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Carbon dioxide in agricultural streams

Magnitude and patterns of an understudied atmospheric carbon source

My Osterman

REFERAT

Koldioxid i jordbruksbäckar – magnitud och mönster hos en understuderad källa av kol till atmosfären

My Osterman

Bäckars roll i den globala kolbudgeten blev länge försummad då de enbart sågs som passiva transportörer av kol från land till hav. Studier har dock visat att bäckar ofta är övermättade på koldioxid (CO_2), vilket gör dem till källor av kol till atmosfären. CO_2 kan härstamma från biologiska processer i bäckarna, införsel från avrinningsområdet eller från geologiska källor, såsom vittring av mineral. Litteratur inom området domineras av studier i skogrika avrinningsområden medan bäckar i jordbruksmark är under-representerade. Studiens syfte var att undersöka partialtrycket av CO_2 (pCO_2) i bäckar i jordbruksdominerade avrinningsområden. Detta gjordes för att öka kunskapen om jordbrukets påverkan på pCO_2 och ge underlag för jordbrukssektorn vid planering av åtgärder för att minska utsläpp av CO_2.

Mätningar av pCO_2 utfördes var 30:e minut med flytande kammare, utrustade med CO_2-sensorer, i tio bäckar i jordbruksdominerade avrinningsområden kring Uppsala från juni till november 2017. Mätningar gjordes även av näringsämnen, organiskt kol, vattenföring och olika kemiska variabler. Korrelationstester utfördes med metoden Kendalls Tau och avrinningsområden avgränsades med geografiska informationssystem (GIS). Datasetet CORINE Land Cover användes för att undersöka markanvändning.

Uppmätta pCO_2-värden var i median mellan 3000 och 10 000 µatm. Vid många tillfällen överskred dock pCO_2 10 000 µatm, vilket var den använda sensorns maximala mätvärde. Korrelation hittades mellan pCO_2 och vattenföring, med negativ korrelation i fem bäckar och positiv i två. Negativa samband hittades mellan pCO_2 och pH samt mellan pCO_2 och löst syre i vattnet. Ingen korrelation hittades mellan pCO_2 och andel jordbruk i avrinningsområdet, halt av näringsämnen eller halt av organiskt kol. De uppmätta pCO_2-värdena var höga jämfört med tidigare studier i skogsdominerade avrinningsområden, vilket kan indikera att förekomst av jordbruk i ett avrinningsområde ökar bäckvattnets koldioxidhalt. Källor till CO_2 i bäckarna bör undersökas vidare, då det är möjligt att en betydande del av koldioxiden har geologiskt ursprung. Metoden att mäta pCO_2 med flytande kammare behöver revideras för att minska sensorns känslighet för kondensation och låga temperaturer samt höja detektionsgränsen.

Nyckelord: Koldioxid, bäckar, jordbruk, avrinningsområde, flytande kammare, Kendalls Tau, CORINE Land Cover

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ABSTRACT

Carbon dioxide in agricultural streams – magnitude and patterns of an understudied atmospheric carbon source

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The role of streams in the global carbon budget was for a long time neglected, since they were considered passive transporters of carbon from land to sea. However, studies have shown that streams are often supersaturated in carbon dioxide (CO_2), making them sources of carbon to the atmosphere. The main sources of stream CO_2 are in-stream mineralization of organic matter and transport of carbon from the catchment. The catchment derived CO_2 could both be of biogenic (respiration) or geogenic (weathering) origin. Most studies regarding the topic rely on measurements carried out in forest-dominated catchments, while agricultural streams are under-represented. The objective of this study was to examine partial pressure of CO_2 (pCO_2) in streams in catchments dominated by agriculture. This was done to increase the knowledge about agricultural influence on stream pCO_2, and to provide a basis for planning mitigation strategies for reducing CO_2 emissions from the agriculture sector.

Sampling was performed in ten streams draining agriculture-dominated catchments around Uppsala, Sweden, from June to November 2017. Measurements of pCO_2 were carried out with floating chambers, equipped with CO_2 sensors. Nutrients, organic carbon, discharge and different chemical variables were also measured. For correlation tests, the method Kendall's Tau was used. Catchments were delineated in a geographic information system (GIS) and the CORINE Land Cover dataset was used to examine land use.

Stream specific median pCO_2 varied from 3000 to 10 000 µatm. In some streams, pCO_2 exceeded 10 000 µatm, which was outside of the sensor's measurement range. Values of pCO_2 were high compared to similar studies in forested catchments, which could indicate that occurrence of agriculture in the catchment increases stream CO_2. Correlation was found between pCO_2 and discharge, with negative correlation in five streams and positive correlation in two. Negative correlation was found between pCO_2 and pH and percentage of dissolved oxygen, respectively. No significant correlation was found between pCO_2 and fraction of agricultural land use, nutrients or organic carbon. Further studies are needed to examine the sources of CO_2, since it is possible that a large part of the CO_2 has a geogenic origin. The floating chamber method should be revised to reduce the sensor's sensitivity to condensation and cold temperatures, and to increase the measuring range.

Keywords: Carbon dioxide, streams, agriculture, catchment, floating chamber, Kendall's Tau, CORINE Land Cover

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PREFACE

This thesis was the final part of the Master Programme in Environmental and Water Engineering at Uppsala University and corresponds to 30 hp. The project was a collaboration between Uppsala University and the Swedish University of Agricultural Sciences in Uppsala. The supervisor was Marcus Wallin, the subject reviewer was Mattias Winterdahl and the examiner was Fritjof Fagerlund, all three active at the Department of Earth Sciences at Uppsala University. This study was supported by the Swedish research council FORMAS (grant 2015-1559) and by the Carl Tryggers Foundation.

Thankfully, I was not alone in completing this thesis and I have many people to thank for their contributions. Marcus Wallin and Mattias Winterdahl gave invaluable guidance and support during the project, from start to finish. Joachim Audet at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences provided guidance and help in the field, without which, this project would not have been possible. Maud Oger, also at the Department of Aquatic Sciences and Assessment, assembled the equipment for CO_2 measurements and carried out field work during the summer before the project officially started. Thomas Grabs, at the Department of Earth Sciences, gave assistance during the GIS-section of the project. Karin Broqvist, student at Uppsala University, collected and analyzed water samples for TOC and DOC.

Lastly, I would like to thank my family and friends for their support during my thesis work. I could not have done this without all of you!

My Osterman
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POPULÄRVETENSKAPLIG SAMMANFATTNING

Koldioxid är en växthusgas som bidrar starkt till uppvärmningen av klimatet och det är därför viktigt att veta hur flödet av koldioxid ser ut i landskapet. Bäckar sågs länge som passiva transportvägar av koldioxid från land till hav, där koldioxiden inte omvandlades eller försvann från vattnet. Sedan början på 1990-talet har det dock visats att bäckarna ofta är övermättade på koldioxid, i och med att de har högre halt av koldioxid än atmosfären, och att de därför släpper ut koldioxid till luften. Det gör dem till aktiva delar av kolcykeln i landskapet och det är viktigt att undersöka hur mycket koldioxid som finns i bäckarna för att veta hur mycket som kan avgå till atmosfären. Exempelvis har det visats att strömmande vatten, såsom bäckar och älvar, släpper ut strax under två miljarder ton kol per år till atmosfären. Det kan jämföras med haven, som istället tar upp omkring två miljarder ton kol per år från atmosfären. Koldioxiden i vattnet kan komma från biologiska processer, såsom nedbrytning av organiskt material, och från geologiska processer, såsom när kolrika mineral bryts ned genom vittring. Jordbruk kan påverka mängden av koldioxid i en bäck, exempelvis då jordbruksmark ofta är gödslad med näringsämnen för att stimulera tillväxt av grödor. Näringsämnena transporteras in till bäcken med vatten från området och kan där öka produktion av organiskt material i vattnet, vilket i sin tur påverkar mängden koldioxid. De få tidigare studier som har gjorts har visat att koldioxidkoncentrationen generellt är högre i jordbruksbäckar jämfört med skogsbäckar.

I detta projekt undersöktes hur mycket koldioxid som fanns i bäckvatten i jordbruksområden. Det har inte gjorts många studier där koldioxidhalt i bäckar i jordbruksmark har undersökts, utan de flesta studier grundas på mätningar från skogsbäckar. Jordbruk täcker i dagsläget ca 40 % av jordens landyta. Eftersom det finns så mycket jordbruksmark är det angeläget att studera koldioxidhalt i bäckar som tar emot vatten från jordbruksområden för att se om det finns skillnader gentemot skogsmark. Om det finns en skillnad bör flödena av koldioxid i landskapet revideras för att inkludera att olika typer av mark, såsom skogs- och jordbruksmark, släpper ut olika mängder av koldioxid till atmosfären.

Under projektets gång studerades partialtryck av koldioxid (pCO_2), ett mått på hur mycket koldioxid som finns i vattnet, i tio bäckar i jordbruksområden omkring Uppsala. Medianvärdet av partialtrycket varierade från 3000 µatm till 10 000 µatm. Partialtrycket var högt jämfört med tidigare studier som har undersökt koldioxid i skogsbäckar. Det kan betyda att jordbruket bidrar till ökade koldioxidhalter i bäckvattnet. Det kan också vara så att vittring av kolrika bergarter och mineral utgör ett avsevärt bidrag av koldioxid, eftersom pCO_2 var så högt. Resultaten från denna studie har visat på höga värden av pCO_2 även jämfört med tidigare studier där koldioxid i jordbruksbäckar studeras och det är viktigt att utröna om bäckarna i studien är representativa för denna typ av undersökning.

Även vattenföring, hur mycket vatten som flödar i bäckarna, undersöktes. Vattenföringen var låg under sommaren och ökade kraftigt under den senare delen av hösten (oktober – november). Det kan förklaras med en ökad mängd nederbörd under denna period. Det fanns i flera bäckar ett samband mellan vattenföring och partialtryck av koldioxid. I fem bäckar minskade pCO_2 då vattenföringen ökade, vilket kan förklaras med att koldioxiden i bäckvattnet blir utspädd då mängden vatten i bäcken ökar. I två bäckar ökade istället pCO_2 då vattenföringen ökade, vilket kan bero på exempelvis att det transporteras in mer kol till bäckarna med regnvatten, eller att det kommer in mer kolrikt grundvatten då vattennivåerna stiger. I projektet togs vattenprover för att mäta hur mycket näringsämnen,

i form av kväve, fosfor, löst organiskt kol och total mängd organiskt kol som fanns i vattnet. Det fanns dock inget samband mellan pCO_2 och halt av näringsämnen eller organiskt kol i vattnet. Det kan tyda på att den koldioxid som finns i vattnet härstammar från vittring av kolrika mineral snarare än från biologiska processer.

Mätningar av koldioxidkoncentration utfördes med plastkammare som flöt på vattenytan, förankrade i bäckkanterna, och utfördes från juni till november 2017. Kamrarna var utformade som uppochnedvända baljor utrustade med sensorer som mätte koldioxidhalt. Sensorerna var känsliga för kondensation, vilket gjorde att några av mätningarna gav bristfälliga resultat eftersom vatten från bäcken kondenserade på insidan av kammaren. Dessutom kunde sensorerna bara mäta koncentrationer upp till 10 000 ppm, vilket var ett problem då vattnet i vissa av bäckarna visade på högre koncentrationer än så, något som både kan bero på faktiska höga koncentrationer och på fel i sensorerna. Det var dock en tillräckligt bra metod för projektets syfte eftersom mätning kan ske under långa tidsperioder under dygnets alla timmar, metoden är relativt billig och mätningarna inte är tidskrävande. Koncentrationen av koldioxid beräknades sedan om till pCO_2. Samband mellan parametrar undersöktes med metoden Kendalls Tau, som är en statistisk metod för att studera hur värden på två variabler korrelerar.

De undersökta bäckarnas höga halter av koldioxid behöver utredas vidare för att se om de är representativa för jordbruksbäckar i allmänhet. Metoden skulle dessutom behöva utvecklas för att minska känsligheten för kondensation och kalla temperaturer, samt för att kunna mäta koncentrationer över 10 000 ppm. Studien bidrog till kunskapen om jordbruksbäckars bidrag till koldioxid i atmosfären och har påvisat att denna typ av utredningar är viktiga för att få en bättre uppskattning av bäckarnas roll i landskapets kolkretslopp.

LIST OF ABBREVIATIONS

CO_2: carbon dioxide

CO_3^{2-}: carbonate ion

DO: dissolved oxygen

DOC: dissolved organic carbon

EC: electric conductivity

H_2CO_3: carbonic acid

HCO_3^-: bicarbonate ion

NH_4^+ -N: ammonium nitrogen

NO_2^-/NO_3^- -N: nitrite and nitrate nitrogen

pCO_2: partial pressure of carbon dioxide

PO_4^{3-} -P: phosphate-phosphorous

q: specific discharge

TOC: total organic carbon

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1. INTRODUCTION

Despite the fact that inland waters, such as lakes, streams, and rivers, cover a relatively small fraction of the Earth's surface, they are active contributors to the global carbon (C) budget through emission of gases such as carbon dioxide (CO_2) and methane (CH_4) (Battin et al., 2009; Bastviken et al., 2011; Tranvik et al., 2009). Knowledge about the natural flow of carbon, globally or within a specific ecosystem, is important for our understanding of the anthropogenic influence on the global climate, and for planning mitigation strategies (Tranvik et al., 2009). Inland waters were previously viewed as passive transporters of carbon from land to sea. This view has been revised, since increased knowledge about biological, chemical and physical processes along the hydrological continuum from soils to the ocean has shown that inland waters are active components in the global C budget (Cole et al., 2007). Inland waters can transport carbon, but there are also processes of degradation in the water that transform the organic carbon to CO_2 and CH_4 that is emitted to the atmosphere during the passage through the hydrological chain of lakes and streams.

Production of CO_2 in a body of water is caused by microbial degradation of organic material in the water and sediments, and by photochemical degradation (Cole et al., 2007). In addition to in situ production, CO_2 can also be transported from surrounding terrestrial areas where CO_2 is produced by root respiration and degradation of soil organic matter. In the presence of carbonate containing minerals in soil and bedrock, stream CO_2 can also have a geogenic origin as a result of weathering processes (Cole et al., 2007). Studies have shown that stream emissions of CO_2 are dominated by carbon with terrestrial origin and that the fraction of CO_2 emissions that originates from carbon produced within the stream increases with stream size (Hotchkiss et al., 2015).

Since the early 1990's, it has been known that inland waters are in many cases supersaturated with CO_2 (Cole et al., 1994; Duarte and Agustí, 1998; Duarte and Prairie, 2005), i.e. the concentration of CO_2 in the water is higher than the concentration of water in thermodynamic equilibrium with the atmosphere. The supersaturation means that inland waters act as sources of CO_2 to the atmosphere and that they emit more CO_2 than they absorb during the course of a year. The supersaturation is caused by a dominance of respiration compared to photosynthesis (net heterotrophy), and transport of CO_2 and organic carbon from the catchment (Hotchkiss et al., 2015). However, in the fourth assessment report, published in 2007 by the United Nations Intergovernmental Panel on Climate Change (IPCC, 2007), inland waters were only included as passive pipes for transport of C from land to sea. Researchers have since then shown that this view is incorrect. For example, Tranvik et al. (2009) showed that inland waters have an important and active role in the global flows of C between land, water, and atmosphere due to the biological and chemical processes in the water (Figure 1). In the following IPCC assessment report (IPCC, 2013), the global carbon budget was revised to include inland waters as active sources of C to the atmosphere and that sediments can act as sinks of C.

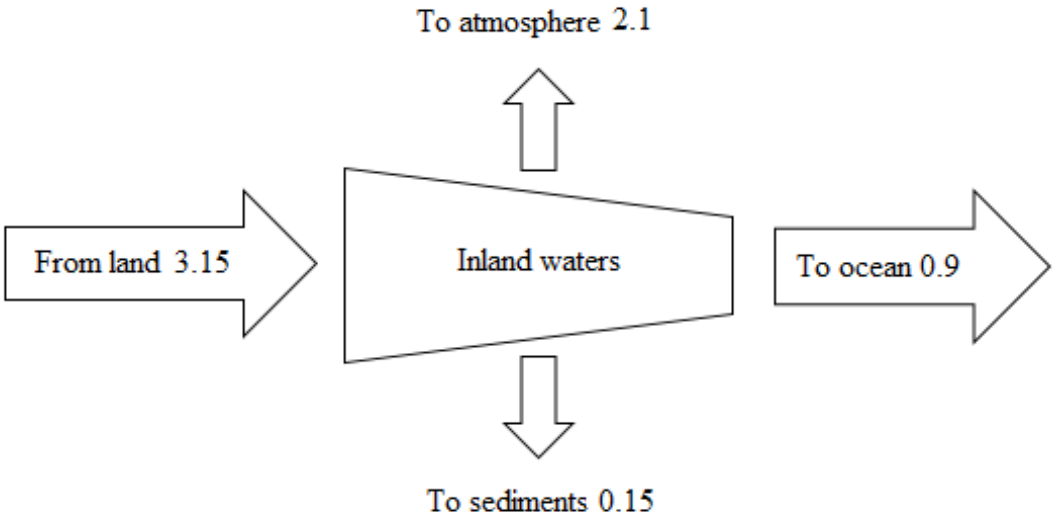

Figure 1: Global transport and emission of carbon through inland waters (Pg C $year^{-1}$) (Raymond et al., 2013; Mendonça et al., 2017).

For many of the studies about carbon emissions from inland waters, the main focus has been on lakes and larger water bodies, while relatively little attention has been given to rivers and streams (Wallin et al., 2013). Streams represent small surface areas individually, but together they drain a large part of the landscape. It is also suggested that the total surface area of streams could in many cases be underestimated due to the difficulties of measuring it with sufficient accuracy (Benstead and Leigh, 2012). According to Raymond et al. (2013), the global carbon emissions from inland waters amount to 2.1 Pg C $year^{-1}$, of which streams and rivers account for 1.8 Pg C $year^{-1}$. This can be compared with the uptake of anthropogenic carbon by the ocean, which has been estimated to 2.0 Pg C $year^{-1}$ (Wanninkhof et al., 2013). It is important to take emissions of CO_2 from streams into account in the landscape C budget, since the uptake of CO_2 from land and vegetation could otherwise be overestimated (Wallin et al., 2013).

