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Carbon dioxide dynamics in agricultural streams

Investigation of two streams draining catchments dominated by agricultural land

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ABSTRACT

In recent years, streams draining agricultural land has been suggested to exhibit high carbon dioxide (CO_2) concentrations when compared to streams draining other land-types. The transport of carbon from land to ocean is mainly occurring through the chain of inland waters, and with agricultural land today representing 40% of all continental area many of these inland waters are influenced by agricultural land. The aim of this study was to improve the understanding of CO_2 dynamics and its control in agricultural streams. Continuous data was collected from two catchments of different scales, near the city of Uppsala, Sweden. Both catchments are typical low-land catchments largely dominated by agricultural land. The measured CO_2 concentrations were analyzed to find temporal variations and differences in dynamics between the catchments. The interplay between CO_2 and parameters such as dissolved oxygen, discharge and conductivity were analyzed to determine the main drivers for CO_2 dynamics.

The findings show supersaturation of CO_2 concentration during the full length of the measurement periods, with mean CO_2 concentrations higher than what have been observed in streams draining other land-type catchments. Diel CO_2 cycles were found throughout most of the measurement periods, where manual measurements were conducted to confirm these findings. The diel CO_2 patterns were suggested to be heavily dependent on in-situ metabolic control while hydrological factors, such as sufficient discharge, seemed to be needed to produce a good diel CO_2 signal. CO_2 build-up is suggested to occur in the catchment soil and, when flushed out after rain events, result in an increasing CO_2 concentration. This might be one important driver for the high levels in CO_2 concentration found in the streams during summer and autumn. Analysis of the catchment areas suggest the percentage of agricultural land and the size of the catchment areas had an impact on hydrology, both for sufficient water flow to exist but also for the CO_2 response after rain events. More research is encouraged, where more parameters should be investigated, such as groundwater inputs and carbonate precipitation.

Keywords: Carbon dioxide, dynamics, streams, agriculture, oversaturation, metabolic control, hyrdological control

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REFERAT

Bäckar som dränerar åkermark har under de senaste åren blivit mer uppmärksammade på grund av nya studier som visat att dessa bäckar tenderar att ha högre CO_2-koncentration än bäckar som dränerar andra marktyper. Idag utgör cirka 40% av all kontinentalyta åkermark, då den huvudsakliga transporten av kol från land till hav sker genom sammankopplade vattendrag är därav en förståelse av åkermarkers dränering till bäckar av stor betydelse. Syftet med studien var att förbättra förståelsen av CO_2-dynamiken och dess påverkan på bäckar i jordbruksdominerade avrinningsområden. Kontinuerlig data samlades in, samt erhölls från tidigare mätningar, från två avrinningsområden med olika storlekar och markfördelningar nära Uppsala. Båda avrinningsområdena var typiska låglandsavrinningsområden som dominerades av åkermark. Data för CO_2-koncentration analyserades för att hitta kort- och långsiktiga variationer i CO_2-dynamiken samt undersöka hur denna dynamik skiljer sig mellan avrinningsområden med olika storlek och markfördelning. Samspelet mellan CO_2 och parametrar såsom vattenlösligt syre, vattenföring och konduktivitet analyserades för att hitta drivkrafter bakom CO_2-dynamiken.

Resultatet visar att de undersökta bäckarna var övermättade med CO_2 under hela mätperioden, samt att medelkoncentrationerna som uppmättes var högre än vad som observerats i bäckar som dränerar andra landtyper. En dygnsvariation av CO_2 observerades under större delar av mätperioderna, manuella prover utfördes för att stärka denna data. Den observerade dygnscykeln av CO_2-koncentrationen konstaterades korrelera med den in-situ metaboliska kontrollen medan hydrologiska faktorer, såsom ett tillräckligt högt vattenflöde, visade sig var viktigt för att en CO_2-dygnscykel ska existera. De mycket höga toppar av CO_2-koncentration som observerats under mätningarna tros bero på ackumulering av CO_2 i avrinningsområdenas marker, vilket under nederbörd utarmas och transporteras till bäcken. Vid jämförelse av de två avrinningsområdena föreslogs den procentuella andelen åkermark och storleken av avrinningsområdet ha en stor påverkan på hydrologin, både för att ett tillräckligt vattenflöde ska existera men också för CO_2-responsen vid större nederbördsmängder. Mer forskning behövs där fler parametrar börs ta i beaktning, till exempel in-situ karbonutfällning och inflöde av CO_2 via grundvatten, för att få en bättre bild över åkermarkens påverkan på CO_2-dynamik i bäckar.

Nyckelord: Koldioxid, koldynamik, bäckar, jordbruk, övermättat, metabolisk kontroll, hydrologisk kontroll

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PREFACE

This master thesis was conducted at Uppsala University in Sweden, with Marcus Wallin, research engineer in landscape carbon balance, as supervisor. The thesis correspond to 30 hp and is the final course in the Mater program in Environmental and Water Engineering. The subject reviewer was Erik Sahlée and examiner was Björn Claremar and Fritjof Fagerlund.

First of I want to thank Marcus Wallin for offering me the possibly to write my master thesis about this new and exciting research area. He has provided the necessary data and experience needed to complete this thesis. He has also given me invaluable support though the whole process, without which this thesis would have not been possible. I would also like to thank Jens Fölster for providing oxygen data in Hågaån and Mikael Östlund for helping me out with water table data in Hågaån after my pressure sensor malfunctioned.

A big thanks goes out to Erik Söderberg and Anna Jansson for the hospitality with providing a place to stay during all my visitations in Uppsala, it means much to me. I would also like to thank Elsa Malmer for great company during my late-night measurement trip, it was nice not being alone at 3 am in a cold and dark forest!

Albin Bostner, Uppsala 2020

POPULÄRVETENSKAPLIG SAMMANFATTNING

Koldioxid (CO_2) har en betydande roll för den naturliga växthuseffekten. Koncentrationen av CO_2 i atmosfären har stor betydelse för styrkan av växthusverkan och förhöjs denna koncentrationen resulteras detta i en förhöjd medeltemperatur, det vi idag kallar global uppvärmning. En bra förståelse för hur CO_2 rör sig mellan olika sfärer, den globala kolcykeln, är därav av hög prioritet. Ett område som under de senaste åren fått mer uppmärksamhet är transporten av kol från land till hav, vilket främst sker genom transport i inlandsvatten. Mycket av den mark som en gång i tiden var skogsmarker är idag transformerad till åkermarker, vilket idag, tillsammans med betesmark, representerar 40% av den kontinentala ytan. Då bäckar som dränerar åkermarker har observerats innehålla högre koncentrationer av CO_2 än bäckar som dränerar andra landtyper är det viktigt att förstå hur denna transformation av landskapet har påverkat koltransporten från land till hav.

Denna studie har inriktas på att undersöka CO_2-koncentration och dynamik i bäckar som dränerar åkermarker, gentemot tidigare studier som främst inriktat sig på bäckar som dränerar skogsmark. Studien undersöker två avrinningsområden som domineras av åkermark. Sensorer placerades ut i bäckar som dränerar dessa avrinningsområden där kontinuerlig data av CO_2 samt andra relevanta parametrar samlades in. Den erhållna CO_2-data analyserades för att undersöka hur CO_2-koncentration uppför sig över korta och långsiktiga tidsperioder i respektive bäck. Samtidigt insamlades data från övriga parametrar, vilket används för att förstå de huvudsakliga drivkrafterna bakom dessa variationer.

Den uppmätta CO_2-koncentrationen i bäckarna underskrider aldrig atmosfärskoncentrationen av CO_2, ca 410 ppm, och visar under vissa perioder på upp till 50 gånger högre värden än atmosfärskoncentrationen. Studien styrker även tidigare observationer där den uppmätta medelkoncentrationen generellt är högre i bäckar som dränerar åkermark än bäckar som dränerar andra landtyper, såsom skogsmark och våtmark. Därav visar detta på att åkermarker, gentemot andra landtyper, bidrar med en hög CO_2-koncentration till bäckar. CO_2-koncentrationen uppvisade en daglig cykel där koncentrationen var som högst under natten och som lägst under dagen. Detta föreslås vara relaterat till samspelet mellan fotosyntes och respiration i bäcken, där fotosyntesen dominerar under dagtid då solen skiner och respiration undernattetid då fotosyntesen avstannat.

Vid undersökning av hur CO_2-koncentrationen i bäckarna reagerade vid större nederbördsmängder föreslogs att ackumulering av CO_2 i avrinningsområdenas mark förekom. Höga temperatur under vår och försommar, tillsammans med den näringsrika och väldränerade marken som återfinns vid åkermarker, tillåter effektiv respiration i marken. När större nederbördmängder faller över avrinningsområdet för vattnet med sig den CO_2 som byggts upp i joden, vilket transporteras ned till bäcken. Detta tros vara en av de orsakerna till de höga CO_2-koncentrationerna som observerats i bäckarna.

Avrinningsområdenas storlek och andel åkermark visar sig betydande för CO_2-dynamiken. Främst föreslås vattenföringen, mängden vatten som strömmar i bäckarna, vara relaterad till avrinningsområdenas uppbyggnad. Desto mer åkermark avrinningsområdet består av, desto snabbare flödar vattnet till bäcken vid nederbörd, vilket beror på den effektiva dränering som åkermark medför. Avrinningsområdets storlek påverkar både volymen nederbörd som faller över avrningsområdet, samt hur lång sträcka vattnet måste färdas innan det når den dränerande bäcken. Detta gör att mindre avrinningsområden med högre andel åkermark dräneras snabbare, vilket ger höga vattenflöden under kort tid, medan större avrinningsområden med lägre andel åkermark får lägre vattenflöden men under en längre tid. Avrinningsområdets uppbyggnad och storlek är därav viktigt både för den hydrologiska kontrollen, men också för hur CO_2 uppför sig vid större nederbördsmängder.

Mer forskning behövs inom detta område där fler parametrar bör undersökas för att få bättre förståelse av drivkrafter bakom den uppmätta CO_2-dynamiken. Även bör utbredningen av åkermark, som föregått sedan bondesamhällets intågande, utvärderas för att se hur det har påverkat transporten av kol från land till hav.

Contents

1 INTRODUCTION

Carbon is stored in the atmosphere, ocean, soil, bedrock and in living biomass and is circulating between these pools through different processes. During shorter geological time scales this movement of carbon is usually in equilibrium but can, for different reasons, be altered (Archer 2010). If the equilibrium is shifted several important processes and functions on Earth can be affected, e.g. if an excess amount of carbon is transferred from soil deposits to the atmosphere the Earth's overall temperature can be increased (IPCC 2013). Hence, a correct description of how the global carbon is cycled is a central basis for understanding one of our times biggest challenge, global warming.

One essential component of the carbon cycle is the transport of carbon from land to ocean, which is mainly occurring through the chain of inland waters i.e. lakes, reservoirs, rivers and streams. In addition to the ocean transport of carbon, these inland waters store carbon in their sediments as well as releasing carbon to the atmosphere in the form of carbon dioxide (CO_2) and methane (CH_4) (Cole et al. 2007). Most river and streams are oversaturated with CO_2 (Raymond et al. 2013; Wallin et al. 2018) due to mineralization of organic matter either in the catchment soil or in-situ the steam. Stream CO_2 could also be derived from direct root-respiration in the catchment (Campeau et al. 2019) or as a weathering product from carbonate containing minerals (Cole et al. 2007).

