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Abstract

Though there is an innumerable amount of freshwater systems, they cover just a small fraction of the Earth's surface area and have been mostly disregarded as an important quantitative element in the carbon cycle on regional or global scales. Recently several studies showed the importance of freshwater systems as a significant source of carbon dioxide (CO_2) emissions. Global estimates show that the amount of carbon (C) exported from terrestrial environments to aquatic systems is on par with the terrestrial uptake of CO_2 via photosynthesis. About half of this C that is exported to aquatic inland ecosystems is transferred back to the atmosphere via outgassing. Most studies have been focused on either lentic or lotic ecosystems and disregarded the connectivity between streams and lakes. This study aims to quantify carbon emissions from a small boreal catchment area in central Sweden. Automatic floating chambers were placed on lake Gäddtjärn, and its connecting streams to measure the CO_2 flux rates. Furthermore the small scale spatial variability of the partial pressure of CO_2 (pCO_2) and CO_2 emission rates along the streams were analysed, results of the lake and its connecting streams have been compared, and the suitability of automatic chambers for CO_2 flux measurements and data reproducibility was tested.

The results showed that all sampling sites across the lake and along the streams were supersaturated in pCO_2 with respect to the atmosphere. Stream pCO_2 was largely influenced by the processes in the lake Gäddtjärn and an upstream wetland. However, the high pCO_2 decreased over a small distance due to the fast process of CO_2 outgassing. Spatial variability of stream CO_2 emission rates was highly controlled by the gas transfer velocities which were positively correlated to the turbulence conditions. Average pCO_2 was similar for lake and streams and in agreement with findings from other studies. Lake CO_2 emission rates were usually lower than stream CO_2 emission rates as a consequence of lower gas transfer velocities.

Findings of this study show that automatic floating chambers are suitable for analyzing CO_2 emissions on lakes, but stream CO_2 emissions seem to be underestimated as a reason of technical (sensor response time) and practical (placement of chambers in turbulent conditions) limitations.

Keywords: CO_2 emissions, floating chamber, gas transfer velocity

Popular Science Summary

An increase of atmospheric greenhouse gas emissions, especially carbon dioxide (CO_2), is the main reason for global warming and raised the discussion about global climate change in the media. CO_2 is largely emitted by the burning of fossil fuels but there are also natural sources. Recently, studies have shown that freshwater systems play an important role in the global carbon cycle, although they only cover a small area of the earth's surface. Global estimates show that the amount of carbon (C) exported from terrestrial environments to aquatic systems is on par with the terrestrial uptake of CO_2 via photosynthesis. About half of this C that is exported to aquatic inland ecosystems is transferred back to the atmosphere via outgassing. Most studies have been focused on either lakes and reservoirs, or streams and rivers disregarding the connectivity between these freshwater systems.

This study focused on measuring CO_2 emissions from a small boreal lake in central Sweden and its connecting streams. Automatic floating chambers (round-shaped plastic prism that are closed to the atmosphere but open at the bottom to the gas source) have been placed along the inlet and outlet stream and across the lake to measure the CO_2 flux from the water to the atmosphere. Furthermore, the small scale variability of the CO_2 emission rates and the partial pressure of CO_2 (pCO_2) were analyzed. Results of lake and stream measurements have been compared, and the suitability of automatic floating chambers for CO_2 flux sampling and data reproducibility was tested.

The results showed that all sampling sites across the lake and along the streams had a much higher CO_2 concentration in the water in comparison to the atmosphere. Thus, they were supersaturated in CO_2 with respect to the atmosphere. Stream pCO_2 was largely influenced by processes in the lake Gäddtjärn and an upstream wetland. But over a small distance the pCO_2 decreased along the streams due to the fast process of CO_2 outgassing. Spatial variability of stream CO_2 emission rates was dependent on the rate of gas exchange across the air-water interface per time (gas transfer velocity). Average pCO_2 was similar for the lake and the streams and in agreement with findings from other studies. Lake CO_2 emission rates were usually lower than stream CO_2 emission rates as a consequence of lower gas transfer velocities.

The tested automatic floating chambers are suitable for measuring CO_2 emissions on lakes. In contrast, stream CO_2 emissions were likely underestimated due to technical (sensor response time) and practical (placement of chambers in turbulent conditions) limitations.

Zusammenfassung

Der kontinuierliche Anstieg von atmosphärischen Treibhausgasen, insbesondere Kohlenstoffdioxid (CO2), ist der Hauptgrund für die Klimaerwärmung und entfacht Diskussion über den globalen Klimawandel in den Medien. CO_2 wird im großen Umfang durch die Verbrennung fossiler Brennstoffe produziert und in die Atmosphäre freigesetzt, aber es gibt ebenfalls natürliche Quellen von CO_2 Emissionen. Aktuelle Studien haben gezeigt, dass auch Süßwasserökosysteme eine wichtige Rolle im globalen Kohlenstoffkreislauf spielen, auch wenn sie nur einen sehr kleinen Anteil der Erdoberfläche repräsentieren. Globale Schätzungen zeigen, dass fast die Hälfte des von der terrestrischen Umwelt zu Inlandwasserökosystemen importierten Kohlenstoffs durch Ausgasungen in die Atmosphäre zurück gelangt. Ein Großteil der Studien untersuchte entweder Seen und Reservoirs oder Flüsse, wenige beachteten die Verbindungen und Interaktionen zwischen diesen Süßgewässern.

Diese Studie untersuchte die CO_2 Emissionen eines kleinen borealen Sees in Mittelschweden und seiner Zu- und Abflüsse. Automatische schwimmende Kammern (Plastikzylinder zur Atmosphäre geschlossen, aber nach unten zur Gasquelle offen) wurden auf dem Zufluss, dem Abfluss und dem See verteilt, um die CO_2 Ausgasung aus den Gewässern in die Atmosphäre zu messen. Weiterhin wurde die räumliche Variabilität der CO_2 Konzentrationen im Wasser (pCO_2) stromabwärts analysiert. Die Ergebnisse der Messungen auf dem See und entlang der Bäche wurden verglichen. Weiterhin wurde die Methode für den generellen Einsatz zur Messung von CO_2 Emissionen aus Gewässern und auf Reproduzierbarkeit getestet.

Die Ergebnisse zeigen, dass an allen Messpunkten entlang der Bäche und auf dem See die CO_2 Konzentration im Wasser höher als in der Atmosphäre war. Das Wasser war also CO_2 übersättigt. pCO_2 entlang der Bäche war stark durch die Prozesse im See und dem Sumpfgebiet beeinflusst. Allerdings geht der Ausgasungsprozess so schnell vonstatten, dass die hohe CO_2 Konzentration im Wasser schon entlang einer kurzen Distanz stromabwärts stark gesunken war. Die räumliche Variabilität der CO_2 Emissionen war von der Rate des Gasaustausches zwischen der Luft-Wasser Grenzfläche pro Zeiteinheit (Gasaustauschgeschwindigkeit) abhängig. Gemessene pCO_2 Mittelwerte im See und den Bächen waren ähnlich und stimmten mit Ergebnissen aus anderen Studien überein. Die CO_2 Emissionen vom See waren meist geringer als von den Bächen, aufgrund der niedrigeren Gasaustauschgeschwindigkeit.

Die Methode ist geeignet, um CO_2 Emissionen von Seen zu untersuchen, aber bei der Untersuchung von Bächen wurden CO_2 Ausgasungen häufig unterbewertet als Folge von technischen (Sensorreaktionszeit) und praktischen (Messung von stark turbulenten Bachabschnitten) Einschränkungen.

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Abbreviations

BLM	Boundary layer model
C	Carbon
CO_2	Carbon dioxide
DIC	Dissolved inorganic carbon
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EC	Eddy Covariance
GHG	Greenhouse gases
k	Gas transfer velocity, piston velocity
kCO_2	Gas transfer velocity for CO_2
k_{600}	Normalised gas transfer velocity to 20°C and for a Sc of 600
NEP	Net ecosystem production
pCO_2	Partial pressure of carbon dioxide
PIC	Particulate inorganic carbon
POC	Particulate organic carbon
Sc	Schmidt number
SRM	Surface renewal model
TOC	Total organic carbon

1 Introduction

Carbon dioxide (CO_2) emissions have been increasing steadily since the industrial revolution, mainly as a consequence of anthropogenic activities like burning fossil fuels and changing the land use. Natural emissions are mainly released by volcanic activities. On a global scale boreal ecosystems are regarded as carbon sinks since they store large amounts of atmospheric CO_2 in their biomass, peatlands and soils (IPCC, 2007). Freshwater systems have so far been mostly disregarded as an important quantitative element in the carbon cycle on regional or global scales (Cole et al., 2007), since they cover just a small fraction of the Earth's surface area (Cole et al., 1994). However, during the last decades several studies have showed the importance of freshwater systems as a significant source of carbon dioxide emissions (Aufdenkampe et al., 2011; Cole et al., 2007, 1994; Tranvik et al., 2009). It is estimated that two thirds of the carbon input from the terrestrial environment to aquatic inland systems are lost via outgassing (48 %) and storage in sediments (~20%). These 2 Pg of carbon lost per year (Tranvik et al., 2009) closely resemble the total global carbon accumulation within the terrestrial ecosystems of the world, called global net ecosystem production (NEP) (Randerson et al., 2002). Thus, an enormous amount is sequestered and or released to the atmosphere as CO_2. The remaining fraction of roughly 30 % is transported to the oceans (Tranvik et al., 2009). Hence, inland waters play an important role in the global carbon cycle being an active component of transport, transformation or storage and they have the potential to affect the climate (Cole et al., 2007).

1.1 The importance of boreal ecosystems

The boreal landscape is highly important in the global carbon (C) cycle not only because it covers a large amount of the global land area. Furthermore, it stores a significant part of the global carbon stock in soils and vegetation (Chapin et al., 2000; Pregitzer and Euskirchen, 2004) and accumulates about 0.6 Pg C yr^{-1} (Goodale et al., 2002). Thus, it is regarded as a net carbon sink (Chapin et al., 2000; Cole et al., 1994; Goodale et al., 2002).

