Quantification of Terrestrial CO$_2$ Sources to a Headwater Stream in a Boreal Forest Catchment

Kvantifiering av terrestriellt CO$_2$ till en bäck i ett borealt vattenavrinningsområde

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Title page: Part of the headwater stream and boardwalks in the Västrabäcken catchment where measurements were done. Photo Audrey Campeau, 2015.

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Abstract

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Carbon Dioxide (CO2) emissions from streams are a significant component of the global carbon cycle. Terrestrial export of CO2 through runoff is increasingly recognized as a major source of CO2 in boreal headwater streams. However, the spatial and temporal distribution of soil water CO2 within the terrestrial landscape remains poorly quantified, contributing to large uncertainties about the origin of CO2 in headwater streams. The riparian zone (i.e. the area with fine sediments and organic rich soils closest to the stream) is accepted as a main contributor of organic carbon to streams, but its importance as a source of CO2 is less evident. Here I evaluate the riparian zone as a main source by quantifying the contribution of lateral CO2 export from the riparian and hillslope zones to a headwater stream in a Swedish boreal catchment. Hourly measurements of CO2 concentration, conductivity, soil temperature and water table levels were taken in the riparian zone and the hillslope from June 2014 to October 2015. The riparian zone accounted for 58-89 % (August 2014 and March respectively) of the total terrestrial CO2 export from the slope to the stream. The hillslope, in turn, became a progressively larger source of CO2 to the stream during high flow events. To identify the drivers behind these zone-dependent and seasonal patterns in CO2 export, the CO2 production dissolved in the groundwater (groundwater-absorbed carbon) was estimated by taking the temporarily stored CO2 into account. The highest groundwater-absorbed carbon was observed during April and May (5.0 and 7.1 g C-CO2 m⁻² month⁻¹ respectively) which is the period with the highest discharge due to snow melt and the initiation of spring production. As such, conventional methods (gas chambers and the gradient method) may underestimate the soil respiration up to 50% during periods of high flow, as they exclude groundwater-absorbed carbon. CO2 consumption was observed in September 2014 and October 2015 (-0.2 and -0.7 g C-CO2 m⁻² month⁻¹ respectively) and may be explained by a major amount of the soil respiration being emitted instead of diluted in the groundwater during periods of low groundwater levels. It can be concluded that, regardless of season, the riparian zone is a major source of CO2 to the headwater stream.

Keywords: Deep soil respiration, headwater streams, lateral CO2 export, CO2 storage, riparian zone, Krycklan

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Populärvetenskaplig sammanfattning

Kvantifiering av terrestriellt CO₂ till en bäck i ett borealt vattenavrinningsområde
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En signifikant mängd koldioxid (CO₂) är lagrad i skog och marken. Marken i barrskogsregionerna förvarar en signifikant mängd CO₂ där det partiella trycket av CO₂ varierar mellan ~10 000 – 50 000 ppm i jämförelse med atmosfären (400 ppm). Mättnaden av CO₂ gör att mycket avdunstar tillbaka till atmosfären. Dock absorberas en del CO₂ av grundvattnet; vilket resulterar i en naturlig transport av CO₂ vidare till ytvattnet där CO₂ absorberas av grundvattnet; vilket resulterar i en naturlig transport av CO₂ vidare till ytvattnet där det kapillära nätverket av bäckar är största recipienten. Det är fortfarande oklart hur transporten av CO₂ är distribuerad i ett vattenavrinningsområde vilket medför brister i förståelsen av den globala uppvärmningen. Därför är en kvantifiering av olika områdets bidrag av CO₂ till bäckarna nödvändig. Två betydande zoner i ett vattenavrinningsområde som troligen bidrar olika är: the riparian zone som är närmast bäcken och består av fina sediment med hög organisk halt och, the hillslope som är resterande område och består av grovkorniga jordar med låg organisk halt. Den förstnämnda misstänks transportera mer CO₂ via grundvattnet på grund av dess närhet till bäcken, höga halter av CO₂ och höga vattenmättnad men detta är ännu inte verifierat. Jag evaluerar the riparian zone som en viktig källa till CO₂ i ett vattenavrinningsområde genom att kvantifiera transporten av CO₂ från de två zonerna. För att förklara varför transporten varierar presenterar jag en ny modell (GVR) som beräknar den månatliga fluktuationen av del av CO₂-produktionen som absorberas i grundvattnet i the riparian zone. Mätningar av data utfördes i Västrabäcken, ett mindre vattenavrinningsområde i ett större område (Krycklan), en transek av tre mätstationer (i bäcken, the riparian zone and the hillslope) installerades i den förmodade grundvattenströmningsriktningen. Resultaten visar på en hög produktion av CO₂ under vårfloden (maj) då en hög grundvattenyta troligen absorberar en signifikant mängd CO₂. Detta kan betyda att jordrespiration under våren underskattas då dagens mätmetoder är begränsade till mätningar i jorden av CO₂ ovan grundvattenytan. Fortsatta studier rekommenderas där GVR-modellen och andra mätmetoder utförs samtidigt för att vidare utröna den kvantitativa underskattningen under perioder med hög grundvattenyta (speciellt under våren). Bidraget från the riparian zone till den totala transporten av CO₂ till bäcken under ett år varierar mellan 58-89 % och det månatliga transportmönstret kunde förklaras med resultaten från GVR-modellen. Resultaten verifierar att oberoende av säsong så är the riparian zone den huvudsakliga laterala koltransporten från landvegetationen; medan the hillslope procentuellt bidrar mer av CO₂ under höga grundvattenflöden.

Nyckelord: Djup jordrespiration, bäckar, lateral CO₂-export, CO₂-lagring, riparianzon, Krycklan

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Abbreviations

a-e  Variables to correct measured CO₂
Ci  Measured CO₂ partial pressure in %
CO₂  Carbon dioxide
C-CO₂  Referring to the carbon part of the carbon dioxide. Used when defining that the units refers solely to the carbon in the carbon dioxide.
CO₃²⁻  Carbonate
DIC  Dissolved inorganic carbon
DOC  Dissolved organic carbon
HCO₃⁻  Bicarbonate
H₂CO₃  Carbonic acid
GMP221  The type of sensor model measuring the CO₂
kp 1, 2  Variables to correct measured CO₂
kt 1-3  Variables to correct measured CO₂
NEE  Net ecosystem exchange
P  Production; the amount of the soil respiration (i.e. CO₂ production) absorbed in the groundwater. Referred to in the text as “groundwater-absorbed carbon”
PIC  Particulate inorganic carbon
POC  Particulate organic carbon
Psyst  Pressure from water pillar pressure and atmospheric pressure on the CO₂ sensor
Q, Q’  Discharge from the catchment, discharge from the slope area
Temp_U  Soil temperature at upslope station (in °C)
Temp_R  Soil temperature at riparian station (in °C)
Tₛ  Soil temperature (in °C)
WT_R  Water table position at the riparian station
WT_U  Water table position at the upslope station
ΔS  Changes in CO₂ storage in the soil water (in both the saturated and the unsaturated zone)
1 Introduction

A significant amount of terrestrial carbon dioxide (CO$_2$) is transported and processed in the freshwater system. Streams are the main pathway for this carbon input to the freshwater system as they are the major link between terrestrial and aquatic ecosystem (Wallin et al., 2013). This is especially true for headwater streams which, with their fine network, reaches remote areas in the landscape. During the last decade, the view of streams being passive carbon transporters in the carbon cycle became discarded and replaced with a theory of them having a more active role (e.g. Battin et al. 2009b; Bonan 2008; Cole et al. 2007); approximately 40 % of global terrestrial carbon entering inland waters is emitted to the atmosphere (Cole et al., 2007). The authors underline the results of emission is likely to be underestimated due to emission data for headwater streams being unavailable. A more recent study can indeed confirm the former statement, and show significant emission from these streams and furthermore estimates that 90 % of the estimated dissolved inorganic carbon (DIC) entering a headwater stream is emitted within the first 200 metres (Öquist et al., 2009). At the regional scale, streams emit almost as much as lakes, while covering a much smaller area (Crawford et al., 2014). If CO$_2$ emissions from streams are not incorporated when estimating the net CO$_2$ sink capacity of a terrestrial forest, an overestimation is done due to the underestimation of terrestrial respiration (Cole et al., 2007).

Arctic and boreal biomes are located between 50°N and 60°N (Lorenz and Lal, 2009). They cover 22 % of the continental area and store 25-35 % of the global soil carbon (Chapin et al., 2000; Bonan, 2008). At these colder latitudes, the consequences of global warming is expected to be strongest (Bonan et al., 1995; Mann et al., 1999). The anticipated increase in temperature and alteration of the hydrological cycle (enhanced periods of drought and heavy rainfalls) (Salinger, 2005; Gedney et al., 2006; Huntington, 2006; Luo, 2007) is likely to have a direct impact on the role of streams in the carbon cycle. An increase in the global runoff is already noticed (Gedney et al., 2006) with the likely consequence of increase in lateral CO$_2$ export from soil to streams in the northern hemisphere (Öquist et al., 2014). Therefore, to be able to correctly incorporate stream CO$_2$ emissions in greenhouse gas balances and predict the impact of global warming on the efflux, it is crucial to understand the hydrobiochemical interaction between terrestrial and aquatic ecosystems in boreal regions.

The CO$_2$ in streams can originate from several sources: stream metabolism, bedrock weathering or terrestrial CO$_2$ input from soil respiration. This terrestrial input originates from the whole catchment. However, the conditions attributing to soil respiration and lateral export of CO$_2$ may differ in different zones in a catchment and it is important to find the hotspots (i.e. zones which contribute to the CO$_2$ in headwater streams by having both high CO$_2$ production and significant lateral export). Two distinctive zones in a catchment that likely differ in intensity of soil respiration and lateral CO$_2$ export is the riparian zone and the distal hillslope (Leith et al., 2015; Pacific et al., 2008). The riparian zone is composed of the area stretching from a stream across its highest flooding plane into the proximal canopy (Sedell et al., 1991). Fine sediments and organic rich humic soil normally characterize this zone, whereas the
hillslope are composed of coarser material such as moraine. It is known that the riparian zone strongly influence the chemical composition on the waters (Smart et al., 2001; Woltemade, 2002; Ågren et al., 2010). Thus, its contribution of CO₂ is believed to be significant larger in comparison to the hillslope.

The importance of the sources contributing to the emitted CO₂ in headwater streams is starting to become unravelled (e.g. Johnson et al. 2008; Hotchkiss et al. 2015; Öquist et al. 2009). It has now become evident that contribution of CO₂ by terrestrial DIC export is more important compared to in-stream metabolism (Hotchkiss et al. 2015; Palmer et al. 2001; Öquist et al. 2009).

Three key studies contributing to this unravelling are: 1) Johnson et al. (2008) who found that in the tropical region, 70% of the evaded CO₂ from headwater streams originated from terrestrial CO₂, 2) Hotchkiss et al. (2015) who concluded that CO₂ emitted from smaller streams was mainly supported by lateral input of terrestrial CO₂, and 3) Pacific et al. (2008) who found the CO₂ production to be higher in the riparian zone (possibly 57% higher compared to the hillslope) but evasion of this was limited by high soil water content. All these results are important steps in the progress to determine the sources contributing to CO₂ in headwater streams. However, there is a significant different in the tropical biomes compared to boreal biomes, and thus, their results are not comparative to the boreal forests. Moreover, Hotchkiss et al. (2015) do not stratify where the terrestrial CO₂ originates from in a boreal forest (i.e. specific zones and where in the soil profile) and Pacific et al. (2008) do not evaluate the part of the soil respiration absorbed below the reported high groundwater table in the riparian zone.

The next step to ascertain all the sources contributing to the CO₂ emissions in stream is to distinguish between the terrestrial sources. To discriminate all contributing sources is necessary in order to understand an important path in the carbon cycle (Dinsmore et al., 2013, 2010; Wallin et al., 2010). Indeed, it is highly topical, as with a warmer climate and a higher variability in the runoff (in response to episodes of heavy rains and periods with drought), the lateral CO₂ export is expected to become a more important part of the carbon cycle.

This study aims to evaluate the importance of the riparian zone as a source of CO₂ to streams, by using a small headwater catchment in northern Sweden as a case study. Based on hourly measurements I quantify the monthly export of CO₂ from the riparian zone and the hillslope. In order to understand the drives behind the lateral CO₂ export from the riparian zone, I quantify the soil respiration dissolved in the groundwater (from here on referred to as the groundwater-absorbed carbon) by adding the temporal storage of CO₂ in the soil water in the riparian zone. A comparison of estimated groundwater-absorbed carbon is performed with existing emission (and respiration) data to evaluate the importance of the aqueous CO₂. The result of the lateral CO₂ export and the soil respiration is finally put in a wider context regarding the zone-dependent quantitative contribution of CO₂ to the headwater stream. I hypothesize that the riparian zone will be a major source (i.e. a hotspot) of the CO₂ to headwater streams throughout the year, yet seasonality may play a role in modulating its relative importance compared to the upper hillslope area. Furthermore, seasonal patterns in soil respiration are the main drivers of the relative importance of the riparian zone as a source of CO₂ to streams.
2 Method

2.1 Field Site

The field survey was executed in Västrabäcken, a northern sub-catchment of the Krycklan catchment. It is positioned at 64°14’N 19°46’E outside of the village Vindeln in northern Sweden (Fig. 1). Västrabäcken belongs to a larger research area, maintained by the Swedish Agriculture University, and is therefore a frequently used study site for several other environmental surveys. Västrabäcken covers 0.12 km² and in its centre flows an approximately 300-400 meters long (depending on season) headwater stream.

![Figure 1](image.png)

*Figure 1. Location of Västrabäcken catchment (a) and locations of the setup of the three stations (b). Modified from Seibert et al. (2009).*

The climate in the catchment is seasonally dependent with a spring flood occurring sometime during April and May. It is responsible for 40-60 % of the yearly discharge (Laudon et al., 2011). Mean annual air temperature (1980-2008) is 1.7 °C. Average air temperature during January and June is -9.6 °C and 14.6 °C respectively. A snow sheet covers the ground approximately 168 days per year (1980-2007) between mid-November to early May. The thickness of the snow sheet varies between 43 and 113 cm with an average thickness of 76 cm. Soil frost occurs during the winters. The maximum depth of the soil frost was measured approximately 1 km from the Västrabäcken (1993-2007) and varied between 2.5 cm and 79 cm. No anomalies of the climate variables occurred during the measurement period compared to mean data from 1980 to 2008 (Haei et al., 2010).
The vegetation is dominated by pines \((\text{Pinus sylvetris})\), with some spruces \((\text{Picea abies})\) growing near the stream. The understory vegetation consists mostly of blue and lingonberry, grasses, mosses and wood horsetail \((\text{Vaccinium myrtillus}, \text{Vaccinium vitis-idaea}; \text{Deschampsia flexuosa}; \text{Sphagnum spp.} \text{ and } \text{Polytrichum commune}; \text{Equisetum sylvaticum})\), the two latter are found in wetter areas. The vegetation is underlain by a 10-15 meters thick moraine layer which was deposited during the last ice age and is, in turn, situated on top of the gneissic bedrock (Leith \textit{et al.}, 2015).

Two distinctive soil types are found in Västrabäcken catchment area. An organic rich soil is found closer to the stream and a podzol farther away from it. The soil profile at 11 metres upslope from the stream is a well-developed iron podzol which stretches down to ~80 cm below surface. The humus, E and B- horizons of the soil profile are 5, 12 and 60 cm thick respectively. Closer to the stream, the soil profile changes to peat underlain by a ticker humus layer and 1 metre from the stream, the peat layer is found down to 90 cm below the surface of which the last 20 cm is a transition zone to the moraine (Nyberg \textit{et al.}, 2001; Bishop \textit{et al.}, 2008).

2.1.1 Site Instrumentation

The data was collected from three measurement stations in an 11 meter transect perpendicular to the stream (i.e. stream - riparian - upslope stations) (Fig. 2). The transect is positioned in an assumed hydrologically restricted area (2530 m²) that contributes ~2% of the total discharge in Västrabäcken catchment. The landscape distribution in the slope is believed to be representative for the whole catchment.

Measurements were taken between 14th of June 2014 and 11th of October 2015. At each station (stream, riparian and upslope), data of groundwater level, temperature, conductivity and partial pressure of CO\(_2\) was measured hourly. CO\(_2\) sensors (of type GMP221) were placed at two depths in the riparian and upslope stations: at ~35 and ~85 cm below surface. These sensors are from here on referred to as shallow and deep measurement sensors. All other sensors (measuring groundwater level, temperature and conductivity) were positioned at ~85 cm below surface. No measurements in the stream occurred during the winter season because the stream freezes. Also, some interruptions occurred in the data collection; these resulting gaps in the time series were filled by interpolation.
Figure 2. Illustration of the slope (2530 m²), a hydrologically restricted area in Västrabäcken catchment, and the division between the zones. The arrows (in red) indicate measurement stations which are positioned one and 11 meters from the stream (named the riparian station and the upslope station respectively). The respective heights at the stations is depth down to the stream bed.

