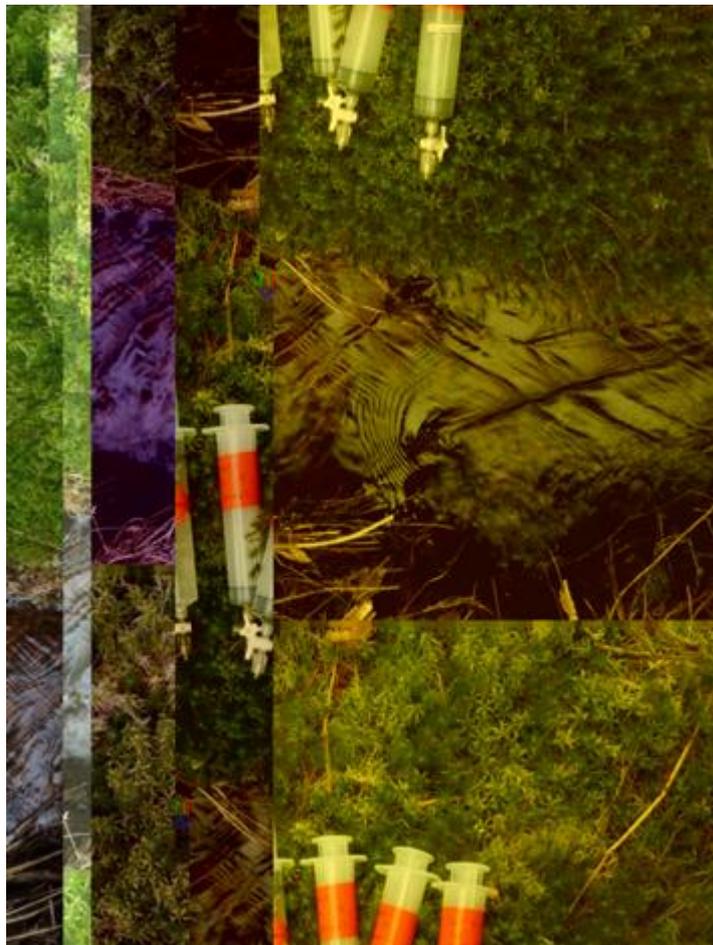


# Estimating CO<sub>2</sub> evasion from streams connected to a boreal lake

– Comparing three different methods

*Šárka Okrouhliková*



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## Abstract

There are different reservoirs of Carbon (C) on Earth and these reservoirs are closely linked to each other by the transport of C across different interfaces. The freshwater environment is one of the interfaces and an active component of the global C cycle. A considerable amount of C is lost through degassing (evasion) of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) from surface waters globally. Evasion is a vertical flux of gasses between the water surface and the atmosphere. Much of the efforts of determining the evasion component have been on lakes and large rivers while less focus has been spent on headwater streams.

Small streams represent a large part of the interface between the soil and the aquatic environment. Peat and boreal forest soils are often rich in C, so the streams, which drain this landscape, are transporting and cycling a large amount of C in different forms.

The aim of this study was to estimate the CO<sub>2</sub> evasion in streams connected to a boreal lake, and to compare three different methods for measuring evasion from those streams. The CO<sub>2</sub> evasion was calculated by a mass balance method, a gas transfer velocity method and a gas transfer coefficient method. The evasion by the gas transfer velocity and the gas transfer coefficient methods were determined using a volatile gas tracer. The CO<sub>2</sub> evasion by the mass balance method was calculated from the differences in CO<sub>2</sub> concentrations along a stream reach.

The study was conducted in the catchment of Lake Gäddejärn, which is situated in the boreal landscape of central Sweden. Four stream sites were selected and the measurements were done twice. The results of this study showed that the evasion of CO<sub>2</sub> from those boreal streams ranged from 2.6 to 12.9 kg C m<sup>-2</sup> yr<sup>-1</sup> based on stream surface area. The evasion rates were largely controlled by variability in discharge and stream morphology. The method comparison showed that the gas transfer velocity and gas transfer coefficient methods showed similar results, on average 15% difference in CO<sub>2</sub> evasion rate. It also showed that the mass balance method is not a good option for those kinds of stream systems. The study concludes that evasion of CO<sub>2</sub> from boreal streams is a significant flux and hence an important term in the landscape C cycle.

**Key words:** Evasion, CO<sub>2</sub>, Boreal

**Hypothesis:** That the three different methods to measure CO<sub>2</sub> evasion show similar results

**Aim:** To estimate the evasion rate and compare three different methods

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## 1. Introduction

Carbon (C) is one of most important chemical elements on Earth since it is the chemical base of all known life. There are two main forms of C: organic (coal, peat, oil....) and inorganic (limestone, dolomite, carbon dioxide). The amount of C on Earth is effectively constant and the paths that C follows in the environment make up the C cycle.

### 1.1. C cycling in aquatic systems

There are three major reservoirs of C – terrestrial, oceanic and atmospheric. C is processed within the different reservoirs and the reservoirs are also closely linked to each other with transport of C across different interfaces. Inland freshwaters is one of those interfaces between land and ocean or atmosphere. Inland freshwaters cover only a relatively small part of the Earth's surface area, approximately 3% (Downing et al, 2006). The freshwater environment is divided into two parts. The main part of the water is in steady freshwater environments called lentic systems (lakes and ponds) and the rest (around 5%) is in flowing freshwater environments called lotic systems (rivers and streams) (Wetzel, 2001). These systems have rarely been considered as potentially important quantitative components of the C cycle at global or regional scales (Cole et al. 2007). During the last decade the role of inland waters in the C cycle has been highlighted and Cole et al. (2007) showed that inland water is not just a passive pipe (Fig 1); instead it is a highly active component of the global C cycle responsible for a significant amount of C being processed and transported across the terrestrial/aquatic/sediment/atmosphere interfaces.

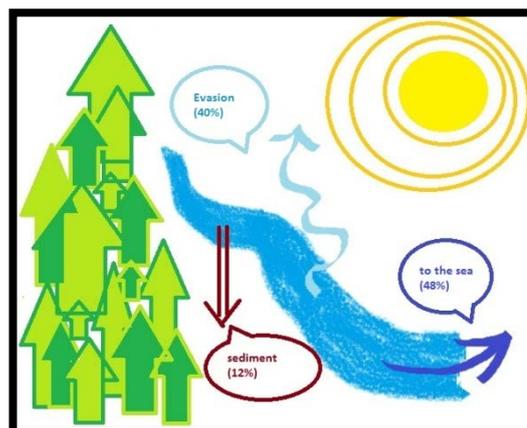


Figure 1: Carbon fluxes in the aquatic C cycle (Cole et al. 2007).

Of the C exported from terrestrial system to inland waters (Fig. 1), 48% is estimated to be transported to the sea, about 40% is lost through degassing (evasion) as carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ) from the water surface, and the remaining 12% are stored in sediments of lakes and ponds (Cole et al, 2007).

## 1.2. The Boreal landscape and influence of streams on C export

The boreal landscape consists of forests, peatlands and water bodies (Reunanen et al., 2001). Streams and rivers in this landscape are constantly transporting and cycling different forms of C (as particulate and dissolved organic carbon (POC and DOC) and as dissolved inorganic carbon (DIC)). This C can derive from both terrestrial and aquatic sources and be of both biogenic and geogenic origin. Export of DIC can be either downstream or vertically through degassing (evasion) of CO<sub>2</sub>.

In this work, the emphasis will be on streams. Streams have heterogeneous and dynamic morphology and chemistry, and the area covered by streams is not well documented at regional or global scales (Cole et al, 2007). Peat and boreal forest soils are often rich in C and the stream systems that drain these soils are often rich in DOC (Laudon et al. 2004) and supersaturated in CO<sub>2</sub> (Wallin et al, 2010; Öquist et al. 2009). In Sweden 90% of the streams have catchment areas smaller than 15 km<sup>2</sup> (Bishop et al. 2008). These small streams represent a large part of the interface between soils and aquatic systems, which makes them highly interesting components in the C cycling of the boreal landscape.