In contrast to terrestrial ecosystems in the boreal zone aquatic systems are regarded as net sources of carbon dioxide (CO_2) (Algesten et al., 2004; Cole et al., 1994). They are usually supersaturated with respect to CO_2 due to high C import rates from inflowing waters as well as high mineralization rates of allochthonous material (Algesten et al., 2004; Cole et al., 1994; del Giorgio et al., 1997). Furthermore, the high density of aquatic ecosystem emphasizes the focus on studying boreal regions.

1.2 Carbon cycle in aquatic systems

Carbon, as the chemical base of organisms, is one of the most important chemical elements on earth. Global carbon models are needed to quantify the inputs and outputs of carbon between the different C reservoirs. Most attention is paid on the major reservoirs: the oceans, the atmosphere and the terrestrial environment, in which C is distributed very unevenly (Atmosphere: ~762 $GtCyr^{-1}$, Oceans: ~38270 $GtCyr^{-1}$, Vegetation, Soil & Detritus: ~2260 $GtCyr^{-1}$) and exchanged via different pathways (IPCC, 2007). It is important to estimate the different fluxes between and within the various reservoirs in order to understand the global carbon cycle.

Firstly, C enters the biosphere via photosynthesis by plants. This process is called gross primary production (GPP) and estimated to be about 100-150 PgC yr^{-1} (Randerson et al., 2002). Large amounts of the CO_2 are incorporated in biomass and support respiration as well as abiotic oxidation. The difference between GPP and total ecosystem respiration is called net ecosystem production (NEP) (roughly 2 Pg C yr^{-1}; Randerson et al., 2002). NEP is the amount of C which can either be stored within the system, e.g. use for biomass production or abiotic storage, or is exported (Cole et al., 2007). Large amounts of C are stored in biomass and soils. Especially boreal ecosystems, including their forests and peatlands, are known to be a large carbon storage pool (Chapin et al., 2000; Pregitzer and Euskirchen, 2004).

However, NEP is in general solely regarded as the difference of GPP and respiration. C losses due to export to aquatic systems are usually not included. Aquatic systems receive carbon via three major pathways: exchange with the atmosphere, release of C from sediments, and input of C species from soils or groundwater (Figure 1). Carbon can be present in different forms: particulate organic carbon (POC), particulate inorganic carbon (PIC), dissolved organic carbon (DOC) or dissolved inorganic carbon (DIC) (Cole et al., 2007; Myrbo, 2012; Striegl and Michmerhuizen, 1998). DIC can be derived from both biogenic, geogenic and atmospheric sources and occurs as dissolved free CO_2 (pCO_2), as carbonic acid (H_2CO_3) or in ionic forms as bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). The present speciation of DIC is pH dependent (Stumm and Morgan, 1996). Biogenic sources are in stream-mineralization of C by microbes, photo-oxidation, and CO_2 inputs via the groundwater derived from soil respiration. Weathering and dissolution of carbonate or silicate minerals represents a geogenic contribution. In addition, undersaturated freshwaters have the potential to absorb CO_2 as an interaction with the atmosphere (Atekwana and Krishnamurthy; 1998).

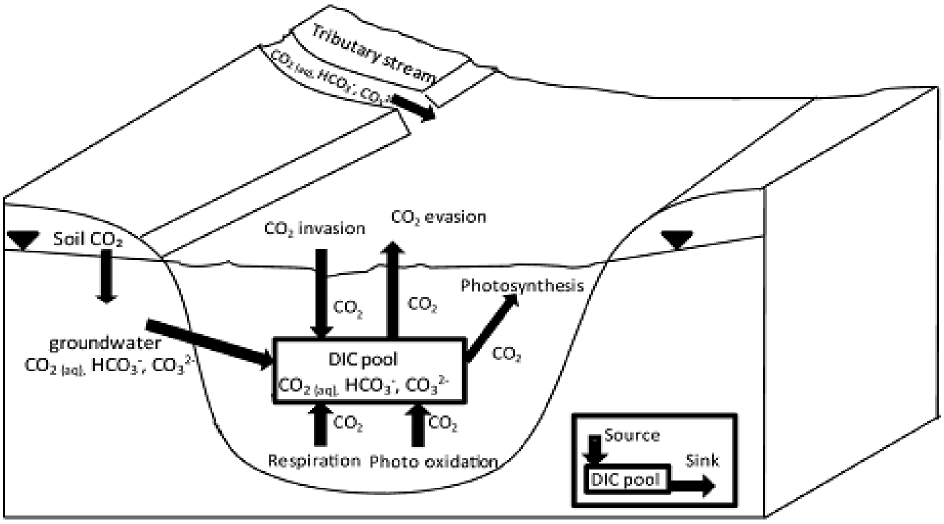

Figure 1: Schematic figure of processes controlling the DIC concentration in freshwater systems. Revised figure from Atekwana & Krishnamurthy (1998).

Mineralization of DOC by bacterial respiration (Jonsson et al., 2001) and photo-oxidation (Graneli et al., 1996) is an important source of CO_2 in freshwater systems. In addition, DOC can be derived from primary production in the water column (autochthounous C) or as input of plant or soil material from the catchment area (allochthonous C) (Jonsson et al., 2001). Allochthonous DOC is thought to be the more important component for the production of CO_2 (Jonsson et al., 2001; Sobek et al., 2003). Additionally, the production of CO_2 within peatlands followed by a DOC export downstream seems to be of a significant magnitude (Algesten et al., 2004).

Lakes can be sites of high C mineralization. C can be fixed in organisms by photochemical reactions, by both phototrophic and heterotrophic organism (Del Giorgio et al., 1999; Tranvik et al., 2009). If respiration rates exceed the CO_2 fixation by phototrophs the lake is net heterotrophic. This results in a supersaturated water column with respect to CO_2 and a concentration gradient. Besides degradation of imported material (Graneli et al., 1996), CO_2 supersaturation can also be a result of microbial respiration both in the sediment and the water column (Jonsson et al., 2001). To reach equilibrium with the atmosphere a CO_2 flux occurs from the lake water to the atmosphere (Del Giorgio et al., 1999). Also by streams and rivers CO_2 can be outgassed to the atmosphere as a result of high respiration rates in sediments and the hyporheic zone (Cole et al. 2007). Thus, both, lakes and streams, can act as net sources of CO_2 and are important components in the global C cycle.

1.3 Gas exchange across the water-atmosphere interface

The diffusive gas exchange across the interface between the water surface and the atmosphere is driven by a concentration gradient. The rate of diffusion depends mainly on two factors: the gas exchange velocity (k) for an individual gas at a certain temperature, and its partial pressure (MacIntyre et al., 2010). The flux can be expressed as the difference between the actual concentration of the gas in the water (c_w) and the gas concentration that the water would have at equilibrium with the atmosphere (c_{sat}). Cole and Caraco (1998) formulated the following:

$$(1) \quad \mathrm{Flux} = \mathrm{k}(\mathrm{p_{gas}}\mathrm{K_H} - \mathrm{c_{sat}}) = \mathrm{k}(\mathrm{c_w} - \mathrm{c_{sat}})$$

where K_h is Henry's constant for the gas at a given temperature, p_{gas} is the partial pressure of the gas in the surface water-atmosphere and k the gas transfer velocity or piston velocity [cm h^{-1}]. The latter is defined as the height of water that is equilibrated with the atmosphere per unit time for a given gas at a given temperature (Cole and Caraco, 1998).

The partial pressure of an individual gas and its gas transfer velocity control the rate of the gas flux across the water-atmosphere interface (MacIntyre et al., 2010). A supersaturation with respect to CO_2 in the water resulting in a concentration gradient between the water surface and the atmosphere is the base for a gas exchange. Fluctuations in CO_2 exchange rates are mainly driven by the high temporal and spatial variability of the CO_2 concentrations in the water due to changes in primary production and ecosystem respiration, which are strongly linked to input of organic and inorganic material from the catchment (Hanson et al., 2003; Prairie et al., 2002). Furthermore, different lake metabolisms, structures in the food-web (Prairie et al., 2002), and varying chemical parameters (Hanson et al., 2004) are also influencing the initial C concentration.

The variability in CO_2 affects the gas exchange. The rate of exchange of a gas across the air-water interface is expressed as gas transfer velocity *k*. *k* is dependent on various factors, such as gas solubility, surface waves, wind speed, wind shear, turbulence, and convective mixing. The main drivers for variability in *k* in lotic and lentic systems are often different (MacIntyre et al., 1995). In lakes and open water systems *k* is largely determined by the wind speed over the water surface (Wanninkhof, 1992), whereas turbulence of the water mass due to discharge variability and stream morphology is the main driver for streams (Hope et al., 2001; Wanninkhof et al., 1990; Wallin et al., 2011). Due to rapid changes in the water turbulence along a stream or due to different wind exposure across a lake there is a high temporal and spatial variability of evasion rates of CO_2 from inland water systems even at a small scale (Cole and Caraco, 1998; Wallin, 2011).

1.4 Methods for measuring CO_2 emissions

There are a variety of methods used to determine CO_2 fluxes but the different characteristics of lentic and lotic systems make it complicated to apply the same techniques for both systems (Wallin et al., 2011). Generally, the different methods can be divided into direct and indirect flux measurement techniques (Guérin et al., 2007). Floating chambers and eddy covariance correlation measure the gas flux directly whereas indirect methods are based on measuring gas concentrations at the air-water gradient together with different measures/estimates of the *k* (Clark et al., 1994) or rely on models that derive emission rates from CO_2 concentrations in the surface water e.g. boundary layer model (BLM) or surface renewal model (SRM) (Cole and Caraco, 1998). Furthermore a mass balance could be used; one of the simplest existing methods that assumes the difference between the input and output of CO_2 in the aquatic system as a measure of the evasion of CO_2.

