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Carbon in Boreal Streams

Isotopic Tracing of Terrestrial Sources

AUDREY CAMPEAU



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Abstract

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The boreal biome comprises vast areas of coniferous forests, dotted with millions of peatlands. Plants harbouring these ecosystems fix CO₂ from the atmosphere, which is later incorporated into the vegetation biomass and subsequently buried in soils. Over the course of millennia, this process has led to the formation of a large repository of organic C, currently stored in boreal soils. Streams draining this landscape are typically enriched with carbon dioxide (CO₂), methane (CH₄) and dissolved organic carbon (DOC). As a consequence, streams tend to emit CO₂ and CH₄ to the atmosphere, two potent greenhouse gases, and thus contribute positively to radiative climate forcing. The sources fuelling C to boreal streams are not well understood. This thesis aims to unravel these sources, and promote a better consolidation of terrestrial and aquatic C biogeochemical processes. The work is largely based on stable and radiogenic C isotope characterization of various dissolved C forms in stream and groundwater, within contrasting ecosystem types across Sweden.

This thesis identifies boreal soils as the main source of CO₂ in streams. Soil respiration (i.e. biogenic sources) overwhelmingly supply CO₂ to streams, leaving only a few exceptions where geogenic CO₂ sources were present. An array of biological processes also transform CO₂ during its transport from soils to streams. These include; methanogenesis, aquatic DOC mineralization and primary production. The majority of C in boreal streams is sustained by the decomposition of recent photosynthates, with ancient C substrates holding a negligible share of the total C export. While these results suggest that the repository of ancient soil organic C is currently stable, within boreal forests and peatlands, the close connection with recently occurring photosynthesis suggest that forecasted alterations in plant C allocation patterns, driven by climate and land-use changes, will produce a rapid response in stream CO₂ emissions. Isotopic characterization of C in stream and groundwater can help reveal these sources and transformation processes, but its interpretation must be made with care.

Audrey Campeau, Department of Earth Sciences, LUVÅL, Villav. 16, Uppsala University, SE-75236 Uppsala, Sweden.

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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

- I **Campeau, A.**, Wallin, M.B., Giesler, R., Löfgren, C., Mörrth, C.M., Schiff, S., Venkiteswaran, J.J., Bishop, K., (2017) Multiple source and sinks of dissolved inorganic carbon across Swedish streams, refocusing the lens of stable C isotopes. *Scientific Reports*, 7(1),9158–4
- II **Campeau, A.**, Bishop, K. Bishop, K. Nilsson, M. B. Klemmedtson, L., Laudon, H., Leith, F. I., Öquist, M., Wallin, M. B., (2018) Stable carbon isotopes reveal soil-stream DIC linkages in contrasting headwater catchments. *Journal of Geophysical Research: Biogeosciences*, 123(1),149-167
- III **Campeau, A.**, Bishop, K. H., Billett, M. F., Garnett, M. H., Laudon, H., Leach, J. A., Nilsson, M. B., Oquist, M. G., Wallin, M. B., (2017) Aquatic export of young dissolved and gaseous carbon from a pristine boreal fen: implication for peat carbon stock stability. *Global Change Biology*, 23(12), 5523-5536.
- IV **Campeau, A.**, Bishop, K., Amvrosiadi, N., Billett, M. F., Garnett, M. H., Laudon, H., Öquist, M. G., Wallin, M. B., (2019) Current forest carbon fixation fuels stream CO₂ emissions. *Nature Communications*, 10(1)

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Additional Papers

In addition, the author has contributed to the following papers, which are not included in the thesis

- I **Campeau, A.**, Lapierre, J. F., Vachon, D. and del Giorgio, P. A. (2014) Regional contribution of CO₂ and CH₄ fluxes from the fluvial network in a lowland boreal landscape of Québec, *Global Biogeochemical Cycles*, 28(1), 57–69
- II **Campeau, A.**, and Del Giorgio, P. A. (2014) Patterns in CH₄ and CO₂ concentrations across boreal rivers: Major drivers and implications for fluvial greenhouse emissions under climate change scenarios, *Global Change Biology*, 20(4), 1075–1088
- III **Campeau, A.**, Abbott, B.W., Baranov, V., Mendoza-Lera, C., Nikolakopoulou, M. Harjung, A., Kolbe, T., Balasubramanian, M. N., Vaessen, T. N., Ciocca, F., Wallin, M. B., Romeijn, P., Antonelli, M., Gonçalves, J. Datry, T., Laverman, A. M., de Dreuzay, J-R., Hannah, D. M., Krause, S., Oldham, C., Pinay, G. (2016) Using multi-tracer inference to move beyond single-catchment ecohydrology. *Earth-Science Reviews* 160,19-42
- IV **Campeau, A.**, Wallin, M. B., Audet, J., Bastviken, D, Bishop, K., Kokic, J., Laudon, H., Lundin, E., Löfgren, S., Natchimuthu, S., Sobek, S., Teutschbein, C., Weyhenmeyer, G.A., Grabs, T. (2017) Carbon dioxide and methane emissions of Swedish low-order streams – a national estimate and lessons learnt from more than a decade of observations. *Limnology and Oceanography Letters* 3(3),156-167
- V **Campeau, A.**, Riml, J., Bishop, K., Wallin, M.B. (in review) Spectral decomposition reveals new perspective on CO₂ concentration patterns and soil-stream linkages in a boreal headwater catchment. *Journal of geophysical research: Biogeosciences*

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Abbreviations

CO ₂	Carbon Dioxide
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
CH ₄	Methane
$\delta^{13}\text{C}$	Stable C Isotope Ratio
^{14}C	Radiocarbon Content
NEE	Net Ecosystem Exchange
NECB	Net Ecosystem Carbon Balance
ABI	Abisko
DAL	Dalarna
KRY	The Krycklan Catchment
LAVI	South-West of Sweden
DEG	Degerö Stormyr
SVB	Svartberget or Site C2
SKOG	Skogaryd or Mineral Site



Prologue

Our planet is equipped with its own thermostat. Life on Earth is self-perpetuated by controlling the amount of greenhouse gases and water present in our atmosphere, hence regulating the climate system. This regulation is partly achieved through biological and geochemical processes circulating carbon between the biosphere, atmosphere, lithosphere and hydrosphere. Together, these mechanisms are termed the *Global Carbon Cycle*. Fossil fuel burning, deforestation and ocean acidification, has and will continue to profoundly alter the natural course of these processes. Today, photosynthetic organisms on land and in oceans, pump over half of the annual CO₂ emissions resulting from human activities. This process dampens our impact on the global carbon cycle, and slows down the rise in radiative climate forcing. But how resilient is the global C cycle? How is it regulated, and how will it respond to forthcoming disturbances? How do these mechanisms also shape important environmental aspects, such as water quality, ecosystem functioning and other societal services. These are the research questions that have led to the scientific discipline of *Carbon Biogeochemistry*, some of which are reflected in the subject of this thesis. Global warming is one of the most defining challenge of our time. The Earth is a source of wonder, but it is also our only home. Understanding it, ultimately means to protect it and ourselves.



Introduction

*“Nothing in life is to be feared, it is only to be understood,
Now is the time to understand more, so that we may fear less.”*
- Marie Curie

Carbon Cycling in the Boreal Biome

The boreal biome forms a large belt encircling the northern high latitudes. It's land cover is composed of a mosaic of coniferous forests and peatlands. Through photosynthesis, the living vegetation found across this remote landscape continuously fix carbon dioxide (CO₂) from the atmosphere. The C entering these ecosystems is then used as building blocks for the vegetation, and later for soil litter formation. Decomposition, carried out by soil microbes and other organisms, returns a fraction of this CO₂ to the atmosphere. The net results of these two counteracting processes, is however, to remove CO₂ from the atmosphere, with boreal ecosystems providing alone ~20% of the global net forest C sink (Pan *et al.*, 2011). Since CO₂ acts as an important greenhouse gas, boreal ecosystems contribute to a net cooling of the climate and neutralize a significant fraction of anthropogenic CO₂ emissions (Chapin *et al.*, 2000, Gauthier *et al.*, 2015, Winkler *et al.*, 2019).

The exchange of CO₂ between boreal ecosystems and the atmosphere, rapidly grows in complexity when considering the role of the hydrosphere (Cole *et al.*, 2007, Tranvik *et al.*, 2009). The boreal biome harbours the world's highest density of freshwater ecosystems; composed of inter-connected lakes, ponds, rivers and streams (Allen & Pavelsky, 2018, Downing *et al.*, 2006, Downing *et al.*, 2012). Freshwater bodies draining the boreal landscape are overwhelmingly enriched with CO₂ (Raymond *et al.*, 2013) and methane (CH₄) (Bastviken *et al.*, 2011) and receive high dissolved organic carbon (DOC) loads (Algesten *et al.*, 2004, Laudon *et al.*, 2011). The greenhouse gas component of aquatic C, comprising CO₂ and CH₄, is rapidly returned to the atmosphere by physical gas exchange. Freshwaters, thus contribute positively to atmospheric climate forcing. A large body of research has been devoted to

quantify freshwater greenhouse gas emissions, in order to better constrain their role in the global C cycle and climate system. These efforts have led to a first integration of freshwater CO₂ emissions in the global C cycle scheme in the most recent IPCC report on climate change (IPCC, 2013). Proceeding from here, this thesis sets out to reveal the sources leading to the presence of C in streams draining boreal ecosystems.

Due to the cold and wet climate conditions prevailing across the boreal biome, decomposition of plant material and soil litter is often incomplete. This has led to the formation of a large repository of soil organic C, slowly expanding over the last ~10 000 years (Holocene), which contributed to cool the climate system (Frolking & Roulet, 2007). The estimated magnitude of this latent C repository currently represents a third of the global soil organic C reserves and is near equivalent to the total atmospheric CO₂ pool (200-500 Pg of C (Bonan & Pollard, 1992, Gorham, 1991, Malhi *et al.*, 1999). Boreal soil C stocks are mostly accumulated in waterlogged environments, such as peatlands and riparian zones. Mobilizing these C stocks, for example through runoff, would have unprecedented consequences for the climate system. Its stability in the face of climate and land-use changes is complex and currently unknown.

Most organisms found across the boreal biome are currently living within their climatic limits. Rising temperatures in these regions will profoundly transform the structure and functioning of boreal ecosystem, more so than in lower latitudes (Gauthier *et al.*, 2015, Jarvis & Linder, 2000). Some of these transformations are already observable, through a northward shift in the tree line and a widespread greening of the northern high latitudes (Piao *et al.*, 2006, Serreze *et al.*, 2000, Winkler *et al.*, 2019). Other disturbances are less progressive and may instead emerge suddenly. An anticipated increase in forest fires frequency, due to a growing water stress and intensified summer heat waves (Bond-Lamberty *et al.*, 2007, Turetsky *et al.*, 2015), coupled with devastating insect outbreaks (Kurz *et al.*, 2008, Stinson *et al.*, 2011), will lead to extensive forest destruction (Lenton *et al.*, 2008). These disturbances will likely alter the boreal biome's C sink capacity and ecosystem level C allocation patterns, which may rapidly feedback on the climate system (Bonan, 2008, Piao *et al.*, 2008). How the C balance of freshwaters systems draining these landscapes will respond to such disturbances is still unclear (Benoy *et al.*, 2007, Campeau & Del Giorgio, 2014, Marchand *et al.*, 2009).