## 1.3. Gas exchange (Evasion) from the water surface

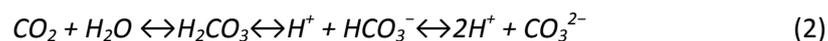
Evasion is a vertical flux characterized by an exchange of gasses between the water surface and the atmosphere. The exchange is diffusive i.e. driven by a concentration gradient with higher concentration of the studied gas in the water than in the atmosphere. CO<sub>2</sub> evasion from streams and rivers has been shown to significantly influence the carbon balance in terrestrial systems (Butman and Raymond, 2011).

CO<sub>2</sub> evasion is dependent on the speciation of DIC:

$$DIC = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \quad (1)$$

where *DIC* is total inorganic carbon,  $[CO_2^*]$  is the sum of carbonic acid concentrations ( $[CO_2]$  and  $[H_2CO_3]$ ),  $[HCO_3^-]$  is the bicarbonate concentration and  $[CO_3^{2-}]$  is the carbonate concentration.

The speciation is controlled by a pH dependent chemical equilibrium:



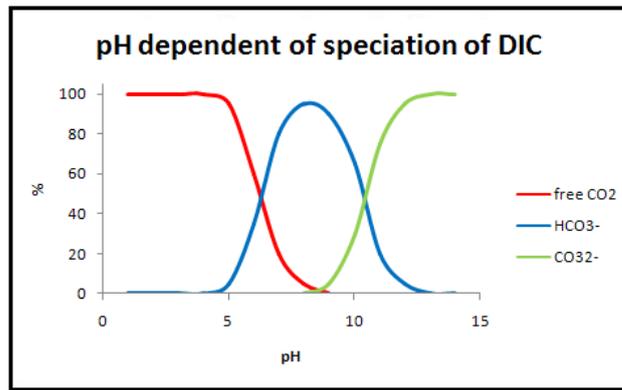


Figure 2: pH dependent chemical equilibrium.

As illustrated in Fig.2, at low pH (<5), DIC is largely in the form of CO<sub>2</sub>; when the pH increases, the HCO<sub>3</sub><sup>-</sup> starts to appear and around pH 6, CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> are both present in the same amount. Near pH 8, the CO<sub>2</sub> disappears, and above pH 8.5, just the HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> are present (Stumm and Morgan, 1996).

#### 1.4. Methods for determining CO<sub>2</sub> evasion

Many different methods for determining CO<sub>2</sub> evasion are used in the literature; in this study three of them are presented.

The simplest method is a **mass balance** method. Different mass balance methods have widely been used on both lentic and lotic systems. The method is based on the assumption that the difference between input and output of CO<sub>2</sub> to/from a water body is equal to the evasion.

The majority of studies about gas transfer between water surface and atmosphere have been done on large lakes or oceans (Johnson, 2010; Kawaba et al., 2003), using the gas transfer velocity ( $K_{TV}$ ). **Gas transfer velocity** is defined as the height of water that equilibrates with the atmosphere per unit time for a given gas and given temperature (Cole and Caraco, 1998; Frankignoulle et al., 1998; Raymond and Cole, 2001).

There are two main methods for determining gas transfer velocity – direct and indirect. Examples of direct methods are eddy correlation techniques or the use of floating chambers. In addition, there are a few indirect methods used in the literature. One of them, which can be used for both lentic and lotic system, is the deliberate tracer approach. This method can be used for measuring either the gas transfer velocity or the gas transfer coefficient for a lake/pond or a specific stream reach.

There is an uncertainty in using the gas transfer velocity for stream systems, because it depends on the depth of water, which can be very variable along a stream. To avoid this uncertainty the **Gas transfer coefficient** ( $K_{CO_2}$ ) can be used. This coefficient can be defined as the portion of gas that is lost over a specific stream reach per unit time (Wallin, 2011). It describes the exchange ability of gas across the water-atmosphere interface (Öquist et al., 2009).

For the **deliberate tracer approach**, a volatile tracer gas is added to the water body and the change in concentration of the tracer is monitored along the stream/river reach of interest. The main requirements for the tracer are that it is volatile and can be related to the gas of interest by known chemical relationships. Propane is often used in such studies and was the choice of tracer in this study due to its well established relationship to  $CO_2$  in terms of gas exchange properties and due to easy and cheap access to the gas.

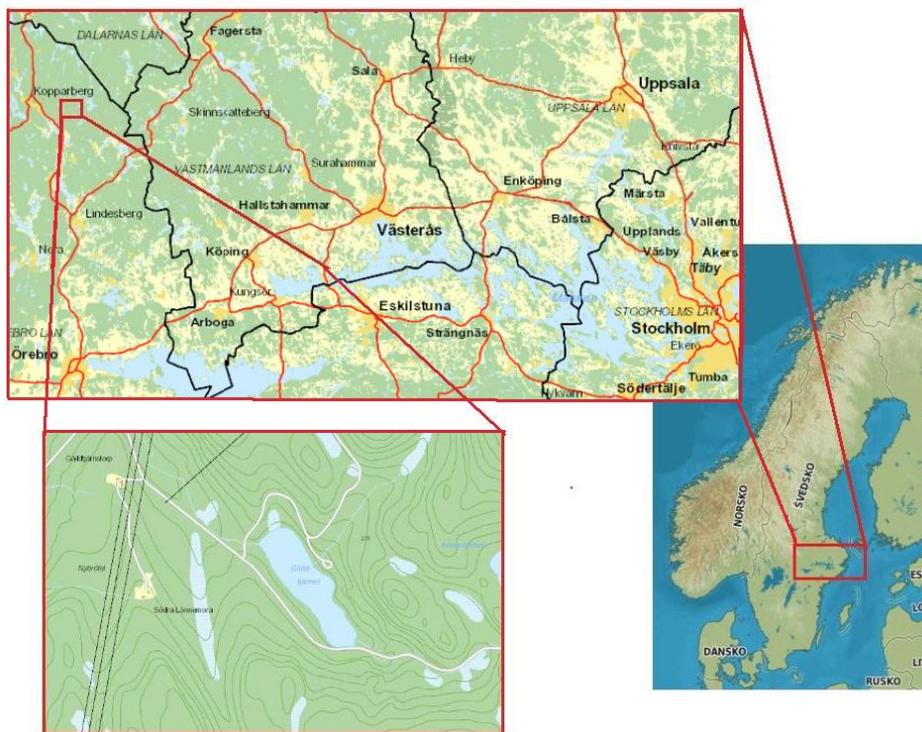
### **1.5. Motivation**

Since a large number of methods to determine  $CO_2$  evasion from streams are used in the literature there is a clear need to compare a number of those methods in order to establish a better understanding of the diffuse loss of C from streams. A method comparison will give a more accurate quantitative estimate of the exchange of  $CO_2$  between water and atmosphere. It will also show the weaknesses and strengths of the different methods used. This information will be useful for future calculations and modelling of the evasion rate from streams and its contribution to the C cycling of the landscape.

## 2. Materials and methods

### 2.1. Site description

The study was conducted in the catchment of Lake Gäddtjärnen (59°51'N; 15°11'E) situated close to Klotten in Örebro Län, Sweden (Sobek et al., 2009). The catchment is situated 65 km northward from Örebro and 140 km westward from Uppsala (Fig. 3). The catchment, covering an area of 1.8 km<sup>2</sup>, drains into the Norrström River. The area of lake Gäddtjärnen is 0.07 km<sup>2</sup> (Sobek et al., 2009; Wachenfeld and Tranvik, 2008).