2.2 Limitations in the Study

The study is limited to a hydrological restricted slope in a boreal catchment in the northern hemisphere. Only the CO₂ form of the DIC pool will be considered, therefore neglecting the respired part converted into bicarbonate (HCO₃⁻). This is a reasonable simplification since it is estimated that the HCO₃⁻ part of the DIC pool is negligible at consistent low pH, which is the condition for this boreal catchment (Maier et al., 2010; Wallin et al., 2010).

The lateral extent of the soil layer of the riparian zone from the headwater stream varies vigorously and, thus, is difficult to restrain (Grabs et al., 2012; Ledesma et al., 2015). The upslope station is supposed to be located in the mineral soil as the CO₂ concentrations in this station are remarkably low (Leith et al., 2015). Therefore, the transition zone of organic to mineral soils is located between the two stations and assumable this transition is just before the upslope station. The selected positions of the measurement stations in the slope were based on previous knowledge of the riparian zone in the Västrabäcken (Ledesma et al., 2015; Seibert et al., 2009; Blomberg, 2009).

The bedrock in the area is, as mentioned earlier, solely crystalline (Leith et al., 2015) leaving out a significant source of HCO₃⁻ from weathering of carbonaceous bedrock. Instead, transformation of CO₂ to HCO₃⁻ may occur via silicate weathering but this is assumed negligible and thus no further evaluation on this topic is done herein.
2.3 Data Treatment

Due to several incidents (such as lightning), some of the sensors broke which resulted in gaps in the measurements (Table 1).

**Table 1.** Summary of periods with missing data and associated sensor where R = riparian and U = upslope.

<table>
<thead>
<tr>
<th>Sensor measuring</th>
<th>Date with missing data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water table at R station</td>
<td>2014: August 17-28, September 2-8 and October 7</td>
</tr>
<tr>
<td>Water table at U station</td>
<td>2014: June 14 - October 16</td>
</tr>
<tr>
<td>Soil Temperature at U station</td>
<td>2015: June 5 - August 4</td>
</tr>
<tr>
<td>CO₂ at R and U station</td>
<td>2014: August 17-28, September 2-8 and October 7</td>
</tr>
<tr>
<td></td>
<td>2015: May 3 - June 10</td>
</tr>
</tbody>
</table>

The missing data of the water table at the riparian station was interpolated (Eq. 1) from the correlation between discharge at Västrabäcken (Q) and available water table data at the riparian station (WT_R) ($R^2 = 0.70$, p-value<<0.005). The same discharge was used to interpolate (Eq. 2) the missing data of water table at upslope station (WT_U) (Eq. 2) ($R^2 = 0.79$, p-value<<0.005).

\[ WT_R = -3.044 \times \ln(Q) + 5.7168 \]  
\[ WT_U = -10.88 \times \ln(Q) + 6.4934 \]  

The soil temperature data at upslope station was completed with a correlation between upslope and riparian stations soil temperature (Temp_U and Temp_R respectively) (Eq. 3) ($R^2 = 0.97$, p-value<<0.005).

\[ Temp_U = 1.24 + 0.84 \times Temp_R \]  

The CO₂ measurements from the sensors contained gaps that was filled with linear interpolation. To gain corrected pCO₂ the CO₂ measurement were adjusted for water temperature and ambient pressure (Eq. 4) with algorithms provided in the manufacture manual for GMP221 and compiled in a compendium by Leith *et al.* (2015) (Eq. 5-15).

\[ P_{sys} = \frac{h \rho \times g}{100} + atm \]  

Where $h =$ water height above bottom of sensor (m), $\rho = 1000$ (fluid density, kg/m³), $g = 9.80665$ (acceleration of gravity, m/s²), $atm =$ atmospheric pressure (hPa). Division by 100 is to convert P to hPa.
\[ \text{CO}_2 \text{ corrected (ppmv)} = \text{CO}_2 \text{ measured} - a - b - c - d - e \]  

where

\[ a = kp1 \times \left( \frac{p_{sys} - 1013}{1013} \right)^2 \]  

\[ b = kp2 \times \left( \frac{p_{sys} - 1013}{1013} \right)^2 \times P_{sys} \]  

\[ c = kt1 \times \left( \frac{25 - T_s}{25} \right)^3 \]  

\[ d = kt2 \times \left( \frac{25 - T_s}{25} \right)^2 \]  

\[ e = 16320 \times (-kt3^2) + kt3 \times \left( \frac{25 - T_s}{25} \right) \]

where \( T_s \) = soil temperature (°C); \( Kp1, Kp2, Kt1, Kt2, Kt3 \) = equation 11-15 and \( P_{sys} \) (hPa) = Pressure compensated for water pillar pressure and atmospheric pressure, from equation 4.

\[
Kp1 = 0.97501 \times C_i^4 + (-54.1519 \times C_i^3) + (479.778 \times C_i^2) + (-11362.8 \times C_i)
\]

\[
kp2 = (-9.3269 \times 0.001 \times C_i^3) + (0.14345 \times C_i^2) + (15.7164 \times C_i)
\]

\[
kt1 = 0.046481 \times C_i^3 + (-1.02280 \times C_i^2) + (-37.4433 \times C_i) + (-49.000)
\]

\[
kt2 = (-3.0166 \times C_i^2) + (-8.8421 \times C_i)
\]

\[
kt3 = 0.000083600 \times C_i^3 + (-0.0024199 \times C_i^2) + (0.066814 \times C_i)
\]

Where \( C_i \) = measured CO\(_2\) partial pressure in %

Appendix I contain the R script with all supplementary info necessary to redo these corrections needed for the measurements from this site.

To get a CO\(_2\) concentration with soil depth, assumptions had to be done as only two point measurements were collected along each station profile. The chosen lower boundary limits for the profiles are described in chapter Hydrological Modelling and are 0.6 and 1.2 meters at riparian and upslope stations respectively. An interpolation of the corrected CO\(_2\) was done between the shallow and deep sensor. Estimation of CO\(_2\) below the deep sensor at the riparian station was not necessary as the sensor was positioned below the active flow depth. In contrast, at the upslope station, the active flow depth was 1.2 m below the surface (35 cm below the deep sensor) and, thus, it was necessary to make an extrapolation. A constant partial pressure of CO\(_2\) from the deep sensor down to 1.2 m was assumed. The partial pressure of CO\(_2\) in the soil above the shallow sensors to the soil surface were linearly extrapolated assuming atmospheric CO\(_2\) (400 ppmv) at the soil-surface value.

The corrected CO\(_2\) was in partial pressure (ppmv) but when estimating the export and the production mg/l is used. This conversion needed an application of Henry’s law. Firstly, Henry’s solubility constant was computed following Weiss (1974) (Eq. 16).
\[ K_h = e^{-58.0931 + 90.5069 \times \left( \frac{100}{T_s \times 273.15} \right)} + 22.294 \times \log \frac{T_s + 273.15}{100} \]  

where \( K_h = \) Henry's Constant, \( T_s = \) Soil temperature (in °C). The measured soil temperature at 0.85 m was used for both the shallow and deep sensor. Henry's Constant was thereafter utilized to get the CO2 concentration in mg/l (Eq. 17).

\[ \text{CO}_2 \text{ mg l}^{-1} = K_h \times p\text{CO}_2 \times \frac{12.01}{1000} \]  

where \( p\text{CO}_2 = \) is the corrected partial pressure of CO2 (in ppmv), 12.01 is molecular weight of carbon divided by \( 10^3 \) to convert g to mg.

### 2.3.1 Hydrological Modelling

Hydrological studies in the catchment have estimated the active flow depth in the groundwater discharge profile (Amvrosiadi, unpublished data). Below the active flow depth, the water moves so slow that it is estimated to not contribute to catchment discharge. Therefore, the active flow depth is the bottom boundary of the discharge profile herein. The discharge profile was divided into 100 layers where the discharge in one particular layer at the riparian station was assumed to originate from the same layer at the upslope (Fig. 3). This is a similar approach as the one used in the riparian integration model (Seibert et al., 2009).

![Figure 3. Conceptual model of the discharge between the two measurement stations, with only a few layers illustrated. The dashed line in the bottom is the stream bed position and also the lower limit of the model. The black dots illustrate approximately measurement depths for the shallow and deep sensors (35 and 85 cm respectively). Note that the deep sensor at the riparian station is not in the figure as it is positioned deeper in the profile. In the applied model, the profile was divided into 100 layers instead of the 6 illustrated layers. The height of each layer at the riparian and upslope stations were 0.6 and 1.2 cm respectively.](image)
To estimate the groundwater flow from the slope at the riparian station, a loop with Darcy’s law (Eq. 18 & 19) was applied with discharge data from a station further downstream. The steps to get the layered discharge model is explained herein and was developed by Amvrosiadi (unpublished).

\[ T = \frac{Q}{\Delta \frac{W}{L}} \]  

[18]

Where \( T \) = transmissivity (area/time), \( Q \) = discharge measurements from downstream station (volume/time), \( \Delta \frac{W}{L} \) = the slope between the water table at the riparian and upslope stations (distance between stations is 10 m) (length). The estimated transmissivity (\( T_{e} \)) was reused in the Darcy’s law in order to get groundwater flow from the slope (\( Q' \)) (Eq. 19). After re-running the equation with the new groundwater flow (\( Q' \)), a new transmissivity was estimated.

\[ Q' = T_{e} \times \Delta \frac{W}{L} \]  

[19]

This new calculated transmissivity was plotted against water table height to get the transmissivity for each soil layer. The transmissivity for a layer was used in Darcy’s law to get that specific layer’s discharge. The result of the groundwater flow profile was applied both at riparian and upslope stations when calculating the CO2 export.

A slope of the water table height at the riparian and upslope stations could not be estimated from middle of July to middle of August 2014 as it appeared as negative. The groundwater flow during these occurrences were put to zero, assuming no lateral flow to the stream.

2.4 Estimations of CO2 Export

The monthly export was calculated by multiplying the CO2 concentration with the discharge for all layers at both riparian station and upslope station and sum it up monthly (Eq. 20).

\[
Monthly \ CO_2 \ export = \sum_{i=0}^{100}(Q_i \times CO_2 \ conc. \ i)
\]

[20]

Where \( Q \) = groundwater flow at the riparian station (m\(^3\) h\(^{-1}\)), \( CO_2 \ conc. \) (mg m\(^{-3}\)) and \( i \) = the \( i^{th} \) layer in the 100 layers that the model is divided in (see again Figure 3 for model structure).

Monthly CO2 export from the riparian zone (i.e. area between the two stations) was estimated by subtracting the upslope CO2 export from the riparian CO2 export (Eq. 21).

\[
CO_2 \ export \ from \ the \ Riparian \ zone = \sum_{i=0}^{100} (RCO_2_{exp.i} - UCO_2_{exp.i})
\]

[21]
where \( R- \) and \( UCO_2\ exp_i \) (mg month\(^{-1}\)) = the monthly export from the riparian station and the upslope station respectively, and \( i \) = the \( i^{th} \) layer of the 100 layers constituting the model entities (Fig. 3).

The monthly \( CO_2 \) export from the hillslope area (the area above the upslope station) was assumed to be equal to the \( CO_2 \) export at the upslope station. Therefore, the \( CO_2 \) export by soil depth in the hillslope is the same as the export profile at the upslope station.

The water table at the upslope station is behaving differently compared to the water table at the riparian station. At high flow conditions, the water table in the upslope station raised a bit higher in comparison to the riparian station. This lead to a few additional layers in the model becoming saturated at the upslope station whereas these layers remained above the water table at the riparian station (between June and July in 2014 and April and May in 2015). The first period had five extra water saturated layers in the upslope whereas the second period had eight additional layers (each layer represents 1.2 cm at the upslope station). The consequences of this was an apparent negative \( CO_2 \) export from the riparian station as the export from the riparian zone is calculated by subtracting the \( CO_2 \) export from the upslope station from the riparian station. These negative layers were deleted and the model was re-run; the affect from deleting these layers will be discussed in the discussion section Zone-dependent \( CO_2 \) Export.

2.5 Estimation of Storage & Groundwater-absorbed Carbon

The soil respiration that dissolves into the groundwater is what eventually will be exported downstream (the origin of this carbon is described in a general background of \( CO_2 \) reservoirs in the northern hemisphere in Appendix II). However, a certain amount of this dissolved \( CO_2 \) will be temporarily stored within the system rather than exported downstream (Figs. 4 and 5). If the timescale is monthly or more detailed, my assumption is that it is necessary to integrate this storage with the \( CO_2 \) export to correctly estimate the soil respiration that is dissolved in the groundwater.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Conceptual distribution of \( CO_2 \) production below ground in soil pore space where UZ = unsaturated zone. Do note that the distribution between the three is not to scale as it is today not verified how the total \( CO_2 \) volume is distributed in an acidic soil. Arrows indicates transport paths for \( CO_2 \): Green arrow = evasion of \( CO_2 \); blue arrow = export of \( CO_2 \).
Figure 5. Conceptual model illustrating the fate of CO₂ production (Rs) where it either stays in the vadose zone of the soil (green part) and might be measured by existing measurement techniques, or is diluted in the groundwater (blue part). Furthermore, a part the CO₂ diluted in the groundwater is temporarily stored (monthly) whereas the rest becomes exported through runoff. The figure is schematic and aims solely to illustrate that an amount of the soil respiration is caught/dissolved in the groundwater and only a part of this is exported and thus the distribution between the fates of the soil respiration is not to scale.

The amount of exported CO₂ is dependent on two variables: the discharge and the CO₂ concentration in the water. A high discharge can result in a large export of CO₂ (Leith et al., 2015; Pacific et al., 2008). Similarly, an intense soil respiration increases the CO₂ concentrations in the groundwater and generates thereby a high export of CO₂ even when the discharge is small. The lateral export of CO₂ would presumably approach, on a long-term basis, the groundwater-absorbed carbon. Therefore, if evaluating annual soil respiration, the sum of the CO₂ export and the evaded CO₂ represents the soil respiration. However, if evaluating how the soil respiration fluctuates on a seasonal, or on an even more short-scaled basis, the part of the respired CO₂ that has not yet been evaded or exported needs to be considered. That is, the changes in the temporarily, short-term storage (S) of CO₂.

The S will change as the part of the respiration being stored will change through time (ΔS). The concept of S and ΔS, when estimating the short-term soil respiration, works the same way as ΔS in a water balance equation: in a long-term, the equation can exclude ΔS as it will be ~ 0 but for instance on a monthly scale, the storage has to be included as a significant part of the what is going to become exported may instead become temporarily stored within the system. The ΔS can be applied in both the unsaturated zone and the saturated zone. Maier et al. (2011) confirmed that the ΔS significantly effects the amount soil respiration in the vadose zone when added to fluxes data in a soil respiration model (a description on conventional measurements to estimate fluxes is found in Appendix III). The storage after a rainfall could hold up to 40 % of the soil respiration, leading to a significant underestimation in soil respiration if the ΔS change was not added into the equation. Maier et al. (2011) brought up to discussion how valid ΔS may be for other sites and suggested that in shallow acidic soils (i.e. low pH), ΔS may be less important. Regardless if this is true, the CO₂ storage in acidic soils occur below the water table. Therefore, if there is a high water table in acidic soils catchments (which is true for the
riparian zone in the slope), $\Delta S$ is needed to be taken into account in order to evaluate the total amount of the soil respiration dissolved in the groundwater and not only the exported part of the soil respiration. Otherwise, a possible underestimation of the soil respiration dissolved in the groundwater may occur. To this day, no one has yet added $\Delta S$ in the equation to estimate the part of the soil respiration dissolving in the groundwater. Further on, the interaction of this part of the soil respiration and CO$_2$ export from the riparian zone and hillslope has not been evaluated.

The groundwater-absorbed carbon is calculated as the differences in carbon that leaves and enters the riparian zone with water flux (CO$_2$ export from the riparian zone) and the difference in storage ($\Delta S$) from one day to another. To estimate the groundwater-absorbed carbon in the riparian zone based on the CO$_2$ export, changes in storage in the riparian zone was accounted for (Eq. 22).

$$P = \text{RZ}_{\text{CO}_2 \text{ exp.}} + \Delta S \quad [22]$$

where $P = \text{the groundwater-absorbed carbon}$, $\text{RZ}_{\text{CO}_2 \text{ exp.}} = \text{the export of CO}_2 \text{ from the riparian zone}$ and $\Delta S = \text{the difference in the stored CO}_2 \text{ in the riparian zone through time}$ (Eq. 23).

$$\Delta S = \sum_{i=0}^{100} (W_{Volume} \times \text{CO}_2 \text{ conc. } i) + (UZ_{WVolume} \times \text{CO}_2 \text{ conc. } i) \quad [23]$$

where $\Delta S = \text{monthly change in stored CO}_2 \text{ in the riparian zone}$, $W_{Volume} = \text{water volume}$, $\text{CO}_2 \text{ conc. } i = \text{mean concentration of riparian and upslope station for } i = \text{the } i^{\text{th}} \text{ layer of the 100 layers constituting the model entities}$. The $\Delta S$ was calculated on a monthly basis, with a positive $\Delta S$ representing a CO$_2$ build-up in the riparian zone due to production exceeding CO$_2$ export and in-situ emission. Contrary, a negative $\Delta S$ represented an emptying of the storage by export and likely in-situ emission exceeding the water diluted production.