Sources of CO₂ in Streams

Over the last decade, boreal freshwater CO₂ emissions have been estimated across a vast range of scales; e.g. catchment scale (Crawford *et al.*, 2013, Kokic *et al.*, 2015, Wallin *et al.*, 2013), regional scale (Campeau *et al.*, 2014, Crawford *et al.*, 2014, Teodoru *et al.*, 2009), national scale (Butman & Raymond, 2011, Humborg *et al.*, 2010, Wallin *et al.*, 2018) and global scale (Raymond *et al.*, 2013). These studies point out to the same conclusion: *streams hold a large relative contribution to CO₂ emissions, despite representing only a small areal coverage*. This disproportionately high contribution is explained by two major factors. Firstly, streams are associated with turbulent flow conditions that triggers rapid atmospheric gas exchange (Raymond *et al.*, 2012, Wallin *et al.*, 2011). Secondly, stream waters are often excessively saturated in CO₂, considered to arise from a close connectivity with catchment soils (Duvert *et al.*, 2018, Hotchkiss *et al.*, 2015, Johnson *et al.*, 2008). Approaches for integrating stream CO₂ emissions into terrestrial C budgets are, however, still unclear (Billett *et al.*, 2015, Raymond *et al.*, 2013). Defining stream CO₂ sources will provide a process-based understanding to help reconcile aquatic and terrestrial components in catchment C budgets.

CO₂ can arise from various biogeochemical processes and C substrates; each associated with different timescales, turnover rates and environmental controls (Figure 1). Given the age of the boreal soil C repository, substrates fueling biogenic CO₂ production in soils through decomposition of organic matter can span from current to ~10 000 years old (Figure 1). The age of DOC circulating within boreal freshwater systems reflects this wide range of substrates (Marwick *et al.*, 2015). Microbial decomposition of DOC within groundwater or surface waters may generate CO₂ with a corresponding range of age (Mayorga *et al.*, 2005, McCallister & del Giorgio, 2012, Raymond *et al.*, 2004). The DOC circulating in freshwaters can also be photo-oxidized once exposed to solar radiation, leading to aquatic CO₂ production (Amon & Benner, 1996, Graneli *et al.*, 1996, Köhler *et al.*, 2002). However, these processes can be reduced in streams shaded by the canopy. Similarly, aquatic microbial decomposition of DOC can be restricted in streams, owing to short water transit times (Catalán *et al.*, 2016). Together, this information suggests that DOC processing in-streams is controlled by a complex set of environmental and hydrological conditions. Its relevance for stream CO₂ emissions is highly variable, and remains unclear.

Within shorter timescales, the photosynthetic activity of the above ground vegetation can directly fuel CO₂ in soils, by directly supporting autotrophic root metabolism (Bond-Lamberty *et al.*, 2004, Hogberg *et al.*, 2001, Kuzyakov & Larionova, 2005) (Figure 1). Microbes and fungi associated with

the root system can also decompose root exudates and other recent photosynthates transported to soils via throughfall and stemflow (Van Hees *et al.*, 2005, Van Stan & Stubbins, 2018) (Figure 1).

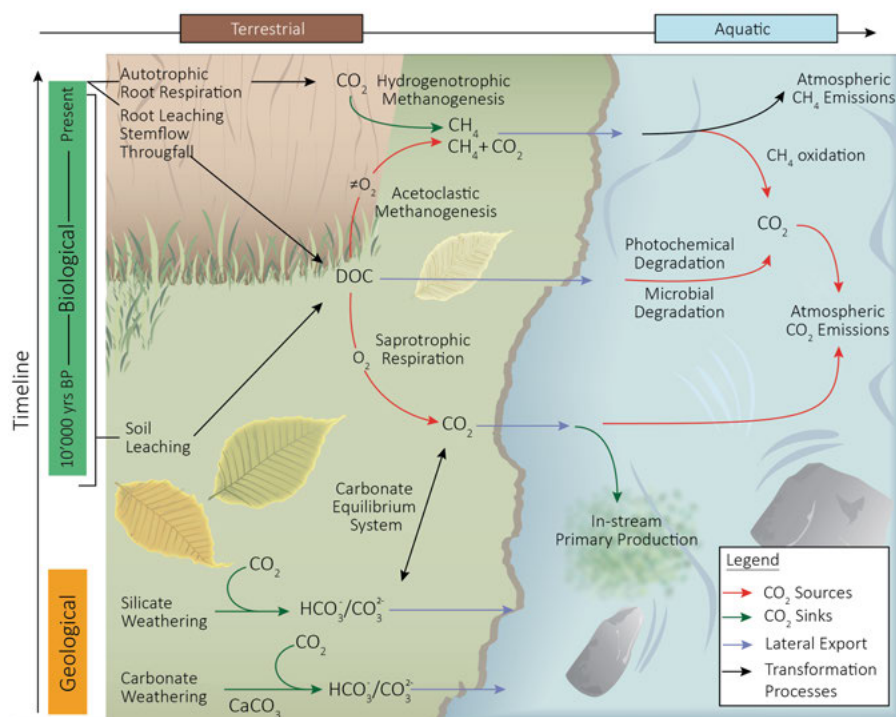


Figure 1. Schematic illustrating the various sources (red arrows), sinks (green arrows), and transformation processes (black arrows) occurring during the lateral export of C (blue arrow) from groundwater (left side) to streams (right side).

Counteracting processes may further contribute to remove CO₂ from stream waters, thus acting as C sinks. Stream primary producers can, much like forests on land, take up ambient CO₂ to be incorporated into the emergent plants and benthic algae inhabiting the streams (Falkowski & Raven, 2013) (Figure 1). Abiotic processes such as chemical weathering consume CO₂ and generate freshwater carbonate alkalinity, that supports life both in freshwaters and oceans (Amiotte Suchet *et al.*, 2003, Meybeck, 1987) (Figure 1). These reactions occur through two distinct chemical pathways; weathering of carbonate or silicate containing minerals. While silicate weathering reaction simply converts CO₂ to HCO₃⁻, the analogous reactions with carbonate containing minerals simultaneously releases geogenic C in the form of CaCO₃ (Figure 1). The weathering processes links the contemporary and geological reservoir of the C cycle and has provided a long-term thermostat, stabilizing the Earth's climate over geological timescales (Berner, 1992, Liu *et al.*, 2011, Walker *et al.*, 1981).

In the absence of oxygen, organic C decomposition gives rise to CH₄ production. Water-logged and organic-rich environments, such as peatlands and riparian zones, are prone to oxygen depletion and thus represent key source areas for methanogenesis (Harriss *et al.*, 1985, Jones & Mulholland, 1998b, Roulet *et al.*, 1992). Streams draining such environments also tend to emit significant amounts of CH₄ to the atmosphere (Campeau *et al.*, 2014, Hope *et al.*, 2001, Wallin *et al.*, 2018). Methanogenesis can occur through two fundamental pathways, acetoclastic methanogenesis, which consumes organic C and generate both CO₂ and CH₄, or hydrogenotrophic methanogenesis, which consumes CO₂ in order to produce CH₄ (Whiticar *et al.*, 1986) (Figure 1). Methanogenesis can thus represent both a source and a sink of CO₂ depending on the pathway prevailing in the environment.

A complex mixture of sources, sinks and transformation processes fuelling C in streams need to be separated. Tracers allowing to partition these processes are necessary to address the sources of C in boreal streams. Each of the above listed processes are associated with specific isotopic fractionations, or with an imprint on the age component of C. These effects can thus be interpreted by C isotopic characterization in streams.

Isotopic Tools to Reveal C sources

Stable Isotope Ratio

The stable C isotope ratio, ¹³C/¹²C ($\delta^{13}\text{C}$) carries the imprint of various sources and transformation processes generating CO₂. Its interpretation can be challenging, owing to the multiple co-founding factors that need disentangling. The first partitioning of CO₂ sources can be made based on the large gap in $\delta^{13}\text{C}$ value that stands between two major C reservoirs; biogenic and geogenic C (Figure 2). Biogenic CO₂ results from the degradation of organic material, which in a C3-plant dominated catchment generates $\delta^{13}\text{C}$ ranging between -33‰ to -24‰ (O'Leary, 1988, Vogel *et al.*, 1993) (Figure 2). Alternatively, geogenic CO₂ results from the dissolution of calcium carbonate (CaCO₃, $\delta^{13}\text{C}=0\text{‰}$), generating a mixture with $\delta^{13}\text{C}=-12\text{‰}$ if reacting with biogenic CO₂ ($\delta^{13}\text{C}=-27\text{‰}$) or $\delta^{13}\text{C}=0\text{‰}$ if reacting with non-carbon bearing acids (Clark & Fritz, 1997, Land, 1980) (Figure 2).

Historically, the separation of these two C sources has involved a simple two end-members mixing ratio, where the range in $\delta^{13}\text{C}$ value is attributed to a combination of the two sources (Deines *et al.*, 1974, Kendall *et al.*, 1992). While this simple scheme can be appropriate in closed systems, it holds a high risk for misinterpretation when CO₂ is also mixing with the atmosphere, such as for shallow groundwater and surface waters (Clark & Fritz, 1997).

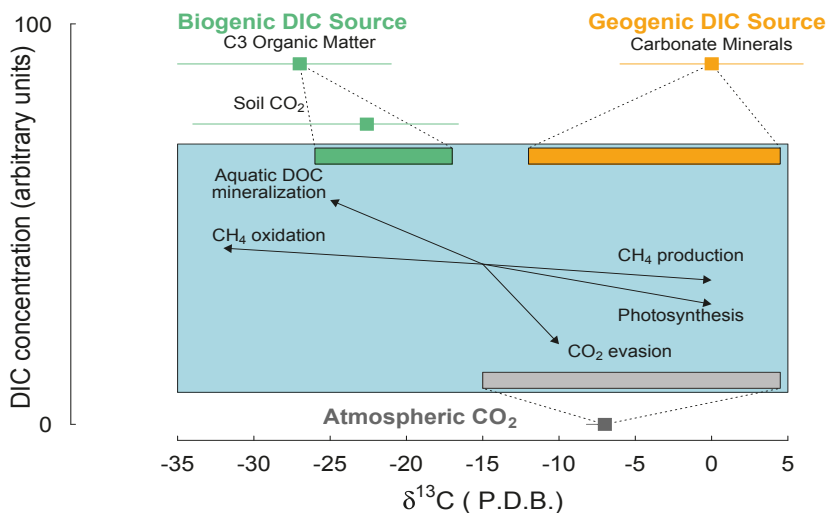


Figure 2. Conceptual scheme illustrating biogeochemical processes controlling stream $\delta^{13}\text{C}$ -DIC values in streams, adapted from Amiotte-Suchet *et al.* (1999) and Alling *et al.* (2012). The x-axis represents the reported range of stream $\delta^{13}\text{C}$ -DIC values and y-axis a gradient in DIC concentration with arbitrary units. The internationally agreed $\delta^{13}\text{C}$ end-members for the biogenic (-27‰) DIC source in a C3-plant dominated catchment (green square) and geogenic (0‰) DIC source (orange) as well as the atmospheric CO_2 (-8.5‰) are represented with their documented range (coloured bars) from Coplen *et al.* (2002). The blue box represents the stream water environment, with the commonly accepted range of $\delta^{13}\text{C}$ -DIC values in equilibrium with each of these three end-members (Biogenic (-26 to -18‰), Geogenic (-12‰ to 5‰), Atmospheric (-15‰ to 8‰), represented in coloured rectangles, along with the isotopic effect of in-stream biogeochemical processes represented as the black arrows (**Paper I**).