Historically, streams and rivers were suggested to be passive transporters of carbon from soils to the ocean (IPCC 2007). More recently, this view has changed and today streams and rivers are suggested to be active sources of CO_2 to the atmosphere (IPCC 2013). Streams and rivers cover only 0.3-0.6% of Earth's surface but are suggested to emit 1.8 Pg C yr^{-1} to the atmosphere, corresponding to 70% of all inland water CO_2 emissions (Raymond et al. 2013). Wallin et al. (2018) estimated that CO_2 and CH_4 emissions from Swedish rivers and streams correspond to roughly 21% of the net C uptake from land use, land use change and forestry in Sweden. Consequently, if this source term would be ignored the terrestrial carbon sequestration would be considerably overestimated.

Despite the suggested importance of inland water CO_2 emissions, there are still critical knowledge gaps in our understanding, especially when it comes to certain land types. Anthropogenic activities have changed the Earth's landscape in several ways, for example through the transformation of forest to agricultural land. Today, roughly 40% of Earth's continental surface is covered by agriculture land (Foley et al. 2005). To fully understand the anthropogenic influence on the global carbon cycle it is important to understand how this transformation of the landscape has affected the C transport in inland waters.

Few studies have investigated CO_2 concentration patterns and emission in rivers and streams draining agricultural areas (Wallin et al. 2020). The studies that exist have indicated a higher concentration of CO_2 in agricultural streams when compared to streams draining other land-use types, such as forest, alpine, mire etc. (Bodmer et al. 2016; Borges et al. 2018; Wallin et al. 2020, 2018). Borges et al. (2018) found that the Meuse river in Belgium showed up to 5 times as high concentrations in agricultural stream than forest streams. The elevated concentration of CO_2 in agricultural streams compared to other stream types is suggested to be an effect of both hydrological and biological related mechanisms such as lower water velocity, which limit atmospheric gas exchange, and high nutrient availability (Bodmer et al. 2016).

Agricultural soil often contains a surplus of nutrients which can be exported to connecting surface waters at precipitation events or through leakage from groundwater to the stream. This bring nutrients such as nitrogen and phosphorus with it, together with organic matter, which increase the quantity of biodegradable material and the efficiency of which microbial life can degrade organic material (Bodmer et al. 2016). CO_2 is also thought to build up in the catchment area and flushed out during heavy precipitation (Wallin et al. 2020).

Agricultural streams tend to have a lower stream-atmosphere gas exchange rate when compared to other stream types, which may play an important role for the stream CO_2 concentration and its dynamics (Bodmer et al. 2016). The lower gas exchange is possibly related to the lower water velocity observed in agricultural streams which result in a lower turbulence (Borges et al. 2018; Kokic et al. 2018). Agricultural land is usually located in flat landscapes as it brings the best conditions for growing crops, but this also decreases water velocity which prevents efficient gas and water exchange (Hall & Ulseth 2020; Wallin et al. 2011). The lower gas exchange enhance the accumulation of CO_2 in the water (Borges et al. 2018). Other typical features of agricultural areas can also play an important role on the carbon dynamics. Efficient drainage systems which are typically found in agricultural soil, in form of pipes and trenches, could support quicker response to hydrological events, whereas high amounts of nutrients and organic matter transported to the stream during hydrological events could spike microbial activity (Wallin et al. 2020).

More research is clearly needed in order to understand how agricultural land effects the carbon transport from land to ocean. This thesis have investigated the quantity, dynamics and main drivers behind temporal variations of CO_2 in two agricultural streams which drains typical low-land catchments. The study was conducted in a headwater- and a fifth order catchment of different size (11.3 km^2 vs. 124.0 km^2) and with different agricultural influence (86% vs. 26%). The study was also complement by previous work in one of the catchments, e.g. Wallin et al. (2020), where CO_2 dynamics were analyzed during the drought of 2018.

1.1 OBJECTIVE & RESEARCH QUESTIONS

The aim of this study was to improve the understanding of CO_2 dynamics and its control in agricultural streams, while also investigate how land use distribution and size of the catchment affect the behavior of CO_2 in the streams they drain. As this research area is new and understudied this study hopes to bring more clarity to the role of agricultural streams in the inland C transport.

The specific research questions were:

- What are the levels of CO_2 concentrations in agricultural streams and which temporal variations can be observed?
- Do the patterns in CO_2 dynamics differ between a headwater- and a fifth order catchment?
- What are the main drivers of the CO_2 dynamics, and do they differ between streams of different size?

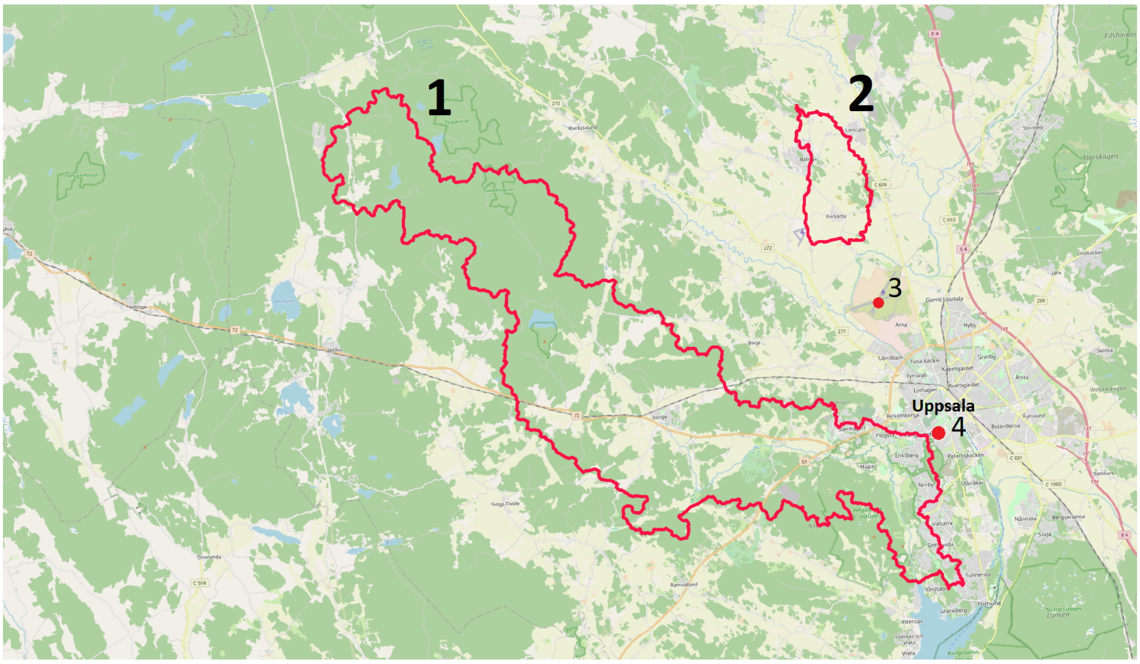
2 METHODS

2.1 SITE DESCRIPTIONS

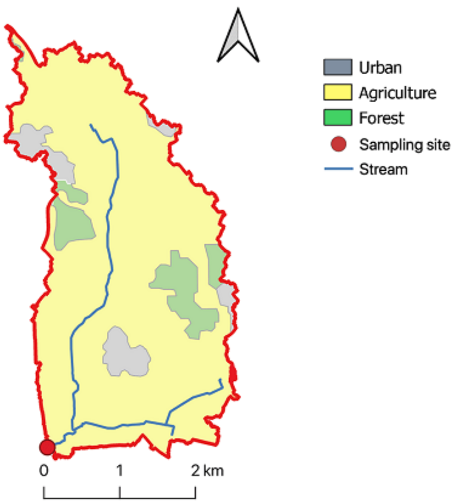
In this study, two catchments (the Hågaån and Sundbromark catchments) near the city of Uppsala, Sweden were investigated (Figure 1a). Uppsala is the fourth-largest city in Sweden with a population of just under 180 000 and is located at the 59°N latitude. The climate is temperate with a mean annual temperature of 5.3°C and with monthly means varying from -5°C (winter) to 16°C (summer). The mean annual precipitation is 535 mm and displays a seasonal pattern with lower monthly precipitation during spring and with higher values typically observed during summer and autumn (Table 1). Spring floods are common as a result of melting snow which accumulate during the cold winter months. The melt water results in high discharge during spring and early summer, despite these month exhibiting limited precipitation. The amount of sunshine per day varies heavily depending on the time of the year, from one hour or less (winter) to 8 or more hours (summer) (Table 1).

Table 1: Monthly and yearly reference values for temperature, precipitation and sunshine based on 30 year mean from 1961-1990. Sunshine data collected from measurement station Stockholm Sol, remaining data collected from Uppsala airport meteorological station, (SMHI 2020).

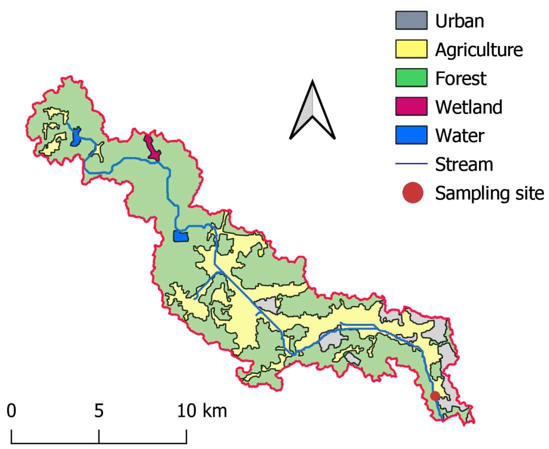
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Okt	Nov	Dec	Year
TEMP [°C]	-4.5	-4.6	-1.1	3.8	10.0	14.6	16.0	14.8	10.6	6.2	1.0	-3.0	5.3
PPT [mm]	37.2	25.3	28.9	28.0	31.8	43.9	71.3	67.3	57.4	49.3	51.1	43.0	534.5
Sunshine [$h \cdot d^{-1}$]	1	2	3	5	8	9	8	6	4	3	1	1	



a) Map over Uppsala and surrounding rural areas. Location and extent of the (1) Hågaån and (2) Sundbromark catchments is represented with red line, Uppsala airport meteorological station (3) and Geocentrum meteorological observatory (4) is marked with red dot.



b) Land use and location of measurement station (red dot) in the Sundbromark-catchment.



c) Land use and location of measurement station (red dot) in the Hågaån-catchment.

Figure 1: Location and land use for each catchment area (CORINE Land Cover 2018; EROS 2017).

2.1.1 Sundbromark

The Sundbromark catchment is located 10 km north of Uppsala at N59°55′ E17°32′ (Figure 1a). The catchment area covers 11.3 km^2 and consist of 86% agricultural land, 6% urban areas and 8% forest land (Figure 1b). The elevation ranges from 41 m.a.s.l. at the highest peaks to 13 m.a.s.l. at the outlet. The catchment soils consist mainly of post glacial clay, especially at lower elevation, and with influence of glacial clay and silt at higher elevations. Carbonate minerals are present in the soils and make the stream water slightly basic, pH = 7.4-8.4. As the major part of the catchment area are covered by agricultural land it is mainly artificially drained where pipes and trenches transport water to the stream (Wallin et al. 2020).