The $\Delta S$ was estimated by the storage of CO$_2$ in the riparian zone. Where the storage was determined by the dissolved concentration of CO$_2$ found in the riparian zone depth (176 m$^2$) down to the active flow at a specific time point. The diluted amount CO$_2$ was estimated from an average between the CO$_2$ concentrations in the riparian and upslope stations for each layer. It was first estimated hourly and then summed up daily. In order to get the amount CO$_2$ (in mg), the averaged CO$_2$ concentration for each layer was multiplied with the volume of water it contained. Both the water in the unsaturated and saturated zones was considered. The inclusion of the unsaturated zone was to prevent the voluminous influence on the delta storage ($\Delta S$) of a raising or decreasing water table, as only a few cm raise of the water table would result in a large increase in the storage. The CO$_2$ amount in the unsaturated zone was estimated from an average of the CO$_2$ concentrations in the layers in the unsaturated zone for both the stations which was then multiplied with the amount of water in the unsaturated zone. This amount was added up with the estimated CO$_2$ from the layers below water table to represent the amount of diluted CO$_2$ in the riparian zone on a daily basis.
The groundwater is constantly supersaturated compared to the atmospheric CO$_2$, so the CO$_2$ invasion from above groundwater is assumed to be negligible whereas the CO$_2$ evasion however is unlikely to be zero. Nevertheless, this is the assumption herein as there was only two measurement points (positioned too deep), and thus the evasion was not possible to estimate. Therefore, the CO$_2$ evasion from the groundwater and the unsaturated zone is omitted herein but will be taken up in the discussion.
3 Results

3.1 Climatic Variables

Means and ranges for climatic variables during a hydrological year between 1st October 2014 to 30th September 2015 are presented in table 2.

Table 2. Climate variables during the studied hydrological year (Oct.-14 to Sept.-15). The precipitation is in mm over the Västrabäcken catchment. Snow is measured from a station nearby and presents how many days the snow was covering the ground. The slope runoff is the runoff from the hydrological restricted area (2354 m²) in the Västrabäcken sub catchment. The results during this measurement period did not show any significantly differences in comparison with means of the climatic parameters measured between 1980 and 2008 (Haei et al., 2010).

<table>
<thead>
<tr>
<th>Climatic variable</th>
<th>Mean/Median (±SD)</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air temperature (°C)</td>
<td>3.0/1.5 (±8.5)</td>
<td>-20.6</td>
<td>28.7</td>
</tr>
<tr>
<td>Soil temperature upslope (°C)</td>
<td>4.5/3.8 (±2.5)</td>
<td>1.3</td>
<td>8.9</td>
</tr>
<tr>
<td>Soil temperature riparian (°C)</td>
<td>3.9/2.9 (±2.8)</td>
<td>0.8</td>
<td>9.1</td>
</tr>
<tr>
<td>Precipitation (mm)</td>
<td>593</td>
<td>~40 % as snow</td>
<td></td>
</tr>
<tr>
<td>Snow (days)</td>
<td>192</td>
<td>1/11-14</td>
<td>14/5-15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(First day)</td>
<td>(Last day)</td>
</tr>
<tr>
<td>Slope runoff (mm)</td>
<td>286</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

During the sampling period (mid-June 2014 to mid-October 2015) climatic data of air temperature, precipitation and snow sheet was measured from a station in the outlet of the catchment whereas soil temperature was measured both in the riparian and upslope stations (Fig. 6). The air and riparian station soil temperature are also displayed in a boxplot in order to better see monthly variations and to easier compare the monthly differences to the values of groundwater-absorbed carbon (Figs. 7 and 8).

The hydrological year was warmer (in average +1.3 °C) in comparisons to air temperature data from the years 1980 to 2008 (Haei et al., 2010); but overall, the values of the climatic parameters (temperature, precipitation, snow cover duration) coincided with previous recordings. Thus, the sampling period occurred during representative climate conditions for the catchment area.
Figure 6. Climatic variables during the measurement period. Left axis is temperature, right axis (top) is precipitation and right axis (bottom) is discharge from the whole catchment area.
Figure 7. Left: Variation of air temperature (°C) within a month measured at the outlet of the catchment. Black line = median, rectangle = 1st and 3rd quartile with the middle of the box being the mean, whiskers = minimum and maximum soil temperature. The air temperature is always above 0 °C from May and onward is. The months that did not have soil temperature measurements for the whole month is excluded (June – 2014 and October – 2015). Right: Monthly boxplot for soil temperature (°C) at the riparian station for the studied period (from 1st July 2014 to 30th September 2015). Black line = median, rectangle = 1st and 3rd quartile with the middle of the box being the mean, whiskers = minimum and maximum soil temperature. Largest ranges appear during the summer months whereas a shift from generally lower to higher temperatures occur in spring and the opposite change during the autumn. The months that did not have soil temperature measurements for the whole month is excluded (June – 2014 and October – 2015).

3.2 CO₂ Concentration

Ranges of the CO₂ concentration throughout the hydrological year (October 2014 to September 2015) is presented in table 3. At a temporal perspective, the CO₂ concentration varies considerably both along the soil profile depth and between stations (Figs. 8 and 9). A seasonal trend is seen with higher CO₂ concentrations during the warmer period of the year (~June to September, based on air temperature in Figures 6 and 7) and lower concentrations during the colder season (October to May). The CO₂ concentrations at 85 cm in the riparian and upslope stations and at 35 cm in the upslope station were significant positively correlated to soil temperatures ($R^2 = 0.73, 0.57, 0.58$, p-values $<<0.005$) whereas the CO₂ concentration at 35 cm in the riparian station was insignificant correlated with soil temperature ($R^2 = 0.04$, p-value $<< 0.005$). No significant correlation was found between CO₂ concentrations and soil water volume or discharge. There was no significant relationship between CO₂ concentrations and the position of the water table, for neither the riparian or upslope stations.
Table 3 Summary of statistic variables for CO$_2$ concentrations (mg C-CO$_2$ l$^{-1}$) for the hydrological year (October 2014 to September 2015).

<table>
<thead>
<tr>
<th>Station and depth</th>
<th>Mean/Median (±SD)</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riparian shallow</td>
<td>17.4/17.0 (±4.0)</td>
<td>8.3</td>
<td>27.6</td>
</tr>
<tr>
<td>Riparian deep</td>
<td>14.5/14.5 (±2.4)</td>
<td>10.4</td>
<td>18.9</td>
</tr>
<tr>
<td>Upslope shallow</td>
<td>2.4/2.05 (±1.0)</td>
<td>1.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Upslope deep</td>
<td>8.9/8.7 (±1.5)</td>
<td>5.6</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Figure 8. Partial pressure of CO$_2$ (ppm, left axis), discharge (m$^3$ h$^{-1}$, right axis) and snow duration throughout the sampling period.
Figure 9. Heatmap of CO₂ concentration profiles in the riparian (upper) and upslope (lower) stations below the groundwater table based on the linear extra- and interpolation.
3.3 Discharge

Flow rates of the groundwater with depth for the entire sampling period is presented in Figure 10. Highest flow rates always appear in the shallower soil and highest flow rates are seen during periods of a shallow water table. The persistent high water table in mid-April to end of May is in response to the seasonal snowmelt. Periods of low flows often occur just after periods of high water tables; a plausible reaction due to a sinking water table in the upslope station is yielding less input of water. In July and August 2014, gaps are seen and is due to these values are erased and assumed to represent no flow as the slope of the water table during these periods appeared as reverted (i.e. flow occurred towards upslope instead of downhill). This is during a period where the water table is extrapolated in the upslope station so an underestimation of the water table position is possible. These gaps coincide with a drought period and very little discharge from the outlet of the catchment.

![Groundwater flow profile throughout the sampling period. The gaps during 2014 is due to the flow is so low that they are below the lowest discharge in the legend.](image)

3.4 CO₂ Export

Export of CO₂ from riparian and upslope station is presented in Figure 11 and is the outcome from multiplying the discharge with the concentration at each depth. The two periods in July and August 2014 that was assumed to have no flow is surrounded by gaps in the export figure; it is due to the export is smaller than the minimum of the heat legend and is only caused by small discharge and not due to low CO₂ concentrations. The highest transports are from shallower layers and when the water table is high, more CO₂ is transported. The monthly export from the slope, the hillslope and the riparian zone is presented in table 4 where the values are normalized by m². The normalization was calculated by total export divided by respective area above the measurement station (slope: 2530 m², hillslope: 2354 m² and riparian zone: 176 m²).
Figure 9 The CO₂ export from the riparian (upper) and upslope (lower) stations (i.e. slope and hillslope export respectively).

Table 4. Normalized CO₂ export from the riparian and upslope stations and the riparian zone and in addition, monthly slope discharge is displayed in column four Bold months represents the hydrological year and a sum of respective values for these months is done in the last row. Do note that these are normalized values and because the area of the riparian zone is much smaller in comparison to the other used areas; its export seems to be 10 times bigger in comparison to what is in total being exported from the slope.

<table>
<thead>
<tr>
<th>Month</th>
<th>CO₂ export from slope (mg C-CO₂ m⁻² month⁻¹)</th>
<th>CO₂ export from hillslope (mg C-CO₂ m⁻² month⁻¹)</th>
<th>CO₂ export from riparian zone (mg C-CO₂ m⁻² month⁻¹)</th>
<th>Groundwater flow (m³ month⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>June (14 days)</td>
<td>73.05</td>
<td>11.43</td>
<td>897.19</td>
<td>18.92</td>
</tr>
<tr>
<td>July</td>
<td>45.83</td>
<td>17.03</td>
<td>430.96</td>
<td>13.95</td>
</tr>
<tr>
<td>August</td>
<td>123.01</td>
<td>55.45</td>
<td>1'026.60</td>
<td>38.68</td>
</tr>
<tr>
<td>September</td>
<td>52.10</td>
<td>11.15</td>
<td>599.90</td>
<td>10.39</td>
</tr>
<tr>
<td>October</td>
<td>165.77</td>
<td>52.11</td>
<td>1'685.93</td>
<td>60.22</td>
</tr>
<tr>
<td>November</td>
<td>243.70</td>
<td>64.43</td>
<td>2'641.46</td>
<td>78.32</td>
</tr>
<tr>
<td>December</td>
<td>168.06</td>
<td>35.92</td>
<td>1'935.44</td>
<td>43.47</td>
</tr>
</tbody>
</table>

2014↑ 2015

<table>
<thead>
<tr>
<th>Month</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>84.56</td>
<td>16.47</td>
<td>995.29</td>
</tr>
<tr>
<td>February</td>
<td>45.03</td>
<td>8.66</td>
<td>531.49</td>
</tr>
<tr>
<td>March</td>
<td>68.49</td>
<td>8.14</td>
<td>875.64</td>
</tr>
<tr>
<td>April</td>
<td>548.74</td>
<td>138.83</td>
<td>6'031.34</td>
</tr>
<tr>
<td>May</td>
<td>745.76</td>
<td>252.71</td>
<td>7'340.25</td>
</tr>
<tr>
<td>June</td>
<td>247.00</td>
<td>57.31</td>
<td>2'783.99</td>
</tr>
<tr>
<td>July</td>
<td>218.20</td>
<td>45.76</td>
<td>2'524.65</td>
</tr>
<tr>
<td>August</td>
<td>145.96</td>
<td>43.40</td>
<td>1'517.77</td>
</tr>
<tr>
<td>September</td>
<td>103.18</td>
<td>22.43</td>
<td>1'183.18</td>
</tr>
<tr>
<td>October (11 days)</td>
<td>29.97</td>
<td>9.82</td>
<td>299.50</td>
</tr>
<tr>
<td><strong>October 2014 to September 2015</strong></td>
<td><strong>2'784.45</strong></td>
<td><strong>746.17</strong></td>
<td><strong>30'046.44</strong></td>
</tr>
</tbody>
</table>
3.5 Export Differences between the Riparian Zone & the Hillslope

Of the total export from the slope area (2530 m²), the riparian zone (176 m²) consistently contributes more compared to the hillslope (2354 m²) (Figs. 13 and 14). Peak CO₂ export in the riparian zone occurred during the snowmelt in April and May (548 and 746 mg C-CO₂ m⁻² month⁻¹ respectively) (Table 4). The major part of this export happened between 10 and 33 cm below surface. A minor peak occurred in November (244 mg C-CO₂ m⁻² month⁻¹) where the highest export appeared in a zone between 37 and 48 cm below surface. The relative contribution from the riparian zone to the total CO₂ export, was highest in March 2015 (88 %) and lowest in August 2014 (53 %).

**Figure 10.** Total and relative zone-dependent CO₂ export from the groundwater to the stream. The total CO₂ export to the stream is highest during snowmelt and a small peak occurs in November. The contribution to the total export from the riparian zone is always bigger in comparison to the export from the hillslope.

**Figure 11.** Bar plot of the monthly contribution of the riparian zone to the slope CO₂ export, expressed in percent.
3.6 Groundwater-absorbed Carbon

The estimated groundwater-absorbed carbon was obtained from the conception model (Eq. 20) and represents the part of the soil respiration diluting into the groundwater. The result is presented in figure 15 where the lowest production (appears negative) is in October (-0.67 g C-CO₂ m⁻² month⁻¹) and the highest production is in May (7.1 g C-CO₂ m⁻² month⁻¹). Do note that June 2014 only contains data for 16 days as the measurements started the 14th of June 2014. This is why June is excluded in the following comparisons of production during the summer months.

![Figure 12. Monthly CO₂ export, ΔS and groundwater-absorbed carbon from/in the riparian zone during the measurement period normalized by m². A positive ΔS indicates refilling of CO₂ in the groundwater whereas a negative indicates emptying in this storage. The former occurs when the groundwater-absorbed carbon exceeds the export. Do also note that June 2014 and October 2015 only have data for 16 and 11 days respectively.](image)

The negative production in September 2014 and October 2015 coincides with months with low discharge. These months are also the first months when the air temperature drops below 0 degrees (Fig. 7, air temperature for October 2015 is not presented in the figure). The production in September had a correlation with air temperature (R² = 0.53, p-value <<0.005).

In early April, the discharge increases due to snowmelt and continues to be large throughout the month. The snow sheet however, is still existing to some extent. In addition this month is represented of the soil temperature being at its lowest (~1.5 °C) and the air temperature still dropping below 0 degrees (with the minimum of -2 °C and 25 % of the hourly temperature measurements being below 0 °C). A positive correlation is seen between the groundwater-absorbed carbon and discharge (R² = 0.50,
p-value<0.005) and becomes even stronger in May (R² = 0.90, p-value<< 0.005). The peak production during May coincides with:

- The later part of the snowmelt when the ground is snow free, approximately in middle of May.
- The water table being at its highest position at the upslope station (~10 cm below surface) consistently high at the riparian station (~ 10 cm below surface).
- The air temperature, for the first time after the winter season, not dropping below 0 °C (Fig. 7).
- The increase in the soil temperature after being consistently low during the winter months (Fig. 8).

May production also correlates well with CO₂ concentrations (R² > 0.70, p-values<< 0.005), riparian and upslope CO₂ export (R² > 0.87, p-values << 0.0005) and soil temperature (R² = 0.69, p-value << 0.005), whereas the production has a weak positive correlation with air temperature (R² = 0.22, p-value < 0.005) (for all correlations: n = 744).

The production and the discharge is decreasing from May until October (table 4). A correlation between the two variables during this season is only seen in June (R² = 0.50, p-value<0.05, n = 720) and thereafter the correlation is in-significant.

During the hydrological year (October 2014 to September 2015) the groundwater volume in the riparian zone correlates positively with the production (R² = 0.31, p-value << 0.005, n = 8496). If comparing the production with the total water volume in the soil (i.e. soil water in the unsaturated zone included) the result was almost the same (a decrease in R² of 1 %). This was also true when comparing production with discharge from the riparian station (i.e. R²=0.30, p-value << 0.005, n = 8496). Furthermore, the riparian zone CO₂ export and production had a weak positive linear correlation, R² = 0.35 (p-value << 0.05, n = 8496), and a slightly stronger polynomial correlation, R² = 0.41 (p-value << 0.05, n = 8496).

The storage of CO₂ in the riparian zone is “refilled” during all months except in September, April, May and October in 2015; during these months, the storage of CO₂ is being “emptied”. Highest refill in storage occurs during March representing low fluctuation of the water table and a low export.

4 Discussion

The source of the CO₂ in headwater streams is starting to become unravelled by different research teams. However, it remains to clearly distinguish where in the surrounding landscape the terrestrial CO₂ originates. This thesis has examined the CO₂ contribution from two well-known zones, the riparian zone and the hillslope area draining to that riparian zone. This will help us to understand the catchment origins of the CO₂ emitted by the stream to the atmosphere, since so much of the stream CO₂ in the study area originates from the catchment. Thus, the aim of this study has been to quantify the terrestrial contribution of CO₂ to the stream and to describe the drivers behind the seasonal and spatial distribution. This was done by calculating zone-dependent CO₂ export from the riparian zone and the hillslope area and furthermore developing the export data to estimate the part of soil respiration dissolved in the soil water in the riparian zone.
4.1 CO₂ Concentrations in the Soil

The CO₂ concentration in a soil profile is a natural first step to determine where the CO₂ is produced and how it moves in the soil. It may indicate high production or storage in the soil. The highest concentration in the riparian station at 30 cm occurred in early spring (April) 2015 (Fig. 9). It might be explained by an increasing density in the snow making a cap on the surface and thus, capturing the CO₂ in the shallower layers (Pacific et al., 2008; Rains et al., 2016). Another or an additional explanation could be increased soil respiration below the snow sheet which might be enhanced by the water input from the snowmelt noticed in other studies (Musselman et al., 2005; Monson et al., 2006). The latter explanation is strengthened by the results of increase in production during this period herein (February to May, fig. 15).