$\delta^{13}\text{C}$ values are typically reported for the total dissolved inorganic C (DIC) pool, which includes dissolved CO_2 gas (carbonic acid: H_2CO_3), but also two ionic forms; bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}). The reported range of $\delta^{13}\text{C}$ -DIC value in flowing waters spans from $+5$ to -35‰ , which exceeds the end-member values for the geogenic and biogenic DIC (Marwick *et al.*, 2015) (Figure 2). This wide range in $\delta^{13}\text{C}$ -DIC values clearly demonstrate that additional processes affect the $\delta^{13}\text{C}$ in surface waters. The relative proportion of the three C forms that comprise DIC is controlled by pH dependent equilibrium reactions, where low pH conditions boost the CO_2 fraction, while high pH conditions increases the relative proportion of ionic forms. Large isotopic equilibrium fractionation occurs when C is exchanged between these three components (Zhang, 1995). This isotopic effect is particularly important in freshwater systems, where supersaturated CO_2 evades to the atmosphere, but

carbonate alkalinity remains in the aqueous phase (Clark & Fritz, 1997, Zeebe & Wolf-Gladrow, 2001). The kinetics of gas exchange in streams is a key process in stream waters, since CO₂ is often found in supersaturation relative to the atmosphere (Figure 2). The DIC concentration and composition, the gas exchange rates, pH and alkalinity together shape the isotopic composition of stream water DIC exchanging with the atmosphere. Recent progress in modelling have allowed to describe this effect in certain environmental conditions. Using the observed $\delta^{13}\text{C}$ -DIC values, these models allow to trace back the mass of CO₂ evaded from streams (Marx *et al.*, 2018, Polsenaere & Abril, 2012, Venkiteswaran *et al.*, 2014).

A large combination of biogeochemical processes may alter the $\delta^{13}\text{C}$ -DIC values in streams including: DOC mineralization, either biological or photochemical, in-stream primary production, methanogenesis and CH₄ oxidation (Figure 2). Taken individually, each of these various processes can be described, but disentangling them simultaneously is challenging. Hence, methods to separate those confounding isotopic effects in order to extract the information held in the observed $\delta^{13}\text{C}$ -DIC values are clearly needed.

Radiocarbon dating

Radiocarbon (¹⁴C) dating is a fundamental technique in biogeochemistry. Historically, it has allowed to reveal key processes controlling the global C cycle and climate (Levin & Heshshaimer, 2000, Oeschger *et al.*, 1975). The β -decay of ¹⁴C, with a half-life of 5'730 years, can be used to trace back the origin of any C bearing molecule, up to around 50'000 years. Nuclear testing in the 1950's has set profound changes in the natural levels of radioactive elements present in our environment, causing a near doubling of the natural ¹⁴C abundance in the atmosphere (Levin & Kromer, 2004, Rafter & Fergusson, 1957) (Figure 3). The exceedance of the natural ¹⁴C abundance in the atmosphere has forced us to reconsider the interpretation of ¹⁴C dating, now precluding a linear translation of the ¹⁴C-content to calendar years (Figure 3).

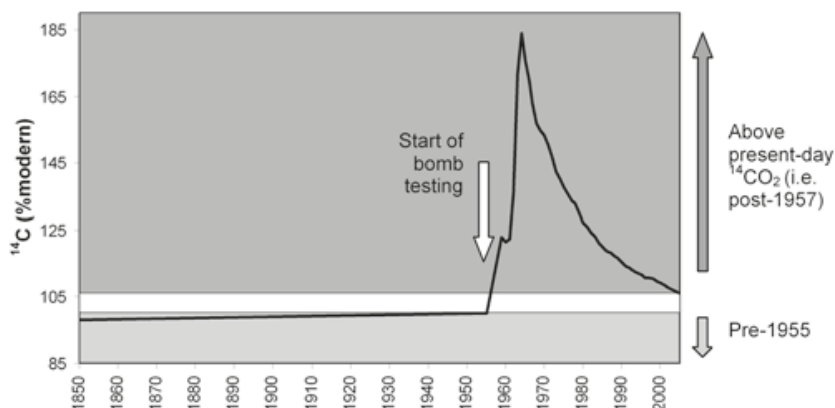


Figure 3. Time series of atmospheric ^{14}C level between the year 1850 and 2000 taken from Evans *et al.* (2007).

The ^{14}C contents are typically reported in terms of relative ^{14}C enrichment in percent modern C (% modern) or in terms of years before present (yrs BP), where 0 BP corresponds to 1950 - beginning of nuclear testing. According to the conventional radiocarbon age (CRA), the ^{14}C content is thus interpreted as follow; $>100\%$ modern indicates a considerable incorporation post-bomb ^{14}C . Its average age can be assigned to either the rising (1950-1964) or falling limb (1964-present) of the bomb atmospheric ^{14}C peak. Alternatively, the ^{14}C content $<100\%$ modern indicate the presence of older material and can be assign to an average CRA calendar year.

While this interpretation may be correct for a selection of standing solid materials, e.g. tree rings, ice and soil cores, it involves several complications for mobile material, such as solutes and gases. For these materials, the average ^{14}C content likely represents a combination of molecules with different origins, with a standard error associated to the average value that remains unknown. Thus an average ^{14}C content of $<100\%$ modern in solutes or gas samples does not preclude the intrusion of post-bomb C. New research is shedding light upon these issues by revealing that microbial decomposition can yield CO_2 with a considerably different ^{14}C -content than its organic C substrate (Dean *et al.*, 2019, Mann *et al.*, 2015, McCallister *et al.*, 2004). This suggest that the average ^{14}C -content of DOC and CO_2 , does in fact represent a mixture of different values. For this reason, the analysis of ^{14}C -content in this thesis specifically avoided potential translation to calendar years. Instead, we focused on relative differences between C species (DOC, CO_2 and CH_4) and their changes over time, to help appropriate differences in C sources and environmental controls.



Objectives and Study Design

*“The world is beautiful to look at,
but it’s even more beautiful to understand”*
- Brian Cox

This thesis sets out to reveal the sources of C in boreal streams. The CO₂ component was given particular emphasis, but CH₄ and DOC were also considered for the significant overlap in their respective cycling, and the major fraction that they form to the total stream C loading. Several different techniques were applied to address C sources in streams. These mostly focused on the use of C isotopes ($\delta^{13}\text{C}$ and ^{14}C), but also on automated logger systems to help monitor changes in soil and stream water hydro-chemical properties over time.

The thesis combined two different approaches: 1) a synthesis of large-scale synoptic surveys of headwaters streams covering different regions of Sweden (Paper I) and 2), three detailed catchment-scale studies within different ecosystem types (Paper II-III-IV) (Figure 4). Through this study design, we aimed to acquire a broad spatial understanding, coupled with a more detailed knowledge of small-scale processes with their temporal variability. The specific objectives for each of the included studies were:

- I. Characterize the sources and sinks of stream water DIC across multiple catchments through the interpretation of the $\delta^{13}\text{C}$ -DIC values (Paper I).
- II. Reveal the biogeochemical processes occurring during the transport of DIC from soils to stream within contrasting ecosystem types (Paper II).
- III. Determine the sources of lateral CO₂, CH₄ and DOC export from a boreal peatland in order to assess the stability of the peat C storage (Paper III)
- IV. Separate the biogeochemical sources of lateral DOC and CO₂ export from an old-growth boreal forested catchment (Paper IV).

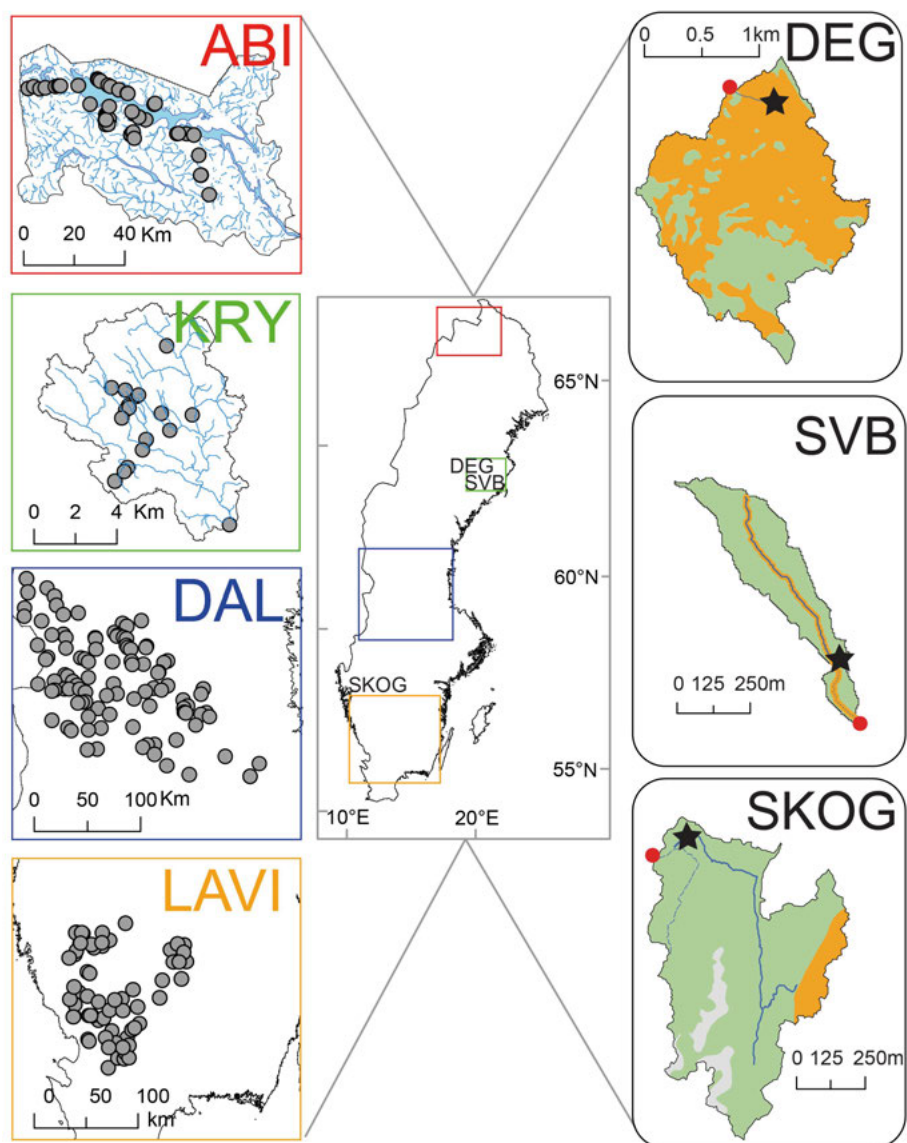


Figure 4. Map of Sweden indicating the location of the four synoptic stream surveys (left side, top-down: ABI, KRY, DAL, LAVI) and three detailed catchment-scale studies (right side, top-down: DEG, SVB, SKOG). Left: the location of each stream sampled in the synoptic surveys are illustrated with grey circles within each regions. Right: the catchment boundaries are delimited with the grey line and specific land covers are illustrated, comprising forests (green) peatlands (orange) and bedrocks outcrop (grey). The blue lines represent the stream line upstream of the transect sampling location (black stars) and the red circles indicate the location of stream flow gauging station.



