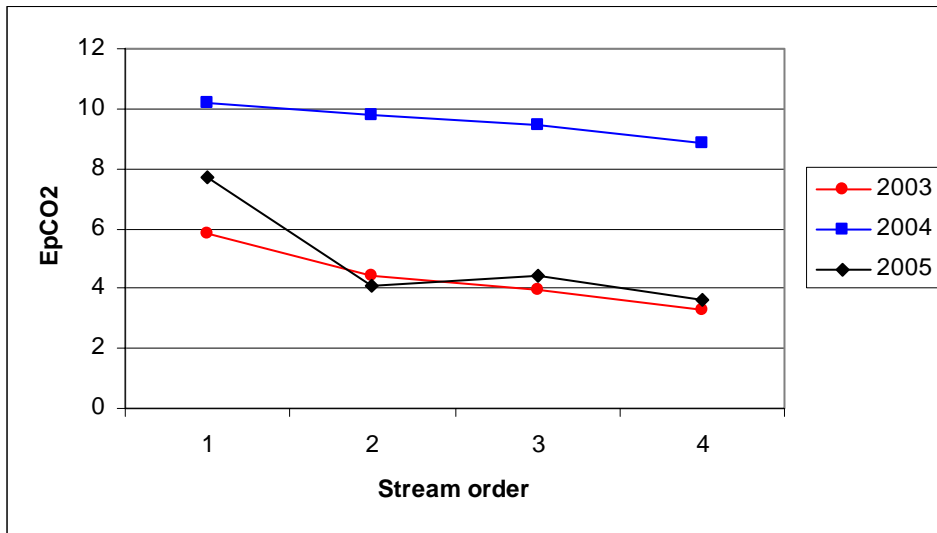


Figure 9. Mean EpCO₂ for each stream order from the surveys of Krycklan in 2003, 2004 and 2005

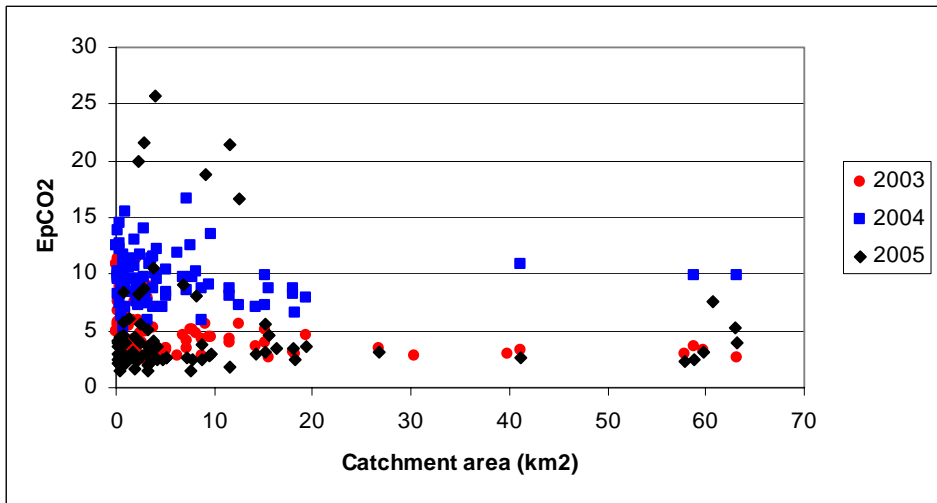


Figure 10. EpCO₂ against catchment area for the study reaches of the surveys of 2003, 2004 and 2005

Time series

The results from the time series of 2003 and 2004 are found in figure11-14. The results for EpCO₂ and instantaneous evasion are presented with an annual mean value. More detailed results with ranging values for variation over year are presented in appendix 2.

There is a wide range in EpCO₂ between the study reaches but also between the years. Generally the annual mean values are higher in 2004 then in 2003 except for study reach 3 and 4 where there are the opposite. Mean annual EpCO₂ for all samples of first order streams, were 11.0 and 11.9 for 2003 and 2004 respectively. Corresponding values for fourth order streams were 2.7 and 6.3. The decrease in EpCO₂ with increased stream order seems to be smaller in 2004. However, the

high values for study reach 3 and 4 have a great influence on the mean value since there are highly supersaturated reaches with a large proportion of mire area, ca 40 percent, in the sub catchment (figure13-14).

