bg-2014-486: "Carbon dioxide transport across the hillslope-riparian-stream continuum in a boreal headwater catchment"

F. I. Leith, K. J. Dinsmore, M. B. Wallin, M. F. Billett, K. V. Heal, H. Laudon, M. G. Öquist, and K. Bishop

Response to Referees

We thank the Associate Editor, and the two Referees for their constructive reviews of the manuscript. We welcome the many positive comments made by the Referees and we are fully able to address all points raised in the reviews and submit a revised manuscript. Both Referees made similar comments: 1. the literature review and discussion largely focus on Sweden and other northern European examples which should be expanded to include other relevant boreal catchments, particularly those in north America and 2. more details should be included regarding the modelling approach used in this study. These two points are addressed first followed by specific points raised by each Referee. Referees' comments are given in italics with page and line numbers referring to the published discussion paper.

1. Expansion of literature review

We agree with the Referees that the manuscript largely focuses on the Krycklan catchment, with many of the comparisons made with similar catchments in Sweden and northern Europe. In order to provide a wider range of examples the literature cited has been changed in a number of places and three additional references have been added (full references are included at the end of this document).

15588 Line 27: the cited literature considering spatial and temporal variability are site specific studies conducted only in Scotland and as indicated by the Referees do not cover the breadth of research on CO_2 evasion. The literature cited here has been changed to better cover spatial variability using Wallin et al. (2014) which examined the spatial variability in CO_2 evasion from 200 headwaters across southern Sweden. The discussion on temporal variability now includes a study which made high temporal CO_2 measurements in Alaska (Crawford et al., 2013) in addition to Dinsmore et al. (2013b) which used high temporal resolution data sets from Canada, Sweden, Finland and the UK. The manuscript has been changed to "Due to the limited numbers of direct measurements of the gas transfer coefficient (KCO_2) (Raymond et al., 2013; Wallin et al., 2011) and the considerable spatial (Wallin et al., 2014) and temporal (Crawford et al., 2013; Dinsmore et al., 2013a) variability in dissolved CO_2 concentrations observed across a wide range of northern latitude catchments, evasion, and the drivers of this flux are likely to be poorly quantified."

15606 Lines 13-18: This section has been significantly modified to include a wider range of studies to investigate the importance of terrestrial inputs to CO_2 processing in streams. This includes examples from tropical (Abril et al., 2014), temperate (Butman and Raymond., 2011) and north American boreal catchments (Crawford et al., 2013). The section now reads: "Terrestrial processes have been shown to have an important role in determining CO_2 export via the aquatic pathway in a wide range of catchments (Abril et al., 2014; Butman and Raymond, 2011; Crawford et al., 2013). The results from this catchment indicate that terrestrial-aquatic export of CO_2 was controlled by riparian water table dynamics, highlighting the potential importance of riparian zones in headwater catchments."

2. Clarification of modelling approach and methods

We thank the Referees for drawing our attention to the need to clarify the methods for modelling water export. Referee #1 suggested adding a figure describing the modelling. During the production of the original manuscript a number of options for a figure were discussed but these were not felt to help in explaining the modelling approach. Instead, Section 2.3 Data processing and analysis, especially from Page 15594 Line 26, has been modified and is included below. Specific points raised by Referee #2 are covered in more detail below. We hope this clarifies the methods.

"The model was constructed by subdividing the 90 cm deep soil profile into 5 cm horizons. The daily lateral water export from each 5 cm soil layer was estimated by combining the measured volumetric water content with lateral saturated hydraulic conductivity estimated by Stähli et al. (2001). Total daily water export from the full soil profile was estimated by adding together the lateral flow from all 5 cm horizons below the daily mean water table. As CO_2 concentration was only measured at two depths (30-40 cm and 60-70 cm) these were assumed to represent the concentration above and below 45 cm depth. Daily average CO_2 concentrations below the water table, in mg CO_2-C L^{-1}, were multiplied by the water export, with CO_2 export expressed in units of mg CO_2-C m^{-2} day^{-1}. The model was run twice to estimate the export from 1. podzol hillslope soils and 2. riparian organic soils. Hillslope export was taken to represent the input of water and CO_2 into the riparian zone with riparian export representing the total terrestrial water and CO_2 export to the stream."

Additional points

Referee #1

"The hypothesis of riparian control on gas export is also evaluated for other catchments and could help frame these results. My question is how often and where would we expect riparian CO_2 controls in streams? Does this extend to the temperate zone or the tropics where soil CO_2 has been used to infer aquatic evasion?"

We comment on 15603 Lines 11-14 that the approach used in this study is suitable due to the nature of the hydrological flowpaths through the catchment, with numerous studies showing that all water exported from the catchment passes through the upper 1 m depth of the riparian zone. The validity of this approach was commented on by Referee #2. The finding of this study that the riparian zone has an important role in controlling CO_2 evasion is therefore dependent on the catchment characteristics (particularly the nature of the hydrological flowpaths and the distribution of organic rich soils within the catchment). 15603 Lines 11-14 have been altered to more clearly explain this. In summary, in areas where there are mineral soils upslope and organic soils close to the stream, the riparian zone will be a major source of CO_2. While the findings from this study could be extrapolated to other catchments, in a range of geographical areas, we feel that due to the wide variety of definitions of riparian zones and the catchment specific nature of the processes then it would be inappropriate to make an overarching statement on how all riparian zones may contribute to CO_2 export in headwaters. This aim of this study was to use a very well defined catchment to show the potential extent of riparian control, so that future studies are aware of the importance of this area and can include it in experimental or modelling exercises in a range of catchments. The final paragraph of the Section 4.3, which discusses the wider implications of the work, has been significantly modified to give a greater range of literature examples (including tropical, temperate and boreal catchments) and to further highlight the importance of riparian zone processes in headwater catchments (15606 Lines 13-18). The new text is included in the response to 15606 Lines 13-18 above.

Referee #2

"A 4m riparian zone on each side is relatively large for many headwater systems, and it is conceivable that hill slope soil CO_2 will contribute consistently more as the riparian area decreases. This cannot be tested here, but discussed."

We agree that the lateral extent of the riparian zone in this catchment contributes to its importance for soil CO_2 export, as shown in this study and for studies to consider TOC also in this catchment (Grabs et al., 2012). The study catchment was chosen due to the consistency of the riparian extent down the stream reach allowing us to upscale from our single transect. At 15603 Lines 11-14 the discussion of the validity of using the riparian export to understand stream water CO_2 dynamics has been changed to include the potential impact of variability in the lateral extent of the riparian zone. The section now reads:

"This approach can be used as the catchment chosen for this study is relatively simple in terms of the water flowpaths (with water transported laterally through the soil at <1 m depth with groundwater and overland flow not significant) and the consistency of the riparian lateral extent down the stream reach. In catchments with more complex hydrology or where the riparian lateral extent is variable, riparian CO_2 export alone may not account for all variability in stream water CO_2 dynamics and additional sources would need to be considered."

"The notion that you can have a large spring pulse from snowmelt moving high volumes of water through relatively low CO_2 environments, contrasts with the episodic nature of infrequent storm events moving overall smaller volumes of water through very high CO_2 environments. This should be highlighted more, with a discussion regarding how the community should better constrain annual estimates of carbon evasion and lateral export across scales. A few sentences to this effect could broaden the work beyond the Krycklan system."

We agree that it is an interesting finding that periods of high riparian CO_2 export can occur during periods of both low and high soil CO_2 concentrations. The importance of the spring snow melt period to annual fluxes of a range of solutes has been widely shown in boreal catchments (Dyson et al., 2010; Laudon et al., 2004). Additionally, in catchments which do not experience large snow melt events, much of the research focus has been on episodic storm events. The importance of capturing hydrological extremes across seasons is now discussed in more detail at 15603 Lines 25-27 in the line "This observed pattern of peaks in CO_2 export suggests that riparian export is a function of both season and runoff. This highlights the importance of capturing hydrological extremes when quantifying annual estimates of downstream export and evasion of CO_2 across catchments and scales."

"More detail within the description on page 15595 would help resolve some confusion as to how the water was modeled, and how hill slope and riparian portions are separated. Presumably the hill slope is added to the riparian water profiles?"

The export of water and CO_2 was calculated per 1 m^{-3} area of hillslope and riparian soils with hillslope export taken to represent the input of water and CO_2 into the riparian zone and riparian export representing the total terrestrial water and CO_2 export to the stream. This distinction has been added to the manuscript at 15595 Lines 6-8.