Methodology

*“Equipped with his five senses,
man explores the universe around him
and calls the adventure Science”
- Edwin Powell Hubble*

Stream Surveys

Synoptic stream surveys were conducted within four distinct geographical regions in Sweden: from north to south, Abisko (ABI), the Krycklan catchment (KRY), Dalarna (DAL) and the South-west coast (LAVI) (Figure 3; Paper I). The study included a total of 326 different stream water chemistry measurements. The studied streams in the DAL (n=101) and LAVI (n=68) region were selected based on a randomized statistical selection and were visited only once, in June 2013 and 2014 respectively. The selected streams were of Strahler order 1 exclusively, contained no lakes within their specific catchment areas and were located away from urbanized or agricultural areas but nonetheless within walking distance of roads. The 18 studied rivers and streams included in KRY were visited at 7 different occasions, for a total of 108 measurements. For ABI, 49 different rivers and stream were visited once in mid-September 2008 and have been previously published in Giesler *et al.* (2013). The sampling in KRY and ABI was undertaken outside the work frame of this thesis. The studied rivers and streams in KRY and ABI spanned from Strahler order 1 to 5. A detailed description of each of the regions and their sampling design is presented in paper I.

Catchment-Scale Studies

Three distinct ecosystem types were considered for the detailed catchment-scale studies (Figure 3). In the north, a boreal oligotrophic fen, Degerö Stormyr (DEG), and a mature boreal forest, Svartberget (*Site C2*) (SVB). In the southwest, a reforested hemi-boreal agricultural area, Skogaryd (*Mineral Site*) (SKOG). All three catchments are involved in the Swedish Infrastructure for Ecosystem Science (SITES; fieldsites.se). A more detailed description of the three catchments (DEG, SVB and SKOG) is presented in paper II, with more specific information regarding the DEG catchment in paper III and SVB catchment paper IV.

The groundwater sampling at the DEG study site consisted of a single vertical peat profile allowing manual groundwater collection, located about 70 m away from the stream initiation point (Figure 5). The groundwater tubes screened across a depth range between 0.25 and 1 m in vertical extent, allowed sampling of peat pore water across the full 4 meters depth profile, divided into six different peat horizons [0–0.25 m, 0.25–0.5 m, 0.5–1 m, 1–2 m, 2–3 m, and 3–4 m] (Figure 5).

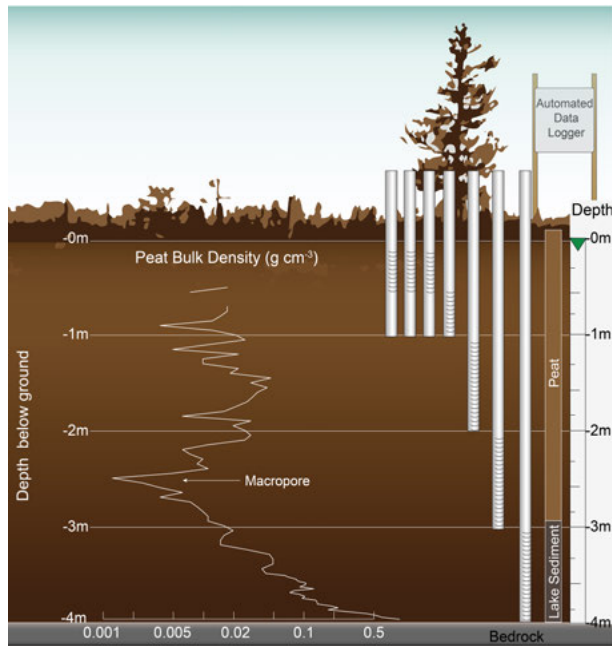


Figure 5. Schematic of the groundwater tubes characterizing the full peat depth profile at Degerö (right side) along with peat bulk density profile (left side) indicating the location of a deep macropore (~2.5m below ground) potentially exporting water and C to the stream.

The groundwater and stream water sampling at SVB and SKOG was designed following a three-level lateral transect; upslope-riparian-stream (Figure 6). The upslope location was situated 10-15 m away from the stream, and the riparian 1-4 m away from the stream. Two different soil depths were considered at both locations, shallow [0 to 0.5m] and deep [0.5 to 1m] below ground surface (Figure 6). Two different sets of groundwater tubes were installed next to each other at each location and depth (Figure 6). The first set was equipped with a manual sampling tube that allowed to suck up water from the ground. The second set was instrumented with automated sensors recording hourly CO₂ concentrations and temperature (Figure 6). A fifth tubes was installed at both locations where water table position was monitored (Figure 6).

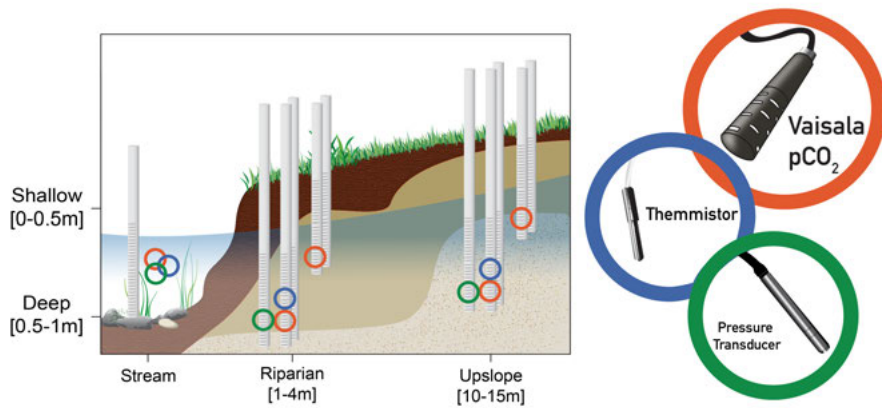


Figure 6. Schematic of the upslope-riparian-stream transect (unscaled) at the SVB catchment indicating the location and depth of each instrument, blank soil tubes were used for manual groundwater collection.

Hourly measurements of CO₂ concentration in stream and groundwater were conducted using Vaisala CARBO- CAP GMP221 nondispersive infrared (NDIR) CO₂ sensors (range from 0-1% to 0-20% depending on the location) (Figure 6). The sensors were enclosed within a water-tight, gas-permeable Teflon membrane (PTFE) and sealed with Plasti Dip (Plasti Dip international, Baine, MN, USA) to ensure that the sensor was protected from water, but remained permeable to gas (Johnson et al., 2010). Water table positions was measured using pressure transducers (MJK 1400, 0–1 m, MJK Automation AB) and water temperature was measured using thermistors (TO3R, TOJO Skogsteknik) that recorded hourly data (Figure 6). All continuously measured data were stored on an external data loggers (CR1000, Campbell Sci.).

Laboratory Water Chemistry Analysis

Groundwater and stream water chemistry was analysed for pH, alkalinity and C concentrations; DIC, CO₂, CH₄, TOC. The groundwater and stream water DIC and CO₂ concentrations were analyzed using the acidified headspace methods (Åberg and Wallin 2014). The pH analysis were conducted in the laboratory using mostly a Mettler Toledo MP 220 pH Meter with an accuracy of ±0.1 units. The groundwater or stream water DOC concentration was analysed in the laboratory using a Shimadzu Total Organic Carbon Analyzer TOC-VCPH, following sample filtration at 0.45 µm in the field. For a subset of samples, additional measurements for δ¹⁸O and δ²H were also performed using a Picarro cavity ringdown laser spectrometer (L2130-i) with a vaporizer module (A0211).

Stable C Isotope Ratio

A total of 535 samples were analysed for δ¹³C-DIC for this thesis work alone, including 360 samples from stream waters, and 175 samples from groundwater. In addition, a total of 44 stream water and groundwater samples were analysed for δ¹³C-CH₄ values and 40 more were analysed for δ¹³C-DOC. Specific analysis of the δ¹³C-CO₂ values was also conducted for a total of 52 groundwater and stream water samples.

The δ¹³C-value for DIC, CO₂, CH₄ and DOC is given as a ratio between the stable ¹³C and ¹²C isotopes, which is then reported in terms of deviation from the standard *Pee- Dee Belemnite* (PDB) in per mille:

$$\delta^{13}C_{sample} = \left(\frac{{}^{13}R_{sample}}{{}^{13}R_{PDB}} - 1 \right) * 10^3 \quad (\text{eq.1})$$

Where δ¹³C sample is the isotopic composition of the sample, expressed in (‰) as a result of the 10³ multiplication factor, and ¹³R is the isotopic ratio of [¹³C]/[¹²C] from the sample and the PDB standard respectively. The standard deviation of the standards were <0.2‰.

The fractionation factor (α or ε) can be used to compare the isotopic ratio of two molecules in different phases, compounds or material. It can reconstruct processes causing or influencing isotopic effects, either kinetic or environmental factors.

$$\alpha_{a-b} = (\delta^{13}C_a + 1000) / (\delta^{13}C_b + 1000) \quad (\text{eq.2})$$

$$\epsilon_{a-b} = (\alpha_{a-b} - 1) * 10^3 \quad (\text{eq.3})$$

Where α is the fractionation factor between the component a and b. The $\delta^{13}\text{C}_a$ and $\delta^{13}\text{C}_b$ is the isotopic ratio of a and b respectively. The α is unit less and often very close to 1 as a result of the very small differences in isotopic ratios. The α factor can be replaced by the ϵ factor, which is expressed in ‰ and more clearly illustrates the change in isotopic composition (Zeebe & Wolf-Gladrow, 2001).

Graphical Techniques

The Miller-Tans (Miller & Tans, 2003) and Keeling (Keeling, 1958) plots were used in Paper I and II to identify and separate DIC sources in groundwater and stream water based on the $\delta^{13}\text{C}$ values. Both graphical techniques are based on the principle of conservation of mass and assume mixing of isotopically distinct C sources (eq.4)

$$\delta^{13}\text{C}_{\text{obs}} \times C_{\text{obs}} = \delta^{13}\text{C}_S \times C_S + \delta^{13}\text{C}_B \times C_B \quad (\text{eq.4})$$

Where ($\delta^{13}\text{C}_{\text{obs}}$) and (C_{obs}) are the observed C isotopic composition and concentration respectively, resulting from a mixture of the C isotopic composition and concentration of the source “S”, for example biogenic or geogenic DIC source ($\delta^{13}\text{C}_S \times C_S$) and background “B” ($\delta^{13}\text{C}_B \times C_B$), represented in the atmospheric CO_2 .