Studies regarding stream emissions of CO_2 and other greenhouse gases have largely been focused on forested catchments (Wallin et al. 2018). In contrast, few studies have focused on stream CO_2 emissions in agricultural areas (Bodmer et al., 2016), a land use type that at present covers roughly 40 % of Earth's land surface (Ramankutty et al., 2008). The few existing studies on stream CO_2 emissions in agricultural areas have shown varying results. Bodmer et al. (2016) measured partial pressure of CO_2 (pCO_2) and emission of CO_2 in Germany and Poland and examined differences between forested and agricultural catchments. They found that pCO_2 was higher in agricultural streams, but that there was no difference in emission of CO_2 between the two land use types. The authors explained that the latter was due to significantly higher discharge and gas transfer velocity in the forest streams. Borges et al. (2018) have examined CO_2 concentration in the river system Meuse in Belgium. They found that the water in the river was supersaturated in CO_2, and the river was therefore a source of CO_2 to the atmosphere. The emission showed a seasonal variability that correlated with variations in discharge. The highest concentrations of CO_2 were observed during periods of low discharge. Systems dominated by agriculture had higher concentrations of CO_2 compared to forested

catchments, which could be related to higher levels of dissolved organic carbon (DOC), particulate organic carbon (POC) and inorganic nitrogen in agricultural catchments.

Agricultural land use in the catchment can affect the concentration of stream CO_2, e.g. by leaching of nutrients. Due to the use of fertilizers, streams in agricultural areas are generally rich in nutrients, which benefits primary production in the water. An increase in primary production leads to uptake of CO_2 and a decrease in emissions of CO_2 to the atmosphere. However, an increase in primary production leads to larger amounts of organic matter and higher rates of degradation, which increases emissions of CO_2 through respiration (Borges et al., 2018). The quality of dissolved organic matter can be different in agricultural streams compared to other land use types (Wilson and Xenopoulos, 2009) and can affect the rate with which microbes degrade the organic matter and in turn the amount of CO_2 that is emitted (Bodmer et al., 2016)

Stream CO_2 emissions in agricultural catchments are understudied, with most of the previous studies mentioned in this introduction. Hence, there is a need for further studies to increase the understanding of the role of agricultural streams in the landscape carbon budget, especially since previous studies have shown higher concentrations of CO_2 in agricultural catchments compared to forested catchments (Bodmer et al., 2016).

1.2. OBJECTIVE AND RESEARCH QUESTIONS

The objective of this project was to assess pCO_2 patterns in low order streams draining catchments with varying degrees of agricultural influence. More specifically, the study aimed to determine to what degree agricultural streams are oversaturated in CO_2 and how variable the CO_2 is in time and space. As stream CO_2 emissions from agricultural areas are understudied, this will be an important contribution to the current understanding of the role of streams in landscape C budgets. The results will also serve as a basis for the agricultural sector when developing mitigation strategies for reducing CO_2 emissions.

Based on studies where CO_2 emissions from agricultural streams were examined, values of pCO_2 in agricultural streams were expected to be significantly higher than in streams in forested catchments (Bodmer et al., 2016; Borges et al. 2018). Furthermore, pCO_2 was expected to correlate negatively with discharge (Borges et al., 2018) and the pCO_2 measurements would display a discernible pattern of diurnal variation in pCO_2, with lower values during daytime and higher values during night.

The following questions were posed:

- To what degree are streams in agricultural areas supersaturated in CO_2?
- Is pCO_2 in streams correlated to the extent of agricultural land in the catchment?
- Is pCO_2 in agricultural streams controlled by variations in discharge?
- Is there a diurnal cycle in pCO_2 in agricultural streams, and if so, how large is it?
- How large is the flux of CO_2 from the agricultural streams to the atmosphere?

2. METHOD, MATERIAL AND THEORY

2.1. THEORY – IN-SITU SINKS AND SOURCES OF CO_2

When organic matter is decomposed by microbes, CO_2 is released through respiration (1), consuming oxygen (O_2). Photosynthesis, the process where living organisms harvest light energy and store it as chemical energy (2), instead consumes CO_2 while producing O_2 (Schlesinger and Bernhardt, 2013b).

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 2830\ kJ \quad (1)$$

$$6H_2O + 6CO_2 + light\ energy \rightarrow C_6H_{12}O_6 + 6O_2 \quad (2)$$

If the rate of respiration is greater than the rate of photosynthesis, an ecosystem is said to be heterotrophic and acts as a source of carbon to the atmosphere (Duarte and Agustí, 1998). If the photosynthesis rate is greater, the ecosystem is autotrophic, acting as a carbon sink. In aquatic ecosystems, the dominance of photosynthesis versus respiration can vary during the course of a day. Concentrations of CO_2 are generally higher during night due to the respiration rate becoming higher than the rate of photosynthesis during low-light conditions (Natchimuthu et al., 2017). During daytime, the opposite is true.

The concentration of CO_2 in an aquatic ecosystem is also closely linked to the carbonate system (Aufdenkampe et al., 2011) where carbonates (H_2CO_3, HCO_3^- and CO_3^{2-}) buffer changes in pH, producing CO_2 (3). As pH decreases, the concentration of hydrogen ions (H^+) increases, shifting the equilibrium to the left in the reaction, producing CO_2. If pH increases, CO_2 is instead consumed, lowering the concentration of CO_2 in the water.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (3)$$

2.2. SITE DESCRIPTION

Within this study, measurements were carried out in ten streams with varying degree of agricultural influence located around Uppsala, Sweden (Figure 2, Appendix D). All ten sites were located in catchments with relatively large agricultural coverage. At one of the sites, Site 3 Sundbromark, an already existing v-notch weir and a stilling well allowed for measuring water level/discharge. At site 5, a small waste water treatment plant is located about 1 km upstream of the sampling point.

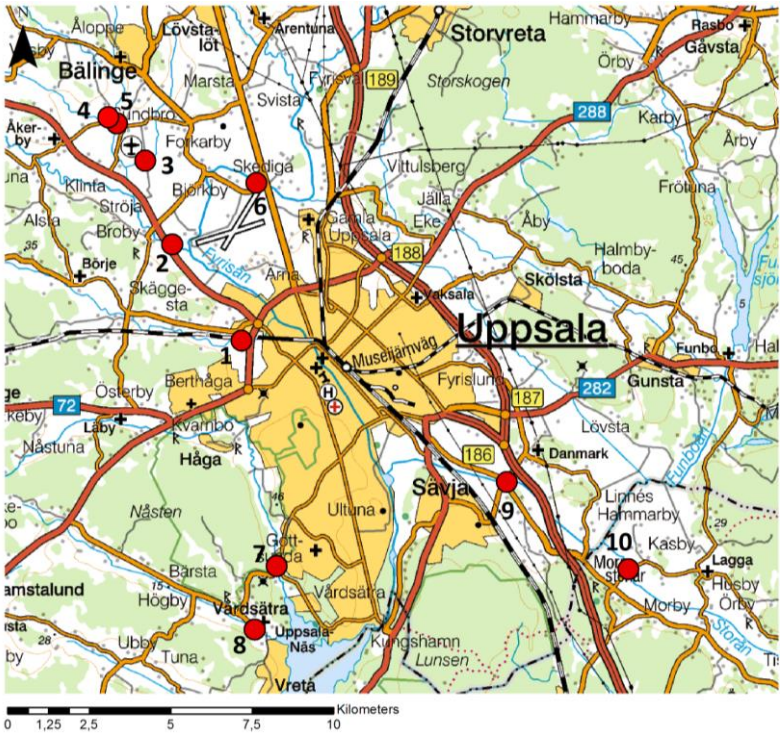

Figure 2: Locations of the study sites around Uppsala. The map was made using material from GSD-Översiktskartan raster (©Lantmäteriet 2010). The green areas represent forests, yellow urban areas and light yellow agricultural areas.

The included streams drain a variety of different land use types, including cropland, pasture, forest and urban areas. All sites were chosen so that agricultural land would cover a relatively large fraction of the catchment area. The Swedish Meteorological and Hydrological Institute (SMHI) have discharge measurement stations in Stabby, close to site 8 and in Fyrisån and Sävjaån. Average temperature and precipitation (Table 1) was calculated using data from SMHI (SMHI, 2017b). The glacial clay, that constitutes a large part of the soils in Uppsala and its surroundings (Sveriges Geologiska Undersökning, 2017a), often contains carbonate that was transported with melted snow and ice from limestone in the Bothnian Sea (Sveriges Geologiska Undersökning, 2017b).

Table 1: Average precipitation (precip.) and temperature (temp.) in Uppsala during the measuring period and averages from the 30-year period of 1961-1990. Data was collected from SMHI (SMHI, 2017b). This period was the only 30-year period readily available from SMHI.

Month	Total precip. (mm)	Average precip. 1961-1990 (mm)	Average temp. (°C)	Average temp. 1961-1990 (°C)
June	49	45	15.1	15.0
July	20	75	17.1	16.4
August	76	65	16.2	15.2
September	76	59	12.6	10.9
October	96	50	7.1	6.4
November	65	52	2.7	1.2

2.3. CATCHMENT DELINEATION AND LAND USE DISTRIBUTION

To delineate catchments, digital elevation models (DEM), i.e. raster files with resolutions of 50×50 m (GSD-Höjddata, grid 50+ nh) and 2×2 m (GSD-Höjddata, grid 2+) containing elevation data, were collected from Lantmäteriet, the Swedish mapping, cadastral and land registration authority. The coordinate system used was SWEREF99 TM. To study land use in the catchments, the dataset CORINE Land Cover 2012 was used. In this dataset, provided by the European Environment Agency, the examined surface area was divided into five main groups: constructed surfaces, e.g. urban areas, agriculture, forest, wetlands and water. The resolution was 50×50 m. The main groups were then divided into classes depending on e.g. land use and vegetation type. In total, the dataset consisted of 44 classes represented by polygons. Combined, the polygons covered the whole area that was examined. The agriculture group contained 11 classes, but only four were relevant around Uppsala. These were: arable land, pasture, complex arable land, and arable land/natural vegetation. Complex arable land was defined as a mix of arable land and pasture where no category covered more than 75 % or less than 25 % of the total surface. Arable land/natural vegetation was land that was dominated by agriculture, but had significant fractions of natural vegetation.

Catchments were delineated using the ArcGIS program ArcMap 10.2. To delineate catchments for sites 6, 8, 9 and 10, DEM files with the resolution 50×50 m were used. The remaining catchments were smaller, or had height differences that were too low to use the 50×50 resolution DEM files. These were delineated using DEM files with a 2×2 m resolution. The 2×2 m DEM files were problematic to use for the large catchments since the files were too large to download and use in ArcGIS. The tools used are available in the Spatial Analyst Toolbox (Figure 3). First, the sinks in the DEM were filled using the tool Fill. A flow direction raster was created using Flow Direction, a tool that calculates the direction of flow for each cell in the surface raster, using the slope of the surface. The outlet was placed at the site location using GPS-coordinates that were collected in the field. The Flow Accumulation tool was used to visualize a stream network in the catchment and to make sure the outlet was placed within the stream. This tool calculates the number of cells that flow into each cell to show where water accumulates in streams. To delineate and create a raster file of the catchment, the tool Watershed was used on the flow direction raster. The catchment area was calculated by converting the raster into a polygon. Lastly, the area of the catchment covered by agriculture or other types of land use was calculated using the CORINE Land Cover data set.

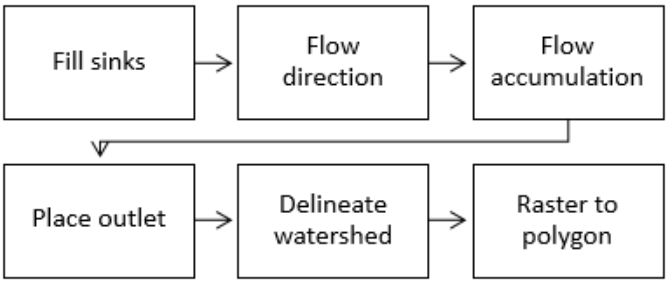

Figure 3: The process of catchment delineation and calculation of catchment area in ArcMap 10.2.

2.4. FIELD MEASUREMENTS AND DATA COLLECTION

2.4.1. CO_2 concentration

The CO_2 measurements were made using a floating chamber method, where a chamber equipped with a CO_2 sensor (CO_2 Engine® ELG, SenseAir AB, Sweden), logger and a 9 V battery attached to the inside (Figure 4) floated on the water surface (Bastviken et al., 2015; Natchimuthu et al., 2017). The measurement range of the CO_2 sensor was 0 - 10 000 ppm. Sensor, logger and battery were protected from water and condensation with plastic boxes. The box containing the sensor also had a condensation trap made with a plastic sheet, since the sensor was sensitive to condensation.

Figure 4: Inside of the chamber at site 7. The white and gold device is the CO_2 sensor. It is connected to a 9 V battery and a cable to collect data. When the chamber was in use, the sensor, battery and cable were protected with plastic casings. The diameter of the chamber was 30 cm.

Concentration of CO_2 and temperature in the chamber was measured and logged every 30 minutes from June 22nd until November 8th, except in cases where measurements were cancelled or failed due to e.g. drying of the stream or malfunctioning sensors. The method is based on the assumption that CO_2 in the chamber was in equilibrium with the CO_2 in the water, and that therefore the measured concentration in the chamber corresponded to the concentration in the water (Bastviken et al., 2015). The outside of the chamber was covered with reflective tape with the aim of minimizing temperature increases due to direct sunlight exposure (Figure 5). Every fortnight, the sites were visited to change batteries, collect data and to dry any condensation from the inside of the chambers.

Figure 5: Chamber in the field at site 7.

At site 3, an additional CO_2 concentration sensor (Eosense Inc., eosGP) was installed on October 11th. The sensor could measure CO_2 concentration up to 20,000 ppm. It was installed to complement measurements from the chamber when the CO_2 concentration exceeded 10,000 ppm and to compare results from the two sensors.

At site 6, an area visible for passers-by, the measurements were cancelled in the middle of September, since the chamber at two occasions had been removed by people passing and the sensor had been damaged. At sites 3 and 4, the measurements were cancelled for a period during the summer (mid-July for site 3 and late June for site 4) due to drying of the streams. The measurements started again on September 14th for site 3 and October 11th for site 4 when the streams were filled with water again.

2.4.2. Additional measurements and data

Measurements of conductivity, temperature, pH and oxygen were carried out with a multiprobe (Hach-Lange) when the sites were visited every fortnight. Water samples were collected for analysis of concentrations of ammonium (NH_4^+-N), nitrite and nitrate (NO_2^- and NO_3^--N), phosphate (PO_4^{3-}-P) and total and dissolved organic carbon (TOC and DOC) at the accredited laboratory at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences. During transport, the samples were kept dark and cool. At each visit to the sites, water depth and width of the streams were estimated along with the degree of vegetation cover.

Daily discharge measurements in Stabby (station 1742), Vattholma (station 2244) and Sävjaån (station 2243) were collected from the SMHI Vattenwebb (SMHI, 2017a). Daily measurements of temperature and pressure in Uppsala were collected from SMHI Öppna Data (SMHI, 2017b). The station used was Uppsala Aut.

Discharge measurements at site 3 started on September 26th. A pressure transducer (MJK 1400) was installed, logging pressure values every 30 minutes, manual measurements of discharge in the stream were carried out with a bucket method every fortnight and the water level above the v-notch in the stream was measured. Relationships between water level recorded by the pressure transducer in a well close by the stream and water level

above the v-notch (4) and between water level and discharge (5) (Appendix C) were found:

$$H = 0.9813P - 0.5306 \quad (4)$$

$$Q = 0.5795H^{2.0477} \quad (5)$$

where P is the water level in the stirring well (m), H is the water level above the bottom of the v-notch (m) and Q is the discharge (m^3s^{-1}). For sites where no discharge data was available, specific discharge from similar catchments were calculated using equation (6):

$$q = \frac{Q}{A} \quad (6)$$

where q is specific discharge ($m\ s^{-1}$), Q is discharge ($m^3\ s^{-1}$) and A is the catchment area (m^2). This was done for sites 1, 2, 3, 4 and 5 during June – September, using SMHI discharge data from Stabby, since the catchments were of similar sizes as Stabby. For sites 4 and 5 during September – November, measurements from Sundbromark (site 3) was used. SMHI data from Vattholma was used for site 6. For sites 7 and 8, SMHI data from Stabby was used. Lastly, for sites 9 and 10, SMHI data was from Sävjaån. The assumption that specific discharge from one catchment can be used to produce reliable results for a proximate catchment is an approximation. Furthermore, in agricultural areas tile drainage systems that affect the hydrology are commonly applied. However, these calculations were used to show variations in discharge in the streams, not absolute values.

2.5. CALCULATIONS

Concentration of CO_2 from the chamber measurements was converted into partial pressure of CO_2 (7), assuming that the gas is ideal, in order to compare the data with previous studies (Natchimuthu et al., 2017):

$$pCO_2 = P_{total} \times \frac{x^g{}_{CO_2}}{10^6} \quad (7)$$

where pCO_2 is the partial pressure of CO_2 (µatm), P_{total} is the pressure in the atmosphere (µatm) and $x^g{}_{CO_2}$ is the concentration of CO_2 inside the chamber (ppm). To see if it was reasonable to use a normalized value of P_{total} instead of daily values, the variance of pressure was calculated for the whole measuring period. The variance was small and a normalized value of 997 000 µatm could be used.

The CO_2 sensors had a measurement range of 0 – 10 000 ppm. The upper limit could be reached both by values being high and by errors caused by e.g. condensation on the sensor (Bastviken et al., 2015). Therefore, a data quality control was performed such that values that were too divergent from the rest of the data series were removed (Figure 6). This was done by calculating, for each value, the median of values from 4 hours before and 4 hours after the measurement. If the observed value deviated with more than 10 % from the median, it was removed (Appendix D), according to recommendations from Bastviken et al. (2015). Furthermore, values of 10 000 ppm were removed in cases where the high values were assumed to stem from errors and not from actual high concentrations, based on values of the other measurements from the site during the same period. A concentration of 10 000 ppm corresponds to pCO_2 of 9970 µatm. Values from when the chamber was lifted every fortnight were removed since CO_2 was then emptied from the chamber.