The mean annual pH for all study reaches ranging from 3.94 to 6.63 for 2003 and 4.09 to 6.48 for 2004. The mean variation between the years is 0.09 pH units. Lowest pH-values are found at the study reaches where the catchments having a large proportion of mire (appendix 2).

The variations over the year in DIC-concentration, $EpCO_2$, and CO_2 evasion for 2004 are found in appendix 1, where one study reach from each stream order is presented. The variation in $EpCO_2$ follows the variation in DIC, but when comparing the reaches with each other show differences between them. Comparatively high DIC-concentration in SR16 did not result in higher $EpCO_2$ than for SR2 and SR7. Differences in pH is the explanation according to figure 1.

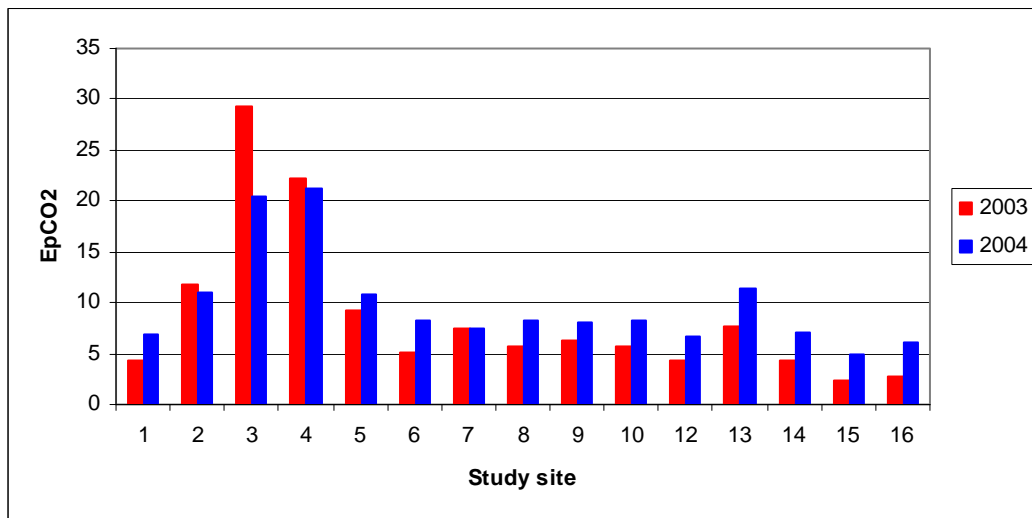


Figure 11. Annual mean $EpCO_2$ for 2003 and 2004 at the 15 study reaches of the time series in Krycklan

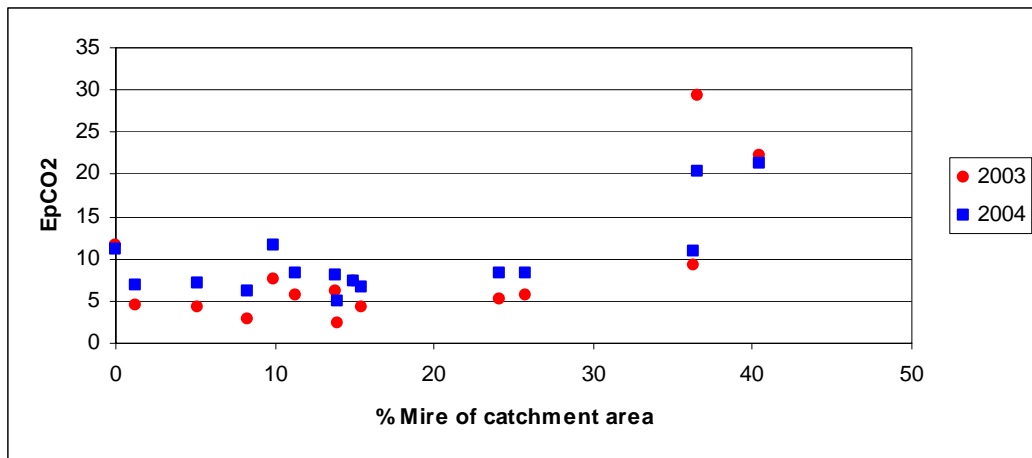


Figure 12. Annual mean $EpCO_2$ for 2003 and 2004 at the 15 study reaches versus percent mire of the catchment area

There is a wide range of annual evasion between the study reaches, from 0.8 and 1.3 g C/m²&year for reach 4 to 87.5 and 271.3 g C/m²&year for reach 16, for 2003, and 2004 respectively (figure 12). Despite much higher EpCO₂ values at reach 4 then at reach 16 (figure 11) the evasion is much smaller. The big difference in flow (table 3) seems to be the explanation to this, since the evasion is flow dependent.