Even though there are a variety of methods that could be used to determine CO_2 fluxes their application is mostly restricted either to lotic or lentic ecosystems. The eddy covariance technique has been widely used on lakes (Åberg et al., 2010; Jonsson et al., 2008; Laurion et al., 2010; Lewicki et al., 2012) but is not suitable for measurements on most lotic systems because it requires a large open water surface around the monitoring point (Jonsson et al., 2008; Wallin et al., 2011). Floating chambers are technically suitable for lotic and lentic systems and have been applied on streams (Beaulieu et al., 2012; Guérin et al., 2007), estuaries (Borges et al., 2004), marshes (Schedlbauer et al., 2012), reservoirs and lakes (Guérin et al., 2007; Soumis et al., 2008; Zhu et al., 2012). However, they have been criticised to underestimate the evasion rates as they influence the gas transfer velocity, reduce surface water turbulence and remove the wind (MacIntyre et al., 1995) while other studies claim an increase of turbulence and an overestimation of flux rates when using chambers on lakes (Vachon et al., 2010).

1.4.1 Gradient flux techniques

Gradient flux techniques determine the CO_2 flux between water and atmosphere indirectly; and include for example BLM and SRM. Generally, the emission is calculated and modelled from the CO_2 concentration in the surface water (Cole and Caraco, 1998). The atmospheric surface layer above a lake is characterized by turbulence, which is thought to be the primary reason for gas transport. Directly below the air-water interface is an aqueous viscous sublayer situated, which is characterized by sharp gradients in both temperature and gas concentration. Underneath this viscous layer a well-mixed bulk water column can be found (Anderson et al., 1999). BLM and SRM characterize the viscous sublayer differently. While it is a homogenous layer with changing thickness depending on wind speed and temperature in BLM, it is thought to be inhomogenous in SRM (Anderson et al., 1999). Thus, SRM is usually preferred because it integrates biogeochemical processes better (Soumis et al., 2008). However, in both approaches the gas flux is driven by a difference in gas concentrations in bulk water and atmosphere and regulated by the bulk transfer velocity, which is highly sensitive to temperature. Thus, the model depends strongly on a precise determination of the temperature. Furthermore detailed knowledge of the CO_2 concentration in both air and water and the gas exchange coefficient is needed (Cole and Caraco, 1998).

1.4.2 Eddy covariance technique

The eddy covariance (EC) technique enables a direct measurement of turbulent scalar flow as such as CO_2 emission from lakes without affecting the natural gas transfer between water and atmosphere (Anderson et al., 1999; Jonsson et al., 2008). The mass flux of CO_2 above the water surface is calculated from the mean covariance of the deviation of the vertical wind speed that occurs across the virtual surface at a certain distance above the water surface and in combination with the mixing ratio of CO_2 (Anderson et al., 1999; Baldocchi, 2003; Guérin et al., 2007).

1.4.3 Tracer gas method

The tracer gas method is widely used in inland water ecosystems (Clark et al., 1994; Cole and Caraco, 1998; Hope et al., 2001; Wanninkhof et al., 1990). It is based on measuring the gas exchange at the water-atmosphere interface using the injection of an inert volatile gas tracer that is not naturally occurring in the water system (e.g. SF_6 or $SF_6/^3He$, C_3H_8, CH_3Cl) (Clark et al., 1994; Cole and Caraco, 1998; Wallin et al., 2011). The tracer gas is released by bubbling into the water of a lotic or lentic system. Concentration measurements are taken over time in the lentic systems or downstream in lotic systems as a measure of the tracer loss. The loss of tracer over time or over the stream reach could then together with known relationships between the gases be used to calculate the k values for the gas of interest (Cole and Caraco, 1998).

1.4.4 Floating chamber method

The method is based on measuring the accumulation or loss of gas concentration over time in a fixed volume (Striegl and Michmerhuizen, 1998). The chamber, which is usually a round shaped or rectangular prism made of plexiglas, plastic, polypropylene or any other lightweight (Guérin et al., 2007) is closed to the surrounding atmosphere but open at the bottom to the gas source (Striegl and Michmerhuizen, 1998). The outer surface is mostly covered with a reflecting material to reduce the warming effect and limit photosynthesis inside the enclosure (Soumis et al., 2008). Lightweight, floating material like polystyrene is attached on the outside to increase buoyancy and ensure a floating device. The most common designs include a sampling tube and a vent on top, so that air samples can be taken manually with the help of syringes. The vent is used to balance the pressure inside the chamber but is closed as soon as the chamber is positioned (Soumis et al., 2008). Then the gas is either pumped directly through an infra-red gas analyser (IRGA) or gas samples are taken from the headspace in regular intervals every 10 to 20 minutes for an one hour time period (Eugster et al., 2003; Soumis et al., 2008) and subsequently, the samples are analyzed using gas chromatography. Automatic chambers which include a sensor that analysis the CO_2

concentrations immediately on site and concentration values can be usually stored in a data logger are more expensive than manual samplings. Hence, only one or few samples can be conducted at one site at the time. Manual measurements can be used numerously but are limited by the sample handling. Treatment steps such as gas transfers into syringes and lab analysis entail risks of inaccuracy and handling errors. However, for both, automatic and manual chamber measurements, a linear regression based on the concentration change as a function of time is used to calculate the flux rates (Soumis et al., 2008). Different experimental set-ups are possible; chambers can be free floating driven by the wind or currents, or be attached as a static device (Schubert et al., 2012; Zhu et al., 2012).

1.5 Objective

Various studies for measuring and estimating the CO_2 flux across the water-atmosphere interface in freshwater systems have been conducted. Since only few methods are suitable for both lentic and lotic systems the majority of studies disregarded the connectivity between streams and lakes and focussed on either of them. The floating chamber has been used on both systems. However, only few studies have been comparing the results obtained from streams and lakes using the same measuring technique and within the same catchment. This study aims to

(1) analyse the small scale variability in pCO_2 and CO_2 emissions along streams, and across the lake using floating chambers,
(2) compare water-atmosphere CO_2 fluxes in streams and lakes located within the same catchment, and
(3) test the suitability of automatic chambers for flux measurements and the data reproducibility.

Measurements focussed on CO_2 emission rates and pCO_2 measurements from a small boreal lake in central Sweden, its inlet and outlet streams. The sampling was conducted two times on the streams and one time on the lake during three different days after the ice melt in May 2013.

2 Methods

2.1 Study Site

Lake Gäddtjärn is a small lake situated in central Sweden in the Örebro region (59°52'N 15°11'E), approximately 17 km east of Kopparberg and 80 km north of Örebro. Gäddtjärn is situated 263 m above sea level and covers an area of roughly 6.2 ha. The lake has two main inlets, Inlet 1 originating in headwater lakes (Prästtjärn, Kringeljärn, Svintjärn), and passing a number of small wetlands before entering Gäddtjärn. Inlet 2 is draining a wetland. The outlet drains into a larger lake, Lake Kölsjön, further downstream. The catchment area covers an area of about 190 ha and is characterised by coniferous and deciduous forest (Vrede et al., 2003). The yearly average temperature is 4.5°C, the average precipitation rate is 995 mm per year (SHMI, 2013).

Lake Gäddtjärn and all sampling sites are shown in Figure 2. Samples were taken on three different days in May 2013, twice on the streams and one time on six different locations at the lake. Twenty sampling locations, ten on each stream, were distributed over a distance of 220 m along the outlet and 530 m along the inlet 1. Inlet 2 stream is not part of this study and was not sampled.

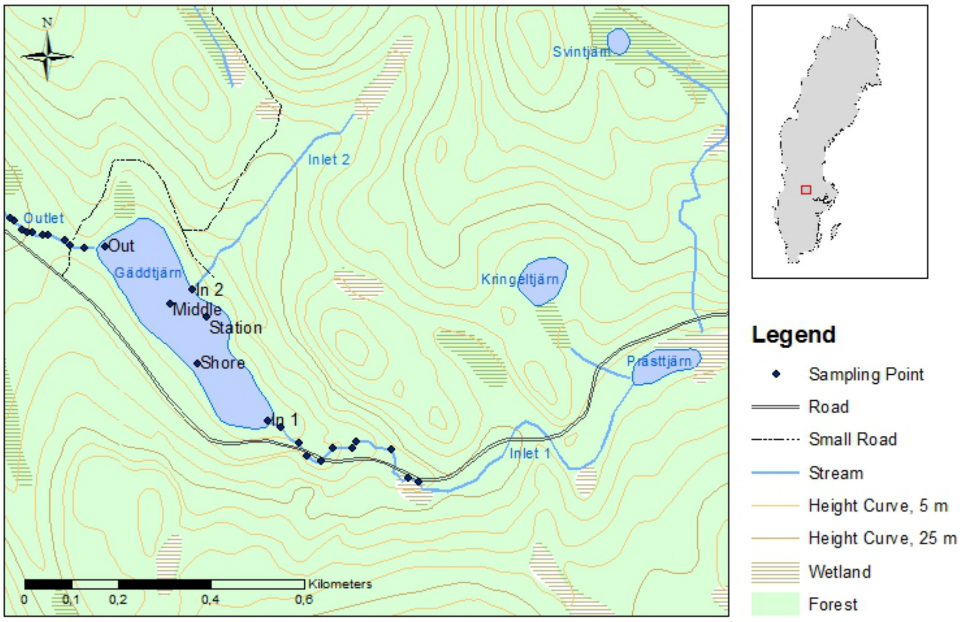

Figure 2: Overview map showing the catchment area of Lake Gäddtjärn and all sample points along the inlet and outlet stream, and in the lake. Inlet stream 1 is draining from three smaller lakes trough wetlands, where the flow path is not clearly defined as one stream. Inlet stream 2 is draining from a wetland and was not sampled.