"...some description regarding how periods when sensors were not submerged were handled within the modeling would be helpful"

The model only calculated lateral CO_2 export below the daily mean water table as only these soil horizons are connected hydrologically. CO_2 concentrations, especially at 30-40 cm depth, from when the sensor was not submerged were not included in the model. This is now made clearer at 15595 Line 5. There were periods, especially in the hillslope when the water table was below the 90 cm depth profile used in the model. During these times it was assumed that there was no lateral flow through the soil profile. As can be seen in Figure 3a, during drier months (in the summer and under snow conditions in winter) there was no flow through the upper 50 cm of the soil profile. Concentrations above the water table are only included in the time series of CO_2 concentrations given in Figure 2a.

15605 - Lines 15-20 - Finally, it is mentioned that the export of soil CO_2 and hence the evasion proportion of the total aquatic carbon flux, was not estimated during storm events however the findings from this work suggest that these could be hotmoments for carbon removal (15605 lines 15-20). I would like to see the authors comment briefly on this.

Evasion was not estimated during the largest storm events, which we assume relates to a lag in water residence times. These storms are very short lived, with the storm peak occurring in a time period of less than 24 hours. As the model calculated the daily riparian export there is a potential time lag between the discharge peak and the peak in riparian export during the largest, but short lived storm events. The results from this study show that periods of high flow, both during storm events and the spring snow melt event, are hotmoments for CO_2 export. This highlights the importance of high frequency measurements, as commented on in the manuscript, but also the study of hydrological extremes in accurately determining annual CO_2 export which is now commented on at 15603 Lines 25-27 with the line "This observed pattern of peaks in CO_2 export suggests that riparian export is a function of both season and runoff. This highlights the importance of capturing hydrological extremes when quantifying annual estimates of downstream export and evasion of CO_2 across catchments and scales."

15588-23, check this value of 205,000 Tg-C yr^{-1}. That would be HUGE!!

Agreed. The value should be 0.205 Tg C yr^{-1} and has been corrected in the manuscript. The incorrect units were taken from the original reference (Humborg et al., 2010).

15588-15589 why would these fluxes be underestimated? They could be completely overestimated!

Agreed. This line has been changed to say that the values could be both under and over represented due to the variability in gas transfer coefficient.

15593 - can you explain / cite what a dipwell is?

Dipwells allow the separation of soil water from the surrounding soil material with this explanation now included at 15593 Lines 9-11. The soil water collected in the dipwell corresponds to the water table depth within the soil profile and also allows sampling of the water for dissolved CO_2 concentration and in a separate dipwell, the water table depth and soil water temperature. The construction of the dipwell is given on 15593 Line 12 and a graphical representation given in Figure 1.

15595 - differences in soil moisture content at 60cm depths are really not significantly different SD on some of these numbers would be appreciated.

Agreed. The SD of the soil moisture values are now included.

15601 - please explain in more detail what transmissivity feedback is.

Transmissivity feedback is defined as the increase in lateral saturated hydraulic conductivity towards the ground surface, resulting in more lateral flow as water table rises into near surface soil horizons. The introduction of the concept on 15601 Line 21 has been changed from 'indicate' to 'defined' to now define the concept, with reference made to the original works to define this term at 15601 Line 20.

15606 - The conclusion points 1&2 are actually not things measured by the work presented. It is understood that these are inferred by changes in concentration and water level. No exchange with the atmosphere was actually quantified. Arrange the conclusion to better match the paper.

Agreed. The first sentence of the conclusion (15606 Lines 20-23) has been modified to highlight the section that was inferred from the results (the numbered points) from what was directly measured and now reads: "CO_2 concentrations were significantly higher in the riparian zone than hillslope soils, which we infer was due to 1. greater production of CO_2 in riparian peats compared to the hillslope pozols and 2. higher water table positions limiting the vertical CO_2 diffusion and exchange with the atmosphere."

Additional references

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Carbon dioxide transport across the hillslope-riparian-stream continuum in a boreal headwater catchment

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Abstract

Headwater streams export CO_2 as lateral downstream export and vertical evasion from the stream surface. CO_2 in boreal headwater streams generally originates from adjacent terrestrial areas, so determining the sources and rate of CO_2 transport along the hillslope-riparian-stream continuum could improve estimates of CO_2 export via the aquatic pathway, especially by quantifying evasion at higher temporal resolutions. Continuous measurements of dissolved CO_2 concentrations and water table were made along the hillslope-riparian-stream continuum in the Västrabäcken sub-catchment of the Krycklan Catchment, Sweden. Daily water and CO_2 export from the hillslope and riparian zone were estimated over one hydrological year (October 2012-September 2013) using a flow-concentration model and compared with measured lateral downstream CO_2 export.

Total water export over the hydrological year from the hillslope was 230 mm yr^{-1} compared with 270 mm yr^{-1} from the riparian zone. This corresponds well (proportional to the relative upslope contributing area) to the annual catchment runoff of 265 mm yr^{-1}. Total CO_2 export from the riparian zone to the stream was 3.0 g CO_2-C m^{-2} yr^{-1}. A hotspot for riparian CO_2 export was observed at 30-50 cm depth (accounting for 71 % of total riparian export). Seasonal variability was high with export peaks during the spring flood and autumn storm events. Downtream lateral CO_2 export (determined from stream water dissolved CO_2 concentrations and discharge) was 1.2 g CO_2-C m^{-2} yr^{-1}. Subtracting downstream lateral export from riparian export (3.0 g CO_2-C m^{-2} yr^{-1}) gives 1.8 g CO_2-C m^{-2} yr^{-1} which can be attributed to evasion losses (accounting for 60 % of export via the aquatic pathway). The results highlight the importance of terrestrial CO_2 export, especially from the riparian zone, for determining catchment aquatic CO_2 losses and the importance of the CO_2 evasion component to carbon export via the aquatic conduit.

1 Introduction

Boreal forests are an important ecosystem within high latitude regions containing a globally significant carbon store in both soils and vegetation (Dunn et al., 2007; Pregitzer and Euskirchen, 2004). The net ecosystem carbon balance (NECB) of individual northern latitude catchments has shown them to be net sinks for carbon (Dinsmore et al., 2010, 2013b; Koehler et al., 2011; Nilsson et al., 2008; Olefeldt et al., 2012; Roulet et al., 2007). In boreal forest catchments, carbon export via the aquatic pathway (consisting of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), particulate organic carbon (POC) plus dissolved and gaseous CO_2 and CH_4) accounted for 4-28 % of carbon uptake via Net Ecosystem Exchange (NEE), representing an important, but spatially and temporally variable component of the NECB (Öquist et al., 2014; Wallin et al., 2013).

Headwater streams are generally supersaturated in CO_2 with respect to the atmosphere, resulting in export via the aquatic conduit consisting of both the downstream lateral export and vertical evasion of CO_2 from the stream surface (Kling et al., 1991). CO_2 evasion has been shown to account for 13-53 % of the total aquatic flux across a range of northern latitude headwater streams (Billett et al., 2004; Öquist et al., 2009; Wallin et al., 2013), representing an important component of the catchment NECB. Low order streams have been observed to have disproportionately high evasion rates (Aufdenkampe et al., 2011; Butman and Raymond, 2011; Raymond et al., 2013). Across Sweden, CO_2 evasion from 1st order streams was estimated at 205,000 Tg C yr^{-1} or 39 % of the total from all streams, despite accounting for only 13 % of the total stream area (Humborg et al., 2010). Quantifying evasion involves combining dissolved CO_2 concentrations and the gas transfer coefficient (KCO_2) (Hope et al., 2001). Due to the limited numbers of direct measurements of the gas transfer coefficient (KCO_2) (Raymond et al., 2013; Wallin et al., 2011) and the considerable spatial ~~and temporal~~ (Wallin et al., 2014) and temporal (Crawford et al., 2013; Dinsmore et al., 2013a) variability in dissolved CO_2 concentrations ~~(Dawson et al., 2001b; Dinsmore et al., 2013a; Hope et al., 2004)~~ observed across a wide range of northern latitude catchments, evasion, and the drivers of this flux are likely to be

~~underestimated~~poorly quantified. To improve understanding of both lateral downstream export and vertical evasion of CO_2 from headwater streams the concentrations and sources of dissolved CO_2 need to be better quantified.