2.1.2 Hågaån

The Hågaån catchment stretches from 22 km north-west of Uppsala to south of the city where the stream drains into Ekoln, a sub-basin of lake Mälaren, N59°80′ E17°60′ (Figure 1a). The catchment area covers 134.0 km^2 and consist of 26% agricultural land, 6% urban areas, 67% forest land and 1% water and wetland (Figure 1c). The elevation ranges from 70 m.a.s.l in north-west to 20 m.a.s.l. at the measurement location and 6 m.a.s.l. at the outlet in Ekoln. Although the catchment is dominated by forest land the stream runs mainly through an agricultural landscape during the downstream half of the catchment area.

2.2 CONTINUOUS SENSOR-BASED MEASUREMENTS

The measurements in the Sundbromark catchment were conducted from 2019-04-16 to 2019-11-06. Power loss reslutet in missing data between 2019-05-11 and 2019-05-21. The measurements in Hågaån was conducted from 2020-02-26 to 2020-08-01. Power loss reslutet in missing data between 2020-03-04 and 2020-03-15. Data used in this report is based on Central European Time (UTC +1).

The sensor based measurement setup used in the current study was almost identical to the one described in Wallin et al. (2020). CO_2 concentration was measured with a EosGP sensor (Eosense, Dartmouth, Canada). To prevent biofouling the CO_2 sensor was covered with copper tape. Stage height (height of the water table) was measured with pressure transducers in Sundbromark (1400, MJK Automation, Sweden) and Hågaån (WT-HR 64K, Intech INSTRUMENTS, New Zealand). For Sundbromark, continuous discharge data was calculated based on stage height data, together with a known stage height-discharge rating curve (Holmqvist 1998; Wallin et al. 2020). A thermocouple (Type T) and a CS547A-L probe (Campbell, UK) were used for temperature and electrical conductivity measurements respectively. For oxygen measurement a minDot oxygen logger (PME, USA) and Aqua TROLL 600 (In-Situ, USA) was used in Sundbromark and Hågaån receptively. The oxygen data collected at Sundbromark was only considered reliable from deployment of the sensor on May 21 to June 27, the later period was only used for illustration purposes due malfunctioning of the oxygen sensor.

The measurement sensors at the Sundbromark catchment, except the pressure transducer, were placed under water connected to a wooden rod just upstream of a V-notch weir (Figure 2). The pressure transducer was placed at a stilling well representing the stream water level at the V- notch weir. For Hågaån, the sensors were tightly connected on an already existing measurement platform (Figure 3), roughly 50 cm below the water surface at the start of the measurements, but had to be manually lowered when the water table dropped during dryer periods. Due to malfunctioning of the pressure transducer in Hågaån, an operational sensor 100 meter downstream was used to obtain water table data.

For both measurement locations a CR1000X data logger was used to sample and store data from the sensors. The measurement interval were 1 minute in Sundbromark and 5 seconds in Hågaån, with 30-min mean values being stored. All analysis was made on the 30 min mean values.

The dataset was complemented with meteorological data including precipitation, air temperature and incoming shortwave radiation (global radiation). Hourly resolution of precipitation and air temperature data was gathered from Uppsala airport meteorological station (SMHI), while data for incoming shortwave radiation (sampled every 10 min) was obtained from Geocentrum meteorological observatory (Uppsala University, department of Earth Sciences). See location of each station in Figure 1a.

Figure 2: The measurement location in the Sundbromark-catchment in May 2018. The sensors, except the pressure transducer, is placed under water on the wooden rod just upstream the V- notch weir.

Figure 3: The measurement location at Hågaån-catchment in February 2020. The left picture exemplifies the stream environment in the catchment area. The right picture shows the measurement setup were the white and black box contains the logger and the battery, respectively. The measurement sensors is placed under water on the black rod which extends into the water.

2.3 SENSOR BASED CALCULATIONS

The CO_2 sensor outputs, which were expressed in ppm, were corrected for variations in temperature and pressure (atmospheric and water depth) using the same method described in Johnson et al. (2010) and Wallin et al. (2020). The output was recalculated and expressed in the unit of mg C L^{-1}.

2.4 MANUAL CO_2 SAMPLING AND ANALYSIS

To validate the sensor based CO_2 measurements, manual samples were collected at the measurement station in Hågaån. The sampling was carried out during a 24 hr period from 2020-05-11 at 11:00 to 2020-05-12 at 9:30, with six sampling occasions evenly distributed during the period. Triplicate samples were taken at each sampling occasion. The samples were collected using the headspace method, which is a technique in which volatile material, in this case CO_2, is extracted from a heavier sample matrix, water, to later by analysed by gas chromatography (Kokic et al. 2015; Wallin et al. 2020). For each sample, 30 ml of stream water was collected using a 60 ml syringe, and where 30 ml of ambient air was introduced to create a headspace. The syringes were shaken for 2 minutes before the headspace volume was transferred to a separate syringe for storage prior to analysis. The samples were analyzed within 24 h. The equilibrated headspace (20-30 ml) was analyzed using an Ultraportable Greenhouse Gas Analyzer (UGGA) (Los Gatos Research, USA) equipped with a soda lime filter and manual injection port. The instrument was calibrated with three known standard CO_2 mixtures (395, 1000 and 5000 ppm). To calculate in situ CO_2 concentration the UGGA-determined ppm-values using Henry's law was used. The law consider stream temperature (Weiss 1974), atmospheric pressure, the added ambient air, as well as ratio between the water and air volume in the syringe.

2.5 CATCHMENT DELINEATION

The delineation of the two catchments was performed in QGIS 3.10 using a high-resolution (30 m) digital elevation model derived from satellite LIDAR data (STRM) (EROS 2017). Land use distribution data was derived from the Corine Land Cover, which is based on the satellite imaging programme, IMAGE2000 (CORINE Land Cover 2018).

2.6 DATA PROCESSING

Matlab 2020a was used for all data analysis. Spearman's rank correlation test was used for local regression analysis of relationships between CO_2 and other relevant parameters. The correlations were considered significant if p- value <0.05.

2.6.1 Continuous Wavelet Transform and Wavelet Coherence Analysis

To study the full CO_2 sequence's variability over time a continuous wavelet transform (CWT) analysis was used. CWT was chosen over Fourier transformation as CWT does not rely on stationary processes, which is advantageous when working with environmental time series for the reason as they exhibit varying mean and variance over time (Riml et al. 2019). CWT is also beneficial for finding localized intermittent periodicities which is not possible with the Fourier transformation (Riml et al. 2019). The analysis was accomplished using the wavelet toolbox in Matlab with the function (cwt). To analyze similarities in the variability of CO_2 with other parameters, a cross wavelet transform (XWT) and wavelet coherence (WTC) were used. These are both combined in the function (wcoherence) in Matlab where they co-operate to both show common power and relative lag between parameters. For all wavelet analysis the wavelet 'morlet' was used.

The Matlab functions cwt and wcoherence produces a so-called scalogram, which is the absolute value of the CWT/WCO plotted with logarithmic frequency on the y-axis and time on the x-axis. The CWT scalogram shows magnitude, i.e. the frequency of co-occurring patterns in the data, by using colors where bright is associated with high magnitude and dark with low magnitude. The WCO scalogram show coherence, i.e. correlation between the two parameters in the time-frequency plane, by also using bright and dark colors to indicate high and low coherence. The scalogram also visualize the "cone of influence" by a white dashed line where edge effect become significant due to limitations of the wavelet, which means that the magnitude/coherence on and inside the white dashed line is not reliable. The WCO analysis display arrows where coherence is high, which is spaced in time and scale, and represent the phase lag between the two parameters. The direction of the arrows corresponds to the unit circle and is directly related to the frequency of which the coherent data exhibit.

2.6.2 Paired O_2-CO_2 Analysis

To analyze the relationship between dissolved oxygen and CO_2 a technique called Paired CO_2-O_2 was used (Vachon et al. 2020). CO_2 and O_2 should theoretically follow a 1:-1 relationship in an aquatic system with no influence of additional drivers, i.e. where the so called respiratory quotient (RQ) and photosynthetic quotient (PQ) is 1. This means that when a CO_2 molecule is consumed by photosynthesis an oxygen molecule is produced, and with the opposite occurring during respiration. If this is not the case there must be other drivers involved, which this technique helps to identify. The analyzing method required recalculation of the measured CO_2 and O_2 concentrations (mg C L^{-1} and mg L^{-1}) to departure concentration values (µmol L^{-1}), where the concentration at equilibrium (atmospheric concentration) was subtracted for both CO_2 and O_2. The departure values were then plotted against each other which generated a concentrated cluster of values, called departure cloud. Depending on the positioning of the departure cloud in the coordinate system, different assumptions could be made concerning processes controlling the observed CO_2 and O_2 patterns (Figure 4). In addition to describe the metabolic control of the system of interest, the analysis can also give valuable information to other chemical and physical processes affecting the C cycling in the aquatic system (Vachon et al. 2020).

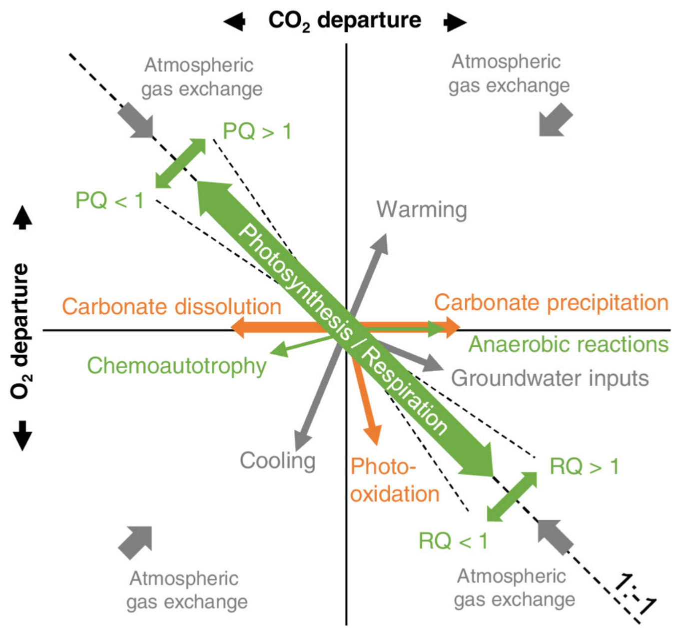


Figure 4: Conceptual figure showing potential role of different drivers when analysing the position of the departure cloud. The arrows in the figure represent biochemical processes (green), chemical processes (orange) and physical/hydrological processes (light gray). The 1:-1 relationship is represented as a dashed line. Figure taken with permission from Vachon et al. (2020).