2.2 Floating Chambers

For the flux measurements circular shaped PE automatic floating chambers developed by David Bastviken and Ingrid Sundgren, Linköping University, Sweden, (Sundgren, 2012) were used. Bastviken supplied the chambers in support of this study. On the inside two smaller plastic boxes were attached. The smaller one, battery box, protects both battery and connection cable from water and condensation. The bigger one contains the CO_2 sensor, CO_2 Engine® ELG made by SenseAir, attached on the lid, which enables direct CO_2 concentration measurements. The sensor box is equipped with ventilation holes on one short side and a slanting plastic sheet to prevent the sensor from condensation water. When the sensor box is closed and attached to the lid the side with the ventilation holes should always be placed on the same side as the sensor. A small air tube attached on the upper side of the chambers enables manual gas sampling. The chamber is covered with a reflecting aluminium foil to reduce the heating effect. Single chambers were placed on ten spots along the inlet and the outlet stream. The chambers were attached to the stream bank with a rope to prevent floating downstream. For the measurements on the lake, three chambers were placed together on the same location to test the reproducibility. All three chambers were attached via the rope to a stone on the bottom of the lake. The flux was measured in five minute intervals for a minimum of two hours on the streams and three hours on the lake. Data from the logger downloaded using an USB connection cable (TTL-232R-3V3) and the software UIP5 provided by SenseAir.

Figure 3: Floating chamber from the downside (left) and upside (right). Battery and sensor box are open. The chamber is covered with aluminium foil to increase reflection and reduce the warming effect. A rope for attaching the chamber and floating elements for increasing buoyancy are fixed on the outside. Gas samples can be taken manually by the valve coupling on the top.

2.3 Water Chemistry parameters and C components

Temperature, conductivity, pH and dissolved oxygen (DO) were measured at every sample location using a HQ40d Portable Multi-parameter Meter (HACH), an 826 portable pH meter (Metronohm) and a HI99300 EC/temp meter (Hanna instruments).

2.3.1 DOC, DIC, POC

For DOC and POC analysis water from Gäddtjärn and the streams was filled into 1 L plastic bottles, stored cool and dark after sampling until the analysis was conducted. For DIC, water was transferred into glass scintillation vials. Samples for DOC were filtered through GF/F glass fibre filters (0.7 µm, Whatman) and analysed using a Portable TOC Analyser (Sievers 900) with a membrane-based conductivity detector. Ammonium persulphate was used as an oxidiser to convert all organic carbon into CO_2. DIC was analysed using the same TOC Analyser. Samples were acidified to shift the DIC speciation to the form of CO_2. For the POC analysis a known water volume was filtered through a GF/F filter. Then, the dried filter was combusted with an elemental analyser (ECS 4010 Elemental Combustion System, CHNS-O).

2.3.2 $p\mathrm{CO_2}$

Partial pressure of CO_2 was directly analysed in field using the headspace equilibration method (Sobek et al., 2003). Water samples were taken with 60 ml polypropylene syringes without any air bubbles. The volume was divided equally in three syringes and ambient air was sucked in the syringes until the ratio of air and water within the syringes was equal. For the lake sampling 30 ml of water and air were used, for the streams 20 ml of each one. After shaking the syringes one minute, the equilibrated air was extracted into another empty syringe, and analysed in a portable infrared gas analyser (IRGA; EGM-3 PP Systems). $p\mathrm{CO_2}$ in the water was calculated from the $p\mathrm{CO_2}$ reading from the IRGA according to Weiss (1974). Henry's constant, K_H, was corrected for the actual temperature and the CO2 concentration in the atmosphere ($\mathrm{CO_{2air}}$), gas ($\mathrm{CO_{2gas}}$) and water ($\mathrm{CO_{2water}}$) phase was calculated from the CO_2 reading using the actual volumes (V), the universal gas constant (R) and the water temperature (T).

$$(2)\quad \mathrm{K_H} = \mathrm{e}^{-58.0931+\frac{90.5069*100}{\mathrm{T}}+22.294*\ln(\frac{\mathrm{T}}{100})}$$

$$(3)\quad \mathrm{CO_{2air}} = \frac{(\mathrm{V_{gas}CO_{2air}})}{\mathrm{RT}}$$

$$(4)\quad \mathrm{CO_{2gas}} = \frac{(\mathrm{CO_{2reading}V_{gas}})}{\mathrm{RT}}$$

$$(5)\quad \mathrm{CO_{2water}} = \mathrm{CO_{2reading}K_HV_{water}}$$

By knowing the CO_2 concentrations in each phase, $p\mathrm{CO_2}$ was calculated using the actual atmospheric pressure (p_{atm}) and the corrected Henry's constant.

$$(6)\quad pCO_2 = \frac{CO_{2\mathrm{gas}}+CO_{2\mathrm{water}}-CO_{2\mathrm{air}}}{V_{water}K_Hp_{atm}}$$

2.4 Emissions of CO_2

The sensor mounted in the floating chambers gave direct values of the CO_2 concentration in the chamber. The CO_2 flux from the water to the atmosphere was calculated using a time series of CO_2 measurements, corrected for the actual temperature and volume, and area of the chamber. Three different time intervals (mostly 15, 30 and 45 minutes) depending on the slope were used to get an average value for the flux rate for a specific area over time. The gas transfer velocity, $k\mathrm{CO}_{2,}$ was calculated based on the equation (1) from Cole and Caraco (1998):

$$(1)\quad \mathrm{CO_2flux} = \mathrm{kCO_2}(\mathrm{pCO_2K_H} - \mathrm{CO_{2sat}}) = \mathrm{kCO_2}(\mathrm{CO_{2water}} - \mathrm{CO_{2sat}})\ ,$$

where K_h is Henry's constant for the CO_2 at a given temperature, pCO_2 is the partial pressure CO_2 in the surface water, and CO_{2sat} the CO_2 concentration the water would have when it is equilibrated with the atmosphere. The gas transfer velocity was normalised to 20°C (k_{600}) using a Schmidt number (Sc) for 20°C according to (Jähne et al., 1987):

$$(7)\quad \mathrm{kCO_2} = \frac{\mathrm{k_{600}}}{(\frac{600}{\mathrm{ScCO_2}})^{-0.66\mathrm{or}-0.5}}$$

$$(8)\quad \mathrm{ScCO_2} = 1841\mathrm{e}^{-0.0549\mathrm{T}}$$

Sc is power dependent, for lower windspeeds (<3.5 m s^{-1}) the power -0.66 is used and for more turbulent waters -0.5. In this study -0.66 was used for lakes and -0.5 for streams. Sc CO_2 is the Schmidt number before normalization to 600, which depends on the water temperature T (°C).

3 Results

3.1 Water Chemistry parameters

Streams

Conductivity was in the range between 16.7 µS cm^{-1} and 48.0 µS cm^{-1} for all stream sites. For the 3rd May it was lowest in the outflow and decreased slightly along the stream. On the 21st May the pattern was reversed and it was highest in the outlet stream. 18 out of 20 measurements on the second sampling day were twice as high as on the first sampling day (Table 1).

pH ranged from 4.69 to 5.57. It was lower closer to the mire outlet and increased slightly along the inlet stream except for the last two sampling points. Dissolved oxygen ranged from 9.2 to 11.6 mg L^{-1}. With the exception of two sampling points it increased along both the inlet and outlet stream, but was higher in the inflow. pH and DO along the streams were only measured on the first sampling day (3rd May). DOC varied from 11,6 to 18,0 mg L^{-1} and with highest DOC concentrations found in the Inlet and lowest in the outlet stream. DIC ranged from 0,7 to 2,5 mg $L^{-1}$and showed a large variability between the stream sampling sites. Generally measured values for all parameters were lower on the first sampling day, due to low flow conditions and consequential less dissolution. Only DOC and DIC for the outlet stream were a little higher on the second sampling day. All detailed data is presented in Table 4 to 6 in the Appendix.

Lake Gäddtjärn

For the lake sampling the variation within each parameter was usually lower than along the streams. pH was in the range from 5.49 to 5.55. The lowest pH was measured at the Station, highest at the Shore. DOC ranged from 11.9 to 12.1. DO varied from 9.7 to 10.1 mg L^{-1}. Conductivity was in the range from 17.3-17.9. Both, lowest conductivity and DO were measured at the In 1 sampling point. DIC varied from 1.4 to 1.5 mg L^{-1} and concentrations were lower on the sampling sites situated further away from the streams (Middle, Station, Shore) (Figure 4).

Table 1: *Mean values (including standard deviation) of chemical and physical parameters of the inlet 1 and outlet stream, and lake Gäddtjärn for the three sampling days. For DOC and DIC only two samples were taken in the inlet stream, and one in the outlet outlet stream. Coefficients of variation are given in % in brackets below.*

	n	**Tempera-ture [°C]**	**pH**	**Conduct-ivity [µS cm^{-1}]**	**DO [mgL^{-1}]**	**DOC [mgL^{-1}]**	**DIC [mgL^{-1}]**
Inlet 1	10	5,4 ± 0,2	4,86 ± 0,1	19,8 ± 0,3	11,1 ± 0,8	12,5 ± 0,04	1,2 ± 0,5
03.05.13		(4,8)	(2,0)	(1,7)	(6,9)	(0,3)	(46,0)
Inlet 1	10	10,7 ± 0,2	4,99 ± 0,1	31,8 ± 11,1	-[a]	16,0 ± 2,8	1,8 ± 1,1
21.05.13		(1,6)	(2,6)	(34,9)	-[a]	(17,6)	(59,7)
Lake	18	11,9 ± 0,8	5,53 ± 0,02	17,7 ± 0,2	9,9 ± 0,1	12,0 ± 0,05	1,4 ± 0,03
07.05.13		(6,6)	(0,4)	(1,2)	(1,3)	(0,4)	(2,3)
Outlet	10	6,1 ± 0,3	5,46 ± 0,1	16,9 ± 0,1	10,5 ± 0,6	12,4	1,6
03.05.13		(4,1)	(1,2)	(0,6)	(5,3)	-	-
Outlet	10	17,4 ± 0,2	5,66[b]	44,4 ± 1,8	-[a]	11,6	0,7
21.05.13		(0,9)	-[b]	(4,1)	-[a]	-	-

[a] no measurements because portable Multi-parameter Meter was not available
[b] only one measurement because pH-Meter was not working properly

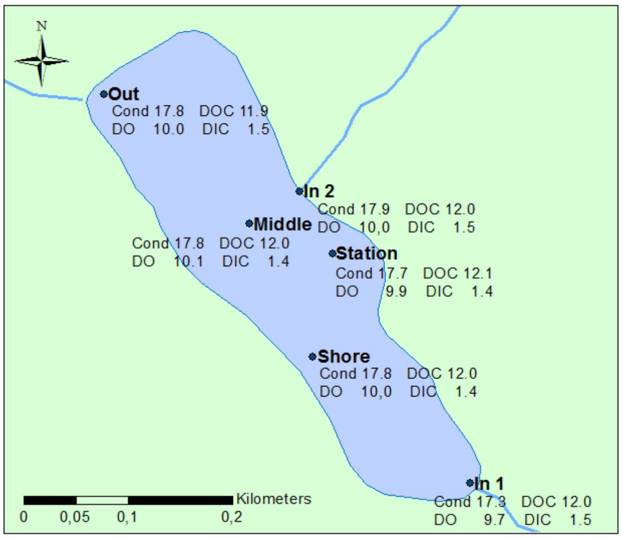

Figure 4: Physical and chemical parameters for the sampling points in lake Gäddtjärn. Conductivity values are given in µS cm^{-1}, DO, DOC and DIC concentrations in mg L^{-1}.