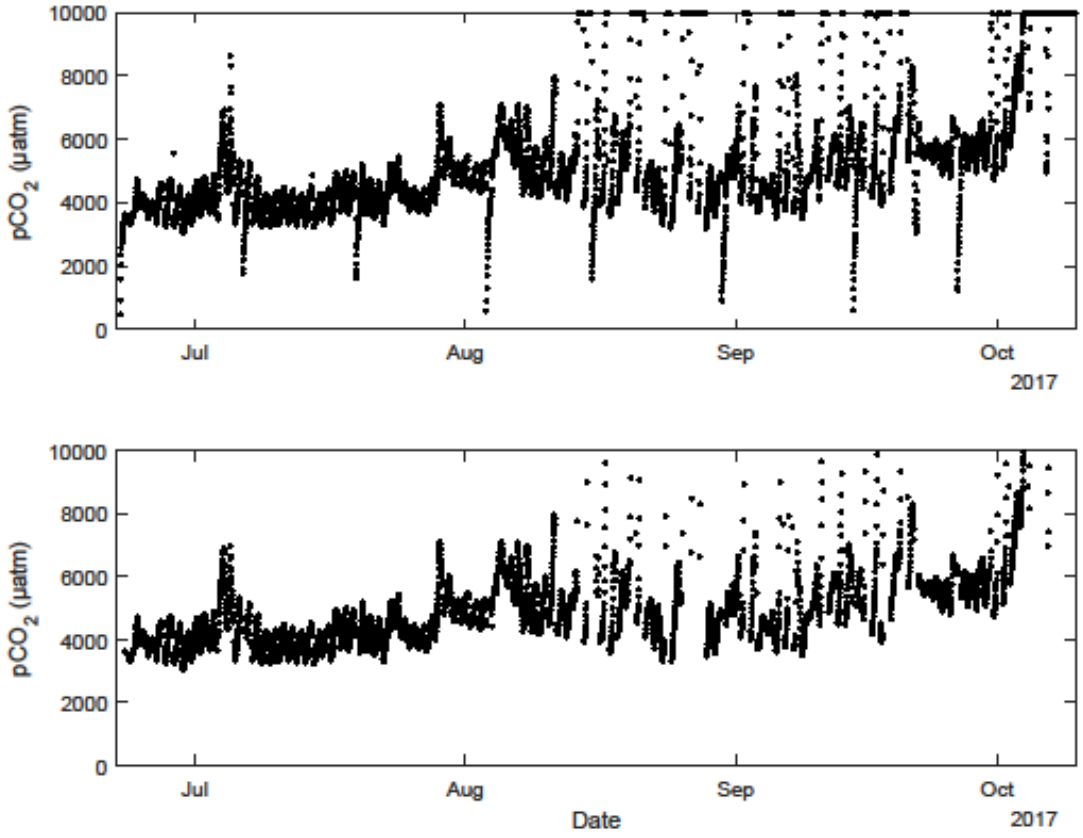

Figure 6: The total series of pCO_2 from site 5 before (a) and after (b) a data quality control was made and data from when the chamber was lifted was removed. Measurements that deviated more than 10 % from the median of measurements from 4 hours before and after the measurement was taken were removed. In this case, values at the upper measurement limit of 9970 µatm were removed since they were assumed to be caused by errors in the sensor, based on the pattern and the values of the data.

After the quality control, median and interquartile range (IQR) of pCO_2 were calculated. The IQR is a measure of variability that is not based on the assumption that data is normally distributed, and is not sensitive to outliers. It is calculated as the difference between the 75^{th} and 25^{th} percentile.

The amplitude of the diurnal variation in pCO_2 indicates the amount of CO_2 that is taken up from the water through photosynthesis and how much is released through respiration over a day. To see whether the diurnal variation correlated with variations in chemical variables or with land use, the amplitude in pCO_2 was calculated each time a water sample was collected, which could only be done if there was a distinguishable pattern of diurnal variation in the data. To calculate the amplitude, minimum and maximum values of pCO_2 from a two-day period were determined. The amplitude was calculated as the difference between the maximum and the minimum values.

The flux of CO_2 from the water to the atmosphere was calculated by using pCO_2 data from when the chambers had been lifted and emptied of CO_2. After the chambers were put back in the water, concentrations of CO_2 started to rise, which resulted in a straight

line of increasing pCO_2 in the data. Linear regression was used to make a trendline through the first 10 measurements after the chamber was lifted (Natchimuthu et al., 2017). The slope of the trendline gave a flux in the unit µatm h^{-1}, which was only used if the R^2 value was larger than 0.9 (Natchimuthu et al., 2017). The flux was then divided with the area of the chamber to give a flux with the unit µatm m^{-2} h^{-1} and the pressure was converted to the unit mg C h^{-1} m^{-2} using the molecular weight of C and the ideal gas law (8), where *n* is the amount of CO_2 (moles), *p* is the pressure of the gas, *V* is the volume, *R* is the ideal gas constant and *T* is the absolute temperature of the gas.

$$n = \frac{pV}{RT} \qquad (8)$$

2.6. STATISTICAL METHODS

All statistical analyses were performed in the program R (R Core Team, 2017). The level of significance was chosen to 0.05, meaning that results were considered significant if the p-value was lower than 0.05. To determine whether data were normally distributed, the Shapiro-Wilks test was used. The null hypothesis of the test is that data are normally distributed and this is rejected if the p-value is below the level of significance (Helsel and Hirsch, 1992).

The Kendalls rank correlation coefficient method, commonly referred to as Kendall's Tau, was used to test for correlation between variables that were not normally distributed. The null hypothesis is that there is no correlation between two groups of data (Helsel and Hirsch, 1992). The null hypothesis is rejected if the p-value is below the significance level, meaning there is a significant correlation between the two data sets. The output Tau lies between -1 and 1 and indicates the strength of the correlation and whether correlation is positive (Tau > 0) or negative (Tau < 0). To study correlation between pCO_2 and land use, median values of pCO_2 during June and July were calculated for each site, since data were most consistent during these months. Correlation between pCO_2 and chemical parameters were examined using values of pCO_2 that corresponded with the time that water samples were collected. For correlation tests between pCO_2 and discharge at sites 6, 7, 8 and 9, daily medians of pCO_2 were used, since discharge data at these sites were daily. The same methods were used to study how chemical variables, discharge and land use correlated with amplitude in diurnal variation and flux of CO_2.

3. RESULTS

3.1. LAND USE IN THE CATCHMENTS

The catchment areas of the investigated streams varied from 9 km^2 for the smallest catchment (site 3) to 780 km^2 for the largest catchment (site 6). The portion of the catchments being used for agriculture varied between 30 % (site 7, Figure 7) and 91 % (site 3). The percentage of forest in the catchments varied between 63 % (site 9) and 5 % (site 3).

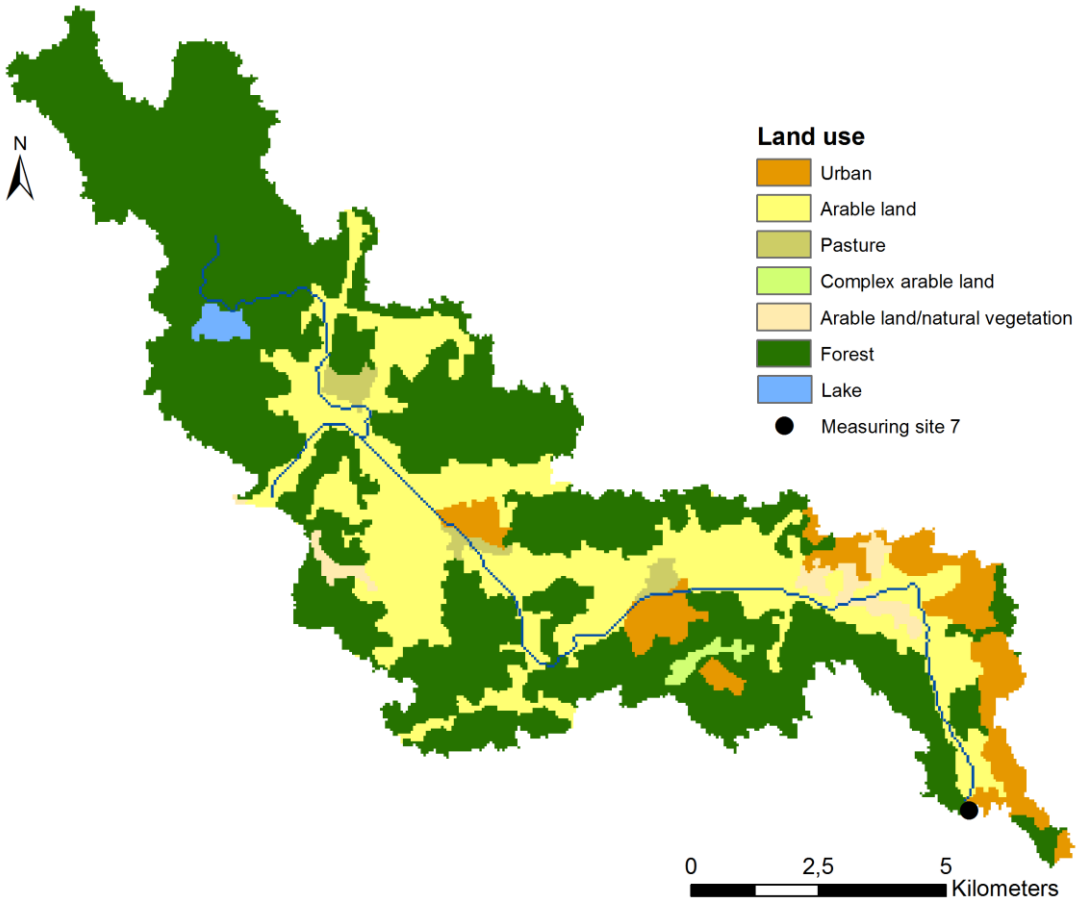

Figure 7: Catchment and land use distribution for site 7. Agriculture covered 30 % of the total area of 105 km^2. The blue line is the stream network that was derived from a DEM file with a resolution of 2×2 m.

Agriculture and forest were the dominating land use types in all catchments (Table 2). All catchments had features of urban areas, except sites 4 and 8. As visible in maps of land use in the catchments (Appendix A), the primary agricultural land use type was arable land.

Table 2: Catchment area and percentage of the catchment consisting of agriculture, forest and urban areas.

Site	Catchment area (km^2)	Agriculture (%)	Forest (%)	Urban (%)
1	25	52	45	2
2	200	42	56	1
3	9	91	5	4
4	14	56	44	0
5	21	46	45	5
6	780	35	59	2
7	105	30	62	6
8	23	39	59	0
9	740	35	63	1
10	210	39	57	1

3.2. FIELD MEASUREMENTS

3.2.1. Partial pressure of CO_2

The median partial pressure of CO_2 from the total measuring period varied between 3115 and 8452 µatm (Table 3, Appendix B). The site with the highest median pCO_2 was site 1, whereas the lowest median pCO_2 was found at site 4. At site 10, the sensor did not record any longer periods of concentrations below 10 000 ppm, which made the measurements from this site of no use for correlation testing and no median values could be calculated.

Table 3: Median, IQR and number of measurements (n) of pCO_2 (µatm), monthly and during the total period.

Month		1	2	3	4	5	6	7	8	9	10
Jun	Median	5212	5767	3359	2709	3880	*NM*	3703	4691	3990	*IQ*
	IQR	1687	1364	1697	375	660	*NM*	503	1244	771	*IQ*
	n	367	395	357	327	382	*NM*	341	368	316	*IQ*
Jul	Median	7219	7639	4042	*D*	4222	5263	4884	7019	*IQ*	*IQ*
	IQR	1759	1825	1778	*D*	905	2307	1124	1997	*IQ*	*IQ*
	n	1397	1420	659	*D*	1416	384	317	305	*IQ*	*IQ*
Aug	Median	8676	*AMR*	*D*	*D*	5062	8586	*IQ*	*IQ*	*IQ*	*IQ*
	IQR	1204	*AMR*	*D*	*D*	1137	2509	*IQ*	*IQ*	*IQ*	*IQ*
	n	1400	*AMR*	*D*	*D*	1078	486	*IQ*	*IQ*	*IQ*	*IQ*
Sep	Median	9405	*AMR*	*IQ*	*D*	5511	*NM*	*IQ*	*IQ*	*IQ*	*IQ*
	IQR	1777	*AMR*	*IQ*	*D*	1226	*NM*	*IQ*	*IQ*	*IQ*	*IQ*
	n	1391	*AMR*	*IQ*	*D*	1053	*NM*	*IQ*	*IQ*	*IQ*	*IQ*
Oct	Median	*AMR*	*AMR*	*IQ*	3190	*IQ*	*NM*	*IQ*	*IQ*	*IQ*	*IQ*
	IQR	*AMR*	*AMR*	*IQ*	701	*IQ*	*NM*	*IQ*	*IQ*	*IQ*	*IQ*
	n	*AMR*	*AMR*	*IQ*	871	*IQ*	*NM*	*IQ*	*IQ*	*IQ*	*IQ*
Nov	Median	*AMR*	*IQ*	*IQ*	2957	*NM*	*NM*	*IQ*	*IQ*	*IQ*	*IQ*
	IQR	*AMR*	*IQ*	*IQ*	1101	*NM*	*NM*	*IQ*	*IQ*	*IQ*	*IQ*
	n	*AMR*	*IQ*	*IQ*	280	*NM*	*NM*	*IQ*	*IQ*	*IQ*	*IQ*
Total period	Median	8452	7307	3645	3115	4679	7064	4019	5484	3990	*IQ*
	IQR	8165	2021	1657	984	1459	3932	1217	2341	771	*IQ*
	n	4555	1815	1016	1478	4929	870	655	673	316	*IQ*

D: The stream was dry
IQ: Data was of insufficient quality
AMR: above measurement range
NM: no measurements were made

A comparison of CO_2 concentration measurements from the two different sensors installed at site 3 showed that the two methods corresponded poorly (Figure 8). However, there was only a limited time where measurements of sufficient quality from the two sensors overlapped enough to compare the data. During this period (October 12th), the chamber sensor values of pCO_2 were approximately 1100 µatm lower than the Eosense sensor, and the slope was not equal to 1 when the datasets were plotted against each other (linear regression: $y = 0.78x-1100$, $p = 6\times10^{-7}$, $n = 49$, $R^2 = 0.43$).

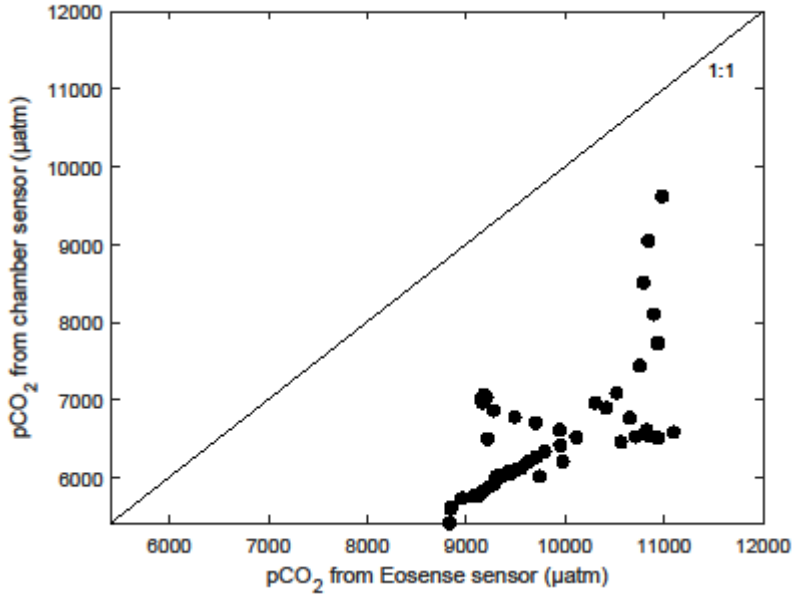

Figure 8: Comparison of pCO_2 values from the new CO_2 sensor and the sensor in the chamber at site 3 during October 12th. The line represents a 1:1 relationship.

The flux of CO_2 from stream water to the atmosphere was possible to calculate at sites 1, 2 and 5 from June to September (Table 4). At the remaining sites, no discernible line of increasing pCO_2 could be found from times when the chamber was lifted. The flux was higher during fall compared to summer at sites 1 and 2. At site 5, there was no visible temporal pattern in flux. The median flux was highest at site 2 and lowest at site 5. On September 26th, it was not possible to calculate the flux for site 1, since no discernible line of increasing pCO_2 was found in the data.

Table 4: Flux of CO_2 from water to atmosphere (mg C h^{-1} m^{-2}).

Date	Site 1	Site 2	Site 5
June 22	260	320	290
July 6	310	290	140
July 19	440	450	160
August 3	590	520	270
August 15	450	490	170
August 30	460	550	170
September 14	720	640	290
September 26	-	580	270
Median	450	505	220

3.2.2. Organic C and nutrient data

The median concentration of $NH4^+$-N was substantially higher in the stream water at site 3 compared to the remaining sites (Table 5). It was roughly 20 times higher than at site 4, which had the lowest median $NH4^+$-N concentration. Site 5 had the highest concentration of NO_2^-/NO_3^--N and there were large variations at sites 3 and 8. Site 8 had the highest median concentration of PO_4^{3-}-P, with the median more than double that of the site with the second highest concentration (site 4). Median concentrations of organic carbon (TOC and DOC) displayed a large variation at site 7 compared to the remaining sites.

Table 5: Median and IQR values of nutrient, TOC and DOC concentrations in the examined streams. It should be noted that measurements at site 6 were cancelled in September, and that measurements at sites 3 and 4 were paused during the summer due to drying of the stream and that this has affected the values.

	NH_4^+-N (µg/L)		**NO_2^-/NO_3^--N (µg/L)**		**PO_4^{3-}-P (µg/L)**		**DOC (mg/L)**		**TOC (mg/L)**	
Site	Median	IQR	Median	IQR	Median	IQR	Median	IQR	Median	IQR
1	25	22	310	1200	49	14	4.4	8.7	4.4	0.2
2	17	7	1560	300	22	8	3.8	1.0	4.0	0.8
3	98	44	680	1860	39	71	7.6	2.3	8.3	2.2
4	5	20	650	630	103	169	10.5	0.2	10.9	0.2
5	22	23	2690	800	51	14	2.2	0.7	2.3	0.9
6	25	19	370	100	6	4	12.8	2.0	12.8	1.9
7	21	17	170	780	14	13	7.6	8.8	7.8	9.1
8	48	32	420	1650	275	173	11.8	5.7	12.7	6.2
9	17	24	4	340	9	21	11.4	0.8	11.4	0.8
10	21	9	100	1030	8	9	6.9	3.5	7.1	2.9

Median and IQR values were also calculated for temperature, pH, conductivity and dissolved oxygen (Table 6). Median temperature was highest at site 6 and lowest at site 4. Measurements were however cancelled during the summer at site 4 and picked up again during fall, making the median temperature lower than at the remaining sites. Median pH was highest at sites 4 and 8 and lowest at site 2, but the variation among all sites was within 0.6 pH units. Site 3 had a median conductivity substantially higher than the other sites and there was also a larger variation in the data. Median dissolved oxygen was highest at site 4 and lowest at site 10. The variation was larger at site 8 than at the other sites.

Table 6: Median and IQR values of temperature, pH, electric conductivity (EC) and dissolved oxygen (DO) during the total measuring period (September – November).