**Figure 3** Location of the Gäddtjärnen catchment.

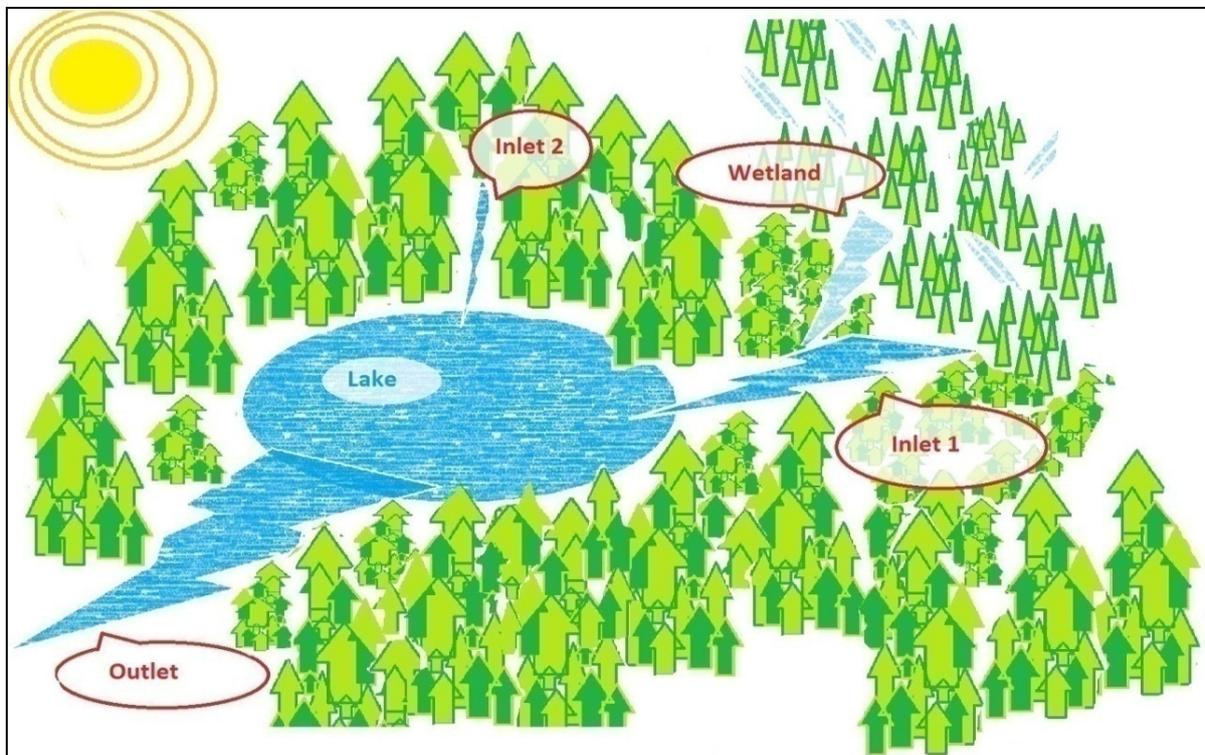
The Gäddtjärnen catchment area is covered by more than 80% forest, which is mostly represented by Norway spruce (*Picea abies*) and Scottish pine (*Pinus sylvestris*). Wetlands and water bodies are sharing 10% of total area (4% and 6% respectively) (<http://www.viss.lst.se>) and 10% is without forest cover (mainly clear cut). Wetlands are dominated by peat moss (*Sphagnum spp.*). The annual mean pH of lake Gäddtjärnen is 5.5 (Wachenfeld and Tranvik, 2008).

Climate is characterized by relatively warm summers and cold winters. Mean annual temperature is 6.4 °C, which varied from -7.5 °C during winter months and around 15°C during summer. The mean annual precipitation is 856 mm (SHMI, 2011). The elevation in the Gäddtjärnen

catchment ranges about 277 m above sea level (<http://www.viss.lst.se>). Podzols are the dominating soil type in upper areas and in the wetlands and riparian peat histosols appears.

For this study, four sites were selected within the catchment (Fig. 4, Fig. 5). Two sites are located at the two main inlets to the lake (Inlet 1 and Inlet 2), one is at the outlet of the lake (Outlet) and one site drains the wetland area upstream of Inlet 1 (Wetland).

Much research concerning C flows and cycling (e.g. terrestrial export, internal lake processes and atmospheric exchange) is conducted in Lake Gäddtjärn and its contributing catchment. This was the motivation behind the selection of the sites used in this study, with an overall aim to construct a complete landscape C budget of the area.



**Figure 4:** Site position in the catchment.



Inlet 1



Inlet 2



Outlet



Wetland

Figure 5: The four investigated stream sites.

At each site, a representative reach of the stream was chosen and used for the study. The reaches were chosen to cover streams with various morphological conditions (steady parts with pools, running turbulent parts etc.). Length, width and depth of the reach were measured at each site (Table 1). The area of the stream surface was calculated from its width and length.

**Table 1: Physical characteristics of stream reaches**

	<b>Length (m)</b>	<b>Width (average) (m)</b>	<b>Depth (average) (m)</b>	<b>Area (m<sup>2</sup>)</b>
<b>Inlet 1</b>	46	0.55	0.18	26.1
<b>Inlet 2</b>	25	0.53	0.26	13.6
<b>Outlet</b>	45	1.3	0.28	58.8
<b>Wetland</b>	44	0.6	0.25	25.8

## **2.2. Field sampling**

The study was conducted during spring 2012 (April/May) on four different streams and at two different occasions.

The field procedure was done in four steps (Fig. 6). The first step included a site selection and measurements of stream width and depth (A). The second step was the flow and residence time determination where the salt dilution method was used (B). The third step was to take headspace samples for CO<sub>2</sub> (C), and the last step was the injection of the volatile gas tracer followed by replicate sampling (D).

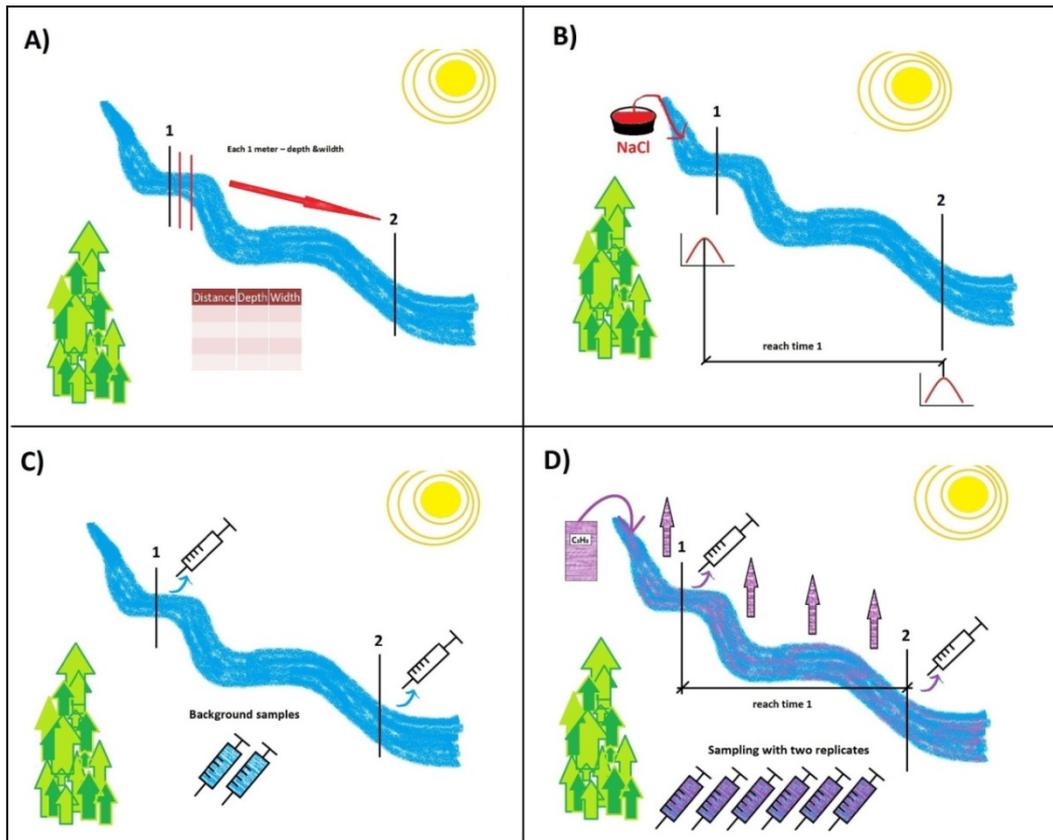


Figure6: Gas tracer method – field sampling.