3.2 pCO$_2$ and turbulence conditions in the streams

All sampling sites were supersaturated in pCO$_2$ with respect to the atmosphere. Values ranged from 917 to 4665 µatm, which is equal to 2.3-11.5 times equilibrium with the atmosphere. Highest pCO$_2$ were found in the inlet stream just after the wetland outlet, and with lowest values observed in the outlet stream. pCO$_2$ decreased along the streams both for the inlet stream from the wetland to the lake and for the outlet stream with increasing distance to the lake (Figure 5). Values were lower for the inlet streams in the beginning of May in comparison to the second sampling day. For the outlet stream the opposite pattern was seen.

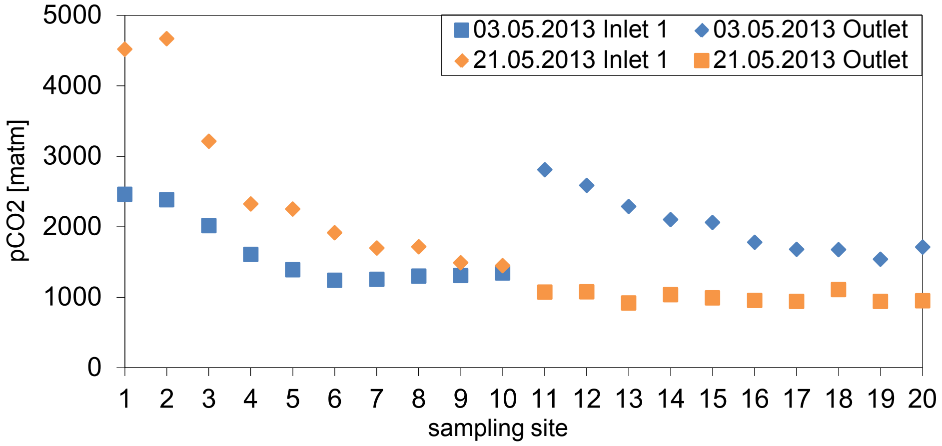

Figure 5: pCO$_2$ measured at 20 different locations along the inlet and outlet stream of Gäddtjärn for two different sampling dates. Sampling points are arranged according to the distance to the lake, from 1 to 10 distance decreases, from 11 to 20 distance increases. The distance between adjacent sampling sites varies between 20 and 80 meters. Lake Gäddtjärn is situated between sampling points 10 and 11.

Surface turbulence of the stream surface was assessed visually at both sampling days and conservatively categorized in low, medium and high turbulence. There was a large variability in the turbulence conditions along the streams and turbulence varied with no relation to the different stream depths. High turbulence conditions had mostly lower pCO$_2$ values, maximum pCO$_2$ in this category was 2286 µatm. The median pCO$_2$ value was lowest (1346 µatm) for the high turbulence category, and similar for sites with low turbulence (1640 µatm) and medium turbulence (1616 µatm). Low turbulence conditions showed smaller CO$_2$ flux rates and k$_{600}$ values. Emissions of CO$_2$ increased with increasing turbulence but median emissions were similar for medium and high turbulent conditions (272 mg CO$_2$-C m^{-2} day^{-1}, 848 mg CO$_2$-C m^{-2} day^{-1}, 897 mg CO$_2$-C m^{-2} day^{-1}; sorted by turbulence in ascending order). The gas transfer velocity showed a similar pattern as for the emissions and increased with rising turbulence. Median k_{600} values increased for each turbulence category (1.4 cm h^{-1}, 4.1 cm h^{-1}, and 5.3 cm h^{-1}). For low turbulence conditions k_{600} values were concentrated around the median, while they spread over a higher range with increasing turbulence (Figure 6).

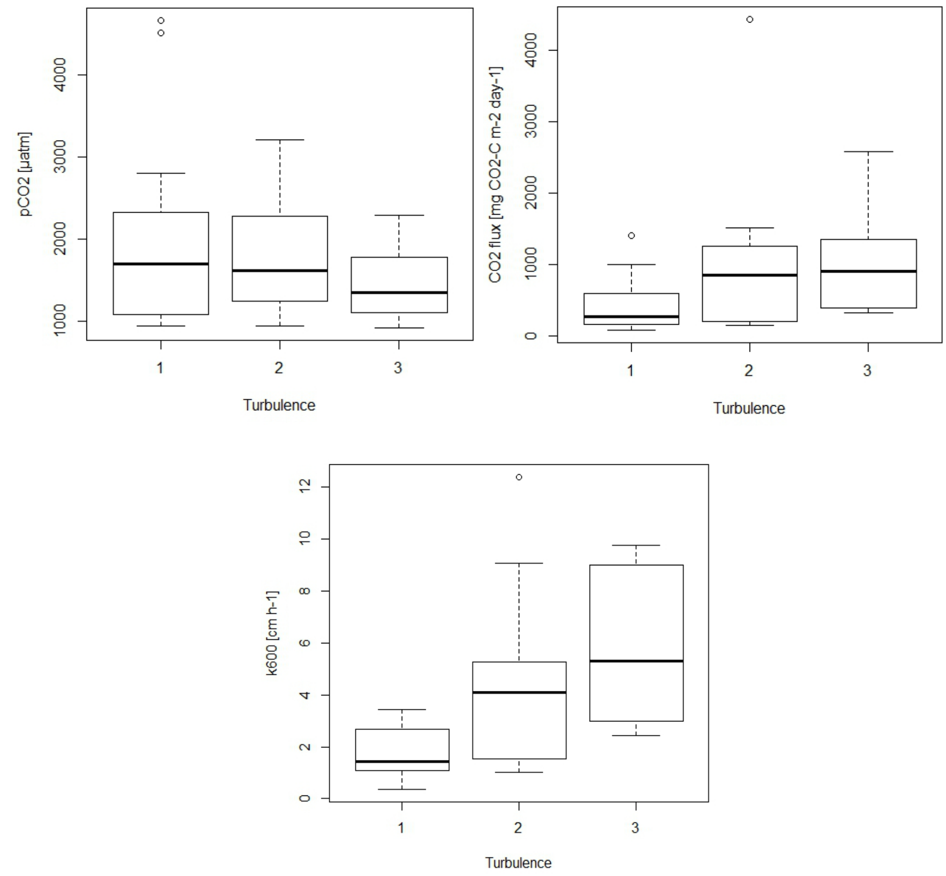

Figure 6: Boxplots for $p\text{CO}_2$, CO_2 flux and $k\text{CO}_2$ in dependence of turbulence conditions (1 – low, 2 – medium, 3 – high turbulence). The solid black line represents the Median, the lower box border the 25%th quartile and the upper box border the 75%th quartile.

3.3 CO_2 emission from the streams

CO_2 flux rates varied from 81 to 4426 mg CO_2-C m^{-2} day^{-1}. Flux rates in the inflow showed similar values for each location on both sampling days, except for the first three spots. The outflow flux rates were much higher on the 3rd May in comparison to the sampling at the end of May (Figure 7).

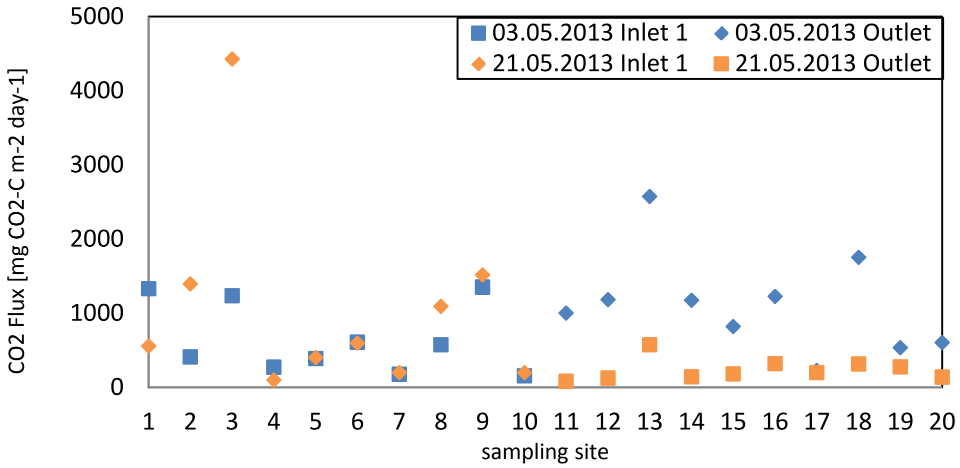

Figure 7: Calculated CO_2 flux [mg CO_2-C m^{-2} day^{-1}] at 20 different locations along the inlet and outlet stream of Gäddtjärn for two different sampling dates. Sampling sites are sorted downstream from 1 to 20. The distance between adjacent sampling sites varies between 20 and 80 meters. Lake Gäddtjärn is situated between sampling points 10 and 11.

3.4 Gas transfer velocities in the streams

The calculated gas transfer velocity k_{600} varied from 0.4 to 12.4 cm h^{-1}. The pattern was similar to the CO_2 flux rates. Median k_{600} value in the outlet (2.9 cm h^{-1}) was higher than for the inlet (2.6 cm h^{-1}) (Figure 8). But the highest value was measured in the inlet stream after the wetland.

