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Quantifying CO2 evasion from a headwater stream-A multidimensional study

Kvantifiering av CO2-avgång från en källnära bäck-En multidimensionell studie

Maria Ingvarsson

ABSTRACT
Quantifying CO_2 evasion from a headwater stream - A multidimensional study

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In order to estimate CO_2 evasion and predict K_{CO2} from a headwater stream in the northern part of Sweden, three different methods have been used. Evasion is the process when carbon dioxide degasses from the surface water of the stream to the atmosphere and K_{CO2} is the gas transfer coefficient. Together with hydrology data, concentration measurements, temperature measurements and pH-sampling, an estimation of CO_2 evasion and estimations of K_{CO2} values have been done. The methods that have been evaluated and compared are, volatile gas tracer injection, where a tracer gas has been injected to the stream. The tracer gas is assumed to have a related degassing trend to the CO_2. Evasion is assumed to depend on discharge, residence time, concentration of carbon dioxide in the stream water and a constant, K_{CO2}. The second method, the chamber method is based on a closed chamber which is laid onto the stream water. The CO_2 evasion is measured directly. The third method is based upon a mass balance model, where the mass of carbon that goes into the system is equal to the mass of carbon that goes out of the system.

The result from the study shows that the measured and calculated evasions have a range between 0.4-3.8 g Carbon year^{-1} m^{-2} catchment area. The gas tracer method gives the highest estimations and the mass balance method gives the lowest. The chamber method probably underestimates evasion because of the reducing turbulence when the chamber is laid on the water. The K_{CO2} values vary between 0 - 0.0644, where the gas tracer and the mass balance methods give the same range and the range of the chamber method is about half. The chamber method does not show any relation between discharge and evasion. The hydrology has large impact on the results.

REFERAT

Kvantifiering av CO$_2$-avgång från en källnära bäck – En multidimensionell studie

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För att uppskatta CO$_2$-avgång och koldioxidöverföringskonstanten, K_{CO2} från en källnära bäck i norra Sverige har tre olika metoder använts. CO$_2$-avgång är processen när koldioxid avgasas från bäckytan till atmosfären på grund av koncentrationsskillnader och K_{CO2} är en gasöverföringskonstant som styr hur mycket som avgasas till atmosfären. Tillsammans med hydrologiska data, koncentrationsmätningar, temperaturmätningar och pH-provtagningar har en uppskattning av CO$_2$-avgång och K_{CO2}-värden gjorts. Tre metoder har utvärderats och jämförts. En är spårgasinjektion, där en spårgas har injicerats i bäcken. Gasen antas diffundera enligt en relation till CO$_2$. Avgången av gas antas bero på vattenföring, uppehållstid av vatten, CO$_2$-koncentration i bäcken samt en koldioxidöverföringskonstant, K_{CO2}. Den andra metoden, kammarmetoden, baseras på att en sluten kammare läggs på ytvattnet på bäcken och koldioxidavgången mäts direkt. Den tredje metoden baseras på en massbalansmodell, där massan koldioxid som flödar in i systemet är lika med massan koldioxid som flödar ut ur systemet.

Resultaten visar att CO$_2$-avgången varierar mellan 0,4-3,8 g kol år^{-1} m^{-2} avrinningsområde. Spårgasmetoden ger de högsta uppskattningarna och massbalans-modellen de lägsta. Kammarmetoden underskattar förmodligen avgången eftersom turbulensen reduceras när kammaren läggs på ytvattnet. K_{CO2} varierar mellan 0-0,0644, där spårgasmetoden och massbalansmetoden har samma område och kammarmetodens område är hälften. Kammarmetoden visar ingen relation mellan vattenföring och CO$_2$-avgång. Hydrologin har stor betydelse för uppskattningen av K_{CO2} och gas avgången.

PREFACE

This master thesis includes 30 hp and is the final moment in my civil engineering studies in Aquatic- and environmental engineering, Uppsala University.

The master thesis has been performed at the Department of Environmental Assessment at Swedish University of Agricultural Sciences. Supervisor has been PhD Student Marcus Wallin. Professor Kevin Bishop has been reviewer, the Department of Environmental Assessment, Swedish University of Agricultural Sciences.

I would like to thank all the people who made this thesis possible, especially Marcus Wallin and Kevin Bishop for all the guidance, all the help and all the good answers on many questions and for encouraging me all the time. Thanks also to Thomas Grabs, Stockholm University for hydrology data, to Peder Blomquist, Umeå University for help in the field and to all other people who somehow have encouraged me during this work.

Uppsala, June 2008
Maria Ingvarsson

POPULÄRVETENSKAPLIG SAMMANFATTNING

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Klimatet är ett hett ämne i den dagliga debatten och faktorerna som påverkar klimatet är många. En ökad växthuseffekt är en av de bidragande orsakerna till att klimatet faktiskt blir varmare och en av de viktigaste växthusgaserna är koldioxid. Koldioxid är en viktig komponent i kolbudgeten. Förståelsen av lagringen och utbytet av kol i och mellan terrestra, akvatiska och atmosfäriska system har stor betydelse i diskussionen om huruvida ekosystem fungerar som källa eller som sänka av atmosfäriskt koldioxid.

En av transportvägarna för koldioxid från terrestra system till atmosfären är genom ytvatten. Denna väg är liten i jämförelse med fotosyntes och markandning men det akvatiska bidraget pågår ständigt. Den senaste uppskattningen av hela den akvatiska kanalen för Sverige är 5.3 g C $år^{-1}$ m^{-2} avrinningsområde (Jonson et al., 2007).

Koldioxid avges till atmosfären via sjöar, vattendrag och hav på grund av en koncentrationsgradient mellan atmosfären och ytvattnet. Denna process kallas CO_2-avgång. I en studie från Amazonas avrinningsområde har det visats att det varje år avgasas 0.5 gigaton koldioxid (Richey et al., 2002). Det är ett stort flöde och ytvattenavgången kan således vara ett betydande bidrag till den globala kolcykeln.

En teori är att CO_2-avgångens storlek beror av avrinning, uppehållstid av vatten, CO_2-koncentration i bäckvatten samt en gasöverföringskonstant, K_{CO2}. Avrinning, uppehållstid och koncentrationer är parametrar som är relativt lätta att mäta medan K_{CO2} inte kan mätas. K_{CO2} är ett mått på variationen i CO_2-avgång och är plats- och tidsspecifik. Den antas variera med flöde, turbulens, vindhastighet, morfologi hos bäcken och klimatet. Om det är möjligt att uppskatta K_{CO2} för olika områden och olika förhållanden kan CO_2-avgången beräknas.

Få undersökningar har gjorts där koldioxidens avgång från bäckar har studerats. I denna studie som har genomförts i norra Sverige har CO_2-avgång och K_{CO2} uppskattats med hjälp av tre olika metoder. Spårgasmetoden är en metod där propangas har injicerats i bäcken. Det har antagits att propangasens avgång är relaterad till avgången hos CO_2. Den andra metoden, kammarmetoden har bestått i att en sluten kammare har lagts på ytvattnet och gasavgången har mätts direkt. Den tredje metoden är en massbalansmodell, där det antas att massan koldioxid i systemet är konstant och inflödet och utflödet av koldioxid balanserar varandra.

Resultatet från studien visar att K_{CO2}-variationen för det här området ligger mellan 0-0,0644, för spårgasmetoden och massbalansmetoden medan kammarmetodens område är hälften, 0-0,0355. Enligt spårgasmetoden är K_{CO2} starkt flödes- och temperaturberoende, medan massbalansmetoden enbart visar på ett flödesberoende. Massbalansmetodens K_{CO2} beror av vilka antaganden på koldioxidkoncentrationen hos det inströmmande grundvattnet till bäcken som görs. Trots att spårgas- och massbalansmetoden har samma

K_{CO_2}-område, skiljer sig den dagliga variationen mellan dessa modeller mycket. Studien visar på komplexiteten i att bestämma gasöverföringskonstanten.

Den årliga CO_2-avgången som beräknats med de olika metoderna visar att spårgasmetoden ger den högsta uppskattningen och massbalansmetoden den lägsta. Det troliga är att kammarmetoden underestimerar CO_2-avgången eftersom en del av ytturbulensen tas bort när kammaren läggs på bäckvattnet. Kammarmetoden ger ingen indikation på att flödet och CO_2-avgången har något samband, den visar dock på en rumslig variation av CO_2-avgång. Allt tyder på att uppskattning av CO_2-avgång är mycket komplext och att det är många processer som styr storleken av koldioxidavgång från bäcken till atmosfären. Studien visar på svårigheten att uppskatta K_{CO_2} och CO_2-avgång utifrån kända parametrar. Naturen är mycket komplex och faktorer som förmodligen har stor betydelse för CO_2-avgången är flödet, turbulensen, omgivande förhållanden, vinden, omblandningsgrad och temperaturer. Parametrarnas olika bidrag är svårt att uppskatta, men det kan konstateras att det finns en stor rumslig variation i K_{CO_2}. För att vidare klarlägga CO_2-avgång och K_{CO_2} behöver flera mätningar göras.

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1. INTRODUCTION

1.1 AIM

The evasion of carbon dioxide, CO_2 from surface water has emerged as an important unknown parameter in the landscape carbon balance. The evasion of CO_2 depends on the concentration of CO_2 in waters and the evasion efficiency which can be described by a term K_{CO2}. This term is not well defined for running waters.

The aim of this study is to compare different methods to estimate the K_{CO2} and CO_2 evasion from a boreal headwater stream. The methods that have been considered are; volatile gas tracer injection, floating chamber and concentration measurements in a mass balance model.

1.2 BACKGROUND

CO_2 is the most important greenhouse gas due to the high amount of it in the atmosphere compared to other gases. It is a central component in the landscape carbon balance. The understanding of storage and exchange of carbon in and between terrestrial, aquatic and atmospheric systems is crucial when discussing if an ecosystem acts as a sink or source for atmospheric CO_2.

One of the conduits for CO_2 from terrestrial systems to the atmosphere is through surface water. The aquatic conduit is small compared to photosynthesis and soil respiration in the terrestrial carbon cycle, but the aquatic conduit is persistent. The most recent estimates of the entire "aquatic conduit" for CO_2 in Sweden are 5.3 g C m^{-2} yr^{-1} (Jonson et al., 2007).

Oceans, lakes, rivers and streams are releasing CO_2 because a concentration gradient between the surface water and the atmosphere exists (Johnson et al., 2007). This process, when CO_2 degasses from the water to the atmosphere is called evasion. For example 0.5 Gt carbon is assumed to degas from the Amazon Basin every year (Richey et al., 2002). This is a large flux and water bodies can account for some of the missing carbon in the global carbon cycle (Billet et al., 2006). The CO_2-cycle can be seen in figure 1.

The research about dissolved organic carbon in streams has been quite extensive, whereas there has not been much focus on the dissolved inorganic carbon in streams where CO_2 is one component. The available estimates of evasion are mostly for lakes and large rivers. Groundwater inflow to the headwater stream usually brings a large amount of dissolved gases and might have an increasing affect on the evasion rate (Hope et al., 2001).
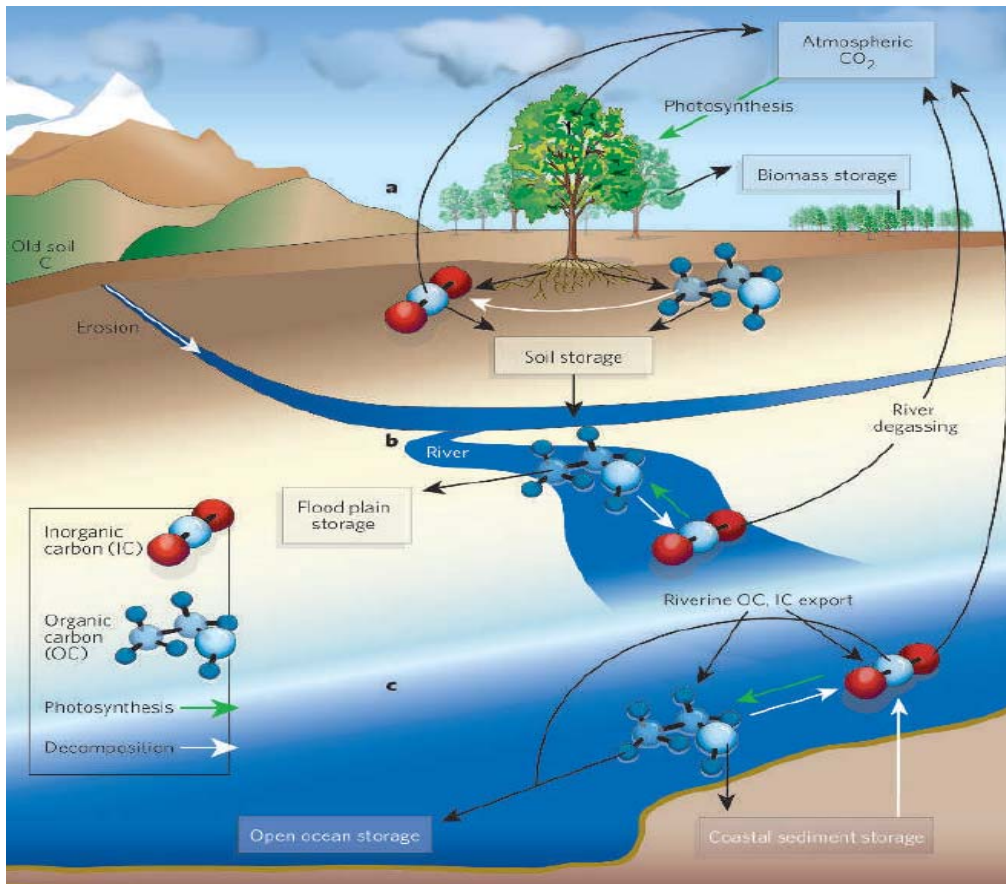
Figure 1 The carbon dioxide cycle. (Raymond, 2005).

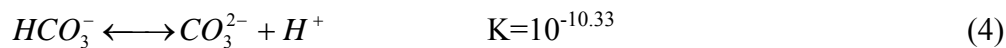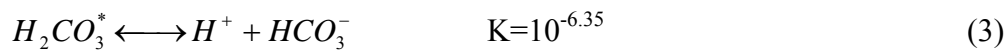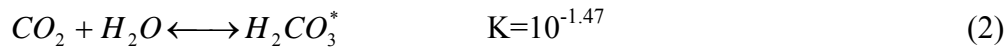## 1.3 CARBON INPUTS AND OUTPUTS TO A HEAD WATER STREAM

Concentrations of DIC (dissolved inorganic carbon) in the stream are the result of an interaction between processes regulating the carbon content. Examples of these processes are primary production, decomposition of organic matter, ground water inflow to a stream and degassing to the atmosphere (Jones et al., 1998).