The extreme fluctuations of CO₂ concentrations during the summer of 2014 in the shallow soil layers and in the stream show how complex and sensitive the system is to influences by different factors (such as water table position and rain events). In the shallow layers at 35 cm in the riparian station, the oscillation in groundwater level causes short periods of the sensor being just below and above the groundwater level. This, in turn, could result in CO₂ being pushed up in the soil profile due to the fluctuating groundwater table. The consequence would be a rapid decrease in CO₂ concentration in these shallow soil layers (Luo and Zhou, 2006, p.64). Then again, the pattern of CO₂ concentration in the stream during the same period closely resembles the fluctuation of the CO₂ concentration in the shallow layers at 30 cm in the riparian station. This might be due to export of the CO₂ from the shallow soil layers at the riparian station feeds the stream with CO₂ throughout periods of low discharge and dry periods. The high CO₂ concentration built up during dry periods is suddenly flushed out as soon it starts to rain and the discharge becomes larger. The consequence is a “flush-out” of the CO₂ in the shallow layers at the riparian station and a subsequent rapid emission of it from the stream and, thus, in-stream CO₂ concentrations decreases. This interpretation is supported by a study by Dinsmore et al. (2013), who presented a correlation between CO₂ concentration decrease in headwater streams in response to high flow events.

The positive correlation between soil temperature and CO₂ concentrations indicate a seasonal trend of higher concentrations during summer months. The seasonal trend agrees with the results of Striegl & Wickland (2001) indicating of a distinct seasonality in the soil CO₂ concentration profile in a young jack pine forest in Canada. The high CO₂ concentrations at the riparian station is believed to be due to the availability of organic carbon that is respired by microbes (Luo & Zhou, 2010, p. 54). The retrieved pattern of higher CO₂ concentration in the shallow part of the profile in the riparian station and, contrary, in the deeper part of the profile in the upslope station described herein have similarly been described from other catchments (Davidson et al., 2006; Pacific et al., 2011). The higher CO₂ concentration in shallower layers compared to in the deeper layers at the riparian station might be explained by: 1) Highest soil respiration appears in the shallow layers where more organic carbon is available and where
also the root zone are found (Lorenz and Lal, 2009, pp.24–37; Luo and Zhou, 2006, pp.79–85), and/or
2) soil respiration is linked to soil water content with highest respiration at an intermediate soil moisture
(Luo and Zhou, 2006, p.92). Both of these statements could potentially explain the noticed pattern.

4.1.1 Uncertainties in the CO2 Concentration Data

The 3 interpolated gaps in the CO2 concentration time-series during 2014 are, to some extent, unreliable
as they coincide with periods of fluctuating concentrations. The interpolation during 2015 is likely more
reliable as during this period little fluctuation appears in the stream sensor which during the last year
resembled at least the shallow sensor in the riparian station. The CO2 concentration profile is estimated
from only two depths (35 and 85 cm) with a linear relation. Thus, the profile may be a bit coarse and
some variations in the concentration with depth might be missing out. However, the linear interpolation
was based on varies studies with more measurement points in the soil profile (Luo and Zhou, 2006,
p.63; Öquist et al., 2009) and thus the CO2 concentration soil profile is assessed to be reliable. The
biggest uncertainty in the CO2 concentration soil profile is the extrapolation done for the upslope station
CO2 concentration below 85 cm to 120 cm, (layers were given the same concentration measured at 85
cm depth). But it is difficult to predict the CO2 concentration for these depths and both higher and lower
concentrations is plausible. As a consequence, the export from the deeper layers may be larger or
smaller. However, the impact of this uncertainty in the model is not likely to be significant, as the CO2
export is lowest in the deepest layers.

4.2 Zone-Dependent CO2 Export

Higher CO2 export is estimated during times the water table is high (Fig. 12 and Table 4). If to believe
reports predicting more intense rain events (e.g. Knapp et al., 2008; Räisänen and Tuomenvirta, 2009),
the importance of lateral CO2 export may increase (Dinsmore et al., 2013; Öquist et al., 2014) as rapid
rain events result in shallower water tables and consequently more of the soil respiration becomes
groundwater-absorbed carbon. Gedney et al. (2006) show on global scale, during the last decade, that
increased runoff could to some degree be explained by decreased evaporation due to stomatal-closure
effects of elevated air CO2 concentration. This should also have the effect of more respired CO2 being
exported through runoff which makes the production model herein even more important. It is difficult
to evaluate if that is already the case but nevertheless, it can be concluded that the main CO2 export is
from the shallower soil layers which are more conductive and the highest CO2 concentration occurs
which is in agreement with a previous study (Leith et al., 2015). This major export in shallower layers
mainly comes from the riparian zone.

The proximity of the riparian zone to the stream, the high content of organic carbon and a shallow
water table are all likely reasons why the riparian zone is the major contributor of the total terrestrial
CO2 export to the headwater stream (Figs. 13 and 14, Table 4). However, the contribution of CO2 from
the hillslope to the headwater stream (between 11 to 42 %) cannot be disregarded and its role as a source is not as insignificant as thought.

The importance of hillslope CO₂ becomes more significant during the two months with highest discharge (April and May). It might be due snowmelt water percolating the soil and pushes the spring production in shallower layers deeper into the soil but also constrains emission from deeper soil respiration. Moreover, the rising groundwater level in result of snowmelt reaches shallower soil layers and “captures” CO₂. If the hydrological cycle will change to fiercer rain events, it might result in a more fluctuating groundwater table in the hillslope allowing the hillslope contribution to become more significant (as in Augusts and May). This concept might be the explanation for the 35 % contribution of total terrestrial CO₂ export from the hillslope CO₂ export during July 2014; the monthly discharge is small, only 13.95 m³ (Table 4), but the major part of this leaves the system as in one event in the middle of July when the groundwater table rises fast. Instead, when intermediate water table is maintained by a more constant groundwater flow at the upslope station (as in July 2015), the importance of hillslope CO₂ export becomes less significant (20 %). Fiercer rain events might result in the hillslope becoming a more important CO₂ source to streams but, on the basis that the riparian zone is, in comparison to the hillslope: more productive, closer to the stream and saturated to a higher level, the riparian zone is consistently the most important terrestrial source. From a forest maintenance perspective, this suggests that changes in the hillslope zone (with for instance through clear cuts) might significantly affect the stream CO₂ emission, if coinciding with a fierce rain event. From a perspective of the carbon cycle, both slope zones are contributing to the CO₂ content of the stream but the riparian zone composes the more important source. It can be concluded from this study that CO₂ can be added to the compounds that the riparian zone controls/highly influence in streams (Vidon et al., 2015; Grabs et al., 2012; Cirmo and McDonnell, 1997).

4.2.1 Comparing the CO₂ Export with Previous Studies

The timing of the peaks in CO₂ export from the riparian station in May 2014 and November 2015 is similar to the pattern of CO₂ export that Leith et al. (2015) estimated for the years 2012 and 2013 in the same stations. Do note that the export from the riparian station is not the same as the export from the riparian zone CO₂ export (where upslope amount has been extracted). However, the peak during winter 2014 occurred one month earlier compared to the peak during winter 2012. There are also differences regarding the amount of CO₂ being exported and between which depths the major export occurred: data from Leith et al. (2015): May 2012 = 522 mg C-CO₂ m⁻² month⁻¹ (highest export between 25-50 cm below surface) and December 2012 = 529 mg C-CO₂ m⁻² month⁻¹ (highest export between 35-40 cm below surface) in comparison to my results: May 2015 = 746 mg C-CO₂ m⁻² month⁻¹ (highest export between 10-33 cm below surface) and November = 244 mg C-CO₂ m⁻² month⁻¹ (highest export 37-48 cm below surface). The difference in CO₂ export between the different years is probably due to natural
variance in a complex system influenced by many variables, such as discharge, freezing zones in the soil, soil temperature and CO\textsubscript{2} evasion from deeper layers.

Furthermore, the annual hillslope CO\textsubscript{2} export estimated herein (746 mg C-CO\textsubscript{2} m\textsuperscript{-2} yr\textsuperscript{-1}) is considerably lower compared to the annual hillslope CO\textsubscript{2} export measured during 2012 and 2013 (1144 mg C-CO\textsubscript{2} m\textsuperscript{-2} yr\textsuperscript{-1}) (Leith et al., 2015). This is also the case on a monthly basis, for instance the hillslope export peak in May: my study = 253 mg C-CO\textsubscript{2} m\textsuperscript{-2} month\textsuperscript{-1} versus 482 mg C-CO\textsubscript{2} m\textsuperscript{-2} month\textsuperscript{-1} (Leith et al., 2015). It is rather surprising that the CO\textsubscript{2} export estimations made herein are lower than those of Leith et al. (2015) as the same discharge profile was used at the upslope station. This was expected to rather result in a possible overestimation of the CO\textsubscript{2} export compared to if a separate discharge profile was calculated at the upslope station. Moreover, I also include deeper layers; down to 1.2 meters compared to the 0.9 meters’ deep model applied by Leith et al. (2015). A reason why this studies values are lower could be that the interpretation of CO\textsubscript{2} concentration with depth was done by a linear interpolation between the sensors whereas Leith et al. (2015) put the shallow sensor to represent the CO\textsubscript{2} concentration for all layers down to 45 cm below surface, whereas deeper layers where represented by the CO\textsubscript{2} concentration from the deep sensor. When applying linear interpolation instead (as in this study), the result is slightly lower CO\textsubscript{2} concentrations in the shallow layers which are layers where CO\textsubscript{2} export is high, and thus, the consequence is less CO\textsubscript{2} export. A gradient in CO\textsubscript{2} concentration is noticed in several other studies (Öquist et al., 2009; Davidson et al., 2006; Welsch and Hornberger, 2004; Maier et al., 2010; Luo and Zhou, 2006, pp.61–70); and the higher export in Leith et al. (2015) is believed to be due to the overestimated CO\textsubscript{2} concentration and to some extent a natural difference.

The total annual export presented herein, 2.8 g C-CO\textsubscript{2} g\textsuperscript{-1} yr\textsuperscript{-1}, is lower compared to previous results from the same catchment which equalled 3.0 and 3.2 g C-CO\textsubscript{2} m\textsuperscript{-2} yr\textsuperscript{-1} (Leith et al., 2015; Öquist et al., 2009). The annual discharge from the slope and the range of CO\textsubscript{2} concentrations (Table 3) for each sensor in this study was similar in Leith et al. (2015). Therefore, the difference in annual CO\textsubscript{2} export might be due to natural variability, as many different variables and their interactions affect the CO\textsubscript{2} export. Another explanation for the lower values presented herein could be due to a more developed model, referring mostly to the hydrological part but also the method to make the CO\textsubscript{2} concentration profile, which increases the accuracy of the results.

4.2.2 Uncertainties in the Estimations of CO\textsubscript{2} Export

As measurements of water table height only were available at two stations, the discharge profile was calculated at the riparian station. Consequently, the CO\textsubscript{2} export from the upslope station is estimated with the discharge profile from riparian station. This approach may underestimate the export of CO\textsubscript{2} from the hillslope due to the transmissivity profile likely being different in the mineral soil of the hillslope, compared to in the organic soil of the riparian zone. This especially applies for the shallower layers as the largest difference in transmissivity seems to be found here (Amvrosiadi, unpublished).
The extremely low CO₂ export in August 2014 may be due to an extrapolated water table at the upslope station underestimating the water level position. Such a deep positioned water table was not observed anywhere in the recordings from this study period and an earlier study (Leith et al., 2015). However, if instead the extrapolation is correctly estimating the height of the water table position, the reason for the low water level might be a dry period, starting in the middle of June and continuing until the middle of August. This latter explanation is strengthened by the decrease in CO₂ concentration in the deep layers at the upslope station where CO₂ might be in situ evaded rather than groundwater exported due to a deep water table; the consequences of this emission is an increase of the CO₂ concentration in the shallower layers. I favour the former explanation, however, due to the uncertainties with extrapolation.

The consequences of the discrepancy of CO₂ export in the shallower layers, where the upslope station have export but not the riparian station, might have resulted in a slightly overestimated export from the riparian zone as these extra layers was deleted. This outcome may indicate of a too detailed model during high flow events and the model might work better if a different shape for the shallow layers was applied. This modification of the layer shape would especially be important during high flow events as it was during such an event the discrepancy occurred of the water table raises much more at the upslope station. However, the extra layers at the upslope station could also be due to an error in the water table measurements, which would lead to no changes in the existing results. Another reason for the discrepancy could be the lack of sufficient data to make a discharge profile at the upslope station. How this would affect the total export is difficult to evaluate. However, even if these layers were deleted, the results are assumed reliable as it only being a few centimetre errors.

4.3 Groundwater-absorbed Carbon

The peak in groundwater-absorbed carbon (in May, Fig. 15) coincides with the period 1) of increase in sun radiation and the start of snowmelt 2) when the air temperature always stays above 0 °C (Fig. 7) ($R^2 = 0.19$, p-value $<< 0.005$), and the first real increase in soil temperature ($R^2 = 0.68$ and 0.44 for riparian and upslope respectively, p-values $<< 0.005$) after winter is noticed (Fig. 8); all parameters triggering input of carbon from root exudation (Kaiser et al., 2010) as well as vegetation growth. As the soil respiration is, to a major part, driven by assimilation from trees (Högberg et al., 2001), the peak during spring (when the water table is high) is expected because the groundwater will be in more close contact with the tree roots. The increase in temperature may also cause winter microbial communities to collapse, and thereby adding more carbon to the soil (Wang et al., 2014; Liptzin et al., 2009; Nemergut et al., 2005). Because of these increases of organic carbon in the soil, the microbial respiration may get fuel and an increase in the CO₂ “by-product” is likely. The emission rates during spring period is expected to be low in comparison to summer months, as most of the CO₂ production is becoming groundwater-absorbed carbon (further discussed in section when comparing result with
emission techniques). When the snowmelt is ending and spring turns to summer (May to June), the groundwater-absorbed carbon declines, as the major part of the soil respiration instead is in situ evaded.

The lowest calculated amounts of groundwater-absorbed carbon during the summer occurred in July 2014 (446 mg C-CO₂ m² month⁻¹); this is much smaller in comparison with July 2015 (2804 mg C-CO₂ m² month⁻¹). If evaluating the climatic variables between the years during the two July months, 2015 is rainier compared to 2014 (total precipitation: 91 mm and 39 mm respectively). Furthermore, during July 2015 the water table fluctuates in the shallower soil whereas during July 2014 the water table is fluctuating more and in deeper soil layers (Fig. 10). The influence of the water table on the groundwater-absorbed carbon is weak during 2015 (R² = 0.13, p-value: 0.03) and insignificant during 2014 (R² = 0.05, p-value > 0.05). The insignificant and significant correlations suggest: the water table might only influence the groundwater-absorbed carbon if it fluctuates in the shallow soil. The theory is strengthened by the fact that July is normally a high productive month with intense soil respiration especially occurring in shallower soil layers) (e.g. Pumpanen et al., 2003), which makes a shallower water table to a greater extent influences the CO₂ production becoming groundwater-absorbed carbon. This leads to an intriguing speculation of higher emission CO₂ production during 2014 (assuming that the emission rate is relatively similar in July 2014 and July 2015) as the deeper water table in 2014 access less CO₂. However, I emphasize that this is not possible to evaluate in this study as the emission rates is dependent on soil water content and other factors, such as soil temperature, leaf area index and fine root biomass (Borken et al., 2002; Hibbard et al., 2005; Ryan and Law, 2005; Canadell et al., 2007, p.27). The suggestion of the water table fluctuation in the shallower soil influencing the groundwater-absorbed carbon is strengthen by the increasing correlation during August months (2015: R² = 0.35 and 0.45, p-values << 0.005 for riparian and upslope water table respectively and 2014: R² = 0.19 and 0.17, p-value << 0.008 and 0.013 for riparian and upslope water table respectively).

The small peak in groundwater-absorbed carbon in November might be explained by possible frost in the shallower soils that traps the soil respiration in the ground and thus in the groundwater. The occasional snow sheet may also prevent the CO₂ to evade. However, a more likely explanation would be the melting of the occasional snow sheet leads to a high water table that absorbs the soil respiration. This may also be true for October 2014 where occasional snow sheet is observed. The melting of existing snow sheet during late autumn months (non-growing season) might cause a larger amount of the soil respiration dissolving in the groundwater. However, this evaluation is impossible without emission data. The results however suggest that further studies during this period might be of interest, as the amount soil respiration dissolving into the groundwater could be significantly larger in comparison to what is being emitted.

The decreasing groundwater-absorbed carbon towards the colder months (August and onward) may be due to an overall decrease in soil respiration as growing season is ending (Pumpanen et al., 2003). Therefore, the calculated level of groundwater-absorbed carbon in August and onwards are not surprising. The groundwater-absorbed carbon cannot become negative, as it appears to be in September
2014 and October 2015. For October 2015 data was only available for the first 11 days so it is possible that the production would be different if computation had been done for the whole month. Another likely explanation that applies for both months could be CO₂ evasion exceeding production rates.