### 2.2.1. Salt dilution method

Prior to the propane injection a pulse injection with  $NaCl$  was made for measurements of discharge ( $Q$ ) and residence time ( $\tau$ ) within the study reach. Before the measurement started, the temperature of water was measured and the salt solution was prepared. Electrical conductivity was measured with probes at each end of the reach using a Campbell CR510 data logger or by manual conductivity probes. The salt solution was added upstream (5-15 m) of the reach and the peak of salt solution was monitored over time at both stations. Residence time of the water within the reach was given as the difference in time between maximum electrical conductivity at the upper and lower station. From the concentration of the salt solution and the integrated conductivity ( $A$ ), the discharge ( $Q$ ) was calculated:

$$Q = V_t * c / A \quad (3)$$

$$c = salt(g) * 1000 / V_t \quad (4)$$

where  $V_t$  is volume of water in salt solution (L) and  $c$  is concentration of salt (g/L).

### 2.2.2. Gas tracer method

Samples for pCO<sub>2</sub> determination were collected at the upper and lower station before the propane was injected (Fig. 7). Propane (AGA gas) was injected through an air curtain creating fine bubbles with a constant rate (1.0 bar) 5-10 m upstream from the study reach. Propane was injected for approximately 15 minutes prior to sampling to achieve equilibrium within the reach (Fig. 8). Stream samples were taken at each end of the study reach using the residence time as time difference for sampling the same water mass. The sampling was repeated twice.



Figure 7: Watersampling.



Figure 8: Propane injection.

### 2.3. Calculations

Three methods for calculating CO<sub>2</sub> evasion were used and compared in this study.

- Mass balance (MB)
- Gas transfer coefficient ( $k_{CO_2}$ )
- Gas transfer velocity ( $k_{TV}$ )

For the **mass balance** approach, the CO<sub>2</sub> concentration difference between the upper and lower reach ends was assumed to represent the amount of CO<sub>2</sub> lost to the atmosphere. This was based on the assumption that no input of water or CO<sub>2</sub> occurred along the study reach:

$$Evasion = \frac{([CO_2]_{UP}] - [CO_2]_{LOW}) * Q}{A} \quad (5)$$

Where  $CO_2_{UP}$  and  $CO_2_{LOW}$  are the amount of  $CO_2$  ( $mg\ C\ L^{-1}$ ) at upper respectively lower reach end,  $Q$  is discharge ( $L\ s^{-1}$ ) and  $A$  is area of the stream surface ( $m^2$ ).

For the **gas transfer coefficient** method, an aeration equation was used. This equation was originally developed by Young and Huryn (1998) but has been widely used for determining  $CO_2$  evasion (Hope et al., 2001; Öquist et al., 2009; Wallin et al., 2011):

$$Evasion = \frac{CO_{2str-atm} * K_{CO_2} * \tau * Q}{A} \quad (6)$$

where,  $Q$  and  $\tau$  are discharge ( $L\ s^{-1}$ ) and residence time (min);  $CO_{2str-atm}$  is the difference between the stream and atmospheric  $CO_2$  concentrations ( $mg\ C\ L^{-1}$ ),  $K_{CO_2}$  is the gas exchange coefficient for carbon dioxide ( $min^{-1}$ ) and  $A$  is area of stream surface ( $m^2$ ).

The following equation was used to determine the gas transfer coefficient for propane (Genereux and Hemond, 1992).

$$K_{C_3H_8} = \frac{1}{\tau} \ln \left( \frac{Q_U c_U}{Q_L c_L} \right) \quad (7)$$

where  $K_{C_3H_8}$  is the gas transfer coefficient for propane ( $min^{-1}$ ),  $\tau$  is the residence time (min),  $Q_U$  and  $Q_L$  are the discharge at the lower and upper station ( $L\ s^{-1}$ ), and  $c_U$  and  $c_L$  are the relative concentrations (area of gas chromatogram peaks) of propane at the upper and lower station, respectively.

The gas exchange coefficient for  $CO_2$  ( $K_{CO_2}$ ) was determined according to the transformation from  $K_{C_3H_8}$  calculated according to Hope et al. (2001):

$$K_{CO_2} = K_{C_3H_8} \left( \frac{d_{CO_2}}{d_{C_3H_8}} \right)^n \quad (8)$$

where,  $K_{C_3H_8}$  is the gas transfer coefficient for propane,  $d_{CO_2}$  and  $d_{C_3H_8}$  are the gas diffusion coefficients for carbon dioxide and propane respectively and  $n$  is a coefficient describing the water surface characteristic. The value of 0.5 was used for  $n$  (Wallin et al. 2011).

The gas diffusion coefficients are temperature dependent and were corrected according to the stream temperature.  $d_{CO_2}$  and  $d_{C_3H_8}$  were corrected according to Jähne et al. (1987) and Wise and Houghton (1966) respectively:

$$d_{CO_2} = 0,9477 \exp^{(0,0274 * T)} \quad (9)$$

$$d_{C_3H_8} = 1,092 \exp^{(0,0235 * T)} \quad (10)$$

The third method was the **gas transfer velocity approach**. The relationship between the gas transfer coefficient,  $K_{CO_2}$  ( $\text{min}^{-1}$ ), and the gas transfer velocity,  $K_{TV}$  ( $\text{cm min}^{-1}$ ), is given in Wanninkhof et al. (1990) using depth,  $z$  (cm), as follows:

$$K_{CO_2} = \frac{K_{TV}}{z} \quad (11)$$

The evasion was then calculated with the  $K_{TV}$  transformed to suitable unit according to:

$$Evasion = CO_{2str-atm} * K_{TV} \quad (12)$$

where the Evasion ( $\text{mg m}^{-2} \text{min}^{-1}$ );  $CO_{2str-atm}$  is the difference between the stream and atmospheric  $CO_2$  concentrations ( $\text{mg C L}^{-1}$ ) and  $K_{TV}$  the gas transfer velocity ( $\text{cm min}^{-1}$ ). All **three methods** used for calculating evasion are summarized in the table 2.

**Table 2: The different methods**

Method	Equation used
<b>Mb</b>	$\frac{(CO_{2UP} - CO_{2LOW}) * Q}{area}$
<b>K<sub>CO2</sub></b>	$\frac{Q * CO_2 * \tau * K_{CO2}}{area}$
<b>K<sub>TV</sub></b>	$CO_2 * K_{TV}$

$CO_2$  in equation for  $K_{CO_2}$  and  $K_{TV}$  in table 2 is the difference between stream and atmosphere  $CO_2$  concentration.

### 3. Results

The two tracer injections were applied on the falling limb of the peak of the spring flood. Discharge (Q) decreased by nearly 50% at all sites between the 1<sup>st</sup> and 2<sup>nd</sup> sampling occasion (Table 3). Consequently, the measured residence times (RT) were almost two times higher at the 2<sup>nd</sup> sampling occasion compared to the 1<sup>st</sup> occasion. The pCO<sub>2</sub> varied from 1107 to 2638 µatm among the different sites with the highest pCO<sub>2</sub> observed at the Outlet and Wetland. The hydrological response on pCO<sub>2</sub> was different among the sites with Inlet 1, Inlet 2 and Wetland showing higher pCO<sub>2</sub> at lower discharge and Outlet showing higher pCO<sub>2</sub> at higher discharge. K<sub>CO2</sub> varied from 0.029 to 0.074 min<sup>-1</sup> among the sites with the highest measured K<sub>CO2</sub> values at Inlet 1 and at Outlet. K<sub>CO2</sub> values were decreasing with discharge at three of the sites (Inlet 1, Inlet 2 and Wetland) but increasing with increased discharge at the Outlet.