Without influences from differences in area and stream length the instantaneous evasion per stream surface area is presented in figure 14.

To make it possible to compare the study reaches with each other, without influences from upstream evasion I assumed that every reach represents just the surrounding area and not totally upstream catchment area (table 3). Using a mean value of the evasion for the 15 reaches of the time series, representing the entire catchment and extrapolate the results with K_{CO2} value from Degerö-Stormyr gave the result of **5.5** and **13.0** g C/m²&year for 2003 and 2004 respectively.

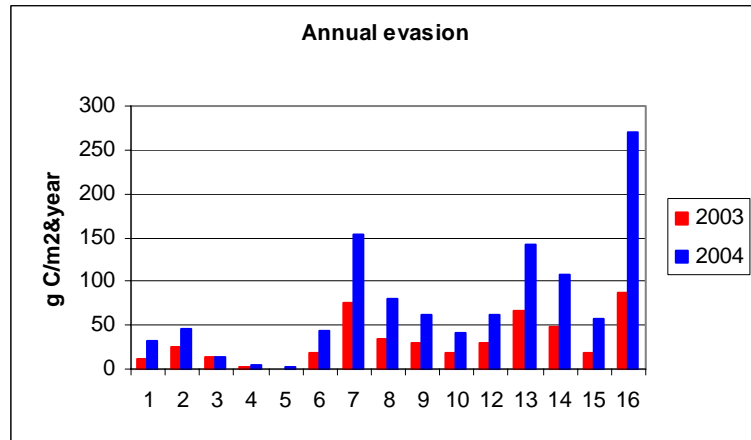


Figure 13. Annual evasion per area rep. each study reach for the 15 study reaches of 2003 and 2004

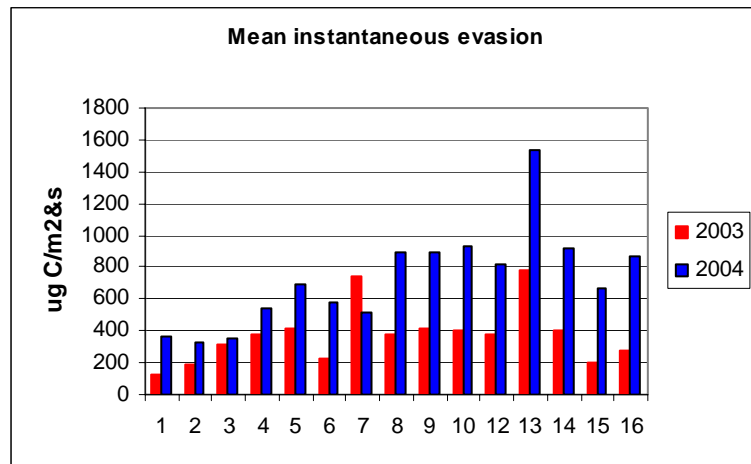


Figure 14. Mean instantaneous evasion per stream surface area for the 15 study reaches of 2003 and 2004

Statistical analysis

Principal components analysis (PCA) where used to determine correlations between different variables in the data set. Different landscape-, chemistry-, and hydrological variables where used, total around 30 variables. The 10 variables which are strongest correlated to each other for the time series of 2003 are presented in figure 15, the variables explain 67% of the variation. EpCO₂, CO₂ evasion are strongly correlated to DIC concentration since there are calculated from DIC. Percent mire is strongly correlated and pH is negative correlated to the evasion of CO₂. Higher proportion mire leads to lower pH due to organic acids, which results in higher EpCO₂ and CO₂ evasion. Increased stream order and catchment area are negatively correlated to the evasion. The negative correlation to forest depends on that smaller amount forest gives higher amount mire which is correlated to the evasion. An annual mean flow is used for all reaches to show the correlation independency of the great differences in flow.