3 RESULTS

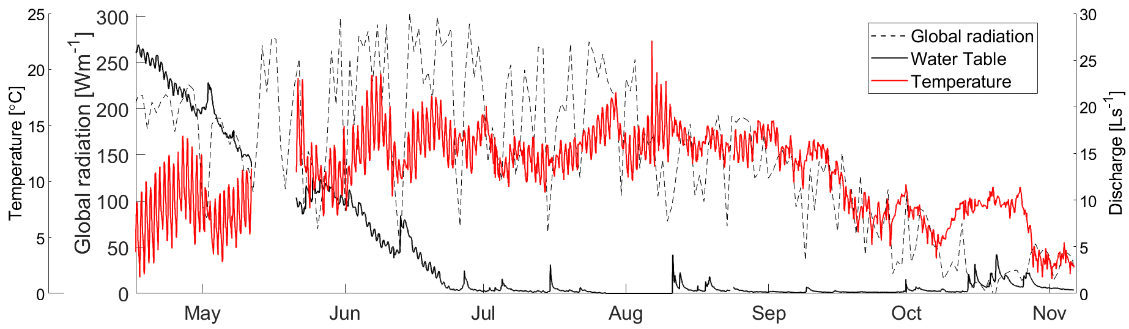
3.1 HYDROLOGICAL AND METEOROLOGICAL CONDITIONS

The mean annual temperature of 2019, measured at the Uppsala airport meteorological station, was 1.7 °C higher than the long term average (30 year mean from 1961-1990), where every month except January, May, July and October had a higher average temperature than normal. The annual precipitation 2019, measured at the Uppsala airport meteorological station, was 173 mm above average and was particularly high in July and August with 107.9 mm and 103.5 mm respectively. The temperature during the early months in 2020 (January-May) was high when compared to the long term average, particular January which was 7.8 °C higher. The precipitation was low during the start of the year (January-April) but had more rainfall in May, June and July than the long term average (Table 2).

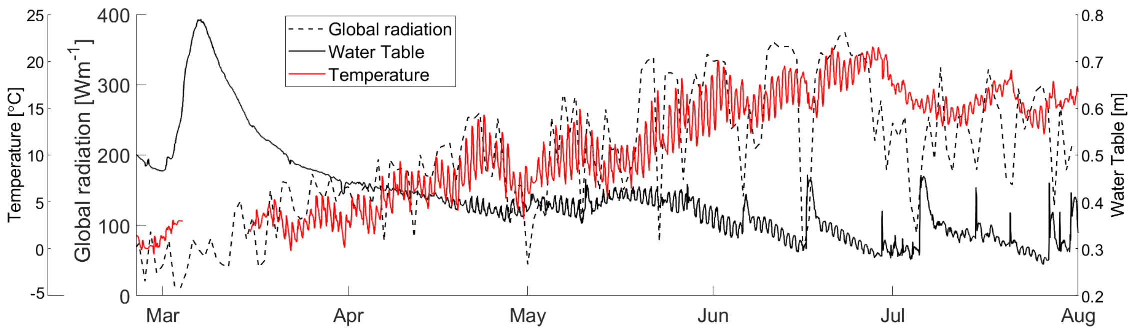
Table 2: Monthly and yearly average temperature and precipitation for 2019 and 2020 for the Sundbromark and Hågaån catchments. Data collected from Uppsala airport meteorological station (SMHI 2020).

2019	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Okt	Nov	Dec	Year
TEMP [°C]	-4.3	0.4	1.4	6.1	9.8	17.0	15.8	16.5	11.4	6.1	2.2	1.4	7.0
PPT[mm]	33.7	27.1	49.7	5.1	57.3	34.8	107.9	103.5	61.2	71.8	78.9	76.5	707.5
2020													
TEMP [°C]	3.3	1.7	2.3	5.7	8.3	17.3	15.4	-	-	-	-	-	-
PPT[mm]	18.6	23.9	23.7	13.3	45.9	73.3	77.6	-	-	-	-	-	-

A diel pattern, a pattern that is reoccurring daily, was observed for water temperature in both streams where the water temperature reached its maximum in the evening and minimum in the morning (Figure 5a, 5b). For both locations, the maximum discharge/water table was observed in early spring while the minimum was observed during summer and fall. For Sundbromark the discharge decreased throughout late spring and early summer to become stable at low flow rates. From 25 July to 11 August the discharge in Sundbromark was either zero or below 0.1 Ls^{-1}. In Hågaån the water table increased considerably in early March which was followed by a rapid drop from middle to end of March. Several rain events occurred in June and July which temporary increased the water table. The global radiation had an average intensity over 200 Wm^{-1} per day in both catchments areas from May to August (July to August for Hågaån), but during winter, early spring and late fall the intensity was considerably lower (<100 Wm^{-1}).



a)



b)

Figure 5: Time series for water temperature, discharge/water table and global radiation (mean per day) in Sundbromark (a) and Hågaån (b). Water temperature and discharge/water table were obtained by sensors at the measurement locations, global radiation was obtained from the meteorological station at Geocentrum in Uppsala.

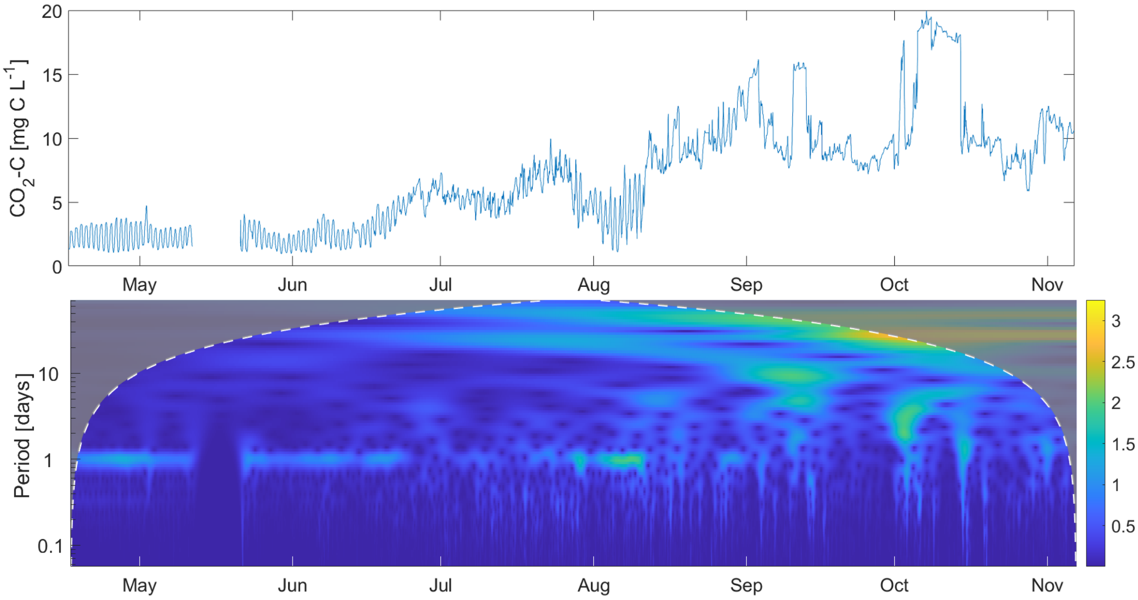
3.2 STREAM CO_2 DYNAMICS

3.2.1 Continuous stream data

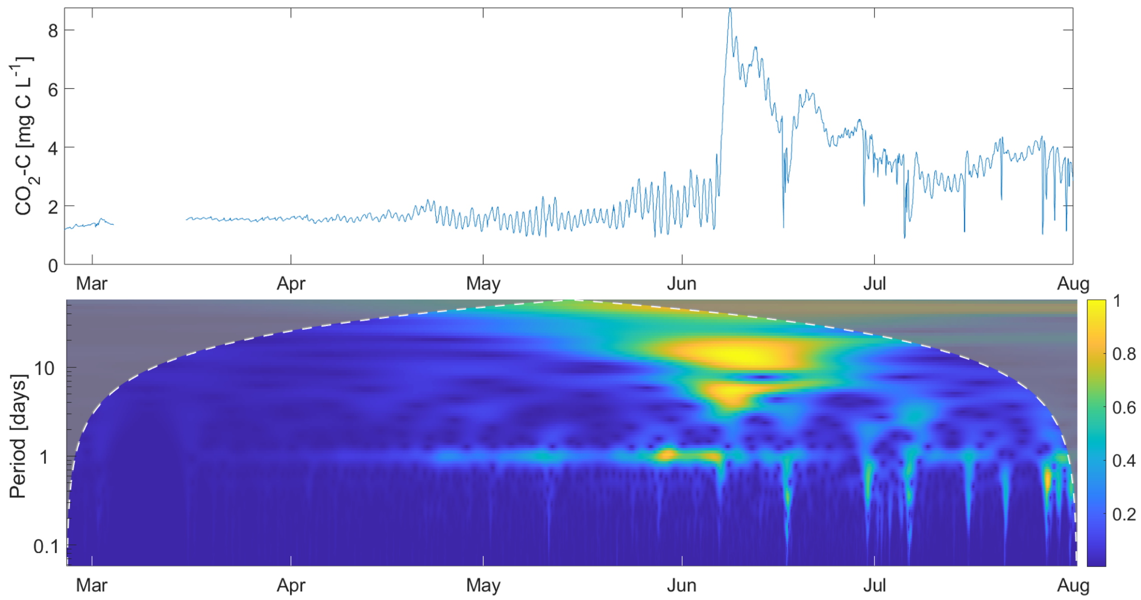
The mean CO_2 concentration (2019-04-16 to 2019-11-06) in Sundbromark was 7.0 mg C L^{-1}, with an interquartile range (IQR) of 6.3 mg C L^{-1}, corresponding to a pCO_2 of 10995 µatm (IQR=9541 µatm). From the start of the measurements, in the middle of April, to the middle of June the mean concentration and variability was lower with 2.2 mg C L^{-1} (IQR=1.35 mg C L^{-1}), the remaining measurement period had a higher variability and a high CO_2 concentration which peaked in the middle of August to November (Figure 6a). The highest levels registered plateaus at 19-20 mg C L^{-1} and was likely a result of the sensor's measurement range. The mean CO_2 concentration in Hågaån (2020-02-25 to 2020-08-01) was 2.6 mg C L^{-1} (IQR=2.0 mg C L^{-1}) corresponding to a pCO_2 of 4524 µatm (IQR=4503 µatm). The mean CO_2 concentration had a low variability until the start of June (IQR=0.3 mg C L^{-1}), although the diel signal increased slightly over time (from 0.1 mg C L^{-1} in the end of March to 1.0 mg C L^{-1} in the end of May). In the start of June, the CO_2 increased sharply and the remaining period had a much higher concentration and variability (4.2 mg C L^{-1}, IQR=1.5 mg C L^{-1}).

From the continuous wavelet transformation (CWT) analysis of CO_2 in Sundbromark, a diel pattern was observed from the start of the measurements to right before July (Figure 6a). During this period the CO_2 data was ”smooth”, where the concentration of CO_2 peaked in the morning, from 6 am to 12 pm, and reached its minimum in the evening, from 6 pm to 12 am. As July passed, the data became more ”rough” and variable, but with the absence of a clear diel cycle. At the end of July to the middle of August an occasional drop in concentration was detected. This period showed a strong diel pattern in the CWT analysis. The corresponding CWT analysis for Hågaån showed a diel pattern in CO_2 for the full measurement period with a periodicity of one day. The highest magnitude was found from the middle of May to August, though the magnitude from middle of June to August was inconsistent (Figure 6b).