**Table 3: Evasion parameters determined for the four stream reaches**

Site	Date	Q l s <sup>-1</sup>	RT min	pCO <sub>2</sub> µatm	K(CO <sub>2</sub> ) min <sup>-1</sup>	K(TV) m min <sup>-1</sup>
Inlet 1	27.4.2012	22.6	3.7	1186	0.050	0.0100
	4.5.2012	10.8	6.2	1295	0.074	0.0127
Inlet 2	27.4.2012	8	8.25	1028	0.031	0.0090
	4.5.2012	3.9	16.3	1278	0.043	0.0126
Outlet	27.4.2012	44.5	5.5	2202	0.064	0.0180
	4.5.2012	23.6	9.3	1107	0.047	0.0131
Wetland	27.4.2012	21.3	6	1833	0.029	0.0083
	4.5.2012	9.7	10.5	2638	0.049	0.0107

#### 3.1. Comparing different methods to determine CO<sub>2</sub> evasion

##### 3.1.1. Spatial patterns

Evasion rates for the two sampling occasions determined by the three different methods are shown in Table 4. K<sub>CO2</sub> and K<sub>TV</sub> numbers were calculated from the propane injection, with the latter numbers determined by multiplying the K<sub>CO2</sub> value by the average depth of the stream reach. At the

1<sup>st</sup> sampling the  $K_{CO_2}$  method produced 9% higher evasion rates than the  $K_{TV}$  method. At the 2<sup>nd</sup> sampling the  $K_{CO_2}$  method produced 15% lower evasion rates at Inlet 1, Outlet and the Wetland than the  $K_{TV}$  method, at Inlet 2 the evasion rate was 40% higher. During the 1<sup>st</sup> sampling occasion the highest measured evasion rates were 447.97 and 368.35  $\mu\text{g C m}^{-2} \text{s}^{-1}$  at the Outlet for  $K_{CO_2}$  and  $K_{TV}$  respectively. The highest evasion rates at the 2<sup>nd</sup> sampling occasion were determined at the Wetland site (278.84 and 346.08  $\mu\text{g s m}^{-2}$  for  $K_{CO_2}$  and  $K_{TV}$  respectively).

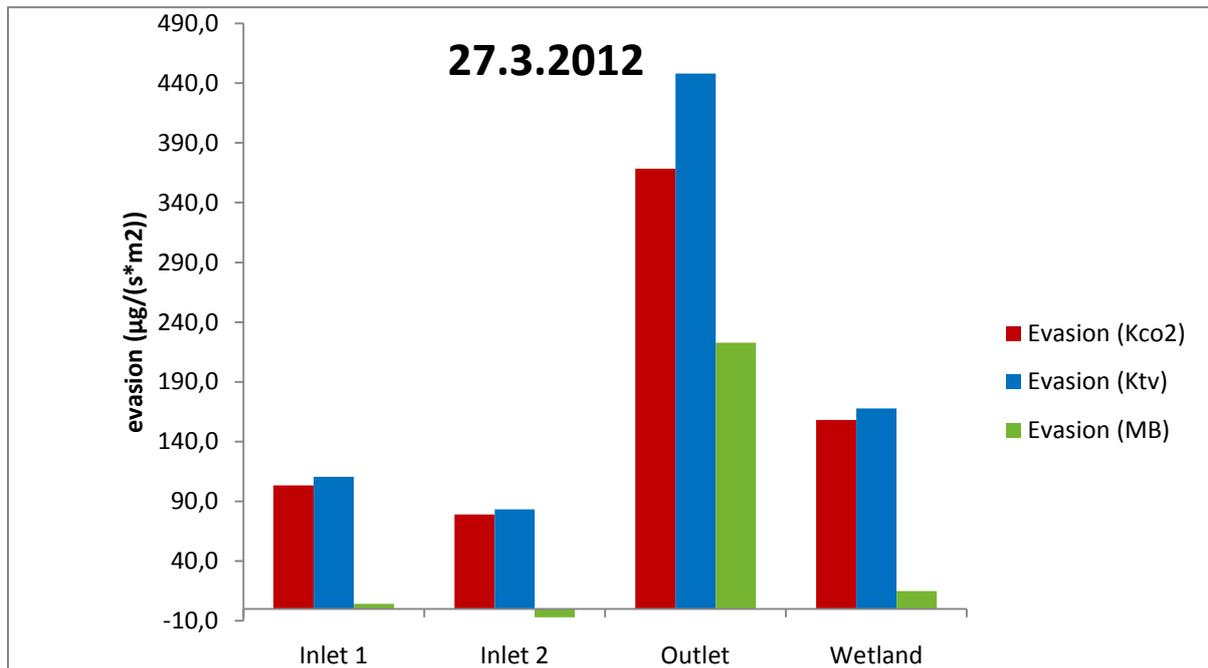
The mass balance method showed generally low evasion rates. At three of the stream reaches (Inlet 1, Inlet 2 and Wetland) the evasion rates by the mass balance method was just 20% of the evasion rates determined by the  $K_{CO_2}$  and  $K_{TV}$  methods. At the Outlet the evasion rate determined by the mass balance method was 50% of the  $K_{CO_2}$  and  $K_{TV}$  methods. At both (1<sup>st</sup> and 2<sup>nd</sup>) sampling occasions the mass balance method showed negative value for Inlet 2 (-6.9 and -33.4 respectively) suggesting an input of water along the reach with higher  $CO_2$  concentration than in the stream.

**Table 4: Evasion rates**

Site	Date	$K (CO_2)$ $\mu\text{g C m}^{-2} \text{s}^{-1}$	$K (TV)$ $\mu\text{g C m}^{-2} \text{s}^{-1}$	MB $\mu\text{g C m}^{-2} \text{s}^{-1}$
Inlet 1	<b>27.4.2012</b>	103	111	4
	<b>4.5.2012</b>	128	134	8
Inlet 2	<b>27.4.2012</b>	79	83	-7
	<b>4.5.2012</b>	156	112	-33
Outlet	<b>27.4.2012</b>	368	448	223
	<b>4.5.2012</b>	90	77	32
Wetland	<b>27.4.2012</b>	158	168	15
	<b>4.5.2012</b>	346	279	44

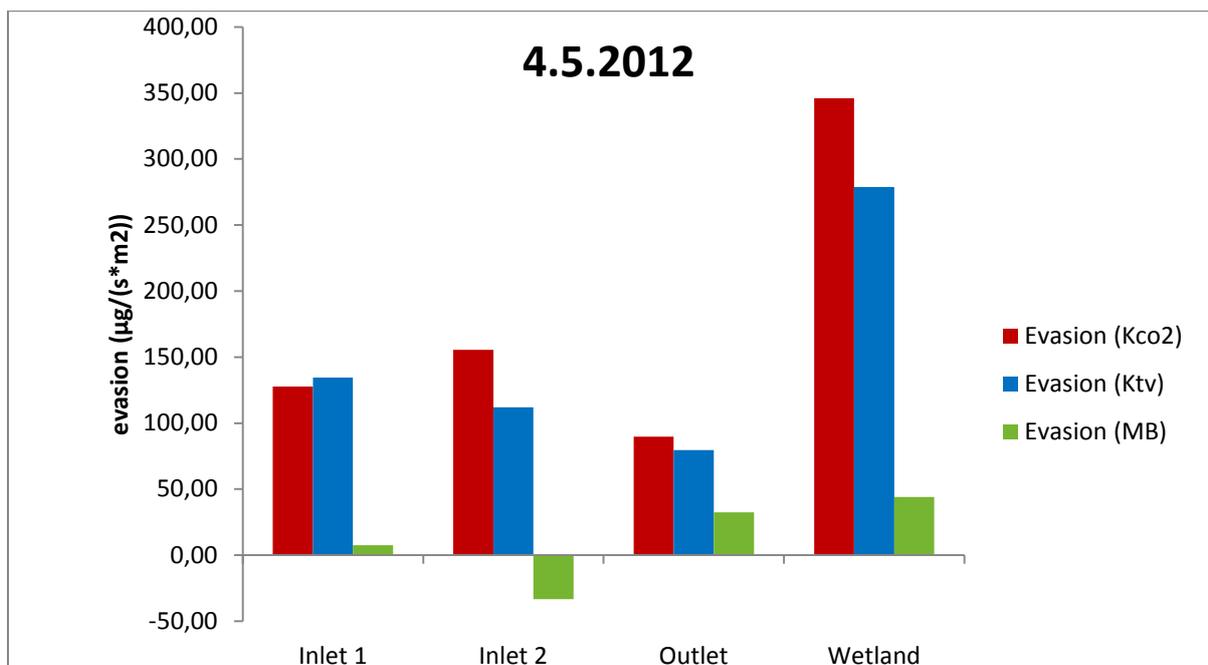
At the 1<sup>st</sup> sampling occasion the highest evasion rates were determined at the Outlet. The evasion rates determined by the  $K_{TV}$  and  $K_{CO_2}$  methods were similar at all sites. The mass balance method generated very low or even negative evasion rates at three of the sites (Fig. 9 and 10). At the Outlet the mass balance method showed higher evasion rates, but still only around half of the other two methods. For the 1<sup>st</sup> sampling occasion the  $K_{CO_2}$  method showed 6% higher evasion rates than  $K_{TV}$  at Inlet 1, Inlet 2 and Wetland; for Outlet it was about 20%. At the 2<sup>nd</sup> sampling only Inlet 2 showed

lower evasion rates with the  $K_{TV}$  than the  $K_{CO_2}$  method, whereas other sites show 20% - 40% higher evasion rates.