To better understand the drivers of stream water CO_2 dynamics an increasing number of studies have made continuous, direct measurements of dissolved CO_2 concentrations in stream waters (using in situ, non-dispersive infra-red (NDIR) CO_2 sensors) giving new insights into diurnal, storm event and seasonal CO_2 dynamics (Dinsmore and Billett, 2008; Dinsmore et al., 2013a; Dyson et al., 2011; Johnson et al., 2006, 2010). Much of the excess CO_2 in temperate and boreal streams originates from terrestrial areas through lateral subsurface transport through the soil (Hope et al., 2004), confirmed by isotope studies in peatland catchments (Garnett et al., 2012; Leith et al., 2014). The concentration of CO_2 in stream water is largely dependent on the concentration in terrestrial source areas and the hydrological connectivity between source areas and the stream channel (Vidon et al., 2010). Despite the apparent importance of soil sources, most studies of stream CO_2 dynamics take the observed response in the stream and link it to terrestrial processes without direct measurements in soils. Quantifying the rate of export of carbon from soil to stream will enable better estimates of CO_2 export via the aquatic pathway and in particular contribute to higher temporal resolution estimates of evasion.

A few studies have made continuous, high frequency CO_2 concentration measurements in soils but are largely restricted to sampling at shallow depths above the water table (Dinsmore et al., 2009; Jassal et al., 2004, 2008; Tang et al., 2003). Higher soil CO_2 concentrations have been observed below the water table and in response to soil re-wetting after storms (Jassal et al., 2005; Rasilo et al., 2012). In soil, CO_2 can be derived from root respiration, soil organic matter decomposition and weathering of carbonate parent material. Mobilisation of CO_2 occurs through the displacement of high CO_2 concentrations in the soil atmosphere, combined with decreased vertical diffusivity as soil pore space becomes saturated (CO_2 diffusion is 10,000 times slower in water than in air) (Šimůnek and Suarez, 1993). This highlights the importance of considering concentration changes over the full soil profile depth, especially in horizons which experience frequent water table fluctuations as transient saturation can increase the lateral export of water and dissolved constituents exponentially (Bishop et al., 2011).

The terrestrial-aquatic interface is a continuum between the wider catchment area (hillslope), riparian zone and stream. Riparian zones in headwater catchments commonly represent a 1-5 m wide area immediately adjacent to the stream (Luke et al., 2007). Common characteristics of the riparian zone are higher water table conditions (Burt et al., 2002), organic rich soils and distinct vegetation composition in comparison to the surrounding hillslope (Lyon et al., 2011). Hence, the riparian zone has been widely shown to be a key area for hydrological, ecological and biochemical processes (Naiman and Décamps, 1997; Vidon et al., 2010). Subsurface hydrological flowpaths converge at the terrestrial-aquatic interface resulting in the riparian zone being the last biogeochemical environment encountered by subsurface water (Bishop et al., 1990; McClain et al., 2003). The riparian zone has been shown to have a stronger hydrological connection to the stream in comparison to groundwater or soil water (Buttle et al., 2004; Stieglitz et al., 2003) and to control stream water chemistry during hydrological events (Bishop et al., 2004). Water and solute transport has been shown to be episodic with hotspots and hotmoments in export (McClain et al., 2003; Vidon et al., 2010), hence the full hillslope-riparian-stream continuum needs to be considered at high temporal resolutions to quantify solute transport across the terrestrial-aquatic interface.

Across five different northern latitude catchments, stream water CO_2 concentrations were shown to be strongly linked to discharge, with the highest 30 % of flow having the greatest impact on lateral CO_2 export (Dinsmore et al., 2013a). DIC export via the aquatic pathway over a 13 year period in a headwater Swedish catchment (the same catchment as this study) was positively correlated with precipitation with export varying from 2.3 to 6.9 g DIC-C m^{-2} yr^{-1} (Öquist et al., 2014). In boreal systems, water and carbon cycles are highly seasonal and strongly linked to the length of the snow covered period in winter and the spring snow melt event. In these systems, snow melt is the major hydrological event of the year, with one example being the Krycklan catchment where 40 to 60 % of the annual runoff occurs during only 10-15 % of the year (Laudon et al., 2011). Snow melt has been shown to be an important period for carbon export via the aquatic pathway both as DOC (Laudon et al., 2004; Nilsson et al., 2008) and gaseous species (Dyson et al., 2011). Another example of the short-term variability in stream water dissolved CO_2 concentrations is the observation in some catchments of bimodal frequency distributions during storms, indicative of two distinct CO_2 sources within the catchment (Dinsmore et al., 2013a). Combining high resolution concentration measurements in both the soil and the stream is a powerful way of studying hydrological and seasonal variability in these catchments. However, previous studies which determined dissolved CO_2 concentrations in riparian soils and streams have used either a limited number of discrete measurements (Hope et al., 2004; Öquist et al., 2009) or did not determine the variability in the depth of lateral subsurface hydrological flowpaths transporting CO_2 to the stream (Rasilo et al., 2012). This is likely to under represent variability in these dynamic systems, especially for short lived hydrological events such as storms.

This study uses high temporal resolution measurements of CO_2 concentrations along a hillslope-riparian-stream continuum in a hydrologically well defined catchment with extensive previous work delineating the hydrological flowpaths along the continuum (Bishop et al., 2004; Seibert et al., 2009; Stähli et al., 2001). This allows the sources of stream water CO_2 to be investigated while estimating the export of water and CO_2 across the terrestrial-aquatic interface. Due to the position of riparian zones within the catchment and the greater potential for CO_2 production in the organic rich riparian soils we hypothesise that it is the riparian zone, rather than the wider catchment area, that is maintaining CO_2 export to streams.

2 Materials & Methods

2.1 Site description

This study was conducted in the 0.13 km^2 forested Västrabäcken subcatchment of the 0.47 km^2 Svartberget catchment, which is part of the wider 68 km^2 Krycklan Catchment (64°14' N, 19°46' E), 50 km northwest of Umeå, Sweden (Laudon et al., 2013).

The altitude of the catchment ranges from 235 to 310 m above sea level (Bishop et al., 1990). Mean annual temperature (1980-2008) is 1.7 °C, with the maximum (14.6 °C) and minimum (-9.6 °C) in July and January, respectively. Mean annual precipitation (1981-2008) is 612 mm, with approximately 35 % falling as snow (Haei et al., 2010). Snow covers the ground on average for 171 days from October to May to a depth of between 43 and 113 cm (1980-2007) (Laudon et al., 2011). The largest hydrological event during the year is a 4-6 week long snow melt period in late April/early May which contributes between 40 and 60 % of annual runoff (Laudon et al., 2011). The Västrabäcken is a 1st order, low pH (range pH 4.5-5.9) with little variability in the bicarbonate equilibrium system (Wallin et al., 2010).

Drainage channels were deepened and widened in the 1920s to improve forest drainage (Bishop et al., 1990). Scots pine (*Pinus sylvestris*) is the dominant tree species in hillslope areas with some Norway spruce (*Picea abies*) nearer to the stream. Understory vegetation is predominately a mix of *Vaccinium myrtillus, Vaccinium vitis-idaea* and grasses (*Deschampsia flexuosa*), with mosses (*Sphagnum spp, Polytrichum commune*) and wood horsetail (*Equisetum sylvaticum*) in the wetter riparian areas.

The bedrock is gneiss overlain by 10-15 m of locally derived glacial till. Soils consist of well-developed iron podzols comprising a surface 5 cm humus layer overlying a 12 cm thick sandy bleached E-horizon and a 60 cm thick B-horizon (Nyberg et al., 2001). The riparian zone formed through the accumulation of organic matter in low lying areas and extends 4 m on either side of the stream channel. Riparian soils consist of ~70 cm thick peat transitioning to the underlying till at ~90 cm depth. Soil organic content is considerably higher in the riparian soil (>80 %) compared to the hillslope podzols (<5 %) (Nyberg et al., 2001). Saturated hydraulic conductivity is about one order of magnitude lower in the riparian zone

(6.2×10^{-6} m s^{-1}) than the hillslope (5.6×10^{-5} m s^{-1}) (Nyberg et al., 2001) decreasing with depth (Stähli et al., 2001). Porosity and water retention were higher in the riparian soil (Nyberg et al., 2001; Stähli et al., 2001). The riparian zone studied is representative of headwater till catchments across the larger Krycklan catchment (Grabs et al., 2012).