This principle, if re-written as a linear relationship, is expressed as equation 5 in terms of the Keeling plot regression, and equation 6 in the Miller-Tans plot regression.

$$\delta^{13}\text{C}_{\text{obs}} = C_B (\delta^{13}\text{C}_B - C_S) \times (1/ C_{\text{obs}}) + \delta^{13}\text{C}_S \quad (\text{eq.5})$$

$$\delta^{13}\text{C}_{\text{obs}} \times C_{\text{obs}} = \delta^{13}\text{C}_S \times C_{\text{obs}} - \delta^{13}\text{C}_B (\delta^{13}\text{C}_B - \delta^{13}\text{C}_S) \quad (\text{eq.6})$$

The $\delta^{13}\text{C}_S$ is found in the intercept of the linear regression in equation 5 or in the slope of the linear regression in equation 6 (Figure 7). Conceptually, the differences between the two regression models imply that the stream $\delta^{13}\text{C}$ -DIC value in equilibrium with atmospheric CO_2 ($\delta^{13}\text{C}_B \times C_B$), must remain fixed across observations in equation 5. However, this requirement can be disregarded in equation 6, since the $\delta^{13}\text{C}_B \times C_B$ is found in the residual variation of the regression line (Figure 7).

In stream waters, DIC can be taken up by primary producers, which has a known apparent fractionation factor of $\alpha_{pp} = 0.975$ according to the C3 plant metabolic pathways (Alling *et al.*, 2012, O'Leary, 1988). In the alternative of DIC consumption by hydrogenotrophic methanogenesis, a range of apparent isotope fractionation factors can be applied $\alpha_{hm} = 1.055$ to 1.085 (Whiticar, 1999). Alternatively, DIC production can occur through acetoclastic methanogenesis, which can be estimated using a range of apparent isotope fractionation factors, $\alpha_{am} = 1.040$ to 1.05576 (Corbett *et al.*, 2013, Whiticar, 1999).

In the case of paper I, the above listed biological processes were considered as additional influences that supplemented the kinetics of CO_2 outgassing in streams. To identify those effects, the $\delta^{13}\text{C}$ were set to the expected $\delta^{13}\text{C}$ -DIC values from the CO_2 evasion model (Venkiteswaran *et al.*, 2014). Deviations from the expected modelled values were quantified and used to determine these additional biogeochemical processes. In paper I and II, estimates of acetoclastic methanogenesis were made setting $\delta^{13}\text{C}$ to the average $\delta^{13}\text{C}$ -DOC value. For hydrogenotrophic methanogenesis, the $\delta^{13}\text{C}$ was instead set to the $\delta^{13}\text{C}$ -DIC source value approximated from the Miller-Tans analysis.

Kinetics of CO_2 Evasion

The kinetic isotopic effect during CO_2 outgassing favours the evasion of $^{12}\text{CO}_2$ and the progressive build-up of $^{13}\text{CO}_2$ in stream water. This isotopic effect is concentration dependant and follows a non-linear relationship. Its influence on the streams $\delta^{13}\text{C}$ -DIC values can be modelled, for example (Polsenaere & Abril, 2012, Venkiteswaran *et al.*, 2014). These models are limited to specific environmental conditions involving that 1) in-stream processes are negligible, 2) organic acids does not affect carbonate alkalinity as CO_2 is evaded 3) carbonate alkalinity is conserved in the streams, and 4) in the case of Venkiteswaran *et al.* (2014), the DIC pool holds no geogenic contribution.

Radiocarbon Dating

A total of 70 water samples were collected and analysed for ^{14}C content in the DEG and SVB catchment, respectively. This data collection represent one of the largest published aquatic ^{14}C sampling effort within a given catchment. At both DEG and SVB, a complete year characterization (May 2015 to June 2016) of the ^{14}C - CO_2 and ^{14}C -DOC was conducted in the stream water. The stream water characterization was complemented with repeated sampling of the connecting groundwater. The groundwater sampling at DEG was distributed vertically, across the full depth peat profile (0 to 4m below surface) (Figure 5). The material characterized for ^{14}C included at DEG included DOC,

CO₂ and CH₄. Dating of the solid soil organic C across peat depth from a separate study was also included (Larsson *et al.*, 2016). At the SVB catchment, the groundwater ¹⁴C characterization focused on ¹⁴C-DOC and ¹⁴C-CO₂, and was distributed horizontally, following the upslope-riparian-stream transect (Figure 6).

Manual spot measurements of ¹⁴C-CO₂ and ¹⁴C-CH₄ were conducted using the super headspace method (Figure 8a) according to (Garnett *et al.*, 2016a) and (Garnett *et al.*, 2016b) respectively. In summary, the method consist in equilibrating a large volume of water with air in a close container, and extracting the headspace to be injected in air bags (CH₄) (Figure 8b) or stored in molecular sieves (CO₂) (Figure 8c).

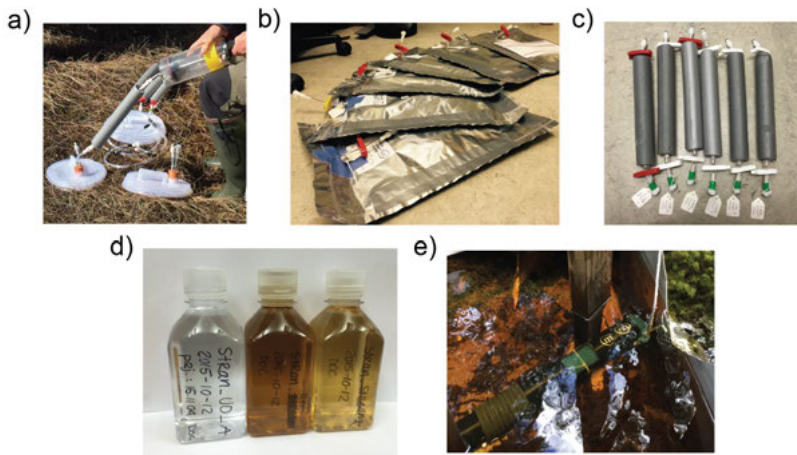


Figure 8. Photo collage of ¹⁴C sampling, a) Jumbo headspace method b) ¹⁴C-CH₄ air bags, c) molecular sieves for ¹⁴C-CO₂ sample storage, d) ¹⁴C-DOC samples in bottles collected at the SVB site, in the stream, riparian and upslope location (left to right) e) passive molecular sieves for time integrated ¹⁴C-CO₂ samples deployed in the SVB stream.

The manual spot measurements for ¹⁴C-DOC were collected in 0.5L bottles in the field and subsequently filtered at 0.7µm in the laboratory (Figure 8d). The manual spot measurement for all C species at SVB and DEG were repeated on 3 different occasions (May, August and October) to help capture the seasonal variability in hydro-climatic conditions that may affect the C sources.

Time-integrated measurements of ¹⁴C-CO₂ in the stream water were conducted using a novel method involving the deployment of passive molecular sieves in the streams (Garnett *et al.*, 2009) (Figure 8e). The sieves were deployed for periods ranging from 4 to 6 weeks. Collectively, these individual measurements provided a complete year characterization of stream water ¹⁴C-CO₂ in both catchments.



Main Findings

“Eureka!”
-Archimedes

Soil-Stream CO₂ linkages

All four papers included in this thesis recognize that stream water CO₂ is primarily sustained by terrestrial sources, transported by inflowing groundwater. Previous studies have put forward this close connection between soil and streams, using mass balance exercises, for example in SVB (Ledesma *et al.*, 2015, Leith *et al.*, 2015, Öquist *et al.*, 2014)), DEG (Leach *et al.*, 2016) and in other catchments world-wide (Duvert *et al.*, 2018, Hope *et al.*, 2004, Hotchkiss *et al.*, 2015). In our case, however, this link was established through C isotope analysis.

Based on a compilation of 318 stream water $\delta^{13}\text{C}$ -DIC values, within different catchments and regions, **paper I** identifies that biogenic soil respiration is the primary source of DIC within four distinct geographical regions in Sweden. This was demonstrated by the close correspondence between the approximated $\delta^{13}\text{C}$ -DIC_{source} from the Miller-Tans plots and the measured $\delta^{13}\text{C}$ -DIC values observed in shallow ground water (Figure 9). In **paper II**, this coupling was further emphasized by simultaneously analysing the stream water and groundwater $\delta^{13}\text{C}$ -DIC values over time from DEG, SKOG and SVB. This analysis demonstrated a close agreement between the $\delta^{13}\text{C}$ -DIC source in streams and groundwaters, further supporting their close connection (Figure 10). In **paper III and IV**, the ^{14}C content of stream water CO₂, DOC and CH₄ over the course of a complete study year was well representative of the connecting groundwater, allowing to identify and partition the contributing hydrological flowpaths. These flowpaths consisted of a deep source area, located at ~2m below ground, supplemented with an intermittent activation of a second flowpath located in the near surface zone of the peat profile.

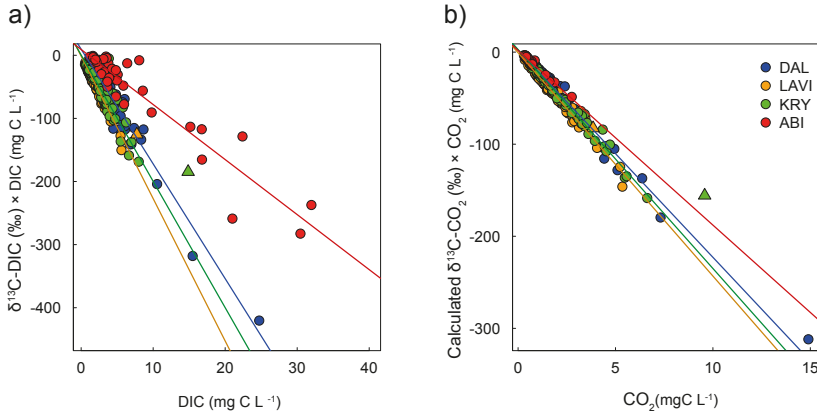


Figure 9. Miller-Tans plot analysis for $\delta^{13}\text{C-DIC}$ values (a) and the calculated $\delta^{13}\text{C-CO}_2$ values (b) presenting the relationship between $\delta^{13}\text{C-DIC} \times \text{DIC}$ as a function of DIC. The points are coloured according to their regions (LAVI, DAL, KRY, ABI). The regression lines are plotted for each individual region and follow the regional colour coding, with the equations listed in Table 2. The triangles represent stream outliers (LAVI n=1, KRY n=1) identified with the Cook's distance and discussed in supplementary materials (**Paper I**).