**Figure 9:** Evasion rates from the four sites at the 1<sup>st</sup> sampling occasion

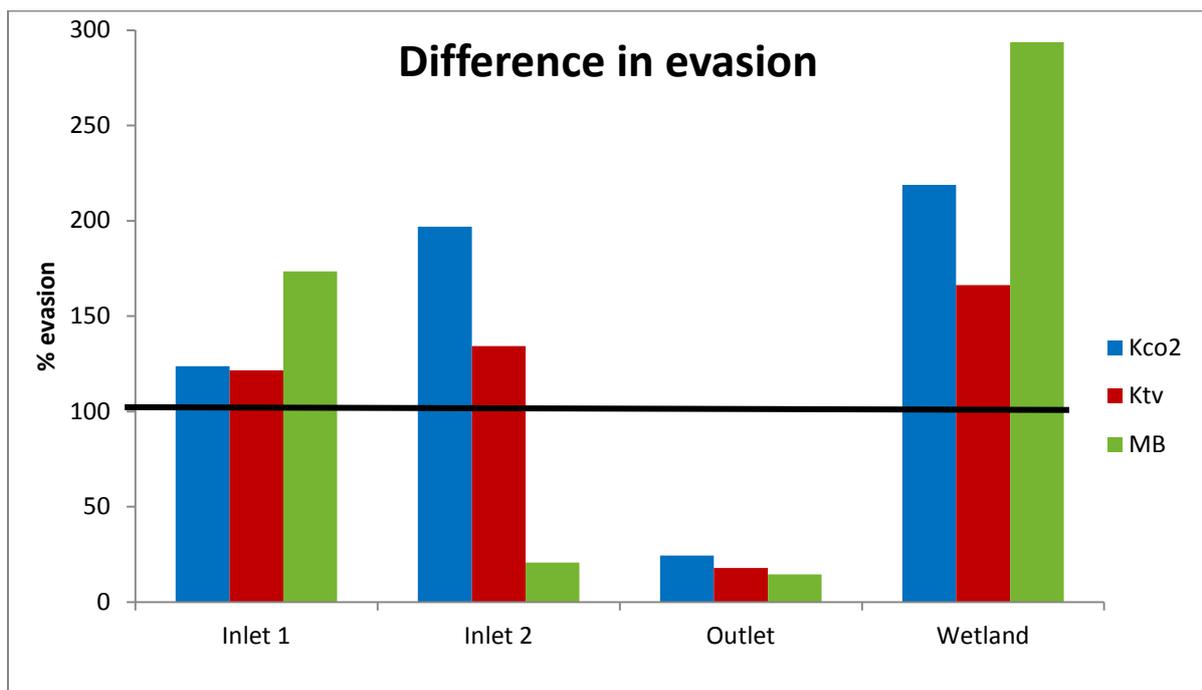
At the 2<sup>nd</sup> sampling occasion, the Wetland showed the highest evasion rates. The values at Inlet 1, Inlet 2 and Outlet were similar. At the Outlet site, the mass balance method showed 60% of  $K_{TV}$  and  $K_{CO_2}$  methods, which was the lowest difference between methods.



**Figure 10:** Evasion rates from the four sites at the 2<sup>nd</sup> sampling occasion

### 3.1.2. Temporal patterns

In Fig. 11 the percentage difference between the 1<sup>st</sup> and 2<sup>nd</sup> sampling occasion is shown. The 1<sup>st</sup> sampling occasion was set to 100% represented by the black line. At the Wetland site a high increase in evasion was obtained by all three methods ( $K_{CO_2}$ ,  $K_{TV}$  and mass balance method) at the second sampling occasion. The biggest site-specific difference between methods was obtained for Inlet 2, where the evasion rate from the mass balance method was nearly four times higher at the 2<sup>nd</sup> sampling. The Wetland showed a high increase in evasion between the two sampling days (about 125%). At the Outlet, a large decrease in evasion rate was determined between the 1<sup>st</sup> and 2<sup>nd</sup> sampling occasion, evasion was about 80 % lower at the 2<sup>nd</sup> sampling day, something that was shown by all methods.



**Figure 11:** Percentage change in CO<sub>2</sub> evasion.

The two sampling occasions were conducted during spring flood on the falling limb of the discharge peak. By comparing two different discharge situations we were able to detect the influence of discharge on evasion rates (Figs. 12-14).

The  $K_{CO_2}$  and  $K_{TV}$  methods showed similar patterns among the sites in the relationship between discharge and evasion rate. At Inlet 1, Inlet 2 and Wetland the evasion rate increased with decreased discharge. The opposite was determined at the Outlet where the evasion decreased with decreasing discharge. The mass balance method showed a similar discharge dependent trend for Inlet 1 and the Wetland as for the  $K_{CO_2}$  and  $K_{TV}$  methods although the percentage difference in evasion was lower. The Outlet was the only site where all three methods were showing similar patterns and evasion rates.

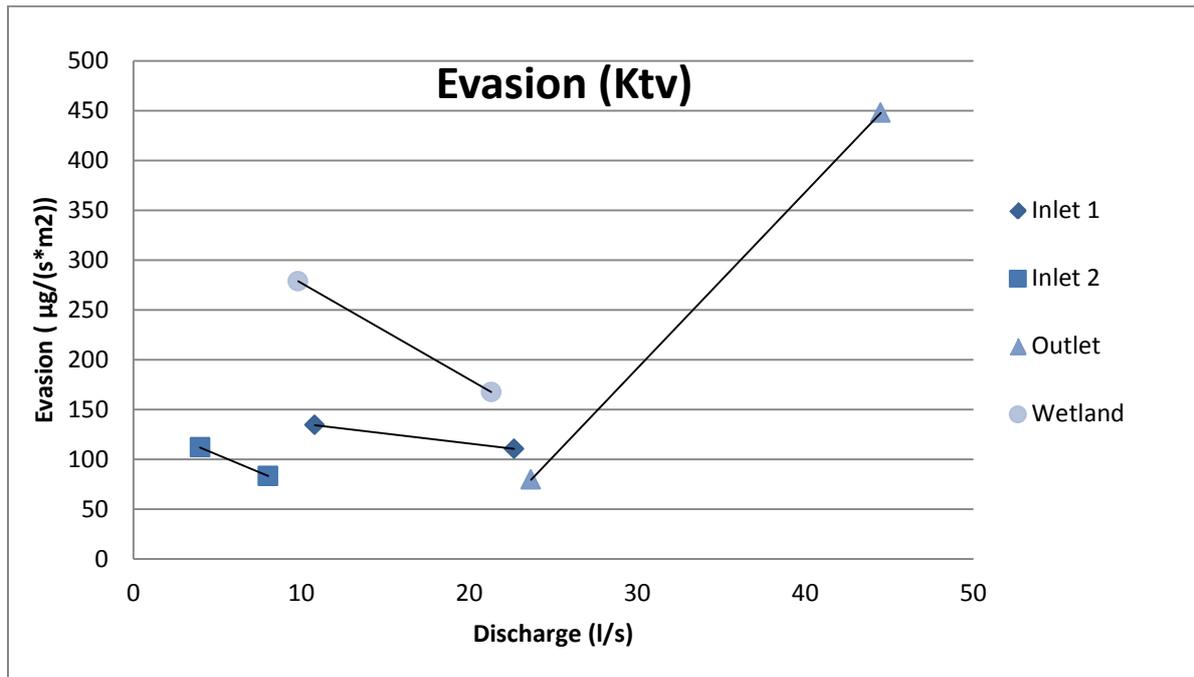


Figure 12: Gas Transfer velocity method: Evasion - Discharge dependence.