2.2 Field Methods

Sampling was carried out in both the hillslope podzol soils (15 m perpendicular to the stream) and riparian zone peat soils (1.5 m from the stream) (Figure 1). At each location~~there were two dipwells for CO_2 measurement~~, two dipwells with a 10 cm perforated sampling window at either 30-40 cm or 60-70 cm depth were installed, with the dipwells separating the soil water from the surrounding soil allowing the measurement of soil water CO_2 concentrations. Dipwells were constructed from 50 mm inner diameter (ID) pipe open at the bottom and sealed at the surface using rubber bungs (Saint Gobain Performance Plastics, France). To prevent damage to the dipwells over winter due to freezing, the short above ground section was covered in insulation foam. Each dipwell contained a Vaisala CARBOCAP GMP221 non-dispersive infra-red (NDIR) CO_2 sensor (range 0-5 %). Prior to deployment, sensors were enclosed in a water-tight, gas-permeable membrane (Johnson et al., 2006, 2010). At each sampling point a third dipwell, constructed from 90 mm ID pipe perforated along its entire 1 m length and open at the bottom, was used for the measurement of water table depth (Level Troll 300, In-situ, USA) and soil temperature (CS457A, Campbell Scientific, USA), with sensors suspended at 90 cm depth. All sensors were connected to a datalogger (CR1000, Campbell Scientific, USA) which recorded measurements at 30 min intervals. The system ran for three months (from 1st July 2012) to allow it to become stabilised and equilibrated before the main measurement period over one hydrological year (1st October 2012 to 30th September 2013). Soil moisture content was recorded by time domain reflectometry (TDR) probes (Laudon et al., 2013; Nyberg et al., 2001).

Measurements were made at one point in the hillslope and riparian zone assuming, as with all transect studies, that these points are representative of the catchment overall. A single transect approach is appropriate for this catchment due to the small area (0.13 km^2)

and limited variability in soils and vegetation (Bishop et al., 1990; Lyon et al., 2011). Furthermore, overland flow or deeper groundwater inputs to the stream have been shown to be limited in this catchment (Laudon et al., 2004; Peralta-Tapia et al., 2014). The sampled riparian zone is consistent with the 13 riparian zones in the wider Krycklan Riparian Observatory (Grabs et al., 2012).

Stream water dissolved CO_2 concentrations (measured using the same Vaisala CO_2 sensors), plus discharge were measured continuously in a heated dam house at the catchment outlet (Laudon et al., 2013), 200 m downstream from and over the same time period as soil measurements.

2.3 Data Processing and analysis

CO_2 sensor output was corrected for temperature and pressure using the method of Tang et al. (2003) but using algorithms supplied by the manufacturer specific to the GMP221 sensors. In addition to atmospheric pressure, the correction also accounted for the head of water above the sensor, related to the water table depth at the time of sampling. Corrected concentrations are given in units of ppmv with mg CO_2-C L^{-1} used for export calculations.

The export of water and CO_2 from each m^2 of hillslope and riparian zone were estimated using a flow-concentration model, a similar approach to the Riparian Integration Model concept used previously in this, and similar, hillslope-riparian systems (Grabs et al., 2012; Seibert et al., 2009). Our study used measured water table positions in the hillslope and riparian zone while previous studies have used a correlation between groundwater and runoff dynamics (Grabs et al., 2012).

The model was constructed by subdividing the 90 cm deep soil profile ~~was subdivided~~ into 5 cm horizons~~with the~~. The daily lateral water export from each 5 cm soil layer was estimated by combining the ~~daily mean water table position with~~ measured volumetric water content ~~and~~ with lateral saturated hydraulic conductivity estimated by Stähli et al. (2001). Total daily water export from the full soil profile was estimated by adding together the ~~flow from each~~ lateral flow from all 5 cm ~~horizon~~ horizons below the daily mean water table. As CO_2 concentration was only measured at two depths (30-40 cm and 60-70 cm) these were assumed to represent the concentration above and below 45 cm depth. Daily average CO_2 concentrations below the water table, in mg CO_2-C L^{-1}, were multiplied by the water export, with CO_2 export expressed in units of mg CO_2-C m^{-2} day^{-1}. The model was run twice to estimate the export from 1. podzol hillslope soils and 2. riparian organic soils. Hillslope export was taken to represent the input of water and CO_2 into the riparian zone with riparian export representing the total terrestrial water and CO_2 export to the stream.

Downstream CO_2 export was determined by multiplying daily mean stream water CO_2 concentration with discharge at the catchment outlet. Based on the assumption that all stream water carbon is derived from terrestrial inputs, evasion was estimated by subtracting the downstream lateral CO_2 export from the export of CO_2 from the riparian zone to the stream. Whilst we recognize this assumption may not be completely met and we may be underestimating total inputs and therefore evasion, in stream processing in this catchment is likely to be minimal due to the low temperatures, pH and short water residence time (Öquist et al., 2009). Our results therefore provide a useful means to consider temporal variability in a flux which is otherwise unmeasurable at high temporal resolution.

3 Results

3.1 Hillslope-riparian hydrological connectivity

Water table was significantly higher in the riparian zone compared to the hillslope, but with similar temporal variability (Figure 2). Mean ($\pm$ SD) hillslope water table during the hydrological year was -63 $\pm$ 16 cm compared with -37 $\pm$ 10 cm in the riparian zone (Table 1). Volumetric soil moisture content was also higher in the riparian zone (mean $\pm$ SD of 0.73 $\pm$ 0.008 and 0.46 $\pm$ 0.004 m^3 m^{-3} at 30 and 60 cm depths respectively) compared to the hillslope (~~0.30~~ 0.50 $\pm$ 0.01 and 0.45 $\pm$ 0.003 m^3 m^{-3} at 30 and 60 cm depths respectively).

Annual mean ($\pm$ SD) soil temperature was 4.1 $\pm$ 3.0 ℃ and 3.9 $\pm$ 3.0 ℃ in the hillslope and riparian zone respectively with a strong seasonal trend (Figure 2). Soil temperature (measured at 70 cm depth) did not fall below freezing, with minimum temperatures in the hillslope (0.8 ℃) and riparian (0.7 ℃) (Table 1) reached at the beginning of May (Figure 2).

Water table was above the 60 cm CO_2 measurement depth for 32 % and 97 % of the time and above the 30 cm depth 7 % and 59 % of the time, in the hillslope and riparian zone respectively. These values describe the relative proportion of the measurement period over which the CO_2 sensors were submerged.

3.2 Hillslope-riparian CO_2 concentrations

CO_2 concentrations were on average higher in the riparian zone than the corresponding depth in the hillslope (Table 1). Highest mean ($\pm$ SD) CO_2 concentrations were at 60-70 cm in the riparian zone (23,100 $\pm$ 4100 ppmv) with lowest at 30-40 cm in the hillslope (4410 $\pm$ 2570 ppmv). At both depths the hillslope and riparian zone CO_2 concentrations were significantly different (Table 1).

There was considerable temporal variability in CO_2 concentration in the hillslope, which displayed a baseline and peak pattern (Figure 2). Baseline concentrations were generally <2000 ppmv. In the winter period (January-March), median concentrations at 60-70 cm depth (1600 ppmv) were 24 % less than those at 30-40 cm depth (2110 ppmv). During drier periods in summer (July-September), the baseline was higher with median concentrations at 60-70 cm (1770 ppmv), 61 % less than those at 30-40 cm depth (4530 ppmv). The range was also higher in summer (7640 and 6470 ppmv at 30-40 and 60-70 cm depths) than in winter (680 and 870 ppmv).

Periodically, sharp increases in hillslope CO_2 concentrations were observed, corresponding to a rise in water table position (Figure 2). CO_2 concentrations in the hillslope had a positive correlation with hillslope water table at 30-40 cm (r^2 = 0.43; $P<0.001$) and 60-70 cm (r^2 = 0.65; $P<0.001$) depths. Over the measurement period the two spikes with the highest CO_2 concentrations (14,100 ppmv and 13,160 ppmv) occurred when the water table was above the level of the deeper (60-70 cm depth) sensor at -41 cm and -51 cm respectively.

CO_2 concentrations in the riparian zone did not display the same baseline and peak pattern as the hillslope. At 60-70 cm depth, CO_2 concentrations peaked at 31,920 ppmv in October before falling to 16,140 ppmv in April (Figure 2). This change in concentration closely followed soil temperature which decreased over a similar period from 9.2 ℃ to the annual minimum of 0.7 ℃ on 26/4/13 (Figure 2), coinciding with minimum CO_2 concentrations. CO_2 concentrations had a weak positive correlation with riparian water table at 30-40 cm (r^2 = 0.12; P<0.001) and a weak negative correlation at 60-70 cm (r^2 = -0.21; P<0.001) depth. At 30-40 cm depth in the riparian zone there was considerably more temporal variability in CO_2 concentrations than at 60-70 cm depth with concentrations at 30-40 cm depth rising during periods of higher water table. Minimum concentrations (4430 ppmv) occurred in April before the spring snow melt event.