The characteristics of the surrounding area have big influence on the carbon input to the stream. If the stream is surrounded by a pine-, spruce-, or leaf forest, wetland or any other type of vegetation, dissolved carbon will exist in organic or inorganic form in different ratios and levels. Depending on the accessible carbon and the groundwater inflow to the stream this will regulate the input of carbon to the stream. DIC concentration and CO_2 solubility in the stream varies between seasons because of big differences in pH, temperature, hydrology and carbon accessibility. Some of the processes regulating the carbon export of organic and inorganic carbon are ground based production, mineralization of CO_2, geohydrological characteristics in combination with water discharge (Jonsson et al, 2007), respiration (Billet at al., 2006) and emissions to the atmosphere.

2. THEORY

2.1 BICARBONATE SYSTEM

The bicarbonate system or the carbonic acid system as it is called is a natural buffer system which has a natural ability to resist pH changes. By a few reactions (eq. 1-4) this course of events can be explained and the components are CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+ and OH^- (Stumm et al., 1996). The amount of one species for a specific time depends on the equilibrium shifting. Factors that affect the reactions are pressure, temperature, pH and concentrations (Grip et al., 2001)

$$CO_2(g) \longleftrightarrow CO_2(aq) \tag{1}$$
$$CO_2 + H_2O \longleftrightarrow H_2CO_3^* \qquad K=10^{-1.47} \tag{2}$$
$$H_2CO_3^* \longleftrightarrow H^+ + HCO_3^- \qquad K=10^{-6.35} \tag{3}$$
$$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+ \qquad K=10^{-10.33} \tag{4}$$

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

2.1.1 pH and temperature dependency

The amount of carbon dioxide in the head water stream is highly dependent on the pH because the hydrogen concentration will regulate the direction of the reactions (eq. 1-4). A simple way to illustrate the amount of the species and the pH dependency is by a partition diagram (fig. 2). A high pH results in a high concentration of CO_3^{2-} and a low pH makes the concentration of $H_2CO_3^*$ dominant. When pH is in the range of 4-7 which is normal for a northern headwater stream, most of the carbon is in the form of HCO_3^- and $H_2CO_3^*$.
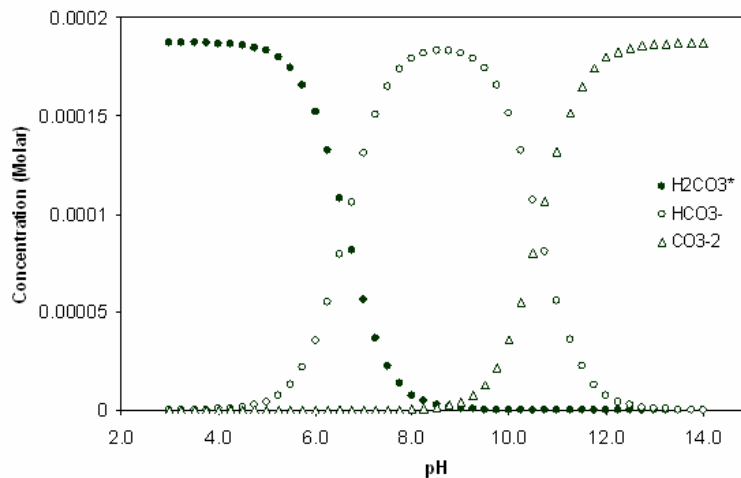

Figure 2 Concentration of species at different pH and at temperature 20° C.

The stream water temperature is of importance for the dissolution degree of the gas in the water. In general, gas solubility decreases with higher temperature (Stumm et al,. 1996). This is illustrated in figure 3.
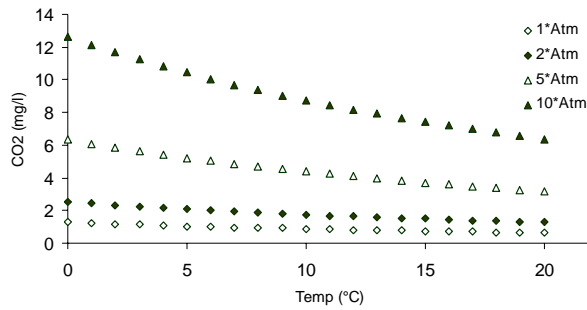
Figure 3 Solubility of CO_2 in water as a function of temperature and different pressures.

2.2 HENRYS LAW

The gas solubility can be expressed with Henrys law (eq. 5) where the partial pressure of a gas is proportional to the liquid-phase concentration. P is the partial pressure (atm), K_H is Henry's constant (atm liter mol^{-1}) and C is the concentration (mol $liter^{-1}$).

$$p = K_H \cdot C \tag{5}$$

K_H is temperature dependent and valid for ideal solutions (Stumm et al., 1996). Equation 6 shows the temperature dependency of K_H. H is a temperature independent equilibrium constant (dimensionless), R is the ideal gas constant (liter atm K^{-1} mol^{-1}) and T is the temperature (K).

$$K_H = \frac{H}{R \cdot T} \tag{6}$$

2.3 IDEAL GAS LAW

The ideal gas law can be expressed by equation 7. P is the pressure (atm), V is the volume (liter), n is the substance amount (mol), R is the ideal gas constant (liter atm K^{-1} mol^{-1}) and T is the temperature (K).

$$p \cdot V = n \cdot R \cdot T \tag{7}$$

Combining equation 5, 6 and 7 gives a good tool for calculating for example the carbon dioxide concentration in different samples.

2.4 EVASION

The concentration of CO_2 in surface water is higher than the surrounding environment and the result of this is that carbon dioxide will degas to the atmosphere. This is an equilibrium reaction between water surface and atmosphere. Factors affecting the evasion rate are turbulence, slope of stream, wind speed, discharge, morphology, depth, width and concentration of carbon dioxide in the stream (Hope et al., 2001). The evasion is assumed to be a function of four parameters; the discharge, the residence time, the CO_2-gas transfer coefficient and the excess of CO_2 in equilibrium with stream water and atmosphere. Equation 8

4

(Hope et al., 2001) describes this, where E is evasion (μmol s^{-1}), Q is the discharge (liter s^{-1}), τ is the residence time (min), K_{CO_2} is the gas transfer constant (min^{-1}) and $CO_{2(str\text{-}atm)}$ is the excess of CO_2 in equilibrium with stream water and atmosphere (μ mol liter^{-1}). This equation is a modified form of the Young and Hyrun (1998) reareation flux formula.

$$E = Q \cdot \tau \cdot K_{CO_2} \cdot CO_{2(str-atm)} \tag{8}$$

2.5 K_{CO2}

One of the components in equation 8 is the gas transfer constant, K_{CO2}, which is a measurement of the variability in evasion. This constant is time and place specific and varies with discharge, turbulence, wind speed, morphology of the stream and the climate. If it would be possible to predict K_{CO2} and relate it to different factors, it would be easy to estimate the evasion.

2.6 VOLATILE GAS TRACER METHOD

By adding propane gas to the stream water, it is possible to study the concentration decrease within a limited stream length assuming that the gas is lost only by evasion. It is assumed that propane gas is degassing at a rate proportional to CO_2. K_{CO2} can be related to the degassing degree of propane gas and thereafter evasion can be estimated.

2.7 CHAMBER METHOD

A closed chamber is laid on the surface water and a CO_2-transmitter is measuring the accumulated carbon dioxide over time, the evasion rate. The CO_2-transmitter is based on a method called IRGA, Infrared Gas Analyzer. In a simple way, it can be described as an IR-light source sending out infrared beams. The CO_2-concentration affects the beams and this is a measure of the gases light absorptions ability (Vaisala, 2007). This will give the gas concentration. The advantage with the chamber method is that it is a direct method and does not influence the system chemically.

2.8 MASS BALANCE MODEL

Relatively little is known about carbon dioxide fluxes within headwater streams and the research about it is sparse. One way to illustrate the fluxes is with a mass balance model. The model is based on conservation of the mass of CO_2 into the system and the mass of CO_2 out of the system with storage in stream not changing (fig. 4). Equation 9 describes this, where E is evasion (μmol s^{-1}), C_{in} and C_{out} (μmol L^{-1}) are the "horizontal" CO_2 concentrations into respective out of the system and $C_{g.w}$ (μmol L^{-1}) is the "vertical" concentration of CO_2 flowing in with the groundwater to the system. Q_{in} and Q_{out} (L s^{-1}) are discharge into and out of the system, Q_{gw} (L s^{-1}) is the groundwater discharge into the system and ΔS (μmol s^{-1}), is the storage. ΔS is assumed to be zero. With this formulation, mass of CO_2 in the box is assumed not to change.

$$E = C_{in} \cdot Q_{in} + C_{gw} \cdot Q_{gw} - C_{out} \cdot Q_{out} + \Delta S \tag{9}$$
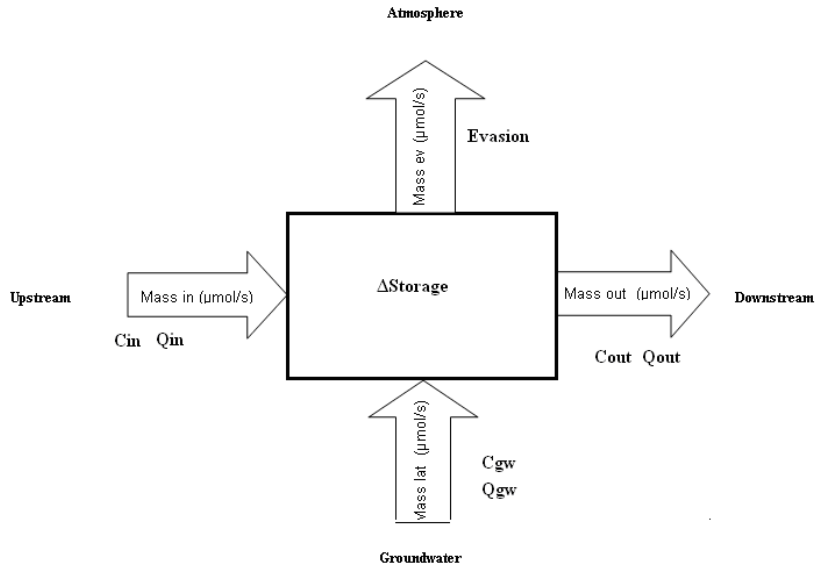
Figure 4 A conceptual model over the fluxes into and out of a head water stream.

3. MATERIAL AND METHODS

3.1 STUDY AREA

The Krycklan catchment (fig. 5) is located in the northern part of Sweden, 60 km northwest of Umeå. It has an area of 67 km^2. The climate is characterized by short summers and long winters, with a snow cover from late October until early May (Laudon et al., 2007). The mean temperature is 0°C and the mean annual precipitation is 600 mm (Laudon et al., 2007). Typical for northern streams are spring flood, coming in late April. The altitude is between 126 and 369 meters above sea level (Ågren, 2007).
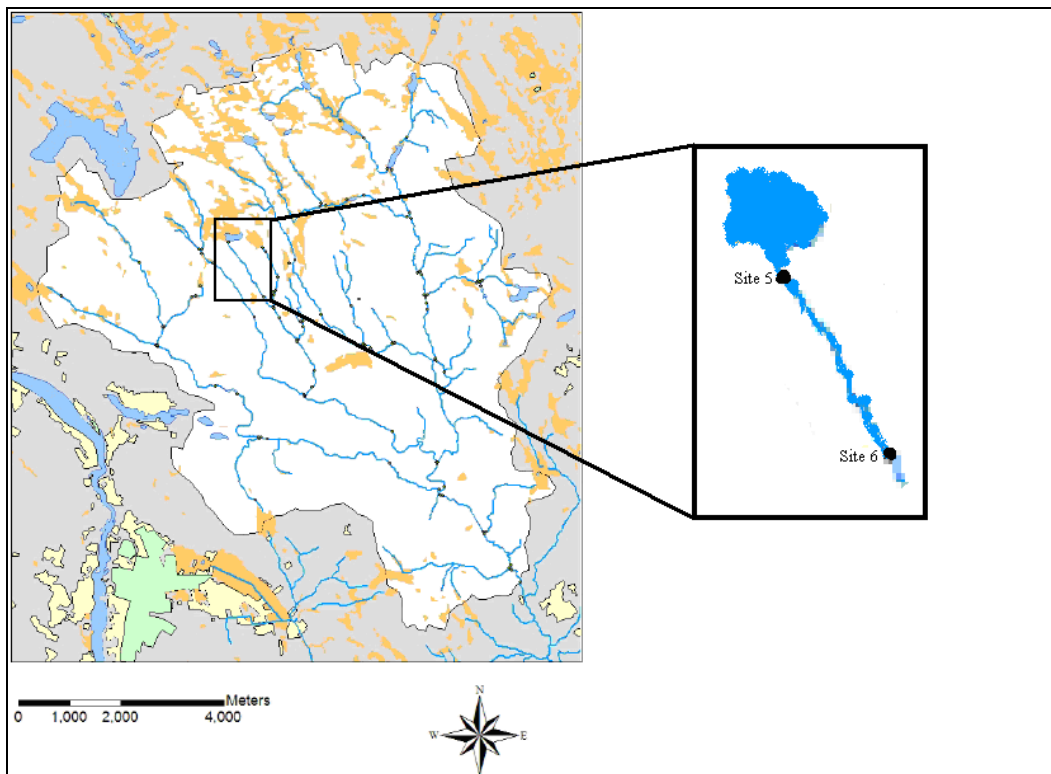

Figure 5 To the left is Krycklan catchment, to the right is the stream section which have been studied.

The vegetation is mostly composed of Norway spruce (Picea abies) and Scots pine (Pinus sylvestris) with a portion of deciduous forest such as birch (Betula ssp), alder (Alnus incana) and willow (Salix ssp) in the lower, wetter riparian zones of the catchment. Mires are a common element within the catchment.

Precambrian gneiss is the dominant bedrock in the area but there is influence of intermediate metavolcanic granite and pegmatite (Ågren, 2007). Sorted sediment such as sand, clay and silt are common due to the inland ice. Iron podzols are dominating the soils in the forest and organic content is large close to the streams (Blomberg, 2008).