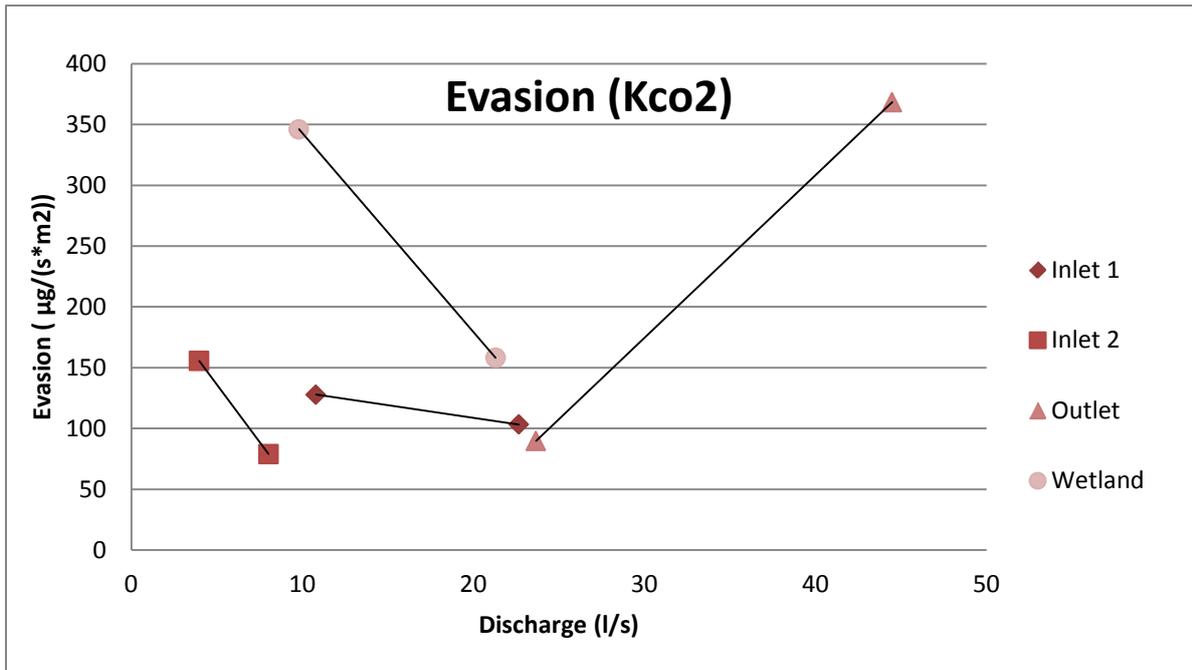


Figure 13: Gas Transfer coefficient method: Evasion - Discharge dependence

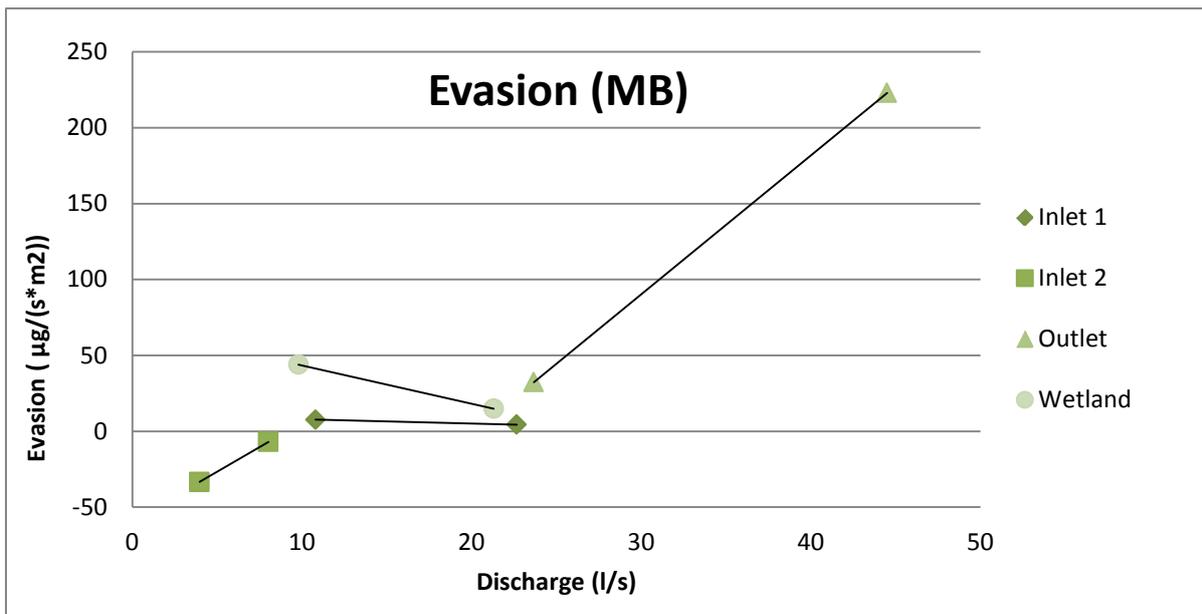


Figure 14: Mass Balance method: Evasion - Discharge dependence.

Relationships between  $K_{CO_2}$  values and discharge (Fig. 15) were showing similar trends as for evasion. With decreasing discharge the K value increased at Inlet 1, Inlet 2 and Wetland. At Outlet, the K value decreased with decreasing discharge.

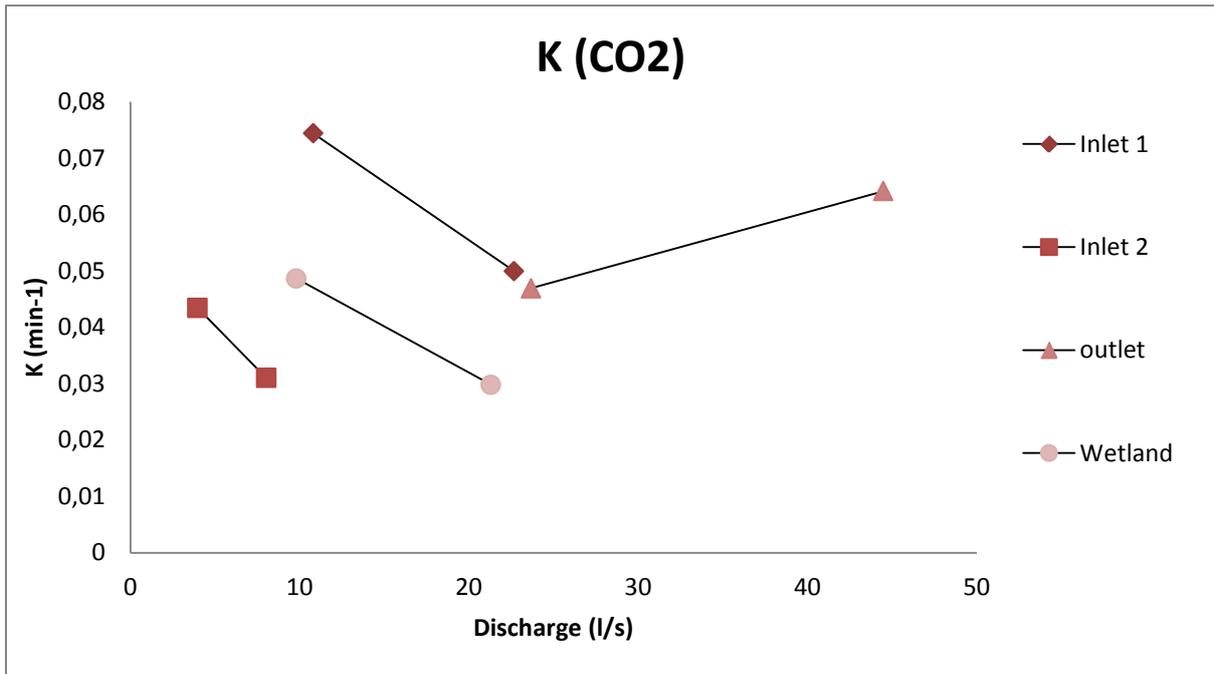


Figure 15:  $K_{CO_2}$  value dependence on Discharge.