3.3 Hillslope-riparian water and CO_2 export

Annual water export from each m^2 of hillslope over the hydrological year was estimated at 230 mm yr^{-1}. Across the year, water export was consistently low with flow largely restricted to below ~50 cm depth. Total monthly export was highest in May (109 mm $month^{-1}$) accounting for 47 % of the annual hillslope water export, due to greater flow at 25-35 cm depth (37 mm $month^{-1}$). Hillslope CO_2 export over the hydrological year was 1144 mg CO_2-C m^{-2} yr^{-1} and followed a similar pattern to water export. CO_2 export was considerably higher in May (482 mg CO_2-C m^{-2} $month^{-1}$), accounting for 42 % of the annual CO_2 export, largely due to considerable export (93 mg CO_2-C m^{-2} $month^{-1}$) from 45-50 cm depth (Figure 3).

3.4 Riparian-stream water and CO_2 export

Annual water export from the riparian zone to the stream channel over the hydrological year was estimated at 270 mm yr^{-1}. Below 65 cm depth, although water export was relatively low (<3 mm $month^{-1}$) it occurred for >97 % of the measurement period. Water export was highest in a zone between 25 and 50 cm depth. At shallower depths (0-25 cm) flow was restricted to the wettest months. Total monthly export was highest in May (49 mm $month^{-1}$) due to dominant flow at 25-50 cm depth with maximum monthly flow (9 mm $month^{-1}$) at 35-40 cm depth.

Total annual CO_2 export from the riparian zone to the stream channel over the hydrological year was estimated at 3008 mg CO_2-C m^{-2} yr^{-1}. Two monthly peaks in riparian CO_2 export to the stream occurred over the hydrological year, in December (529 mg CO_2-C m^{-2} $month^{-1}$) and May (522 mg CO_2-C m^{-2} $month^{-1}$). CO_2 export was highest in a narrow zone between 25 and 50 cm depth (Figure 3). In December, water flow (5 mm $month^{-1}$) and CO_2 export (77 mg CO_2-C m^{-2} $month^{-1}$) were highest from 35-40 cm depth. In May, maximum flow of both water and CO_2 was from the same depth (35-40 cm) at 9 mm $month^{-1}$ and 96 mg CO_2-C m^{-2} $month^{-1}$.

3.5 Downstream CO_2 export and evasion

Total catchment runoff over the hydrological year was 265 mm yr^{-1} (Figure 4). Total downstream lateral CO_2 export from the catchment was estimated at 1183 mg CO_2-C m^{-2} yr^{-1}. There was considerable temporal variability in the downstream lateral export of CO_2 from the catchment, related to temporal variability in discharge (Figure 4). Median downstream lateral export was 1.2 mg CO_2-C m^{-2} day^{-1} with two large spikes (57 and 35 mg CO_2-C m^{-2} day^{-1}) corresponding to sudden increases in discharge after storm events. Over the same period the input of CO_2 from the soil to the stream was 3008 mg CO_2-C m^{-2} yr^{-1}. Based on the assumption that all stream water CO_2 is derived from soil input then by subtraction 1825 mg CO_2-C m^{-2} yr^{-1} is lost between the soil and the stream (i.e. evasion from the stream surface), which accounted for 60 % of export via the aquatic pathway (Figure 4).

4 Discussion

4.1 Hillslope-riparian CO_2 concentrations

It was hypothesised that CO_2 concentrations would be higher in the riparian zone as a result of enhanced production (by decomposition of soil organic matter and root respiration) due to the higher organic matter content of riparian peat (>80 %) compared to hillslope podzols (<5 %) (Nyberg et al., 2001) and greater mobilisation of CO_2 due to the generally wetter conditions found in riparian zones (Burt et al., 2002). Changes in the soil water content can result in: 1. initial displacement of high CO_2 concentration soil atmosphere as soils become saturated and 2. decreased vertical diffusion as soil pore space becomes saturated with water. Weathering of carbonate parent material can also contribute but carbonate bedrock is not found in this catchment (Wallin et al., 2013). Mean hillslope concentrations (Table 1) are within the range ($\sim$400 to $\sim$10,000 ppmv) reported by studies conducted in similar forest podzol soils (Jassal et al., 2004, 2005; Tang et al., 2003). Mean riparian concentrations at 30-40 cm depth were similar to those in a Finnish riparian zone at the same depth (14,200-16,500 ppmv) (Rasilo et al., 2012) but CO_2 concentrations at 60-70 cm depth were considerably higher (Table 1).

There was considerable temporal variability in CO_2 concentrations, especially in the hillslope, corresponding to water table fluctuations (Figure 2). The CO_2 concentrations in the hillslope podzol soils over the measurement period, with peaks of 14,100 ppmv and 13,160 ppmv, both occurred during high water table conditions, as also observed by Rasilo et al. (2012). During the winter months (January-April) when the water table was generally low, CO_2 concentrations remained relatively stable at $\sim$2000 ppmv (Figure 2) suggesting that the vertical exchange of CO_2 is greater than the lateral export during these periods (Dyson et al., 2011).

Temporal variability in riparian zone CO_2 concentrations was more pronounced at 30-40 cm depth which can largely be attributed to water table fluctuations (the sensor was below the water table for 59 % of the measurement period). The 60-70 cm sampling depth was below the water table for 97 % of the measurement period with water table variability alone unlikely to explain the observed pattern in riparian CO_2 concentrations. CO_2 concentration was linked to soil temperature, which had a strong seasonal cycle (Figure 2) suggesting root respiration and/or organic matter decomposition, driven by changes in soil temperature, provides an additional control on CO_2 concentrations. During periods of generally high water tables in the riparian zone, such as during the spring snow melt event in May, concentrations increased (Figure 2) again highlighting the importance of water table fluctuations on CO_2 concentrations in soils.

Overall, the large temporal variability in porewater CO_2 concentration, especially in the hillslope, can largely be attributed to water table fluctuations altering the rate of CO_2 mobilisation and vertical diffusion of CO_2 stored in soil pore space. This confirms the results of others who measured higher CO_2 concentrations during periods of water table fluctuation (Jassal et al., 2005; Rasilo et al., 2012). The importance of the water table for CO_2 concentration dynamics suggests that pore water CO_2 concentration differences between the hillslope and the riparian zone are strongly influenced by the altered diffusion gradient and surface exchange of CO_2 with the atmosphere; the riparian zone had continually higher water tables than the hillslope (Figure 2). However, despite the importance of water table fluctuations, most of the existing studies involving continuous use of CO_2 sensors have been focused predominately above the water table, potentially missing this observation (Jassal et al., 2004, 2005; Tang et al., 2003). This highlights the importance of considering CO_2 concentration changes over the full soil profile depth, especially in horizons which experience frequent fluctuations between wet and dry conditions. In this study, CO_2 concentrations were only determined at two sampling depths (30-40 cm and 60-70 cm). In the riparian zone the shallower measurement depth was below the water table 59 % of the time giving a range of measurements under saturated and unsaturated conditions. The deeper measurement point was below the water table 97 % of the time giving concentrations under saturated conditions. These two sampling depths therefore gave a good overall representation of soil conditions, and their respective CO_2 concentrations.

4.2 Hillslope-riparian-stream water and CO_2 export

The total export of water per m^2 of hillslope was 230 mm yr^{-1} and from the riparian zone 270 mm yr^{-1}. Both estimates correspond well (proportional to the relative upslope contributing area) to the annual catchment runoff of 265 mm yr^{-1}. The lateral movement of water along the hillslope-riparian-stream continuum is dependent on a number of assumptions, principally that lateral subsurface flow is the dominant hydrological pathway and that these flowpaths are perpendicular to the stream. These assumptions have been validated for the study catchment by the observed planar nature of the water table (Cory et al., 2007) and through stable isotope studies (Laudon et al., 2004; Peralta-Tapia et al., 2014). Alternative flowpaths, such as overland flow and groundwater recharge are not important at this site (Grabs et al., 2012). Downslope lateral water flow occurs in saturated soils, with minimal lateral flow occurring above the water table, in accordance with the transmissivity feedback conceptualisation of subsurface flows in shallow till catchments (Bishop et al., 2011; Rodhe, 1989).