	Temperature (°C)		pH		EC (µS/cm)		DO (%)	
Site	Median	IQR	Median	IQR	Median	IQR	Median	IQR
1	11	3.7	7.8	0.2	580	60	60	19
2	11	3.5	7.5	0.1	560	240	52	10
3	11	5.8	7.7	0.4	1080	510	53	13
4	5.5	5.3	8.0	0.2	510	100	82	6
5	12	4.5	8.1	0.1	670	110	78	9
6	18	2.2	7.7	0.04	450	30	43	12
7	13	5.2	7.9	0.2	520	100	61	21
8	12	3.9	8.0	0.4	730	240	75	56
9	16	7.7	7.9	0.06	590	60	56	12
10	14	3.7	7.7	0.2	760	60	24	21

3.2.3. Discharge

In all streams, specific discharge was low during summer with small variations . In October, there was a large increase in specific discharge in the SMHI discharge measuring stations Sävja, Stabby and Vattholma (Figure 9). The peak in specific discharge in Sundbromark (site 3) came later, in November (Figure 10). The maximum and minimum values of specific discharge were higher in Stabby than in the remaining streams. Sävja and Sundbromark displayed the lowest values of specific discharge.

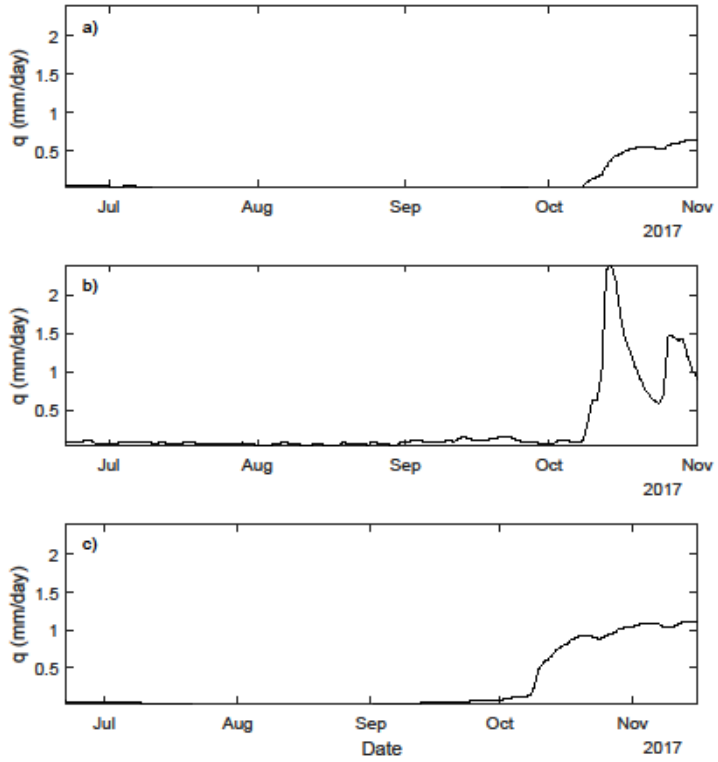

Figure 9: Specific discharge at Sävjaån (a) Stabby (b) and Vattholma (c) was plotted using discharge data from SMHI (SMHI 2017a).

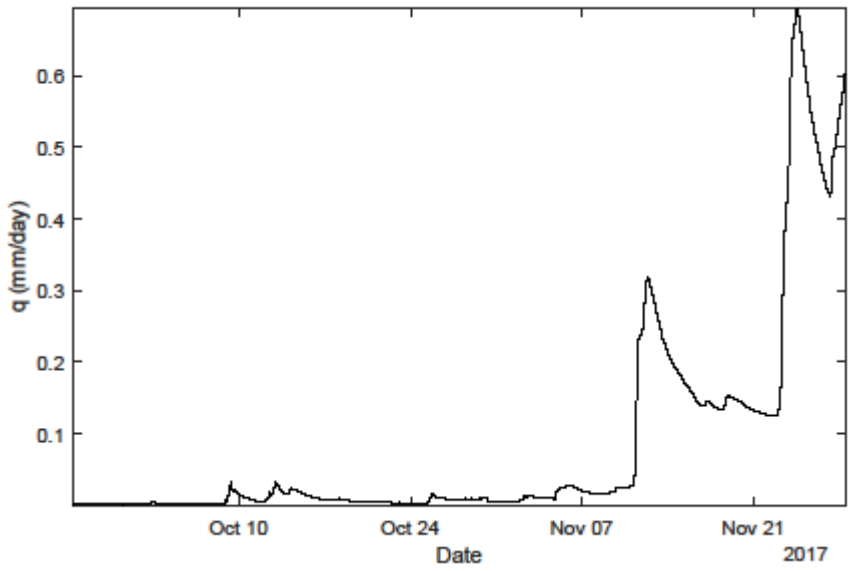

Figure 10: Specific discharge at site 3 in Sundbromark. Discharge was measured at a weir in Sundbromark during October – November.

3.3. SPATIAL ANALYSIS

3.3.1. Spatial patterns in pCO_2

Partial pressure of CO_2 showed no significant correlation with the percentage of agricultural land use in the catchments (Figure 11,Table 7), nor with the percentage of forests or urban areas.

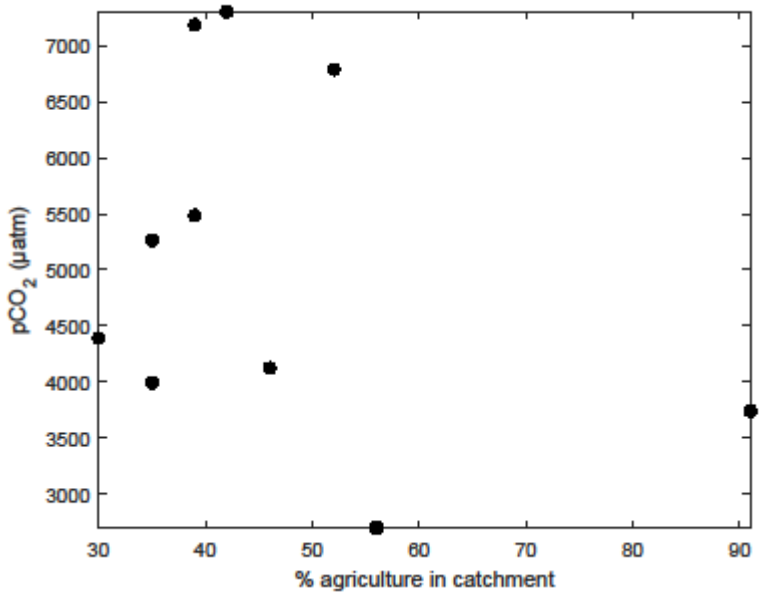

Figure 11: Medians of pCO_2 from summer (June – July) plotted against percentage of catchment covered by agriculture. No significant correlation was found.

There was no significant correlation between pCO_2 and TOC or pCO_2 and DOC when measurements from all sites covering the total period were combined (Figure 12, Table 7). Similarly, no correlation was found with concentration of nutrients (NH_4^+-N, NO_2^- /NO_3^--N and PO_4^{3-}-P) and pCO_2 (Figure 13).

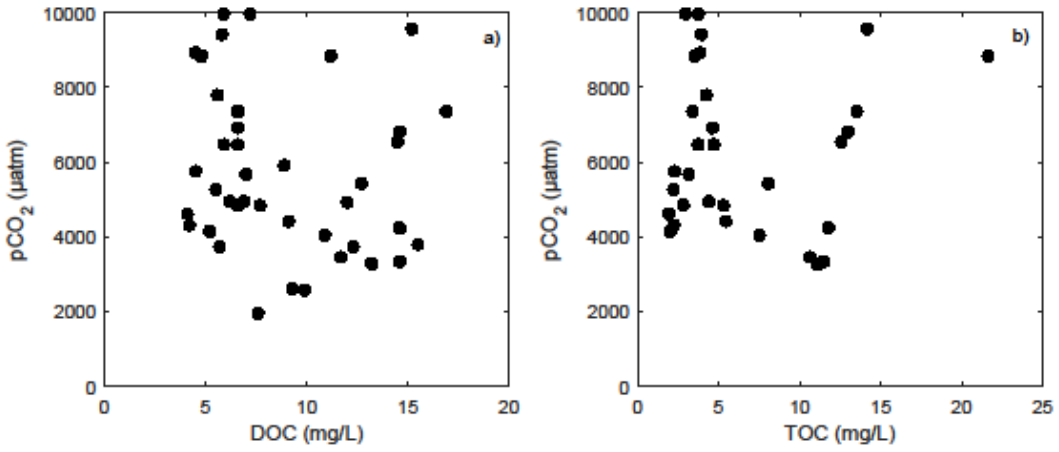

Figure 12: Values of DOC (a) and TOC (b) plotted against median pCO_2 values. No significant correlation was found between pCO_2 and concentrations of DOC and TOC.

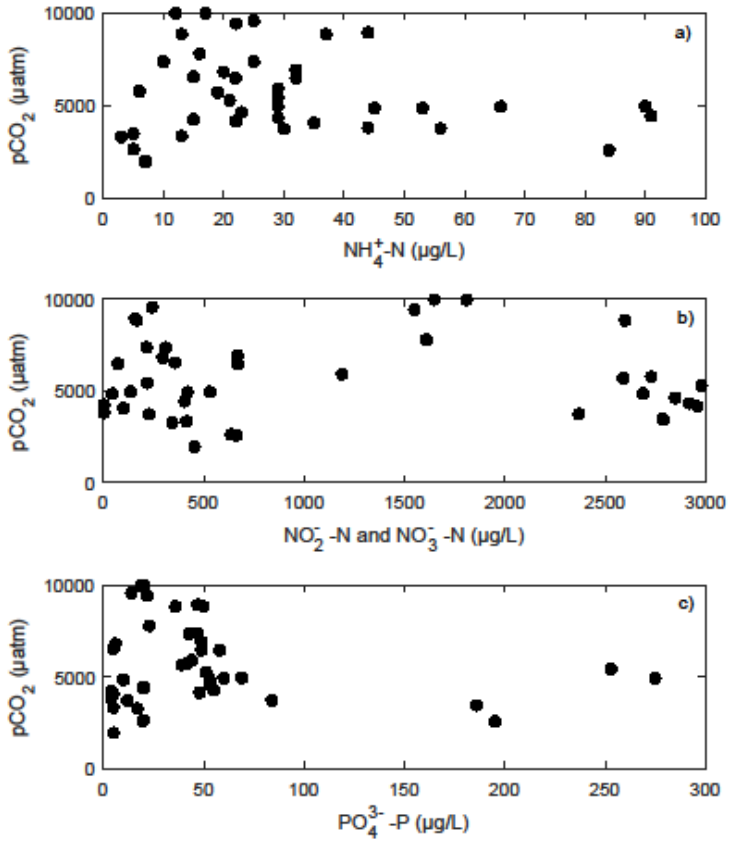

Figure 13: Concentrations of nutrients NH_4^+-N (a), NO_2^-/NO_3^--N (b) and PO_4^- -P (c) plotted against median values of pCO_2 at each site except site 10. No significant correlations were found.

When combining all data for all sites covering the entire study period, correlation was studied between pCO_2 and temperature, pH, conductivity and dissolved oxygen (DO). Two significant correlations were found (Figure 14, Table 7). pCO_2 and pH displayed a negative correlation whereas the correlation between pCO_2 and DO showed a decrease in pCO_2 with increasing percentage of DO in the water. Linear and negative relationships were found between pCO_2 and pH (pCO_2 = -5960pH+52682, $p<0.05$, R^2= 0.45, n=40) and DO (pCO_2=-62DO+9622, $p<0.05$, R^2=0.3, n=40) (Figure 14), using linear regression. The variables were normally distributed.

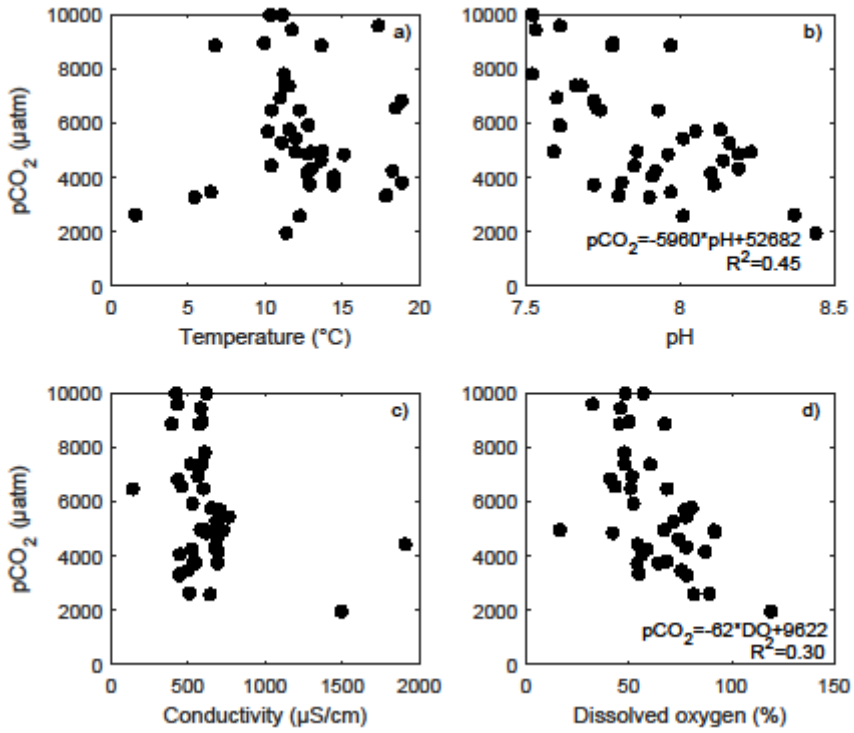

Figure 14: pCO_2 plotted against temperature (a), pH (b), electric conductivity (c) and dissolved oxygen, DO (d). Significant relationships ($p < 0.05$) were found between pCO_2 and pH and pCO_2 and DO. Equations from regressions are written out in the respective plots.

Table 7: Results from correlation analysis, using Kendall's Tau, between pCO_2 and different variables. Tau < 0 indicates a negative correlation. For significant correlations ($p < 0.05$), p-values are written in bold.

Variable	p	n	Tau
Catchment area	0.36	9	0.28
% agriculture	0.92	9	-0.03
% forest	0.95	9	0
% urban	0.92	9	-0.03
NH_4^+-N	0.90	40	-0.04
NO_2/NO_3-N	0.96	40	-0.01
PO_4^{3-}-P	0.71	40	-0.04
DOC	0.18	40	-0.15
TOC	0.93	31	0.01
Temperature	0.25	40	-0.13
pH	**<0.0001**	40	-0.44
Conductivity	0.15	40	-0.16
Dissolved oxygen	**0.0002**	40	-0.41

3.3.2. Flux of CO_2 from stream water

Significant correlations were found between flux of CO_2 from water to atmosphere and NO_2^-/NO_3^--N, PO_4^{3-}-P, pH, conductivity and DO, respectively, when measurements from all sites over the entire period were studied (Table 8). Correlation between flux and NO_2^-/NO_3^--N showed a decrease in flux as NO_2^-/NO_3^--N increased. The same was found for correlation with PO_4^{3-}-P, pH and conductivity. The correlation between flux and DO was negative.

Table 8: Results of correlation testing, using Kendall's Tau, between flux of CO_2 from stream water to the atmosphere and different chemical variables. Tau < 0 indicates a negative correlation. For significant correlations ($p < 0.05$), p-values are written in bold.

Variable	p	n	Tau
NH_4^+-N	0.35	23	-0.14
NO_2^-/NO_3^--N	**0.002**	23	-0.48
PO_4^{3-}-P	**0.02**	23	-0.34
DOC	0.44	23	0.12
TOC	0.13	20	0.25
Temperature	0.27	23	-0.17
pH	**0.0002**	23	-0.57
Conductivity	**0.0003**	23	-0.53
Dissolved oxygen	**<0.0001**	23	-0.66
pCO_2	**0.0008**	20	0.57

3.3.3. Diurnal pattern in pCO_2

Correlation between amplitude of the diurnal variation in pCO_2 and different chemical variables was tested using measurements from all sites during the whole period (Table 9). Significant correlation was found for NO_2^-/NO_3^--N, DOC, TOC, temperature and conductivity. The amplitude decreased when NO_2^-/NO_3^--N, temperature and conductivity increased and increased with increasing DOC and TOC.

Table 9: Results of correlation analysis, using Kendall's Tau, between amplitude of the diurnal variation in pCO_2 and different chemical variables. Tau < 0 indicates a negative correlation. For significant correlations, p-values are written in bold.

Variable	p	n	Tau
NH_4^+-N	0.94	11	0.02
NO_2^-/NO_3^--N	**0.01**	11	-0.59
PO_4^{3-}-P	0.39	11	-0.20
DOC	**0.04**	11	0.48
TOC	**0.03**	8	0.64
Temperature	**0.03**	11	-0.53
pH	0.11	11	-0.37
Conductivity	**0.03**	11	0.53
Dissolved oxygen	0.65	11	-0.13

3.4. TEMPORAL CORRELATION ANALYSIS

3.4.1. Temporal patterns in pCO_2

There was a significant correlation between discharge and pCO_2 at all sites except at sites 8 and 9 (Table 10). Five sites (1, 2, 3, 6 and 7) showed negative correlation (Tau < 0), i.e. pCO_2 decreased with increasing discharge, whereas two sites (4 and 5) showed a positive correlation (Tau > 0).

Table 10: Summary of results of correlation analysis, using Kendall's Tau, between discharge and pCO_2. Tau < 0 indicates that pCO_2 decreases with increasing discharge. For sites with significant correlation between pCO_2 and discharge, p-values are written in bold.

Site	Period	p	n	Tau
1	Jun – Aug	**<0.0001**	71	-0.47
2	Jun – Aug	**0.0006**	40	-0.43
3	Oct – Nov	**<0.0001**	1625	-0.46
4	Oct – Nov	**<0.0001**	1149	0.13
5	Oct – Nov	**<0.0001**	288	0.45
6	Jun – Jul	**<0.0001**	22	-0.73
7	Jun – Jul	**<0.0001**	22	-0.63
8	Jun – Jul	0.09	17	-0.30
9	Jul	0.40	8	0.29

For sites 1 and 2, only summer data (Jun – Aug) was used for the correlation analysis, since CO_2 data from that period was of better quality than during fall and within the measurement range, which was not the case during fall (Figure 15).