In this study, a stream section of approximately 1.5 km within the Krycklan catchment has been studied (fig. 5). The northern and the southern points of the stream section will be referred to as site 5 and site 6 (fig. 6), where site 5 is an outlet from a lake and site 6 is 1.5 km downstream that point. Altitude varies between 283 to 231 meter for site 5 and site 6 respectively. Both at site 5 and site 6 there is a dam for measuring discharge. Table 1 shows the land compositions for the two sites.
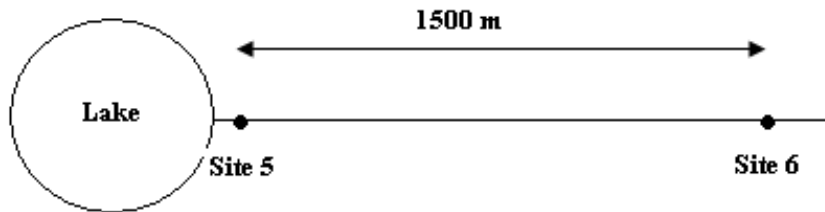

Figure 6 Site 5 and site 6 locations to each other and to the lake.

Table 1: The ratios of water, forest and mire for site 5 and site 6.

Site	Catchment area (km^2)	Water (%)	Forest (%)	Mire (%)
5	0.95	4.7	59	36.3
6	1.3	3.1	72.8	24.1

3.2 REGULAR SAMPLING PROGRAM

Within the Krycklan catchment study (CCREW, 2007) a regular sampling program has been going on since 2003. 15 sites within the catchment where monitored and stream samples where taken once a month with higher intense during spring flood, totally ca 25 sampling occasions a year. Site 5 and 6 where two of the sampling sites where pH, stream water temperature and carbon dioxide concentration in the stream water where measured.

3.3 CONCENTRATION MEASUREMENTS

In a laboratory, glass vials (22.5 ml) where prepared. Between the years of 2004 - 2005 the glass vials volume was 60 ml. The preparing was done by adding 0.6% hydrochloric acid to the vials and an air tight lid was put on. The air in the vials was replaced with nitrogen equilibrated so there was atmospheric pressure in the vials when sample was added.

A syringe was rinsed three times with stream water before the sample was taken. This was done in the field. During the year of 2004-2005 a sample of 15 ml stream water was injected in an air tight vial and since 2006 the sample volume was 5 ml. The vials where stored in a refrigerator until gas chromatography was done to analyze the content of carbon dioxide and propane when tracer experiment has been made. The gas chromatogram gave the ppm-content of carbon dioxide under

laboratory conditions. This value was used to calculate the dissolved inorganic carbon content in the water sample.

The calculated concentrations of CO_2-C (mg L^{-1}) in the stream have been used for estimating evasion and K_{CO2}. Between the days where data was missing, a linear relationship has been assumed.

3.4 DISCHARGE MEASUREMENT

3.4.1 Salt dilution method

Salt dilution is a method for measuring stream discharge based on the conductivity of salt in water (Moore, 2005). A known amount of salt (approximately 100g/10 L s^{-1}) is mixed and poured into the water. The salt gives raise to an electrical conductivity and it is possible to calculate the discharge in the stream (eq. 10). A conductivity probe is placed downstream. This is connected to a data logger and measured values are stored.

$$Q = \frac{V}{k \cdot \Delta t \sum \left[EC(t) - EC_{bg} \right]}$$
(10)

Q = discharge (L s^{-1})
V = volume salt solution (L)
k = calibrated constant
EC = electrical conductivity
EC_{bg} = background electrical conductivity

The discharge has been calculated in a special data program, Q-salt. The program is based upon conductivity, time and salt amount. Input parameters to the program are k, mass of salt, distance to the probe, injection time, minimum conductivity, maximum conductivity, background conductivity, start point and end point.

Salt dilution was used as a complement to the gas tracer injection in order to estimate the residence times and to achieve the discharge.

3.4.2 Water height and pressure transmitter measurement

At site 5 and site 6 there are water height and pressure transmitters installed. These collect and store water level and pressure useful for calculating the discharge. Water level and pressure are converted to discharge via a rating curve.

3.4.3 Discharge at the measuring station

About 1 km away from the study area (fig. 7), there is a measuring station (dam house) on another stream. Continuous discharge measurement is done every hour. Estimating the discharge at site 5 and site 6 has been done with the specific discharge from the measuring station, $q_{station}$ and the areas of site 5 and site 6. Q_5 and Q_6 are the discharge for respectively site and A_5 and A_6 are the areas for the sites (eq. 11 & 12).

$$Q_5 = q_{station} \cdot A_5 \qquad (11)$$
$$Q_6 = q_{station} \cdot A_6 \qquad (12)$$

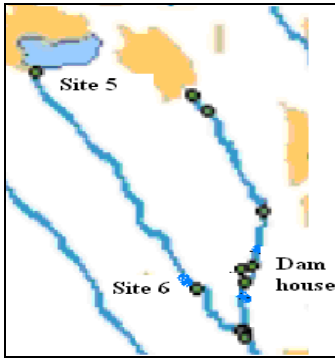Between site 5 and site 6, discharges have been assumed to decrease linearly and are referred to as Q_{5-6}.

Figure 7 The measuring stations (dam house) location in relation to site 5 and site 6.

3.5 VOLATILE GAS TRACER INJECTION

3.5.1. Field procedure

Three conductivity probes were placed into the stream water with approximately ten meters between (fig. 8). The probes were placed so the water easily could flow through them. The conductivity probes were connected to a Campbell CR10x logger which stored the measured values. With the salt dilution method (3.4.1) the discharge and the residence time of the stream water was measured.
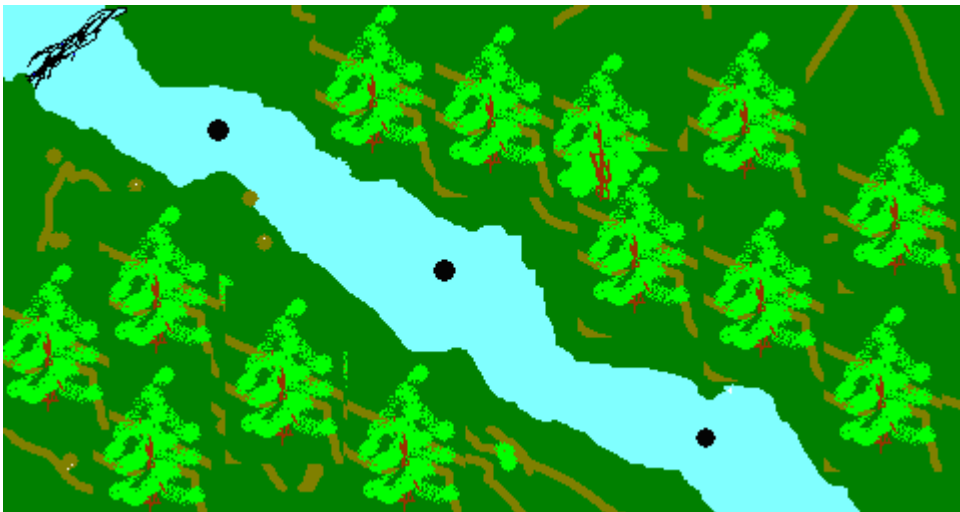

Figure 8 A view of the stream, where the black dots symbolize the probes.

When the salt had passed the water in the study area, propane gas was injected approximately 10 meter upstream the first probe. This was done by connecting a propane gas container to an air curtain, created for making fine bubbles. The air

curtain was approximately 30 cm long and was placed along the stream width so the gas could be spread in a homogenous way. Propane gas was bubbled into the stream with a constant rate at a fixed pressure. The gas was allowed to bubble for about ten minutes to be sure the gas was dissolved over the whole reach.

Water samples were taken (3.3) at the same places as the probes where, with two replicates. Transport time between the probes was used to decide when the samples were taken with the idea being that a "package" of water was followed downstream. Samples were analyzed for carbon dioxide and propane on a gas chromatograph. In connection with volatile gas tracer injection, pH sample and water temperature were taken, width and depth of the stream were measured on the sample day.

3.5.2 Calculations

A yearly carbon dioxide evasion has been calculated and estimated based upon the volatile gas tracer injection. Equation 8 has been used to calculate the evasion on a daily basis, between the years of 2004-2007. To get an integrated estimation, the stream section has been divided into 15 parts, where all the calculations have been done separately. The discharge, the stream water temperature and the partial pressure of CO_2 were assumed to change linearly between site 5 and 6. In the last step, where evasion (g C year^{-1} m^{-2} catchment) has been calculated, the contributes of the 15 parts have been added and divided by the whole catchment area.

The first term in equation 8 is the discharge, Q (L s^{-1}), where daily mean values have been used. There was a big lack of discharge data from site 5 and site 6, therefore Q_5, Q_6, and Q_{5-6} have been used (3.4.3).

The second term in the equation is the residence time, τ (min^{-1}). This variable has been estimated by plotting the measured discharge against the measured residence time. In the calculations the empirical relationship between those two variables has been used.

The third term, K_{CO2}, has been calculated with equation 13 (Hope et al., 2001) and the propane constant, $K_{propane}$ has been calculated with equation 14.

$$K_{CO_2} = K_{propane}(d_{CO_2}/d_{propane})^n \tag{13}$$

$$K_{propane} = \frac{1}{\tau}\ln\left(\frac{C_3H_{8,up}}{C_3H_{8,low}} \cdot \frac{Q_{up}}{Q_{low}}\right) \tag{14}$$

$$d_{CO_2} = 1.005 \cdot \exp^{(0.0231x)} \tag{15}$$

$$d_{propane} = 1.092 \cdot \exp^{(0.0235x)} \tag{16}$$

d_{CO2} and $d_{propane}$ (eq. 15 and eq. 16) are temperature dependence constants, where x is stream water temperature (Celcius). n in equation 13 is a turbulence dependent constant and was assumed to be 0.5. τ is residence time (min^{-1}), C_3H_{8up} and C_3H_{8low} are propane concentrations upstream and downstream, Q_{up} and Q_{low} are upstream and downstream discharge (L s^{-1})

The measured discharge has been plotted against the ratio between propane concentration upstream and downstream. The empirical relation between those two variables has been used in equation 14. Q_{low} was assumed to be the upstream discharge times the area increase in percent. The area increase was assumed to be 1.36 %. The stream water temperature in equation 15 and 16 has been taken from the regular sampling program and from logger data. For days with no available data, a linear change between the days with available data has been assumed.

The fourth term in the evasion equation (eq. 8) is the excess of CO_2 in equilibrium with atmosphere and stream (μmol L^{-1}) and is calculated with equation 17.

$$CO_{2(stream-atm)} = (p_{CO_2} - 370) \cdot K_H \tag{17}$$

p_{co2} (ppm) is the partial pressure of CO_2 and is determined from the regular sampling program. The carbon dioxide in air is assumed to be 370 ppm at all days. K_H is Weiss temperature dependency (Weiss, 1974) and is described in equation 18, where T is the stream water temperature (K).

$$Kh = e^{(-58.0931+(90.5069 \cdot (100/T))+22.294 \cdot \ln(T/100))}) \tag{18}$$

K_{CO2} has been calculated with equation 13 on a daily basis and the carbon dioxide evasion has been calculated with equation 8 on a daily basis.

3.6 FLOATING CHAMBER

3.6.1 Field procedure
A closed chamber (fig. 9) was laid on the stream surface water to measure the carbon dioxide evasion. Two different sizes of chambers have been used depending on the stream size. The dimensions and the volumes of the chambers can be seen in table 2. Effective volume was the estimated volume over the water surface when laid on the surface water.

Table 2 Dimensions of the chambers.

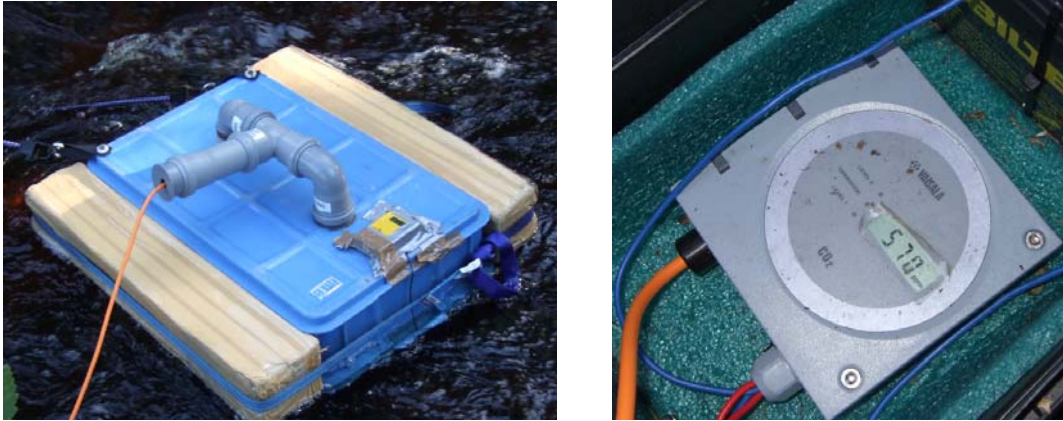|	"Blue" chamber	"Grey" chamber
Width (cm)	36.5	26
Length (cm)	56	36
Height (cm)	13	11
Total volume (cm^3)	26572	10296
Effective volume(cm^3)	23506	8424

Figure 9 The left picture shows the chamber and the right picture shows the Vaisala, carbon dioxide transmitter.

Attached to the sides of the chambers was styrofoam, for enhancing the floating capacity. On the top of the chamber, a carbon dioxide gauge was attached through a tube. The carbon dioxide transmitter (fig. 9) was attached to a Campbell logger and carbon dioxide accumulation (ppm) was measured and stored. Temperature was measured in the chamber during the measurement. Apart from the carbon dioxide measuring with the chamber method, carbon dioxide sample of the water (3.3) and pH-sample have been taken and the stream water temperature was measured.

3.6.2 Sampling sites

The chamber was placed at site 6 and on three different turbulent conditions within 10 m of stream reach. One transect sampling with the chamber method was done where evasion was measured every hundred meter between site 5 and site 6. In this case, the chamber has been laid on water surface with medium turbulence.