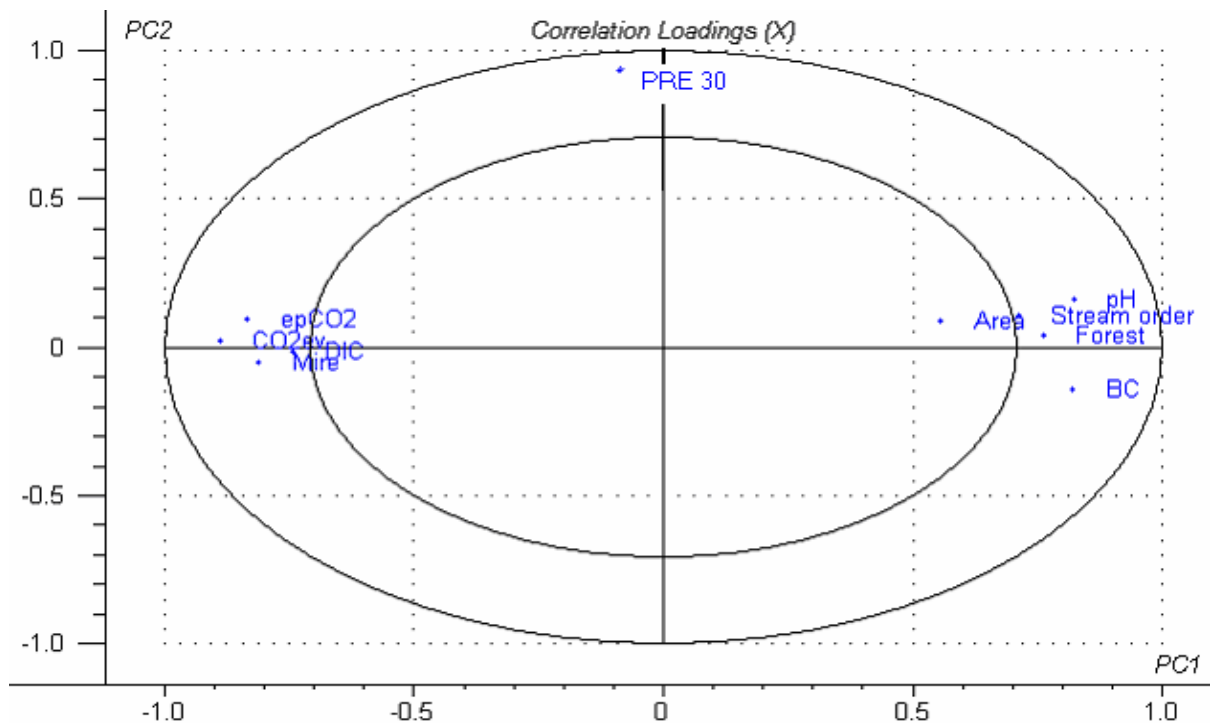


Figure 15. Correlation loading of PCA for Krycklan time series of 2003. The variables explain 67 % of the variation

Variables	Explanation
EpCO ₂	CO ₂ in times of overpressure
CO ₂ ev	Evasion of CO ₂ per square meter stream surface area
DIC	DIC-concentration
Mire	Percent mire within catchment
PRE 30	Precipitation last 30 days
Area	Catchment area
Forest	Percent forest within catchment
pH	pH-value
Stream order	Number of stream order (1-4)
BC	Concentration of base cations

Discussion

The results from this study show that the loss of carbon from a boreal headwater catchment is somewhere between 2 and 13 g C/m²&year. This seems rather realistic when comparing with similar studies done in a peat land area in Brocky Burn, Scotland which shows a loss of 14 g C/m²&year (Hope et al. 2001). It also shows that earlier studies in Sweden seem to have underestimated the loss from streams, 0.5 g C/m²&year (Algesten et al. 2004). As mentioned before the study by Algesten is based on partial pressures of 3-5 times above equilibrium with atmosphere. However, this study show that EpCO₂ in headwater streams varies between 1.5 and 30 times overpressure, and that the annual mean EpCO₂ at many sites especially high up in the catchment is over 10 times overpressure. The super saturation of carbon dioxide in stream water in Krycklan is very high compared to results from similar studies in similar areas. Annual mean EpCO₂ is almost at the same levels as for the highest in comparing studies (table 7) The wide range of the annual evasion arises from the variation between the years and if the calculations are based on the surveys or the time series.