The distribution of CO_2 data in Sundbromark during the full measurement period was multimodal and had four distinct peaks at 1.5, 2.9, 5.3 and 9.3 mg C L^{-1} (Figure 7a). For the individual months, April, May, July, August and October the distribution was bi-modal, for the remaining months no distinguishable distribution was observed. In Hågaån a distribution with a distinct peak of 1.5 mg C L^{-1} was observed (Figure 7b).

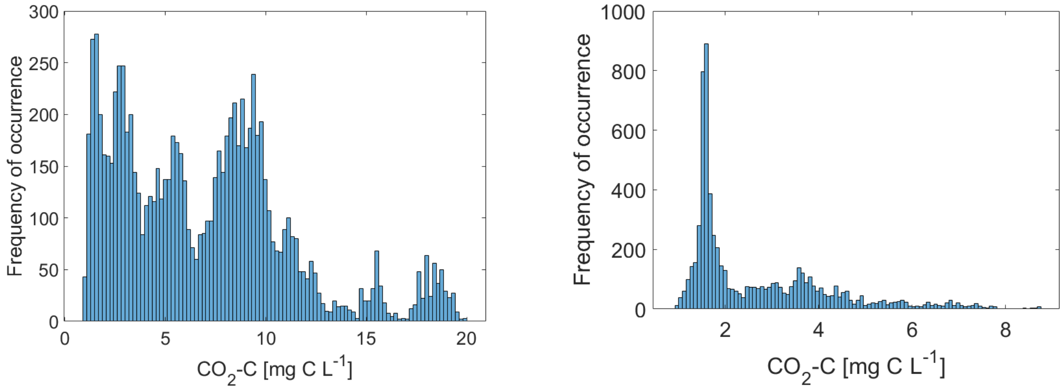


a)



b)

Figure 6: Time series (top) and CWT scalogram (bottom) for CO_2 in Sundbromark (a) and Hågaån (b). The bright areas in the CWT scalogram indicates a high magnitude, meaning that nearby data follow similar periodicities. The white dashed line indicates the ”cone of influence” where edge effects occur, i.e area on and outside the line is not reliable. During May (Sundbromark) and March (Hågaån) data is missing which interrupts the time series and scalograms.



a) b)

Figure 7: Distribution of CO_2 data for full measurement period in Sundbromark (a) and Hågaån (b).

3.2.2 Manual sampling

The manual samples collected in Hågaån (2020-05-11 11:00 to 2020-05-12 09:30) exhibited a clear variation of CO_2 concentration during the sampling period, with a minimum of 1.3 mg C L^{-1} (15:00) and maximum of 2.4 mg C L^{-1} (03:30). The manual samples followed the same diel pattern as the sensor data and had an offset of ca. 0.1 mg C L^{-1} on average compared with the sensor data (Figure 8). Methane (CH_4) showed an opposite trend where lowest concentration was observed during the night/morning and the highest during the evening (Appendix A.1).

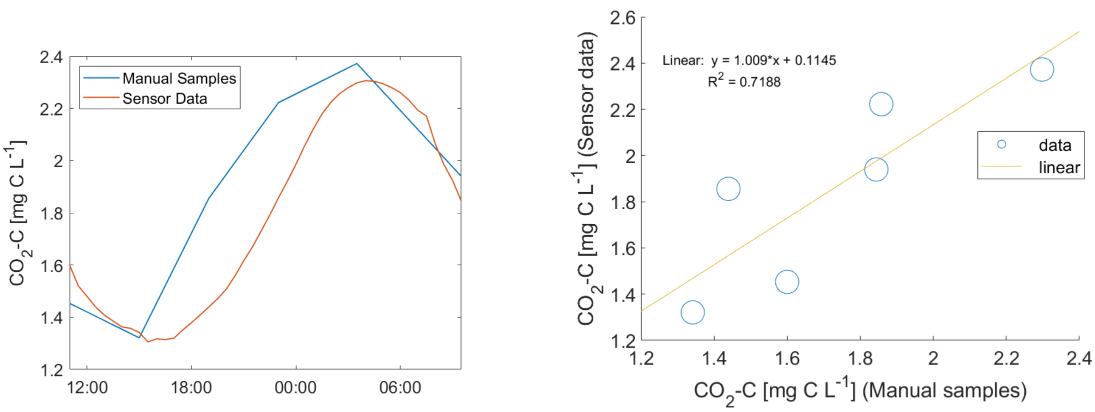


Figure 8: Time series (left) of CO_2 for manual samples and sensor data in Hågaån (2020-05-11 11:00 to 2020-05-12 09:30). Linear fitting (right) for relationship between manual samples and sensor data.

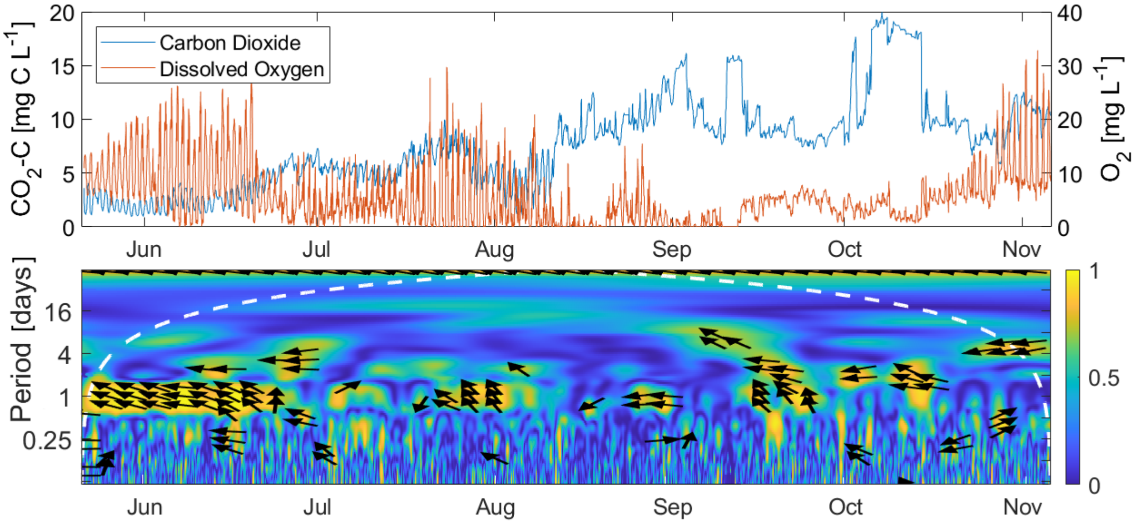
3.3 CONTROLS ON CO_2 DYNAMICS

3.3.1 Metabolic control

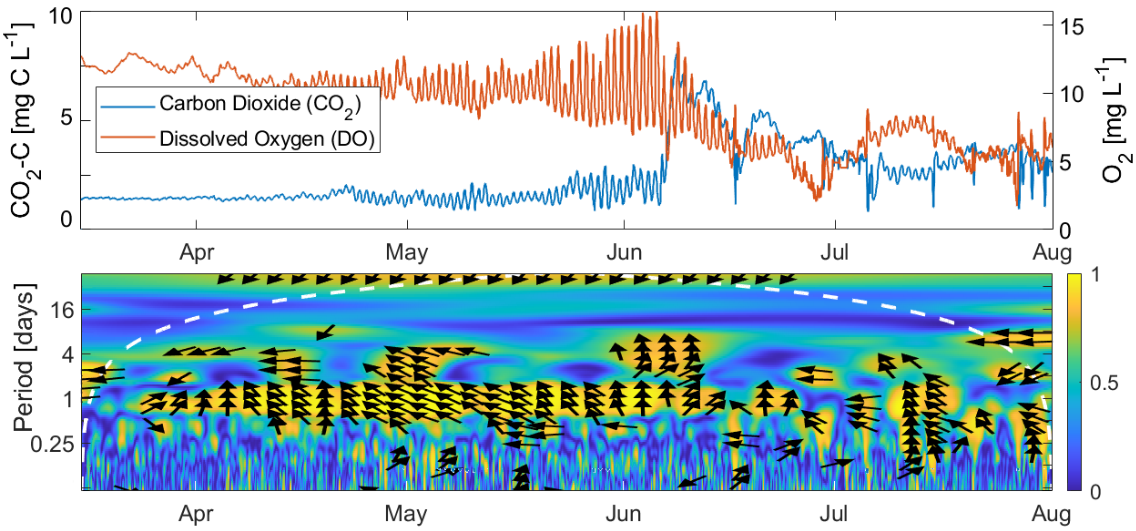
For Sundbromark, the highest dissolved oxygen (DO) concentration was observed during the summer and lowest during the fall (Figure 9a). For Hågaån, the maximum concentration was observed in the spring and lowest during the summer period (Figure 9b). In general, the CO_2 concentration displayed a negative correlation compared to DO, where CO_2 was high when DO was low and vice versa, indicating an interplay between CO_2 and DO. During the first ten days after deployment of the oxygen sensor in Sundbromark the mean DO was 10.1 mg L^{-1}. The DO reached maximum concentration in the afternoon/evening, from 2 pm to 6 pm, and descended to minimum during the night/morning, from 12 am to 4 am (Appendix A.2). The same pattern was observed in Hågaån for the full measurement period.

Wavelet coherence (WCO) analysis of CO_2 and DO in Sundbromark showed a good coherence with a periodicity of one day from the start of measurement period (21 May) to the end of June (Figure 9a). Correlation with a periodicity of one day was sporadically visible throughout the remaining measurement period. WCO analysis of CO_2 and DO in Hågaån displayed a coherence from end of April to July (Figure 9b). The arrows show a relative lag of approximately 0.4 periods (10h), meaning that the CO_2 diel cycle lags ten hours behind the DO diel cycle.

Paired CO_2- O_2 analysis during the first 10 days after deployment in Sundbromark depicts the departure cloud to lie slightly negative on the y axis and positive on the x axis, 196 mmol L^{-1} CO_2 and -55 mmol L^{-1} O_2 (Figure 10). For Hågaån, departure clouds from Paired CO_2- O_2 analysis during March, April and May showed a higher variability in O_2 than CO_2, and where June and July had a much higher CO_2 variability (Figure 11). In both catchment areas, the CO_2 concentration was always supersaturated while the O_2 concentration was pending between being supersaturated and unsaturated.



a)



b)

Figure 9: Time series (top) and WCO scalogram (bottom) for CO_2 and DO in (a) Sundbromark and (b) Hågaån. The brighter areas indicates high coherence while arrows in this area indicates the time lag between variables. The white dashed line indicates the "cone of influence" where edge effects occur in the coherence data, i.e data on and outside the line is not reliable.