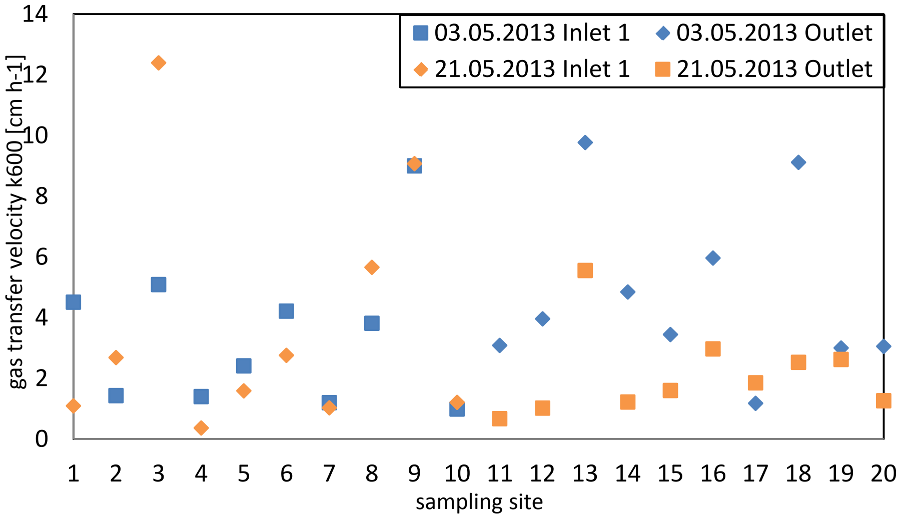

Figure 8: Calculated gas transfer velocities [cm h^{-1}] at 20 different locations along the inlet and outlet stream of Gäddtjärn for two different sampling dates. Sampling sites are sorted downstream from 1 to 20. The distance between adjacent sampling sites varies between 20 and 80 meters. Lake Gäddtjärn is situated between sampling points 10 and 11.

3.5 $p\mathrm{CO_2}$ and CO_2 emission from the lake

On the lake, three replicates of chamber measurements were conducted on each sampling point. The mean values and standard deviations for $p\mathrm{CO_2}$, CO_2 flux and $k\mathrm{CO_2}$ are shown in Figure 9. Mean $p\mathrm{CO_2}$ values varied between 1826-2219 µatm. The highest $p\mathrm{CO_2}$ was measured on the sampling points Out, and In 2, and lowest values at the Shore. Standard deviation was highest for the Shore (± 109 µatm) and lowest for In 1 (± 6 µatm). Mean flux rates varied from 415 to 882 mg CO_2-C m^{-2} day^{-1}. The highest CO_2 emission rates were measured on the sampling points Middle, and Station. The same pattern was observed for the gas transfer velocity. The Middle and Station sampling points are situated further away from the lake shore. Mean k_{600} was in the range of 1,9 to 4,2 cm h^{-1}. Standard deviation was highest for the Shore and lowest for the Out.

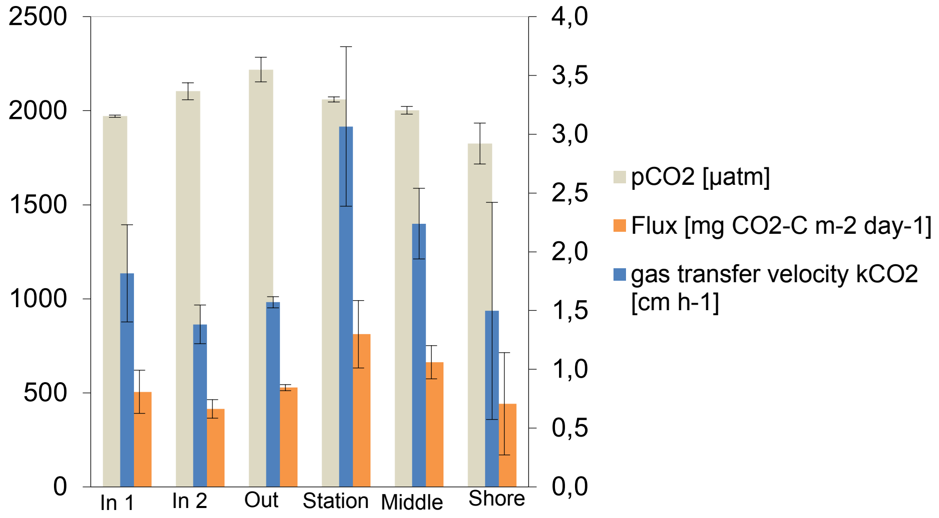

Figure 9: Mean values of partial pressure of CO_2, CO_2 flux and gas transfer velocity kCO_2 for six different locations on lake Gäddtjärn. pCO_2 was highest at the outlet sampling point. CO_2 flux and and kCO_2 were highest on the Station. For kCO_2 the right y-axis app applies. Standard deviation for the three replicates is indicated with error bars. For the flux rate of In 1 only two replicates were taken.

3.6 Comparison between lake Gäddtjärn and its connecting streams

Median values for pCO_2 ranged from 971 to 2080 µatm, lowest concentrations were found in the outlet stream and highest in the inlet stream. Median lake pCO_2 (2031 µatm) was similar to the Inlet pCO_2 (2080 µatm) from 21st May. Median CO_2 flux rates varied tenfold from 186 to 1087 mg CO_2-C m^{-2} day^{-1}, both extremes found measured in the outlet stream. CO_2 flux rate for the lake was similar to the median flux in Inlet 1. Median k_{600} varied between 1.7 to 3.7 cm h^{-1}, again showing lowest and highest gas transfer velocities in the Outlet stream. Generally the variability for all parameters within the lake was much lower than for the stream measurements (Table 2).

Table 2: *Median values for partial pressure of CO_2, calculated CO_2-Flux and gas exchange coefficients k for the streams and lake Gäddtjärn on the different sampling days. Minimum and maximum values are given below in brackets.*

	n	**pCO$_2$** [µatm]	**Flux** [mg CO$_2$-C m^{-2} day^{-1}]	**k_{600}** [cm h^{-1}]
Inlet 1	10	1366	489,2	3,1
03.05.13		(1238-2456)	(154-1349)	(1,0-9,0)
Inlet 1	10	2080	572,9	2,1
21.05.13		(1445-4665)	(95-4426)	(0,4-9,1)
Gäddtjärn	18	2031	516,7	2,3
07.05.13		(1826-2219)	(415-812)	(1,9-4,2)
Outlet	10	1917	1087,4	3,7
03.05.2013		(1538-2805)	(227-2573)	(1,2-9,8)
Outlet	10	971	186,1	1,7
21.05.13		(917-1104)	(81-571)	(0,7-5,6)

4 Discussion

4.1 Spatial variability in pCO_2 and relationship to DOC and DIC

All stream and lake sites were supersaturated in pCO_2 with respect to the atmosphere, which is in agreement with previous studies for aquatic ecosystems in boreal regions (Kokic, 2012; Öquist et al., 2009; Sobek et al., 2003; Wallin et al., 2013). Using an atmospheric pressure of 407 ppm, this reflects a supersaturation of 2.3 to 11.5 times the atmospheric pressure.

Lake Gäddtjärn

Lake C is received via different processes; inflow of C-rich groundwater or surface water, release from sediments, or biological production within the water column. A study on 33 Swedish lakes by Sobek et al. (2003) suggested that C imported as DOC from the terrestrial environment is regarded as the main driver for the observed CO_2 oversaturation in boreal regions. In this study DOC had the largest proportion of all C species, followed by DIC and POC. However, there was no correlation between DOC and lake pCO_2.

Streams

Stream pCO_2 was strongly correlated to DIC ($r^2 = 0,98$) and to DOC ($r^2 = 0,75$). Looking at the stream measurements separately for each sampling day shows that DOC was strongly related to stream pCO_2 ($r^2 = 0,97$) during low flow conditions at the second sampling but not at all at the first sampling. These findings could indicate that mineralization of allochthonous DOC to CO_2 was not of that high importance during early spring but productivity of microbes and bacteria as well as photo-oxidation increased till the end of May. Furthermore it is likely that soil respiration rates increased as well. During the first sampling day stream $p\mathrm{CO}_2$ was probably more influenced by an input of CO_2 via the soil pore water or groundwater (Jonsson et al., 2008; Striegl and Michmerhuizen, 1998).

4.1.1 Spatial variability in $p\mathrm{CO}_2$

Lake Gäddtjärn

Spatial variations in $p\mathrm{CO}_2$ were not that strong as for the streams. However, $p\mathrm{CO}_2$ increased across the lake from the inlet stream to the outlet stream with the highest $p\mathrm{CO}_2$ measured at the Out sampling point. The lower $p\mathrm{CO}_2$ close to Inlet 1 was a reason of the low $p\mathrm{CO}_2$ input from the inlet stream. So the CO_2 concentration in the lake got diluted by the inflowing stream water. Based on higher $p\mathrm{CO}_2$ measurements close to Inlet 2 it could be assumed that the input of CO_2 from Inlet 2 (which was not sampled) was higher.

Streams

The measured $p\mathrm{CO}_2$ in the streams shows a high variability on a small spatial scale. Stream $p\mathrm{CO}_2$ decreased downstream from the mire outlet to the lake, indicating that $p\mathrm{CO}_2$ is lost en route. It is likely that the inlet stream received most CO_2 from the wetland than from internal production in the stream itself. In the outlet stream $p\mathrm{CO}_2$ decreased with increasing distance to the lake at the beginning of May but did not show a significant trend at the end of May. Since the first sampling day was conducted just two days after the ice breakup of the lake, the decreasing pattern in CO_2 along the outlet stream was likely an effect of rapid loss of CO_2 that has been accumulated in the lake under the ice during the winter. The elevated CO_2 signal from the lake was then gone at the second sampling occasion and the $p\mathrm{CO}_2$ in the outlet stream was probably in equilibrium between groundwater input and vertical loss of CO_2, keeping the $p\mathrm{CO}_2$ at a relatively stable level along the stream.