Comparing the methods at Degerö-Stormyr shows that the real evasion seems to be somewhere between using the reaeration flux equation by Young and Huryn (1998) and the wind dependent evasion flux equation from water surfaces by Wanninkhof (1992). Using the factor of 5.7 when recalculate the annual evasion to extrapolated values is simplifications but since it is based on experimental measurement in stream it assumes to be rather appropriate.

Uncertainties about the K_{CO2}-value is however a problem. It seems like using the flow dependent equation by Jones and Mulholland is a rather rough simplification of estimating K_{CO2}. The equation is the result of experiments were propane was used as tracer gas. The evasion equation by Young and Huryn was used in a study from Scotland by Hope et al. (2001) were they also calculated K_{propane} in an experimental way. Figure 16 show how this values correspond to the K_{propane} values from equation 15 by Jones and Mulholland at the same flows. The K_{propane}-values from the study by Hope et al. are measured at different study reaches which also show that there is a great spatial variation.

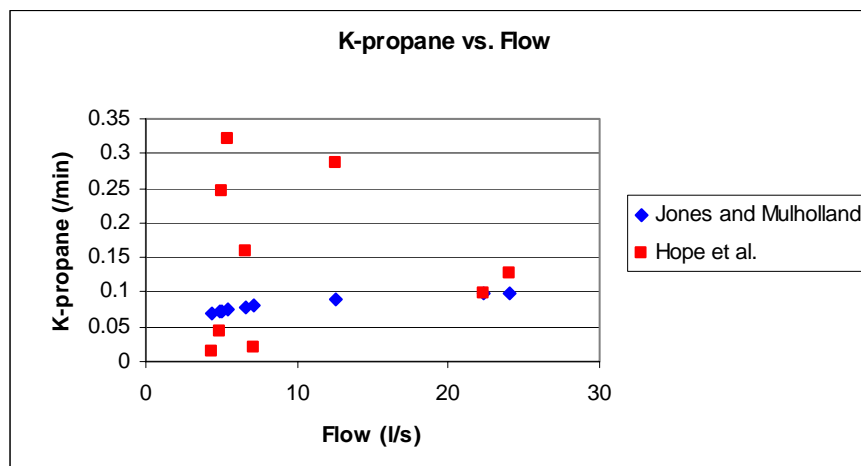


Figure 16. $K_{propane}$ vs. flow for the study by Hope et al. compared to the flow dependent equation by Jones and Mulholland.

Since I have not used tracer experiments like in the studies by Hope et al. (2001) and Jones and Mulholland (1998), measurements of the stream morphology is important for the evasion when using the reaeration flux equation by Young and Huryn (1998), since τ , reach travel time is dependent of the volume of the study reach. I have used mean values of width and depth for each stream order based on simplified measurements when sampling.

Both the annual and spatial variation of CO₂ evasion is to a great extent regulated by water discharge when using the reaeration flux equation by Young and Huryn (1998) (figure 6 and 19). Partly because the evasion is dependent of the flow due to the equation, but also because it seems like discharge and pH is regulating the variation of EpCO₂ (figure 6, 18-19 and table 8-9).

Comparison to other studies

Similar studies in temperate and boreal regions are done and shown in table 7. The selection includes only those references from which such an annual flux estimate is available or can readily calculated and emphasizes studies carried out in peat land systems.

	EpCO ₂	CO ₂ evasion (g C/m ² &year)	Reference
Rivers			
This study	1.5-30	2-13	
Brocky Burn, Scotland	1.2-7.6	14	Hope et al. (2001)
Walker Branch, Tennessee	1.0-10.1	2-4	Jones & Mulholland (1998)
Boreal rivers, Sweden	3-5	0.11-0.57	Algesten et al. (2004)
Arctic rives, Alaska	1-2.8		Kling et al. (1992)
Lakes			
Arctic lakes, Alaska	0.3-10.7		Kling et al. (1992)
Boreal lakes, Sweden	3-5	0.6-5.1	Algesten et al. (2004)

Table 7. A summary of carbon dioxide flux data from published studies of gaseous evasion from streams, rivers and lakes in temperate and boreal regions. The evasion is expressed as loss of carbon per square meter catchment area

Conclusions

The super saturation of carbon dioxide in stream in the head water catchment of Krycklan is very high and well correlated to the proportion of mire in the catchment area.