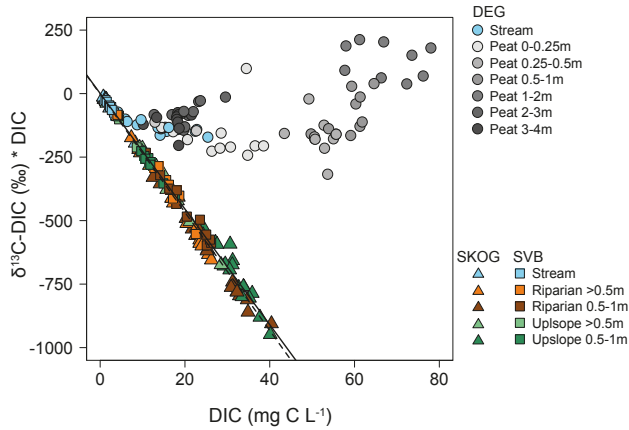


Figure 10. Miller-Tans plots showing $\delta^{13}\text{C-DIC} \times \text{DIC}$ and DIC concentration in the SKOG (triangles), SVB (squares), and DEG (circles) catchment. The symbols are coloured according to their locations/depth (see legend). The full line represents the linear regression model for SVB: $\delta^{13}\text{C-DIC} \times \text{DIC} = -22.76 \times \text{DIC} + 0.62$, $n=50$, $R^2=0.99$, $p<0.0001$, and dotted line represents SKOG: $\delta^{13}\text{C-DIC} \times \text{DIC} = -23.25 \times \text{DIC} - 2.22$, $n=82$, $R^2=0.99$, $p<0.0001$ (**Paper II**).

Passive Pipes and Active Reactors

Stream water CO₂ supersaturation relative to the atmosphere was widespread across all surveyed streams (**paper I**), and constant over time in all three catchment scale studies (**paper II-IV**). This supported previous findings that streams act as ubiquitous sources of atmospheric CO₂ within Sweden (Humborg *et al.*, 2010, Wallin *et al.*, 2018). Two conflicting views concerning the sources for these emissions are found in the literature, 1) streams are *passive conduits*, simply relocating groundwater CO₂ to the atmosphere (Crawford *et al.*, 2015, Leith *et al.*, 2015, Winterdahl *et al.*, 2016), or 2) streams are *active reactors* that generate CO₂ through in-stream biogeochemical reactions (Campeau & Del Giorgio, 2014, Lapierre *et al.*, 2013, Mayorga *et al.*, 2005).

Through the analysis of the stream water $\delta^{13}\text{C}$ -DIC values in **paper I and II**, we established that both of these views are valid. Atmospheric CO₂ evasion was considered the sole fate of CO₂ in a number of streams, thus supporting the conceptualization of streams as passive pipes (Figure 11 and 12). Secondary sources and sinks, associated with in-stream primary production, DOC mineralization through photochemical or biological reactions and anaerobic processes were also significant in some streams, thus validating the active reactor conceptualization (Figure 11 and 12). These secondary processes have a significant influence on both $\delta^{13}\text{C}$ -DIC values and DIC fluxes.

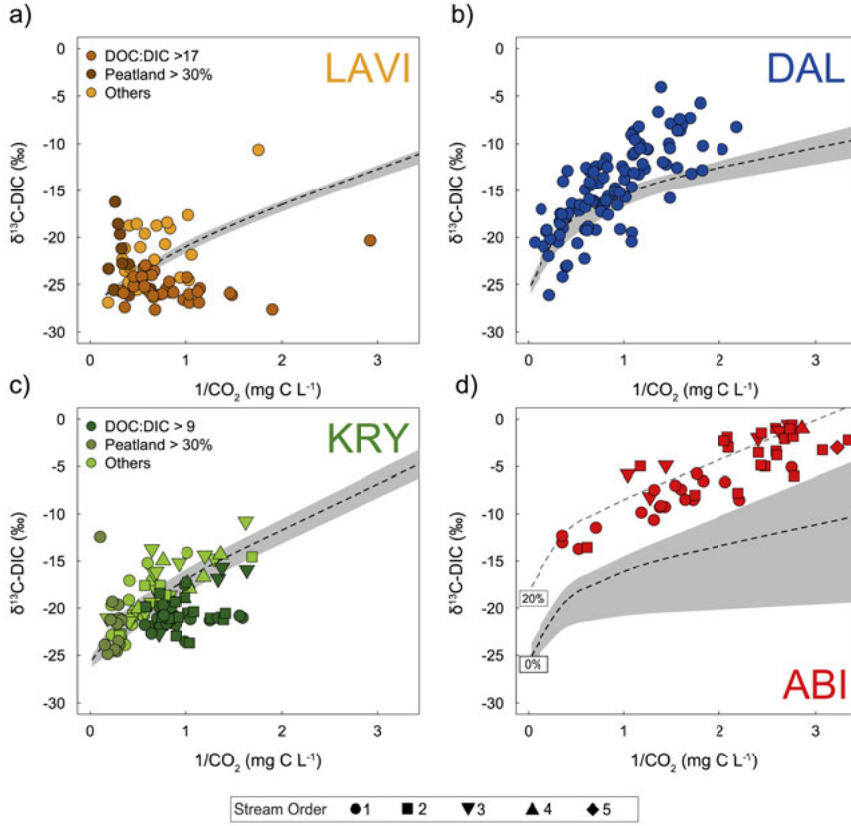


Figure 11 Scatterplots showing the relationship between $\delta^{13}\text{C-DIC}$ and the inverted CO_2 concentration [$1/\text{CO}_2$], comparing stream observations with modelled trajectories of $\delta^{13}\text{C-DIC}$ evolution with CO_2 evasion for the streams in a) LAVI, b) DAL, c) KRY and d) ABI from Giesler *et al.* (2013). The mean modelled trajectories are represented as the black dotted line with the grey area illustrating the upper and lower prediction boundaries. Each point represents a different stream observation. In the case of (a) and (c) certain streams were also colored to identify streams with DOC:DIC ratios above the regional average, and peatland cover >30%. In the case of (c) and (d) different symbols were attributed to the Strahler stream order (1-5). In (d), additional curves represent the shift in modelled CO_2 evasion with 20%, contribution of geogenic DIC source (initial $\delta^{13}\text{C-DIC}$ value = -20‰) (**Paper I**).

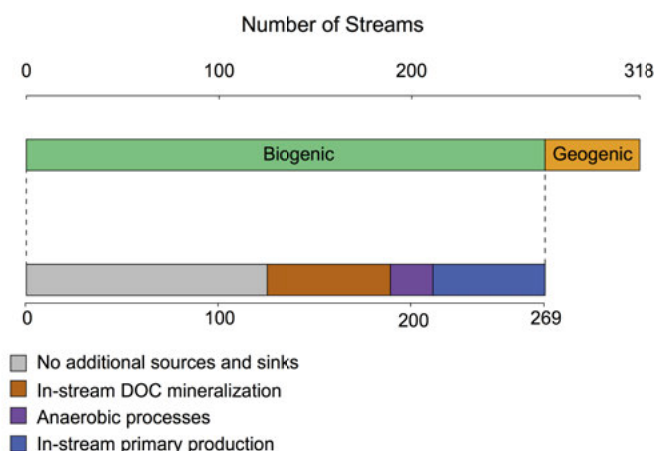


Figure 12. Synthesis scheme representing the identified dominant DIC sources and sinks for the studied streams (n=318). The top bar shows the separation between streams with strictly biogenic DIC sources (n=269) (green) or with a detected geogenic DIC influence (n=49) (orange). The bottom bar represents the streams within the category of biogenic DIC sources for which additional DIC sources and sinks are important. All streams were considered to be affected by CO₂ evasion. The grey area represents the streams with no detectable additional influence besides CO₂ evasion to the atmosphere (n=126). The brown area represents streams where DOC mineralization was identified (n=64). The purple area represents the streams likely influenced by anaerobic processes (n=22). The blue area represents the streams possibly influenced by in-stream primary production (n=58) (**Paper I**).

The concept of active reactors extend beyond stream waters. Groundwater, also appeared as areas of intensive C transformation. Methanogenesis, associated with peat-rich environments found in the different types of studied catchments DEG, SVB and SKOG, had a dominant influence on the catchment scale DIC cycling (**Paper II**). These areas comprised a large boreal fen (DEG), where hydrogenotrophic methanogenesis consumes groundwater DIC (**Paper II-III**), an organic-rich riparian zone (SVB), where acetoclastic methanogenesis likely sustained groundwater DIC production, and a previously unrecognized hydrological source associated with an upstream peatland (SKOG), that contributed disproportionately to the catchment total C export relative to its areal coverage. The similarity between ¹⁴C-CO₂ and ¹⁴C-CH₄ at DEG further reinforced the close source connections between the two C-species (**Paper III**). Collectively, these results demonstrate that the catchment-scale cycling of CO₂ is intertwined with that of CH₄. Depository environments, poor in oxygen and rich in CH₄, are widespread across the boreal biome (Gorham, 1991, Nilsson *et al.*, 2001, Yu, 2012). They likely play a predominant role in modulating and transforming CO₂ exported to freshwaters.

Stability of the Boreal C Repository

In both the DEG and SVB catchment, the ^{14}C content of dissolved C species was remarkably different from the age of the standing soil OC, indicating little remobilization of ancient peat C stocks in both catchments (**Paper III, IV**). Projecting the total ^{14}C export at DEG relative to the hydrological conditions over the last 12 years indicated that inter-annual shifts in discharge will have a negligible influence on the age of lateral C export from DEG (Figure 13). This boreal fen has been spared from human disturbances and remains in relative pristine condition. Studies in peatlands that were disturbed by human activities, demonstrate that ancient C stocks can be remobilized through the aquatic pathway (Butman *et al.*, 2014, Evans *et al.*, 2014, Moore *et al.*, 2013). Our study suggest that in the absence of such disturbances, C losses from boreal peatlands should remain limited.

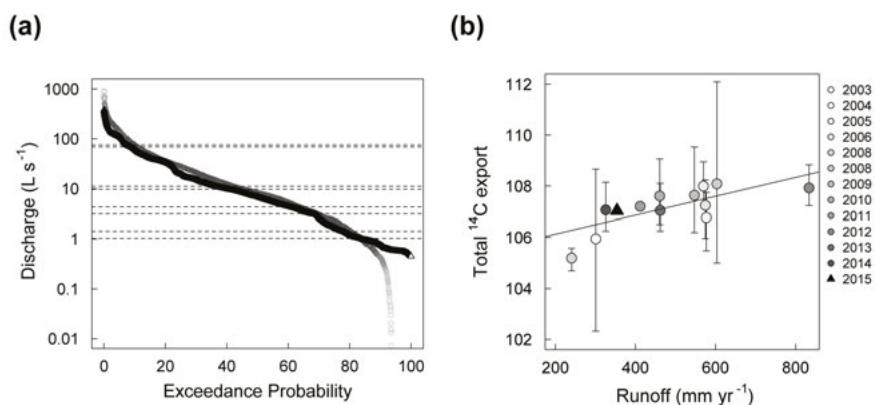


Figure 13. a) Flow duration curve of the stream for each year between 2003 and 2014 (circles in grey scales) and during the study year (black triangle; 2015), with flow conditions at the time of stream water ^{14}C -DOC sample collection identified as dotted lines. b) the estimated annual weighted average ^{14}C content of total C export (Total ^{14}C exp) for each year between 2003-2016, in relation to the annual runoff expressed in mm, with the bars representing the uncertainty of each prediction, and the solid line representing the least-square linear regression model (Total $^{14}\text{Cexp} = 105.2 + \text{Runoff} \times 0.004$, $R^2=0.53$, $n=12$, $p=0.004$) (**Paper III**).