3.6.3 Calculations

The ideal gas law (eq. 7) was used to calculate the CO_2-carbon mole amount, where V is the effective volume of the chamber, R is 0.08206, T is the temperature in the chamber and p is the determined partial pressure of CO_2. This is converted to evasion ($\mu g\ C\ m^{-2}\ s^{-1}$) with equation 19, where M_c ($g\ mol^{-1}$) is the mole mass for carbon, A is the chamber area (m^2) and t is the time (s).

$$C_{CO_2} = \frac{p \cdot V \cdot M_C}{R \cdot T \cdot A \cdot t} \cdot \qquad (19)$$

K_{CO2} has been calculated with equation 8; the discharge, the residence time and the excess of carbon dioxide between stream and atmosphere has been estimated and calculated in the same way as in the volatile gas tracer method. The excess carbon dioxide pressure has been calculated with equation 17. From the transect calculations, one K_{CO2} value for each spot is achieved. These have been used to calculate a yearly evasion for the stream section where K_{CO2} was assumed to be constant over the year.

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3.7 MASSBALANCE MODEL

The stream section has been divided in 15 "boxes". K_{CO_2} and evasion have been calculated for each "box" (fig.4) with equation 8 and 9. "Horizontal" concentrations and flows have been assumed in the same way as in the volatile gas tracer experiment. Groundwater flow, Q_{gw} has been assumed to be the difference between the outflow, Q_{out} and the inflow, Q_{in}. Groundwater concentration of carbon dioxide into the stream is assumed to be 606 (μ mol L^{-1}), supported by 36 soil water data (Öqvist, 2007) from the depth of 15- 60 cm where a mean value was used. These data came from another stream area in the catchment of Krycklan.

For each day evasion and K_{CO_2} was calculated. Discharge, residence times and excess carbon in equilibrium between the atmosphere and stream have been estimated and calculated in the same way as in the volatile gas tracer experiment.

4. RESULTS

4.1 CO_2 CONCENTRATION IN STREAM WATER

A spatial and yearly variation of the carbon dioxide concentrations in the stream water was existing (fig. 10-13). In general the concentrations where higher at site 5 than at site 6. This is probably a result of the lake being a carbon dioxide source. Between site 5 and 6, groundwater enters with some CO_2 (assuming a "gaining reach") to the stream and evasion to the atmosphere. These two combine to give the change in stream CO_2 between sites 5 and 6. A seasonal variation could be seen (fig. 10-13), especially at site 5 where the high peaks of the concentrations could be a result of respiration being higher than the photosynthesis in the lake. This often occurs during late spring or summer, when the temperature in the lake is rising. The reason for site 6 not to answer to this respond could be that a large amount of the carbon dioxide goes away with evasion.
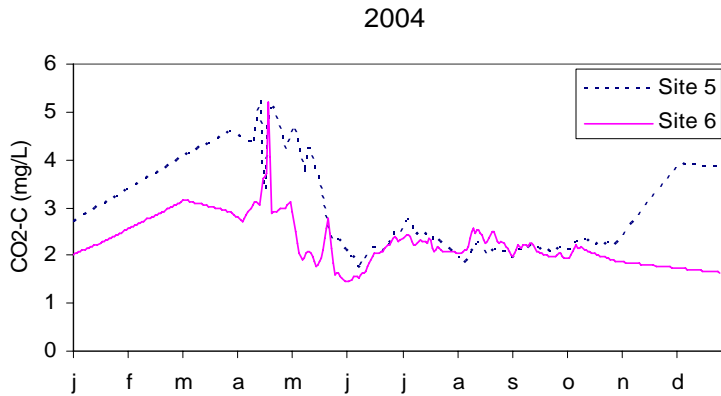
Figure 10 CO_2-C concentrations in stream water at site 5 and 6 based on sampling every 2-4 weeks for the year of 2004.
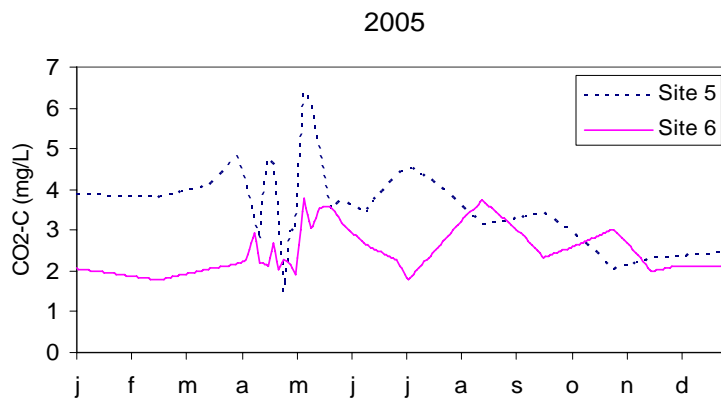
Figure 11 CO_2-C concentrations in stream water at site 5 and 6 based on sampling every 2-4 weeks for the year of 2005.
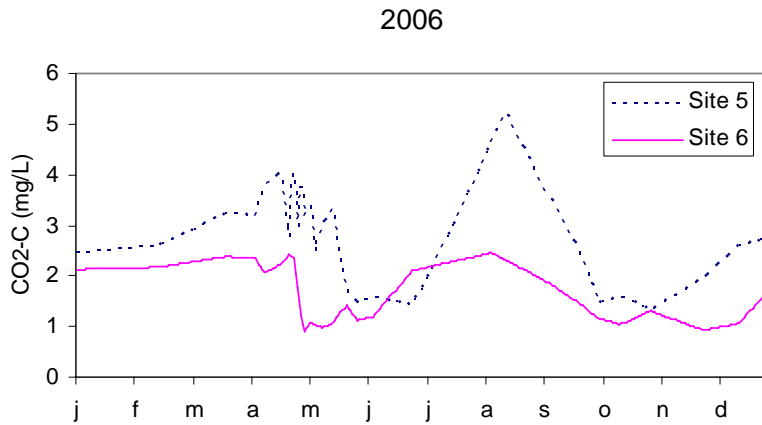
2006

Figure 12 CO_2-C concentrations in stream water at site 5 and 6 based on sampling every 2-4 weeks for the year of 2006.
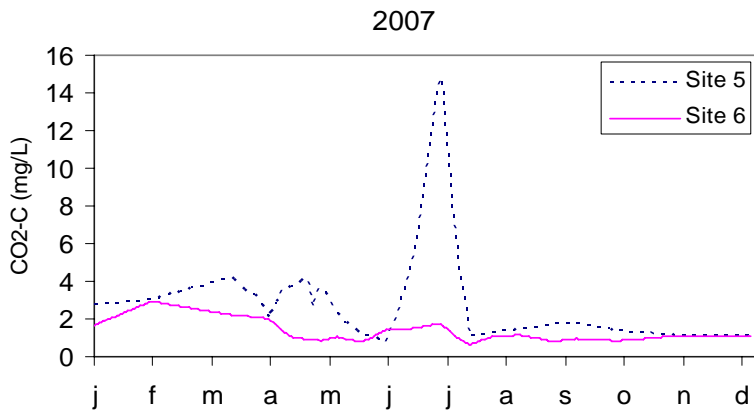
2007

Figure 13 CO_2-C concentrations in stream water at site 5 and 6 based on sampling every 2-4 weeks for the year of 2007.

Figure 14 shows the carbon dioxide concentrations changing with discharge for two different years and for two sites. A strong relation between the CO_2-C and the discharge could not be seen.
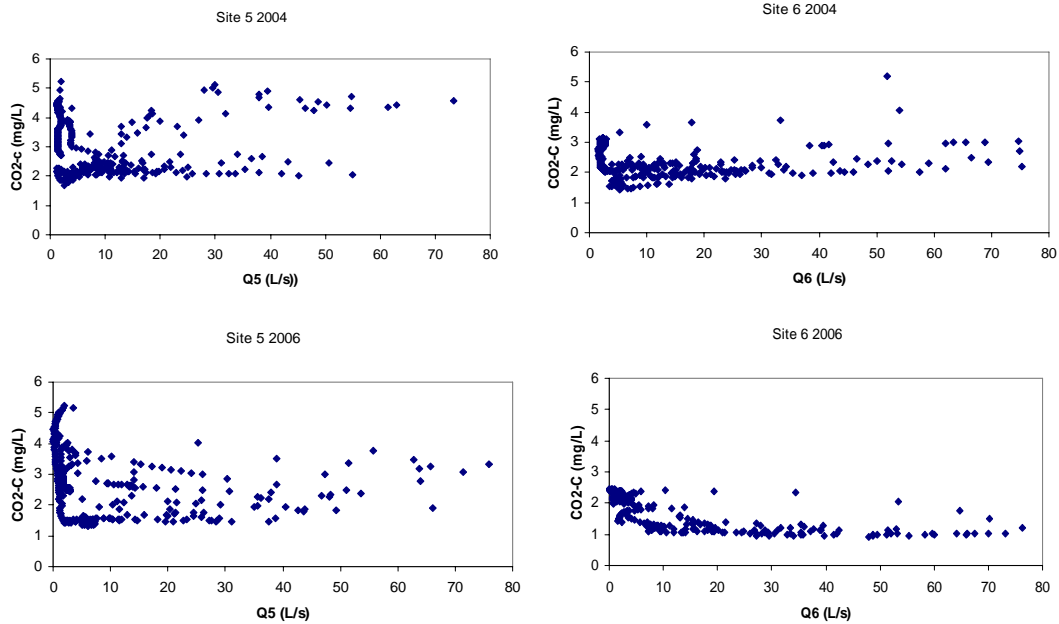
16

Figure 14 Estimated CO_2-C concentrations in stream water as a function of discharge. To the left for site 5 and to the right for site 6, in upper row for the year 2004 and in the lower the year of 2006.

4.1.1 Downstream gradient

There are variations of carbon dioxide concentrations and discharge in the headwater stream transect between site 5 and site 6 (fig. 15 & 17). The variations of pH and the stream water temperature as a function of distance from the lake can be seen in figure 16 and 18. These values are based on measured values from two occasions.

The data from the two transect (fig. 15 & 17) shows a similar pattern according to the CO_2-C concentrations in the stream section. This pattern indicates that the concentration of CO_2-C in the stream water not only depends on the distance from the lake. This could indicate that different concentrations of carbon dioxide enter with groundwater inflow to the stream.
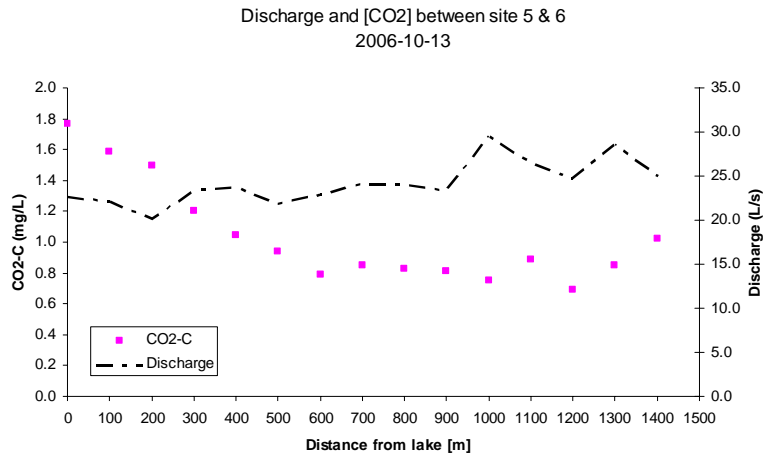
Figure 15 Measured CO_2-C concentrations and measured discharge between site 5 and site 6 as a function of distance from the lake.
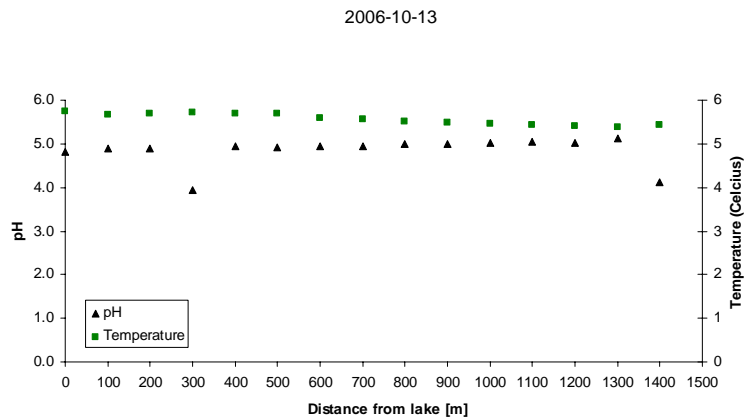

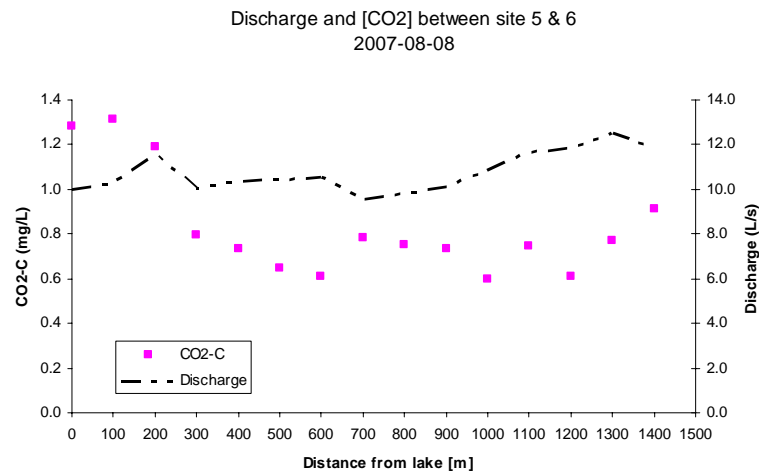**Figure 16** Measured pH and measured stream water temperatures as a function of distance from the lake.