The evasion of carbon dioxide from Swedish boreal headwaters is higher than earlier estimations, and is a persistent term that has to be taken account when discussing the carbon budget.

A large part of the carbon dioxide seems to degas shortly after that the groundwater enters the stream according to the study at Degerö-Stormyr.

Improved measurements of the gas specific transfer coefficient, K_{propane} and the relationship to K_{CO_2} should get more appropriate results when using this method.

Due to the great daily and spatial variation in evasion it is difficult to upscale daily values to annual, and calculate a total evasion for the entire catchment based on sampling at 15 sites.

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Appendix 1

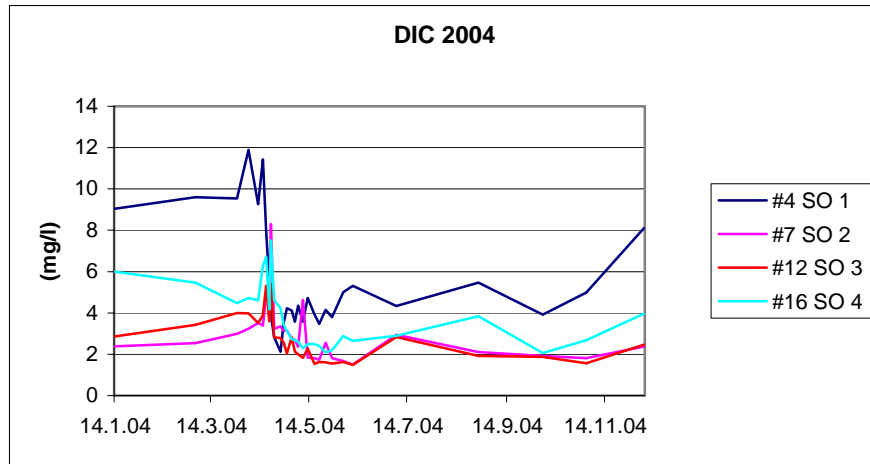


Figure 17. The variation in DIC-concentration for 2004 at four study reaches with different stream order

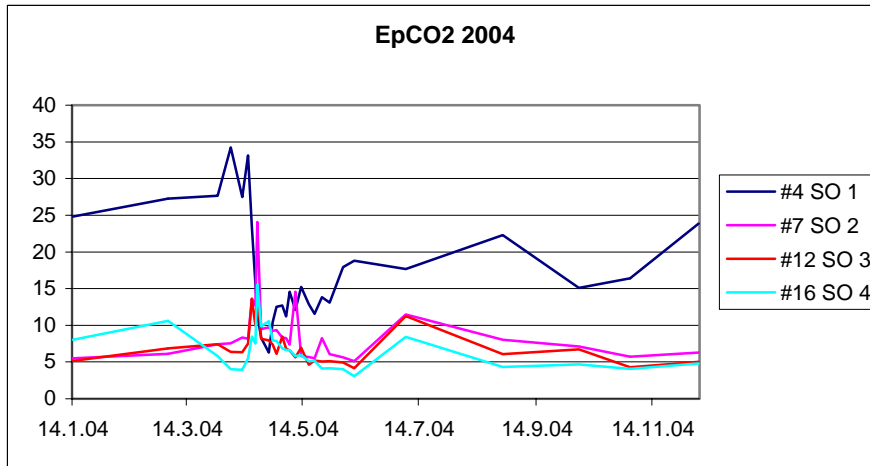


Figure 18. The variation in EpCO₂ for 2004 at four study reaches with different stream order