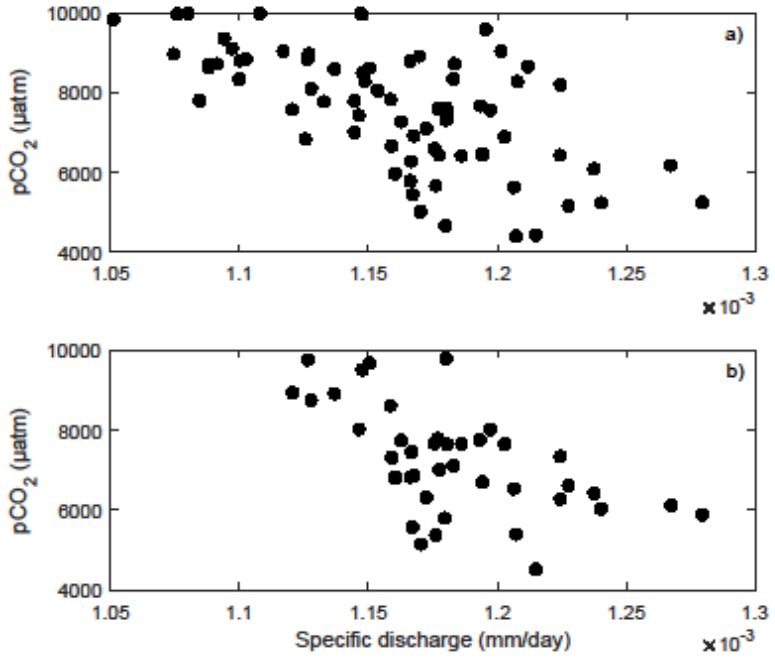

Figure 15: pCO_2 plotted against specific discharge during June – August at site 1 (a) and June – July at site 2 (b). A significant and negative correlation ($p < 0.05$) was found at both sites with pCO_2 decreasing with increasing discharge.

A significant correlation between continuous pCO_2 and discharge was found at sites 3, 4 and 5 (Figure 16, Figure 17). At site 3, the correlation was negative. At sites 4 and 5, pCO_2 and discharge correlated positively.

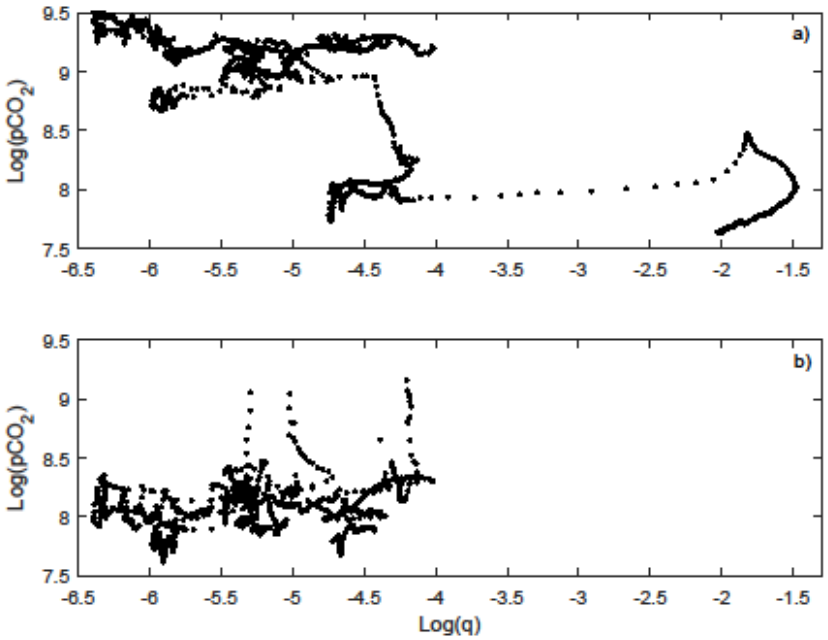

Figure 16: Logarithm of pCO_2 and specific discharge (q) during fall at sites 3 (a) and 4 (b). Significant correlation between pCO_2 and discharge was found at both sites. At site 3, the correlation was negative. At site 4, a positive correlation was found.

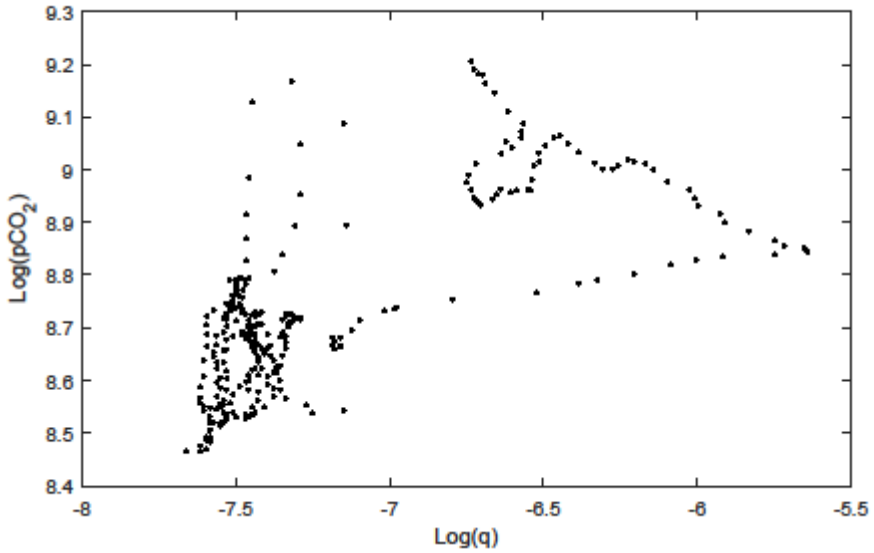

Figure 17: Logarithm of pCO_2 and specific discharge (q) at site 5. A significant and positive correlation was found between the variables.

At sites 6, 7, 8 and 9, only summer pCO_2 data was examined for correlation with discharge, since the quality of the data was best during this period (Figure 18).

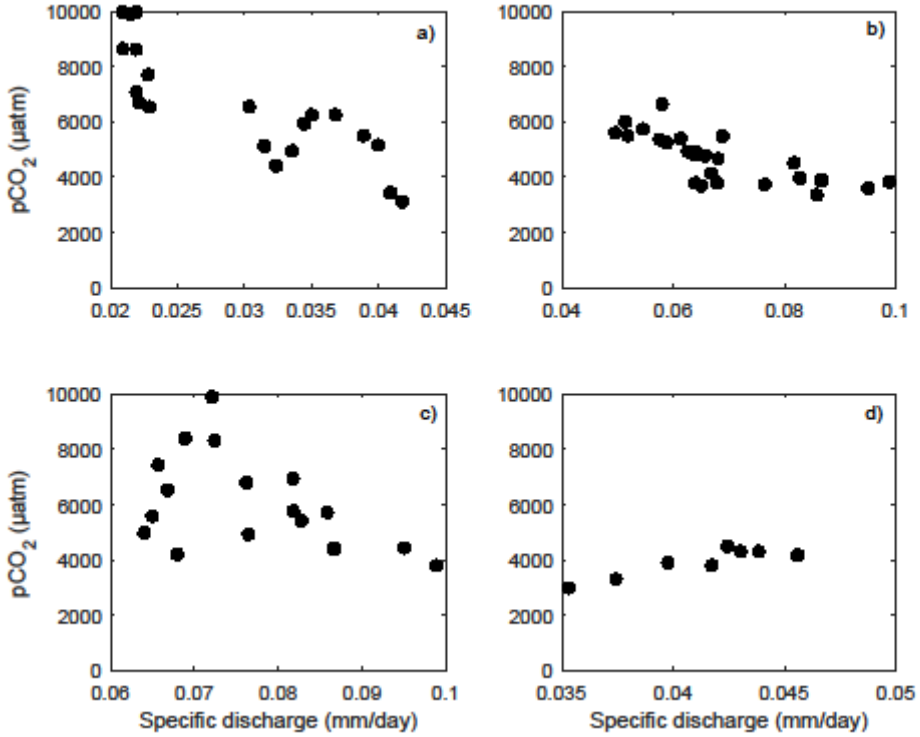

Figure 18: pCO_2 plotted against specific discharge for sites 6–9. Significant and negative correlations were found at site 6 and 7 using Kendall's Tau. No significant correlation was found at sites 8 and 9.

The temporal variation in pCO_2 was examined by looking at the amplitude in diurnal variation (Figure 19). This could be calculated at sites 1, 2 and 5 (Table 11). However, only data collected during summer proved sufficient for calculating the amplitude, since there was no clearly discernible pattern of diurnal variation during fall. The amplitude showed a decreasing pattern from summer to fall and was largest for sites 1 and 2.

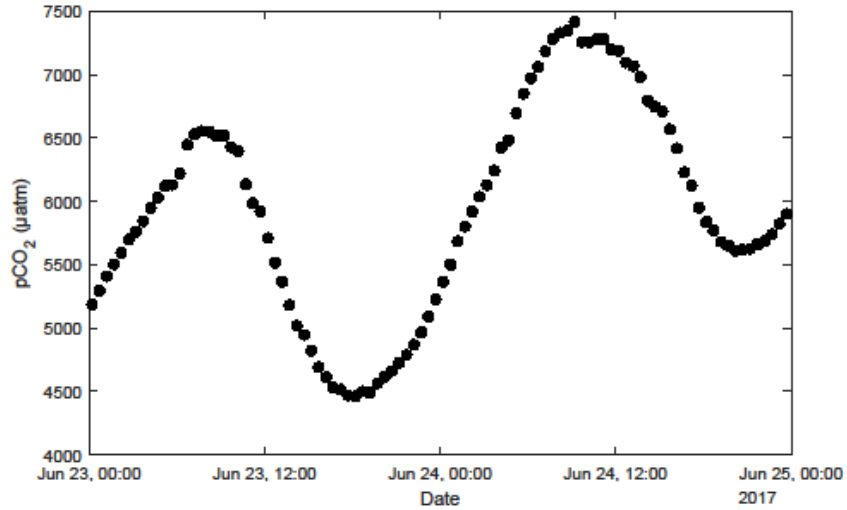

Figure 19: Example of diurnal variation in pCO_2 at site 2 during 48 hours from June 23 to June 25.

Table 11: Amplitude of diurnal variation of pCO_2 at sites 1, 2, and 5. Dates were chosen so they corresponded to the dates when water samples were collected. No calculation of amplitude was possible on August 2nd at site 2 since no clearly discernible diurnal variation was found at that time.

	Amplitude of diurnal pCO_2 variation (µatm)		
Date	Site 1	Site 2	Site 5
June 23	2350	2960	1430
July 7	2320	2150	1440
July 18	2060	1460	1230
August 2	1850	-	890

3.4.2. Flux of CO_2 from stream water

The flux of CO_2 from stream water to the atmosphere was tested for correlation over time with discharge (Table 12). The results showed significant correlation at two out of three sites where the flux decreased with increasing discharge.

Table 12: Results of correlation testing with Kendall's Tau between discharge and flux of CO_2 from stream water to atmosphere for sites 1, 2 and 5. Tau < 0 indicates a negative correlation. For significant correlations ($p < 0.05$), p-values are written in bold.

Site	p	n	Tau
1	**<0.05**	6	-0.87
2	**<0.05**	6	-0.87
5	0.25	6	-0.41

4. DISCUSSION

4.1 PARTIAL PRESSURE OF CO_2 IN AGRICULTURAL STREAMS

Measurements of pCO_2 in agricultural streams around Uppsala gave useful results in all streams, except at site 10. The results could be used for correlation analysis and showed that pCO_2 values in the examined streams were high, compared to published data from other streams.

The site specific medians of pCO_2 observed in the current study were all higher than pCO_2 observed in the forested Krycklan catchment, Northern Sweden (Wallin et al., 2013). This result was in accordance with results from previous studies (Bodmer et al. 2016; Borges et al. 2018) from Germany and Belgium that have found generally higher stream pCO_2 in agricultural areas compared to forested areas. However, the levels of pCO_2 in streams around Uppsala were on average two times higher than found in the given studies (Bodmer et al., 2016; Borges et al., 2018). The high levels indicate that there must be a geogenic source of carbon for the stream of the current study, such as weathering of carbonate minerals. This is supported by the mineralogy of the glacial clay soils in the area, which are known to contain carbonates (SGU, 2017). Further studies are encouraged

to examine the sources of CO_2 in these streams, both to determine whether the high pCO_2 levels are caused by geogenic carbon input or if there are biogenic sources that can maintain the high levels observed and to examine how agriculture in the catchments affect carbon inputs and in situ production.

Significant correlation was found between pCO_2 and discharge. At five sites (1, 2, 3, 6 and 7), the correlations were negative, which agreed with results by Borges et al. (2018) found in streams and rivers in Belgium and with a previous study in the Krycklan catchment (Winterdahl et al., 2016). A possible explanation for the decrease in pCO_2 is that raising groundwater tables activate flow paths that are not rich in CO_2, which in turn causes a dilution of CO_2 in the stream water (Winterdahl et al., 2016). At two sites (4 and 5), a positive correlation was found, which has also been found in a previous study (Dinsmore et al. 2013). A positive correlation between pCO_2 and discharge can have a number of possible explanations. Due to an uneven distribution in specific runoff, there can be an addition of runoff from areas of the catchment rich in CO_2 during rain events (Dinsmore et al., 2013), which would result in a positive correlation. A rise of the groundwater table during rain events can also cause additions of carbon-rich groundwater to the streams, which would also cause a rise in CO_2 concentration along with increasing discharge. The hydrological pathways in agricultural landscapes are heavily affected by man-made structures, mainly related to drainage. Most fields contain (more or less effective) drainage pipes in the soil, which control water pathways and transport of solutes including carbon to the stream (Elmquist, 2014). Due to this manipulation, concentration-discharge patterns are often very variable both in time and space, making the interpretation of correlations between pCO_2 and discharge in the catchments of this study complicated.

No significant correlation was found between pCO_2 and land use. The topic of how pCO_2 varies with land use has not been extensively examined in the literature. Further studies with a larger number of sites are needed to test the hypothesis that there is a correlation between the variables. However, there are many factors that affect the concentration of carbon dioxide in a stream, and assuming that only agriculture has an effect on the concentration is a simplification. The catchments are heterogenous in character, even though they have similar percentages of agriculture. There are physical processes, such as variations in discharge and gas exchange with the atmosphere, that affect stream pCO_2, along with biological processes such as respiration and photosynthesis. It would be of use to further study catchments with a larger range in percentage of agriculture and other land use types, applying the same method at each site, to see whether pCO_2 varies with catchment land use. The results were also affected by limitations in data quality, since there were only ten sites to rely on for the analysis, and site 10 did not produce useful results.

When pCO_2 and DOC were studied, no significant correlation was found. This result was not in agreement with Bodmer et al. (2016), where the authors found a significant and positive relationship between pCO_2 and DOC in streams draining agricultural areas. Also, no correlation was found between pCO_2 and TOC, which was also the case in a study at the Krycklan catchment (Winterdahl et al., 2016) and in a Canadian study (Koprivnjak et al., 2010). The latter suggested that the lack of correlation between pCO_2 and TOC indicates that the main source of carbon dioxide in the water is not in-stream decomposition of dissolved organic matter, but rather that it is transported into the stream from sources in the catchment. In the current project, the objective was to quantify the CO_2 in the streams rather than examine which processes it originates from. The

correlation between pCO_2 and TOC, and possible explanations for it, is something that further studies are encouraged to examine.

The concentration of nutrients (NH_4^+-N, NO_2^-/NO_3^--N and PO_4^{3-}-P) displayed no significant correlation with pCO_2. The results are in contrast to the results from Bodmer et al. (2016) where pCO_2 was found to correlate positively and linearly with total concentrations of phosphorous and nitrogen. A possible explanation could be that photosynthetic processes and respiration of organic matter do not control the concentration of CO_2 as much as other processes in the streams, such as inputs of C from the catchment. It could also be due to that photosynthesis is not nutrient limited but limited by other factors such as light.

Correlation tests were performed between pCO_2 and temperature, pH, conductivity and dissolved oxygen, respectively. The significant and negative relationship found between pCO_2 and pH is logical due to the close connection within carbonate equilibrium. In the chain of equilibrium reactions, H_2CO_3 reacts with H^+ and HCO_3^-, producing CO_2. When pH increases, less CO_2 will be produced, which is consistent with the results from the correlation test in this study. There was also a significant and negative relationship between pCO_2 and dissolved oxygen, with pCO_2 values decreasing with increasing dissolved oxygen in the water. This result is logical, considering that respiration and photosynthesis are occurring in the water, with O_2 being consumed as CO_2 is produced in the first process, and O_2 being produced and CO_2 consumed in the latter. The result is also consistent with the diurnal cycles of pCO_2 visible in the measurements. During night, respiration is dominant compared to photosynthesis, making pCO_2 values rise (Schlesinger and Bernhardt, 2013a). During the day, photosynthesis becomes dominant, consuming CO_2 and producing O_2, which is visible in the clear diurnal variation in the pCO_2 data. A strong decrease in pCO_2 with increasing dissolved oxygen has been found in previous studies using floating CO_2 chambers in Swedish lakes (Natchimuthu et al., 2017).

When the amplitude in the diurnal cycle in pCO_2 was used for correlation tests, significant and negative correlation was found between amplitude and NO_2^-/NO_3^--N, temperature and conductivity. Significant positive correlation with amplitude was found with TOC and DOC, respectively. The small number of values (n = 11) needs to be noted when discussing these results. They give an indication of drivers of the diurnal pattern in pCO_2, but further studies are needed to examine whether correlation differs e.g. between catchments with varying land use or if there is a variation over time. A clear diurnal variation in pCO_2 has been noted in inland waters (Natchimuthu et al., 2017; Åberg et al., 2010) and streams specifically (Parker et al., 2007), and it is suggested that the variation patterns are more pronounced during warm periods when the biota in the streams is in a growing-phase (Åberg et al., 2010).

Many of the correlation tests were performed with a relatively small number of data from study sites that in some cases did not produce reliable results. While the data in the correlation tests were chosen because they were thought to be representative, it is likely that measuring errors have affected the results. Therefore, correlation between variables should be interpreted as indicators, rather than definite evidence that correlation exists. Further studies are encouraged to explore the topic in depth.

4.2 FLUX OF CO_2

The estimated values of CO_2 flux between water and atmosphere were of similar magnitude as seen in a previous study (Bastviken et al., 2015), where flux was measured in a Swedish lake using the floating chamber method. However, flux values were higher than those found in the Krycklan catchment (Wallin et al., 2013). As in this study, there was a large range in flux values. Recent studies have shown that anchored floating chambers measuring CO_2 in running waters tend to overestimate fluxes of greenhouse gases (Lorke et al., 2015), which is something that needs to be taken into consideration when evaluating the results. Furthermore, all results in this study rely on a small number of measurements, and should be interpreted as indications of relationships, rather than evidence.