Transmissivity feedback, which has been widely observed in this catchment, ~~indicates that~~ is defined as the increase in lateral saturated hydraulic conductivity ~~increases toward~~ towards the soil surface, resulting in more lateral flow as water table rises into near surface soil horizons (Bishop et al., 1990, 2004; Laudon et al., 2004). The drier hillslope podzol soils had a greater potential to store water without increasing water table (Seibert et al., 2003), limiting the time in which high water table conditions occurred; mean water position in the hillslope was -63 cm. Water table only moved into higher lateral hydraulic conductivity horizons during the spring snow melt event in May when 42 % of annual hillslope CO_2 export occurred, emphasising the importance of the spring snow melt event in this system. The results from this study show that maximum water export occurs where water table position and soil hydrological properties (lateral hydraulic conductivity and soil water content) combine to produce the set of conditions most conducive to water flow, in agreement with the transmissivity feedback ~~principal~~principle.

The concept of a riparian chemosphere has been conceptualised by and shown to exist in the catchment studied here (Bishop et al., 2004; Seibert et al., 2009), with the chemistry of water flowing laterally through the catchment determined by soil interactions. The final soil encountered by subsurface waters (in this study the riparian peat soils) will determine the composition of water transported across the terrestrial-aquatic interface (Bishop et al., 2004). Over the hydrological year, total CO_2 export per m^2 of hillslope was 1144 mg CO_2-C m^{-2} yr^{-1} with export from the riparian zone estimated at 3008 mg CO_2-C m^{-2} yr^{-1}. The organic rich peat soils of the riparian zone therefore represent a significantly greater CO_2 export source than the podzol hillslope soils, despite accounting for <10 % of the catchment area. This can be related to the higher measured CO_2 concentrations (Figure

2). The importance of riparian-stream CO_2 export is in agreement with the results for other catchments (Peter et al., 2014; Rasilo et al., 2012) and for TOC in this catchment (Grabs et al., 2012).

Few studies have estimated carbon export across the terrestrial aquatic interface, especially for CO_2. The total annual export of CO_2 in this study (3.0 g CO_2-C m^{-2} yr^{-1}) was similar, given the large inter-annual variability, to the estimate for DIC (3.2 g DIC m^{-2} yr^{-1}) produced from spot measurements (Öquist et al., 2009) and the 2.3-6.9 g DIC m^{-2} yr^{-1} estimated over a longer period (1997-2009) in the same catchment (Öquist et al., 2014). As expected, CO_2 export was lower than in peat dominated catchments in Sweden (3.1-6.0 g CO_2-C m^{-2} yr^{-1}) (Nilsson et al., 2008) and Scotland (11.2-15.5 g CO_2-C m^{-2} yr^{-1}) (Dinsmore et al., 2010, 2013b).

The results of this study suggest that the riparian zone, and not the wider hillslope, is the dominant source of CO_2 entering the stream but the contribution of the riparian zone to water and CO_2 transport has been shown to be episodic, resulting in hotspots and hotmoments when export is greatest (McClain et al., 2003; Vidon et al., 2010). CO_2 export was highest in a narrow band between 30 and 50 cm depth, which accounted for 71 % of CO_2 export. The results from this study suggest that the riparian zone contains two distinct sources of CO_2 export; high export rates at 30 to 50 cm depth as water table moves into more superficial horizons and a deeper (>65 cm depth) continuous but smaller export (Figure 3). The presence of these two water sources in this catchment has also been shown isotopically (Peralta-Tapia et al., 2014) and indicated by the observed bimodal frequency distributions in stream water CO_2 concentrations during storm events (Dinsmore et al., 2013a). Therefore, the riparian export rates of water and CO_2 measured here can be used to explain the observed changes in stream water CO_2 concentrations. ~~The~~ This approach can be used as the catchment chosen for this study is relatively simple in terms of the ~~catchment characteristics and water flowpaths . Water is~~ water flowpaths (with water transported laterally through the soil at <1 m depth with groundwater and overland flow not significant~~. However, this may not be the case in other~~) and the consistency of the riparian lateral extent down the stream reach. In catchments with more complex hydrology or where the riparian lateral extent is variable, riparian CO_2 export alone may not account for all variability in stream water CO_2 dynamics and additional sources would need to be considered.

Peaks in water and CO_2 export occurred in late autumn (October-December) and May. The export of water from the riparian zone was highest during May at 49 mm month^{-1} when the spring snow melt event occurred, accounting for 18 % of the annual water export from the riparian zone. In May, at the onset of spring snow melt, CO_2 concentrations were close to minimum values of 3840 ppmv and 14,400 ppmv at 30-40 and 60-70 cm depths in the riparian zone, resulting in relatively low CO_2 export despite large water export at this time. In October-December, despite only moderate water export, CO_2 export was high (275-529 mg CO_2-C m^{-2} month^{-1}) (Figure 3). During these months, CO_2 concentrations in the riparian soil were at or close to their maximum values (Figure 2), coinciding with maximum soil water DOC concentrations in late summer/autumn observed in the catchment (Lyon et al., 2011). ~~The importance of export from certain horizons in the soil profile found in this study suggests that hotspots occur both spatially throughout the soil profile and temporally~~This observed pattern of peaks in CO_2 export suggests that riparian export is a function of both season and runoff. This highlights the importance of capturing hydrological extremes when quantifying annual estimates of downstream export and evasion of CO_2 across catchments and scales.

The lateral export of riparian dissolved CO_2 is therefore the main source of stream water CO_2, with the amount of CO_2 exported related to the depth of water flow through the riparian zone. The riparian export of CO_2 can therefore be used as an estimate of the catchment CO_2 export to partition the export of CO_2 via the aquatic conduit.

4.3 Downstream CO_2 export and evasion

Total downstream lateral CO_2 export, calculated from the CO_2 concentration and discharge at the catchment outlet, over the hydrological year was 1.2 g CO_2-C m^{-2} yr^{-1}. This is within the range 0.9-1.3 g CO_2-C m^{-2} yr^{-1} of estimates for the same catchment (Öquist et al., 2009) and a peatland catchment in southern Scotland (Dinsmore et al., 2010, 2013b). Due to the greater range in discharge (0.02-15.3 L s^{-1}) than dissolved CO_2 concentrations (daily mean CO_2 concentration ranged from 1.8-7.2 mg CO_2-C L^{-1}); discharge had a greater influence on temporal variability in downstream lateral CO_2 export (Figure 4).

By subtracting downstream lateral CO_2 export (1183 mg CO_2-C m^{-2} yr^{-1}) from the estimate of soil export over the same period (3008 mg CO_2-C m^{-2} yr^{-1}), an estimated 1825 mg CO_2-C m^{-2} yr^{-1} was released to the stream but not accounted for by downstream lateral export. Photosynthetic uptake by aquatic plants or in stream respiration is unlikely to be important in this catchment due to the short water residence times (typically $\sim$4.5 hrs) and the low temperatures (Öquist et al., 2009). Hence the remaining CO_2 is likely to be evaded from the stream surface. Our evasion estimate from the stream surface (1825 mg CO_2-C m^{-2} yr^{-1}) was at the lower end of evasion rates determined from direct point measurements in the same catchment (Wallin et al., 2011). However, evasion accounted for 60 % of export via the aquatic pathway supporting previous findings of the rapid CO_2 loss from the stream (Öquist et al., 2009).

Estimating evasion rate based on this approach is dependent on two assumptions: 1. all stream water CO_2 is derived from lateral soil inputs from the riparian zone and 2. a short water transport time between the riparian zone and the stream to allow rapid exchange of water and CO_2 during events. In headwater systems, in-stream productivity (through biological respiration and photo-degradation of DOC) is limited by the cold temperatures, low pH and short water residence times (Dawson et al., 2001a). Additionally, CO_2 evasion from headwater streams has been widely shown to be composed predominately of recently fixed, plant derived CO_2 transported from the surrounding soil (Billett et al., 2012; Leith et al., 2014). The transport time for water between the riparian zone and the stream varied with depth from <1 hour at <15 cm depth up to $\sim$25 hours at >70 cm depth. The lateral exchange of water and CO_2 between the riparian zone and the stream was rapid enough for the approach to be valid at the daily scale that was used in the model. Additionally, the total volume of water exported from the riparian zone (270 mm yr^{-1}) corresponded well with the annual runoff from the catchment (265 mm yr^{-1}) suggesting that no other inputs of water are contributing. Riparian CO_2 export to the stream is therefore sustaining the lateral downstream export and vertical evasion of CO_2.