Figure 17 Measured CO_2-C concentrations and measured discharge between site 5 and site 6 as a function of distance from the lake.
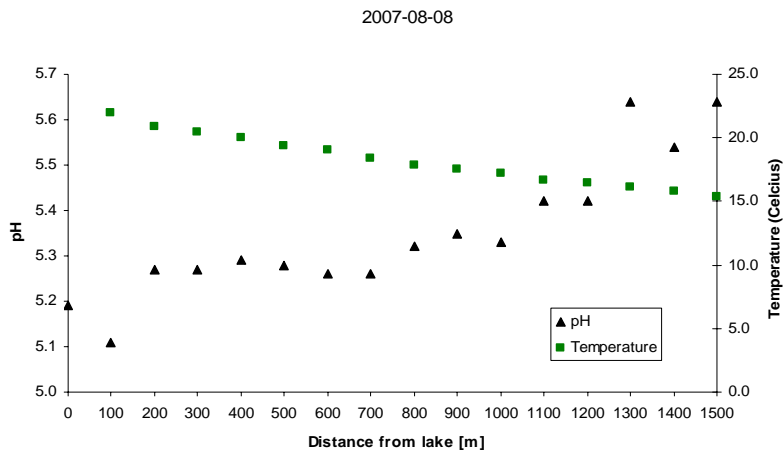
18

2007-08-08

Figure 18 Measured pH and measured stream water temperatures as a function of distance from the lake.

4.2 VOLATILE GAS TRACER INJECTION

4.2.1 Estimations

There exists an empirical relationship between residence time and discharge (fig. 19). In the methods where residence time is approximated this relationship (eq. 20) has been used. τ is the residence time (min^{-1}) and Q is the discharge (L s^{-1}).

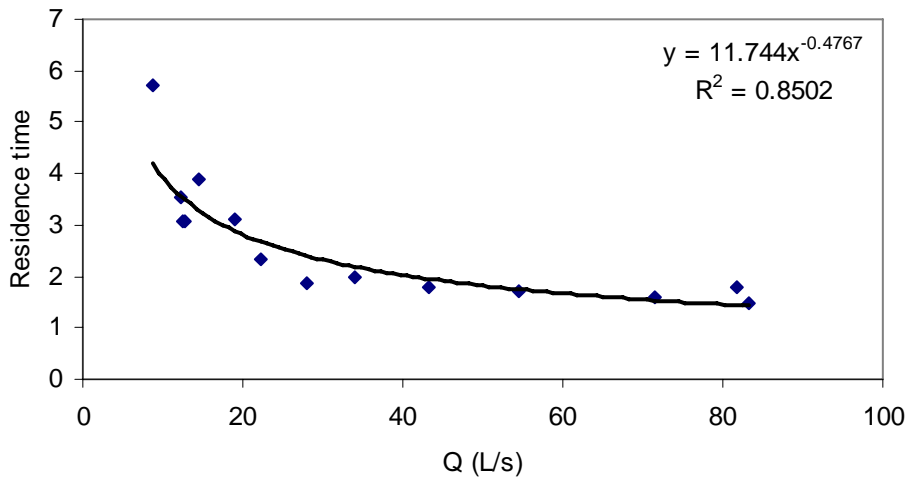

$$y = 11.744x^{-0.4767}$$
$$R^2 = 0.8502$$

Figure 19 Residence time for stream water as a function of discharge, measured with the salt dilution method in volatile gas tracer experiment.

$$\tau = 11.744 \cdot Q^{-0.4767} \tag{20}$$

Figure 20 is the result of the propane ratio as a function of discharge. The relation between these variables (eq. 21) has been used in equation 14. These equations together result in equation 22, where Q is the discharge (L s^{-1}) and τ is the residence time (eq. 20).

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This estimation of $K_{propane}$ has limitations. Under low discharge conditions the curve will rise, and if the discharge get higher then 76 (L s^{-1}), $K_{propane}$ will be negative, so when the discharge is higher than 76 L s^{-1} an limit has been set.
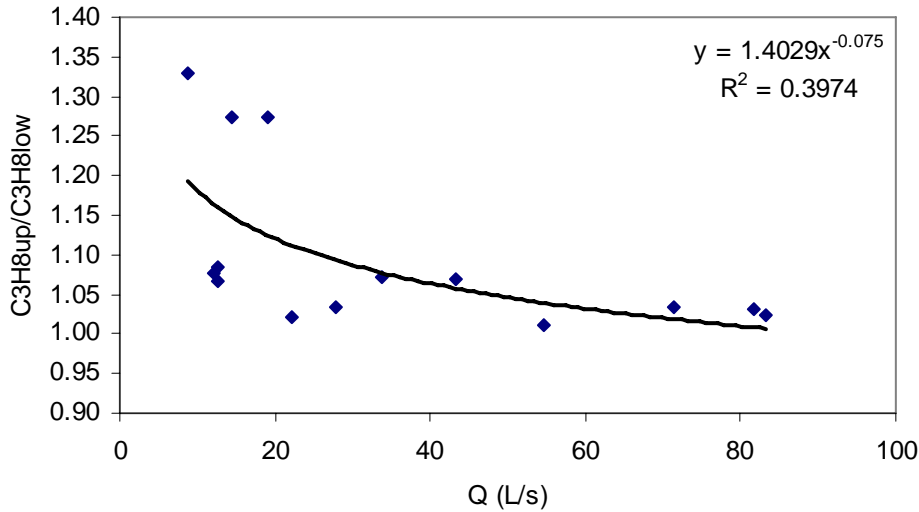

Figure 20 Propane ratio as a function of discharge measured with the tracer gas experiment.

$$\frac{C_3 H_{8,up}}{C_3 H_{8,low}} = 1.40 \cdot Q^{-0.075} \tag{21}$$

$$K_{propane} = \frac{1}{\tau} \ln\left(1.38 \cdot Q^{-0.075}\right) \tag{22}$$

4.2.2 Variations in K_{CO2}

With equation 13 and the assumptions that have been done, K_{CO2} values have been calculated on a daily basis. This has been done both for site 5 and site 6 for the four years. Table 3 shows the maximum and minimum, standard deviation and median for the calculated K_{CO2}-values. Volatile gas tracer injection method gives a range for K_{CO2} between 0.00003-0.0613.

Figure 21-24 shows the K_{CO2}-values as a function of the days for the years 2004-2007. K_{CO2} is inversely proportional to the discharge. At low discharge the K_{CO2} values is high and larger discharge yields a decrease in K_{CO2} (fig. 25). A higher stream water temperature yields a larger K_{CO2} value (fig. 26).

Table 3 Variations in K_{CO_2} calculated with the gas tracer method for the years of 2004-2007.

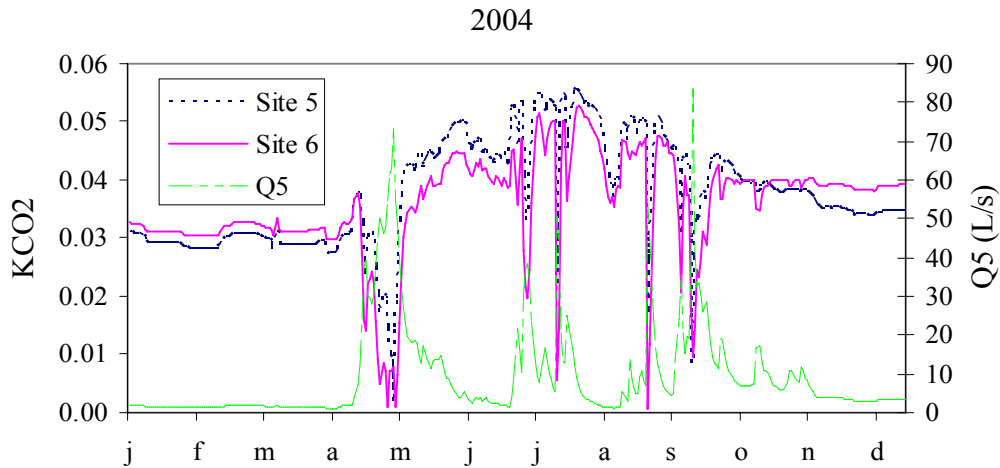|		Site 6	Site5
2004	K_{max}	0.0529	0.0556
	K_{min}	0.0008	0.0020
	Std.dev	0.0091	0.0092
	Median	0.0384	0.0360
2005	K_{max}	0.0508	0.0613
	K_{min}	0.0014	0.0033
	Std.dev	0.0080	0.0095
	Median	0.0363	0.0372
2006	K_{max}	0.0482	0.0545
	K_{min}	0.00003	0.0002
	Std.dev	0.0090	0.0090
	Median	0.0344	0.0342
2007	K_{max}	0.0534	0.0582
	K_{min}	0.0072	0.0049
	Std.dev	0.0067	0.0073
	Median	0.0373	0.0377

Figure 21 Estimated K_{CO_2} values for site 5 and site 6 as a function of day for the year of 2004.

2005

Figure 22 Estimated K_{CO2} values for site 5 and site 6 as a function of day for the year of 2005.
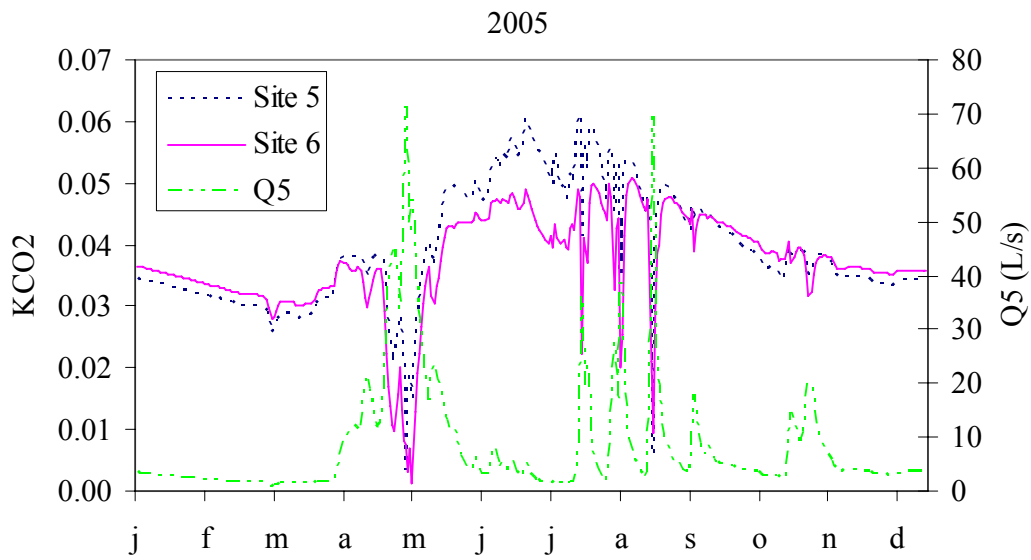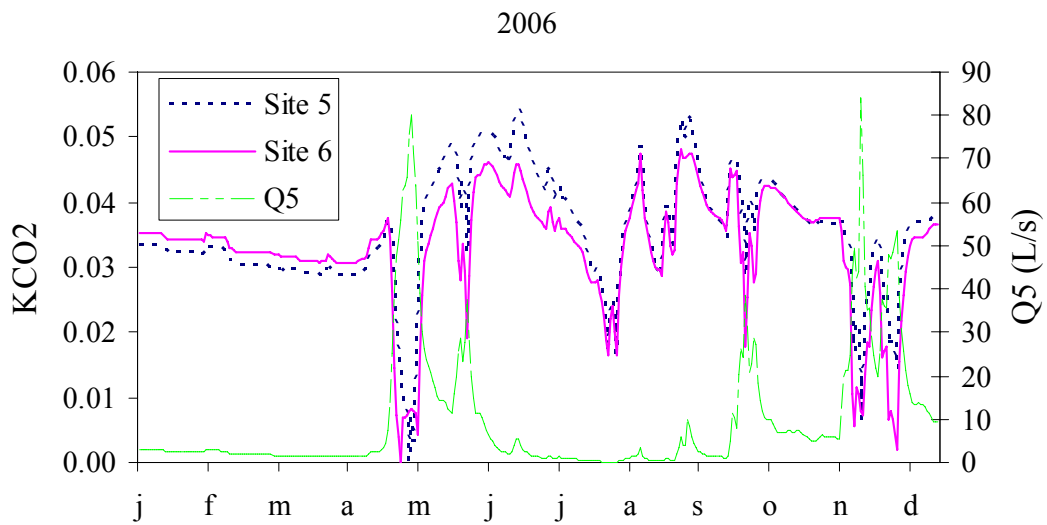
2006

Figure 23 Estimated K_{CO2} values for site 5 and site 6 as a function of day for the year of 2006.
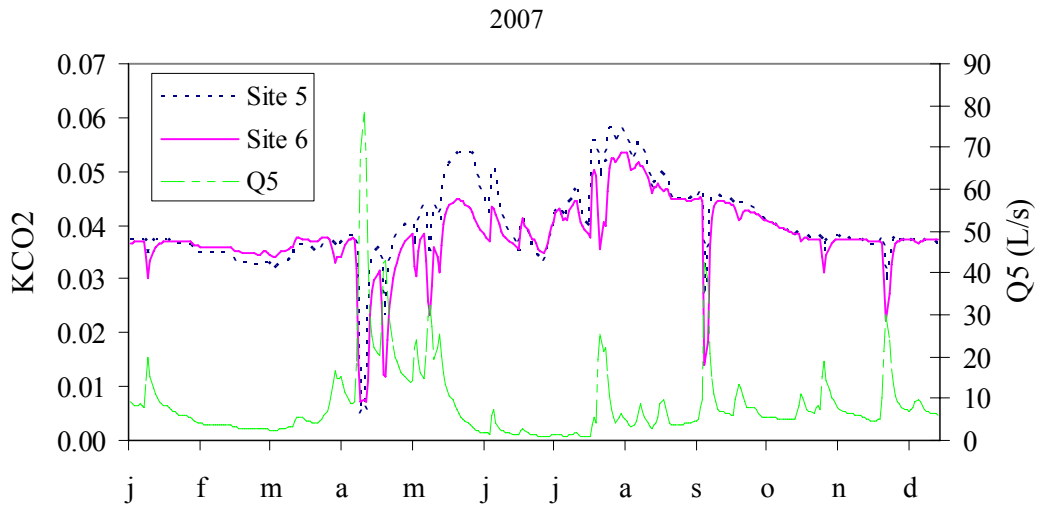
Figure 24 Estimated K_{CO_2} values for site 5 and site 6 as a function of day for the year of 2007.
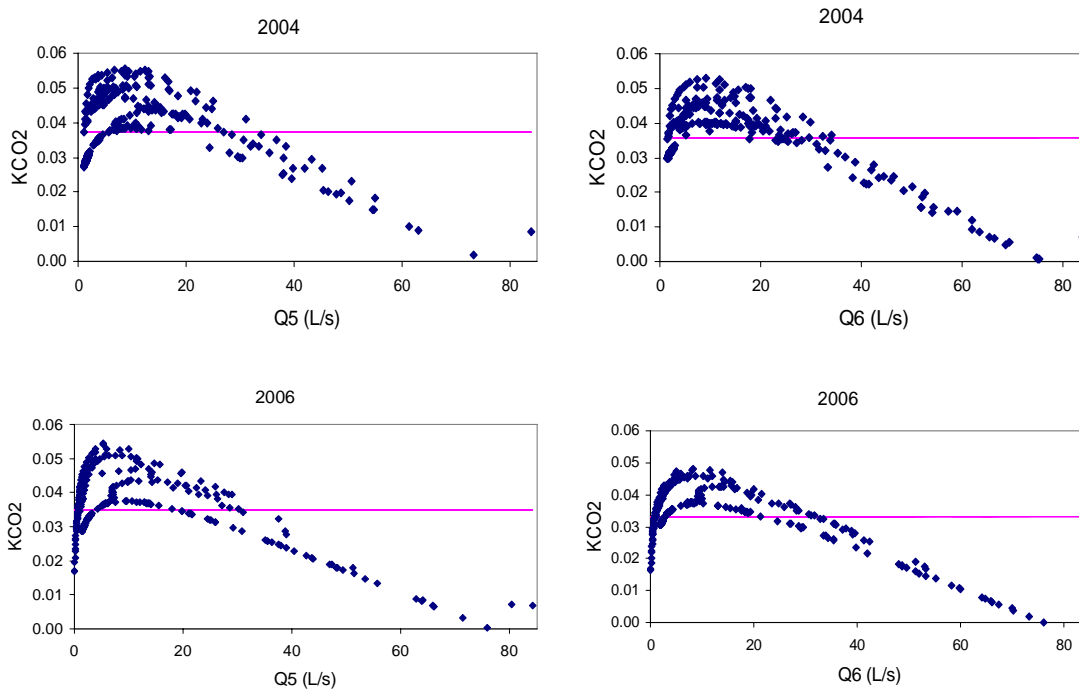