That a seemingly equal amount of the groundwater-absorbed carbon is produced in a summer month (July and maybe August) and a winter month (December to January) suggest that: 1) the winter soil respiration might be much larger if groundwater-absorbed carbon was to be added to the soil respiration, and 2) a significant amount of the soil respiration occurs in the deeper soil layers as groundwater-absorbed carbon is captured in the deep lying water tables during the winter months (Especially in January and December). That soil respiration is influenced by temperature (e.g. Davidson et al., 2006) strengthens the fact that deeper soil respiration might be more active during the winter months where the temperature is more stable and seldom below 0 °C.

### 4.3.1 Groundwater-absorbed Carbon and Export

The coinciding peaks of production and export (Fig. 15) are reasonable, as soil respiration at its highest should result in high export of CO₂. This is true when the water table is high enough so that the soil respiration part dissolving in the groundwater becomes significant. The interaction of high water table and high soil respiration should result in peaks in groundwater-absorbed carbon, as likely is the case during May. Whereas either low water table or soil respiration result in intermediate groundwater-absorbed carbon which may be the case during November.

In April, the export exceeds the production, and thus, emptying the CO₂ storage in the riparian zone soil. This might be due the spring production has not yet started whereas the snowmelt has resulting in a major CO₂ lateral export with little refilling. When the conditions for production are more favourable (in May), the groundwater-absorbed carbon catches up with the high export and the out- and input are more or less in equilibrium (ΔS ~ 0).

### 4.3.2 Groundwater-absorbed Carbon in the Hillslope

The coupling between CO₂ export and production in the riparian zone might tell us something about the groundwater-absorbed CO₂ in the hillslope if the model was to be applied there. In this case, as the export from the hillslope is much lower in comparison to the export from the riparian zone, the production would also be expected to be lower. This interpretation agrees with Pacific et al. (2008) who suggested that there is a higher soil respiration in the riparian zone compared to the hillslope. To verify that this theory is applicable in the groundwater-absorbed carbon, the ΔS would be needed to take into consideration. However, if the water table is deeper in the ground (as in the hillslope), the ΔS might be as Maier et al. (2010) pointed out not necessary. More measurements are needed to further evaluate this.
4.3.3 Storage

On an annual basis, the ΔS (the difference in riparian zone CO₂ export and groundwater-absorbed carbon) would be expected to be in-significant compared to the annual export when estimating the production. As such, the groundwater-absorbed carbon may be estimated based on the CO₂ export. Based on the hydrological year between October-2014 and September-2015, the ΔS is positive: 815 mg C-CO₂ m⁻² yr⁻¹ (or a total increase for the riparian zone of ~140 g C-CO₂ yr⁻¹), which represent 2.6 % of the annual production. This may be due to margin of errors in the data collecting but they are more or less assumed to be cancelled out at a large scale. Most likely, however, this change in storage is due to natural differences in build-up and flush-out of CO₂, in and from, the riparian zone.

The overall CO₂ storage in the riparian zone is decreasing in two periods throughout the hydrological year: during spring flood and in the autumn. During all the other months, there is a refilling of the storage. The positive ΔS during the winter agrees with the new general idea that soil respiration occurs during the winter season even though it is small in comparison to the growing season respiration (Seok et al., 2015; Liptzin et al., 2009). A refilling of the storage would be expected to occur when the groundwater-absorbed carbon is high. This is not the case in the model presented herein (referring to April and May). As Maier et al. (2010) pointed out, the change in CO₂ storage is complex. They noticed an increase in vadose zone storage during heavy rainfall, increasing soil water content in the shallow soil layers, and a decreasing groundwater table whereas a decrease the storage coincided with increasing heights of the groundwater table (this would presumably after the heavy rainfall). Therefore, a possible explanation for depletion in storage during April, is that the water table raises considerably and due to the fast rate, instead of “absorbing” CO₂, it may push it further up in the soil profile. However, another possible explanation would be that, due to the increase in the water table, discharge increases and drains the storage; an emptying that continues in May. As soon as the growing season starts (presumably sometime during June), the storage starts to becomes refilled which is continuing during the summer months.

During the late autumn and the winter season (October 2014 to March 2015), only ΔS has a strong positive correlation with production (R² = >0.80, p-values << 0.005). The strong correlation indicates that the change in storage is controlled by the production which agrees with what Maier et al. (2010) found regarding the importance of ΔS during the cold season. The emptying of the CO₂ storage in September 2014 might be explained by several components acting together: firstly, there isn’t much rain and thus the most of the CO₂ production in the vadose zone is likely to be stored in the air pore space, secondly, the water table is stagnating which limits the “capturing” of new groundwater-absorbed carbon and thus only what is produced below the water table is adding to the storage. These are circumstances known to not favour soil respiration. Furthermore, the growing season have likely ended and thus the CO₂ production is smaller. In October 2014 instead, a refill is noticed and might be due to a colder adaptive microbial biota are established and also using up all carbon left from the growing season. This might also be the reason for the continuing refill during November and December together.
with the on and off snow cap that might slow down the evasion of CO\textsubscript{2} and thus the fluctuating groundwater table captures the CO\textsubscript{2} production which leads to increasing the CO\textsubscript{2} export. January and February may be a continuation of winter microbial biota activity along with low groundwater flow. Highest refill in storage occurs in March 2015, a month with similar conditions as January and February. Why a sudden increase in the refilling occurs are difficult to ascertain. However, it might be explained by a build-up in storage in the saturated and the unsaturated zone by: 1) the snow sheet slows down the evasion of the CO\textsubscript{2} production in the shallower layers; 2) the stagnated groundwater level makes it possible for slow CO\textsubscript{2} emission during winter from deeper layers; 3) a continuously CO\textsubscript{2} production in the deeper layers increases the storage in the groundwater (which has low fluctuation of the water table and also low CO\textsubscript{2} export due to small discharge. The soil respiration during winter months are complex and not very well studied, especially not in the deeper soils (below \textasciitilde30) (e.g. Brooks et al., 2005), but the increase in $\Delta S$ in this study might in general be explained by major microbial respiration occurs in the deep soil layers where the soil temperature still is in favour (above 0 °C degrees).

### 4.3.4 Spring Groundwater-absorbed Carbon compared to CO\textsubscript{2} Production

The groundwater-absorbed carbon calculated herein only represents the dissolved part of the respired CO\textsubscript{2} but the major amount of the respiration is generally being \textit{in situ} evaded. Most research has focused on measuring this \textit{in situ} CO\textsubscript{2} evasion and many equal these estimations to the total respiration. However, Maier et al. (2011) found that up to 40 % of the respiration can temporarily be stored in the soil pore space and I show that when the water level is high, more CO\textsubscript{2} is stored/produced in the groundwater. This quantity is not captured in emission measurements and neither in CO\textsubscript{2} export measurements. The ratio between CO\textsubscript{2} emission and dissolution has so far been unknown. But by monthly comparing my results of production to already made research on CO\textsubscript{2} emission and soil respiration, it is possible to evaluate the importance of the part of the soil respiration that is captured in the groundwater. The pattern in the measured monthly CO\textsubscript{2} emission from Pumpanen et al. (2003) during spring shows low emission that is increasing onwards. They made measurements during June 1997 to December 1999 in a Scots pine forest of CO\textsubscript{2} efflux CO\textsubscript{2} concentration and reveal highest effluxes during the snow free summer period. What is noticeable in the study is that during the snowmelt, the soil water content doubles but the evasion is continuously low. On contrary, the groundwater-absorbed carbon in this study is high during the snowmelt period. This highlights that emission data misses out on soil respiration dissolving in the groundwater and thus, if assimilating effluxes to soil respiration, the production would be low during snowmelt and then increase rapidly. But if the groundwater-absorbed carbon computed by the model presented herein were added, the soil respiration would likely have the rapid increase earlier as the groundwater-absorbed carbon is peaking during the snowmelt. This statement holds when continuing comparing the groundwater-absorbed carbon with other research (below).
Raich et al. (2002) reviews data from two localities of boreal woodlands that have a similar climate to the site in this project. Their estimations of the seasonal respiration is similar to the site described by Pumpanen et al. (2003) with highest respiration during summer. However, there is no data at snow sheet but assumption can be made if looking into general climate data in their respective regions. For one of the two localities (in Alaska, -64.8 N, 148.3 W), snowmelt normally ends in end of April, and the emission during May is approximately 0.1 g C m\(^{-2}\) day\(^{-1}\) but during one of the four years 0.5 g C-CO\(_2\) m\(^{-2}\) day\(^{-1}\) (Gulledge and Schimel, 2000). The snowmelt at the other locality (in Canada, -55.7 N, 97.9 W) occurred sometime during April when their estimated emission rate was 0.2 g m\(^{-2}\) day\(^{-1}\) (Savage et al., 1997). During the same months, my estimation of the groundwater-absorbed carbon is 0.17 and 0.23 g m\(^{-2}\) day\(^{-1}\) (April and May respectively). If the similarity of their sites to Västrabäcken generate similar respiration data (i.e. comparable emission data), the quantity of the groundwater-absorbed carbon is comparable with respiration being emitted during snowmelt. Thus, if the groundwater-absorbed carbon had been measured in their studies, the total respiration may have been the double compared to their reported soil respiration. The position of the water table is important as the quantity of groundwater-absorbed carbon is likely only comparable to emission data at sites with high water tables. As is often the case in riparian zones.

More recent research than the comparison with the two previous studies (i.e. (Raich et al., 2002; Pumpanen et al., 2003) may better capture respirations rates during snowmelt periods as the techniques have been improved; Monson et al. (2006) reports a six fold increase in soil respiration during snowmelt which they measured with gas chambers. Regardless of this increase, the accountable soil respiration was only a fraction of the NEE they estimated from an eddy covariance tower. Which might be due to the chamber measurements fails to capture the amount of CO\(_2\) becoming groundwater-absorbed carbon. Thus, there may be a possible underestimation of soil respirations contribution to the NEE. This claim could be strengthened or weakened if information of the groundwater table was presented and most likely, the statement would hold if the water table at the site were close to the surface. Continuously, the estimated soil respiration is in quantity (range and seasonal: 7.4 - 47.6 and 17 mmols C m\(^{-2}\) day\(^{-1}\)) comparable to the groundwater-absorbed carbon estimations (April and May: 14.3 and 19.1 mmols C m\(^{-2}\) day\(^{-1}\) respectively) and thereby, the soil respiration could be by maximum the double.

It is likely that a major of the respired CO\(_2\) during the summer season evades and therefore less is becoming groundwater-absorbed carbon. However, during spring when low emissions are seen (i.e. accepted in general as indicating low CO\(_2\) production), the groundwater-absorbed carbon is high. Therefore, an underestimation of soil respiration during spring may occur in seasonal dependent boreal forests if not the groundwater-absorbed carbon is taken into account. If this is to be true, up to the double amount CO\(_2\) production occurs in spring months during, and direct after, snowmelt. The distribution of the soil respiration between emission and groundwater-absorbed carbon could be assessed if measurement of the \textit{in situ} evasion is performed simultaneously with the model presented herein. Furthermore, assessment is possible of if the groundwater-absorbed carbon input increases soil
respirations’ influence of net ecosystem exchange (NEE) if the NEE was estimated, by for instance measurements collected by an eddy covariance tower.

4.3.5 Uncertainties in the Estimation of Groundwater-absorbed Carbon & ΔS

The groundwater-absorbed carbon is estimated from two variables (export of CO₂ and ΔS). The heterogeneity in soil CO₂ storage is extensive (Jassal et al., 2005; Maier et al., 2010) and to calculate the change in this storage for a larger area (176 m²) with only two measurement stations might make the ΔS variable a bit too generalized. One of these measurement stations that was used was assumed to represent humus soil (representative of high CO₂ concentration) and the other one a moraine (representative of low CO₂ concentration). This may contribute to uncertainties regarding production, as the ΔS estimation is generalized from available data. It is however, difficult to estimate the impact from this error and how more detailed data would affect ΔS.

Another issue with the estimation of ΔS is the influence of changes in water volume. If only the change in storage would be estimated for CO₂ in the groundwater, a small rise in the water table (few cm), would increase the stored CO₂ immensely due to large increase in the volume of water in the riparian zone. In a trial to eliminate or at least reduce the influence of the groundwater volume, the CO₂ amount dissolved in the water in the unsaturated zone was included. The relation between the CO₂ amount in the water in the unsaturated zone and the CO₂ amount in the groundwater for the downslope area varied substantially. During low water levels, naturally more CO₂ was stored in the unsaturated zone as the extent of this zone increased. The influence of the groundwater volume change on ΔS is assessed to be reduced to such an extent that the ΔS is reliable regarding this aspect.

To further improve the estimation of ΔS, the storage of CO₂ in the air pore space could be added as the CO₂ in the unsaturated zone is majorly focused in the air pore space. As estimated in this study, the CO₂ amount in the unsaturated zone may be slightly underestimated. More CO₂ measurement points in the riparian zone to estimate ΔS would increase the accuracy of the ΔS and thus, refine the production model.

The unsaturated CO₂ amount is estimated from an average of the CO₂ concentration between the surface (assumed to be atmospheric CO₂ concentration: 400 ppmv) and the shallow sensor. Together with the volume of water in the unsaturated zone, the CO₂ amount is estimated. If the spatial distribution of the water in the unsaturated zone could be mapped, the estimated CO₂ amount may increase as the ratio of air:water in the pore space is generally decreasing towards the groundwater table (one exception may be during rainfall where water is percolating the soil). Moreover, as the CO₂ concentration measured in the shallow sensor is supersaturated compared to the surface, the CO₂ amount in the unsaturated zone would likely increase.
5 Summary & Conclusions

Previous quantifications of the aquatic CO₂ export from the riparian zone and hillslope to headwater streams do not represent the part of the soil respiration that is absorbed in the groundwater. This due to the exclusion, in these models, of the changes in the temporarily stored CO₂ in the riparian zone (i.e. ΔS). Furthermore, estimations of the soil respiration based on measurements of either the emitted CO₂ (with for instance the well-used gas chambers) or the difference in CO₂ concentrations in unsaturated soils (the gradient method) fail to include the respired CO₂ absorbed in the groundwater. The model presented in this study fills this gap of knowledge by adding the temporary storage of CO₂ to the zone-dependent CO₂ groundwater export across a hillslope-riparian-stream transect. The results show that the highest amount of the groundwater-absorbed carbon coincided with periods of high groundwater levels. This is likely a result of a larger degree of the soil respiration becomes groundwater-absorbed carbon during flood events, rather than evaded in situ. Especially high groundwater-absorbed carbon was noticed during the snowmelt, when high groundwater levels coincided with the likely spring production. During these periods, the conventional methods used today to estimate the CO₂ production very likely fail to account for a large amount of the soil respiration and thus, underestimates the soil respiration with the consequences of: 1) misjudging the start of the spring production (so it seems to start later on the year than it actually is), 2) overestimating the local net primary production and 3) possibly underestimating the contribution of soil respiration to the NEE resulting in misinterpretations of the carbon exchange in the terrestrial ecosystem. This likely underestimation of soil respiration when only making measurements with conventional methods was confirmed by the comparison of the groundwater-absorbed carbon with existing evasion data which, indicated that up to half of the soil respiration is missed during spring. Future approaches should therefore advisably combine emission and aqueous CO₂ data to quantify the CO₂ production in the riparian zone and the hillslope in river catchments.

The temporal pattern of the groundwater-absorbed carbon did not differ as much between summer and winter as shown by models estimating the soil respiration. Possibly, the microbial respiration takes place at deeper soil levels than the root respiration. As such, the proximity of CO₂ production to the groundwater may lead to that, a relatively larger amount of the produced CO₂ becomes absorbed in the groundwater (instead of being in situ evaded) during winters. Alternatively, this effect is due to frost capping which captures the produced CO₂ in the soil. In this model, apparent “negative” CO₂ productions in the aqueous soil CO₂ pool may be calculated if emission exceeds the production; this might be adjusted by complementary in situ evasion data. The climatic main drivers behind the groundwater-absorbed carbon differed throughout the seasons where for instance the soil temperature was an important variable during the spring (i.e. March to May). The increase in the soil temperature, likely affected the soil respiration positively and thus, a cause for these high productive months.
Further studies are recommended where \( \Delta S \) for the hillslope is added to hillslope CO\(_2\) export estimates, as this could deepen our understanding of the drivers behind the terrestrial CO\(_2\) export. It could furthermore contribute with new knowledge regarding how soil respiration in deeper soil layers varies throughout the year, which today is not very well understood. The model can for certain be developed, which would make it possible to produce refined results, perform studies on more detailed temporal scales and evaluate the production laterally. Improvements could be done with for instance more CO\(_2\) concentration measurements which likely would increase the accuracy of the \( \Delta S \). If, in addition, measurements of CO\(_2\) in the vadose zone was included, the accuracy of \( \Delta S \) would furthermore increase and result in the first CO\(_2\) production profile accounting for all important soil respiration variables known today (lateral export, evasion and \( \Delta S \) of CO\(_2\)).