This study was only done on two different sampling days at a distance of three weeks so that statements regarding temporal variability cannot be made. However, differences between the sampling days were found. The two stream samplings have been conducted in the beginning of May, right after the ice melt, and three weeks later. At the first sampling, $p\mathrm{CO}_2$ was higher in the outlet stream than in the inlet stream due to a CO_2 accumulation under the lake ice during winter. Inlet stream $p\mathrm{CO}_2$ was lower, probably because production of CO_2 in the wetland was still low. In the end of May, $p\mathrm{CO}_2$ was low in the outlet because the productivity of the lake was still low, so was the C import from the lake. The major C import came probably from the groundwater, sediments or through production of CO_2 in the stream water. The inlet showed much higher $p\mathrm{CO}_2$ values on the end of May, especially right after the mire outlet values increased twofold. Measurements agreed with the seasonal variation of CO_2 production in aquatic ecosystems, with relation to higher C concentrations in early spring due to an accumulation under the ice and low C concentrations in late spring (Weyhenmeyer et al., 2012).

4.2 CO_2 emissions to the atmosphere

CO_2 flux rates were within the range (lower half) of values found in the literature (Table 3). The range in CO_2 flux rates for the lake was smaller than for the streams, where the lowest and highest flux rates were found. Across the lake lower CO_2 emission rates were measured at the sampling points close to the shore (Shore, In 1, In 2, Out). The middle of the lake was more wind-exposed which resulted in higher gas transfer velocities and higher flux rates.

Streams

The spatial variability of k and CO_2 emission rates for streams was very high. It is thought that stream CO_2 flux rates depend on C concentrations in the water (Halbedel and Koschorreck, 2013), on discharge (Hope et al., 2001) and turbulence conditions (Wallin et al., 2011). A significant correlation between pCO_2 and CO_2 evasion as proposed in other studies (Halbedel and Koschorreck, 2013) could not be found neither for the lake nor the streams. Discharge was not measured in this study, however it could be seen on site that the discharge was much higher in the beginning than in the end of May. Thus, for the inlet stream flux rate and discharge were negatively related, while outlet flux rates and discharge were related positively. The different behaviour underlines that discharge is not the only variable influencing the CO_2 emission rate from streams. In this study high turbulence was associated with a larger range in CO_2 flux rates and higher median values. There was no distinct correlation between CO_2 emission rates and turbulence (Figure 6, p.15). However, lowest CO_2 flux rates were measured at sampling points with calm water surface (pools). Turbulence is influenced by stream morphology and discharge. A relationship between stream depth and turbulence was not found. However, it should be regarded that the stream depth varied on a very small scale since the bottom was characterised by a lot of large rocks.

4.3 Comparison between lake Gäddtjärn and streams

As supposed, the variability for all chemical and physical parameters within the lake was much lower than for measurements along the streams, because the small lake Gäddtjärn represents a more coherent water body.

A clear trend as found by Kokic (2012) showing that emissions from the streams were much higher than emissions from the lake was not found. But $p\mathrm{CO}_2$, CO_2 emissions to the atmosphere and the gas transfer velocities were spatially much more variable in the inlet and outlet streams than compared to the lake. Thus, a generalization is difficult to make. However, lake Gäddtjärn plays an important role, as it is connecting inlet and outlet stream. Both streams are influenced by the C inputs from either the wetland or the lake. With increasing distance these sources become neglectable and the groundwater input will determine the downstream characteristics. The inlet stream which is draining a wetland receives high inputs of CO_2 rich soil pore water, which leads to high C concentrations in the stream (Hope et al. 2001). However, this phenomenon does not appear all year round. Due to lower temperatures and less sunlight the production of CO_2 in wetland and lakes decreases in winter, so does the C input to the flowing waters. In contrast to the closed ice cover on lakes, ice layers on wetlands are often interrupted by holes (personal observations), so that CO_2 is outgassed. In lakes CO_2 is accumulated under the ice and increasing C concentrations are delivered to the outlet. As a consequence C concentrations were high in the beginning of May, so were the emissions of CO_2. At the end of May the discharge decreased, but the water that reached the lake was richer in C because the wetlands productivity increased. However, the increased C concentration in the inlet stream did not have any effect on the concentration in the outlet, which was quiet low at this time. It is assumed that the lake water diluted the C-rich inflowing water and output concentrations were low because lake-turnover did not have started.

CO_2 emissions in streams and lakes are supposed to be controlled by different mechanisms. Hydrological conditions (e.g. discharge) and stream morphology determine mostly the stream emissions (Hope et al., 2001, Wanninkhof, 1990), while CO_2 emissions from lakes are driven by wind speed and the C concentration in the water (Wanninkhof, 1992). This study did not focus on the different drivers and only stream morphology was analysed. Thus, no detailed conclusions can be drawn regarding the main driving components. However, stream depth was not a good predictor for CO_2 emissions due to a large variability on a small spatial scale. For both lakes and streams no correlation between DOC/DIC and emissions to the atmosphere could be found. But stream $p\mathrm{CO}_2$ was more driven by DOC and DIC than in lakes, probably indicating that biological activity in the wetland was already present in contrast to the lake. However, this statement should be treated carefully due to the little amount of data.

4.4 Comparison to other studies

Several studies to quantify CO_2 emission from lakes or streams in boreal ecosytems have been conducted. Table 3 shows a selection of studies, most of them based on the experimental determination of k, usually using the gas tracer method. Values obtained in this study agree mostly with the literature. The observed range of pCO_2 from 917 to 4665 μatm agrees well with findings from studies in other boreal areas as well as with the findings from Kokic (2012) and Okrouhlíková (2012), who analysed the catchment area of Gäddtjärn. Comparing the results to these two studies, stream CO_2 emission rates and stream k_{600} were very low and not even in the same range, whereas lake CO_2 flux rates and lake k_{600} were twice as high. In relation to other literature lake emissions were high and maybe a bit overestimated. Alternatively, the high values could just be a consequence of the short sampling period, since lake measurements were only conducted one day. Most other studies sampled all year round, which leads to smaller average and median values due to very low emission rates expected during the summer period. For stream measurements, results for CO_2 flux rates and gas transfer velocities from this study were quite low in comparison to other studies and probably underestimated.

Table 3: *Summary of CO_2 emission rates and k_{600} values for streams and lakes obtained from different studies in aquatic boreal regions.*

	pCO$_2$	**CO$_2$ flux rate [g C m^{-2} yr^{-}**		**K$_{600}$ [cm h^{-1}]**		**Reference**
	[µatm]	**Lakes**	**Streams**	**Lakes**	**Streams**	
Central Sweden Gäddtjärn	917-4665	96-372	29-1616	1.2-5.2	0.4-12.4	This study[1]
Central Sweden Gäddtjärn	1028-2638	-	2428-14129	-	49.8-78.6	(Okrouhlíková, 2012)[2]
Central Sweden Gäddtjärn	970-4995*	14.5-172,3	3000-16279*	0.87-1.5	39-303*	(Kokic, 2012)[2]
North Sweden Krycklan	713-6253	-	59.9-51271	-	6.9-101.1	(Wallin et al., 2011)[2]
North Sweden Krycklan	722-24167	-	1455-6411	-	-	(Wallin et al., 2013)[2]
East Canada Ontario	3200-9320	76-4346		-	-	(Billett and Moore, 2008)[1]
North Sweden Öreälven	-	38-105	142-800	-	-	(Jonsson et al., 2007)[3]
Entire Sweden	794-1950	31.9-88.3	473-3032	2.1	26.3-64.5	(Humborg et al., 2010)[4]
Boreal & Arctic	1100-1300	130	560	4	13.1	(Aufdenkampe et al., 2011)[5]

* only values for Gäddtjärn inflow and outflow taken into account

[1] k directly determined by floating chambers

[2] based on an experimentally determined k

[3] literature-based k

[4] modelled-based k

[5] summarizing paper of results from existing studies using a variety of methods

4.5 Assessment of the method

4.5.1 Data Reproducibility

Reproducibility of data is one of the key elements while testing a new method. In this study, three chambers where set up at the same sampling point on the lake to test the reproducibility. The coefficient of variation (CV) at the different sampling points varied in most cases between 3 and 22 %, but was at one sampling point 61 %.

4.5.2 Importance for current research questions

Studies (Jonsson et al., 2007; Teodoru et al., 2009) rely often on an average gas exchange velocity, regardless of spatial or temporal variability of k_{600}, but generalized k_{600} values introduce a large source of uncertainty in C budgets and can lead to underestimations or overestimations of C fluxes to the atmosphere. With the floating chamber method it is possible to calculate gas transfer velocities directly from the CO_2 flux rates. As shown in a study by Wallin et al. (2011) the CO_2 flux from the water surface to the atmosphere was largely controlled by k_{600} ($r^2 = 0.8$). Thus, the gas transfer coefficient/gas transfer velocity is of high importance for estimations of C fluxes on a large scale and automatic floating chambers are very useful in the determination of k both on a spatial and temporal scale.

4.5.3 Handling and technical limitations

The use of the automatic floating chambers used in this study is a cheap, uncomplicated and time-saving method. Long laboratory analyses are not needed, since the sensor gives direct values of CO_2 concentrations in the gas-filled chamber. Especially the aspect of taking measurements in particular time intervals from short term (1 second) to long term (~ 6 months) makes it an attractive method. Once installed, measurements can be taken without the necessary attendance of personal. Due to the cheap cost, many measurement units could be used measuring over the same time period. In total we used 20 units at the same time. Thus, advantageous is the possibility to perform many measurements over a large area simultaneously. However, the method is largely dependent on the quality of the sensor. The sensor, CO_2 Engine ELG, itself has a rather low accuracy (± 30 ppm) and the response time, <25 sec gas diffusion time (Senseair, n.d.), seemed to be slower in practice. This is probably affected by the instalment of the sensor in the protecting box that reduced the response time. Furthermore, the sensor in the chamber showed a high sensitivity regarding battery capacity. Though a change of battery is supposed by the manufacturer only at voltage levels lower than 4.75 V, some measurements already failed at 7 V voltage level during the initial testing. It is recommended to check the battery capacity regularly and replace the batteries, especially before longer measuring periods.