Figure 25 Estimated K_{CO_2}-values as a function of discharge with the gas tracer method. The upper figures are from 2004, site 5 and site 6 and the lower figures are from 2006, site 5 and 6. The line in each diagram is the average KCO_2.
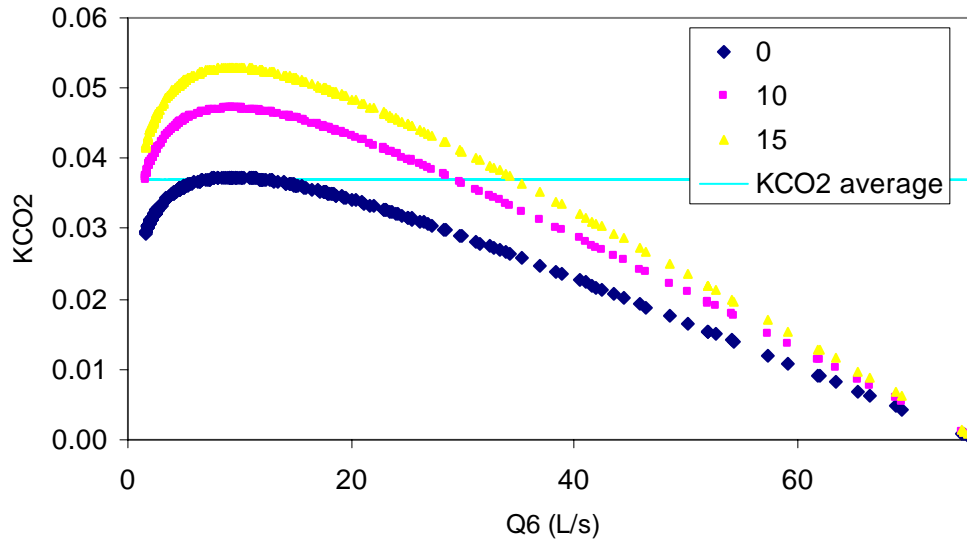
Figure 26 The temperature dependency of estimated KCO_2 with discharge.

4.2.3 Yearly estimation of evasion

From calculations and assumptions from the volatile gas tracer injection experiment yearly evasion budgets have been calculated. Daily carbon dioxide evasion has been calculated with equation 8. The result is presented in table 4. The range of evasion is between 1.7-2.8 (g C $year^{-1}$ m^{-2} catchment area). The catchment area includes all of what is upstream from the south point. All evasion from lake and streams leading to the lake has been ignored. Figure 27-30 shows the calculated evasions on a daily basis for the year 2004-2007. The evasions are higher at site 5 than site 6 and there are fluctuations over the year. Figure 31 shows evasion (g C day^{-1} m^{-2} stream area) as a function of discharge. For low discharge (< 20 L s^{-1}), higher evasion can be seen with increasing discharge. Higher discharge results in a decreasing trend with this method.

Table 4 Estimated evasion (g C $year^{-1}$ m^{-2} catchment area) for the years 2004-2007 with the gas tracer method.

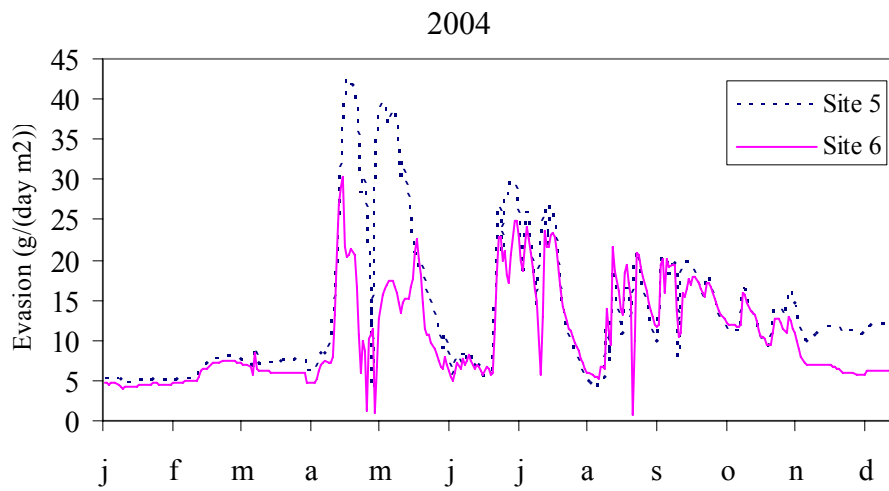| Year	Evasion
2004	2.8
2005	3.4
2006	1.7
2007	2.0

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Figure 27 Estimated evasions (g day^{-1} m^{-2} stream area) as a function of days for the year of 2004, with the volatile gas tracer experiment.

Figure 28 Estimated evasion (g day^{-1} m^{-2} stream area) as a function of days for the year of 2005, with the volatile gas tracer experiment.

2006

Figure 29 Estimated evasion (g day^{-1} m^{-2} stream area) as a function of days for the year of 2006, with the volatile gas tracer experiment.

2007

Figure 30 Estimated evasion (g day^{-1} m^{-2} stream area) as a function of days for the year of 2007, with the volatile gas tracer experiment.
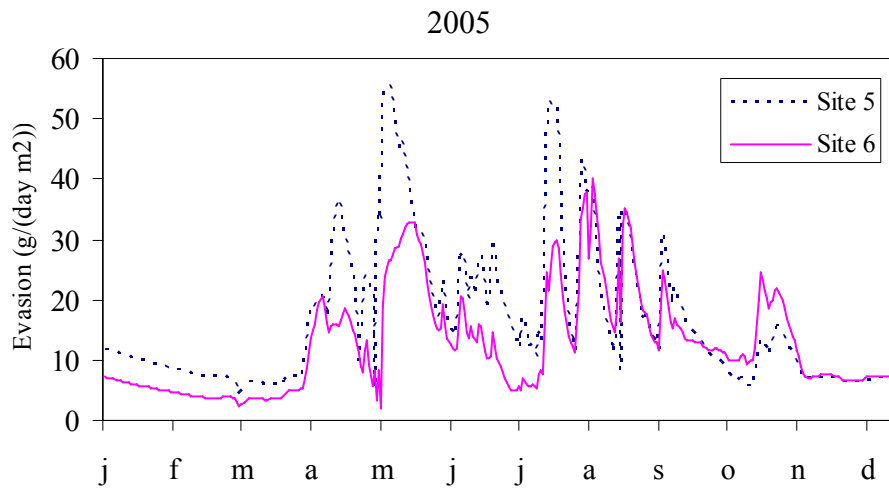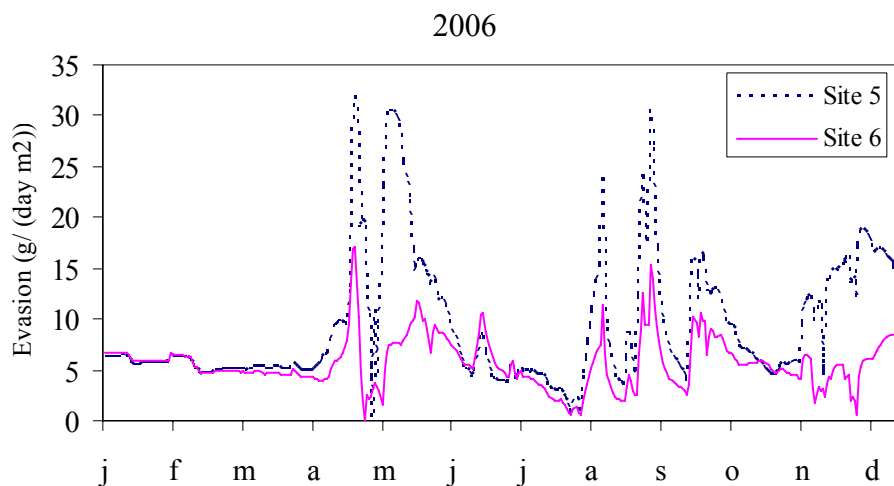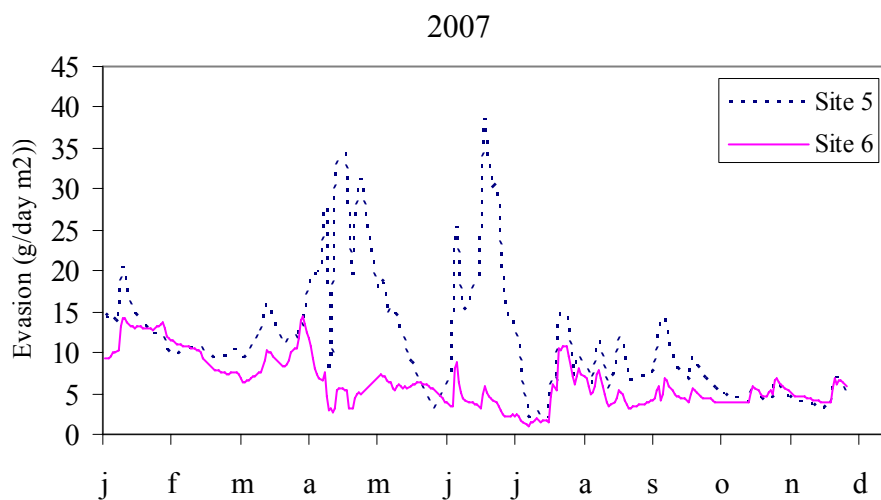
2005

2005
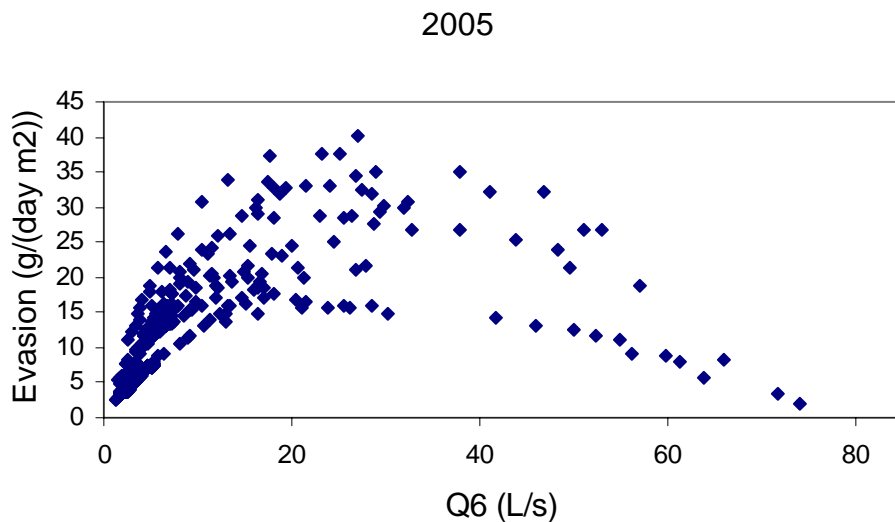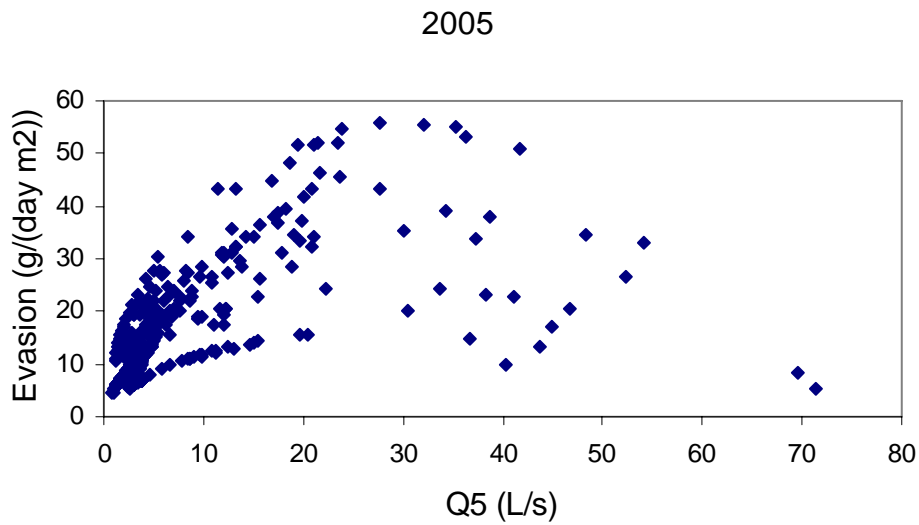
Figure 31 Estimated evasion (g C day^{-1} m^{-2} stream area) as a function of discharge. The upper diagram is for site 5 and the lower diagram is for site 6.