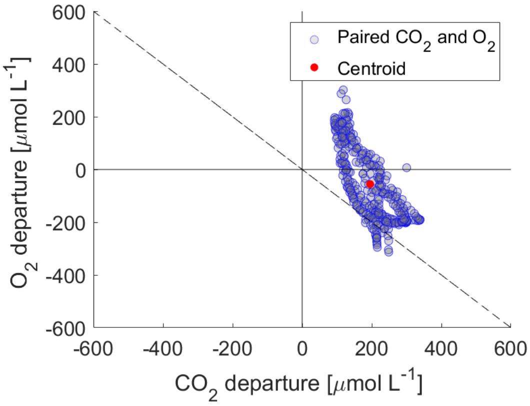


Figure 10: Paired CO_2- O_2 analysis for Sundbromark during the first 10 days after deployment (2019-04-16 to 2019-04-26). For Matlab code see Appendix B.1.

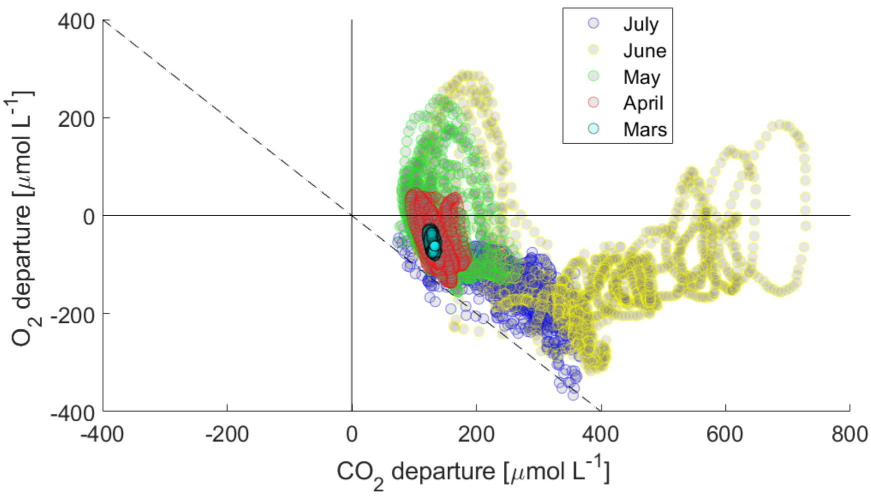


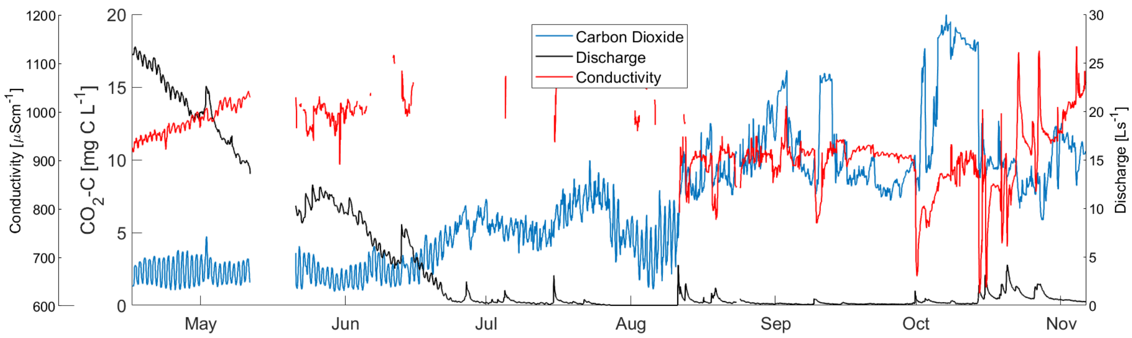
Figure 11: Paired CO_2- O_2 analysis for Hågaån during the full measurement period. For Matlab code see Appendix B.2.

3.3.2 Hydrological control

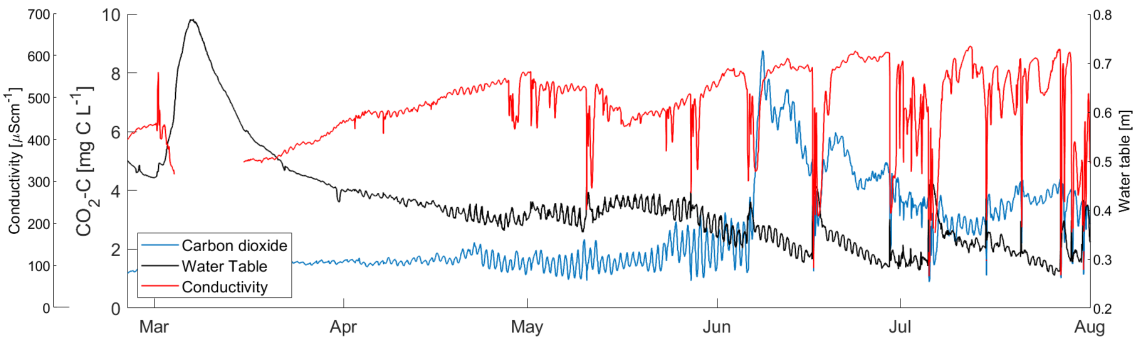
Due to malfunctioning sensor, continuous conductivity data was only obtained from August to the end of measurement period for Sundbromark. Data collected before this period were inconsistent. In Hågaån the conductivity data were consistent over the full measurement period. There was a clear interplay between conductivity and discharge/water table for both catchments, were conductivity decreased in response to increased discharge/water table during rain events (Figure 12a, 12b). For the majority of the rain events the conductivity recovered quickly to preexisting values after the event.

For Sundbromark, the discharge decreased from start of the measurements to late June where it became stable at low flow rates, around 0.4 Ls^{-1} (Figure 12a). During this period the CO_2 data displayed a rather constant daily mean concentration and with a "smooth" and pronounced diel variability. From July and onwards the CO_2 data displayed much higher concentrations and at the same time the variability was more rugged and flashy. In

August the discharge was either zero or bellow 0.1 Ls^{-1} which lead to temporary low CO_2 concentration. Similar to Sundbromark, the daily mean CO_2 concentration in Hågaån was relatively stable and with clear diel cycle developing from April, which got further pronounced in May/early June. The CO_2 concentration dynamics for the remaining measurement period was more rugged and flashy (Figure 12b).



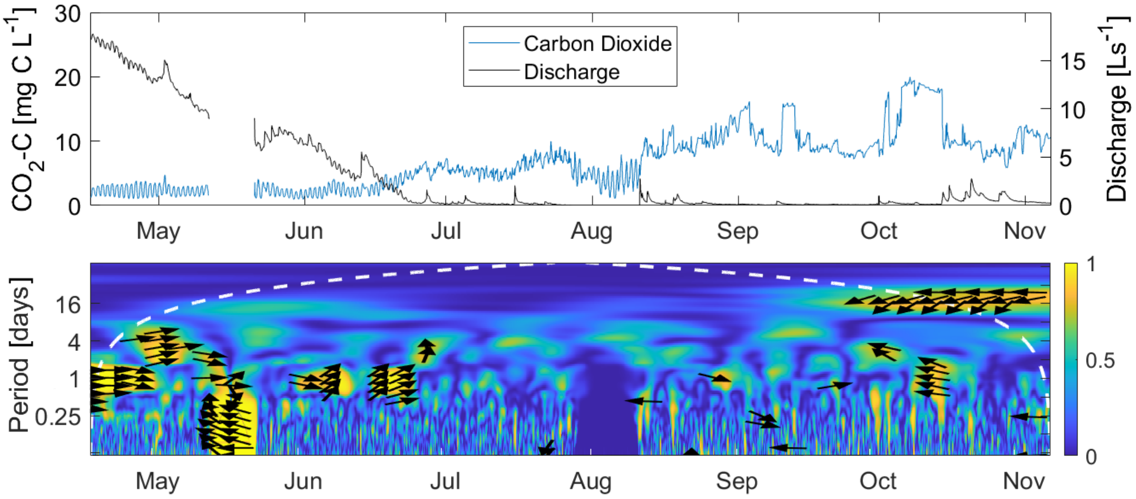
a)



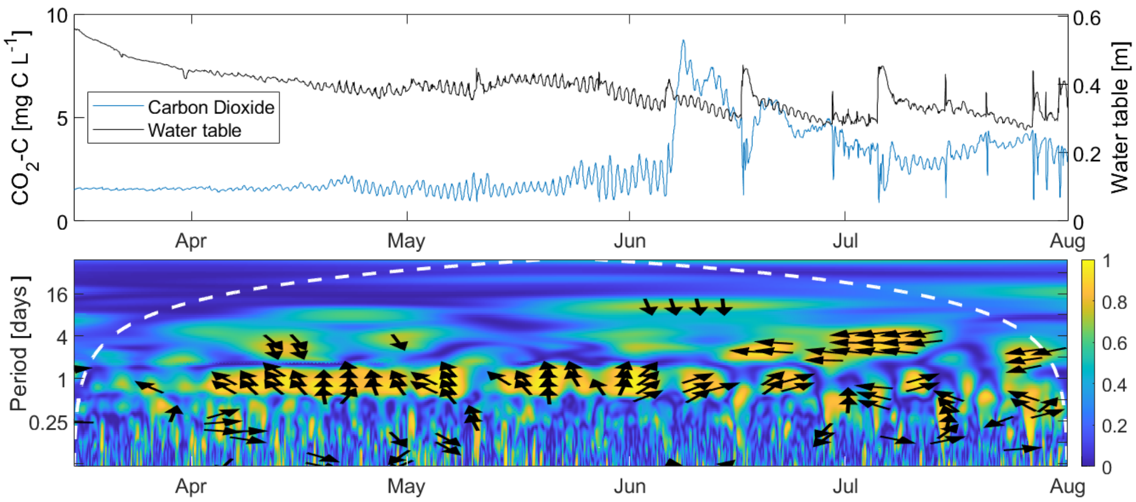
b)

Figure 12: Time series for conductivity, CO_2 and discharge/water table for Sundbromark (a) and Hågaån (b).

The WCO analysis between discharge and CO_2 in Sundbromark showed a weak coherence during the measurement period (Figure 13a). Inconsistent coherence with the periodicity of one day, with a light positive delay, was observed from middle of March until July, while the later period showed no detectable diel pattern. The WCO analysis between water table and CO_2 for Hågaån showed a high coherence from April to July, with a periodicity of one day. However, the coherence was interrupted temporally by increases in water table at rain events (Figure 13b).