A significant and negative correlation between flux of CO_2 from the water to the atmosphere and discharge was found at sites 1 and 2. A significant and positive correlation between flux and pCO_2 was also found at these sites. Looking at the results from correlation tests between pCO_2 and discharge, there is a possible explanation to these findings, as pCO_2 decreases with increasing discharge. Higher discharge leads to lower pCO_2, which in turn results in a lower flux of CO_2 to the atmosphere. However, studies have shown that the gas transfer velocity, which affects the rate with which CO_2 exits the stream water, correlates with discharge (Melching and Flores, 1999; Raymond et al., 2012). The gas transfer velocity commonly increases with discharge, which would lead to higher flux.

As was the case with pCO_2, the negative correlation between flux and pH is logical due to the close connection within the carbonate system. When pH increases, more CO_2 is shifted to other dissolved inorganic carbon forms. When there is less CO_2 in the water, the flux is reduced, which is confirmed by the positive correlation between flux and pCO_2. Similarly, the negative correlation between flux and DO can be explained by the negative correlation between pCO_2 and DO. The flux displayed a negative correlation with conductivity and this result cannot be explained by any correlation between pCO_2 and conductivity. There is a possibility that this correlation is spurious, if conductivity correlates with discharge, which has not been examined in this study.

4.3 METHOD

The floating chamber method to derive continuous CO_2 concentration data has advantages and disadvantages. Since data is logged with an interval that can be adjusted by the user, the resolution can be adapted according to the needs of the study. The method produces a continuous series of data over multiple seasons and during the whole day, which is an advantage compared to measuring CO_2 manually. Studies with manual sampling tend to rely on measurements carried out during daytime in summer (Bastviken et al., 2015), since measuring is easiest during these times. The floating chamber method captured temporal variations in CO_2 concentration in streams, since it clearly showed a diurnal and seasonal variation. Also, the flux of CO_2 can easily be estimated from the chamber sensor data at deployment with no additional measurements needed

(Natchimuthu et al., 2017). The method is relatively inexpensive compared with other methods of measuring stream CO_2 concentration (Bastviken et al., 2015) and the cost of labor is low since the sites are only visited fortnightly. Furthermore, malfunctioning sensors can quickly be replaced without a large cost.

Based on previous studies of CO_2 in streams, the concentration of CO_2 was not expected to exceed 10 000 ppm, and therefore, the measurement range of the CO_2 sensors (0 – 10 000 ppm) was not assumed to be a problem when planning the study. However, the concentrations reached the upper limit at most sites at some point during the study period, making data difficult to use. In addition, the CO_2 sensors are sensitive to condensation, since they are built for indoor use. To determine whether some of the high concentrations measured were caused by a high degree of condensation would require further analysis. In addition, the sensors or the power supply (the 9 V battery) appeared to be sensitive to cold temperatures, since the sensors stopped working when the temperature dropped during the fall. As a result, data was not recorded for some periods. Furthermore, it became evident that sites should be located in areas that are hidden from people to minimize the risk of the chamber being picked up or damaged. This was the case at site 6 where measurements were cancelled since people passing by repeatedly tampered with the equipment. At site 10, the chamber did not work well and did not produce useful results. It is unclear what the reason for this was, since the sensor seemed to be working. Possible explanations are that condensation was a larger problem at this site, and that this affected the sensor or that concentrations constantly exceeded 10,000 ppm.

During a limited time in the fall, a comparison between the floating chamber sensor and the Eosense sensor was carried out at site 3. There was generally a large deviation in pCO_2 (~1000 µatm) between the two sensors, with the Eosense measuring higher values. However, there was only a short time when the datasets overlapped enough to compare the results. Due to the Eosense sensor's higher measuring range, it seems to be more suitable to use for measuring the high CO_2 concentrations observed in these agricultural streams. However, the chamber sensors were calibrated prior to the study but for the Eosense sensor, factory calibration was used. Further evaluation with equal calibration procedures of the different sensors is needed.

When catchments were delineated in ArcGIS, two different resolutions of DEM files were used. The 50×50 m DEM files were too coarse to use for the small catchments, since the area around Uppsala is relatively flat. The 2×2 m DEM files became too large to use for the large catchments, but produced useful results for the small catchments. However, using the 2×2 m resolution has a disadvantage in that it is sensitive to roads and bridges, in some cases cutting off the catchment making it smaller than it is in reality. The DEM resolution sensitivity of watershed delineation has been noted in previous studies (Wu et al., 2007). This should be taken into consideration when choosing DEM files for the watersheds and observed when working with the delineation, so that areas of the watershed do not get cut off by roads and bridges.

There is a need of a large number of discharge measurements in order to produce a more reliable rating curve for calculating discharge. In the current study, the number of discharge measurements was small, which has likely resulted in some degree of error in the discharge measurements at Sundbromark (site 3).

4.4 RECOMMENDATIONS FOR FURTHER RESEARCH

Further studies are encouraged to continue studying stream CO_2 concentration and flux in agricultural streams in order to improve the knowledge about the role of streams in the landscape C budget. Especially, further work is needed to trace the sources of CO_2 in these streams and both geogenic and biogenic contributions of stream CO_2 should be examined. For example, pCO_2 has been shown to be significantly linked to the quality of dissolved organic matter in streams (Bodmer et al., 2016). There is need of an investigation regarding how representative these streams are for agricultural stream pCO_2, since the values of pCO_2 found are generally higher than those found in previous studies in agricultural streams (Borges et al., 2018; Bodmer et al., 2016). It should be noted, however, that those studies relied on other methods than the ones used here. If the sensors had not been sensitive to cold temperatures and condensation, measurements would have been continued for a longer period during the fall and the beginning of winter. Further studies should strive to measure during multiple seasons to examine the seasonal variability of pCO_2 in these streams, especially during late fall and winter, since this period is under-represented in the literature (Bastviken et al., 2015).

When designing future studies to investigate the effects of agricultural land use on stream CO_2, a more complete range in agriculture area coverage would be preferable. In this study, most catchments had an agricultural coverage of about 30 – 50 %. A larger range would perhaps increase the knowledge about how pCO_2 varies between catchments with different land use characteristics. If possible, water sampling should be done more frequently than during this study to provide a larger set of data for investigating potential connections between the other chemical parameters and pCO_2. Further investigations concerning the hydrological control on stream pCO_2 in catchments dominated by agriculture are needed since the hydrology and likely also the CO_2 sources are spatiotemporally very variable in these systems.

5. CONCLUSIONS

The main conclusion of this study was that agricultural streams around Uppsala are rich in CO_2, compared to previous studies on stream pCO_2. Further studies are needed to determine the source of CO_2 in the streams and whether these streams are representative for agricultural streams in general. Studies of agricultural influence on stream pCO_2 and flux should be integrated into the landscape carbon budget and used as a basis for the agricultural sector when mitigation strategies are developed for reducing greenhouse gas emissions. Since stream pCO_2 was linked to discharge, the discharge-concentration effects should be considered when performing studies on the topic. A connection between stream pCO_2 and the extent of agricultural land in the catchment could not be found. Further studies are encouraged to keep exploring effects of agriculture on stream pCO_2. The flux and diurnal cycling of pCO_2 in the examined streams could be quantified, but should be explored further, using more reliable methods that are suitable for running water, in order to investigate the effects of agriculture on these patterns. Finally, the floating chamber method provides a useful tool for measuring stream CO_2 concentrations with a high resolution. However, problems regarding the measurement range and condensation sensitivity of the sensor should be solved to avoid loss of data.

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APPENDIX

A. LAND USE IN THE CATCHMENTS

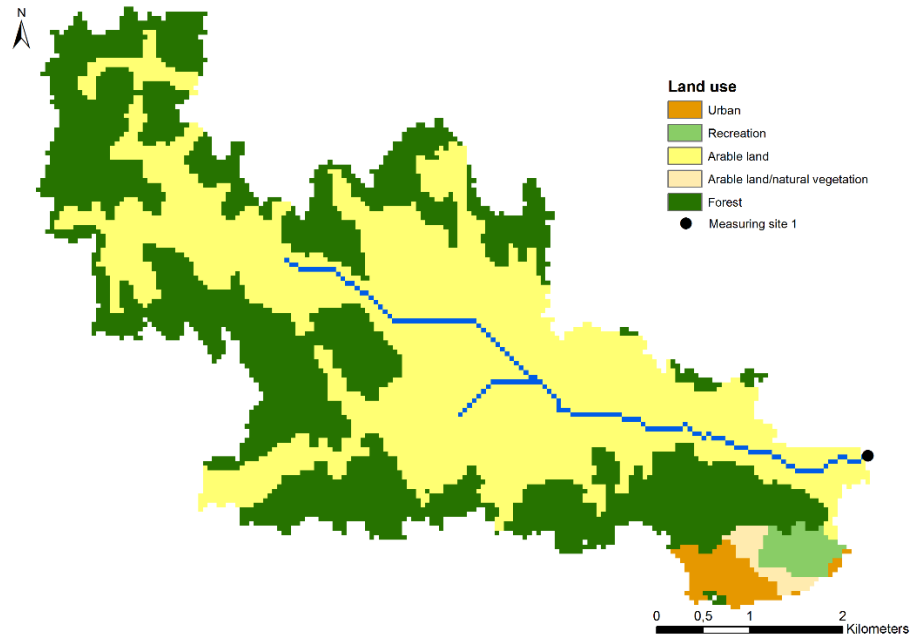

Figure 20: Catchment area and land use distribution in the catchment of site 1. The catchment was delineated using a DEM file with a resolution of 2×2 m.

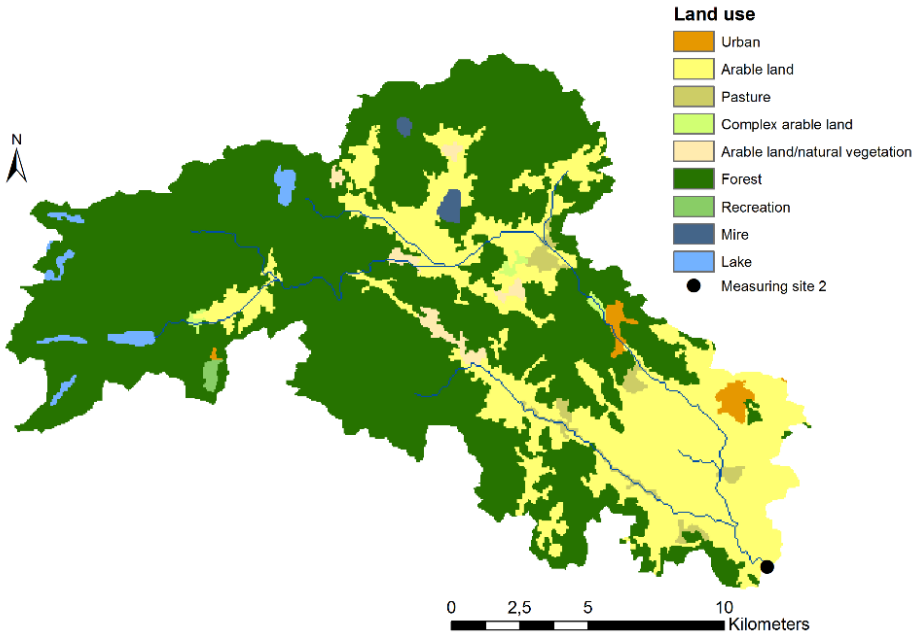

Figure 21: Catchment area and land use distribution in the catchment of site 2. The catchment was delineated using a DEM file with a resolution of 2×2 m.

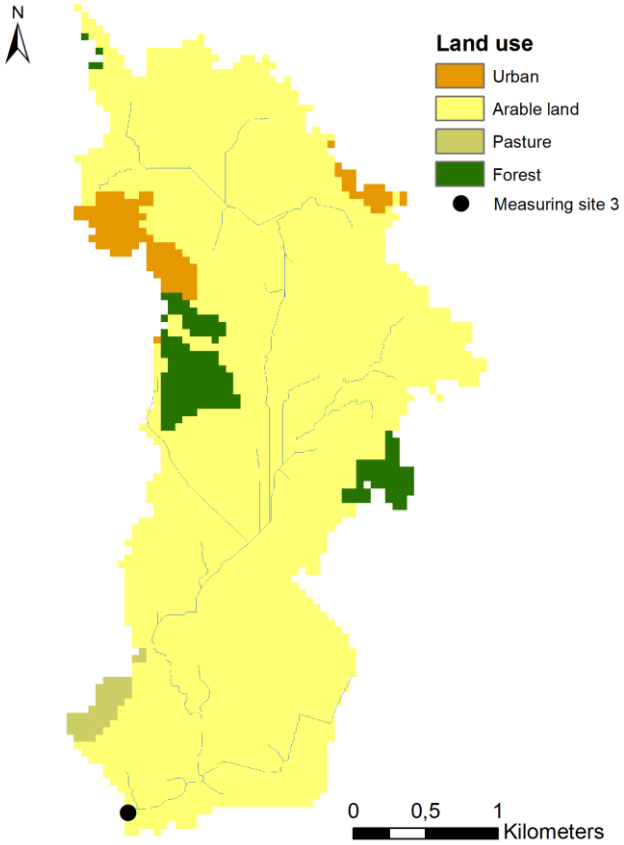

Figure 22: Catchment area and land use distribution in the catchment of site 3. The catchment was delineated using a DEM file with a resolution of 2×2 m.

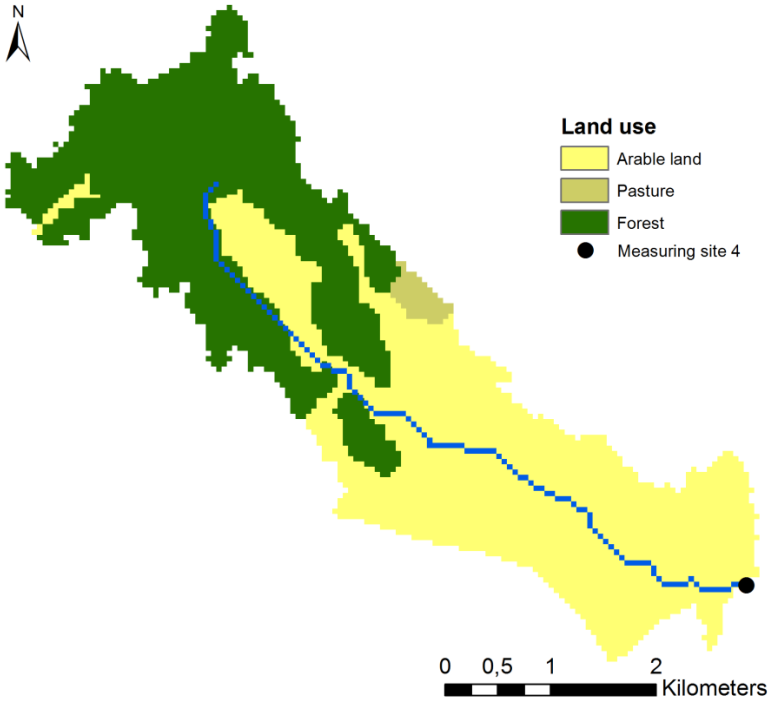

Figure 23: Catchment area and land use distribution in the catchment of site 4. The catchment was delineated using a DEM file with a resolution of 2×2 m.

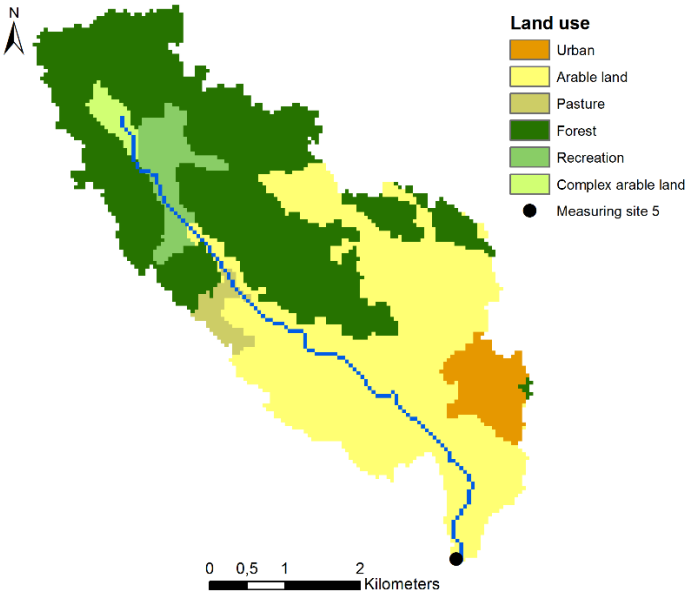

Figure 24: Catchment area and land use distribution in the catchment of site 5. The catchment was delineated using a DEM file with a resolution of 2×2 m.

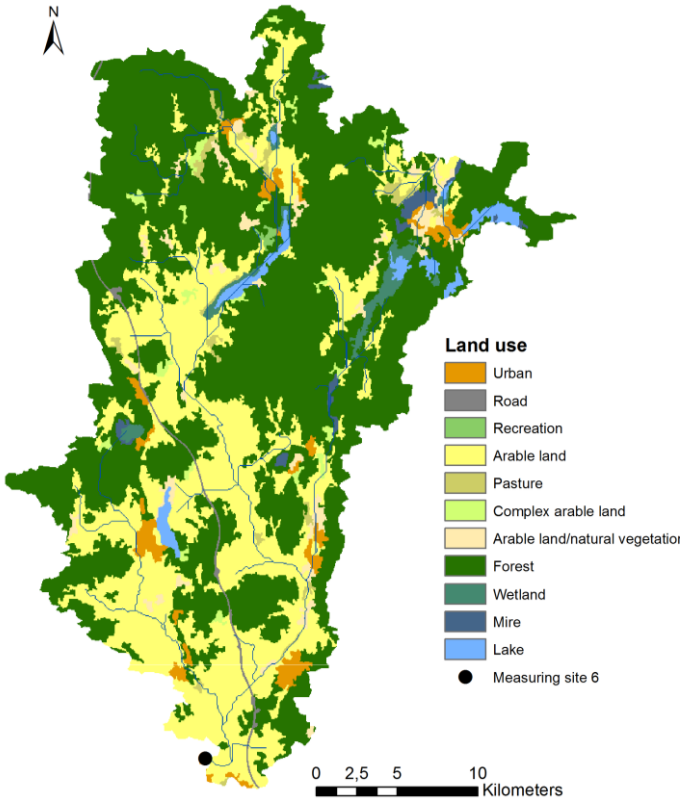

Figure 25: Catchment area and land use distribution in the catchment of site 6. The catchment was delineated using a DEM file with a resolution of 50×50 m.