4.3 FLOATING CHAMBER

4.3.1 Measured evasion

Figure 32 shows one curve of the CO_2-accumulation when chamber is laid on the surface water. Figure 33 shows the measured evasions as a function of the discharge. No relation between discharge and evasion could be seen.
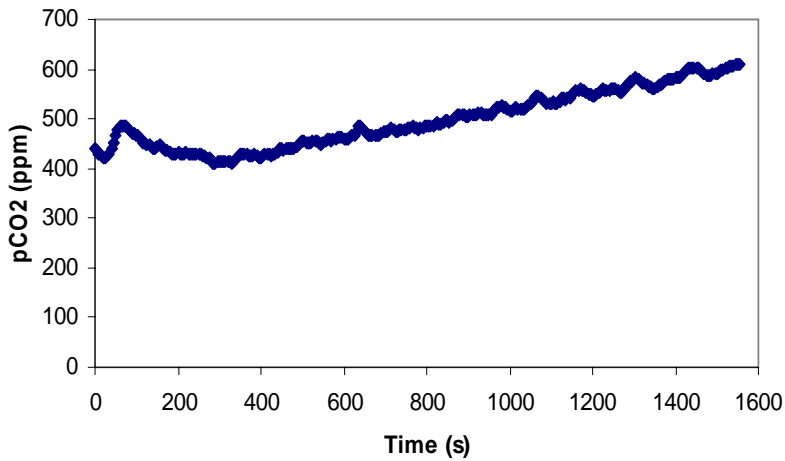
Figure 32 Accumulated carbon dioxide (ppm) over time, measured with the chamber method.
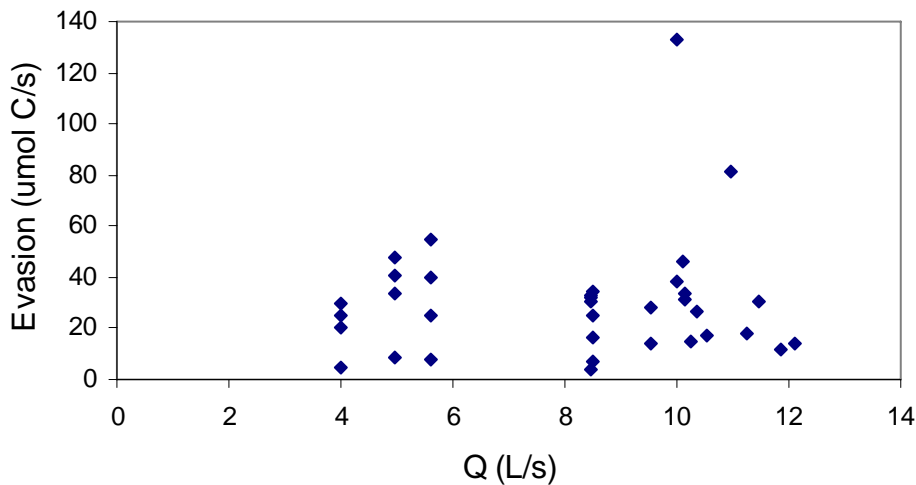
Figure 33 Measured evasion as a function of the flow, with the chamber method.

4.3.2 Variations in K_{CO_2}

The measured evasions from the chamber method has a range between 2.4 - 79.7 (ugC s^{-1} m^{-2} stream area), where the lowest one is from a low turbulence situation at site 6 and the highest one is from a medium turbulence situation, approximately 200 meters from the lake. Those evasion rates are equivalent to K_{CO_2}–values between 0.0013 and 0.0355, which have been calculated with equation 8 and the assumptions done in the gas tracer method. Average K_{CO_2}-value for the transect is 0.015 and the standard deviation is 0.0078, where the same values for site 6 is 0.0097respectively 0.0060.

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Figure 34 shows the CO_2-C concentration as a function of K_{CO2}, and in the same diagram the discharge as a function of K_{CO2} in the stream water is showed. The result in this graph is both from site 6 and from the transect measuring.
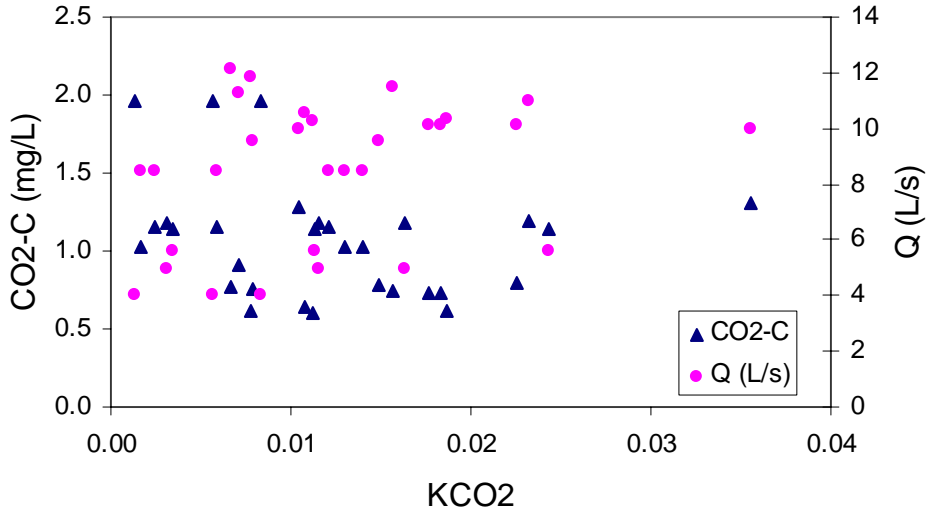
Figure 34 Calculated K_{CO2} values as a function of carbon dioxide concentration (mg L^{-1}) in the stream and as a function of discharge.

There was spatial variations in K_{CO2} for different discharge and different turbulence levels at site 6 (fig. 35). In general, a higher turbulence gives a higher K_{CO2}-value. This experiment is only for relatively small discharge and nothing can be said about turbulence and K_{CO2} for higher discharge.

Figure 35 K_{CO2} as a function of discharge for three different turbulence levels, measured with the chamber method.

4.3.3 Downstream transect

Figure 36 shows the K_{CO_2} variations as a function of distance from the lake. The altitudes are also shown in the same figure. 200 meters from the lake the highest K_{CO_2} could be seen. A small K_{CO_2} existed close to the lake and after this the highest K_{CO_2} in the transect could be seen. Afterwards there was a more or less decreasing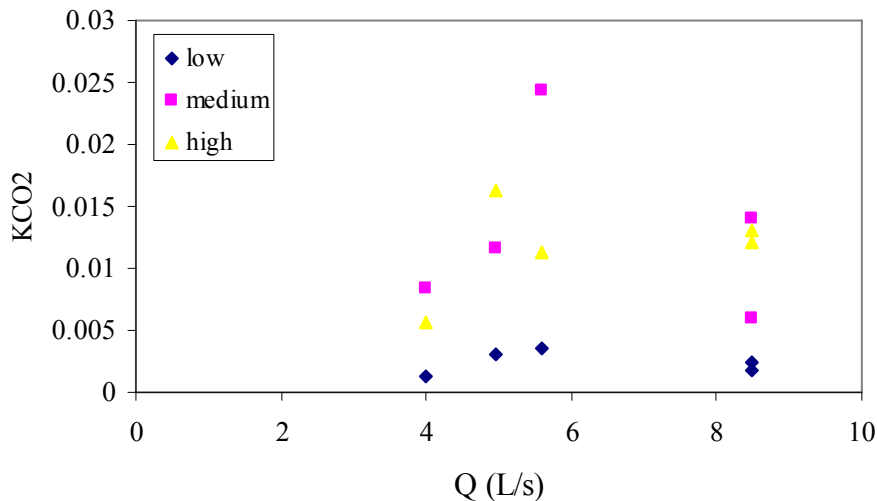 trend. The variability in K_{CO_2} for this day and this section was 0.0067 – 0.0355. The discharge varied between 10.0 and 12.1 L/s.
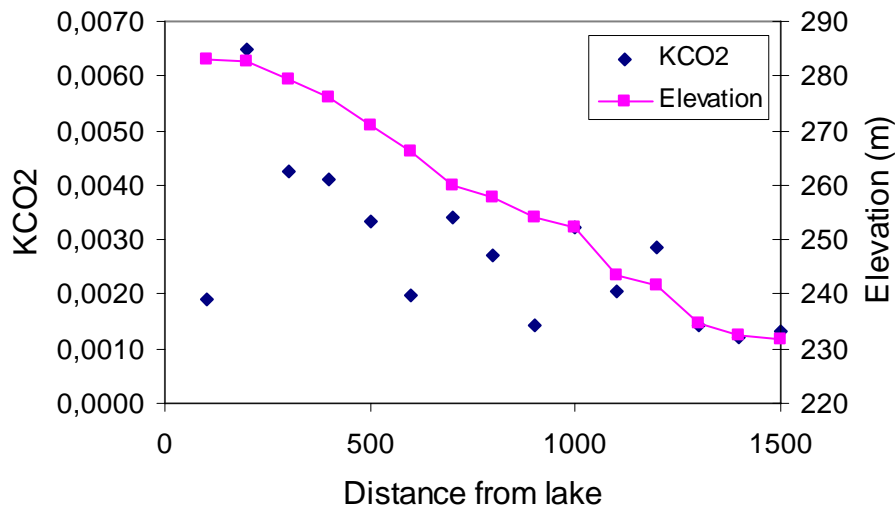

Figure 36 K_{CO_2} as a function of distance from the lake, calculated with the chamber method. In the same diagram is elevation as a function of distance from lake.

4.3.4 Yearly estimation of evasion

The discharge, residence time, temperature and other parameters has been assumed in the same way as in the gas tracer method. If K_{CO_2} is assumed to have the values as in the transect (fig. 36) and if K_{CO_2} is assumed to be constant over the year, this will result in the yearly evasion (g C year^{-1} m^{-2} catchment) presented in table 5.

Table 5 Estimated evasion (g C year^{-1} m^{-2} catchment) for the years 2004-2007 calculated with the chamber method.

Year	Evasion
2004	1.4
2005	1.5
2006	0.9
2007	0.9

4.4 MASS BALANCE MODEL

4.4.1 Variations in K_{CO_2}

With the mass balance model, K_{CO_2} values have been calculated on a daily basis, with equation 8 & 9. Table 6 shows the result of the range within in the sites and the years. An increase of the discharge yields an increase in K_{CO_2} (fig. 37).
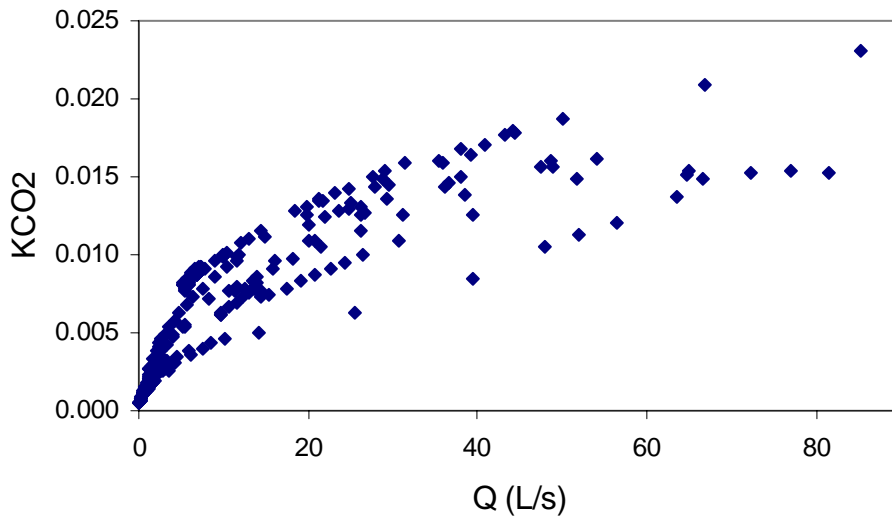
Figure 37 Estimated K_{CO2} as a function of discharge for site 5 and year 2006, with the mass balance model.

Table 6 Estimated variations in K_{CO2} calculated with the mass balance model.

		Site 6	Site 5
2004	K_{max}	0.0177	0.0130
	K_{min}	0.0001	0.0009
	Std.dev	0.0034	0.0020
	Median	0.0046	0.0038
2005	K_{max}	0.0181	0.0098
	K_{min}	0.0005	0.0012
	Std.dev	0.0029	0.0014
	Median	0.0046	0.0028
2006	K_{max}	0.0636	0.0231
	K_{min}	0.0010	0.0005
	Std.dev	0.0122	0.0048
	Median	0.0047	0.0031
2007	K_{max}	0.0644	0.0208
	K_{min}	0.0020	0.0015
	Std.dev	0.0106	0.0043
	Median	0.0111	0.0070

4.4.2 Yearly estimation of evasion

Evasion was calculated on a daily basis and on a yearly basis with equation 8 and the assumptions that have been done. The result can be seen in table 7. Evasion ranges between 0.4 -0.8 (g C $year^{-1}$ m^{-2} catchment).

Table 7 Evasion (g C year^{-1} m^{-2} catchment) for the years 2004-2007 calculated with the mass balance model.

Year	Evasion
2004	0.6
2005	0.4
2006	0.8
2007	0.7

4.5 COMPARING THE METHODS

4.5.1 Variations in K_{CO2}

Figure 38 shows the K_{CO2} values with different methods on a specific day. The tracer method gives a higher K_{CO2} value than the other methods. In the diagram are also the carbon dioxide concentrations of the stream water for the particular day. Table 8 shows the range of K_{CO2} with the different methods. In figure 39 the measured K_{CO2} values are shown as a function of the measured discharge, with the chamber method and with the gas tracer method.

Table 8 The estimated K_{CO2} ranges with the different methods.