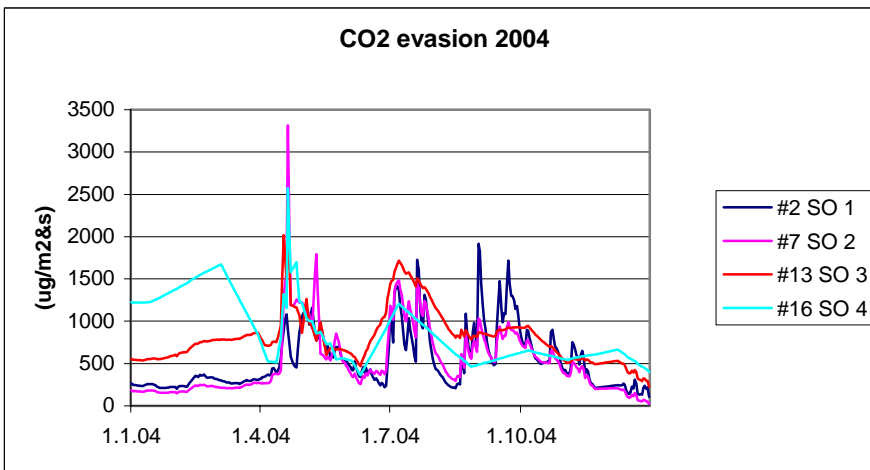


Figure 19. The variation in CO₂ evasion for 2004 at four study reaches with different stream order

Appendix 2

Study reach	EpCO ₂ range (mean) 2003	EpCO ₂ range (mean) 2004	pH mean 2003	pH mean 2004
1	2.5-6.7 (4.4)	3.8-25.8 (6.9)	5.37	5.40
2	3.4-24.6 (11.7)	5.6-21.8 (11.1)	5.13	5.05
3	8.6-62.0 (29.3)	10.3-26.2 (20.4)	3.94	4.09
4	4.1-33.0 (22.3)	6.4-35.2 (21.2)	4.32	4.47
5	5.3-20.0 (9.2)	7.0-16.9 (10.9)	5.03	4.89
6	2.8-7.4 (5.2)	3.5-15.7 (8.2)	5.58	5.45
7	3.7-12.0 (7.4)	2.1-24.8 (7.4)	4.48	5.03
8	3.9-9.2 (5.7)	3.8-15.5 (8.3)	5.35	5.34
9	3.6-9.7 (6.2)	3.3-15.5 (8.0)	5.71	5.76
10	4.0-8.5 (5.7)	3.7-15.9 (8.3)	5.35	5.26
12	2.5-7.4 (4.3)	3.2-15.6 (6.6)	5.64	5.56
13	3.8-16.4 (7.6)	5.7-30.4 (11.5)	5.83	5.76
14	2.4-7.7 (4.3)	1.7-14.6 (7.0)	6.28	6.25
15	1.7-4.5 (2.3)	2.6-8.5 (5.0)	6.54	6.37
16	1.6-8.1 (2.8)	3.1-16.0 (6.1)	6.63	6.48

Table 8. Ranging and annual mean EpCO₂ and annual mean pH for the 15 sub catchment used in the time series

Study reach	Instantaneous evasion (µg C/m ² &s) range (mean) 2003	Instantaneous evasion (µg C/m ² &s) range (mean) 2004	Annual evasion (g C/m ² &yr) 2003	Annual evasion (g C/m ² &yr) 2004
1	24-361 (132)	86-2711 (369)	11.1	31.0
2	22-1261 (187)	24-1287 (321)	26.3	44.9
3	20-3672 (320)	55-1768 (349)	12.6	13.6
4	26-2412 (376)	107-1917 (535)	3.2	4.5
5	59-1156 (416)	187-1714 (698)	0.8	1.3
6	55-536 (230)	89-1672 (577)	18.0	44.5
7	36-710 (743)	22-3314 (522)	75.4	153.0
8	140-743 (381)	197-2027 (895)	34.9	80.3
9	112-924 (410)	179-2222 (892)	28.8	61.6
10	120-824 (404)	205-2114 (928)	18.2	41.1
12	152-757 (381)	225-2365 (812)	30.0	62.7
13	279-1918 (782)	759-4684 (1531)	66.1	142.6
14	178-851 (398)	87-2221 (922)	47.2	107.8
15	112-541 (197)	241-1296 (663)	17.7	58.3
16	84-1109 (274)	362-2575 (873)	87.5	271.3

Table 9. Instantaneous evasion per stream surface area and annual evasion per area representing each study reach for the 15 sub catchment used in the time series