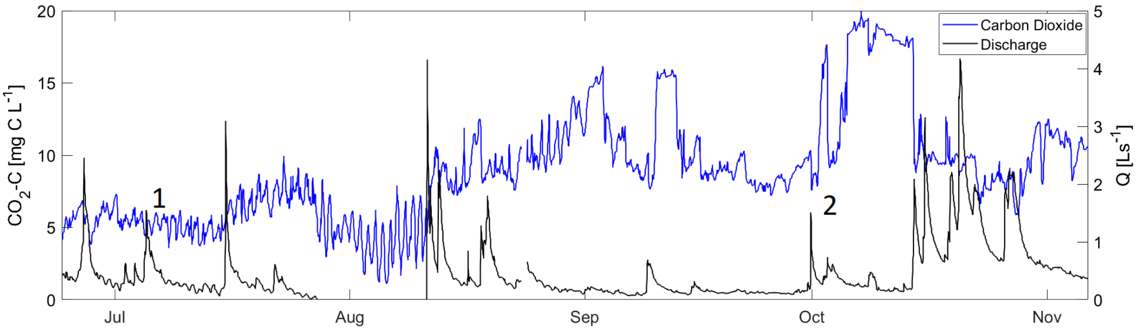
a)



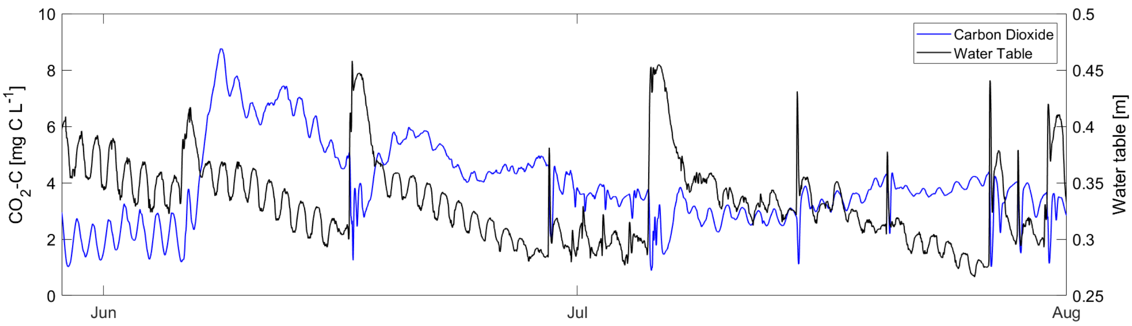
b)

Figure 13: Time series (top) and WCO scalogram (bottom) for CO_2 and discharge/water table in Sundbromark (a) and Hågaån (b). The brighter areas in the WCO indicates high coherence, while arrows indicates lag between the parameters. The white dashed line indicates the "cone of influence" where edge effects occur in the coherence data, i.e data on and outside the line is not reliable. For Sundbromark, data is missing in May which interupts the time series and scalogram.

For Sundbromark, the response in stream CO_2 concentration during temporal increases in discharge varied throughout the year (Figure 14a). A rain event in early July, resulted in an anticlockwise CO_2-discharge hysteresis loop where the minimum CO_2 concentration was reached before the maximum discharge was observed during the event. In contrast, rain event in October displayed a clockwise hysteresis loop where the maximum CO_2 is reached before the maximum discharge was observed during the event (Appendix A.3). However, analysis of several rain events showed no consistency in the CO_2-discharge response in Sundbromark that could be related to a specific time period. The first major rain event (start of June) in Hågaån increased the concentration of CO_2 by approximately 4 times from pre-event levels. The elevated CO_2 concentration level then steadily declined until the start of July after it started to slowly increase for the rest of measurement period (Figure 14b). During all of the later rain events in Hågaån anticlockwise CO_2-water table hysteresis loops were observed, i.e. the CO_2 concentration dropped temporally during the rain event to later return to the pre-event concentration.



a) From 2019-06-24 to 2019-11-06



b) From 2020-05-29 to 2020-08-01

Figure 14: Time series for CO_2 and discharge/water table for Sundbromark (a) and Hågaån (b) during period of co-occurring rain events.

4 DISCUSSION

4.1 CO_2 CONCENTRATION IN AGRICULTURAL STREAMS

Results from high frequency sensor measurements of stream CO_2 concentration in the Sundbromark and Hågaån catchments showed supersaturation during the full length of the measurement periods. The observed mean CO_2 concentrations were generally higher than what have been previously documented for streams draining forested catchments (Bodmer et al. 2016; Wallin et al. 2014). Thus, the results agree with the literature were agricultural streams are suggested to have higher CO_2 concentrations compared to streams draining other land-use types (Bodmer et al. 2016; Borges et al. 2018; Wallin et al. 2020, 2018). However, the observed mean CO_2 concentration in Sundbromark was higher than what have earlier been observed in agricultural streams. When compared with results from Wallin et al. (2018) and Wallin et al. (2020), Sundbromark showed twice as high CO_2 concentration, even though Wallin et al. (2020) was conducted in the same stream the year before. Worth mentioning is that the measurement period in Sundbromark, from the current study, was from late spring to late fall, a period which tend to have higher concentrations of CO_2 (Wallin et al. 2020). From August to November the concentration reaches values of 19-20 mg C L^{-1} in Sundbromark which is very high compared to the rest of the measurements.

The CO_2 concentration displayed in general a high variability, with variabilities existing on time scales ranging from hourly to seasonal. Compared to earlier literature the CO_2 concentration variability in both catchments exceeded what has been previously documented in agricultural streams (Bodmer et al. 2016; Borges et al. 2018; Wallin et al. 2020, 2018). Analysis of CO_2 time series (Figure 6) display a low variability during the spring, and considerably higher dynamics observed during the summer and autumn. The increase in stream discharge, in accordance to rain events, tend to have a high impact on the variability in CO_2 concentration which increases considerably after these events. These observations was also observed in Wallin et al. (2020) with rapid and high pulses in late summer/autumn, occurring in accordance to rain events, and a lower flux in spring/early summer representing a strong diel cycle.

On a seasonal scale, the CO_2 concentration in Sundbromark and Hågaån catchments followed similar trends as CO_2 variability, where concentrations was generally low in spring and higher in the summer and autumn. This is likely an effect of the temperature controlled respiration that is promoted during the summer and autumn periods (Nishizaki & Carrington 2014). The CWT analysis of CO_2 (Figure 6) revealed that both streams had clear diel patterns in CO_2 concentration during parts of the measurement periods, meaning that they follow a reoccurring daily pattern (Crawford et al. 2017; Wallin et al. 2020). The maximum concentrations were observed in the morning (6am to 12pm) and the minimum in the evening (6pm to 12am). This result was supported by the manual measurements conducted in Hågaån which confirmed the diel pattern captured by the sensor measurements.

4.2 DIFFERENCES IN CO_2 BETWEEN CATCHMENT

The Sundbromark (headwater catchment) and Hågaån (fifth order catchment) streams displayed seasonal CO_2 concentration patterns which were similar, although the measurement periods were different for the two catchments, May to November 2019 and March to August 2020 for Sundbromark and Hågaån respectively. By inspecting the same time periods, for the different years, shows the Hågaån initially have a low CO_2 concentration (May to June) but during the turn of June dramatically increases and have a higher concentration during the later period (June till August). Sundbromark instead have a more subtile increase during the later period but reaches considerably higher values in September to October where time series in Hågaån are missing. Both the highest mean and maximum CO_2 concentration was found in Sundbromark, which might be related to both size and land use of the catchment. Hågaån did however have a shorter measurement period which was carried out during spring and early summer, a period which tend to have lower CO_2 concentration when compared to summer and autumn. If longer time series existed for Hågaån, which extended throughout summer and autumn, the same high mean and maximum CO_2 concentrations found in Sundbromark could have been observed in Hågaån as well.

The CWT analysis of the CO_2 concentration (Figure 6) indicated a diel cycle during the spring and early summer in both streams. However, the diel cycle in Hågaån ceased in the end of July, while it in the Sundbromark stream ended in late June. The Sundbromark stream displayed a stronger diel in CO_2 cycle than the Hågaån stream during the spring, while the period June to August showed much lower variability. The distribution in CO_2 concentration data was very different between the two streams (Figure 7). Sundbromark had a multimodal distribution with several distinct peaks, while the Hågaån stream only showed one distinct peak. Though the distributions are measured in different years, it still gives an indication that Sundbromark have a higher and more irregular variability in CO_2 when compared to the Hågaån stream. This could possibly be related to the more extensive measurement period in Sundbromark which include the summer and autumn month, periods which the Hågaån measurement period does not include.

The analysis of rain events in Sundbromark showed no consistency in the CO_2 concentration-discharge hysteresis loops that could be referred to a certain periods of measurements. This was in contrast to data collected the year before where certain forms of the CO_2 concentration-discharge hysteresis loops were related to specific time periods (Wallin et al. 2020). For Hågaån, the first summer rain, which occurred in early June, caused the CO_2 concentration to increase fourfold (Figure 14b). In contrast, the following rain events that occurred caused anticlockwise CO_2 concentration-discharge hysteresis loops, where the stream water CO_2 concentration was diluted and dropped temporally.

4.3 MAIN DRIVERS OF CO_2 DYNAMICS

The WCO analysis between CO_2 and DO showed a strong diel control during spring and early summer in both streams (Figure 9). As both streams are open with limited canopy cover the stream surface, it is likely that the high sunlight exposure stimulate an effective primary production during day-time. The interplay between primary production in day-time and a strong respiration signal increasing the CO_2 concentration during night-time resulted in a negative correlation between DO and CO_2 (Nishizaki & Carrington 2014), which can be seen in the WCO analysis when inspecting the phase lag. When comparing the WCO between CO_2 and DO (Figure 9) to the CWT analysis of CO_2 (Figure 6), the coherence and magnitude in the two wavelet transformations coincide. This indicates that the interplay between CO_2 and DO is important for the CO_2 diel cycle. Metabolic control on the stream CO_2 was also present during the high CO_2 concentration period observed during the summer and autumn. By inspecting the time series for CO_2 and DO in the Hågaån stream (Figure 9b), a drop in DO concentration was observed after the rapid increase in CO_2 concentration in early June. No coherence in the WCO analysis can be observed during the remaining period, but DO still exhibits a diel cycle meaning that metabolic control is still occurring. This suggest that a metabolic control was present throughout the whole measurement period.

The WCO analysis between discharge/water table and CO_2 concentration showed a weak coherence in Sundbromark, while Hågaån showed a good coherence for most of the measurement period. The main difference between the catchments, regarding hydrology factors, is the flow rate, where the Sundbromark catchment suffers from low flow rates from late June till end of measurement period (Figure 13a) while an analyze of water table in the Hågaån stream does not indicate low flow rates (Figure 13b), even though having less precipitation (Figure 5). Coherence was sporadically observed during the first two months in Sundbromark, when discharge was still high. In contrast, no coherence was found during the remaining period, when discharge was low. This might therefore suggest that sufficient water flow is needed for a correlation between CO_2 and discharge/water table to exist. It could also imply that both discharge/water table and CO_2 have their own diel cycles, and when water flow is low the diel discharge cycle is too weak to produce measurable fluctuations. That would mean it is a correlation and not a causation.

Rain events influenced the diel cycle temporarily as the WCO analysis between CO_2 and discharge/water table was interrupted after rain events. This was especially noticeable in Hågaån during June and July (Figure 6b). This suggests an interplay between hydrological and biological controls on the stream CO_2 concentration, and that the dominating control is dependent on the hydrometeorological conditions. A similar interplay has previously been observed in nutrient poor alpine systems (Peter et al. 2014).

During the first summer rain in the Hågaån catchment, which occurred in early June, the CO_2 concentration increased fourfold (Figure 14b). As no process in the stream is likely to be the main cause for this rapid increase in CO_2, the excess in CO_2 must originate from external sources. One plausible source is CO_2 buildup in the catchment soils, a theory which have been proposed in earlier studies (Wallin et al. 2020). Before the rain event in June, no significant amount of precipitation had occurred during the last month. As respiration in soil is high during this period (Phillips & Nickerson 2015), it is likely that CO_2 that have been accumulated in the soil was flushed out in accordance to the rain event. The rain events which followed the first summer rain occurred more frequent and were instead showing anticlockwise CO_2 concentration-discharge hysteresis loops, where the CO_2 concentration was temporally diluted. This might suggest that the majority of the accumulated soil CO_2 was flushed out during spring/early summer, and that buildup of new soil CO_2 between the rain events was not enough to counteract the dilution effect from the runoff water.