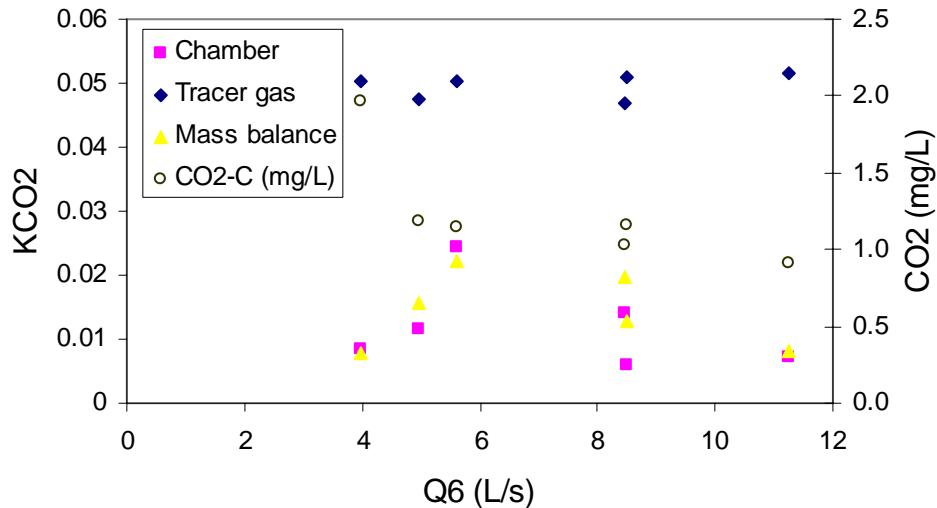| Method	K_{CO2}
Gas tracer	0.00003-0.0613
Chamber	0.0013-0.0355
Mass balance	0.0001-0.0644

Figure 38 K_{CO2} values from site 6 as a function of discharge and carbon dioxide concentration as a function of discharge, calculated and measured with the different methods.
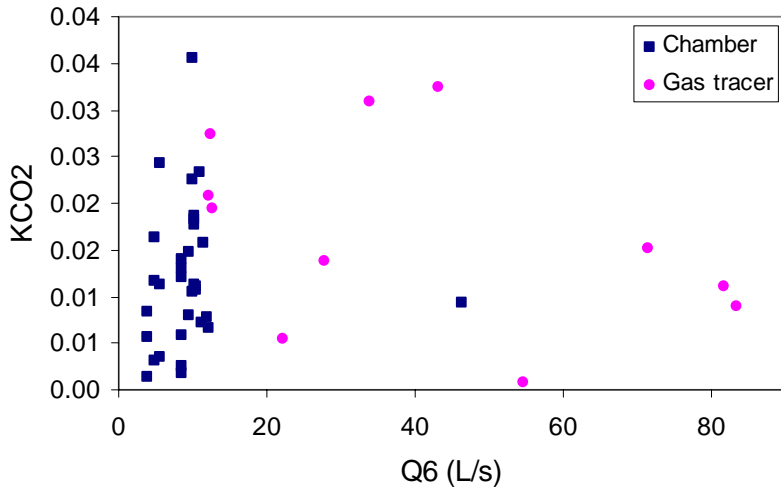
Figure 39 The actual K_{CO_2} values that have been measured as a function of the measured discharged, with the chamber method and the gas tracer method.

There where variations in KCO_2 over the one year with the three methods (fig. 40). Even though the gas tracer method and the mass balance methods have the same range (tab. 8) of K_{CO_2}, the daily estimated values differ between the two methods.
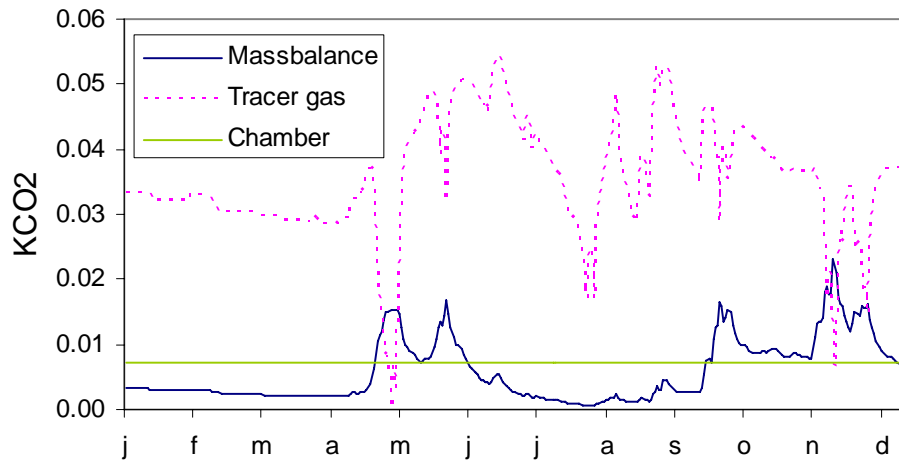
Figure 40 Estimated K_{CO_2} as a function of days, calculated with mass balance, tracer gas and chamber methods. This is from year 2006 and site 5.

In figure 41, the yearly K_{CO_2} values are presented as a function of discharge. The gas tracer method and the mass balance method show different patterns, the mass balance method gives an increasing K_{CO_2} with discharge, whereas the gas tracer method show an increasing in KCO_2 with low discharge, but an decreasing with higher discharges.

Figure 41 Estimated KCO_2 values as a function of discharge. This is from site 6 and year 2006.

4.5.2 Yearly estimation of evasion

Table 9 gives a summary of the yearly estimations of evasion with the three methods. Figure 42 shows the evasion (g day^{-1} m^{-2} stream area) as a function o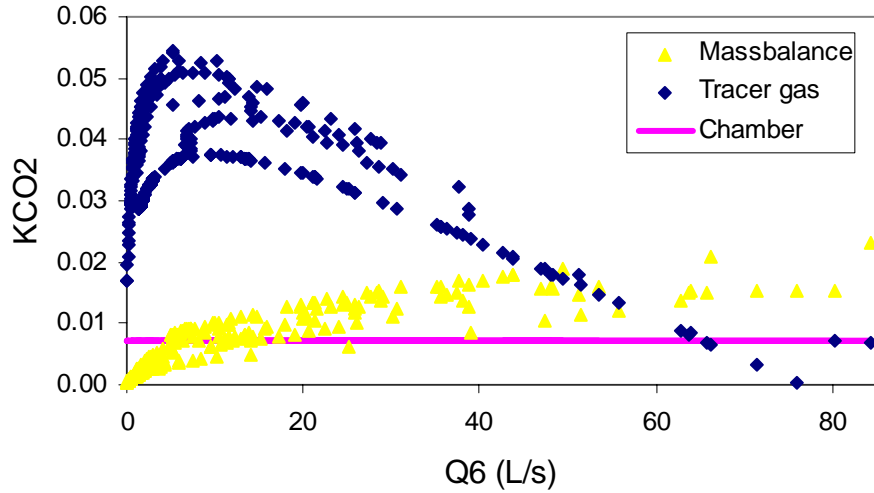f discharge. It can be seen that the tracer method yields the highest values. Figure 43 shows the evasion (g day^{-1} m^{-2} stream area) as a function of days. The fluctuations of the evasion with the tracer method and the chamber method are in first case a result of the discharge.

Table 9 The evasion (g C year^{-1} m^{-2} catchment area) calculated with the different methods.

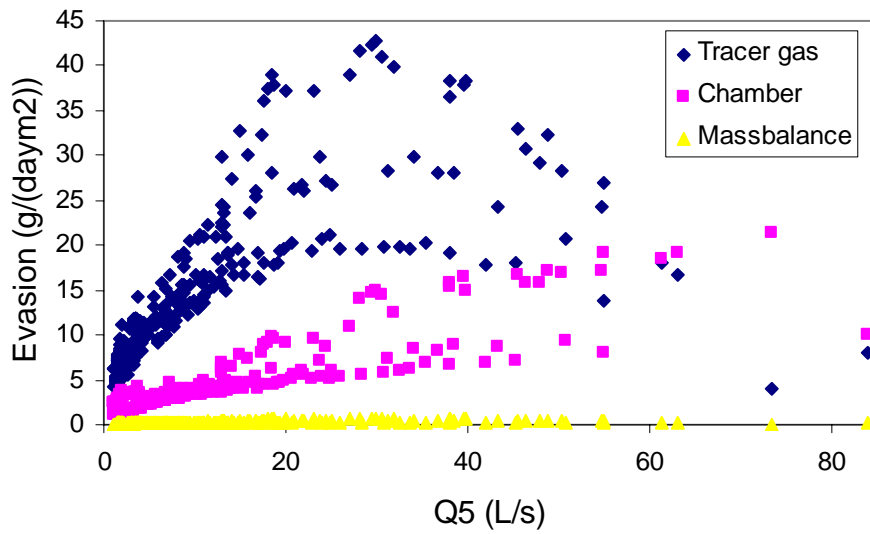| Year	Gas tracer	Chamber	Mass balance
2004	3.8	1.4	0.6
2005	3.4	1.5	0.4
2006	1.7	0.9	0.8
2007	2.0	0.9	0.7

Figure 42 Estimated evasion as a function of discharge with the three methods. This is from site 5, the year of 2004.
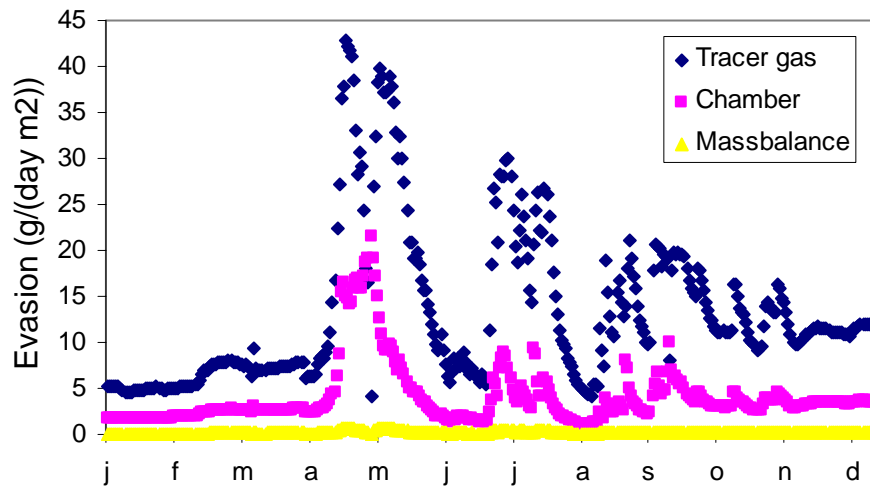

Figure 43 Estimated evasion as a function of day for the methods, this is from site 5, the year of 2004.

5. DISCUSSION

5.1 CONCENTRATIONS OF CO_2 IN STREAM

The range of CO_2 concentrations in stream water is between 0.5 to 7 mg CO_2-C L^{-1}. There is also a set of seasonal and spatial patterns of CO_2 variation in the stream. Usually the CO_2 concentration is higher at site 5 than at site 6 which is reasonable since the lake close to site 5 acts as a CO_2 source.

The pattern of CO_2 variation along the stream water, however, is not only related to the distance from the lake. While the lake contributes to the downstream pattern, it is not the only controlling factor. Other important factors that control the downstream pattern are the degassing of CO_2 and diffuse inputs of groundwater along the stream.

5.2 VOLATILE GAS TRACER METHOD

The value of K_{CO2} is an important control on the rate of degassing from the stream. According to figure 21-24, K_{CO2} has a nonlinear relationship with flow, as measured using the tracer gas injections. At low flow, the water will have longer residence times and the potential for degassing increases. The values of K_{CO2} increases slightly as flow increase to about 5 L/s, then decreases steadily as flow increases further. The variation of K_{CO2} is indirectly seasonal because of the discharge. The way K_{CO2} has been calculated with this method has limitations; equation 14 is only valid for discharge less than 76 L/s. If it would be possible to fit the curve in figure 20 in a better way, better approximations of K_{CO2} could be achieved.

Using the estimate of K_{CO2} based on flow, and daily concentrations of CO_2 interpolated from the manual observations every two weeks, the evasion of CO_2 from the stream reach was calculated using equation 8. The years 2004-2005 gave higher estimated evasion of CO_2 than years 2006-2007. The difference can partly be related to different discharges, as some years are rainy and some years are dry. This will affect the discharge largely and indirectly the evasion. Between the years of 2004-2005 and 2006-2007, there was also a change in methods that might have affected the carbon dioxide values measured in the water samples.

One interesting observation from the flux estimates is that the hydrology affects the results more than the concentration. Stream water has partial pressure between 2000-8000 µatm, whereas the discharge has a range between 10-80 L/s. Thus the concentration differs only by a factor 4 while the discharge differs by a factor of 8.

5.3 CHAMBER METHOD

The chamber method of estimating K_{CO2} shows no relation between measured evasion and discharge, but the turbulence level is important for the evasion rate. A higher turbulence level yields a higher evasion and a higher K_{CO2}. If the turbulence is higher, the water will mix better and result in more CO_2 at the water surface and the potential for evasion increases.

The yearly estimate of evasion based on the chamber method does not include any variations in K_{CO2} over the year. If the value used for K_{CO2} is an average of the different turbulence situations, it still might be a good approximation. This method probably underestimates the evasion, though, because the turbulence at the water surface is reduced when the chamber is laid on the water. The advantage with this method is that the evasion is measured directly.

5.4 MASS BALANCE MODEL

The limitation with this method is that one must assume a value for the CO_2 concentration of the ground water entering the stream section. This in turn regulates the evasion and the K_{CO2}. Higher discharge generates higher K_{CO2} values. This method yields low estimates of the evasion relative to the other terms, and this is because of the assumptions. This method does not take the processes within the stream water into consideration.

5.5 COMPARING THE METHODS

Estimation of K_{CO2} is a complex problem since it depends on many factors. The use of different methods have yielded different values of K_{CO2} and provided some insight into the difficulty of estimating K_{CO2}. Even though the gas tracer and the mass balance methods have the same range of K_{CO2}, the daily values differ (fig. 40). The gas tracer method yields lower estimates of K_{CO2} at higher discharge, while the mass balance method yields higher K_{CO2} with higher discharge. The stream water temperature (fig. 26) is an important factor regulating K_{CO2} in the gas tracer method. The floating chamber shows no relation between discharge and evasion while in the gas tracer method, a relation between those parameters has been found. The gas tracer method takes evasion from a larger stream area into account, and indicates that evasion is related to the discharge. The chamber method shows a large spatial variation of evasion within a limited stream area. This demonstrates that the turbulence levels have a large impact on the evasion and on K_{CO2}. The estimates of K_{CO2} strongly influence the calculation of CO_2 evasion, and the key contribution of this thesis has been to explore the variability in estimates of K_{CO2} based on different methods.

5.6 BEST ESTIMATE OF K FOR THIS REACH AND THE VARIABLITY IN K

The gas tracer method and the mass balance method give the same range of K_{CO2}, whereas the chamber method gives half the range. A reasonable estimation of K_{CO2} for this area is 0 - 0.0644.

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