The riparian zone is independently of season the major contributor to CO\(_2\) in the stream (between 58-89 \%) in comparison to the distal hillslope. A drive behind the CO\(_2\) export was found to be the groundwater-absorbed carbon but during some months, stored CO\(_2\) was also exported. The contribution of CO\(_2\) from the hillslope to the headwater stream increases during intense rain events, but in comparison to the riparian zone it is still small. The CO\(_2\) production dissolving into the groundwater in the riparian zone is likely much larger in comparison to the hillslope, as the CO\(_2\) export follows the pattern of the groundwater-absorbed carbon. In, this study, it can be confirmed that the riparian zone is a hotspot and therefore a significant terrestrial source of headwater stream CO\(_2\). Even with the expected increase in lateral CO\(_2\) export, its role as a main source will not likely change. In fact, due to the extremely CO\(_2\) saturated conditions in the zone, the consequences might be that the riparian zone becomes an even more important source. To fully understand how the global warming and the expected change in precipitation pattern in the northern hemisphere will affect the riparian zone as a main source, future questions to answer could be: how old is the carbon being exported? secondly, will the expected increase in export mobilize older carbon and thus, change the carbon balance in the riparian zone?
6 Acknowledgements

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7 References


Appendix I – Rstudio script with corrections for Vaisala GMP221

Temperature & Pressure Correction

Calculate correct CO2

ASSUMED DEPTHS OF VALUES AS IN BELOW SURFACE#

* P_transducer (in both R and U):
  # UPSLOPE  900 mm RIPARIAN  830 mm
* Bottom of sensors (i.e sensor head):
  # S [350 mm] D [850 mm]
* Top of sensors (account for 109 mm length of sensor, model GMP221): S [241 mm]
  # D [741 mm]

  (Sensor position - length of sensor = Top of sensor)

* WT above sensors:
  # R_S [P_transducer -480] R_D [P_transducer +20]
  # U_S [P_transducer -550] U_D [P_transducer -50]

  the water height from the P_transducer - the difference to the sensors position =
  #
  water height above sensor)

* WT limit when CO2_sensor might read air:
  #
  deep: value of WTcorr is lower than -82 = Sensor in Water
  #
  shallow: value of WTcorr is lower than -32 = Sensor in Water

  Treshold D: WTcorr > -82 --> in air
  #
  S: WTcorr > -32 --> in air

(I have added 3 cm to the Sensor position to be sure the whole shield is under water)

EXPLANATION OF DATAFRAME VARIABLES

** Ci_XX: pCO2 in %

** Head_XX: WT (mm) above CO2_sensor bottom (Bottom in S = 35, D = 85), ("P_transducer"

  "CO2_sensor" [position] = "Water height above CO2_sensor" (mm)) in this case: 900 [U] (or 850

  [R]) - S[350] or D[850] =

  R_S: -480 or R_D: +20  U_S: -550 or U_D: -50

** PHead_XX: converting Head_XX to Meter

** CO2corrRDSPsys_XX: Pressure compensated for Water pillar pressure AND atm. pressure

(Note! X [hPA] = Y/100 [P] ; 1 Pascal [N/m^2] --> 1 [(kg*m/s^2)/m^2]

  (Pressure on sensor[(kg*m/s^2)/m^2 N/s^2]= ((water height [m]*density of fluid

  [kg/m^3]*gravity [m/s^2]) / 100) + atm pressure [hPa])

# STEP 1 SET UP WORKING AREA AND CREATE VARIABLES

47
# STEP 1 FOR RIPARIAN DEEP SENSOR

```r
#Create a Matrix to put calculation results in
CO2corrRD = matrix(0, nrow=length(DATA$RECORD), ncol=16, byrow=F)

#Define Column names for matrix
colnames(CO2corrRD)=c("Ci_RD","Head_RD","PHead_RD","Psys_RD",
"kp1_RD","kp2_RD","kt1_RD","kt2_RD","kt3_RD",
"aRD","bRD","cRD","dRD","eRD",
"CO2_RDc","CO2_RD_Dif")

CO2corrRD = as.data.frame(CO2corrRD)

# FILL COLUMNS
#"Ci_RD" #pCO2 Riparian Deep in %
CO2corrRD$Ci_RD = DATA$CO2_RD/10000

#"Head_RD": Riparian Deep Water Table above sensor Head (mm).
#Sensor at 850 mm, WT should be: P_Transducer_depth - CO2_sensor_depth = 950 -
# 850 --> 100 #Mean of PT is used if PT does not exist
CO2corrRDS$Head_RD = DATA$R_PTcorr+20

#"PHead_RD" #Convert Head (mm) to Head (m), CO2 sensor lays at 850 m below ground
CO2corrRDS$PHead_RD = (CO2corrRDS$Head_RD)/1000

#"Psys_RD" #Pressure compensated for water height above the sensor in hPa
CO2corrRDS$Psys_RD = (((CO2corrRDS$PHead_RD*1000*9.80665)/100)+(DATA$AP))
```

# STEP 1 FOR RIPARIAN SHALLOW SENSOR

```r
#Create a Matrix to put calculation results
CO2corrRS = matrix(0, nrow=length(DATA$RECORD), ncol=16, byrow=F)

#Define Column names for matrix
colnames(CO2corrRS)=c("Ci_RS","Head_RS","PHead_RS","Psys_RS",
"kp1_RS","kp2_RS","kt1_RS","kt2_RS","kt3_RS",
"aRS","bRS","cRS","dRS","eRS",
"CO2_RSc","CO2_RS_Dif")

#Convert the matrix to a dataframe so that I can directly refer to the column names
CO2corrRS = as.data.frame(CO2corrRS)

# FILL COLUMNS
#"Ci_RS" #pCO2 Riparian Shallow in %
CO2corrRS$Ci_RS = DATA$CO2_RS/10000

#"Head_RS" #Water Table above sensor Head (CO2 sensor head at 350 m belowground) (mm),
#Accounts for Shallow Sensor is 480 mm above P_transducer which is at 830.
CO2corrRSP$Head_RS= DATA$R_PTcorr-480

summary(DATA$R_PTcorr)
summary(CO2corrRSP$Head_RS)

# "PHead_RS" #Convert Head (mm) to Head (m)
CO2corrRSP$PHead_RS = (CO2corrRSP$Head_RS)/1000

#"Psys_RS" #Pressure compensated for water height above the sensor in hPa
CO2corrRSP$Psys_RS = (((CO2corrRSP$PHead_RS*1000*9.80665)/100)+(DATA$AP))
```

# STEP 1 FOR UPSLOPE DEEP SENSOR

48
Create a Matrix to put calculation results
Deep sensors don’t need 17 column (extra column for Temp) because measured and not modeled
CO2corrUD=matrix(0,nrow=length(DATAS$RECORD), ncol=16, byrow=F)
Define Column names for matrix
colnames(CO2corrUD)=c("Ci_UD","Head_UD","PHead_UD","Psyst_UD",
  "kp1_UD","kp2_UD","kt1_UD","kt2_UD","kt3_UD",
  "aUD", "bUD","cUD","dUD","eUD",
  "CO2_UDc","CO2_UD_Dif")
Convert the matrix to a dataframe so that I can directly refer to the column names
CO2corrUD=as.data.frame(CO2corrUD)

"Ci_UD" #pCO2 Riparian Deep in %
CO2corrUD$Ci_UD= DATA$CO2_UD/10000

"Head_UD" #head W (mm) above CO2_sensor Approximation is used
CO2corrUD$Head_UD= (DATA$U_PTcorr-50)

"PHead_UD" #Convert Head (mm) to Head (m)
CO2corrUD$PHead_UD=CO2corrUD$Head_UD/1000

# Pressure compensated for water heigh above the sensor in (hPa)
CO2corrUD$Psyst_UD=(((CO2corrUD$PHead_UD*1000*9.80665)/100)+(DATA$AP))

Create a Matrix to put calculation results
CO2corrUS=matrix(0,nrow=length(DATAS$RECORD), ncol=16, byrow=F)
Define Column names for matrix
colnames(CO2corrUS)=c("Ci_US","Head_US","PHead_US","Psyst_US",
  "kp1_US","kp2_US","kt1_US","kt2_US","kt3_US",
  "aUS", "bUS","cUS","dUS","eUS",
  "CO2_USc","CO2_US_Dif")
Convert the matrix to a dataframe so that I can directly refer to the column names
CO2corrUS=as.data.frame(CO2corrUS)

"Ci_US" #pCO2 Upslope shallow %
CO2corrUS$Ci_US= DATA$CO2_US/10000

"Head_US" # Convert Head (mm) to Head (m)
CO2corrUS$Head_US= (DATA$U_PTcorr-550)

"PHead_US" # Convert Head (mm) to Head (m)
CO2corrUS$PHead_US=as.numeric((CO2corrUS$PHead_US/1000),na.rm=FALSE)

# Pressure compensated for water heigh above the sensor in (hPa)

Create a Matrix to put calculation results
CO2corrSTM=matrix(0,nrow=length(DATAS$RECORD), ncol=16, byrow=F)
Define Column names for matrix
colnames(CO2corrSTM)=c("Ci_STM","Head_STM","Psys_STM","kp1_STM","kp2_STM","kt1_STM","kt2_STM","kt3_STM","aSTM","bSTM","cSTM","dSTM","eSTM","CO2_STMMe","CO2_STM_Dif")

#Convert the matrix to a dataframe so that I can directly refer to the column names
CO2corrSTM=as.data.frame(CO2corrSTM)

# "Ci_STM"  #pCO2 Riparian Deep in %
CO2corrSTM$Ci_STM= DATA$CO2_STM/10000

# "Head_STM"             #Stream Water Table (above Head expressed in mm)
# Assume that CO2 sensor in stream is at the same place a Pressure Transducer.
# If NA --> mean of STM_WL is used.
CO2corrSTM$Head_STM= ifelse(is.na(DATA$STM_WL),
mean(DATA$STM_WL,na.rm=T), DATA$STM_WL)

# "Psys_STM"                               #Calculate Pressure compensated for sensor depth. Psys in hPa
CO2corrSTM$Psys_STM =(((CO2corrSTM$PHead_STM*1000*9.80665)/100)+(DATA$AP))

# STEP 2               CALCULATE CONSTANTS FOR THE VAISALA_CORRECTION              #

##                                           RIPARIAN_DEEP constants
##Calculate first series constants ##
CO2corrRD$kp1_RD=(0.97501*(CO2corrRD$Ci_RD)^4)+(-
54.1519*(CO2corrRD$Ci_RD)^3)+(479.778*(CO2corrRD$Ci_RD)^2)+(-
11362.8*(CO2corrRD$Ci_RD))

CO2corrRD$kp2_RD=((-
9.3269*0.001)*(CO2corrRD$Ci_RD^3))+(0.14345*(CO2corrRD$Ci_RD^2))+(15.7164*(CO2corrRD$Ci_RD))

CO2corrRD$kt1_RD=(0.046481*(CO2corrRD$Ci_RD^3))+(-1.02280*(CO2corrRD$Ci_RD^2))+(-
37.4433*CO2corrRD$Ci_RD)+(-49.000)

CO2corrRD$kt2_RD=(-3.0166*(CO2corrRD$Ci_RD^2))+(-8.8421*CO2corrRD$Ci_RD)

CO2corrRD$kt3_RD=(0.000083600*(CO2corrRD$Ci_RD^3))+(-
0.0024199*(CO2corrRD$Ci_RD^2))+(-0.066814*CO2corrRD$Ci_RD)

#Calculate second series of constants
CO2corrRD$sRD=CO2corrRD$kp1_RD*((CO2corrRD$Psys_RD-1013)/(1013)^2)

CO2corrRD$bRD=CO2corrRD$kp2_RD*((CO2corrRD$Psys_RD-1013)/(1013)^2)

CO2corrRD$cRD=CO2corrRD$kt1_RD*((25-DATA$Temp_R)/25)^3

CO2corrRD$dRD=CO2corrRD$kt2_RD*((25-DATA$Temp_R)/25)^2

CO2corrRD$eRD=16320*(((-CO2corrRD$kt3_RD)^2)+CO2corrRD$kt3_RD)*((25-
DATA$Temp_R)/25)

##                                           RIPARIAN_SHALLOW constants

##Calculate first series constants ##
CO2corrRD$kp1_RD=((CO2corrRD$Ci_RD*0.97501)^4)+(-
54.1519*(CO2corrRD$Ci_RD)^3)+(479.778*(CO2corrRD$Ci_RD)^2)+(-
11362.8*(CO2corrRD$Ci_RD))

CO2corrRD$kp2_RD=((-
9.3269*0.001)*(CO2corrRD$Ci_RD^3))+(0.14345*(CO2corrRD$Ci_RD^2))+(15.7164*(CO2corrRD$Ci_RD))

CO2corrRD$kt1_RD=(0.046481*(CO2corrRD$Ci_RD^3))+(-1.02280*(CO2corrRD$Ci_RD^2))+(-
37.4433*CO2corrRD$Ci_RD)+(-49.000)

CO2corrRD$kt2_RD=(-3.0166*(CO2corrRD$Ci_RD^2))+(-8.8421*CO2corrRD$Ci_RD)

CO2corrRD$kt3_RD=(0.000083600*(CO2corrRD$Ci_RD^3))+(-
0.0024199*(CO2corrRD$Ci_RD^2))+(-0.066814*CO2corrRD$Ci_RD)

#Calculate second series of constants
CO2corrRD$sRD=CO2corrRD$kp1_RD*((CO2corrRD$Psys_RD-1013)/(1013)^2)

CO2corrRD$bRD=CO2corrRD$kp2_RD*((CO2corrRD$Psys_RD-1013)/(1013)^2)

CO2corrRD$cRD=CO2corrRD$kt1_RD*((25-DATA$Temp_R)/25)^3

CO2corrRD$dRD=CO2corrRD$kt2_RD*((25-DATA$Temp_R)/25)^2

CO2corrRD$eRD=16320*(((-CO2corrRD$kt3_RD)^2)+CO2corrRD$kt3_RD)*((25-
DATA$Temp_R)/25)
CO2corrRS$kp1_RS=(0.97501*(CO2corrRS$Ci_RS^4))+(-54.1519*(CO2corrRS$Ci_RS^3))+(479.778*(CO2corrRS$Ci_RS^2))+(-11362.8*(CO2corrRS$Ci_RS))

CO2corrRS$kp2_RS=(-9.3269*0.001)*(CO2corrRS$Ci_RS^3)+(0.14345*(CO2corrRS$Ci_RS^2))+(-15.7164*CO2corrRS$Ci_RS)

CO2corrRS$kt1_RS=(0.046481*(CO2corrRS$Ci_RS^3))+(-1.02280*(CO2corrRS$Ci_RS^2))+(-37.4433*(CO2corrRS$Ci_RS))+(-49)

CO2corrRS$kt2_RS=(-3.0166*(CO2corrRS$Ci_RS^2))+(-8.8421*CO2corrRS$Ci_RS)

CO2corrRS$kt3_RS=(0.000083600*(CO2corrRS$Ci_RS^3))+(-0.0024199*(CO2corrRS$Ci_RS^2))+(-0.066814*(CO2corrRS$Ci_RS))

#Calculate second series of constants

CO2corrRS$aRS=CO2corrRS$kp1_RS*(((CO2corrRS$Psys_RS-1013)/1013)^2)

CO2corrRS$bRS=CO2corrRS$kp2_RS*(((CO2corrRS$Psys_RS-1013)/1013)*CO2corrRS$Psys_RS)

CO2corrRS$cRS=CO2corrRS$kt1_RS*(((25-DATA$Temp_R)/25)^3)

CO2corrRS$dRS=CO2corrRS$kt2_RS*(((25-DATA$Temp_R)/25)^2)

CO2corrRS$eRS=16320*(-(CO2corrRS$kt3_RS^2)+CO2corrRS$kt3_RS)*((25-DATA$Temp_R)/25)

##                                    #########      UPSLOPE_DEEP constants

#Calculate first series constants

CO2corrUD$kp1_UD=(0.97501*((DATA$CO2_UD)/10000)^4)+(-54.1519*((DATA$CO2_UD)/10000)^3))+(479.778*((DATA$CO2_UD)/10000)^2))+(11362.8*(DATA$CO2_UD)/10000)

CO2corrUD$kp2_UD=(((-9.3269*0.001)*)((DATA$CO2_UD/10000)^3))+(0.14345*DATA$CO2_UD/10000)^2))+(15.7164*(DATA$CO2_UD/10000))

CO2corrUD$kt1_UD=(0.046481*(DATA$CO2_US/10000)^3))+(-1.02280*(DATA$CO2_US/10000)^2))+(-37.4433*(DATA$CO2_US/10000))+(-49)

CO2corrUD$kt2_UD=(-3.0166*(DATA$CO2_US/10000)^2))+(-8.8421*(DATA$CO2_US/10000))

CO2corrUD$kt3_UD=(0.000083600*(DATA$CO2_US/10000)^3))+(-0.0024199*(DATA$CO2_US/10000)^2))+(-0.066814*(DATA$CO2_US/10000))

#Calculate second series of constants

CO2corrUD$aUD=CO2corrUD$kp1_UD*(((CO2corrUD$Psys_UD-1013)/1013)^2)

CO2corrUD$bUD=CO2corrUD$kp2_UD*(((CO2corrUD$Psys_UD-1013)/1013)*CO2corrUD$Psys_UD)

CO2corrUD$cUD=CO2corrUD$kt1_UD*(((25-DATA$Temp_Ucorr)/25)^3)