When comparing Sundbromark and Hågaån concerning differences in water flow and CO_2 response from rain events, the differences could originate from land use and size in receptive catchment. The Sundbromark catchment consists of a high percentage of agricultural land (86%) while Hågaån instead is dominated by forestry, with only a quarter agricultural land (26%). The flat landscapes and artificially drained fields which agricultural land is associated with would make Sundbromark drain more effectively, thus giving the runoff water in Sundbromark a lower retention time. Sundbromark does also have a tenth of the catchment area than that of Hågaån, contributing to a lower total water volume which is flushed out more quickly as the travel distance for the water is be shorter. This may explain the rapid water flow peaks in Sundbromark, opposite from Hågaån where rain events causes more stretched out responses (Figure 14). This suggest that the percentage of agricultural land and size of catchment area have a profound impact on hydrology, both for sufficient water flow to exist but also CO_2 response from rain events.

Paired CO_2-O_2 analysis in Sundbromark and Hågaån indicated that respiration was stronger than photosynthesis during each measurement period (Figure 10, 11). By inspecting Figure 4, other factors relevant to the behavior of the paired CO_2-O_2 pattern can be suggested, these include: groundwater inputs of CO_2, carbonate precipitate, photo oxidation and anaerobic reactions. Anaerobic reactions is known to occur in Hågaån from manual measurements (Figure 15) but how much of an effect it has on the overall CO_2 concentration is unknown. Carbonate being present in the soil is know in Sundbromark and is suggested to be a source of CO_2. These factors have not been a main focus, and has thus not been investigated thoroughly in this report. Further studies are encouraged, while also investigating photo oxidation and groundwater control by,for example, isotope analysis.

5 CONCLUSIONS

The findings regarding CO_2 concentration agree with earlier research where supersaturation of CO_2 concentration were observed during full length of measurement period. Mean CO_2 concentrations were also found having higher levels than what have been observed in streams draining forested catchments. Seasonal variations in CO_2 concentration was strong, with large differences between early spring and summer/autumn. Diel CO_2 cycles was confirmed during most part of the measurement periods, where maximum concentration was found during the night and minimum during the day. External manual measurements in confirmed these findings. Analyses show that the diel CO_2 are heavily dependent on metabolic control in-situ the stream, while hydrological factors, such as sufficient discharge, appear to be needed for a diel cycle to exist. Rain events are suggested to have impact on the CO_2 concentration, this by temporal interruptions of the diel CO_2 after precipitation. CO_2 response suggest that CO_2 build up is occurring in catchment, which when flushed out produces spikes in CO_2 concentration which increases the mean CO_2 during the rest of the measurement. This may therefore be one of the most important drivers for high CO_2 concentrations observed in agricultural streams. Analysis of the different catchment areas suggest the percentage of agricultural land and size of the catchments have a profound impact on hydrology, both for sufficient water flow to exist but also for how the CO_2 concentration respond during rain events. More research is encouraged, where more parameters, such as groundwater inputs of CO_2, carbonate precipitate, photo oxidation and anaerobic reactions, should be investigated as it might be important for the dynamic of CO_2 in agricultural streams.

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APPENDIX

A. FIGURES

A.1

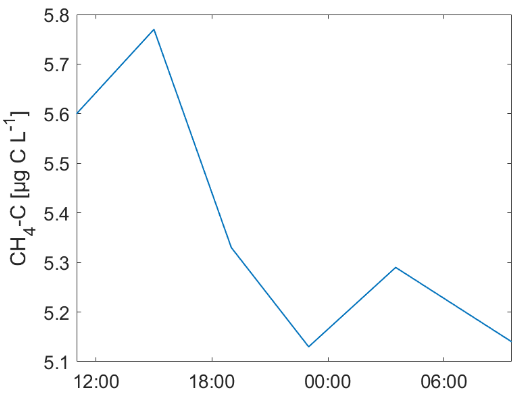

Figure 15: Manual samples of CH_4 in Hågaån (2020-05-11 11:00 to 2020-05-12 09:30).

A.2

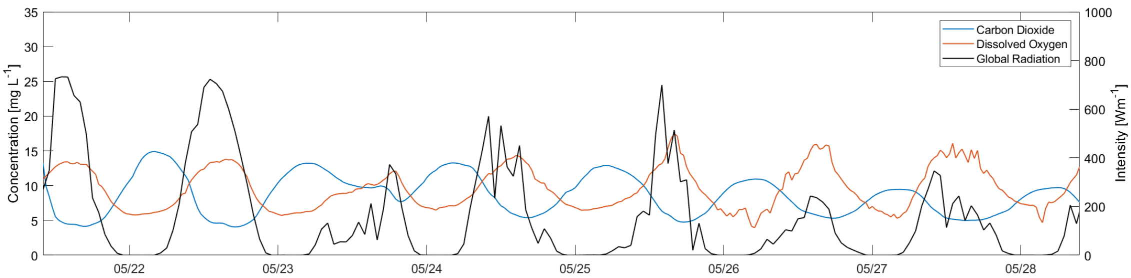

Figure 16: Time series for CO_2, DO and Global Radiation during the first 10 days of measurements in Sundbromark. Note that both DO and CO_2 are in mg L^{-1}.

A.3

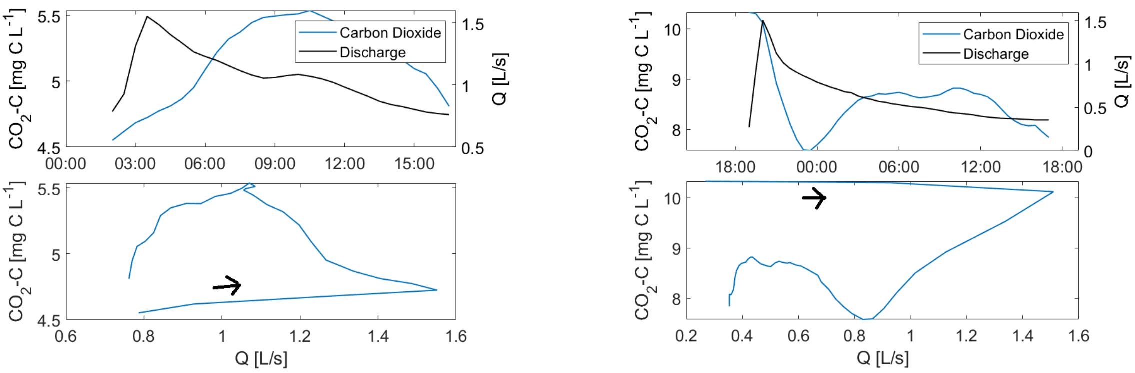

Figure 17: Rain event 1 (left) and rain event 2 (right) and CO_2 concentration-discharge hysteresis loops in Sundbromark.

B. MATLAB CODE FOR PAIRED O_2-CO_2 ANALYSIS

B.1 Sundbromark

```
%% Retriving relevant data
T=readtable('Measurement_data_2019.xlsx','PreserveVariableNames',true);
DepatureCO2=table2array(T(:,13)); %Departure CO2 [\mumol L^-1]
DepatureDO=table2array(T(:,14));  %Departure CDO [\mumol L^-1]

%% Scatter plots between CO2 departure and DO departure (21-05-2019 to 28-05-2019)

scatter(DepatureCO2(1676:2011),DepatureDO(1676:1676+2011),'o','MarkerEdgeColor','blue',...
'MarkerFaceColor',[0.5,0.5,0.5],'MarkerFaceAlpha',.2,'MarkerEdgeAlpha',.5)
hold on

% Calculate and plot Centriod
CentroidDO=mean(DepatureDO(1676:1676+335));
CentroidCO2=mean(DepatureCO2(1676:1676+335));
plot(CentroidCO2,CentroidDO,'r.','MarkerSize',20)
set(gca,'fontsize',15)

%Adding axis limits, 1:-1 line, labels and legend
hold on
x=(-600:1:600);
y=(600:-1:(-600));
plot(x,y,'k--')
```

```
set(gca,'fontsize',15)
xL = xlim;
yL = ylim;
line([0 0], yL,'Color','black');  %y-axis
line(xL, [0 0],'Color','black');  %x-axis
ylabel('O_2 departure [\mumol L^{-1}] ')
xlabel('CO_2 departure [\mumol L^{-1}] ')
legend('Paired CO_2 and O_2','Centroid')
set(gcf,'color','w'); %Makes the background white
```

B.2 Hågaån

```
%% Retriving relevant data
T=readtable('Measurement_data_2020.xlsx','PreserveVariableNames',true);
DepatureCO2=table2array(T(:,13)); %Departure CO2 [\mumol L^-1]
DepatureDO=table2array(T(:,14));  %Departure DO [\mumol L^-1]

%% Scatter plots between CO2 departure and DO departure for each month

%July
scatter(DepatureCO2(6068:7555),DepatureDO(6068:7555),'o','MarkerEdgeColor','blue',...
'MarkerFaceColor',[0.5,0.5,0.5],'MarkerFaceAlpha',.2,'MarkerEdgeAlpha',.5)
set(gca,'fontsize',10)
hold on

%June
scatter(DepatureCO2(4628:6034),DepatureDO(4628:6034),'o','MarkerEdgeColor','yellow',...
'MarkerFaceColor',[0.5,0.5,0.5],'MarkerFaceAlpha',.2,'MarkerEdgeAlpha',.5)
set(gca,'fontsize',10)
hold on

%May
scatter(DepatureCO2(3140:4627),DepatureDO(3140:4627),'o','MarkerEdgeColor','green',...
'MarkerFaceColor',[0.5,0.5,0.5],'MarkerFaceAlpha',.2,'MarkerEdgeAlpha',.5)
set(gca,'fontsize',10)
hold on

%April
```

```
scatter(DepatureCO2(1700:3139),DepatureDO(1700:3139),'o','MarkerEdgeColor','red',...
'MarkerFaceColor',[0.5,0.5,0.5],'MarkerFaceAlpha',.2,'MarkerEdgeAlpha',.5)
set(gca,'fontsize',10)

hold on
%Mars
scatter(DepatureCO2(912:1699),DepatureDO(912:1699),'o','MarkerEdgeColor','black',...
'MarkerFaceColor','cyan','MarkerFaceAlpha',.2,'MarkerEdgeAlpha',.5)
set(gca,'fontsize',10)
hold on

%Adding axis limits, 1:-1 line, labels and legend
x=(-400:1:400);
y=(400:-1:(-400));
plot(x,y,'k--')
set(gca,'fontsize',10)
xL = xlim;
yL = ylim;
line([0 0], yL,'Color','black');  %y-axis
line(xL, [0 0],'Color','black');  %x-axis
set(gca,'fontsize',13)
ylabel('O_2 departure [\mumol L^{-1}] ')
xlabel('CO_2 departure [\mumol L^{-1}]')
legend('July','June','May','April','Mars')
set(gcf,'color','w'); %Makes the background white
```