All measurements should be treated carefully. In an initial test, where the chambers where placed all in the same small room, they showed significantly different values, though the sensors were calibrated. To increase the reliability and comparability between the measurements, the same chambers where placed on the same sampling site on both stream sampling days, a strategy that is recommended.

Studies using floating chambers are in disagreement regarding the flux rates. Some authors (Billett and Moore, 2008; MacIntyre et al., 1995) criticise them to underestimate emission rates since they reduce surface water turbulence and remove the wind effect while Vachon et al. (2010) showed a higher turbulence inside the sampling area created by the chamber's walls. Independent from this discordance can be said, that the use of chambers is restricted to low or medium turbulence conditions when using them in streams. At high turbulent sites the chambers cannot be attached properly and with a high risk of flipping over. Furthermore, we found that on very turbulent sites a kind of foam was accumulated around and under the chamber during the measurements. This could potentially inhibit the flux rates and partly explain the lower CO_2 emission rates from the streams in comparison to other literature.

5 Conclusion

This study emphasises that boreal streams and lakes are supersaturated in CO_2 with respect to the atmosphere. It shows that C emissions from boreal waters play an important role in the C cycle and should be included in ecosystem C balances.

pCO_2 along the streams was very variable in space and time, and variability was largely driven by the processes in the lake Gäddtjärn and the wetland. Thus higher concentrations were found close to the lake directly after the ice melt (CO_2 had been accumulated in the water body), and the wetland in late spring. However, the high pCO_2 decreased over a small distance due to the fast process of CO_2 outgassing. The relation of CO_2 concentration to discharge had a different temporal pattern for the inlet and outlet stream. During low flows concentrations in the inlet stream were high, while concentrations in the outlet stream were low. However, it is assumed that the differences in concentration were more influenced by the C input then the discharge. Spatial variability of stream CO_2 emission rates was highly controlled by the gas transfer velocities which were positively correlated to the turbulence conditions.

pCO_2 was similar for the lake and the streams and in agreement with findings from other studies. Nevertheless, the spatial variability was much higher along the streams. Lake CO_2 emission rates covered the lower range of stream CO_2 emission rates as a consequence of lower gas transfer velocities. Generally, the variability for all chemical parameters within the lake was much lower than for the stream measurements.

The automatic floating chambers used in this study are suitable for analyzing CO_2 emissions from lakes but our findings of limitations regarding the data reproducibility and sensor response time should be considered. Stream CO_2 emissions and k values were probably underestimated as a reason of the limitation and uncertainties associated with both the specific method and with the general problem of placing chambers on streams . It is likely that the floating chambers reduced the surface turbulence and hence influencing the measured gas transfer velocity, as already claimed in other studies. In addition, placing a floating chamber on a representative site in a stream characterized by large geomorphological variability is a general problem of the method application. For further research we recommend comparative studies with automatic/manual floating chambers and another methods such as for example tracer injection experiments.

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Appendix

Table 4: *Chemical and physical parameters on six different sampling points on lake Gäddtjärn from the 7th May 2013.*

Sampling Site	**Temperature (°C)**	**pH**	**Conductivity [µS cm^{-1}]**	**DO [mg L^{-1}]**	**DO [%]**	**DOC [mg L^{-1}]**	**DIC [mg L^{-1}]**	**pCO$_2$ [µatm]**	**Flux [mg CO$_2$-C m^{-2} day^{-1}]**	**kCO$_2$ [cm h^{-1}]**	**k_{600} [cm h^{-1}]**
In 1	12,8	5,53	17,3	9,7	93,8	12,0	1,5	1971	506	1,8	2,4
In 2	12,5	5,54	17,9	10,0	95,5	12,0	1,5	2104	415	1,4	1,8
Out	10,7	5,54	17,8	10,0	91,6	11,9	1,5	2219	528	1,6	2,2
Station	11,9	5,49	17,7	9,9	94,0	12,1	1,4	2060	812	3,1	4,2
Middle	11,4	5,54	17,8	10,1	93,8	12,0	1,4	2002	663	2,2	3,1
Shore	12,4	5,55	17,8	10,0	95,4	12,0	1,4	1826	441	1,5	2,0

Table 5: *Chemical and physical parameters along the inlet 1 and outlet stream of lake Gäddtjärn from the 3rd May 2013, put in order upstream-downstream. DOC, DIC and POC was only measured on three different locations: close to the mire outlet, at the discharge stations at the inlet stream and outlet stream. Conductivity was not measured for the sampling locations 18-20 due to a salt injection.*

Sampling Site		**Temperature** [°C]	**pH**	**Conductivity** [µS/cm]	**DO** [mg L^{-1}]	**DOC** [mg L^{-1}]	**DIC** [mg L^{-1}]	**POC** [mg L^{-1}]	**Depth** [cm]	**Turbulence**[a]	p**CO$_2$** [µatm]	**Flux** [mg CO$_2$-C m^{-2} day^{-1}]	k**CO$_2$** [cm h^{-1}]	k_{600} [cm h^{-1}]
1	**Inlet 1**	5,7	4,79	20,1	10,8	12,5	1,5	0,3	16	2	2456	1330	3,0	4,5
2	**Inlet 1**	5,9	4,78	20,1	10,4				48	1	2382	408	0,9	1,4
3	**Inlet 1**	5,5	4,81	19,7	10,9				9	3	2015	1231	3,4	5,1
4	**Inlet 1**	5,3	4,85	19,4	11,4				40	1	1605	270	0,9	1,4
5	**Inlet 1**	5,3	4,92	19,8	11,5				24	3	1388	387	1,9	2,4
6	**Inlet 1**	5,4	4,95	19,4	11,6	12,5	0,8	0,1	11	2	1238	607	3,1	4,2
7	**Inlet 1**	5,5	4,98	19,4	11,5				22	2	1251	173	0,9	1,2
8	**Inlet 1**	5,5	4,96	19,7	11,6				22	3	1297	571	3,0	3,8
9	**Inlet 1**	5,0	4,70	19,8	11,6				11	3	1304	1350	7,0	9,0
10	**Inlet 1**	5,2	4,69	20,4	9,2				36	1	1343	154	0,8	1,0
11	**Outlet**	6,8	5,45	17,01	9,8				45	1	2805	1001	2,3	3,1
12	**Outlet**	6,1	5,32	16,98	10,1	12,4	1,6	0,6	36	2	2585	1179	3,1	4,0
13	**Outlet**	6,1	5,57	16,91	10,2				19	3	2286	2573	7,6	9,8
14	**Outlet**	6,1	5,45	16,9	10,5				34	2	2098	1174	3,7	4,9
15	**Outlet**	6,0	5,47	16,8	10,6				27	1	2056	818	2,6	3,4
16	**Outlet**	6,1	5,45	16,7	10,8				35	3	1777	1223	4,6	6,0
17	**Outlet**	6,0	5,50	16,9	9,7				17	1	1676	227	0,9	1,2
18	**Outlet**	6,0	5,42	-	11,2				15	3	1674	1752	7,2	9,1
19	**Outlet**	5,9	5,46	-	11,1				25	2	1538	531	2,4	3,0
20	**Outlet**	6,0	5,47	-	11,1				37	1	1710	601	2,4	3,1

[a] Turbulence classification: 1- low, 2 – medium, 3 – high turbulence

Table 6: *Chemical and physical parameters along the inlet 1 and outlet stream of lake Gäddtjärn from the 21st May 2013, put in order upstream-downstream. DOC, DIC and POC was only measured on three different locations: close to the mire outlet, at the discharge stations at the inlet stream and outlet stream. pH was only measured on three sites because the pH meter was not working properly. POC and DO were not measured at this sampling day.*

Sampling Site		Temperature [°C]	pH	Conductivity [µS/cm]	DOC [mg L^{-}	DIC [mg L^{-1}]	Depth [cm]	Turbulence[a]	pCO$_2$ [µatm]	Flux [mg CO$_2$-C*m²*day]	kCO$_2$ [cm h^{-1}]	k_{600} [cm h^{-1}]
1	**Inlet 1**	10,9	4,9	19	18,0	2,5	33	1	4514	554	0,8	1,1
2	**Inlet 1**	11,0		17			39	1	4665	1395	2,3	2,7
3	**Inlet 1**	10,8		21			10	2	3211	4426	10,7	12,4
4	**Inlet 1**	10,8		20			36	1	2322	95	0,3	0,4
5	**Inlet 1**	10,7		39			21	1	2248	398	1,4	1,6
6	**Inlet 1**	10,6	5,08	39	14,0	1,0	11,5	1	1912	592	2,1	2,8
7	**Inlet 1**	10,6		36			33	2	1694	197	0,8	1,0
8	**Inlet 1**	10,6		39			10	2	1713	1089	4,3	5,7
9	**Inlet 1**	10,5		44			6	2	1486	1513	6,9	9,1
10	**Inlet 1**	10,5		44			17	1	1445	197	0,9	1,2
11	**Outlet**	17,7		42			32	1	1068	81	0,5	0,7
12	**Outlet**	17,6	5,66	42	11,6	0,7	48	1	1073	123	0,8	1,0
13	**Outlet**	17,5		44			13	3	917	571	4,2	5,6
14	**Outlet**	17,4		44			20	2	1031	141	0,9	1,2
15	**Outlet**	17,3		48			26	1	989	176	1,5	1,6
16	**Outlet**	17,3		44			26	3	952	315	2,7	3,0
17	**Outlet**	17,3		44			7	2	940	196	1,4	1,9
18	**Outlet**	17,3		44			12	3	1104	314	1,9	2,5
19	**Outlet**	17,2		46			26	1	938	274	2,4	2,6
20	**Outlet**	17,3		46			25	1	946	134	1,0	1,3

[a] Turbulence classification: 1- low, 2 – medium, 3 – high turbulence