CO2corrUD$dUD=CO2corrUD$kt2_UD*(((25-DATA$Temp_Ucorr)/25)^2)

CO2corrUD$eUD=16320*(-(CO2corrUD$kt3_UD^2)+CO2corrUD$kt3_UD)*((25-DATA$Temp_Ucorr)/25)

##                                    #########      UPSLOPE_SHALLOW constants

#Calculate first series constants

CO2corrUS$kp1_US=(0.97501*((DATA$CO2_US)/10000)^4)+(-54.1519*((DATA$CO2_US)/10000)^3))+(479.778*((DATA$CO2_US)/10000)^2))+(11362.8*(DATA$CO2_US)/10000)

CO2corrUS$kp2_US=(((-9.3269*0.001)*)((DATA$CO2_US/10000)^3))+(0.14345*DATA$CO2_US/10000)^2))+(15.7164*(DATA$CO2_US/10000))

CO2corrUS$kt1_US=(0.046481*(DATA$CO2_US/10000)^3))+(-1.02280*(DATA$CO2_US/10000)^2))+(-37.4433*(DATA$CO2_US/10000))+(-49)


CO2corrUS$kt3_US=(0.000083600*(DATA$CO2_US/10000)^3))+(-0.0024199*(DATA$CO2_US/10000)^2))+(-0.066814*(DATA$CO2_US/10000))

#Calculate second series of constants


## Calculate first series constants (Pressure)
CO2corrSTMkp1_STM = (0.97501 * (DATA$CO2_STM) / 10000)^4 + (-54.1519 * (DATA$CO2_STM) / 10000)^3 + (479.778 * (DATA$CO2_STM) / 10000)^2 + (-11362.8 * (DATA$CO2_STM) / 10000)
CO2corrSTMkp2_STM = ((-9.3269 * 0.001) * (DATA$CO2_STM) / 10000)^3 + (0.14345 * (DATA$CO2_STM) / 10000)^2 + (15.7164 * (DATA$CO2_STM) / 10000)
CO2corrSTMkt1_STM = (0.046481 * (DATA$CO2_STM) / 10000)^3 + (-1.02280 * (DATA$CO2_STM) / 10000)^2 + (-37.4433 * (DATA$CO2_STM) / 10000) + (-49)
CO2corrSTMkt2_STM = (-3.0166 * (DATA$CO2_STM) / 10000)^2 + (-8.8421 * (DATA$CO2_STM) / 10000)
CO2corrSTMkt3_STM = (0.000083600 * (DATA$CO2_STM) / 10000)^3 + (-0.0024199 * (DATA$CO2_STM) / 10000)^2 + (0.066814 * (DATA$CO2_STM) / 10000)

## Second series of constants
CO2corrSTMsaSTM = CO2corrSTMkp1_STM * ((DATA$STMPsys_STM - 1013) / 1013)^2
CO2corrSTMsbSTM = CO2corrSTMkp2_STM * ((DATA$STMPsys_STM - 1013) / 1013) * DATA$STMPsys_STM
CO2corrSTMscSTM = CO2corrSTMkt1_STM * ((25 - DATA$Temp_STM) / 25)^3
CO2corrSTMsdSTM = CO2corrSTMkt2_STM * ((25 - DATA$Temp_STM) / 25)^2
CO2corrSTMseSTM = 16320 * (- (CO2corrSTMkt3_STM)^2 + CO2corrSTMkt3_STM) * ((25 - DATA$Temp_STM) / 25)

## INFO TO EASE UP YOUR HEAD
# If sensor is above water, put in "air"-column (DATA$CO2_RDcorr_air) and set old column-row (DATA$CO2_RDcorr) to Na.
# Treshold D: WTcorr > -85 --> in air        # See intro for information if you can't remember
# S: WTcorr > -35 --> in air
## Calculate corrected CO2 and other variables
CO2corrRD_CO2_RDc = DATA$CO2_RD - (CO2corrRD_aRD) - (CO2corrRD_bRD) - (CO2corrRD_cRD) - (CO2corrRD_dRD) - (CO2corrRD_eRD)
CO2corrRD_CO2_RD_Dif = (DATA$CO2_RD - CO2corrRD_CO2_RDc) / DATA$CO2_RD

# Calculate corrected pCO2
CO2corrRDpCO2_RDc = DATA$CO2_RD - (CO2corrRDaRDpCO2) - (CO2corrRDbRDpCO2) - (CO2corrRDeRDpCO2)

# If sensor is above water, put in "air"-column (DATA$CO2_cwg_RD) and set old column-row (DATA$CO2_cwg_RD) to Na.
CO2corrRS$CO2_RSc = DATA$CO2_RS - (CO2corrRS$aRS) - (CO2corrRS$bRS) - (CO2corrRS$cRS) - (CO2corrRS$dRS) - (CO2corrRS$eRS)
CO2corrRS$CO2_RS_Dif = (DATA$CO2_RS - CO2corrRS$CO2_RSc) / DATA$CO2_RS
head(CO2corrRS) # check

# Define a new column in Stran with the corrected data and set values to NA where CO2_Sensor is in AIR (e.g. U_PT<199 or U_PT<719)
CO2corrRS$CO2_RSc <- as.numeric(CO2corrRS$CO2_RSc)
DATA$CO2_cwg_RS = CO2corrRS$CO2_RSc
summary(CO2corrRS$CO2_RSc)
DATA$CO2_RS_corr = as.numeric(DATA$CO2_RS_corr)

CO2corrUD$CO2_UDc = DATA$CO2_UD - (CO2corrUD$aUD) - (CO2corrUD$bUD) - (CO2corrUD$cUD) - (CO2corrUD$dUD) - (CO2corrUD$eUD)
CO2corrUD$CO2_UD_Dif = (DATA$CO2_UD - CO2corrUD$CO2_UDc) / DATA$CO2_UD
CO2corrUD$CO2_UDc = as.numeric(CO2corrUD$CO2_UDc)
DATA$CO2_cwg_US = CO2corrUS$CO2_USc # cwg stands for corrected with gaps (gaps are not filled)
summary(DATA$CO2_cwg_US)

# Obs! DATA refers to a df where setup of Date and time is already done

CO2corrUS$CO2_USc = as.numeric(CO2corrUS$CO2_USc)
DATA$CO2_cwg_US = CO2corrUS$CO2_USc

# Calculate corrected pCO2
CO2corrSTM$CO2_STMc = DATA$CO2_STM - (CO2corrSTM$aSTM) - (CO2corrSTM$bSTM) - (CO2corrSTM$cSTM) - (CO2corrSTM$dSTM) - (CO2corrSTM$eSTM)
CO2corrSTM$CO2_STM_Dif = (DATA$CO2_STM - CO2corrSTM$CO2_STMc) / DATA$CO2_STM
CO2corrSTM$CO2_STMc = as.numeric(CO2corrSTM$CO2_STMc)
DATA$CO2_cwg_STM = CO2corrSTM$CO2_STMc
summary(DATA$CO2_cwg_STM)

# Set values to NA where CO2_Sensor is in AIR:
DATA$CO2_STM_corr = as.numeric((CO2corrSTM$CO2_STMc<0 ? NA, CO2corrSTM$CO2_STMc), na.rm=FALSE)
# DEFINE AN AIR-column If Sensor is above water, put in "air"-column (DATA$CO2_RDcorr_air) and set old column-row (DATA$CO2_RDcorr) to Na.
# PLUS : Define Data type and specify that NA's should be interpreted as NA's
DATA$CO2_STM_corr_air = as.numeric((DATA$CO2_STM_corr_air<0 ? NA, CO2corrSTM$CO2_STMc), na.rm=FALSE)

Interpolation of Gaps in Data and Separation when the Sensor is Measuring in the Air versus Groundwater

# DATA$CO2RD_all_wg <- (CO2corrRD$CO2_RSc)
DATA$CO2RS_all_wg <- (CO2corrRS$CO2_RS)
summary(DATA$CO2RS_all_wg)
DATA$CO2UD_all_wg <- (CO2corrUD$CO2_UDc)
summary(DATA$CO2UD_all_wg)
DATA$CO2US_all_wg <- (CO2corrUS$CO2_USc)
summary(DATASCO2US_all_wg)
DATASCO2STM_all_wg <- (CO2corrSTM$CO2_STMc)
summary(CO2corrSTM$CO2_STMc)
# Divide air and water CO2 concentrations into different columns,
# Estimated if WT higher than 32 --> sensor in air
DATASU_WT_approxE = abs(DATASU_WT_approxE)
DATASR_WT_approxE = abs(DATASR_WT_approxE)
summary(DATASU_WT_approxE)
summary(DATASR_WT_approxE)
# RD
DATASCO2_RDcorr=ifelse(DATASR_WT_approxE>(82), NA, CO2corrRD$CO2_RDc)
DATASCO2_RDcorr_air =ifelse(((82)>DATA$R_WT_approxE & (82)=DATA$R_WT_approxE),
NA, CO2corrRD$CO2_RDc)
# RS
DATASCO2_RScorr=ifelse(DATASR_WT_approxE>(32), "NA", CO2corrRS$CO2_RScc)
DATASCO2_RScorr_air =ifelse((32.01)>DATA$R_WT_approxE, "NA", CO2corrRS$CO2_RScc)
# UD
DATASCO2_UDcorr=ifelse(DATASU_WT_approxE>(90), NA, CO2corrUD$CO2_UDc)
DATASCO2_UDcorr_air = ifelse((90.01)>DATA$U_WT_approxE, NA, CO2corrUD$CO2_UDc)
# US
DATASCO2_UScorr = ifelse(DATASU_WT_approxE>(32), NA, CO2corrUS$CO2_USc)
DATASCO2_UScorr_air = ifelse((32.01)>DATA$U_WT_approxE, NA, CO2corrUS$CO2_USc)
# Convert to numeric
DATASCO2_RDcorr_air=as.numeric(DATASCO2_RDcorr_air)
DATASCO2_RScorr_air=as.numeric(DATASCO2_RScorr_air)
DATASCO2_UScorr_air=as.numeric(DATASCO2_UScorr_air)
DATASCO2_UDcorr_air=as.numeric(DATASCO2_UDcorr_air)
# Script-part explanation: filling in the gaps in the CO2-data set - This, in order to make triangle interpolation of CO2 by depth
# DATASCO2RD_all = ifelse(is.na(DATASCO2RD_all), na.approx(DATASCO2RD_all),
DATASCO2RD_all)
DATASCO2RS_all = ifelse(is.na(DATASCO2RS_all), na.approx(DATASCO2RS_all),
DATASCO2RS_all)
DATASCO2UD_all = ifelse(is.na(DATASCO2UD_all), na.approx(DATASCO2UD_all),
DATASCO2UD_all)
DATASCO2US_all = ifelse(is.na(DATASCO2US_all), na.approx(DATASCO2US_all),
DATASCO2US_all)
DATASCO2STM_all = ifelse(is.na(DATASCO2STM_all), na.approx(DATASCO2STM_all),
DATASCO2STM_all)
Appendix II - Carbon Cycling in the Northern Hemisphere

Terrestrial Reservoirs

Forests
The carbon uptake and release in forests is strongly influenced by seasonality. Uptake in forests occurs through: photosynthesis, tree growth, forest ageing and carbon decomposition in soil; whereas carbon release takes place through root respiration, tree mortality, microbial decomposition of litter, degradation and disturbance. These mechanisms are divided into the gross primary production (GPP) (i.e. biomass produced of primary producers) and the respiration (i.e. chemical energy used for maintenance). The difference of these is equal to the net primary production (NPP) (i.e. the amount biomass fixed in new production). For example, atmospheric CO₂ is consumed by plant photosynthesis whereas root respiration and microbial respiration simultaneously releases CO₂. The carbon sequestration potential of forests is strongly dependent on soil respiration (Högberg et al., 2001). The root respiration can release >50 % of the photosynthesized carbon (Lambers et al., 1996; Ryan et al., 1997). The net balance between these two processes can change from net CO₂ uptake to net source depending on landscape type and seasonality. Yet, in sum, the forests act as a carbon bonder of CO₂ to organic carbon which is subsequently deposited in the soil (Bonan et al., 1995; Whalen et al., 1991; Lorenz and Lal, 2009).

The ground vegetation carbon uptake is estimated to 2,6 Pg C year⁻¹ of which the boreal forest uptake is responsible for approximately 0,47-0,7 Pg C year⁻¹ (Lorenz and Lal, 2009) and, in total, the boreal forests contain 13 % of the global carbon biomass (Dunn et al., 2007). The uptake of carbon in forests is through atmospheric CO₂, carbon oxide (CO) and methane gas (CH₄). But as the CH₄ influxes in a boreal forest is small (1 Tg CH₄ yr⁻¹) (Bonan et al., 1995; Whalen et al., 1991), CO₂ and CO is the dominant gases assimilated to organic matter.

Soils
The CO₂ in the soil originates from several sources with a major amount coming from soil respiration (Luo and Zhou, 2006; Reardon et al., 1979), which is considered the “the main door” for CO₂ to leave plants (Schlesinger and Andrews, 2000). Respiration is divided into autotrophic and heterotrophic respiration, where the former is constituted by microbial respiration and the latter is the uptake of energy from inorganic substances by trees. It is difficult to pinpoint a certain method for major CO₂ created in soil respiration as for example root respiration can account for 10 to 90 % of the soil respiration (Luo and Zhou, 2006, p.42). Highest CO₂ production activity is noticed in the shallowest soil layer where the majority of organic carbon in soils is found in the upper soil layer (Maier et al., 2010). The production is decreasing with depth (Davidson et al., 2006; Jassal et al., 2004). It is from the upper soil layers, root respiration and degradation of fresh litter from the terrestrial vegetation transfer the carbon in organic
matter into the soil. Soil microbiota (i.e. fungi, micro fauna and bacteria) feeds on the soil litter and releases nutrients and CO₂, CH₄, H₂O. They also transform the organic matter in soils from coarse particulate to dissolved molecules which can be composed of glucose, proteins, aromatic compounds and especially humic and fulvic acids (Schlesinger and Bernhardt, 2013, p.160).

The metabolic pathways leading to production of CO₂ is the result of oxic respiration from root or microbes (Ekblad and Högborg, 2001). The decomposition rate (i.e. soil microbial activity) is dependent on temperature (Valentini et al., 2000), moisture and the litter chemical compound (Schlesinger and Bernhardt, 2013, p.161; McTiernan et al., 2003). The turnover time of carbon in soils is dependent on climate, vegetation, parent material and topography and ranges from years to centuries (Trumbore and Harden, 1997; Trumbore, 1997) where carbon turnover rate in soils increases with increased temperature (Bonan, 2008). For instance, during the first year in Arctic areas, litter decomposition (i.e. “mass remaining of original litter after a period of incubation”) has reached 20 % (Luo & Zhou, 2010, p. 51). In addition to temperature, the process can be speeded up depending on several other abiotic factors such as the access to water and oxygen, (Luo & Zhou, 2010, p. 55) but also the litter quality (for example, access to N and C:N ratios) affects the time of decomposition (Norby et al., 2007).

The partial pressure of CO₂ (pCO₂) in the pore water of soils can be highly oversaturated compared to the atmosphere (Battin et al. 2009), not seldom up to two orders of magnitude in comparison (Aucour et al., 1999). Supersaturated soil conditions result in streams receiving a substantial amount of CO₂ through percolation which ultimately results in rapid CO₂ efflux from streams (Battin et al. 2009).

Other ways of CO₂ to find its way into the soil would be through erosion of carbonaceous bedrocks (CaCO₃) as this process releases HCO₃⁻.

**Peatlands**

Peatland consist of incomplete OM decomposition. Due to cold climate, the microbial degradation cannot keep up with the production consequently resulting in accumulation (Gorham, 1991; Post et al., 1982) (i.e. net primary production (NPP) is larger compared to decomposition). Northern peatlands cover only 3 % of the earth’s surface (Clymo et al., 1998) but contain approximately 450 Pg C of the overall annual store (Gorham, 1991; Wu et al., 2012). The accumulation of carbon in peatland is a slow process (at a rate of 2-7 g C m⁻²y⁻¹ (Cole et al., 2007)) but has being ongoing since the beginning of the Holocene (last ~11700 BP) (Yu et al., 2009); The peatlands act as a sink of CO₂ but a net source of CH₄. The balance between the two is highly dependent on the climate where increased precipitation (as is predicted in northern hemisphere) risks to decrease the carbon sequestration (Belyea and Malmer, 2004). Carbon is normally emitted as CH₄ and is responsible for 10 % of wetland emission (Wu et al., 2012).
The Freshwater System

The role of inland waters in the carbon cycle was earlier believed to act as passive transporters of the carbon from the terrestrial area and to the oceans. This view has slowly been changing over the past decades and they are now also considered for their contribution in OM degradation and transformation during the transport (Battin et al., 2009; Cole et al., 2007; Richey et al., 2002; Tranvik et al., 2009). This new function may contribute to substantially more CO₂ emissions from inland waters to the atmosphere. Terrestrial OM inputs to the freshwater system are important and a majority becomes either sedimented or outgassed and the remaining are transported to the oceans (Bonan, 2008). A major part of the carbon outgassed is in the form as CO₂ (Aufdenkampe et al., 2011). The outgas fluxes for inland waters have increased throughout the years as more data is gathered and improved (>0,8 to 1,2 to 1,4 and recent 1,8 Pg C yr⁻¹ (Aufdenkampe et al., 2011; Battin et al., 2009; Cole et al., 2007; Raymond et al., 2013).