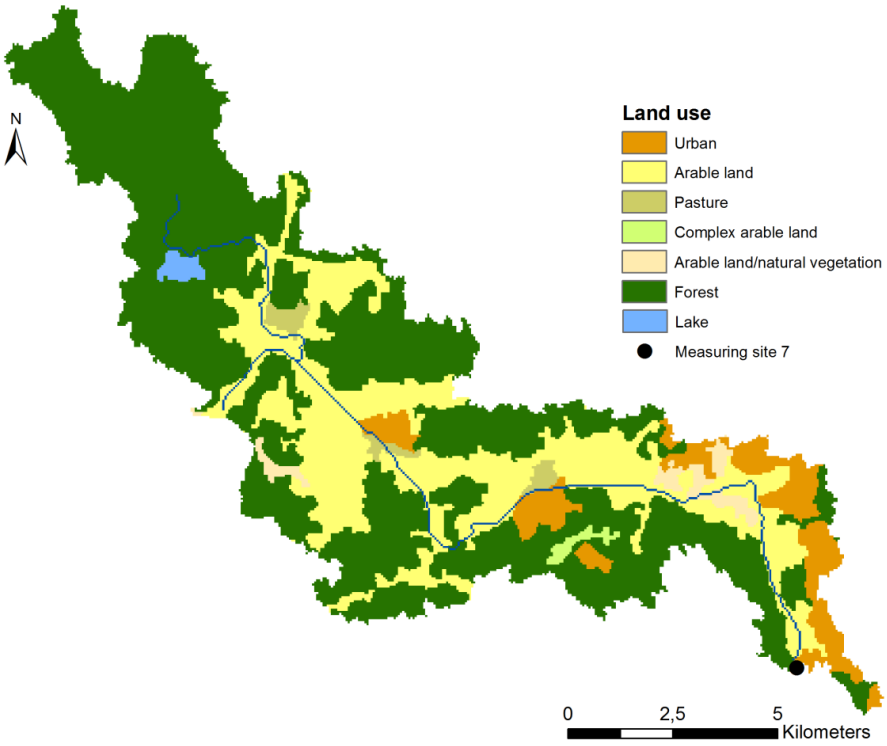

Figure 26: Catchment area and land use distribution in the catchment of site 7. The catchment was delineated using a DEM file with a resolution of 2×2 m.

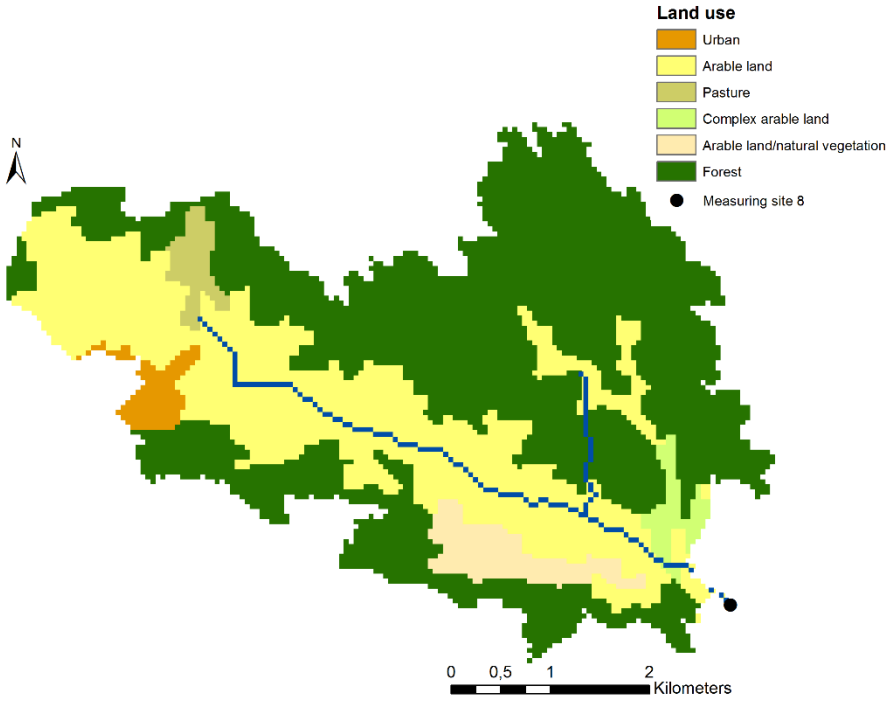

Figure 27: Catchment area and land use distribution in the catchment of site 8. The catchment was delineated using a DEM file with a resolution of 50×50 m.

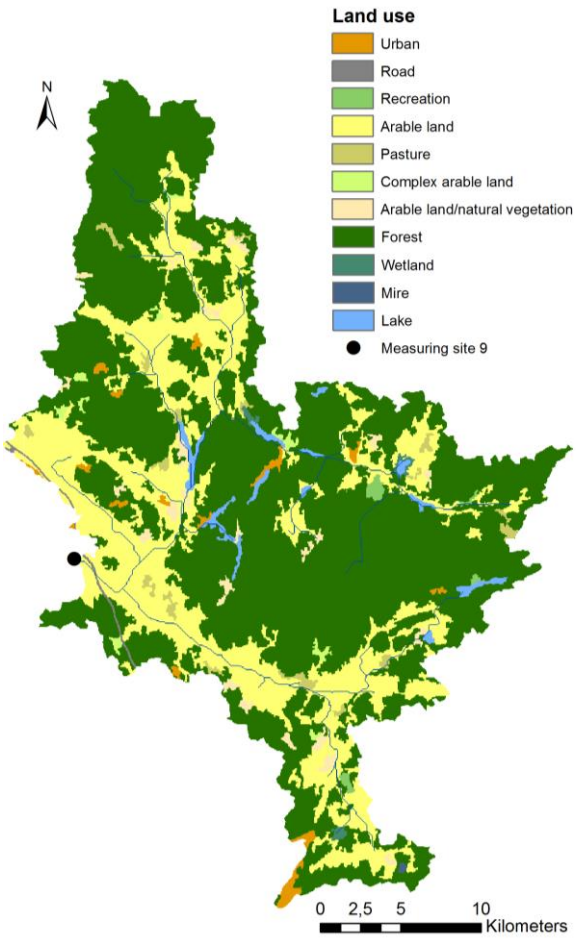

Figure 28: Catchment area and land use distribution in the catchment of site 9. The catchment was delineated using a DEM file with a resolution of 50×50 m.

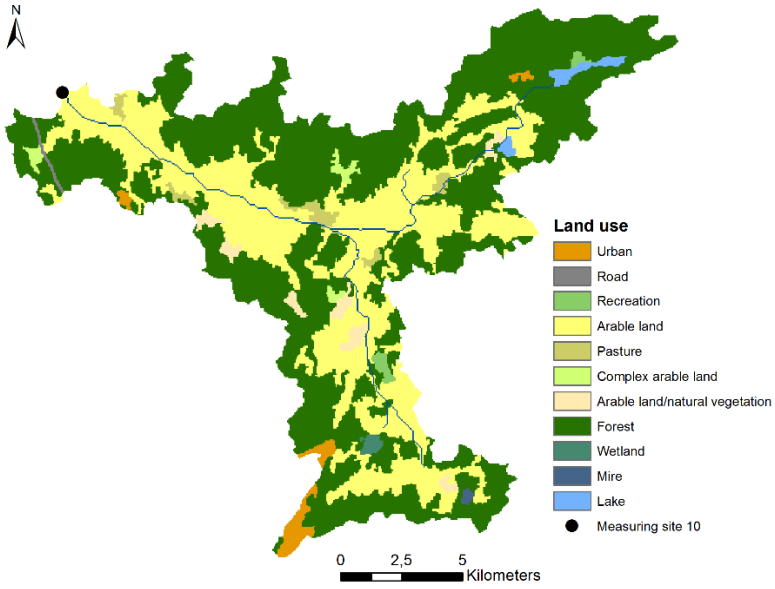

Figure 29: Catchment area and land use distribution in the catchment of site 10. The catchment was delineated using a DEM file with a resolution of 50×50 m.

B. MEASUREMENTS OF CO_2 CONCENTRATION

Raw data from measurements of CO_2 concentration at sites 1 – 10. All graphs represent measurements from the chambers, except at site 3 where measurements using the Eosense CO_2 sensor are also included in a separate graph. Values from when the sensor indicated that there was an error have been removed from the data.

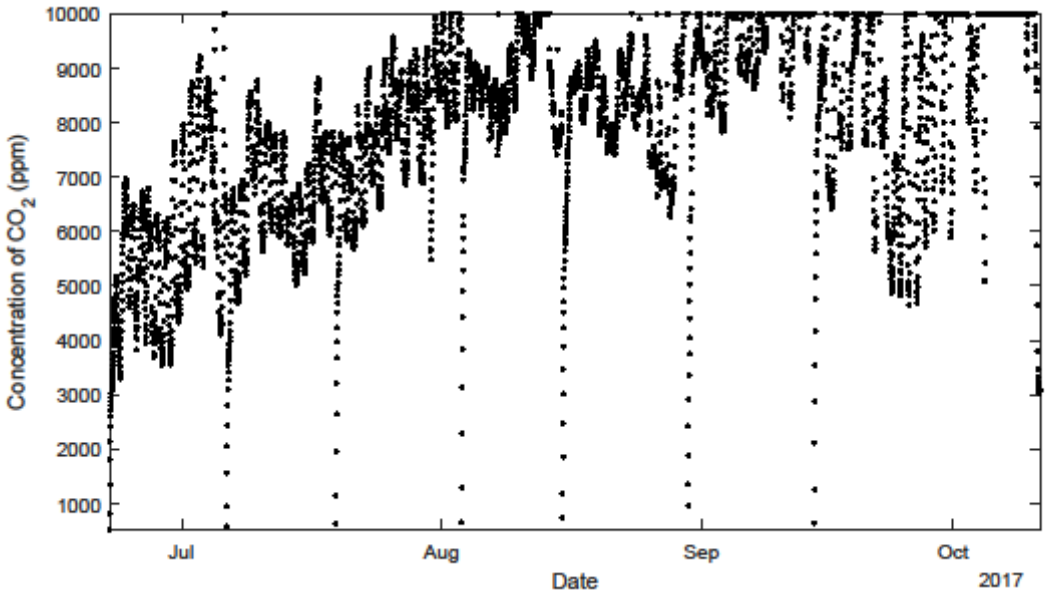

Figure 30: Concentration of CO_2 at site 1 during the whole measuring period.

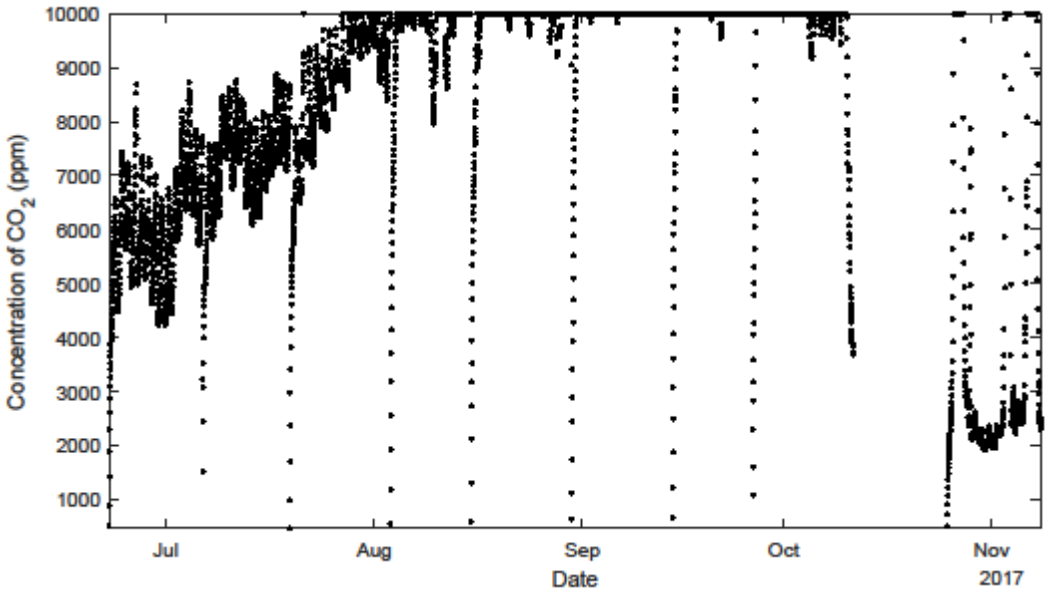

Figure 31: Concentration of CO_2 at site 2 during the whole measuring period.

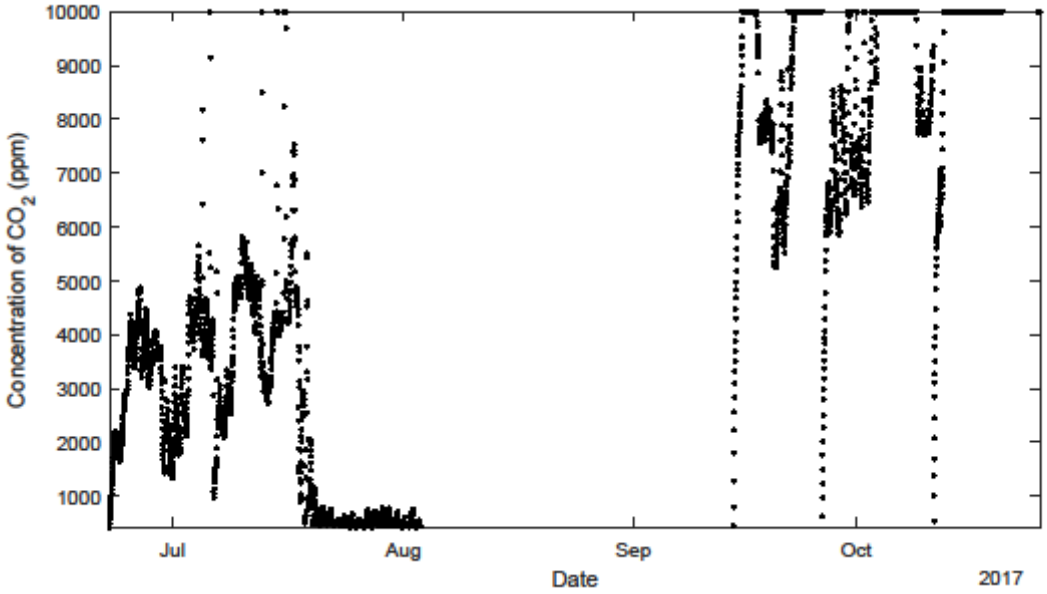

Figure 32: Concentration of CO_2 at site 3 during the whole measuring period from the chamber measurements.

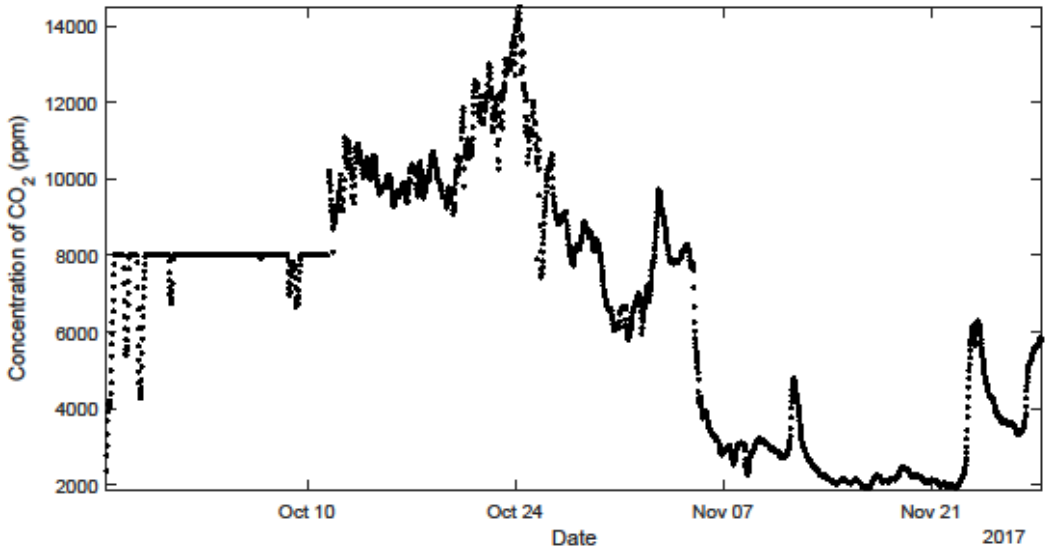

Figure 33: Concentration of CO_2 at site 3 with measurements from the new sensor that had an upper detection limit of 20 000 ppm.

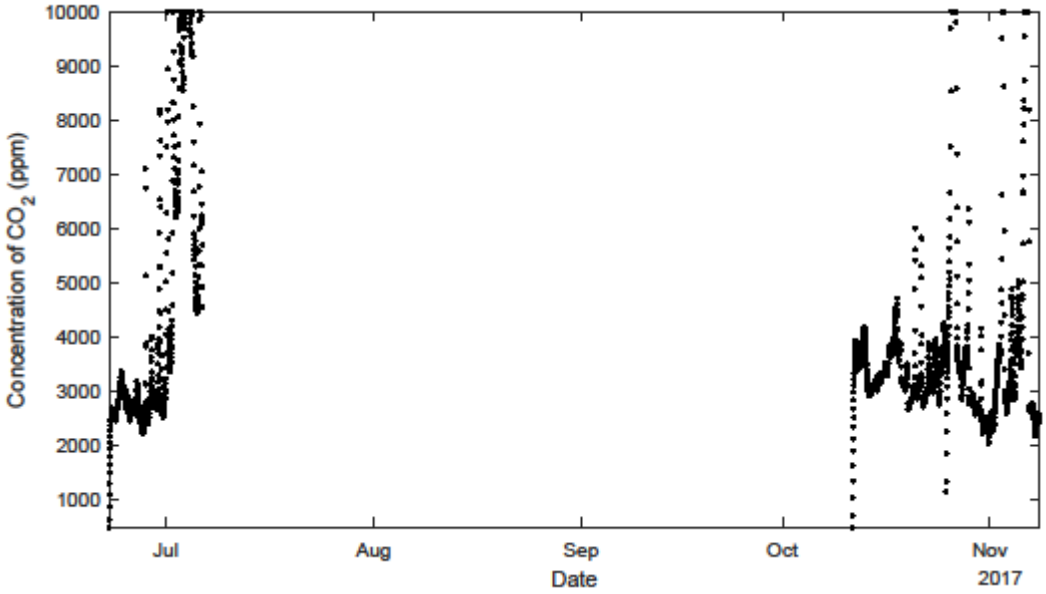

Figure 34: Concentration of CO_2 at site 4 during the whole measuring period.