There was considerable temporal variability in the evasion estimate (Figure 4) related to variability in CO_2 dynamics in both the terrestrial (Figure 2) and aquatic systems (Figure 4). During the two largest storm events, in which discharge increased suddenly over a very short time period (<1 day), downstream lateral export spiked but without a corresponding increase in soil export. Evasion was therefore not estimated during these periods. This also occurred during the onset of the spring flood. This suggests that during storms there may be a rapid input of overland flow or direct channel water input contributing to discharge without interacting with the soil. The model used to estimate soil CO_2 export did not include overland flow so may be underestimating the total flow of water and CO_2 into the stream during storm events. Overland flow has been shown to be a relatively minor flowpath within the Västrabäcken catchment (Grabs et al., 2012; Peralta-Tapia et al., 2014). However, during the spring flood, up to 20 % of stream runoff was found to be derived from snow melt transported via overland flow (Laudon et al., 2004). Thus during the spring snow melt period, water and CO_2 stored within the snowpack may be an additional export source, bypassing the soil profile. In two Finnish catchments, CO_2 concentrations in the snow pack of 500-1900 ppmv were recorded (Dyson et al., 2011) with snow melt estimated to contribute 35-46 % of downstream lateral CO_2 export during the spring snow melt period (Dinsmore et al., 2011). Over the course of the spring snow melt event in the same Finnish catchments the isotopic signature of evaded CO_2 showed a decreasing contribution from recently fixed, plant derived CO_2 from near surface soil horizons with a corresponding increase in the atmospheric CO_2 component, likely derived from the melting snow pack (Billett et al., 2012). In some headwater catchments, the effects of melt water and overland flow would need to be accounted for in annual estimates of riparian CO_2 export.

Although the annual estimate of riparian export and evasion in the study compare well to estimates from discrete measurements (Öquist et al., 2009), the results of this study highlight the importance of high frequency, direct measurements of CO_2 concentrations given the high temporal variability in CO_2 dynamics in the terrestrial and aquatic systems. Terrestrial processes ~~, especially riparian water table dynamics, have~~ have been shown to have an important role in determining CO_2 export via the aquatic pathway in a wide range of catchments (Abril et al., 2014; Butman and Raymond, 2011; Crawford et al., 2013) . The results from this catchment indicate that terrestrial-aquatic export of CO_2 was controlled by riparian water table dynamics, highlighting the potential importance of riparian zones in headwater catchments. ~~Carbon export via the aquatic pathway positively has been shown to be positively correlated with precipitation (Öquist et al., 2014) .~~ Changes in climate, especially greater variability in precipitation patterns (IPCC, 2007), have the potential to alter riparian water table dynamics and ~~the~~ since carbon export via the aquatic pathway has been shown to be positively correlated with precipitation (Öquist et al., 2014) , impact on the export of CO_2 to streams ~~impacting on~~ and the NECB of boreal headwater catchments.

5 Conclusions

CO_2 concentrations were significantly higher in the riparian zone than hillslope soils~~principally~~ , which we infer was due to 1. greater production of CO_2 in riparian peats compared to the hillslope pozols and 2. higher water table positions limiting the vertical CO_2 diffusion and exchange with the atmosphere. The ~~riparian zone was therefore the main source of stream water~~ results of this study suggest that the riparian zone, and not the wider hillslope, is the dominant source of CO_2 entering the stream with a hotspot for export observed at 30-50 cm depth (accounting for 71 % of total riparian export). Seasonal variability was high with peaks in export during the spring flood and autumn storm events highlighting the importance of high frequency measurements in this very dynamic system.

Downstream CO_2 export (determined from stream water dissolved CO_2 concentrations and discharge) was 1.2 g CO_2-C m^{-2} yr^{-1}. Subtracting downstream lateral export from riparian input (3.0 g CO_2-C m^{-2} yr^{-1}) gives 1.8 g CO_2-C m^{-2} yr^{-1} which can be attributed to evasion losses (accounting for 60 % of export via the aquatic pathway). The results highlight the importance of terrestrial CO_2 export, especially from the riparian zone, for determining catchment aquatic CO_2 losses and especially for maintaining the high evasion fluxes from boreal headwater streams.

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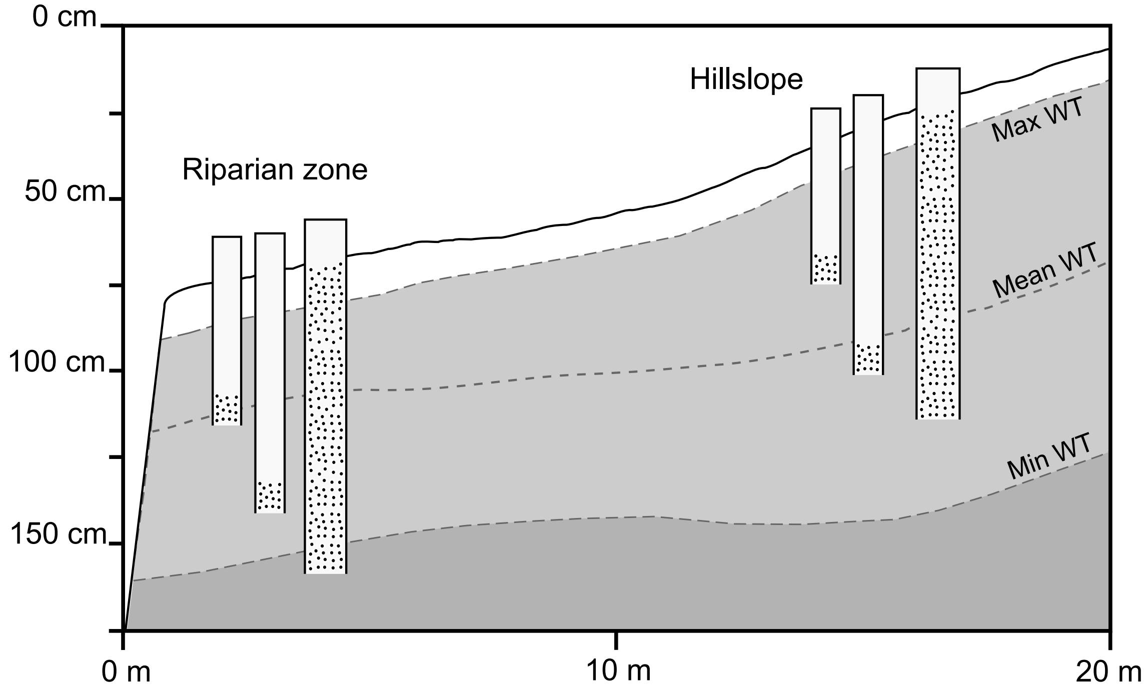

Figure 1. Schematic of the hillslope-riparian transect used in this study. CO_2 sensors were installed in dipwells with sampling windows at 30-40 cm and 60-70 cm depth. An additional dipwell for water table and soil temperature was perforated along the full length to 90 cm depth. Grey box indicates the zone of transient saturation (between max and min water table positions) over the hydrological year.