Lakes
Lakes normally are a net source of CO₂ emission but at the same time carbon is available to be deposited in the sediments (Cole et al., 2007). This is explained by, respiration (R) have access to the large amount of terrestrial carbon input, which can be equal to or larger than GPP in freshwater systems. This makes it possible for the net ecosystem production (NEP) (the part of GPP that is not mineralized) in lakes to be negative due to GPP in freshwater ecosystems can be much smaller than R (NEP ~ GPP-R)(Cole et al., 2007; Del Giorgio and Peters, 1994).

The deposition of carbon in lakes is estimated to be 0,03-0,07 Pg C yr⁻¹ and the preservation time (>10 000 years) is much longer compared to forest and soils. The majority of organic carbon (OC) found in lakes is in the form of dissolved organic carbon (DOC) while the fraction most often deposited is in the form of particulate organic carbon (POC). The greater productivity of lakes compared to oceans, is seen in the higher areal rates (i.e. rates area⁻¹) of OC deposition. The difference in areal rates is also explained by the dominance of OC in the distribution between inorganic carbon (IC) and OC, the high preservation rate and rapid sediment accumulation (Cole et al., 2007).

Compared to the atmospheric CO₂ concentration (390 parts per million (ppm)), water bodies are most commonly supersaturated (pCO₂ exceeding 10 000 ppm) and therefore act as a source of CO₂ (Cole et al. 2007; Marotta et al. 2009; Sobek et al. 2005). Global net flux of carbon from lakes are estimated to 0,07-0,15 Pg y⁻¹ (Cole et al., 2007; Bastviken et al., 2011), where lake CH₄ efflux is responsible for approximately 5 to 33 % (i.e. 0,006-0,036 Pg C y⁻¹; Bastviken et al. 2004)).

Streams
Carbon in streams is likely derived from multiple sources. The source of carbon can be biogenic: OM inputs from water percolating soil, photo-oxidation, microbial C-mineralization activity; or geogenic: weathering of carbonate or silicate minerals and atmospheric outgassing (i.e. the water and atmosphere
exchange of CO₂) (Krenz, 2013). The dominated bio-genic source in small streams is allochthonous terrestrial OM. This is especially seen in upland and wetland areas (Hope et al., 1994; Palmer et al., 2001; Wetzel, 1992). A major amount of the allochthon terrestrial contents does not enter the sea even though they are highly recalcitrant. Either it gets degraded by microbial communities or re-deposited and stored in the floor of reservoirs (Marwick et al., 2015; Schlesinger & Bernhardt, 2013).

The chemistry of the streams is largely controlled of the above-mentioned carbon sources. The CO₂ in rivers and streams are from groundwater inputs of OC origin from respiration in the soil system, hyporheic zone respiration or autochthonous respiration (i.e. respiration in streams)(Cole et al., 2007). Wetzel (1992) writes the efficiency of inorganic and organic chemical loading in streams is dependent on soil saturation and therefore flooding. The pH in streams is majorly controlled by rock weathering. The major amount of HCO₃⁻ in rivers comes from silicate weathering (and carbonate weathering in areas those bedrocks are present) where CO₂ is a reactant and HCO₃⁻ is a product (Cole et al., 2007).

As for lakes, the water in streams is supersaturated regarding CO₂ and CH₄ compared to CO₂ atmosphere pressure. This, due to export of the contents from soil pore water (Battin et al., 2009; Campeau & Del Giorgio, 2014; Wallin et al., 2010) resulting in partial pressure in rivers varying between 1000-12 000< ppm (Richey et al., 2002; Aufdenkampe et al., 2011; Johnson et al., 2008; Humborg et al., 2010).

**Carbon Dynamics in Streams**

Carbon in streams can be presented in four different forms: DIC, DOC, particulate inorganic carbon (PIC) and POC; where DOC < 0,45 micrometer < POC. POC size range from 0,5 micrometres to 1 millimetre with three subdivisions and contributes to only 10 % of the carbon export via freshwater. However, large pulses of POC can also occurs during specific times of the seasons (e.g. high flow) (Billett et al., 2012).

In headwater streams, particulate matter (PM) is normally dominating as carbon containers but decreases along the flow path and transform into dissolved matter (DM) which becomes the dominated carbon container. PM ratio increase due to PM along the river generally gets degraded and rivers has in comparison to headstreams a smaller terrestrial edge (Schlesinger & Bernhardt, 2013, p. 312). The DOC in streams originates mostly from terrestrial vegetation. DOC is seen as recalcitrant but in an environment with increased lit and oxygen, the decomposition is facilitated (Schlesinger & Bernhardt, 2013, pp. 136–141, 285, 312).

The DIC form is dependent on pH and can be found as dissolved CO₂, HCO₃⁻ and carbonate CO₃²⁻ (i.e. carbonic acid (H₂CO₃)). The variables controlling riverine DIC dynamics can be separated into two groups (Abril et al., 2003; Amiotte-Suchet et al., 1999; Tamooh et al., 2013):
Watershed inputs

— input of terrestrial organic,
— weathering of silicate/carbonate minerals (Si-Ca min.) in the bedrock and
— ratio of GW discharge to surface runoff

In-stream processes

— CO₂ exchange with atmosphere,
— dissolution or precipitation of Si-Ca minerals,
— primary production
— respiration

Due to the many processes influencing the DIC pool, the concentration can vary substantially between both catchments and seasons (Campeau and Del Giorgio, 2014; Crawford et al., 2014). The seasonal patterns of CO₂ concentration are also inconsistent (Dawson et al., 2009; Sobek et al., 2005). However, seasonal fluctuations of CH₄ is more consistent with peaks in warm and low flow periods (Campeau and Del Giorgio, 2014; Wallin et al., 2014).

The source of DIC is difficult to ascertain due to the complexity of the variables (i.e. hydrology, geology, geomorphology, size of stream, productivity and seasonal variations in temperature and discharge) affecting the processes and the interaction between the variables.

In Västrabäcken, no carbonated CO₂ is found as the bedrock is magmatic/metamorphic granite/gneissic. So left of DIC sources is input of terrestrial organic that is respired either by roots or microbial activity. The CO₂ concentrations in groundwater in Västrabäcken is supersaturated (Leith et al., 2015).
Appendix III – Soil Respiration Measurement Methods

There are several methods available to measure soil respiration: micro-meteorological instruments (such as eddy covariance towers), gas chambers and the gradient method (using in-situ sensors). Gas chambers are most commonly used and they measure fluxes of CO$_2$ released from the soil surface. However, the in-situ sensors are becoming more and more popular (Maier and Schack-Kirchner, 2014) and not seldom, more than one of these measurement techniques are used to conduct a survey (Riveros-Iregui et al., 2008; Rains et al., 2016).

Gas chambers can be either dynamic or static and are furthermore classified as either open or closed. The dynamic chambers allow continuous flow of air from the chamber to the measurement sensor and, thus, a direct measurement of the CO$_2$ concentration is done. The static chambers, on the other hand, trap CO$_2$ in the chamber and measure the change in CO$_2$ concentration over time (Luo and Zhou, 2006, pp.161–185). The choice of which gas chamber to use depends mainly on the environment being measured (Livingston and Hutchinson, 1995). The analysing of the CO$_2$ gas by the chambers is often done by an infrared gas analyser (IRGA) of the nondispersive infrared (NDIR) type (except the static chamber method, which uses a gas chromatograph).

The gradient method is based on that the movement of gas in soil is mainly controlled by molecular diffusion. By taking samples from several depths in a soil profile, a gradient of CO$_2$ concentration is retrieved. From this, the flux from different depths can be calculated and, thus, the vertical difference of soil respiration in a soil profile is estimated (De Jong and Schappert, 1972). With recently developed in-situ sensors that continuously measures the CO$_2$ concentration, the gradient method is gaining popularity as they can at a very detailed scale evaluate the temporal and vertical variation of soil respiration (Tang et al., 2003; Vargas et al., 2011; Maier and Schack-Kirchner, 2014).

Micrometeorological methods can also estimate soil CO$_2$ fluxes (Dugas, 1993) but they are not as frequently used to measure soil respiration and soil CO$_2$ fluxes as the other methods. However, they normally are positioned somewhere between just above the ground to above the treetops and, thus, they constitute the only measurement technique that may capture data of the groundwater-absorbed carbon. This is because the groundwater-absorbed carbon is transported to a nearby headwater stream where a major of it is emitted (Wallin et al., 2013; Hotchkiss et al., 2015; Leith et al., 2015). To my knowledge, it has not yet been possible to differentiate the groundwater-absorbed carbon from the other CO$_2$ fluxes by measurements performed by an eddy covariance tower. Moreover, no other measurement technique has been utilized to measure the groundwater-absorbed carbon. Therefore, to provide an insight of the currently main used measurement techniques to estimate soil respiration, the different chambers and the gradient method will be described in more detail. In addition, the sensors normally used in the gradient method is used in this study, which makes an explanation relevant. The micro-meteorological method will only be briefly described, as it is not often used to only estimate soil respiration. But still,
it is considered as an important method measuring closely related parameters involving the soil respiration (e.g. Baldocchi, 2003; Hirano et al., 2003; Misson et al., 2007; Rains et al., 2016).

**Dynamic Chambers**
The dynamic chambers can be either open or closed. The closed chamber measures the increase of the CO₂ concentration where the rate is comparative to the CO₂ efflux:

\[
F = \frac{(C_f - C_i)V}{\Delta tA}
\]

where \( F \) = CO₂ fluxes, \( C_f \) = Initial CO₂ concentration, \( C_i \) = End CO₂ concentration, \( V \) = Volume in the chamber, \( \Delta t \) = time difference between \( C_i \) and \( C_e \) and \( A \) = area the chamber is covering. The method is not reliable if the measurement is so long that it alters the CO₂ gradient. This related to that increased CO₂ concentrations in the chamber slows down the input of new CO₂, which ultimately results in underestimations of the CO₂ flux.

The open dynamic chamber allows air outside the chamber to flow through the chamber. The difference in CO₂ concentration between the air flowing in and the air flowing out is utilized together with the rate of airflow to calculate the CO₂ flux:

\[
F = \frac{u_0C_0 - u_eC_e}{A}
\]

where \( C \) = CO₂ concentration in air, \( u \) = airflow rate and \( A \) = area the chamber is covering. The 0 and e subscripts refer to the air entering and leaving the chamber, respectively. This system is sensitive to differences in pressure between air outside and inside the chamber. The consequence of such a difference is that an additional airflow can be generated, resulting in erroneous CO₂ efflux measurements. This is often compensated by keeping a constant over or under pressure inside the chamber (Luo & Zhou 2006, pp.163–170).

**Static Chambers**
The static chamber can be either of an open model or of a gas chromatograph. The closed chamber contains a chemical absorbent, of either alkali solution (NaOH or KOH) or soda lime (NaOH and Ca(OH)₂), that absorbs the CO₂ molecules inside the chamber. The alkali trapping method is the oldest soil respiration measurement method, but it is rarely used today in contrast to the soda lime method, which is very commonly used, as it is inexpensive and easy to manage. Both of these methods need to be processed in a lab.

The CO₂ fluxes from the alkali trapping method is estimated by titrating an alkali solution with HCl to gain a pH-value. From there, the flux is gained by the CO₂ amount absorbed (\( C_{\text{trap}} \)) over the absorbent time (\( \Delta t_{\text{abs}} \)):

\[
F = \frac{C_{\text{trap}} - C_{\text{blank}}}{\Delta t_{\text{abs}}A}
\]

Where \( C_{\text{blank}} \) = CO₂ in a control solution of the absorbant to eliminate biases of the solution and \( A \) = area the chamber cover.
The soda lime trapping method utilizes the natural reaction of CO$_2$ to form carbonates. As a result of this reaction, the soda lime gains weight. After a sampling period, which is typically around 24 hours, the weight difference before and after the measurement is comparative to the absorption of CO$_2$ if a correction factor is used (Luo and Zhou, 2006, pp.170–174).

Both the alkali trapping method and the soda lime method is sensitive to outer factors. The former technique is less sensitive to changes in concentration and size of the alkali solution and chamber size but very sensitive to absorption times. The CO$_2$ effluxes estimated with the soda lime method is noticed to be a bit coarse compared to the dynamic methods; an underestimating is noticed of high CO$_2$ fluxes and an overestimating of low CO$_2$ fluxes. Therefore, calibration curves may be needed (Luo and Zhou, 2006, pp.161–185).

If the static chambers are not correctly used, the mixing of CO$_2$ in the chamber becomes insufficient and a CO$_2$ concentration gradient builds up inside the chamber with lower concentrations in the upper part of the chamber. The sample of CO$_2$ from the chamber is often taken from the upper part and thus, underestimation of CO$_2$ fluxes is done. However, the errors and uncertainties of these techniques are well known as they have been used for a long time. Therefore, detailed information on how to use the cambers has been drawn up to minimize the errors. So when used methodically correct, both techniques are potentially inexpensive and reliable to use (De Jong et al., 1979; Luo and Zhou, 2006, pp.161–185; Dossa et al., 2015).

The other way to use static chambers is by a gas chromatograph. The chambers have a syringe opening on the top which is used for withdrawal of air samples from inside the chamber. The CO$_2$ concentrations from the syringe are analysed in a gas chromatograph with the same equation used as for the closed dynamic chamber.

**Gradient Method**

As the gradient method is based on that the major transport of CO$_2$ in the soil is controlled by molecular diffusion, the flux can be calculated with Fick’s first law:

\[
F_{CO_2}(z) = -D_s \frac{dC}{dz}
\]

Where $F_{CO_2}(z)$ = the CO$_2$ flux from depth $z$, $D_s$ = the effective gas diffusion coefficient of CO$_2$, $dC$= difference in concentration and $dz$= depth of the layer. There has been numerous ways of developing the gradient method by adding other transport mechanisms in a try to more realistic reflect the soil properties (Maier and Schack-Kirchner, 2014; Jassal et al., 2004; Turcu et al., 2005; Tang et al., 2003; Jassal et al., 2005). It has also been adapted to measure CO$_2$ efflux from soils covered by a snow layer (Rains et al., 2016; Liptzin et al., 2009). Early on, the in-situ measurements were done with an air-permeable hydrophobic poly-propylene tube buried in the soil at the desired depth. Gas samples were taken from desired soil depth and was then measured by pushing the gas through the IRGA. This method was limited to make point measurements and therefore data series missed out rapid temporal changes (Maier and Schack-Kirchner, 2014). Another version enabling continuous measurement, was made by
directly coupling an IRGA to the tube so the CO₂ concentration was circulated through the IRGA (Maier and Schack-Kirchner, 2014). Recently developed sensors (mostly referred to as “solid-state CO₂ sensors”), have an IRGA directly built in to the sensor (Tang et al., 2003). These sensors are heavily reduced in size and allows in-situ measurements with minimized disturbance of the environment after installation. They allow continuous data acquisition of the CO₂ concentration and require little monitoring in the field compared to older devices. The sensor is covered with a water resistant cape and can be put in the soil at any desired depth. The CO₂ flows through the cape and gets measured in partial pressure. Depending on the model, the raw data often needs corrections for temperature and air pressure.

Uncertainties in results from the gradient method increases if: the diffusivity in the soil is too low, the air-filled porosity is lower than 12% of the total porosity, other transport than diffusion is happening (for instance ebullition, i.e. sudden release of CO₂ in bubbles) or horizontal heterogeneity in soil CO₂ concentration occur. The uncertainties generated from these conditions are especially expressed in the Dₛ and, thus, can generate high uncertainties in the results. Results from the gradient method in comparison with measurements done with chambers seems to give similar fluxes. Exception is during and after rainy periods, when the soil water content increases. A condition influencing the Dₛ and therefore causing high uncertainties in fluxes estimated with the gradient method (Maier and Schack-Kirchner, 2014).

**Micro-meteorological Instrumentation**

Bowen ratio/energy balance systems (BREB+) and Eddy covariance towers are two micro-meteorological instruments. The BREB+ is positioned just above the surface and measures both CO₂ and vapour fluxes (Held et al., 1990). However, this system seems to have been abandoned (not found in any recent literature) and most likely it has been replaced by other methods. Eddy covariance towers measure net ecosystem exchange where CO₂ fluxes from soil are embedded. This data can be extracted by utilizing micro-meteorological theory but a description of the procedure will be excluded herein. They normally gather data for a larger area (hundreds of meters to several kilometres away from the tower), and thus, are mainly used for estimations at a regional scale, such as ecosystem exchanges (Baldocchi, 2003; Dugas, 1993). However, it is possible to measure CO₂ fluxes on a local scale. Rains et al. (2016) made simultaneously measurements of the eddy covariance and a chamber to evaluate CO₂ effluxes during winter.

**Infrared Gas Analyser (IRGA)**

The technique behind an IRGA is based on that specific gasses absorb specific wavelengths of infrared light and creates an attenuation of the light. The CO₂ concentration is measured by lighting the infrared light on the CO₂ flowing into the sensor and then measure how much of the light the gas absorbs. The sensor used in this study was an IRGA.