### 3.2. Up scaling to annual fluxes

To obtain annual fluxes (Table 5), the average evasion rates based on stream surface area for each site and occasion were calculated. The fluxes were based on the  $K_{CO_2}$  and  $K_{TV}$  methods. The mass balance method was not included because the values were very low. At the 1<sup>st</sup> sampling, the Outlet showed the highest ( $12.9 \text{ kg m}^{-2} \text{ yr}^{-1}$ ) and Inlet 2 shows the lowest ( $2.5 \text{ kg m}^{-2} \text{ yr}^{-1}$ ). At the 2<sup>nd</sup> sampling, the Wetland showed the highest ( $9.85 \text{ kg m}^{-2} \text{ yr}^{-1}$ ) and the Outlet showed the lowest ( $2.62 \text{ kg m}^{-2} \text{ yr}^{-1}$ ).

The difference between the 1<sup>st</sup> and 2<sup>nd</sup> sampling was high. The Outlet showed the highest evasion during the 1<sup>st</sup> sampling and the lowest during the 2<sup>nd</sup> sampling. The average from the 1<sup>st</sup> and 2<sup>nd</sup> sampling occasion showed low evasion rates from Inlet 1 and Inlet 2 and high evasion rate from the Outlet and Wetland.

**Table 5: Average annual evasion rates and K values**

Site	Date	Evasion $\text{kg m}^{-2} \text{ yr}^{-1}$	Average Evasion $\text{kg m}^{-2} \text{ yr}^{-1}$
Inlet 1	27.4.2012	3.4	3.9
	4.5.2012	4.5	
Inlet 2	27.4.2012	2.6	3.4
	4.5.2012	4.2	
Outlet	27.4.2012	12.9	7.7
	4.5.2012	2.6	
Wetland	27.4.2012	5.1	7.5
	4.5.2012	9.8	

## 4. Discussion

### 4.1. Comparing methods

The results from the gas transfer coefficient and gas transfer velocity methods showed similar results. However, the results for both methods were based on the same gas tracer measurements. The gas transfer velocity method is highly dependent of the average depth of stream. Although we made detailed measurements of the stream depth along the study reaches, the estimate of the average stream depth is uncertain and it was concluded that this is a major disadvantage of the gas transfer velocity method. We found the gas transfer coefficient method most convenient to use for these kinds of boreal streams.

The mass balance method showed lower/negative values at the study sites. By comparing the three methods, the evasion rates from the mass balance method corresponded to just 3 - 20% of the evasion rates produced by the  $K_{CO_2}$  method at three of four sites. The exception was the Outlet where the mass balance method corresponded to 50%. The mass balance method is a simple method which has been used in different environments, but since it does not account for groundwater and soil inputs it is not suitable to use in these kinds of boreal streams. This was confirmed by the better correspondence between the mass balance and the tracer based methods at the Outlet site where the stream  $CO_2$  is regulated mostly by lake processes and where the morphology of the stream channel indicates that the soil-stream connection is low.

### 4.2. Stream morphology

Turbulence within stream reaches control the evasion rates to a great extent (Hope et al. 2001; Wallin et al. 2011). The turbulence is created by the stream channel morphology and discharge conditions. Inlet 1, Inlet 2 and the Wetland reaches are showing similar patterns – increased evasion with decreased discharge. Those three stream channels have similar morphology – streams with a well-defined channel and with a bottom free from rocks. The Outlet showed the opposite pattern, increased evasion with increased discharge. Compared to the other three channels, this pattern can be explained by the different morphology of the stream and by the fact that the stream contains many large rocks and small falls. Higher discharge and hence velocity will create higher turbulence and an increased evasion in this channel type. In Figure 16, two conceptual streams with different morphology can be seen. The left picture illustrates a stream where more turbulence and hence also higher evasion occurs with lower discharge. The right picture shows the opposite where turbulence and evasion is increased with higher discharge. This is a conceptual explanation on how we believe turbulence, discharge and evasion are connected in streams with different geomorphological conditions.

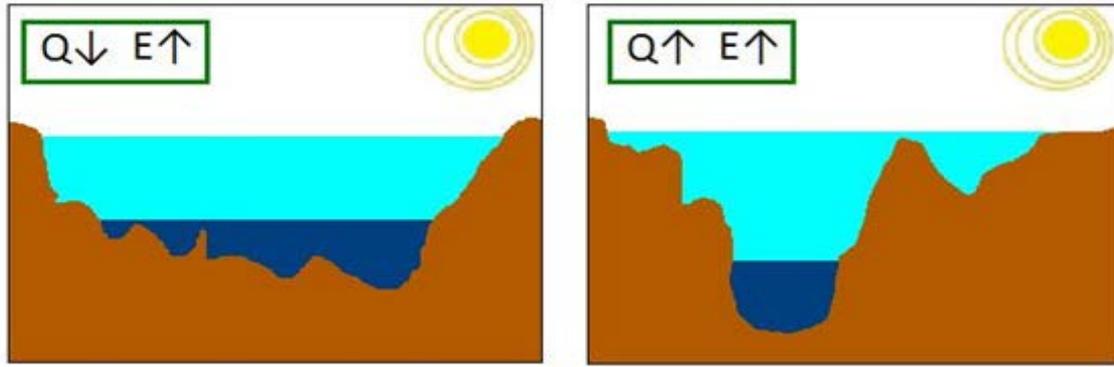


Figure 16: Stream morphology

#### 4.3. Comparison to other studies

Results from similar studies of CO<sub>2</sub> evasion from streams and rivers are shown in table 6. All presented data are based on experimental determination of *k* and CO<sub>2</sub> evasion and is expressed per stream surface area.

Our study showed relatively high evasion rates compared to similar studies. The studies from Northern Sweden (Öquist et al., 2009 and Wallin et al., 2011) showed higher values of pCO<sub>2</sub> but lower evasion rates. In Scotland Hope et al. (2001) estimated a large range in CO<sub>2</sub> evasion from a peatland stream. Results from USA (Jones and Mulholland, 1998 and Butman and Raymond, 2011) show lower evasion rates than this study even though pCO<sub>2</sub> is higher. However, the stream channel morphology has high influence on evasion rates and conclusions concerning evasion rates based on just pCO<sub>2</sub> are very uncertain.

Table 6: Summary of CO<sub>2</sub> evasion data from published studies of streams in boreal landscape

Region	pCO <sub>2</sub> µatm	Evasion kg m <sup>-2</sup> yr <sup>-1</sup>	Reference
Central Sweden	1028-2638	2.56 – 12.87	This study
Northern Sweden	2015-7838	2.36	Öquist et al., 2009
Northern Sweden	722-24167	0.59-5.44	Wallin et al., 2011
Scotland, UK	420-4500	0.095-16.75	Hope et al., 2001
Entire, USA	1588-4326	0.88-4	Butman and Raymond, 2011
Tennessee, USA	360-6228	0.69-1.64	Jones and Mulholland, 1998

## 5. Conclusions

The gas transfer velocity and gas transfer coefficient methods can be used for estimating evasion rates in the boreal landscape. For streams, the gas transfer coefficient method is more suitable, because the average depth is not needed. The mass balance method is not suitable for determining CO<sub>2</sub> evasion in these kinds of boreal streams.

Discharge and morphology of the stream influence the degree of turbulence and were identified as the most influential components to determine evasion rate besides CO<sub>2</sub> concentration.

The result from this study showed that the evasion rates from small boreal streams are high and should be considered as a part of the landscape C cycle.

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