From Leaves to Streams

The systematic gap in ^{14}C content between CO_2 and DOC, prevailing in both DEG and SVB throughout the studied year, was one of the most surprising result of this thesis (Figure 14). In both catchments, the ^{14}C - CO_2 was constant across locations and sampling periods, but the ^{14}C -DOC was considerably more variable. This aspect was even more striking at the SVB catchment,

where ^{14}C -DOC spanned from 50 to 117 %modern, while the ^{14}C - CO_2 remained stable, ranging from 99 to 107 %modern in the same waters (Figure 14). This gap highlighted differences in the sourcing and turn-over rates of DOC and CO_2 . In addition, contrasts in the ^{14}C distribution of CO_2 and DOC across the vertical peat profile at DEG further indicated that these two compounds are subject to different turnover times, but also to different hydro-physical processes controlling their respective transport across depth.

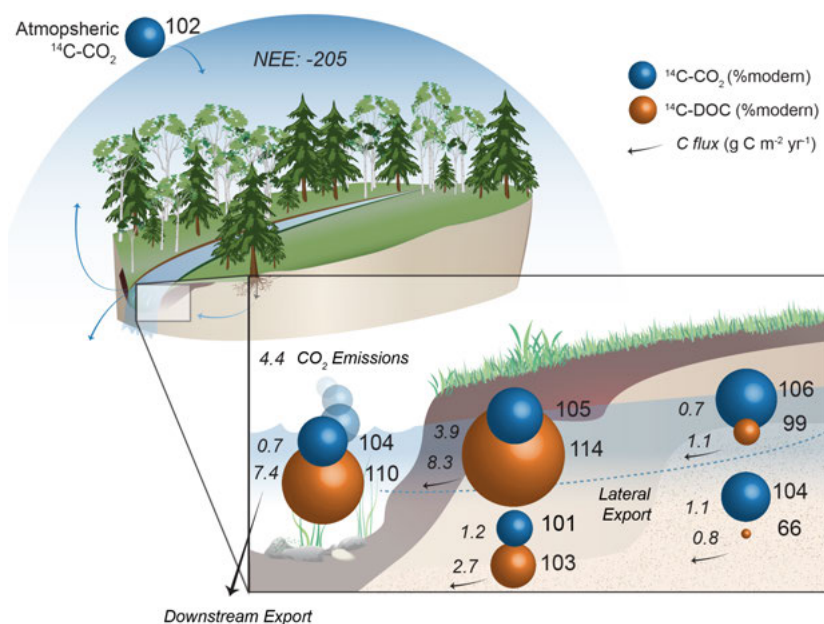


Figure 14. This schematic (unscaled) includes the forest NEE and the lateral and downstream CO_2 and DOC export and stream CO_2 emissions, along with their cumulative annual ^{14}C content represented by the sizes of the spheres (blue (^{14}C - CO_2) and orange (^{14}C -DOC)), at the three locations along the Upslope-Riparian-Stream transect, and depth (shallow [0-0.5 m] and deep [0.5-1 m]). Mass of C export ($\text{g C m}^{-2} \text{ yr}^{-1}$) are written on the left side of each spheres and in *italic*, while the ^{14}C -contents are written on the right side (**Paper IV**).

In the SVB catchment, we were able to elaborate on the drivers behind this disconnect in the cycling of DOC and CO_2 (**Paper IV**). The steadiness of the ^{14}C - CO_2 represented well the current atmospheric ^{14}C - CO_2 levels, indicating a constant and rapid cycling. We connected this source to currently occurring forest C fixation, and the ensuing soil respiration carried out by roots and microbes mineralizing recent photosynthates. In the light of these results, we conclude that stream CO_2 emissions will rapidly feedback on the anticipated future changes in forest C sink capacity and C allocation patterns driven by climate and land-use changes in the boreal biome.

Lessons Learned from Isotopic Tracing of C Sources

Separating multiple co-occurring isotopic effects is certainly the most challenging aspect in the interpretation of stream water $\delta^{13}\text{C}$ -DIC values. While there are no perfect ways to address these issues, a few alternative methods have been developed in this thesis to circumvent some of these problems. Our approach began by describing some of the key well-described isotopic effects on $\delta^{13}\text{C}$ -DIC values. This was followed by a second analysis focusing on the residual variation of $\delta^{13}\text{C}$ -DIC values.

The pH Effect

The composite nature of DIC and its isotopic composition [H_2CO_3 , HCO_3^- , CO_3^{2-}] was the first key-isotopic effect considered in the analysis of $\delta^{13}\text{C}$ -DIC values. The pH was the best explanatory variable for $\delta^{13}\text{C}$ -DIC value across the streams surveyed in **paper I** (Figure 15). This relationship is not attributed to differences in C sourcing, but rather to the isotopic effect of CO_2 evasion, where CO_2 escapes to the atmosphere and leaves behind ionic DIC forms. These ionic forms have a higher affinity for ^{13}C isotopes, which leads to large equilibrium isotopic effects in combination with kinetic fractionation (Zhang, 1995). In streams with high CO_2 supersaturation and low pH, this isotopic effect will remain low, but for streams with high buffering capacity, this will have a substantial effect on $\delta^{13}\text{C}$ -DIC values (Figure 15). If neglected, this effect will lead to misguided interpretations of C sources. As such, analysis of stream water $\delta^{13}\text{C}$ -DIC values across variable temporal and spatial scales should begin with a contextualization with pH and carbonate alkalinity, which in our case was achieved by deriving the $\delta^{13}\text{C}$ - CO_2 values (**Paper I**).

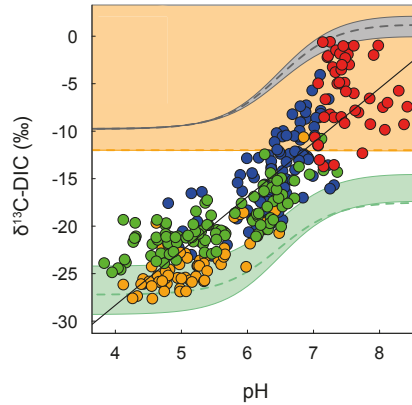


Figure 15. Scatterplots showing the relationship between $\delta^{13}\text{C-DIC}$ as a function of pH, with the solid black line representing the least square linear regression model, the green area representing $\delta^{13}\text{C-DIC}$ in equilibrium with soil CO_2 (-23 to -28‰), the grey area representing equilibrium with atmospheric CO_2 (-8.5‰) the orange area representing the conventional threshold where geogenic DIC sources are considered possible. Each dot represents a different stream observation and is colored according to its region (DAL, LAVI, KRY and ABI) (**Paper I**).

Filtering out CO_2 evasion

The kinetics of stream water CO_2 evasion is a second key isotopic effect that can be well-described through modelling (Polsenaere & Abril, 2012, Venkiteswaran *et al.*, 2014). By quantifying this isotopic effect for multiple streams, we were able to identify secondary isotopic effects and connect them to different biogeochemical processes. While we recommend to use caution when quantify CO_2 evasion based on $\delta^{13}\text{C-DIC}$ observations, we also highlight novel opportunities to unravel the presence of additional mechanisms regulating DIC concentration in surface waters using $\delta^{13}\text{C-DIC}$ values (**Paper I**).

Miller-Tans Plot

The Keeling plot is a well-known graphical technique, but requires fixed background conditions that can rarely be validated in field conditions. The Miller-Tans graphical technique is less notorious in comparison, but allows for background conditions to vary between sampling points. Consequently, this graphical technique proved to be more valuable for separating and approximating stream $\delta^{13}\text{C}$ sources between multiple catchments scattered through time and space. This method clearly revealed distinct groups in $\delta^{13}\text{C-DIC}$ values, which were not distinguishable using the Keeling plot technique or a basic distribution of values.

Tracing Hydrological Flowpaths

An array of isotopes and chemical compounds can be used to trace hydrological flowpaths (Abbott *et al.*, 2016). Because C transformations typically leave an imprint on the $\delta^{13}\text{C}$ value and ^{14}C content, they too can be used as tracers. This thesis contains several examples where hydrological information could be derived from C isotopes. In DEG, a deep hydrological flowpath, ~2m below ground surface, was found to support ~70% of the total aquatic C export (**Paper II**). In the same catchment, a 9-day lag was identified between the different contributing areas exporting CO_2 to the stream (**Paper II**). A deep hydrological flowpath, transporting ancient DOC, was revealed in the upslope soils at the SVB catchment (**Paper IV**). In the SKOG catchment, the disagreement between the stream water and the groundwater $\delta^{13}\text{C}$ -DIC values suggested a methanogenic source that was not captured by our groundwater characterization. This revealed a previously unaccounted hydrological source from an upstream peatland (**Paper II**), which comprised only 6.5% of the total catchment area, but dominated the lateral C export.



Conclusions & Future Perspectives

” Science never solves a problem without creating ten more ”
– George Bernard Shaw

This thesis has provided new information on the sources of C in boreal streams. Most striking, was the rich complexity of processes shaping the export of C from soils to streams. Stream CO₂ arises from multiple sources and sinks (**Paper I & II**), but is mostly driven by fast-cycling processes within the connecting soils (**Paper III and IV**). These findings open up to new questions such as; how to better capture the complexity in stream C sources across large spatial scales and how to track potential shifts in C sources in response to climate and land-use changes.

Developing Better Indicators

This thesis recommends that future studies aim to combine catchment C budgets with a determination of stream C sources and sinks. The integration of lateral C export into catchment scale budget is complex, and mass balance exercises will not fully capture the relationships between different flux components. These attempts can be supported by the interpretation of large-scale patterns in $\delta^{13}\text{C}$ values and ^{14}C -contents, but can we derive better indicators that would facilitate a large-scale determination of stream C sources? Methanogenic processes are important in the cycling of CO₂ at the catchment scale (**Paper I-III**) and may respond differently to warming and water stress (Campeau & Del Giorgio, 2014, Updegraff *et al.*, 2001). The CH₄ in surface waters tend to be controlled locally (Stanley *et al.*, 2016), but is often associated with specific environments, e.g. peatlands and riparian zones (Wallin *et al.*, 2014), or certain landscape features, e.g. flat topography (Campeau *et al.*, 2014, Jones & Mulholland, 1998a). Floodable lands have recently been identified as key areas controlling the C supply to freshwaters (Abril & Borges, 2019). This aspects is surely relevant to headwater systems, including ephemeral streams, for which the true areal extent still remains unknown (Allen & Pavelsky, 2018, Benstead & Leigh, 2012, Bishop *et al.*, 2008). The C that is

supplied to streams by these intermittently flooded areas needs further assessment. Developing remote sensing tools to map methane-rich environments and intermittently flooded areas could possibly help better describe these influences at larger spatial scales. In-stream primary production has a poor predictability (Lamberti & Steinman, 1997), but accessibility to light (Mulholland *et al.*, 2001) and application of fertilizers associated with agriculture (Gücker *et al.*, 2009) are major controls that could potentially be described at large spatial scales. In-stream DOC processing has been studied extensively, new concepts relating to hydrological controls are emerging in the literature, for example, the pulse shunt concept (Raymond *et al.*, 2016), providing a framework to dynamically address the influence of residence time (Catalán *et al.*, 2016) and stream size (Hotchkiss *et al.*, 2015). These effects may, someday, be quantifiable by remote sensing methodologies.