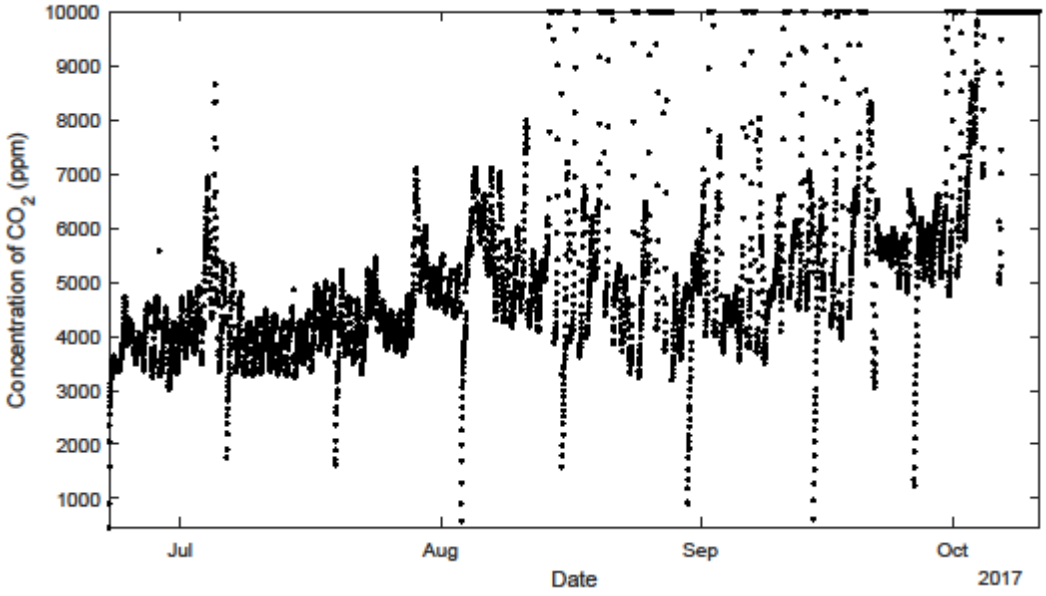

Figure 35: Concentration of CO_2 at site 5 during the whole measuring period.

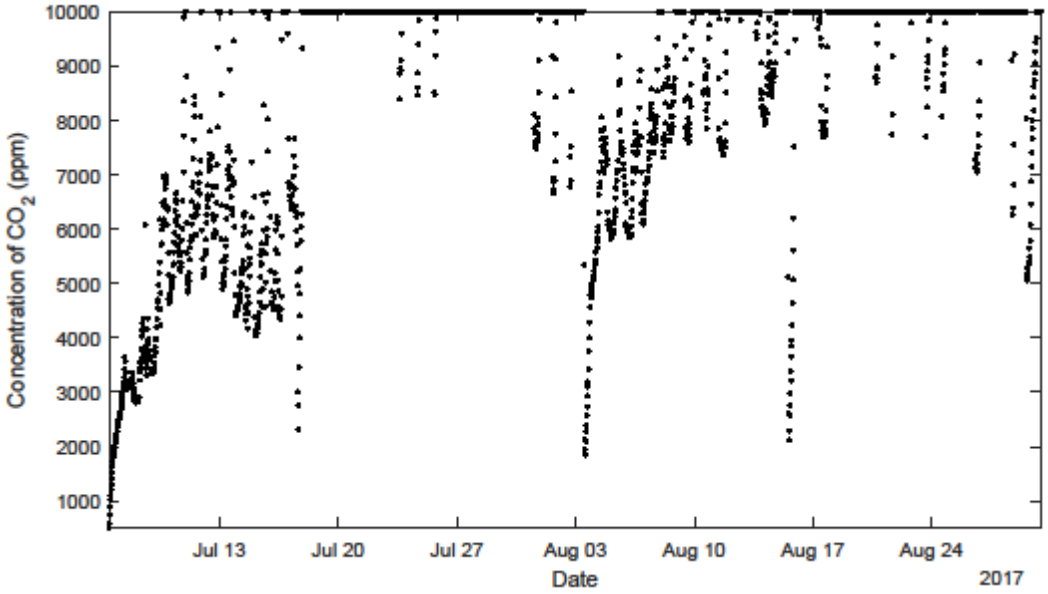

Figure 36: Concentration of CO_2 at site 6 during the whole measuring period.

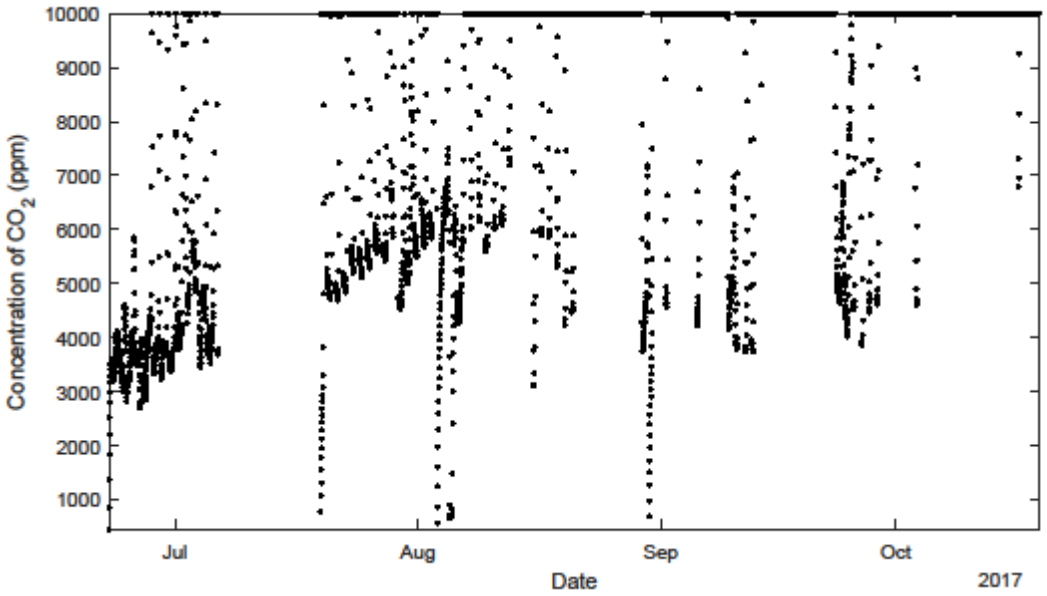

Figure 37: Concentration of CO_2 at site 7 during the whole measuring period.

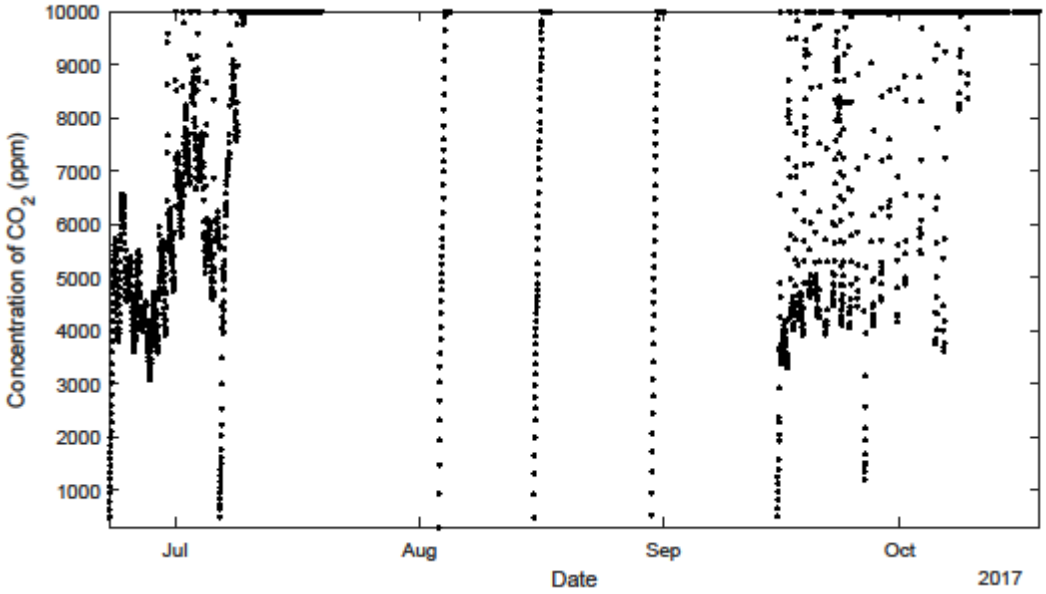

Figure 38: Concentration of CO_2 at site 8 during the whole measuring period.

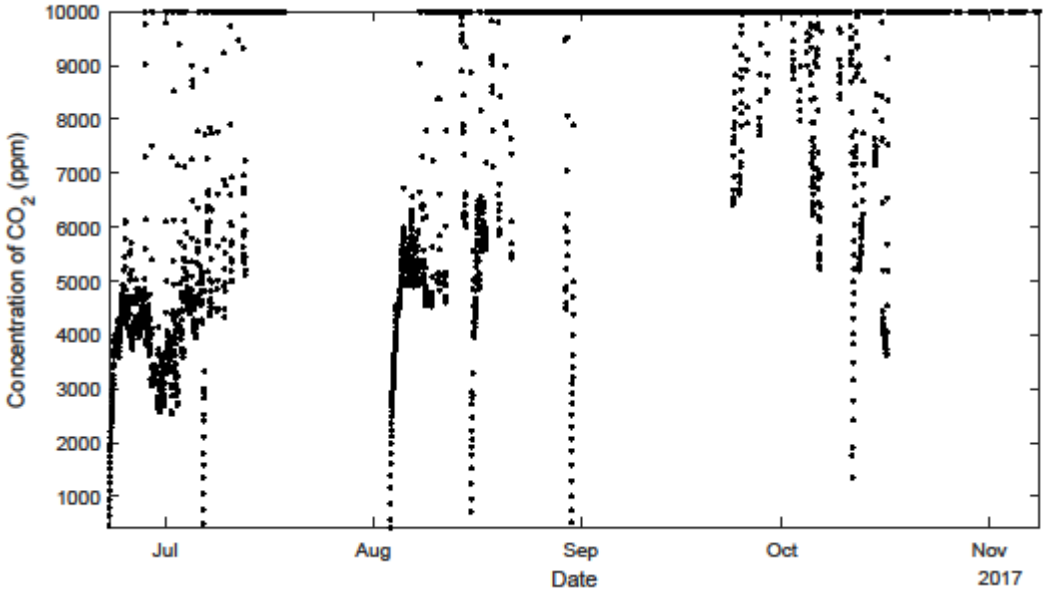

Figure 39: Concentration of CO_2 at site 9 during the whole measuring period.

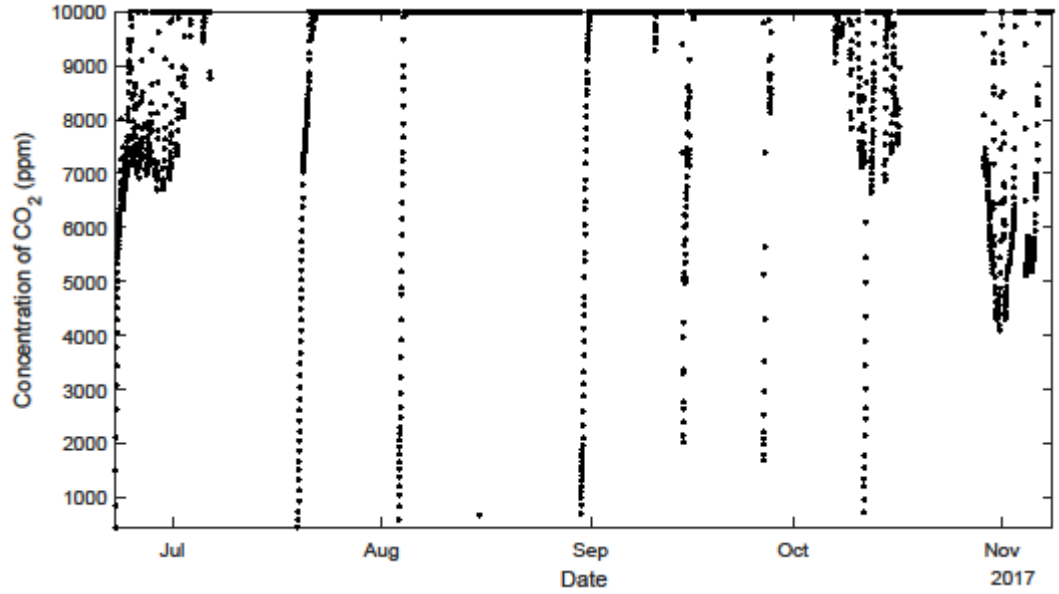

Figure 40: Concentration of CO_2 at site 10 during the whole measuring period.

C. RATING CURVE

The following rating curve was used to calculate discharge from height above the v-notch, which was given from pressure measurements at Sundbromark (site 3):

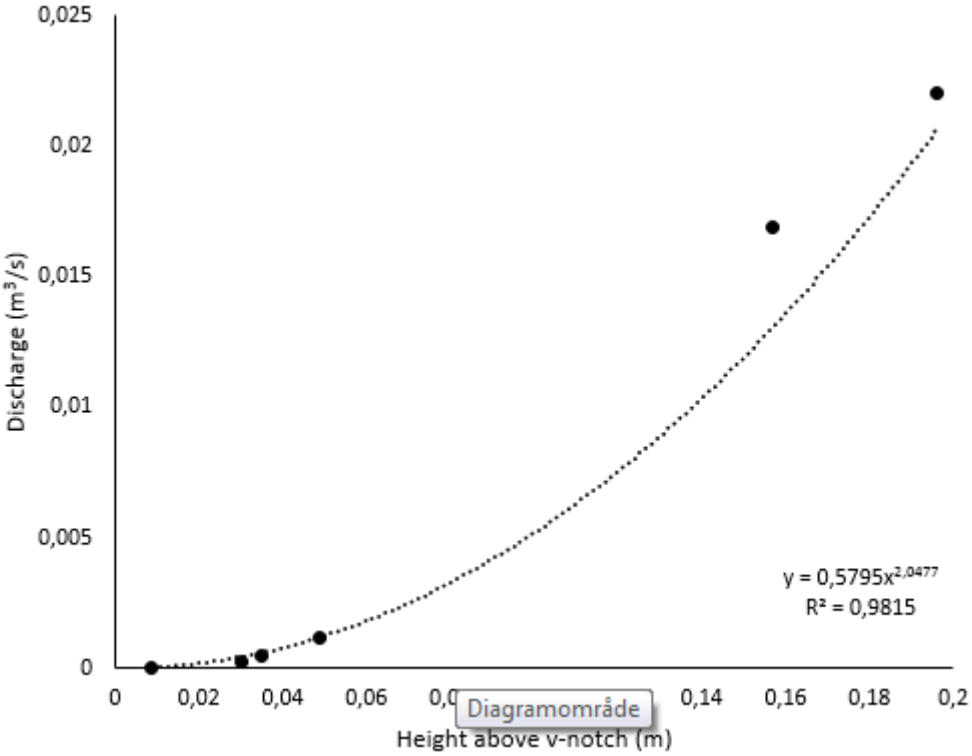

Figure 41: Rating curve for calculating discharge from pressure measurements that gave height above the v-notch at Sundbromark (site 3).

D. COORDINATES FOR FIELD SITES

Table 12: Summary of field sites and coordinates. X and Y coordinates are given in the coordinate system SWEREF99 TM and were collected using a GPS in the field.

Site	Name	X	Y
1	Librobäck	6 639 450	645 052
2	Jumkilsån	6 642 417	642 917
3	Sundbromark	6 644 998	642 090
4	Åloppebäcken	6 646 322	640 955
5	Trollbäcken	6 646 140	641 207
6	Fyrisån	6 644 305	645 507
7	Hågaån	6 632 527	646 124
8	Näsviken	6 630 572	645 445
9	Sävjaån	6 635 102	653 197
10	Storån	6 632 424	656 935

E. MATLAB CODE FOR DATA QUALITY CONTROL

The following code was used to perform quality control on data from site 5.

```
%Quality control for data from site 5
%Values that deviate > 10 % from the median of values +/- 4 h relative
%to the time for the measurement are removed

%Reading carbon dioxide concentration data from site 5
Upp5_june=xlsread('Upp5_monthly.xlsx');
Upp5_CO2=Upp5_june(:,2);
ExDates5 = Upp5_june(:,1);

%Defining vectors
subset=zeros;
Upp5_CO2filtered=zeros;
deviation=zeros;
date=zeros;

%The loop collects all values that fulfill the filter's requirements
%and adds them to a new vector
for i=10:395
    subset=[Upp5_CO2(i-8) Upp5_CO2(i-7) Upp5_CO2(i-6) Upp5_CO2(i-5)
    Upp5_CO2(i-4) Upp5_CO2(i-3) Upp5_CO2(i-2) Upp5_CO2(i-1)
    Upp5_CO2(i+1) Upp5_CO2(i+2) Upp5_CO2(i+3) Upp5_CO2(i+4)
    Upp5_CO2(i+5) Upp5_CO2(i+6) Upp5_CO2(i+7) Upp5_CO2(i+8)];
    deviation(i)=abs((median(subset)-Upp5_CO2(i))/median(subset));
    if deviation(i) < 0.1 && Upp5_CO2(i) < 10000
%Values are added to the new vector if they deviate < 10 % from the
median of +/- 4 h and if they do not equal 10 000 ppm (values of
10 000 ppm are assumed to be caused by errors)
        Upp5_CO2filtered(i)=Upp5_CO2(i);
        date(i)=ExDates5(i);
% Dates of the measurements are collected into a date vector
    end
end
```

```
%Removing zero values from the filtered data and the date vector
Upp5CO2filtrerad_nozeros=Upp5_CO2filtered(Upp5_CO2filtered~=0);
date_final=date(date~=0);

%Converting the Excel date number format to MATLAB dates
timevector_filtered = datetime(date_final,'ConvertFrom','excel');
t_unfiltered=datetime(ExDates5,'ConvertFrom','excel');

CO2_upp1_aug=[date_final; Upp5CO2filtrerad_nozeros]';

%Plotting series before and after filtering
plot(timevector_filtered,Upp5CO2filtrerad_nozeros,'.')
xlabel('Date')
ylabel('Concentration of CO2 (ppm)')
title('After filtering')
figure
plot(t_unfiltered, Upp5_CO2, '.')
title('Before filtering')
xlabel('Date')
ylabel('Concentration of CO2 (ppm)')
```