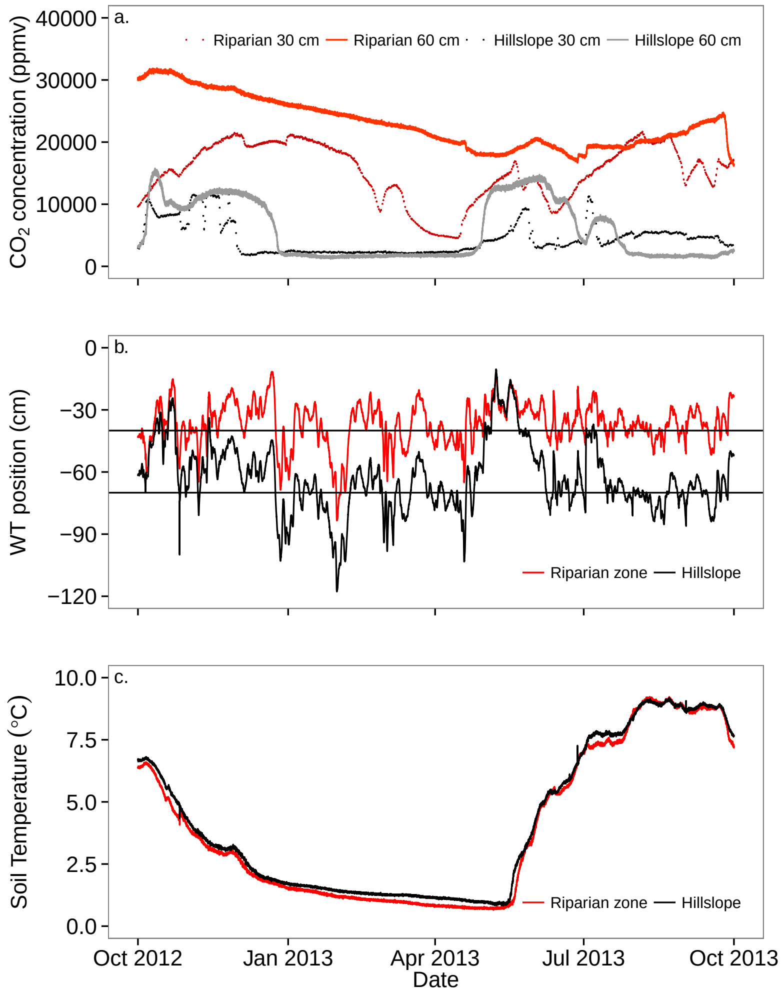

Figure 2. Time series of hillslope and riparian zone a. CO_2 concentrations sampled at 30-40 cm and 60-70 cm depths, b. water table and c. soil temperature across the full measurement period. Horizontal lines in b. highlight the deepest depths sampled by the 30-40 cm and 60-70 cm depth CO_2 sensors.

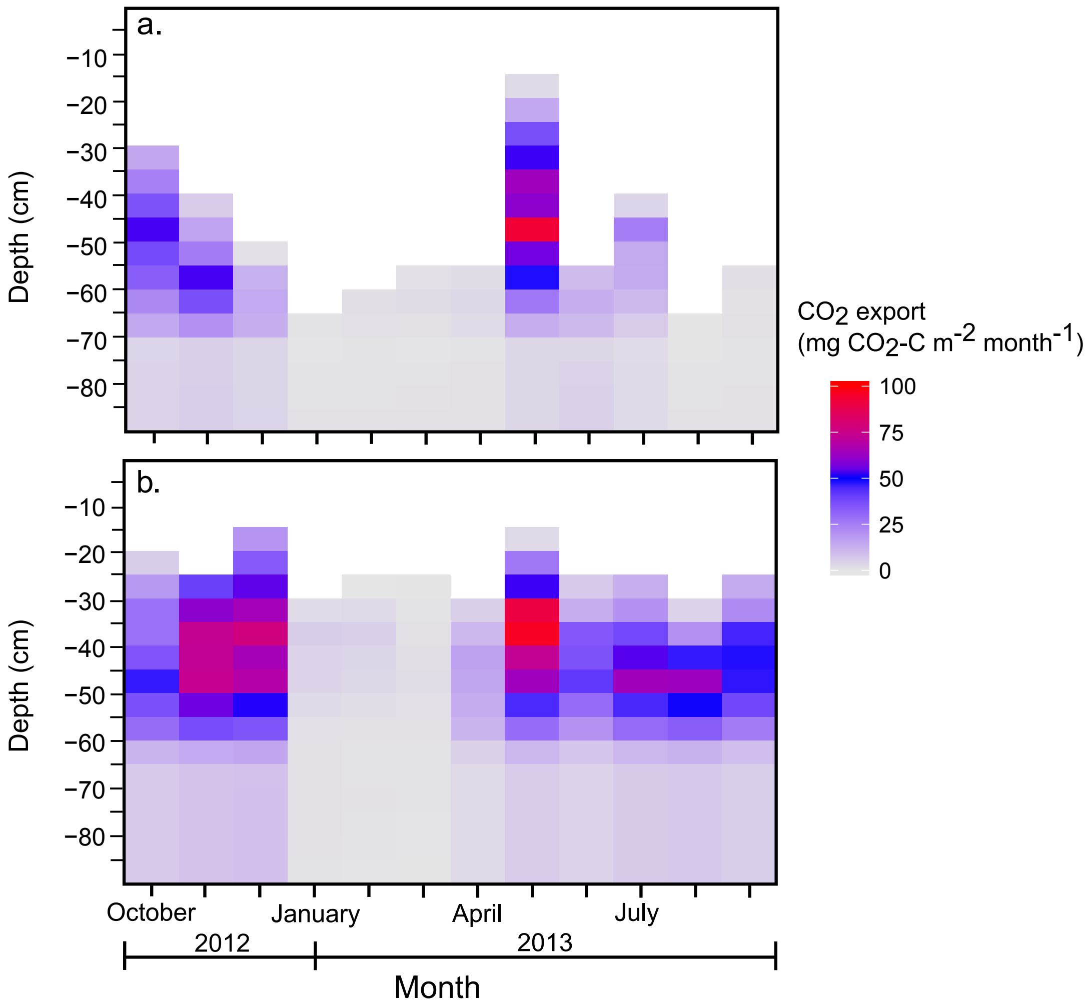

Figure 3. Total monthly export of CO_2 from the a. hillslope and b. riparian zone across the measurement period

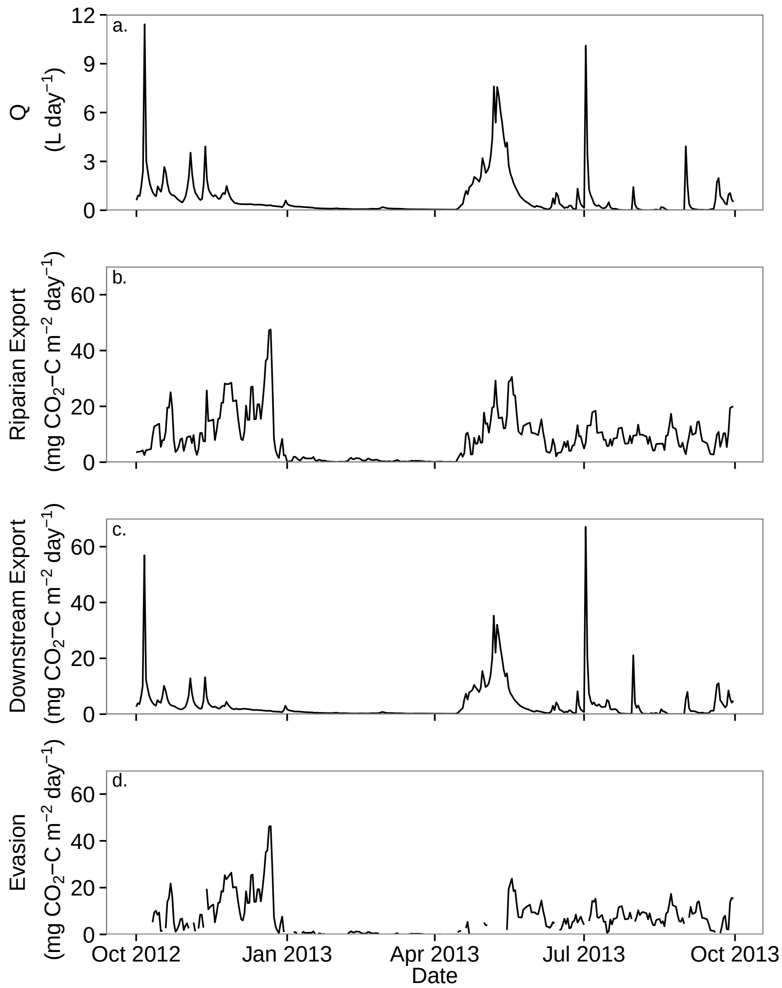

Figure 4. Mean daily a. discharge (Q), b. CO_2 export from the riparian zone to the stream, c. downstream lateral CO_2 export and d. vertical CO_2 evasion over the hydrological year.

Table 1. Mean (min-max) calculated from all continuous measurements over the hydrological year (1st October 2012 - 30th September 2013) in the hillslope and riparian zone. Significant differences between the hillslope and riparian zone sampling points (at P<0.01) are indicated by **.

	Hillslope	**Riparian**
Water table depth (cm)**	-63 (-118 to -10)	-37 (-83 to -12)
Temperature (℃)**	4.1 (0.8-9.2)	3.9 (0.6-9.2)
CO_2 (ppmv) 30-40 cm**	4410 (1680-11,730)	15,130 (4430-21,730)
CO_2 (ppmv) 60-70 cm**	5790 (1170-15,770)	23,100 (16,140-31,920)