A False Impression of Stability

While this thesis demonstrates that the age component of C mobilized through the aquatic pathway in a pristine boreal fen (DEG) is resilient to changes in hydro-climatic conditions, the boreal forest catchment (SVB) revealed an ancient DOC source in the upslope groundwater. Why aged DOC is mobilized in this catchment remains unclear. An aged C component re-emerges further downstream of the Krycklan river, this time in the form of CO₂ (Figure 16). How the occurrence of this aged-CO₂ in the Krycklan river catchment could be connected to the same old-DOC pool found in the upslope groundwater remains to be determined. Alternatively, both aged-DOC and CO₂ may simply be co-transported with deep groundwater emerging in different sections of the catchment. Further isotopic characterization across this catchment could help elucidate the hydrological sources and fate associated with this old DOC and CO₂ pool and whether fast-cycling CO₂ sources are, or not, ubiquitous in this catchment.

A predominant hydrological flowpath in the boreal fen (DEG), located about 2 m below ground, feeds most of the C found in the connecting stream. While this deep pathway surprisingly transports relatively fresh DOC, CO₂ or CH₄, it may relocate ancient particulate organic C (POC), which was not measured in the study. How the potential seeping of aged-POC affects the stability and the C budget of the peatland is still unquantified. An extreme summer-heat-wave in 2018 lowered the groundwater level at Degerö further than at any time since measurements began at this location. Such extreme events, would expose new peat depths to oxygen and promote the mineralization of older peat material. How such conditions affects the remobilization of ancient C towards the atmosphere has yet to be determined.

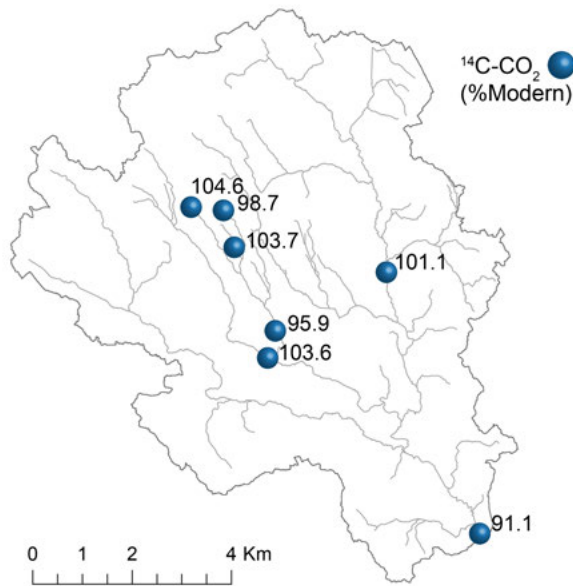


Figure 16. Map of the Krycklan river catchment showing the location of time-integrated $^{14}\text{C-CO}_2$ samples in stream waters collected between 2015-07-08 to 2015-08-06 with their ^{14}C -content expressed in %modern (Campeau A., unpublished data).

The close connection between aquatic and terrestrial CO_2 sources, gives rise to suspicion that anticipated changes in the forest C balance and C allocation will be mirrored in aquatic ecosystems. While a connection to current forest activity could be made based on the $^{14}\text{C-CO}_2$, the specific biological pathways giving rise to groundwater CO_2 could not be separated. This limits our capacity to predict how changes in forest C allocation patterns will be reflected in the source and magnitude of lateral C export. Forest manipulation, e.g. interrupting the flow of energy to the root system, could help further separate the various respiratory processes associated with the lateral C export, i.e. autotrophic/heterotrophic, but these questions remain to be explored.

At last, little of what has been concluded in this thesis should be extrapolated across the boreal biome without caution. The heterogeneity of this landscape is far too great to be represented by this collection of studies. Our understanding of biogeochemical processes in high-latitude ecosystems has been said to be strongly biased towards Sweden (Metcalf *et al.*, 2018). More studies in other regions of the boreal biome and within different ecosystem types will be needed to develop a broader picture of C sources in boreal streams.

Sammanfattning på svenska

Den boreala biomen bildar ett stort bälte som omger jordens nordliga latituder. Landskapet består av en mosaik av barrskog, torvmark samt sjöar och vattendrag. Genom fotosyntes fixerar den levande vegetationen som finns här kontinuerligt koldioxid (CO_2) från atmosfären. Detta kol används som byggstenar för vegetation vilken senare bryts ned och lagras in markens kollager.

Genom nedbrytning, utförd av markmikrober och andra organismer, återförs en viss del av detta kol till atmosfären. Nettoresultatet av dessa två motverkande processer är emellertid oftast att CO_2 avlägsnas från atmosfären, och där boreala ekosystem representerar $\sim 20\%$ av den globala kolsänkan utförd av skogsmark. Eftersom CO_2 fungerar som en viktig växthusgas bidrar boreala ekosystem till en nettoavkylning av klimatet och neutraliserar en betydande del av det antropogena CO_2 -utsläppet.

Utbytet av CO_2 mellan boreala ekosystem och atmosfären blir dock mer komplext när man inkluderar hydrosfären. Den boreala biomen har världens högsta täthet av sötvattenekosystem, bestående av sjöar, dammar, älvar samt bäckar. Dessa sötvattenförekomster som dränerar det boreala landskapet är i de flesta fall övermättade med CO_2 och metan (CH_4) i förhållande till atmosfären. Dessutom transporteras mycket löst organiskt kol (DOC) till sjöar och vattendrag från avrinningsområdets kolrika marklager. CO_2 och CH_4 i dessa vatten returneras snabbt till atmosfären genom fysiskt gasutbyte. Boreala sötvatten bidrar därmed positivt till halter av växthusgaser i atmosfären.

Under de senaste decennierna har försökt gjorts till att kvantifiera utsläpp av växthusgaser från sötvatten, detta för att bättre kunna förstå dess roll i den globala kolcykeln och i förlängningen jordens klimatsystem. Dessa ansträngningar har lett till en första integrering av CO_2 -utsläpp från sötvatten i den senaste IPCC-rapporten om klimatförändringar (2013), där den globala kolcykeln beskrivs.

Denna avhandling syftar till med förståelsen om växthusgasemissioner från sötvatten sam bas försöka ta ett steg till och förstå de källor av kol som gör att små vattendrag som dränerar boreala ekosystem ofta är övermättade med avseende på CO_2 . Dessa små vattendrag utgör en proportionellt liten andel av den totala ytan av sötvatten men bidrar samtidigt med en stor andel av de totala

CO₂-emissionerna. CO₂ i små vattendrag kan härröra från flera källor. En växande forskning har visat att grundvatteninflödet av CO₂ är tillräckligt för att förklara mycket av de CO₂ emissioner och nedströms export som observerats i vattendrag. Dessa slutsatser har till stor del baserats på massbalansberäkningar, men där det fortfarande saknas en tydlig processförståelse.

En stor mängd biologiska och geokemiska källor och processer kan generera CO₂ till grund- och bäckvatten. De biologiska källorna, autotrofisk och heterotrofisk respiration, utförs av mikroorganismer, svampar och växtrötter. Geokemiska källor involverar mestadels vittring av silikat- eller karbonat innehållande mineral och vilket konsumerar CO₂ och producerar alkalinitet. I frånvaro av syre kan CH₄-producerande bakterier ändra CO₂-balansen genom att antingen producera CH₄ tillsammans med CO₂ (acetoklastisk metanogenes) eller konsumera CO₂ till CH₄-produktion (hydrogenotrofisk metanogenes). I bäckvattnet kan primär produktion också konsumera CO₂ via fotosyntes, medan mikroorganismer samtidigt kan bryta ned löst organiskt kol och bilda CO₂. Dessutom kan fotokemisk nedbrytning av organiskt material bryta ned löst organiskt kol och därmed producera CO₂. Dessa olika källor, sänkor och transformationsprocesser måste separeras för att förstå hur kol omsätts och transporteras mellan mark, vatten och atmosfär i det boreala landskapet.

Åldersbestämning av kol kan vara en metod för att förstå de olika processer som reglerar CO₂ i rinnande vatten. CO₂ i grund- och bäckvatten kan ha sitt ursprung från nedbrytningsprocesser som ägt rum det senaste året, men också från nedbrytning av gammalt markkol, som i Sverige kan vara upp till ~ 10 000 år gammal (början av Holocen). Skillnaden mellan dessa tidsskalor är fundamental för vår processförståelse, men är information som oftast saknas eller bortses från när det gäller CO₂ i vattendrag.

Denna avhandling baseras i stor utsträckning på karaktärisering av naturlig förekomst av stabila och radioaktiva kolisotoper i grund- och bäckvatten. Studien har inkluderat de olika formerna av kol samt provtagning av olika ekosystemtyper över hela Sverige med syftet att ta fram en så god förståelse som möjligt rörande mark-vatten interaktioner. Medan den stabila isotopen (¹³C) bär avtrycket av flera källor och transformationsprocesser, ger den radioaktiva isotopen (¹⁴C) en uppskattning av den tidsskala involverad för att producera CO₂.

Resultaten från isotopanalyserna visar att boreal mark är huvudkällan för CO₂ i bäckvatten. Markrespiration (dvs biologisk nedbrytning av organisk material) producerar CO₂ som transporteras till dränerande vattendrag och där skapar ett övertryck i förhållande till atmosfären. I ett fåtal undantag visade resultaten på att geologiska CO₂-källor (vittring av karbonat innehållande min-

eral) bidrog. En rad biologiska processer omvandlar också CO₂ under transporten från mark till vatten, eller i vattendraget. Dessa inkluderar; metanogener, DOC-mineralisering och primärproduktion i vattendraget.

Majoriteten av CO₂ i små boreala vattendrag upprätthålls genom det senaste årets kolfixering av vegetationen. Detta tyder på snabb omsättning och transport från mark till vatten och där antika kolsubstrat utgör en mycket liten andel av den producerade CO₂ som når vattendrag. Dessa resultat visar desutom att lagret av organiskt kol i boreal skogs- och torvmark för närvarande är stabilt. Dock indikerar den direkta kopplingen mellan vattendragets CO₂ och skogens fotosyntetiska aktivitet att förändringar i kolinbindningsmönstret i det boreala landskapet, drivna av klimat och markanvändning, kan ge direkta effekter på CO₂ emissioner från små vattendrag.



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— Isaac Newton

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